Phosphine-Mediated Cyclopentannulation of Arenes and Heteroarenes

A thesis submitted for the partial fulfillment of the degree of Doctor of Philosophy

by

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Dedicated

to my beloved teacher

Nimai Bhanja

Declaration

The work presented in this thesis titled "***Phosphine-Mediated Cyclopentannulation of Arenes and Heteroarenes***" 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 bona fide record of original work done by me and all sources listed within have been detailed in the bibliography.

Bishnupada Satpathi

Date: 6th July 2019

Place: IISER Mohali

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.

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Place: IISER Mohali

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Summary

The five-membered carbocycles are recognized as essential class of substructures widely present in natural products and pharmaceutically active molecules. They are often utilized as key building block for the synthesis of complex targets. On the other hand, arene and heteroarene-fused carbocycles are abundant in a diverse range of bioactive natural products and pharmaceutically relevant molecules. Among them, indanes and pentannulated heteroarenes consisting of indole, thiophene, benzothiophene, benzofuran, and furans have occupied a distinct place in pharmaceuticals and found broad application in material science especially in organic semiconducting materials and optoelectronics. The importance of cyclopentanoids inspired the development of numerous synthetic strategies to access pentannulated arenes and heteroarenes by utilizing precious metals and organocatalysts. However, the development of general, efficient, and atom-economic organocatalytic methods starting from the readily accessible materials remain an emerging research area.

The thesis entitled "*Phosphine-Mediated Cyclopentannulations of Arenes and Heteroarenes*" describes the efforts towards the development of novel phosphine-mediated strategies for the pentannulation of arenes and heteroarenes. 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 various organophosphine mediated strategies such as [3+2], [4+1], [2+2+1] cycloaddition reactions, Rauhut-Currier (RC) reaction, and Morita-Baylis-Hillman (MBH) reaction leading to a wide variety of cyclopentanoids.

Our ongoing research interest in developing of new organocatalytic strategies for the cyclopenta-fused arenes and heteroarenes, we designed substrates amenable to an intramolecular Morita-Baylis-Hillman (IMBH) reaction by tethering the enone and carbonyl functionalities *ortho* to each other. The second section of the thesis demonstrates an efficient intramolecular MBH reaction of β-mono- and β,β-disubstituted enones. In an attempt to develop an enantioselective IMBH reaction several solvent and catalyst combinations were evaluated. An excellent enantioinduction was realized with the bifunctional phosphine only in hexafluoroisopropanol (HFIP) solvent. A diverse range of cyclopenta[*b*]annulated arenes and heteroarenes synthesized from easily accessible starting materials in excellent yields and short reaction time.

Summary

Continued research interest in developing new strategies for the cyclopentannulation prompted us to design the dienone-aldehyde substrate amenable to an intramolecular MBH (IMBH) reaction. The third section discusses a highly enantioselective IMBH reaction of δ-mono and δ,δ-disubstituted dienones to access cyclopenta-fused arenes and heteroarenes. This work represents the first enantioselective intramolecular MBH reaction of dienones. The reaction mechanism was elucidated through control experiments. Further, the IMBH adducts were elaborated to 3,4-disubstituted fluorenones *via* a one-pot telescopic method.

The fourth section describes a phosphine and water-mediated intramolecular reductive cyclization reaction of α-substituted dienone-aldehydes to afford the highly functionalized cyclopenta-fused arenes and heteroarenes bearing two contiguous stereogenic centers, one of them being an all-carbon quaternary center, in good yields and diastereoselectivities. Interestingly, this result represents the first metal- and hydride free intramolecular reductive aldol reaction of α-substituted dienones. The role of water and mechanistic details were thoroughly elucidated by means of control experiments. After the successful establishment of an intramolecular reductive aldol reaction, a series of serendipitous one-step elaborations of reductive aldol products were established. These strategies describe efficient access to indeno-[1,2-*b*]furanones, indeno[1,2-*b*]pyrans, and dibenzo[*a*,*h*]-azulen-8-ones.

List of Abbreviations

Ac	acetyl
aq	aqueous
atm	atmospheric
BINAP	2,2'-bis(diphenylphosphino)-1,1' binaphthyl
BINOL	1,1′-Binaphthalene-2,2′-diol
Bn	benzyl
Bz	benzoyl
Boc	*tert*-butyloxycarbonyl
brs	broad singlet
calcd	calculated
cod	cyclooctadiene
d	day(s)
d	doublet
DABCO	1,4-diazabicyclo[2.2.2]octane
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCE	1,2-dichloroethane
DCM	dichloromethane
dd	doublet of a doublet
ddd	doublet of a doublet of doublet
DMAP	4-dimethylaminopyridine
DMF	*N*,*N'*-dimethyl formamide
DMSO	dimethyl sulfoxide
dq	doublet of a quartet
dr	diastereomeric ratio
dt	doublet of a triplet
ee	enantiomeric excess
eq.	equivalents
ESI	electron spray ionization
FT-IR	Fourier-transform infrared spectroscopy
h	hour(s)
HFIP	1,1,1,3,3,3-hexafluoroisopropanol

