Synthesis of New Class of Cyclopropanes and Their Unusual Synthetic Transformations

A thesis submitted for the partial fulfillment of

the degree of Doctor of Philosophy

by

UTTAM K. MISHRA

Department of Chemical Sciences

Indian Institute of Science Education and Research (IISER) Mohali

Sector 81, Knowledge City, S. A. S. Nagar, Manauli PO, Mohali, 140306, Punjab, India.

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Dedicated

to my beloved grandmother and father

Late Smt. Jayanti Mishra

and

Sri Haradhan Mishra

DECLARATION

The work presented in this thesis titled "***Synthesis of new class of cyclopropanes and their unusual synthetic transformations***" has been carried out by me under the supervision of **Dr. Sripada S. V. Rama Sastry** in the Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Mohali.

This work has not been submitted in part or full for a degree, diploma or a fellowship to any other university or institute.

Whenever contributions of others are involved, every effort is made to indicate this clearly with due acknowledgments of collaborative work and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Uttam K. Mishra

Date:

Place:

In my capacity as the supervisor of the candidate's thesis work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Sripada S. V. Rama Sastry
Associate Professor
Department of Chemical Sciences
Indian Institute of Science Education and Research Mohali

Date:

Place:

CONTENTS

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Uttam K. Mishra

SUMMARY

Organic molecules are the art of nature. Nature provides sophisticated targets which enable organic chemists to discover the potential synthetic strategies. Nature has endowed all types of carbo- and heterocycles with different ring sizes. Among them, three-membered carbocycles are recognized as essential subunits of complex molecular architectures and have occupied a distinct place in organic synthesis. These small carbocycles are commonly known as cyclopropanes, which attracted much attention of the organic community.

The enormous reactivity of cyclopropanes makes them to serve as useful synthetic building blocks in modern organic synthesis. Moreover, these small carbocycle subunits are often found in many biologically active natural products and pharmaceuticals. The impressive pharmacological activities and the industrial relevance of cyclopropanes have motivated several researchers to study cyclopropanes and their derivatives. Nowadays, the development of new synthetic methods for the synthesis of cyclopropanes has become a great interest of organic chemists. In the past few decades, multiple numbers of strategies have been developed towards the synthesis of cyclopropanes. Among them, the Corey-Chaykovsky cyclopropanation reaction is a metal-free cyclopropanation strategy triggered by sulfur ylides. The Corey-Chaykovsky cyclopropanation reaction can be defined as the Michael addition of sulfur ylides to the *α,β*–unsaturated systems, and subsequent 1,3-elimination of the leaving group leading to cyclopropanes. As such, sulfur ylides have found wide applications in transition metal catalysis as metal carbenoids and tremendous use in organic transformation as nucleophiles. Despite tremendous advancements in sulfur ylide chemistry, there still remains huge scope for the development of efficient processes to achieve the complex molecular architectures.

The thesis entitled "*Synthesis of new class of cyclopropanes and their unusual synthetic transformations*" describes the efforts towards the synthesis of unusual cyclopropanoids and their synthetic elaborations to achieve the privileged bioactive molecular scaffolds. The content of the thesis has been divided into four sections. In all the sections, a brief introduction is provided, the compounds are sequentially numbered (bold), and references are marked sequentially as superscript and listed at the end of the thesis.

The first section highlights sulfur ylides mediated strategies for the synthesis of cyclopropanes and the unusual reactions promoted by sulfoxonium ylides.

The second section of the thesis demonstrates a series of unprecedented diastereoselective synthesis of cyclopropanoids *via* unusual cyclization pathways triggered by the DOSM (dimethyloxosulfoniummethylide). These strategies provide efficient routes to access cyclopropa-fused tetralones and indeno-spirocyclopropanes in excellent yields. The methods described herein are straightforward and mechanistically fascinating, and establish novel substrate-based diversity-oriented strategies. Further, to illustrate the synthetic utility of these methods, we have successfully demonstrated a series of serendipitous one-step elaborations to access the privileged scaffolds such as fluorenones, indenones, and tetralones.

The successful development of unexpected reactions facilitated by DOSM for the synthesis of unusual cyclopropanoids (described in Section 2) motivated us to apply these ylides to other substrate designs. A thorough literature survey suggested that there are no applications of sulfur ylides in a desymmetrization process yet. Thus, keeping the idea of desymmetrization process which is a powerful strategy to achieve complex architectures, we designed the symmetric enone-enones appended to the aryl backbone and employed in the reaction with DOSM. The third section discusses the reaction of DOSM with the designed symmetric substrates, the reaction efficiently generated highly functionalized cyclopropanoids in excellent yields. Further, one-step serendipitous elaboration of the products provided access to privilege scaffolds such as fluorenones, indenones, and naphthaphenones. The investigation about the mechanism of product formation indicated that the strategies presented herein are straightforward under the mild reaction conditions.

After the successful demonstration of mild and straightforward protocols for the synthesis of unusual cyclopropanoids promoted by DOSM (as described in Sections 2 and 3), we considered the development of ring-opening reactions of the cyclopropanes. Due to the unusual reactivity of the cyclopropane ring, they can undergo a variety of ring-opening cyclization reactions in the presence of suitable chemical reagents. In the past few decades, several strategies regarding cyclopropane ring-opening enabled by suitable activating reagents have been developed, which include the limitations, such as (i) the reactions are catalyzed by Lewis or Brønsted acids or metal catalyst under vigorous reaction conditions, (ii) the reactions catalyzed

by organocatalysts are less explored, and (iii) the reactions associated with cyclopropyl aryl ketones (monoactivated cyclopropanes) required stoichiometric amount of acids and harsh reaction conditions.

The fourth section describes an unprecedented metal- and acid-free ring-opening/recyclization cascade of cyclopropyl aryl ketones. These strategies provided pentannulated aromatics such as 2-(2-hydroxyethyl)indenones, 2-styryl-3-arylindenones, and 2,3-disubstituted fluorenones in moderate to good yields. The mechanistic details are elucidated by thoroughly performing the control experiments. The key features of these strategies are (i) readily accessible starting materials, (ii) the ease of operation, and (iii) high atom economy.

The development of green and sustainable chemistry is of significance in modern organic synthesis. The "green chemistry" and "sustainable chemistry" involves the idea of increasing efficiency and decreasing waste in synthetic sequences. The productivity of a synthetic sequence can be improved by developing reactions under one-pot. Hayashi defines a one-pot synthesis as "a strategy to improve the efficiency of a chemical reaction, whereby a reactant is subjected to successive chemical reactions in just one reactor." The advantages of one-pot process are (i) it reduces the number of steps compare to other multistep process, (ii) it avoids the wastage of raw materials during purification and isolation of intermediates, and (iii) it saves the loss of time, labour, and yield losses of the product.

The appendix part demonstrated the diversity-oriented one-pot trimetallic orthogonal process for the synthesis of cyclohepta[*b*]indoles. A series of serendipitous one-step elaboration of cyclohepta[*b*]indoles were also established. These strategies described efficient access to dihydrocyclohepta[*b*]indoles, dihydroindolotropones, and indolotropones. We believed that these multicatalytic one-pot processes are the easiest route to access the privileged bioactive scaffolds. These one-pot strategies could be applied towards the synthesis of natural products.

LIST OF ABBREVIATIONS

Ac	Acetyl
Aq	Aqueous
ABq	AB quartet
Atm	Atmospheric
BBEDA	*N,N'*-bis-(benzylidene)ethylenediamine
Bn	Benzyl
Boc	*tert*-butyloxycarbonyl
Brs	broad singlet
calcd	calculated
cbz	carboxybenzyl
CFL	compact fluorescent lamp
d	doublet
DABCO	1,4-diazabicyclo[2.2.2]octane
DBU	1,8-diazabicylo[5.4.0]undec-7-ene
dba	dibenzylideneacetone
DCE	dichloro ethane
DCM	dichloro methane
dd	doublet of doublet
ddd	doublet of a doublet of doublet
DMA	dimethylacetamide
DMAP	4-dimethylaminopyridine
DME	dimethoxyethane
DMF	*N,N'*-dimethyl formamide
DMSO	dimethyl sulfoxide
DOSM	dimethyloxosulfoniummethylide
dq	doublet of quartet
dpbp	2,2'-bis(diphenylphosphino)benzophenone
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppp	1,3-bis(diphenylphosphino)propane

dr	diasteriomeric ratio
dt	doublet of triplet
ee	enantiomeric excess
eq	equivalents
ESI	electron spray ionization
FT-IR	Fourier transform infrared spectroscopy
h	hour(s)
HRMS	high resolution mass spectrum
Hz	Hertz
ppm	parts per million
IBX	2-iodoxybenzoic acid
J	coupling constant
LDA	lithium di-isopropyl amide
m	multiplet
mg	milli gram(s)
MHz	mega hertz
min	minute(s)
mL	milliliter(s)
mmol	milli mole(s)
m.p.	melting point
MS	molecular sieves
m/z	mass/charge
NBS	*N*-bromosuccinimide
NIS	*N*-iodosuccinimide
PTSA	*p*-toluenesulfonic acid
q	quartet
qd	quartet of doublet
RT	room temperature
s	singlet
t	triplet
t-Bu	*tert*-butyl

td	triplet of doublet
TMEDA	tetramethylethylenediamine
Tf	trifluoromethanesulfonate
TFAA	trifluoroacetic anhydride
TFE	trifluoroethanol
TMS	trimethylsilyl
tert	tertiary
THF	tetrahydrofuran
THA	tetrahexylammonium
TMS	tetramethylsilane
TLC	thin layer chromatography

Section 1

General introduction about cyclopropanoids

Organic molecules are the art of nature. Nature provides sophisticated targets which enable organic chemists to discover the potential synthetic strategies. However, nature has endowed all types of carbo- and heterocycles with different ring sizes. Among them, three-membered carbocycles are recognized as essential subunits of complex molecular architecture and have occupied a distinct place in organic synthesis. These small carbocycles are commonly known as cyclopropanes, which attracted much attention of the organic community.

Cyclopropanes are valuable molecular scaffolds in organic chemistry. They show unique and versatile reactivity due to their inherent angle strain, high π-character, and intrinsic torsional strain. The enormous reactivity of cyclopropanes makes them to serve as useful synthetic building blocks in modern organic synthesis. Moreover, these small carbocycle subunits are

often found in many biologically active natural products and pharmaceuticals. Most of the cyclopropane containing natural products have been isolated from fungi, plants, or microorganisms. The large complex molecular structure containing small cyclopropane motif displayed a wide range of biological activities spanning from enzyme inhibitions, herbicidal, antifungal, antibacterial, antibiotic, insecticidal, antimetastatic (anticancer), plant growth, antiviral, and fruit ripening control. An overview of natural products and their synthetic derivatives, which constitute a cyclopropane ring, is presented in Fig. 1.[1]

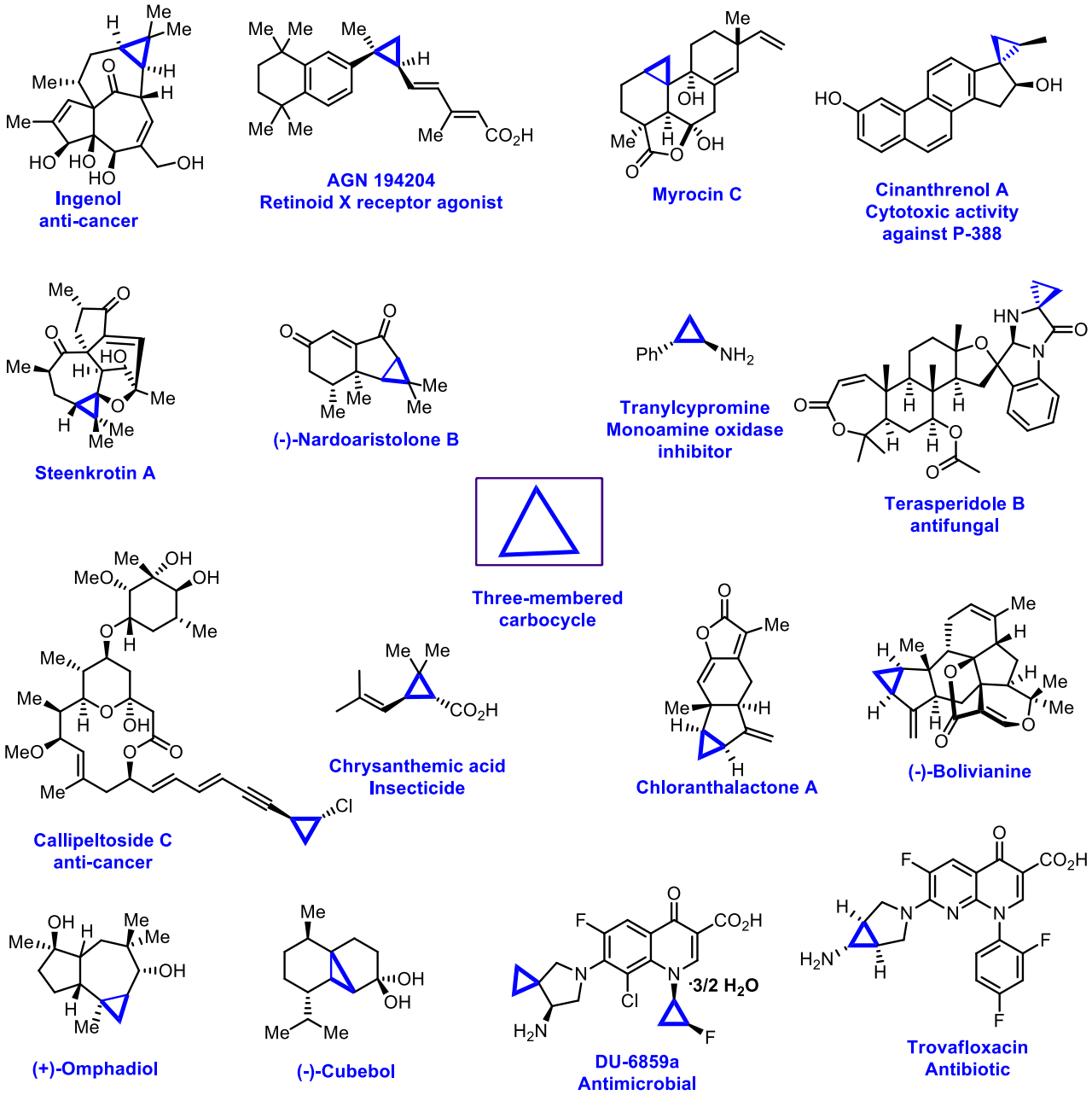
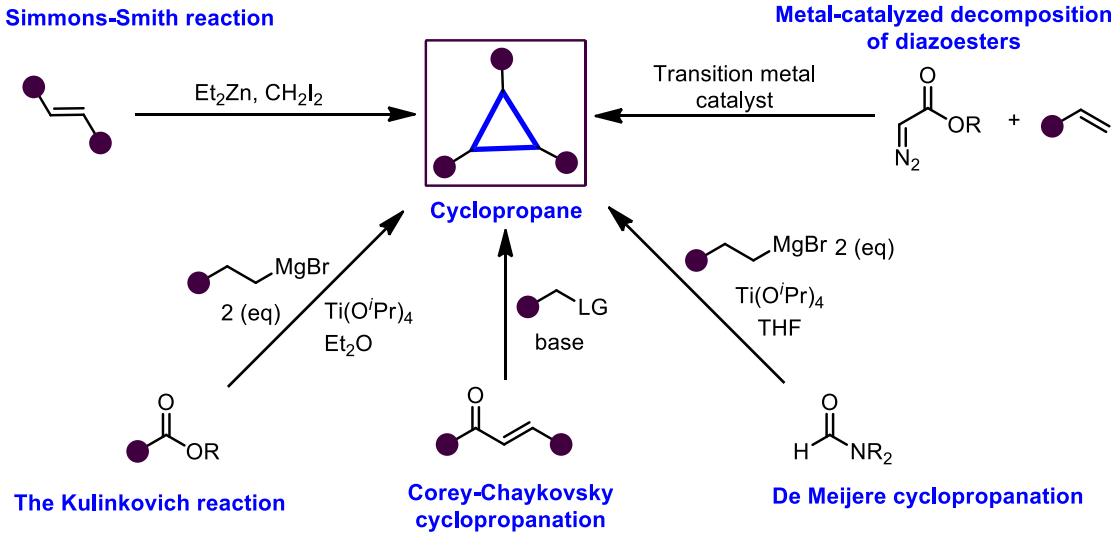


Figure 1: Representative cyclopropane ring containing bioactive natural products

The impressive pharmacological activities and the industrial relevance of cyclopropanes have motivated several researchers to study cyclopropanes and their derivatives. Nowadays, the development of new synthetic methods for the synthesis of cyclopropanes has become a great interest of organic chemists. In the past few decades, multiple numbers of strategies have been developed towards the synthesis of cyclopropanes. Some of the classical synthetic routes for the synthesis of cyclopropanes or their derivatives have included in this context, such as (a) The Simmons-Smith cyclopropanation reaction, (b) The metal-catalyzed cyclopropanation reactions involving the decomposition of diazoesters, (c) The Corey-Chaykovsky cyclopropanation reaction (reactions mediated by ylides), (d) The Kulinkovich cyclopropanation reaction (reactions usually follow the nucleophilic addition-ring closure sequence) and (e) The De Meijere cyclopropanation reaction, Scheme 1.[2] Among all these methods, the Corey-Chaykovsky cyclopropanation reaction is a metal-free cyclopropanation strategy triggered by sulfur ylides.



Scheme 1: Some methods for the synthesis of substituted cyclopropanes

The Corey-Chaykovsky cyclopropanation reaction can be defined as the Michael addition of sulfur ylides to the *α,β*–unsaturated system, and subsequent 1,3-elimination of the leaving group leading to cyclopropanes. This reaction can also be applied for the synthesis of epoxides and aziridines by the addition of sulfur ylides to carbonyls and imines, respectively.[3]

The Corey-Chaykovsky reagents are commonly known as sulfur ylides, one of the most relevant reagents in organic synthesis. They have found wide applications in transition metal catalysis as metal carbenoids and tremendous use in organic transformation as nucleophiles. The

first isolation of sulfur ylides was reported by Ingold and Jessop in 1930.[4] However, the actual stepwise development of the sulfur ylides was initiated from the 1960's towards the synthesis of small carbo- and heterocycles. These ylides could be prepared by the treatment of their salts with an appropriate base at ambient temperature. Structurally they can be defined as the zwitterions that possess the adjacent opposite charges. The zwitterionic ylides have been used so far as nucleophilic one-carbon synthons in most of the relevant organic transformations. The stability of these ylides depends on (a) the nature of substituents attached to the sulfur atom, and (b) delocalization of negative charge constitute by carbon atom over the sulfur atom.

However, depending on their stability, they could be classified into two categories: (i) Sulfonium ylides, and (ii) Sulfoxonium ylides, Fig. 2. The detailed investigation of these two types of ylides passes the information that they are mainly used to synthesize small ring compounds such as epoxides, aziridines, and cyclopropanes. The traditional synthetic methods on cyclopropanations and some unexpected reactions triggered by these nucleophilic ylides are discussed in the next few subsections.

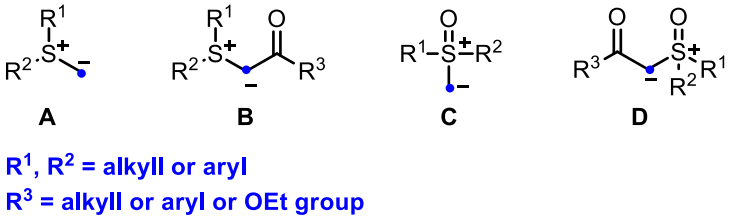
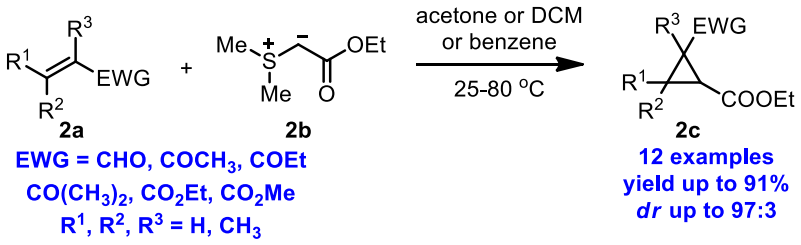


Figure 2: Typical sulfonium and sulfoxonium ylides

1.1. Reactions promoted by sulfur ylides

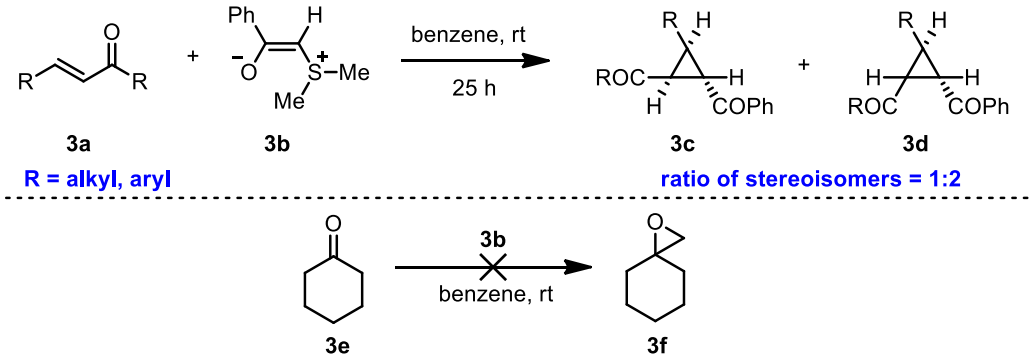
1.1.1. Synthesis of cyclopropanes by sulfonium ylides

In 1967, Payne *et al.*[5] developed the stable sulfonium ylide **2b** and introduced in the cyclopropanation reaction with *α,β*-unsaturated compounds **2a**, Scheme 2. A variety of cyclopropyl derivatives **2c** were synthesized in excellent yields with high diastereoselectivities. In this reaction, it was observed that the stereoisomers where the groups EWG and COOEt are in *trans* to each other predominante over other stereoisomers. In 1969, Amel *et al.* utilized similar sulfonium ylides towards the synthesis of cyclopropanes.



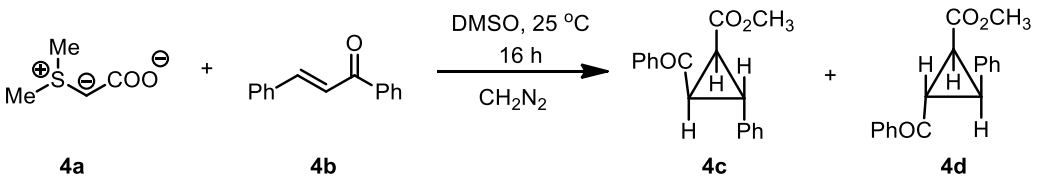
Scheme 2: Payne's synthesis of cyclopropanes

In 1967, Trost *et al.*[6] came up with a new stable sulfonium ylide **3b** and utilized in the synthesis of cyclopropanes **3c** and **3d**, Scheme 3. The reaction of ylide **3b** with chalcones **3a** at rt yielded a mixture of cyclopropanes in the ratio of 1:2. The observation of the formation of cyclopropanes indicates the similar behavior of sulfonium ylide **3b** like typical sulfoxonium ylides. However, the reaction of cyclohexanone **3e** with ylide **3b** failed to give corresponding epoxide **3f** due to less nucleophilicity of the ylide.



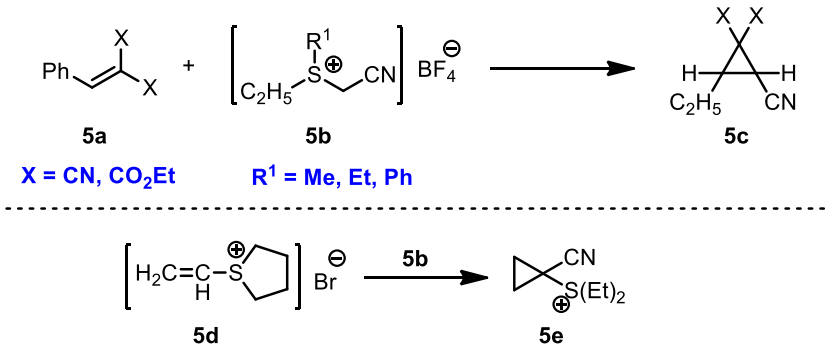
Scheme 3: Trost's synthesis of cyclopropanes

In 1970, Trost *et al.*[7] reported the synthesis of cyclopropane derivatives under very mild reaction conditions. The *α,β*-unsaturated ketone **4b** converted to a variety of cyclopropane carboxylate anions in the presence of stable sulfonium ylide **4a**, Scheme 4. Subsequently, cyclopropane carboxylate anions were transformed into a mixture of cyclopropane derivatives **4c** and **4d** in a 1:1.5 ratio by the treatment with diazomethane.



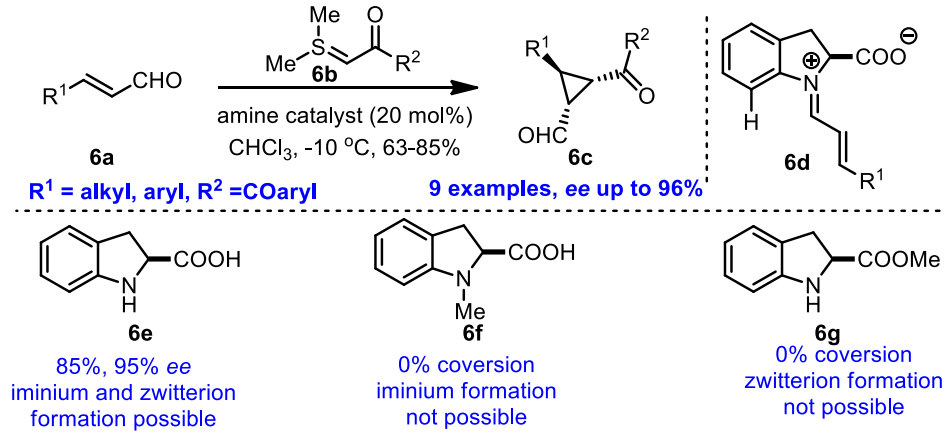
Scheme 4: Trost's synthesis of cyclopropanes

In 1972, Gosselck *et al.*[8] adopted a new stable cyano sulfonium ylides and employed in the cyclopropanation reactions. The reaction of *α,β*-unsaturated compounds **5a** with ylides **5b,** resulted in the formation of cyclopropane derivatives **5c**, Scheme 5. The substrate **5d** also delivered cyclopropane by reacting with the ylide **5b**.



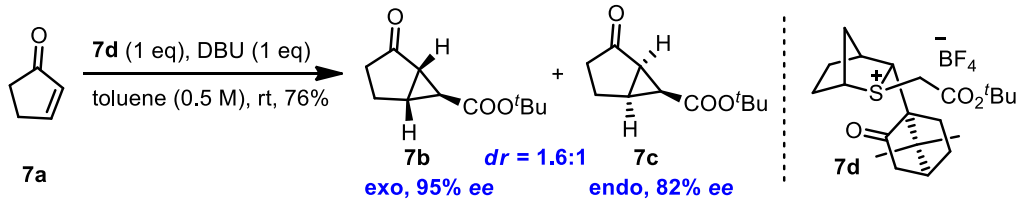
Scheme 5: Gosselck's synthesis of cyclopropanes

In 2005, MacMillan *et al.*[9] documented the cyclopropanation of *α,β*-unsaturated compounds **6a** mediated by stable sulfonium ylides **6b** and organocatalyst **6e** in an enantioselective manner as shown in Scheme 6. Different kinds of cyclopropane derivatives **6c** were prepared in high enantioselectivity *via in situ* formations of iminium and zwitterion intermediate **6d**. The reaction of **6a** could not provide the desired product **6c** when the reaction was catalyzed by **6f** or **6g**, indicating that the formation of iminium and zwitterion is necessary for these transformations.



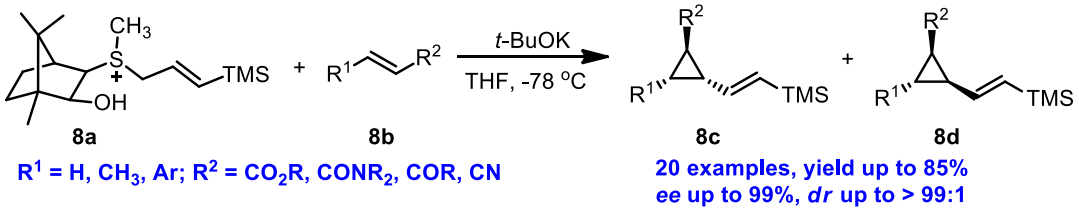
Scheme 6: MacMillan's synthesis of cyclopropanes

In 2006, Aggarwal *et al.*[10] have reported an enantioselective cyclopropanation reaction by utilizing sulfonium salt **7d**, Scheme 7. The reaction involves *in situ* generated ester-stabilized sulfonium ylide from **7d** with cyclopentenone **7a** to produce **7b** and **7c** in good enantioselectivity and low diastereoselectivity. They also applied this strategy to other carbocycles bearing an enone system to generate ester-containing cyclopropanes.



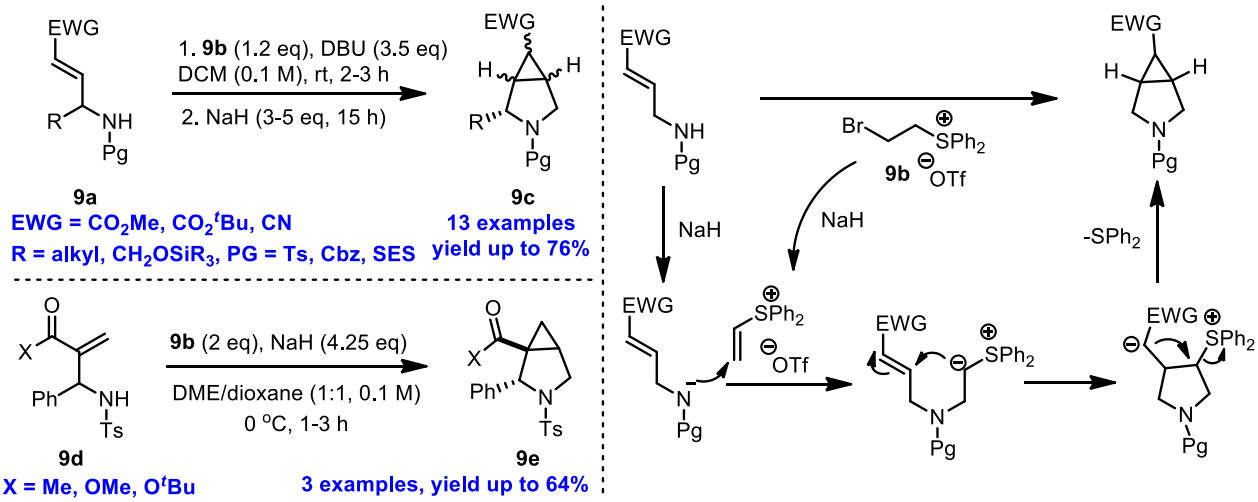
Scheme 7: Aggarwal's enantioselective synthesis of cyclopropanes

In 2006, Tang *et al.*[11] introduced camphor based exo- or endo-sulfonium ylides in the cyclopropanation reaction of *α,β*-unsaturated systems, Scheme 8. The reaction of **8b** with exo-sulfonium salt **8a** in presence of *t*-BuOK delivered the mixture of cyclopropanes **8c** and **8d** in good yields with excellent enantio- and diastereoselectivities. A diverse range of enantiopure vinylcyclopropane derivatives were made by employing these methods with no detectable epoxide formation.



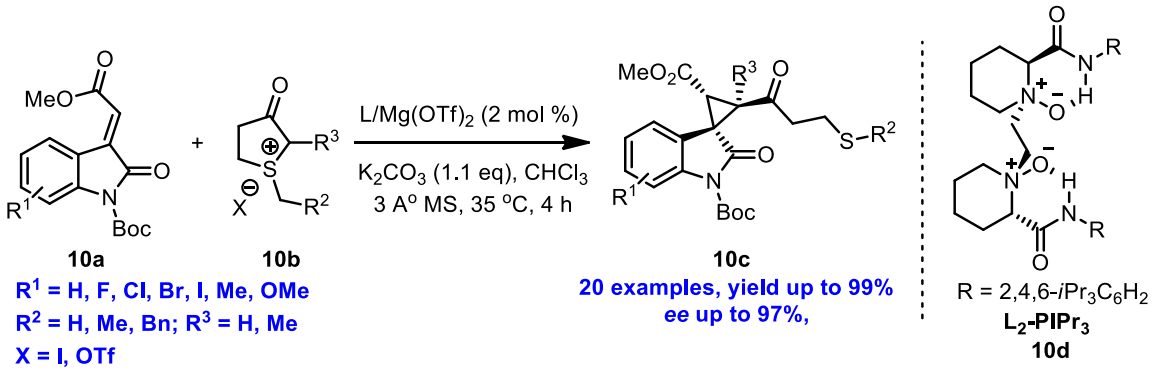
Scheme 8: Tang's synthesis of cyclopropanes

In 2013, McGarrigle *et al.*[3] reported the synthesis of fused cyclopropane derivatives by using sulfonium salt **9b**, Scheme 9. The reaction of **9a** with the sulfonium salt **9b** under the base mediated reaction conditions generated **9c** in moderate to good yields. They employed the same ylide for the conversion of **9d** to **9e** in good yields. The formation of **9c** follows the mechanism described in Scheme 9.



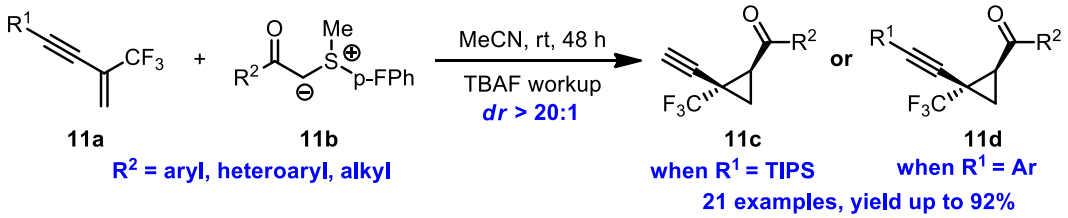
Scheme 9: McGarrigle's synthesis of cyclopropanes

In 2018, Feng *et al.*[12] developed the strategy to generate spiro-cyclopropyloxindoles **10c** in an enantiomeric fashion by utilizing chiral ligand **10d**, Scheme 10. The reaction involves the sulfur ylides (**10b**) ring-opening and asymmetric cyclopropantion reaction of **10a** by employing chiral complex ligand **10d** to access spiro-cyclopropyloxindoles **10c** in excellent yields with high enantioselectivities.



Scheme 10: Feng's asymmetric synthesis of cyclopropanes

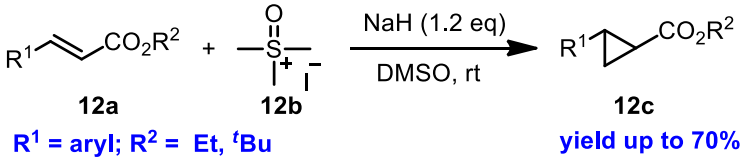
In 2019, Liu *et al.*[13] employed the stable sulfonium ylides **11b** towards the synthesis of cyclopropanes **11c** or **11d** in a diastereoselective manner, Scheme 11. A series of enynes **11a** bearing trifluoromethyl groups were employed under the reaction conditions to deliver cyclopropanes **11c** or **11d** in excellent yields. Herein, the trifluoromethyl group plays an important role in the formation of cyclopropanes. In 2020, Liu *et al.* have reported a similar kind of transformation by using sulfonium ylides.



Scheme 11: Liu's synthesis of cyclopropanes

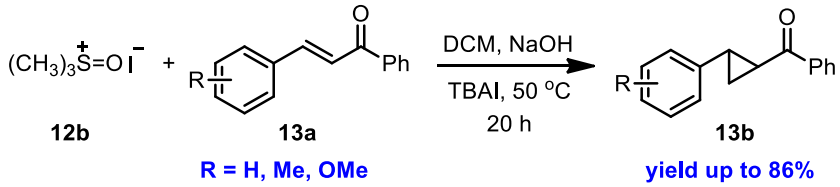
1.1.2. Synthesis of cyclopropanes by sulfoxonium ylides

In 1965, Weinstock *et al.*[14] reported a facile stereoselective synthesis of cyclopropanes **12c** by utilizing trimethylsulfoxonium salt **12b**, Scheme 12. A wide variety of cyclopropane derivatives **12c** were synthesized from a variety of *α,β*-unsaturated esters **12a** under the mild reaction conditions. In this reaction, the product is almost entirely *trans*-selective.



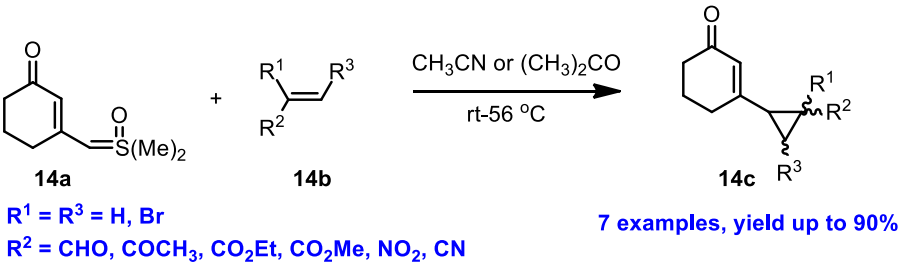
Scheme 12: Weinstock's synthesis of cyclopropanes

In 1973, Markl *et al.*[15] highlighted the formation of cyclopropanes **13b** from the reaction of *α,β*-unsaturated ketones **13a**, and *in situ* generated dimethyloxosulfonium methylide from **12b**, Scheme 13. A variety of enones **13a** were well-tolerated under the reaction conditions.



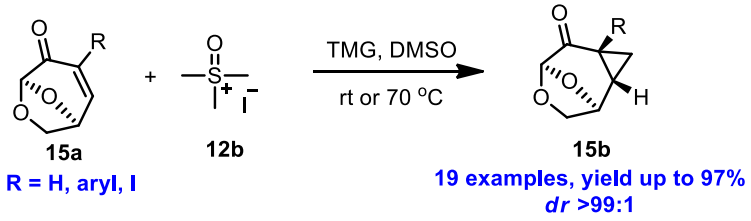
Scheme 13: Markl's synthesis of cyclopropanes

In 1973, Marino *et al.*[16] employed vinyl sulfoxonium ylide **14a** as Michael donor towards the synthesis of vinyl cyclopropanes **14c**, Scheme 14. The treatment of sulfoxonium ylide **14a** with various Michael acceptors **14b** delivered vinyl cyclopropanes **14c** in excellent yields.



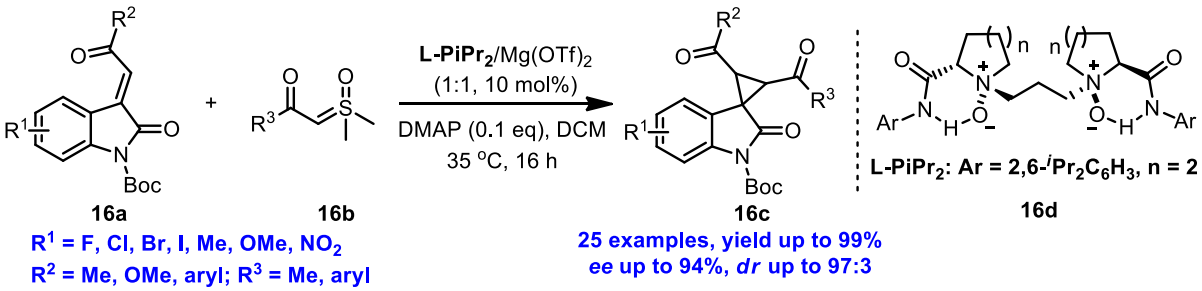
Scheme 14: Marino's synthesis of cyclopropanes

In 2017, Greatrex *et al.*[17] developed the cyclopropanation strategy of (-)-Levoglucosenone derivatives **15a** by utilizing *in situ* generated sulfoxonium ylide from **12b**, Scheme 15. Various Levoglucosenone derivatives **15a** undergo cyclopropanation reaction in the presence of trimethyl sulfoxonium salt **12b** under the 1,1,3,3-tetramethylguanidine (TMG) mediated reaction conditions, which resulted in cyclopropanes **15b** in excellent yields with good diastereoselectivities.



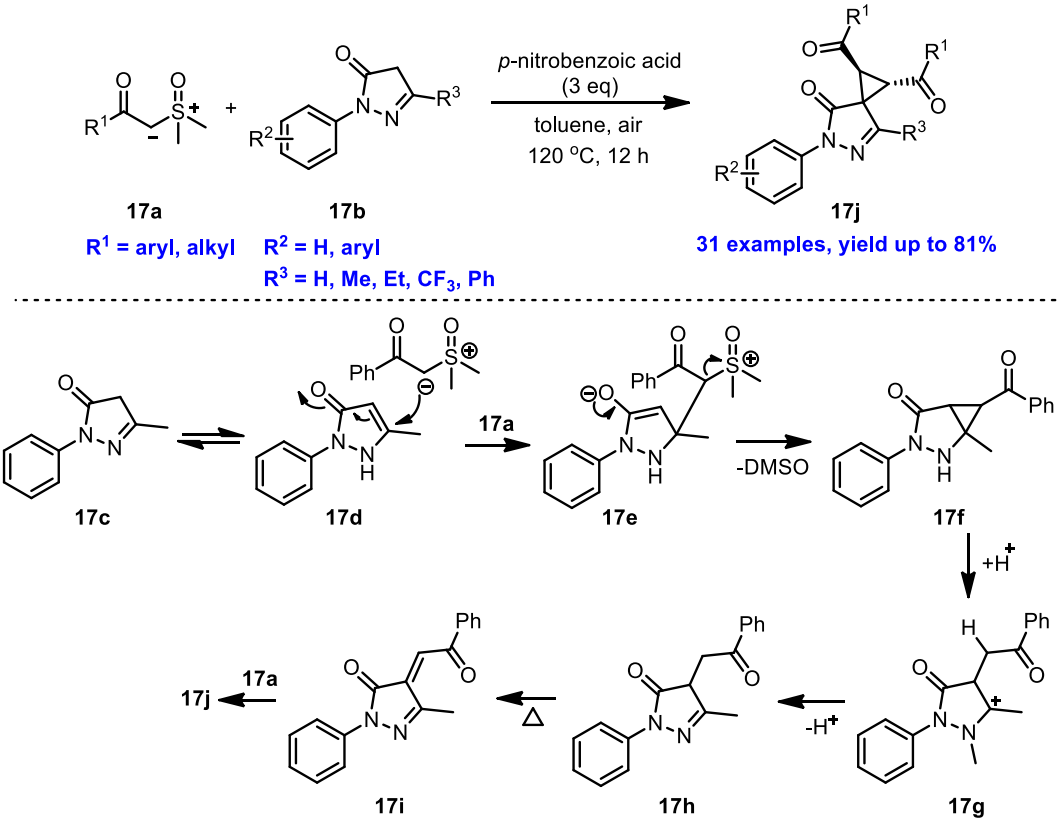
Scheme 15: Greatrex's synthesis of cyclopropanes

In 2018, Cao and Feng[18] have discovered the synthesis of spiro-cyclopropyl oxindoles **16c** from the reaction of sulfoxonium ylides **16b** with oxindoles **16a** in an asymmetric fashion by employing **16d** as the chiral complex catalyst, Scheme 16. A series of oxindoles **16a** and sulfoxonium ylides **16b** were well-tolerated under the reaction conditions to generate spiro-cyclopropyl oxindoles **16c** in excellent yields with high diastereo- and enantioselectivities.



Scheme 16: Cao and Feng's synthesis of cyclopropanes

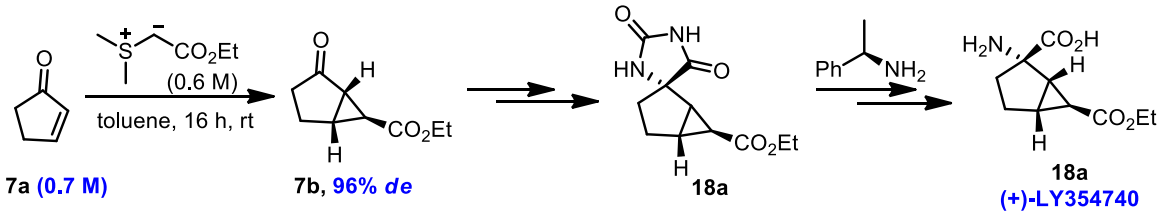
In 2019, Xu *et al.*[19] adopted a one-pot annulation strategy to achieve spiro-cyclopropane skeletons. A variety of spiro-cyclopropane fused pyrazoline-5-one derivatives **17j** were prepared from the reaction of pyrazoline-5-ones **17b** and sulfoxonium ylides **17a** in the presence of an acid, Scheme 17. The following described mechanism explains the formation of the products.



Scheme 17: Xu's synthesis of cyclopropanes

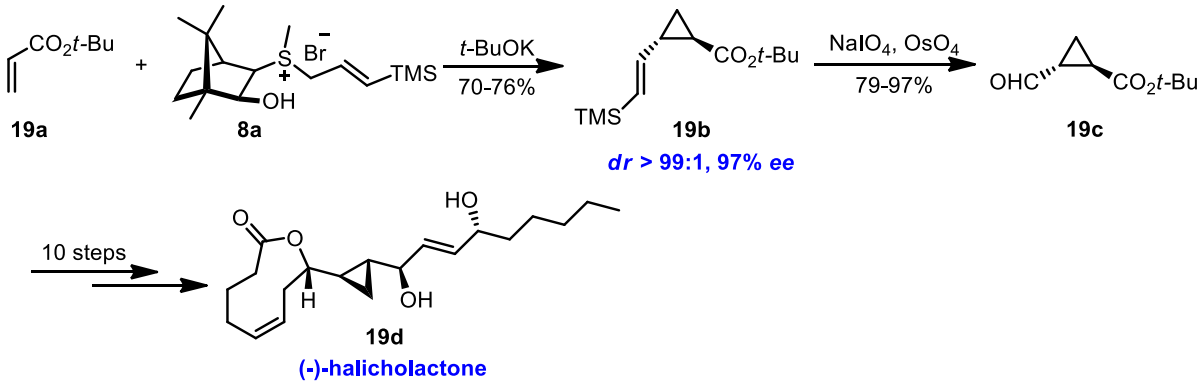
1.2. Applications of sulfur ylides towards the synthesis of natural products

In 2006, Aggarwal *et al.*[10] achieved the stereoselective synthesis of (+)-LY354740 by utilizing sulfonium ylide in the cyclopropanation reaction, Scheme 18. The cyclopropanation of cyclopentenone **7a** in the presence of sulfonium ylide **7d** generated **7b** in high diastereoselectivity. The skeleton of **18a** was constructed after a few synthetic transformations of **7b**. The synthesis of the natural product **18b** was accomplished by a few diastereoselective transformations of **18a**.



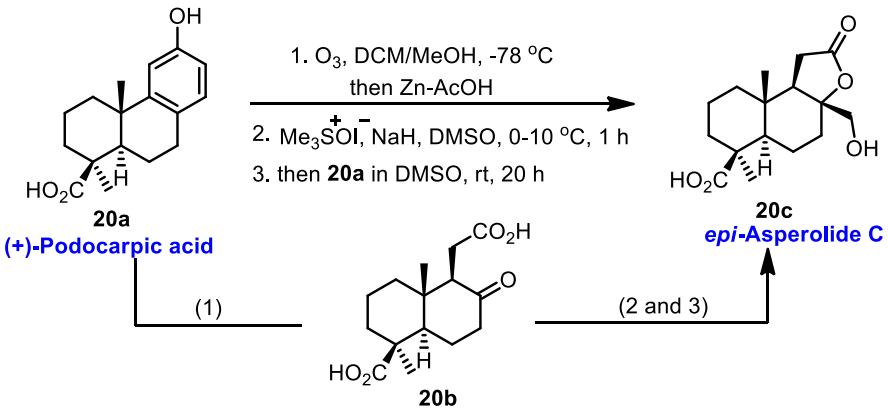
Scheme 18: Aggarwal's stereoselective synthesis of (+)-LY354740

In 2009, Tang *et al.*[20] developed the synthesis of chiral vinyl cyclopropane **19b** by the reaction of camphor derived sulfonium salt **8a** and an acrylate **19a** in the presence of *t*-BuOK, Scheme 19. By employing this strategy, they have adopted the synthesis of (-)-halicholactone **19d**. Towards this, they have converted the vinyl cyclopropane **19b** to **19c** *via* oxidative cleavage of the alkene. Subsequently, the natural product (-)-halicholactone **19d** was achieved by accumulating ten-step synthetic transformations.



Scheme 19: Tang's total synthesis of (-)-halicholactone

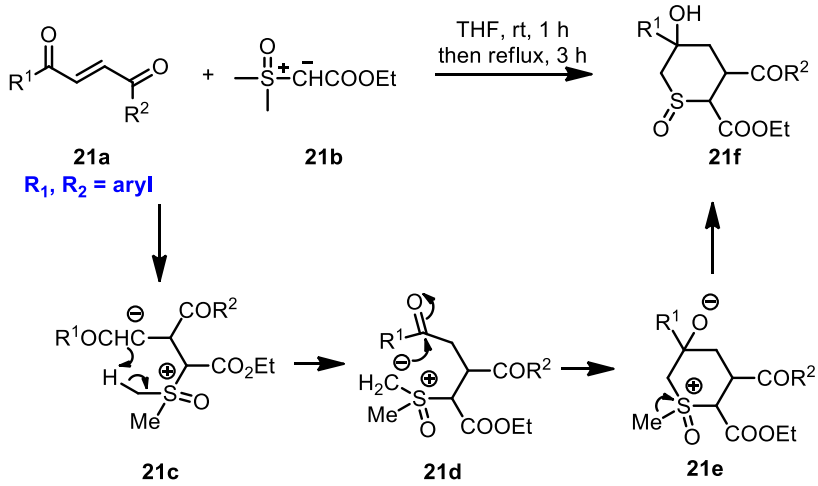
In 2019, Kokotos *et al.*[21] have demonstrated the unusual reaction towards the synthesis of *γ*-lactones enabled by trimethylsulfoxonium ylide and they have applied their strategy towards the total synthesis of the natural product (+)-Asperolide C, Scheme 20. The natural product **20c** could be achieved in a two-step protocol starting from (+)-podocarpic acid **20a**. The ozonolysis reaction of commercially available (+)-podocarpic acid **20a** and subsequent Zn-AcOH mediated reduction of resulting hydroperoxide provided the keto diacid **20b**. In the last step, they employed the lactonization conditions, where the use of trimethylsulfoxonium ylide afforded the product **20c** in 24% yield over two-steps. It was realized that the isolated product **20c** was the epimer of (+)-Asperolide C.



Scheme 20: Kokotos's synthesis of (+)-Asperolide C

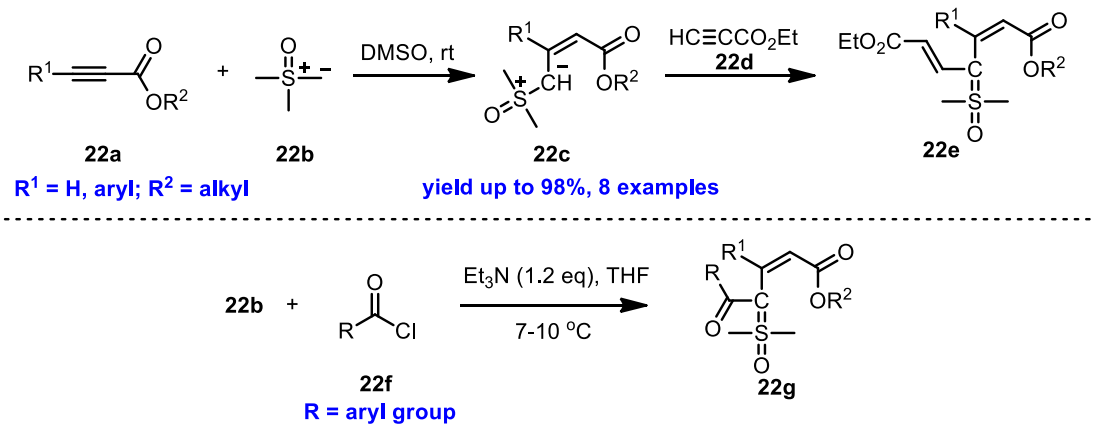
1.3. Unusual reactions mediated by sulfoxonium ylides

In 1967, Nozaki *et al.*[22] developed the construction of six-membered heterocycles *via* an intermolecular ylide (**21b**) addition to chalcones **21a**, Scheme 21. The initial adduct **21c** formed by the Michael addition of the ylide, and it converted to the zwitterion **21d** *via* 1,5-proton shift and subsequent elimination of methyl group delivered **21f** in good yields.



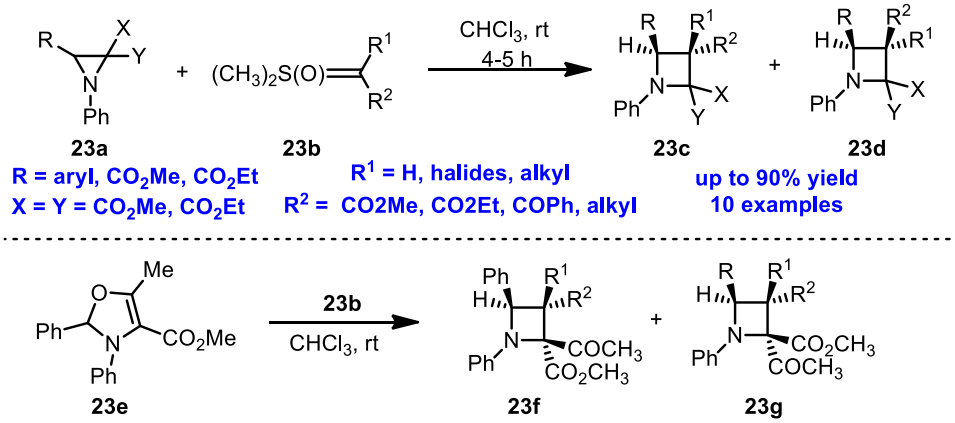
Scheme 21: Nozaki's synthesis of sulfur containing heterocycles

In 1968, Kishida *et al.*[23] reported an unprecedented Michael addition of sulfoxonium ylide **22b** to the activated alkynes **22a** to furnish the sulfoxonium ylides **22c** in good to excellent yields, Scheme 22. Further, the treatment of these products **22c** with different electrophiles **22d** or **22f** lead to the formation of ylides **22e** or **22g**, respectively.



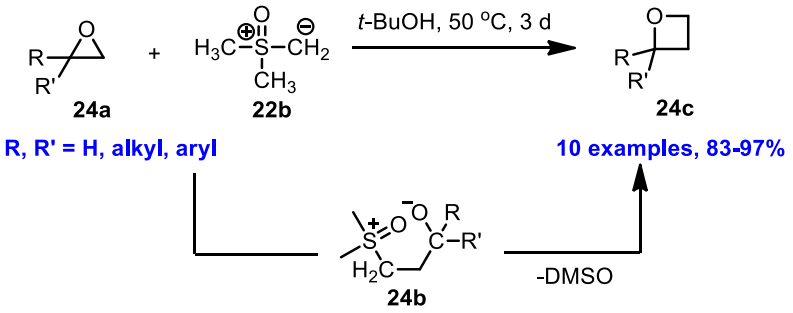
Scheme 22: Kishida's synthesis of stable sulfoxonium ylides

In 1975, Carrie *et al.*[24] first employed the ylides **23b** as a nucleophilic trigger for the ring-opening of aziridines **23a** or 4-oxazoline **23e** to generate the respective epimeric azetidines **23c** and **23d** or **23f** and **23g**, Scheme 23. A series of azetidines were synthesized in good yields owing to their versatility in organic synthesis.



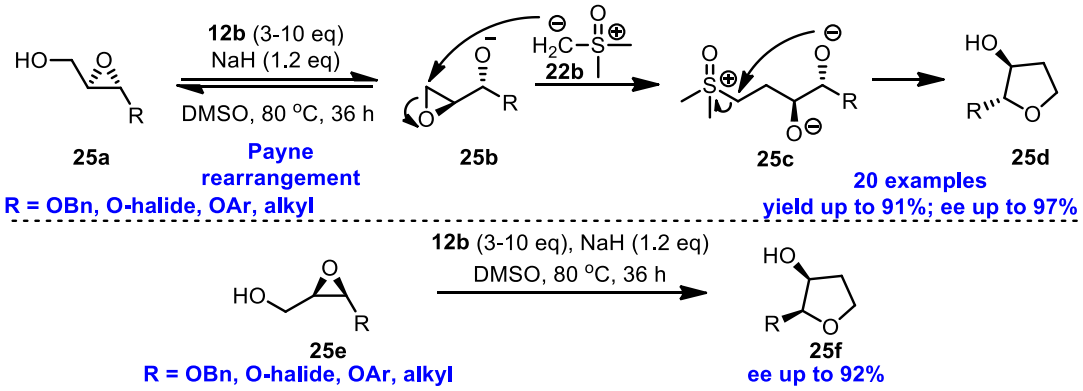
Scheme 23: Carrie's synthesis of azetidines

In 1983, Okuma *et al.*[25] developed the synthesis of oxetanes by utilizing oxosulfonium ylides as methylene group transfer reagent, Scheme 24. The reaction of ylide **22b** with epoxides **24a** afforded the oxetanes **24c** in good to excellent yields. It is believed that the reaction proceeds *via* the formation of the intermediate **24b**. In 1987, Fitton *et al.* also introduced a similar epoxide ring-opening reaction by employing the ylide **22b**.



Scheme 24: Carrie's synthesis of azetidines

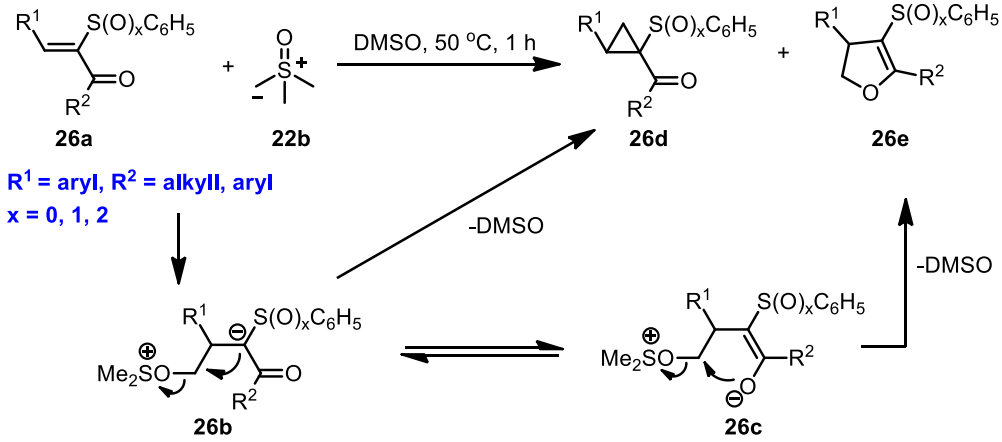
In 2004, Borhan *et al.*[26] docoumented the enantioselective synthesis of 2,3-disubstituted tetrahydrofurans from epoxyalcohols *via* ring expansion assisted by sulfoxonium ylides, Scheme 25. The epoxyalcohols **25a** underwent *in situ* Payne rearrangement in the presence of a base (NaH) to generate **25b**. Subsequent ring-opening of epoxides by ylide **22b** and recyclization provided **25c** in excellent yields and high enantioselectivities. It was observed that the *cis*-disubstituted THFs **25f** and *trans*-disubstituted THFs **25d** were obtained from *cis*-epoxides **25e** and *trans*-epoxides **25a**, respectively.



Scheme 25: Borhan's synthesis of tetrahydrofurans

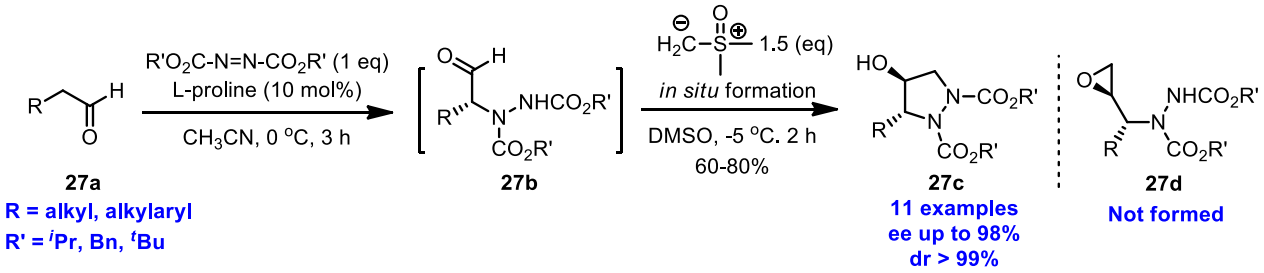
In 2005, Piras *et al.*[27] have demonstrated an unexpected reaction of **26a** by utilizing the Corey's ylide **22b** in a regioselective manner, Scheme 26. The reaction of **26a** with the ylide **22b** furnished a mixture of compounds **26d** and **26e**. The ratio of these compounds (**26d**:**26e**) depends on the nature of R^1 and R^2 or the oxidation state of the sulfur atom. The desired **26d** were obtained most probably through the formation of intermediate **26b**, and the intermediate

26c led to the formation of side products **26e**. In 2014, Budynina *et al.* described a similar cyclization reaction by utilizing the sulfoxonium ylide **22b**.



Scheme 26: Piras's synthesis of dihydrofurans

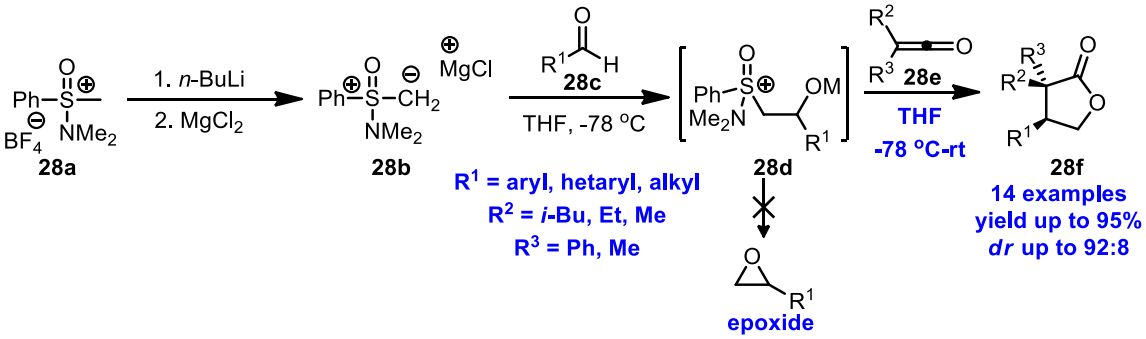
In 2012, Sudalai *et al.*[28] adopted a one-pot process towards the synthesis of 4-hydroxypyrazolidine derivatives **27c** *via* a consecutive *α*–amination and Corey-Chaykovsky reaction of aldehydes **27a**, Scheme 27. However, they did not observe the formation of **27d** in the Corey-Chaykovsky reaction of **27a**. A wide variety of 4-hydroxypyrazolidine derivatives were synthesized with excellent enantio- and diastereoselectivities.



Scheme 27: Sudalai's synthesis of 4-hydroxypyrazolidines

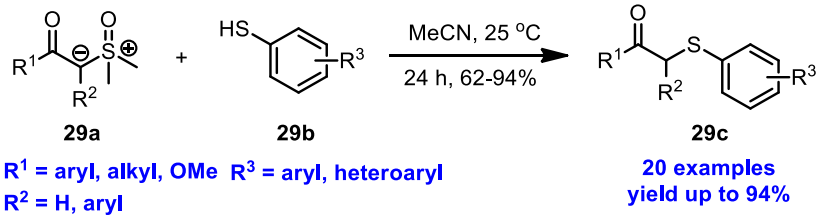
In 2013, Kerrigan *et al.*[29] came up with an intermolecular reaction of sulfoxonium ylide **28b** with aldehydes **28c** and ketenes **28e** that provided *γ*-lactones **28f** in excellent yields and high diastereoselectivities, Scheme 28. The use of metal salt additive plays a vital role in this reaction system. The metal salt $MgCl_2$ mainly activates the aldehydes to increase the yield of the products

28f. The mild reaction conditions (-78 ^{o}C) suppressed the formation of epoxide from the intermediate **28d**.



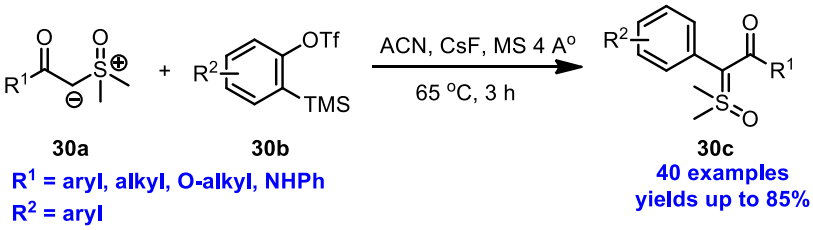
Scheme 28: Kerrigan's synthesis of γ-lactones

In 2016, Burtoloso *et al.*[30] highlighted the use of sulfoxonium ylides **29a** to access β–keto thioesters **29c** from aryl thiols **29b**, Scheme 29. The reaction involves the initial protonation of ylides **29a** facilitated by acidic aryl thiols **29b** to liberate sulfoxonium salt and nucleophilic thiolate. Subsequent nucleophilic attack of thiolate to sulfonium salt leads to the formation of **29c** through the displacement of DMSO. The reaction conditions are straightforward and no need for extra catalysts for these transformations.



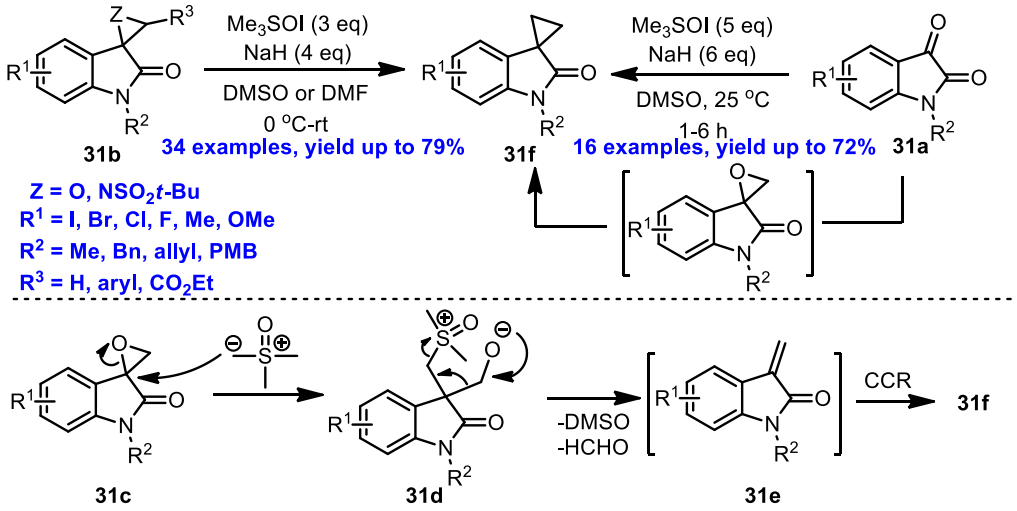
Scheme 29: Burtoloso's synthesis of β–keto thioesters

In 2018, Burtoloso *et al.*[31] described the reaction of sulfoxonium ylides **30a** and *in situ* generated arynes from **30b** towards the synthesis of α-aryl-β-ketosulfoxonium ylides **30c** in good yields, Scheme 30. A series of α-aryl-β-ketosulfoxonium ylides were accessed by employing this strategy under mild reaction conditions. This reaction has an advantage; α-aryl-β-ketosulfoxonium ylides could not be accessed by performing the reactions with sulfonium ylides or diazo ketones.



Scheme 30: Burtoloso's synthesis of aryl ketosulfoxonium ylides

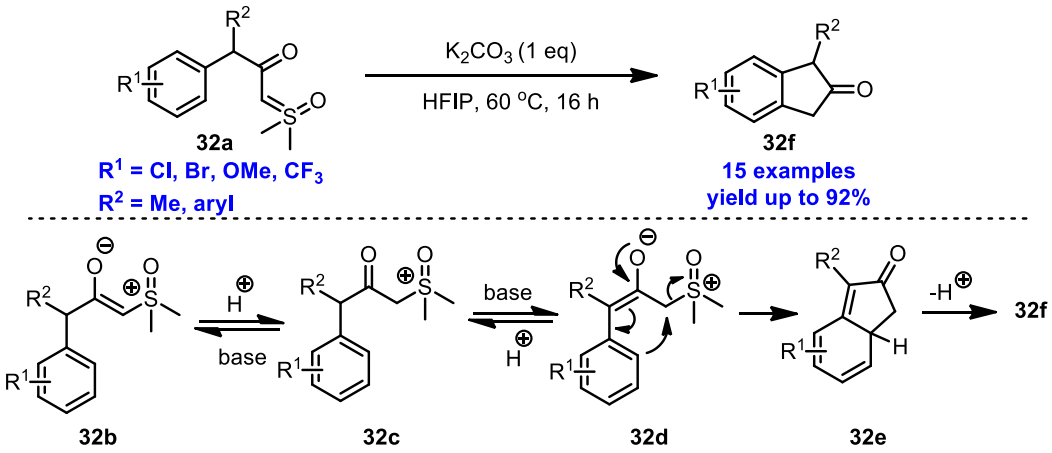
In 2018, Hajra *et al.*[32] have demonstrated the one-pot synthesis of spiro cyclopropyl oxindoles **31f** through the Corey-Chaykovsky reactions (CCR) from isatins **31a** or spiroepoxy- or spiroaziridine oxiindoles **31b**, Scheme 31. The nucleophilic attack of the ylide **22b** to epoxide resulted in the formation of **31d**, which upon subsequent elimination of DMSO and HCHO provided **31e**. The intermediate **31e** followed by CCR delivered **31f**. On the other hand, the conversion of isatins **31a** to **31f** involves a consecutive CCR involving the intermediate **31c**.



Scheme 31: Hajra's synthesis of spirocyclopropyl oxindoles

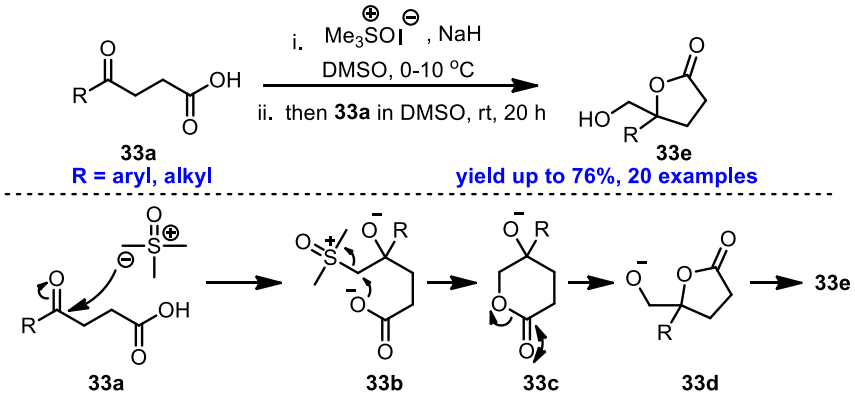
In 2019, Aissa *et al.*[33] utilized *α*-carbonyl sulfoxonium ylides **32a** towards the cyclization reactions in the presence of a base and HFIP at 60 ºC for 16 h, Scheme 32. Thus, the reaction of ylides **32a** under K_2CO_3/HFIP reaction conditions delivered **32f** *via* intramolecular cyclization. Similar product formation was observed in the case of bezofurans and *N*-*p*-toluenesulfonyl indoles in the presence of K_2CO_3/HFIP. In the absence of HFIP, no product formation was

observed, which indicates the HFIP has a crucial role in this transformation. The proposed mechanistic pathway in Scheme 32 supports for the conversion of **32a** to **32f**.



Scheme 32: Aissa's cyclization reaction of *α*-keto sulfoxonium ylides

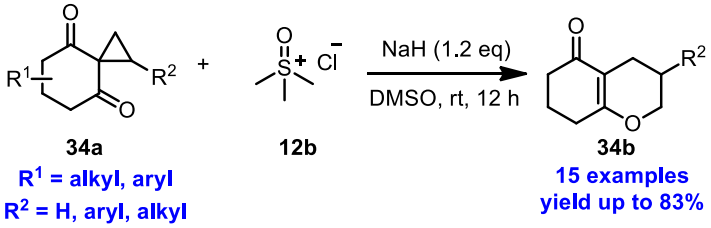
In 2019, Kokotos *et al.*[21] designed ketoacids **33a** that undergo cyclization reactions by employing dimethyloxosulfonium methylide **22b** (Corey's ylide), Scheme 33. The ketoacids **33a** under the Corey-Chaykovsky reaction conditions furnished *γ*-lactones **33e** in good yields. The reaction proceeds by initial nucleophilic attack of the ylide **22b** to generate **33b**, which through cyclization/recyclization and protonation afforded *γ*-lactones **33e**.



Scheme 33: Kokotos's synthesis of *γ*-lactones

In 2020, Yakura *et al.*[34] have developed the synthesis of substituted benzopyran-5-ones **34b** *via* ring-opening and recyclization of spirocyclopropanes **34a** enabled by sulfoxonium ylide

22b generated from **12b**, Scheme 34. A wide range of benzopyran-5-ones **34b** were synthesized in good to excellent yields by cyclopropane ring-opening in a regioselective manner.



Scheme 34: Yakura's synthesis of benzopyran-5-ones

Thus, despite tremendous advancements in sulfur ylide chemistry, there still remains lack of efficient processes to achieve the complex molecular architecture. Thus, the background of the sulfur ylide chemistry inspires us to emerge the development in sulfur chemistry by contributing easy and straightforward synthetic strategies.

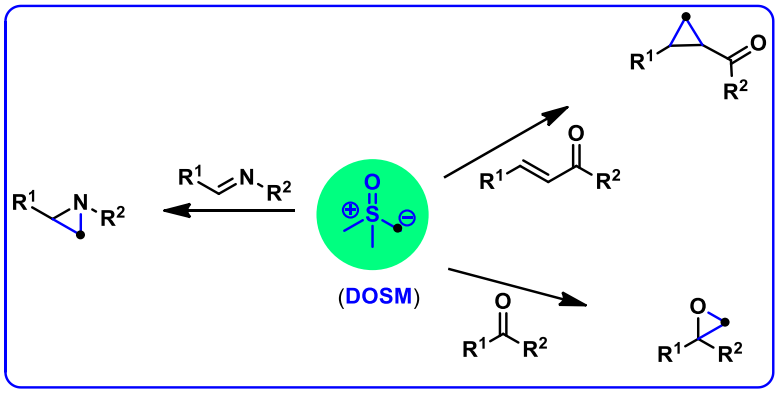
Section 2

Unexpected reactions mediated by the Corey-Chaykovsky reagent: Synthesis of unusual cyclopropanoids

Over many decades, small yet complex molecular scaffolds have attracted the attention of the scientific community because of their biological significance in several drug discovery programs.[35] However, increasingly complex biological targets have evolved, which involve tougher challenges in the development of new synthetic strategies. Therefore, it is essential to develop contemporary and relevant approaches to liberate novel molecular architectures. In the past few decades, several methods have been developed to achieve complex molecular architecture. Among them, organic transformations mediated by sulfur ylides have played significant roles in organic synthesis.[36]

Sulfur ylides are the most useful reagents in organic synthesis.[37] Typically, they can be described as carbanions connected to an adjacent sulfur atom bearing positive charge. Their stability mainly depends on the nature of substitutions attached to the sulfur atom and electronic delocalization in the molecular structure. As for example, ketosulfonium and ketosulfoxonium ylides are comparatively most stable than typical sulfur ylides, herein the presence of a heteroatom connected to the sulfur center enhances stability of the ylides. However, among the sulfur ylides, dimethyloxosulfonium methylide (DOSM) is a versatile methylene group transfer agent commonly famous as Corey-Chaykovsky reagent, which can be easily prepared *in situ* reaction from trimethysulfoxonium iodide.[14]

The chemistry involving these ylides has emerged dramatically over the last 50 years since the pioneering work of Johnson, Corey and Chaykovsky in the 1960s (Johnson-Corey-Chaykovsky reaction).[38] The Johnson-Corey-Chaykovsky reaction involves the reaction of sulfur ylide with electrophiles such as carbonyls, imines and electron-deficient olefins, which result in the formation of corresponding epoxides, aziridines and cyclopropane derivatives, respectively, Scheme 35.[39]

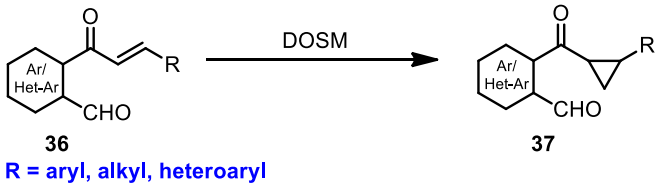


Scheme 35: Common synthetic applications of the Johnson-Corey-Chaykovsky reaction

Among the privileged compounds, cyclopropanes have always fascinated the organic chemists.[40] The high level of strain and conformational rigidity of cyclopropanes offer the distinct properties to medicinal chemists. Further, several biologically active natural products and pharmaceutically relevant compounds along with many marketed drugs possess cyclopropane structural units.[41] Consequently, they have found widespread application in modern synthetic organic chemistry. Because of their unique steric and electronic properties, the

strained three-membered carbocycles can be converted to new molecular entities by a variety of ring opening transformation.[42] These impressive features motivated organic chemists to develop inspirational methods for the synthesis of cyclopropanes.

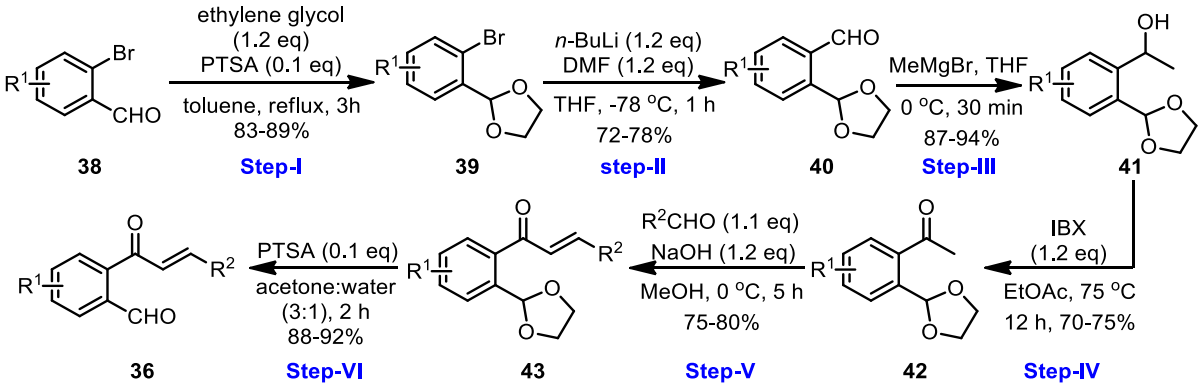
As part of our ongoing research programs,[43] it necessitated us to access the cyclopropyl keto-aldehydes **37**. Thus, towards the synthesis of the cyclopropyl keto-aldehydes **37**, we intended to perform the cyclopropanation reaction of enone-aldehydes **36** with DOSM (Corey's ylide) as depicted in Scheme 36.



Scheme 36: Hypothesis to access the cyclopropyl keto-aldehydes **37**

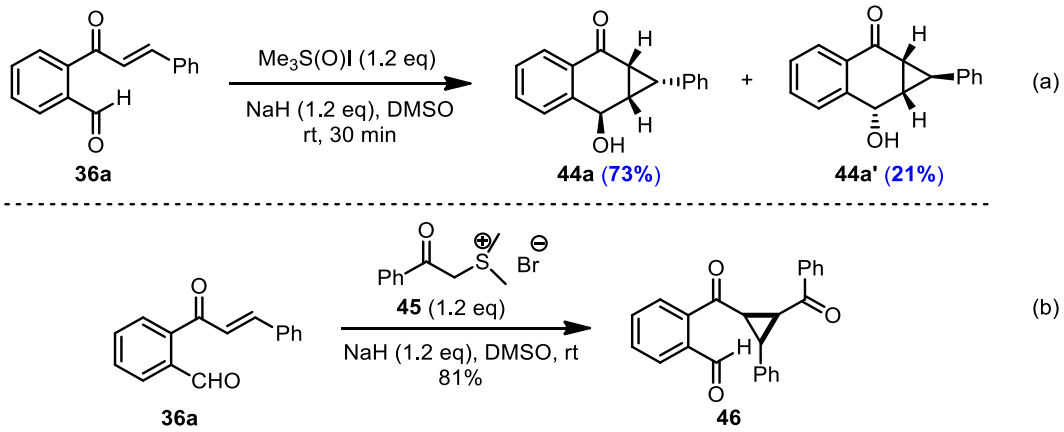
2.1: Results and discussions

With the desire to access the cyclopropyl keto-aldehydes of the type **36b** *via* Corey-Chaykovsky reaction, we have initiated the studies to synthesize the proposed enone-aldehydes **36**, Scheme 37. The enone-aldehydes **36** can be easily synthesized by an efficient six-step protocol starting from 2-bromobenzaldehydes **37**. The reaction of **37** with ethylene glycol in the presence of a catalytic amount of PTSA afforded 2-bromoacetals **38**. *n*-Butyllithium-mediated formylation of **38** generated **39**, which upon treatment with MeMgBr yielded **40**. The IBX oxidation of **40** afforded ketones **41**. Subsequent aldol condensation reaction of **41** with appropriate aldehydes under basic conditions delivered corresponding **42**. Finally, PTSA-mediated deprotection of the acetal functionality in **42** produced desired enone-aldehydes **36**.



Scheme 37: Synthesis of the enone-aldehydes **36**

After the successful synthesis of the enone-aldehyde **36a**, we performed the cyclopropanation reaction as shown in Scheme 38 (a). But the reaction failed to give the desired cyclopropyl keto-aldehyde **37a** (when R = Ph). However, unexpected products **44a** and **44a'** were isolated in 5:1 diastereomeric ratio in 94% (combined yield). Surprisingly, while the cyclopropyl keto-aldehyde **36a** was treated with a stabilized ylide such as **45**, it resulted in the formation of cyclopropane **46** in 81% yield, Scheme 38 (b).[44]

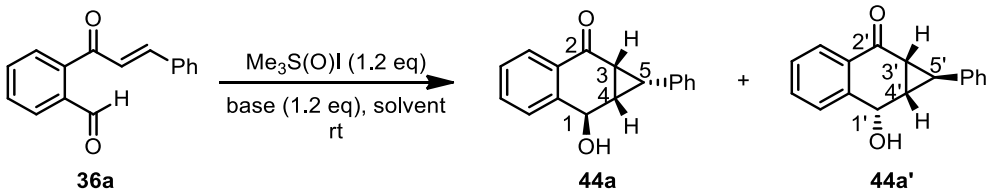


Scheme 38: Corey-Chaykovsky reaction with the substrate **36a**

Having realized the unprecedented nature of the formation of **44a**, we initiated the optimization study by choosing 2-cinnamoylbenzaldehyde **36a** as a model substrate. A variety of bases and solvents combinations were tested and the results are compiled in Table 1. Among the commonly employed Brønsted bases (KOH, K_2CO_3, K^{t}OBu, NaH), NaH was found to be most effective to deliver the desired product **44a** in very good yields, Table 1. The structure of cyclopropanoids **44a** and **44a'** were carefully deduced from the IR, NMR, and HRMS data. The presence of a broad absorption band at 3398 cm^{-1} indicates the presence of secondary alcohol and a sharp band at 1661 cm^{-1} is the indication of the presence of a carbonyl group in the IR spectrum, which indicates the formation of the product **44a**. In the ^{1}H-NMR spectrum (see Fig. 3), the presence of a singlet at δ 5.18 ppm indicates C-1 methine proton, a broad singlet at δ 3.26 ppm indicates the presence of -OH functionality, a triplet at δ 6.84 ppm indicates C-4 methine proton and a multiplet at δ 2.63-2.51 ppm indicates C-3 and C-5 methine protons. In ^{13}C-NMR spectrum (see Fig. 4), presence of a peak at δ 196.6 ppm indicates the presence ketone (C-2), a peak at δ 66.1 ppm indicates carbon (C-1) and the peaks at δ 29.5, 28.3, 27.3 indicate the respective cyclopropane carbons (C-3, C-4, C-5). Thus the ^{1}H- and ^{13}C-NMR data confirmed the

formation of the product **44a**. The assigned structure of **44a** was further confirmed by HRMS data which showed the presence of a protonated molecular ion peak at m/z 251.1081 $(M+H)^+$ corresponding to the formula $C_{17}H_{15}O_2$ with the calculated value of 251.1072.

Table 1: Optimization of reaction parameters with **36a**



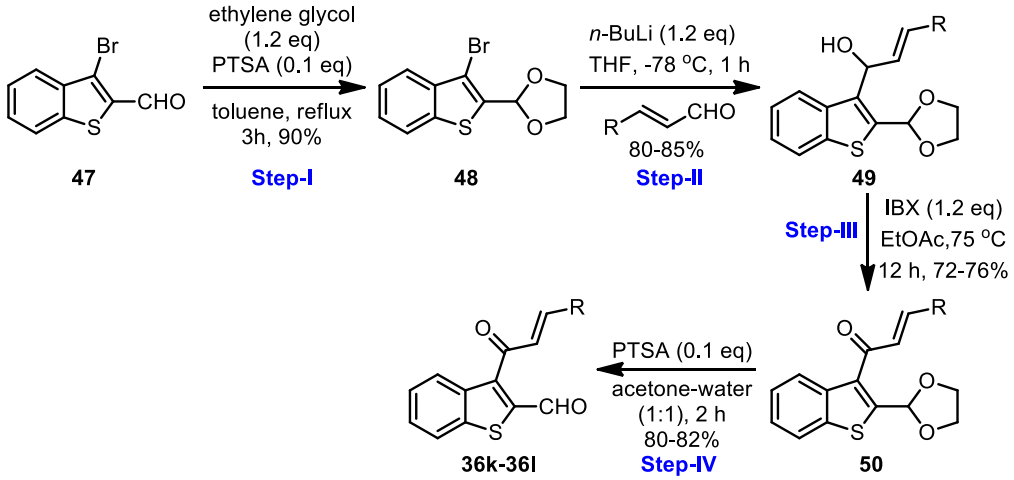
36a **44a** **44a'**

Entry	Base	Solvent	Time (h)	Yield[a] (%) (44a/44a')
1	KOH	DMSO	1	53/10
2	K_2CO_3	DMSO	1	34/7
3	**NaH**	**DMSO**	**0.5**	**73/21**
4	K^{t}OBu	DMSO	0.5	70/16
5	NaH	DMF	1	71/19
6	NaH	THF	1	Trace/-
7	NaH	1,4-dioxane	1	-
8	NaH	Toluene	1	-
9	NaH	Nitroethane	1	-
10	NaH	Chloroform	1	Trace/-

The other diastereomer **44a'** was also confirmed by the IR, NMR, and HRMS data. The presence of a broad absorption band at 3388 cm^{-1} indicates the presence of secondary alcohol and a sharp band at 1664 cm^{-1} is the indication of the presence of a carbonyl group in the IR spectrum, which indicates the formation of the product **44a'**. In the ^{1}H-NMR spectrum (see Fig. 5), presence of a doublet at δ 5.38 ppm indicates C-1' methine proton, a multiplet at δ 2.68-2.56 ppm indicates C-3' and C-4' methine protons, a multiplet at δ 2.55-2.49 ppm indicates C-5' methine proton and a broad singlet at δ 2.43 ppm indicates the presence of -OH functionality. In ^{13}C-NMR spectrum (see Fig. 6), appearance of a peak at δ 194.2 ppm indicates the presence of an unsaturated ketone (C-2'), a peak at δ 65.5 ppm indicates methine carbon (C-1') and the peaks

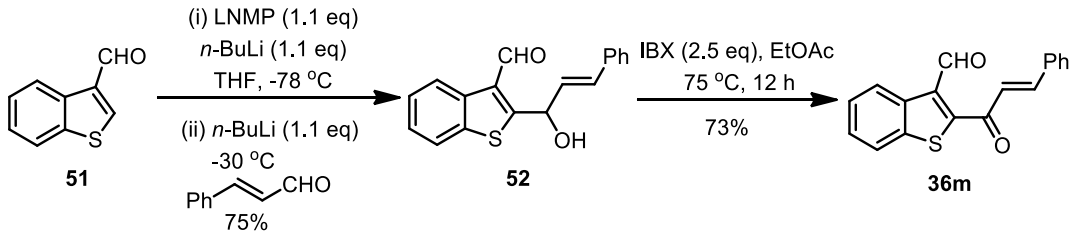
at δ 36.1, 29.7, 29.2 ppm indicate the cyclopropane carbons (C-3', C-4', C-5'). Thus the ^{1}H- and ^{13}C-NMR data and also the HRMS data indicated the formation of product **44a'**.

With the optimal reaction condition in hand, we next investigated the scope and generality of the reaction. Towards this, a variety of enone-aldehydes appended to the aromatic backbone were synthesized by following the six-step protocol described in Scheme 37. Benzothiophene-based substrates were accessed by following either a four-step protocol (Scheme 39) or a two-step protocol (Scheme 40). The enone-aldehydes **36k-36l** can be easily prepared from 3-bromo-benzothiophene-2-carboxaldehyde **47**. The PTSA-catalyzed aldehyde protection of **47** in the presence of ethylene glycol delivered the formation of bromoacetal **48**. The *n*-BuLi mediated alkylation of **48** in the presence of appropriate enals generated allyl alcohols **49**. Subsequently, the IBX oxidation of **49** at 75 ^{o}C afforded enones **50**, which followed by acetal deprotection in the presence of the catalytic amount of PTSA provided the enone-aldehydes **36k-36l**.



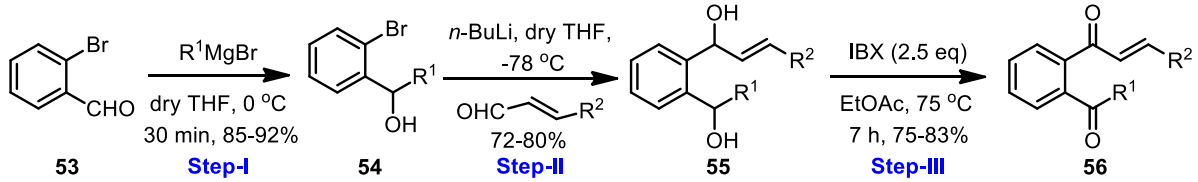
Scheme 39: Synthesis of enone-aldehydes **36k-36l**

The enone-aldehyde **36m** was prepared by following the literature method.[45] *n*-BuLi mediated C-2 alkylation of 3-benzothiophene carboxaldehyde **51** with appropriate enal provided allyl alcohol **52** through *in situ* masking of aldehyde functionality by lithium N-methylpiperazine (generated from NMP and *n*-BuLi). The allyl alcohols **52** followed by IBX oxidation generated desired enone-aldehyde **36m**.



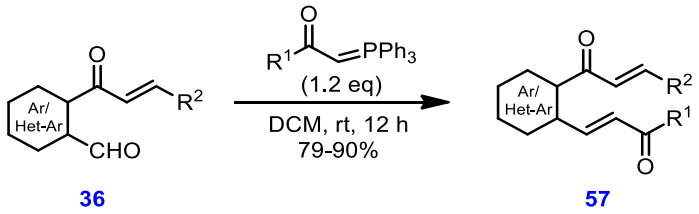
Scheme 40: Synthesis of the enone-aldehyde **36m**

On the other hand, the enone-ketones **56** can be synthesized by following a three-step protocol starting from *o*-Bromobenzaldehydes **53**, Scheme 41.[45] The Grignard reaction of 2-bromobenzaldehydes **53** generated 2-bromobezyl alcohols **54**. Direct alkylation of **54** formed diols **55** under the *n*-BuLi mediated reaction. The IBX mediated oxidation of diols **55** delivered desired enone-ketones **56**.



Scheme 41: Synthesis of enone-ketones **56**

The substrates bearing enone-enone functionality could be achieved by following a one-step protocol starting from the enone-aldehydes **36**, Scheme 42. The treatment of Wittig salt with the enone-aldehydes **36** at room temperature delivers the desire enone-enones **57**. By following this protocol, we have synthesized a wide variety of enone-enones **57a-57j**.



Scheme 42: Synthesis of enone-enones **57**

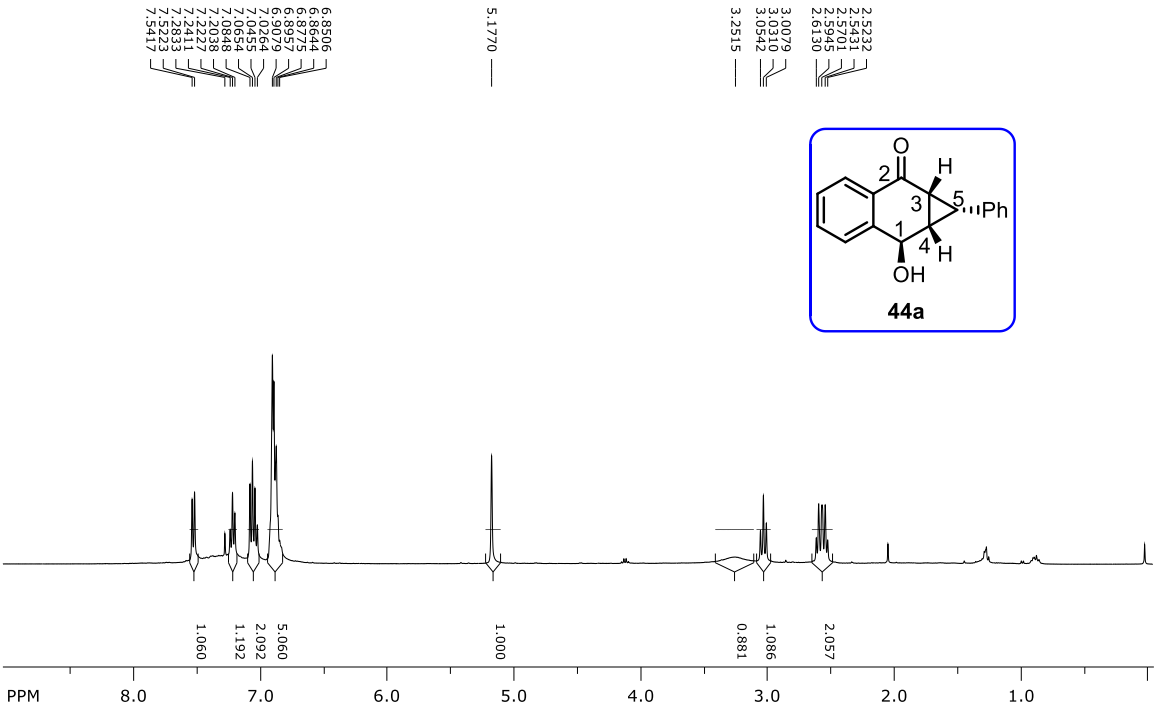


Figure 3: ^{1}H-NMR spectrum of **44a**

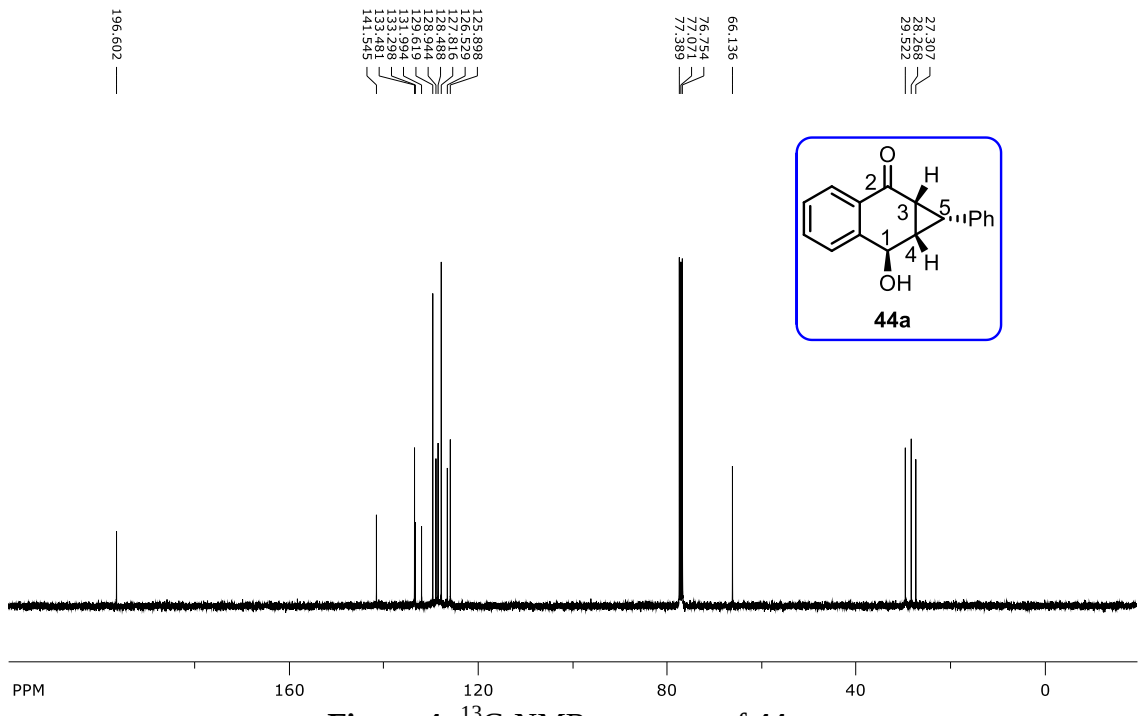


Figure 4: ^{13}C-NMR spectrum of **44a**

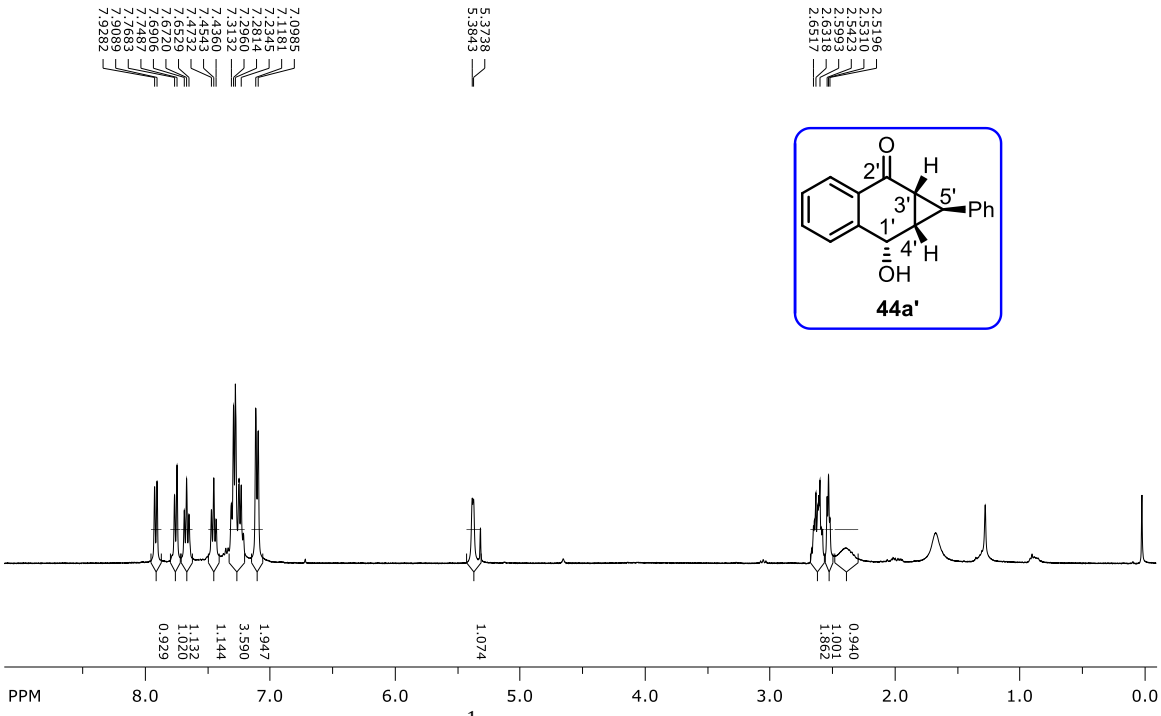


Figure 5: ^{1}H-NMR spectrum of **44a'**

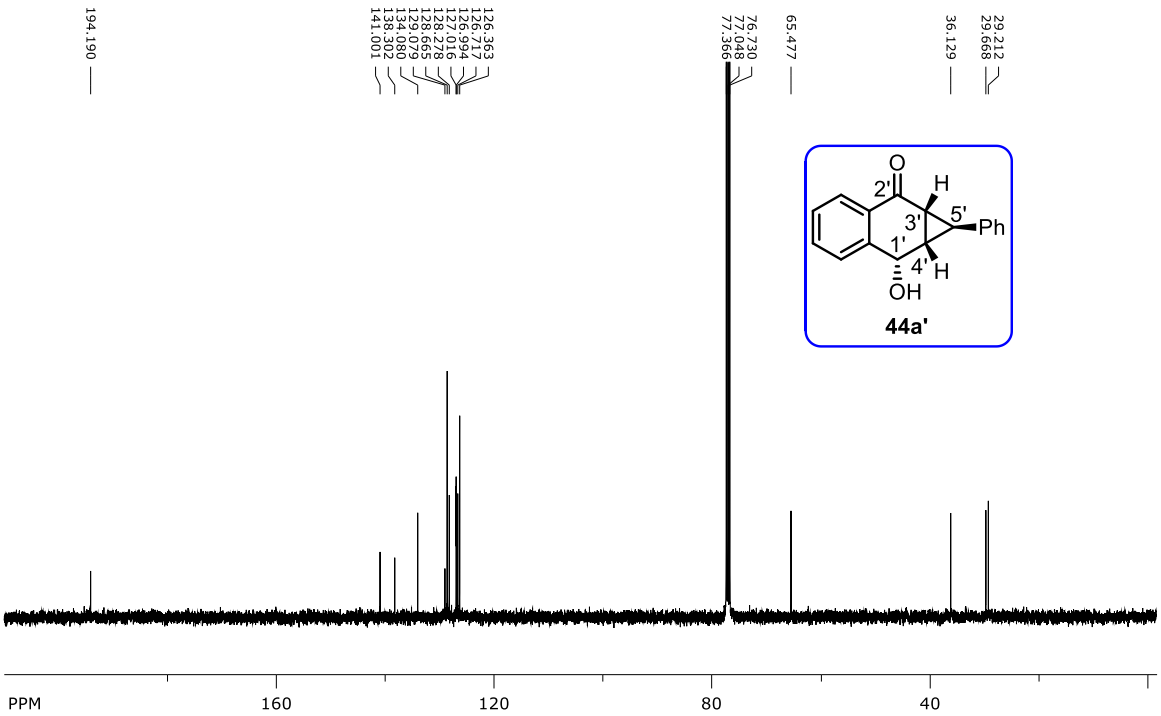


Figure 6: ^{13}C-NMR spectrum of **44a'**

A wide range of enone-aldehydes were subjected to the optimized reaction conditions to generate the respective cyclopropa-fused tetralones **44b-44m** in good to excellent yields, Table 2. The substrates containing electron-donating and electron-withdrawing substituents on the enone moiety as well as on the aromatic backbone were well-tolerated under the optimized conditions. The substrate with an aliphatic group on the enone moiety also delivered the respective cyclopropa-fused tetralone **44h** in excellent yield. To further extend our strategy, the *β*-alkyl and *β*-aryl-substituted enones appended to benzothiophene **36k-36m** were subjected to the optimized conditions and generated the respective tetralones **44k-44m** in good to excellent yields. The fluorinated compounds are very important due to their unique biological properties. Therefore, fluorinated cyclopropa-fused tetralones **44d and 44i** were also accessed by this method in excellent yield. The structure of the major diastereomer and the relative stereochemistry was confirmed from the X-ray diffraction analysis of **44a** and assigned to other products in analogy, Fig. 7.