List of Abbreviations

HRMS	high-resolution mass spectrum
Hz	Hertz
IBX	2-iodoxybenzoic acid
Ipc*	diisopinocamphenyl
J	coupling constant
LG	leaving group
m	multiplet
mg	milligram(s)
MHz	megahertz
min	minute(s)
mL	milliliter(s)
mmol	millimole(s)
M.P	melting point
MS	molecular sieves
m/z	mass/charge
NMF	N-methylformamide
ppm	parts per million
^{n}Pr	*n*-propyl
p-TSA	*para*-toluenesulfonic acid
q	quartet
qd	quartet of doublet
rt	room temperature
s	singlet
sept	septet
t	triplet
^{t}Bu	*tert*-butyl
td	triplet of a doublet
tert	tertiary
TFE	2,2,2-trifluoroethanol
TFT	α,α,α-trifluorotoluene
THF	tetrahydrofuran

TMS	trimethylsilyl
TMS	tetramethylsilane
Ts	tosyl
TLC	thin layer chromatography

Section 1

General Introduction About Cyclopentanoids

The five-membered carbocycles are recognized as essential class of substructures widely present in natural products and pharmaceutically active molecules. They are often utilized as crucial building block for the synthesis of complex targets. Cyclopentane fused carbocycles also frequently encountered in nature. Polyfunctionalized cyclopentanes exhibit excellent biological activities, such as Ticagrelor is a marketed drug employed for the treatment of platelet aggression inhibitor. Pactamycin shows promising antiviral and anti-tumor activity. Marine secondary metabolite Vannusal B, isolated from *Euplotes vannus*, is an anti-fungal agent, Fig. 1.[1]

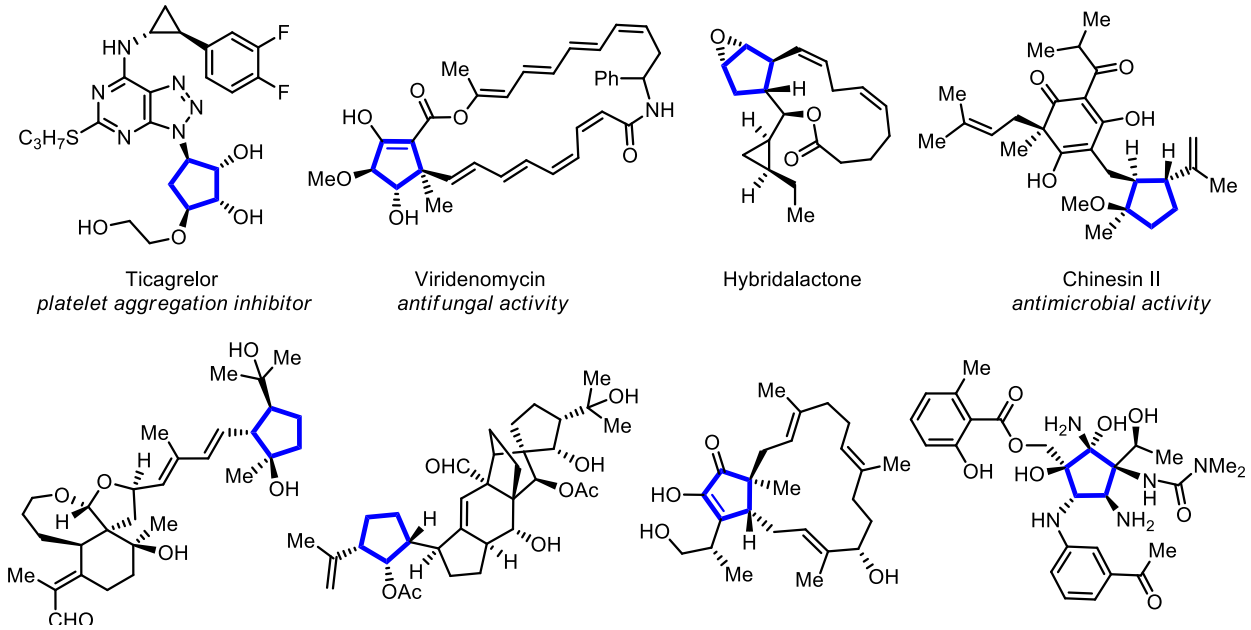


Figure 1: Natural products and pharmaceutically important molecules possessing cyclopentanes

On the other hand, heteroarene fused cyclopentanes are also abundant in a diverse range of active pharmaceutical ingredients, natural products, and organic materials.[2] Among them, pentannulated heteroarenes consisting of indole, pyrrole, benzofuran, and furans have occupied a distinct place in organic synthesis. For example, cyclopenta[*b*]indole core containing natural product Polyveoline, an indolosesqiterpene isolated from *Polyalthia suaveolens*, exhibits anti-parasitic activity. Spiroindimicin B isolated from marine actinomycete *Streptomyces* shows anti-cancer activity. The cyclopenta-fused pyrrole macrocycle, Roseophilin isolated from *Streptomyces griscovirides* is an antibiotic and anti-cancer agent. (–) Nakadomarin-A a furan alkaloid shows kinase-4 inhibitory activity and antibacterial activity. An orally active vasodilatory, antiplatelet and cytoprotective agent, prostacyclin analog Beraprost also possess a cyclopenta-fused benzofuran moiety, Fig. 2.[3] Furthermore, cyclopenta[*b*]annulated thiophene and benzothiophenes find potential applications in organic semiconductors since their incorporation drastically influences the electronic properties of the semiconductors.[4]

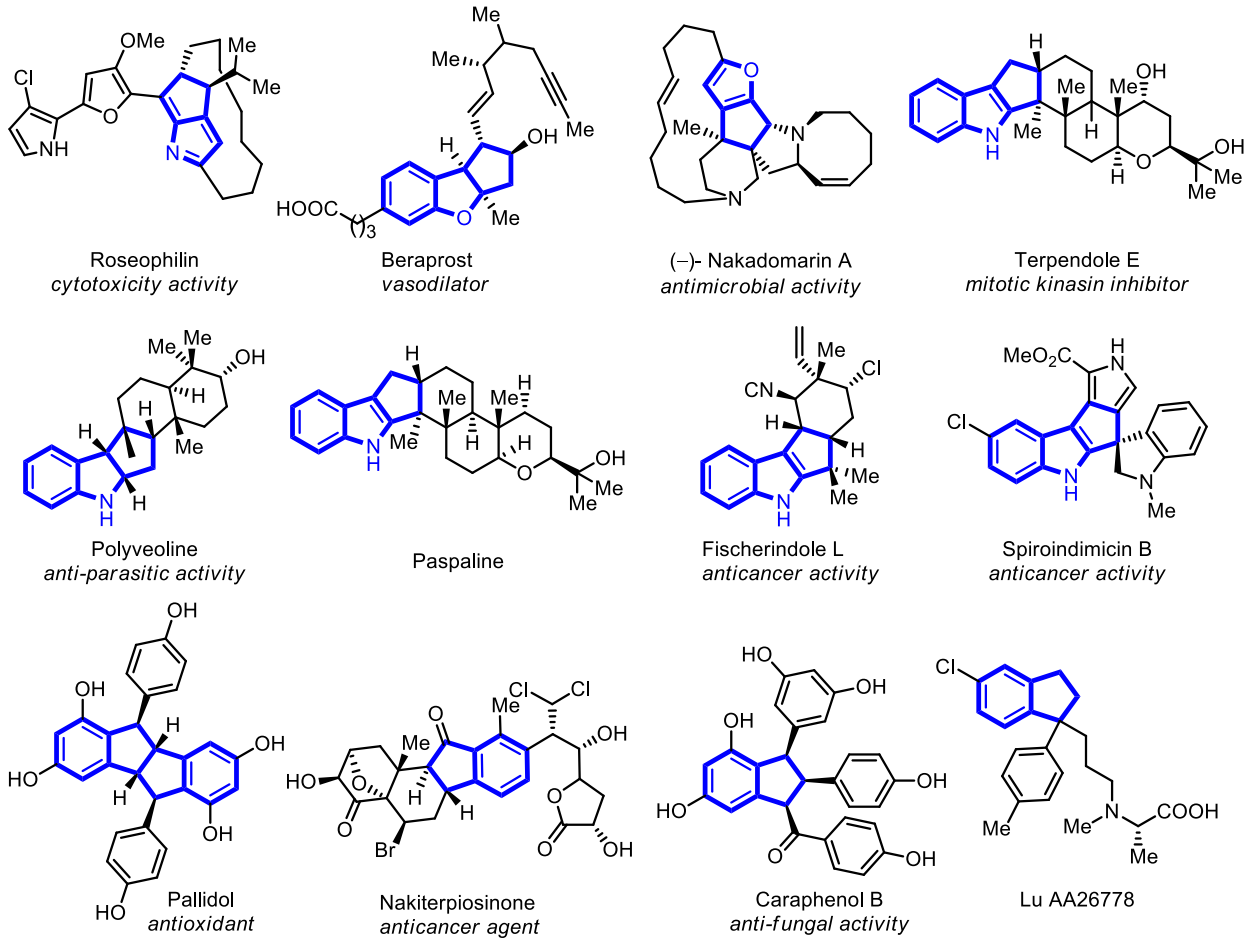


Figure 2: Representative examples of bioactive cyclopenta-fused arenes and heteroarenes