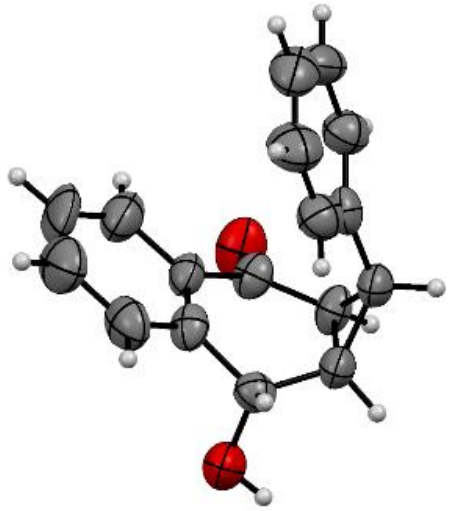
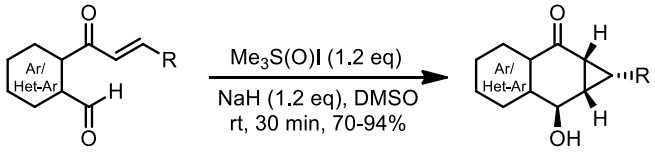
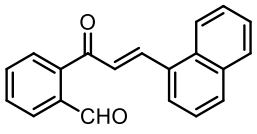
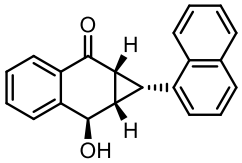
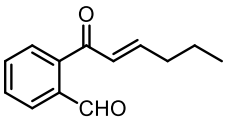
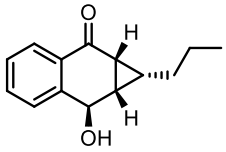
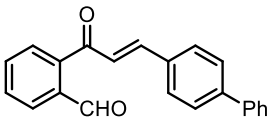
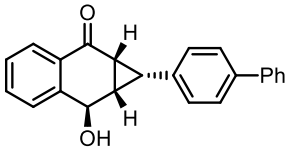
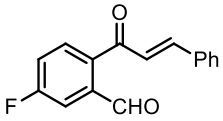
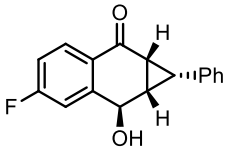
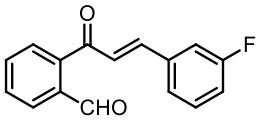
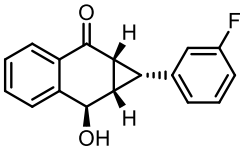
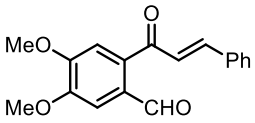
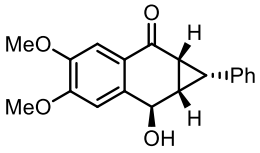
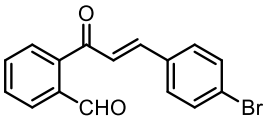
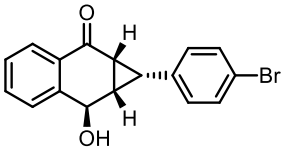
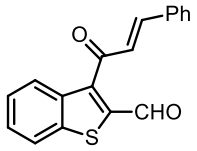
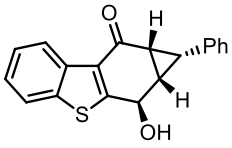
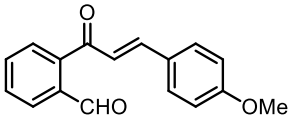
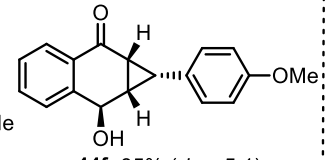
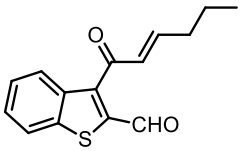
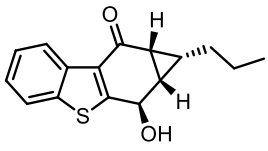
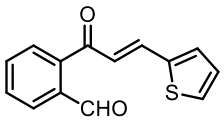
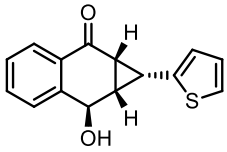
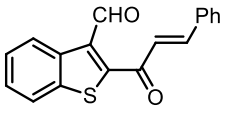
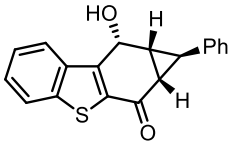


Figure 7: ORTEP diagram of **44a**, ellipsoid probability (50%)

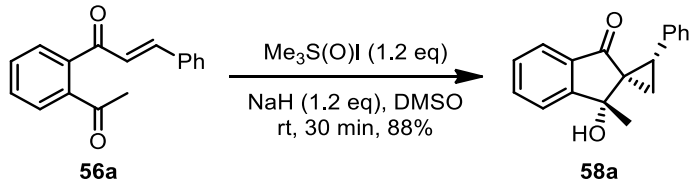
Table 2: Reactions of enone-aldehydes under the optimized conditions



36 **44**

Entry	Substrate	Product	Entry	Substrate	Product
1	 **36b**	 **44b**, 88% (*dr* = 2.5:1)	7	 **36h**	 **44h**, 89% (*dr* = 3:1)
2	 **36c**	 **44c**, 81% (*dr* = 5:1)	8	 **36i**	 **44i**, 92% (*dr* = 3:1)
3	 **36d**	 **44d**, 85% (*dr* = 2.5:1)	9	 **36j**	 **44j**, 88% (*dr* = 2.5:1)
4	 **36e**	 **44e**, 83% (*dr* = 5:1)	10	 **36k**	 **44k**, 70% (*dr* = 2.5:1)
5	 **36f**	 **44f**, 85% (*dr* = 5:1)	11	 **36l**	 **44l**, 72% (*dr* = 3:1)
6	 **36g**	 **44g**, 88% (*dr* = 5:1)	12	 **36m**	 **44m**, 71% (*dr* = 2.5:1)

Encouraged by the results obtained for enone-aldehydes appended to aryl and heteroaryl backbones, we initiated our investigation about the scope and generality of the reaction with enone-ketones such as **56a**. Towards that, the substrate **56a** was subjected to optimized conditions. The reaction, in an unexpected manner generated the indeno-spirocyclopropane **58a** in excellent yield and in very short reaction time, Scheme 43.



56a **58a**

Scheme 43: Synthesis of indeno-spirocyclopropane **58a**

The structure of the indeno-spirocyclopropane **58a** was deduced from the analysis of spectral data. The presence of the absorption band at 3408 cm^{-1} indicates the presence of alcohol functionality and a peak at 1702 cm^{-1} is the indication of the presence of ketone functionality, which indicates the formation of **58a**. In the ^{1}H-NMR spectrum (see Fig. 8), the appearance of a triplet at δ 3.04 ppm (J = 8.7 Hz) indicates the methine proton (C-4), a multiplet at δ 2.07-2.01 ppm indicates the methylene protons (C-5), a doublet of doublet at δ 1.86 ppm (J = 9.3 and 4.4 Hz) indicates the presence of -OH proton and a snglet at δ 1.72 ppm indicates the presence of methyl group confirmed the formation of **58a**. In the ^{13}C-NMR spectrum (see Fig. 9), a signal at δ 200.6 ppm indicates the presence of carbonyl group (C-3), a signal at δ 75.3 ppm indicates the -OH connected carbon (C-1), signals at δ 47.3, 35.0 and 26.9 ppm are the indication of the aliphatic carbons (C-2, C-4 and C-5) and a signal at δ 19.8 ppm indicates the presence of methyl carbon (C-6) established the structure **58a**. In the high-resolution mass spectrum, presence of a peak at m/z 287.1037 $(M+Na)^{+}$ corresponding to the formula $C_{18}H_{16}NaO_2$ with the calculated value of 287.1048 which further supported the product formation.

Having realized the formation of the indeno-spirocyclopropanes, we have synthesized a diverse set of enone-ketones **56b-56j** and subjected to the optimized conditions to access the indeno-spirocyclopropanes, Table 3. The alkyl and aryl-substituted ketones appended to the aromatic backbone delivered the indeno-spirocyclopropanes **58b-58j** in good to excellent yields. The substrates bearing enone moiety with alkyl, aryl and heteroaryl groups at *β*-position (**58b-58j**) were well-tolerated under the optimized conditions. The presence of strong electron-

donating groups (such as -OMe) and as well as electron-withdrawing groups on aryl backbones (**58h-58i**), displayed no significant impact on the reaction efficiency. The structures and relative stereochemistry of major isomers were confirmed by the X-ray diffraction analysis of **58i**, Fig. 10.

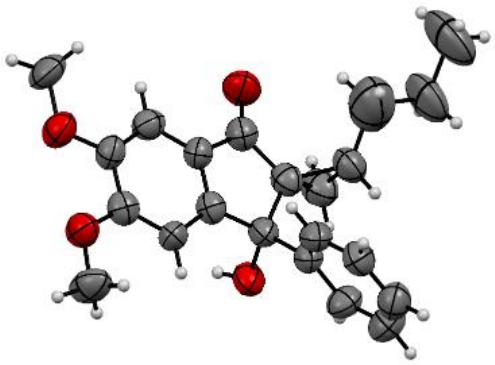
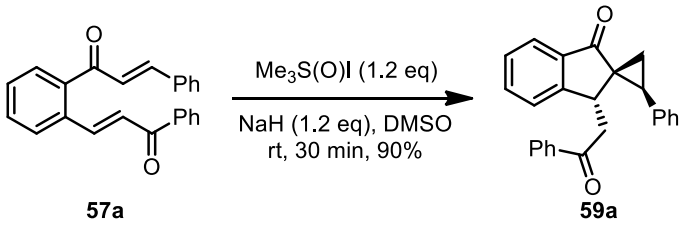


Figure 10: ORTEP diagram of **58i**, ellipsoid probability (50%)

After realizing the efficient and facile transformation of enone-aldehydes or enone-ketones, we considered the reaction of enone-enones appended to aryl and heteroaryl backbones under the prototypical conditions. Thus initially we have prepared the enone-enone **57a** (described in Scheme 42) and subjected to the optimized reaction conditions. The reaction delivered the indeno-spirocyclopropane **59a** in excellent yield, Scheme 44.



Scheme 44: Synthesis of indeno-spirocyclopropane **59a**

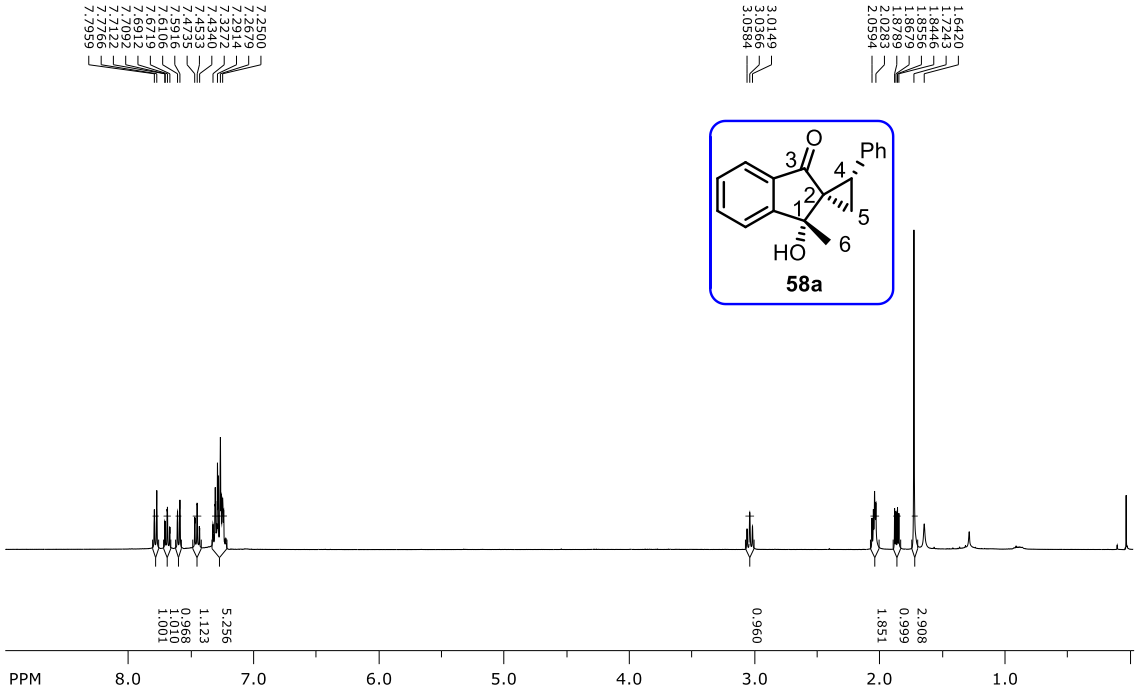


Figure 8: ^{1}H-NMR spectrum of **58a**

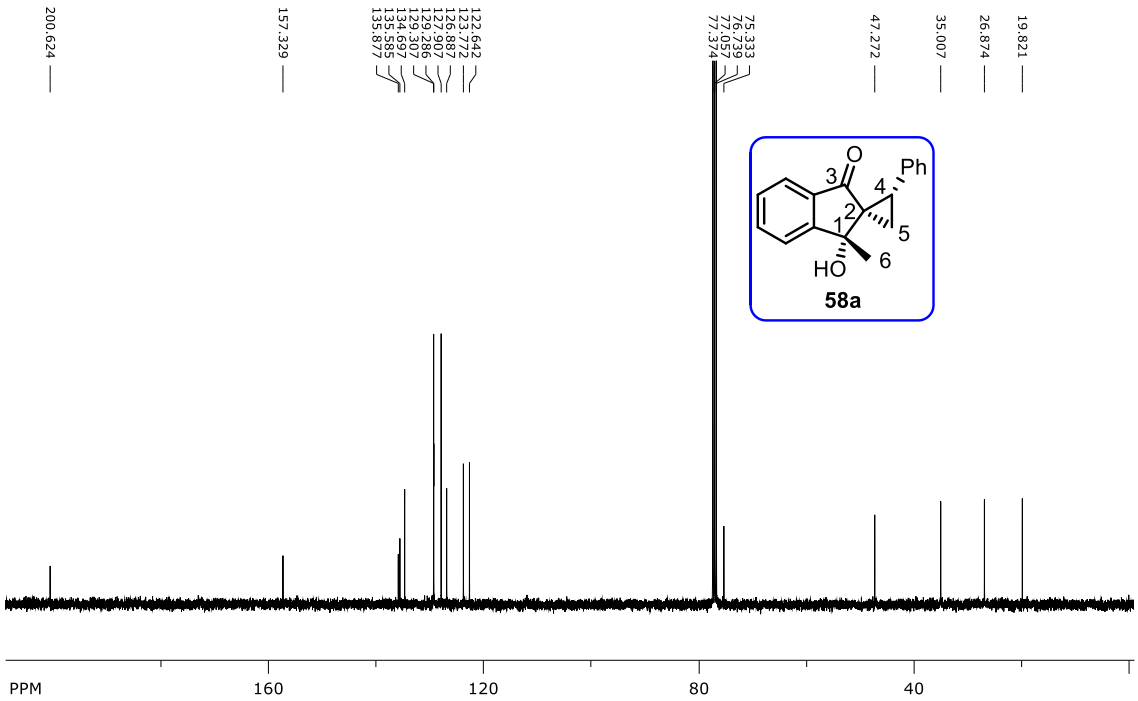
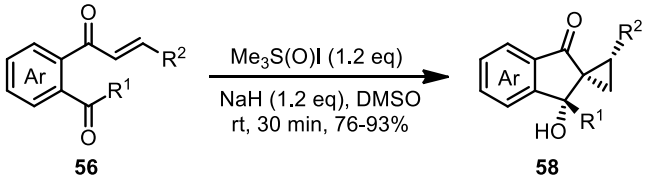
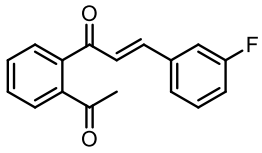
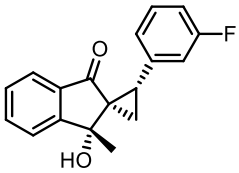
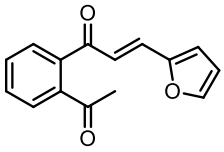
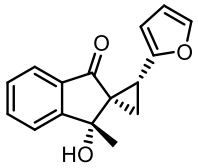
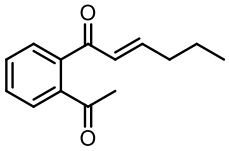
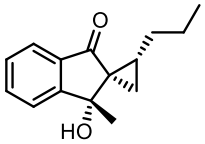
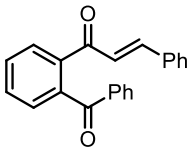
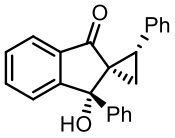
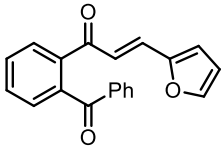
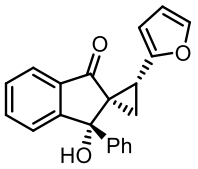
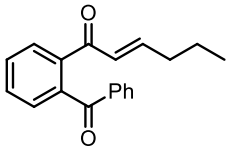
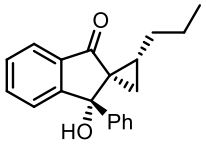
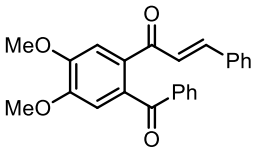
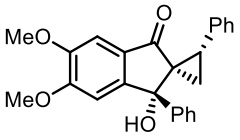
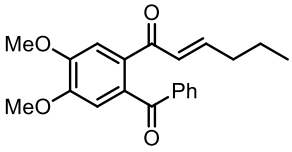
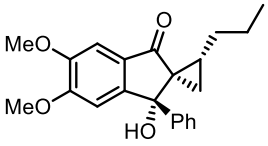
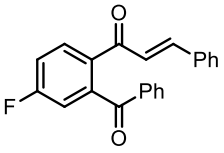
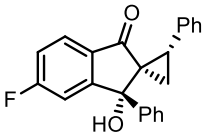


Figure 9: ^{13}C-NMR spectrum of **58a**

Table 3: Reactions of enone-ketones under the optimized conditions



56 **58**

Entry	Substrate	Product
1	 **56b**	 **58b**, 76% (*dr* = 3:1)
2	 **56c**	 **58c**, 77% (*dr* = 3:1)
3	 **56d**	 **58d**, 80% (*dr* = 2:1)
4	 **56e**	 **58e**, 80% (*dr* = 3.3:1)
5	 **56f**	 **58f**, 91% (*dr* = 2.5:1)
6	 **56g**	 **58g**, 84% (*dr* = 3:1)
7	 **56h**	 **58h**, 91% (*dr* = 3:1)
8	 **56i**	 **58i**, 93% (*dr* = 4:1)
9	 **56j**	 **58j**, 91% (*dr* = 2.4:1)

The structure of **59a** was deduced from the spectral data. In the IR spectrum, sharp absorption bands at 1703 cm^{-1} and 1699 cm^{-1} indicate the presence of two carbonyl groups in the product **59a**. In the ^{1}H-NMR spectrum (see Fig. 11), the presence of doublet of doublet at δ 4.15

ppm (J = 7.9 and 3.3 Hz) and at δ 2.83 ppm (J = 18.6 and 3.4 Hz) indicate methylene protons (C-4), a triplet at δ 3.32 ppm (J = 8.4 Hz) indicates methine proton (C-3), a doublet of doublet at δ 2.61 ppm (J = 18.3 and 8.1 Hz) indicates methine proton (C-6) and the doublet of doublet at δ 1.87 ppm (J = 7.7 and 4 Hz) and δ 1.69 ppm (J = 9.3 and 4.2 Hz) indicate the methylene proton (C-7) given the confirmation of the formation of **59a**. In the ^{13}C-NMR spectrum (see Fig. 12), signals at δ 203.8 and 198.0 ppm indicate the presence of the carbonyl groups (C-1 and C-5), the signals at δ 42.3, 41.9, 39.8, 30.8 and 22.9 ppm are the indication of the presence of the aliphatic carbons, respectively (C-3, C-4, C-2, C-6 and C-7), also further indicated the formation of **59a**. Finally, the presence of a protonated molecular ion peak at m/z 353.1558 $(M+H)^+$ corresponding to the formula $C_{25}H_{21}O_2$ with the calculated value of 353.1542 in mass spectrum confirmed the product **59a**.

After confirming the structure of the indeno-spirocyclopropanes under the optimized reaction conditions by the analysis of spectral data, we initiated the evaluation of substrate scope. Towards this, the optimized conditions were employed to a wide variety of enone-enones **57b-57j** bearing different steric and electric features, Table 4. The aryl and alkyl groups at R^1 as well as the aryl, heteroaryl or alkyl groups at R^2 were well-tolerated under the optimized conditions. The substrates containing electron-donating and electron-withdrawing groups on the aromatic backbone also generated the indeno-spirocyclopropanes **59g-59h** in excellent yields. The reaction of enone-enones appended to the heteroaryl backbone proceeded smoothly to deliver the desired indeno-spirocyclopropanes **59i** in good yield in short reaction time. The structure and relative stereochemistry of the major isomer was confirmed by the X-ray diffraction analysis of **59e**, Fig. 13.

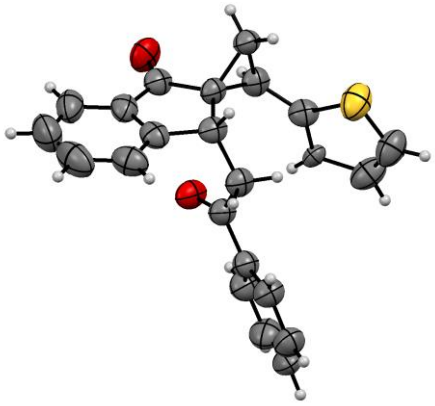


Figure 13: ORTEP diagram of **59e**, ellipsoid probability (50%)

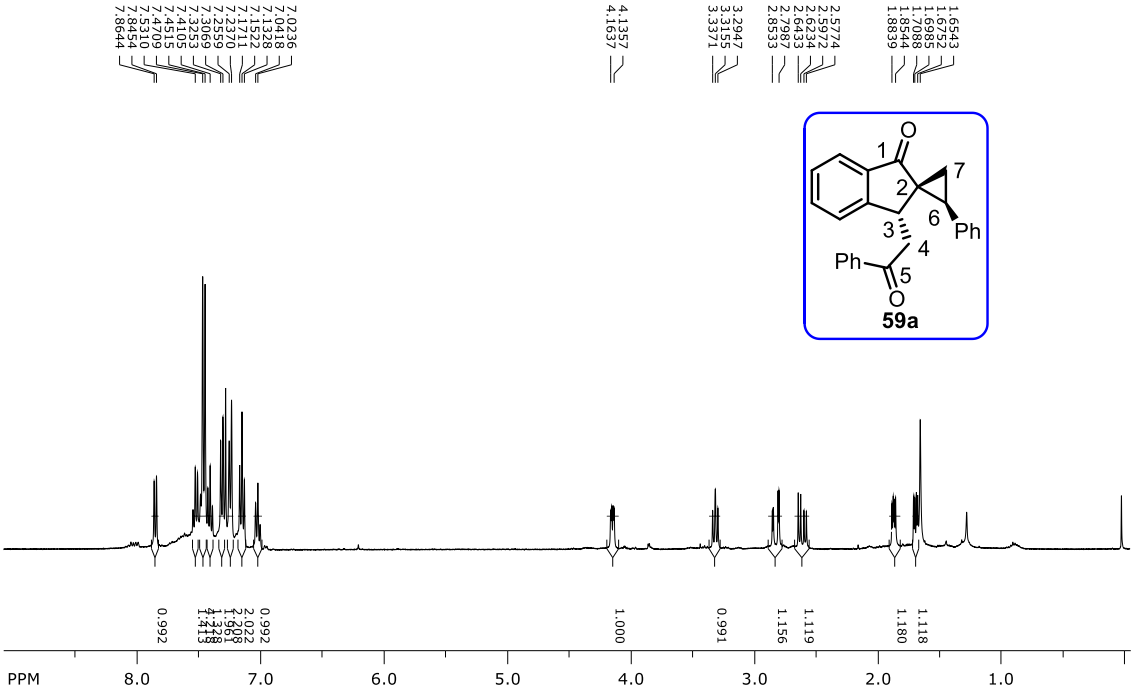


Figure 11: ^{1}H-NMR spectrum of **59a**

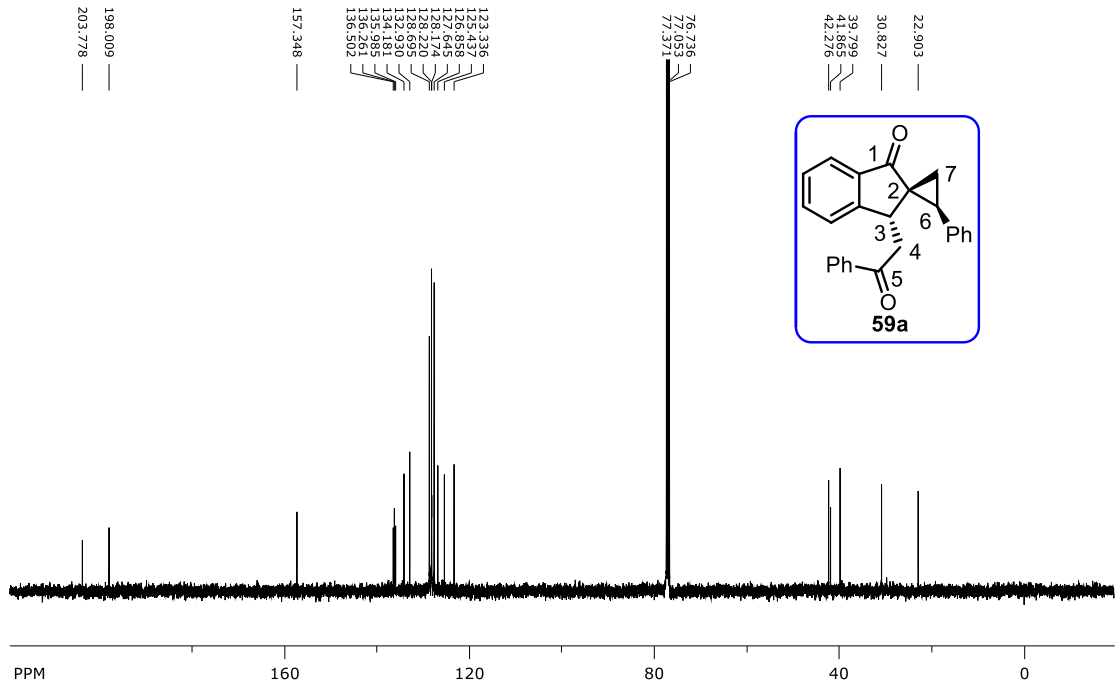
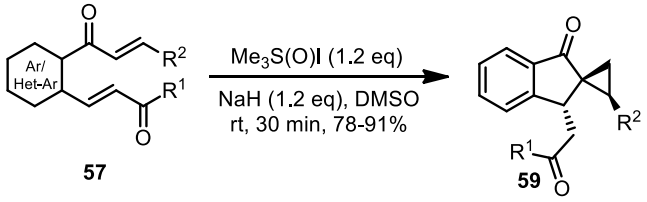
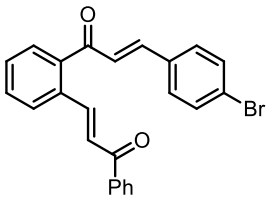
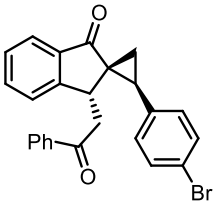
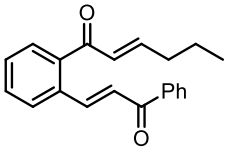
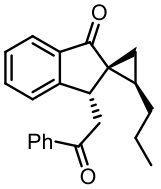
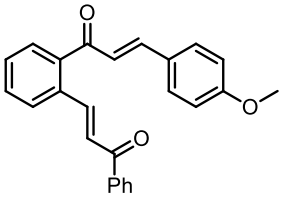
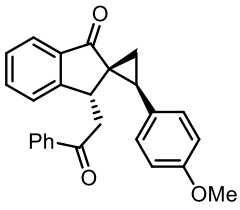
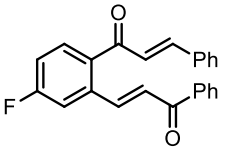
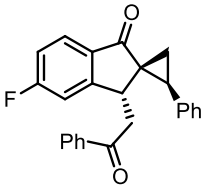
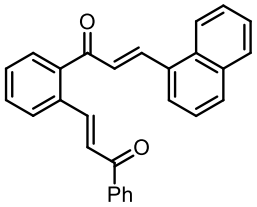
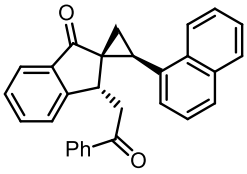
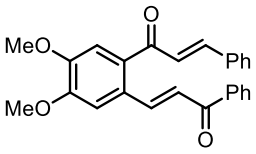
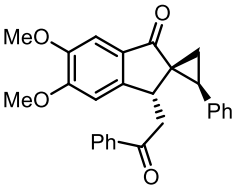
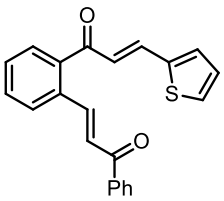
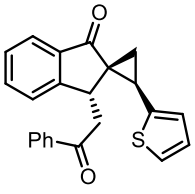
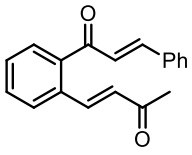
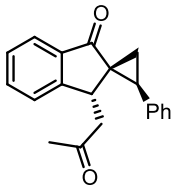
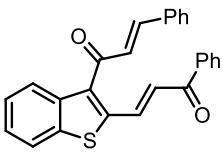
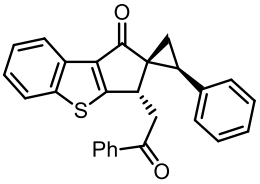


Figure 12: ^{13}C-NMR spectrum of **59a**

Table 4: Reactions of enone-enones under the optimized conditions

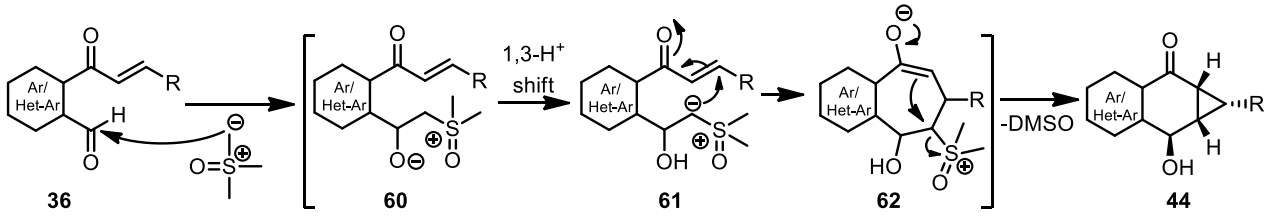


57 **59**

Entry	Substrate	Product	Entry	Substrate	Product
1	 **57b**	 **59b**, 91% (*dr* = 3.3:1)	5	 **57f**	 **59f**, 82% (*dr* = 3:1)
2	 **57c**	 **59c**, 83% (*dr* = 5:1)	6	 **57g**	 **59g**, 78% (*dr* 5:1)
3	 **57d**	 **59d**, 85% (*dr* = 5:1)	7	 **57h**	 **59h**, 87% (*dr* = 6:1)
4	 **57e**	 **59e**, 88% (*dr* = 3:1)	8	 **57i**	 **59i**, 85% (*dr* = 3:1)
			9	 **57j**	 **59j**, 81% (*dr* = 2:1)

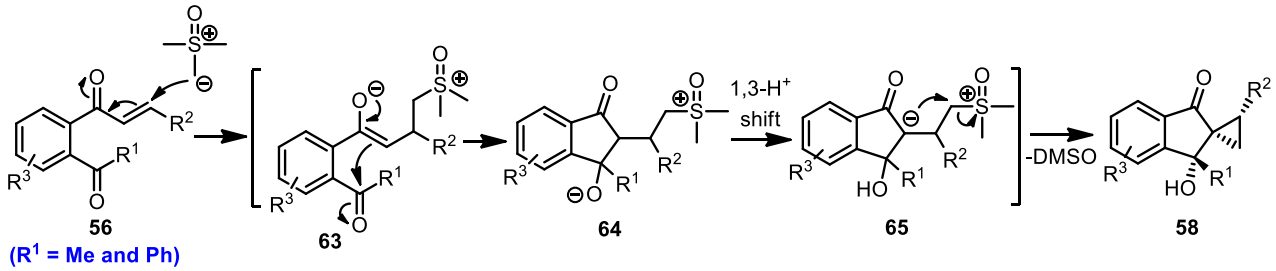
2.2: Plausible mechanism of the reactions involving enone-aldehydes, enone-ketones and enone-enones

The mechanism for the formation of **44** is believed to involve an initial aldol-type reaction of the ylide (DOSM) with **36** generating the 1,4-zwitterionic species **60**, Scheme 45. A subsequent 1,3-proton shift followed by an intramolecular Michael addition to the enone functionality deliveres the enolate **62**. The nucleophilic displacement of the dimethylsulfoxonium group from the enolate **62** leads to the formation of **44**.



Scheme 45: Plausible mechanism for the formation of **44a-44m**

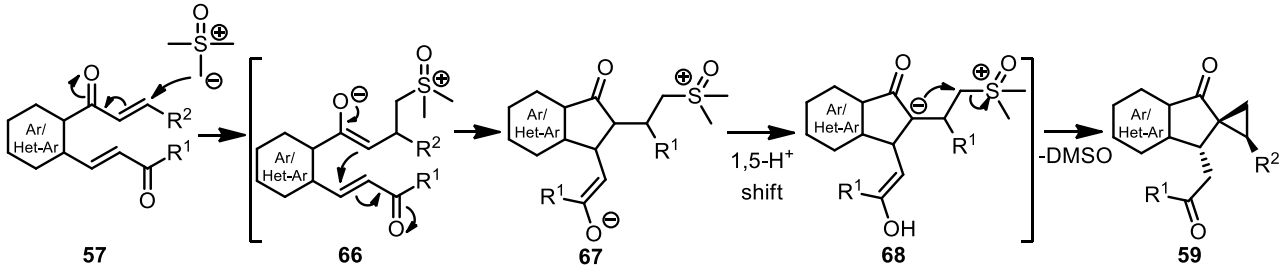
All the enone-ketones delivered the indeno-spirocyclopropanes **58a-58j** by reacting with the ylide (DOSM) presumably *via* the following mechanism, Scheme 46. The mechanism involves sequential intermolecular Michael/aldol reactions of **56** to generate the intermittent enolate **63**. The enolate **63** undergoes an intramolecular aldol-type reaction to furnish the 1,6-zwitterion **64**. An eventual 1,3-proton shift deliveres the enolate **65**, which enables the formation of **58** by the displacement of the DMSO (dimethylsulfoxide) group.



Scheme 46: Plausible mechanism for the formation of **58a-58j**

The formation of the product **59a-59j** derived from the corresponding enone-enones can be explained by considering a Michael/Michael reaction sequence on **57**, Scheme 47. The initial intermolecular Michael reaction of the ylide (DOSM) with **57** deliveres the enolate **66**, which subsequently undergoes an intramolecular Michael reaction to generate the 1,8-zwitterionic species **67**. A 1,5-proton shift of the zwitterionic species **67** leads to the formation of the enolate

68. Finally, the elimination of the dimethylsulfoxide group from the enolate **68** facilitates the formation of products **59**.



Scheme 47: Plausible mechanism for the formation of **59a-59j**

2.3. Synthetic utility of the cyclopropanoids 44, 58, and 59

2.3.1: Synthesis of 1,2-disubstituted tetralones

The tetralone scaffold is frequently encountered in a number of bioactive natural products such as catalponol, isocatalponol, isoshinanolone, palmarumycin, aristelegones A-B and schiffnerone-B, Fig. 14.[46] The compounds possessing tetralone moiety show excellent biological activities, such as catalponol, isocatalponol, isoshinanolone, Palmarumycin exhibit antileishmanial, anti-diabetic, antifungal, antibacterial, and herbicidal activities. The natural tetralones aristelegone-A and aristelegone-B were isolated from the root and stem of *Aristolochia elegants* and exhibit insecticidal and repellent activities. The tetralone schiffnerone-B was isolated only from the wood of *Dysoxylum schiffneri* and displays antitumor activity. The tetralone moiety is considered as a very useful building block in organic synthesis as well. Moreover, the tetralones are also used as precursors in the synthesis of several natural products.[47]

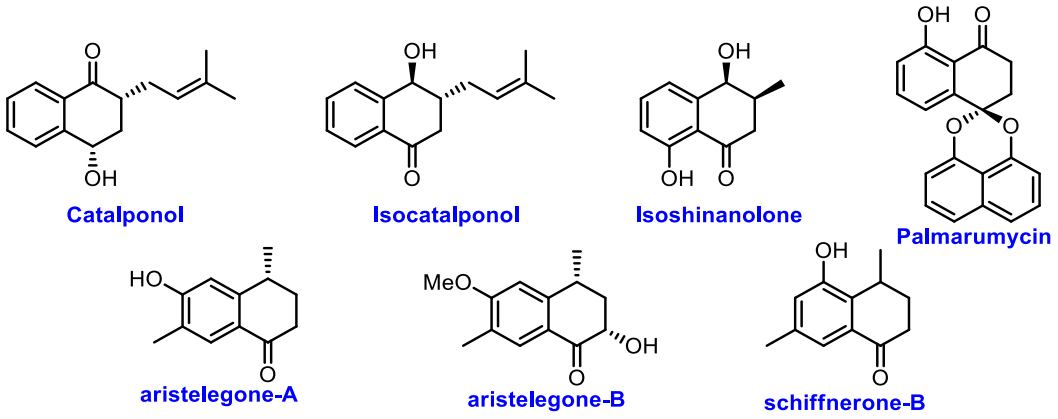
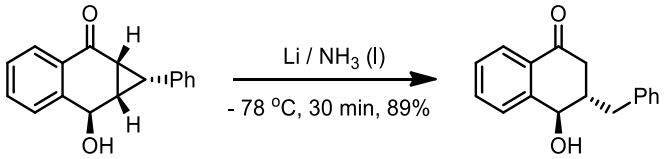


Figure 14: Representative natural products containing the 1-tetralone moiety

Because of the significance of tetralones, the development of new synthetic route to access them is of great interest in organic synthesis. It was hypothesized that the cyclopropyl ring in **44a** can undergo ring-opening of the cyclopropane under Li/liq. NH_3 conditions, Scheme 48. It is well known that the maximum overlapped cyclopropane bond with the π-orbital system of the carbonyl group preferentially cleaves.[48] Accordingly, we have applied Li/liq. NH_3 conditions to the product **44a**. Interestingly, the reaction of **44a** under Li/liq. NH_3 conditions yielded the *trans*-1,2-disubstituted tetralone **69a** in 89% yield. The presence of a doublet at δ 4.72 ppm (J = 6.4 Hz) indicates the methine proton (C-1), the doublet of doublet at δ 3.11 ppm (J = 13.6 and 5 Hz) and δ 2.86 ppm (J = 16.6 and 3.9 Hz) indicate the methylene proton (C-3), a doublet of doublet at δ 2.69 ppm (J = 13.4 and 8.3 Hz) indicates the -OH proton, a multiplet at δ 2.56-2.44 ppm indicates the methylene proton (C-5), and a multiplet at δ 2.42-2.33 ppm indicates the methine proton (C-4) in the ^{1}H-NMR spectrum (see Fig. 15) and in the ^{13}C-NMR spectrum (see Fig. 16), the presence of carbonyl signal at δ 197.1 (C-2) and four aliphatic signals (C-1, C-3, C-4, and C-5) confirmed the product formation.



44a **69a**

Scheme 48: Synthesis of *trans*-1,2-disubstituted tetralone **69a**

Few other tetralone analogues **69b-69e** were synthesized by employing the same protocol, Table 5. The structure and the relative stereochemistry were confirmed by the X-ray diffraction analysis of **69a**.

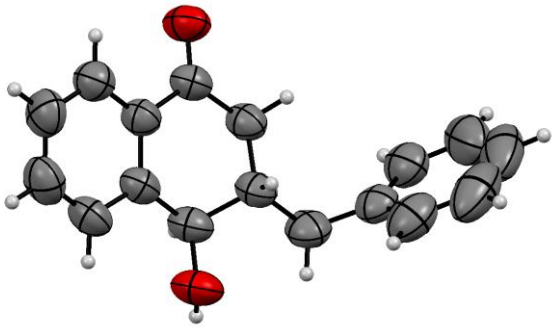


Figure 17: ORTEP diagram of **69a**, ellipsoid probability (50%)

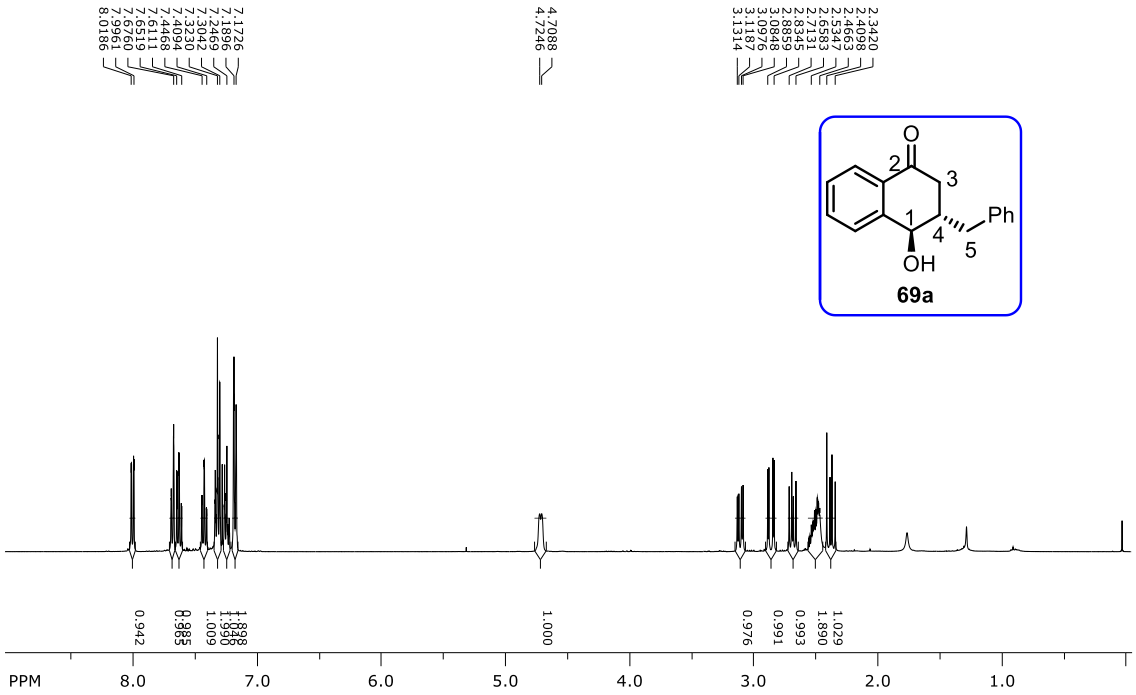


Figure 15: ^{1}H-NMR spectrum of **69a**

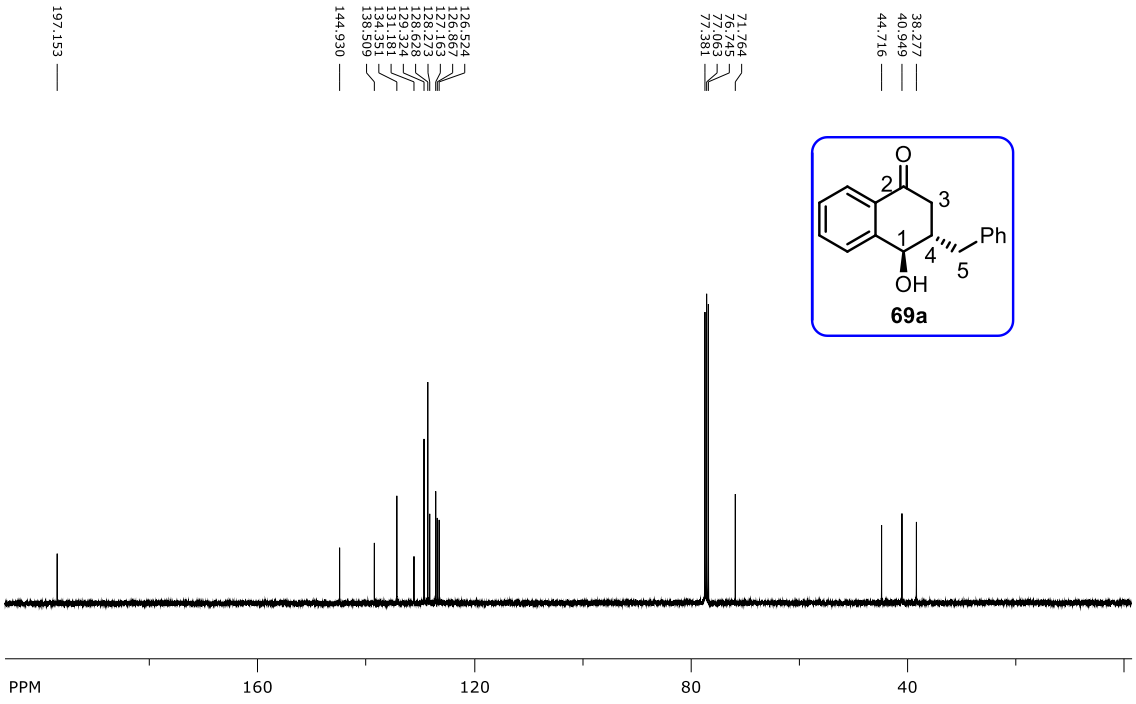
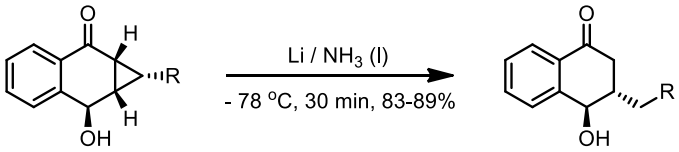
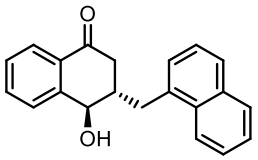


Figure 16: ^{13}C-NMR spectrum of **69a**

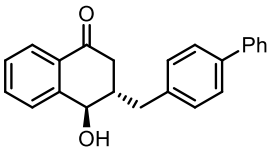
Table 5: Synthesis of *trans*-1,2-disubstituted tetralone analogs **69**



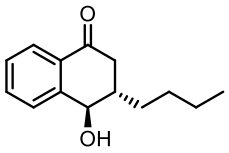
44 **69**



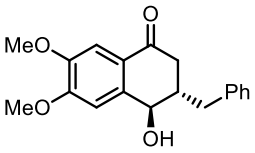
69b, 83%



69c, 88%

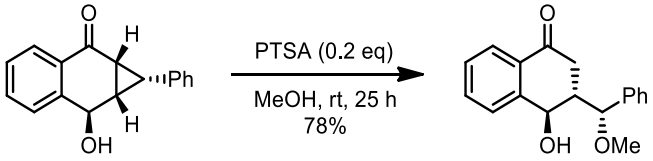


69d, 88%



69e, 85%

In the similar fashion, it was also envisioned that the product **44a** could undergo the ring-opening of cyclopropane under the acidic conditions in the presence of a suitable nucleophile.[49] Towards this, the reaction of **44a** was done in the presence of a catalytic amount of PTSA in methanol leading to the formation of *trans*-1,2-disubstituted tetralone **70a** in 78% yield, Scheme 49. The product **70a** contains three contiguous stereogenic centers.



44a **70a**

Scheme 49: Synthesis of *trans*-1,2-disubstituted tetralone **70a**

Few other tetralones **70b-70e** were also prepared by employing the same conditions, Table 6. The structure and the relative stereochemistry of the product were confirmed in analogy with the single crystal X-ray diffraction analysis of **70b**, Fig. 18. These results also provide the information that this strategy could perhaps apply to other analogous nucleophile-mediated ring openings for the synthesis of a diverse range of tetralones.

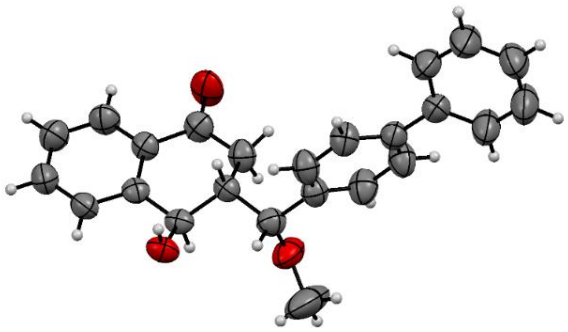
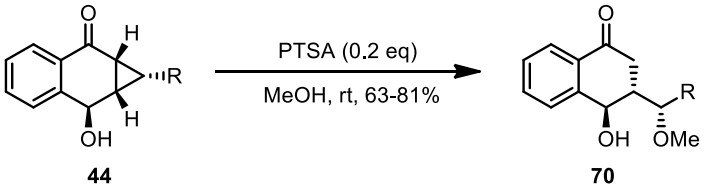
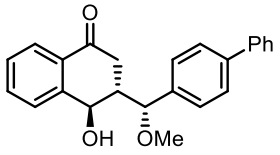


Figure 18: ORTEP diagram of **70b**, ellipsoid probability (50%)

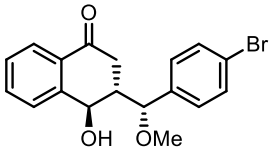
Table 6: Synthesis of *trans*-1,2-disubstituted tetralone analogs **70**



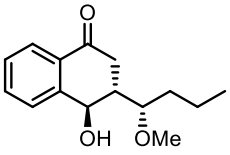
44 **70**



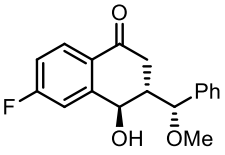
70b, 40 h, 79%



70c, 22 h, 75%



70d, 12 h, 63%



70e, 42 h, 81%

2.3.2: Synthesis of 2-styrylindenones

Indenones are privileged structural scaffolds widely occur in many natural products. Some of the biologically active compounds such as alcoholic fermentation activator, estrogen receptor, neo-lignan and acredinone A are listed in Fig. 19.[50] These structural units exhibit a broad spectrum of bioactivity profiles and often serve as useful intermediates in natural product synthesis. In the Figure xx, the first compound shows the activity towards alcochol fermentation and the second compound acts as an estrogen receptor. The indenone neo-lignan was isolated from the fruits of *Virola sebifera* and shows anti-tumor activity. Whereas, acredinone A used as K^+ channel inhibitor.

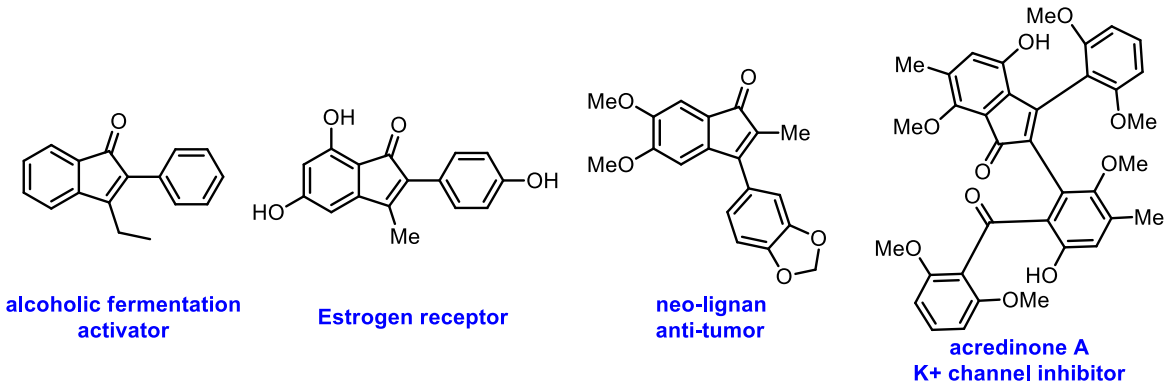
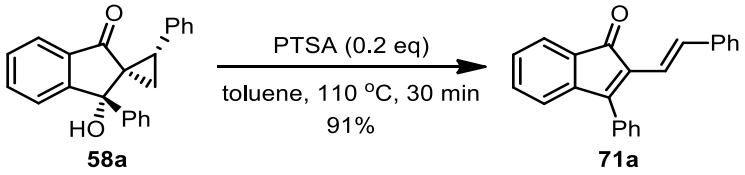


Figure 19: Representative examples of bioactive 2,3-substituted indenones

The interesting biological properties of indenones prompted us to develop new synthetic methods. In the past decades, many approaches have been developed to access the indenones, but the conventional methods generally require multistep sequences and/or have limited scope. Herein, we considered the synthetic transformation of indeno-spirocyclopropanes **58a** to indenones **71a**, Scheme 50. It was hypothesized that the bisbenzylic *tert*-alcohol could be activated under the acidic conditions and the cyclopropane moiety might anchimerically assist the developing cationic center, thereby a skeletally reorganized product could be observed. Accordingly, the treatment of **58a** with a catalytic amount of PTSA at an elevated temperature generated 2-styrylindenone **71a** in excellent yield.



Scheme 50: Synthesis of 2-styrylindenone **71a**

Under the same conditions two more indenone derivatives **71b-71c** were synthesized, Table 7. The structure of 2-styrylindenones was confirmed by the analysis of ^{1}H-NMR and ^{13}C-NMR spectral data, Fig. 20 and 21, respectively. A plausible mechanism for the formation of **71** is proposed in Table 7.

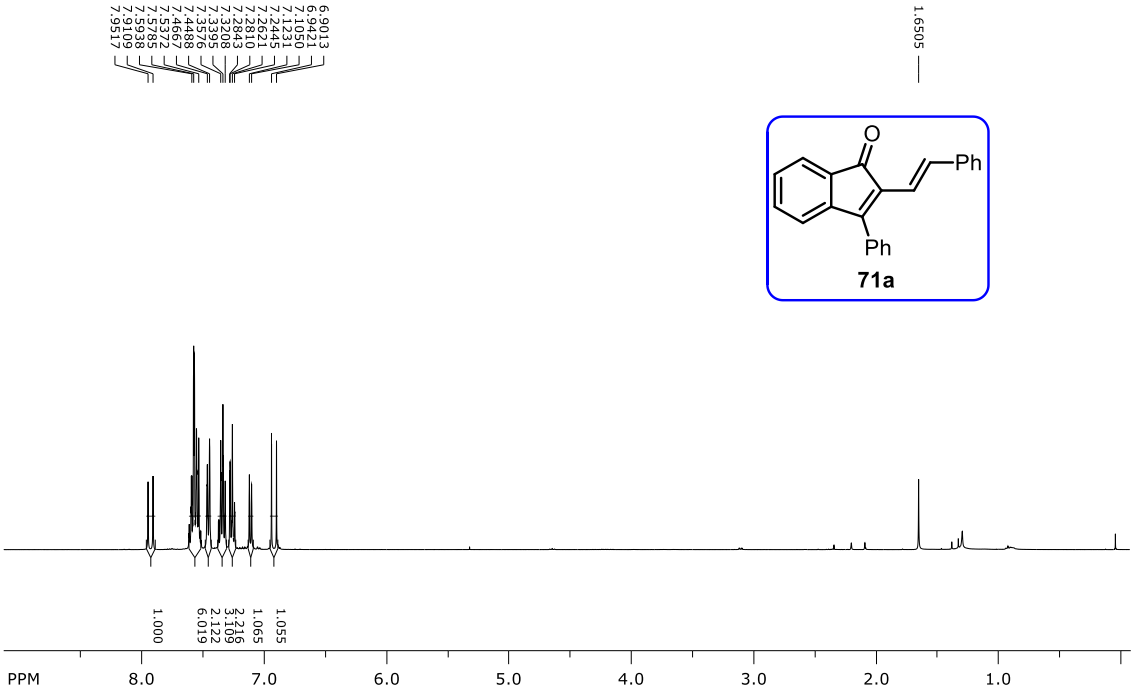


Figure 20: ^{1}H-NMR spectrum of **71a**

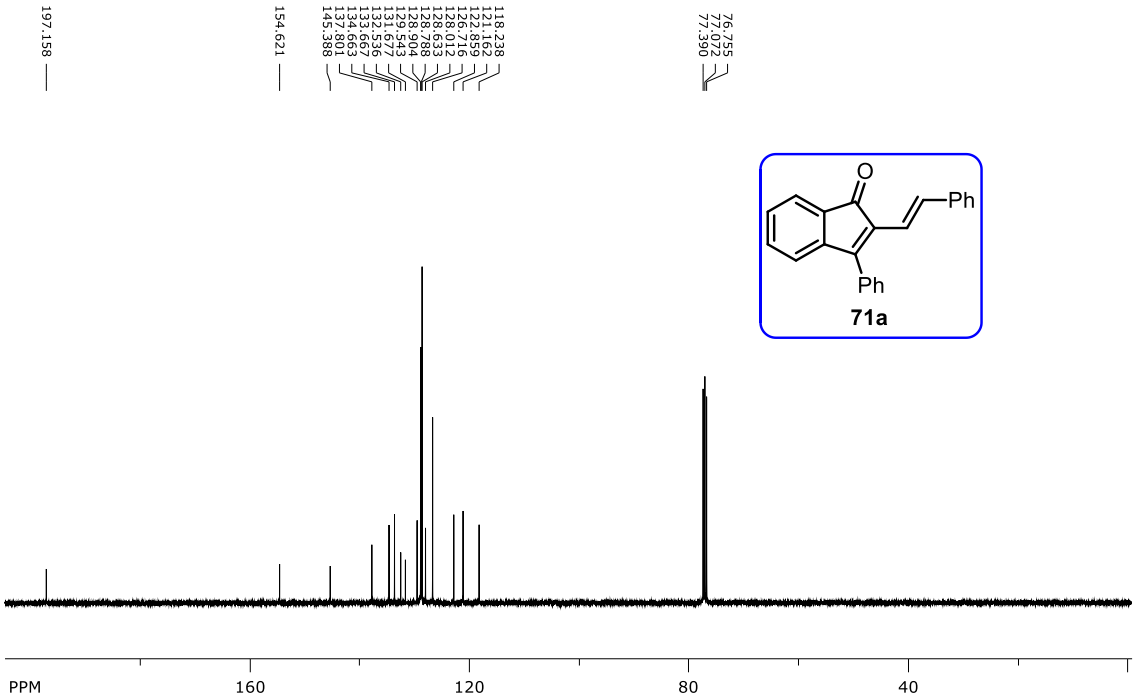
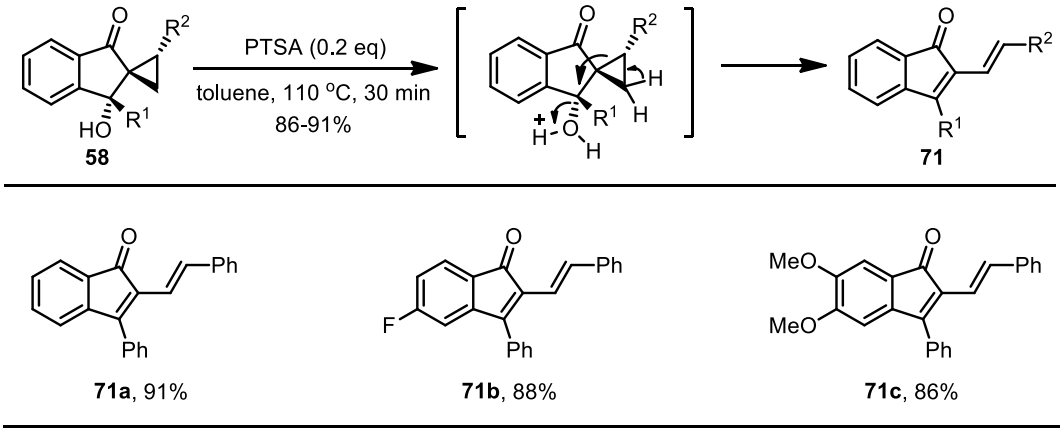


Figure 21: ^{13}C-NMR spectrum of **71a**

Table 7: Synthesis of 2-styrylindenone analogs **71**



2.3.3: Synthesis of fluorenones

Fluorenone is a privileged motif which is commonly found in many natural products and biologically active molecules. It can also serve as photocatalyst in organic synthesis. Some of the representative examples of fluorenone containing natural products are summarized in Fig. 22.[51] Among them, Dengibsinin exhibits high biological activities including neuroprotective, anti-tumor effects, etc. In 1984, Sunil and coworkers first isolated dendroflorin from *D. densiflorum* Lindl, which exhibits higher antioxidant activity. In 2011, Wang and co-workers reported the isolation of caulophyline A from the radix of *Caulophyllum robustum* Maxim. The caulophyline A shows anti-myocardial ischemia activity. Kinafluorenone is an example of benzo[*b*]fluorenone motif containing natural product which usually displays antibiotic activities. Moreover, the fluorenones have found wide application in materials chemistry as well. Thus, the biological features of fluorenone influenced us to develop new synthetic strategies to access the fluorenone derivatives.

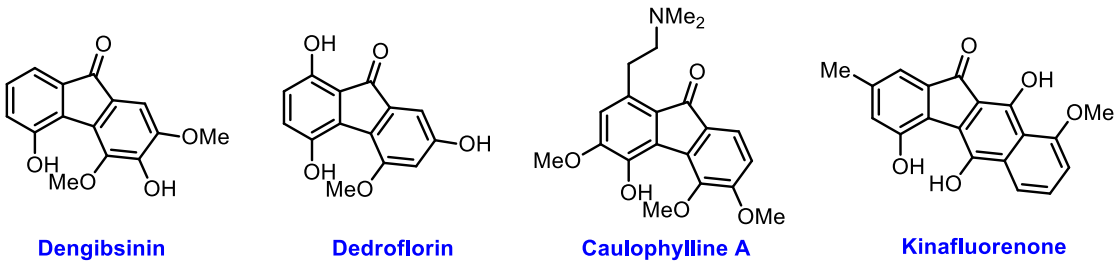
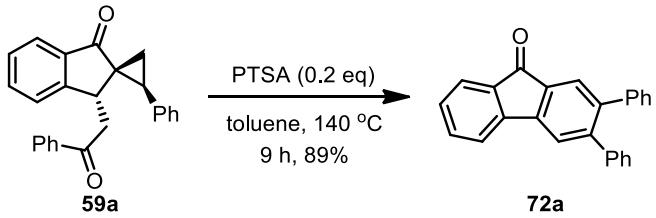


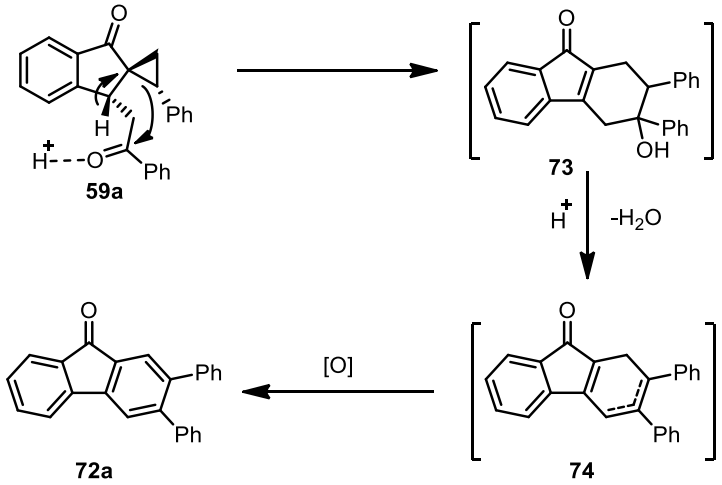
Figure 22: Representative examples of fluorenone natural products

It was assumed that the product **59a** could be converted to a new molecular architecture under the acidic conditions, Scheme 51. Accordingly, the reaction of **59a** was carried out in the presence of a catalytic amount of PTSA with azeotropic removal of water. The reaction efficiently generated the formation of 2,3-diarylfluorenone **72a** in 89% in a serendipitous manner. The structure of the 2,3-diarylfluorenone **72a** was deduced by careful analysis of IR, NMR (see Fig. 23 and 24) and HRMS data.



Scheme 51: Synthesis of fluorenone **72a**

As of the mechanism, the reaction is believed to involve a sequential proton elimination, cyclopropane ring-opening and nucleophilic attack onto ketone to furnish tetrahydrofluorenone **73**, Scheme 52. The elimination of water generates the dihydrofluorenone **74**, which upon aerobic oxidative aromatization deliveres **72a**.



Scheme 52: Plausible mechanism for the synthesis of fluorenones

To validate the generality of this unprecedented observation, a few more fluorenones **72b-72f** were prepared under the optimized conditions, Table 8. The structure was confirmed by the single crystal X-ray diffraction analysis of **72a**, Fig. 25.

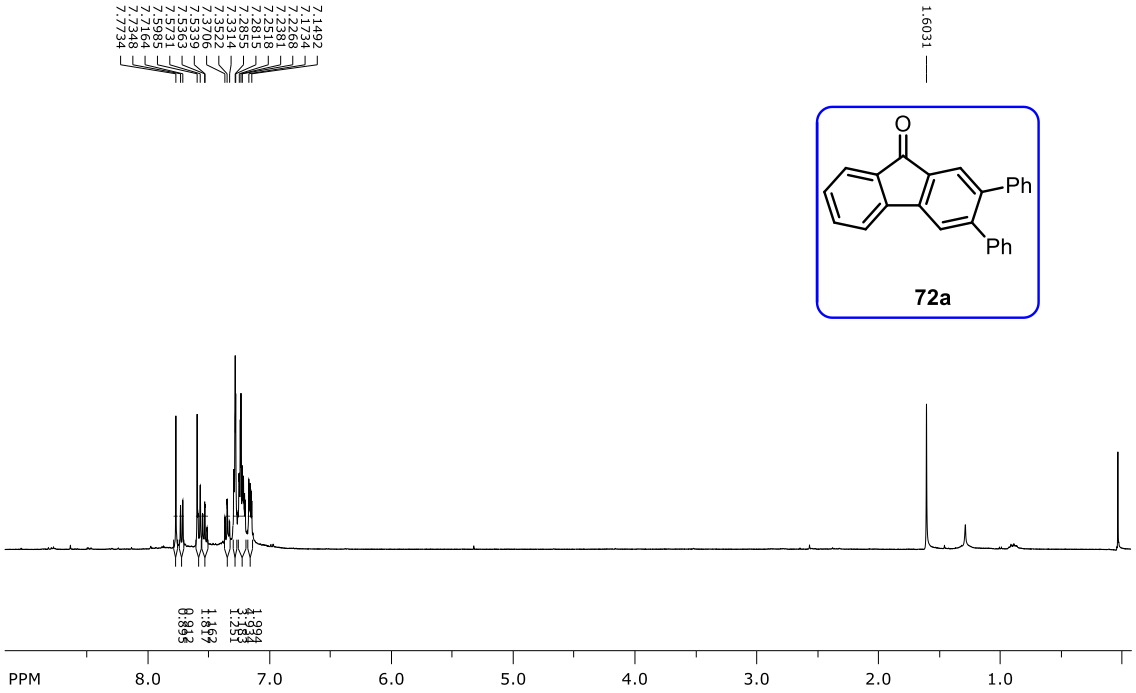


Figure 23: ^{1}H-NMR spectrum of **72a**

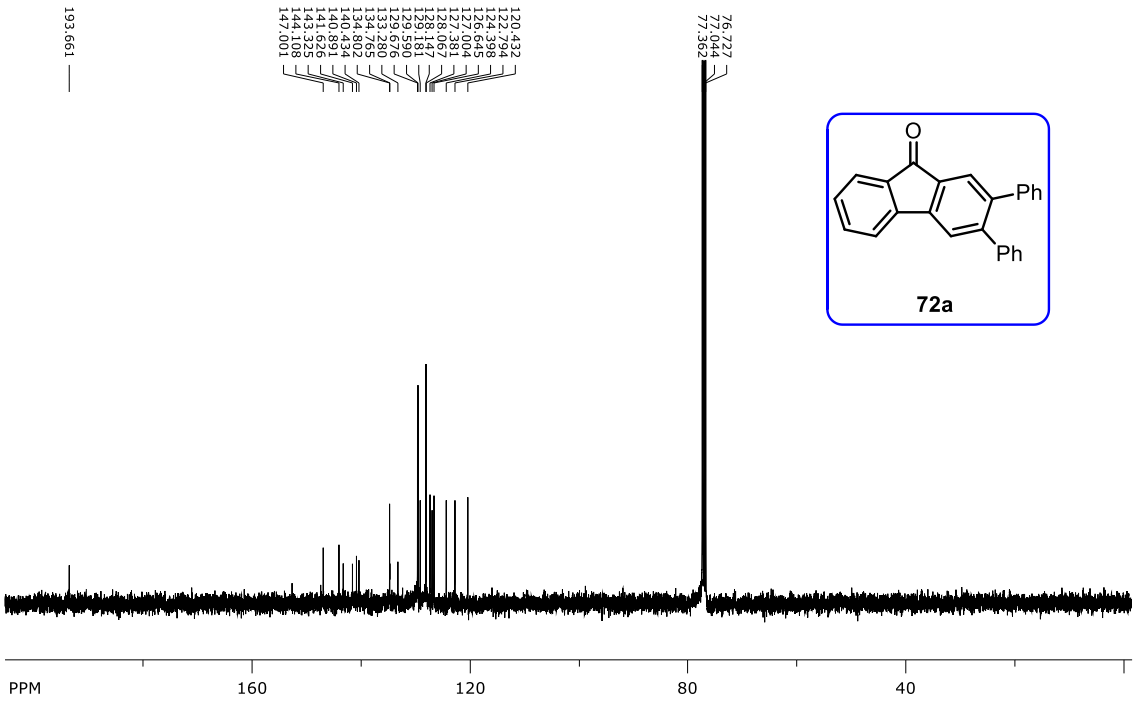


Figure 24: ^{13}C-NMR spectrum of **72a**

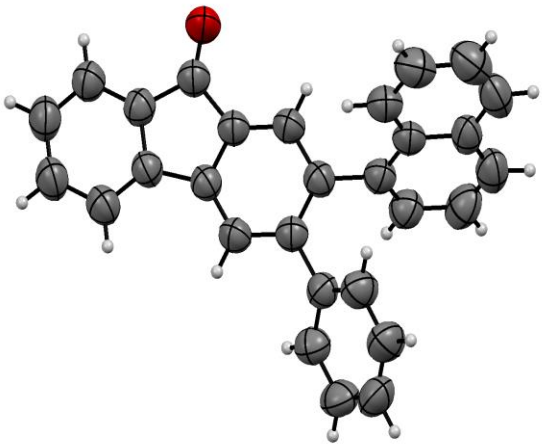
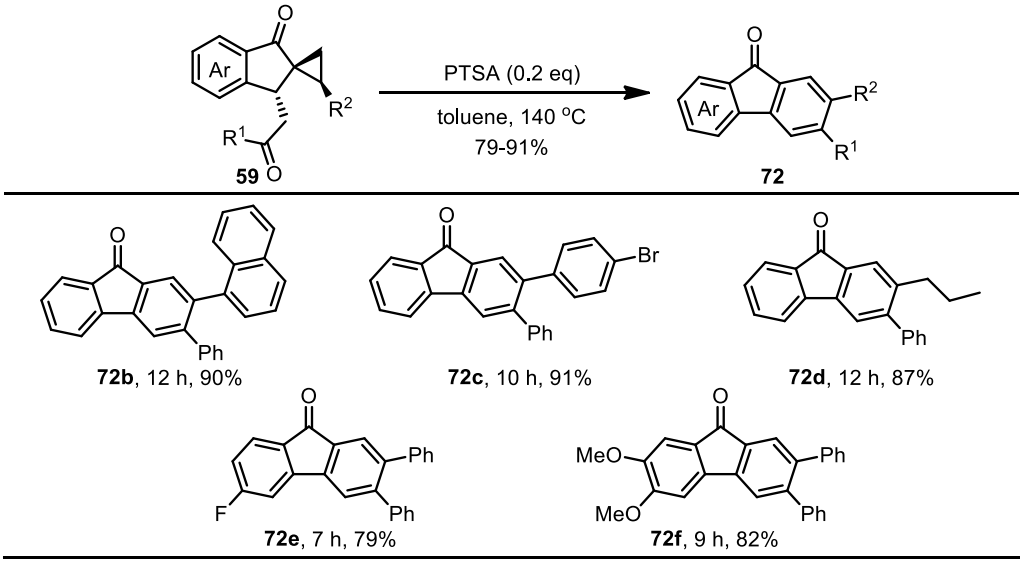


Figure 25: ORTEP diagram of **72a**, ellipsoid probability (50%)

Table 8: Synthesis of fluorenone analogs **72**



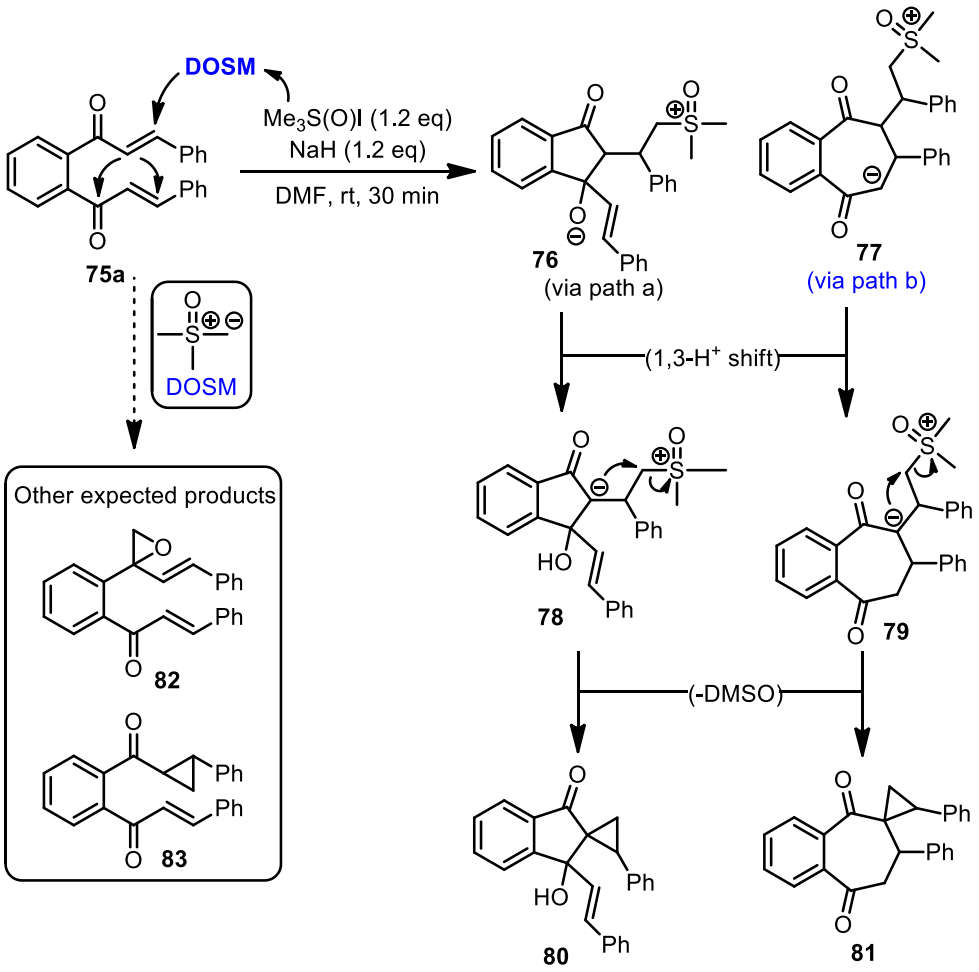
In conclusion, we have developed a series of unprecedented diastereoselective synthesis of cyclopropanoids *via* unusual cyclization pathways triggered by the DOSM. These strategies provide efficient routes to access cyclopropa-fused tetralones and indeno-spirocyclopropanes in excellent yields. The methods described herein are straightforward and mechanistically fascinating, and symbolize as novel substrate-based diversity-oriented strategies. Further, to illustrate the synthetic utility of these methods, we have successfully demonstrated a series of serendipitous one-step elaborations to access the privileged scaffolds such as tetralones, indenones and fluorenones.

Section 3

Desymmetrization reactions promoted by sulfur ylides: Synthesis of unusual cyclopropanoids

The successful development of the unexpected reactions facilitated by DOSM for the synthesis of unusual cyclopropanoids (described in Section 2) motivated us to apply these ylides to other substrate designs. A thorough literature survey suggested that there are no applications in a desymmetrization process yet by employing sulfur ylides. Thus, keeping the idea of desymmetrization process which is a powerful strategy to achieve complex architectures,[52] we designed the symmetric substrate **75a** and employed in the reaction with DOSM.[53]

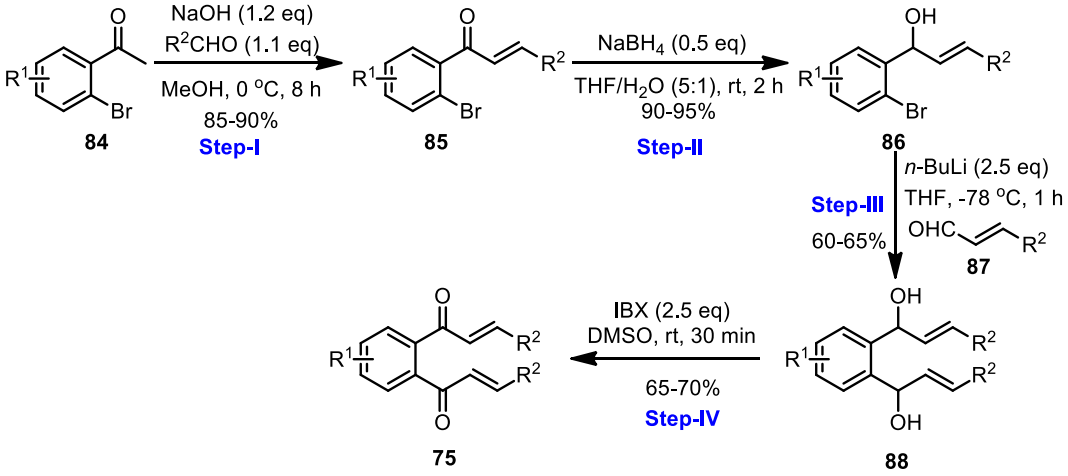
It was hypothesized that the DOSM initially could add in a Michael fashion and subsequently either through an aldol-type reaction (path-a) or a Michael reaction (path-b) could generate the zwitterionic species **76** or **77**, respectively, Scheme 53.[54] A concomitant 1,3-proton shift could provide enolates **78** or **79**, respectively. The elimination of the dimethylsulfoxide from the enolates could provide indanone **80** or fused-cycloheptanedione **81**, respectively. On the other hand, the substrate **75a** could lead to the formation of epoxide **82** or cyclopropane **83** under the reaction conditions.



Scheme 53: Our hypothesis for the desymmetrization of enone-enone **75a**

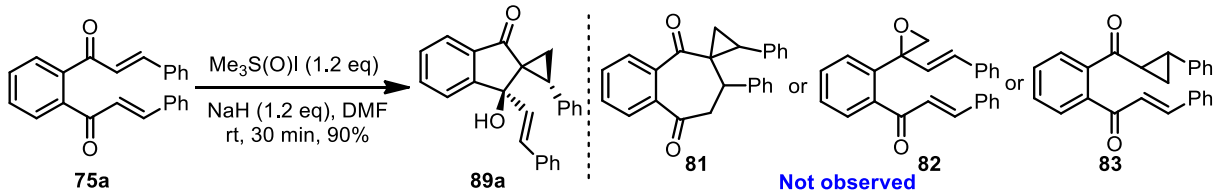
3.1: Results and discussion

To validate our hypothesis described in the Scheme 53, we commenced synthesizing the substrate **75**, Scheme 54. The enone-enone **75** can be achieved in a four-step protocol starting from 2'-bromoacetophenones **84**. The aldol reaction of **84** with aldehydes under the base mediated reaction conditions generated 2'-bromoenones **85**. The $NaBH_4$ mediated chemoselective reduction of ketone in **85** at rt provided 2'-bromoenols **86**. The *n*-BuLi mediated alkylation of **86** with appropriate enals **87** at -78 ^oC generated diols **88**. Subsequently, the IBX oxidation of **88** furnished enone-enones **75**.



Scheme 54: Synthesis of enone-enones **75**

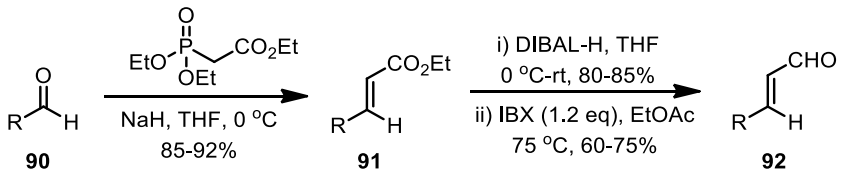
Accordingly, we have started the optimization study with the enone-enone **75a** as the model substrate, Scheme 55. Prompted by our earlier success with Corey's ylide (DOSM) on enone substrates (described in section 2), we have employed the prototypical conditions during the initial screening with **75a**. Interestingly, under these conditions, the enone-enone **75a** exclusively delivered indanone **89a** in 90% yield with 2.5:1 diastereomeric ratio within a short reaction time. The formation of the expected fused-cycloheptanedione **81** or epoxide **82** or cyclopropane **83** was not detected.



Scheme 55: Synthesis of indeno-spirocyclopropane **89a**

The structure of indanone **89a** was deduced from the analysis of the spectral data. In the IR-spectrum, the presence of an absorption band at 3424 cm^{-1} is an indication of the presence of tertiary alcohol functionality and a band at 1697 cm^{-1} indicates the presence of the carbonyl functionality. In the ^{1}H-NMR spectrum (see Fig. 26), the appearance of doublets at δ 6.93 ppm (*J* = 15.9 Hz) and δ 6.30 ppm (*J* = 15.9 Hz) indicate the two *trans* olefinic protons (C-6 and C-7), a triplet at δ 2.97 ppm (*J* = 8.7 Hz) indicates C-4 methine proton, a singlet at δ 2.43 ppm indicates the presence of -OH functionality, two multiplets at δ 2.08-2.05 and δ 1.84-1.81 ppm indicate C-5 methylene protons. In ^{13}C-NMR spectrum (see Fig. 27), the presence of a peak at δ 200.5 ppm indicates the presence of the ketone (C-3), a peak at δ 78.3 ppm indicates aliphatic carbon (C-1) and the peaks at δ 47.8, δ 36.9 and δ 18.9 ppm are the indication of the presence of the cyclopropane carbons (C-2, C-4 and C-5). Thus the ^{1}H-NMR and ^{13}C-NMR data confirms the formation of the product **89a**. The assigned structure of **89a** was further confirmed by HRMS data which showed the presence of a protonated molecular ion peak at m/z 353.1549 $(M+H)^{+}$ corresponding to the formula $C_{25}H_{21}O_2$ with the calculated value of 353.1542.

After realizing a facile transformation of enone-enone **75a** to highly functionalized indanone **89a** possessing three contiguous stereogenic centers, we sought to investigate the scope and generality of the reaction. Towards this, a diverse set of enone-enones were synthesized by following the protocol described in Scheme 54. All the enals **92** employed in this study can be synthesized by an efficient three-step protocol described in Scheme 56. The Horner-Wadsworth-Emmons (HWE) reaction of aldehydes **90** leading to the formation of *α,β*-unsaturated esters **91**, which followed by DIBAL-H reduction and IBX oxidation delivered enals **92**.[55]



Scheme 56: Synthesis of substituted enals **92**

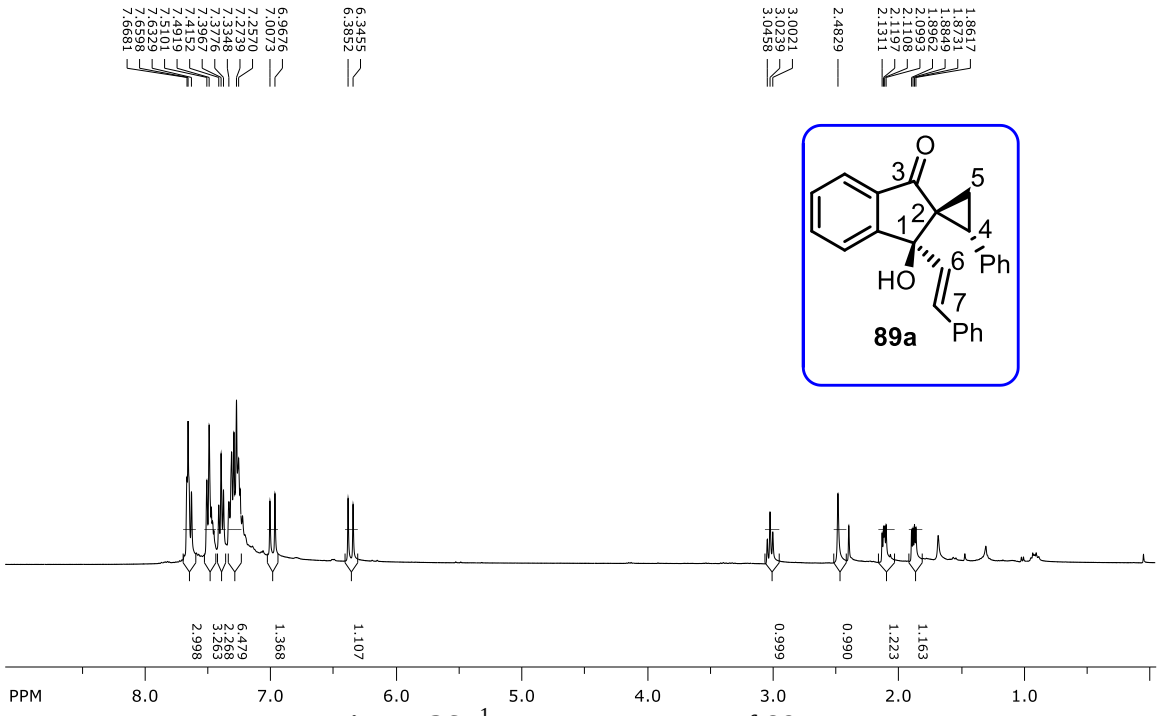


Figure 26: ^{1}H-NMR spectrum of **89a**

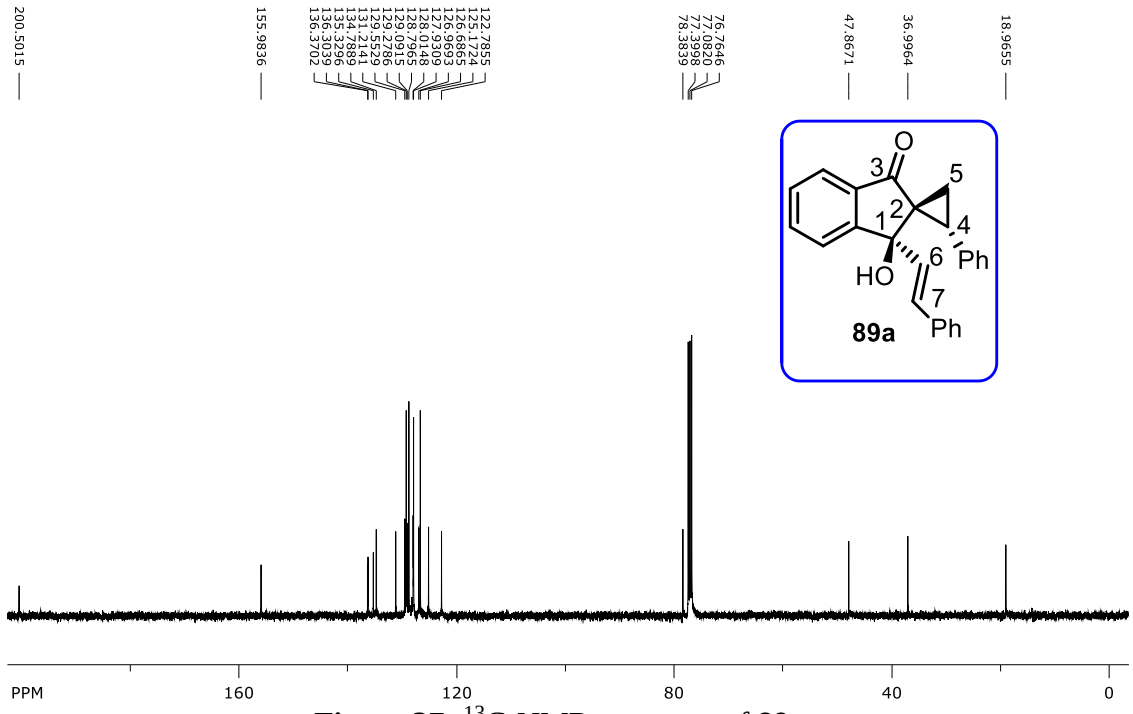


Figure 27: ^{13}C-NMR spectrum of **89a**

To validate the generality of this method, all the enone-enones **75b-75k** were subjected to the optimized reaction conditions to afford indeno-spirocyclopropanes **89b-89k**, Table 9. It was realized that the reaction proceeds with least electronic and steric effects and proceeded smoothly within 30 minutes. There was no noticeable impact on the yield while the substrates bearing electron-donating groups on the aromatic backbone as well as on the enone moiety were treated under the optimized conditions (entry 3, 4, and 6-9). The substrate containing electron-withdrawing group on the enone moiety was well-tolerated under the reaction conditions (entry 5). The reaction was also general with the substrates bearing aliphatic group on the enone moiety (entry 10). With the analysis of the ^{1}H-NMR of the crude reaction mixture, we have determined the diastereoselectivity in each case. The structures and relative stereochemistry of the major isomers were assigned in analogy with the X-ray diffraction analysis of **89h**, Fig. 28.

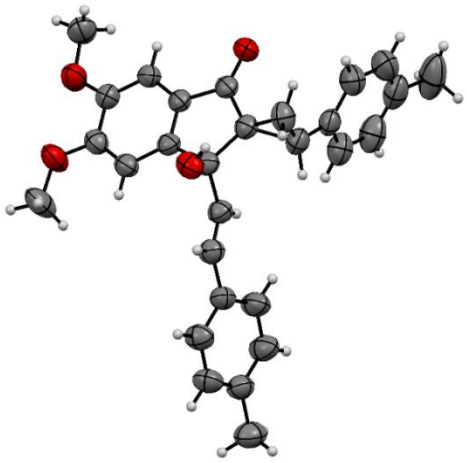
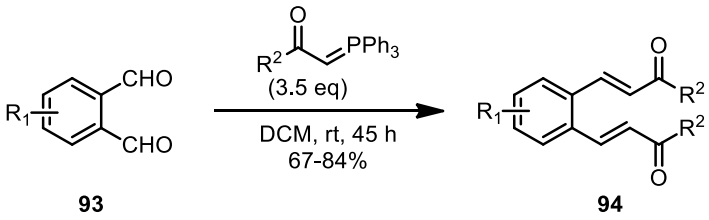


Figure 28: ORTEP diagram of **89h**, ellipsoid probability (50%)

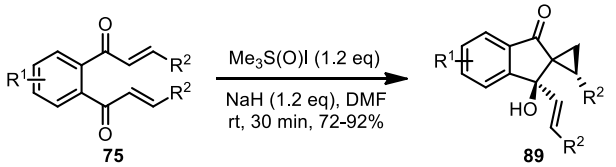
Encouraged by the aforementioned results obtained with enone-enones **75**, the strategy was extended to other symmetric enone-enones **94**.[56] Thus, we synthesized the enone-enones **94** by following the literature report, Scheme 57.[57]



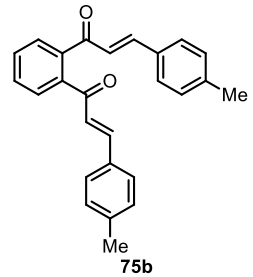
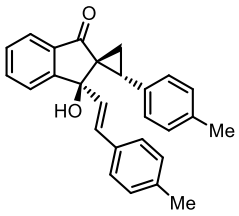
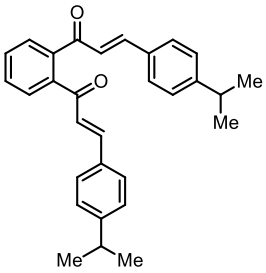
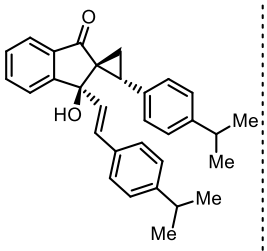
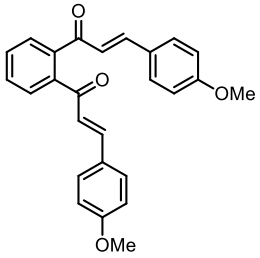
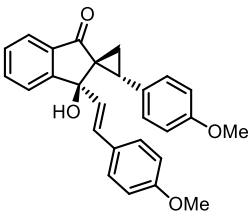
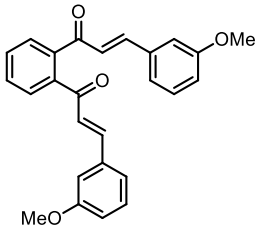
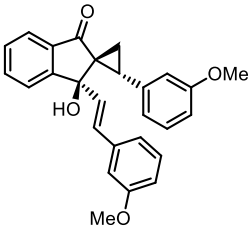
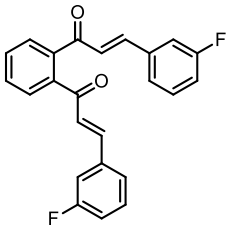
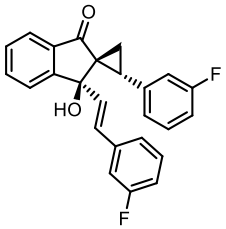
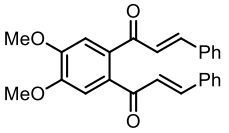
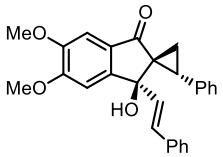
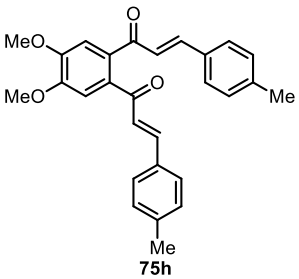
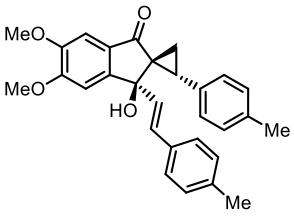
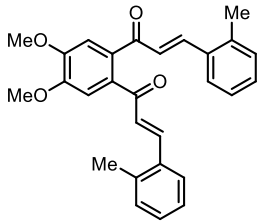
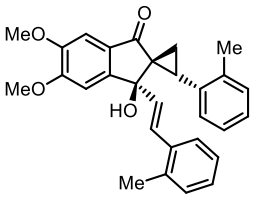
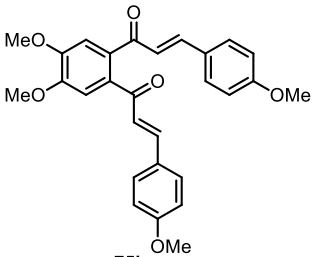
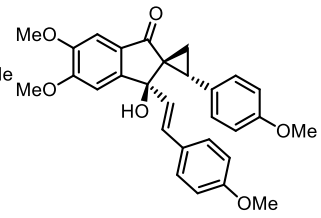
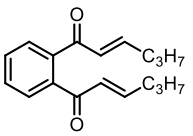
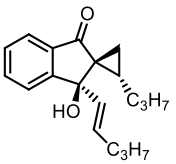
93 **94**

Scheme 57: Synthesis of enone-enones **94**

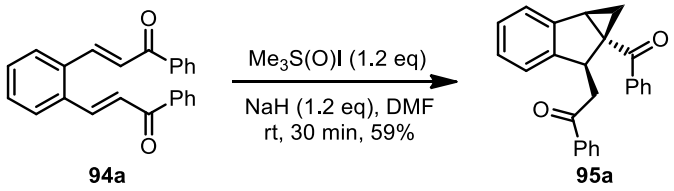
Table 9: Reactions of enone-enones under the optimized conditions



75 89

Entry	Substrate	Product
1	 **75b**	 **89b**, 92% (*dr* = 2.5:1)
2	 **75c**	 **89c**, 82% (*dr* = 2.5:1)
3	 **75d**	 **89d**, 87% (*dr* = 2:1)
4	 **75e**	 **89e**, 78% (*dr* = 3:1)
5	 **75f**	 **89f**, 80% (*dr* = 2.5:1)
6	 **75g**	 **89g**, 87% (*dr* = 3:1)
7	 **75h**	 **89h**, 88% (*dr* = 2:1)
8	 **75i**	 **89i**, 88% (*dr* = 3:1)
9	 **75j**	 **89j**, 84% (*dr* = 2.5:1)
10	 **75k**	 **89k**, 72% (*dr* = 2.5:1)

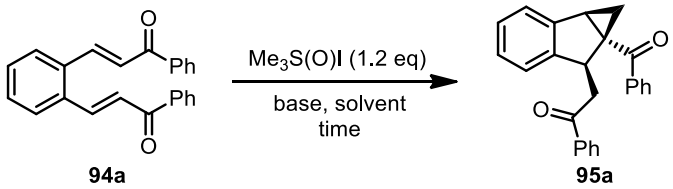
To our surprise, the reaction of the enone-enone **94a** resulted in the formation of cyclopropafused indane **95a** in 59% yield in 2.5:1 diastereoselectivity, Scheme 58. In this reaction, we did not observe the formation of any other side product. Further to improve the yield of the product, we optimized the reaction conditions with different base and solvent combinations, but there was no impact on the yield of the product, Table 10. During the reaction, some amount of starting material was realized to be decomposing, which could be the possible reason for the less yield of the product.