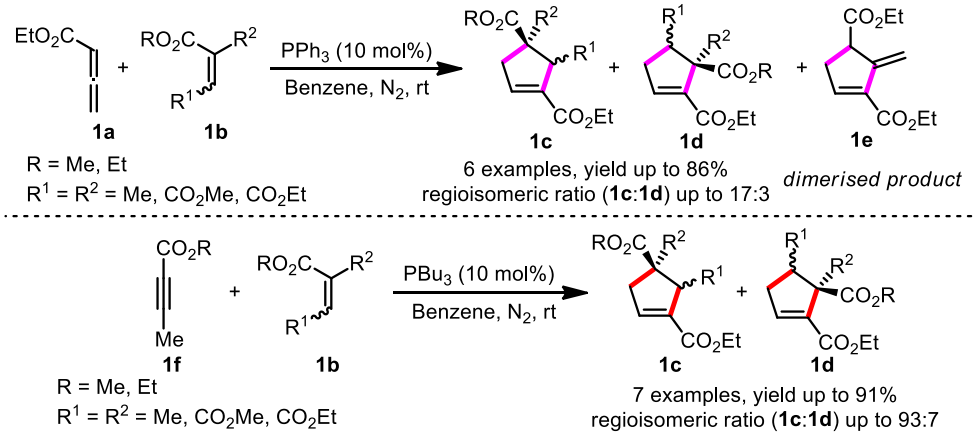
The cyclopentannulated arenes (indane and indene), one of the most important carbocycles, serve as an essential central structure in many natural products. They exhibit diverse biological activities such as antiallergic, antimicrobial, including antitumor, anti-hypercholesterolemic properties, and often found in active pharmaceuticals. For example, the resveratrol derived, Caraphenol B isolated from *Caragana sinica* shows promising anti-fungal activity. Another resveratrol dimer, Pallidol is widely found in red wine with antioxidant activity. A protease inhibitor, Crixivan marketed as an anti-HIV drug also possesses a functionalized indane moiety, Fig. 2.[5] They are also employed as versatile chiral ligands and organocatalysts in organic synthesis.[6] Besides, these indanes are useful in material science.[7]

These aforementioned importances of cyclopentanoids in the area of synthetic organic chemistry, pharmaceuticals, and materials science hold the key for the ever-growing interest to develop efficient synthetic protocols. Past few decades, enormous numbers of method have been

developed by employing precious metal (Pd, Au, Pt, Ru, Rh, and Ir) catalysis.[8] Though metals exhibit a high level of selectivity, the major drawback is the toxicity originating from metal contamination in pharmaceuticals. Recently organocatalytic approaches (N-heterocyclic carbenes (NHCs), organophosphines and amines) received remarkable attention due to their operational simplicity, atom economic and less toxic nature. Toward this, various organophosphine mediated strategies such as [3+2], [4+1], [2+2+1] cycloaddition reactions, Rauhut-Currier (RC) reaction, and Morita-Baylis-Hillman (MBH) reaction have been reported.[9] In the next few subsections, a few important metal-free methods leading to a wide variety of cyclopentanoids are described.

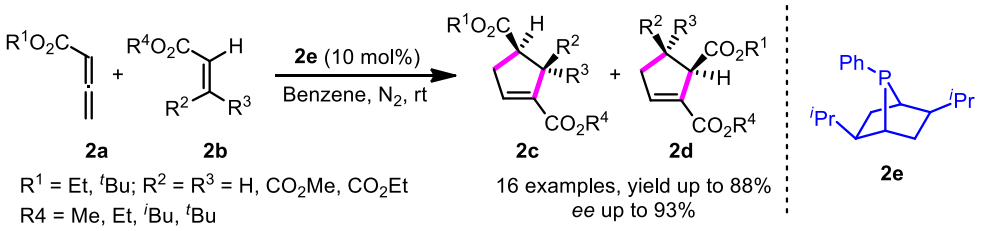
1.1: [3+2] cyclization based approaches for the synthesis of cyclopentanes

In 1995, Lu *et al.*[10] documented an unprecedented intermolecular phosphine catalyzed [3+2] cycloaddition reaction. The reaction of 2,3-butadienoates **1a** or 2-butynoates **1f** with activated alkenes resulted in the formation of highly substituted cyclopentenes **1c** and **1d** in good yields and regioisomeric ratio, albeit small amount of dimerized product of allenoate **1e** also was observed, Scheme 1. This reaction opened a new avenue in the area of phosphine catalysis.



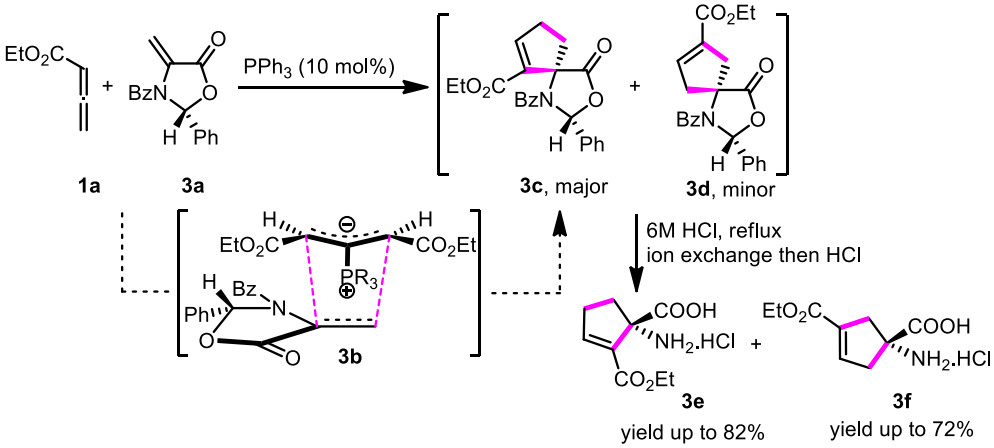
Scheme 1: Lu's [3+2] for the synthesis of cyclopentenes

In 1997, Zhang *et al.*[11] reported the first asymmetric Lu [3+2] annulation by employing the rigid-bridged chiral phosphines **2e,** Scheme 2. A wide variety of substituted cyclopentenes **2c** and **2d** were synthesized in good yields and excellent enantio- and regioselectivities. The sterically hindered alkenes influenced the better enantioinduction in the product.



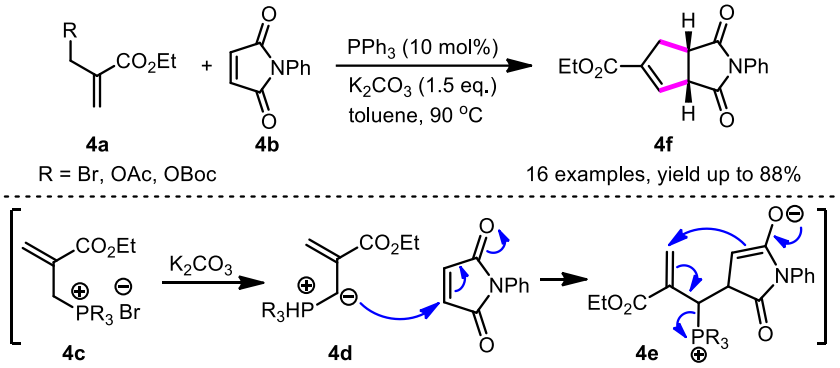
Scheme 2: Zhang's asymmetric cyclopentene synthesis

In 1997, Pyne *et al.*[12] described the synthesis of spirocyclic L-glutamates by employing [3+2] cycloaddition reaction, Scheme 3. A variety of L-glutamate analogs **3c** and **3d** were synthesized in good yields and moderate regioselectivities, owing to their medicinal importance. The cyclic α-amino acids **3e** and **3f** also were achieved *via in-situ* hydrolysis of **3c** and **3d** respectively.



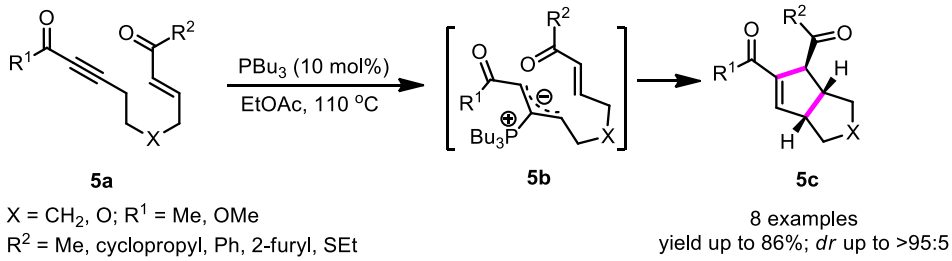
Scheme 3: Pyne's synthesis of spirocyclic L-glutamates

In 2003, Lu *et al.*[13] first employed activated allyl bromides **4a**, which can be obtained easily from Baylis-Hillman adducts, as C_3 component in a [3+2] cyclization, Scheme 4. The reaction of maleimide **4b** with allyl bromides **4a** furnished the annulated cyclopentenes **4f** in good yields. The initial formation of a phosphonium salt **4c** converts to the corresponding ylide **4d** in the presence of a base and subsequently undergoes the Michael addition and cyclization leading to the desired products.