Scheme 58: Synthesis of cyclopropa-fused indane **95a**

The structure of **95a** was deduced from the analysis of IR, ^{1}H-NMR, ^{13}C-NMR spectrum. In the IR spectrum, the appearance of two bands at 1683 cm^{-1} and 1607 cm^{-1} indicate the presence of the two carbonyl functionalities in the product. In the ^{1}H-NMR spectrum (see Fig. 29), the presence of a doublet of doublet at δ 4.65 ppm (J = 9.3 and 4.4 Hz) indicates methine proton (C-3), doublet of doublet at δ 3.46 ppm (J = 18 and 4.5 Hz) and δ 3.25 ppm (J = 18 and 9.4 Hz) indicate the methylene protons (C-2), a doublet of doublet at δ 2.99 ppm (J = 8.3 and 3.9 Hz) indicates methine proton (C-5) and doublet of doublet at 2.07 ppm (J = 8.3 and 4.9 Hz) and 0.69 ppm (J = 4.9 and 4.2 Hz) indicate the methylene protons (C-6) confirms the formation of **95a**. In the ^{13}C-NMR spectrum (see Fig. 30), signals at δ 200.6 and 198.1 ppm indicate the presence of the carbonyl carbons (C-1 and C-7), signals at δ 44.6, 43.0, 41.3, 35.8 and 18.3 ppm are the indication of the presence of the aliphatic carbons (C-2, C-3, C-4, C-5 and C-6), respectively, also supports the formation of **95a**. An analysis of HRMS data showed the presence of a molecular ion peak at m/z 375.1379 $(M+Na)^{+}$ corresponding to the molecular formula $C_{25}H_{20}NaO_2$ (with the calculated value of 375.1361), which further confirmed the product **95a**. The structure and the relative stereochemistry of the major diastereomer were confirmed by the X-ray diffraction analysis of **95a**, Fig. 31.

Table 10: Optimization of reaction parameters with **95a**



Entry	Solvent	Temperature (^{o}C)	Time (min)	Yield[a] (%)
1	DCM	RT	30	Trace
2	$CHCl_3$	RT	30	Trace
3	DCE	RT	30	30%
4	Toluene	RT	-	-
5	**DMF**	**RT**	**15**	**59%**
6	DMSO	RT	15	58%
7	ACN	RT	30	47%
8	DMSO/THF (1:1 v/v)	RT	45	50%
9	DMF	-20	40	57%
10	DMF	-30	120	56%

[a]Isolated yields after column chromatography.

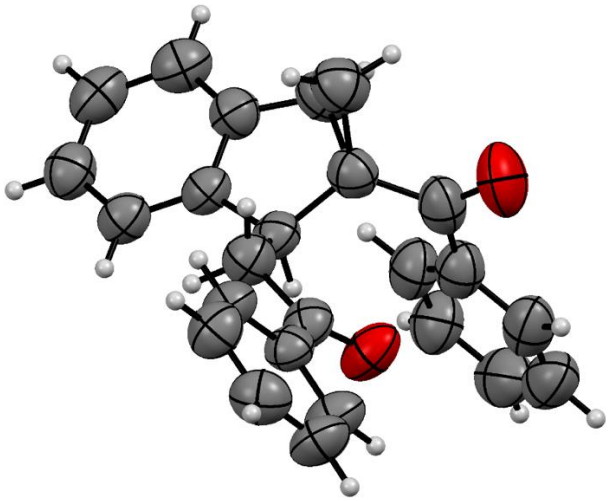


Figure 31: ORTEP diagram of **95a**, ellipsoid probability (50%)

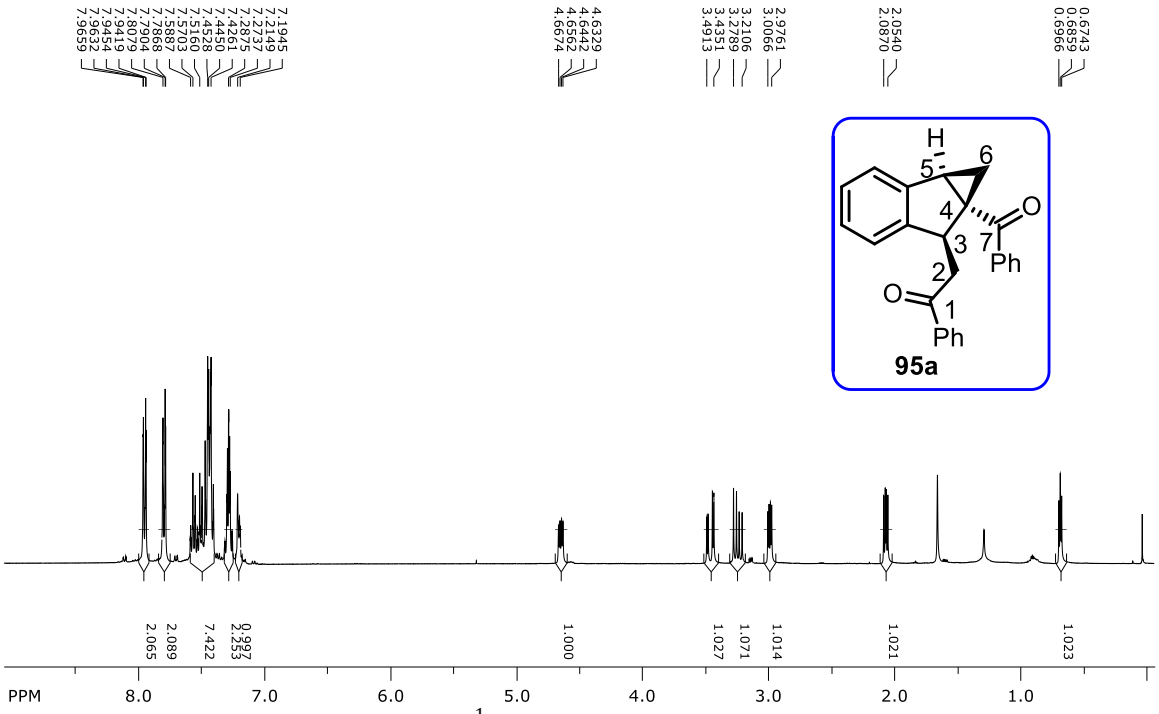


Figure 29: ^{1}H-NMR spectrum of **95a**

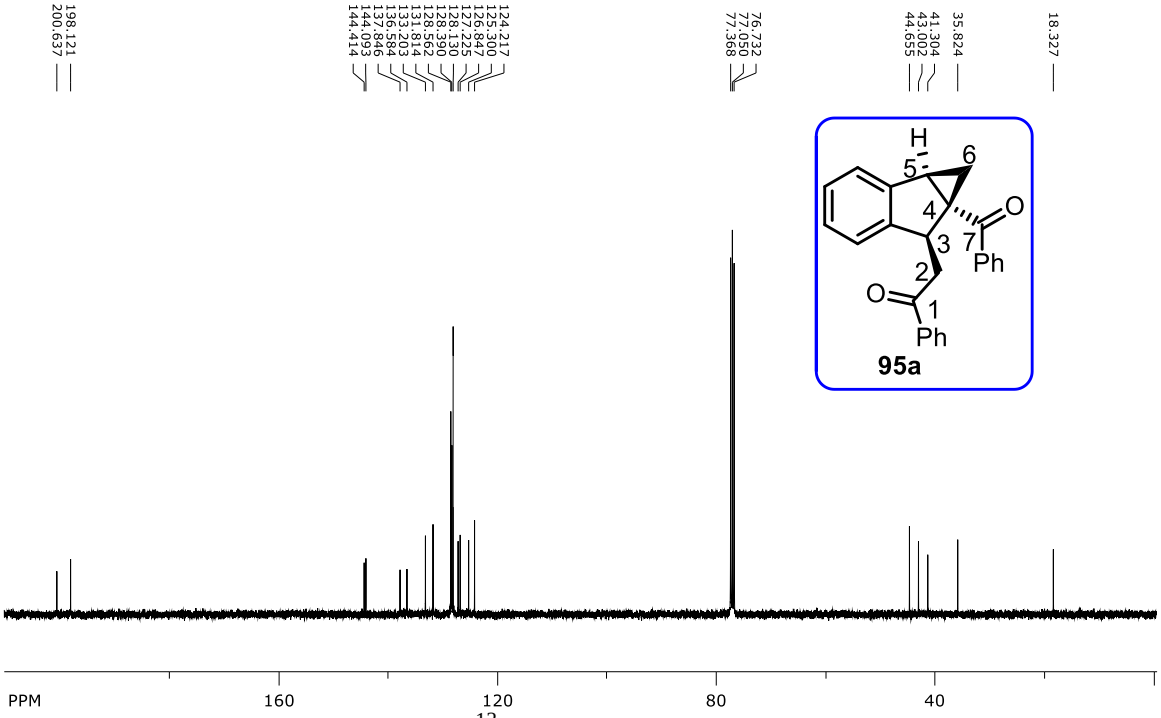
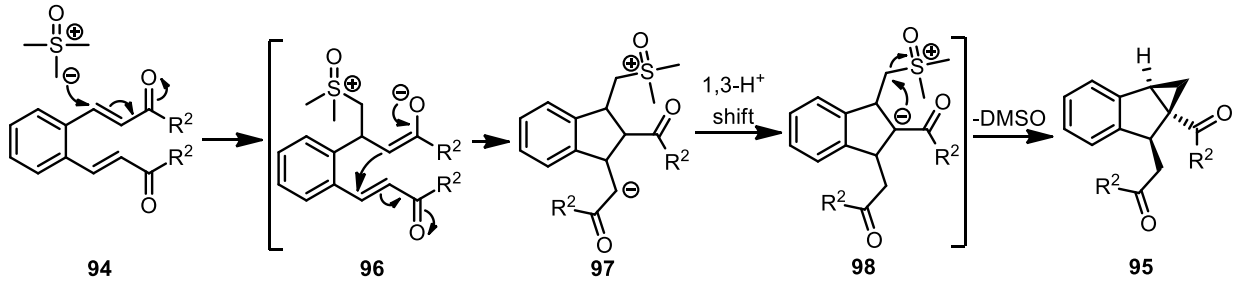


Figure 30: ^{13}C-NMR spectrum of **95a**

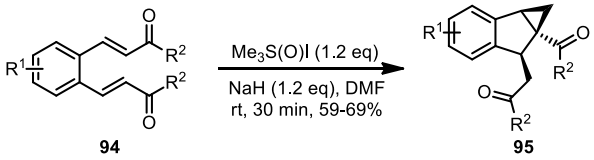
After realizing the formation of **95a**, we started to explore the substrate scope. For this, a series of enone-enones **94a-94j** were prepared by following the described procedures in Scheme 57. The optimized reaction conditions were applied to the enone-enones **94b-94j** to afford cyclopropa-fused indanes **95b-95j**, Table 11. The enone-enones possessing electron-withdrawing and electron-donating groups were reacted smoothly under the optimized reaction conditions (entry 8 and 5). The substrates with strong electron-donating group on the aryl backbone were also well-tolerated under the prototypical conditions (entry 9-10).

A plausible mechanistic pathway for the formation of product **95** is described in Scheme 59. The in situ generated sulfoxonium ylide attacks the enone moiety in **94** in a Michael fashion to generate enolates **96**, which subsequently through intramolecular Michael reaction deliveres the zwitterions **97**. The zwitterions **97** generate the intermediates **98** by a concomitant 1,3-proton shift, which followed by elimination of dimethyl sulfoxide provide **95**.

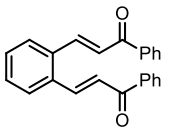
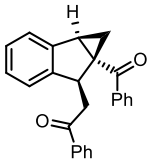
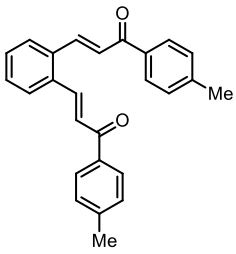
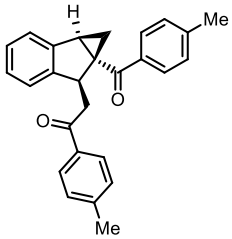
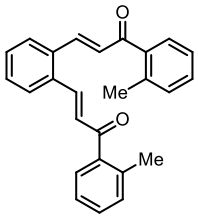
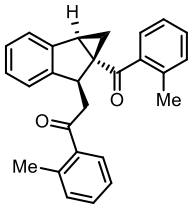
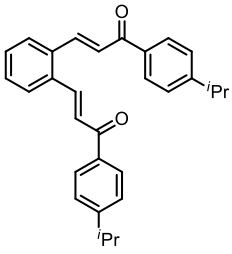
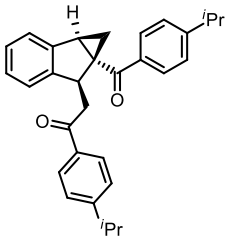
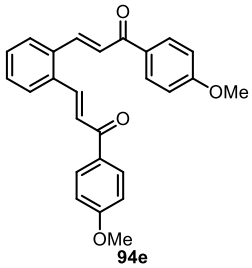
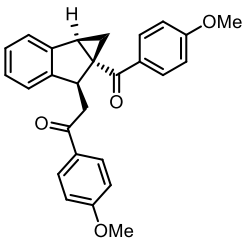
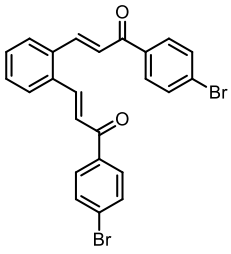
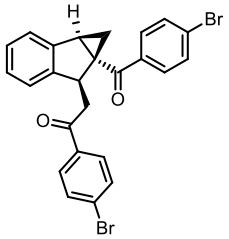
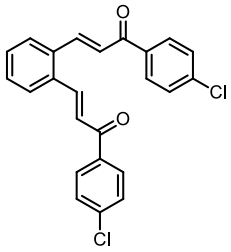
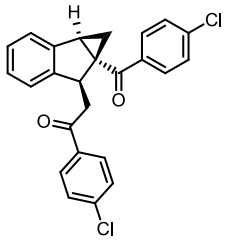
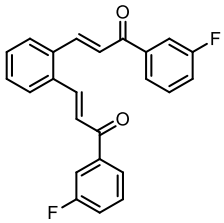
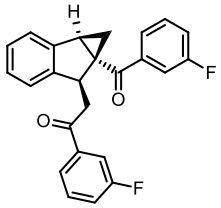
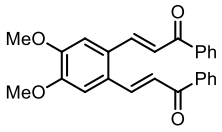
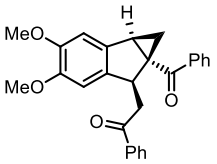
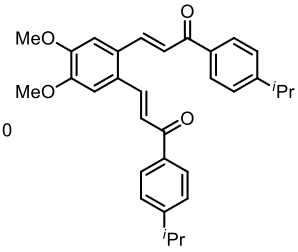
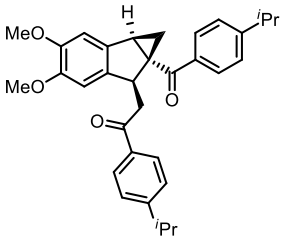


Scheme 59: Plausible mechanism for the Synthesis of cyclopropa-fused indanes **95**

Table 11: Reactions of enone-enones under the optimized conditions



94 **95**

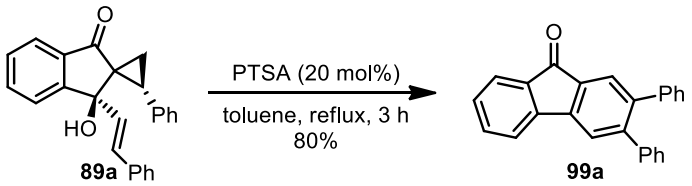
Entry	Substrate	Product
1	 **94a**	 **95a**, 59% (*dr* = 2.5:1)
2	 **94b**	 **95b**, 62% (*dr* = 2.5:1)
3	 **94c**	 **95c**, 67% (*dr* = 3:1)
4	 **94d**	 **95d, 61%** (*dr* = 2.5:1)
5	 **94e**	 **95e, 64%** (*dr* = 2.5:1)
6	 **94f**	 **95f**, 60% (*dr* = 3:1)
7	 **94g**	 **95g**, 69% (*dr* = 3:1)
8	 **94h**	 **95h**, 61% (*dr* = 3:1)
9	 **94i**	 **95i**, 58% (*dr* = 3:1)
10	 **94j**	 **95j**, 63% (*dr* = 3:1)

3.2: Synthetic utility of cyclopropanoids 89 and 95

After successful establishment of the synthesis of unusual cyclopropanoids, the synthetic elaboration of **89** and **95** were considered.

3.2.1: Synthesis of fluorenones

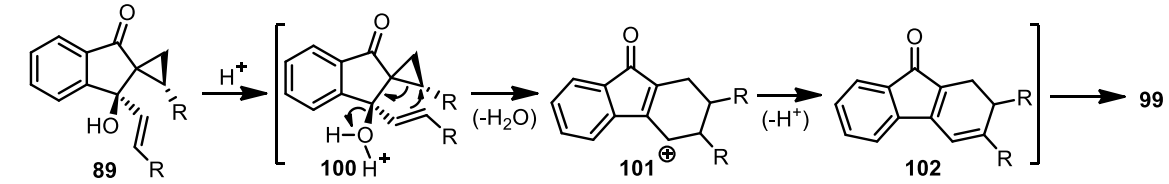
The presence of various functional groups and spirocyclopropane ring in the cyclopropanoid **89** indicates the high reactivity of **89**. Based on their reactivity, it was envisioned that **89** could undergo cationic cyclization reaction under acidic conditions. To validate our hypothesis, the reaction of **89a** was conducted in the presence of a catalytic amount of PTSA in toluene at reflux temperature, Scheme 60. Surprisingly, the reaction of **89a** exclusively delivered fluorenone **99a** in 80% yield.

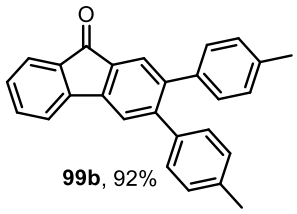


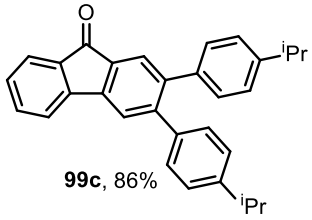
Scheme 60: Synthesis of fluorenone **99a**

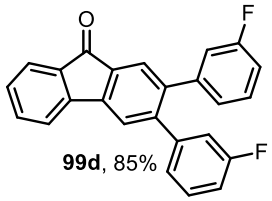
Fluorenone derivatives are privileged structures commonly present in many natural products and several biologically active molecules.[51] They have found wide-spread applications in photoelectronics, optics and organic semiconducting materials.[58] Owing to their significance, several types of fluorenone analogous were synthesized in good to excellent yields, Table 12. As of the mechanism, in the presence of an acid, the allylic-benzylic alcohol moiety is activated to generate intermediate **100**. The intermediate **100** through a formal homo-nazarov-type cyclization, generates tetrahydrofluorenyl cation **101**. The species **101** delivers fluorenone **99** *via* an intermediate **102**, through deprotonation and aromatization.

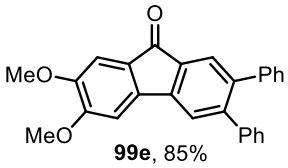
Table 12: Substrate Scope

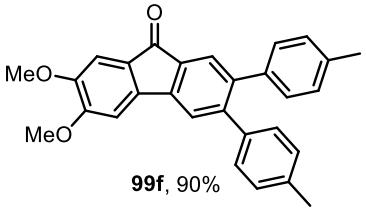






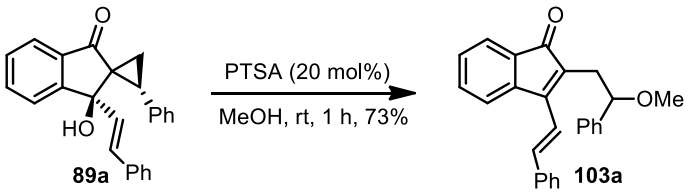






3.2.2: Synthesis of indenones

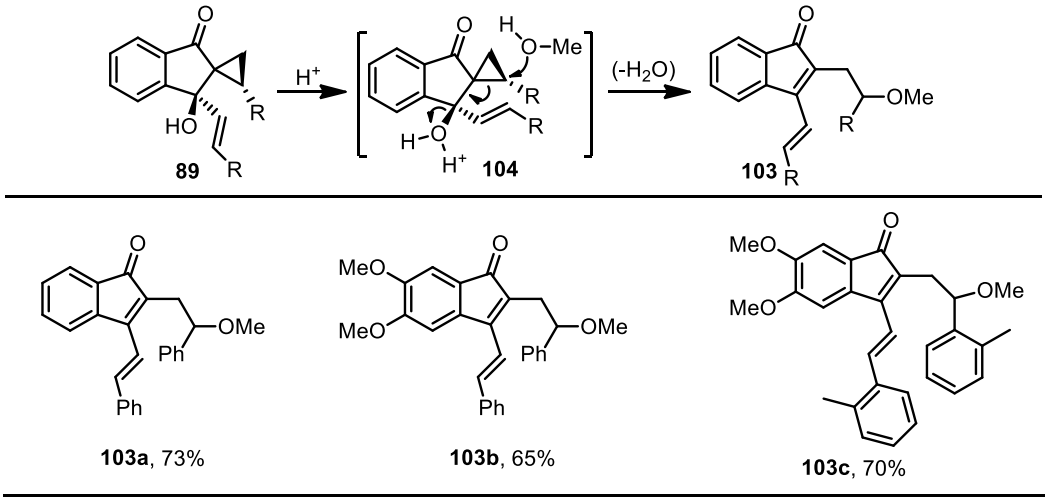
We noticed an interesting observation during the optimization of reaction parameters for the conversion of **89a** to **99a**, Scheme 60. When the cyclopropanoids **89a** were treated with the catalytic amount of PTSA in methanol solvent, resulted in the formation of *β*-styryl indenone **103a** in good yield.



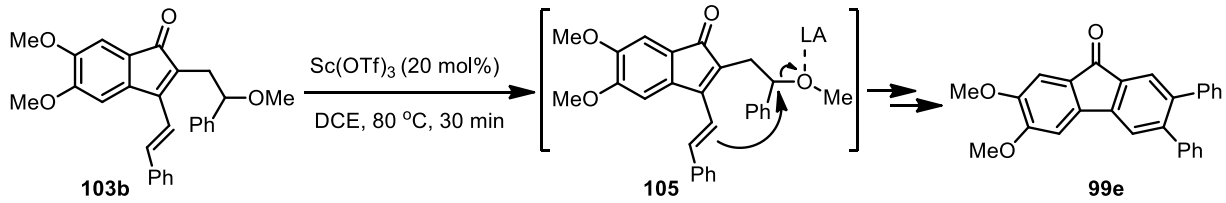
Scheme 61: Synthesis of indenone **103a**

Few more indenone analogous **103b-103c** were prepared owing to their importance,[59] Table 13. The product **103** was formed from **89** *via* the intermediate **104** as depicted in Table 13. However, we did not observe the formation of the respective fluorenone.

Table 13: Substrate Scope



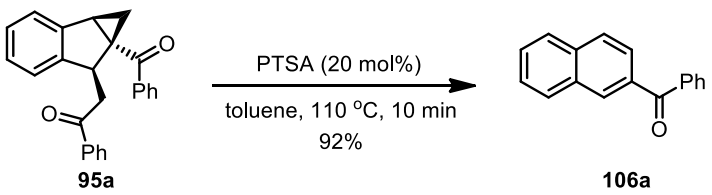
The PTSA catalyzed reaction of **89** in methanol did not result in the formation of fluorenone but an interesting observation was made while the reaction was conducted in the presence of $Sc(OTf)_3$. The reaction of **103b** in the presence of catalytic amount of $Sc(OTf)_3$ in DCE at 80 ^oC resulted in the formation of fluorenone **99e**, presumably *via* the intermediate **105**, Scheme 62.



Scheme 62: Synthesis of fluorenone **99e**

3.2.3: Synthesis of 2-naphthaphenones

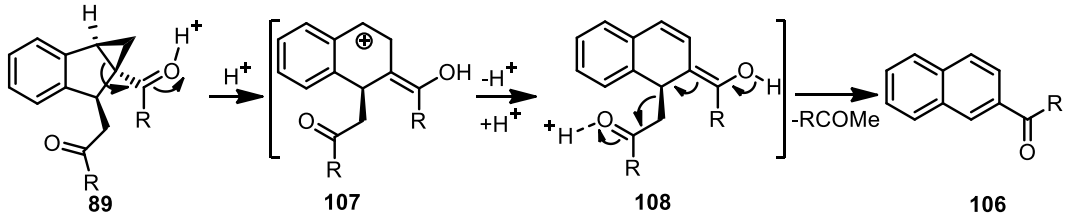
Our earlier success in PTSA mediated cyclopropane ring-opening inspired us to apply the strategy to other unusual cyclopropanoids to access the privileged compounds.[44] Thus, in order to achieve new molecular entities, we performed the reaction of **95a** in the presence of a catalytic amount of PTSA in toluene at 110 ^oC. Before performing the reaction, it was anticipated that by activation of cyclopropyl keto moiety in **95a**, the C-C bond which experiences better overlapping with the carbonyl group could cleave. Thereby, the reaction of **95a** yielded 2-naphthapphenone **106a** in excellent yield, Scheme 63.

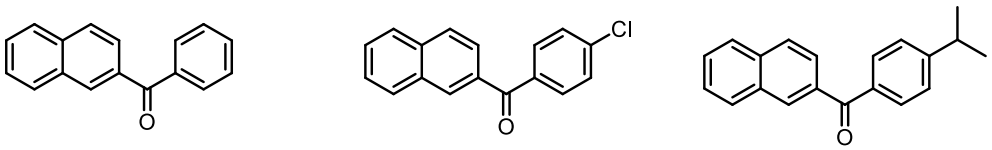


Scheme 63: Synthesis of 2-naphthaphenone **106a**

Naphthalene moiety is an important core frequently found in many biologically active natural products.[60] Natural products embody naphthalene moiety, such as Nafcillin, Naproxen, Cambinol, and Velpatasvir showed broad biological activity. Moreover, the naphthalene derivatives serve as semiconductor. Thus, due to these impressive properties of naphthalene moiety, two more analogous of 2-naphthaphenone were synthesized in excellent yields, Table 14. For the transformation of **89** to **106**, a plausible mechanism is proposed in Table 14. The keto group attached to the cyclopropane ring is activated by PTSA and subsequently the cyclopropane ring cleaves to generate the intermediate **107**. The intermediate **107** *via* dehydrogenation provides **108**, which followed by retro-Michael reaction affords **106**.

Table 14: Substrate Scope





In conclusion, we have demonstrated the DOSM promoted synthesis of densely functionalized cyclopropanoids. Further, one-step serendipitous elaboration of the products provided access to privilege scaffolds such as fluorenones, indenones and naphthaphenones. The investigation about the mechanism of product formation indicated that the strategies presented herein are very straightforward under the mild reaction conditions.

Section 4

Ring-opening and recyclization reactions of mono-activated cyclopropanes enabled by DMSO

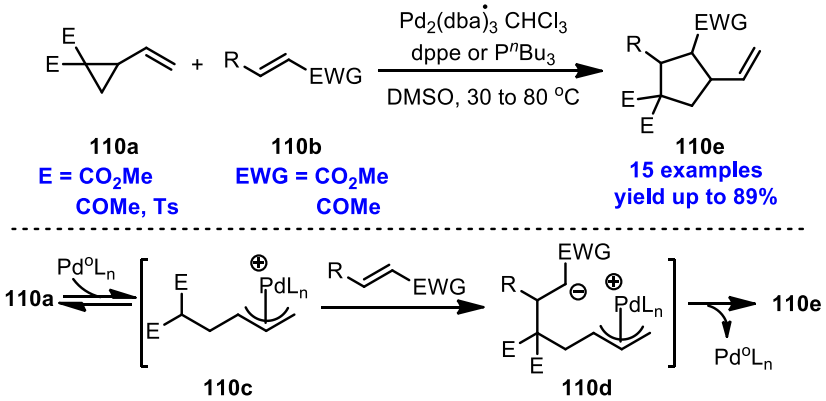
After the successful demonstration of mild and straightforward protocols for the synthesis of unusual cyclopropanoids promoted by DOSM (as described in Sections 2 and 3), we considered the ring-opening of the cyclopropane motif by employing organocatalysts. Due to the unusual reactivity of the cyclopropane ring, they can undergo a variety of ring-opening cyclization reactions in the presence of suitable chemical reagents.[2] However, there are two types of cyclopropane ring-opening reactions, assisted either by electrophiles or nucleophiles. In the past few decades, several strategies regarding cyclopropane ring-opening enabled by suitable

activating reagents have been developed, but nucleophile assisted ring-opening reactions of unactivated cyclopropanes are limited. There are four major classes of cyclopropanes (a) donor-acceptor cyclopropanes, (b) cyclopropanes containing two geminal electron-withdrawing groups, (c) vinyl cyclopropanes, and (d) monoactivated cyclopropanes, that rapidly undergo ring-opening cyclization reaction influenced by suitable reagents. Some of the cyclopropane ring-opening reactions are demonstrated in the following.

In 1982, Dieter *et al.*[61] introduced the hard Lewis acid-catalyzed ring cleavage of cyclopropyl ketone **109a** towards the synthesis of nucleophile added product **109b** in excellent yields, Scheme 64. The cleavage of the cyclopropyl ring depends on the nature of electrophiles or nucleophiles present in the reaction medium. Herein, the whole reaction represents electrophiles assisted cyclopropane ring-opening of **109a**.

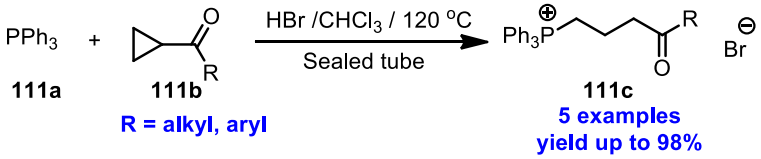
Scheme 64: Dieter's Lewis acid catalyzed ring-opening of cyclopropane

In 1985, Tsuji *et al.*[62] reported a palladium-catalyzed cycloaddition reaction of vinylcyclopropanes **110a** with electron-deficient olefins **110b** for the synthesis of highly substituted functionalized cyclopentanes **110e** in good yields, Scheme 65. The following described mechanism in Scheme 65 attributed to the formation of the product **110e**.



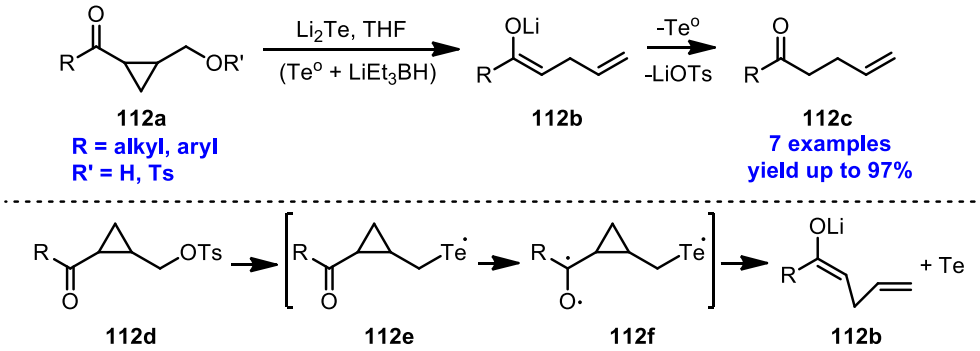
Scheme 65: Tsuji's [3+2] cycloaddition reaction *via* ring-opening of vinycyclopropane

In 1987, Cristau *et al.*[63] first unfolded the concept of cyclopropane ring-opening strategy triggered by nucleophilic organo-phosphines, Scheme 66. The reaction of cyclopropyl ketones **111b** and triphenylphosphine **111a** in the presence of HBr afforded phosphonium salts **111c** in excellent yields.



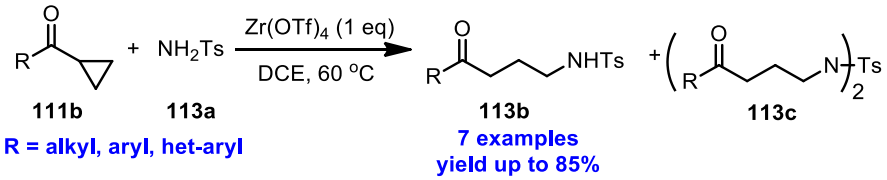
Scheme 66: Cristau's organocatalytic ring-opening of cyclopropanes

In 2004, Dittmer *et al.*[64] demonstrated tellurium-triggered ring-opening of cyclopropyl ketones **112a** to generate the corresponding enolates **112b**, which upon protonation delivered homoallylic ketones **112c** in excellent yields, Scheme 67. The plausible mechanism for the formation of the product is depicted in Scheme 67. This strategy provides enolates **112b** without using any strong bases or strong Lewis acids.



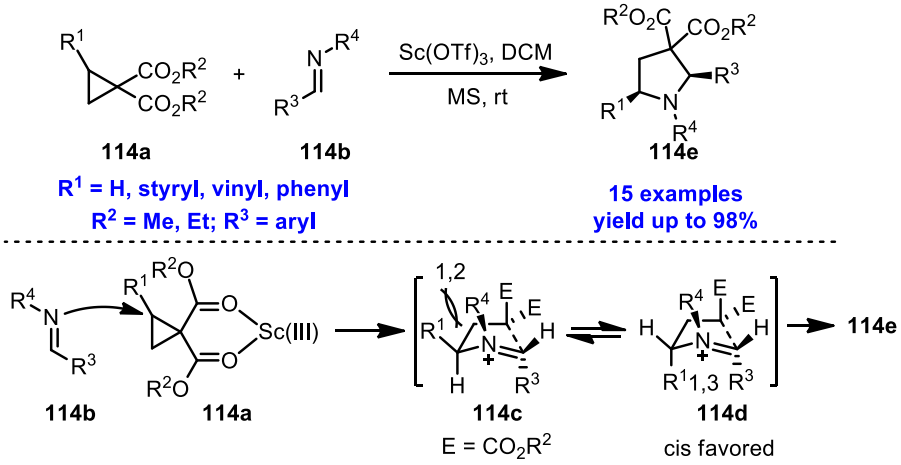
Scheme 67: Dittmer's ring-opening of cyclopropanes by the action of tellurium

In 2004, Shi *et al.*[65] developed $Zr(OTf)_4$ promoted ring-opening reaction of cyclopropyl aryl ketones **111b** in the presence of sulfonamides **113a** to provide **113b** in good yields, Scheme 68. Under the reaction conditions, the dimerized product **113c** was detectable in some cases.



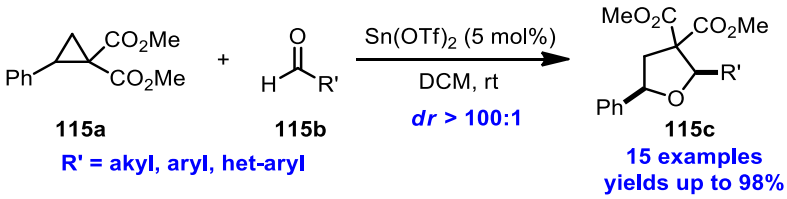
Scheme 68: Shi's Lewis acid mediated ring-opening of cyclopropane

In 2006, Tang *et al*.[66] described Lewis acid-mediated ring-opening/recyclization reaction of cyclopropanes **114a** with imines **114b**, Scheme 69. In the presence of $Sc(OTf)_3$, the reaction efficiently delivered substituted pyrrolidines **114e** in high diastereoselectivities. A plausible mechanistic path for the formation of the product is depicted in Scheme 69. The cyclopropane moiety of **114a** is activated *via* the coordination of ester groups with $Sc(OTf)_3$ and subsequently *via* S_N2 attack of imine **114b** generated zwitterionic intermediate **114c** or **114d**, which through cyclization produced **114e**. In this reaction, the formation of *cis*-isomer is favored over *trans*-isomer because of the steric hindrance between R^1 and R^4 is depicted in **114d**.



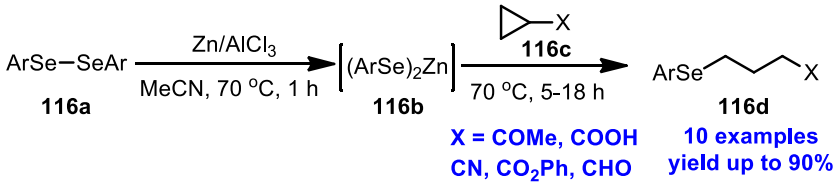
Scheme 69: Tang's Lewis acid mediated cyclopropane ring-opening reaction

In 2008, Johnson *et al*.[67] established [3+2] annulation reaction between activated cyclopropanes **115a** and aldehydes **115b** enabled by Lewis acid catalyst $Sn(OTf)_2$, which resulted in the formation of *cis*-2,5-disubstituted tetrahydrofurans **115c** in high diastereoselectivities, Scheme 70.



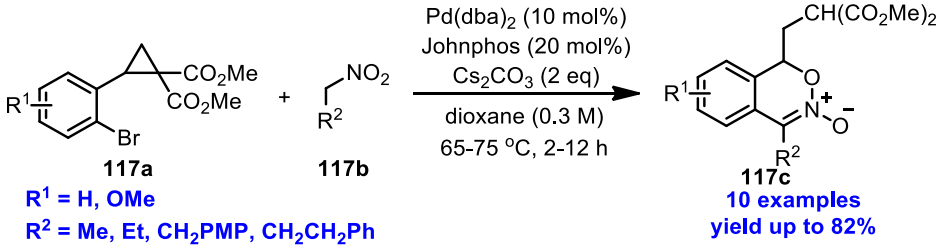
Scheme 70: Johnson's Lewis acid mediated [3+2] annulation reaction

In 2009, Movassagh *et al.*[68] introduced Zn/$AlCl_3$-assisted cleavage of diselenides **116a** and subsequent rupture of cyclopropane ring **116c** to generate the product **116d** in good to excellent yields, Scheme 71. A wide variety of organoselenium compounds were accessed under neutral and mild reaction conditions owing to their importance in organic synthesis.



Scheme 71: Movassagh's Lewis acid mediated ring-opening of cyclopropanes

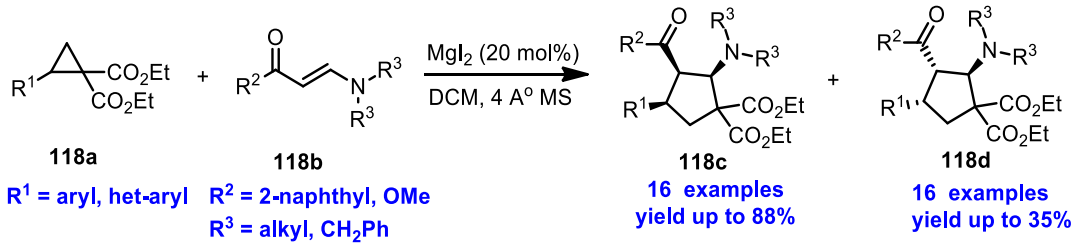
In 2016, Mikhaylov *et al.*[69] demonstrated $Pd(dba)_2$/Johnphos catalyzed C-C coupling of **117a** with nitroalkanes **117b** and subsequent intramolecular cyclization to obtain 1*H*-2,3-benzoxazine 3-oxides **117c** in good yields, Scheme 72. It was realized that the ring-opening of the cyclopropane moiety is a faster process than the coupling reaction.



Scheme 72: Mikhaylov's annulation reaction with cyclopropanes

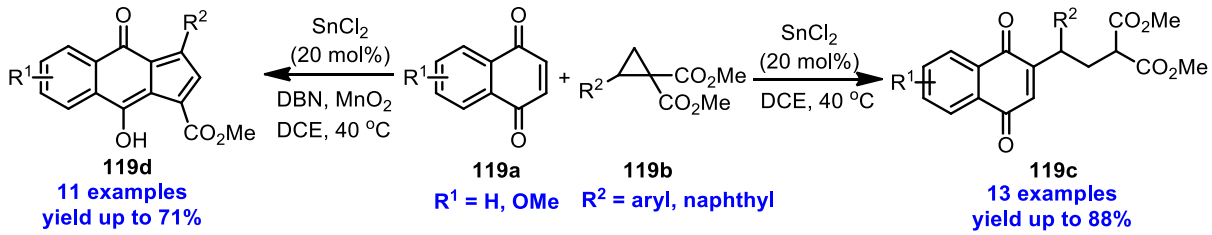
In 2016, Banerjee *et al.*[70] developed Lewis acid-catalyzed [3+2] annulation strategy by the reaction of cyclopropanes **118a** and enamines **118b** towards the synthesis of cyclopentane

derivatives **118c** and **118d** as a diastereomeric mixture, Scheme 73. The cyclopropanes **118a** undergo ring-opening through activation assisted by the Lewis acid MgI_2.



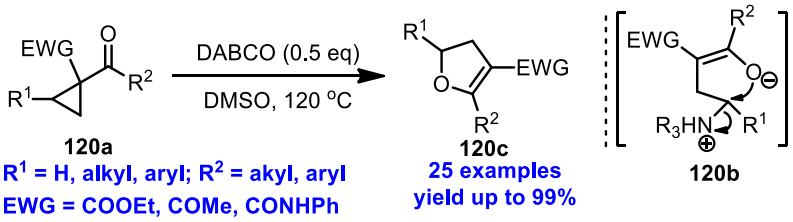
Scheme 73: Banerjee's [3+2] annulation reaction of cyclopropanes and enamines

In 2017, Werz *et al.*[71] highlighted the cyclopropane ring-opening by *in situ* generated naphthoquinone radical, Scheme 74. The reaction of naphthoquinones **119a** and activated cyclopropanes **119b** in the presence of Lewis acid $SnCl_2$ delivered **119c** in excellent yields. However, interestingly, in the presence of a base, the reaction of **119a** and **119b** generated cyclopentannulated product **119d** in moderate to good yields. The key to the success of this reaction is the *in situ* transformation of electrophilic naphthoquinone to nucleophilic naphthoquinone in the presence of $SnCl_2$.



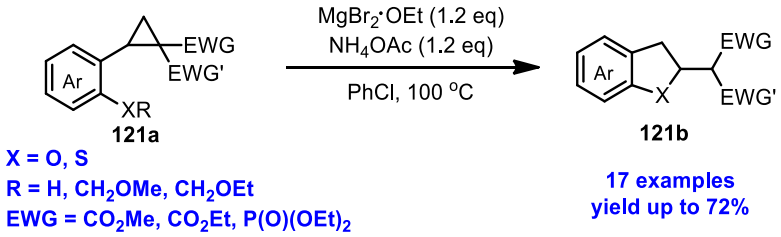
Scheme 74: Werz's coupling reaction of cyclopropanes and naphthoquinones

In 2017, Xu *et al.*[72] reported the synthesis of 2,3-dihydrofurans **120c** *via* organocatalytic ring expansion of cyclopropyl ketones **120a**, Scheme 75. A wide range of 2,3-dihydrofurans were accessed in high yields with exclusive regioselectivity by utilizing this strategy. The reaction of cyclopropyl ketones **120a** exclusively provided **120c** through the formation of the intermediate **120b**.



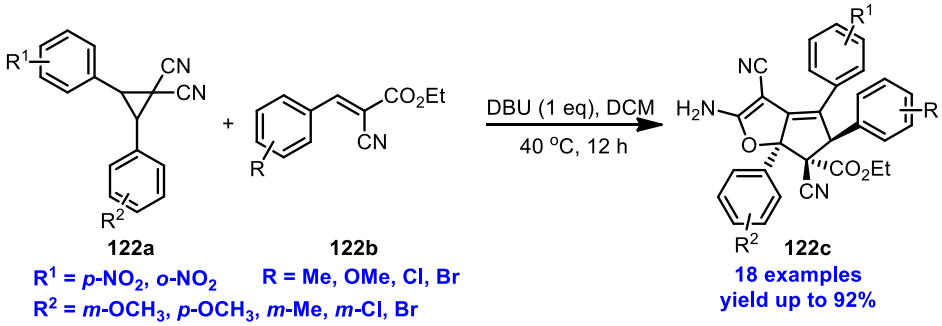
Scheme 75: Xu's organocatalytic cyclopropane ring opening reaction

In 2018, Trushkov *et al.*[73] introduced the synthesis of oxygen and sulfur-containing heterocycles **121b** by Lewis acid-catalyzed intramolecular cyclopropane ring-opening of **121a**, Scheme 76. A diverse set of cyclopropane bearing substrates were well tolerated under the optimize reaction conditions.



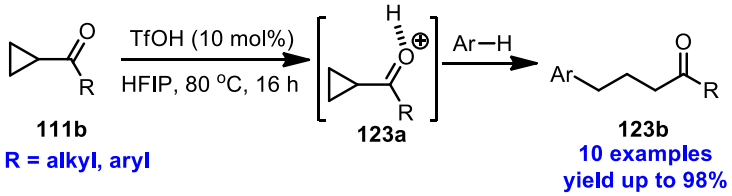
Scheme 76: Trushkov's Lewis acid catalyzed cyclopropane ring-opening/cyclization reaction

In 2018, Wang *et al.*[74] developed DBU promoted [3+2] annulation reaction of nitroarylcyclopropane-1,1-dicarbonitriles **122a** and 3-aryl-2-cyanoacrylates **122b** towards the synthesis of cyclopenta[*b*]furan derivatives **122c** in excellent yields with high stereoselectivity, Scheme 77. The mild reaction conditions and the easily accessible starting materials make this strategy a practical process towards the synthesis of cyclopenta[*b*]furan derivatives.



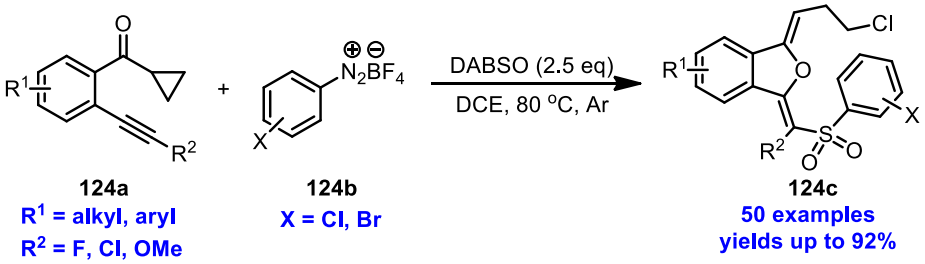
Scheme 77: DBU-mediated cyclopropane ring opening reaction

In 2018, Moran *et al.*[75] documented Brønsted acid promoted ring cleavage of monoactivated cyclopropanes **111b** in HFIP solvent to afford **123b** in good to excellent yields, Scheme 78. The formation of **123b** can be rationalized by considering the formation of the intermediate **123a**. The convertion of **111b** to **123b** proceeded smoothly under the reaction conditions due to the generation of superior Brønsted acid catalyst from TfOH in HFIP solvent.



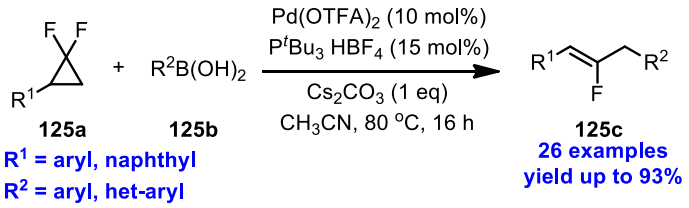
Scheme 78: Moran's Brønsted acid catalyzed cyclopropane ring-opening reaction

In 2019, Jiang *et al.*[76] reported an unprecedented stereoselective synthesis of highly functionalized substituted (*Z*,*Z*)-isobenzofurans **124c** by DABSO mediated radical-induced reaction of **124a** and **124b**, Scheme 79. A diverse range of substituted (*Z*,*Z*)-isobenzofurans were accessed in good to excellent yields by employing this strategy.



Scheme 79: Jiang's radical-induced cyclopropane ring-opening/cyclization reaction

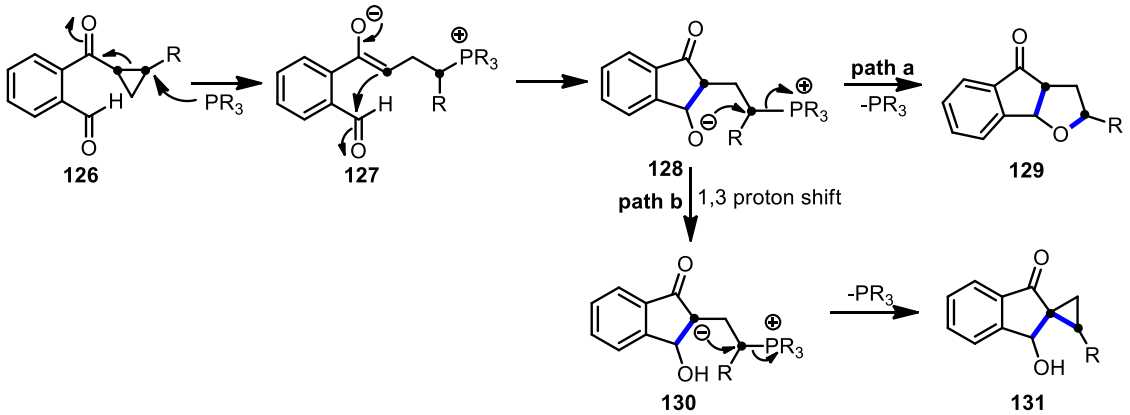
In 2019, Fu *et al.*[77] established the cross-coupling reaction between *gem*-difluorinated cyclopropanes **125a** and boronic acids **125b** *via* palladium-catalyzed *in situ* ring-opening of cyclopropane moiety, Scheme 80. The palladium-catalyzed cross-coupling reaction resulted in 2-fluoroallylic moiety **125c** in moderate to excellent yields.



Scheme 80: Pd-catalyzed cross-coupling reaction of cyclopropanes and boronic acids

The aforementioned literature survey highlights few important aspects of cyclopropane ring-opening reactions: (i) the reactions are catalyzed by Lewis or Brønsted acids or metal catalyst under vigorous reaction conditions, (ii) the reactions catalyzed by organocatalysts are less explored, and (iii) the reactions associated with cyclopropyl aryl ketones (monoactivated cyclopropanes) required stoichiometric amount of acids and harsh reaction conditions.

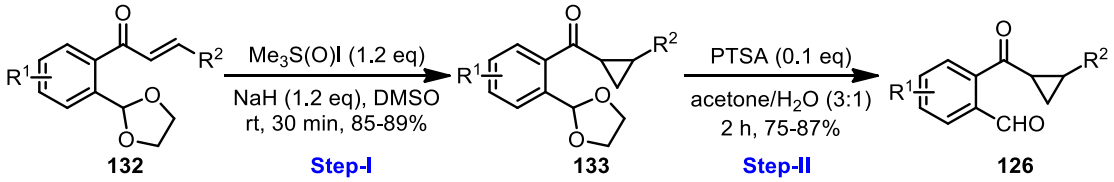
Thus, these limitations influenced us to design the cyclopropyl aryl ketones **126**, and it was envisioned that **126** could undergo the cyclopropane ring-opening under the nucleophilic organophosphine mediated reaction conditions, Scheme 81.[78] It was also anticipated that the nucleophilic phosphine could attack the cyclopropane ring moiety to generate the zwitterionic species **127** and subsequent recyclization (intramolecular aldol type reaction) could provide the intermediate **128**. Now, the intermediate **128** could deliver the product **129** through the nucleophilic displacement of the phosphonium group *via* path a. On the other hand, a 1,3-proton shift of the intermediate **128** could yield another zwitterionic species **130**, followed by nucleophilic displacement of the phosphonium group could lead to the formation of **131** *via* path b.



Scheme 81: Our hypothesis for the organocatlytic cyclopropane ring-opening reaction

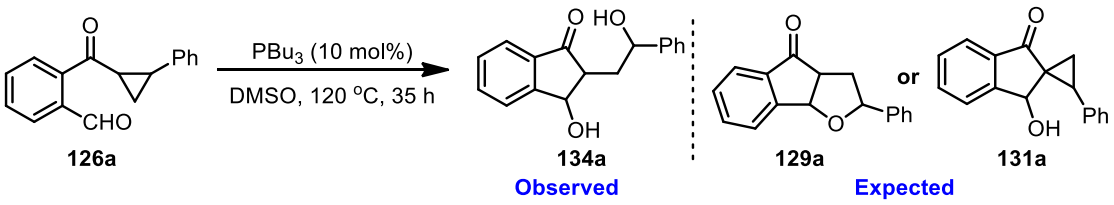
4.1: Results and discussion:

To substantiate our hypothesis presented in Scheme 81, we started synthesizing the designed substrates **126**. The cyclopropyl keto-aldehydes **126** can be synthesized in a two-step protocol starting from the compounds **132**, Scheme 82. The compounds **132** can be easily accessible by following a protocol developed by our research group.[44] The cyclopropanation reaction of **132** delivered **133**, which followed by deprotection of acetal group under the appropriate reaction conditions, afforded the desired cyclopropyl keto-aldehydes **126**.



Scheme 82: Synthesis of cyclopropyl keto-aldehydes **126**

Accordingly, we have initiated an optimization study to evaluate the optimization conditions to deliver the expected products (mentioned in Scheme 81) by considering 2-(2-phenylcyclopropanecarbonyl)benzaldehyde **126a** as a model substrate. Thus, the substrate **126a** was subjected to the phosphine mediated reaction conditions in DMSO at 130 ^{o}C, which resulted in the formation of **134a** with no noticeable formation of either **129a** or **131a**, Scheme 83.[79] Having realized the formation of **134a**, we made several efforts to improve the yield of the product **134a**. Towards this, different kinds of phosphines and solvent combinations were tested, and the results are summarized in Table 15. Among the commonly employed phosphine catalysts, PBu_3 and PCy_3 were found to deliver **134a** in moderate yields (Table 15, entries 1-2). However, surprisingly, when the reaction was carried out in the absence of phosphine catalyst, it also resulted in the formation of **134a** (Table 15, entry 9). This result indicated that there is no role of phosphine catalyst in the formation of the product **134a**.

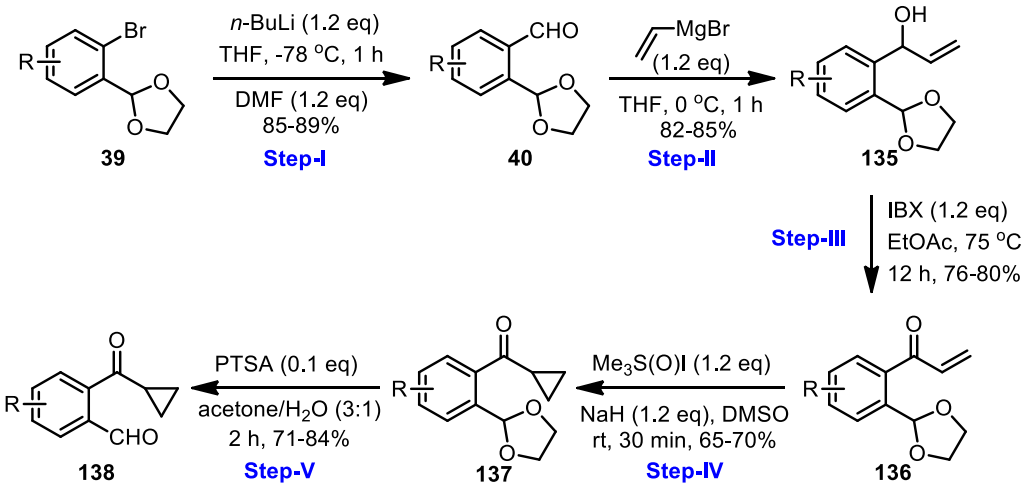


Scheme 83: Phosphine mediated reaction of cyclopropyl keto-aldehydes **126a**

Table 15: Optimization of reaction parameters

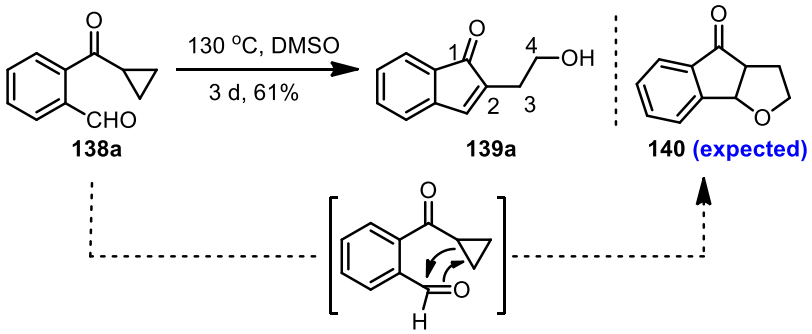
Entry	Catalyst (mol%)	Solvent	Temperature (^{o}C)	Time (d)	Yields (%)
1	PBu_3	DMSO	130	3	72
2	PCy_3	DMSO	130	3	73
3	PPh_3	DMSO	130	5	-
4	PCy_3	DMF	130	4	-
5	PCy_3	CAN	Reflux	4	-
6	PCy_3	1,4-dioxane	130	4	-
7	PCy_3	THF	Reflux	4	-
8	PCy_3	Toluene	Reflux	5	-
9	**-**	**DMSO**	**130**	**3**	**73**

Encouraged by this result, we applied this strategy to the less explored and less reactive monoactivated cyclopropyl keto-aldehydes **138** to undergo the cyclopropane ring-opening reaction, which is extremely challenging.[65,80] Thus, we initiated our efforts towards the synthesis of **138** by following a five-step protocol starting from **39**, Scheme 84. Direct *n*-BuLi mediated formylation of **39** afforded **40**, which followed by Grignard reaction, delivered **135**. The IBX oxidation of **135** yielded **136**. Cyclopropanation of **136** by using Corey's ylide provided **137**, which under acidic medium underwent deprotection of acetal group to deliver the desired cyclopropyl keto-aldehydes **138**.



Scheme 84: Synthesis of monoactivated cyclopropyl keto-aldehydes **138**

As per the plan, the cyclopropyl keto-aldehyde **138a** was heated at 130 ^{o}C in DMSO for three days which resulted in the formation of indenone **139a** in good yield, Scheme 85. However, under these conditions, the formation of **140** was not observed. To further improve the efficiency of the reaction, we commenced our efforts to optimize the reaction conditions. During the optimization, we realized that there was a pronounced dependence of temperature and solvent on the product formation. For example, when **138a** was heated in dimethylformamide (DMF), acetonitrile or 1,4-dioxane, **138a** remained as such (Table 16, entries 1-3). But when **138a** was heated in toluene, 1,2-dichloromethane, it resulted in the formation of oxidized product **141** (Table 16, entries 4-5). These results indicated an important role of the solvent (dimethylsulfoxide, DMSO) in the formation of the product **139a**. The role of the solvent was further evident when **138a** was heated neat, in which case only acid **141** was observed (Table 16, entry 6). Interestingly, no product formation was observed when **138a** was heated at lower temperature (Table 16, entries 7-8). Overall, this process represents the first uncatalyzed ring-opening/recyclization of cyclopropyl aryl ketones.

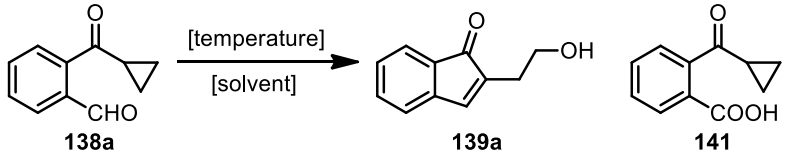


Scheme 85: Synthesis of indenone **139a**

The structure of indenone **139a** was deduced from the IR, NMR and HRMS data. The presence of a broad absorption band at 3405 cm^{-1} is the indication of the presence of primary alcohol functionality in the product and a sharp band at 1709 cm^{-1} indicates the unsaturated cyclic ketone in the IR spectrum of the product **139a**. In the ^{1}H-NMR spectrum (see Fig. 32), the presence of a triplet at δ 3.82 ppm (J = 6.1 Hz) indicates the -OH connected aliphatic C-4 methylene protons, a multiplet at δ 2.60-2.56 ppm indicates the C-3 methylene protons and a broad singlet at δ 2.15 ppm indicates the presence of -OH functional group. In ^{13}C-NMR spectrum (see Fig. 33), presence of a peak at δ 199.0 ppm indicates the carbonyl functionality

(C-1), a peak at δ 61.2 ppm indicates the -OH connected methylene carbon (C-4) and a peak at δ 28.7 ppm indicates aliphatic carbon (C-3). Thus the ^{1}H-NMR and ^{13}C-NMR data supported the formation of the product **139a**. The formation of the product **139a** was further confirmed by HRMS data where the presence of a (M-OH) peak at m/z 157.0653 corresponding to the formula $C_{11}H_9O$ with the calculated value of 157.0642.

Table 16: Optimization of reaction parameters with **138a**



138a **139a** **141**

Entry	Solvent	Temperature (^{o}C)	Time (d)	Yield (%)
1	DMF	130	5	-
2	CH_3CN	Reflux	5	-
3	1,4-dioxane	Reflux	5	-
4	toluene	110	3	85[141]
5	1,2-DCE	Reflux	3	91[141]
6	-	130	4	75[141]
7	DMSO	80	5	-
8	DMSO	110	5	-
9	**DMSO**	**130**	**3**	**61**

With the optimization reaction conditions in hand, we next turned our attention to investigate the substrate scope of the reaction. Towards this, we synthesized a wide range of cyclopropyl keto aldehydes **138a-138c** and **126a-126j** by following the procedures described in Scheme 84 and 82, respectively. Under the optimized reaction conditions, unsubstituted cyclopropanes (**138b** and **138c**) worked efficiently to deliver the corresponding products (Table 17, entries 1-2). Even the cyclopropanes possessing alkyl groups and aryl groups containing either electron-donating group or electron-withdrawing group at R^1 were well-tolerated under the optimized conditions (Table 17, entries 4 and 7-9). However, the substrates bearing electron-donating or electron-withdrawing groups on the arene backbone under the optimized conditions have no noticeable impact on the yield of the product (Table 17, entries 10-12 and 5-6). During the study of substrate scope evaluation, we never realized the formation of alcohol elimination product (leading to 2-vinylindenones).

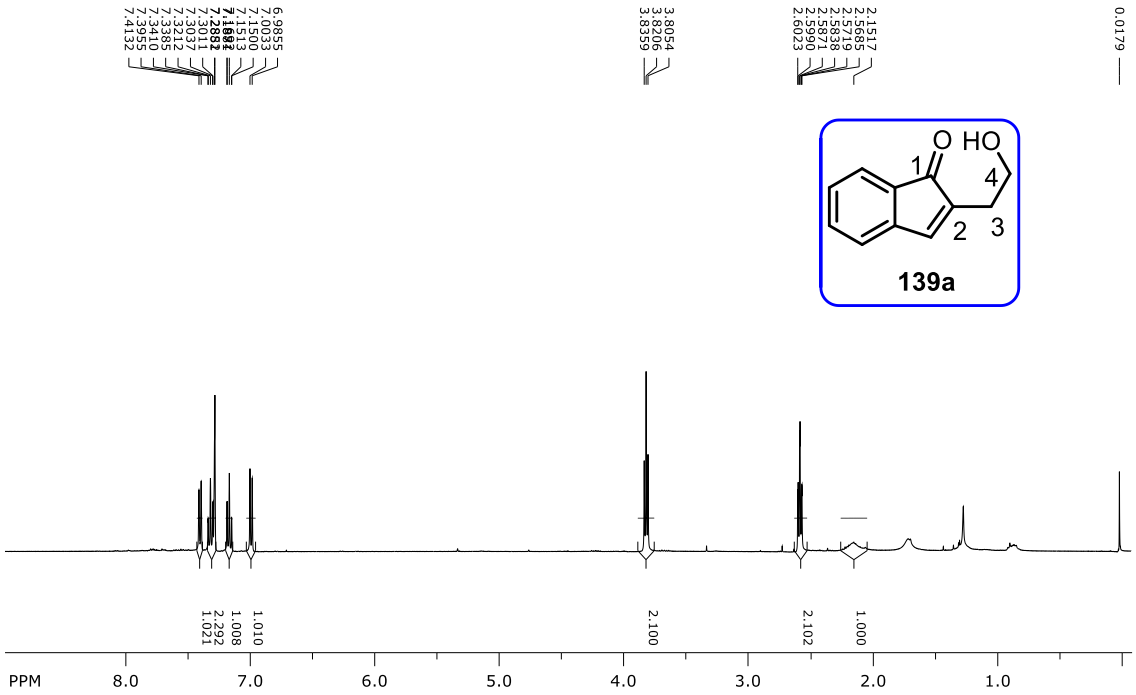


Figure 32: ^{1}H-NMR spectrum of **139a**

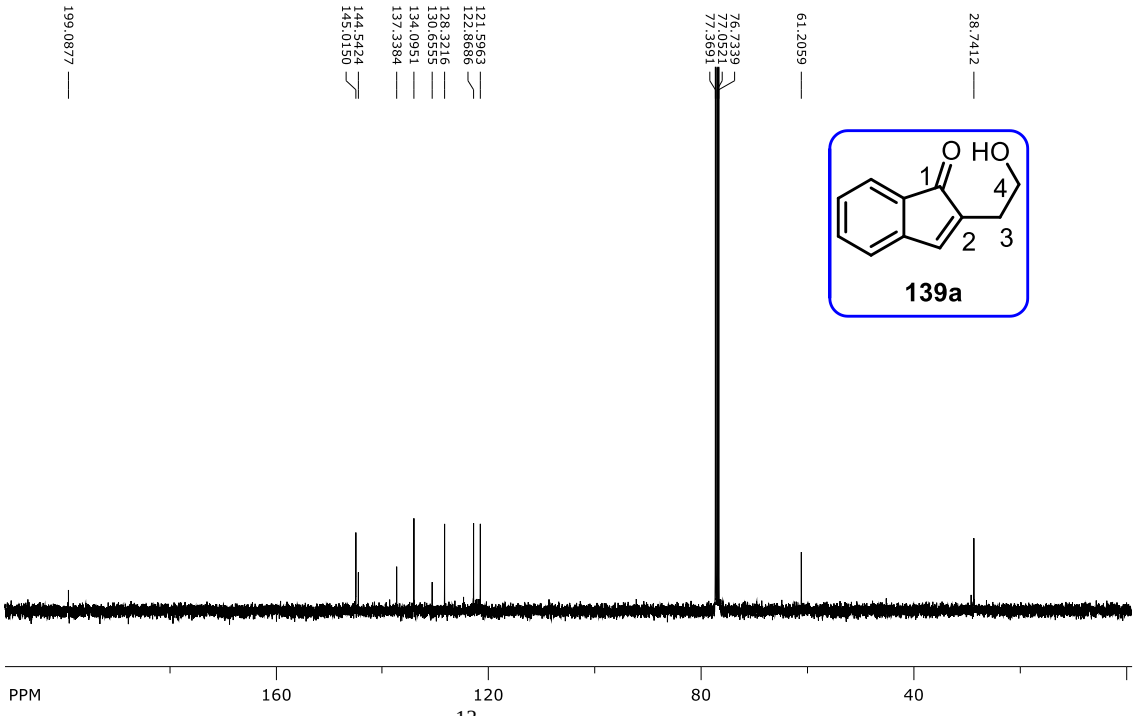
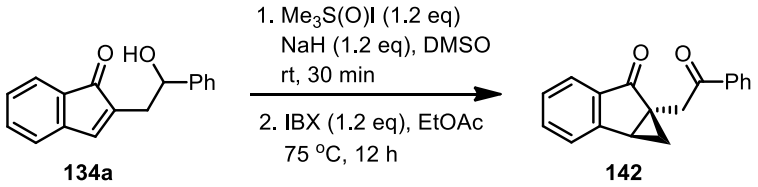


Figure 33: ^{13}C-NMR spectrum of **139a**

To confirm the structure of **134** or **139** by the X-ray diffraction analysis, a representative compound **134a** was converted in a two-step protocol to **142**, Scheme 86. The Corey's ylide mediated cyclopropanation reaction of **134a**, and subsequent IBX oxidation delivered **142**. The X-ray structure of **142** confirms the structure of **134a** (and as such those of **134** and **139**), Fig. 34.



134a **142**

Scheme 86: Synthetic transformations of **134a**

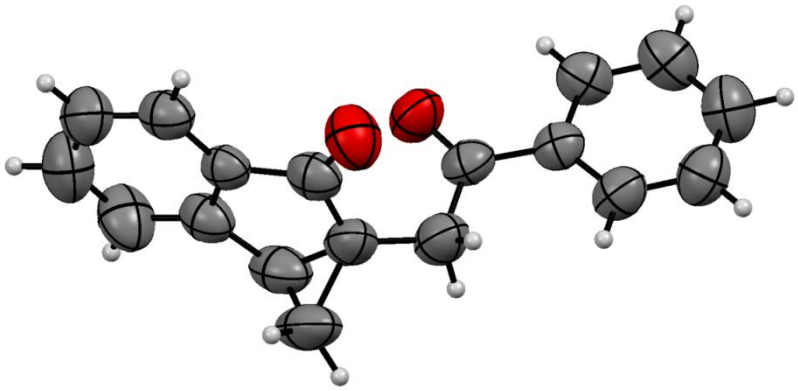
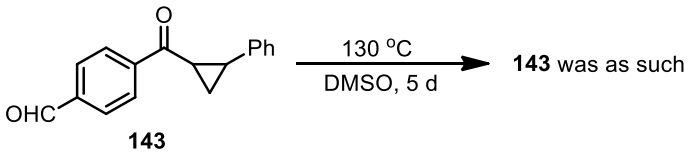


Figure 34: ORTEP diagram of **142**, ellipsoid probability (50%)

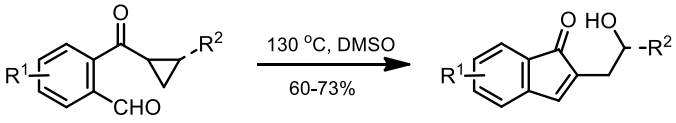
On the other hand, the substrate **143** bearing aldehyde functionality *para* to the cyclopropyl keto group under the optimized reaction conditions remained as such even after the prolonged reaction time, Scheme 87. This result is indicating that the formation of indenone was the driving force for the otherwise-difficult cyclopropane ring-opening.



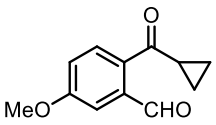
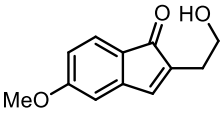
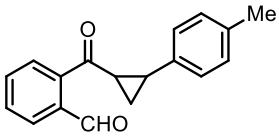
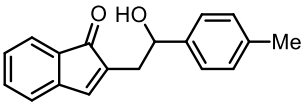
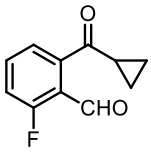
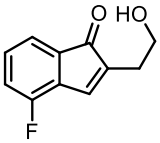
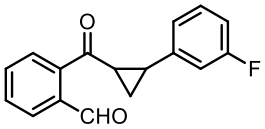
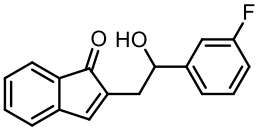
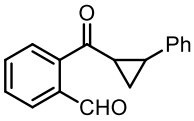
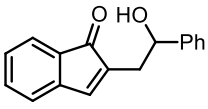
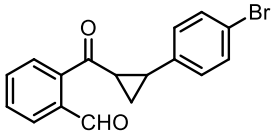
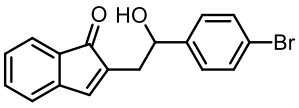
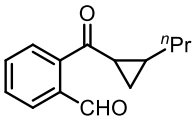
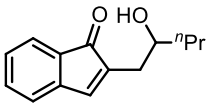
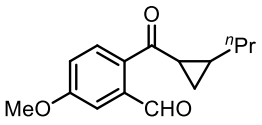
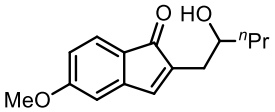
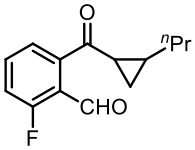
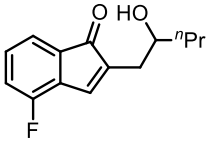
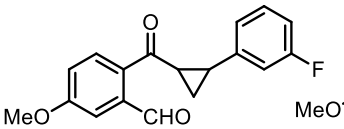
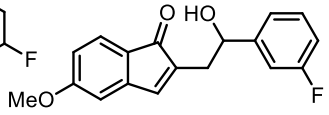
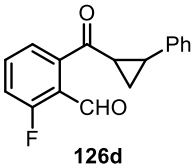
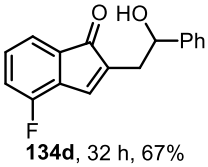
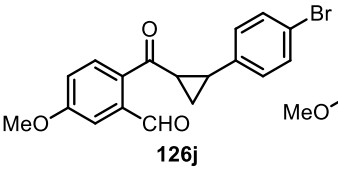
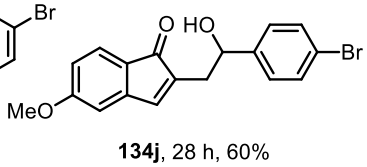
143

Scheme 87: Reaction of **143** under prototypical conditions

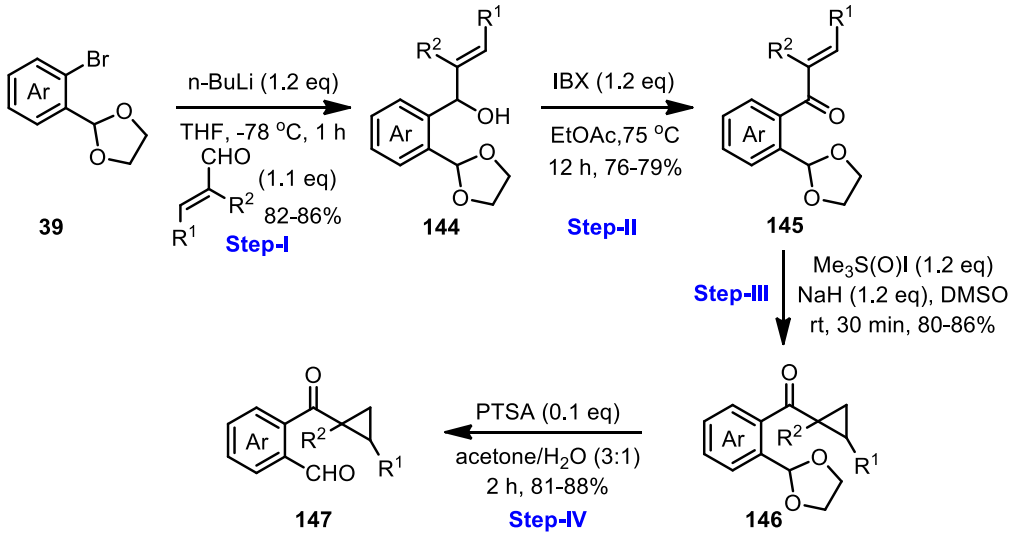
Table 17: Reactions of cyclopropyl keto-aldehydes under the optimized conditions



138 or 126 **139 or 134**

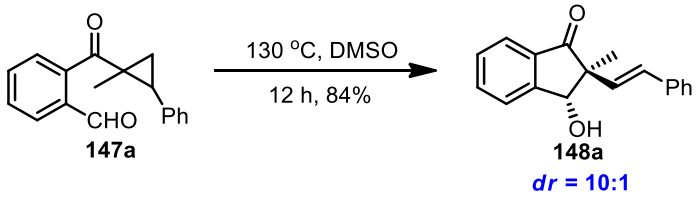
Entry	Substrate	Product	Entry	Substrate	Product
1	 **138b**	 **139b**, 74 h, 63%	7	 **126e**	 **134e**, 45 h, 70%
2	 **138c**	 **139c**, 70 h, 66%	8	 **126f**	 **134f**, 36 h, 66
3	 **126a**	 **134a**, 35 h, 73%	9	 **126g**	 **134g**, 32 h, 63%
4	 **126b**	 **134b**, 33 h, 62%	10	 **126h**	 **134h**, 32 h, 63%
5	 **126c**	 **134c**, 40 h, 60%	11	 **126i**	 **134i**, 20 h, 63%
6	 **126d**	 **134d**, 32 h, 67%	12	 **126j**	 **134j**, 28 h, 60%

After detailed investigation on the reactivity of monosubstituted and disubstituted cyclopropanes under the optimal reaction conditions, the strategy was extended to test the reactivity of 1,1,2-trisubstituted cyclopropyl ketones **147** under the reaction conditions. All the 1,1,2-trisubstituted cyclopropyl ketones **147** employed in this study were synthesized by following a four-step protocol starting from **39**, Scheme 88. Direct *n*-BuLi mediated alkylation of **39** provided **144**, which through IBX oxidation delivered **145**. The Corey's ylide mediated cyclopropanation reaction of **145** generated **146**, which, followed by PTSA-catalyzed deprotection of acetal group afforded **147**.



Scheme 88: Synthesis of cyclopropyl keto-aldehydes **147**

Accodingly, the 1,1,2-trisubstituted cyclopropyl ketone **147a** was subjected to the optimized reaction conditions, Scheme 89. An unexpected product **148a** formation was observed in good yield with good diastereoselectivity. The product **148a** possess two contiguous stereogenic centers, one of them is an all-carbon quaternary center.



Scheme 89: Synthesis of 2,2-disubstituted-3-hydroxyindanone **148a**

Due to the biological importance of the highly functionalized substituted indanones,[43] some other analogous **148b-148d** and **149a-149b** were synthesized in good yields, Table 18. Interestingly, substrates bearing aliphatic group at R^1 provided terminal olefins under the optimal reaction conditions (Table 18, entries 5-6). The structure including the relative stereochemistry of the major diastereomer was confirmed from the X-ray diffraction analysis of **148a**, Fig. 35.

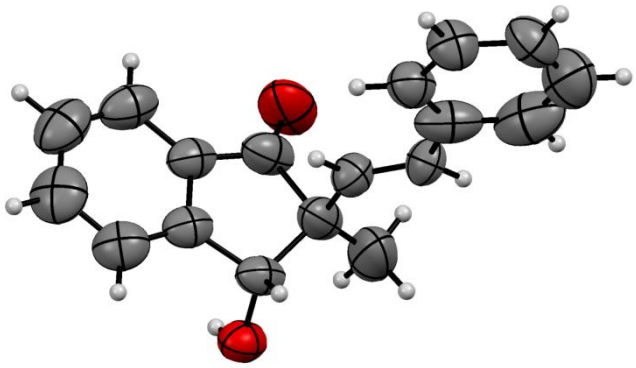
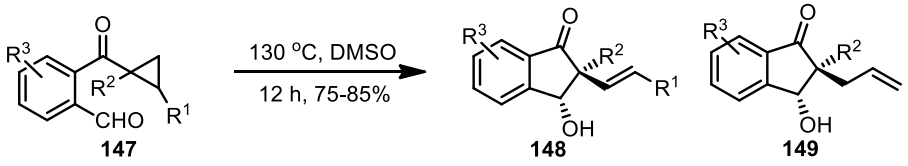
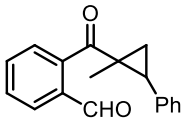
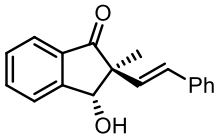
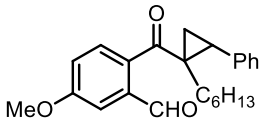
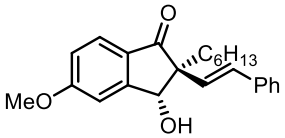
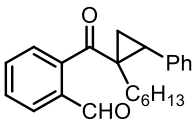
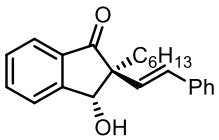
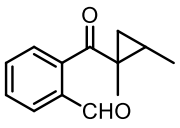
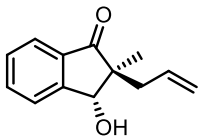
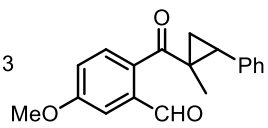
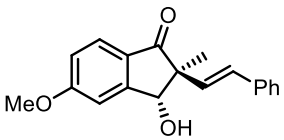
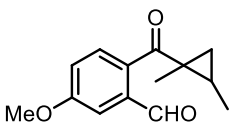
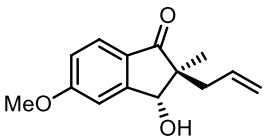


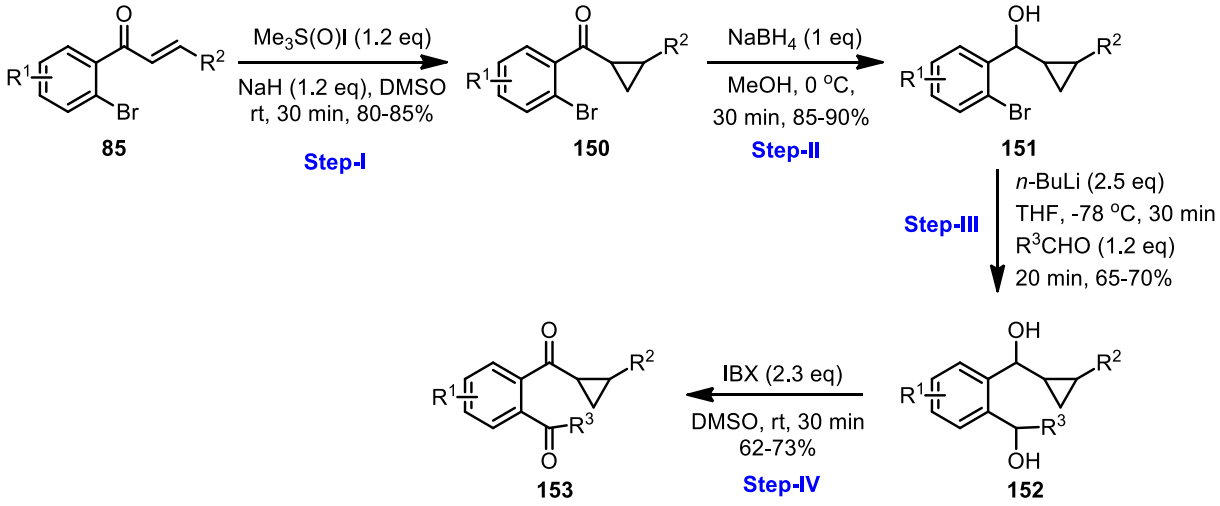
Figure 35: ORTEP diagram of **148a**, ellipsoid probability (50%)

Table 18: Reactions of cyclopropyl keto-aldehydes under the optimized conditions



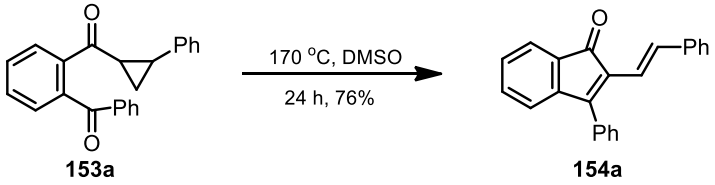
Entry	Substrate	Product	Entry	Substrate	Product
1	 **147a**	 **148a**, 84% (*dr* = 10:1)	4	 **147d**	 **148d**, 75% (*dr* = 10:1)
2	 **147b**	 **148b**, 81% (*dr* = 10:1)	5	 **147e**	 **149a**, 85% (*dr* = 3:1)
3	 **147c**	 **148c**, 78% (*dr* = 10:1)	6	 **147f**	 **149b**, 83% (*dr* = 2:1)

After realizing the efficient and facile tranceformations of mono-, di- and trisubstituted cyclopropyl keto aldehydes, the reaction of cyclopropyl keto-ketones **153** was considered. Towards this, the cyclopropyl keto-ketones **153** were prepared by following a four-step protocol starting from **85**, Scheme 90. The cyclopropanation reaction of **85** provided **150** which upon $NaBH_4$ reduction led to **151**. The *n*-BuLi mediated alkylation of **151** in the presence of benzaldehyde provided **152**, which, followed by IBX oxidation generated the desired cyclopropyl keto-ketones **153**.



Scheme 90: Synthesis of (2-benzoylaryl)(2-arylcyclopropyl)methanone **153**

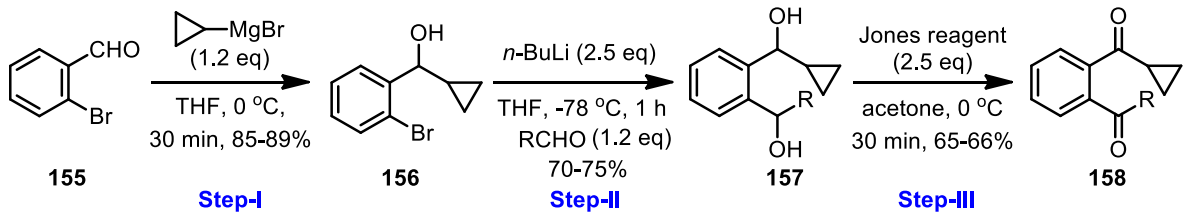
However, when the cyclopropyl keto-ketone **153a** was subjected to the optimal reaction conditions (as mentioned in case of cyclopropyl keto-aldehydes), no product formation was observed and starting material remained as such even after prolonged reaction time. But when the reaction temperature was elevated to 170 °C, an unprecedented formation of 2-styryl-3-phenylindenone **154a** was realized in good yield, Scheme 91.



Scheme 91: Synthesis of 2-styryl-3-arylindesnone **154a**

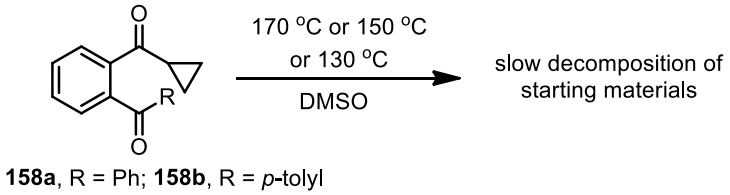
Having realized an unprecedented result,[81] the reaction of unsubstituted cyclopropyl keto-ketones **158** was also considered under the prototypical conditions. The cyclopropyl keto-ketones

158 can be easily achieved by following an efficient three-step protocol, Scheme 92. The Grignard reaction of **155** delivered **156** in a short reaction time. The *n*-BuLi mediated alkylation of **156** in the presence of appropriate aldehydes yielded diols **157**, which, followed by Jones oxidation provided **158**.



Scheme 92: Synthesis of (2-benzoylaryl)(cyclopropyl)methanone **158**

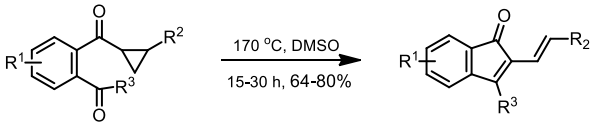
Under the optimized reaction conditions, all the cyclopropyl keto-ketones **153a-153k** delivered 2-styryl-3-arylindenone **154a-154k** in good yields, Table 19. The substrates possessing electron-rich as well as electron-poor substituents at R^2 were well-tolerated (entries 5 and 7). The substrates containing *ortho*-tolyl substituents **153d** and **153e** efficiently delivered the corresponding product under the optimized conditions (entries 4-5). Substrates with electron-donating groups on the arene backbone smoothly generated the respective products (entries 6-11). The product **154c**, with the presence of pyrene ring, shows interesting physicochemical properties (see Fig. 36 and 37). The compound **154k** represents the analogue of natural products, such as paucifloral F, ampelopsin D, caraphenol B, and others.[82] However, the unsubstituted cyclopropyl keto-ketones **158a** and **158b** failed to deliver the corresponding indenones even at lower temperature, Scheme 93.



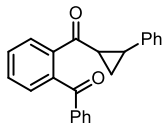
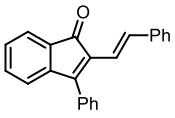
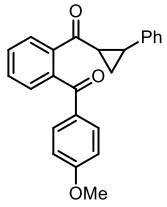
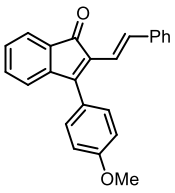
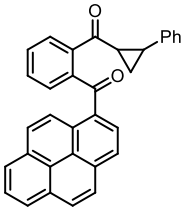
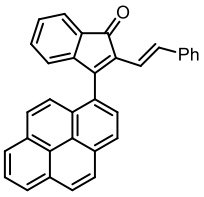
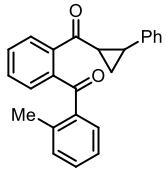
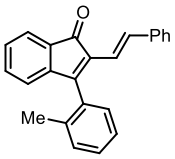
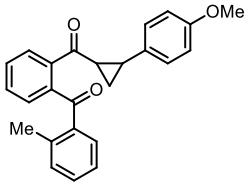
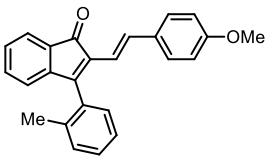
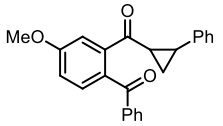
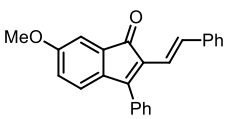
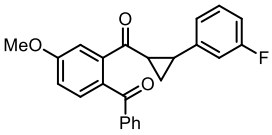
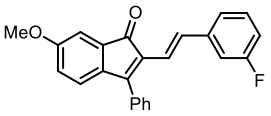
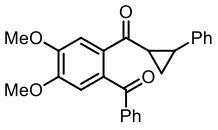
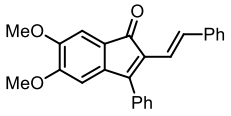
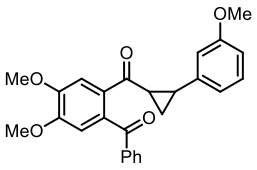
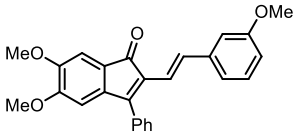
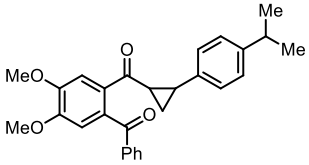
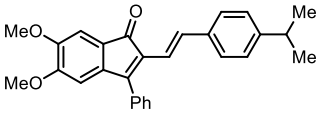
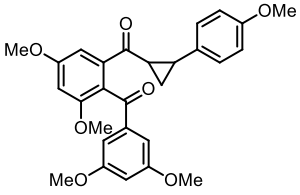
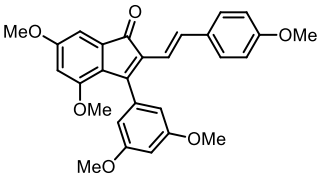
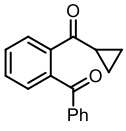
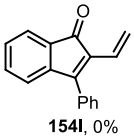
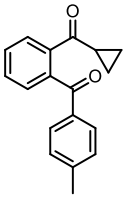
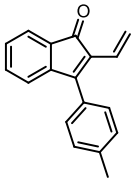
158a, R = Ph; **158b**, R = *p*-tolyl

Scheme 93: Reaction of unsubstituted cyclopropyl keto-ketones **158a** and **158b**

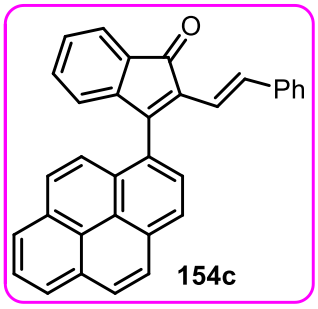
Table 19: Reaction of cyclopropyl keto-ketones under the optimized conditions



153 **154**

Entry	Substrate	Product
1	 **153a**	 **154a**, 24 h, 76%
2	 **153b**	 **154b**, 15 h, 76%
3	 **153c**	 **154c**, 9 h, 65%
4	 **153d**	 **154d**, 26 h, 68%
5	 **153e**	 **154e**, 3 h, 75%
6	 **153f**	 **154f**, 26 h, 79%
7	 **153g**	 **154g**, 30 h, 74%
8	 **153h**	 **154h**, 12 h, 80%
9	 **153i**	 **154i, 16 h, 65%**
10	 **153j**	 **154j**, 5 h, 75%
11	 **153k**	 **154k**, 1 h, 64%
12	 **158a**	 **154l**, 0%
13	 **158b**	 **154m**, 0%

Photophysical properties of 154c: Photophysical properties of **154c** having the pyrene residue were recorded in different solvents.



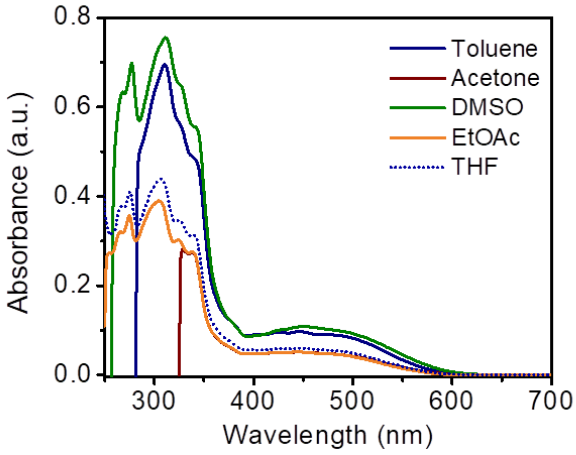


Figure 36: UV-vis absorption spectra of **154c** (15 μM) in different solvents

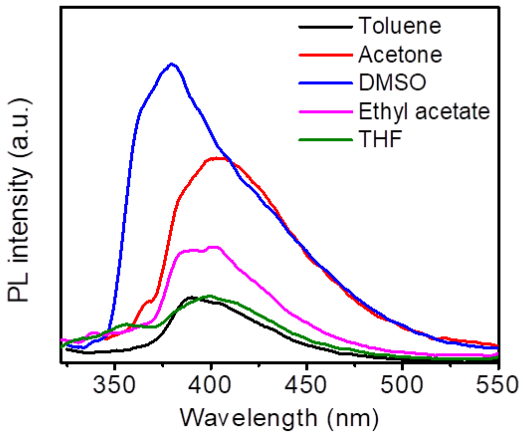
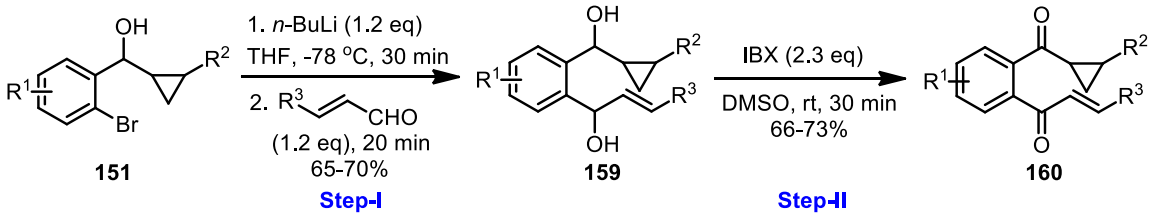


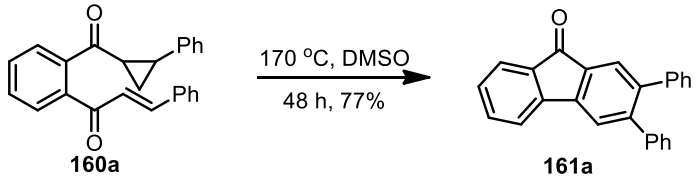
Figure 37: Fluorescence emission spectra of **154c** (15 μM) in different solvents

With the successful establishment of facile transformations of cyclopropylketo-aldehydes and cyclopropyl keto-ketones, the reaction of cyclopropyl keto-enones **160** was also considered. The cyclopropyl keto-enones **160** can be easily prepared by following a three-step protocol, Scheme 94. Direct *n*-BuLi mediated alkylation of **151** in the presence of appropriate enals provided **159**, which were easily converted to the desired cyclopropyl keto-enones **160** *via* IBX oxidation.



Scheme 94: Synthesis of cyclopropyl keto-enones **160**

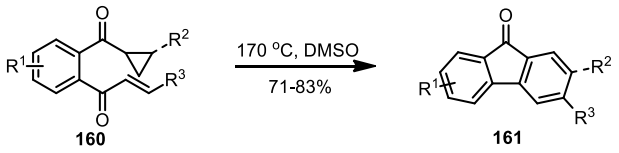
To our surprise, the reaction of cyclopropyl keto-enone **160a** under the prototypical reaction conditions (as mentioned for cyclopropyl keto-ketones) furnished 2,3-disubstituted fluorenone **161a** in good yield, Scheme 95.



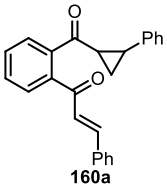
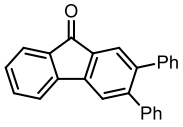
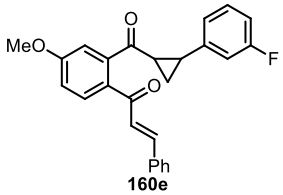
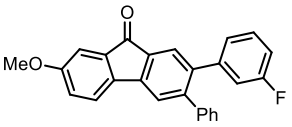
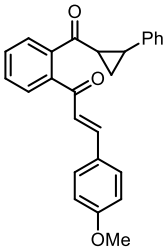
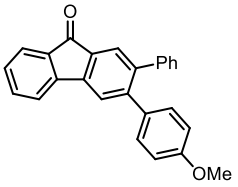
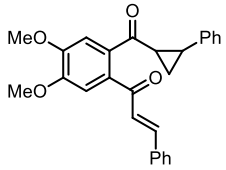
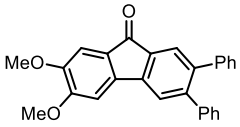
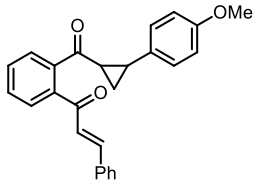
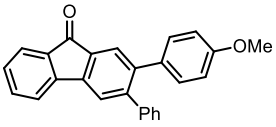
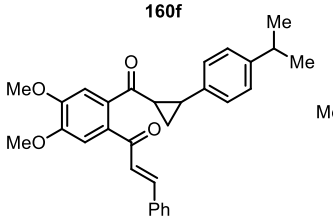
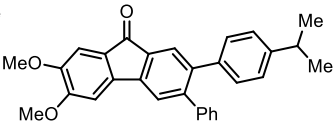
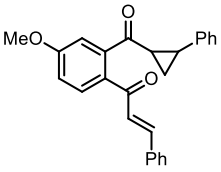
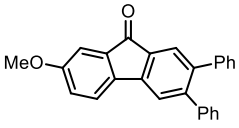
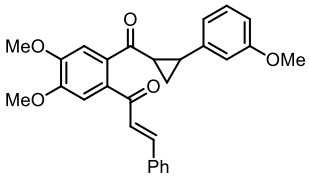
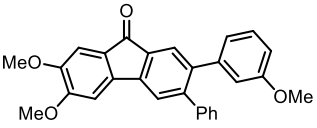
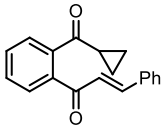
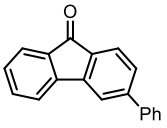
Scheme 95: Synthesis of 2,3-disubstituted fluorenone **161a**

Realizing the importance of fluorenone moiety in natural products chemistry as well as in material science,[83] few more fluorenone analogous **161b-161h** were accessed in good yields by employing this strategy, Table 20. Interestingly, the unsubstituted cyclopropyl keto-enone **160i** (when R^1, R^2 = H, R^3 = Ph) also successfully delivered the monosubstituted fluorenone **161i** in 74% yield (entry 9).

Table 20: Reaction of cyclopropyl keto-enones under the optimized conditions



160 **161**

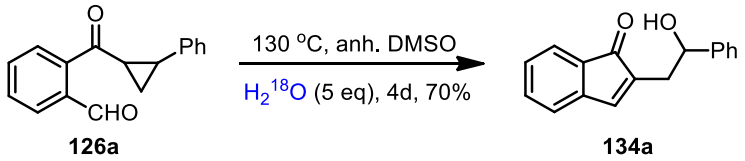
Entry	Substrate	Product	Entry	Substrate	Product
1	 **160a**	 **161a**, 48 h, 77%	5	 **160e**	 **161e**, 48 h, 71%
2	 **160b**	 **161b**, 20 h, 83%	6	 **160f**	 **161f**, 24 h, 83%
3	 **160c**	 **161c**, 30 h, 83%	7	 **160g**	 **161g**, 12 h, 80%
4	 **160d**	 **161d**, 30 h, 83%	8	 **160h**	 **161h**, 18 h, 73%
			9	 **160i**	 **161i**, 48 h, 74%

4.2: Mechanistic Insights:

As we observed during the optimization of the reaction conditions (Table 16) that the reaction is proceeding only in DMSO, suggesting that there is a crucial role of DMSO in the aforementioned transformations. Thus, to gain the mechanistic insights of the afforementioned transformations, we have performed a few control experiments as described below.

1. The reaction of 126a in the presence of $H_2{}^{18}O$

The reaction of **126a** was conducted in the presence of $H_2{}^{18}O$ in anhydrous DMSO and the product **134a** was isolated in 70% yield. The isolated product (**134a**) was analyzed by HRMS. The data indicated that there was no incorporation of ^{18}O in the product. This result indicated that the source of hydroxyl group in **134a** is not water.



126a **134a**

Scheme 96: Reaction of **126a** in the presence of $H_2{}^{18}O$

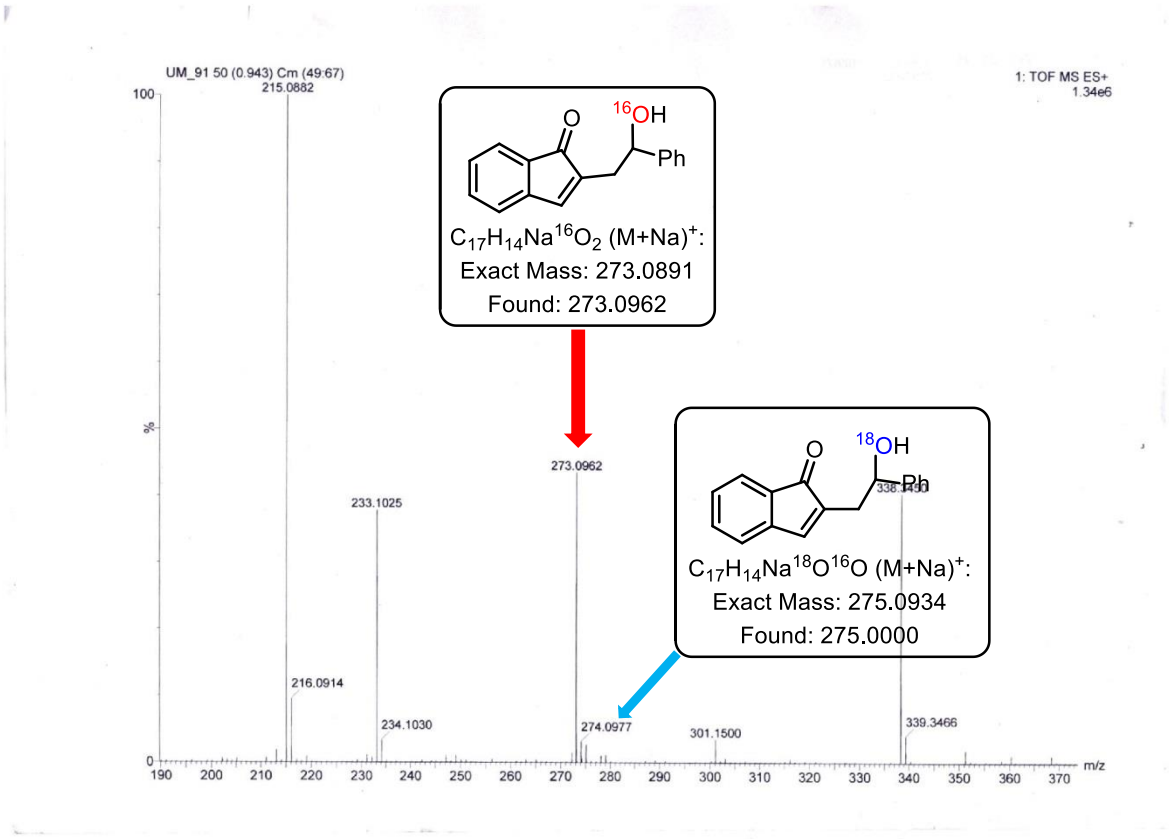
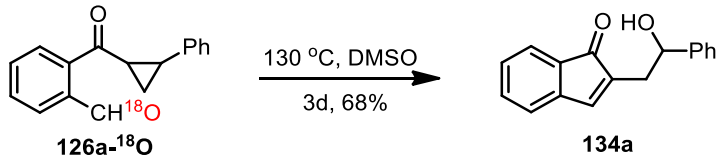


Figure 38: HRMS spectrum of **126a**

2. The reaction of ^{18}O-labelled cyclopropyl keto-aldehyde (126a-^{18}O).

The reaction of ^{18}O-labelled cyclopropyl keto-aldehyde (**126a-^{18}O**)[84] in DMSO resulted in the formation of **134a** in 68% yield. The isolated product was subjected to HRMS analysis, which showed that the product **134a** was devoid of ^{18}O. This result indicated that the source of hydroxyl group in **134a** was not aldehyde functionality.



126a-^{18}O **134a**

Scheme 97: Reaction of **126a-^{18}O**

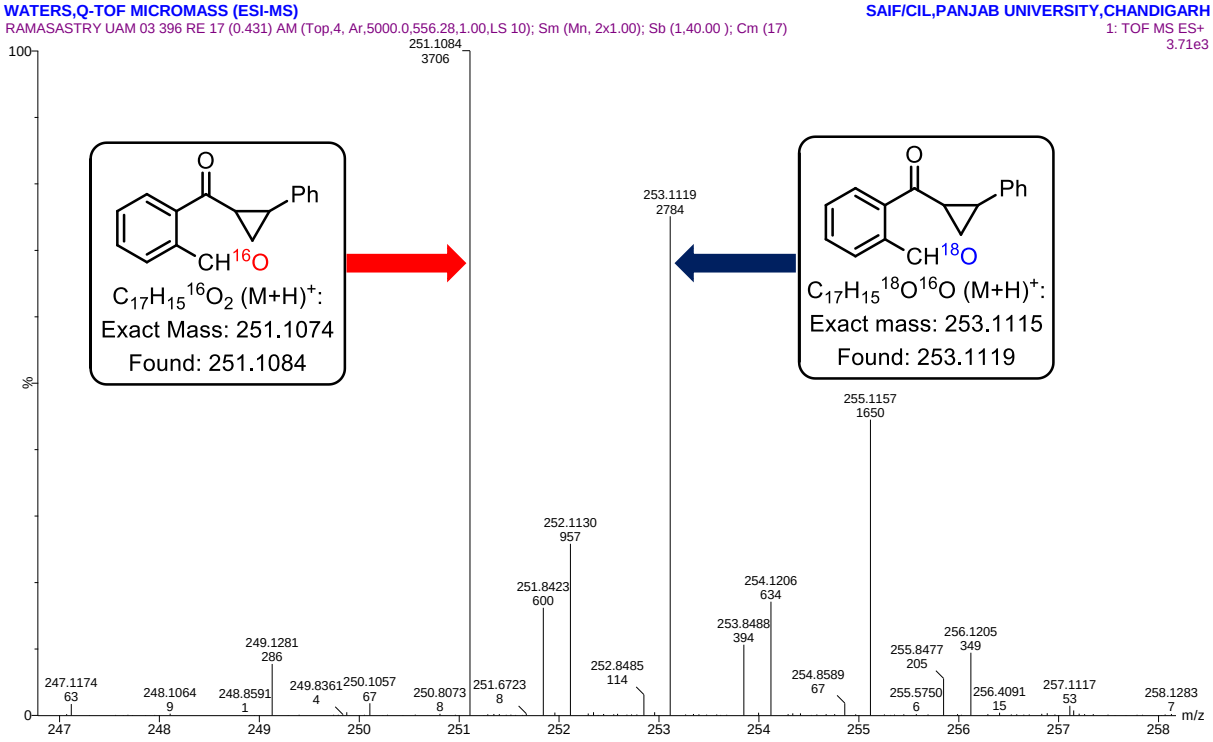


Figure 39: HRMS spectrum of ^{18}O-labelled cyclopropylketo-aldehyde **126a-^{18}O**

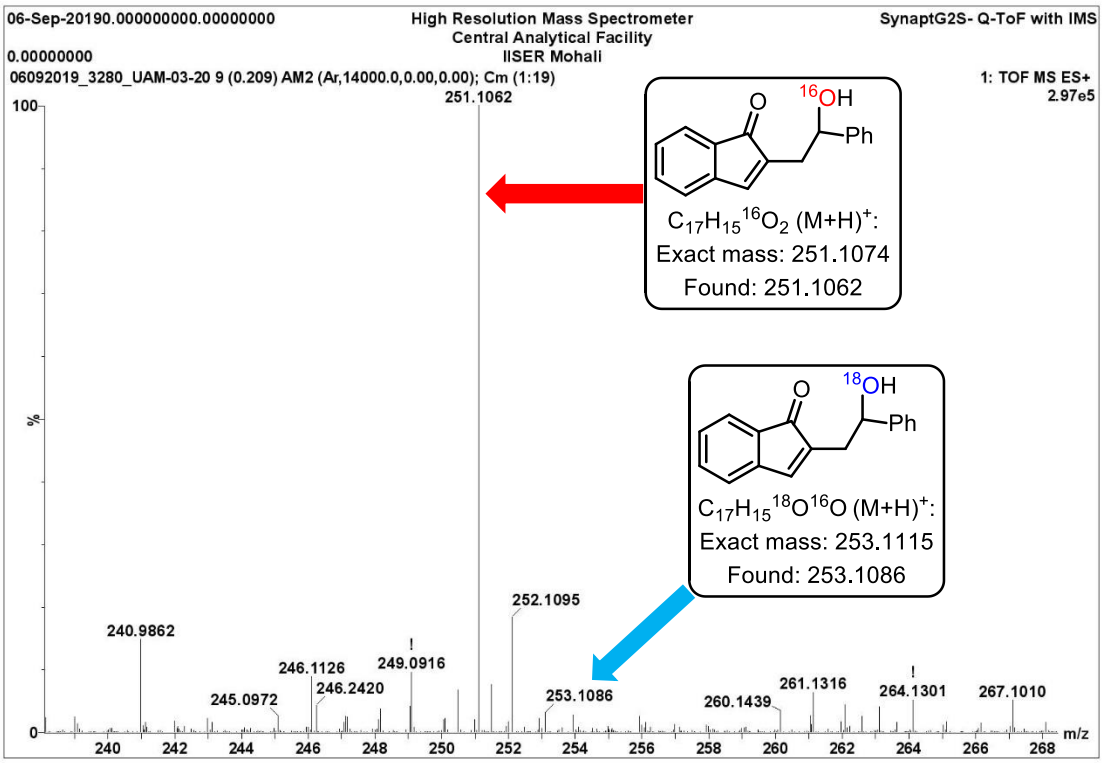


Figure 40: HRMS spectrum of **134a** (from the reaction of **126a**)

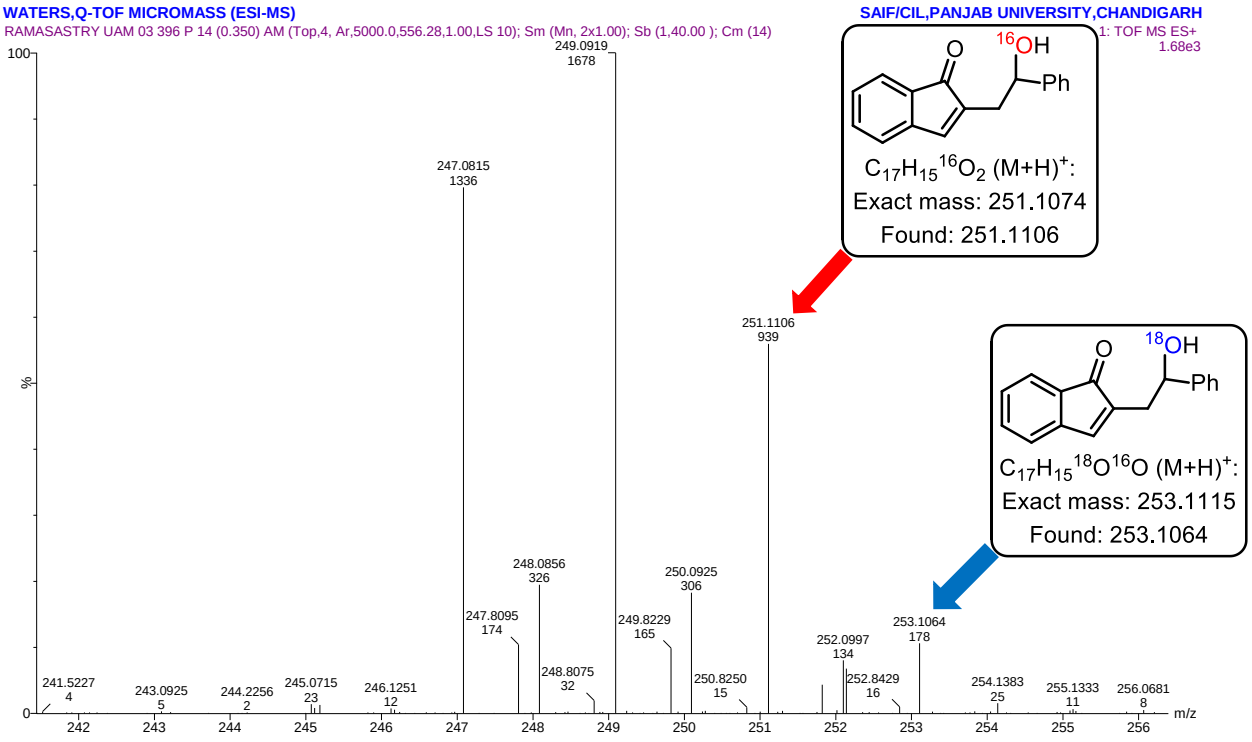
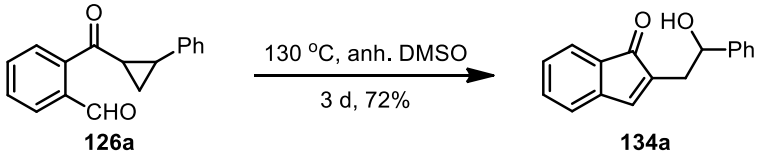


Figure 41: HRMS spectrum of **134a** (from the reaction of **126a-^{18}O**)

3. The reaction of 126a in anhydrous DMSO

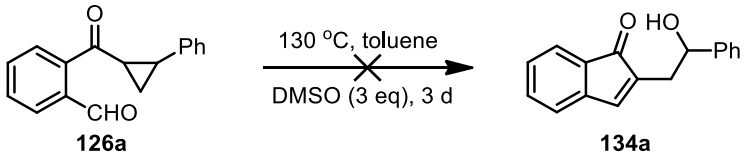
The reaction of **126a** in anhydrous DMSO was performed to ascertain whether water assists DMSO to perform certain function during the transformation. The result in Scheme **98** indicates that DMSO has an independent role in promoting the formation of **134a**.



Scheme 98: Reaction of **126a** in anhydrous DMSO

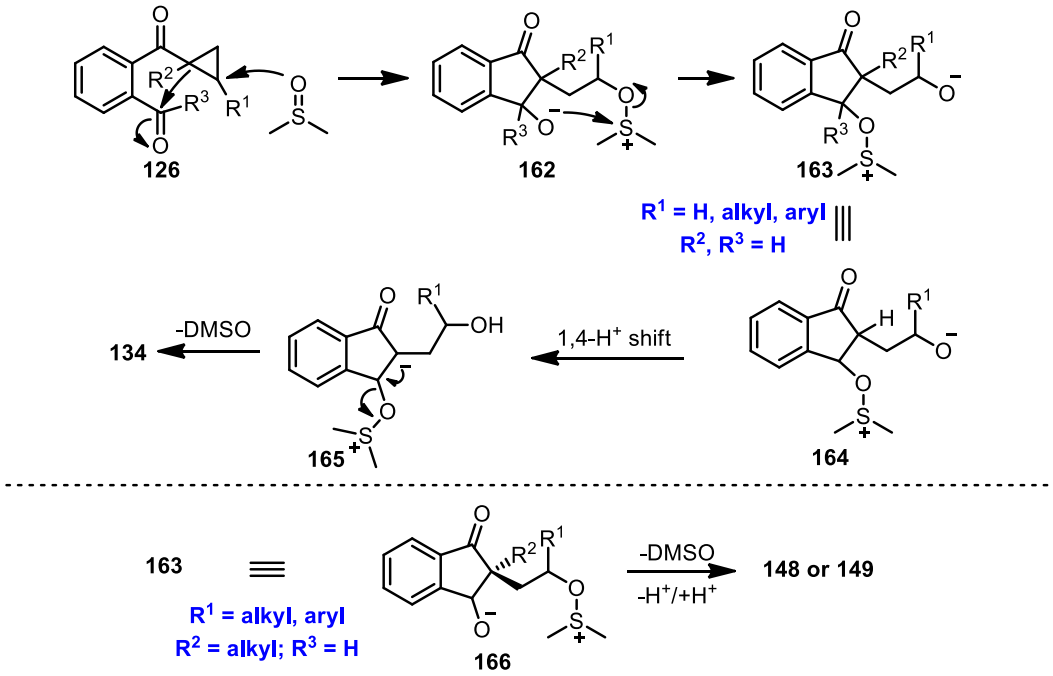
4. The reaction of 126a in a binary solvent system with controlled amount of DMSO

Having realized the critical role of DMSO in promoting the reaction, we intended to ascertain whether the reaction can be performed under a controlled amount of DMSO, Scheme 99. Thus, the reaction of **126a** was performed in toluene-DMSO (3 eq) at 130 °C. But, after 3 days, it was found that half the amount of the starting compound (**126a**) decomposed and rest remained as such. This result indicates that the reaction requires the exclusive presence of DMSO.



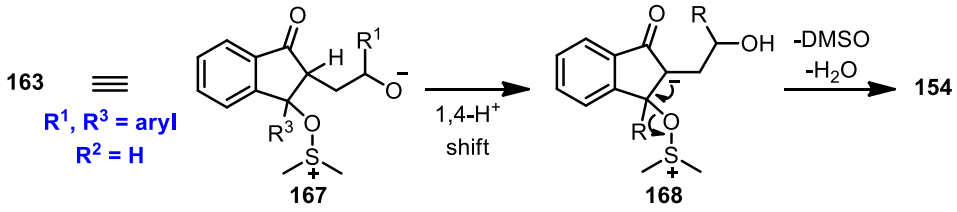
Scheme 99: Reaction of **126a** in the presence of 3 equivalents of DMSO

Based on the above control experimental results and the related literature reports,[85] a plausible mechanistic pathway is proposed in Scheme 100. The transformation of **126** to **134** and **138** to **139** is proposed to involve the DMSO-assisted ring-opening of cyclopropyl ketones **126** and **138**, Scheme 100. The zwitterionic species **162** resulted by the initial attack of DMSO and reorganizes to the intermediate **163** (or **164**). Through a 1,4-proton shift, **164** transforms to **165**, with concomitant elimination of dimethylsulfoxide (DMSO) generates indenones **134**. On the other hand, formation of **148** or **149** involves the intermediate **166**. The intermediate **166** provides the indenones **148** or **149** *via* the elimination of DMSO and subsequently through deprotonation/protonation sequence.



Scheme 100: Plausible mechanism for the formation of **134**, **139** and **148**, **149**

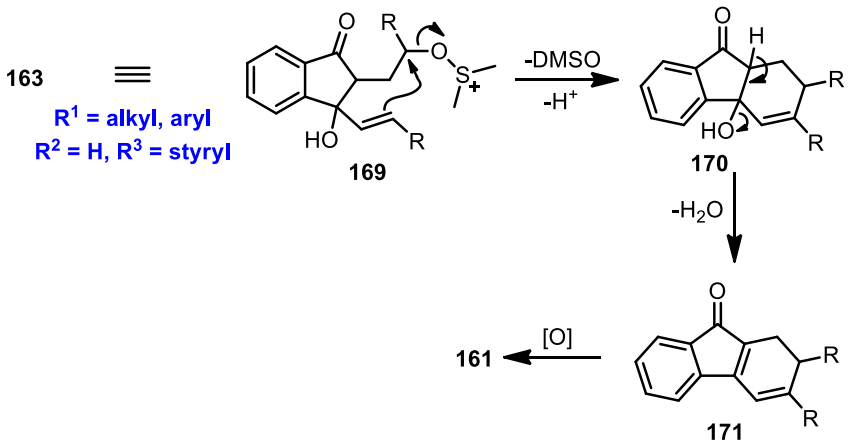
A plausible mechanism for the transformation of **153** to **154** is presented in the Scheme 101. The mechanistic pathway involves the formation of zwitterionic species **167**, which upon a 1,4-proton shift, generates **168**. Now, the intermediate **168** delivers **154** *via* the elimination of DMSO and water.



Scheme 101: Plausible mechanism for the formation of **153-154**

The formation of **160** also follows the proposed mechanistic pathway presented in Scheme 102. A cascade process, as depicted in **169** and **170**, might be responsible in the formation of 2,3-disubstituted fluorenones **161**. Thus, the sequential ene-type cyclization,

deprotonation and dehydration reactions generate dihydrofluorenone **171**, which, followed by oxidative aromatization delivers **161**.



Scheme 102: Plausible mechanism for the formation of **160-161**

In conclusion, we have presented an unprecedented metal- and acid-free ring-opening/recyclization cascade of cyclopropyl aryl ketones. These strategies provided us pentannulated aromatics such as 2-(2-hydroxyethyl)indenones, 2,2-disubstituted-3-hydroxyindanones, 2-styryl-3-arylindenones, and 2,3-disubstituted fluorenones. The mechanistic details are elucidated by thoroughly performing the control experiments. The key features of these strategies are (i) readily accessible starting materials, (ii) the ease of operation, and (iii) high atom economy.

Appendix

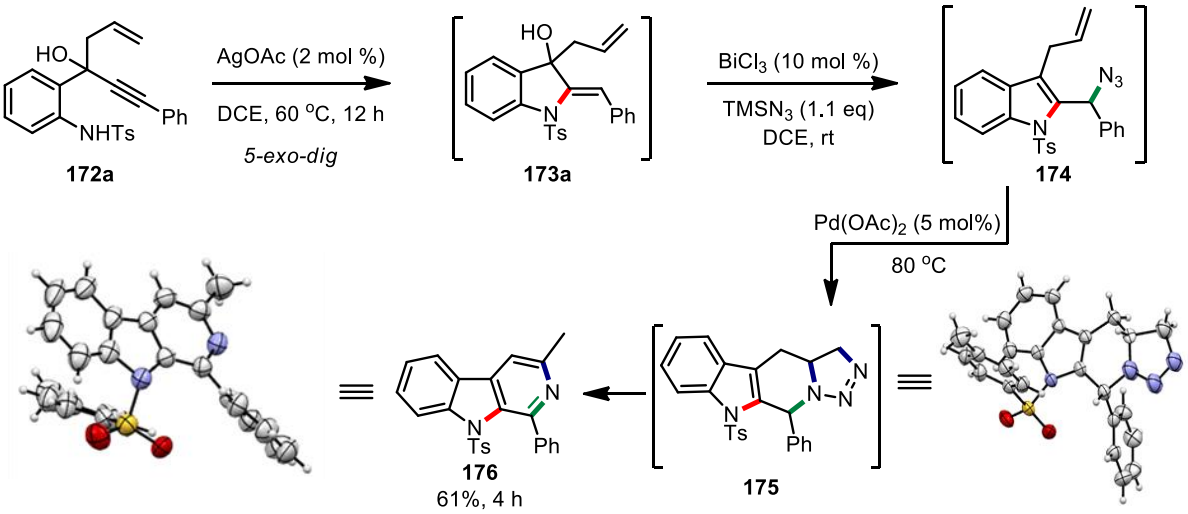
Synthesis of cyclohepta[*b*]indoles, indolotropones, and tetrahydrocarbazoles in a one-pot multicatalytic process

The development of green and sustainable chemistry is of significance in modern organic chemistry. The "green chemistry" and "sustainable chemistry" involves the idea of increasing efficiency and decreasing waste in synthetic sequences.[86] The productivity of a synthetic series can be improved by employing the reactions under one-pot. Hayashi defines a one-pot synthesis as "a strategy to improve the efficiency of a chemical reaction, whereby a reactant is subjected to successive chemical reactions in just one reactor."[87] The advantages of one-pot process are (i) it reduces the number of steps compare to other multistep process, (ii) it avoids the wastage of raw materials during purification and isolation of intermediates, and (iii) it saves the loss of time, labour, and yield losses of the product.[88]

Consequently, such methods are usually superior to stepwise approaches. To further improve the efficiency of these processes, the recent chemist has been focused on developing one-pot sequences, including multistep reactions. However, the discovery of such processes is not common and also challenging. The evolution of such methods is complicated by compatibility between different catalytic systems present in the reaction medium and the selectivity issues. Despite these disadvantages of this process, several numbers of successful applications of this concept have been reported in the literature.[89]

In this direction, our group has recently reported the successful development of a few one-pot bi- and trimetallic orthogonal catalytic approaches for the synthesis of complex indole derivatives.[90] Among them, very recently, we have reported the synthesis of *β*-carbolines *via* one-pot triple orthogonal-relay catalysis, depicted in scheme 103.[91] The triple relay catalysis, which is the combination of silver, bismuth and palladium catalysts applied for the synthesis of *β*-carbolines. The reaction sequence follows a one-pot cascade involving an intramolecular hydroamination, Friedel-Crafts-type dehydrative azidation and an unprecedented pyridine annulation of the ε,ω-unsaturated azides.

Inspired by this background, we intended to develop a one-pot process associated with four metal catalysts towards the synthesis of indolotropones. The whole process represents one-pot quadruple orthogonal relay catalysis. To the best of our knowledge, reactions promoted by four orthogonal relay metal catalytic systems in one-pot manner are not reported thus far.



Scheme 103: Synthesis of *β*-carboline **176**

Indolotropone is a class of seven-membered ring fused indole. The indolotropone motif is frequently encountered in numerous natural and non-natural pharmaceutical products and displays a broad spectrum of biological activities.[92] The biological profile of these molecules has attracted the remarkable interest from the pharmaceutical industry. Therefore, the efficient synthesis of indolotropone has become the key interest for organic chemist in recent years. Some of the natural and non-natural products possessing indolotropone motif are depicted in Fig. 42.

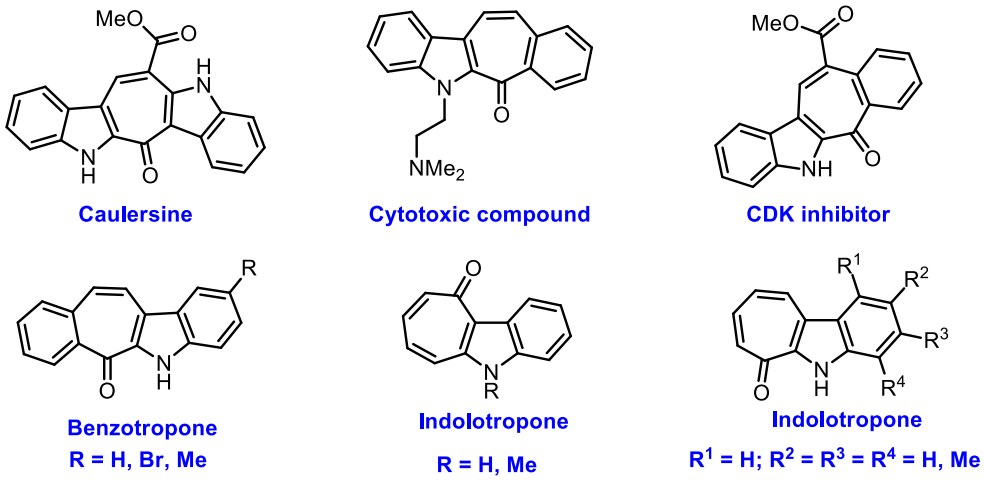
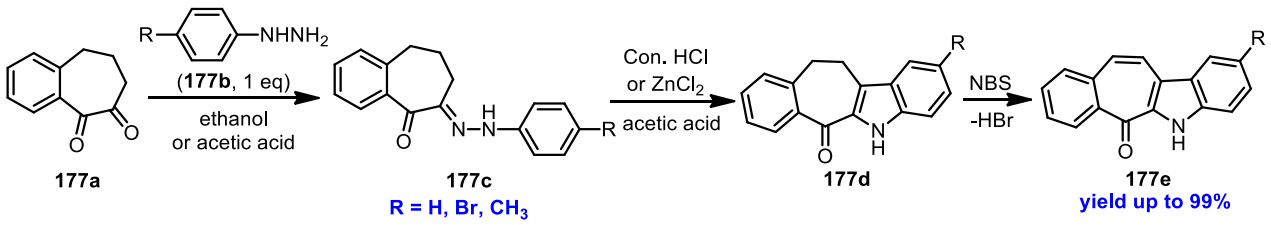


Figure 42: Few indolotropone containing natural and non-natural products

The development of general and efficient protocols to synthesize the indolotropone derivatives remains challenging. Moreover, they are assembled in a multi-step manner due to lack of efficient annulation strategy. As our current research activities focus on the efficient synthesis of complex indole derivatives owing to their importance in natural products and pharmaceuticals,[93] we planned to develop a one-pot strategy for the synthesis of indolotropones. The absence of one-pot strategy towards the synthesis of indolotropones, prompted us to design a substrate to achieve indolotropones. Few strategies are described for the synthesis of indolotropones in the following.

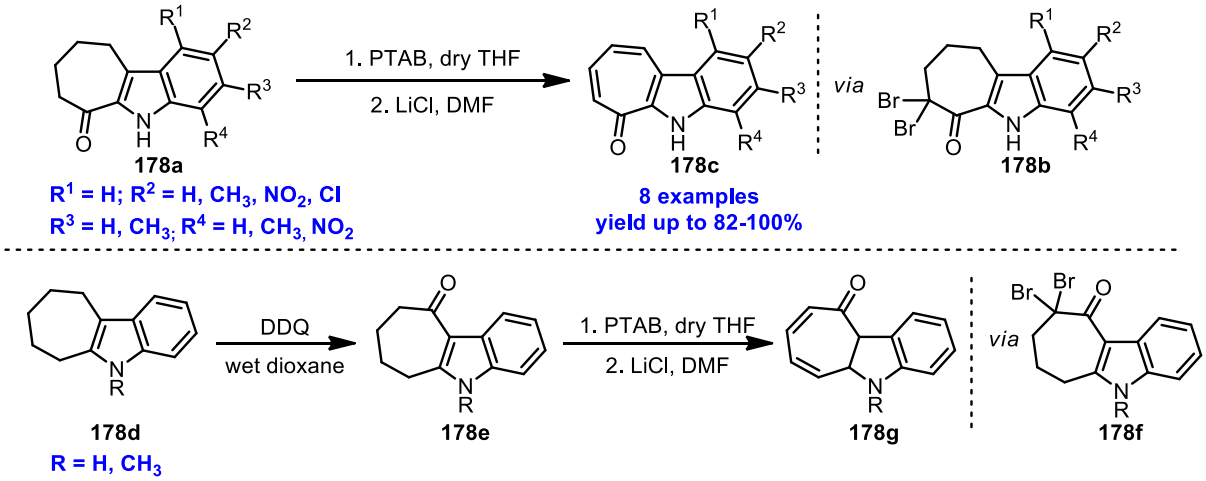
In 1972, Fujimori *et al.*[94] reported the synthesis of benzotropones by following a multistep strategy, Scheme 104. The compound **177a** in ethanol or acetic acid in the presence of hydrazines **177b** afforded the formation of the corresponding hydrazones **177c**. The compound **177c** underwent Fischer indolization by the action of zinc chloride or concd. hydrochloric acid in

acetic acid to deliver **177d**. The NBS mediated reaction of **177d** furnished benzotropones **177e** in excellent yields.



Scheme 104: Fujimori's synthesis of benzotropones

In 1976, Fujimori *et al.*[95] developed a step-wise process towards the synthesis of indolotropones, Scheme 105. The reaction of **178a** with phenyltrimethylammonium tribromide (PTAB) in dry THF generated the intermediate **178b**, which by the action of LiCl in DMF delivered indolotropones **178c** in excellent yields. On the other hand, they have also established the synthesis of indolotropones **178g** by following the multistep sequences depicted in Scheme 105. The compound **178d** rapidly undergo the reaction with DDQ in wet dioxane to deliver the corresponding product **178e**. The reaction of **178e** with PTAB in dry THF afforded the dibromination product **178f**, which by the treatment with LiCl in DMF delivered indolotropones **178g**.



Scheme 105: Fujimori's synthesis of indolotropones

The cyclohepta[*b*]indole motif is an important structural unit, commonly found in a variety of natural and as well as non-natural pharmaceutical products.[96] Compounds containing

this motif show a broad spectrum of biological activities, such as inhibition of adipocyte fatty-acid binding protein (A-FABP), inhibition of leukotriene production p53, deacetylation of histones, anti-HIV activities and antituberculosis activities. Therefore, the biological profiles of this structural motif have attracted the attention of the scientific community. This structural motif often has been synthesized by employing Fischer indole synthesis. But this method has some limitations although it is a very robust and useful reaction. The Fischer indole type synthesis is not suitable for the synthesis of unsymmetrically functionalized cyclohepta[*b*]indoles, since product mixtures are inevitable.[92] Therefore, to overcome these synthetic difficulties, synthetic organic chemists focused on the development of numerous synthetic efforts to access this structural motif. Though several methods are available for the synthesis of cyclohepta[*b*]indoles, but these methods require multistep sequences associating laborious isolation and purification procedures,[97] which limit the generality and synthetic utility of such methods. To overcome these limitations, we intended to develop sequential one-pot multicatalytic approaches to access a diverse range of cyclohepta[*b*]indoles.

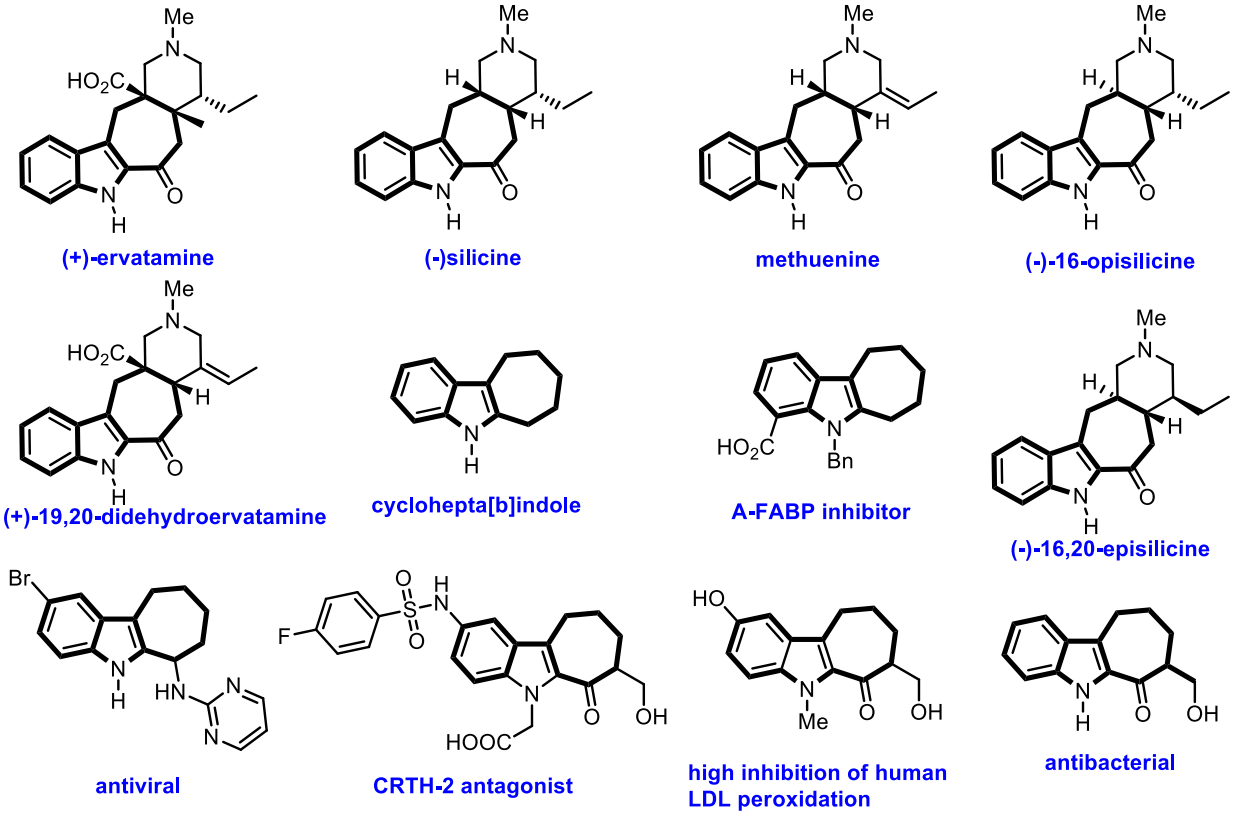
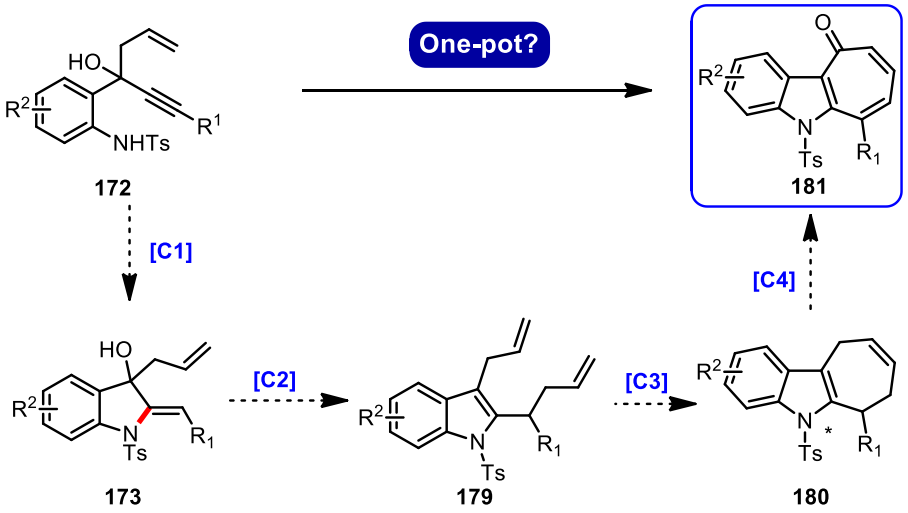


Figure 43: Representative bioactive cyclohepta[*b*]indole natural products

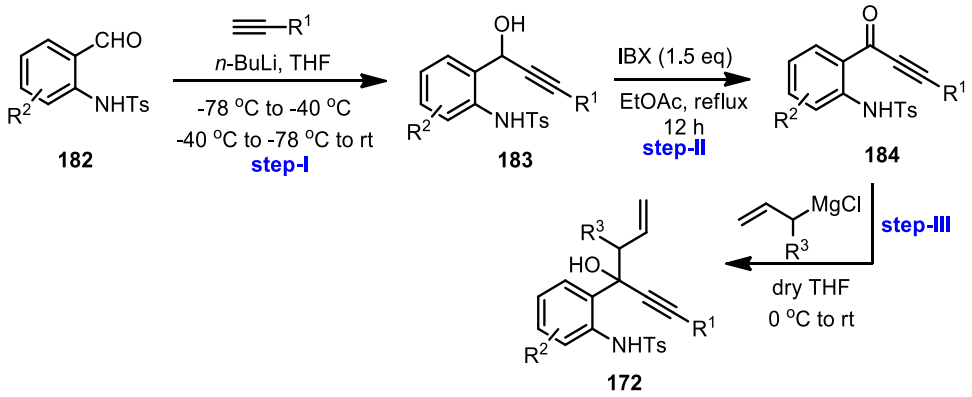
5.1: Results and discussion:

Prompted by our earlier developed one-pot relay catalytic processes, we initiated our studies towards the development of an efficient one-pot approach for the synthesis of indolotropones. Initially, we envisioned that a 5-*exo*-*dig* cyclization of 3-(2-aminophenyl)-5-hexenyn-3-ols **172** promoted by an appropriate metal catalyat C1 could provide the indolines **173**, Scheme 106.[91,98] The **173** could be converted to **179** involving 1,3-allylic alcohol isomerization (1,3-AAI) and dehydrative nucleophilic allylation cascade enabled by C2 catalyst. It was further hypothesized that a catalyst C3 mediated ring closing metathesis (RCM) in **179** could provide tetrahydrocyclohepta[*b*]indoles **180**. Finally, C4-catalyzed allylic oxidation of **180** and subsequent dehydrogenation under appropriate reaction conditions could generate our desired indolotropones **181**.



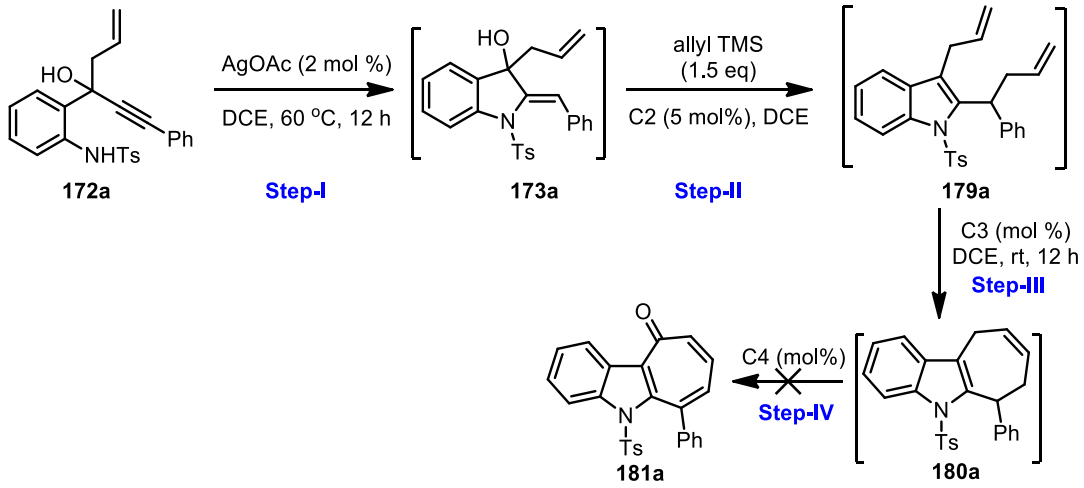
Scheme 106: Hypothesis for the one-pot synthesis of indolotropones

A modular access of the 3-(2-aminophenyl)-5-hexenyn-3-ols **172** can be achieved from the amino benzaldehydes **182** by following an efficient three straightforward steps developed by our research group.[91] *n*-BuLi assisted addition of alkynes to amino benzaldehydes **182** produced ynols **183**. The IBX oxidation of ynols **183** delivered the ynones **184**. Further, the treatment of allylmagnesium chlorides with ynones **183** provided our desired starting material **172**, Scheme 107.



Scheme 107: Synthesis of 3-(2-aminophenyl)-5-hexenyn-3-ols **172**

In order to validate our hypothesis presented in Scheme 106, we initiated our efforts towards identifying an efficient catalytic system by considering enynol **172a** as the model substrate. During initial studies, a step-wise protocol was followed with a goal to combine appropriately to a one-pot process for the synthesis of indolotropone **181a**, Scheme 108.



Scheme 108: Multicatalytic synthesis of indolotropone **181a** in one-pot process

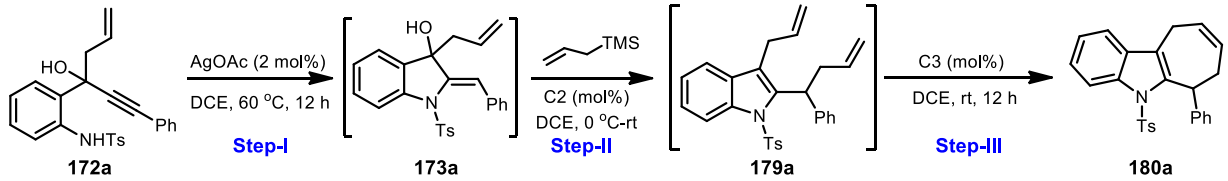
At the beginning, AgOAc catalyzed intramolecular hydroamination condition reported by our group was employed for the transformation of **172a** to produce desired 5-*exo-dig* product **173a** with excellent chemo- and regioselectivity.[91] Next, for the cascade 1,3-AAI/nucleophilic allylation to achieve **179a**, we screened various Lewis acids. Our initial attempts with Lewis acids, such as $In(OTf)_3$ or $FeCl_3$ were unsuccessful for the conversion of **173a** to **179a** (Table 21,

entries 1 and 2). However, the desired product **179a** was formed in poor yield when the Lewis acid $Bi(OTf)_3$ was employed as catalyst. After having an initial success with $Bi(OTf)_3$ for the formation of **179a**, subsequently we moved to the next step to achieve **180a**. The RCM reaction of **179a** with Grubbs' first generation catalyst (G-I) at rt delivered the desired product **180a** in 34% yield in one-pot manner (Table 21, entry 3). Further attempts were made to improve the yield of **180a** with other different Lewis acids as well as Brønsted acids in step-2 (Table 21). However, among several Lewis acids screened, $InCl_3$, $BiCl_3$ and $ZnCl_2$ catalyzed reactions provided the desired product **180a** in good yields (Table 21, entries 13, 18-19, and 21). As a result, AgOAc, $InCl_3$, and G-I were the evaluated catalyst for the transformation of **172a** to **180a** in one-pot process.

During the screening in step-3, it was found that the **179a** was remained as such when lower amount of either G-I or G-II was introduced in the reaction (Table 21, entries 25-28). Interestingly, while the purified sample of **179a** was subjected to the RCM reaction conditions resulted in the formation of **180a** in excellent yields (Table 21, entries 23-24). This result indicating that the G-I or G-II catalyst would have deactivated by the other catalysts present in the one-pot process. The poisoning or deactivation of catalyst explained the no formation of **180a** in the cases where the lower quantity of either G-I or G-II catalyst was used. Having realized the deactivation of C3 catalyst in one-pot process, a little higher amount of catalyst C3 which is slightly more than the integrated amount of C1 and C2 required for the successful transformation.

Having optimized the reaction conditions for step-I, step-II, and step-III, we next focused on the optimization of reaction conditions for the transformation of **180a** to indolotropone **181a**, Scheme 108. To achieve the indolotropone **181a**, a brief screening was performed with different oxidizing reagents and different solvent combinations in one-pot process. However, all the attempts for the transformation of **180a** to indolotropone **181a** were unsuccessful. Therefore, we developed one-pot synthesis of cyclohepta[*b*]indoles.

Table 21: Optimization of reaction parameters with **172a**



Entry	C-1 (2 mol%)	C-2 (5 mol%) / conditions	C-3 (mol%) / conditions	Solvent	Yield (%)
1[a]	AgOAc	$In(OTf)_3$/RT/22 h	-	DCE	-
2[b]	AgOAc	$FeCl_3$/RT/25 h	-	DCE	-
3	AgOAc	$Bi(OTf)_3$/RT/20 h	G-I (15)/16 h	DCE	34
4	AgOAc	TMSOTf/RT/22 h	G-I (15)/12 h	DCE	47
5	AgOAc	$La(OTf)_3$/RT/26 h	G-I (15)/23 h	DCE	-
6	AgOAc	$Zn(OTf)_2$/RT/24 h	G-I (15)/19 h	DCE	-
7	AgOAc	$BiCl_3$/RT/23 h	G-I (15)/13 h	DCE	55
8	AgOAc	$ZnCl_2$/RT/24 h	G-I (15)/10 h	DCE	70
9	AgOAc	$Sc(OTf)_3$/RT/21 h	G-I (15)/15 h	DCE	53
10[a]	AgOAc	$Yb(OTf)_3$/RT/24 h	G-I (15)/18 h	DCE	-
11[a]	AgOAc	CSA/RT/22 h	G-I (15)/15 h	DCE	-
12[a]	AgOAc	PTSA/RT/25 h	G-I (15)/18 h	DCE	-
13	AgOAc	$InCl_3$/RT/20 h	G-I (15)/12 h	DCE	67
14	AgOAc	$BiBr_3$/RT/24 h	G-I (15)/15 h	DCE	40
15	AgOAc	TFA/RT/24 h	G-I (15)/17 h	DCE	37
16[a]	AgOAc	$HClO_4$/RT/23 h	G-I (15)/20 h	DCE	-
17[a]	AgOAc	$ClCH_2COOH$/RT/25 h	G-I (15)/22 h	DCE	-
18	AgOAc	$BiCl_3$/0 °C-RT /25 h	G-I (15)/12 h	DCE	74
19	AgOAc	$ZnCl_2$/0 °C-RT /26 h	G-I (15)/12 h	DCE	71
20[a]	AgOAc	$Sc(OTf)_3$/0 °C-RT /27 h	G-I (15)/15 h	DCE	-
21	AgOAc	$InCl_3$/0 °C-RT /21 h	G-I (15)/10 h	DCE	75
22	AgOAc	$BiBr_3$/0 °C-RT /24 h	G-I (15)/17 h	DCE	47
23[c]	AgOAc	$InCl_3$/RT/21 h	G-II (5)/1 h	DCE	95
24[c]	AgOAc	$InCl_3$/ RT/21 h	G-I (5)/1 h	DCE	93
25[d]	AgOAc	$InCl_3$/RT/20 h	G-I (5)/12 h	DCE	-
26[d]	AgOAc	$InCl_3$/RT/20 h	G-I (10)/12 h	DCE	-
27[d]	AgOAc	$InCl_3$/RT/20 h	G-II (5)/12 h	DCE	-

[a]Starting material as such in step-II. [b]Decomposition of starting material **172a**. [c]Reaction with purified **179a**; yield of step-III alone. [d]Starting material as such in step-III.

Thus, the model substrate **172a** through a sequential catalytic process integrated by Ag/In/Ru metal-catalyst delivered the cyclohepta[*b*]indole **180a** in moderate yield. 2 mol% AgOAc, 5 mol% $InCl_3$, and 15 mol% G-I were the evaluated optimal conditions for step-I, step-II, and step-III, respectively. The formation of cyclohepta[*b*]indole **180a** was confirmed by the help of IR, ^{1}H-NMR, and ^{13}C-NMR spectrum analysis. In IR spectrum, the presence of an absorption band at 1453 cm^{-1} indicates the presence of C=C bond in the product **180a**. In the ^{1}H-NMR spectrum (see Fig. 44), presence of a multiplet at δ 5.93-5.990 ppm and a doublet of triplet at δ 5.55 ppm (*J* = 5.1 and 2.7 Hz) indicate the two C-3 and C-4 olefinic protons, a broad singlet at δ 5.38 ppm indicates the C-1 methine proton, a multiplet at δ 3.58-3.54 ppm indicates C-5 methylene protons, a multiplet at δ 2.95-2.91 ppm and a doublet of doublet of doublet at δ 2.69 ppm (*J* = 14.6, 8.4 and 5.6 Hz) indicate the another C-2 methylene protons, a siglet at δ 2.28 ppm indicates the methyl group from tosyl moiety. In ^{13}C-NMR spectrum (see Fig. 45), presence of the peaks at δ 41.3, δ 34.1, and δ 24.8 ppm are indication of the presence of three aliphatic carbons (C-5, C-2, and C-1), and a peak at δ 21.4 ppm iindicates the methyl carbon from tosyl group. Thus, the spectral data of ^{1}H-NMR and ^{13}C-NMR supports for the formation of the product **180a**. The structure of **180a** was further confirmed by the presence of a peak at m/z 414.1512 $(M+H)^+$ corresponding to the formula $C_{26}H_{24}NO_2S$ with the calculated value of 414.1528 in the HRMS spectrum. The structure was confirmed from the X-ray diffraction analysis of **180j** and assigned to other products in analogy, Fig. 46.

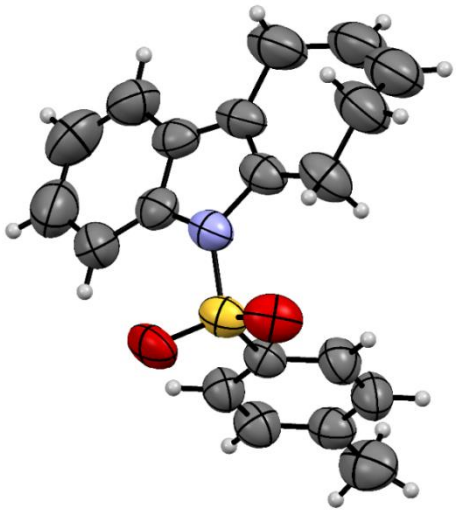


Figure 46: ORTEP diagram of **180j**, ellipsoid probability (50%)

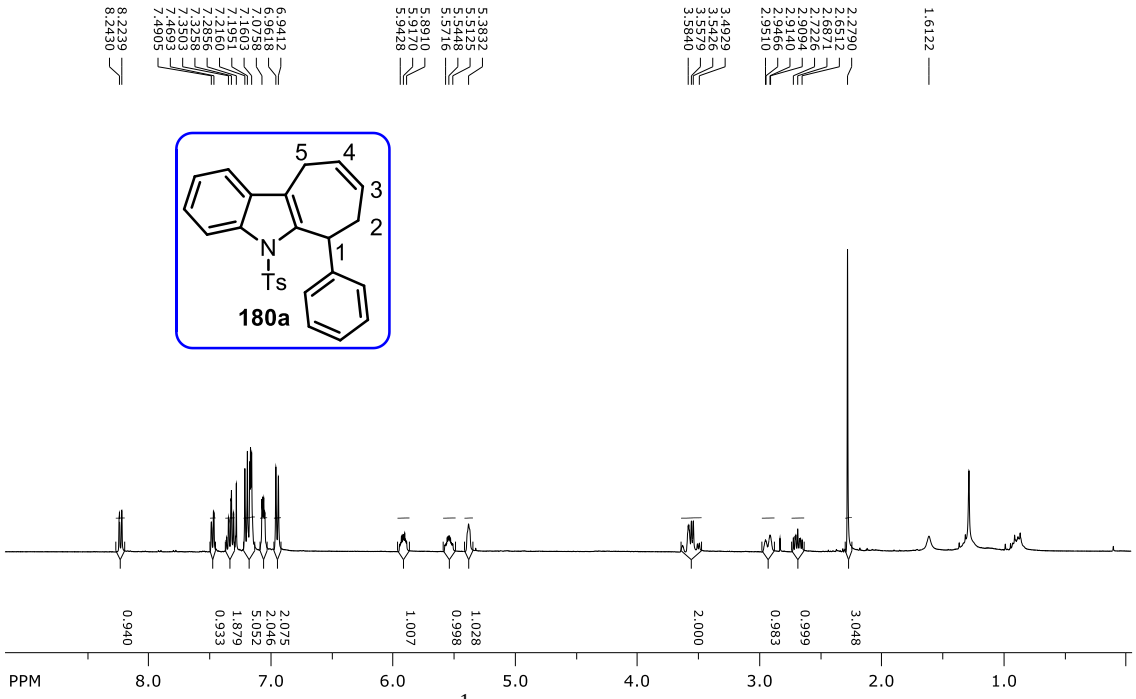


Figure 44: ^{1}H-NMR spectrum of **180a**

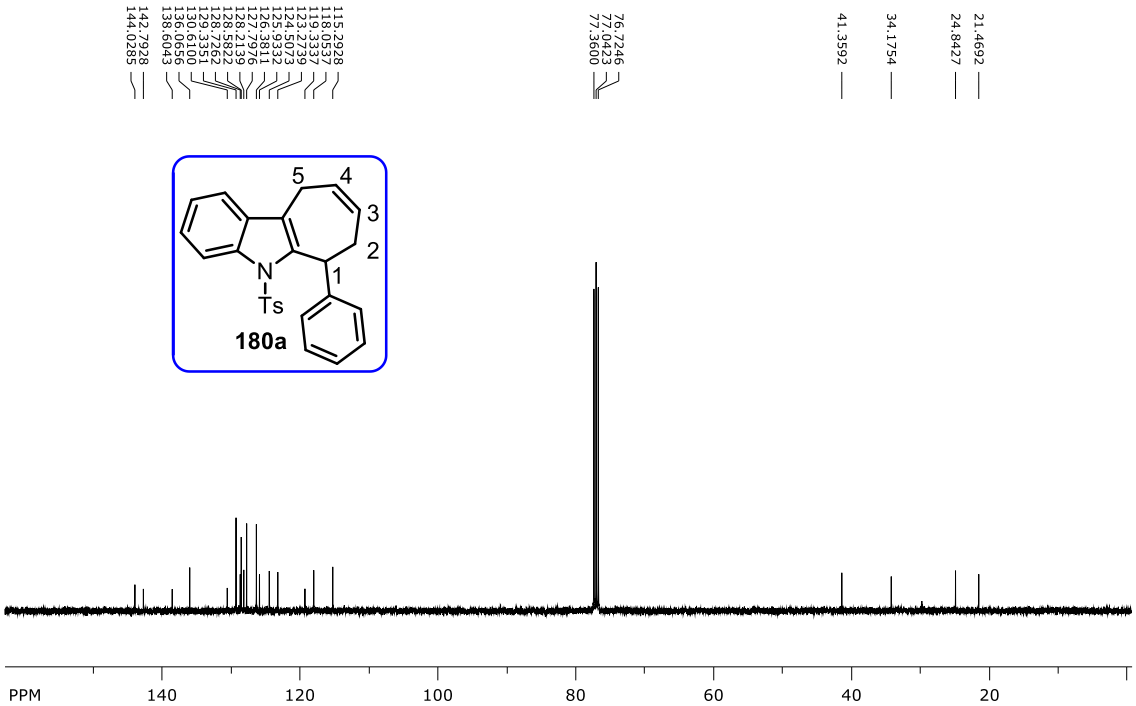
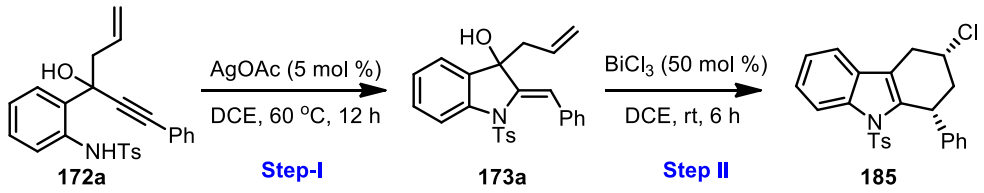


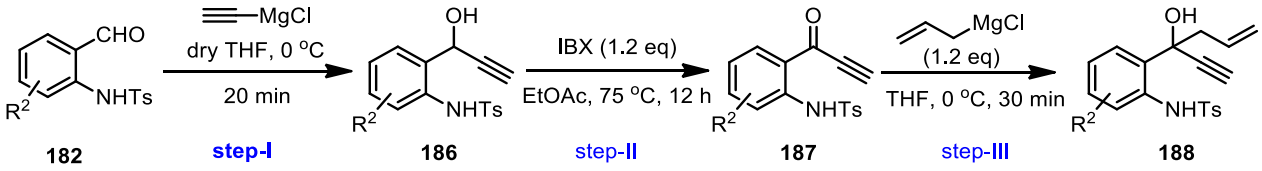
Figure 45: ^{13}C-NMR spectrum of **180a**

To our surprise, the yield losses in the formation of the cyclohepta[*b*]indoles could be explained by considering the formation of **185a** in the step-II, Scheme 109. The enynol **172a** under the catalytic AgOAc reaction conditions delivered indolyl alcohol **173a** *via* 5-*exo-dig* cyclization reaction, Scheme 109. The $BiCl_3$-catalyzed reaction of **173a** provided the formation of tetrahydrocarbazole **185** in 87% yield *via* the halo-Prins-type carbocyclization reaction.



Scheme 109: Formation of side product **185**

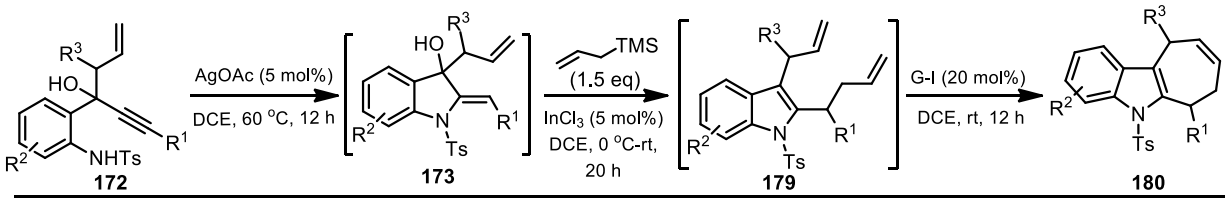
With the optimized conditions in hand, we began the examination to explore the general scope of this strategy with various designed substrates. Towards this, we synthesized a wide range of enynols **172a-172j** by following a three-step protocol, scheme 107. The enynols **188a-188c** possessing the unsubstituted alkyne moiety were synthesized by following a two-step protocol, scheme 110.

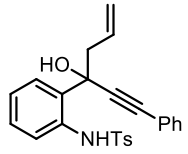
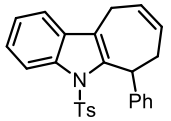
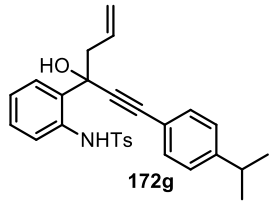
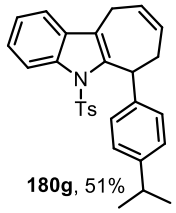
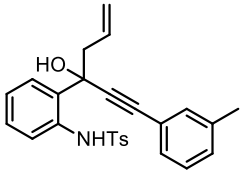
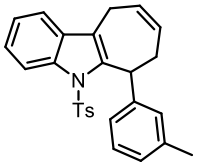
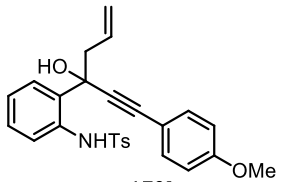
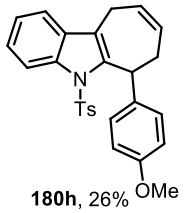
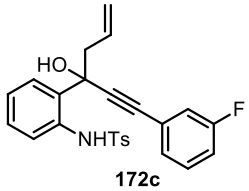
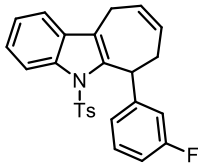
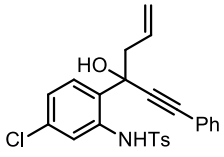
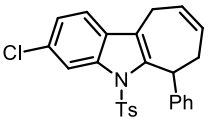
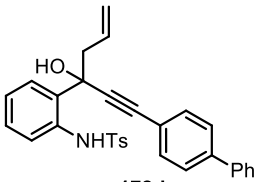
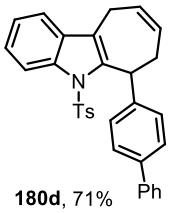
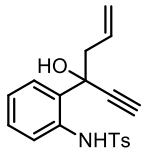
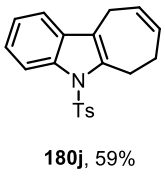
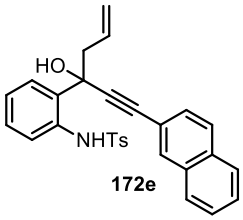
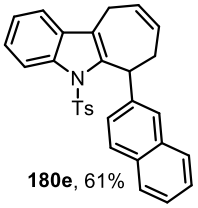
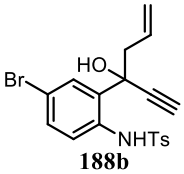
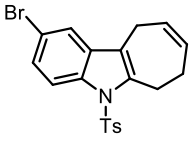
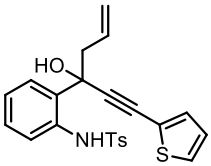
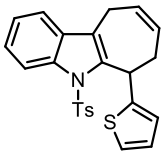
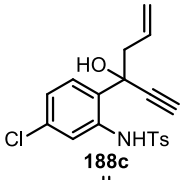
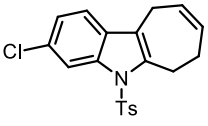
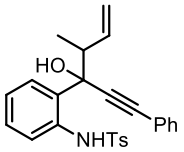
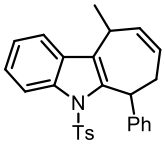


Scheme 110: Synthesis of enynols **188a-188c**

All the enynols **172a-172j** and **188a-188c** were subjected to the optimized reaction conditions, and we observed the effect of some interesting electronic and steric factors in the formation of respective products **180a-180m**, Table 22. The substrates with electron-donating group on the alkyne moiety (entries 2 and 7-8, Table 22) under the optimized conditions delivered the respective products in less yields than expected. The formation of the side product **185** explained the low yield on the formation of product **180**. The reaction of the substrate containing electro-withdrawing group on the alkyne chain (entry 3) generated the respective product in moderate to good yield. Moreover, under the optimized conditions, the product cyclohepta[*b*]indole containing heteroaryl group (entry 6) was isolated in good yield.

Table 22: One-pot synthesis of cyclohepta[*b*]indoles under the optimized conditions

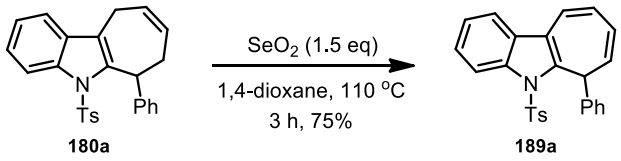


Entry	Substrate	Product	Entry	Substrate	Product
1	 **172a**	 **180a**, 75%	7	 **172g**	 **180g**, 51%
2	 **172b**	 **180b**, 65%	8	 **172h**	 **180h**, 26%
3	 **172c**	 **180c**, 85%	9	 **172i**	 **180i**, 83%
4	 **172d**	 **180d**, 71%	10	 **188a**	 **180j**, 59%
5	 **172e**	 **180e**, 61%	11	 **188b**	 **180k**, 52%
6	 **172f**	 **180f**, 56%	12	 **188c**	 **180l**, 56%
			13	 **172j**	 **180m**, 0%

The substrates with unsubstituted alkyne functionality (entries 10-12) were also well tolerated under the optimized reaction conditions. However, after several of our efforts, the conversion of the enynol with 1-methylallyl system **172j** to our desired product **180m** was remained unsuccessful because it was not a suitable substrate for the RCM reaction.

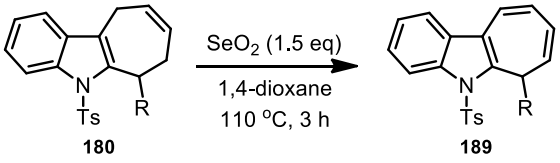
5.2: Synthetic utility of cyclohepta[*b*]indoles:

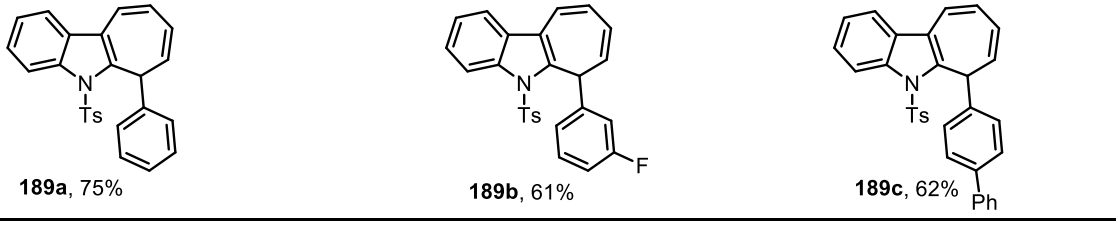
After the successful development of one-pot trimetallic approaches for the synthesis of otherwise difficult-to-access cyclohepta[*b*]indoles **180**, we turned our attention towards the demonstration of the synthetic utility of these products. We made an observation among several of our attempts during the optimization in the last step (Scheme 108) to achieve indolotropones in a one-pot manner. To our delight, when the purified product **180a** was treated with a stoichiometric amount of SeO_2 generated dihydrocyclohepta[*b*]indole **189a** exclusively in good yield, Scheme 111.[99] To explore the generality of this unprecedented observation, few other cyclohepta[*b*]indoles **180c-180d** were also subjected to the optimized conditions, Table 23. The optimization conditions provided general access to dihydrocyclohepta[*b*]indoles **189b-189c** in moderate yields. Thus this method was an alternative synthetic route of otherwise difficult-to-access dihydrocyclohepta[*b*]indoles.



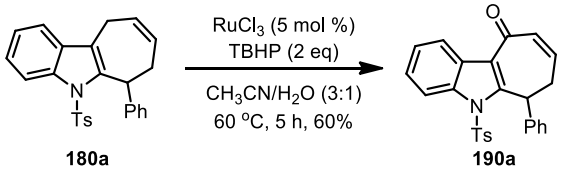
Scheme 111: Synthesis of dihydrocyclohept[*b*]indole **189a**

Table 23: Substrate Scope:



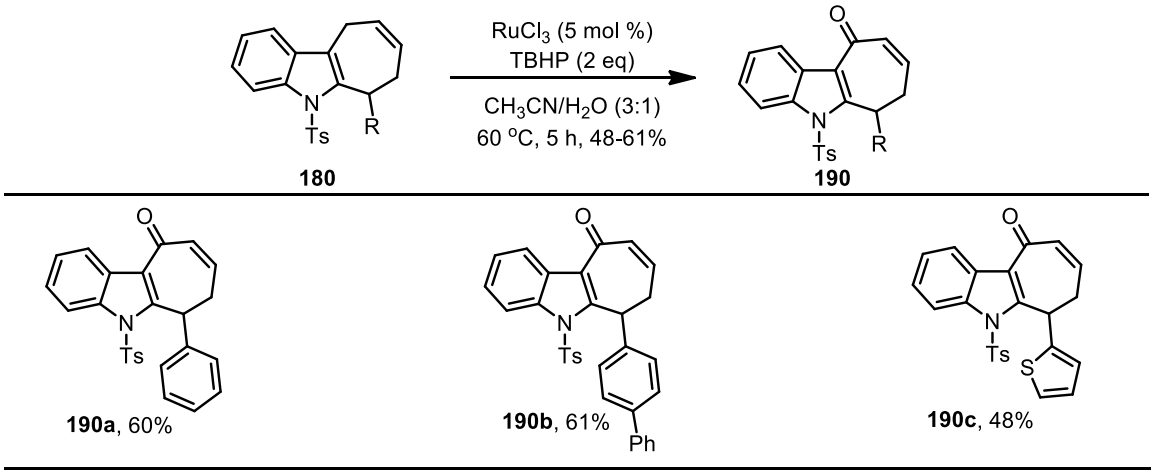


Next, we noticed another surprising observation during the optimization of the reaction conditions in the last step (Scheme 108) towards the synthesis of indolotropones. The reaction of **108a** mediated by the $RuCl_3$ catalyst led to dihydroindolotropone **190a** in 60% yield, Scheme 1112. Having realized the formation of **190a**, few more other dihydroindolotropone derivatives **190b-190c** were synthesized by employing the same reaction conditions, Table 24.

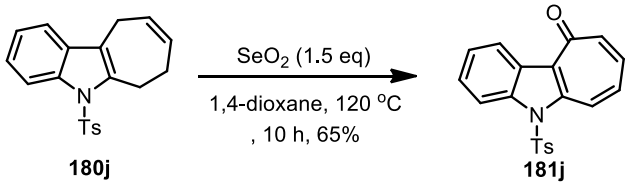


Scheme 112: Synthesis of dihydroindolotropone **190a**

Table 24: Substrate Scope:



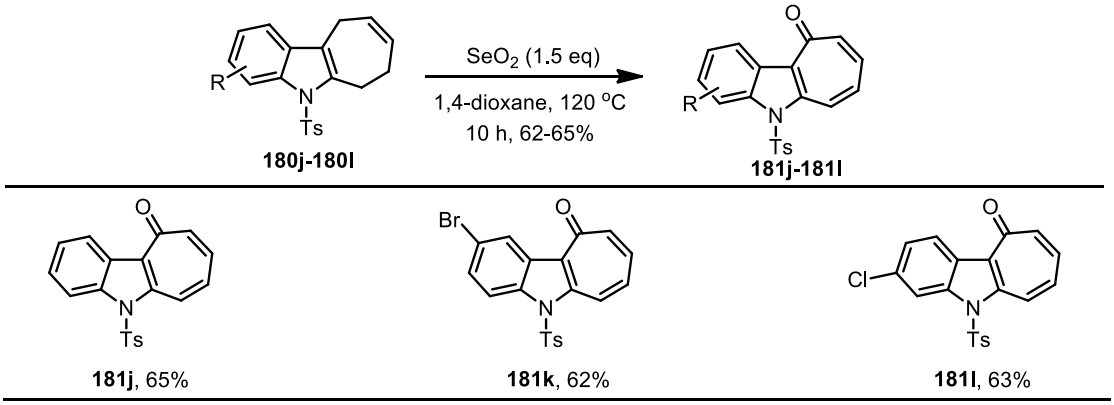
However, among the several attempts towards the synthesis of indolotropones, the stoichiometric amount of SeO_2 mediated reaction of the purified sample **180j** furnished the indolotropone **181j** exclusively.



Scheme 113: Synthesis of indolotropone **181j**

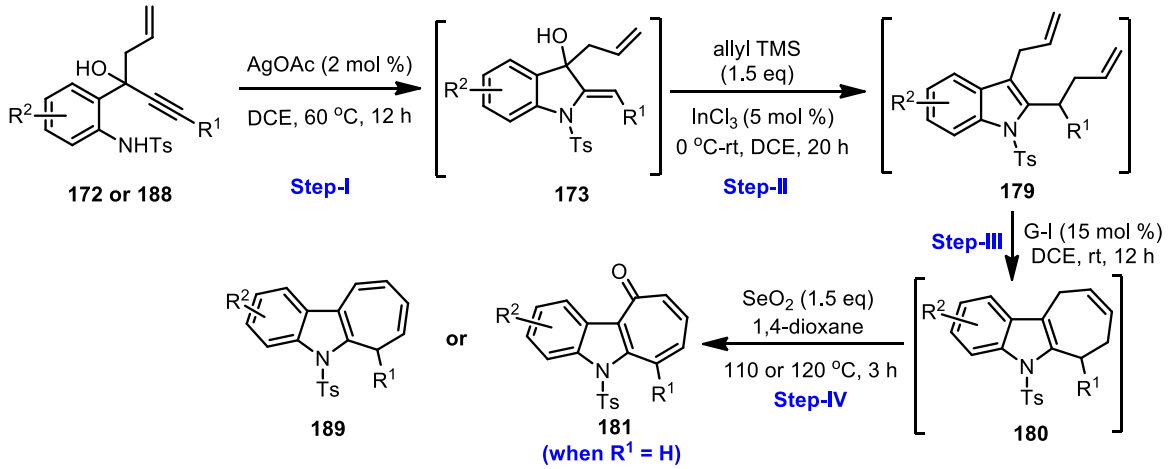
As we mentioned earlier, the indolotropone is an important motif frequently present in a numerous number of biologically active molecules and pharmaceuticals.[100] Moreover, complex molecules possessing these motifs have broad biological profiles (See Fig. 43). Encouraged by their biological features, the organic chemists have motivated towards the discovery of the synthetic strategy to access indolotropones. In this direction, we employed the same reaction protocol to few other substrates to access the indolotropones **181j-181l**, Table 25.

Table 25: Substrate Scope:



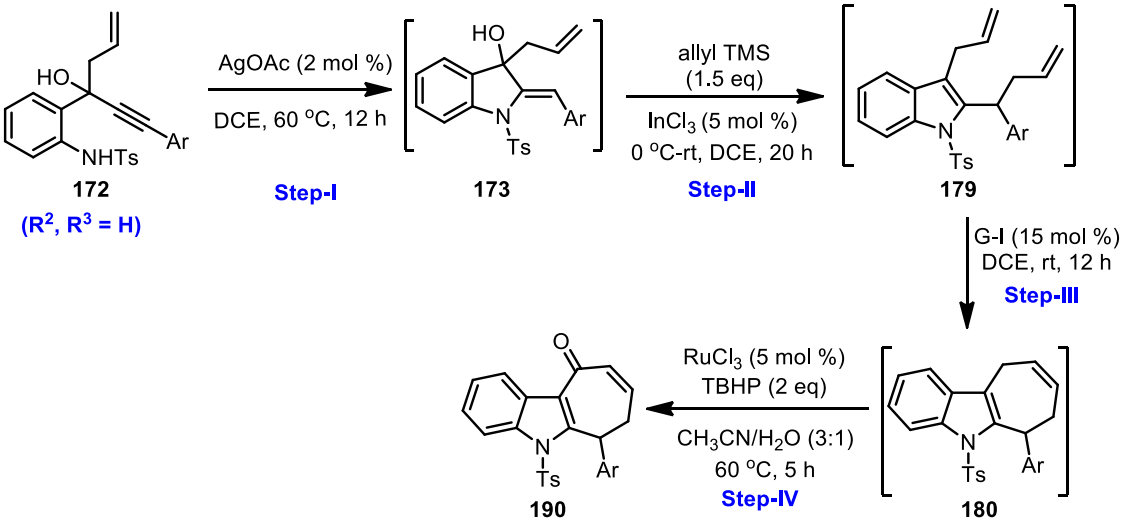
5.3: One-pot quadruple reactions:

In line with our successful development of efficient one-step synthetic protocols for the synthesis of **189**, **190**, and **181** from **180**, we intended to apply these protocols to access these respective products in a one-pot manner starting from the enynols **172**, Scheme 114. To develop the multicatalytic one-pot strategy, we have used four metal-catalysts sequentially to achieve the respective products **189**, **190**, and **181**. Thus, the whole process represents a one-pot tetrametallic orthogonal tandem process.[101] Accordingly, we have subjected the enynols **172** to a sequential catalytic one-pot system, which integrated by Ag/In/Ru/Se, resulted in the desired product **189** in moderate yield. However, the enynols **188** (when R = H) under the Ag/In/Ru/Se-catalyzed reaction conditions delivered the indolotropones **181** exclusively in poor yield, Scheme 114. Interestingly, the reaction of enynols **172** catalyzed by Ag/In/Ru (II)/Ru(III) furnished the product **190** in poor yield, Scheme 115.



Scheme 114: One-pot synthesis of indolotropones **181** and dihydrocyclohepta[*b*]indoles **189**

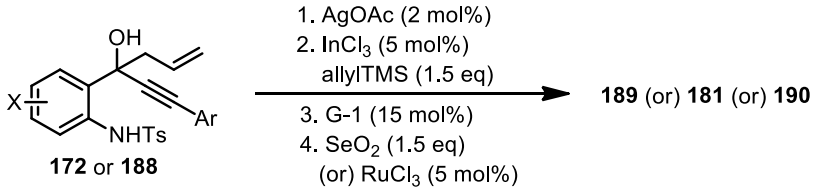
To make this protocol general to all the enynols, few other indolotropones, dihydrocyclohepta[*b*]indoles, and dihydroindolotropone were accessed in a one-pot manner by employing the same reaction conditions, Table xx.



Scheme 115: Multicatalytic one-pot synthesis of dihydroindolotropones **190**

In conclusion, we have demonstrated the diversity-oriented one-pot trimetallic and tetrametallic orthogonal process for the synthesis of cyclohepta[*b*]indoles and indolotropones. We believed that these multicatalytic one-pot processes are the easiest route to access the privileged compounds. These one-pot strategies could be applied towards the synthesis of natural products.

Table 26: Substrate Scope:



172 or **188**

189a, Ar = Ph, 52%	**181j**, Ar = Ph, 35%	**190a**, Ar = Ph, 35%
189b, Ar = (*m*-F)C_6H_4, 36%	**181k**, Ar = Ph, X = Br, 32%	**190b**, Ar = (*p*-Ph)C_6H_4

CONCLUSIONS

In conclusion, we have described a series of unprecedented diastereoselective synthesis of cyclopropanoids *via* unusual cyclization pathways triggered by the DOSM. These strategies provide efficient routes to access cyclopropa-fused tetralones and indeno-spirocyclopropanes in excellent yields. Further, the synthetic utility of these products was established *via* a series of serendipitous one-step elaborations to access the privileged scaffolds such as tetralones, indenones and fluorenones. This strategy was extended to another designed symmetric substrates possessing enone-enone. Towards this, we have demonstrated the DOSM promoted synthesis of densely functionalized cyclopropanoids. Further, one-step serendipitous elaboration of the products provided access to privilege scaffolds such as fluorenones, indenones and naphthaphenones. After the successful demonstration of mild and straightforward protocols for the synthesis of unusual cyclopropanoids promoted by DOSM, we have described an unprecedented metal- and acid-free ring-opening/recyclization cascade of cyclopropyl aryl ketones. These strategies provided us pentannulated aromatics such as 2-(2-hydroxyethyl)indenones, 2,2-disubstituted-3-hydroxyindanones, 2-styryl-3-arylindenones, and 2,3-disubstituted fluorenones.

Continued research interest in developing new strategies to achieve the complex molecular architecture prompted us to develop the diversity-oriented one-pot trimetallic and tetrametallic orthogonal process for the synthesis of cyclohepta[*b*]indoles and indolotropones. We believed that these multicatalytic one-pot processes are the easiest route to access privileged compounds.

EXPERIMENTAL SECTION

General experimental methods: All the starting compounds and catalysts employed in this study were procured from Sigma-Aldrich and were used without further purification. For thin layer chromatography (TLC), silica aluminium foils with fluorescent indicator 254 nm (from Aldrich) were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), and acetic acid (10 mL) in ethanol (900 mL) followed by heating. Column chromatography was performed using SD Fine silica gel 100-200 mesh (approximately 15–20 g per 1 g of the crude product). Dry THF was obtained by distillation over sodium and stored over sodium wire. IR spectra were recorded on a Perkin–Elmer FT IR spectrometer as thin films or KBr pellet, as indicated, with ν_{max}^{-1}. Melting points were recorded on a digital melting point apparatus Stuart SMP30. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker Biospin Advance III FT-NMR spectrometer. NMR shifts are reported as delta (δ) units in parts per million (ppm) and coupling constants (*J*) are reported in Hertz (Hz). The following abbreviations are utilized to describe peak patterns when appropriate: br=broad, s=singlet, d=doublet, t=triplet, q=quartet and m=multiplet. Proton chemical shifts are given in δ relative to tetramethylsilane (δ 0.00 ppm) in $CDCl_3$ or in $(CD_3)_2SO$ (δ 2.50 ppm) or in $(CD_3)_2CO$ (δ 2.05 ppm). Carbon chemical shifts are internally referenced to the deuterated solvent signals in $CDCl_3$ (δ 77.1 ppm) or in $(CD_3)_2SO$ (δ 39.5 ppm) or in $(CD_3)_2CO$ at δ 29.9 and 206.7. Single crystal X-ray analysis was carried on a Rigaku XtaLAB mini X-ray diffractometer. High-resolution mass spectra were recorded on a Waters QTOF mass spectrometer.

General procedure-1: Synthesis of the enone-aldehydes 36a-36j

Step-I: A 50 mL RB flask was charged with 2-bromobenzaldehydes **38** (500 mg, 2.70 mmol), toluene (10 mL), ethylene glycol (1.2 eq) and PTSA (0.1 eq) and the whole mixture was refluxed at 150 ^{o}C by connecting to a Dean-Stark set-up. The reaction continued until **38** disappeared (as monitored by TLC). The reaction mixture was cooled to room temperature and quenched by the addition of aqueous sodium bicarbonate solution (5 mL). Majority of the volatile components were removed under reduced pressure and the residue was extracted with ethyl acetate (2x3 mL).

The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using hexanes/ethyl acetate (9:1) as eluent to afford 2-bromoacetals **39** in 83-89%.

Step-II: To a solution of **39** (600 mg, 2.62 mmol) in anhydrous THF (5 mL) at -78 ^{o}C was added *n*-BuLi (1.6 M in hexane, 1.9 mL, 3.14 mmol). After 15 min, DMF (0.24 ml, 3.14 mmol) at the same temperature was added and the reaction mixture was stirred for an additional 30 min. The mixture was warmed to room temperature over 30 min. The reaction progress was monitored by TLC. Reaction mixture was quenched with saturated aqueous ammonium chloride solution and extracted with ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (9:1) as eluent to afford the aldehyde **40** in 72-78% yield.

Step-III: To a solution of **40** (400 mg, 2.25 mmol) in THF (5 mL) at 0 ^{o}C under nitrogen atmosphere, MeMgBr (3 M in THF, 0.9 mL, 2.7 mmol) was added dropwise over 5 min and the reaction mixture was stirred for an additional 30 min. The reaction progress was monitored by TLC and the reaction mixture was quenched with saturated aqueous ammonium chloride solution and extracted with ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using hexanes/ethyl acetate (7:3) as eluent to afford alcohols **41** in 87-94%.

Step-IV: Compound **41** (1.80 mmol) was dissolved in ethyl acetate (10 mL), and IBX (1.5 eq, 2.71 mmol) was introduced. The resulting reaction mixture was immersed in an oil bath and stirred at 75 °C until compound **41** disappeared as monitored by TLC. The reaction was cooled to room temperature and filtered through Buchner funnel. The filter cake was washed with ethyl acetate (3x2 mL). Organic extracts were combined and worked up using saturated sodium bicarbonate solution to remove excess iodobenzoic acid. The extract was dried over anhydrous sodium sulphate and concentrated under reduced vacuum. The residue was purified by silica gel column chromatography using hexane/ethyl acetate (5:1) as eluent to afford the compound **42** in 70-75% yield.

Step-V: The ketoacetal **42** (290 mg, 1.51 mmol) was dissolved in MeOH, and benzaldehyde (1.1 eq, 1.66 mmol) and NaOH (1.2 eq, 72.5 mg, 1.81 mmol) were introduced at 0 ^{o}C. The reaction mixture was then stirred at 0 ^{o}C until the reactant **42** disappeared as monitored by TLC. The reaction mixture was quenched with saturated aqueous ammonium chloride solution and

extracted with ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate as eluent (5:1) to afford compound **43** in 75-80% yield.

Step-VI: Compound **43** (280 mg, 1 mmol) was dissolved in acetone/water (5 mL, 3:1) mixture in an oven dried round bottom flask and PTSA (0.1 eq) was added and stirred at rt until the reactant **43** disappeared as monitored by TLC. The reaction mixture was quenched with saturated aqueous sodium bicarbonate solution and extracted with ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (9:1) as eluent to afford compound **36** in 88-92% yield.

General procedure-2: Synthesis of the enone-aldehydes 36k-36l and 36m

The procedures described for the synthesis of **36a-36j** (Scheme 37) were followed for the conversion of **47** to **36k-36l**. The enone-aldehyde **36m** was prepared by following the literature method.[45]

General procedure-3: Synthesis of the enone-ketones 56a-56j

All the enone-ketones (**56a-56j**) employed in this study were synthesized following a three-step protocol described in the literature.[45]

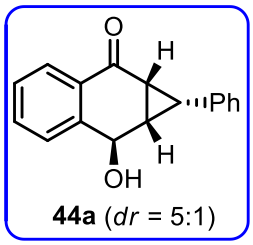
General procedure-4: Synthesis of the enone-enones 57a-57j

The enone-aldehyde **36** (1.0 eq) was dissolved in dry DCM (3 mL) in an oven dried round bottom flask and the Wittig salt (1.2 eq) was added and stirred at rt until the reactant **36** disappeared as monitored by TLC. The reaction mixture was quenched with saturated aqueous ammonium chloride solution and extracted with DCM. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (5:1 to 4:1) as eluent to afford compound **57** in 79-90% yield.

General procedure-5: DOSM reaction with 36, 56, and 57

A mixture of sodium hydride (60% in oil, 20.3 mg, 0.51 mmol) and trimethyloxosulfonium iodide (111.8 mg, 0.51 mmol) was placed in an oven dried flask and DMSO (4 mL) was added to the mixture. After the evolution of hydrogen ceased, the milky solution turned clear and the reaction mixture was stirred for 15 min. The compound **36** or **56** or **57** (100 mg, 0.42 mmol) was dissolved in DMSO (1 mL) and was added to the clear solution dropwise over a period of 5-10 min and stirred at rt until the reactant **36** or **56** or **57** disappeared as monitored by TLC. The reaction mixture was quenched with ice-water and extracted with diethyl ether. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (5:1 to 3:2) as eluent to afford **44** and **44' or 58** or **59**.

7-Hydroxy-1-phenyl-7,7a-dihydro-1*H*-cyclopropa[*b*]naphthalen-2(1a*H*)-one (44a)

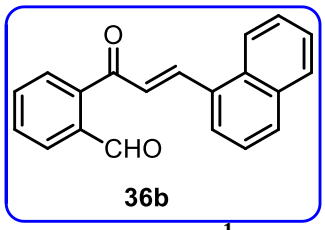


44a (*dr* = 5:1)

Major: This compound was isolated as pale orange solid. Following the general procedure-5, 100 mg of **36a** afforded 77 mg of **44a** (73% yield). M.P = 120-123 ^{o}C. R_f = 0.3 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3398, 3061, 1661, 1597, 1348, 1009, 766. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.53 (d, *J* = 7.76 Hz, 1H), 7.22 (t, *J* = 7.48 Hz, 1H), 7.10-7.01 (m, 2H), 6.94-6.83 (m, 5H), 5.18 (s, 1H), 3.26 (br. s, 1H), 3.03 (t, *J* = 9.28 Hz, 1H), 2.63-2.51 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.6, 141.5, 133.5, 133.3, 131.9, 129.6 (2CH), 128.9, 128.5, 127.8 (2CH), 126.5, 125.9, 66.1, 29.5, 28.3, 27.3. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{15}O_2$ $(M+H)^+$: 251.1072, Found: 251.1081.

Minor: This compound was isolated as pale yellow solid. Following the general procedure-5, 100 mg of **36a** afforded 22 mg of **44a'** (21% yield). M.P = 139-143 ^{o}C. R_f = 0.6 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3388, 2935, 1664, 1605, 1291, 1028, 748. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.67 (t, *J* = 7.1 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.33-7.21 (m, 3H), 7.11 (d, *J* = 7.1 Hz, 2H), 5.38 (d, *J* = 4.6 Hz, 1H), 2.68-2.56 (m, 2H), 2.55-2.49 (m, 1H), 2.43 (br. s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 194.2, 141.0, 138.3, 134.1, 129.1, 128.7 (2CH), 128.3, 127.0, 126.9, 126.7, 126.4 (2CH), 65.5, 36.1, 29.7, 29.2.

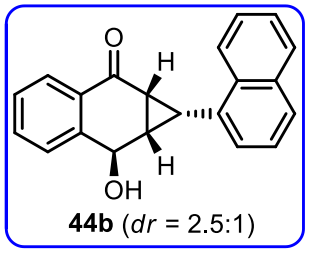
(*E*)-2-(3-(Naphthalen-1-yl)acryloyl)benzaldehyde (36b)



36b

This compound was isolated as pale yellow solid. Following the general procedure-1, 200 mg of **43b** (R = 1-naphthyl) afforded 155 mg of **36b** (89% yield). M.P = 96-98 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3059, 2849, 1696, 1595, 1348, 1211, 1018, 777. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.28 (s, 1H), 8.42 (d, *J* = 15.9 Hz, 1H), 8.11-8.04 (m, 2H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.93-7.88 (m, 2H), 7.81-7.69 (m, 3H), 7.62-7.52 (m, 3H), 7.36 (d, *J* = 15.9 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.9, 191.3, 143.6, 141.8, 135.8, 133.7, 133.3, 131.6, 131.5, 131.4, 131.2, 129.7, 128.9, 128.6, 128.0, 127.2, 126.4, 125.5 (2CH), 123.1. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{15}O_2$ $(M+H)^+$: 287.1072, Found: 287.1084.

7-Hydroxy-1-(naphthalen-1-yl)-7,7a-dihydro-1*H*-cyclopropa[*b*]naphthalen-2(1a*H*)-one (44b)



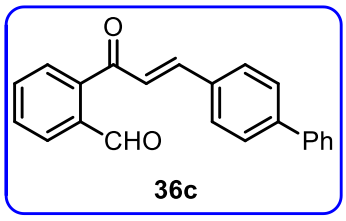
44b (*dr* = 2.5:1)

Major: This compound was isolated as pale brown semisolid. Following the general procedure-5, 100 mg of **36b** afforded 60.5 mg of **44b** (58% yield). R_f = 0.3 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3402, 3050, 1662, 1600, 1293, 1010, 736. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.24 (d, *J* = 8.3 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.53 (td, *J* = 7.6 and 1.2 Hz, 1H), 7.46-7.36 (m, 3H), 7.08 (td, *J* = 7.5 and 1.3 Hz, 1H), 6.98-6.89 (m, 3H), 6.79 (d, *J* = 7.6 Hz, 1H), 5.17 (s, 1H), 3.31 (t, *J* = 9.2 Hz, 1H), 3.03-2.76 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.8, 141.5, 133.2, 133.1, 132.6, 131.9, 129.3, 128.5, 128.4 (2CH), 128.2, 127.3, 126.2, 125.9, 125.6, 124.5, 124.4, 66.3, 28.5, 28.1, 27.7. **HRMS (ESI):** *m/z* calcd for $C_{21}H_{17}O_2$ $(M+H)^+$: 301.1229, Found: 301.1227.

Minor: This compound was isolated as pale brown semisolid. Following the general procedure-5, 100 mg of **36b** afforded 31.5 mg of **44b'** (30% yield). R_f = 0.6 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3416, 3054, 1664, 1599, 1336, 1288, 1027, 776. **Minor a: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.20 (d, *J* = 8.3 Hz, 1H), 8.06-8.0 (m, 1H), 7.91-7.77 (m, 5H), 7.76-7.68 (m, 2H), 7.45-7.40 (m, 2H), 5.51 (br. s, 1H), 2.98 (t, *J* = 4.9 Hz, 1H), 2.73 (dt, *J* = 8.1 and 5.6 Hz, 1H), 2.64 (dd, *J* = 8.1 and 4.2 Hz, 1H), 2.51 (br. s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.1, 141.0, 134.2, 133.9, 133.6, 132.7, 129.3, 128.6, 128.3, 128.1, 127.1, 126.7, 126.6, 126.1, 125.2, 124.9, 123.9, 65.6, 33.8, 27.9, 27.3. **Minor b: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.64-7.58

(m, 2H), 7.58-7.45 (m, 8H), 7.35 (t, *J* = 7 Hz, 1H), 4.26 (d, *J* = 7.3 Hz, 1H), 3.53 (t, *J* = 8.1 Hz, 1H), 2.26 (dd, *J* = 7.5 and 4.5 Hz, 1H), 2.05 (dd, *J* = 8.9 and 4.5 Hz, 1H), 1.70 (d, *J* = 8.1 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.5, 153.9, 136.3, 134.7, 133.0, 132.9, 129.4, 129.3, 128.7, 128.2, 126.6, 126.0, 125.8, 125.5, 125.1, 123.1, 122.8, 69.3, 44.0, 31.7, 18.3.

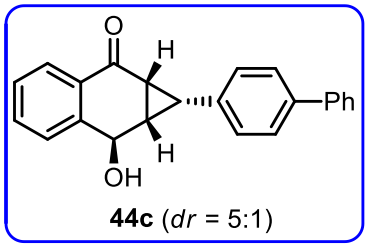
(*E*)-2-(3-([1,1'-Biphenyl]-4-yl)acryloyl)benzaldehyde (36c)



36c

This compound was isolated as pale orange solid. Following the general procedure-1, 200 mg of **43c** (R = (*p*-C_6H_5)C_6H_4) afforded 153 mg of **36c** (87% yield). M.P = 122-126 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3032, 1696, 1593, 1328, 1215, 984, 762. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.22 (s, 1H), 8.04 (d, *J* = 7.1 Hz, 1H), 7.75-7.62 (m, 9H), 7.55 (d, *J* = 15.9 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 7.3 Hz, 1H), 7.29 (d, *J* = 16 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 194.3, 191.2, 146.6, 143.8, 141.8, 139.9, 135.6, 133.3, 133.1, 131.0, 129.6, 129.2 (2CH), 128.9 (2CH), 128.5, 128.1, 127.7 (2CH), 127.1 (2CH), 125.7. **HRMS (ESI):** *m/z* calcd for $C_{22}H_{17}O_2$ $(M+H)^+$: 313.1229, Found: 313.1245.

1-([1,1'-Biphenyl]-4-yl)-7-hydroxy-7,7a-dihydro-1*H*-cyclopropa[*b*]naphthalen-2(1a*H*)-one (44c)



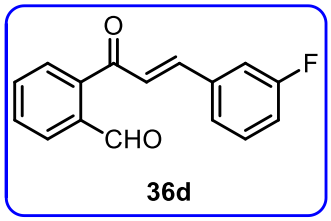
44c (*dr* = 5:1)

Major: This compound was isolated as pale yellow liquid. Following the general procedure-5, 100 mg of **36c** afforded 68 mg of **44c** (65% yield). R_f = 0.3 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3394, 3031, 1659, 1488, 1348, 1007, 761. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.64 (dd, *J* = 7.9 and 1.3 Hz, 1H), 7.89-7.34 (m, 4H), 7.33-7.29 (m, 1H), 7.27-7.21 (m, 1H), 7.17-7.07 (m, 4H), 7.01 (d, *J* = 7.6 Hz, 2H), 5.25 (s, 1H), 3.09 (t, *J* = 9.3 Hz, 1H), 2.71 (ddd, *J* = 9.5, 7.3 and 1.2 Hz, 1H), 2.60 (ddd, *J* = 9, 7.4 and 1.5 Hz, 1H), 2.48 (br. s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.1, 141.3, 140.5, 139.3, 133.5, 132.4, 132.1, 130.1 (2CH), 128.8, 128.7, 128.6 (2CH), 127.2, 126.8 (2CH), 126.4 (2CH), 126.1, 66.3, 29.0, 28.3, 27.2. **HRMS (ESI):** *m/z* calcd for $C_{23}H_{19}O_2$ $(M+H)^+$: 327.1385, Found: 327.1371.

Minor: This compound was isolated as pale yellow solid. Following the general procedure-5, 100 mg of **36c** afforded 17 mg of **44c'** (16% yield). M.P = 191-195 ^{o}C. R_f = 0.6 (hexane/EtOAc

= 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3392, 3022, 1660, 1479, 1343, 1076, 759. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.95 (dd, *J* = 7.6 and 1.2 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.69 (td, *J* = 7.6 and 1.2 Hz, 1H), 7.61-7.52 (m, 4H), 7.47 (q, *J* = 7.8 Hz, 3H), 7.39-7.34 (m, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 5.42 (br. s, 1H), 2.73-2.63 (m, 2H), 2.58 (t, *J* = 4.7 Hz, 1H), 2.28 (br. s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 194.0, 140.9, 140.5, 139.9, 137.4, 134.1, 129.1, 128.8 (2CH), 128.3, 127.4, 127.3 (2CH), 127.0, 126.9 (2CH), 126.8 (2CH), 126.7, 65.5, 36.2, 29.4, 29.3.

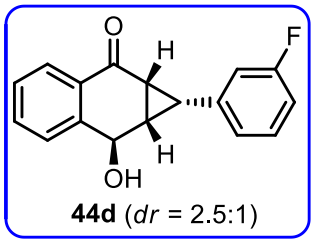
(*E*)-2-(3-(3-Fluorophenyl)acryloyl)benzaldehyde (36d)



36d

This compound was isolated as pale yellow solid. Following the general procedure-1, 200 mg of **43d** (R = (*m*-F)C_6H_4) afforded 150 mg of **36d** (88% yield). M.P = 160-165 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3060, 1693, 1467, 1385, 1174, 1054, 757. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.18 (s, 1H), 8.07-7.98 (m, 1H), 7.77-7.66 (m, 3H), 7.45 (d, *J* = 16 Hz, 1H), 7.42-7.33 (m, 2H), 7.31-7.26 (m, 1H), 7.22 (d, *J* = 16.1 Hz, 1H), 7.18-7.10 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 194.1, 191.1, 163.0 (d, *J* = 245.8 Hz), 145.1 (d, *J* = 2.5 Hz), 141.4, 136.4 (d, *J* = 7.7 Hz), 135.6, 133.4, 131.2, 130.6 (d, *J* = 8.2 Hz), 129.9, 128.4, 126.9, 124.6 (d, *J* = 2.7 Hz), 117.9 (d, *J* = 21.2), 114.7 (d, *J* = 21.8). **HRMS (ESI):** *m/z* calcd for $C_{16}H_{12}FO_2$ $(M+H)^+$: 255.0821, Found: 255.0810.

1-(3-Fluorophenyl)-7-hydroxy-7,7a-dihydro-1*H*-cyclopropa[*b*]naphthalen-2(1a*H*)-one (44d)

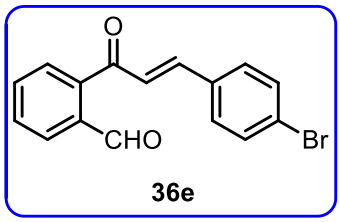


44d (*dr* = 2.5:1)

Major: This compound was isolated as pale yellow semisolid. Following the general procedure-5, 100 mg of **36d** afforded 68.5 mg of **44d** (65% yield). R_f = 0.3 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3466, 2937, 1738, 1370, 1235, 1020, 809, 757. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.59 (dd, *J* = 8 and 1.4 Hz, 1H), 7.32-7.26 (m, 1H), 7.17-7.08 (m, 2H), 6.92-6.82 (m, 1H), 6.71 (dd, *J* = 7.7 and 1 Hz, 1H), 6.67-6.54 (m, 2H), 5.19 (s, 1H), 3.01 (t, *J* = 9.3 Hz, 1H), 2.87 (br. s, 1H), 2.68-2.52 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.9, 161.9 (d, *J* = 245.1 Hz), 141.2, 135.8 (d, *J* = 7.6 Hz), 133.7, 131.9, 129.4 (d, *J* = 8.3 Hz), 128.9, 128.8, 126.0, 125.4 (d, *J* = 2.8 Hz), 116.6 (d, *J* = 21.3 Hz), 113.6 (d. *J* = 21.0 Hz), 66.0, 28.9 (d, *J* = 2 Hz), 28.2, 27.1. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{14}FO_2$ $(M+H)^+$: 269.0978, Found: 269.0990.

Minor: This compound was isolated as pale yellow solid. Following the general procedure-5, 100 mg of **36d** afforded 21 mg of **44d'** (20% yield). M.P = 104-107 ^{o}C. R_f = 0.6 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3377, 2923, 1661, 1439, 1347, 1011, 764. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.91 (dd, *J* = 7.8 and 1.2 Hz, 1H), 7.80-7.73 (m, 1H), 7.68 (td, *J* = 7.6 and 1.5 Hz, 1H), 7.50-7.42 (m, 1H), 7.25 (td, *J* = 8.1 and 6.1 Hz, 1H), 6.97-6.87 (m, 2H), 6.84-6.77 (m, 1H), 5.38 (d, *J* = 4.6 Hz, 1H), 2.65-2.56 (m, 2H), 2.55-2.46 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.8, 162.9 (d, *J* = 245.1 Hz), 141.0 (d, *J* = 7.9 Hz), 140.8, 134.2, 130.2 (d, *J* = 8.4 Hz), 128.9, 128.3, 127.1, 126.7, 122.1 (d, *J* = 2.7 Hz), 113.9 (d, *J* = 21 Hz), 113.3 (d, *J* = 22.2 Hz), 65.3, 36.0, 29.3, 29.2 (d, *J* = 1.8 Hz).