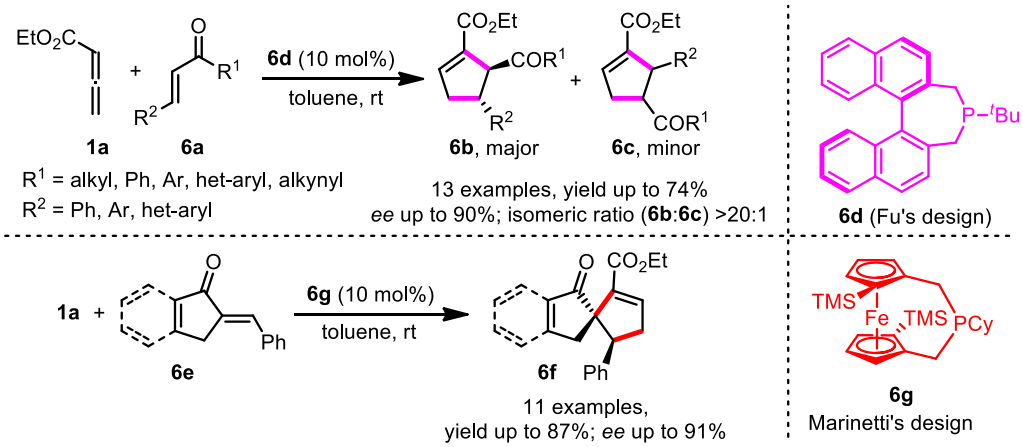
Scheme 4: Lu's [3+2] annulation of MBHADs

In 2003, Krische *et al.*[14] came up with an intramolecular version to overcome the regioselectivity issue in the formal Lu [3+2] cyclization, Scheme 5. The intramolecularly tethered enone-ynone functionalities of **5a** undergo regioselective cycloaddition reaction *via* a zwitterionic intermediate **5b**, in the presence of tributylphosphine to deliver the diquinanes **5c** in good yields and excellent diastereoselectivities.



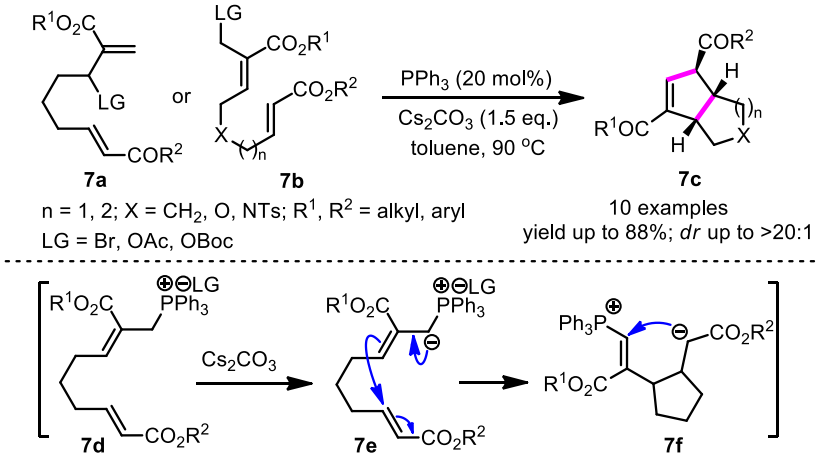
Scheme 5: Krische's synthesis of diquinanes

In 2006, Fu *et al.*[15] have demonstrated an asymmetric [3+2] cycloaddition of allene **1a** with chalcones **6a,** Scheme 6. By employing the Gladiali's phosphepine **6d**, an array of densely substituted cyclopentenes **6b** and spirocyclic indanes **6f** were synthesized in excellent yields and enantioselectivities. Later Marinetti *et al.*[16] also described similar cycloaddition reaction by utilizing ferrocene-based chiral phosphine **6g**.



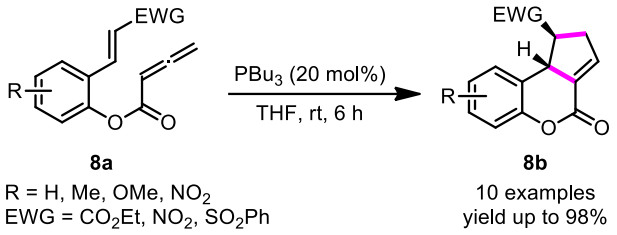
Scheme 6: Fu's and Marinetti's asymmetric cyclopentene synthesis

In 2007, Tang *et al.*[17] have constructed [n.3.0] ring systems *via* an intramolecular ylide annulation, Scheme 7. The Morita-Baylis-Hillman adducts (MBHADs) and activated olefins were tethered intramolecularly to deliver the annulated cyclopentenes **7c** in excellent diastereoselectivities, under phosphine catalysis *via* an in situ generation of ylide **7e** and subsequent cyclization.