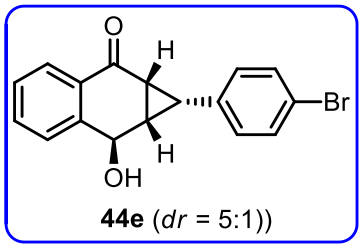
(*E*)-2-(3-(4-Bromophenyl)acryloyl)benzaldehyde (36e)



36e

This compound was isolated as pale yellow solid. Following the general procedure-1, 200 mg of **43e** (R = (*p*-Br)C_6H_4) afforded 162 mg of **36e** (92% yield). M.P = 134-137 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2881, 1691, 1594, 1485, 1326, 1219, 981, 769. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.18 (s, 1H), 8.02 (d, *J* = 6.68 Hz, 1H), 7.75-7.63 (m, 3H), 7.56 (d, *J* = 8.28 Hz, 2H), 7.46-7.38 (m, 3H), 7.21 (d, *J* = 16.1 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 194.1, 191.1, 145.3, 141.5, 135.6, 133.4, 133.1, 132.3 (3CH), 131.1, 129.9 (2CH), 128.4, 126.3, 125.4. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{12}BrO_2$ $(M+H)^+$: 315.0021, Found: 315.0006.

1-(4-Bromophenyl)-7-hydroxy-7,7a-dihydro-1*H*-cyclopropa[*b*]naphthalen-2(1a*H*)-one (44e)



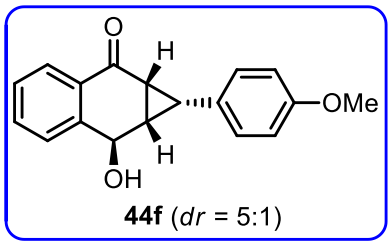
44e (*dr* = 5:1))

Major: This compound was isolated as pale white solid. Following the general procedure-5, 100 mg of **36e** afforded 65.5 mg of **44e** (63% yield). M.P = 195-197 ^{o}C. R_f = 0.3 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3399, 2950, 1659, 1489, 1348, 1295, 1009, 763. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58 (dd, *J* = 7.7 and 1.2 Hz, 1H), 7.34- 7.28 (m, 1H), 7.16-7.08 (m, 2H), 7.05-7.00 (m, 2H), 6.84-6.73 (m, 2H), 5.16 (d, *J* = 4.6 Hz, 1H), 2.94 (t, *J* = 9.3 Hz, 1H), 2.77 (d, *J* = 6.6 Hz, 1H), 2.66-2.51 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.9, 141.2, 133.8, 132.4, 131.8, 131.2

(2CH), 130.9 (2CH), 128.92, 128.90, 126.0, 120.5, 66.0, 28.7, 28.1, 27.1. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{14}BrO_2$ $(M+H)^+$: 329.0177, Found: 329.0190.

Minor: This compound was isolated as pale orange semisolid. Following the general procedure-5, 100 mg of **36e** afforded 21 mg of **44e'** (20% yield). R_f = 0.6 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3444, 2928, 1663, 1491, 1289, 1072, 764. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.92 (d, *J* = 6.8 Hz, 1H), 7.78-7.39 (m, 2H), 7.50-7.39 (m, 3H), 7.0 (d, *J* = 8.6 Hz, 2H), 5.39 (t, *J* = 16.1 Hz, 1H), 2.64-2.53 (m, 2H), 2.49 (t, *J* = 4.6 Hz, 1H), 2.34 (d, *J* = 8.6 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 139.8, 140.8, 137.4, 134.2, 131.7 (2CH), 128.9, 128.4, 128.1 (2CH), 127.1, 126.7, 120.7, 65.3, 35.9, 29.2, 29.0.

7-Hydroxy-1-(4-methoxyphenyl)-7,7a-dihydro-1*H*-cyclopropa[*b*]naphthalen-2(1a*H*)-one (44f)

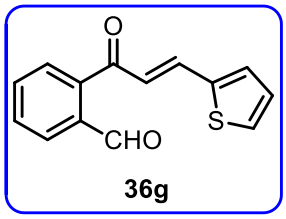


44f (*dr* = 5:1)

Major: This compound was isolated as pale green solid. Following the general procedure-5, 100 mg of **36f** afforded 63 mg of **44f** (60% yield). M.P = 152-156 ^oC. R_f = 0.3 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3431, 2958, 1657, 1607, 1513, 1351, 1245, 1026, 764. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58 (d, *J* = 8.16 Hz, 1H), 7.28-7.23 (m, 1H), 7.12-7.06 (m, 2H), 6.86-6.80 (m, 2H), 6.47-6.39 (m, 2H), 5.17 (s, 1H), 3.60 (s, 3H), 2.96 (t, *J* = 3.2 Hz, 1H), 2.88 (br. s, 1H), 2.61-2.47 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.4, 157.9, 141.6, 133.5, 132.0, 130.6 (2CH), 128.8, 128.5, 125.9, 125.3, 113.3 (2CH), 66.2, 55.1, 28.6, 28.3, 27.3. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{16}NaO_3$ $(M+Na)^+$: 303.0997, Found: 303.1014.

Minor: This compound was isolated as pale yellow solid. Following the general procedure-5, 100 mg of **36f** afforded 26.5 mg of **44f'** (25% yield). M.P = 143-146 ^oC. R_f = 0.6 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3428, 2928, 1700, 1609, 1515, 1250, 1034, 832, 733. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.67-7.61 (m, 2H), 7.52-7.45 (m, 1H), 7.19-7.13 (m, 2H), 6.90-6.85 (m, 2H), 4.62 (br. s, 1H), 3.81 (s, 3H), 2.99 (dd, *J* = 9.2 and 7.7 Hz, 1H), 2.21 (br. s, 1H), 1.98-1.88 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.5, 158.6, 154.0, 136.4, 134.7, 129.4, 129.1, 128.9 (2CH), 125.9, 122.7, 114.0 (2CH), 69.4, 55.3, 44.9, 34.4, 19.2.

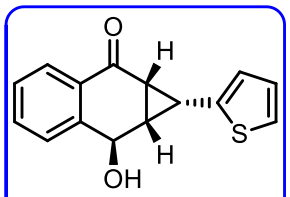
(*E*)-2-(3-(Thiophen-2-yl)acryloyl)benzaldehyde (36g)



36g

This compound was isolated as pale orange solid. Following the general procedure-1, 200 mg of **43g** (R = 2-thienyl) afforded 144 mg of **36g** (85% yield). M.P = 69-72 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3106, 1696, 1585, 1281, 1209, 1020, 712. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.11 (s, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.66-7.55 (m, 4H), 7.40 (d, *J* = 4.9 Hz, 1H), 7.26 (d, *J* = 3.2 Hz, 1H), 7.01 (t, *J* = 4.3 Hz, 1H), 6.97 (d, *J* = 15.8 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.3, 191.2, 141.6, 139.5, 139.1, 135.6, 133.3, 132.7, 131.1, 130.1, 129.4, 128.6, 128.4, 124.2. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{11}O_2S$ $(M+H)^+$: 243.0480, Found: 243.0490.

7-Hydroxy-1-(thiophen-2-yl)-7,7a-dihydro-1*H*-cyclopropa[*b*]naphthalen-2(1a*H*)-one (44g)



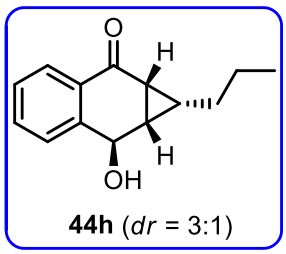
44g (*dr* = 5:1)

Major: This compound was isolated as pale gray solid. Following the general procedure-5, 100 mg of **36g** afforded 74 mg of **44g** (70% yield). M.P = 150-152 ^{o}C. R_f = 0.3 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3387, 2928, 1662, 1350, 1288, 1012, 700. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.69 (d, *J* = 7.6 Hz, 1H), 7.38-7.33 (m, 1H), 7.24-7.14 (m, 2H), 6.83 (d, *J* = 5.1 Hz, 1H), 6.52-6.43 (m, 2H), 5.27 (s, 1H), 2.97 (t, *J* = 9.1 Hz, 1H), 2.73-2.51 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.0, 141.7, 135.7, 133.6, 131.7, 129.0, 128.6, 128.2, 126.3, 126.1, 124.7, 65.9, 29.5, 28.0, 23.1. **HRMS (ESI):** *m/z* calcd for $C_{15}H_{12}NaO_2S$ $(M+Na)^+$: 279.0456, Found: 279.0443.

Minor: This compound was isolated as pale brown solid. Following the general procedure-5, 100 mg of **36g** afforded 19 mg of **44g'** (18% yield). M.P = 108-111 ^{o}C. R_f = 0.6 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3439, 3076, 1665, 1601, 1290, 1029, 760, 700. **Minor a: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.91 (dd, *J* = 7.7 and 1.3 Hz, 1H), 7.72-7.64 (m, 3H), 7.55-7.49 (m, 1H), 7.15 (dd, *J* = 5.1 and 1.2 Hz, 1H), 6.87 (dt, *J* = 3.4 and 1 Hz, 1H), 4.78 (d, *J* = 9 Hz, 1H), 2.31 (d, *J* = 8.8 Hz, 1H), 2.03 (dd, *J* = 9.2 and 4.8 Hz, 1H), 1.99-1.93 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.6, 153.8, 142.0, 134.9, 129.5, 128.4, 127.1 (2CH), 125.9, 124.4, 123.7, 69.4, 37.0, 29.0, 25.0. **Minor b: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.77 (dd, *J* = 13.7 and 7.8 Hz, 2H), 7.49-7.43 (m, 1H), 7.21 (dd, *J* = 5.1 and 1.2 Hz, 1H), 7.02 (dd, *J* = 5.1 and 3.7 Hz, 1H), 6.95-6.90 (m, 2H), 5.37 (dd, *J* = 8.6 and 5.1 Hz, 1H), 3.19 (dd, *J* = 9.0 and 7.8 Hz, 1H),

2.76-2.71 (m, 1H), 2.70-2.60 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.5, 160.2, 140.9, 134.2, 128.9, 127.4, 126.7 (2CH), 125.4, 124.5, 122.8, 65.3, 45.1, 30.1, 20.6.

7-Hydroxy-1-propyl-7,7a-dihydro-1*H*-cyclopropa[*b*]naphthalen-2(1a*H*)-one (44h)

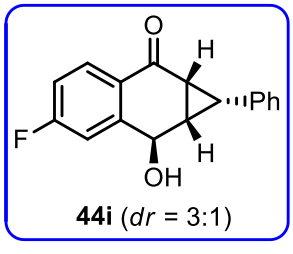


44h (*dr* = 3:1)

Major: This compound was isolated as pale yellow semisolid. Following the general procedure-5, 100 mg of **36h** afforded 72.5 mg of **44h** (68% yield). R_f = 0.3 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3398, 2959, 1661, 1353, 1291, 1009, 763. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.89 (dd, *J* = 7.8 and 1.2 Hz, 1H), 7.63-7.55 (m, 1H), 7.49-7.45 (m, 1H), 7.39 (td, *J* = 7.6 and 1.2 Hz, 1H), 5.06 (s, 1H), 2.90 (br. s, 1H), 2.26-2.15 (m, 2H), 1.69-1.58 (m, 1H), 1.28-1.14 (m, 2H), 1.09-0.97 (m, 1H), 0.94-0.82 (m, 1H), 0.70 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.6, 142.9, 134.1, 132.1, 129.2, 129.0, 126.1, 65.4, 27.9, 27.0, 26.2, 25.0, 22.8, 13.5. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{17}O_2$ $(M+H)^+$: 217.1229, Found: 217.1221.

Minor: This compound was isolated as pale brown semisolid. Following the general procedure-5, 100 mg of **36h** afforded 22.5 mg of **44h'** (21% yield). R_f = 0.6 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3415, 2958, 1662, 1457, 1339, 1292, 1020, 725. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.85 (dd, *J* = 7.7 and 1.1 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.62 (td, *J* = 7.5 and 1.3 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 5.26 (d, *J* = 4.6 Hz, 1H), 2.12-2.03 (m, 2H), 1.53-1.30 (m, 6H), 0.92 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.9, 141.1, 133.8, 129.5, 128.0, 126.8, 126.5, 65.8, 34.5, 32.8, 27.5, 26.4, 22.4, 13.8.

5-Fluoro-7-hydroxy-1-phenyl-7,7a-dihydro-1*H*-cyclopropa[b]naphthalen-2(1a*H*)-one (44i)



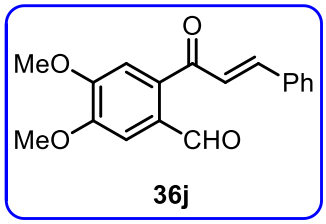
44i (*dr* = 3:1)

Major: This compound was isolated as pale yellow solid. Following the general procedure-5, 100 mg of **36i** afforded 68.5 mg of **44i** (65% yield). M.P = 100-104 ^oC. R_f = 0.3 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3399, 3056, 1662, 1606, 1494, 1351, 1249, 1009, 700. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 (dd, *J* = 8.7 and 5.7 Hz, 1H), 6.96-6.88 (m, 5H), 6.76 (dd, *J* = 8.8 and 2.4 Hz, 1H), 6.68 (td, *J* = 8.4 and 2.4 Hz, 1H), 5.12 (s, 1H), 3.71 (br. s, 1H), 3.05 (t, *J* = 9.28 Hz, 1H), 2.56 (d, *J* = 9.4 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.4, 165.5 (d, *J* = 254 Hz), 144.5 (d, *J* = 8.3 Hz), 133.0, 129.5 (2CH), 128.8 (d, *J* =

9.3 Hz), 128.5 (d, *J* = 2.6 Hz), 127.9 (2CH), 126.8, 115.9 (d, *J* = 21.9 Hz), 115.3 (d, *J* = 21.5 Hz), 65.7 (d, *J* = 0.8 Hz), 29.5, 28.1, 27.5. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{14}FO_2$ $(M+H)^+$: 269.0978, Found: 269.0965.

Minor: This compound was isolated as pale brown liquid. Following the general procedure-5, 100 mg of **36i** afforded 25.5 mg of **44i'** (24% yield). R_f = 0.6 (hexane/EtOAc = 3/2). **IR (thin film, neat):** 3411, 2900, 1667, 1605, 1488, 1266, 1074, 755, 697. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.93 (dd, *J* = 8.6 and 5.8 Hz, 1H), 7.45 (dd, *J* = 9.6 and 2.1 Hz, 1H), 7.33-7.20 (m, 3H), 7.14-7.06 (m, 3H), 5.33 (br. s, 1H), 2.75 (d, *J* = 5.6 Hz, 1H), 2.65-2.58 (m, 1H), 2.56 (dd, *J* = 8.2 and 4.1 Hz, 1H), 2.50 (t, *J* = 7.8 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 192.9, 166.7 (d, *J* = 253.7 Hz), 144.4 (d, *J* = 8.3 Hz), 138.1, 130.1 (d, *J* = 9.4 Hz), 128.7 (2CH), 127.1, 126.3 (2CH), 125.5 (d, *J* = 2.8 Hz), 115.8 (d, *J* = 22 Hz), 113.9 (d. *J* = 23.2 Hz), 65.3 (d, *J* = 1 Hz), 35.8, 29.8, 29.0.

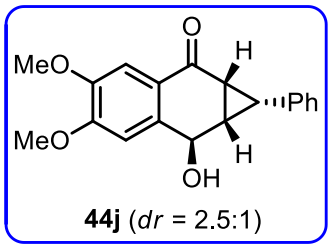
2-Cinnamoyl-4,5-dimethoxybenzaldehyde (36j)



36j

This compound was isolated as pale yellow solid. Following the general procedure-1, 200 mg of **43j** (4,5-OMe, R = Ph) afforded 148 mg of **36j** (85% yield). M.P = 126-129 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2939, 1682, 1592, 1351, 1282, 1122, 983, 760. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.13 (s, 1H), 7.62-7.53 (m, 4H), 7.48-7.41 (m, 3H), 7.23 (d, *J* = 16 Hz, 1H), 7.13 (s, 1H), 4.03 (s, 3H), 4.02 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.3, 189.8, 152.8, 150.9, 147.0, 136.9, 134.2, 131.2, 129.5, 129.1 (2CH), 128.6 (2CH), 126.3, 110.7, 109.9, 56.5, 56.3. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{17}O_4$ $(M+H)^+$: 297.1127, Found: 297.1115.

7-Hydroxy-4,5-dimethoxy-1-phenyl-7,7a-dihydro-1*H*-cyclopropa[*b*]naphthalen-2(1a*H*)-one (44j)



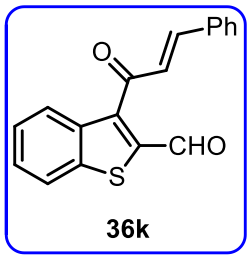
44j (*dr* = 2.5:1)

Major: This compound was isolated as pale brown semisolid. Following the general procedure-5, 100 mg of **36j** afforded 67 mg of **44j** (64% yield). R_f = 0.3 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3438, 2936, 1648, 1597, 1512, 1349, 1269, 1065, 782. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.02 (s, 1H), 6.97-6.87 (m,

5H), 6.52 (s, 1H), 5.08 (s, 1H), 3.80 (s, 3H), 3.75 (s, 3H), 3.05-2.95 (m, 2H), 2.61-2.47 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.0, 153.4, 149.0, 136.1, 133.4, 129.4 (2CH), 127.8 (2CH), 126.6, 125.2, 110.3, 107.1, 65.8, 55.9, 55.8, 29.2, 27.4, 27.1. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{19}O_4$ $(M+H)^+$: 311.1283, Found: 311.1289.

Minor: This compound was isolated as pale yellow solid. Following the general procedure-5, 100 mg of **36j** afforded 23 mg of **44j'** (22% yield). M.P = 153-156 ^oC. R_f = 0.6 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3417, 2933, 1664, 1597, 1506, 1281, 1028, 757. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.42 (s, 1H), 7.35-7.29 (m, 2H), 7.26-7.24 (m, 1H), 7.21 (s, 1H), 7.14-7.08 (m, 2H), 5.34 (d, *J* = 4.9 Hz, 1H), 4.0 (s, 3H), 3.96 (s, 3H), 2.63-2.56 (m, 2H), 2.51 (t, *J* = 9.3 Hz, 1H), 2.15 (br. s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 192.8, 154.1, 148.9, 138.5, 135.4, 128.7, 128.6, 127.8, 126.9, 126.3, 121.9, 108.7, 108.5, 65.4, 56.2, 56.1, 35.9, 29.8, 29.1.

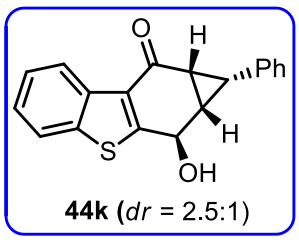
3-Cinnamoylbenzo[*b*]thiophene-2-carbaldehyde (36k)



36k

This compound was isolated as pale orange solid. Following the general procedure-2, 200 mg of **50k** (R = Ph) afforded 140 mg of **36k** (80% yield). R_f = 0.5 (hexane/EtOAc = 9/1). M.P = 104-107 ^oC. **IR (thin film, neat):** ν_{max}/cm^{-1} 3051, 1662, 1593, 1507, 1344, 1197, 1122, 977, 736. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.25 (s, 1H), 7.99 (dd, *J* = 10.9 and 8.4 Hz, 2H), 7.67 (d, *J* = 15.9 Hz, 1H), 7.62-7.56 (m, 3H), 7.53-7.43 (m, 4H), 7.31 (d, *J* = 16.1 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 189.6, 184.4, 148.1, 143.8, 143.6, 141.8, 137.5, 133.8, 131.6, 129.2 (2CH), 128.9 (2CH), 128.5, 127.1, 126.0, 125.6, 123.3. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{13}O_2S$ $(M+H)^+$: 293.0636, Found: 293.0641.

2-Hydroxy-1-phenyl-1a,2-dihydro-1*H*-benzo[*b*]cyclopropa[4,5]benzo[1,2-*d*]thiophen-8(8a*H*)-one (44k)

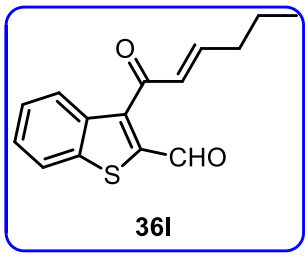


44k (*dr* = 2.5:1)

This compound was isolated as pale yellow liquid. Following the general procedure-5, 100 mg of **36k** afforded 73 mg of **44k** (70% yield). R_f = 0.3 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3290, 2979, 1730, 1372, 1279, 1184, 1037, 718. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.39 (d, *J* = 8.1 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.92-6.78 (m, 3H), 5.32 (d, *J* = 6.8

Hz, 1H), 3.49 (d, *J* = 9 Hz, 1H), 3.0 (t, *J* = 9.4 Hz, 1H), 2.60-2.48 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 190.9, 155.3, 138.2, 134.7, 133.2, 129.7, 129.1 (2CH), 128.0 (2CH), 126.7, 125.6, 125.5, 125.0, 121.8, 62.5, 28.8, 28.4, 27.9. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{15}O_2S$ $(M+H)^+$: 307.0793, Found: 307.0779.

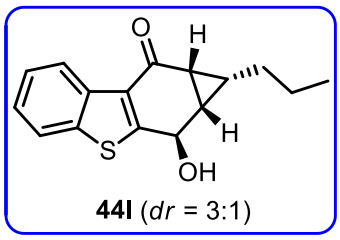
(*E*)-3-(Hex-2-enoyl)benzo[*b*]thiophene-2-carbaldehyde (36l)



36l

This compound was isolated as pale yellow solid. Following the general procedure-2, 200 mg of **50l** (R = *n*-propyl) afforded 137.5 mg of **36l** (82% yield). M.P = 65-68 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2960, 1670, 1509, 1267, 1198, 980, 737. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.18 (s, 1H), 7.94 (ddt, *J* = 7.2, 2.2 and 1.2 Hz, 2H), 7.57 (ddd, *J* = 8.3, 7 and 1.3 Hz, 1H), 7.53-7.45 (m, 1H), 7.01-6.88 (m, 1H), 6.69 (dt, *J* = 15.9 and 1.5 Hz, 1H), 2.33 (qd, *J* = 7.2 and 1.5 Hz, 2H), 1.60-1.50 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 190.1, 184.3, 154.6, 143.8, 143.2, 141.7, 137.5, 132.0, 128.5, 125.8, 125.6, 123.2, 34.9, 21.1, 13.8. **HRMS (ESI):** *m/z* calcd for $C_{15}H_{15}O_2S$ $(M+H)^+$: 259.0793, Found: 259.0780.

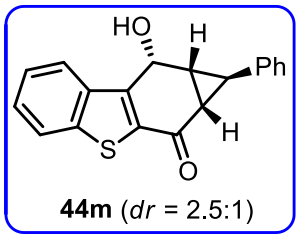
2-Hydroxy-1-propyl-1a,2-dihydro-1*H*-benzo[*b*]cyclopropa[4,5]benzo[1,2-*d*]thiophen-8(8a*H*)-one (44l)



44l (*dr* = 3:1)

This compound was isolated as pale brown semisolid. Following the general procedure-5, 100 mg of **36l** afforded 74 mg of **44l** (70% yield). R_f = 0.3 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3379, 2959, 1639, 1462, 1391, 1202, 1030, 749. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.54 (dd, *J* = 7.6 and 1.6 Hz, 1H), 7.74 (dd, *J* = 7.3 and 1 Hz, 1H), 7.45-7.33 (m, 2H), 5.17 (d, *J* = 8.6 Hz, 1H), 3.68 (d, *J* = 9.3 Hz, 1H), 2.21-2.16 (m, 1H), 2.14-2.08 (m, 1H), 1.65-1.55 (m, 1H), 1.32-1.22 (m, 2H), 1.20-1.10 (m, 1H), 1.09-0.99 (m, 1H), 0.74 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 191.5, 157.7, 138.6, 134.9, 129.6, 125.8, 125.79, 125.70, 122.0, 62.3, 28.8, 27.3, 25.4, 24.7, 22.8, 13.6. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{17}O_2S$ $(M+H)^+$: 273.0949, Found: 273.0949.

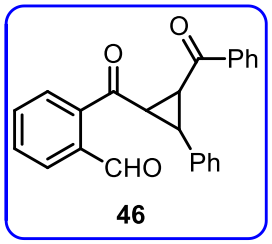
8-Hydroxy-1-phenyl-8,8a-dihydro-1*H*-benzo[*b*]cyclopropa[4,5]benzo[1,2-*d*]thiophen-2(1a*H*)-one (44m)



44m (*dr* = 2.5:1)

This compound was isolated as pale yellow semisolid. Following the general procedure-5, 100 mg of **36m** afforded 74 mg of **44m** (71% yield). R_f = 0.3 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3397, 2927, 1638, 1461, 1266, 1024, 750. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.96-7.79 (m, 1H), 7.67-7.60 (m, 1H), 7.40-7.33 (m, 2H), 7.04 (d, *J* = 7.3 Hz, 2H), 6.93 (t, *J* = 7.3 Hz, 2H), 6.89-6.82 (m, 1H), 5.51 (s, 1H), 3.07 (t, *J* = 9.5 Hz, 1H), 2.87 (br. s, 1H), 2.70-2.56 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 190.6, 142.9, 142.5, 137.7, 136.9, 133.1, 128.9 (2CH), 128.1 (2CH), 127.6, 126.8, 124.9, 123.8, 123.2, 61.1, 28.9, 28.4, 28.3. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{15}O_2S$ $(M+H)^+$: 307.0793, Found: 307.0779.

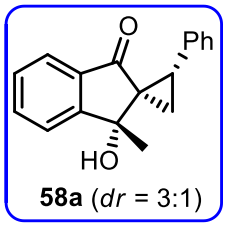
2-(2-Benzoyl-3-phenylcyclopropanecarbonyl)benzaldehyde (46)



46

This compound was isolated as pale brown solid. Following the general procedure-5 (with dimethyl(2-oxo-2-phenylethyl)sulfonium bromide ylide **45**), 100 mg of **36a** afforded 122 mg of **46** (81% yield). M.P = 74-76 ^oC. R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2923, 1688, 1451, 1219, 1013, 750, 695. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.16 (s, 1H), 8.02 (dd, *J* = 8.3 and 1 Hz, 2H), 7.97-7.93 (m, 1H), 7.89-7.84 (m, 1H), 7.67-7.63 (m, 2H), 7.62-7.57 (m, 1H), 7.50-7.43 (m, 2H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.37-7.31 (m, 3H), 3.51 (t, *J* = 6.2 Hz, 1H), 3.48-3.43 (m, 1H), 3.32 (dd, *J* = 9 and 6.1 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.7, 194.4, 192.4, 141.0, 137.8, 136.8, 136.0, 133.6, 132.9, 131.8, 129.3, 128.9 (2CH), 128.7 (2CH), 128.5, 128.4 (2CH), 127.5, 126.5 (2CH), 38.1, 37.8, 32.8. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{18}NaO_3$ $(M+Na)^+$: 377.1154, Found: 377.1163.

1'-Hydroxy-1'-methyl-2-phenylspiro[cyclopropane-1,2'-inden]-3'(1'*H*)-one (58a)

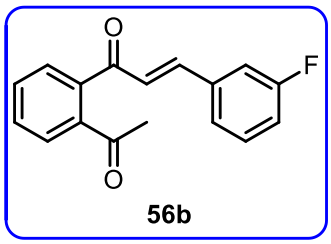


58a (*dr* = 3:1)

This compound was isolated as pale brown semisolid. Following the general procedure-5, 100 mg of **56a** afforded 93 mg of **58a** (88% yield). R_f = 0.5 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 3408, 2972, 1702, 1324, 1120, 1001, 768. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.81-7.76 (m, 1H),

7.69 (td, *J* = 7.5 and 1.2 Hz, 1H), 7.6 (dt, *J* = 7.6 and 0.9 Hz, 1H), 7.45 (td, *J* = 7.5 and 1 Hz, 1H), 7.34-7.22 (m, 5H), 3.04 (t, *J* = 8.7 Hz, 1H), 2.07-2.01 (m, 2H), 1.86 (dd, *J* = 9.3 and 4.4 Hz, 1H), 1.72 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.6, 157.3, 135.9, 135.6, 134.7, 129.3 (2CH), 129.2, 127.9 (2CH), 126.9, 123.8, 122.6, 75.3, 47.3, 35.0, 26.9, 19.8. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{16}NaO_2$ $(M+Na)^+$: 287.1048, Found: 287.1037.

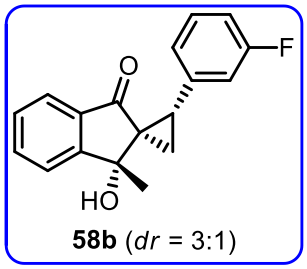
(*E*)-1-(2-Acetylphenyl)-3-(3-fluorophenyl)prop-2-en-1-one (56b)



56b

This compound was isolated as pale yellow liquid. Following the general procedure-3, 200 mg of **55b** (R^1 = Me, R^2 = (*m*-F)C_6H_4) afforded 156 mg of **56b** (79% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3066, 1690, 1676, 1445, 1263, 1144, 767. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.86-7.76 (m, 1H), 7.59 (td, *J* = 6.7 and 1.6 Hz, 2H), 7.53-7.49 (m, 1H), 7.35-7.17 (m, 4H), 7.10-7.03 (m, 2H), 2.56 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.9, 195.7, 162.9 (d, *J* = 245.4 Hz), 143.1 (d, *J* = 2.5 Hz), 140.1, 138.5, 136.8 (d, *J* = 7.8 Hz), 131.8, 130.5, 130.4, 128.9, 128.1, 127.4, 124.4 (d, *J* = 2.7 Hz), 117.3 (d, *J* = 21.3 Hz), 114.5 (d, *J* = 21.8 Hz), 28.2. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{14}FO_2$ $(M+H)^+$: 269.0978, Found: 269.0965.

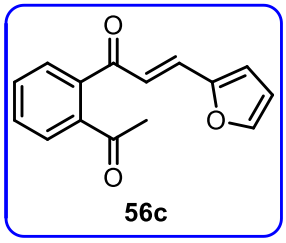
2-(3-Fluorophenyl)-1'-hydroxy-1'-methylspiro[cyclopropane-1,2'-inden]-3'(1'*H*)-one (58b)



58b (*dr* = 3:1)

This compound was isolated as pale brown semisolid. Following the general procedure-5, 100 mg of **56b** afforded 80 mg of **58b** (76% yield). R_f = 0.5 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 3437, 2923, 1706, 1607, 1318, 1007, 762. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.79 (d, *J* = 7.7 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.40 Hz, 1H), 7.27-7.22 (m, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 7.0-6.91 (m, 2H), 3.0 (t, *J* = 8.7 Hz, 1H), 2.02 (dd, *J* = 7.9 and 4.5 Hz, 1H), 1.95-1.85 (m, 2H), 1.72 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.4, 162.5 (d, *J* = 243.6 Hz), 157.3, 138.5 (d, *J* = 7.6 Hz), 135.7, 134.9, 129.4, 129.2 (d, *J* = 8.2 Hz), 125.0 (d, *J* = 2.7 Hz), 123.8, 122.7, 116.3 (d, *J* = 21.5 Hz), 113.8 (d, *J* = 20.9 Hz), 75.2, 47.3, 34.2 (d, *J* = 1.9 Hz), 26.9, 19.9. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{15}FNaO_2$ $(M+Na)^+$: 305.0954, Found: 305.0944.

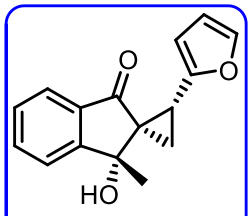
(*E*)-1-(2-Acetylphenyl)-3-(furan-2-yl)prop-2-en-1-one (56c)



56c

This compound was isolated as pale brown semisolid. Following the general procedure-3, 200 mg of **55c** (R^1 = Me, R^2 = 2-Furyl) afforded 148 mg of **56c** (75% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3131, 1685, 1600, 1264, 1016, 757, 593. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.72 (d, *J* = 7.1 Hz, 1H), 7.62-7.50 (m, 4H), 7.20 (d, *J* = 15.7 Hz, 1H), 7.05 (d, *J* = 15.7 Hz, 1H), 6.67 (d, *J* = 3.4 Hz, 1H), 6.53-6.47 (m, 1H), 2.57 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.8, 194.8, 151.1, 145.2, 139.8, 139.4, 131.4, 131.1, 130.5, 128.5, 128.1, 122.9, 116.2, 112.7, 28.6. **HRMS (ESI):** *m/z* calcd for $C_{15}H_{12}NaO_3$ $(M+Na)^+$: 263.0684, Found: 263.0670.

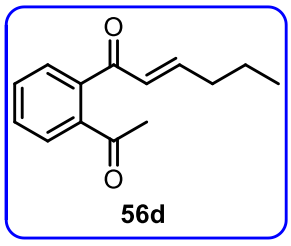
2-(Furan-2-yl)-1'-hydroxy-1'-methylspiro[cyclopropane-1,2'-inden]-3'(1'*H*)-one (58c)



58c (*dr* = 3:1)

This compound was isolated as pale brown semisolid. Following the general procedure-5, 100 mg of **56c** afforded 82 mg of **58c** (77% yield). R_f = 0.5 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 3415, 2972, 1707, 1320, 1114, 1002, 763. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.73 (dd, *J* = 15.3 and 7.8 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 3.7 Hz, 1H), 6.39-6.34 (m, 1H), 6.29 (d, *J* = 3.2 Hz, 1H), 2.84 (t, *J* = 8.7 Hz, 1H), 1.99 (dd, *J* = 7.8 and 4.4 Hz, 1H), 1.92 (br. s, 1H), 1.87 (dd, *J* = 9.3 and 4.4 Hz, 1H), 1.68 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.8, 157.1, 150.5, 141.6, 135.7, 134.8, 129.4, 123.7, 122.7, 110.4, 108.3, 75.2, 46.3, 26.8, 26.3, 19.1. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{13}O_3$ $(M-H)^+$: 253.0865, Found: 253.0846.

(*E*)-1-(2-Acetylphenyl)hex-2-en-1-one (56d)

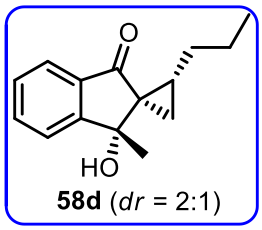


56d

This compound was isolated as pale yellow semisolid. Following the general procedure-3, 200 mg of **55d** (R^1 = Me, R^2 = n-propyl) afforded 163.5 mg of **56d** (83% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2961, 2873, 1687, 1663, 1357, 1262, 977, 765. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.71 (d, *J* = 7.3 Hz, 1H), 7.60-7.48 (m, 2H), 7.43 (d, *J* = 7.1 Hz, 1H), 6.62-6.52 (m, 1H), 6.47 (d, *J* = 16.1 Hz, 1H), 2.53 (s, 3H), 2.21 (q, *J* = 6.9 Hz, 2H), 1.57-1.37 (m, 2H), 0.92 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ

200.0, 196.3, 150.4, 140.1, 138.7, 131.5, 130.4, 130.1, 128.6, 128.1, 34.6, 28.3, 21.2, 13.7. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{16}NaO_2$ $(M+Na)^+$: 239.1048, Found: 239.1041.

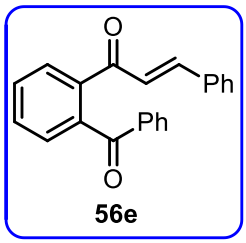
1'-Hydroxy-1'-methyl-2-propylspiro[cyclopropane-1,2'-inden]-3'(1'*H*)-one (58d)



58d (*dr* = 2:1)

This compound was isolated as pale brown semisolid. Following the general procedure-5, 100 mg of **56d** afforded 85 mg of **58d** (80% yield). R_f = 0.5 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 3437, 2961, 1698, 1461, 1323, 1115, 946, 765. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.76-7.70 (m, 2H), 7.68 (td, *J* = 8 and 1.1 Hz, 1H), 7.48 (td, *J* = 7.4 and 1.1 Hz, 1H), 1.88 (br. s, 1H), 1.81-1.66 (m, 3H), 1.56-1.51 (m, 1H), 1.50 (s, 3H), 1.38-1.21 (m, 3H), 0.9 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 203.3, 157.5, 135.9, 134.5, 129.2, 123.7, 122.3, 75.5, 44.5, 32.1, 28.2, 26.3, 23.1, 22.5, 13.8. **HRMS (ESI):** *m/z* calcd for $C_{15}H_{19}O_2$ $(M+H)^+$: 231.1385, Found: 231.1377.

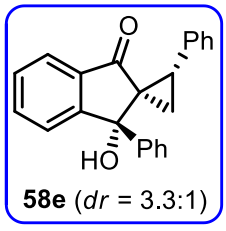
(*E*)-1-(2-Benzoylphenyl)-3-phenylprop-2-en-1-one (56e)



56e

This compound was isolated as pale yellow liquid. Following the general procedure-3, 200 mg of **55e** (R^1 = Ph, R^2 = Ph) afforded 162 mg of **56e** (82% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3061, 1661, 1601, 1449, 1281, 1022, 931, 753. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.92-7.86 (m, 1H), 7.85-7.78 (m, 2H), 7.69-7.61 (m, 2H), 7.58-7.47 (m, 5H), 7.46-7.31 (m, 5H), 7.23 (d, *J* = 15.9 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.4, 192.3, 145.9, 140.7, 139.3, 137.2, 134.5, 133.1, 131.3, 130.8, 130.1, 129.7 (2CH), 128.9 (3CH), 128.8, 128.5 (2CH), 128.4 (2CH), 123.9. **HRMS (ESI):** *m/z* calcd for $C_{22}H_{17}O_2$ $(M+H)^+$: 313.1229, Found: 313.1243.

1'-Hydroxy-1',2-diphenylspiro[cyclopropane-1,2'-inden]-3'(1'*H*)-one (58e)

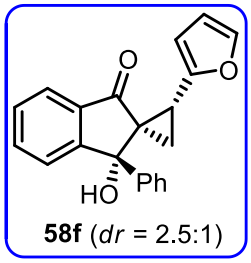


58e (*dr* = 3.3:1)

This compound was isolated as pale yellow solid. Following the general procedure-5, 100 mg of **56e** afforded 83.5 mg of **58e** (80% yield). M.P = 102-104 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3429, 3030, 1700, 1602, 1325, 1037, 760, 700. **^{1}H NMR (400 MHz,**

$CDCl_3$): δ 7.70-7.67 (m, 1H), 7.64 (td, *J* = 7.5 and 1.1 Hz, 1H), 7.49 (td, *J* = 7.5 and 1 Hz, 1H), 7.46-7.41 (m, 3H), 7.40-7.33 (m, 3H), 7.26-7.16 (m, 3H), 7.11-7.06 (m, 2H), 2.42 (s, 1H), 2.24-2.13 (m, 2H), 1.93 (dd, *J* = 8.9 and 4 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.9, 157.6, 143.4, 136.9, 135.1, 134.9, 129.4, 128.9 (2CH), 128.4 (2CH), 127.7 (2CH), 127.6, 126.8, 126.3 (2CH), 125.5, 122.5, 80.6, 50.5, 38.4, 19.6. **HRMS (ESI):** *m/z* calcd for $C_{23}H_{18}NaO_2$ $(M+Na)^+$: 349.1204, Found: 349.1220.

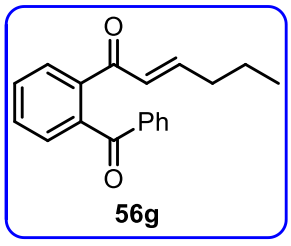
2-(Furan-2-yl)-1'-hydroxy-1'-phenylspiro[cyclopropane-1,2'-inden]-3'(1'*H*)-one (58f)



58f (*dr* = 2.5:1)

This compound was isolated as pale brown liquid. Following the general procedure-5, 100 mg of **56f** afforded 95.5 mg of **58f** (91% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3432, 3061, 1703, 1602, 1319, 1185, 757. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.65 (d, *J* = 7.6 Hz, 1H), 7.60 (td, *J* = 7.5 and 1.1 Hz, 1H), 7.47-7.36 (m, 6H), 7.35-7.29 (m, 1H), 7.25 (d, *J* = 1 Hz, 1H), 6.29 (dd, *J* = 3.2 and 1.7 Hz, 1H), 6.15 (d, *J* = 3.2 Hz, 1H), 2.92 (br. s, 1H), 2.09-1.99 (m, 2H), 1.9 (dd, *J* = 8.2 and 3.3 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.6, 157.9, 150.4, 142.8, 141.6, 136.4, 135.1, 129.3, 128.3 (2CH), 127.5, 126.4 (2CH), 125.5, 122.6, 110.2, 108.2, 80.2, 49.2, 30.5, 19.4. **HRMS (ESI):** *m/z* calcd for $C_{21}H_{16}NaO_3$ $(M+Na)^+$: 339.0997, Found: 339.0989.

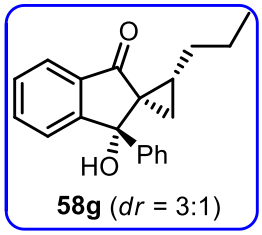
(*E*)-1-(2-Benzoylphenyl)hex-2-en-1-one (56g)



56g

This compound was isolated as pale yellow liquid. Following the general procedure-3, 200 mg of **55g** (R^1 = Ph, R^2 = *n*-propyl) afforded 150 mg of **56g** (76% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2962, 2873, 1656, 1620, 1182, 980, 766, 705. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.81-7.73 (m, 3H), 7.59 (dd, *J* = 5.7 and 3.3 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.49 (dd, *J* = 5.6 and 3.2 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 6.78 (dt, *J* = 15.6 and 6.9 Hz, 1H), 6.54 (d, *J* = 15.7 Hz, 1H), 2.22-2.13 (m, 2H), 1.48-1.38 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.3, 193.0, 151.3, 140.4, 139.3, 137.2, 133.1, 130.9, 130.1, 129.7 (2CH), 128.86, 128.84, 128.4 (2CH), 128.3, 34.7, 21.2, 13.7. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{18}NaO_2$ $(M+Na)^+$: 301.1204, Found: 301.1195.

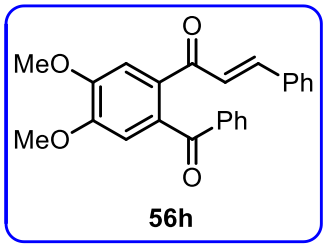
1'-Hydroxy-1'-phenyl-2-propylspiro[cyclopropane-1,2'-inden]-3'(1'*H*)-one (58g)



58g (*dr* = 3:1)

This compound was isolated as pale yellow solid. Following the general procedure-5, 100 mg of **56g** afforded 88.5 mg of **58g** (84% yield). M.P = 99-103 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3445, 2959, 1696, 1602, 1323, 1195, 759. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.74 (d, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.35-7.30 (m, 2H), 7.29-7.22 (m, 3H), 2.61 (d, *J* = 4 Hz, 1H), 1.61-1.55 (m, 2H), 1.42 (dd, *J* = 7.9 and 4 Hz, 1H), 1.32-1.14 (m, 1H), 1.10-0.99 (m, 2H), 0.98-0.88 (m, 1H), 0.72 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 203.9, 157.9, 143.4, 136.8, 134.8, 129.2, 128.1 (2CH), 127.2, 126.2 (2CH), 125.5, 122.2, 80.7, 47.7, 35.7, 28.3, 22.9, 22.6, 13.8. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{20}NaO_2$ $(M+Na)^+$: 315.1361, Found: 315.1352.

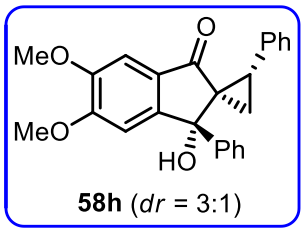
(*E*)-1-(2-Benzoyl-4,5-dimethoxyphenyl)-3-phenylprop-2-en-1-one (56h)



56h

This compound was isolated as pale yellow solid. Following the general procedure-3, 200 mg of **55h** (4,5-OMe, R^1 = Ph, R^2 = Ph) afforded 159 mg of **56h** (80% yield). M.P = 182-184 ^{o}C. R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3007, 1655, 1598, 1451, 1354, 1201, 1119, 976, 769. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.78-7.70 (m, 2H), 7.56-7.49 (m, 1H), 7.49-7.41 (m, 3H), 7.41-7.33 (m, 6H), 7.07 (s, 1H), 7.02 (d, *J* = 15.9 Hz, 1H), 4.04 (s, 3H), 3.96 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.9, 191.5, 151.3, 150.1, 145.0, 137.8, 134.5, 133.9, 133.0, 132.5, 130.6, 129.5 (2CH), 128.9 (2CH), 128.45 (2CH), 128.41 (2CH), 124.6, 111.7, 111.4, 56.4, 56.3. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{21}O_4$ $(M+H)^+$: 373.1440, Found: 373.1432.

1'-Hydroxy-5',6'-dimethoxy-1',2-diphenylspiro[cyclopropane-1,2'-inden]-3'(1'*H*)-one (58h)

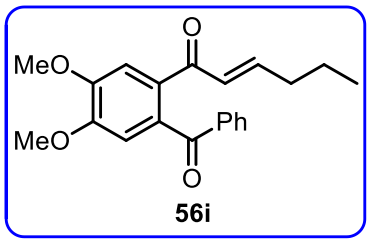


58h (*dr* = 3:1)

This compound was isolated as pale yellow solid. Following the general procedure-5, 100 mg of **56h** afforded 94.5 mg of **58h** (91% yield). M.P = 218-220 ^{o}C. R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3495, 3012, 1697, 1593, 1499, 1272, 1025, 753. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.47-7.41 (m, 2H), 7.40-7.33 (m, 3H), 7.25-7.15 (m, 3H), 7.09 (s, 1H), 7.08-7.04 (m, 2H), 6.82 (s, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 2.53

(br. s, 1H), 2.14-2.05 (m, 2H), 1.86 (dd, *J* = 7.3 and 2.7 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.6, 155.5, 152.3, 150.8, 143.4, 135.4, 130.2, 128.9 (2CH), 128.4 (2CH), 127.6 (2CH), 127.5, 126.7, 126.2 (2CH), 106.5, 103.1, 80.4, 56.4, 56.2, 50.7, 37.6, 18.9. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{23}O_4$ $(M+H)^+$: 387.1596, Found: 387.1579.

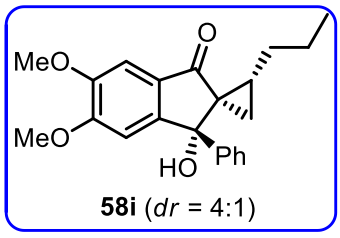
(*E*)-1-(2-Benzoyl-4,5-dimethoxyphenyl)hex-2-en-1-one (56i)



56i

This compound was isolated as pale yellow solid. Following the general procedure-3, 200 mg of **55i** (4,5-OMe, R^1 = Ph, R^2 = *n*-propyl) afforded 149 mg of **56i** (75% yield). M.P = 84-86 ^oC. R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2960, 1665, 1594, 1348, 1280, 1113, 984, 752. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.71 (d, *J* = 7.7 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.21 (s, 1H), 7.0 (s, 1H), 6.68-6.59 (m, 1H), 6.35 (d, *J* = 15.6 Hz, 1H), 3.98 (s, 3H), 3.91 (s, 3H), 2.10 (q, *J* = 7.1 Hz, 2H), 1.42-1.32 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.7, 192.2, 150.9, 150.3, 150.0, 137.7, 133.7, 132.9, 132.4, 129.6 (2CH), 128.8, 128.4 (2CH), 111.7, 111.4, 56.26, 56.24, 34.6, 21.1, 13.7. **HRMS (ESI):** *m/z* calcd for $C_{21}H_{23}O_4$ $(M+H)^+$: 339.1596, Found: 339.1579.

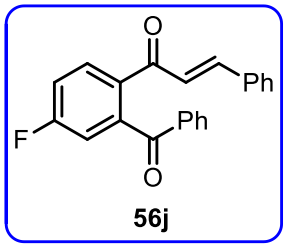
1'-Hydroxy-5',6'-dimethoxy-1'-phenyl-2-propylspiro[cyclopropane-1,2'-inden]-3'(1'*H*)-one (58i)



58i (*dr* = 4:1)

This compound was isolated as pale gray solid. Following the general procedure-5, 100 mg of **56i** afforded 97 mg of **58i** (93% yield). M.P = 167-169 ^oC. R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3446, 2957, 1681, 1596, 1498, 1290, 1124, 857. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.35-7.17 (m, 5H), 7.14 (s, 1H), 6.75 (s, 1H), 3.93 (s, 3H), 3.82 (s, 3H), 2.71 (br, s, 1H), 1.60-1.49 (m, 3H), 1.34 (dd, *J* = 7.8 and 3.9 Hz, 1H), 1.08-0.95 (m, 2H), 0.86-0.77 (m, 1H), 0.69 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.5, 155.4, 152.4, 150.8, 143.3, 130.0, 128.1 (2CH), 127.0, 125.5 (2CH), 106.2, 102.8, 79.8, 56.4, 56.2, 47.8, 31.8, 28.3, 24.8, 23.2, 13.9. **HRMS (ESI):** *m/z* calcd for $C_{22}H_{25}O_4$ $(M+H)^+$: 353.1753, Found: 353.1736.

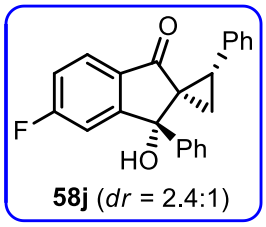
(*E*)-1-(2-Benzoyl-4-fluorophenyl)-3-phenylprop-2-en-1-one (56j)



56j

This compound was isolated as pale yellow liquid. Following the general procedure-3, 200 mg of **55j** (4-F, R^1 = Ph, R^2 = Ph) afforded 160 mg of **56j** (81% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3063, 1666, 1600, 1449, 1280, 1214, 1025, 771, 698. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.96 (dd, *J* = 8.6 and 5.2 Hz, 1H), 7.83-7.77 (m, 2H), 7.60-7.51 (m, 4H), 7.47-7.38 (m, 5H), 7.35-7.29 (m, 1H), 7.27-7.20 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.9, 190.1, 164.17 (d, *J* = 254.5 Hz), 146.2, 143.9 (d, *J* = 7.1 Hz), 136.6, 134.9 (d, *J* = 3.1 Hz), 134.3, 133.4, 131.4 (d, *J* = 8.8 Hz), 130.9, 129.5 (2CH), 129.0 (2CH), 128.6 (2CH), 128.5 (2CH), 122.9, 116.7 (d, *J* = 21.4 Hz), 116.3 (d, *J* = 23.2 Hz). **HRMS (ESI):** *m/z* calcd for $C_{22}H_{16}FO_2$ $(M+H)^+$: 331.1134, Found: 331.1121.

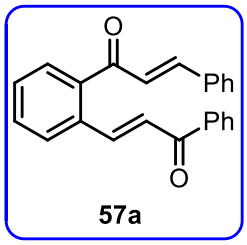
6'-Fluoro-1'-hydroxy-1',2-diphenylspiro[cyclopropane-1,2'-inden]-3'(1'*H*)-one (58j)



58j (*dr* = 2.4:1)

This compound was isolated as pale yellow liquid. Following the general procedure-5, 100 mg of **56j** afforded 95 mg of **58j** (91% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3422, 3062, 1700, 1602, 1331, 1260, 1036, 878, 732. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.66-7.56 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 6.1 Hz, 3H), 7.26-7.18 (m, 3H), 7.17-7.11 (m, 1H), 7.07 (d, *J* = 6.8 Hz, 3H), 3.04-2.92 (m, 1H), 2.20 (t, *J* = 8.7 Hz, 1H), 2.10 (dd, *J* = 8.3 and 4.5 Hz, 1H), 1.92 (dd, *J* = 9.2 and 4.5 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.4, 166.6 (d, *J* = 252.9 Hz), 152.3 (d, *J* = 2.6 Hz), 148.7 (d, *J* = 9.4 Hz), 137.6, 135.5, 132.0, 130.1, 129.7, 129.0 (2CH), 128.6 (2CH), 128.5 (2CH), 128.2, 127.4 (d, *J* = 3.3 Hz), 126.8 (2CH), 124.7 (d, *J* = 9 Hz), 117.9, 114.3 (d, *J* = 23.2 Hz), 109.9 (d, *J* = 25.7 Hz). **HRMS (ESI):** *m/z* calcd for $C_{23}H_{17}FNaO_2$ $(M+Na)^+$: 367.1110, Found: 367.1094.

(*E*)-3-(2-Cinnamoylphenyl)-1-phenylprop-2-en-1-one (57a)

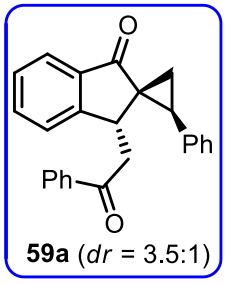


57a

This compound was isolated as pale yellow semisolid. Following the general procedure-4, 150 mg of **36a** afforded 180 mg of **57a** (83% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3060, 1661, 1601, 1328, 1214, 1015, 754, 695. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.06-

7.97 (m, 3H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.62-7.54 (m, 5H), 7.54-7.45 (m, 3H), 7.45-7.38 (m, 4H), 7.19 (d, *J* = 16.1 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.2, 190.9, 146.9, 142.8 (2CH), 140.3, 137.9, 134.4, 134.3, 132.8, 131.0, 130.9, 129.7, 129.0 (2CH), 128.7 (2CH), 128.6, 128.5 (3CH), 127.8, 126.2, 125.4. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{19}O_2$ $(M+H)^+$: 339.1385, Found: 339.1369.

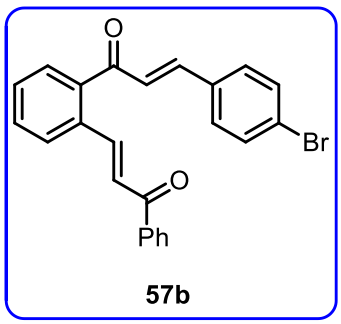
3'-(2-Oxo-2-phenylethyl)-2-phenylspiro[cyclopropane-1,2'-inden]-1'(3'*H*)-one (59a)



59a (*dr* = 3.5:1)

This compound was isolated as pale yellow solid. Following the general procedure-5, 100 mg of **57a** afforded 94 mg of **59a** (90% yield). M.P = 111-114 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3056, 1703, 1603, 1289, 1005, 753, 695. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.86 (d, *J* = 7.8 Hz, 1H), 7.56-7.48 (m, 2H), 7.46 (d, *J* = 7.8 Hz, 3H), 7.43-7.38 (m, 1H), 7.31 (d, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 2H), 7.02 (t, *J* = 7.3 Hz, 1H), 4.15 (dd, *J* = 7.9 and 3.3 Hz, 1H), 3.32 (t, *J* = 8.4 Hz, 1H), 2.83 (dd, *J* = 18.6 and 3.4 Hz, 1H), 2.61 (dd, *J* = 18.3 and 8.1 Hz, 1H), 1.87 (dd, *J* = 7.7 and 4 Hz, 1H), 1.69 (dd, *J* = 9.3 and 4.2 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 203.8, 198.0, 157.3, 136.5, 136.3, 135.9, 134.2, 132.9, 128.7 (2CH), 128.2 (3CH), 128.1, 127.6 (3CH), 126.8, 125.4, 123.3, 42.3, 41.9, 39.8, 30.8, 22.9. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{21}O_2$ $(M+H)^+$: 353.1542, Found: 353.1558.

(*E*)-3-(4-Bromophenyl)-1-(2-((*E*)-3-oxo-3-phenylprop-1-en-1-yl)phenyl)prop-2-en-1-one (57b)

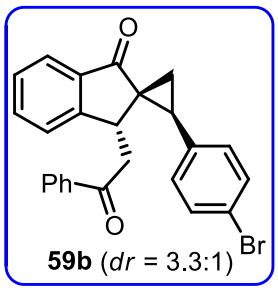


57b

This compound was isolated as pale yellow solid. Following the general procedure-4, 150 mg of **36e** afforded 169 mg of **57b** (85% yield). M.P = 147-150 ^oC. R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3060, 1659, 1601, 1319, 1214, 1012, 819, 749. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.04-7.94 (m, 3H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 7.4 Hz, 1H), 7.62-7.52 (m, 5H), 7.52-7.45 (m, 3H), 7.45-7.39 (m, 3H), 7.17 (d, *J* = 15.9 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 194.7, 190.7, 145.2, 142.7, 140.1, 137.8, 134.5, 133.3, 132.9, 132.3 (2CH), 131.2, 129.9 (2CH),

129.7, 128.7 (3CH), 128.6 (2CH), 127.8, 126.6, 125.4, 125.3. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{18}BrO_2$ $(M+H)^+$: 417.0490, Found: 417.0472.

2-(4-Bromophenyl)-3'-(2-oxo-2-phenylethyl)spiro[cyclopropane-1,2'-inden]-1'(3'*H*)-one (59b)



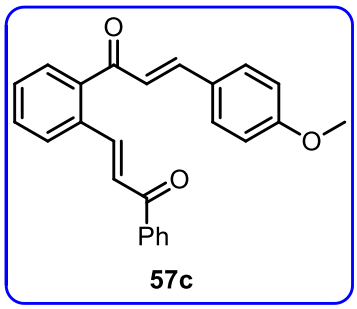
59b (*dr* = 3.3:1)

This compound was isolated as pale white solid. Following the general procedure-5, 100 mg of **57b** afforded 94 mg of **59b** (91% yield). M.P = 166-171 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3056, 1699, 1603, 1489, 1288, 1008, 752.

Major: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 7.5 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.55-7.52 (m, 1H), 7.42 (t, *J* = 8.2 Hz, 2H), 7.39-7.33 (m, 3H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 4.17 (dd, *J* = 6.7 and 2.1 Hz, 1H), 2.93 (dd, *J* = 18.6 and 4.2 Hz, 1H), 2.71 (dd, *J* = 18.6 and 6.6 Hz, 1H), 1.82 (dd, *J* = 7.7 and 4.3 Hz, 1H), 1.71 (dd, *J* = 9.3 and 4.2 Hz, 1H), 1.49 (dd, *J* = 8.9 and 5 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 203.5, 197.5, 157.2, 137.4, 136.1, 135.3, 134.3, 133.2, 131.7 (2CH), 131.1, 130.1, 128.4 (2CH), 128.1, 127.5 (2CH), 125.1, 123.4, 120.8, 44.7, 42.0, 39.5, 30.7, 22.5.

Minor: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.8 Hz, 1H), 7.62 (t, *J* = 5.5 Hz, 2H), 7.52-7.47 (m, 4H), 7.47 (s, 3H), 7.14 (d, *J* = 8.2 Hz, 3H), 4.35 (dd, *J* = 8.3 and 4.4 Hz, 1H), 3.50-3.30 (m, 2H), 3.24-3.12 (m, 2H), 2.00 (dd, *J* = 8.1 and 4.9 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.6, 198.5, 156.0, 136.3, 135.9, 134.8, 134.2, 133.7, 130.9 (2CH), 130.0 (2CH), 128.8 (2CH), 127.8, 127.7 (2CH), 125.2, 123.2, 120.6, 43.2, 41.8, 41.2, 36.5, 18.2. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{20}BrO_2$ $(M+H)^+$: 431.0647, Found: 431.0627.

(*E*)-3-(4-Methoxyphenyl)-1-(2-((*E*)-3-oxo-3-phenylprop-1-en-1-yl)phenyl)prop-2-en-1-one (57c)

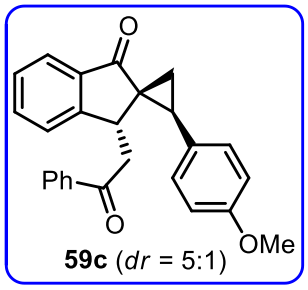


57c

This compound was isolated as pale yellow solid. Following the general procedure-4, 150 mg of **36f** afforded 185 mg of **57c** (89% yield). M.P = 115-118 ^oC. R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3061, 1594, 1511, 1255, 1174, 1020, 829, 750. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.03-7.94 (m, 3H), 7.83 (d, *J*

= 7.8 Hz, 1H), 7.64-7.44 (m, 9H), 7.41 (d, *J* = 15.9 Hz, 1H), 7.06 (d, *J* = 15.9 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 2H), 3.86 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.3, 190.9, 162.0, 146.9, 142.9, 140.8, 137.9, 134.2, 132.8, 130.7, 130.4 (2CH), 129.7, 128.7 (2CH), 128.6 (3CH), 127.7, 127.0, 125.2, 124.2, 114.5 (2CH), 55.4. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{21}O_3$ $(M+H)^+$: 369.1491, Found: 369.1479.

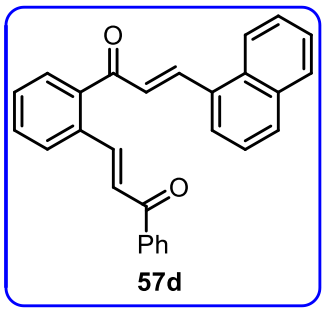
2-(4-Methoxyphenyl)-3'-(2-oxo-2-phenylethyl)spiro[cyclopropane-1,2'-inden]-1'(3'*H*)-one (59c)



59c (*dr* = 5:1)

This compound was isolated as pale yellow semisolid. Following the general procedure-5, 100 mg of **57c** afforded 87 mg of **59c** (83% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2925, 1701, 1606, 1515, 1250, 1033, 753. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.85 (d, *J* = 7.6 Hz, 1H), 7.55-7.40 (m, 6H), 7.36-7.30 (m, 2H), 7.15-7.10 (m, 2H), 6.65-6.60 (m, 2H), 4.16 (dd, *J* = 7.1 and 3.9 Hz, 1H), 3.56 (s, 3H), 3.25 (t, *J* = 8 Hz, 1H), 2.94 (dd, *J* = 18.5 and 4 Hz, 1H), 2.67 (dd, *J* = 18.3 and 7.1 Hz, 1H), 1.82 (dd, *J* = 7.8 and 4.2 Hz, 1H), 1.69 (dd, *J* = 9.3 and 4.2 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 204.0, 197.8, 158.5, 157.4, 136.5, 136.1, 134.1, 132.9, 129.4, 128.2 (2CH), 127.8, 127.7 (2CH), 127.6, 125.2, 123.3, 114.1 (2CH), 113.9, 55.0, 42.2, 41.5, 39.6, 30.9, 22.7. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{23}O_3$ $(M+H)^+$: 383.1647, Found: 383.1629.

(*E*)-3-(Naphthalen-1-yl)-1-(2-((*E*)-3-oxo-3-phenylprop-1-en-1-yl)phenyl)prop-2-en-1-one (59d)

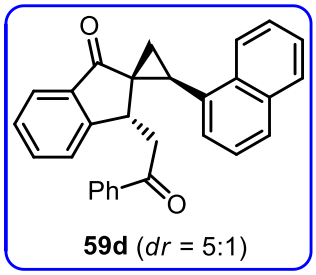


57d

This compound was isolated as pale yellow liquid. Following the general procedure-4, 100 mg of **36b** afforded 181 mg of **57d** (89% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3059, 1642, 1601, 1315, 1215, 1015, 742, 695. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.44 (d, *J* = 15.7 Hz, 1H), 8.15-8.09 (m, 2H), 8.03-7.99 (m, 2H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.92-7.85 (m, 3H), 7.77-7.74 (m, 1H), 7.65-7.60 (m, 1H), 7.59-7.49 (m, 5H), 7.49-7.43 (m, 3H), 7.30 (d, *J* = 14.9 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 194.7, 190.8, 143.6, 142.9, 140.4, 137.9, 134.6, 133.7, 132.8, 131.7, 131.6, 131.23, 131.21, 129.8, 128.8 (2CH), 128.7 (2CH), 128.6 (2CH), 128.5, 127.9,

127.1, 126.4, 125.5, 125.4 (2CH), 123.2. **HRMS (ESI):** *m/z* calcd for $C_{28}H_{21}O_2$ $(M+H)^+$: 389.1542, Found: 389.1525.

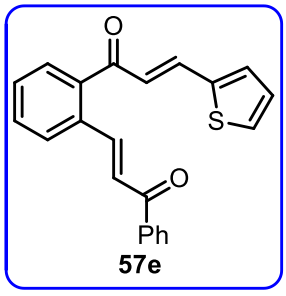
2-(Naphthalen-1-yl)-3'-(2-oxo-2-phenylethyl)spiro[cyclopropane-1,2'-inden]-1'(3'*H*)-one (59d)



59d (*dr* = 5:1)

This compound was isolated as pale white solid. Following the general procedure-5, 100 mg of **57d** afforded 88 mg of **59d** (85% yield). M.P = 144-147 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2924, 1452, 1365, 1169, 1025, 892, 749, 668. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.02 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 7.1 Hz, 1H), 7.73-7.68 (m, 1H), 7.59-7.43 (m, 6H), 7.40-7.34 (m, 2H), 7.26 (t, *J* = 8 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 2H), 6.82 (d, *J* = 7.6 Hz, 2H), 4.27 (t, *J* = 6.4 Hz, 1H), 3.72 (t, *J* = 8.8 Hz, 1H), 2.57-2.39 (m, 2H), 2.14 (dd, *J* = 8.3 and 3.9 Hz, 1H), 1.90 (dd, *J* = 9.2 and 3.8 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 204.3, 197.5, 157.7, 135.9, 135.6, 134.4, 133.7, 133.4, 132.7, 132.2, 128.6, 128.0, 127.9 (2CH), 127.7, 127.4 (2CH), 126.8, 125.8, 125.7, 125.66, 125.63, 124.2, 123.3, 42.0, 41.3, 39.4, 30.6, 21.6. **HRMS (ESI):** *m/z* calcd for $C_{29}H_{23}O_2$ $(M+H)^+$: 403.1698, Found: 403.1715.

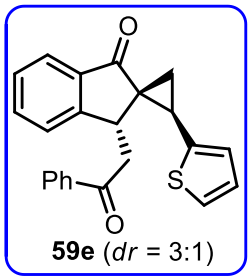
(*E*)-1-(2-((*E*)-3-Oxo-3-phenylprop-1-en-1-yl)phenyl)-3-(thiophen-2-yl)prop-2-en-1-one (57e)



57e

This compound was isolated as pale brown semisolid. Following the general procedure-4, 150 mg of **36g** afforded 183 mg of **57e** (86% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3065, 1660, 1585, 1278, 1214, 1015, 748. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.01-8.11 (m, 3H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 15.9 Hz, 1H), 7.62-7.43 (m, 7H), 7.40 (d, *J* = 15.7 Hz, 1H), 7.31 (d, *J* = 3.4 Hz, 1H), 7.07 (t, *J* = 4.4 Hz, 1H), 6.98 (d, *J* = 15.6 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 194.4, 190.9, 142.8, 140.3, 139.8, 139.0, 137.9, 134.4, 132.8, 132.5, 131.0, 129.8, 129.7, 128.7 (2CH), 128.6 (3CH), 128.5, 127.8, 125.3, 124.8. **HRMS (ESI):** *m/z* calcd for $C_{22}H_{17}O_2S$ $(M+H)^+$: 345.0949, Found: 345.0932.

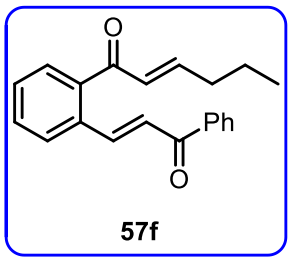
3'-(2-Oxo-2-phenylethyl)-2-(thiophen-2-yl)spiro[cyclopropane-1,2'-inden]-1'(3'*H*)-one (59e)



59e (*dr* = 3:1)

This compound was isolated as pale yellow solid. Following the general procedure-5, 100 mg of **57e** afforded 92 mg of **59e** (88% yield). M.P = 161-164 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3062, 1703, 1603, 1290, 1210, 999, 752, 693. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.85 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.57-7.47 (m, 3H), 7.44-7.33 (m, 3H), 7.02 (d, *J* = 5.1 Hz, 1H), 6.84 (d, *J* = 3.4 Hz, 1H), 6.74 (t, *J* = 4 Hz, 1H), 4.17 (dd, *J* = 8.1 and 3.4 Hz, 1H), 3.43 (t, *J* = 8 Hz, 1H), 2.98 (dd, *J* = 18.6 and 3.2 Hz, 1H), 2.72 (dd, *J* = 18.5 and 8.2 Hz, 1H), 1.83-1.72 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 203.2, 198.0, 157.2, 140.9, 136.6, 136.0, 134.3, 132.9, 128.3 (2CH), 127.7 (3CH), 127.5, 126.1, 125.5, 124.2, 123.4, 41.8, 41.7, 40.0, 25.8, 24.9. **HRMS (ESI):** *m/z* calcd for $C_{23}H_{19}O_2S$ $(M+H)^+$: 359.1106, Found: 359.1124.

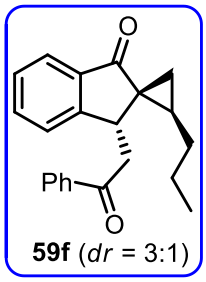
(*E*)-1-(2-((*E*)-3-Oxo-3-phenylprop-1-en-1-yl)phenyl)hex-2-en-1-one (57f)



57f

This compound was isolated as pale yellow liquid. Following the general procedure-4, 100 mg of **36h** afforded 189 mg of **57f** (84% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2961, 2872, 1661, 1612, 1279, 1214, 1015, 978, 751. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.01 (d, *J* = 7.3 Hz, 2H), 7.95 (d, *J* = 15.9 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.62-7.54 (m, 1H), 7.55-7.44 (m, 5H), 7.39 (d, *J* = 15.7 Hz, 1H), 6.77 (dt, *J* = 15.7 and 6.8 Hz, 1H), 6.53 (d, *J* = 16.1 Hz, 1H), 2.26 (q, *J* = 7.3 Hz, 2H), 1.55-1.45 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.8, 190.6, 152.9, 142.8, 140.4, 137.9, 134.1, 132.8, 130.7, 130.6, 129.6, 128.7 (2CH), 128.6 (3CH), 127.6, 124.9, 34.8, 21.2, 13.7. **HRMS (ESI):** *m/z* calcd for $C_{21}H_{21}O_2$ $(M+H)^+$: 305.1542, Found: 305.1530.

3'-(2-Oxo-2-phenylethyl)-2-propylspiro[cyclopropane-1,2'-inden]-1'(3'*H*)-one (59f)

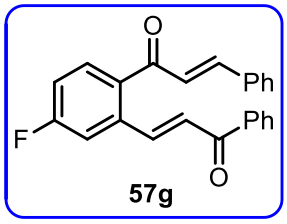


59f (*dr* = 3:1)

This compound was isolated as pale yellow liquid. Following the general procedure-5, 100 mg of **57f** afforded 86 mg of **59f** (82% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2953, 2854, 1698, 1605, 1338, 1212, 967, 750. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.98-7.94 (m,

2H), 7.82-7.77 (m, 1H), 7.64-7.56 (m, 2H), 7.54-7.42 (m, 4H), 4.11 (t, *J* = 4 Hz, 1H), 3.30 (dd, *J* = 8 and 4 Hz, 2H), 1.88 (t, *J* = 8 Hz, 1H), 1.73-1.60 (m, 2H), 1.38-1.33 (m, 1H), 1.33-1.19 (m, 2H), 1.15 (dd, *J* = 8.7 and 4.5 Hz, 1H), 0.86 (t, *J* = 8 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 204.4, 198.6, 156.4, 137.7, 136.5, 133.8, 133.5, 128.7 (2CH), 128.1 (2CH), 127.6, 125.2, 122.8, 44.6, 41.4, 40.2, 34.0, 28.0, 22.9, 20.7, 13.8. **HRMS (ESI):** *m/z* calcd for $C_{22}H_{23}O_2$ $(M+H)^+$: 319.1698, Found: 319.1682.

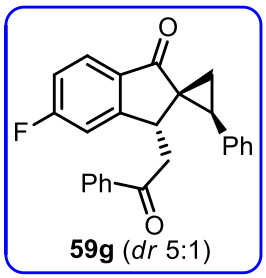
(*E*)-3-(2-Cinnamoyl-5-fluorophenyl)-1-phenylprop-2-en-1-one (57g)



57g

This compound was isolated as pale yellow semisolid. Following the general procedure-4, 150 mg of **36i** afforded 167 mg of **57g** (79% yield). M.P = 167-169 ^oC. R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3067, 1662, 1602, 1330, 1219, 1015, 767, 695. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.06-7.95 (m, 3H), 7.70 (dd, *J* = 8.6 and 5.6 Hz, 1H), 7.63-7.56 (m, 3H), 7.55-7.47 (m, 3H), 7.46-7.34 (m, 5H), 7.26-7.21 (m, 1H), 7.19 (d, *J* = 16 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.5, 190.5, 163.9 (d, *J* = 250.9 Hz), 146.9, 141.6 (d, *J* = 1.9 Hz), 137.6 (d, *J* = 3.3 Hz), 137.5, 136.4 (d, *J* = 3 Hz), 134.3, 133.0, 131.2 (d, *J* = 8.8 Hz), 131.1, 129.1 (2CH), 128.7 (2CH), 128.67 (2CH), 128.61 (2CH), 126.9, 125.9 (d, *J* = 35 Hz), 116.5 (d, *J* = 21.5 Hz), 114.5 (d, *J* = 22.5 Hz). **HRMS (ESI):** *m/z* calcd for $C_{24}H_{18}FO_2$ $(M+H)^+$: 357.1291, Found: 357.1269.

5'-Fluoro-3'-(2-oxo-2-phenylethyl)-2-phenylspiro[cyclopropane-1,2'-inden]-1'(3'*H*)-one (59g)

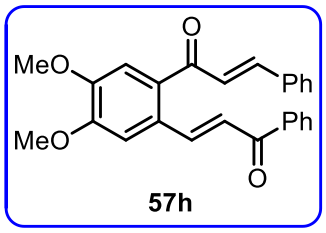


59g (*dr* 5:1)

This compound was isolated as pale yellow solid. Following the general procedure-5, 100 mg of **57g** afforded 81.5 mg of **59g** (78% yield). M.P = 130-135 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2914, 1702, 1609, 1269, 1225, 1088, 748, 698. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.85 (dd, *J* = 8.3 and 5.4 Hz, 1H), 7.50-7.44 (m, 3H), 7.35-7.29 (m, 2H), 7.26-7.22 (m, 2H), 7.19-7.08 (m, 4H), 7.07-7.02 (m, 1H), 4.11 (dd, *J* = 8.1 and 3.2 Hz, 1H), 3.30 (dd, *J* = 9.2 and 7.9 Hz, 1H), 2.83 (dd, *J* = 18.6 and 3.2 Hz, 1H), 2.59 (dd, *J* = 18.7 and 8.2 Hz, 1H), 1.86 (dd, *J* = 7.7 and 4.3 Hz, 1H), 1.73 (dd, *J* = 9.4 and 4.3 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.9, 197.7, 166.8 (d, *J* = 253.8 Hz), 160.1 (d, *J* = 9.7 Hz),

136.2 (d, *J* = 23.9 Hz), 133.1, 132.4 (d, *J* = 1.7 Hz), 128.7 (2CH), 128.3 (3CH), 128.1, 127.6 (3CH), 126.9, 125.5 (d, *J* = 10.2 Hz), 115.7 (d, *J* = 23.5 Hz), 112.6 (d, *J* = 22.9 Hz), 42.0, 41.8, 39.7 (d, *J* = 1.9 Hz), 30.9, 22.8. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{20}FO_2$ $(M+H)^+$: 371.1447, Found: 371.1465.

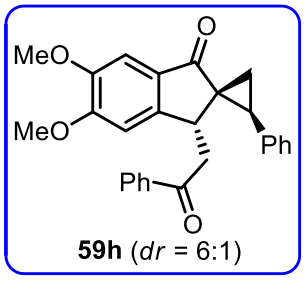
(*E*)-3-(2-Cinnamoyl-4,5-dimethoxyphenyl)-1-phenylprop-2-en-1-one (57h)



57h

This compound was isolated as pale yellow solid. Following the general procedure-6, 150 mg of **36j** afforded 175 mg of **57h** (87% yield). M.P = 156-159 ^oC. R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2933, 1658, 1595, 1511, 1276, 1132, 1017, 768. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.04-7.92 (m, 3H), 7.62-7.52 (m, 4H), 7.49-7.39 (m, 5H), 7.29-7.24 (m, 2H), 7.20-7.12 (m, 2H), 4.05 (s, 3H), 3.99 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.9, 191.4, 151.0, 150.2, 146.2, 143.1, 138.0, 134.4, 134.1, 132.6, 130.9, 129.0 (2CH), 128.7 (2CH), 128.55 (2CH), 128.54 (2CH), 127.9, 126.4, 124.1, 111.4, 109.5, 56.3, 56.2. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{23}O_4$ $(M+H)^+$: 399.1596, Found: 399.1580.

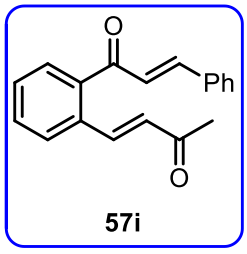
5',6'-Dimethoxy-3'-(2-oxo-2-phenylethyl)-2-phenylspiro[cyclopropane-1,2'-inden]-1'(3'*H*)-one (59h)



59h (*dr* = 6:1)

This compound was isolated as pale yellow semisolid. Following the general procedure-5, 100 mg of **57h** afforded 90 mg of **59h** (87% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2939, 1688, 1595, 1498, 1307, 1118, 1018, 760. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.51-7.44 (m, 3H), 7.34-7.25 (m, 5H), 7.19 (t, *J* = 8 Hz, 2H), 7.06-7.01 (m, 1H), 6.93 (s, 1H), 4.10 (dd, *J* = 8.7 and 3.3 Hz, 1H), 3.94 (s, 3H), 3.85 (s, 3H), 3.28 (dd, *J* = 9 and 7.8 Hz, 1H), 2.78-2.69 (m, 1H), 2.63-2.55 (m, 1H), 1.83 (dd, *J* = 7.6 and 4.2 Hz, 1H), 1.65 (dd, *J* = 9.3 and 4.2 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.4, 198.8, 154.8, 152.7, 149.5, 136.6, 136.5, 133.0, 128.7 (2CH), 128.4, 128.3 (2CH), 128.1, 127.7 (3CH), 126.8, 107.2, 104.0, 56.2, 56.1, 42.9, 42.2, 39.7, 30.4, 22.2. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{25}O_4$ $(M+H)^+$: 413.1753, Found: 413.1735.

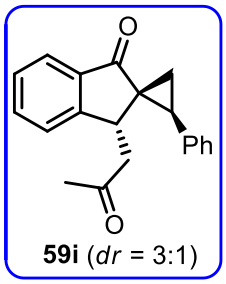
(*E*)-4-(2-Cinnamoylphenyl)but-3-en-2-one (57i)



57i

This compound was isolated as pale yellow liquid. Following the general procedure-4, 150 mg of **36a** afforded 159.5 mg of **57i** (90% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3061, 1666, 1602, 1257, 1210, 977, 755. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.89 (d, *J* = 16.4 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.69 (dd, *J* = 7.5 and 1.6 Hz, 1H), 7.62-7.57 (m, 3H), 7.56-7.50 (m, 2H), 7.46-7.41 (m, 3H), 7.23 (d, *J* = 16.1 Hz, 1H), 6.65 (d, *J* = 16.4 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.7, 194.8, 146.9, 141.7, 139.6, 134.3, 134.2, 131.3, 131.1, 130.0, 129.6, 129.1 (2CH), 128.9, 128.6 (2CH), 127.6, 125.9, 26.9. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{17}O_2$ $(M+H)^+$: 277.1229, Found: 277.1234.

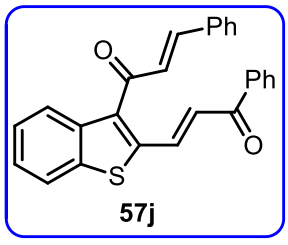
3'-(2-Oxopropyl)-2-phenylspiro[cyclopropane-1,2'-inden]-1'(3'*H*)-one (59i)



59i (*dr* = 3:1)

This compound was isolated as pale yellow liquid. Following the general procedure-5, 100 mg of **57i** afforded 89.5 mg of **59i** (85% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2924, 1700, 1606, 1464, 1201, 1159, 1040, 701. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.45-7.38 (m, 2H), 7.37-7.31 (m, 2H), 7.30-7.23 (m, 3H), 3.93 (dd, *J* = 7.3 and 3.7 Hz, 1H), 3.24 (t, *J* = 8.7 HZ, 1H), 2.29 (dd, *J* = 18.7 and 3.7 Hz, 1H), 2.10 (dd, *J* = 18.8 and 7.3 Hz, 1H), 1.79 (dd, *J* = 7.6 and 4.2 Hz, 1H), 1.63 (dd, *J* = 9.3 and 4.2 Hz, 1H), 1.57 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 206.5, 203.6, 157.3, 136.3, 135.9, 134.2, 128.7 (3CH), 128.3, 127.6, 126.9, 125.1, 123.3, 46.9, 41.8, 39.3, 30.6, 29.7, 23.1. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{19}O_2$ $(M+H)^+$: 291.1385, Found: 291.1399.

(*E*)-3-(3-Cinnamoylbenzo[*b*]thiophen-2-yl)-1-phenylprop-2-en-1-one (57j)

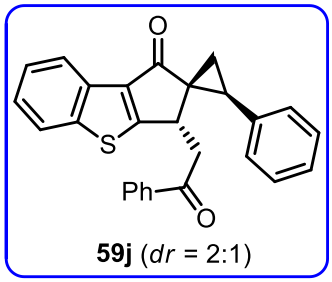


57j

This compound was isolated as pale yellow solid. Following the general procedure-4, 150 mg of **36k** afforded 165.5 mg of **57j** (82% yield). M.P = 136-139 ^oC. R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3061, 1658, 1594, 1498, 1203, 1014, 693. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.16 (d, *J* = 15.4 Hz, 1H), 8.02-7.97 (m, 2H), 7.93-7.87 (m, 2H), 7.66 (d, *J* = 16.1 Hz, 1H), 7.63-7.57 (m, 3H), 7.52-7.41 (m, 8H), 7.24 (d, *J* = 16.1

Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 190.4, 189.7, 147.1, 141.6, 139.5, 138.9, 138.3, 137.6, 135.5, 134.2, 133.1, 131.2, 129.1 (2CH), 128.8 (2CH), 128.7 (2CH), 128.6 (2CH), 127.2, 127.0, 126.0, 125.7, 124.4, 122.4. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{19}O_2S$ $(M+H)^+$: 395.1106, Found: 395.1124.

3-(2-Oxo-2-phenylethyl)-2'-phenylspiro[benzo[*b*]cyclopenta[*d*]thiophene-2,1'-cyclopropan]-1(3*H*)-one (59j)



59j (*dr* = 2:1)

This compound was isolated as pale yellow solid. Following the general procedure-5, 100 mg of **57j** afforded 84 mg of **59j** (81% yield). M.P = 111-113 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3060, 1661, 1455, 1393, 1222, 1018, 703.

Major: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08-7.99 (m, 5H), 7.62 (q, *J* = 6.8 Hz, 2H), 7.55-7.47 (m, 4H), 7.32-7.24 (m, 3H), 3.49-3.42 (m, 1H), 3.21-3.10 (m, 2H), 2.86-2.81 (m, 1H), 2.10 (dt, *J* = 9 and 4.8 Hz, 1H), 1.76 (dd, *J* = 11.9 and 7.5 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.3, 196.8, 150.5, 139.95, 138.3, 137.1, 136.5, 135.5, 133.4, 128.8 (2CH), 128.4 (2CH), 128.3 (2CH), 126.4, 125.7 (2CH), 125.45, 125.0, 123.55, 121.93, 34.9, 30.6, 25.5, 21.2, 20.9.

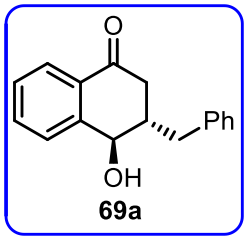
Minor: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.1 Hz, 2H), 7.46-7.33 (m, 5H), 7.17-7.02 (m, 5H), 6.97-9.90 (m, 2H), 3.40-3.32 (m, 1H), 2.94-2.87 (m, 1H), 2.69 (dt, *J* = 8.4 and 4.5 Hz, 1H), 2.05-1.97 (m, 1H), 1.90 (dq, *J* = 8.9 and 4.4 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.2, 197.0, 150.6, 139.91, 138.2, 137.2, 136.7, 135.4, 133.3, 128.7 (2CH), 128.6 (2CH), 128.2 (2CH), 126.6, 125.9 (2CH), 125.42, 124.9, 123.54, 121.99, 34.5, 30.7, 24.9, 21.0, 20.8. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{21}O_2S$ $(M+H)^+$: 409.1262, Found: 409.1242.

General procedure-6: Synthesis of *trans*-1,2-disubstituted tetralones 69a-69e

To an oven dried 100 mL two neck RB flask, 50 mL of distilled liquid ammonia was taken and kept at –78 ^oC. Then, 0.1 g of lithium was introduced to the liquid ammonia solution and stirred until the color of the solution turned to deep blue. A THF (3 mL) solution of **44a** (100 mg, 0.4 mmol) was added dropwise to liquid ammonia and stirred for another 20 min. The reaction mixture was taken out from –78 ^oC and was kept at 0 ^oC by opening two necks of the RB flask, until the complete evaporation of liquid ammonia. Then the reaction mixture was quenched by

adding saturated aqueous ammonium chloride solution and extracted with ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (4:1 to 5:2) as eluent to afford compound **69a** in 89% yield.

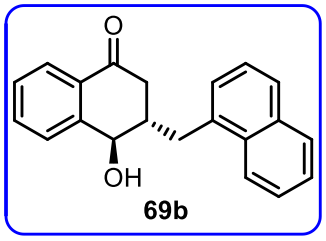
3-Benzyl-4-hydroxy-3,4-dihydronaphthalen-1(2*H*)-one (69a)



69a

This compound was isolated as pale brown solid. Following the general procedure-6, 100 mg of **44a** afforded 90 mg of **69a** (89% yield). R_f = 0.5 (hexane/EtOAc = 7.5/2.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 3401, 2922, 1676, 1599, 1298, 1032, 763, 703. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.01 (dd, *J* = 7.8 and 1.2 Hz, 1H), 7.71-7.66 (m, 1H), 7.66-7.60 (m, 1H), 7.46-7.40 (m, 1H), 7.35-7.29 (m, 2H), 7.28-7.22 (m, 1H), 7.21-7.16 (m, 2H), 4.72 (d, *J* = 6.4 Hz, 1H), 3.11 (dd, *J* = 13.6 and 5 Hz, 1H), 2.86 (dd, *J* = 16.6 and 3.9 Hz, 1H), 2.69 (dd, *J* = 13.4 and 8.3 Hz, 1H), 2.52-2.70 (m, 2H), 2.42-2.33 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.1, 144.9, 138.5, 134.3, 131.2, 129.3 (2CH), 128.6 (2CH), 128.3, 127.2, 126.9, 126.5, 71.8, 44.7, 40.9, 38.3. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{16}NaO_2$ $(M+Na)^+$: 275.1048, Found: 275.1030.

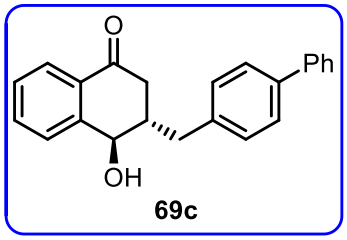
4-Hydroxy-3-(naphthalen-1-ylmethyl)-3,4-dihydronaphthalen-1(2*H*)-one (69b)



69b

This compound was isolated as pale yellow solid. Following the general procedure-6, 100 mg of **44b** afforded 84 mg of **69b** (83% yield). M.P = 139-141 ^oC. R_f = 0.5 (hexane/EtOAc = 7.5/2.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 3438, 2928, 1675, 1600, 1600, 1297, 771. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.08-8.01 (m, 2H), 7.91-7.87 (m, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.75-7.71 (m, 1H), 7.70-7.64 (m, 1H), 7.53-7.49 (m, 2H), 7.48-7.41 (m, 2H), 7.31 (d, *J* = 1 Hz, 1H), 4.86 (t, *J* = 7.2 Hz, 1H), 3.80 (dd, *J* = 13.7 and 4.9 Hz, 1H), 2.95 (dd, *J* = 13.7 and 9 Hz, 1H), 2.87 (dd, *J* = 16.9 and 4.2 Hz, 1H), 2.77-2.66 (m, 1H), 2.47 (dd, *J* = 16.9 and 10.3 Hz, 1H), 2.28 (d, *J* = 6.8 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.8, 144.7, 134.8, 134.3, 134.1, 131.8, 131.3, 128.9, 128.4, 127.6, 127.5, 127.2, 126.9, 126.1, 125.7, 125.4, 123.7, 72.6, 43.8, 41.3, 35.9. **HRMS (ESI):** *m/z* calcd for $C_{21}H_{19}O_2$ $(M+H)^+$: 303.1385, Found: 303.1368.

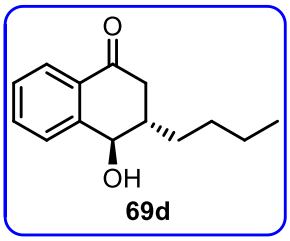
3-([1,1'-Biphenyl]-4-ylmethyl)-4-hydroxy-3,4-dihydronaphthalen-1(2*H*)-one (69c)



69c

This compound was isolated as pale yellow solid. Following the general procedure-6, 100 mg of **444c** afforded 89 mg of **69c** (88% yield). M.P = 158-162 ^{o}C. R_f = 0.5 (hexane/EtOAc = 7.5/2.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 3387, 2918, 1683, 1602, 1486, 1296, 1019, 761. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.04 (dd, *J* = 7.8 and 1.2 Hz, 1H), 7.73-7.69 (m, 1H), 7.69-7.64 (m, 1H), 7.62-7.54 (m, 5H), 7.49-7.44 (m, 3H), 7.29-7.25 (m, 2H), 4.80-4.72 (m, 1H), 3.15 (dd, *J* = 13.4 and 5.1 Hz, 1H), 2.93 (dd, *J* = 16.8 and 3.8 Hz, 1H), 2.77 (dd, *J* = 13.6 and 8.4 Hz, 1H), 2.62-2.52 (m, 1H), 2.49-2.40 (m, 1H), 2.12 (d, *J* = 6.1 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.9, 144.8, 140.8, 139.5, 137.5, 134.4, 131.2, 129.8 (2CH), 128.8 (2CH), 128.3, 127.4 (2CH), 127.2, 127.1, 127.0 (2CH), 126.9, 71.8, 44.7, 40.9, 37.9. **HRMS (ESI):** *m/z* calcd for $C_{23}H_{21}O_2$ $(M+H)^+$: 329.1542, Found: 329.1526.

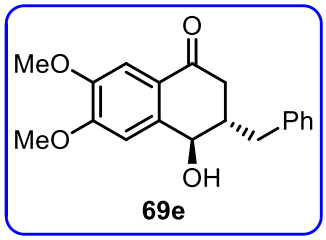
3-Butyl-4-hydroxy-3,4-dihydronaphthalen-1(2*H*)-one (69d)



69d

This compound was isolated as pale gray solid. Following the general procedure-6, 100 mg of **44h** afforded 89 mg of **69d** (88% yield). M.P = 63-65 ^{o}C. R_f = 0.5 (hexane/EtOAc = 7.5/2.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 3415, 2928, 1679, 1601, 1298, 1030, 767. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.03 (dd, *J* = 7.8 and 1.2 Hz, 1H), 7.71-7.67 (m, 1H), 7.66-7.61 (m, 1H), 7.47-7.40 (m, 1H), 4.70 (d, *J* = 7.8 Hz, 1H), 3.01 (dd, *J* = 16.9 and 4.2 Hz, 1H), 2.41 (dd, *J* = 16.9 and 10 Hz, 1H), 2.26-2.16 (m, 1H), 2.11 (br. s, 1H), 1.83-1.74 (m, 1H), 1.51-1.40 (m, 1H), 1.39-1.29 (m, 4H), 0.93 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.5, 145.0, 134.2, 131.2, 128.2, 127.2, 126.8, 72.4, 42.9, 41.1, 31.5, 28.6, 22.8, 13.9. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{19}O_2$ $(M+H)^+$: 219.1385, Found: 219.1392.

3-Benzyl-4-hydroxy-6,7-dimethoxy-3,4-dihydronaphthalen-1(2*H*)-one (69e)



69e

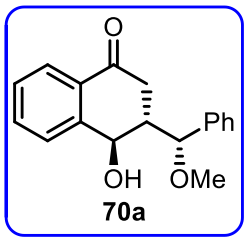
This compound was isolated as pale white solid. Following the general procedure-6, 100 mg of **44j** afforded 86 mg of **69e** (85% yield). M.P = 145-147 ^{o}C. R_f = 0.5 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 3404, 2921, 1676, 1599, 1297, 1029, 760, 702.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (s, 1H), 7.36-7.30 (m, 2H), 7.28-7.22 (m, 1H), 7.22-7.18 (m, 2H), 7.16 (s, 1H), 4.67 (d, *J* = 6.8 Hz, 1H), 4.0 (s, 2H), 3.94 (s, 3H), 3.13 (dd, *J* = 13.6 and 5 Hz, 1H), 2.80 (dd, *J* = 16.6 and 3.7 Hz, 1H), 2.72 (dd, *J* = 13.7 and 8.3 Hz, 1H), 2.54-2.43 (m, 1H), 2.40-2.31 (m, 1H), 2.10 (br. s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.7, 154.2, 148.9, 139.9, 138.6, 129.3 (2CH), 128.6 (2CH), 126.5, 124.6, 108.6, 108.1, 71.9, 56.2, 56.1, 45.4, 40.8, 38.4. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{21}O_4$ $(M+H)^+$: 313.1440, Found: 313.1463.

General procedure-7: Synthesis of tetralones 70a-70e

The compound **44a** (100 mg, 0.4 mmol) was dissolved in methanol in an oven dried round bottom flask and PTSA (12 mg, 0.08 mmol) was added and stirred at rt until **44a** disappeared as monitored by TLC. Then the reaction mixture was quenched by adding saturated aqueous sodium bicarbonate solution and the methanol solvent was removed by reduced pressure and the crude reaction mixture was extracted with ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (5:1 to 4:1) as eluent to afford compound **70a** in 78% yield.

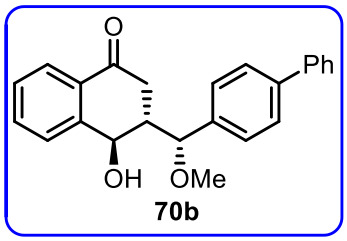
4-Hydroxy-3-(methoxy(phenyl)methyl)-3,4-dihydronaphthalen-1(2*H*)-one (70a)



70a

This compound was isolated as pale yellow solid. Following the general procedure-7, 100 mg of **44a** afforded 88 mg of **70a** (78% yield). M.P = 105-107 ^oC. R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3424, 2933, 1677, 1601, 1297, 1102, 1001, 766. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.96 (dd, *J* = 7.8 and 1.2 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.63 (td, *J* = 7.6 and 1.2 Hz, 1H), 7.44-7.37 (m, 3H), 7.32-7.30 (m, 3H), 4.97 (d, *J* = 9.3 Hz, 1H), 4.65 (d, *J* = 3.4 Hz, 1H), 3.64 (br. s, 1H), 3.37 (s, 3H), 2.67-2.55 (m, 2H), 2.50-2.37 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.0, 145.9, 137.6, 134.2, 130.5, 128.6 (2CH), 128.1, 127.7, 127.2 (2CH), 126.5, 126.4, 83.8, 68.7, 57.6, 48.5, 37.6. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{17}O_3$ $(M-H)^+$: 281.1178, Found: 281.1154.

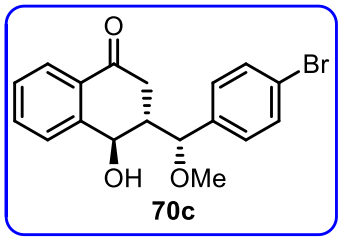
3-([1,1'-Biphenyl]-4-yl(methoxy)methyl)-4-hydroxy-3,4-dihydronaphthalen-1(2*H*)-one (70b)



70b

This compound was isolated as pale brown solid. Following the general procedure-7, 100 mg of **44c** afforded 86.5 mg of **70b** (79% yield). M.P = 156-158 ^{o}C. R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3441, 2927, 1676, 1600, 1298, 1098, 764. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.98 (dd, *J* = 7.8 and 1.2 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.67-7.59 (m, 5H), 7.51-7.44 (m, 2H), 7.43-7.36 (m, 4H), 5.02 (dd, *J* = 9 and 2.9 Hz, 1H), 4.71 (d, *J* = 3.2 Hz, 1H), 3.64 (d, *J* = 4.2 Hz, 1H), 3.41 (s, 3H), 2.71-2.60 (m, 2H), 2.65-2.45 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.9, 145.9, 141.1, 140.6, 136.7, 134.2, 130.6, 128.8 (2CH), 127.7, 127.6 (2CH), 127.5, 127.4 (2CH), 127.1 (2CH), 126.6, 126.5, 83.6, 68.7, 57.7, 48.6, 37.7. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{22}NaO_3$ $(M+Na)^+$: 381.1467, Found: 381.1486.

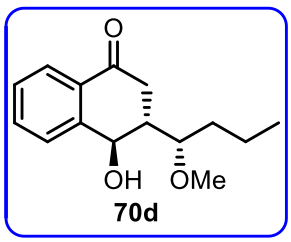
3-((4-Bromophenyl)(methoxy)methyl)-4-hydroxy-3,4-dihydronaphthalen-1(2*H*)-one (70c)



70c

This compound was isolated as pale yellow solid. Following the general procedure-7, 100 mg of **44e** afforded 82 mg of **70c** (75% yield). M.P = 140-142 ^{o}C. R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3422, 2926, 1679, 1599, 1298, 1099, 764. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.97 (dd, *J* = 7.8 and 1.2 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.64 (td, *J* = 7.5 and 1.3 Hz, 1H), 7.58-7.52 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.23-7.18 (m, 2H), 4.96 (d, *J* = 7.1 Hz, 1H), 4.64 (d, *J* = 2.9 Hz, 1H), 3.36 (s, 3H), 3.31 (d, *J* = 3.4 Hz, 1H), 2.61-2.43 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.7, 145.6, 137.1, 134.3, 131.8 (2CH), 130.5, 128.8 (2CH), 127.9, 126.7, 126.4, 121.9, 82.7, 68.7, 57.7, 48.7, 37.2. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{18}BrO_3$ $(M+H)^+$: 361.0439, Found: 361.0421.

4-Hydroxy-3-(1-methoxybutyl)-3,4-dihydronaphthalen-1(2*H*)-one (70d)

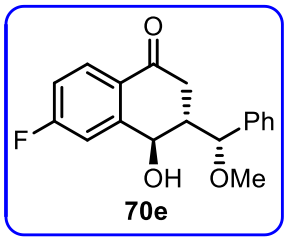


70d

This compound was isolated as pale yellow liquid. Following the general procedure-7, 100 mg of **44h** afforded 72 mg of **70d** (63% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3433,

2932, 1681, 1601, 1458, 1299, 1090, 769. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.02 (dd, *J* = 7.8 and 1.2 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.65 (td, *J* = 7.6 and 1.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 5.07 (d, *J* = 7.6 Hz, 1H), 3.70 (d, *J* = 3.4 Hz, 1H), 3.51 (ddd, *J* = 8.6, 4.2 and 2 Hz, 1H), 3.47 (s, 3H), 2.67-2.58 (m, 1H), 2.55-2.48 (m, 2H), 1.79-1.69 (m, 1H), 1.62-1.36 (m, 3H), 1.0 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.9, 146.4, 134.2, 130.5, 127.6, 126.6, 126.1, 82.3, 69.3, 58.3, 44.3, 38.3, 32.1, 19.5, 14.1. **HRMS (ESI):** *m/z* calcd for $C_{15}H_{20}NaO_3$ $(M+Na)^+$: 271.1310, Found: 271.1337.

6-Fluoro-4-hydroxy-3-(methoxy(phenyl)methyl)-3,4-dihydronaphthalen-1(2*H*)-one (70e)



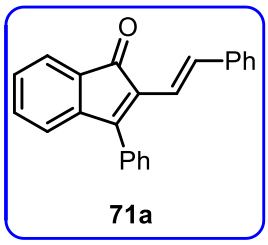
70e

This compound was isolated as pale yellow solid. Following the general procedure-7, 100 mg of **44i** afforded 91 mg of **70e** (81% yield). M.P = 116-118 ^{o}C. R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3414, 2895, 1676, 1605, 1452, 1258, 1101, 830, 708. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.96 (dd, *J* = 8.8 and 5.9 Hz, 1H), 7.48-7.38 (m, 3H), 7.37-7.30 (m, 3H), 7.03 (td, *J* = 8.4 and 2.3 Hz, 1H), 4.94 (dd, *J* = 9.7 and 2.6 Hz, 1H), 4.69 (d, *J* = 3.2 Hz, 1H), 4.10 (d, *J* = 4.2 Hz, 1H), 3.36 (s, 3H), 2.62-2.53 (m, 2H), 2.45-2.34 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.7, 166.6 (d, *J* = 254.4 Hz), 149.74 (d, *J* = 8.7 Hz), 137.4, 129.70 (d, *J* = 9.6 Hz), 128.7 (2CH), 128.1, 127.1 (2CH), 127.06 (d, *J* = 2.5 Hz), 115.23 (d, *J* = 22.1 Hz), 113.27 (d, *J* = 22.9 Hz), 83.47 (d, *J* = 6.8 Hz), 68.5, 57.6, 48.4, 37.5. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{18}FO_3$ $(M+H)^+$: 301.1240, Found: 301.1256.

General procedure-8: Synthesis of 2-styrylindenones 71a-71c

58a (100 mg, 0.31 mmol) was dissolved in toluene and PTSA (10.5 mg, 0.06 mmol) was added and stirred at 110 ^{o}C until the reactant **58a** disappeared as monitored by TLC. Then the reaction mixture was quenched with saturated aqueous sodium bicarbonate solution. Solvent was removed under reduced pressure and the crude reaction mixture was extracted with ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (5:1) as eluent to afford compound **71a** in 91% yield.

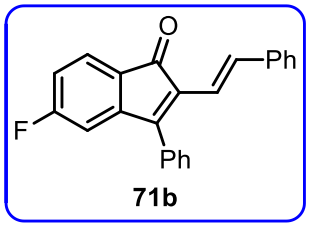
(*E*)-3-Phenyl-2-styryl-1*H*-inden-1-one (71a)



71a

This compound was isolated as pale brown solid. Following the general procedure-8, 100 mg of **58a** afforded 86 mg of **71a** (91% yield). M.P = 137-139 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3057, 1708, 1601, 1361, 1173, 954, 712. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.93 (d, *J* = 16.1 Hz, 1H), 7.62-7.51 (m, 6H), 7.48-7.43 (m, 2H), 7.38-7.31 (m, 3H), 7.28-7.24 (m, 2H), 7.11 (d, *J* = 7.1 Hz, 1H), 6.92 (d, *J* = 16.4 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.1, 154.6, 145.4, 137.8, 134.7, 133.7, 132.5, 131.7, 129.5, 128.9 (3CH), 128.8, 128.6 (4CH), 128.0, 126.7 (2CH), 122.8, 121.2, 118.2. **HRMS (ESI):** *m/z* calcd for $C_{23}H_{17}O$ $(M+H)^+$: 309.1279, Found: 309.1299.

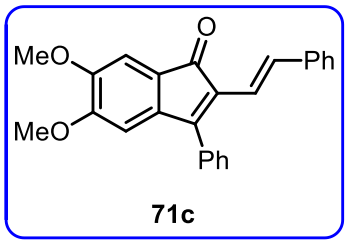
(*E*)-6-Fluoro-3-phenyl-2-styryl-1*H*-inden-1-one (71b)



71b

This compound was isolated as pale brown solid. Following the general procedure-8, 100 mg of **58j** afforded 84 mg of **71b** (88% yield). M.P = 115-118 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3057, 1708, 1596, 1465, 1363, 1202, 1079, 950, 720. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.93 (d, *J* = 16.2 Hz, 1H), 7.63-7.49 (m, 6H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 1H), 6.94-6.86 (m, 2H), 6.83 (dd, *J* = 8.5 and 1.9 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** 195.4, 166.6 (d, *J* = 252.9 Hz), 152.3, 148.7 (d, *J* = 9.4 Hz), 137.6, 135.5, 132.0, 130.1, 129.7, 129.0 (2CH), 128.6 (2CH), 128.5 (2CH), 128.2, 127.4 (d, *J* = 3.3 Hz), 126.8 (2CH), 124.7 (d, *J* = 9.8 Hz), 117.9, 114.3 (d, *J* = 23.2 Hz), 109.9 (d, *J* = 25.7 Hz). **HRMS (ESI):** *m/z* calcd for $C_{23}H_{14}FO$ $(M-H)^+$: 325.1029, Found: 325.1045.

(*E*)-5,6-Dimethoxy-3-phenyl-2-styryl-1*H*-inden-1-one (71c)



71c

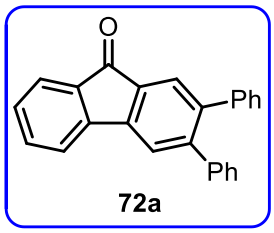
This compound was isolated as pale violet solid. Following the general procedure-8, 100 mg of **58h** afforded 82 mg of **71c** (86% yield). M.P = 170-172 ^{o}C. R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2922, 1707, 1589, 1489, 1357, 1215, 1089, 700. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.84 (d, *J* = 16.4 Hz, 1H), 7.61-7.53 (m, 4H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.29 (s, 1H), 7.23 (t, *J* = 7.1

Hz, 1H), 7.17 (s, 1H), 6.86 (d, *J* = 16.4 Hz, 1H), 6.65 (s, 1H), 3.96 (s, 3H), 3.90 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.6, 153.4, 152.9, 149.2, 139.9, 137.9, 133.5, 132.7, 129.4, 128.9 (2CH), 128.6 (2CH), 128.5 (2CH), 128.0, 127.8, 126.6 (2CH), 124.1, 118.4, 107.4, 105.6, 56.4, 56.4. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{21}O_3$ $(M+H)^+$: 369.1491, Found: 369.1474.

General procedure-9: Synthesis of fluorenones 72a-72f

59a (100 mg, 0.28 mmol) was dissolved in toluene and PTSA (9.7 mg, 0.06 mmol) was added. The reaction mixture was stirred at 140 ^oC with Dean-Stark set-up until the reactant **59a** disappeared as monitored by TLC. Then the reaction mixture was quenched with saturated aqueous sodium bicarbonate solution and the toluene solvent was removed by reduced pressure and the crude reaction mixture was extracted with ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (19:1) as eluent to afford **72a** in 89% yield.

2,3-Diphenyl-9*H*-fluoren-9-one (72a)

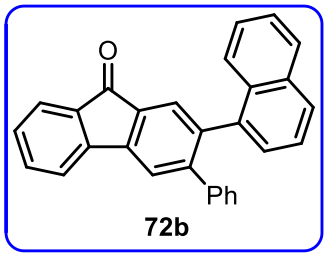


72a

This compound was isolated as pale brown solid. Following the general procedure-9, 100 mg of **59a** afforded 84 mg of **72a** (89% yield). M.P = 178-179 ^oC. R_f = 0.5 (hexane/EtOAc = 9.5/0.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2933, 1669, 1595, 1507, 1459, 1282, 1058, 759. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.77 (s, 1H), 7.73 (d, *J* = 7.3 Hz, 1H), 7.62-7.56 (m, 2H), 7.56-7.51 (m, 1H), 7.35 (td, *J* = 7.3 and 1 Hz, 1H), 7.30-7.20 (m, 8H), 7.16 (dd, *J* = 6.8 and 2.9 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.7, 147.0, 144.1, 143.3, 141.6, 140.9, 140.4, 134.8, 134.7, 133.3, 129.7 (2CH), 129.6 (2CH), 129.2, 128.1 (2CH), 128.0 (2CH), 127.4, 127.0, 126.6, 124.4, 122.8, 120.4. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{17}O$ $(M+H)^+$: 333.1279, Found: 333.1298.

2-(Naphthalen-1-yl)-3-phenyl-9*H*-fluoren-9-one (72b)

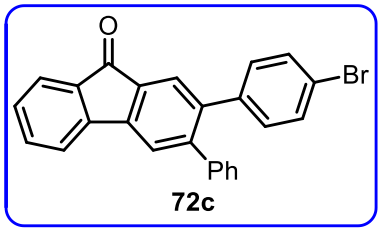
This compound was isolated as pale orange solid. Following the general procedure-9, 100 mg of **59d** afforded 95 mg of **72b** (90% yield). M.P = 205-207 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3055, 1712, 1612, 1450, 1183, 775, 745, 700.



72b

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.6 Hz, 1H), 7.79-7.69 (m, 5H), 7.63 (d, *J* = 7.4 Hz, 1H), 7.57 (td, *J* = 7.5 and 1.2 Hz, 1H), 7.45 (ddd, *J* = 8.1, 6.7 and 1.3 Hz, 1H), 7.41-7.33 (m, 3H), 7.20 (dd, *J* = 7.1 and 1.2 Hz, 1H), 7.16-7.06 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.6, 148.4, 144.2, 143.7, 140.7, 140.0, 138.2, 134.83, 134.80, 133.5, 132.8, 131.9, 129.3, 128.8 (2CH), 128.3, 128.1, 127.8 (2CH), 127.7 (2CH), 127.3, 126.1, 125.8, 125.7, 125.0, 124.4, 122.5, 120.5. **HRMS (ESI):** *m/z* calcd for $C_{29}H_{19}O$ $(M+H)^+$: 383.1436, Found: 383.1423.

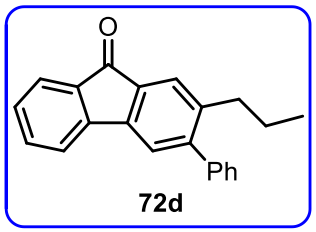
2-(4-Bromophenyl)-3-phenyl-9*H*-fluoren-9-one (72c)



72c

This compound was isolated as pale brown solid. Following the general procedure-9, 100 mg of **59b** afforded 87 mg of **72c** (91% yield). M.P = 156-160 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9.5/0.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2923, 1713, 1612, 1447, 1180, 1069, 1007, 749. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.75-7.69 (m, 2H), 7.60-7.51 (m, 3H), 7.40-7.29 (m, 6H), 7.23-7.17 (m, 2H), 7.03 (d, *J* = 8.1 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.5, 146.9, 143.9, 143.6, 140.5, 140.2, 139.4, 134.9, 134.7, 133.4, 131.3 (4CH), 129.5 (2CH), 129.3, 128.3 (2CH), 127.6, 126.3, 124.5, 122.9, 121.3, 120.5. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{15}BrNaO$ $(M+Na)^+$: 433.0204, Found: 433.0193.

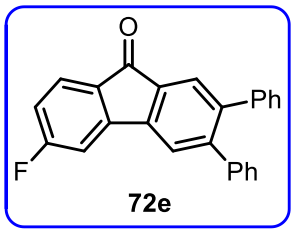
3-Phenyl-2-propyl-9*H*-fluoren-9-one (72d)



72d

This compound was isolated as brown semisolid. Following the general procedure-9, 100 mg of **59f** afforded 82 mg of **72d** (87% yield). R_f = 0.5 (hexane/EtOAc = 9.5/0.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2959, 1712, 1608, 1453, 1182, 976, 702. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.68 (dt, *J* = 7.2 and 0.9 Hz, 1H), 7.63 (s, 1H), 7.51-7.41 (m, 5H), 7.38-7.34 (m, 3H), 7.32-7.29 (m, 1H), 2.61-2.53 (m, 2H), 1.60-1.49 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 194.1, 148.3, 144.5, 141.7, 141.6, 141.3, 134.7, 134.6, 133.3, 128.8, 128.7 (2CH), 128.3 (2CH), 127.5, 125.3, 124.3, 122.2, 120.1, 35.0, 24.1, 13.9. **HRMS (ESI):** *m/z* calcd for $C_{22}H_{19}O$ $(M+H)^+$: 299.1436, Found: 299.1447.

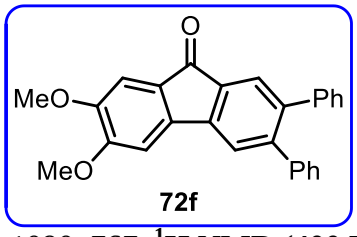
6-Fluoro-2,3-diphenyl-9*H*-fluoren-9-one (72e)



72e

This compound was isolated as pale brown solid. Following the general procedure-9, 100 mg of **59g** afforded 74.5 mg of **72e** (79% yield). M.P = 160-162 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9.5/0.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2926, 1712, 1612, 1480, 1179, 1082, 766, 700. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.77 (s, 1H), 7.72 (dd, *J* = 8.1 and 5.1 Hz, 1H), 7.57 (s, 1H), 7.31-7.28 (m, 2H), 7.27-7.23 (m, 4H), 7.22-7.18 (m, 2H), 7.17-7.14 (m, 2H), 7.04-6.95 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 191.8, 167.3 (d, *J* = 253.9 Hz), 147.2 (d, *J* = 10 Hz), 147.0, 142.3, 141.7 (d, *J* = 2.3 Hz), 140.6, 140.2, 133.7, 130.8 (d, *J* = 2.4 Hz), 129.6 (2CH), 129.5 (2CH), 128.2 (2CH), 128.1 (2CH), 127.5, 127.1, 126.6, 126.5 (d, *J* = 10.2 Hz), 123.0, 115.6 (d, *J* = 23.1 Hz), 108.6 (d, *J* = 24.2 Hz). **HRMS (ESI):** *m/z* calcd for $C_{25}H_{16}FO$ $(M+H)^+$: 351.1185, Found: 351.1168.

2,3-Dimethoxy-6,7-diphenyl-9*H*-fluoren-9-one (72f)



72f

This compound was isolated as pale brown solid. Following the general procedure-9, 100 mg of **59h** afforded 78 mg of **72f** (82% yield). M.P = 149-152 ^{o}C. R_f = 0.5 (hexane/EtOAc = 8.5/1.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2928, 1705, 1592, 1494, 1278, 1212, 1090, 767. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.66 (s, 1H), 7.44 (s, 1H), 7.28-7.26 (m, 3H), 7.25 (s, 1H), 7.24-7.19 (m, 5H), 7.17-7.13 (m, 2H), 7.06 (s, 1H), 4.03 (s, 3H), 3.97 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 192.9, 154.7, 149.9, 146.4, 142.9, 141.1, 140.6, 140.5, 139.1, 133.9, 129.7 (2CH), 129.5 (2CH), 128.1 (2CH), 128.0 (2CH), 127.5, 127.3, 126.9, 126.2, 121.7, 107.2, 103.5, 56.4, 56.3. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{21}O_3$ $(M+H)^+$: 393.1491, Found: 393.1482.

General procedure-10: Synthesis of enone-enones 75a-75k

Step-I: The compound **84** (300 mg, 1.51 mmol; when R^1 = H, R^2 = Ph) and the corresponding aldehyde (1.1 eq, 1.65 mmol) were dissolved in MeOH (5 mL) and NaOH (1.2 eq, 72.5 mg, 1.81 mmol) was introduced at 0 $^{\circ}$C. The reaction mixture was then stirred at 0 $^{\circ}$C until the reactant **84** disappeared as monitored by TLC. The reaction mixture was quenched with saturated aqueous ammonium chloride solution and extracted with ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was

purified by silica gel column chromatography using hexane/ethyl acetate as eluent (5:1) to afford compound **85** in 85-90% yield.

Step-II: The compound **85** (200 mg, 0.69 mmol) was dissolved in THF/H_2O (5 mL, 5:1) in an oven dried round bottom flask and the $NaBH_4$ (13 mg, 0.35 mmol) was introduced portion wise to the reaction mixture over five minutes and stirred at rt until the reactant **85** disappeared as monitored by TLC. The reaction mixture was quenched with saturated aqueous ammonium chloride solution and the THF solvent was removed under reduced pressure and the residue was extracted with ethyl acetate (2x3 mL). The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (4:1) as eluent to afford compound **86** in 90-95%.

Step-III: To a solution of **86** (180 mg, 0.62 mmol) in anhydrous THF (5 mL) at -78 $^{\circ}$C was added *n*-BuLi (1.6 M in hexane, 0.97 mL, 1.56 mmol). After 15 min, corresponding enal **87** (90.4 mg, 0.68 mmol) was added at the same temperature and the reaction mixture was stirred for an additional 30 min. The mixture was warmed to room temperature over 30 min. The reaction progress was monitored by TLC. Reaction mixture was quenched with saturated aqueous ammonium chloride solution and extracted with ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (7:3) as eluent to afford the compound **88** in 60-65% yield.

Step-IV: The compound **88** (120 mg, 0.35 mmol) was dissolved in DMSO in an oven dried round bottom flask and IBX (245 mg, 0.88 mmol) was added and stirred at rt until the reactant **88** disappeared as monitored by TLC. The reaction mixture was quenched with the cold water and filtered through Buchner funnel. The filter cake was washed with ethyl acetate (3x2 mL). Organic extracts were combined and worked up using saturated sodium bicarbonate solution to remove excess iodobenzoic acid and DMSO. The extract was dried over anhydrous sodium sulphate and concentrated under reduced vacuum. The residue was purified by silica gel column chromatography using hexane/ethyl acetate (4:1) as eluent to afford the compound **75a-75k** in 65-70% yield.

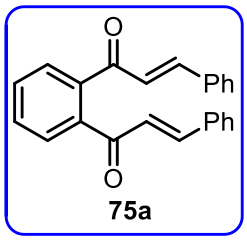
General procedure-11: Synthesis of enone-enones 94a-94j

The compounds **94a-94j** were synthesized by following the literature report.[57]

General procedure-12: DOSM reaction with enone-enones 75a-75k and 94a-94j

A mixture of sodium hydride (60% in oil, 20.3 mg, 0.51 mmol) and trimethyloxosulfonium iodide (111.8 mg, 0.51 mmol) was placed in an oven dried flask and DMF (4 mL) was added to the mixture. After the evolution of hydrogen ceased, the milky solution turned clear and the reaction mixture was stirred for 15 min. The compound **75** (100 mg, 0.29 mmol; when R^1 = H, R^2 = Ph) was dissolved in DMF (1 mL) and was added to the clear solution dropwise over a period of 5-10 min and stirred at rt until the reactant **75** disappeared as monitored by TLC. The reaction mixture was quenched with ice-water and extracted with ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (4:1 to 7:3) as eluent to afford **75a75k**, where the minor diastereomer eluted first and the major one later. The above described procedures are followed for the synthesis of **94a-94j**.

(2*E*,2'*E*)-1,1'-(1,2-Phenylene)bis(3-phenylprop-2-en-1-one) (75a)

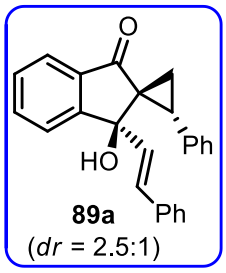


75a

This compound was isolated as pale yellow liquid. Following the general procedure-10, 100 mg of **88** (R^1 = H, R^2 = Ph) afforded 67.5 mg of **75a** (68% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3061, 1644, 1597, 1449, 1333, 1216, 1017, 753, 978, 684. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.76-7.70 (m, 2H), 7.67-7.62 (m, 2H), 7.57-7.52 (m, 4H), 7.50 (d, *J* = 16.0 Hz, 2H), 7.42-7.35 (m, 6H), 7.18 (d, *J* = 16.0 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 194.4 (2C), 145.8 (2C), 140.0 (2C), 134.5 (2C), 130.79 (2C), 130.71 (2C), 128.9 (4C), 128.6 (2C), 128.5 (4C), 125.5 (2C). **HRMS (ESI):** *m/z* calcd for $C_{24}H_{19}O_2$ $(M+H)^+$: 339.1385, Found: 339.1378.

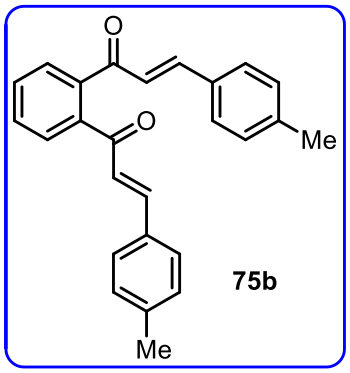
(*E*)-1'-Hydroxy-2-phenyl-1'-styrylspiro[cyclopropane-1,2'-inden]-3'(1'*H*)-one (89a)

This compound was isolated as pale yellow solid. Following the general procedure-12, 50 mg of **75a** afforded 47 mg of **89a** (90% yield). M.P = 157-158 ^oC. R_f = 0.5 (hexane/EtOAc = 8/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3424, 3027, 1697, 1603, 1328, 741, 694. **^{1}H NMR (400 MHz,**



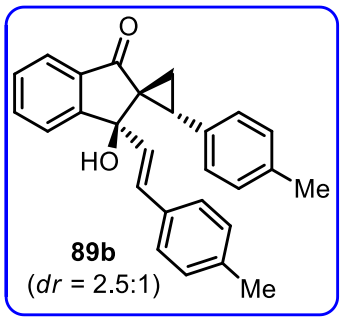
$CDCl_3$): δ 7.62-7.58 (m, 3H), 7.46-7.41(m, 3H), 7.36-7.32 (m, 2H), 7.28-7.17 (m, 6H), 6.93 (d, *J* = 15.9 Hz, 1H), 6.30 (d, *J* = 15.9 Hz, 1H), 2.97 (t, *J* = 8.7 Hz, 1H), 2.43 (s, 1H), 2.08-2.05 (m, 1H), 1.84-1.81 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.5, 155.9, 136.37, 136.30, 135.3, 134.7, 131.2, 129.5, 129.2 (2C), 129.0, 128.7 (2C), 128.0, 127.9 (2C), 126.9, 126.6 (2C), 125.1, 122.7, 78.3, 47.8, 36.9, 18.9. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{21}O_2$ $(M+H)^+$: 353.1542, Found: 353.1549.

(2*E*,2'*E*)-1,1'-(1,2-Phenylene)bis(3-(*p*-tolyl)prop-2-en-1-one) (75b)



This compound was isolated as pale brown solid. Following the reaction procedure-10, 100 mg of **88** (R^1 = H, R^2 = *p*-tolyl) afforded 62.5 mg of **75b** (63% yield). M.P = 162-164 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3026, 2922, 1645, 1597, 1512, 1328, 1285, 814. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.68-7.67 (m, 2H), 7.60-7.59 (m, 2H), 7.74 (d, *J* = 16 Hz, 2H), 7.41-7.39 (m, 4H), 7.16-7.14 (m, 4H), 7.10 (d, *J* = 16 Hz, 2H), 2.34 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 194.6 (2C), 145.9 (2C), 141.2 (2C), 140.1 (2C), 131.7 (2C), 130.6 (2C), 129.6 (4C), 128.5 (6C), 124.6 (2C), 21.5 (2C). **HRMS (ESI):** *m/z* calcd for $C_{26}H_{23}O_2$ $(M+H)^+$: 367.1698, Found: 367.1689.

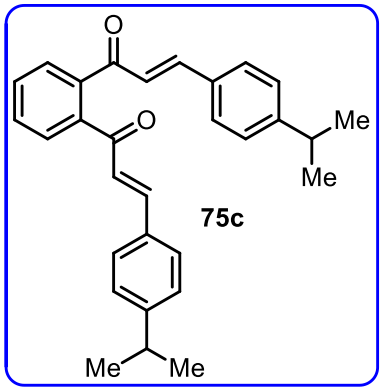
(*E*)-1'-Hydroxy-1'-(4-methylstyryl)-2-(*p*-tolyl)spiro[cyclopropane-1,2'-inden]-3'(1'*H*)-one (89b)



This compound was isolated as pale brown liquid. Following the general procedure-12, 50 mg of **75b** afforded 48 mg of **89b** (92% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3418, 2923, 1697, 1515, 1326, 1010. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.69-7.63 (m, 3H), 7.51-7.45 (m, 1H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.22-7.08 (m, 6H), 6.94 (d, *J* = 15.9 Hz, 1H), 6.30 (d, *J* = 15.9 Hz, 1H), 2.98 (t, *J* = 8.7 Hz, 1H), 2.38 (s, 3H), 2.33 (s, 3H), 2.23 (brs, 1H), 2.11 (dd, *J* = 8.2 and 4.5 Hz, 1H), 1.86 (dd, *J* = 9.3 and 4.4 Hz, 1H). **NMR (100 MHz, $CDCl_3$):** δ 200.5, 156.0, 137.9, 136.5, 136.4, 134.7, 133.7, 132.2, 130.1, 129.5, 129.4 (2C), 129.1 (2C), 128.9,

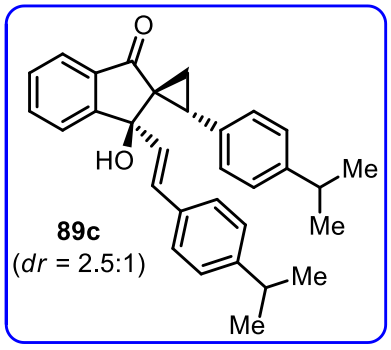
128.7 (2C), 126.6 (2C), 125.1, 122.8, 78.5, 47.9, 36.8, 21.3, 21.2, 18.9. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{25}O_2$ $(M+H)^+$: 381.1855, Found: 381.1843.

(2*E*,2'*E*)-1,1'-(1,2-Phenylene)bis(3-(4-isopropylphenyl)prop-2-en-1-one) (75c)



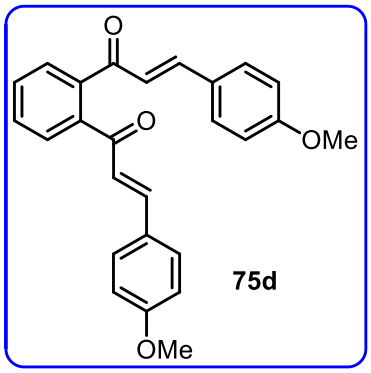
This compound was isolated as pale brown liquid. Following the general procedure-10, 100 mg of **88** (R^1 = H, R^2 = (*p*-^{i}Pr)C_6H_4) afforded 69.5 mg of **75c** (70% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2961, 1638, 1597, 1327, 1216, 1018, 827. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.75-7.69 (m, 2H), 7.67-7.61 (m, 2H), 7.51-7.43 (m, 6H), 7.25 (d, *J* = 7.3 Hz, 4H), 7.13 (d, *J* = 16.1 Hz, 2H), 2.99-2.88 (m, 2H), 1.27 (d, *J* = 6.8 Hz, 12H). **NMR (100 MHz, $CDCl_3$):** δ 194.7 (2C), 152.1 (2C), 145.9 (2C), 140.1 (2C), 132.2 (2C), 130.7 (2C), 128.7 (4C), 128.6 (2C), 127.1 (4C), 124.7 (2C), 34.1 (2C), 23.8 (4C). **HRMS (ESI):** *m/z* calcd for $C_{30}H_{31}O_2$ $(M+H)^+$: 423.2324, Found: 423.2316.

(*E*)-1'-Hydroxy-2-(4-isopropylphenyl)-1'-(4-isopropylstyryl)spiro[cyclopropane-1,2'-inden]-3'(1'*H*)-one (89c)



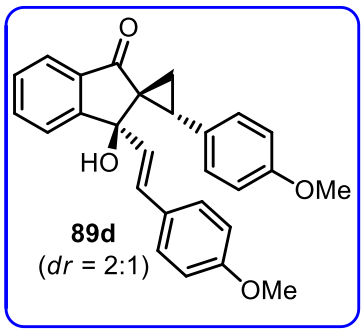
This compound was isolated as pale red semi-solid. Following the general procedure-12, 50 mg of **75c** afforded 43 mg of **89c** (82% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3427, 2960, 1708, 1463, 1328, 1009, 821, 768. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.69-7.63 (m, 3H), 7.51-7.45 (m, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.18 (q, *J* = 8.1 Hz, 4H), 6.94 (d, *J* = 15.9 Hz, 1H), 6.31 (d, *J* = 15.9 Hz, 1H), 3.01-2.84 (m, 3H), 2.19 (brs, 1H), 2.11 (dd, *J* = 8.3 and 4.4 Hz, 1H), 1.87 (dd, *J* = 9.2 and 4.5 Hz, 1H), 1.28 (d, *J* = 6.6 Hz, 6H), 1.25 (dd, *J* = 7.0 and 2.1 Hz, 6H). **NMR (100 MHz, $CDCl_3$):** δ 200.5, 155.9, 148.9, 147.3, 136.4, 134.7, 133.8, 132.6, 130.2, 129.5, 129.1 (2C), 128.8, 126.8 (2C), 126.7 (2C), 125.9 (2C), 125.1, 122.7, 78.5, 47.9, 36.9, 33.9, 33.7, 23.97 (2C), 23.94 (2C), 19.2. **HRMS (ESI):** *m/z* calcd for $C_{31}H_{33}O_2$ $(M+H)^+$: 437.2481, Found: 437.2444.

(2*E*,2'*E*)-1,1'-(1,2-Phenylene)bis(3-(4-methoxyphenyl)prop-2-en-1-one) (75d)



This compound was isolated as pale yellow solid. Following the reaction procedure-10, 100 mg of **88** (R^1 = H, R^2 = (*p*-OMe)C_6H_4) afforded 60.5 mg of **75d** (61% yield). R_f = 0.5 (hexane/EtOAc = 7/3). M.P = 112-114 ^oC. **IR (thin film, neat):** ν_{max}/cm^{-1} 2959, 2838, 1640, 1598, 1511, 1304, 1255, 1173, 1026, 829. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.68-7.66 (m, 2H), 7.60-7.57 (m, 2H), 7.47-7.45 (m, 4H), 7.42 (d, *J* = 16 Hz, 2H), 7.01 (d, *J* = 16 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 4H), 3.82 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 194.6 (2C), 161.7 (2C), 145.7 (2C), 140.2 (2C), 130.5 (2C), 130.3 (4C), 128.4 (2C), 127.2 (2C), 123.4 (2C), 114.3 (4C), 55.4 (2C). **HRMS (ESI):** *m/z* calcd for $C_{26}H_{23}O_4$ $(M+H)^+$: 399.1596, Found: 399.1558.

1'-Hydroxy-2-(4-methoxyphenyl)-1'-((*E*)-4-methoxystyryl)spiro[cyclopropane-1,2'-inden]-3'(1'*H*)-one (89d)

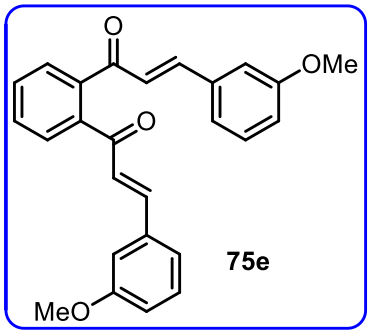


This compound was isolated as pale red semi-solid. Following the reaction procedure-12, 50 mg of **75d** afforded 45.5 mg of **89d** (87% yield). R_f = 0.5 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3450, 2928, 1705, 1606, 1513, 1249, 1175, 1034, 825. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.70-7.62 (m, 3H), 7.50-7.45 (m, 1H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 6.95-6.87 (m, 3H), 6.83 (d, *J* = 8.3 Hz, 2H), 6.20 (d, *J* = 15.9 Hz, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 3.01-2.93 (m, 1H), 2.32 (brs, 1H), 2.08 (dd, *J* = 8.1 and 4.6 Hz, 1H), 1.85 (dd, *J* = 9.3 and 4.4 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.6, 159.5, 158.4, 156.1, 136.4, 134.7, 130.2 (2C), 129.5, 128.9, 128.5, 127.8 (2C), 127.3, 125.1, 122.7, 114.2 (2C), 113.3 (2C), 78.4, 55.4, 55.2, 48.0, 36.6, 29.7, 19.0. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{24}NaO_4$ $(M+Na)^+$: 435.1572, Found: 435.1550.

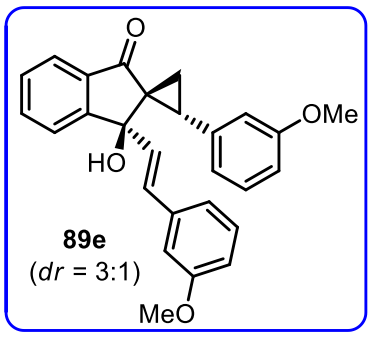
(2*E*,2'*E*)-1,1'-(1,2-Phenylene)bis(3-(3-methoxyphenyl)prop-2-en-1-one) (75e)

This compound was isolated as pale yellow solid. Following the reaction procedure-10, 100 mg of **88** (R^1 = H, R^2 = (*m*-OMe)C_6H_4) afforded 62.5 mg of **75e** (63% yield). M.P = 117-119 ^oC. R_f

= 0.5 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 2938, 2836, 1644, 1602, 1487, 1260, 1047, 772, 679. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.71-7.48 (m, 2H), 7.63-7.62 (m, 2H), 7.43 (d, *J* = 16 Hz, 2H), 7.29-7.25 (m, 2H), 7.13 (d, *J* = 16 Hz, 2H), 7.11-7.09 (m, 2H), 7.02 (s, 2H), 6.92 (d, *J* = 8.2 Hz, 2H), 3.79 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 194.4 (2C), 159.8 (2C), 145.7 (2C), 139.9 (2C), 135.8 (2C), 130.8 (2C), 129.9 (2C), 128.6 (2C), 125.7 (2C), 121.2 (2C), 116.7 (2C), 113.1 (2C), 55.3 (2C). **HRMS (ESI):** *m/z* calcd for $C_{26}H_{23}O_4$ $(M+H)^+$: 399.1596, Found: 399.1568.

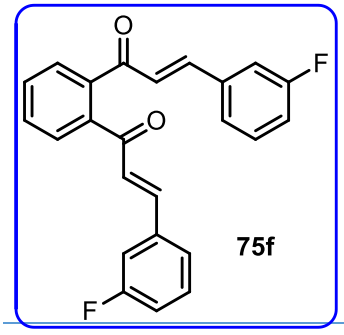


(*E*)-1'-Hydroxy-2-(3-methoxyphenyl)-1'-(3-methoxystyryl)spiro[cyclopropane-1,2'-inden]-3'(1'*H*)-one (89e)



This compound was isolated as yellowish brown semi-solid. Following the general procedure-12, 50 mg of **75e** afforded 40 mg of **89e** (78% yield). R_f = 0.5 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3445, 2937, 1708, 1603, 1464, 1158, 1046, 774. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.64-7.63 (m, 3H), 7.47-7.43 (m, 1H), 7.28-7.24 (m, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 6.97 (s, 1H), 6.90 (d, *J* = 15.9 Hz, 1H), 6.84-6.73 (m, 4H), 6.30 (d, *J* = 15.9 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 2.97-2.92 (m, 1H), 2.27 (brs, 1H), 2.09-2.05 (m, 1H), 1.84-1.81 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.3, 159.9, 159.1, 155.8, 137.7, 136.9, 136.3, 134.8, 131.5, 129.7, 129.6, 129.0, 128.8, 125.1, 122.8, 121.7, 119.1, 115.3, 113.5, 112.1, 112.0, 78.3, 55.2, 55.1, 47.8, 36.8, 19.0. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{24}NaO_4$ $(M+Na)^+$: 435.1572, Found: 435.1572.

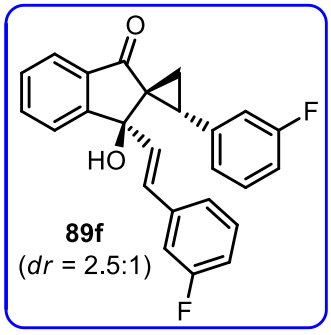
(2*E*,2'*E*)-1,1'-(1,2-Phenylene)bis(3-(3-fluorophenyl)prop-2-en-1-one) (75f)



This compound was isolated as pale yellow liquid. Following the general procedure-10, 100 mg of **88** (R^1 = H, R^2 = (*m*-F)C_6H_4) afforded 64.5 mg of **75f** (65% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3073, 1660, 1607, 1583, 1487, 1447,

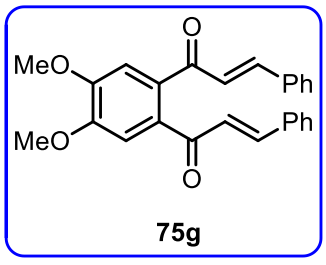
1297, 1245, 785. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.09-7.99 (m, 1H), 7.75-7.71 (m, 1H), 7.69-7.60 (m, 2H), 7.48-7.42 (m, 2H), 7.40-7.15 (m, 8H), 7.14-7.06 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.9 (2C), 162.9 (d, *J* = 245.6 Hz, 2C), 144.2 (d, *J* = 2.5 Hz, 2C), 139.8, 136.7 (d, *J* = 7.6 Hz, 2C), 131.0, 130.5 (d, *J* = 8.1 Hz, 2C), 128.6, 126.3, 124.5 (d, *J* = 2.9 Hz, 2C), 117.6 (d, *J* = 21.3 Hz, 2C), 114.6 (d, *J* = 21.8 Hz, 2C). **^{19}F NMR (374 MHz, $CDCl_3$):** δ -112.3. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{17}F_2O_2$ $(M+H)^+$: 375.1197, Found: 375.1196.

(*E*)-2-(3-Fluorophenyl)-1'-(3-fluorostyryl)-1'-hydroxyspiro[cyclopropane-1,2'-inden]-3'(1'*H*)-one (89f)



This compound was isolated as pale yellow liquid. Following the general procedure-12, 50 mg of **75f** afforded 41.5 mg of **89f** (80% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3424, 2924, 1703, 1612, 1587, 1489, 1442, 1140, 777. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.73-7.64 (m, 3H), 7.55-7.48 (m, 1H), 7.39-7.31 (m, 1H), 7.28-7.22 (m, 2H), 7.17 (d, *J* = 10.0 Hz, 1H), 7.05-6.91 (m, 5H), 6.33 (d, *J* = 15.9 Hz, 1H), 2.95 (t, *J* = 8.7 Hz, 1H), 2.25 (brs, 1H), 2.13-2.05 (m, 1H), 1.89 (dd, *J* = 9.2 and 4.5 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.9, 163.2 (d, *J* = 244.5 Hz), 162.5 (d, *J* = 243.9 Hz), 155.6, 138.5 (d, *J* = 7.6 Hz), 137.9 (d, *J* = 7.6 Hz), 136.2, 135.1, 132.2, 130.3 (d, *J* = 8.5 Hz), 129.8, 129.3 (d, *J* = 8.5 Hz), 128.2 (d, *J* = 2.1 Hz), 125.1, 125.0 (d, *J* = 2.7 Hz), 122.9, 122.5 (d, *J* = 2.5 Hz), 116.2 (d, *J* = 21.5 Hz), 114.9 (d, *J* = 21.4 Hz), 114.0 (d, *J* = 20.9 Hz), 113.2 (d, *J* = 21.4 Hz), 78.2, 47.7, 36.1 (d, *J* = 1.3 Hz), 18.9. **^{19}F NMR (374 MHz, $CDCl_3$):** δ -113.0, -113.8. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{18}F_2NaO_2$ $(M+Na)^+$: 411.1173, Found: 411.1164.

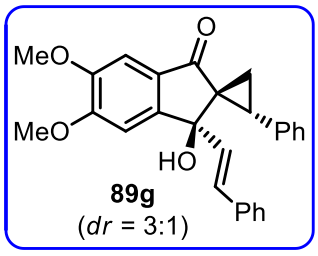
(2*E*,2'*E*)-1,1'-(4,5-Dimethoxy-1,2-phenylene)bis(3-phenylprop-2-en-1-one) (75g)



This compound was isolated as pale brown solid. Following the reaction procedure-10, 100 mg of **88** (R^1 = OMe, R^2 = H) afforded 59.5 mg of **75g** (60% yield). M.P = 125-128 ^oC. R_f = 0.5 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 2932, 2853, 1656, 1597, 1352, 1283, 1163, 978, 772. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.50-7.43 (m, 4H), 7.42 (d, *J* = 16 Hz, 2H), 7.37-7.35 (m, 6H), 7.18 (s, 2H), 7.06 (d, *J*

= 16 Hz, 2H), 4.00 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.7 (2C), 150.7 (2C), 145.2 (2C), 134.5 (2C), 133.3 (2C), 130.6 (2C), 128.9 (4C), 128.4 (4C), 126.0 (2C), 111.2 (2C), 56.3 (2C). **HRMS (ESI):** *m/z* calcd for $C_{26}H_{23}O_4$ $(M+H)^+$: 399.1596, Found: 399.1588.

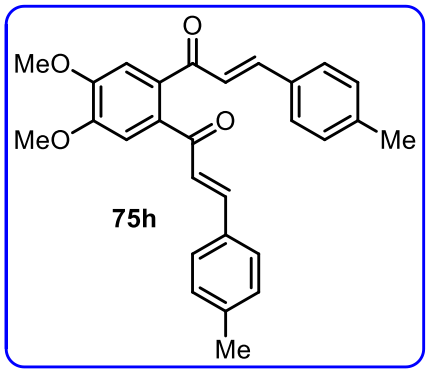
(*E*)-1'-Hydroxy-5',6'-dimethoxy-2-phenyl-1'-styrylspiro[cyclopropane-1,2'-inden]-3'(1'*H*)-one (89g)



89g
(*dr* = 3:1)

This compound was isolated as pale-yellow liquid. Following the reaction procedure-12, 50 mg of **75g** afforded 45 mg of **89g** (87% yield). R_f = 0.5 (hexane/EtOAc = 4/6). **IR (thin film, neat):** ν_{max}/cm^{-1} 3382, 3028, 2932, 1667, 1498, 1290, 697. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.47 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.30-7.18 (m, 6H), 7.02 (d, *J* = 9.8 Hz, 2H), 6.93 (d, *J* = 15.7 Hz, 1H), 6.30 (d, *J* = 15.9 Hz, 1H), 3.93 (s, 3H), 3.85 (s, 3H), 2.93 (t, *J* = 8.7 Hz, 1H), 2.36 (brs, 1H), 2.06-2.03 (m, 1H), 1.79-1.76 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.0, 155.3, 150.8, 150.7, 136.2, 135.5, 131.2, 129.5, 129.2 (2C), 128.9, 128.8 (2C), 128.0, 127.8 (2C), 126.8, 126.6 (2C), 106.0, 103.4, 78.1, 56.4, 56.1, 47.8, 36.2, 18.2. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{25}O_4$ $(M+H)^+$: 413.1753, Found: 413.1745.

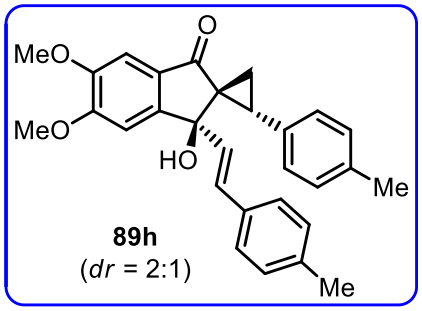
(2*E*,2'*E*)-1,1'-(4,5-Dimethoxy-1,2-phenylene)bis(3-(*p*-tolyl)prop-2-en-1-one) (75h)



75h

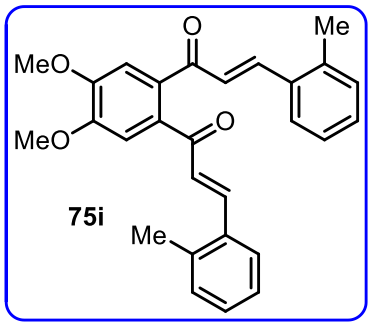
This compound was isolated as pale brown semisolid. Following the general procedure-10, 100 mg of **88** (R^1 = OMe, R^2 = (*p*-tolyl) afforded 63.5 mg of **75h** (64% yield). R_f = 0.5 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 2928, 1596, 1352, 1284, 720, 813. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.46-7.37 (m, 6H), 7.22-7.15 (m, 6H), 7.04 (d, *J* = 15.7 Hz, 2H), 4.02 (s, 6H), 2.38 (s, 6H). **NMR (100 MHz, $CDCl_3$):** δ 193.9 (2C), 150.7 (2C), 145.4 (2C), 141.2 (2C), 133.4 (2C), 131.8 (2C), 129.7 (4C), 128.5 (4C), 125.2 (2C), 111.2 (2C), 56.3 (2C), 21.6 (2C). **HRMS (ESI):** *m/z* calcd for $C_{28}H_{27}O_4$ $(M+H)^+$: 427.1909, Found: 427.1901.

(*E*)-1'-Hydroxy-5',6'-dimethoxy-1'-(4-methylstyryl)-2-(*p*-tolyl)spiro[cyclopropane-1,2'-inden]-3'(1'*H*)-one (89h)



This compound was isolated as pale brown solid. Following the general procedure-12, 50 mg of **75h** afforded 46 mg of **89h** (88% yield). M.P = 152-155 ^{o}C. R_f = 0.5 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3444, 2928, 1698, 1595, 1499, 1288, 1022, 806. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.40 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.17-7.03 (m, 6H), 6.92 (d, *J* = 15.9 Hz, 1H), 6.28 (d, *J* = 15.9 Hz, 1H), 3.96 (s, 3H), 3.88 (s, 3H), 2.98-2.86 (m, 2H), 2.39 (s, 3H), 2.32 (s, 3H), 2.09-2.01 (m, 1H), 1.78 (dd, *J* = 9.3 and 4.6 Hz, 1H). **NMR (100 MHz, $CDCl_3$):** δ 199.2, 155.2, 150.9, 150.8, 137.9, 136.3, 133.5, 132.5, 130.2, 129.5, 129.4 (2C), 129.1 (2C), 128.8, 128.6 (2C), 126.6 (2C), 106.0, 103.4, 78.2, 56.4, 56.2, 47.9, 36.1, 21.25, 21.2, 18.2. **HRMS (ESI):** *m/z* calcd for $C_{29}H_{29}O_4$ $(M+H)^+$: 441.2066, Found: 441.2058.

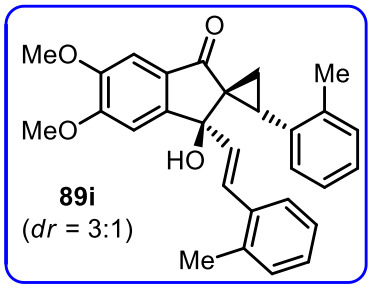
(2*E*,2'*E*)-1,1'-(4,5-Dimethoxy-1,2-phenylene)bis(3-(*o*-tolyl)prop-2-en-1-one) (75i)



This compound was isolated as pale yellow semisolid. Following the general procedure-10, 100 mg of **88** (R^1 = OMe, R^2 = *m*-tolyl) afforded 66.5 mg of **75i** (67% yield). R_f = 0.5 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 2928, 1656, 1594, 1351, 1283, 987, 729. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 15.8 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.28-7.16 (m, 8H), 7.03 (d, *J* = 15.8 Hz, 2H), 4.02 (s, 6H), 2.34 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.6 (2C), 150.7 (2C), 142.5 (2C), 138.3 (2C), 133.4 (2C), 130.8 (4C), 130.4 (2C), 127.0 (2C), 126.5 (2C), 126.3 (2C), 111.2 (2C), 56.3 (2C), 19.7 (2C). **HRMS (ESI):** *m/z* calcd for $C_{28}H_{27}O_4$ $(M+H)^+$: 427.1909, Found: 427.1901.

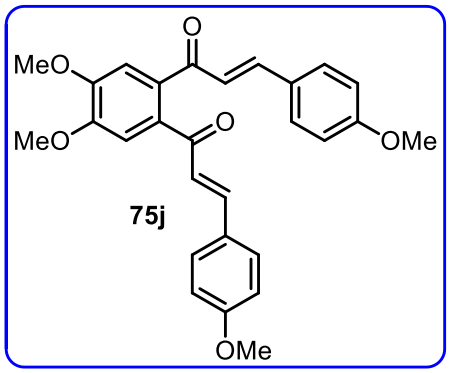
(*E*)-1'-Hydroxy-5',6'-dimethoxy-1'-(2-methylstyryl)-2-(*o*-tolyl)spiro[cyclopropane-1,2'-inden]-3'(1'*H*)-one (89i)

This compound was isolated as pale yellow liquid. Following the general procedure-12, 50 mg of **75i** afforded 46 mg of **89i** (88% yield). R_f = 0.5 (hexane/EtOAc = 3/2). **IR (thin film, neat):**



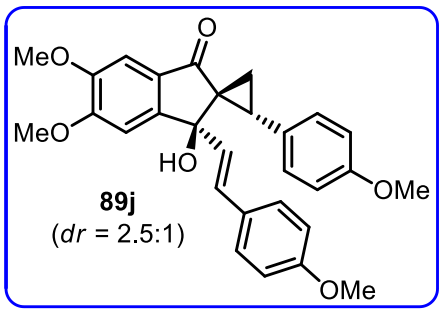
ν_{max}/cm^{-1} 3418, 2941, 1699, 1595, 1499, 1289, 1003, 734. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.47 (d, *J* = 6.3 Hz, 1H), 7.29-7.24 (m, 1H), 7.21-7.11 (m, 6H), 7.04-7.03 (m, 3H), 6.30 (d, *J* = 15.8 Hz, 1H), 3.94 (s, 3H), 3.84 (s, 3H), 2.81-2.77 (m, 1H), 2.61 (s, 1H), 2.42 (s, 3H), 2.40 (s, 3H), 1.78-1.74 (m, 1H), 1.26-1.24 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.0, 155.2, 150.8, 150.6, 137.3, 135.8, 135.4, 134.6, 130.8, 130.5, 129.7, 129.6, 129.2, 127.9, 127.8, 127.1, 126.2, 125.58, 125.52, 106.1, 103.5, 78.3, 56.4, 56.1, 47.4, 34.8, 20.8, 20.0, 17.3. **HRMS (ESI):** *m/z* calcd for $C_{29}H_{29}O_4$ $(M+H)^+$: 441.2066, Found: 441.2058.

(2*E*,2'*E*)-1,1'-(4,5-Dimethoxy-1,2-phenylene)bis(3-(4-methoxyphenyl)prop-2-en-1-one) (75j)



This compound was isolated as pale yellow liquid. Following the general procedure-10, 100 mg of **88** (R^1 = OMe, R^2 = (*p*-OMe)C_6H_4) afforded 62.5 mg of **75g** (63% yield). R_f = 0.5 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 2936, 1597, 1511, 1353, 1255, 1173, 1029, 829. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.43 (d, *J* = 8.0 Hz, 4H), 7.38 (d, *J* = 15.9, 2H), 7.17 (s, 2H), 6.93 (d, *J* = 16.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 4H), 3.99 (s, 6H), 3.81 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.9 (2C), 161.7 (2C), 150.5 (2C), 145.0 (2C), 133.5 (2C), 130.2 (4C), 127.2 (2C), 124.0 (2C), 114.3 (4C), 111.1 (2C), 56.3 (2C), 55.4 (2C). **HRMS (ESI):** *m/z* calcd for $C_{28}H_{27}O_6$ $(M+H)^+$: 459.1808, Found: 459.1789.

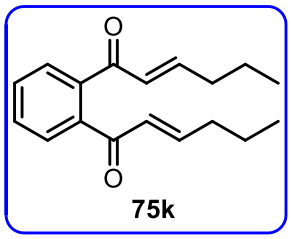
(*E*)-1'-Hydroxy-5',6'-dimethoxy-2-(4-methoxyphenyl)-1'-(4-methoxystyryl)spiro[cyclopropane-1,2'-inden]-3'(1'*H*)-one (89j)



This compound was isolated as pale brown liquid. Following the general procedure-12, 50 mg of **75j** afforded 44 mg of **89j** (84% yield). R_f = 0.5 (hexane/EtOAc = 1/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3452, 2937, 1698, 1595, 1513, 1287, 1247, 1175, 734. **^{1}H NMR (400 MHz, $CDCl_3$):**

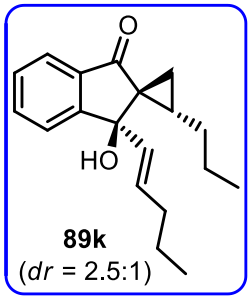
δ 7.04 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.01 (d, *J* = 7.1Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 6.83-6.78 (m, 3H), 6.14 (d, *J* = 15.9 Hz, 1H), 3.96 (m, 3H), 3.85 (m, 3H), 3.81 (m, 3H), 3.76 (m, 3H), 2.88 (t, *J* = 8.4 Hz, 1H), 2.03-1.99 (m, 1H), 1.76-1.73 (m, 1H), 1.28-1.23 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.3, 159.4, 158.3, 155.2, 151.0, 150.7, 130.1 (2C), 129.5, 129.06, 129.03, 128.3, 127.8 (2C), 127.5, 114.1 (2C), 113.2 (2C), 106.0, 103.3, 78.2, 56.4, 56.1, 55.3, 55.1, 48.0, 35.8, 18.3. **HRMS (ESI):** *m/z* calcd for $C_{29}H_{28}NaO_6$ $(M+Na)^+$: 495.1784, Found: 495.1730.

(2*E*,2'*E*)-1,1'-(1,2-Phenylene)bis(hex-2-en-1-one) (75k)



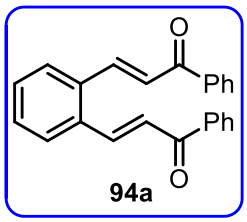
This compound was isolated as pale yellow liquid. Following the general procedure-10, 100 mg of **88** afforded 67 mg of **75k** (68% yield). Rf = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2960, 2872, 1657, 1621, 1465, 1297, 977. **^{1}H NMR (400 MHz, CDCl3):** δ 7.60-7.51 (m, 4H), 6.73-6.63 (m, 2H), 6.48 (d, *J* = 15.8 Hz, 2H), 2.28-2.17 (m, 4H), 1.53-1.42 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (100 MHz, CDCl3):** δ 194.9 (2C), 151.2 (2C), 139.8 (2C), 130.4 (2C), 129.8 (2C), 128.4 (2C), 34.7 (2C), 21.2 (2C), 13.7 (2C). **HRMS (ESI):** *m/z* calcd for $C_{18}H_{23}O_2$ $(M+H)^+$: 271.1698, Found: 271.1686.

(*E*)-1'-Hydroxy-1'-(pent-1-en-1-yl)-2-propylspiro[cyclopropane-1,2'-inden]-3'(1'*H*)-one (89k)



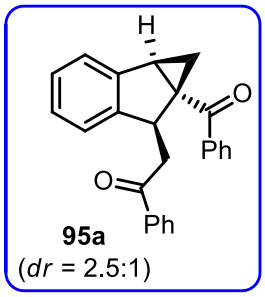
This compound was isolated as pale yellow liquid. Following the general procedure-12, 50 mg of **75k** afforded 38 mg of **89k** (72% yield). Rf = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3428, 2924, 2860, 1709, 1601, 1465, 1121, 981. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.71 (dd, *J* = 7.6 and 0.6 Hz, 1H), 7.66-7.61 (m, 1H), 7.59-7.53 (m, 1H), 7.46 (t, *J* = 7.3 Hz, 1H), 5.92-5.82 (m, 1H), 5.38 (d, *J* = 15.5 Hz, 1H), 2.15-2.0 (m, 2H), 1.76-1.61 (m, 3H), 1.51-1.41 (m, 3H), 1.40-1.35 (m, 1H), 1.34-1.18 (m, 3H), 0.94 (t, *J* = 7.3 Hz, 3H), 0.87 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 203.4, 156.5, 136.4, 134.4, 131.9, 129.9, 129.2, 124.9, 122.3, 78.2, 44.7, 34.2, 33.8, 28.2, 23.0, 22.5, 21.5, 13.8, 13.7. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{25}O_2$ $(M+H)^+$: 285.1855, Found: 285.1847.

(2*E*,2'*E*)-3,3'-(1,2-Phenylene)bis(1-phenylprop-2-en-1-one) (94a)



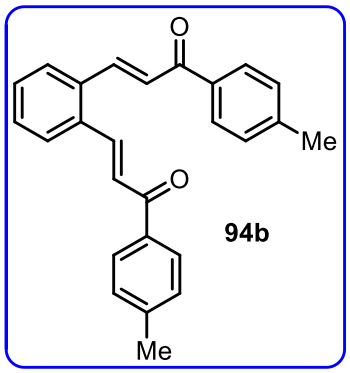
This compound was isolated as pale yellow solid. Following the general procedure-11, 100 mg of **93** (R^1 = H with R^2 = Ph) afforded 181 mg of **94g** (72% yield). M.P = 120-122 ^oC. R_f = 0.5 (hexane/EtOAc = 8.5/1.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 3060, 2927, 1662, 1605, 1447, 1302, 1016, 975, 695. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.18 (d, *J* = 15.5 Hz, 2H), 8.02 (d, *J* = 7.6 Hz, 4H), 7.71-7.69 (m, 2H), 7.59-7.55 (m, 2H), 7.50-7.40 (m, 8H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 190.0 (2C), 141.6 (2C), 137.8 (2C), 135.3 (2C), 133.0 (2C), 130.2 (2C), 128.7 (4C), 128.6 (4C), 128.1 (2C), 125.9 (2C).

2-(6a-Benzoyl-1,1a,6,6a-tetrahydrocyclopropa[*a*]inden-6-yl)-1-phenylethanone (95a)



This compound was isolated as colorless solid. Following the general procedure-12, 50 mg of **94a** afforded 31 mg of **95a** (59% yield). R_f = 0.5 (hexane/EtOAc = 9/1). M.P = 110-113 ^oC. **IR (thin film, neat):** ν_{max}/cm^{-1} 2920, 1683, 1448, 1202, 980, 709. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.99-7.93 (m, 2H), 7.84-7.77 (m, 2H), 7.60-7.39 (m, 7H), 7.32-7.25 (m, 2H), 7.24-7.18 (m, 1H), 4.65 (dd, *J* = 9.3 and 4.4 Hz, 1H), 3.46 (dd, *J* = 18 and 4.5 Hz, 1H), 3.25 (dd, *J* = 18 and 9.4 Hz, 1H), 2.99 (dd, *J* = 8.3 and 3.9 Hz, 1H), 2.07 (dd, *J* = 8.3 and 4.9 Hz, 1H), 0.69 (dd, *J* = 4.9 and 4.2 Hz, 1H). **NMR (100 MHz, $CDCl_3$):** δ 200.6, 198.1, 144.4, 144.1, 137.8, 136.6, 133.2, 131.8, 128.6, 128.4, 128.1 (2C), 127.2, 126.8, 125.3, 124.2, 44.6, 43.0, 41.3, 35.8, 18.3. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{20}NaO_2$ $(M+Na)^+$: 375.1361, Found: 375.1379.

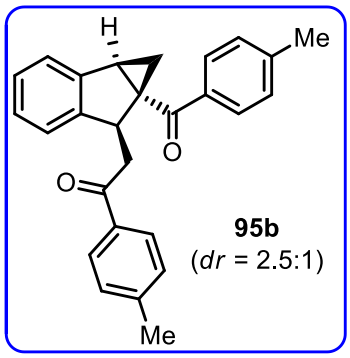
(2*E*,2'*E*)-3,3'-(1,2-Phenylene)bis(1-(*p*-tolyl)prop-2-en-1-one) (94b)



This compound was isolated as pale yellow solid. Following the general procedure-11, 100 mg of **93** (R^1 = H with R^2 = *P*-tolyl) afforded 190 mg of **94b** (69% yield). M.P = 99-103 ^oC. R_f = 0.5 (hexane/EtOAc = 8.5/1.5). **IR (thin film, neat):** ν_{max}/cm^{-1} xx. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.17 (d, *J* = 15.5 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 4H), 7.72-7.69 (m, 2H), 7.46-7.40 (m, 4H), 7.29 (d, *J* =

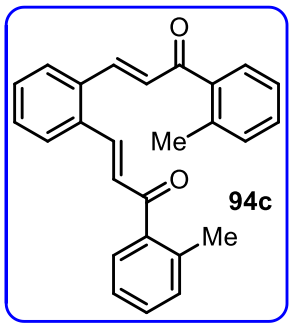
15.5 Hz, 4H), 2.43 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 189.6 (2C), 143.8 (2C), 141.3 (2C), 135.5 (2C), 135.3 (2C), 130.0 (2C), 129.4 (4C), 128.7 (4C), 128.1 (2C), 126.1 (2C), 21.7 (2C).

2-(6a-(4-Methylbenzoyl)-1,1a,6,6a-tetrahydrocyclopropa[*a*]inden-6-yl)-1-(*p*-tolyl)ethanone (95b)



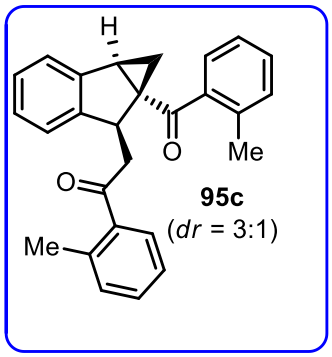
This compound was isolated as colorless solid. Following the general procedure-12, 50 mg of **94b** afforded 33.5 mg of **95b** (62% yield). M.P = 117-120 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3028, 2922, 1672, 1606, 1262, 1179, 981. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.81 (d, *J* = 7.8 Hz, 2H), 7.67 (d, *J* = 7.7 Hz, 2H), 7.39-7.38 (m, 1H), 7.24-7.15 (m, 7H), 4.63-4.60 (m, 1H), 3.40-3.35 (m, 1H), 3.22-3.15 (m, 1H), 2.93-2.90 (m, 1H), 2.38 (s, 3H), 2.36(s, 3H), 2.01-1.98 (m, 1H), 0.63-0.60 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.2, 197.7, 144.5, 144.2, 143.9, 142.4, 135.1, 134.2, 129.2 (2C), 129.1 (2C), 128.3 (2C), 128.2 (3C), 127.1, 126.8, 125.3, 124.2, 44.9, 42.9, 41.2, 35.5, 21.6, 18.2. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{24}NaO_2$ $(M+Na)^+$: 403.1674, Found: 403.1671.

(2*E*,2'*E*)-3,3'-(1,2-Phenylene)bis(1-(*o*-tolyl)prop-2-en-1-one) (94c)



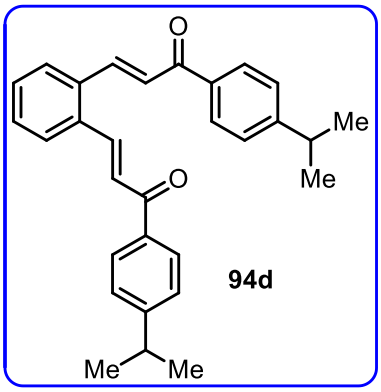
This compound was isolated as pale yellow solid. Following the general procedure-3, 100 mg of **93** (R^1 = H with R^2 = *m*-tolyl) afforded 232 mg of **94c** (84% yield). M.P = 96-99 ^{o}C. R_f = 0.5 (hexane/EtOAc = 6/4). **IR (thin film, neat):** ν_{max}/cm^{-1} 3062, 2964, 2927, 1667, 1645, 1602, 1299, 1213, 978, 732. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.78 (d, *J* = 15.8 Hz, 2H), 7.66-7.64 (m, 2H), 7.50-7.40 (m, 4H), 7.41-7.37 (m, 2H), 7.28-7.22 (m, 4H), 7.02 (d, *J* = 15.8 Hz, 2H), 2.45 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.6 (2C), 142.5 (2C), 138.5 (2C), 137.1 (2C), 134.9 (2C), 135.5 (2C), 130.8 (2C), 130.3 (2C), 130.2 (2C), 128.2 (2C), 128.1 (2C), 125.6 (2C), 20.3 (2C). **HRMS (ESI):** *m/z* calcd for $C_{26}H_{23}O_2$ $(M+H)^+$: 367.1698, Found: 367.1687.

2-(6a-(2-Methylbenzoyl)-1,1a,6,6a-tetrahydrocyclopropa[*a*]inden-6-yl)-1-(o-tolyl)ethanone (95c)



This compound was isolated as pale yellow solid. Following the general procedure-12, 50 mg of **94c** afforded 36 mg of **95c** (69% yield). M.P = 125-128 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3067, 3022, 2928, 1670, 1478, 1457, 977, 758, 739. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.36-7.27 (m, 3H), 7.25-7.21 (m, 4H), 7.18-7.15 (m, 3H), 7.11-7.07 (m, 1H), 4.64-4.60 (m, 1H), 3.34-3.28 (m, 1H), 3.19-3.11 (m, 1H), 2.97-2.94 (m, 1H), 2.52 (s, 3H), 2.47 (s, 3H), 2.03-2.00 (m, 1H), 0.80-0.78 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 204.2, 202.0, 144.5, 143.6, 138.7, 138.1, 137.2, 136.9, 132.2, 131.5, 131.3, 129.8, 128.8, 127.0, 126.9, 126.5, 125.7, 125.4, 125.1, 123.9, 45.7, 42.9, 42.7, 37.2, 21.7, 20.7, 19.8. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{24}NaO_2$ $(M+Na)^+$: 403.1674, Found: 403.1668.

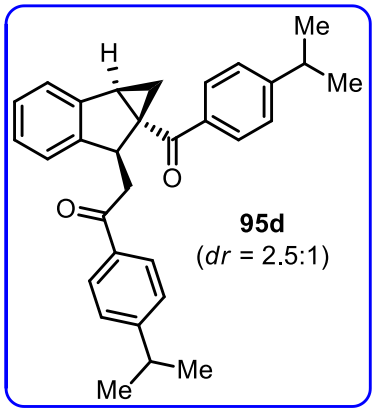
(2*E*,2'*E*)-3,3'-(1,2-Phenylene)bis(1-(4-isopropylphenyl)prop-2-en-1-one) (94d)



This compound was isolated as colorless solid. Following the general procedure-11, 100 mg of **93** (R^1 = H with R^2 = (*p*-^{i}Pr)C_6H_4) afforded 222 mg of **94d** (71% yield). M.P = 124-126 ^{o}C. R_f = 0.5 (hexane/EtOAc = 8.5/1.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 3061, 2962, 2929, 1662, 1608, 1567, 1474, 1326, 1011, 764. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.20 (d, *J* = 15.5 Hz, 2H), 8.01 (d, *J* = 8.2 Hz, 4H), 7.73-7.71 (m, 2H), 7.48-7.44 (m, 4H), 7.36 (d, *J* = 8.2 Hz, 4H), 3.03-2.96 (m, 2H), 1.30 (s, 6H), 1.29 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 189.4 (2C), 154.5 (2C), 141.3 (2C), 135.7 (2C), 135.4 (2C), 130.0 (2C), 128.9 (4C), 128.2 (2C), 126.8 (4C), 126.0 (2C), 34.2 (2C), 23.7 (4C). **HRMS (ESI):** *m/z* calcd for $C_{30}H_{30}NaO_2$ $(M+Na)^+$: 445.2143, Found: 445.2158.

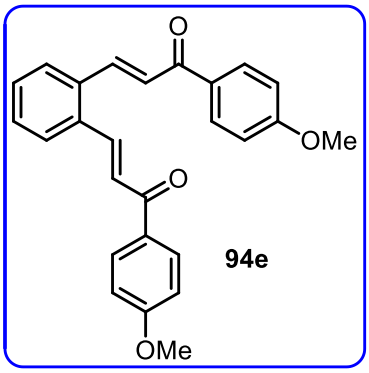
2-(6a-(4-Isopropylbenzoyl)-1,1a,6,6a-tetrahydrocyclopropa[*a*]inden-6-yl)-1-(4-isopropylphenyl)ethanone (95d)

This compound was isolated as pale yellow liquid. Following the general procedure-12, 50 mg of **94d** afforded 32 mg of **95d** (61% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):**



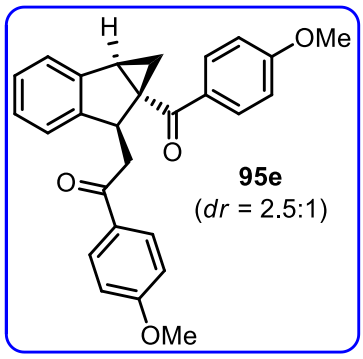
ν_{max}/cm^{-1} 2962, 2928, 1680, 1606, 1378, 1236, 982. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.39-7.37 (m, 1H), 7.27-7.20 (m, 6H), 7.17-7.16 (m, 1H), 4.65-4.63 (m, 1H), 3.41-3.35 (m, 1H), 3.25-3.19 (m, 1H), 2.95-2.89 (m, 3H), 1.99-1.96 (m, 1H), 1.25-1.22 (m, 12H), 0.64-0.62 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.0, 197.7, 154.6, 153.1, 144.5, 144.3, 135.3, 134.5, 128.4 (2C), 128.3 (2C), 127.1, 126.7, 126.6 (2C), 126.5 (2C), 125.3, 124.1, 44.8, 42.9, 41.2, 35.3, 34.2, 34.1, 23.73, 23.71, 23.6 (2C), 18.2. **HRMS (ESI):** *m/z* calcd for $C_{31}H_{32}NaO_2$ $(M+Na)^+$: 459.2300, Found: 459.2322.

(2*E*,2'*E*)-3,3'-(1,2-Phenylene)bis(1-(4-methoxyphenyl)prop-2-en-1-one) (94e)



This compound was isolated as pale yellow solid. Following the general procedure-11, 100 mg of **93** (R^1 = H with R^2 = (*p*-OMe) afforded 200 mg of **94e** (67% yield). M.P = 140-143 ^{o}C. R_f = 0.5 (hexane/EtOAc = 7.5/2.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2934, 2839, 1655, 1604, 1261, 1170, 1020, 834. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.19 (d, *J* = 15.5 Hz, 2H), 8.07 (d, *J* = 8.8 Hz, 4H), 7.73-7.70 (m, 2H), 7.47-7.43 (m, 4H), 6.99 (d, *J* = 8.8 Hz, 4H), 3.90 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 188.3 (2C), 163.5 (2C), 141.0 (2C), 135.5 (2C), 130.9(4C), 130.8 (2C), 129.9 (2C), 128.2 (2C), 125.9 (2C), 113.9 (4C), 55.5 (2C).

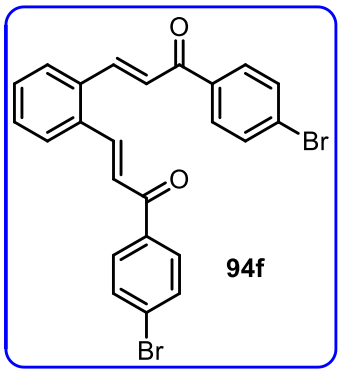
2-(6a-(4-Methoxybenzoyl)-1,1a,6,6a-tetrahydrocyclopropa[*a*]inden-6-yl)-1-(4-methoxyphenyl)ethanone (95e)



This compound was isolated as pale yellow liquid. Following the general procedure-12, 50 mg of **94e** afforded 32.5 mg of **95e** (64% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2933, 2842, 1672, 1600, 1257, 1169, 1028. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.40-7.36 (m, 1H), 7.24-7.22 (m, 2H), 7.18-7.16 (m, 1H),

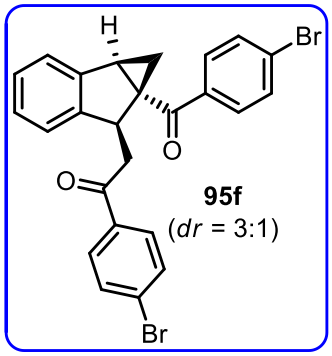
6.89-6.87 (m, 4H), 4.63-4.61 (m, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 3.38-3.33 (m, 1H), 3.23-3.17 (m, 1H), 2.90-2.87 (m, 1H), 1.97-1.94 (m, 1H), 0.62-0.59 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.9, 196.6, 163.4, 162.6, 144.6, 144.2, 130.4 (2C), 130.3 (2C), 130.2, 129.7, 127.1, 126.7, 125.3, 124.1, 113.67 (2C), 113.64 (2C), 55.4, 55.3, 45.2, 42.7, 41.0, 34.9, 18.0. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{24}NaO_4$ $(M+Na)^+$: 435.1572, Found: 435.1566.

(2*E*,2'*E*)-3,3'-(1,2-Phenylene)bis(1-(4-bromophenyl)prop-2-en-1-one) (94f)



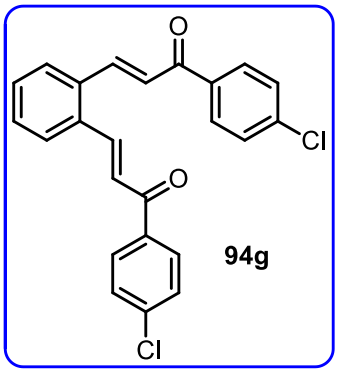
This compound was isolated as pale yellow solid. Following the general procedure-11, 100 mg of **93** (R^1 = H with R^2 = (*p*-Br)C_6H_4) afforded 268 mg of **94f** (73% yield). M.P = 138-140 ^oC. R_f = 0.5 (hexane/EtOAc = 8.5/1.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 3061, 2925, 1663, 1603, 1586, 1214, 1007, 758. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.21 (d, *J* = 8.5 Hz, 2H), 7.93 (d, *J* = 8.5 Hz, 4H), 7.76-7.71 (m, 2H), 7.67 (d, *J* = 8.5 Hz, 4H), 7.53-7.47 (m, 2H), 7.40 (d, *J* = 15.5 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 188.8 (2C), 142.1 (2C), 136.5 (2C), 135.2 (2C), 132.0 (4C), 130.3 (2C), 130.1 (4C), 128.3 (2C), 128.2 (2C), 125.4 (2C).

2-(6a-(4-Bromobenzoyl)-1,1a,6,6a-tetrahydrocyclopropa[*a*]inden-6-yl)-1-(4-bromophenyl)ethanone (95f)



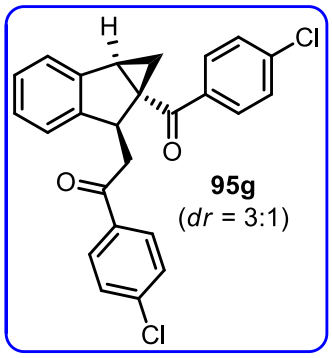
This compound was isolated as pale yellow solid. Following the general procedure-12, 50 mg of **94f** afforded 30.8 mg of **95f** (60% yield). M.P = 170-173 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3070, 2926, 1683, 1585, 1264, 1070, 756. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.78-7.76 (m, 2H), 7.64-7.62 (m, 2H), 7.58-7.53 (m, 4H), 7.42-7.40 (m, 1H), 7.27-7.26 (m, 2H), 7.16-7.14 (m, 1H), 4.52-4.48 (m, 1H), 3.44-3.39 (m, 1H), 3.15-3.08 (m, 1H), 2.96-2.93 (m, 1H), 2.04-2.01 (m, 1H), 0.63-0.61 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.4, 197.1, 144.1, 143.5, 136.5, 135.0, 131.9 (2C), 131.7 (2C), 129.7 (2C), 129.6 (2C), 128.5, 127.4, 127.0, 126.6, 125.1, 124.3, 44.6, 42.8, 41.1, 35.9, 18.2. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{17}Br_2O_2$ $(M-H)^+$: 506.9595, Found: 506.9576.

(2*E*,2'*E*)-3,3'-(1,2-Phenylene)bis(1-(4-chlorophenyl)prop-2-en-1-one) (94g)



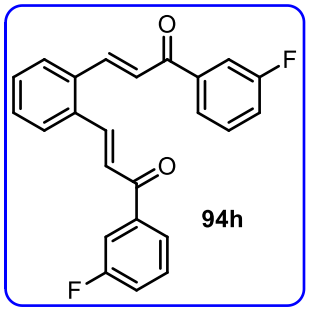
This compound was isolated as colorless solid. Following the general procedure-11, 100 mg of **93** (R^1 = H with R^2 = (*p*-Cl)C_6H_4) afforded 240 mg of **94g** (79% yield). M.P = 162-163 ^oC. R_f = 0.5 (hexane/EtOAc = 8.5/1.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 1661, 1604, 1328, 1214, 1009, 826, 756, 477. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.18 (d, *J* = 15.5 Hz, 2H), 7.98 (d, *J* = 7.6 Hz, 4H), 7.71-7.70 (m, 2H), 7.48-7.46 (m, 6H), 7.39 (d, *J* = 15.5 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 188.5 (2C), 142.0 (2C), 139.5 (2C), 136.1 (2C), 135.2 (2C), 130.3 (2C), 130.0 (4C), 129.0 (4C), 128.2 (2C), 125.4 (2C).

2-(6a-(4-Chlorobenzoyl)-1,1a,6,6a-tetrahydrocyclopropa[*a*]inden-6-yl)-1-(4-chlorophenyl)ethanone (95g)



This compound was isolated as colorless solid. Following the general procedure-12, 50 mg of **94g** afforded 36 mg of **95g** (69% yield). M.P = 170-173 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3068, 1674, 1588, 1400, 1260, 1090, 981, 750. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.84 (d, *J* = 7.9 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.42-7.35 (m, 5H), 7.29-7.23 (m, 2H), 7.17-7.15 (m, 1H), 4.52-4.49 (m, 1H), 3.45-3.39 (m, 1H), 3.16-3.09 (m, 1H), 2.95-2.92 (m, 1H), 2.03-2.00 (m, 1H), 0.63-0.60 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.2, 196.9, 144.2, 143.5, 139.7, 138.0, 136.1, 134.6, 129.6 (2C), 129.5 (2C), 128.9 (2C), 128.7 (2C), 127.4, 127.0, 125.2, 124.3, 44.7, 42.9, 41.1, 35.8, 18.1. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{18}Cl_2NaO_2$ $(M+Na)^+$: 443.0582, Found: 443.0577.

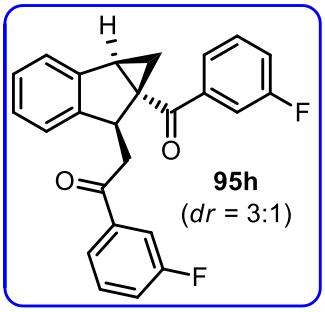
(2*E*,2'*E*)-3,3'-(1,2-Phenylene)bis(1-(3-fluorophenyl)prop-2-en-1-one) (94h)



This compound was isolated as pale yellow solid. Following the general procedure-11, 100 mg of **93** (R^1 = H with R^2 = (*m*-F)C_6H_4) afforded 190 mg of **94h** (68% yield). M.P = 139-142 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 1665, 1585,

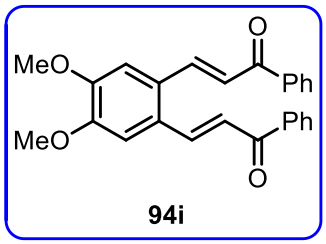
1442, 1246, 1169, 758. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.20 (d, *J* = 15.5 Hz, 2H), 7.82 (d, *J* = 7.7 Hz, 2H), 7.73-7.70 (m, 4H), 7.51-7.46 (m, 4H), 7.39 (d, *J* = 15.5 Hz, 2H), 7.31-7.27 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 188.53, 188.51, 162.9 (d, *J* = 246.6 Hz), 142.2 (3C), 139.9 (d, *J* = 6.1 Hz), 135.2 (2C), 130.4 (4C), 130.3, 128.2 (3C), 125.4 (2C), 124.3 (d, *J* = 2.8 Hz), 120.1 (d, *J* = 21.4 Hz), 115.3 (d, *J* = 22.2 Hz). **^{19}F NMR (374 MHz, $CDCl_3$):** δ -111.5.

2-(6a-(3-Fluorobenzoyl)-1,1a,6,6a-tetrahydrocyclopropa[*a*]inden-6-yl)-1-(3-fluorophenyl)ethanone (95h)



This compound was isolated as pale orange semi-solid. Following the general procedure-12, 50 mg of **94h** afforded 32 mg of **95h** (61% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3072, 2926, 1687, 1588, 1443, 1248, 746, . **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.70 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 9.5 Hz, 1H), 7.51-7.49 (m, 2H), 7.44-7.33 (m, 4H), 7.29-7.27 (m, 2H), 7.20-7.16 (m, 2H), 4.57-4.54 (m, 1H), 3.45-3.41 (m, 1H), 3.18-3.11 (m, 1H), 2.98-2.95 (m, 1H), 2.05-2.02 (m, 1H), 0.65-0.63 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.9, 196.8, 163.9, 162.8 (d, *J* = 246.7 Hz), 144.1, 143.5, 140.0, 130.3 (d, *J* = 7.6 Hz), 129.9 (d, *J* = 8.0 Hz), 127.4, 127.0, 125.2, 124.3, 123.8 (d, *J* = 3.0 Hz), 123.7 (d, *J* = 2.9 Hz), 120.3 (d, *J* = 21.3 Hz), 118.8 (d, *J* = 21.3 Hz), 115.3, 115.0 (d, *J* = 3.2 Hz), 114.8, 44.4, 43.0, 41.2, 36.0, 18.4. **^{19}F NMR (374 MHz, $CDCl_3$):** δ -111.6, -111.9. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{18}F_2NaO_2$ $(M+Na)^+$: 411.1173, Found: 411.1168.

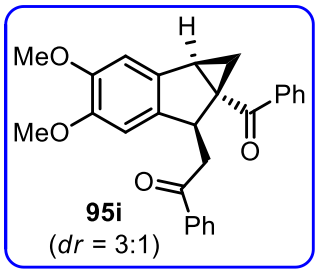
(2*E*,2'*E*)-3,3'-(4,5-Dimethoxy-1,2-phenylene)bis(1-phenylprop-2-en-1-one) (94i)



This compound was isolated as pale yellow solid. Following the general procedure-11, 100 mg of **93** (R^1 = OMe with R^2 = Ph) afforded 150 mg of **94i** (73% yield). M.P = 135-139 ^{o}C. R_f = 0.5 (hexane/EtOAc = 7.5/2.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2935, 1660, 1597, 1510, 1277, 1204, 1017, 696. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.17 (d, *J* = 15.5 Hz, 2H), 8.00 (d, *J* = 7.4Hz, 4H), 7.59-7.56 (m, 2H), 7.51-7.47 (m, 4H), 7.32 (d, *J* = 15.5 Hz, 2H), 7.16 (s, 2H), 3.99 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 190.3

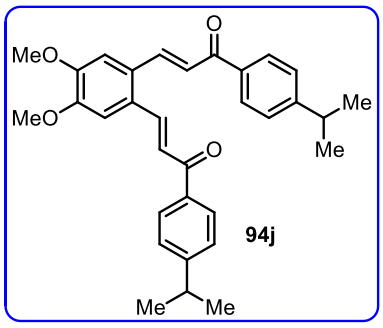
(2C), 150.8 (2C), 141.3 (2C), 138.0 (2C), 132.8 (2C), 128.9 (2C), 128.6 (4C), 128.5 (4C), 124.3 (2C), 109.7 (2C), 56.1 (2C).

2-(6a-Benzoyl-3,4-dimethoxy-1,1a,6,6a-tetrahydrocyclopropa[*a*]inden-6-yl)-1-phenylethanone (95i)



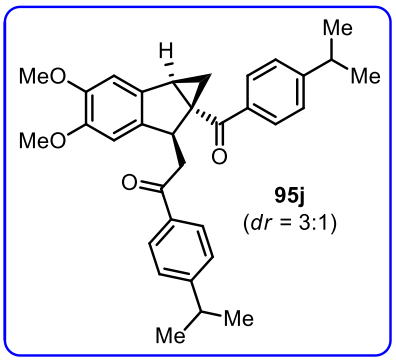
This compound was isolated as pale yellow solid. Following the general procedure-12, 50 mg of **94i** afforded 30 mg of **95i** (58% yield). R_f = 0.5 (hexane/EtOAc = 4/1). M. P = 125-127 ^{o}C. **IR (thin film, neat):** ν_{max}/cm^{-1} 3000, 2934, 1673, 1504, 1247, 1216, 1109, 979. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.92 (d, *J* = 7.7 Hz, 2H), 7.77 (d, *J* = 7.7 Hz, 2H), 7.56-7.51 (m, 1H), 7.49-7.47 (m, 1H), 7.44-7.39 (m, 4H), 6.94 (s, 1H), 6.67 (s, 1H), 4.57-4.54 (m, 1H), 3.92 (s, 3H), 2.97 (s, 3H), 3.39-3.33 (s, 1H), 3.25-3.18 (m, 1H), 2.88-2.85 (m, 1H), 2.01-1.98 (m, 1H), 0.67-0.65 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.6, 198.2, 148.5, 148.4, 137.8, 136.6, 136.3, 135.6, 133.2, 131.8, 128.5 (2C), 128.3 (2C), 128.1 (2C), 128.0 (2C), 108.5, 107.4, 56.1, 56.0, 44.6, 43.3, 42.1, 35.7, 18.6. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{24}NaO_4$ $(M+Na)^+$: 435.1572, Found: 435.1590.

(2*E*,2'*E*)-3,3'-(4,5-Dimethoxy-1,2-phenylene)bis(1-(4-isopropylphenyl)prop-2-en-1-one) (94j)



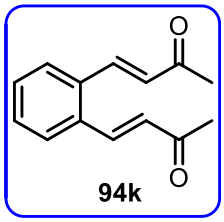
This compound was isolated as pale yellow solid. Following the general procedure-11, 100 mg of **93** (R^1 = OMe with R^2 = (*p*-^{i}Pr)C_6H_4) afforded 188 mg of **94j** (76% yield). M.P = 127-130 ^{o}C. R_f = 0.5 (hexane/EtOAc = 7.5/2.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2964, 2931, 1660, 1604, 1511, 1277, 1027, 1012. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.16 (d, *J* = 15.4 Hz, 2H), 7.96 (d, *J* = 7.6 Hz, 4H), 7.35-7.31 (m, 6H), 7.16 (s, 2H), 3.99 (s, 6H), 3.01-2.94 (m, 2H), 1.28 (s, 6H), 1.27 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 189.8 (2C), 154.3 (2C), 150.7 (2C), 141.0 (2C), 135.9 (2C), 129.0 (2C), 128.8 (4C), 126.7 (4C), 124.5 (2C), 109.8 (2C), 56.1 (2C), 34.2 (2C), 23.7 (4C). **HRMS (ESI):** *m/z* calcd for $C_{32}H_{35}O_4$ $(M+H)^+$: 483.2535, Found: 483.2531.

2-(6a-(4-Isopropylbenzoyl)-3,4-dimethoxy-1,1a,6,6a-tetrahydrocyclopropa[*a*]inden-6-yl)-1-(4-isopropylphenyl)ethanone (95j)



This compound was isolated as pale yellow semi solid. Following the general procedure-12, 50 mg of **94j** afforded 31.5 mg of **95j** (63% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2962, 2928, 1680, 1606, 1461, 982, 759. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.28-7.24 (m, 4H), 6.92 (s, 1H), 6.68 (s, 1H), 4.60-4.57 (m, 1H), 3.91 (s, 3H), 3.83 (s, 3H), 3.30-3.24 (m, 2H), 2.96-2.91 (m, 2H), 2.82-2.80 (m, 1H), 1.96-1.93 (m, 1H), 1.25 (s, 12H), 0.65-0.63 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.1, 198.0, 154.7, 153.2, 148.4, 148.3, 136.4, 135.8, 135.2, 134.5, 128.4 (4C), 126.6 (2C), 126.5 (2C), 108.5, 107.3, 56.0, 44.8, 43.2, 42.0, 35.2, 34.25, 34.22, 23.7 (2C), 23.6 (3C), 18.4. **HRMS (ESI):** *m/z* calcd for $C_{33}H_{36}NaO_4$ $(M+Na)^+$: 519.2511, Found: 519.2508.

(3*E*,3'*E*)-4,4'-(1,2-Phenylene)bis(but-3-en-2-one) (94k)

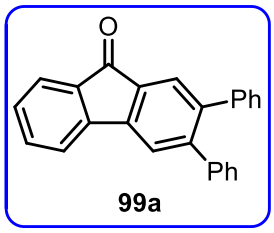


This compound was prepared by following the procedure as described in the literature. **^{1}H NMR (400 MHz, CDCl3):** δ 7.87 (d, *J* = 16 Hz, 2H), 7.64-7.55 (m, 2H), 7.46-7.38 (m, 2H), 6.63 (d, *J* = 16 Hz, 2H), 2.41 (s, 6H).

General procedure-13: Synthesis of fluorenones 99a-99f

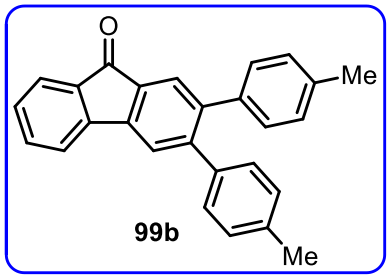
A mixture of compound **89** (50 mg, 0.14 mmol) in toluene and PTSA (4.9 mg, 0.03 mmol) was stirred at 140 °C until the reactant **89** disappeared as monitored by TLC. The reaction mixture was quenched with saturated aqueous sodium bicarbonate solution, the solvent was removed under reduced pressure and the crude reaction mixture was extracted with ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated by reduced pressure. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (9:1) as eluent to deliver compound **99a-99f**.

2,3-Diphenyl-9*H*-fluoren-9-one (8a)[44]



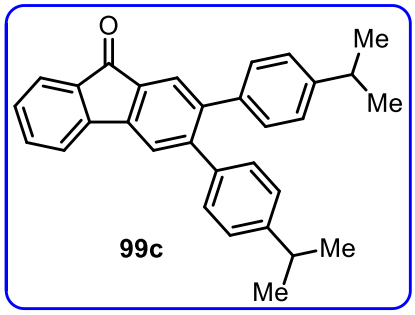
This compound was isolated as pale brown solid. Following the general procedure-13, 50 mg of **89a** afforded 38 mg of **99a** (80% yield). M.P = 178-179 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9.5/0.5).

2,3-Di-*p*-tolyl-9*H*-fluoren-9-one (99b)



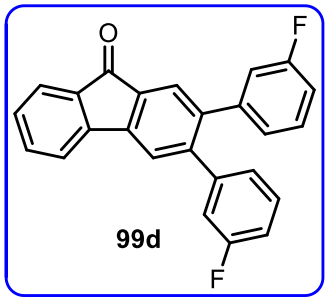
This compound was isolated as pale yellow semi solid. Following the general procedure-13, 50 mg of **89b** afforded 43.6 mg of **99b** (90% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3026, 2922, 1645, 1597, 1512, 1328, 1285, 814. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.71-7.67 (m, 2H), 7.54-7.49 (m, 3H), 7.33-7.29 (m, 1H), 7.08 (s, 4H), 7.03 (s, 4H), 2.34 (s, 3H), 2.31 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.7, 146.9, 144.2, 143.0, 141.4, 138.1, 137.6, 137.1, 136.6, 134.79, 134.74, 133.0, 129.49 (2C), 129.42 (2C), 129.0, 128.88 (2C), 128.81 (2C), 126.7, 124.3, 122.8, 120.3, 21.2, 21.1. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{21}O$ $(M+H)^+$: 361.1592, Found: 361.1567.

2,3-Bis(4-isopropylphenyl)-9*H*-fluoren-9-one (99c)



This compound was isolated as pale brown solid. Following the general procedure-13, 50 mg of **89c** afforded 41 mg of **99c** (86% yield). M.P = 133-134 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3026, 2922, 1645, 1597, 1512, 1328, 1285, 814. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.73 (s, 1H), 7.69-7.67 (m, 1H), 7.55-7.49(m, 3H), 7.32-7.30 (m, 1H), 7.11 (s, 4H), 7.06 (s, 4H), 2.88-2.85 (m, 2H), 1.25-1.21 (m, 12H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.7, 148.0, 147.5, 146.9, 144.2, 143.0, 141.5, 138.4, 137.9, 134.8, 134.7, 133.0, 129.5 (2C), 129.4 (2C), 129.0, 126.7, 126.1 (2C), 126.0 (2C), 124.3, 122.8, 120.3, 33.7, 33.6, 23.9 (4C). **HRMS (ESI):** *m/z* calcd for $C_{31}H_{29}O$ $(M+H)^+$: 417.2218, Found: 417.2206.

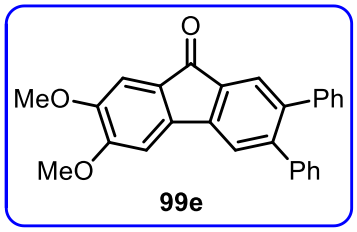
2,3-bis(3-Fluorophenyl)-9*H*-fluoren-9-one (99d)



99d

This compound was isolated as pale yellow solid. Following the general procedure-13, 50 mg of **89f** afforded 40.5 mg of **99d** (78% yield). M.P = 132-134 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2925, 1714, 1612, 1584, 1452, 1287, 1176, 897, 752. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.77-7.70 (m, 2H), 7.62-7.51 (m, 3H), 7.41-7.34 (m, 1H), 7.27-7.19 (m, 2H), 7.04-6.91 (m, 5H), 6.86 (d, *J* = 9.6 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.3, 162.5 (d, *J* = 245.4 Hz), 162.5 (d, *J* = 244.9 Hz), 145.6 (d, *J* = 1.5 Hz), 143.8, 143.7, 142.6 (d, *J* = 7.8 Hz), 142.3 (d, *J* = 7.8 Hz), 140.3 (d, *J* = 1.8 Hz), 134.9, 134.6, 133.7, 129.9, 129.8, 129.7, 129.5, 126.5, 125.4, 125.35, 125.32, 124.5, 122.6, 120.6, 116.6 (d, *J* = 7.4 Hz), 116.4 (d, *J* = 7.4 Hz), 114.6 (d, *J* = 20.8 Hz), 114.2 (d, *J* = 21.1 Hz). **^{19}F NMR (374 MHz, $CDCl_3$):** δ -112.7, -113.0. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{15}F_2O$ $(M+H)^+$: 369.1091, Found: 369.1065.

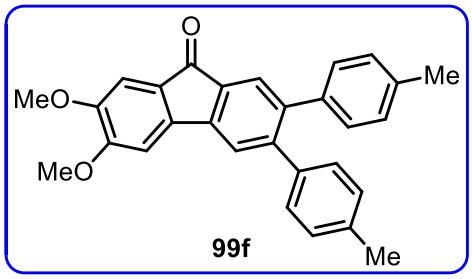
2,3-Dimethoxy-6,7-diphenyl-9*H*-fluoren-9-one (99e)[44]



99e

This compound was isolated as pale brown solid. Following the general procedure-13, 50 mg of **89g** afforded 40.5 mg of **99f** (85% yield). M.P = 149-152 ^{o}C. R_f = 0.5 (hexane/EtOAc = 8.5/1.5).

2,3-Dimethoxy-6,7-di-*p*-tolyl-9*H*-fluoren-9-one (99f)



99f

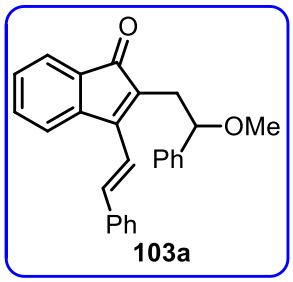
This compound was isolated as pale brown solid. Following the general procedure-13, 50 mg of **89h** afforded 42.9 mg of **99e** (90% yield). M.P = 200-203 ^{o}C. R_f = 0.5 (hexane/EtOAc = 8/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3026, 2922, 1645, 1597, 1512, 1328, 1285, 814. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.61 (s, 1H), 7.37 (s, 1H), 7.26-7.22 (m, 2H), 7.07 (s, 4H), 7.02 (s, 4H), 4.00 (s, 3H), 3.94 (s, 3H), 2.33 (s, 3H), 2.31 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.0, 154.5, 149.7, 146.3, 142.5, 140.4, 139.2, 138.2, 137.6, 136.9, 136.4, 133.6, 129.4 (2C),

129.3 (2C), 128.8 (2C), 128.7 (2C), 127.5, 126.2, 121.7, 107.1, 103.3, 56.3, 56.2, 21.2, 21.1. **HRMS (ESI):** *m/z* calcd for $C_{29}H_{25}O_3$ $(M+H)^+$: 421.1804, Found: 421.1797.

General procedure-14: Synthesis of indenones 103a-103c

Compound **89** (50 mg, 0.14 mmol) was dissolved in MeOH in an oven dried round bottom flask and PTSA (4.9 mg, 0.03 mmol) was introduced and stirred at rt until the reactant **89** disappeared as monitored by TLC. The reaction mixture was quenched by adding saturated aqueous sodium bicarbonate solution, the solvent was removed under reduced pressure and the crude reaction mixture was extracted with ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (4:1) as eluent to afford compound **103a-103c.**

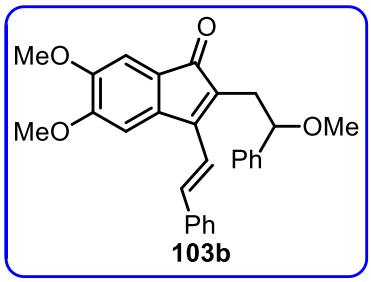
(*E*)-2-(2-Methoxy-2-phenylethyl)-3-styryl-1*H*-inden-1-one (103a)



103a

This compound was isolated as pale orange semi-solid. Following the general procedure-14, 50 mg of **89a** afforded 38 mg of **103a** (73% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2924, 1697, 1661, 1456, 1100, 955, 700. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.49-7.41 (m, 5H), 7.39-7.36 (m, 3H), 7.34-7.28 (m, 5H), 7.26-7.23 (m, 1H), 7.21-7.15 (m, 1H), 6.90 (d, *J* = 16.6 Hz, 1H), 4.41 (t, *J* = 6.7 Hz, 1H), 3.22 (s, 3H), 3.02-2.97 (m, 1H), 2.77-2.72 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.2, 152.6, 144.0, 141.6, 136.6, 136.3, 132.9, 132.1, 131.9, 129.1, 128.8 (2C), 128.4, 128.3, 127.7, 127.3 (2C), 126.5 (2C), 122.3, 121.0, 120.4, 82.5, 57.0, 32.7. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{22}NaO_2$ $(M+Na)^+$: 389.1517, Found: 389.1496.

(*E*)-5,6-Dimethoxy-2-(2-methoxy-2-phenylethyl)-3-styryl-1*H*-inden-1-one (103b)

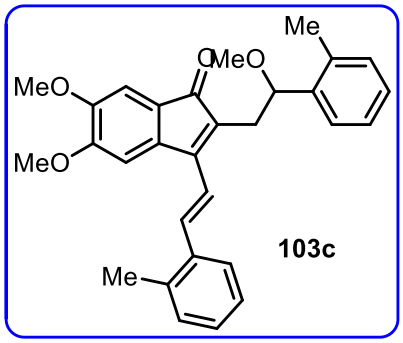


103b

This compound was isolated as pale yellow semi-solid. Following the general procedure-14, 50 mg of **89g** afforded 34 mg of **103b** (65% yield). R_f = 0.5 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 2935, 1699, 1599, 1498, 1280, 1218, 1011, 701. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48-7.40 (m, 4H), 7.38-7.28 (m,

5H), 7.24-7.20 (m, 2H), 7.10 (s, 1H), 6.97 (s, 1H), 6.81 (d, *J* = 16.6 Hz, 1H), 4.40 (t, *J* = 6.7 Hz, 1H), 3.95 (s, 3H), 3.90 (s, 3H), 3.23 (s, 3H), 2.98-2.93 (m, 1H), 2.73-2.68 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.7, 152.1, 151.4, 148.5, 141.6, 138.4, 136.6, 135.7, 131.0, 129.0, 128.8 (2C), 128.3 (2C), 127.7, 127.2 (2C), 126.5 (2C), 124.3, 120.4, 107.0, 106.0, 82.6, 56.9, 56.4, 56.3, 32.8. **HRMS (ESI):** *m/z* calcd for $C_{28}H_{26}NaO_4$ $(M+Na)^+$: 449.1729, Found: 449.1720.

(*E*)-5,6-Dimethoxy-2-(2-methoxy-2-(*m*-tolyl)ethyl)-3-(3-methylstyryl)-1*H*-inden-1-one (103c)



This compound was isolated as pale brown solid. Following the general procedure-14, 50 mg of **89i** afforded 36 mg of **103c** (70% yield). R_f = 0.5 (hexane/EtOAc = 8/2). M. P = 98-101 ^oC. **IR (thin film, neat):** ν_{max}/cm^{-1} 2933, 2834, 1694, 1585, 1257, 1483, 1360, 1214, 757. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.69 (d, *J* = 16.5 Hz, 1H), 7.57-7.54 (m, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.27-7.26 (m, 1H), 7.24-7.16 (m, 3H), 7.11-7.09 (m, 3H), 7.01 (s, 1H), 6.87 (d, *J* = 16.5 Hz, 1H), 4.69-4.66 (m, 1H), 3.95 (s, 3H), 3.90 (s, 3H), 3.19 (s, 3H), 2.88-2.83 (s, 1H), 2.71-2.66 (m, 1H), 2.45 (s, 3H), 2.38 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.1, 152.1, 151.7, 148.4, 140.0, 138.7, 136.4, 135.78, 135.72, 136.6, 131.0, 130.6, 130.4, 128.9, 127.2, 126.4, 126.1, 125.6, 125.5, 124.2, 121.2, 107.0, 79.2, 56.8 (2C), 56.3, 31.9, 19.9, 19.1. **HRMS (ESI):** *m/z* calcd for $C_{30}H_{30}NaO_4$ $(M+Na)^+$: 477.2042, Found: 477.2042.

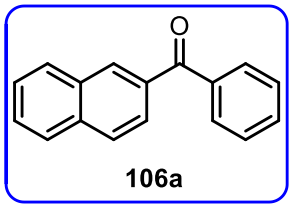
General procedure-15: Synthesis of fluorenone 99e

The compound **103b** (50 mg, 0.12 mmol) was dissolved in DCE in an oven dried round bottom flask. The catalyst $Sc(OTf)_3$ (11.5 mg, 0.02 mmol) was introduced to the reaction mixture and stirred at 80 $^\circ$C until the reactant **103b** disappeared as monitored by TLC. The reaction mixture was quenched by adding saturated aqueous sodium bicarbonate solution, the solvent was removed under reduced pressure and the crude reaction mixture was extracted with ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (4:1) as eluent to afford compound **99e.**

General procedure-16: Synthesis of 2-naphthaphenones 106a-106c

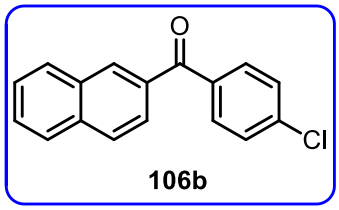
The compounds **106a-106c** were synthesized by following the general procedure-13.

Naphthalen-2-yl(phenyl)methanone (106a)[57(d)]



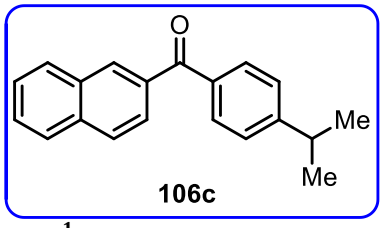
This compound was isolated as pale yellow liquid. Following the general procedure-16, 50 mg of **95a** afforded 30.5 mg of **106a** (92% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3058, 1655, 1597, 1287, 1116, 750. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.26 (s, 1H), 7.94 (s, 2H), 7.91 (d, *J* = 8.1 Hz, 2H), 7.86 (d, *J* = 7.40, 2H), 7.65-7.57 (m, 2H), 7.56-7.49 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.8, 137.9, 135.2, 134.8, 132.4, 132.2, 131.9, 130.1 (2C), 129.4, 128.3 (2C), 128.33, 127.8, 126.8, 125.8.