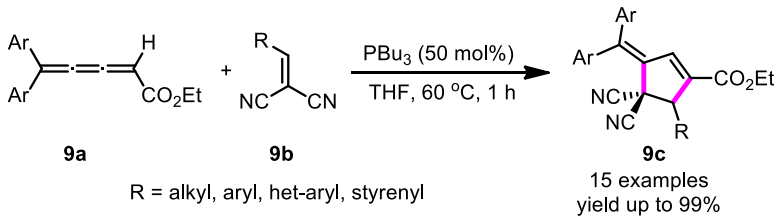
Scheme 7: Tang's intramolecular [3+2] cycloaddition

In 2007, Kwon *et al.*[18] developed an efficient intramolecular [3+2] cycloaddition reaction of 2-styrenyl allenoates **8a**, Scheme 8. The intramolecular cyclization provided cyclopentene fused dihydrocoumarines **8b** in excellent yields and exclusive diastereoselectivities in the presence of tributylphosphine. An exclusive solvent and catalyst dependent reactivity of allenoates **8a** also was observed in this study.



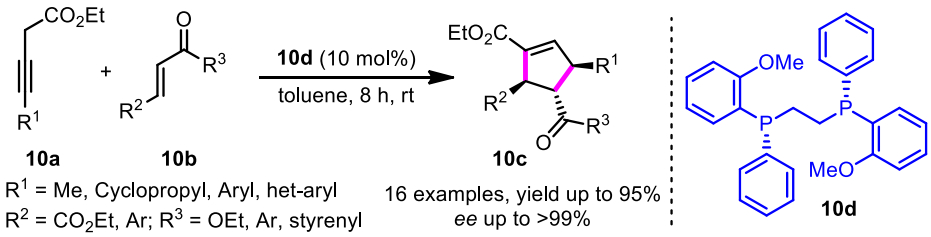
Scheme 8: Kwon's synthesis of cyclopentene fused dihydrocoumarines

In 2009, Shi *et al.*[19] have exploited 2,3,4-pentatrienoates **9a** in the [3+2] cycloaddition reaction as a three carbon synthon, Scheme 9. The reaction between trienoates **9a** and arylmethylidenemalononitriles **9b** generated the cycloadducts **9c** in moderate to excellent yields.



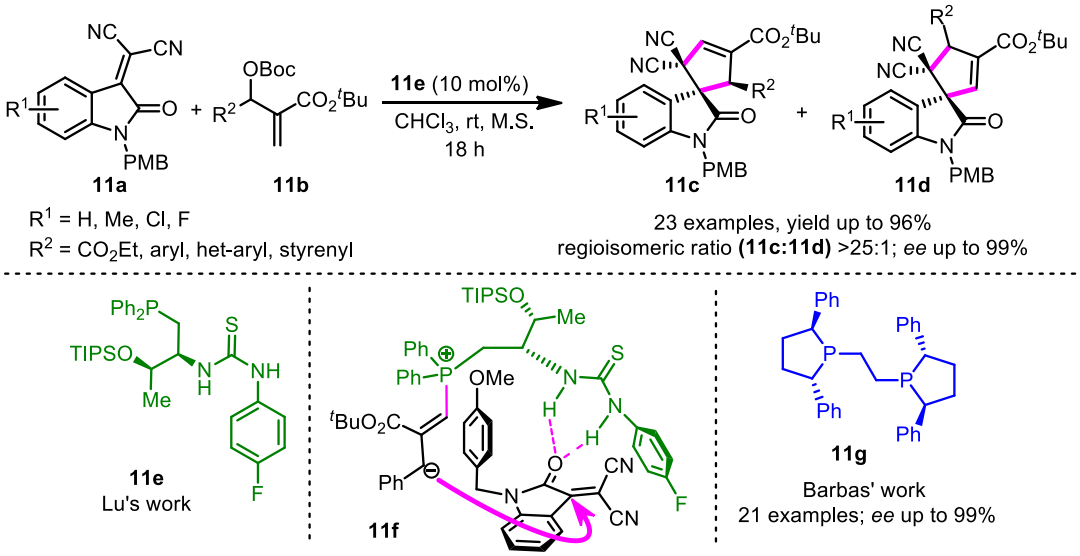
Scheme 9: Shi's synthesis of cyclopentenes using 2,3,4-pentatrienoates

In 2010, Loh *et al.*[20] have introduced 3-butynoates **10a** in an asymmetric [3+2] cycloaddition reaction as a C_3 precursor. In the presence of chiral bidentate phosphine **10d** (*R*,*R*-DIPAMP), 3-butynoate **10a** undergoes in situ isomerization to generate the corresponding allenoate. Subsequently, the reaction of allenoates with chalcones **10b** delivered the highly substituted cyclopentenes **10c** in excellent yields and enantioselectivities, Scheme 10. This reaction has an advantage, the exclusive formation of α-addition product can be obtained, unlike Fu's and Marinetti's approach, where the regioisomeric mixture was observed, Scheme 6.