(4-Chlorophenyl)(naphthalen-2-yl)methanone (106b)[57(e)]



This compound was isolated as pale yellow solid. Following the general procedure-16, 50 mg of **95g** afforded 29.5 mg of **106b** (93% yield). M.P = 124-126 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3062, 1655, 1587, 1466, 1289, 1234, 1089, 774. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.25 (s, 1H), 7.99-7.93 (m, 4H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.67-7.62 (m, 1H), 7.61-7.57 (m, 1H), 7.52 (d, *J* = 6.8 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.5, 138.8, 136.1, 135.3, 134.4, 132.2, 131.8, 131.5 (2C), 129.4, 128.7 (2C), 128.52, 128.50, 127.8, 126.9, 125.6.

(4-Isopropylphenyl)(naphthalen-2-yl)methanone (106c)



This compound was isolated as pale yellow solid. Following the general procedure-16, 50 mg of **95d** afforded 30 mg of **106c** (95% yield). M.P = 87-89 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2962, 1651, 1626, 1352, 1237, 1116, 779. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.27 (s, 1H), 7.93-7.89 (m, 4H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.62-7.52 (m, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 3.07-2.94 (m, 1H), 1.32 (s, 3H), 1.30 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.5, 153.9, 135.5, 135.1, 132.2, 131.6, 130.5 (2C), 129.3, 128.3,

128.20, 127.8, 126.7, 126.4 (2C), 125.9, 34.3, 23.7 (2C). **HRMS (ESI):** *m/z* calcd for $C_{20}H_{19}O$ $(M+H)^+$: 275.1436, Found: 275.1419.

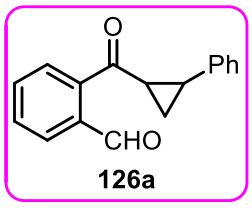
General procedure-17: Synthesis of cyclopropyl keto-aldehydes 126a-126j

The cyclopropyl keto-aldehydes (**126a-126j**) were synthesized from **132** in a two-step protocol, Scheme 82. The representative general procedures for the transformation of **132** to **126** were follows as described in the literature.[44]

General procedure-18: Phosphine mediated reaction of cyclopropyl keto-aldehyde 126a

The compound **126a** (50 mg, 0.28 mmol) was dissolved in DMSO in an oven dried 10 mL round bottom flask and tributyl phosphine (10 mol%) was introduced and placed in a 130 ^oC preheated oil bath. The flask was sealed with a condenser circulated by cold water and was stirred until the compound **126a** disappeared as monitored by TLC. The reaction was cooled to room temperature and quenched by adding cold water and extracted with diethyl ether (2x2 mL). The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (7/3) as eluent to afford **134a** (72% yield).

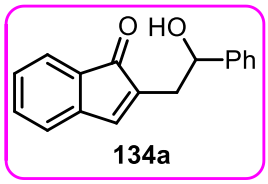
2-(2-Phenylcyclopropanecarbonyl)benzaldehyde (126a)



126a

This compound was isolated as pale yellow liquid. Following the general procedure-17, 100 mg of **133** afforded 73.5 mg of **126a** (86% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2932, 1695, 1665, 1520, 1394, 1224, 995, 750. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.21 (s, 1H), 7.94-7.92 (m, 1H), 7.79-7.77 (m, 1H), 7.66-7.62 (m, 2H), 7.33-7.30 (m, 2H), 7.24-7.22 (m, 1H), 7.19-7.17 (m, 2H), 2.82-2.72 (m, 2H), 2.04-1.99 (m, 1H), 1.68-1.60 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.1, 191.6, 141.8, 139.8, 135.5, 133.1, 131.5, 129.1, 128.6 (2C), 128.3, 126.8, 126.2 (2C), 32.6, 31.3, 20.2. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{15}O_2$ $(M+H)^+$: 251.1072, Found: 251.1062.

2-(2-Hydroxy-2-phenylethyl)-1*H*-inden-1-one (134a)



134a

This compound was isolated as pale yellow solid. Following the general procedure-18, 50 mg of **126a** afforded 36.5 mg of **134** (73% yield). M.P = 75-77 ^{o}C. R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3417, 2925, 1706, 1604, 1458, 1296, 1052, 751. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.39-7.36 (m, 3H), 7.34-7.31 (m, 2H), 7.29-7.26 (m, 2H), 7.16-7.13 (m, 2H), 6.94 (d, *J* = 7.1Hz, 1H), 4.92 (m, 1H), 2.75-2.72 (m, 2H), 2.69 (brs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.1, 145.8, 145.5, 143.7, 136.5, 134.0, 130.5, 128.4 (2CH), 128.3, 127.8, 125.7 (2 CH), 122.9,121.6, 72.8, 35.3. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{13}O$ $(M\text{-}OH)^+$: 233.0966, Found: 233.0950.

General procedure-19: Synthesis of cyclopropyl keto-aldehydes 138a-138c

Step-I: The compound **39** (300 mg, 1.31 mmol; when R = H) was taken in an oven-dried long neck round-bottom flask with a magnetic stirring bar and the flask was sealed with a rubber septum. Anhydrous THF (5 mL) was added through rubber septum by syringe under an nitrogen atmosphere. Now the flask was kept at -78 $^{\circ}$C and *n*-BuLi (1.6 *M* in hexane, 0.98 mL, 1.57 mmol) was added dropwise to the reaction mixture over 5 min. After 25 min, DMF (0.12 mL, 1.57 mmol) was added at the same temperature and the reaction mixture was stirred for an additional 30 min. The mixture was warmed to room temperature over 30 min. The reaction progress was monitored by TLC. The reaction mixture was quenched with saturated aqueous ammonium chloride solution and extracted with ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (4:1) as eluent to afford the compound **40** in 89% yield.

Step-II: Compound **40** (when R = H, 200 mg, 1.12 mmol) was taken in an oven-dried round-bottom flask containing a magnetic stirring bar and sealed with a rubber septum. Anhydrous THF (5 mL) was added through rubber septum by syringe under an N_2 atmosphere and the flask was kept at 0 ^{o}C. At the same temperature, vinyl magnesium bromide (1.3 mmol) was added dropwise over 5 min and the reaction mixture was stirred for an additional 50 min. The reaction progress was monitored by TLC. Upon complete consumption of the starting compound, the reaction mixture was then quenched with saturated aqueous ammonium chloride solution and

extracted with ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (7/3) as eluent to afford 197 mg of compound **135** (85% yield).

Step-III: An oven dried 50 mL round bottom flask containing a magnetic stirring bar was charged with compound **135** (150 mg, 0.73 mmol, when R = H) and IBX (1.2 eq, 0.87 mmol). Ethyl acetate (10 mL) was added and the reaction mixture was kept at 70 ^{o}C. The reaction mixture was then stirred until the compound **135** disappeared as monitored by TLC. The reaction was then cooled to room temperature and filtered through Buchner funnel. The filter cake was washed with ethyl acetate (3x10 mL). Organic extracts were combined and washed with saturated sodium bicarbonate solution to remove excess iodobenzoic acid. The organic extract was dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane/ethyl acetate (4/1) as eluent to afford 119 mg of compound **136** in 80% yield.

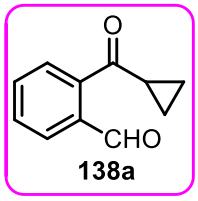
Step-IV: The compound **136** (when R = H) was converted to **137** (when R = H) by following the procedure described in literature.

Step-V: The deprotection of compound **137** (when R = H) was done by using the standard reaction conditions reported in the literature[1] to deliver **138** in 81% yield.

General procedure-20: Synthesis of indanones 134a-134j and 139a-139c under heating conditions

The compound **138a** (50 mg, 0.28 mmol, when R^1, R^2 = H) was dissolved in DMSO in an oven dried 10 mL round bottom flask and was placed in a 130 ^{o}C preheated oil bath. The flask was sealed with a condenser circulated by cold water and was stirred until the compound **138a** disappeared as monitored by TLC. The reaction was cooled to room temperature and quenched by adding cold water and extracted with diethyl ether (2x2 mL). The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (7/3) as eluent to afford **139a** (30.5 mg, 61% yield).

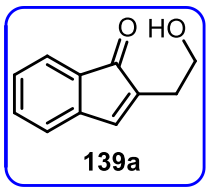
2-(Cyclopropanecarbonyl)benzaldehyde (138a)



138a

This compound was isolated as pale green semi-solid. Following the general procedure-19, 100 mg of **137a** (when R = H) afforded 65 mg of **138a** (81% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3010,1694, 1692, 1381, 1225, 991, 738. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.18 (s, 1H), 7.94-7.92 (m, 1H), 7.87-7.85 (m, 1H), 7.70-7.61 (m, 2H), 2.56-2.50 (m, 1H), 1.36-1.32 (m, 2H), 1.18-1.13 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 203.3, 191.7, 142.2, 135.4, 133.0, 131.4, 128.8, 128.3, 20.7, 12.8 (2C). **HRMS (ESI):** *m/z* calcd for $C_{11}H_{11}O_2$ $(M+H)^+$: 175.0759, Found: 175.0750.

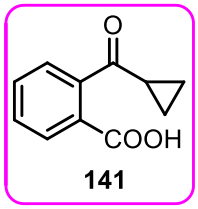
2-(2-Hydroxyethyl)-1*H*-inden-1-one (139a)



139a

This compound was isolated as pale brown semi-solid. Following the general procedure-20, 50 mg of **138a** afforded 31.5 mg of **139a** (61% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3405, 2924, 1709, 1605, 1047, 749, 710. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.40 (d, *J* = 7.0 Hz, 1H), 7.34-7.28 (m, 2H), 7.18-7.14 (m, 1H), 6.99 (d, *J* = 7.1 Hz, 1H), 3.82 (t, *J* = 6.1 Hz, 2H), 2.60-2.56 (m, 2H), 2.15 (br. s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.0, 145.0, 144.5, 137.3, 134.0, 130.6, 128.3, 122.8, 121.5, 61.2, 28.7. **HRMS (ESI):** *m/z* calcd for $C_{11}H_9O$ $(M-OH)^+$: 157.0653, Found: 157.0642.

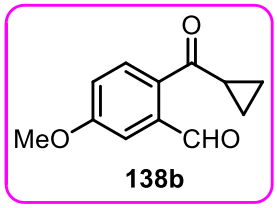
2-(Cyclopropanecarbonyl)benzoic acid (141)



141

This compound was isolated as pale yellow liquid. Following the general procedure-20 (by using DCE as solvent), 50 mg of **138a** afforded 50 mg of **141** (91% yield). R_f = 0.5 (hexane/EtOAc = 3/7). **IR (thin film, neat):** ν_{max}/cm^{-1} 3209, 3012, 1730, 1694, 1382, 1224, 766. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.00 (d, *J* = 1.9 Hz, 1H), 7.67-7.60 (m, 1H), 7.57-7.53 (m, 1H), 7.50-7.48 (m, 1H), 7.16 (br. s, 1H), 2.28 (s, 1H), 1.32 (s, 2H), 1.08 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.1, 144.1, 132.9 (2C), 130.2, 129.9 (2C), 126.6, 21.7, 12.1. **HRMS (ESI):** *m/z* calcd for $C_{11}H_9O_2$ $(M-OH)^+$: 173.0603, Found: 173.0594.

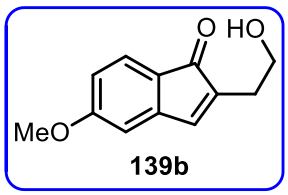
2-(Cyclopropanecarbonyl)-5-methoxybenzaldehyde (138b)



138b

This compound was isolated as pale yellow solid. Following the general procedure-19, 100 mg of **137b** (when R = 5-OMe) afforded 69.5 mg of **138b** (84% yield). M.P = 77-78 ^{o}C. R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2852, 1698, 1680, 1568, 1389, 1239, 1121, 995, 755. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.22 (s, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.38 (d, *J* = 2.7 Hz, 1H), 7.16-7.13 (m, 1H), 3.90 (s, 3H), 2.59-2.55 (m, 1H), 1.31-1.27 (m, 2H), 1.13-1.08 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.0, 192.1, 162.2, 138.5, 134.1, 131.0, 118.6, 112.2, 55.7, 19.6, 12.4 (2C). **HRMS (ESI):** *m/z* calcd for $C_{12}H_{13}O_3$ $(M+H)^+$: 205.0865, Found: 205.0852.

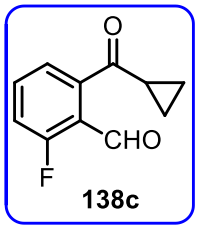
2-(2-Hydroxyethyl)-5-methoxy-1*H*-inden-1-one (139b)



139b

This compound was isolated as pale brown semi-solid. Following the general procedure-20, 50 mg of **138b** afforded 31.5 mg of **139b** (63% yield). R_f = 0.5 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 3418, 2925, 1703, 1597, 1471, 1233, 1093, 780. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37 (d, *J* = 7.8 Hz, 1H), 7.14-7.13 (m, 1H), 6.57-6.53 (m, 2H), 3.85 (s, 3H), 3.81 (t, *J* = 6.0 Hz, 2H), 2.59-2.56 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.6, 164.9, 147.2, 142.7, 139.2, 124.8, 123.3, 110.7, 109.4, 61.2, 55.7, 29.0. **HRMS (ESI):** *m/z* calcd for $C_{12}H_{13}O_3$ $(M+H)^+$: 205.0865, Found: 205.0852.

2-(Cyclopropanecarbonyl)-6-fluorobenzaldehyde (138c)

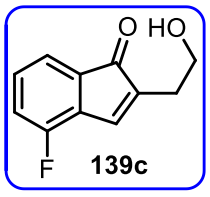


138c

This compound was isolated as pale yellow solid. Following the general procedure-19, 100 mg of **137c** (when R = 6-F) afforded 61.5 mg of **138c** (75% yield). M.P = 75-77 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2920, 1698, 1660, 1568, 1389, 1239, 1121, 995, 755. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.30 (s, 1H), 7.66-7.60 (m, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.32-7.28 (m, 1H), 2.34-2.27 (m, 1H), 1.35-1.30 (m, 2H), 1.14-1.08 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 203.7 (d, *J* = 1.9 Hz), 187.6 (d, *J* = 4.6 Hz), 162.8 (d, *J* = 258.3 Hz), 143.4, 134.8 (d, *J* = 9.6 Hz), 123.42, 123.40, 118.7 (d, *J* = 21.4 Hz), 21.1, 12.8 (2C). **^{19}F NMR (467.5 MHz, CDCl3):** δ -117.8. **HRMS (ESI):** *m/z* calcd for $C_{11}H_{10}FO_2$ $(M+H)^+$: 193.0665, Found: 193.0658.

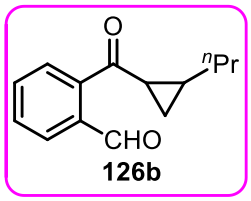
4-Fluoro-2-(2-hydroxyethyl)-1*H*-inden-1-one (139c)

This compound was isolated as pale brown semi-solid. Following the general procedure-20, 50 mg of **138c** afforded 33 mg of **139c** (66% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3419, 2922, 1712, 1607, 1471, 1244, 1044. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.45 (q, J = 1.5 Hz, 1H), 7.24-7.20 (m, 1H), 7.18-7.13 (m, 1H), 7.04 (td, J = 8.5 and 0.8 Hz, 1H), 3.81 (t, J = 6.1 Hz, 2H), 2.58 (td, J = 6.1 and 1.4 Hz, 2H), 2.14 (brs, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 197.6 (d, *J* = 2.9 Hz), 154.8 (d, *J* = 252.6 Hz), 139.8, 137.32 (d, *J* = 2.9 Hz), 132.9 (d, *J* = 4.3 Hz), 130.5 (d, *J* = 6.5 Hz), 129.3 (d, *J* = 15.8 Hz), 122.6 (d, *J* = 21.7 Hz), 119.0 (d, *J* = 2.2 Hz), 61.0, 28.6. **^{19}F NMR (467.5 MHz, CDCl3):** δ -122.4. **HRMS (ESI):** *m/z* calcd for $C_{11}H_{10}FO_2$ $(M+H)^+$: 193.0665, Found: 193.0663.



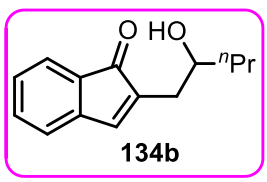
2-(2-Propylcyclopropanecarbonyl)benzaldehyde (126b)

This compound was isolated as colorless liquid. Following the general procedure-17, 100 mg of **133b** (R^1 = H, R^2 = ^{n}Pr) afforded 66.5 mg of **126b** (80% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2959, 1698, 1682, 1594, 1402, 1221, 1018, 764. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.1 (s, 1H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 7.4 Hz, 1H), 7.67-7.63 (m, 1H), 7.61-7.57 (m, 1H), 2.29-2.25 (m, 1H), 1.70-1.67 (m, 1H), 1.57-1.53 (m, 1H), 1.48-1.37 (m, 4H), 1.04-1.00 (m, 1H), 0.94-0.90 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.8, 191.7, 142.4, 135.3, 133.0, 131.2, 128.7, 128.1, 35.3, 28.6, 28.4, 22.3, 20.1, 13.3. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{17}O_2$ $(M+H)^+$: 217.1229, Found: 217.1224.



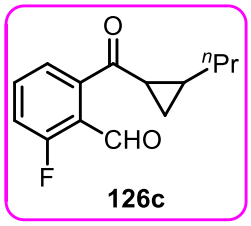
2-(2-Hydroxypentyl)-1*H*-inden-1-one (134b)

This compound was isolated as pale yellow liquid. Following the general procedure-20, 50 mg of **126b** afforded 31 mg of **134b** (62% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3445, 2926, 1711, 1560, 1462, 1044, 751. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.38 (d, *J* = 7.0 Hz, 1H), 7.32-7.26 (m, 2H), 7.16-7.13 (m, 1H), 6.97 (d, *J* = 7.1 Hz, 1H), 3.81 (brs, 1H), 2.56-2.51 (m, 1H), 2.41-2.35 (m, 1H), 2.20 (brs, 1H), 1.52-1.35 (m, 4H), 0.95-0.89 (m, 3H).**^{13}C NMR**



(100 MHz, $CDCl_3$): δ 199.2, 145.4, 144.6, 137.2, 134.0, 130.6, 128.5, 122.8, 121.5, 70.2, 39.4, 33.3, 18.9, 14.0. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{15}O$ $(M\text{-}OH)^+$: 199.1123, Found: 199.1105.

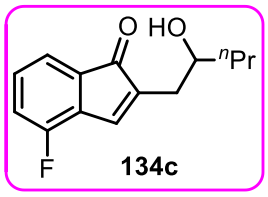
2-Fluoro-6-(2-propylcyclopropanecarbonyl)benzaldehyde (126c)



126c

This compound was isolated as pale yellow liquid. Following the general procedure-17, 100 mg of **133c** (R^1 = 6-F, R^2 = ^{n}Pr) afforded 66 mg of **126c** (78% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3082, 3004, 2873, 2930, 1783, 1703, 1699, 1402, 1256, 803. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.28 (s, 1H), 7.65-7.60 (m, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.30-7.25 (m, 1H), 2.09-2.05 (m, 1H), 1.70-1.67 (m, 1H), 1.57-1.53 (m, 1H), 1.47-1.33 (m, 4H), 1.02-0.97 (m, 1H), 0.94-0.91 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 203.1 (d, *J* = 1.6 Hz), 187.5 (d, *J* = 5.2 Hz), 162.6 (d, *J* = 258.0 Hz), 143.5, 134.8 (d, *J* = 9.3 Hz), 123.38, 123.30 (d, *J* = 3.5 Hz), 118.5 (d, *J* = 21.4 Hz), 35.4, 28.8, 28.2, 22.2, 20.0, 13.8. **^{19}F NMR (374 MHz, CDCl3):** δ -117.8. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{16}FO_2$ $(M+H)^+$: 235.1134, Found: 335.1126.

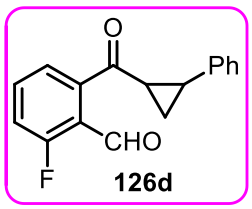
4-Fluoro-2-(2-hydroxypentyl)-1*H*-inden-1-one (134c)



134c

This compound was isolated as pale yellow liquid. Following the general procedure-20, 50 mg of **126c** afforded 30 mg of **134c** (60% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3419, 2959, 1713, 1611, 1471, 1241, 988, 761. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45 (s, 1H), 7.23-7.21 (m, 1H), 7.18-7.13 (m, 1H), 7.04 (t, *J* = 8.5 Hz, 1H), 3.82-3.81 (m, 1H), 2.56-2.52 (m, 1H), 2.42-2.36 (m, 1H), 2.04 (brs, 1H), 1.52-1.36 (m, 4H), 0.95-0.92 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.8, 154.8 (d, *J* = 252.2 Hz), 140.1, 137.3 (d, *J* = 2.6 Hz), 132.9 (d, *J* = 4.7 Hz), 130.5 (d, *J* = 6.3 Hz), 129.4 (d, *J* = 16.6 Hz), 122.5 (d, *J* = 21.5 Hz), 119.0 (d, *J* = 2.3 Hz), 70.1, 39.4, 33.2, 18.9, 14.0, **^{19}F NMR (374 MHz, CDCl3):** δ -122.4. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{16}FO_2$ $(M+F)^+$: 335.1134, Found: 235.1122.

2-Fluoro-6-(2-phenylcyclopropanecarbonyl)benzaldehyde (126d)

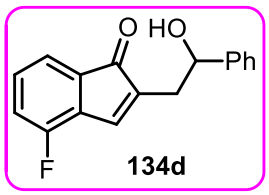


126d

This compound was isolated as pale yellow liquid (as mixture with deprotected aldehyde A, A:B = 5:1). Following the general procedure-17, 100 mg of **133d** (R^1 = 2-F, R^2 = Ph) afforded 65 mg of **126d** (mixture)

(75% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3050, 3000, 2850, 2900, 1780, 1700, 1695, 1400, 1250, 800. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.27 (s, 1H, B), 7.58-7.52 (m, 1H, B), 7.37-7.30 (m, 1H), 7.28-7.23 (m, 2H), 7.21-7.13 (m, 2H), 7.11 (d, *J* = 8.3 Hz, 3H), 7.08 (s, 1H, B), 6.11 (s, 1H), 4.0-3.9 (m, 1H), 3.92-3.79 (m, 3H), 2.82-2.76 (m, 1H, B), 2.76-2.68 (m, 1H), 2.62-2.56 (m, 1H), 2.51-2.45 (m, 1H, B), 2.0-1.94 (m, 1H, B), 1.89-1.82 (m, 1H), 1.64-1.57 (m, 1H, B), 1.54-1.47 (m, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 203.3 (d, *J* = 1.7 Hz), 201.7 (d, *J* = 1.8, B), 187.4 (d, *J* = 5.4 Hz, B), 161.4 (d, *J* = 250.9 Hz), 143.5, 143.2 (B), 140.3, 139.9 (B), 135.0 (d, *J* = 9.1 Hz, B), 131.1 (d, *J* = 9.0 Hz), 128.6 (2C), 126.8 (B), 126.7, 126.3 (B), 126.0, 123.3 (d, *J* = 3.4 Hz), 122.3 (d, *J* = 3.4 Hz), 122.2 (d, *J* = 12.3 Hz, B), 118.8 (d, *J* = 21.4 Hz), 117.3 (d, *J* = 22.2 Hz), 98.6 (d, *J* = 4.5 Hz), 65.5 (d, *J* = 15.5 Hz), 65.4, 34.2, 32.8 (B), 31.2 (B), 30.2, 20.4, 20.1 (B). **^{19}F NMR (467.5 MHz, CDCl3):** δ -115.3 and -117.8. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{14}FO_2$ $(M+H)^+$: 269.0978, Found: 269.0988.

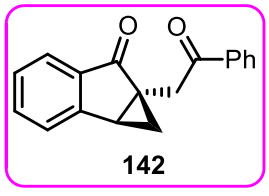
4-Fluoro-2-(2-hydroxy-2-phenylethyl)-1*H*-inden-1-one (134d)



134d

This compound was isolated as pale yellow liquid. Following the general procedure-20, 50 mg of **126d** afforded 33.5 mg of **134d** (67% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3419, 1713, 1610, 1470, 1242, 1050, 795, 701, 544. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.38-7.32 (m, 5H), 7.29-7.25 (m, 1H), 7.21-7.20 (m, 1H), 7.16-7.11 (m, 1H), 7.03-6.99 (m,1H), 4.94-4.91 (m, 1H), 2.74-2.73 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.6, 154.8 (d, *J* = 252.4 Hz), 143.6, 140.5, 136.6 (d, *J* = 2.3 Hz), 132.8 (d, *J* = 4.4 Hz), 130.6 (d, *J* = 6.2 Hz), 129.3 (d, *J* = 16.2 Hz), 128.5 (2C), 127.8, 125.7 (2C), 122.5 (d, *J* = 21.4 Hz), 119.0 (d, *J* = 2.5 Hz), 72.7, 35.1. **^{19}F NMR (374 MHz, CDCl3):** δ -112.2. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{10}FO$ $(M-OH)^+$: 251.0872, Found: 251.0866.

6a-(2-Oxo-2-phenylethyl)-1,6a-dihydrocyclopropa[a]inden-6(1a*H*)-one (142)

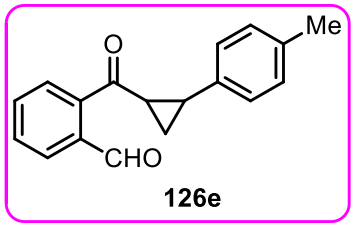


142

This compound was isolated as colorless solid. Following the general procedure-17, 100 mg of **134a** afforded 75 mg of **142** (71% yield). M.P = 93-94 °C. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2925, 1712, 1683, 1609, 1217, 1002, 750. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 1H)), 7.61-7.57 (m, 1H), 7.52-7.44 (m, 4H), 7.33-

7.28 (m, 1H), 4.24 (d, *J* = 18.2 Hz, 1H), 3.22 (d, *J* = 18.2 Hz, 1H), 2.91-2.88 (m, 1H), 1.62-1.59 (m, 1H), 1.51-1.49 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 203.1, 196.9, 154.4, 141.9, 136.3, 133.7, 133.3, 128.6 (2C), 128.1 (2C), 126.8, 125.0, 124.5, 38.6, 37.4, 33.5, 26.9. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{15}O_2$ $(M+H)^+$: 263.1072, Found: 263.1064.

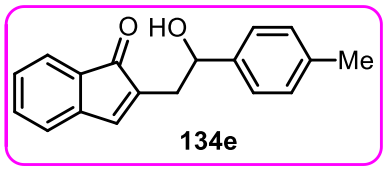
2-(2-(*p*-Tolyl)cyclopropanecarbonyl)benzaldehyde (126e)



126e

This compound was isolated as pale yellow liquid. Following the general procedure-17, 100 mg of **133e** (R^1 = H, R^2 = *p*-tolyl) afforded 72 mg of **126e** (84% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2931, 1694, 1665, 1519, 1393, 1226, 995, 751. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.24 (s, 1H), 7.96-7.94 (m, 1H), 7.81-7.79 (m, 1H), 7.68-7.63 (m, 2H), 7.16-7.14 (m, 2H), 7.10-7.08 (m, 2H), 2.82-2.71 (m, 2H), 2.35 (s, 3H), 2.05-2.00 (m, 1H), 1.66-1.63 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.2, 191.7, 141.8, 136.7, 136.5, 135.5, 133.1, 131.5, 129.3 (2C), 129.1, 128.3, 126.1 (2C), 32.6, 31.3, 21.0, 20.1. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{17}O_2$ $(M+H)^+$: 265.1229, Found: 265.1240.

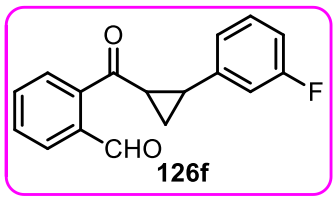
2-(2-Hydroxy-2-(p-tolyl)ethyl)-1*H*-inden-1-one (134e)



134e

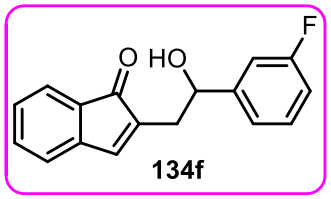
This compound was isolated as pale yellow semi-solid. Following the general procedure-20, 50 mg of **126e** afforded 35 mg of **134e** (70% yield). R_f = 0.5 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 3433, 2923, 1709, 1605, 1447, 1060, 748. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.41 (d, *J* = 7.0 Hz, 1H), 7.33-7.30 (m, 2H), 7.20-7.15 (m, 4H), 6.97 (d, *J* = 7.1 Hz, 1H), 4.93-4.90 (m, 1H), 2.76-2.74 (m, 2H), 2.58-2.57 (m, 1H), 2.36 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.1, 145.7, 144.5, 140.8, 137.3, 136.6, 134.0, 130.6, 129.1 (2C), 128.3, 125.7 (2C), 122.8, 121.6, 72.7, 35.2, 21.6. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{17}O_2$ $(M+H)^+$: 265.1229, Found: 265.1241.

2-(2-(3-Fluorophenyl)cyclopropanecarbonyl)benzaldehyde (126f)



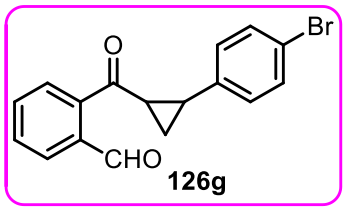
This compound was isolated as pale yellow semi-solid. Following the general procedure-17, 100 mg of **133f** (R^1 = H, R^2 = *m*-FC_6H_4) afforded 70 mg of **126f** (81% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3068, 1710, 1694, 1589, 1275, 1008, 785, 688. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.22 (s, 1H), 7.96-7.94 (m, 1H), 7.80-7.78 (m, 1H), 7.70-7.64 (m, 2H), 7.31-7.26 (m, 1H), 7.01-6.99 (m, 1H), 6.97-6.92 (m, 1H), 6.87 (d, *J* = 9.9 Hz, 1H), 2.84-2.73 (m, 2H), 2.05-2.00 (m, 1H), 1.67-1.62 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.0, 191.6, 163.0 (d, *J* = 245.0 Hz), 142.5 (d, *J* = 7.4 Hz), 141.5, 135.4, 133.2, 131.6, 130.1 (d, *J* = 8.5 Hz), 129.4, 128.2, 121.1 (d, *J* = 2.8 Hz), 113.7 (d, *J* = 21.0 Hz), 113.0 (d, *J* = 21.8 Hz), 32.5, 30.5 (d, *J* = 1.8 Hz), 20.3. **^{19}F NMR (374 MHz, CDCl3):** δ -112.9. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{14}FO_2$ $(M+H)^+$: 269.0978, Found: 269.0974.

2-(2-(3-Fluorophenyl)-2-hydroxyethyl)-1*H*-inden-1-one (134f)



This compound was isolated as pale yellow semi-solid. Following the general procedure-20, 50 mg of **126f** afforded 33 mg of **134f** (66% yield). R_f = 0.5 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 3429, 2916, 1708, 1605, 1455, 1246, 747. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.42 (d, *J* = 7.0 Hz, 1H), 7.34-7.28 (m, 2H), 7.20-7.12 (m, 4H), 7.00-6.95 (m, 2H), 4.97-4.93 (m, 1H), 2.93-2.92 (m, 1H), 2.81-2.68 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.2, 163.0 (d, *J* = 244.6 Hz), 146.5 (d, *J* = 6.5 Hz), 146.2, 144.3, 136.1, 134.1, 130.5, 130.0 (d, *J* = 8.1 Hz), 128.4, 123.0, 121.7, 121.3 (d, *J* = 2.7 Hz), 114.4 (d, *J* = 21.0), 112.6 (d, *J* = 21.9 Hz), 72.1 (d, *J* = 1.2 Hz), 35.5. **^{19}F NMR (374 MHz, CDCl3):** δ -112.7. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{12}FO$ $(M-OH)^+$: 251.0872, Found: 251.0861.

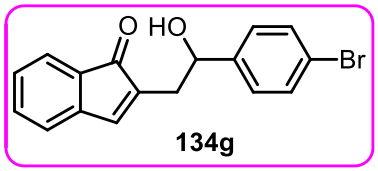
2-(2-(4-Bromophenyl)cyclopropanecarbonyl)benzaldehyde (126g)



This compound was isolated as pale yellow solid. Following the general procedure-17, 100 mg of **133g** (R^1 = H, R^2 = *p*-BrC_6H_4) afforded 72 mg of **126g** (84% yield). M.P = 75-77 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3066, 1700, 1694, 1489, 1277, 1009, 760. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.22 (s, 1H), 7.95 (d, *J* = 7.4 Hz,

1H), 7.78-7.76 (m, 1H), 7.70-7.66 (m, 2H), 7.45 (d, *J* = 7.7 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 2.81-2.68 (m, 2H), 2.05-2.00 (m, 1H), 1.66-1.63 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.0, 191.6, 141.5, 138.9, 135.4, 133.2, 131.7 (2C), 131.6, 129.5, 128.2, 127.9 (2C), 120.5, 32.5, 30.5, 20.1. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{14}BrO_2$ $(M+H)^+$: 329.0177, Found: 329.0194.

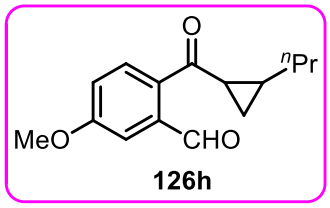
2-(2-(4-Bromophenyl)-2-hydroxyethyl)-1*H*-inden-1-one (134g)



134g

This compound was isolated as pale yellow semi-solid. Following the general procedure-20, 50 mg of **126g** afforded 31.5 mg of **134g** (63% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3433, 2924, 1713, 1603, 1489, 1070, 1010, 757. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.49-7.47 (m, 2H), 7.41 (d, *J* = 7.0 Hz, 1H), 7.34-7.26 (m, 3H), 7.20-7.17 (m, 2H), 6.98 (d, *J* = 7.0 Hz, 1H), 4.94-4.91 (m, 1H), 2.87-2.86 (m, 1H), 2.75-2.72 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.2, 146.2, 144.3, 142.7, 136.1, 134.1, 131.5 (2C), 130.5, 128.5, 127.5 (2C), 123.0, 121.7, 121.3, 721, 35.5. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{12}BrO_2$ $(M-H)^+$: 327.0021, Found: 327.0001.

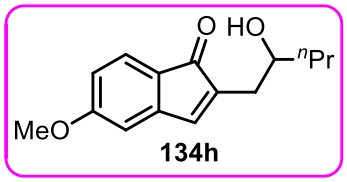
5-Methoxy-2-(2-propylcyclopropanecarbonyl)benzaldehyde (126h)



126h

This compound was isolated as pale yellow liquid. Following the general procedure-17, 100 mg of **133h** (R^1 = 5-OMe, R^2 = ^{n}Pr) afforded 69 mg of **126h** (81% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2960, 2930, 2873, 1698, 1601, 1598, 1358, 1038, 924, 733. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.21 (s, 1H), 7.90 (d, *J* = 8.6 Hz, 1H), 7.38 (d, *J* = 2.6 Hz, 1H), 7.15-7.13 (m, 1H), 3.91 (s, 3H), 2.33-2.31 (m, 1H), 1.68-1.63 (m, 1H), 1.55-1.50 (m, 1H), 1.48-1.39 (m, 4H), 1.00-0.92 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.6, 192.0, 162.1, 138.5, 134.4, 130.8, 118.6, 112.1, 55.7, 35.4, 27.8, 27.5, 22.3, 19.6, 13.8. **HRMS (ESI):** *m/z* calcd for $C_{15}H_{19}O_3$ $(M+H)^+$: 247.1334, Found: 247.1322.

2-(2-Hydroxypentyl)-5-methoxy-1*H*-inden-1-one (134h)

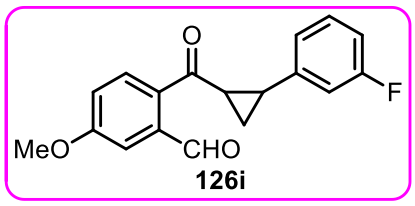


134h

This compound was isolated as pale yellow solid. Following the general procedure-20, 50 mg of **126h** afforded 31.5 mg of **134h** (63% yield). M.P = 78-80 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR**

(thin film, neat): ν_{max}/cm^{-1} 3445, 2958, 1699, 1615, 1596, 1432, 1290, 709. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.34 (d, *J* = 7.8 Hz, 1H), 7.12 (s, 1H), 6.55-6.50 (m, 2H), 3.83 (s, 3H), 3.81-3.77 (m, 1H), 2.54-2.49 (m, 1H), 2.40-2.34 (m, 1H), 1.51-1.35 (m, 4H), 0.94-0.91 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.8, 164.9, 147.9, 143.1, 139.1, 124.8, 123.3, 110.6, 109.4, 70.1, 55.6, 39.4, 33.5, 18.9, 14.0. **HRMS (ESI):** *m/z* calcd for $C_{15}H_{17}O_2$ $(M\text{-}OH)^+$: 229.1229, Found: 229.1225.

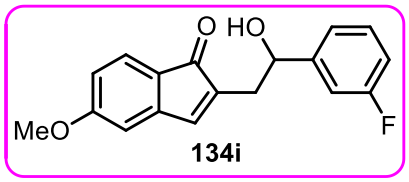
2-(2-(3-Fluorophenyl)cyclopropanecarbonyl)-5-methoxybenzaldehyde (126i)



126i

This compound was isolated as pale yellow solid. Following the general procedure-17, 100 mg of **133i** (R^1 = 5-OMe, R^2 = *m*-FC_6H_4) afforded 71.5 mg of **126i** (83% yield). M.P = 93-96 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2935, 2356, 1694, 1598, 1451, 1289, 1076, 786, 689. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.24 (s, 1H), 7.85 (d, *J* = 8.6 Hz, 1H), 7.39-7.38 (m, 1H), 7.28-7.21 (m, 1H), 7.13-7.10 (m, 1H), 6.98-6.91 (m, 2H), 6.86-6.84 (m, 1H), 2.80-2.70 (m, 2H), 1.97-1.94 (m, 1H), 1.59-1.56 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.5, 192.0, 162.5, 142.6, 138.8, 133.4, 131.0, 130.1, 130.1 (d, *J* = 8.5 Hz), 122.1 (d, *J* = 2.7 Hz), 118.6, 113.7 (d, *J* = 21.0 Hz), 112.9 (d, *J* = 21.8 Hz), 112.6, 55.8, 31.4, 30.0 (d, *J* = 1.3 Hz), 19.8. **^{19}F NMR (374 MHz, CDCl3):** δ -112.9. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{16}FO_3$ $(M+H)^+$: 299.1083, Found: 299.1068.

2-(2-(3-Fluorophenyl)-2-hydroxyethyl)-5-methoxy-1*H*-inden-1-one (134i)

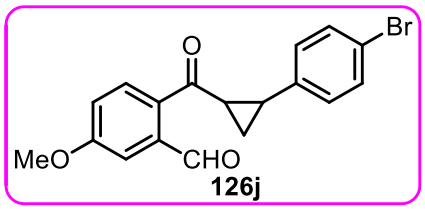


134i

This compound was isolated as pale yellow solid. Following the general procedure-20, 50 mg of **126i** afforded 31.5 mg of **134i** (63% yield). M.P = 82-84 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3466, 2924, 1699, 1615, 1474, 1258, 1092, 799, 462. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.35-7.33 (m, 1H), 7.31-7.25 (m, 1H), 7.13-7.09 (m, 2H), 7.01 (s, 1H), 6.96-6.91 (m, 1H), 6.53-6.51 (m, 2H), 4.92-4.89 (m, 1H), 3.82 (s, 3H), 3.29 (brs, 3H), 2.77-2.64 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.8, 165.0, 163.0 (d, *J* = 244.4 Hz), 147.0, 146.6 (d, *J* = 6.7 Hz), 143.8, 138.0, 129.9 (d, *J* = 8.2 Hz), 125.0, 123.1, 121.3 (d, *J* = 2.8 Hz), 114.3 (d, *J* = 20.9 Hz), 112.6 (d, *J* = 21.8 Hz), 110.8, 109.6, 72.1 (d,

J = 1.2 Hz), 55.7, 35.8. **^{19}F NMR (374 MHz, CDCl3):** δ -112.8. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{14}FO_2$ $(M+Na)^+$: 281.0978, Found: 281.0981.

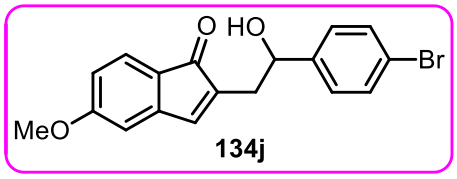
2-(2-(4-Bromophenyl)-cyclopropanecarbonyl)-5-methoxybenzaldehyde (126j)



126j

This compound was isolated as pale yellow solid. Following the general procedure-17, 100 mg of **133j** (R^1 = 5-OMe, R^2 = *p*-BrC_6H_4) afforded 74 mg of **126j** (86% yield). M.P = 118-120 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2939, 1694, 1651, 1595, 1287, 1074, 615, 519. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.25 (s, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.43-7.37 (m, 3H), 7.11-7.09 (m, 1H), 7.04 (d, *J* = 7.8 Hz, 2H), 3.90 (s, 3H), 2.77-2.66 (m, 2H), 1.98-1.93 (m, 1H), 1.59-1.54 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.4, 191.9, 162.4, 139.1, 138.8, 133.4, 131.6 (2C), 131.0, 127.9(2C), 120.4, 118.5, 112.6, 55.8, 31.4, 29.8, 19.6. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{16}BrO_3$ $(M+H)^+$: 359.0283, Found: 359.0277.

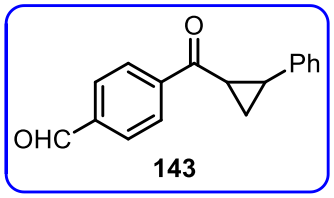
2-(2-(4-Bromophenyl)-2-hydroxyethyl)-5-methoxy-1*H*-inden-1-one (134j)



134j

This compound was isolated as pale yellow solid. Following the general procedure-20, 50 mg of **126j** afforded 30 mg of **134j** (60% yield). M.P = 127-129 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3430, 2923, 1698, 1618, 1594, 1472, 1233. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45 (m, 2H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.25-7.23 (m, 2H), 6.99 (s, 1H), 6.54-6.52 (m, 2H), 4.91-4.88 (m, 1H), 3.83 (m, 3H), 2.73-2.69 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.8, 165.0, 147.0, 143.9, 142.8, 137.9, 131.4(2CH), 127.4 (2CH), 125.0, 123.1, 121.2, 110.9, 109.6, 72.1, 55.7, 35.8. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{15}BrNaO_3$ $(M+Na)^+$: 381.0102, Found: 381.0114.

4-(2-Phenylcyclopropanecarbonyl)benzaldehyde (143)



143

This compound was isolated as pale yellow solid. Following the general procedure-17, 100 mg of **133k** (R^1 = H, R^2 = Ph, para aldehyde) afforded 74 mg of **143** (87% yield). M.P = 70-73 ^oC. R_f =

0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3031, 1709, 1660, 1572, 1401, 1219, 1027, 988, 834. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.06 (s, 1H), 8.13-8.07 (m, 2H), 7.96-7.91 (m, 2H), 7.33-7.28 (m, 2H), 7.25-7.20 (m, 1H), 7.19-7.15 (m, 2H), 2.93-2.87 (m, 1H), 2.76-2.70 (m, 1H), 1.98-1.92 (m, 1H), 1.65-1.59 (m, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 198.0, 191.6, 141.9, 140.0, 138.9, 129.8 (2C), 128.7 (2C), 128.6 (2C), 126.9, 126.2 (2C), 30.8, 29.9, 19.8. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{15}O_2$ $(M+H)^+$: 251.1072, Found: 251.1062.

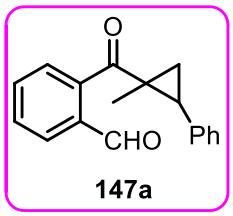
General procedure-21: Synthesis of cyclopropyl keto-aldehydes 147a-147f

The compounds **147a-147f** were synthesized by following the procedure described for the synthesis of compound **126a-126j** (see Scheme 82).

General procedure-22: Synthesis of 2,2-disubstituted-3-hydroxyindanones (148a-148d, 149a-149b)

The compounds (**148a-148d**, **149a-149b**) were synthesized by following the described procedure 20.

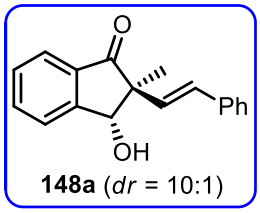
2-(1-Methyl-2-phenylcyclopropanecarbonyl)benzaldehyde (147a)



147a

This compound was isolated as pale yellow liquid. Following the general procedure-21, 100 mg of **146a** (R^1 = Ph, R^2 = Me) afforded 75 mg of 1**47a** (87% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3071, 1702, 1694, 1576, 1454, 1202, 983, 759. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.07 (s, 1H), 7.92-7.90 (m, 1H), 7.70-7.65 (m, 1H), 7.62-7.58 (m, 1H), 7.38-7.34 (m, 5H), 7.28-7.24 (m, 1H), 3.03-2.99 (m, 1H), 2.00-1.97 (m, 1H), 1.44-1.41 (m, 1H), 0.93 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 208.5, 190.9, 142.1, 136.6, 133.9, 133.5, 131.9, 129.4, 129.3 (2C), 126.9, 126.4, 35.1, 33.5, 22.4, 15.4. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{17}O_2$ $(M+H)^+$: 265.1229, Found: 265.1223.

(*E*)-3-Hydroxy-2-methyl-2-styryl-2,3-dihydro-1*H*-inden-1-one (148a)

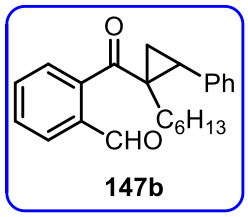


148a (*dr* = 10:1)

This compound was isolated as pale yellow solid. Following the general procedure-22, 50 mg of **147a** afforded 42 mg of **148a** (84% yield). M.P =

75-77 °C. R_f = 0.5 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 3425, 2924, 1699, 1607, 1448, 1288, 1051, 746. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.83 (d, *J* = 7.6 Hz, 1H), 7.79-7.72 (m, 2H), 7.56-7.52 (m, 1H), 7.40-7.38 (m, 2H), 7.33-7.28 (m, 2H), 7.26-7.22 (m, 1H), 6.64 (d, *J* = 16.3 Hz, 1H), 6.42 (d, *J* = 16.3 Hz, 1H), 5.37 (d, *J* = 6.2 Hz, 1H), 2.33 (d, *J* = 7.2 Hz, 1H), 1.41 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 205.4, 152.5, 136.8, 135.5, 134.3, 131.1, 130.6, 129.6, 128.5 (2C), 127.6, 126.3 (3C), 125.8, 124.1, 57.2, 18.7. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{15}O_2$ $(M-H)^+$: 263.1072, Found: 263.1066.

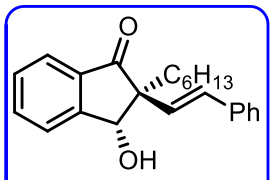
2-(1-Hexyl-2-phenylcyclopropanecarbonyl)benzaldehyde (147b)



147b

This compound was isolated as pale yellow semi-solid. Following the general procedure-21, 100 mg of **146b** (R^1 = Ph, R^2 = C_6H_3) afforded 75 mg of **147b** (85% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2928, 1703, 1668, 1455, 1203, 758, 699. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.13 (s, 1H), 7.97 (d, *J* = 7.56, 1H), 7.69-7.59 (m, 2H), 7.53-7.51 (m, 1H), 7.38-7.34 (m, 2H), 7.31-7.26 (m, 3H), 2.89-2.85 (m, 1H), 1.97-1.93 (m, 1H), 1.65-1.60 (m, 1H), 1.47-1.43 (m, 1H), 1.21-1.17 (m, 2H), 1.10-0.90 (m, 7H), 0.77-0.73 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 206.5, 190.8, 141.6, 136.4, 134.3, 133.2, 130.5, 129.9, 129.1 (2C), 128.3 (2C), 127.3, 126.9, 39.3, 34.9, 31.2, 29.1, 28.7, 27.4, 22.3, 18.7, 13.9. **HRMS (ESI):** *m/z* calcd for $C_{23}H_{27}O_2$ $(M+H)^+$: 335.2011, Found: 335.2023.

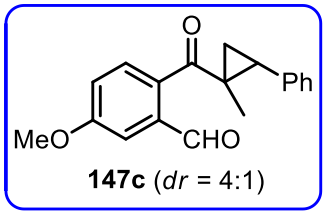
(*E*)-2-Hexyl-3-hydroxy-2-styryl-2,3-dihydro-1*H*-inden-1-one (148b)



148b (*dr* = 10:1)

This compound was isolated as pale yellow liquid. Following the general procedure-22, 50 mg of **147b** afforded 40.5 mg of **148b** (81% yield). R_f = 0.5 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 3434, 2928, 1703, 1694, 1605, 1466, 969, 748. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.77-7.71 (m, 2H), 7.54-7.50 (m, 1H), 7.40-7.38 (m, 2H), 7.33-7.28 (m, 2H), 7.26-7.22 (m, 1H), 6.64 (d, *J* = 16.4 Hz, 1H), 6.51 (d, *J* = 16.4 Hz, 1H), 5.41 (s, 1H), 2.24-2.22 (m, 1H), 1.98-1.90 (m, 1H), 1.77-1.70 (m, 1H), 1.37-1.31 (m, 8H), 0.89-0.83 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 204.6, 152.6, 137.0, 135.3, 135.0, 130.62, 130.60, 129.5, 128.5 (2C), 127.5, 126.2 (2C), 125.3, 123.8, 60.6, 34.1, 31.5, 29.9, 24.6, 22.6, 14.0. **HRMS (ESI):** *m/z* calcd for $C_{23}H_{27}O_2$ $(M+H)^+$: 335.2011, Found: 335.2024.

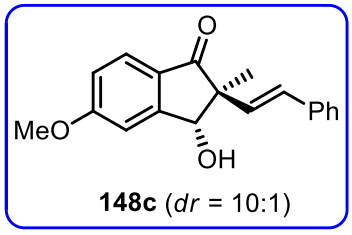
5-Methoxy-2-(1-methyl-2-phenylcyclopropanecarbonyl)benzaldehyde (147c)



147c (*dr* = 4:1)

This compound was isolated as pale yellow liquid (mixture of diastereomers A:B = 4:1). Following the general procedure-21, 100 mg of **146c** (R^1 = 5-OMe, R^2 = Ph) afforded 77 mg of **147c** (88% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2938, 1698, 1600, 1494, 1263, 1011, 700. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.05 (s, 1H), 10.03 (s, 1H, diastereomer B), 7.41-7.39 (m, 1H), 7.38-7.37 (m, 1H), 7.35-7.31 (m, 2H), 7.27-7.23 (m, 3H), 7.16-7.13 (m, 1H), 3.91 (s, 3H, diastereomer B), 3.88 (s, 3H), 2.89 (dd, *J* = 7.4 and 9.1 Hz, 1H), 2.29 (d, *J* = 1.35 Hz, diastereomer B), 1.97 (dd, *J* = 9.2 and 4.5 Hz, 1H), 1.37 (dd, *J* = 7.2 and 4.6 Hz, 1H), 0.98 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$, diastereomer A):** δ 206.9, 190.8, 160.6, 144.2, 136.6, 136.0, 134.4, 129.8, 129.2 (2C), 128.7, 128.4 (2C), 126.9, 119.5, 114.7, 55.73, 34.5, 33.7, 21.5, 15.9. **^{13}C NMR (125 MHz, $CDCl_3$, diastereomer B):** δ 198.6, 190.6, 161.1, 138.9, 137.5, 135.4, 134.8, 131.0, 129.0, 128.5, 128.2, 126.4, 119.3, 113.2, 55.7, 34.4, 27.5, 23.6, 13.7. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{19}O_3$ $(M+H)^+$: 295.1334, Found: 295.1320.

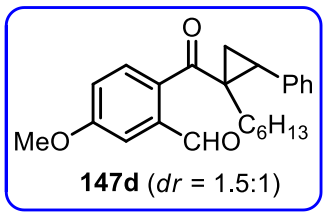
(*E*)-3-hydroxy-5-methoxy-2-methyl-2-styryl-2,3-dihydro-1*H*-inden-1-one (148c)



148c (*dr* = 10:1)

This compound was isolated as pale brown semi-solid. Following the general procedure-22, 50 mg of **147c** afforded 39 mg of **148c** (78% yield). R_f = 0.5 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 2925, 1760, 1606, 1492, 1291, 1251, 1023, 754. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.75 (d, *J* = 8.5 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.31 (dd, *J* = 13.0 and 7.6 Hz, 2H), 7.23 (t, *J* = 6.9 Hz, 1H), 7.19 (s, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 6.64 (d, *J* = 16.2 Hz, 1H), 6.43 (d, *J* = 16.2 Hz, 1H), 5.31 (d, *J* = 2.9 Hz, 1H), 3.95 (s, 3H), 2.31 (d, *J* = 5.6 Hz, 1H), 1.39 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 203.7, 166.0, 155.6, 136.9, 131.4, 130.4, 128.5 (2C), 127.6, 127.3, 126.3 (2C), 125.9, 117.7, 108.7, 57.4, 55.85, 55.84, 18.8. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{19}O_3$ $(M+H)^+$: 295.1334, Found: 295.1324.

2-(1-Hexyl-2-phenylcyclopropanecarbonyl)-5-methoxybenzaldehyde (147d)

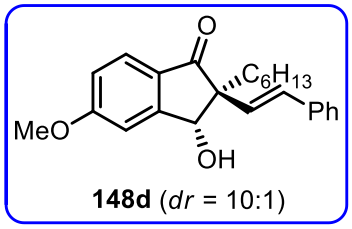


147d (*dr* = 1.5:1)

This compound was isolated as pale yellow semi-solid (mixture of diastereomers A:B = 1.5:1). Following the general procedure-21, 100 mg of **146d** (R^1 = 5-OMe, R^2 = C_6H_{13}) afforded 77 mg of **147d** (86%

yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2929, 1698, 1601, 1495, 1285, 1029, 699. **Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.11 (s, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.55-7.51 (m, 2H), 7.31 (s, 2H), 7.16 (dd, *J* = 8.4 and 1.5 Hz, 2H), 7.06 (s, 1H), 3.94 (s, 3H), 2.76 (t, *J* = 5.3 Hz, 3H), 2.04-1.95 (m, 1H), 1.39-1.29 (m, 6H), 0.98 (brs, 3H), 0.76 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 204.3, 190.9, 161.1, 144.1, 137.4, 136.5, 135.3, 131.3, 129.7, 129.0 (2C), 128.4, 119.1, 112.9, 55.7, 39.3 (2C), 31.3, 29.6, 29.1, 27.6, 22.3, 13.9. **Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.14 (s, 1H), 7.49 (s, 1H), 7.42-7.34 (m, 7H), 3.92 (s, 3H), 1.68-1.58 (m, 4H), 1.50-1.41 (m, 2H), 1.24-1.16 (m, 3H), 1.14-1.05 (m, 3H), 0.93-0.88 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.3, 190.7, 161.2, 144.0, 137.8, 135.2, 133.9, 129.7, 129.3 (2C), 128.6, 126.9, 119.3, 112.5, 55.7, 33.7 (2C), 31.6, 29.5, 28.8, 27.1, 22.6, 17.2, 14.1. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{29}O_3$ $(M+H)^+$: 365.2117, Found: 365.2128.

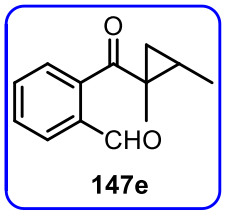
(*E*)-2-hexyl-3-hydroxy-5-methoxy-2-styryl-2,3-dihydro-1*H*-inden-1-one (148d)



148d (*dr* = 10:1)

This compound was isolated as pale yellow liquid. Following the general procedure-22, 50 mg of **147d** afforded 37.5 mg of **148d** (75% yield). R_f = 0.5 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 3430, 2926, 1694, 1599, 1489, 1261, 1156, 748. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.74 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.24 (t, *J* = 6.9 Hz, 1H), 7.18 (s, 1H), 7.03 (dd, *J* = 8.7 and 0.2 Hz, 1H), 6.63 (d, *J* = 16.4 Hz, 1H), 6.53 (d, *J* = 16.4 Hz, 1H), 5.35 (d, *J* = 3.9 Hz, 1H), 3.95 (s, 3H), 2.25 (d, *J* = 8.2 Hz, 1H), 1.29-1.21 (m, 10H), 0.85 (t, J = 6.5 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.9, 165.9, 155.7, 137.1, 131.1, 130.3, 128.6 (2C), 128.0, 127.5, 126.4, 126.3, 125.5, 117.5, 108.3, 60.6, 55.8, 34.4, 31.6, 30.0, 29.7, 24.8, 22.7, 14.1. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{29}O_3$ $(M+Na)^+$: 365.2117, Found: 365.2125.

2-(1,2-Dimethylcyclopropanecarbonyl)benzaldehyde (147e)

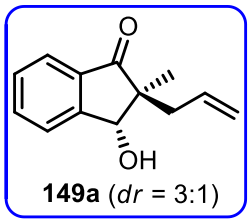


147e

This compound was isolated as colorless liquid. Following the general procedure-21, 100 mg of **146e** (R^1 = Me, R^2 = Me) afforded 67.5 mg of **147e** (82% yield). M.P = 99-103 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2970, 1703, 1691, 1576, 1210, 983, 745. **^{1}H NMR (400**

MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.62-7.58 (m, 1H), 7.54-7.50 (m, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 1.58-1.56 (m, 1H), 1.20 (s, 3H), 1.16-1.15 (m, 3H), 0.56-0.55 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 209.2, 190.8, 142.3, 133.7, 133.4, 131.0, 129.3, 126.5, 31.3, 25.9, 24.6, 14.6, 13.4. **HRMS (ESI):** *m/z* calcd for $C_{13}H_{15}O_2$ $(M+H)^+$: 203.1072, Found: 203.1061.

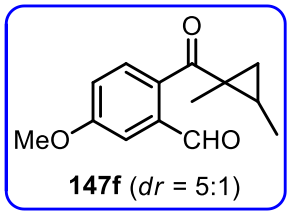
2-Allyl-3-hydroxy-2-methyl-2,3-dihydro-1*H*-inden-1-one (149a)



149a (*dr* = 3:1)

This compound was isolated as pale yellow liquid (mixture of diastereomers A:B = 3:1). Following the general procedure-22, 50 mg of **147e** afforded 42.5 mg of **149a** (85% yield). R_f = 0.5 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 3426, 2976, 1699, 1606, 1293, 986, 765. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.81-7.67 (m, 4H), 7.55-7.46 (m, 1H, diastereomer B), 5.86-5.68 (m, 1H), 5.20-5.13 (m, 2H), 5.11 (d, *J* = 9.9 Hz, 1H, diastereomer B), 5.06-4.96 (m, 1H, diastereomer B), 2.46 (d, *J* = 7.3 Hz, 2H), 2.14 (brs, 1H), 1.73 (d, *J* = 5.8 Hz, 1H, diastereomer B), 1.28 (s, 3H, diastereomer B), 1.17 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 207.6, 152.9, 135.4 (2C), 134.9 (diastereomer B), 134.5 (diastereomer B), 133.9, 129.5 (diastereomer B), 129.4, 125.7, 125.6 (diastereomer B), 123.7, 123.6 (diastereomer B), 118.8, 118.3 (diastereomer B), 78.7 (diastereomer B), 74.8, 54.3, 53.9 (diastereomer B), 40.6, 38.7 (diastereomer B), 21.6 (diastereomer B), 18.6. **HRMS (ESI):** *m/z* calcd for $C_{13}H_{13}O_2$ $(M-H)^+$: 201.0916, Found: 201.0981.

2-(1,2-Dimethylcyclopropanecarbonyl)-5-methoxybenzaldehyde (147f)

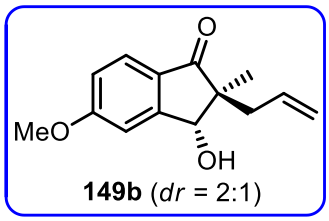


147f (*dr* = 5:1)

This compound was isolated as pale yellow liquid (mixture of diastereomers A:B = 5:1). Following the general procedure-21, 100 mg of **146f** (R^1 = 5-OMe, R^2 = Me) afforded 68.5 mg of **147f** (81% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2968, 1694, 1673, 1602, 1495, 1275, 1031, 836. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.0 (s, 1H), 9.95 (s, 1H, diastereomer B), 7.44 (d, *J* = 1.7 Hz, 1H, diastereomer B), 7.41 (d, *J* = 1.6 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.14 (dd, *J* = 8.4 and 1.3 Hz, 1H), 3.89 (s, 3H), 1.98 (s, 3H, diastereomer B), 1.86 (d, *J* = 6.9 Hz, 2H, diastereomer B), 1.66-1.59 (m, 1H), 1.59-1.50 (m, 1H), 1.28 (s, 3H), 1.21 (d, *J* = 6.1 Hz, 3H), 0.56-0.51 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 207.5, 197.8

(diastereomer B), 190.7, 190.6 (diastereomer B), 160.9 (diastereomer B), 160.6, 144.2 (diastereomer B), 140.1 (diastereomer B), 137.1 (diastereomer B), 135.9, 135.2 (diastereomer B), 134.9, 130.7 (diastereomer B), 128.8, 119.6, 119.4 (diastereomer B), 113.4, 112.4 (diastereomer B), 55.7, 31.3, 24.9, 23.9, 15.3, 15.1 (diastereomer B), 13.5, 11.4 (diastereomer B). **HRMS (ESI):** *m/z* calcd for $C_{14}H_{17}O_3$ $(M+H)^+$: 233.1178, Found: 233.1167.

2-Allyl-3-hydroxy-5-methoxy-2-methyl-2,3-dihydro-1*H*-inden-1-one (149b)



149b (*dr* = 2:1)

This compound was isolated as pale yellow liquid (mixture of diastereomers A:B = 2:1). Following the general procedure-22, 50 mg of **147f** afforded 41.5 mg of **149b** (83% yield). R_f = 0.5 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 3424, 2926, 1691, 1597, 1492, 1258, 1104, 1027, 915. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.72 (d, *J* = 4.2 Hz, 1H, diastereomer B), 7.70 (d, *J* = 4.0 Hz, 1H), 7.16 (d, *J* = 2.2 Hz, 1H), 7.14 (d, *J* = 2.2 Hz, 1H, diastereomer B), 7.03 (t, *J* = 2.7 Hz, 1H), 7.01 (t, *J* = 3.2 Hz, 1H, diastereomer B), 5.84-5.76 (m, 1H, diastereomer B), 5.75-5.65 (m, 1H), 5.19-5.13 (m, 2H, diastereomer B), 5.13-5.08 (m, 2H), 5.05-4.99 m, 1H, diastereomer B), 4.93 (brs, 1H), 3.94 (s, 3H, diastereomer B), 3.93 (s, 3H), 2.49-2.46 (m, 2H, diastereomer B), 2.46-2.42 (m, 2H), 1.68 (brs, 1H), 1.64 (brs, 1H, diastereomer B), 1.28 (s, 3H, diastereomer B), 1.16 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$, Diastereomer A):** δ 205.7, 165.9, 156.1, 134.1, 127.6, 125.5, 118.6, 117.6, 108.5, 74.7, 55.8, 54.4, 40.7, 18.7. **^{13}C NMR (125 MHz, $CDCl_3$, Diastereomer B):** δ 205.6, 165.9, 156.2, 135.3, 128.0, 125.4, 118.1, 117.6, 108.4, 78.7, 55.8, 54.0, 39.1, 21.8. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{17}O_3$ $(M+H)^+$: 233.1178, Found: 233.1168.

General procedure-23: Synthesis of cyclopropyl keto-ketones 153a-153k

All the starting compounds (**153**) employed in this study were synthesized by following the procedure reported in literature. Cyclopropanation of **85** leading to **150** was performed by following the standard reaction conditions described in Scheme 82. The alcohols **M** were synthesized from the compound **150** by $NaBH_4$ reduction. The conversion of **150** to **153a-153k** was achieved by following the procedure described in Scheme 84.

General procedure-24: Synthesis of cyclopropyl keto-ketones 158a-158b

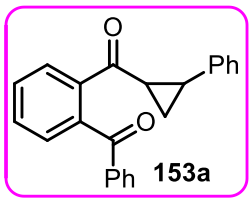
Step-I and Step-II: The reactions were performed by following the general procedure described in Scheme 84.

Step-III: The compound **157** (100 mg, 0.39 mmol, when, R = Ph) was dissolved in acetone in an oven dried round-bottom flask and kept at 0 ^{o}C. The Jones reagent (2.5 eq) was added drop wise over 10 minutes. The reaction mixture was then stirred until **157** disappeared as monitored by TLC. The reaction mixture was filtered through celite. The filter cake was washed with ethyl acetate (3x5 mL). Organic extracts were combined and washed with saturated sodium bicarbonate solution. The organic layer was dried over anhydrous sodium sulphate and concentrated under reduced vacuum. The residue was purified by silica gel column chromatography using hexane/ethyl acetate (4/1) as eluent to afford **158a** (64 mg, 65% yield).

General procedure-25: Synthesis of 2-styryl-3-arylindesnones 154a-154m

The compounds **154a-154m** were synthesized by following the described procedure 20.

(2-Benzoylphenyl)(2-phenylcyclopropyl)methanone (153a)

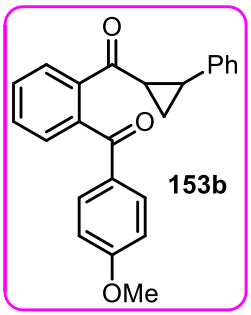


153a

This compound was isolated as pale yellow solid. Following the general procedure-23, 100 mg of **152** (R^1 = H, R^2, R^3 = Ph) afforded 69 mg of **153a** (70% yield). M.P = 120-122 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3061, 1667, 1596, 1581, 1449, 1076, 696. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.92-7.90 (m, 1H), 7.73 (d, *J* = 7.3 Hz, 2H), 7.61-7.52 (m, 3H), 7.45-7.37 (m, 3H), 7.28-7.24 (m, 2H), 7.21-7.18 (m, 1H), 7.05 (d, *J* = 7.1 Hz, 2H), 2.74-2.69 (m, 1H), 2.49-2.44 (m, 1H), 1.72-1.68 (m, 1H), 1.47-1.43 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.4, 197.4, 140.3, 140.0, 138.9, 137.1, 132.9, 131.7, 129.8, 129.4 (2C), 128.5 (4C), 128.4 (2C), 126.6, 126.1 (2C), 31.1, 30.8, 20.0. **HRMS (ESI):** *m/z* calcd for $C_{23}H_{18}NaO_2$ $(M+Na)^+$: 349.1204, Found: 349.1219.

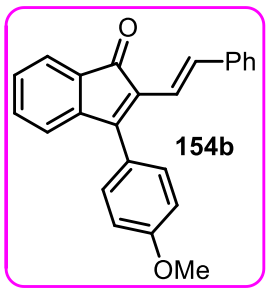
(2-(4-Methoxybenzoyl)phenyl)(2-phenylcyclopropyl)methanone (153b)

This compound was isolated as pale yellow liquid. Following the general procedure-23, 100 mg of **152b** (R^1 = H, R^2 = Ph, R^3 = *p*-$OMeC_6H_4$) afforded 71.5 mg of **153b** (72% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3062, 2360, 1661, 1597, 1398, 1222, 931,



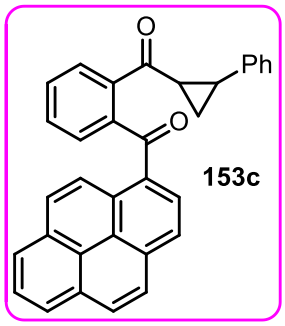
609. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.87 (d, *J* = 7.2 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.58-7.53 (m, 2H), 7.42-7.40 (m, 1H), 7.27-7.23 (m, 2H), 7.20-7.17 (m, 1H), 7.05-7.03 (m, 2H), 6.85 (d, *J* = 7.7 Hz, 2H), 3.83 (s, 3H), 2.70-2.69 (m, 1H), 2.49-2.46 (m, 1H), 1.74-1.72 (m, 1H), 1.43-1.42 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.7, 196.2, 163.5, 140.5, 138.9, 131.9 (2CH), 131.5, 130.2, 129.6, 128.5 (3CH), 128.3, 126.6, 126.1 (2CH), 113.7 (2CH), 55.5, 31.3, 30.8, 20.2. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{20}NaO_3$ $(M+Na)^+$: 379.1310, Found: 379.1324.

(*E*)-3-(4-Methoxyphenyl)-2-styryl-1*H*-inden-1-one (154b)



This compound was isolated as pale red solid. Following the general procedure-25, 50 mg of **153b** afforded 36 mg of **1544b** (76% yield). M.P = 110-112 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3065, 1705, 1604, 1508, 1455, 953, 719. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.87 (d, *J* = 16.4 Hz, 1H), 7.52-7.50 (m, 3H), 7.45-7.43 (m, 2H), 7.35-7.29 (m, 3H), 7.26-7.21 (m, 2H), 7.13-7.07 (m, 3H), 6.90 (d, *J* = 16.4 Hz, 1H), 3.91 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.1, 160.6, 154.6, 145.3, 137.9, 134.1, 133.4, 131.9, 130.2 (2CH), 128.8, 128.6 (2CH), 128.1, 127.8, 126.6 (2CH), 124.8, 122.6, 121.1, 118.4, 114.3 (2CH), 55.4. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{19}O_2$ $(M+H)^+$: 339.1385, Found: 339.1392.

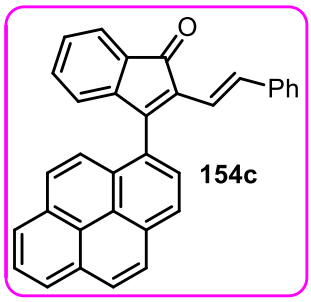
(2-(2-Phenylcyclopropanecarbonyl)phenyl)(pyren-1-yl)methanone (153c)



This compound was isolated as pale brown liquid. Following the general procedure-23, 100 mg of **152c** (R^1 = H, R^2 = Ph, R^3 = $C_{16}H_9$) afforded 63 mg of **153c** (64% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3040, 1660, 1594, 1505, 1237, 1027, 742, 710. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.13 (d, *J* = 9.2 Hz, 1H), 8.16-8.06 (m, 3H). 8.00-7.98 (m, 1H), 7.91-7.78 (m, 4H), 7.72-7.71 (m, 1H), 7.54-7.53 (m, 1H), 7.44-7.43 (m, 2H), 7.07-7.00 (m, 3H), 6.75 (d, *J* = 7.3 Hz, 2H), 2.57-2.54 (m, 1H), 2.13-2.08 (m, 1H), 1.43-1.41 (m, 1H), 1.17-1.16 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.0, 199.2, 141.7, 140.9, 139.9, 134.1, 131.5, 131.2, 131.0, 130.8, 130.6 (2C), 129.94, 129.92,

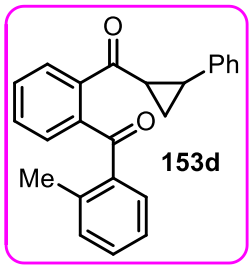
129.89, 128.9, 128.4 (3C), 128.1, 127.1, 126.57, 126.51, 126.3, 126.0 (2C), 125.4, 124.8, 124.2, 123.6, 32.1, 30.9, 20.1. **HRMS (ESI):** *m/z* calcd for $C_{33}H_{23}O_2$ $(M+H)^+$: 451.1698, Found: 451.1677.

(*E*)-3-(Pyren-1-yl)-2-styryl-1*H*-inden-1-one (154c)



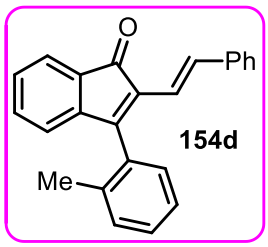
This compound was isolated as pale yellow solid. Following the general procedure-25, 50 mg of **153c** afforded 32 mg of **154c** (65% yield). M.P = 197-200 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2924, 1709, 1596, 1455, 1178, 849, 718. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.31 (d, *J* = 7.8 Hz, 1H), 8.26 (d, *J* = 7.6 Hz, 1H), 8.22-8.14 (m, 3H), 8.07-8.01 (m, 4H), 7.89 (d, *J* = 16.3 Hz, 1H), 7.61-7.59 (m, 1H), 7.25-7.21 (m, 4H), 7.16-7.11 (m, 3H), 6.73-6.71 (m, 1H), 6.65 (d, *J* = 16.3 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.2, 154.7, 146.7, 137.5, 134.7, 133.9, 132.0, 131.4, 131.2, 130.95, 130.93, 128.9, 128.8, 128.5 (2C), 128.4, 128.1, 128.0, 127.4, 127.3, 126.6 (2C), 126.4, 126.3, 125.85, 125.84, 125.3, 125.1, 124.9, 124.6, 122.7, 121.7, 118.5. **HRMS (ESI):** *m/z* calcd for $C_{33}H_{21}O$ $(M+H)^+$: 433.1592, Found: 433.1448.

(2-(2-Methylbenzoyl)phenyl)(2-phenylcyclopropyl)methanone (153d)



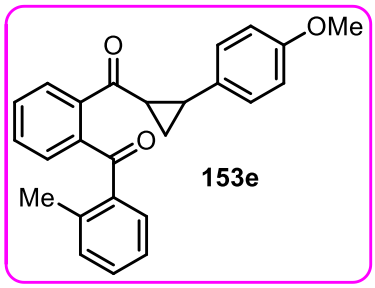
This compound was isolated as pale yellow liquid. Following the general procedure-23, 100 mg of **152d** (R^1 = H, R^2 = Ph, R^3 = *m*-MeC_6H_4) afforded 67.5 mg of **153d** (68% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3062, 2928, 1667, 1594, 1571, 1486, 927. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.81-7.79 (m, 1H), 7.59-7.52 (m, 3H), 7.42-7.39 (m, 1H), 7.32-7.27 (m, 1H), 7.25-7.23 (m, 2H), 7.15-7.11 (m, 1H), 7.09-7.07 (d, *J* = 7.6 Hz, 2H), 2.67-2.66 (m, 1H), 2.64 (s, 3H), 2.45-2.41 (m, 1H), 1.71-1.66 (m, 1H), 1.48-1.43 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.8, 199.0, 140.9, 140.5, 140.1, 139.8, 137.2, 131.6, 131.5, 131.1, 130.6, 130.4, 129.4, 128.4 (2C), 127.9, 126.6, 126.1 (2C), 125.1, 31.8, 30.7, 21.1, 19.9. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{20}NaO_2$ $(M+Na)^+$: 363.1361, Found: 363.1372.

(*E*)-2-Styryl-3-(o-tolyl)-1*H*-inden-1-one (154d)



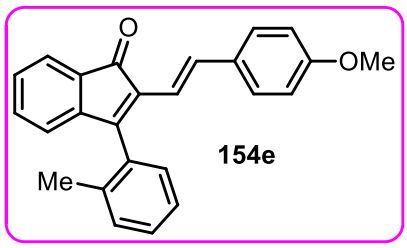
This compound was isolated as pale yellow liquid. Following the general procedure-25, 50 mg of **153d** afforded 32 mg of **154d** (68% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3059, 3022, 1712, 1605, 1595, 1487, 1267, 720. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.73 (d, *J* = 16.4 Hz, 1H), 7.49 (d, J = 6.9 Hz, 1H), 7.38-7.32 (m, 5H), 7.28-7.24 (m, 4H), 7.21-7.18 (m, 2H), 6.72 (d, *J* = 7.08 Hz, 1H), 6.57 (d, *J* = 16.4 Hz, 1H), 2.26 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.2, 155.8, 146.0, 137.6, 136.1, 134.1, 133.9, 132.2, 131.2, 130.8, 129.7, 129.09, 129.02, 128.6 (2CH), 128.3, 128.0, 126.6 (2CH), 126.1, 122.6, 121.2, 118.2, 20.1. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{19}O$ $(M+H)^+$: 323.1436, Found: 323.1455.

(2-(2-(4-Methoxyphenyl)cyclopropanecarbonyl)phenyl)(o-tolyl)methanone (153e)



This compound was isolated as pale yellow liquid. Following the general procedure-23, 100 mg of **152e** (R^1 = H, R^2 = p-$OMeC_6H_4$, R^3 = *m*-MeC_6H_4) afforded 67.5 mg of **153e** (68% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2932, 2836, 1668, 1600, 1573, 1398, 1302, 989, 700, 639. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.75-7.73 (m, 1H), 7.53-7.45 (m, 3H), 7.36-7.32 (m, 1H), 7.26-7.23 (m, 1H), 7.19-7.17 (m, 1H), 7.09-7.06 (m, 1H), 6.97-6.94 (m, 2H), 6.79-6.76 (m, 2H), 3.73 (s, 3H), 2.59 (m, 3H), 2.55-2.52 (m, 1H), 2.37-2.32 (m, 1H), 1.62-1.57 (m, 1H), 1.38-1.33 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.9, 199.0, 158.4, 140.9, 140.6, 139.8, 137.2, 132.0, 131.6, 131.5, 131.0, 130.6, 130.4, 129.4, 127.9, 127.3 (2C), 125.1, 113.8 (2C), 55.3, 31.8, 30.4, 21.1, 19.6. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{23}O_3$ $(M+H)^+$: 371.1647, Found: 371.1637.

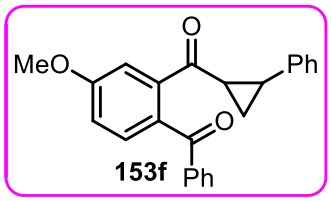
(*E*)-2-(4-Methoxystyryl)-3-(o-tolyl)-1*H*-inden-1-one (154e)



This compound was isolated as pale red liquid. Following the general procedure-25, 50 mg of **153e** afforded 35.5 mg of **154e** (75% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2955, 2836, 1712, 1601, 1575, 1510, 1539,

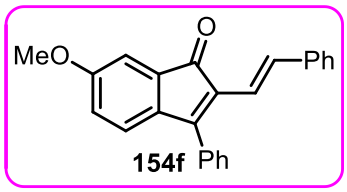
925, 449. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.69 (d, *J* = 16.4 Hz, 1H), 7.48 (d, *J* = 6.9 Hz, 1H), 7.38-7.32 (m, 2H), 7.33-7.29 (m, 3H), 7.26-7.24 (m, 2H), 7.20-7.18 (m, 1H), 6.82-6.80 (m, 2H), 6.71 (d, *J* = 7.2 Hz, 1H), 6.44 (d, *J* = 16.4 Hz, 1H), 3.78 (s, 3H), 2.26 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.4, 159.6, 154.5, 146.3, 136.1, 133.8, 133.7, 132.3, 131.2, 130.8, 130.5, 130.0, 128.9, 128.5, 128.3, 128.0 (2C), 126.1, 122.6, 120.9, 116.2, 114.0 (2C), 55.3, 20.1. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{21}O_2$ $(M+H)^+$: 353.1542, Found: 353.1530.

(2-Benzoyl-5-methoxyphenyl)(2-phenylcyclopropyl)methanone (153f)



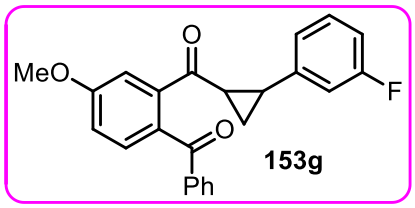
This compound was isolated as pale yellow liquid. Following the general procedure-23, 100 mg of **152f** (R^1 = 5-OMe, R^2,R^3 = Ph) afforded 69.5 mg of **153f** (70% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3061, 3029, 2839, 1668, 1652, 1566, 934, 718. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.72 (d, *J* = 7.7 Hz, 2H), 7.55-7.51 (m, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.40-7.37 (m, 1H), 7.25-7.22 (m, 3H), 7.19-7.17 (m, 1H), 7.03 (d, *J* = 7.4 Hz, 3H), 3.87 (s, 3H), 2.57-2.53 (m, 1H), 2.48-2.47 (m, 1H), 1.70-1.67 (m, 1H), 1.43-1.42 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.9, 196.4, 161.1, 142.8, 140.0, 137.6, 132.7, 131.7, 131.3, 129.6 (2C), 128.46 (2C), 128.40 (2C), 126.6, 126.1 (2C), 115.4, 114.0, 55.7, 32.2, 31.1, 20.4. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{21}O_3$ $(M+H)^+$: 357.1491, Found: 357.1497.

(*E*)-6-Methoxy-3-phenyl-2-styryl-1*H*-inden-1-one (154f)



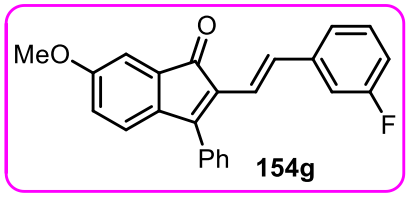
This compound was isolated as pale pink solid. Following the general procedure-25, 50 mg of **153f** afforded 37.5 mg of **154f** (79% yield). M.P = 100-102 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3059, 1705, 1609, 1447, 1358, 1023, 784. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.82 (d, *J* = 16.3 Hz, 1H), 7.57-7.48 (m, 5H), 7.42-7.40 (m, 2H), 7.31-7.27 (m, 2H), 7.23-7.19 (m, 1H), 7.11 (s, 1H), 6.97 (d, *J* = 8.04 Hz, 1H), 6.84 (d, *J* = 16.3 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 3.84 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.8, 161.0, 155.7, 137.9, 137.1, 133.8, 133.4, 132.7, 129.5, 128.8 (2C), 128.58 (2C), 128.54 (2C), 127.8, 127.7, 126.5 (2C), 122.1, 118.3, 116.5, 110.5, 55.8. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{19}O_2$ $(M+H)^+$: 339.1385, Found: 339.1369.

(2-Benzoyl-5-methoxyphenyl)(2-(3-fluorophenyl)cyclopropyl)methanone (153g)



This compound was isolated as pale yellow liquid. Following the general procedure-23, 100 mg of **152g** (R^1 = 5-OMe, R^2 = *m*-FC_6H_4, R^3 = Ph) afforded 67.5 mg of **153g** (68% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3061, 3008, 2941, 1728, 1673, 1615, 1076, 1000, 662, 575. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.71 (d, *J* = 7.68 Hz, 2H), 7.55-7.51 (m, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.40-7.37 (m, 2H), 7.24 (s, 1H), 7.18-7.15 (m, 1H), 7.04-7.02 (m, 1H), 6.87-6.81 (m, 2H), 6.70 (d, *J* = 10.4 Hz, 1H), 3.88 (s, 3H), 2.53-2.46 (m, 2H), 1.71-1.68 (m, 1H), 1.42-1.39 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.7, 196.3, 162.9 (d, *J* = 244.2), 161.2, 142.8, 142.7 (d, *J* = 7.7 Hz), 137.5, 132.8, 131.4 (d, *J* = 3.0 Hz), 129.9 (d, *J* = 8.4 Hz), 129.6 (2C), 128.4 (2C), 128.0, 121.9 (d, *J* = 2.7 Hz), 115.4, 114.0, 113.4 (d, *J* = 20.9 Hz), 113.0 (d, *J* = 21.8 Hz), 55.7, 32.3, 30.5 (d, *J* = 1.7 Hz), 20.4. **^{19}F NMR (374 MHz, CDCl3):** δ -113.2. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{20}FO_3$ $(M+H)^+$: 375.1396, Found: 375.1406.

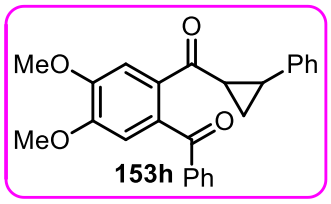
(*E*)-2-(3-Fluorostyryl)-6-methoxy-3-phenyl-1*H*-inden-1-one (154g)



This compound was isolated as pale blue solid. Following the general procedure-25, 50 mg of **153g** afforded 35 mg of **154g** (74% yield). M.P = 162-164 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2353, 1704, 1699, 1432, 774, 680, 585. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.78 (d, *J* = 16.4 Hz, 1H), 7.56-7.51 (m, 5H), 7.25-7.24 (m, 1H), 7.17-7.15 (m, 1H), 7.12-7.02 (m, 2H), 6.99-6.97 (m, 1H), 6.92-6.90 (m, 1H), 6.83-6.75 (m, 2H), 3.84 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.6, 163.1 (d, *J* = 243.6 Hz), 161.2, 156.6, 140.4 (d, *J* = 7.7 Hz), 136.9, 133.8, 132.5, 132.0 (d, *J* = 2.7 Hz), 130.0 (d, *J* = 8.3 Hz), 129.7, 128.9 (2C), 128.4 (2C), 127.4, 122.6 (d, *J* = 2.7 Hz), 122.3, 119.5, 116.5, 114.4 (d, *J* = 21.4 Hz), 112.5 (d, *J* = 19.3), 110.5, 55.3. **^{19}F NMR (374 MHz, CDCl3):** δ -113.6. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{18}FO_2$ $(M+H)^+$: 357.1291, Found: 357.1330.

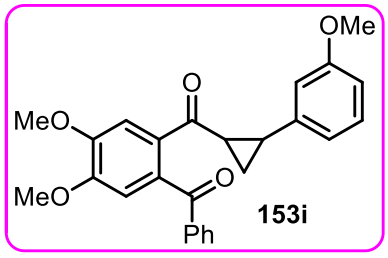
(2-Benzoyl-4,5-dimethoxyphenyl)(2-phenylcyclopropyl)methanone (153h)

This compound was isolated as pale yellow liquid. Following the general procedure-23, 100 mg of **152h** (R^1 = 4,5-OMe, R^2,R^3 = Ph) afforded 70.5 mg of **153h** (71% yield). R_f = 0.5



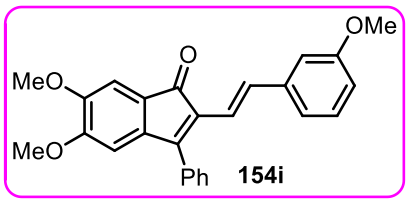
(hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3060, 3029, 3006, 2851, 1711, 1673, 1667, 1431, 762, 562. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.70 (d, *J* = 7.6 Hz, 2H), 7.54-7.51 (m, 1H), 7.39-7.34 (m, 3H), 7.26-7.23 (m, 2H), 7.20-7.18 (m, 1H), 7.01 (d, *J* = 7.1 Hz, 2H), 6.95 (s, 1H), 3.94 (s, 3H), 3.91 (s, 3H), 2.57-2.56 (m, 1H), 2.39-2.38 (m, 1H), 1.61-1.59 (m, 1H), 1.37-1.36 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.3, 197.0, 151.6, 149.6, 140.1, 137.5, 133.9, 132.8, 132.2, 129.3 (2C), 128.47 (2C), 128.44 (2C), 126.5, 126.1 (2C), 111.3, 110.0, 56.3 (2C), 31.5, 30.6, 20.1. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{23}O_4$ $(M+H)^+$: 387.1596, Found: 387.1612.

(2-Benzoyl-4,5-dimethoxyphenyl)(2-(3-methoxyphenyl)cyclopropyl)methanone (153i)



This compound was isolated as pale yellow liquid. Following the general procedure-23, 100 mg of **152i** (R^1 = 4,5-OMe, R^2 = *m*-C_6H_4, R^3 = Ph) afforded 72.5 mg of **153i** (73% yield). R_f = 0.5 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 3058, 3005, 2938, 1710, 1667, 1596, 1515, 1281, 810, 639. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.70 (d, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.54-7.34 (m, 3H), 7.18-7.14 (m, 1H), 6.95 (s, 1H), 6.74-6.72 (m, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 6.56 (s, 1H), 3.95 (s, 3H), 3.91 (s, 3H), 3.76 (s, 3H), 2.58-2.56 (m, 1H), 2.37-2.35 (m, 1H), 1.60-1.58 (m, 1H), 1.37-1.36 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.3, 197.0, 159.6, 151.6, 149.6, 141.7, 137.4, 133.9, 132.8, 132.1, 129.4, 129.3 (2C), 128.4 (2C), 118.4, 112.1, 111.7, 111.3, 111.0, 56.33, 56.31, 55.2, 31.4, 30.5, 20.1. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{25}O_5$ $(M+H)^+$: 417.1702, Found: 417.1692.

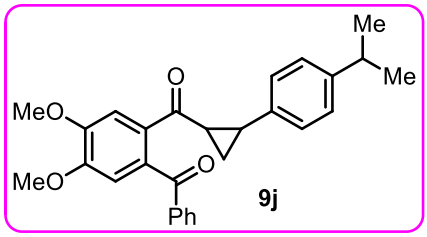
(*E*)-5,6-Dimethoxy-2-(3-methoxystyryl)-3-phenyl-1*H*-inden-1-one (154i)



This compound was isolated as pale blue solid. Following the general procedure-25, 50 mg of **153i** afforded 31 mg of **154i** (65% yield). M.P = 134-136 ^oC. R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2929, 2853, 1703, 1588, 1549, 1493, 1296, 1007, 507. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.78 (d, *J* = 16.3 Hz, 1H), 7.58-7.50 (m, 1H), 7.55-7.52 (m, 2H), 7.51-7.50 (m, 1H), 7.26 (s, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.14

(s, 1H), 7.02-7.01 (m, 1H), 6.94-6.93 (m, 1H), 6.83-6.76 (m, 2H), 6.62 (s, 1H), 3.93 (s, 3H), 3.87 (s, 3H), 3.80 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.6, 159.7, 153.5, 152.9, 149.1, 139.8, 139.4, 133.3, 132.6, 129.5, 129.4, 128.9 (2C), 128.4 (2C), 127.9, 124.0, 119.1, 118.7, 111.3, 112.0, 107.4, 105.6, 56.4, 56.3, 55.2. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{23}O_4$ $(M+H)^+$: 399.1596, Found: 399.1606.

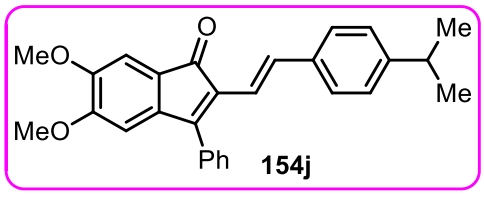
(2-Benzoyl-4,5-dimethoxyphenyl)(2-(4-isopropylphenyl)cyclopropyl)methanone (153j)



This compound was isolated as pale yellow liquid. Following the general procedure-23, 100 mg of **152j** (R^1 = 4,5-OMe, R^2 = *p*-^{i}prC$_6$H$_4$, R^3 = Ph) afforded 66 mg of **153j** (67% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3006, 2960, 1667, 1596, 1567, 1027, 999, 815, 782. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.71-7.69 (m, 2H), 7.54-7.50 (m, 1H), 7.39-7.35 (m, 3H), 7.13-7.11 (m, 2H), 6.96-6.94 (m, 3H), 3.95 (s, 3H), 3.91 (s, 3H), 2.88-2.85 (m, 1H), 2.57-2.54 (m, 1H), 2.38-2.35 (m, 1H), 1.60-1.56 (m, 1H), 1.38-1.34 (m, 1H), 1.23 (s, 3H), 1.21 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.4, 197.1, 151.6, 149.6, 147.3, 137.5, 137.4, 133.9, 132.8, 132.2, 129.3 (2C), 128.4 (2C), 126.5 (2C), 126.1 (2C), 111.3, 111.0, 56.32, 56.30, 33.7, 31.4, 30.5, 24.0 (2C), 20.0. **HRMS (ESI):** *m/z* calcd for $C_{28}H_{29}O_4$ $(M+H)^+$: 429.2066, Found: 429.2051.

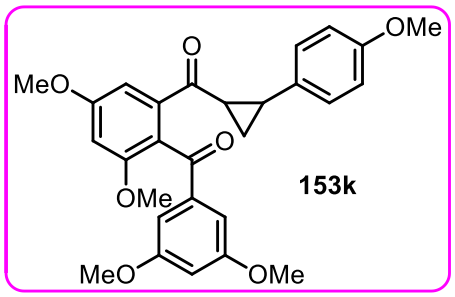
(*E*)-2-(4-Isopropylstyryl)-5,6-dimethoxy-3-phenyl-1*H*-inden-1-one (154j)

This compound was isolated as pale blue solid. Following the general procedure-25, 50 mg of



153j afforded 40 mg of **154j** (75% yield). M.P = 162-164 ^{o}C. R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2959, 1705, 1588, 1548, 1493, 1413, 1029, 823. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.79 (d, *J* = 16.3 Hz, 1H), 7.58-7.50 (m, 5H), 7.34 (d, *J* = 7.7 Hz, 2H), 7.17-7.13 (m, 3H), 6.78 (d, *J* = 16.3 Hz, 1H), 6.61 (s, 1H), 3.92 (s, 3H), 3.86 (s, 3H), 2.89-2.87 (m, 1H), 1.24 (s, 3H), 1.22 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.7, 152.8, 152.7, 149.0, 148.8, 140.0, 135.6, 135.5, 132.7, 129.3, 128.9 (2C), 128.5 (2C), 128.2, 126.68 (2C), 126.60 (2C), 124.0, 117.6, 107.4, 105.5, 56.4, 56.3, 33.9, 23.9 (2C). **HRMS (ESI):** *m/z* calcd for $C_{28}H_{26}O_3$ $(M)^+$: 410.1882, Found: 410.1937.

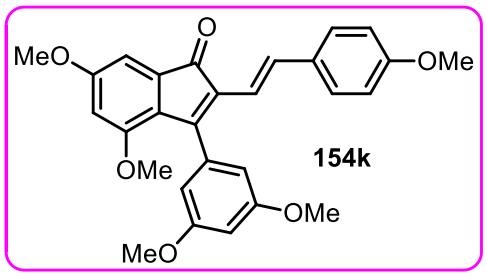
(2,4-Dimethoxy-6-(2-(4-methoxyphenyl)cyclopropanecarbonyl)phenyl)(3,5-dimethoxyphenyl)methanone (153k)



This compound was isolated as pale yellow liquid. Following the general procedure-23, 100 mg of **152k** (R^1 = 2,4-OMe, R^2 = 4-OMeC_6H_4, R^3 = 3,5-OMeC_6H_3) afforded 61.5 mg of **153k** (62% yield). R_f = 0.5 (hexane/EtOAc = 3/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 2930, 2835, 1709, 1601, 1575, 1455, 1304, 973, 945, 712, 450. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.01-6.96 (m,3H), 6.91 (d, *J* = 2.3 Hz, 2H), 6.81-6.78 (m, 2H), 6.66 (d, *J* = 2.0 Hz, 1H), 6.60 (t, *J* = 2.3 Hz, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 3.76 (s, 6H), 3.69 (s, 3H), 2.60-2.57 (m, 1H), 2.46-2.44 (m, 1H), 1.72-1.68 (m, 1H), 1.42-1.38 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.6, 195.7, 161.2, 160.6 (2C), 158.4, 158.3, 140.0, 139.8, 132.0, 127.3 (2C), 122.1, 113.8 (2C), 106.6 (2C), 105.6, 105.1, 101.8, 56.1, 55.7, 55.4 (2C), 55.3, 30.7, 30.4, 19.6. **HRMS (ESI):** *m/z* calcd for $C_{28}H_{29}O_7$ $(M+H)^+$: 477.1913, Found: 477.1898.

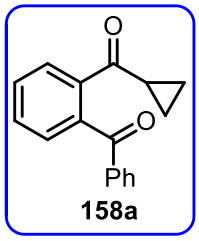
(*E*)-3-(3,5-Dimethoxyphenyl)-4,6-dimethoxy-2-(4-methoxystyryl)-1*H*-inden-1-one (154k)

This compound was isolated as pale blue solid. Following the general procedure-25, 50 mg of **153k** afforded 30.5 mg of **154k** (64% yield). M.P = 184-186 °C. R_f = 0.5 (hexane/EtOAc = 1/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2837, 1703, 1601, 1508, 1455, 1248, 998, 735. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.69 (d, *J* = 16.4 Hz, 1H), 7.32 (s, 1H), 7.28 (d, *J* = 16.6 Hz, 1H), 6.83-6.78 (m, 3H), 6.60-6.56 (m, 3H), 6.53-6.52 (m, 1H), 6.39-6.38 (m, 1H), 3.84 (s, 3H), 3.82 (s, 6H), 3.79 (s, 3H), 3.59 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.9, 162.5, 160.1 (2C), 159.2, 156.0, 154.9, 136.4, 134.9, 131.8, 130.9, 127.9, 127.7 (2C), 123.0, 116.6, 114.0 (2C), 106.5 (2C), 104.0, 102.6, 101.1, 55.9, 55.6, 55.5, 55.4, 55.3. **HRMS (ESI):** *m/z* calcd for $C_{28}H_{27}O_6$ $(M+H)^+$: 459.1808, Found: 459.1817.



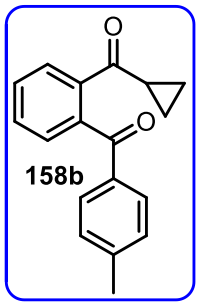
(2-Benzoylphenyl)(cyclopropyl)methanone (158a)

This compound was isolated as pale yellow liquid. Following the general procedure-24, 100 mg of **157a** (R = Ph) afforded 64.5 mg of **158a** (65% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR**



(thin film, neat): ν_{max}/cm^{-1} 3062, 1684, 1663, 1597, 1387, 1275, 1226, 992. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.98-7.94 (m, 1H), 7.76-7.72 (m, 2H), 7.62-7.57 (m, 2H), 7.53 (tt, *J* = 7.2 and 1.3 Hz, 1H), 7.46-7.38 (m, 3H), 0.96-0.90 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 201.7, 197.7, 140.2, 139.4, 137.2, 132.9, 131.5, 129.9, 129.5 (2C), 128.45, 128.41 (2C), 19.3, 12.6 (2C). **HRMS (ESI):** *m/z* calcd for $C_{17}H_{15}O_2$ $(M+H)^+$: 251.1072, Found: 251.1065.

(2-(Cyclopropanecarbonyl)phenyl)(*p*-tolyl)methanone (158b)



This compound was isolated as pale yellow liquid. Following the general procedure-24, 100 mg of **157b** (R = *P*-MeC_6H_4) afforded 65.5 mg of **158b** (66% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3010, 1681, 1610, 1604, 1384, 1282, 1226, 995, 929. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.0-7.93 (m, 1H), 7.67 (d, *J* = 10.1 Hz, 2H), 7.61 (dd, *J* = 6.8 and 5.2 Hz, 2H), 7.47-7.41 (m, 1H), 7.24 (d, *J* = 9.9 Hz, 2H), 2.51-2.44 (m, 1H), 2.41 (s, 3H), 1.09-1.02 (m, 2H), 0.99-0.91 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 201.9, 197.4, 143.9, 140.4, 139.3, 134.7, 131.4, 129.8 (2C), 129.7, 129.1 (2C), 128.4, 128.3, 21.7, 19.4, 12.6 (2C). **HRMS (ESI):** *m/z* calcd for $C_{18}H_{17}O_2$ $(M+H)^+$: 265.1229, Found: 265.1225.

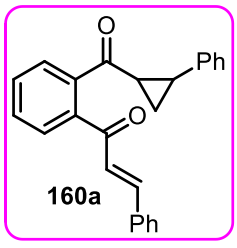
General procedure-26: Synthesis of cyclopropyl keto-enones 160a-160i

The reactions were performed by following the general described procedure 23.

General procedure-27: Synthesis of 2,3-disubstituted fluorenones 161a-161i

The compounds **161a-161i** were synthesized by following the described procedure 20.

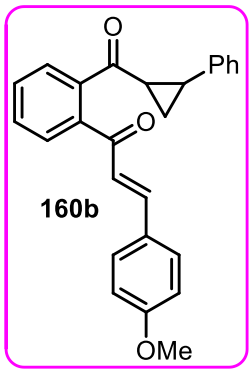
(*E*)-3-Phenyl-1-(2-(2-phenylcyclopropanecarbonyl)phenyl)prop-2-en-1-one (160a)



This compound was isolated as pale yellow liquid. Following the general procedure-26, 100 mg of **159a** (R^1 = H, R^2,R^3 = Ph) afforded 71 mg of **160a** (72% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3029, 3061, 1711, 1668, 1651, 1605, 1482, 1124, 531. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.79-7.77 (m, 1H), 7.58-7.54 (m, 3H), 7.49-7.47 (m, 2H), 7.38-7.32 (m, 3H), 7.28-7.19 (m, 4H), 7.07-7.01 (m, 3H), 2.67-2.64 (m, 2H), 1.92-1.87 (m, 1H), 1.55-

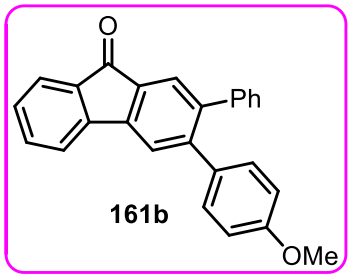
1.52 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.0, 195.6, 145.3, 140.07, 140.03, 139.8, 134.4, 131.3, 130.7, 130.4, 128.9 (2CH), 128.5 (2CH), 128.4 (2CH), 128.3, 128.2, 126.6, 126.3, 126.1 (2CH), 32.1, 32.1, 20.2. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{20}NaO_2$ $(M+Na)^+$: 375.1361, Found: 375.1345.

(*E*)-3-(4-Methoxyphenyl)-1-(2-(2-phenylcyclopropanecarbonyl)phenyl)prop-2-en-1-one (160b)



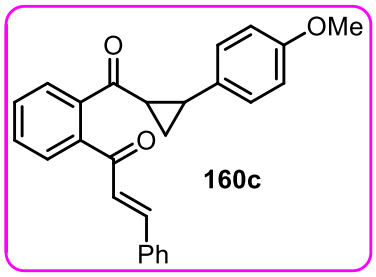
This compound was isolated as pale yellow liquid. Following the general procedure-26, 100 mg of **159b** (R^1 = H, R^2 = Ph, R^3 = *p*-$OMeC_6H_4$) afforded 72 mg of **160b** (73% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3032, 2838, 1667, 1600, 1571, 1127, 930, 532. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.76-7.74 (m, 1H), 7.55-7.54 (m, 3H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.30-7.18 (m, 4H), 7.06 (d, *J* = 7.5 Hz, 2H), 6.94-6.87 (m, 3H), 3.83 (s, 3H), 2.66-2.63 (m, 2H), 1.90-1.89 (m, 1H), 1.52-1.51 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.3, 195.5, 161.7, 145.5, 140.16, 140.12, 139.9, 131.2, 130.3 (2C), 130.2, 128.4 (2C), 128.24, 128.21, 127.1, 126.5, 126.1 (2C), 124.0, 114.3 (2C), 55.4, 32.3, 31.2, 20.3. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{22}NaO_3$ $(M+Na)^+$: 405.1467, Found: 405.1451.

3-(4-Methoxyphenyl)-2-phenyl-9*H*-fluoren-9-one (161b)



This compound was isolated as pale yellow solid. Following the general procedure-27, 50 mg of **160b** afforded 39 mg of **161b** (83% yield). M.P = 154-156 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3057, 2934, 2836, 1713, 1607, 1589, 1438, 1246, 736, 529. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.55-7.48 (m, 5H), 7.28-7.17 (m, 5H), 7.05-7.02 (m, 3H), 6.78 (d, *J* = 8.0 Hz, 2H), 3.78 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.0, 158.8, 144.3, 143.4, 143.2, 140.3, 136.1, 134.56, 134.50, 131.4 (2C), 129.7 (2C), 129.1, 128.1, 127.9, 127.8 (2C), 126.6, 124.0, 119.9, 119.2, 113.6, 112.9 (2C), 55.1. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{19}O_2$ $(M+H)^+$: 363.1385, Found: 363.1330.

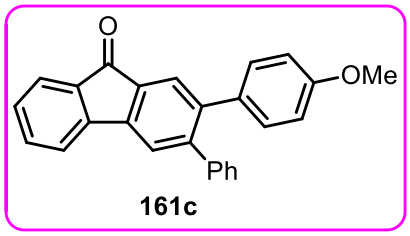
(*E*)-1-(2-(2-(4-Methoxyphenyl)cyclopropanecarbonyl)phenyl)-3-phenylprop-2-en-1-one (160c)



160c

This compound was isolated as pale yellow liquid. Following the general procedure-26, 100 mg of **159c** (R^1 = H, R^2 = *p*-$OMeC_6H_4$, R^3 = Ph) afforded 67 mg of **160c** (68% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3060, 2836, 1668, 1610, 1575, 1495, 1249, 820, 599, 484. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.79-7.77 (m, 1H), 7.58-7.55 (m, 2H), 7.49-7.47 (m, 2H), 7.41-7.35 (m, 4H), 7.30 (d, *J* = 16.1 Hz, 1H), 7.03 (d, *J* = 16.8 Hz, 1H), 7.00-6.98 (m, 2H), 6.79-6.77 (m, 2H), 3.76 (s, 3H), 2.61-2.56 (m, 2H), 1.88-1.86 (m, 1H), 1.49-1.47 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.1, 195.6, 158.4, 145.4, 140.0, 139.9, 134.4, 132.0, 131.2, 130.6, 130.3, 128.9 (2C), 128.4 (2C), 128.29, 128.21, 127.3 (2C), 126.3, 113.9 (2C), 55.3, 32.2, 30.9, 20.0. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{22}NaO_3$ $(M+Na)^+$: 405.1467, Found: 405.1446.

2-(4-Methoxyphenyl)-3-phenyl-9*H*-fluoren-9-one (161c)

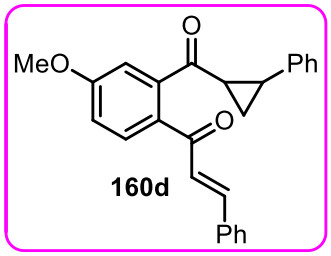


161c

This compound was isolated as pale yellow solid. Following the general procedure-27, 50 mg of **160c** afforded 39 mg of **161c** (83% yield). M.P = 160-162 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3058, 1713, 1615, 1452, 1397, 833, 730. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.71 (s, 1H), 7.68 (d, *J* = 7.3 Hz, 1H), 7.53-7.49 (m, 3H), 7.30-7.26 (m, 4H), 7.20-7.18 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 3.77 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.7, 158.6, 146.7, 144.1, 142.9, 141.2, 141.1, 134.78, 134.73, 133.2, 132.7, 130.7 (2C), 129.5 (2C), 129.0, 128.1 (2C), 127.2, 126.5, 124.3, 122.8, 120.3, 113.5 (2C), 55.2. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{18}NaO_2$ $(M+Na)^+$: 385.1204, Found: 385.1208.

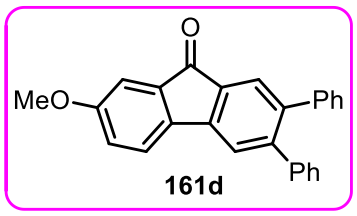
(*E*)-1-(4-Methoxy-2-(2-phenylcyclopropanecarbonyl)phenyl)-3-phenylprop-2-en-1-one (160d)

This compound was isolated as pale yellow liquid. Following the general procedure-26, 100 mg of **159d** (R^1 = 4-OMe, R^2,R^3 = Ph) afforded 71 mg of **160d** (72% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3028, 1661, 1601, 1575, 1495, 1449, 1308, 1142, 1078,



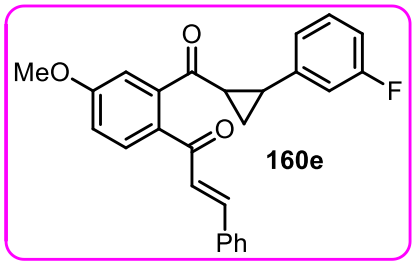
628. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.69 (d, *J* = 8.5 Hz, 1H), 7.53-7.51 (m, 2H), 7.46 (d, *J* = 16.0 Hz, 1H), 7.39-7.38 (m, 3H), 7.25-7.21 (m, 2H), 7.18-7.14 (m, 2H), 7.08-7.06 (m, 3H), 7.02 (d, *J* = 8.5 Hz, 1H), 3.88 (s, 3H), 2.72-2.67 (m, 1H), 2.49-2.48 (m, 1H), 1.94-1.92 (m, 1H), 1.53-1.52 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.9, 192.1, 161.8, 145.0, 144.1, 140.1, 134.6, 131.0, 130.7, 130.6, 128.9 (2C), 128.47 (2C), 128.44 (2C), 126.5, 126.2 (2C), 124.7, 115.1, 113.5, 55.7, 33.2, 31.2, 20.4. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{23}O_3$ $(M+H)^+$: 383.1647, Found: 383.1632.

(7-Methoxy-2,3-diphenyl-9*H*-fluoren-9-one (161d)



This compound was isolated as pale yellow solid. Following the general procedure-27, 50 mg of **160d** afforded 39 mg of **161d** (83% yield). M.P = 198-199 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2940, 2355, 1706, 1609, 1464, 1435, 966, 766. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.68 (s, 1H), 7.44-7.40 (m, 2H), 7.25-7.17 (m, 9H), 7.12-7.11 (m, 2H), 7.00-6.98 (m, 1H), 3.86 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.5, 160.0, 147.1, 143.7, 140.9, 140.5, 140.3, 136.6, 136.5, 133.4, 129.6 (2C), 129.5 (2C), 128.1 (2C), 128.0 (2C), 127.3, 126.8, 126.6, 122.0, 121.4, 120.3, 109.4, 55.7. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{19}O_2$ $(M+H)^+$: 363.1385, Found: 363.1418.

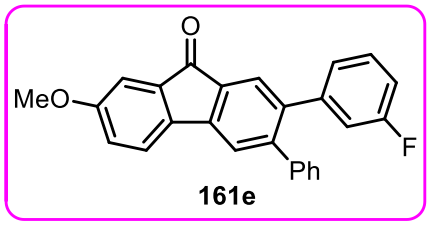
(*E*)-1-(2-(2-(3-Fluorophenyl)cyclopropanecarbonyl)-5-methoxyphenyl)-3-phenylprop-2-en-1-one (160e)



This compound was isolated as pale yellow liquid. Following the general procedure-26, 100 mg of **159e** (R^1 = 5-OMe, R^2 = *m*-FC_6H_4, R^3 = Ph) afforded 69 mg of **160e** (70% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3060, 2940, 2840, 1674, 1661, 1308, 1677, 707. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.71 (d, *J* = 8.4 Hz, 1H), 7.53-7.47 (m, 3H), 7.39 (s, 3H), 7.20-7.15 (m, 2H), 7.06-7.01 (m, 2H), 6.87-6.83 (m, 2H), 6.78 (d, *J* = 10.1 Hz, 1H), 3.88 (s, 3H), 2.72-2.67 (m, 1H), 2.45-2.44 (m, 1H), 1.94-1.90 (m, 1H), 1.51-1.48 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.7, 191.7, 162.9 (d, *J* = 244.2 Hz), 161.9, 145.1, 144.2, 142.9 (d, *J* = 7.5 Hz), 134.5, 130.9,

130.7 (d, *J* = 9.3 Hz), 129.9 (d, *J* = 8.5 Hz), 128.9 (2C), 128.5, 128.4 (2C), 124.3, 122.0 (d, *J* = 2.5 Hz), 115.1, 113.4, 113.3 (d, *J* = 7.2 Hz), 113.1, 55.7, 33.2, 30.5 (d, *J* = 1.8 Hz), 20.3. **^{19}F NMR (374 MHz, CDCl3):** δ -113.2. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{22}FO_3$ $(M+H)^+$: 401.1553, Found: 401.1573.

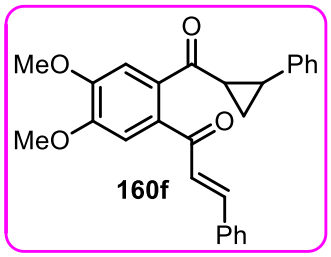
(2-(3-Fluorophenyl)-7-methoxy-3-phenyl-9*H*-fluoren-9-one (161e)



161e

This compound was isolated as pale yellow solid. Following the general procedure-27, 50 mg of **160e** afforded 34 mg of **161e** (71% yield). M.P = 193-195 ^oC. R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3059, 1713, 1606, 1486, 1025, 874, 530. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.65 (s, 1H), 7.43-7.41 (m, 2H), 7.26-7.23 (m, 4H), 7.17-7.16 (m, 3H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.89-6.87 (m, 2H), 6.81 (d, *J* = 10.0 Hz, 1H), 3.86 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.3, 162.4 (d, *J* = 244.1 Hz), 161.0, 147.1, 144.1, 142.8 (d, *J* = 7.8 Hz), 140.5, 139.0 (d, *J* = 2.4 Hz), 136.5 (d, *J* = 10.4 Hz), 133.4, 129.5, 129.46, 129.44 (2C), 128.2 (2C), 127.5, 126.4, 125.4 (d, *J* = 2.6 Hz), 122.1, 121.5, 120.4, 116.5 (d, *J* = 21.8), 113.8 (d, *J* = 20.3), 109.5, 55.8. **^{19}F NMR (374 MHz, CDCl3):** δ -113.4. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{18}O_2$ $(M+H)^+$: 381.1291, Found: 381.1308.

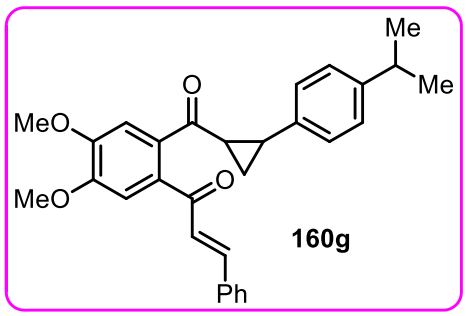
(*E*)-1-(4,5-Dimethoxy-2-(2-phenylcyclopropanecarbonyl)phenyl)-3-phenylprop-2-en-1-one (160f)



160f

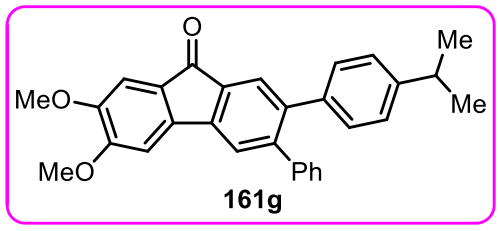
This compound was isolated as pale yellow solid. Following the general procedure-26, 100 mg of **259f** (R^1 = 4,5-OMe, R^2,R^3 = Ph) afforded 69 mg of **160f** (70% yield). M.P = 155-157 ^oC. R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3005, 2937, 2851, 1711, 1661, 1567, 1496, 873, 737. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45-7.44 (m, 2H), 7.37-7.36 (m, 3H), 7.27-7.15 (m, 5H), 7.04 (s, 1H), 7.00-6.98 (m, 2H), 6.94 (d, *J* = 16.1 Hz, 1H), 3.94 (s, 6H), 2.60-2.54 (m, 2H), 1.85-1.82 (m, 1H), 1.48-1.47 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.1, 194.8, 151.2, 150.2, 144.7, 140.0, 134.4, 133.6, 133.2, 130.6, 128.9 (2C), 128.4 (4C), 126.8, 126.5, 126.0 (2C), 111.1, 110.9, 56.3, 56.2, 32.6, 31.1, 20.7. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{25}O_4$ $(M+H)^+$: 413.1753, Found: 413.1771.

(*E*)-1-(2-(2-(4-Isopropylphenyl)cyclopropanecarbonyl)-4,5-dimethoxyphenyl)-3-phenylprop-2-en-1-one (160g)



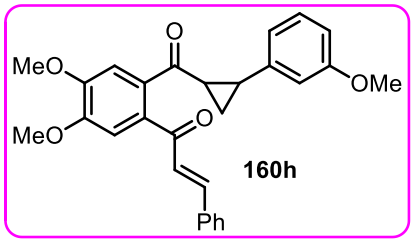
This compound was isolated as pale brown liquid. Following the general procedure-26, 100 mg of **159g** (R^1 = 4,5-OMe, R^2 = *p*-^{i}prC$_6$H$_4$, R^3 = Ph) afforded 67 mg of **160g** (68% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2960, 1661, 1596, 1516, 1449, 1397, 1018, 818, 771. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.46-7.44 (m, 2H), 7.38-7.36 (m, 3H), 7.28-7.24 (m, 2H), 7.09 (s, 1H), 7.07-7.04 (m, 2H), 6.97-6.92 (m, 3H), 3.95 (s, 6H), 2.87-2.83 (m, 1H), 2.59-2.54 (m, 2H), 1.84-1.82 (m, 1H), 1.47-1.46 (m, 1H), 1.22 (s, 3H), 1.20 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 200.3, 195.0, 151.2, 150.1, 147.2, 144.7, 137.3, 134.4, 133.6, 133.1, 130.6, 128.9 (2C), 128.4 (2C), 126.8, 126.5 (2C), 126.0 (2C), 111.0, 110.9, 56.3 (2C), 33.7, 32.6, 31.1, 24.03, 24.01, 20.8. **HRMS (ESI):** *m/z* calcd for $C_{30}H_{31}O_4$ $(M+H)^+$: 455.2222, Found: 455.2203.

2-(4-Isopropylphenyl)-6,7-dimethoxy-3-phenyl-9*H*-fluoren-9-one (161g)



This compound was isolated as pale yellow solid. Following the general procedure-27, 50 mg of **160g** afforded 38 mg of **161g** (80% yield). M.P = 210-212 ^{o}C. R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2960, 1703, 1615, 1593, 1495, 1451, 1323, 773, 613. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.64 (s, 1H), 7.39 (s, 1H), 7.25-7.19 (m, 6H), 7.07-7.03 (m, 5H), 4.00 (s, 3H), 3.94 (s, 3H), 2.87-2.81 (m, 1H), 1.22 (s, 3H), 1.20 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 192.9, 154.6, 149.7, 147.5, 146.3, 142.5, 141.2, 140.6, 139.2, 137.8, 133.8, 129.55 (2C), 129.54 (2C), 128.0 (2C), 127.5, 127.1, 126.2, 126.0 (2C), 121.7, 107.1, 103.4, 56.3, 56.2, 33.7, 23.9 (2C). **HRMS (ESI):** *m/z* calcd for $C_{30}H_{27}O_3$ $(M+H)^+$: 435.1960, Found: 435.1943.

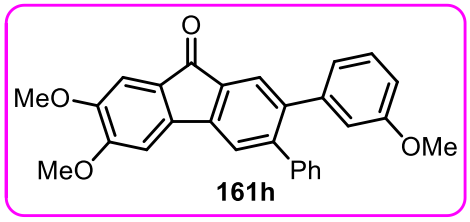
(*E*)-1-(4,5-Dimethoxy-2-(2-(3-methoxyphenyl)cyclopropanecarbonyl)phenyl)-3-phenylprop-2-en-1-one (160h)



160h

This compound was isolated as pale brown liquid. Following the general procedure-26, 100 mg of **159h** (R^1 = 4,5-OMe, R^2 = *m*-$OMeC_6H_4$, R^3 = Ph) afforded 65 mg of **160h** (66% yield). R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2936, 1661, 1601, 1516, 1495, 1351, 772, 572. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48-7.46 (m, 2H), 7.40-7.38 (m, 3H), 7.30-7.25 (m, 2H), 7.18-7.14 (m, 1H), 7.06 (s, 1H), 6.97 (d, *J* = 16.0 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 6.62-6.59 (m, 2H), 3.98 (s, 6H), 3.75 (s, 3H), 2.62-2.56 (m, 2H), 1.86-1.84 (m, 1H), 1.49-1.48 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.2, 194.9, 159.6, 151.2, 150.1, 144.9, 141.7, 134.4, 133.6, 133.1, 130.6, 129.4, 128.9 (2C), 128.4 (2C), 126.7, 118.3, 112.0, 111.7, 111.0, 110.8, 56.3 (2C), 55.1, 32.5, 31.1, 20.8. **HRMS (ESI):** *m/z* calcd for $C_{28}H_{27}O_5$ $(M+H)^+$: 443.1858, Found: 443.1842.

2,3-Dimethoxy-7-(3-methoxyphenyl)-6-phenyl-9*H*-fluoren-9-one (161h)

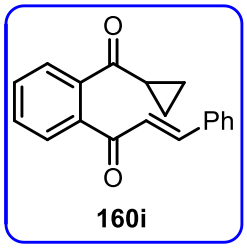


161h

This compound was isolated as pale yellow solid. Following the general procedure-27, 50 mg of **11h** afforded 35 mg of **12h** (73% yield). M.P = 185-187 ^oC. R_f = 0.5 (hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2930, 1704, 1594, 1495, 1287, 1216, 772. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.65 (s, 1H), 7.41 (s, 1H), 7.27-7.24 (m, 3H), 7.23 (s, 1H), 7.21-7.18 (m, 2H), 7.12 (t, *J* = 7.9, 1H), 7.04 (s, 1H), 6.76-6.72 (m, 2H), 6.64-6.63 (m, 1H), 4.00 (s, 3H), 3.94 (s, 3H), 3.61 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 192.9, 159.1, 154.6, 149.8, 146.4, 142.9, 141.7, 141.1, 140.0, 139.1, 133.8, 129.4 (2C), 129.0, 128.1 (2C), 127.5, 127.2, 126.0, 122.1, 121.7, 114.7, 113.2, 107.2, 103.4, 56.39, 56.31, 55.1. **HRMS (ESI):** *m/z* calcd for $C_{28}H_{23}O_4$ $(M+H)^+$: 423.1596, Found: 423.1588.

(*E*)-1-(2-(Cyclopropanecarbonyl)phenyl)-3-phenylprop-2-en-1-one (160i)

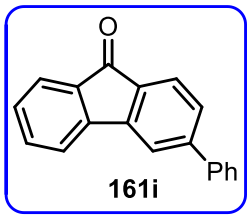
This compound was isolated as pale yellow liquid. Following the general procedure-26, 100 mg of **159i** (R = Ph) afforded 64.5 mg of **160i** (65% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3069, 1674, 1660, 1604, 1447, 1384, 1226, 995. **^{1}H NMR (500 MHz,**



160i

$CDCl_3$): δ 7.85-7.82 (m, 1H), 7.61-7.57 (m, 2H), 7.57-7.54 (m, 1H), 7.54-7.50 (m, 2H), 7.40-7.33 (m, 4H), 7.08 (d, J = 16.2 Hz, 1H), 2.48-2.41 (m, 1H), 1.25-1.20 (m, 2H), 1.06-1.0 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 203.2, 195.9, 145.4, 140.1, 139.9, 134.5, 131.2, 130.6, 130.3, 130.2, 128.9, 128.5, 128.4, 128.3, 128.2, 126.5, 20.2, 12.8 (2C). **HRMS (ESI):** *m/z* calcd for $C_{19}H_{17}O_2$ $(M+H)^+$: 277.1229, Found: 277.1216.

3-Phenyl-9*H*-fluoren-9-one (161i)



161i

This compound was isolated as pale brown semi-solid. Following the general procedure-27, 50 mg of **160i** afforded 34.5 mg of **161i** (74% yield). R_f = 0.5 (hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2926, 1709, 1614, 1450, 1300, 1097, 911. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.74-7.71 (m, 2H), 7.69-7.63 (m, 3H), 7.53-7.47 (m, 4H), 7.45-7.42 (m, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 193.6, 147.9, 145.2, 144.1, 140.2, 143.7, 134.6, 132.9, 129.2, 128.9 (2C), 128.4, 127.9, 127.2 (2C), 124.7, 124.3, 120.3, 119.2. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{13}O$ $(M+H)^+$: 257.0966, Found: 257.0962.

General procedure-28: Synthesis of 3-(2-aminophenyl)hex-5-en-1-yn-3-ols 172a-172j

All the 3-(2-aminophenyl)hex-5-en-1-yn-3-ols (**172**) employed in this study were synthesized by following a three-step protocol developed by our research group.[91]

General procedure-29: Optimisation of the reaction parameters (Table 21)

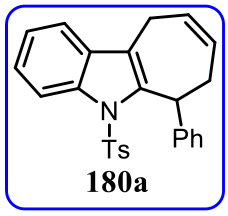
A 5 mL glass vial was charged with **172a** (0.1 mmol), AgOAc (2 mol%) in DCE (1 mL) and stirred at 60 ^oC. After the disappearance of **172a**, allyl-TMS (1.5 eq) and C2 (5 mol%) were introduced at an appropriate temperature (see Table 21) and left stirring at room temperature until the intermediate **173a** disappeared (by TLC). Upon complete formation of the intermediate **179a**, C3 (Grubbs' 1st or 2nd generation catalysts) was introduced at room temperature (see Table 21) and continued stirring at room temperature until intermediate **179a** disappeared (by TLC). The reaction mixture was then quenched with saturated aqueous $NaHCO_3$ (1 mL) and extracted with EtOAc (2×2 mL). The combined organic layers were washed with brine, dried

over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by alumina column chromatography (5% EtOAc/hexanes) to afford **180a**.

General procedure-30: One-pot synthesis of tetrahydrocyclohepta[*b*]indoles

A 5 mL glass vial was charged with 3-(2-aminophenyl)hex-5-en-1-yn-3-ol **172** (0.1 mmol), AgOAc (2 mol%) in DCE (1 mL) and stirred at 60 ^oC. After the disappearance of **172**, allyl-TMS (1.5 eq) and $InCl_3$ (5 mol%) were introduced at 0 ^oC and continued stirring at room temperature until intermediate **173** disappeared as monitored by TLC. After complete formation of **179**, Grubbs' 1st generation catalyst (15 mol%) was added to the reaction mixture at room temperature and continued stirring at room temperature until the intermediate **179** disappeared (by TLC). The reaction mixture was then quenched with saturated aq. $NaHCO_3$ (1 mL) and extracted with EtOAc (2×2 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by alumina column chromatography (5% EtOAc/hexanes) to afford **180**.

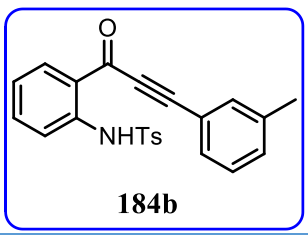
6-Phenyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (180a)



180a

This compound was isolated as colorless viscous liquid. Following the reaction procedure-30, 40 mg of **172a** afforded 29.5 mg of **180a** (75% yield). R_f = 0.5 (hexane/EtOAc = 9.5/0.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 3029, 1737, 1493, 1453, 1170, 747. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.25-8.22 (m, 1H), 7.49-7.47 (m, 1H), 7.37-7.29 (m, 2H), 7.22-7.16 (m, 5H), 7.07 (dd, *J* = 6.6 and 2.9 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 5.93-5.90 (m, 1H), 5.55 (dt, *J* = 5.1 and 2.7 Hz, 1H), 5.38 (brs, 1H), 3.58-3.54 (m, 2H), 2.95-2.91 (m, 1H), 2.69 (ddd, *J* = 14.6, 8.4 and 5.6 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144, 142.7, 138, 136, 130.6, 129.3 (2C), 128.7 (2C), 128.5 (2C), 128.2, 127.7 (2C), 126.3 (2C), 125.9, 124.5, 123.2, 119.3, 118, 115.2, 41.3, 34.1, 24.8, 21.4. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{24}NO_2S$ $(M+H)^+$: 414.1528, Found: 414.1512.

4-Methyl-*N*-(2-(3-(*m*-tolyl)propioloyl)phenyl)benzenesulfonamide (184b)

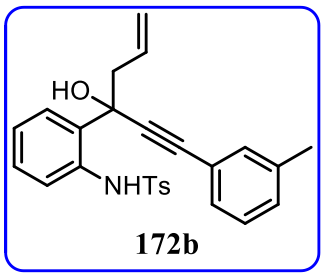


184b

This compound was isolated as pale yellow solid by following the reaction procedure-28. M.P = 147-150 ^oC. R_f = 0.5 (hexane/EtOAc = 6/4). **IR (thin film, neat):** ν_{max}/cm^{-1} 3200, 2924, 2193, 1611, 1490,

1158, 754. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.31 (dd, *J* = 7.8 and 1.5 Hz, 1H), 7.8 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.56-7.46 (m, 3H), 7.34 (d, *J* = 5.1 Hz, 2H), 7.29-7.24 (m, 3H), 7.16 (t, *J* = 7.7 Hz, 1H), 2.41 (s, 3H), 2.38 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 180.5, 144.1, 140.9, 138.7, 136.4, 135.7, 134.8, 133.6, 132.2, 130.3, 129.8 (2C), 128.7, 127.3 (2C), 122.6, 122.5, 119.4, 118.4, 95.7, 86.4, 21.6, 21.2. **HRMS (ESI):** *m/z* calcd for $C_{23}H_{19}NO_3S$ $(M+H)^+$: 390.1164, Found: 390.1148.

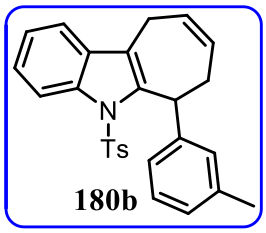
_N_-(2-(3-Hydroxy-1-(_m_-tolyl)hex-5-en-1-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (172b)



172b

This compound was isolated as colorless liquid by following the reaction procedure-28. R_f = 0.5 (hexane/EtOAc = 6.5/2.5). **IR (thin film, neat):** 3451, 2964, 2231, 1588, 1494, 1333, 1160, 749. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.4 (brs, 1H), 7.8 (d, *J* = 8.3 Hz, 2H), 7.76-7.69 (m, 1H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.31 (s, 1H), 7.27-7.14 (m, 5H), 7.09-6.98 (m, 1H), 5.90-5.78 (m, 1H), 5.19 (dd, *J* = 10.3 and 1.2 Hz, 1H), 5.06 (d, *J* = 17.1 Hz, 1H), 3.8 (brs, 1H), 2.68-2.53 (m, 2H), 2.37 (brs, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.8, 138.2, 137.2, 135.7, 132.3, 132.2, 130.0, 129.8, 129.7 (2C), 129.1, 128.9, 128.5, 128.3, 127.2 (2C), 123.4, 121.6, 120.8, 120.1, 88.9, 88.3, 74.8, 47.5, 21.5, 21.2. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{25}NNaO_3S$ $(M+Na)^+$: 454.1453, Found: 454.1437.

6-(_m_-Tolyl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[_b_]indole (180b)

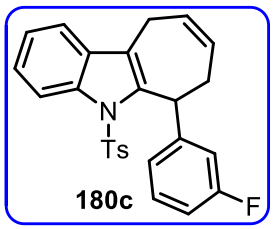


180b

This compound was isolated as pale yellow solid. Following the reaction procedure-30, 40 mg of **172b** afforded 26.5 mg **180b** (65 % yield). M.P = 90-92 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9.5/0.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2926, 1737, 1453, 1368, 1170, 746. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.07 (d, *J* = 7.8 Hz, 1H), 7.58-7.56 (m, 1H), 7.37-7.33 (m, 4H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.12-7.07 (m, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.96-6.79 (m, 2H), 5.88-5.84 (m, 1H), 5.48-5.47 (m, 1H), 5.25 (brs, 1H), 3.54-3.52 (m, 2H), 2.84-2.81 (m, 1H), 2.70-2.65 (m, 1H), 2.26 (s, 3H), 2.17 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.9, 142.5, 138.6, 137.1, 136, 130, 129.3, 129.2 (2C), 128.8, 128.1 (2C), 127.6, 126.6, 126.3 (2C), 125.6, 124.4, 123.2,

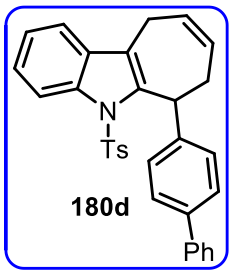
119.1, 118, 115.2, 41.2, 34.2, 24.8, 21.4 (2C). **HRMS (ESI):** *m/z* calcd for $C_{27}H_{26}NO_2S$ $(M+H)^+$: 428.1684, Found: 428.1678.

6-(3-Fluorophenyl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (180c)



This compound was isolated as pale brown solid. Following the reaction procedure-30, 40 mg of **172c** afforded 34 mg **180c** (85 % yield). M.P = 104-106 ^oC. R_f = 0.5 (hexane/EtOAc = 9.5/0.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2926, 1736, 1589, 1452, 1369, 748. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.29-8.27 (m, 1H), 7.5 (dd, *J* = 7.6 and 1 Hz, 1H), 7.35 (m, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.15 (td, *J* = 7.9 and 6.1 Hz, 1H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.84 (td, *J* = 8.4 and 2.6 Hz, 1H), 6.62 (dd, *J* = 10.3 and 1.7 Hz, 1H), 5.92 (dd, *J* = 6.5 and 4.3 Hz, 1H), 5.53 (dt, *J* = 5.1 and 2.7 Hz, 1H), 5.37 (brs, 1H), 3.63-3.50 (m, 2H), 2.96-2.92 (m, 1H), 2.67 (ddd, *J* = 14.5, 8.3 and 5.7 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.51 (d, *J* = 243.0 Hz), 145.4 (d, *J* = 6.7 Hz), 144.3, 137.7, 136.1 (d, *J* = 17.6 Hz), 130.4, 129.5, 129.4 (2C), 129.2 (d, *J* = 8.2 Hz), 128.4 (d, *J* = 1.1 Hz), 126.1 (2C), 124.8, 124.2 (d, *J* = 2.7 Hz), 123.4, 119.7, 118.2, 115.6, 115.4, 115.3, 112.7 (d, *J* = 21.1 Hz), 41.1 (d, *J* = 1.3 Hz), 34, 24.7, 21.4. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -114.2. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{23}FNO_2S$ $(M-H)^+$: 430.1277, Found: 430.1258.

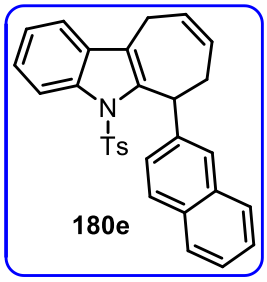
6-([1,1'-Biphenyl]-4-yl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (180d)



This compound was isolated as colorless solid. Following the reaction procedure-30, 40 mg of **172d** afforded 28.7 mg of **180d** (71 % yield). M.P = 169-171 ^oC. R_f = 0.5 (hexane/EtOAc = 9.5/0.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2927, 1486, 1454, 1367, 1169, 758. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.30-8.25 (m, 1H), 7.61-7.55 (m, 2H), 7.53-7.49 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.40-7.31 (m, 5H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 6.91 (d, *J* = 8.3 Hz, 2H), 6.01-5.93 (m, 1H), 5.59 (td, *J* = 5.2 and 2.6 Hz, 1H), 5.42 (brs, 1H), 3.68-3.53 (m, 2H), 2.98 (dd, *J* = 14.7 and 2 Hz, 1H), 2.72 (ddd, *J* = 14.5, 8.3, and 5.9 Hz, 1H), 2.19 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.9, 141.9, 140.9, 138.7, 138.5, 136.24, 136.21, 130.5, 129.3 (2C), 129.1 (2C), 128.9, 128.7 (2C), 128.5, 127.1, 126.9 (2C), 126.4 (2C), 126.2 (2C), 124.6,

123.3, 119.2, 118.1, 115.3, 41.0, 34.1, 24.7, 21.4. **HRMS (ESI):** *m/z* calcd for $C_{32}H_{28}NO_2S$ $(M+H)^+$: 490.1841, Found: 490.1820.

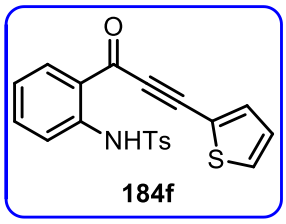
6-(Naphthalen-2-yl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (180e)



180e

This compound was isolated as pale yellow liquid. Following the reaction procedure-30, 40 mg of **172e** afforded 24.3 mg of **180e** (61% yield). R_f = 0.5 (hexane/EtOAc = 9.5/0.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2924, 1454, 1365, 1169, 1126, 809, 746, 664. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.36-8.29 (m, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.60-7.52 (m, 1H), 7.49-7.31 (m, 6H), 7.11 (s, 1H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.54 (d, *J* = 8.1 Hz, 2H), 5.99-5.89 (m, 1H), 5.54-5.44 (m, 2H), 3.69-3.56 (m, 2H), 3.08-3.98 (m, 1H), 2.77 (ddd, *J* = 14.5, 8.3 and 5.6 Hz, 1H), 1.99 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.8, 139.9, 138.3, 136.3, 136, 133, 132, 130.4, 128.9 (2C), 128.5, 127.7, 127.4, 127.3, 127.27, 127.23, 125.8 (2C), 125.4, 125.2, 124.6, 123.2, 119.1, 118.1, 115.2 (2C), 41.4, 33.9, 24.6, 21.2. **HRMS (ESI):** *m/z* calcd for $C_{30}H_{26}NO_2S$ $(M+H)^+$: 464.1684, Found: 464.1668.

4-Methyl-N-(2-(3-(thiophen-2-yl)propioloyl)phenyl)benzenesulfonamide (184f)

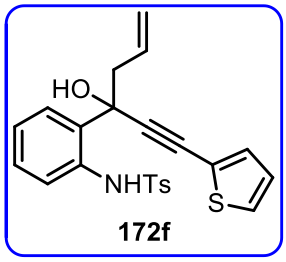


184f

This compound was isolated as pale yellow solid by following the reaction procedure-28. M.P = 166-168 ^oC. R_f = 0.5 (hexane/EtOAc = 6/4). **IR (thin film, neat):** ν_{max}/cm^{-1} 3109, 2916, 2187, 1609, 1489, 1260, 1157, 914. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 11.25 (s, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 7.1 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.63-7.57 (m, 2H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.20-7.12 (m, 2H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 180, 144.1, 140.8, 137.3, 136.4, 135.7, 134.5, 132.4, 129.8 (2C), 128, 127.3 (2C), 122.7, 122.4, 119.3, 118.5, 91.4, 89.4, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{16}NO_3S_2$ $(M+H)^+$: 382.0572, Found: 382.0555.

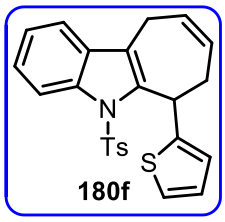
***N*-(2-(3-Hydroxy-1-(thiophen-2-yl)hex-5-en-1-yn-3-yl)phenyl)-4 methylbenzenesulfonamide (172f)**

This compound was isolated as pale yellow liquid by following the reaction procedure-28. R_f = 0.5 (hexane/EtOAc = 6.5/2.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 3432, 3228, 2221, 1704, 1584,



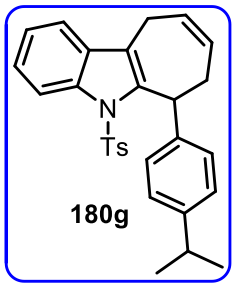
1337, 1160, 661. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.21 (s, 1H), 7.80 (d, *J* = 7.3 Hz, 2H), 7.60 (dd, *J* = 11.1 and 8.2 Hz, 2H), 7.33 (d, *J* = 4.9 Hz, 1H), 7.30-7.22 (m, 4H), 7.08-7.00 (m, 2H), 5.89-5.77 (m, 1H), 5.23 (d, *J* = 10.3 Hz, 1H), 5.10 (d, *J* = 17.1 Hz, 1H), 3.32 (s, 1H), 2.66-2.55 (m, 2H), 2.38 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.8, 137.2, 135.7, 132.9, 131.9, 129.7 (2C), 129.6, 129.2, 128.5, 128, 127.2 (2C), 127.1, 123.5, 121.5, 121.2, 120.2, 92.9, 81.5, 75, 47.3, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{23}H_{21}NNaO_3S_2$ $(M+Na)^+$: 446.0861, Found: 446.0855.

6-(Thiophen-2-yl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (180f)



This compound was isolated as pale yellow liquid. Following the reaction procedure-30, 40 mg of **172f** afforded 22.3 mg of **180f** (56% yield). R_f = 0.5 (hexane/EtOAc = 9.5/0.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2924, 1735, 1597, 1367, 1170, 662. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.29-8.24 (m, 1H), 7.45 (dt, *J* = 7.7 and 0.8 Hz, 1H), 7.40-7.35 (m, 3H), 7.35-7.30 (m, 1H), 7.12 (dd, *J* = 5.1 and 1.2 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.8 (dd, *J* = 5 and 3.5 Hz, 1H), 6.6 (dt, *J* = 3.5 and 1 Hz, 1H), 5.89-5.83 (m, 1H), 5.75-5.63 (m, 2H), 3.63-3.45 (m, 2H), 2.93-2.85 (m, 1H), 2.79-2.70 (m, 1H), 2.31 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 146.6, 144.3, 138.9, 136.1, 136.0, 130.5, 129.5 (2C), 127.9, 127.3, 126.4 (2C), 126.1, 125.3, 124.7, 123.7, 123.4, 119.5, 118.2, 115.4, 37, 34.5, 25.5, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{22}NO_2S_2$ $(M+H)^+$: 420.1092, Found: 420.1076.

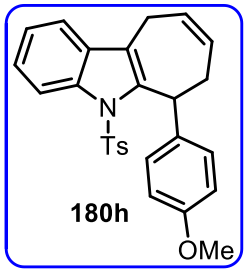
6-(4-Isopropylphenyl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (180g)



This compound was isolated as colorless liquid. Following the reaction procedure-30, 40 mg of **172g** afforded 20.4 mg of **180g** (51% yield). R_f = 0.5 (hexane/EtOAc = 9.5/0.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2920, 1602, 1451, 1172, 1090, 673. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.22 (d, *J* = 7.5 Hz, 1H), 7.48-7.46 (m, 1H), 7.35-7.30 (m, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.03-6.98 (m, 4H), 6.94 (d, *J* = 8.2 Hz, 2H), 5.95-5.89 (m, 1H), 5.59-5.54 (m, 1H), 5.36 (brs, 1H), 3.58-3.54 (m, 1H), 2.92-2.84 (m, 2H), 2.69-2.62 (m, 1H), 2.27 (s, 3H), 1.6 (s, 1H), 1.26 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 146.3, 143.9, 140, 139, 136.1, 136, 130.6, 129.2 (2C), 128.8, 128.4 (2C), 128, 126.4 (2C), 125.7 (2C), 124.4, 123.2, 119.1, 118,

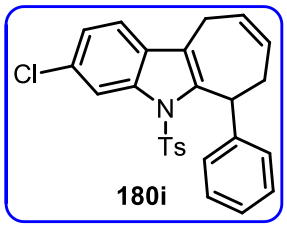
115.2, 40.9, 34.2, 33.5, 24.9, 24.15, 24.10, 21.4. **HRMS (ESI):** *m/z* calcd for $C_{29}H_{30}NO_2S$ $(M+H)^+$: 456.1997, Found: 456.1980.

6-(4-Methoxyphenyl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (180h)



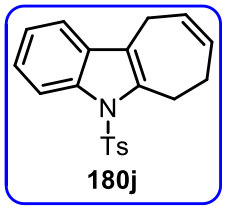
This compound was isolated as Pale yellow liquid. Following the reaction procedure-30, 40 mg of **172h** afforded 10.4 mg of **180h** (26% yield). R_f = 0.5 (hexane/EtOAc = 9.5/0.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2929, 1453, 1374, 1171, 704, 665, 583. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.26-8.22 (m, 1H), 7.50-7.46 (m, 1H), 7.38-7.30 (m, 2H), 7.25-7.20 (m, 2H), 6.99-6.94 (m, 4H), 6.71-6.66 (m, 2H), 5.97-5.89 (m, 1H), 5.56 (dt, *J* = 5.1 and 2.7 Hz, 1H), 5.32 (brs, 1H), 3.79 (s, 3H), 3.60-3.52 (m, 2H), 2.95-2.87 (m, 1H), 2.64 (ddd, *J* = 14.5, 8.3 and 5.9 Hz, 1H), 2.29 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 157.9, 143.9, 138.9, 136.2, 136.1, 134.9, 130.5, 129.5 (2C), 129.2 (2C), 128.9, 128.2, 126.3 (2C), 124.4, 123.2, 119, 118, 115.2, 113.1 (2C), 55.1, 40.5, 34.2, 24.7, 21.4. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{26}NO_3S$ $(M+H)^+$: 444.1633, Found: 444.1614.

3-Chloro-6-phenyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (180i)



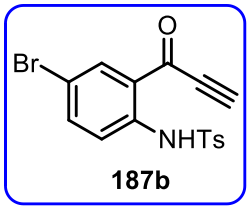
This compound was isolated as colorless oil. Following the reaction procedure-30, 40 mg of **172i** afforded 33 mg of **180i** (83% yield). R_f = 0.5 (hexane/EtOAc = 9.5/0.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2925, 1597, 1452, 1370, 1172,811, 745, 667. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.28 (s, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.24-7.13 (m, 5H), 7.07-6.94 (m, 4H), 5.95-5.84 (m, 1H), 5.54 (d, *J* = 2.2 Hz, 1H), 5.34 (brs, 1H), 3.62-3.42 (m, 2H), 2.91 (d, *J* = 13.7 Hz, 1H), 2.73-2.61 (m, 1H), 2.3 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.4, 142.4, 139.3, 136.4, 135.8, 130.5, 129.5 (2C), 129.1, 128.8, 128.5 (2C), 127.9, 127.8 (2C), 126.4 (2C), 126, 123.8, 118.9, 118.8, 115.4, 41.3, 34.1, 24.7, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{23}ClNO_2S$ $(M+H)^+$: 448.1138, Found: 448.1121.

5-Tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (180j)



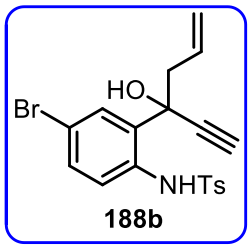
This compound was isolated as colorless solid. Following the reaction procedure-28, 40 mg of **188a** afforded 23.5 mg of **180j** (59% yield). M.P = 85-87 ^{o}C. R_f = 0.5 (hexane/EtOAc = 9.5/0.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2924, 1597, 1453, 1369, 1170, 747. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.22 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.6 Hz, 2H), 7.40-7.38 (m, 1H), 7.31-7.24 (m, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 6.00-5.97 (m, 2H), 3.41 (d, *J* = 1.5 Hz, 2H), 3.24 (ddd, *J* = 6.2, 4.3 and 1.7 Hz, 2H), 2.48-2.44 (m, 2H), 2.35 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.4, 137, 136.3, 135.7, 131.3, 130.7, 129.7 (2C), 129.1, 126.2 (2C), 124, 123.2, 118.3, 117.7, 114.8, 26.4, 25.2, 22.9, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{20}NO_2S$ $(M+H)^+$: 338.1215, Found: 338.1202.

***N*-(4-bromo-2-propioloylphenyl)-4-methylbenzenesulfonamide (187b)**



This compound was isolated as pale yellow solid by following the reaction procedure-28. M.P = 144-145 ^{o}C. R_f = 0.5 (hexane/EtOAc = 6/4). **IR (thin film, neat):** ν_{max}/cm^{-1} 2925, 2100, 1626, 1479, 1388, 1215, 1165, 660. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.91 (s, 1H), 8.31 (dd, *J* = 2 and 0.4 Hz, 1H), 7.80-7.72 (m, 2H), 7.66-7.59 (m, 2H), 7.30-7.25 (m, 2H), 3.64 (s, 1H), 2.40 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 178.6, 144.6, 139.9, 138.9, 137.1, 135.9, 129.9 (2C), 127.3 (2C), 123.1, 120.0, 115.1, 83.1, 79.2, 21.6. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{11}BrNO_3S$ $(M-H)^+$: 375.9641, Found: 375.9626.

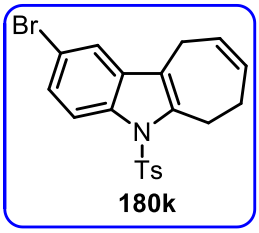
***N*-(4-bromo-2-(3-hydroxyhex-5-en-1-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (188b)**



This compound was isolated as pale yellow liquid by following the reaction procedure-28. R_f = 0.5 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 2925, 2113, 1597, 1486, 1384, 1335, 1163, 660. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.12 (s, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 2.4 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.37-7.30 (m, 1H), 7.26 (d, *J* = 8.3 Hz, 2H), 5.79-5.66 (m, 1H), 5.18 (dd, *J* = 10.3 and 1.2 Hz, 1H), 4.99 (dd. *J* = 17.1 and 1.2 Hz, 1H), 3.7 (brs, 1H), 2.82 (s, 1H), 2.51-2.40 (m, 2H), 2.38 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.1, 136.7, 134.8, 132.0, 131.6, 131.3, 131.2, 129.8 (2C), 127.1 (2C), 121.8, 121.3, 116.4, 83.4, 76.9,

73.7, 46.9, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{17}BrNO_3S$ $(M-H)^+$: 418.0111, Found: 418.0095.

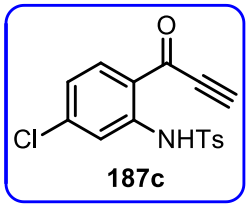
2-Bromo-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (180k)



180k

This compound was isolated as colorless solid. Following the reaction procedure-30, 40 mg of **188b** afforded 20.5 mg of **180k** (52% yield). M.P = 176-178 ^oC. R_f = 0.5 (hexane/EtOAc = 9.5/0.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2925, 1596, 1451, 1370, 1161, 913, 744. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.09 (d, *J* = 8.8 Hz, 1H), 7.59 (dd, *J* = 6.8 and 1.6 Hz, 2H), 7.51 (d, *J* = 2 Hz, 1H), 7.35 (dd, *J* = 8.8 and 2 Hz, 1H), 7.22 (d, *J* = 8 Hz, 2H), 6.01-5.91 (m, 2H), 3.37-3.32 (m, 2H), 3.21 (ddd, *J* = 6.1, 4.3 and 1.8 Hz, 2H), 2.48-2.39 (m, 2H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.8, 138.5, 136.0, 134.5, 132.5, 131.4, 129.9 (2C), 128.9, 126.7, 126.3 (2C), 120.6, 117.6, 116.8, 116.2, 26.4, 25.1, 22.8, 21.6. **HRMS (ESI):** m/z calcd for $C_{20}H_{17}BrNO_2S$ $(M-H)^+$: 414.0168, Found: 414.0151.

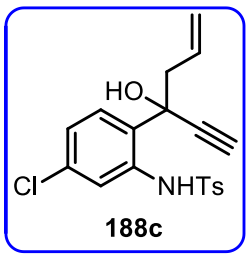
***N*-(5-Chloro-2-propioloylphenyl)-4-methylbenzenesulfonamide (187c)**



187c

This compound was isolated as a pale green solid by following the reaction procedure-28. M.P = 142-143 ^oC. R_f = 0.5 (hexane/EtOAc = 6/4). **IR (thin film, neat):** ν_{max}/cm^{-1} 3190, 2923, 2100, 1622, 1598, 1562, 1164, 938. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 11.13 (s, 1H), 8.16 (d, *J* = 8.6 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 1.7 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.08 (dd, *J* = 8.6 and 2 Hz, 1H), 3.58 (s, 1H), 2.42 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 178.8, 144.6, 142.9, 142.1, 136.2, 136, 129.9 (2C), 127.3 (2C), 122.9, 119.9, 117.9, 83.2, 79.5, 21.6. **HRMS (ESI):** m/z calcd for $C_{16}H_{13}ClNO_3S$ $(M+H)^+$: 334.0305, Found: 334.0290.

***N*-(5-Chloro-2-(3-hydroxyhex-5-en-1-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (188c)**

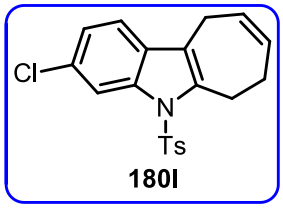


188c

This compound was isolated as pale yellow liquid by following the reaction procedure-28. R_f = 0.5 (hexane/EtOAc = 7.5/2.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 3445, 2982, 2116, 1658, 1599, 1493, 1164, 661. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.17 (s, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 2.2 Hz,

1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.30 (s, 1H), 7.28 (s, 1H), 6.99 (dd, *J* = 8.6 and 2.2 Hz, 1H), 5.80-5.69 (m, 1H), 5.20 (dd, *J* = 10.3 and 1 Hz, 1H), 5.02 (d, *J* = 17.1 Hz, 1H), 3.37 (d, *J* = 4.4 Hz, 1H), 2.81 (s, 1H), 2.54-2.42 (m, 2H), 2.40 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.2, 136.8, 136.7, 134.9, 131.3, 129.8 (2C), 129.5, 127.7, 127.2 (2C), 123.3, 121.4, 119.9, 83.6, 76.6, 73.9, 47, 21.5. **HRMS (ESI):** m/z calcd for $C_{19}H_{18}ClNNaO_3S$ $(M+Na)^+$: 398.0594, Found: 398.0577.

3-Chloro-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (180l)



180l

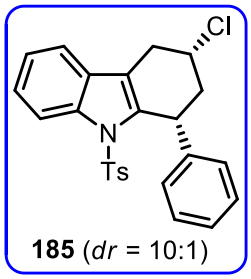
This compound was isolated as pale brown solid. Following the reaction procedure-30, 40 mg of **188c** afforded 22.3 mg of **180l** (56% yield). M.P = 95-97 ^oC. R_f = 0.5 (hexane/EtOAc = 9.5/0.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2926, 1737, 1598, 1460, 1371, 1166, 811. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.26 (d, *J* = 1.7 Hz, 1H), 7.65-7.60 (m, 2H), 7.31-7.28 (m, 1H), 7.26-7.23 (m, 2H), 7.23-7.21 (m, 1H), 6.0-5.94 (m, 2H), 3.38 (dd, *J* = 2.9 and 1.5 Hz, 2H), 3.19 (ddd, *J* = 6.2, 4.3 and 2 Hz, 2H), 2.49-2.41 (m, 2H), 2.38 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.8, 137.7, 136.2, 136.1, 131.3, 129.94 (2C), 129.90, 129.2, 128.9, 126.3 (2C), 123.8, 118.5, 117.8, 114.9, 26.3, 25.1, 22.8, 21.6. **HRMS (ESI):** m/z calcd for $C_{20}H_{17}ClNO_2S$ $(M-H)^+$: 370.0667; Found: 370.0656.

General procedure-31: Synthesis of 1,3-di-substituted tetrahydrocarbazole 185

A 5 mL glass vial was charged with **172a** (0.1 mmol), AgOAc (2 mol%) in DCE (1 mL) and stirred at 60 ^oC. After disappearance of **172a**, BiX_3 (X = Cl, Br, 50 mol%) was introduced at room temperature and continued stirring at room temperature until intermediate **173a** disappeared. The reaction mixture was then quenched with saturated aqueous $NaHCO_3$ (1 mL) and extracted with EtOAc (2×2 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by alumina column chromatography (5% EtOAc/hexane) to afford the final product **185**.

3-Chloro-1-phenyl-9-tosyl-2,3,4,9-tetrahydro-1*H*-carbazole (185)

This compound was isolated as colorless oil. Following the reaction procedure-30, 40 mg of **172a** afforded 36.5 mg of **185** (87% yield). R_f = 0.3 (hexane/EtOAc = 4/6). **IR (thin film, neat):**



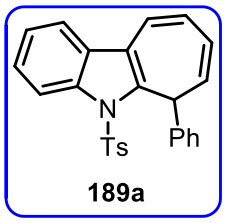
185 (*dr* = 10:1)

ν_{max}/cm^{-1} 2927, 1597, 1493, 1453, 1370, 1172, 746, 667. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.05 (d, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.37-7.29 (m, 3H), 7.23-7.19 (m, 4H), 7.07-7.04 (m, 2H), 7.03-7.01 (d, *J* = 8.2 Hz, 2H), 4.81 (t, *J* = 8.3 Hz, 1H), 4.32-4.25 (m, 1H), 3.38-3.33 (m, 1H), 3 (ddd, *J* = 15.5, 10.3 and 2.8 Hz, 1H), 2.91-2.86 (m, 1H), 2.31 (s, 3H), 2.07 (td, *J* = 12.8 Hz, 1H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 144.8, 144.1, 137.7, 136.4, 135.5, 129.3 (2C), 129.1, 128.4 (2C), 127.6 (2C), 126.4, 126.3 (2C), 124.9, 123.6, 120.3, 118.4, 115.4, 54.2, 46.1, 42.5, 33, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{23}ClNO_2S$ $(M+H)^+$: 436.1138, Found: 436.1124.

General procedure-32: Synthesis of dihydrocyclohept[*b*]indoles 189

The compound **180** was prepared using reaction procedure-30. Compound **180** (0.11 mmol) was dissolved in 1,4-dioxane in an oven dried round bottom flask, SeO_2 (1.5 eq) was added to the reaction mixture. The reaction mixture was then stirred at 110 ^{o}C until the reactant **180** disappeared. The reaction mixture was filtered through celite with DCM. The combined organic layers were concentrated under reduced pressure. The residue was purified by alumina column chromatography (5% EtOAc/hexane) to afford **189.**

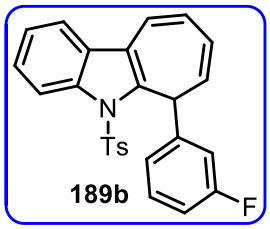
6-Phenyl-5-tosyl-5,6-dihydrocyclohepta[*b*]indole (189a)



189a

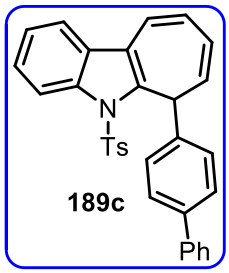
This compound was isolated as a pale brown liquid. Following the procedure-32, 40 mg of **180a** afforded 31 mg of **189a** (78% yield). R_f = 0.4 (hexane/EtOAc = 9.5/0.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2924, 1735, 1492, 1372, 1170, 747. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.37 (d, *J* = 8.1 Hz, 1H), 7.65-7.61 (m, 1H), 7.54-7.50 (m, 2H), 7.43-7.33 (m, 2H), 7.05 (dd, *J* = 19.9 and 7.5 Hz, 5H), 6.98-6.92 (m, 3H), 6.39-6.29 (m, 2H), 6.22 (d, *J* = 9.5 Hz, 1H), 6.08-6.03 (m, 1H), 2.29 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 144.8, 140.2, 136.8, 135.2, 133.3, 129.6 (2C), 128.5, 128.2, 127.7, 127.6 (2C), 127.4, 126.9 (2C), 126.5 (2CH), 126, 124.8, 123.8, 121.7, 120.2, 118.6, 115.6, 39.7, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{22}NO_2S$ $(M+H)^+$: 412.1371, Found: 412.1376.

6-(3-Fluorophenyl)-5-tosyl-5,6-dihydrocyclohepta[*b*]indole (189b)



This compound was isolated as a pale brown liquid. Following the reaction procedure-32, 40 mg of **180c** afforded 24.2 mg of **189b** (61% yield). R_f = 0.4 (hexane/EtOAc = 9.5/0.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 3026, 1734, 1588, 1372, 1170, 754. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.39 (d, *J* = 8.3 Hz, 1H), 7.67-7.63 (m, 1H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.46-7.34 (m, 2H), 7.07-7.01 (m, 3H), 6.98 (d, *J* = 10.8 Hz, 1H), 6.80-6.74 (m, 2H), 6.48 (d, *J* = 10.5 Hz, 1H), 6.41-6.31 (m, 2H), 6.21 (d, *J* = 9.5 Hz, 1H), 6.07-6.01 (m, 1H), 2.3 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.3 (d, *J* = 243.2 Hz), 145.1, 142.8 (d, *J* = 6.6 Hz), 136.9, 135.3, 132.5, 129.6 (2C), 128.9 (d, *J* = 8.1 Hz), 128.6, 128.4, 127.7, 126.6, 126.4 (2C), 125.1, 123.9, 122.7 (d, *J* = 2.7 Hz), 121.9, 120.3, 118.7, 115.6, 113.9 (d, *J* = 22.4 Hz), 112.8 (d, *J* = 21.1 Hz), 39.4 (d, *J* = 1.4 Hz), 21.5. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -114.0. **HRMS (ESI):** m/z calcd for $C_{26}H_{19}FNO_2S$ $(M-H)^+$: 428.1119, Found: 428.1107.

6-([1,1'-Biphenyl]-4-yl)-5-tosyl-5,6-dihydrocyclohepta[*b*]indole (189c)



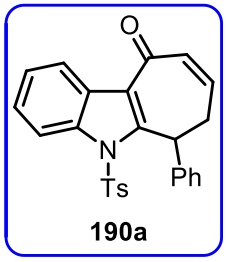
This compound was isolated as pale yellow solid. Following the reaction procedure-32, 40 mg of **180d** afforded **189c** (62% yield). M.P = 173-175 ^oC. R_f = 0.4 (hexane/EtOAc = 9.5/0.5). **IR (thin film, neat):** ν_{max}/cm^{-1} 3028, 1734, 1597, 1451, 1169, 747. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.41-8.38 (m, 1H), 7.68-7.65 (m, 1H), 7.56-7.51 (m, 4H), 7.45-7.31 (m, 7H), 7.05-6.98 (m, 5H), 6.44-6.38 (m, 1H), 6.37-6.31 (m, 1H), 6.26 (d, *J* = 9.3 Hz, 1H), 6.12-6.06 (m, 1H), 2.25 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.9, 140.8, 139.4, 138.9, 136.9, 135.3, 133.2, 129.5 (2C), 128.7 (2C), 128.5, 128.2, 127.6, 127.4 (2C), 127.3, 127, 126.9 (2C), 126.5 (2C), 126.3 (2CH), 124.9, 123.8, 121.8, 120.2, 118.6, 115.6, 39.5, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{32}H_{26}NO_2S$ $(M+H)^+$: 488.1684, Found: 488.1666.

General procedure-33: Synthesis of dihydroindolotropones 190

The compound **180** was prepared using reaction procedure-32. Compound **180** (0.11 mmol) was dissolved in CH_3CN-H_2O (3:1) mixture in an oven dried round bottom flask, TBHP (aqueous, 2 eq) was added to the reaction mixture and then $RuCl_3$ (5 mol%) was added. The reaction mixture was stirred at 60 ^oC until the reactant **180** disappeared. The reaction mixture was then quenched

with saturated aq. $NaHCO_3$ (1 mL) and extracted with EtOAc (2×2 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by alumina column chromatography (5% EtOAc/hexane) to afford **190**.

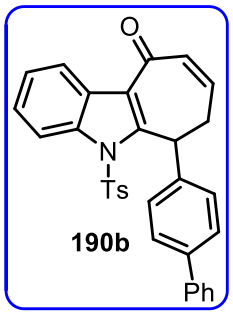
6-Phenyl-5-tosyl-6,7-dihydrocyclohepta[*b*]indol-10(5H)-one (190a)



190a

This compound was isolated as a pale brown liquid. Following the reaction procedure-33, 40 mg of **180a** afforded 24.6 mg of **190a** (60% yield). R_f = 0.3 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 2924, 1657, 1452, 1370, 1172, 750. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.33 (dt, *J* = 8.3 and 1 Hz, 1H), 7.75-7.69 (m, 1H), 7.49-7.40 (m, 3H), 7.28-7.25 (m, 2H), 7.20-7.13 (m, 3H), 6.99-6.92 (m, 4H), 6.17 (dd, *J* = 12.2 and 1.7 Hz, 1H), 5.68 (dd, *J* = 6.0 and 3.3 Hz, 1H), 3.37-3.22 (m, 2H), 2.27 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.5, 145.3, 144.2, 136.4, 135.9, 135.1, 131.8, 129.6 (2C), 129.3, 128.8 (2C), 128.5, 127.5 (2C), 127.1, 126.6 (2C), 125.6, 124.3, 118.2, 117.9, 115.3, 47.6, 36.8, 21.5. **HRMS (ESI):** m/z calcd for $C_{26}H_{22}NO_3S$ $(M+H)^+$: 428.1320; Found: 428.1303.

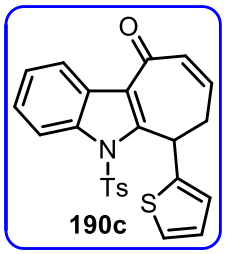
6-([1,1'-Biphenyl]-4-yl)-5-tosyl-6,7-dihydrocyclohepta[*b*]indol-10(5*H*)-one (190b)



190b

This compound was isolated as pale yellow solid. Following the reaction procedure-33, 40 mg of **180d** afforded 25 mg of **190b** (61% yield). M.P = 167-168 ^oC. R_f = 0.3 (hexane/EtOAc = 7/3). **IR (thin film, neat):** 2917, 1729, 1596, 1443, 1168, 1090, 760. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.67-8.63 (m, 1H), 8.36-8.31 (m, 1H), 7.59-7.54 (m, 2H), 7.50-7.41 (m, 4H), 7.42-7.36 (m, 3H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.89 (d, *J* = 8.3 Hz, 2H), 6.28 (d, *J* = 4.2 Hz, 2H), 5.88 (t, *J* = 4.2 Hz, 1H), 3.31-3.24 (m, 1H), 3.07-2.99 (m, 1H), 2.18 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 188.3, 146.9, 145.3, 140.4, 139.7, 138.9, 136.9, 136.4, 135.2, 134.6, 129.5 (2C), 128.9 (2C), 128.8 (2C), 127.9, 127.4, 126.97 (2C), 126.90 (2C), 126.6 (2C), 125.9, 125.1, 123.1, 123.0, 114.7, 39.7, 34.7, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{32}H_{26}NO_3S$ $(M+H)^+$: 504.1633, Found: 504.1642.

6-(Thiophen-2-yl)-5-tosyl-6,7-dihydrocyclohepta[*b*]indol-10(5*H*)-one (190c)



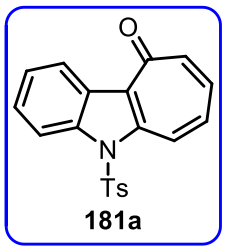
190c

This compound was isolated as a pale brown solid. Following the reaction procedure-33, 40 mg of **180f** afforded 19.7 mg of **190c** (48% yield). M.P = 138-140 ^{o}C. R_f = 0.3 (hexane/EtOAc = 7/3). **IR (thin film, neat):** ν_{max}/cm^{-1} 2925, 1732, 1657, 1374, 1171, 749. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.3 (d, *J* = 8.4 Hz, 1H), 7.7 (d, *J* = 7.3 Hz, 1H), 7.51-7.38 (m, 5H), 7.11 (dd, *J* = 5.1 and 1.2 Hz, 1H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.76 (dd, *J* = 5.1 and 3.4 Hz, 1H), 6.56 (d, *J* = 3.4 Hz, 1H), 6.21 (d, *J* = 12.2 Hz, 1H), 5.96 (s, 1H), 3.29 (d, *J* = 4.2 Hz, 2H), 2.31 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 198.2, 145.4, 143.8, 139.5, 135.8, 135.3, 131.5, 129.7 (2C), 129.3, 128.4, 126.8, 126.6 (2C), 125.8, 125.7, 124.9, 124.4, 118.1, 117.6, 115.4, 48.2, 32.5, 21.6. **HRMS (ESI):** m/z calcd for $C_{24}H_{20}NO_3S_2$ $(M+H)^+$: 434.0885, Found: 434.0868.

General procedure-34: Synthesis of Indolotropones 181

The compound **180** was prepared using reaction procedure-3. Compound **180** (0.08 mmol) was dissolved in 1,4-dioxane in an oven dried round bottom flask, SeO_2 (1.5 eq) was added to the reaction mixture. The reaction mixture was stirred at 120 ^{o}C until the reactant **180** disappeared. The reaction mixture was filtered through celite with DCM. The combined organic layers were concentrated under reduced pressure. The residue was purified by alumina column chromatography (5% EtOAc/hexane) to afford **181.**

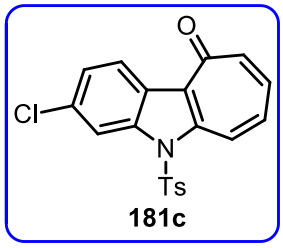
5-Tosylcyclohepta[*b*]indol-10(5*H*)-one (181a)



181a

This compound was isolated as a pale brownish solid. Following the reaction procedure-34, 30 mg of **180j** afforded 20.3 mg of **181a** (65% yield). M.P = 169-173 ^{o}C. R_f = 0.3 (hexane/EtOAc = 5/5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2925, 1733, 1620, 1514, 1377, 1175, 747. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.71 (d, *J* = 12.7 Hz, 1H), 8.44 (d, *J* = 8.6 Hz, 1H), 7.88 (d, *J* = 8 Hz, 1H), 7.86 (d, *J* = 12 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.61 (ddd, *J* = 8.5, 7.2 and 1.2 Hz, 1H), 7.51-7.45 (m, 1H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.14 (dd, *J* = 12.7 and 2.7 Hz, 1H), 7.08 (dd, *J* = 12 and 2.7 Hz, 1H), 2.35 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 187.4, 146.1, 138.8, 137.7, 137.2, 136.7, 134.8, 130.2 (2CH), 129.5, 128.7, 127.3, 126.6, 126.5 (2CH), 126.4, 125.1, 119.5, 115.9, 21.7. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{16}NO_3S$ $(M+H)^+$: 350.0851, Found: 350.0834.

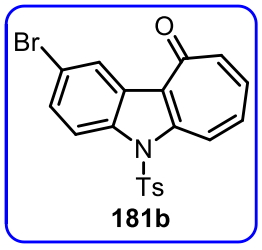
3-Chloro-5-tosylcyclohepta[*b*]indol-10(5*H*)-one (181c)



181c

This compound was isolated as brownish solid. Following the reaction procedure-34, 30 mg of **180l** afforded 19.4 mg of **181c** (62% yield). M.P = 212-214 ^{o}C. R_f = 0.3 (hexane/EtOAc = 5/5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2925, 1732, 1612, 1514, 1415, 1171, 659. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.63 (d, *J* = 13 Hz, 1H), 8.47 (d, *J* = 1.7 Hz, 1H), 7.80 (s, 1H), 7.77 (d, *J* = 4.8 Hz, 1H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.46 (dd, *J* = 8.6 and 1.7 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.12 (dd, *J* = 13 and 2.7 Hz, 1H), 7.07 (dd, *J* = 12 and 2.7 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 187.2, 146.4, 138.9, 138.0, 137.5, 137.0, 134.8, 134.6, 130.4 (2C), 129.0, 126.6 (2C), 126.1, 125.8 (2C), 125.7, 120.3, 115.9, 21.7. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{15}ClNO_3S$ $(M+H)^+$: 384.0461, Found: 384.0446.

2-Bromo-5-tosylcyclohepta[*b*]indol-10(5*H*)-one (181b)



181b

This compound was isolated as a pale brownish solid. Following the reaction procedure-34, 30 mg of **180k** afforded 20 mg of **181b** (64% yield). M.P = 218-220 ^{o}C. R_f = 0.3 (hexane/EtOAc = 5/5). **IR (thin film, neat):** ν_{max}/cm^{-1} 2925, 1623, 1517, 1380, 1172, 749. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.65 (d, *J* = 12.8 Hz, 1H), 8.32 (d, *J* = 8.8 Hz, 1H), 8.00 (d, *J* = 2 Hz, 1H), 7.75 (d, *J* = 12.4 Hz, 1H), 7.70-7.64 (m, 3H), 7.24 (d, *J* = 8 Hz, 2H), 7.14 (dd, *J* = 12.8 and 2.8 Hz, 1H), 7.06 (dd, *J* = 12.2 and 2.8 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 187.2, 146.4, 139.3, 138.4, 136.9, 135.8, 134.5, 131.5, 130.3(2C), 129.0, 128.9, 126.5 (2C), 126.0, 125.2, 122.3, 118.6, 117.4, 21.7. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{15}BrNO_3S$ $(M+H)^+$: 427.9956, Found: 427.9939.

General procedure-35: One-pot Synthesis of dihydrocyclohept[*b*]indoles 189

A 5 mL glass vial was charged with **172** (0.09 mmol), AgOAc (2 mol%) in DCE (1 mL) and stirred at 60 ^{o}C. After disappearance of **172**, allyl-TMS (1.5 eq) and $InCl_3$ (5 mol%) were introduced at 0 ^{o}C and continued stirring at 0 ^{o}C-rt until intermediate **173** disappeared. On complete formation of intermediate **179**, G-I (15 mol%) was introduced and continued stirring at room temperature until intermediate **179** disappeared. After complete formation of **180**, the solvent DCE was removed by reduced pressure and then 1,4-dioxane solvent was added to the

residue and SeO_2 (1.5 eq) was added to the reaction mixture and stirred at 110 ^oC until the intermediate **180** disappeared. The reaction mixture was filtered through celite with DCM. The combined organic layers were concentrated under reduced pressure. The residue was purified by alumina column chromatography (5% EtOAc/hexane) to afford **189**.

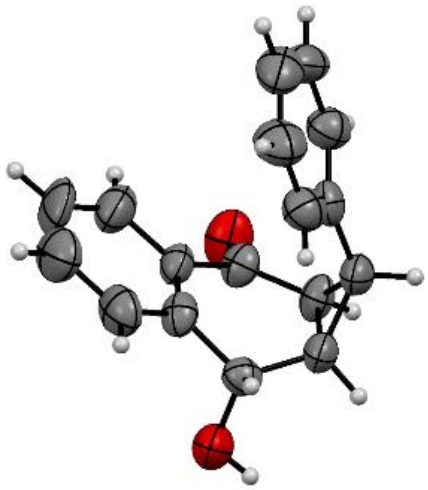
General procedure-36: One-pot Synthesis of dihydroindolotropones 190

A 5 mL glass vial was charged with **188** (0.1 mmol), AgOAc (2 mol%) in DCE (1 mL) and stirred at 60 ^oC. After disappearance of **188**, allyl-TMS (1.5 eq) and $InCl_3$ (5 mol%) were introduced at 0 ^oC and continued stirring at 0 ^oC-rt until intermediate **173** disappeared. On complete formation of intermediate **179**, G-I (15 mol%) was introduced and continued stirring at room temperature until intermediate **179** disappeared. After complete formation of **180**, the solvent DCE was removed by reduced pressure and CH_3CN-H_2O (3:1) was added to the residue, TBHP (aqueous, 2 eq) and then $RuCl_3$ (5 mol%) was added to the reaction mixture. The reaction mixture was then stirred at 60 ^oC until the reactant **180** disappeared. The reaction mixture was then quenched with saturated aqueous $NaHCO_3$ (1 mL) and extracted with EtOAc (2×2 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by alumina column chromatography (5% EtOAc/hexane) to afford **190**.

General procedure-37: One-pot Synthesis of indolotropones 181

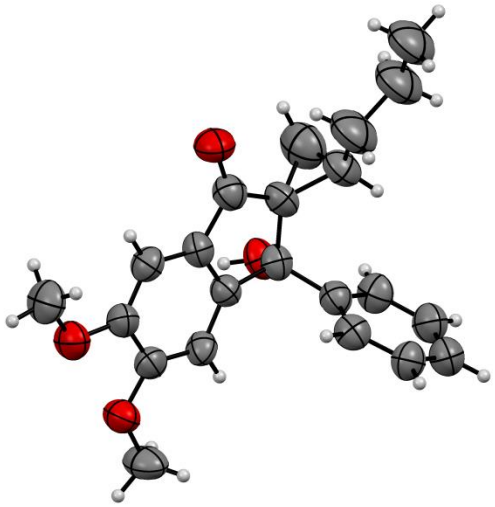
The reaction was performed as in the procedure described for the one-pot synthesis of dihydrocyclohepta[*b*]indoles **189** [representative procedure-35].

Table 27: General data and structure refinement parameters for 44a



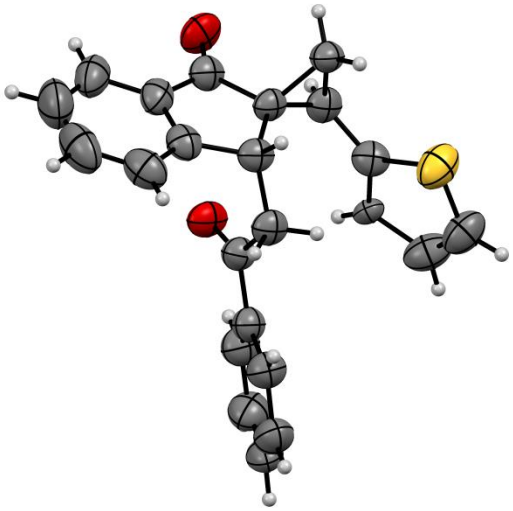
Empirical formula	$C_{17}H_{14}O_2$
Formula weight	250.28
Temperature/K	298
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.550(4)
b/Å	8.868(2)
c/Å	12.114(4)
α/°	90
β/°	105.063(11)
γ/°	90
Volume/Å^3	1301.9(6)
Z	4
ρ_{calc}g/cm^3	1.277
μ/mm^{-1}	0.083
F(000)	528.0
Crystal size/mm^3	0.3 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71075)
2Θ range for data collection/°	6.724 to 54.964
Index ranges	$-16 \leq h \leq 11$, $-11 \leq k \leq 8$, $-15 \leq l \leq 15$
Reflections collected	6620
Independent reflections	2925 [R_{int} = 0.0829, R_{sigma} = 0.1229]
Data/restraints/parameters	2925/0/173
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0839, wR_2 = 0.1944
Final R indexes [all data]	R_1 = 0.1944, wR_2 = 0.2604
Largest diff. peak/hole / e Å^{-3}	0.20/-0.22
CCDC	1855673

Table 28: General data and structure refinement parameters for 58i



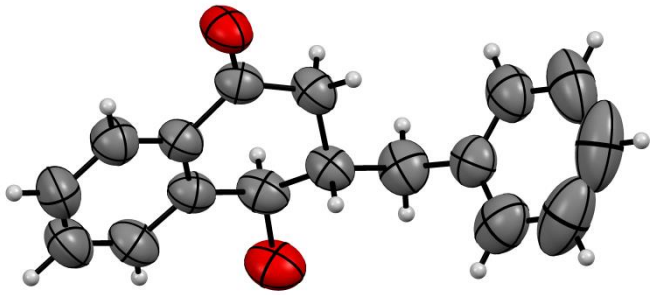
Empirical formula	$C_{22}H_{24}O_4$
Formula weight	352.41
Temperature/K	298.0
Crystal system	Triclinic
Space group	P-1
a/Å	7.4337(9)
b/Å	16.5499(13)
c/Å	17.4774(12)
α/°	115.629(7)
β/°	98.851(9)
γ/°	92.296(9)
Volume/Å^3	1901.8(3)
Z	4
ρ_{calc}g/cm^3	1.231
μ/mm^{-1}	0.084
F(000)	752.0
Crystal size/mm^3	0.4 × 0.3 × 0.3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.266 to 65.504
Index ranges	-10 ≤ h ≤ 10, -24 ≤ k ≤ 24, -26 ≤ l ≤ 22
Reflections collected	15993
Independent reflections	12180 [R_{int} = 0.0451, R_{sigma} = 0.1249]
Data/restraints/parameters	12180/0/452
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.1164, wR_2 = 0.3173
Final R indexes [all data]	R_1 = 0.2660, wR_2 = 0.4582
Largest diff. peak/hole / e Å^{-3}	0.75/-0.63
CCDC	1855911

Table 29: General data and structure refinement parameters for 59e



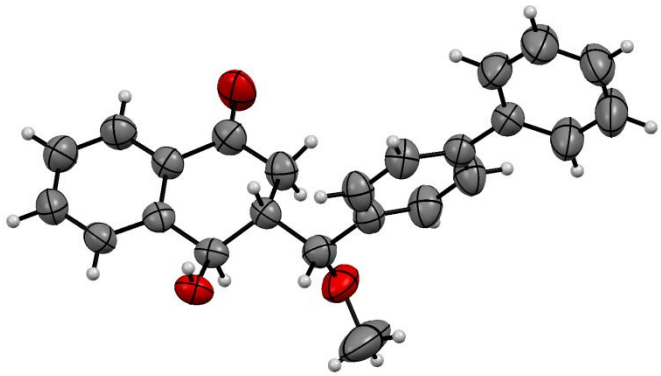
Empirical formula	$C_{23}H_{18}O_2S$
Formula weight	358.43
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.8749(3)
b/Å	15.6150(9)
c/Å	19.5294(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1791.56(18)
Z	4
ρ_{calc}g/cm^3	1.329
μ/mm^{-1}	0.195
F(000)	752.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.92 to 50.054
Index ranges	$-6 \leq h \leq 4$, $-18 \leq k \leq 16$, $-22 \leq l \leq 22$
Reflections collected	10443
Independent reflections	3108 [R_{int} = 0.0681, R_{sigma} = 0.0621]
Data/restraints/parameters	3108/0/236
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0772, wR_2 = 0.2167
Final R indexes [all data]	R_1 = 0.0851, wR_2 = 0.2393
Largest diff. peak/hole / e Å^{-3}	0.89/-0.66
Flack parameter	-0.01(9)
CCDC	1855912

Table 30: General data and structure refinement parameters for 69a



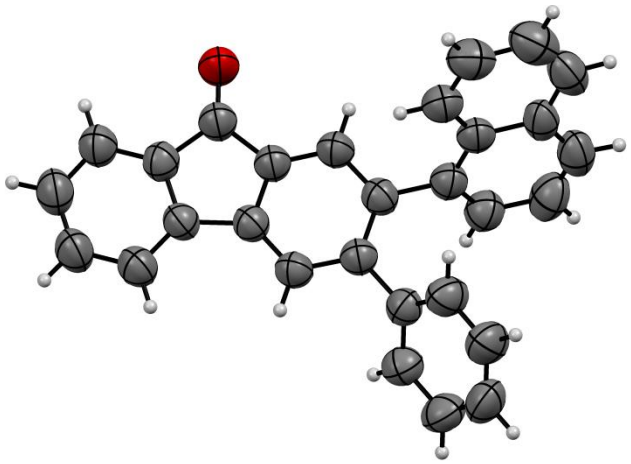
Empirical formula	$C_{17}H_{16}O_2$
Formula weight	252.30
Temperature/K	298.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.918(2)
b/Å	12.7502(12)
c/Å	9.7371(16)
α/°	90
β/°	94.511(17)
γ/°	90
Volume/Å^3	1351.3(4)
Z	4
ρ_{calc}g/cm^3	1.240
μ/mm^{-1}	0.080
F(000)	536.0
Crystal size/mm^3	0.3 × 0.3 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.274 to 65.48
Index ranges	$-14 \leq h \leq 5$, $-16 \leq k \leq 19$, $-14 \leq l \leq 14$
Reflections collected	6988
Independent reflections	4429 [R_{int} = 0.0431, R_{sigma} = 0.1084]
Data/restraints/parameters	4429/0/174
Goodness-of-fit on F^2	0.994
Final R indexes [I>=2σ (I)]	R_1 = 0.0788, wR_2 = 0.1922
Final R indexes [all data]	R_1 = 0.2421, wR_2 = 0.2928
Largest diff. peak/hole / e Å^{-3}	0.21/-0.16
CCDC	1855913

Table 31: General data and structure refinement parameters for 70b



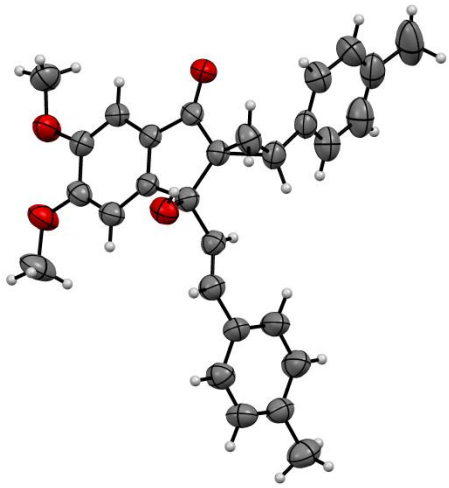
Empirical formula	$C_{24}H_{22}O_3$
Formula weight	358.41
Temperature/K	296.15
Crystal system	Triclinic
Space group	P-1
a/Å	10.929(4)
b/Å	11.823(4)
c/Å	17.435(6)
α/°	101.104(9)
β/°	97.099(9)
γ/°	116.493(8)
Volume/Å^3	1921.3(11)
Z	4
ρ_{calc}g/cm^3	1.239
μ/mm^{-1}	0.081
F(000)	760.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.008 to 49.992
Index ranges	$-12 \leq h \leq 12$, $-14 \leq k \leq 13$, $-20 \leq l \leq 20$
Reflections collected	22995
Independent reflections	6732 [R_{int} = 0.0790, R_{sigma} = 0.0909]
Data/restraints/parameters	6732/0/491
Goodness-of-fit on F^2	0.943
Final R indexes [I>=2σ (I)]	R_1 = 0.0602, wR_2 = 0.1420
Final R indexes [all data]	R_1 = 0.1455, wR_2 = 0.1875
Largest diff. peak/hole / e Å^{-3}	0.18/-0.23
CCDC	1871641

Table 32: General data and structure refinement parameters for 72a



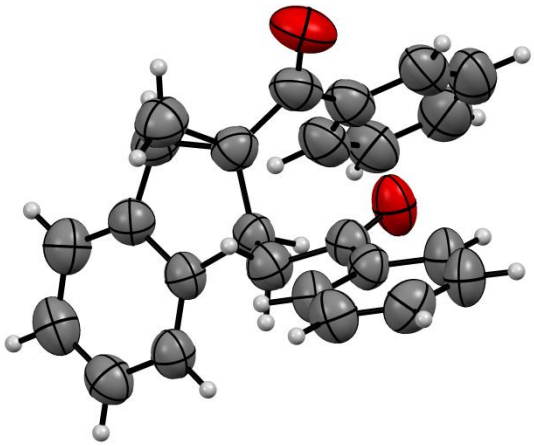
Empirical formula	$C_{29}H_{18}O$
Formula weight	382.43
Temperature/K	298.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.3374(12)
b/Å	8.7031(13)
c/Å	31.909(5)
α/°	90
β/°	93.112(8)
γ/°	90
Volume/Å^3	2034.7(5)
Z	4
ρ_{calc}g/cm^3	1.248
μ/mm^{-1}	0.074
F(000)	800.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.33 to 50.048
Index ranges	$-7 \leq h \leq 8$, $-10 \leq k \leq 10$, $-37 \leq l \leq 37$
Reflections collected	15398
Independent reflections	3592 [R_{int} = 0.0613, R_{sigma} = 0.0370]
Data/restraints/parameters	3592/0/271
Goodness-of-fit on F^2	1.097
Final R indexes [I>=2σ (I)]	R_1 = 0.0698, wR_2 = 0.1627
Final R indexes [all data]	R_1 = 0.1116, wR_2 = 0.1911
Largest diff. peak/hole / e Å^{-3}	0.15/-0.14
CCDC	1855918

Table 33: General data and structure refinement parameters for 89h



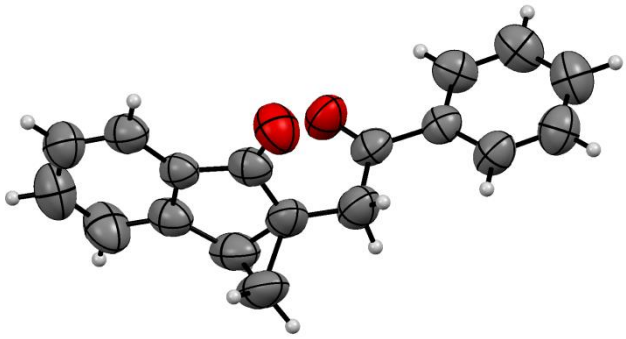
Empirical formula	$C_{29}H_{28}O_4$
Formula weight	440.51
Temperature/K	298.00(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	13.1713(8)
b/Å	10.2547(7)
c/Å	35.1953(18)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4753.8(5)
Z	8
ρ_{calc}g/cm^3	1.231
μ/mm^{-1}	0.081
F(000)	1872.0
Crystal size/mm^3	0.4 × 0.4 × 0.35
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.166 to 50
Index ranges	$-12 \leq h \leq 15$, $-12 \leq k \leq 12$, $-41 \leq l \leq 41$
Reflections collected	13893
Independent reflections	4181 [R_{int} = 0.0504, R_{sigma} = 0.0601]
Data/restraints/parameters	4181/0/303
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0570, wR_2 = 0.1345
Final R indexes [all data]	R_1 = 0.0925, wR_2 = 0.1692
Largest diff. peak/hole / e Å^{-3}	0.22/-0.19
CCDC	1917783

Table 34: General data and structure refinement parameters for 95a



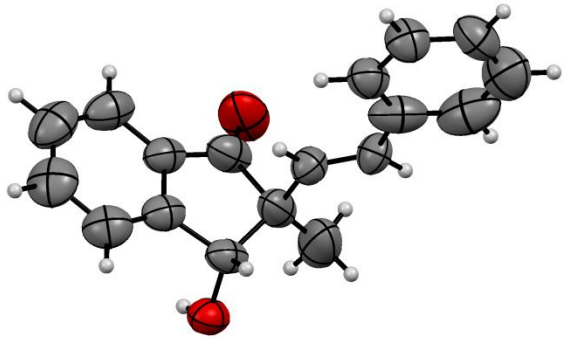
Empirical formula	$C_{25}H_{20}O_2$
Formula weight	352.41
Temperature/K	298.0(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.914(2)
b/Å	24.209(4)
c/Å	10.247(3)
α/°	90
β/°	109.27(3)
γ/°	90
Volume/Å^3	1853.3(9)
Z	4
ρ_{calc}g/cm^3	1.263
μ/mm^{-1}	0.079
F(000)	744.0
Crystal size/mm^3	0.3 × 0.25 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.39 to 49.998
Index ranges	$-8 \leq h \leq 9$, $-27 \leq k \leq 28$, $-12 \leq l \leq 12$
Reflections collected	6942
Independent reflections	3275 [R_{int} = 0.0716, R_{sigma} = 0.1169]
Data/restraints/parameters	3275/0/244
Goodness-of-fit on F^2	0.989
Final R indexes [I>=2σ (I)]	R_1 = 0.0755, wR_2 = 0.1760
Final R indexes [all data]	R_1 = 0.1851, wR_2 = 0.2462
Largest diff. peak/hole / e Å^{-3}	0.20/-0.18
CCDC	1918037

Table 35: General data and structure refinement parameters for 142



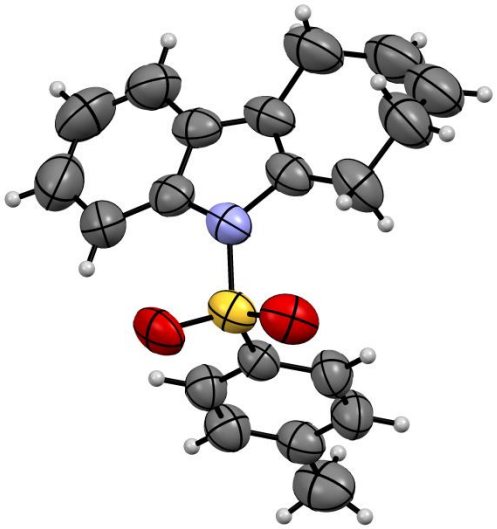
Empirical formula	$C_{36}H_{28}O_4$
Formula weight	524.58
Temperature/K	298.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.9866(6)
b/Å	14.0592(12)
c/Å	33.190(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2793.5(5)
Z	4
ρ_{calc}g/cm^3	1.247
μ/mm^{-1}	0.080
F(000)	1104.0
Crystal size/mm^3	0.3 × 0.3 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.702 to 50
Index ranges	$-7 \leq h \leq 1$, $-16 \leq k \leq 11$, $-39 \leq l \leq 37$
Reflections collected	7566
Independent reflections	4584 [R_{int} = 0.0490, R_{sigma} = 0.0650]
Data/restraints/parameters	4584/0/361
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0670, wR_2 = 0.1596
Final R indexes [all data]	R_1 = 0.1035, wR_2 = 0.2035
Largest diff. peak/hole / e Å^{-3}	0.20/-0.22
Flack parameter	0.4(10)
CCDC	1970555

Table 36: General data and structure refinement parameters for 148a



Empirical formula	$C_{18}H_{16}O_2$
Formula weight	264.31
Temperature/K	298.0(2)
Crystal system	Trigonal
Space group	R-3
a/Å	19.9046(17)
b/Å	19.9046(17)
c/Å	18.9361(19)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	6497.2(13)
Z	18
ρ_{calc}g/cm^3	1.216
μ/mm^{-1}	0.078
F(000)	2520.0
Crystal size/mm^3	0.25 × 0.25 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.392 to 65.414
Index ranges	-19 ≤ h ≤ 22, -27 ≤ k ≤ 5, -26 ≤ l ≤ 10
Reflections collected	5406
Independent reflections	4491 [R_{int} = 0.0225, R_{sigma} = 0.0909]
Data/restraints/parameters	4491/0/190
Goodness-of-fit on F^2	0.951
Final R indexes [I>=2σ (I)]	R_1 = 0.0671, wR_2 = 0.1465
Final R indexes [all data]	R_1 = 0.1978, wR_2 = 0.2200
Largest diff. peak/hole / e Å^{-3}	0.15/-0.24
CCDC	1971535

Table 37: General data and structure refinement parameters for 180j



Empirical formula	$C_{20}NO_2S$
Formula weight	337.45
Temperature/K	293
Crystal system	Monoclinic
Space group	C2/c
a/Å	16.978(5)
b/Å	11.307(3)
c/Å	18.072(5)
α/°	90
β/°	100.741(15)
γ/°	90
Volume/Å^3	3408.5(17)
Z	8
ρ_{calc}g/cm^3	1.3151
μ/mm^{-1}	0.202
F(000)	1425.6
Crystal size/mm^3	0.27 × 0.24 × 0.22
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.04 to 50.06
Index ranges	$-20 \leq h \leq 14$, $-12 \leq k \leq 13$, $-21 \leq l \leq 21$
Reflections collected	6802
Independent reflections	2976 [R_{int} = 0.0723, R_{sigma} = 0.0634]
Data/restraints/parameters	2976/0/217
Goodness-of-fit on F^2	1.288
Final R indexes [I>=2σ (I)]	R_1 = 0.0708, wR_2 = 0.1921
Final R indexes [all data]	R_1 = 0.0987, wR_2 = 0.2270
Largest diff. peak/hole / e Å^{-3}	0.47/-0.41
CCDC	1520411

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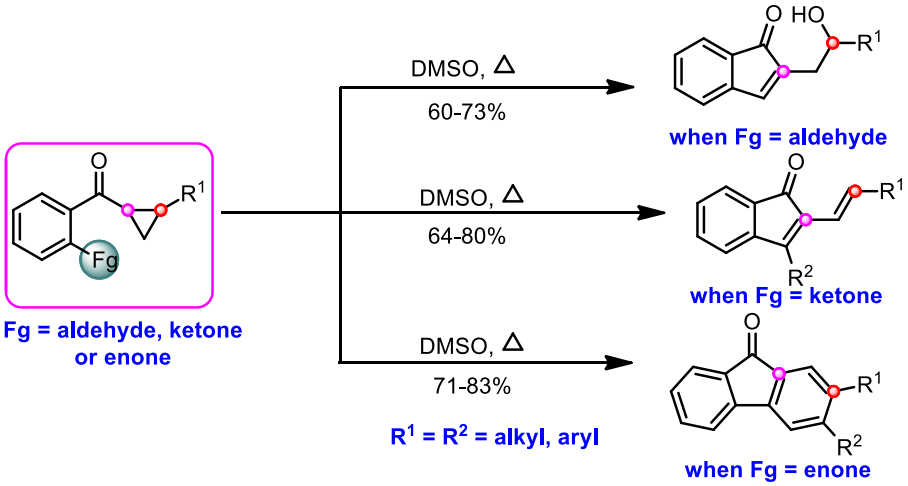
LIST OF PUBLICATIONS

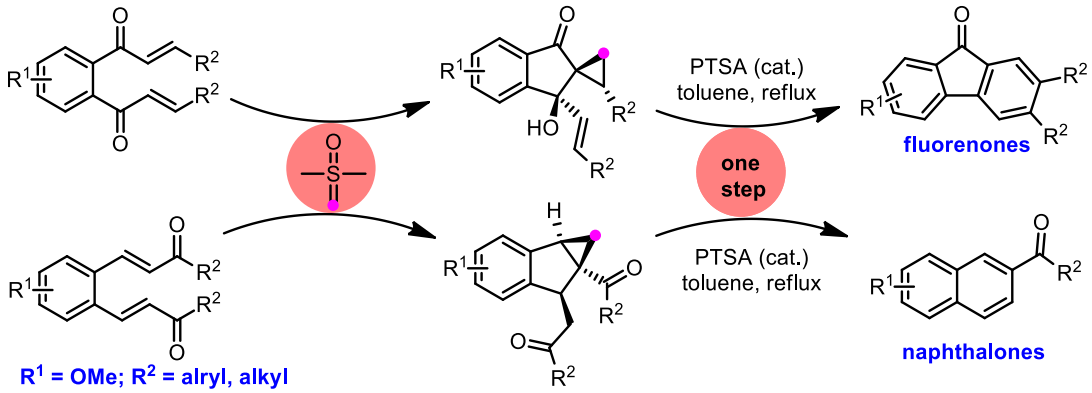
(1) *"Ring-Opening/Recyclization Cascades of Mono-Activated Cyclopropanes"*

Mishra, U. K.;[#] Patel, K.;[#] Ramasastry, S. S. V. *Org. Lett.* **2020**, *22*, 3815.



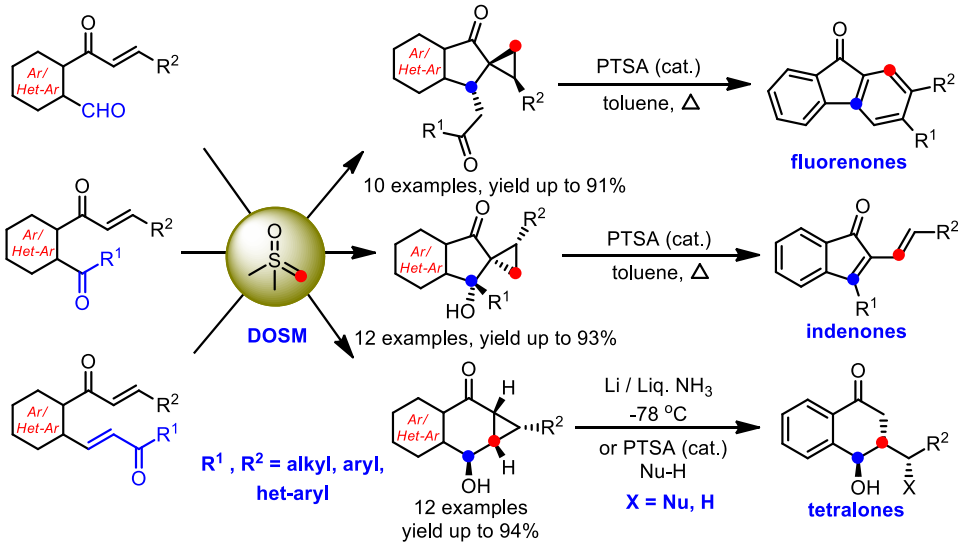
(2) "Beyond the Corey-Chaykovsky Reaction: Synthesis of Unusual Cyclopropanoids via Desymmetrization and Thereof"

Patel, K.;[#] Mishra, U. K.;[#] Mukhopadhyay, D.; Ramasastry, S. S. V. *Chem. Asian J.* **2019**, *14*, 4568.



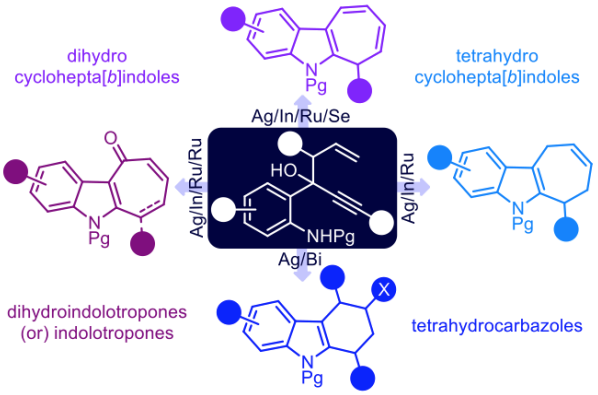
(3) *"Synthesis of Cyclopropanoids via Substrate-Based Cyclization Pathways"*

Mishra, U. K.; Patel, K.; Ramasastry, S. S. V. *Org. Lett.* **2019**, *21*, 175.



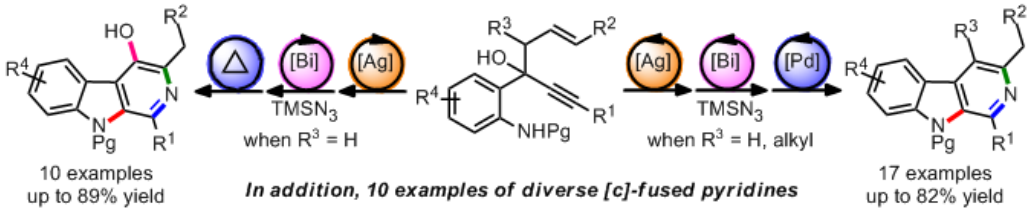
(4) *"One-Pot Multicatalytic Approaches for the Synthesis of Cyclohepta[b]indoles, Indolotropones, and Tetrahydrocarbazoles"*

Mishra, U. K.; Yadav, S.; Ramasastry, S. S. V. *J. Org. Chem.* **2017**, *82*, 6729.



(5) *"One-Pot Trimetallic Relay Catalysis: A Unified Approach for the Synthesis of β-Carbolines and Other [c]-Fused Pyridines"*

Dhiman, S.; Mishra, U. K.; Ramasastry, S. S. V. *Angew. Chem. Int. Ed.* **2016**, *55*, 7737.



ABOUT THE AUTHOR

The author, Mr. Uttam K. Mishra was born at East Medinipur, West Bengal. After his initial schooling at Amarshi, he received a B.Sc. degree in Chemistry from Midnapore College, Vidyasagar University in 2012. After obtaining a Masters degree from Vidyasagar University, Midnapore, in 2014, he joined the research group of Dr. S. S. V. Ramasastry at the Indian Institute of Science Education and Research (IISER) Mohali, as a Ph.D. student in August 2015. He passed the comprehensive examination in August 2016. Presently, he is working as a Senior Research Fellow of IISER Mohali in the Department of Chemical Sciences.

CONFERENCES ATTENDED

- *One-pot synthesis of annulated heteroarenes*
  Poster presentation at the 'Recent Advances in Organic and Bioorganic and Chemistry **(RAOBC)**', IISER Mohali, India, 22-24th March 2019.

- *New strategies for the synthesis of unusual cyclopropanoids and their unexpected transformations*
  Poster presentation at the 'Recent Advances in Bioorganic and Medicinal Chemistry **(RABMC-2019)** Symposium', NIPER Mohali, India, 30th August 2019.

- *Synthesis of cyclohepta[b]indoles and indolotropones in a one-pot multicatalytic process*
  Poster presentation at the Emerging Trends in Drug Developments and Natural Products **(ETDDNP-2018)**, University of Delhi, India, 12-14th January 2018.

- *Multicatalytic one-pot synthesis of cyclohepta[b]indoles and indolotropones*
  Poster presentation at the **ACS on Campus Roadshow**, IISER Mohali, India, 9th February 2018.

- *One-pot multicatalysis for the synthesis of annulated heteroarenes*
  Oral presentation at the XIII JNOST-Organic Chemistry Conference **(JNOST-OCC)**, Banaras Hindu University, India, 9-12th November 2017.