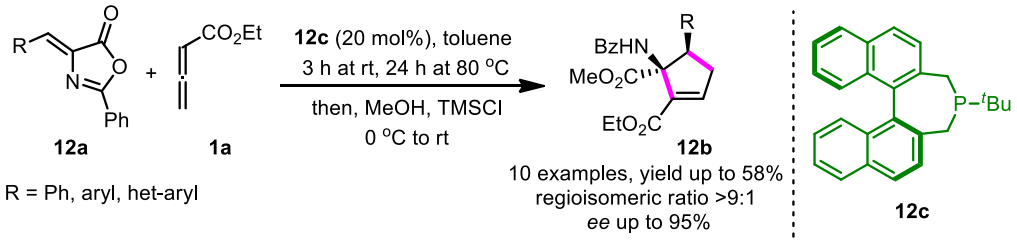
Scheme 10: Loh's asymmetric synthesis of cyclopentenes

In 2011, Lu[21] and Barbas, III[22] independently reported an asymmetric intermolecular cycloaddition reaction of methyleneindolinones **11a** with Morita–Baylis–Hillman adducts **11b**, Scheme 11. Lu has introduced an L-threonine derived bifunctional phosphine **11e** for the transformation. The reaction proceeds through an initial zwitterion formation and subsequent Michael addition *via* the transition state **11f** leading to the formation of functionalized spirocyclopentenes **11c** and **11d** in excellent enantioselectivities and regioisomeric ratio. On the other hand, Barbas employed the bidentate chiral phosphine **11g** [(+)-Ph-BPE], to generate the enantioenriched spirocyclopenteneoxindoles.



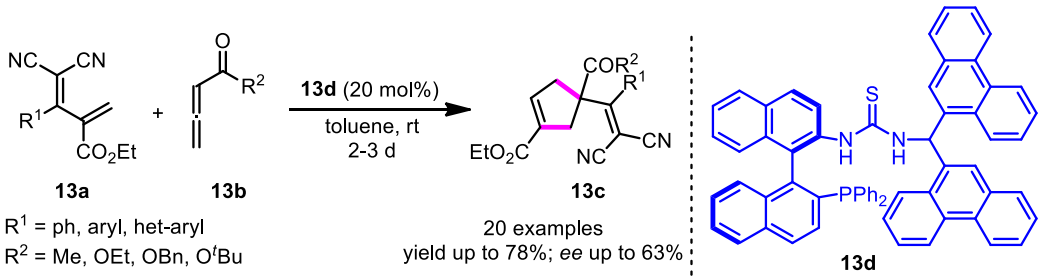
Scheme 11: Lu's and Barbas' synthesis of enantioselective spirocyclopenteneoxindoles

In 2012, Jorgensen *et al.*[23] demonstrated enantioselective one-pot synthesis of cyclic α-amino esters, Scheme 12. (S)-^{t}Bu-BINEPINE **12c** mediated [3+2] cycloaddition reaction of olefinic azalactone **12a** with allenoates **1a** generated spiro-lactones, which upon in situ hydrolysis furnished cyclopentenes **12b** in high regio- and enantioselectivities.



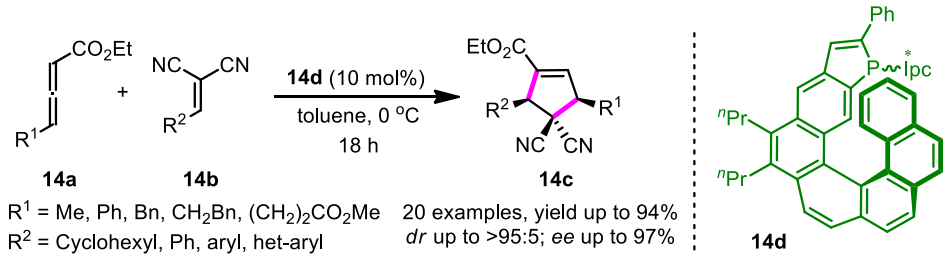
Scheme 12: Jorgensen's asymmetric cycloaddition of azalactone

In 2013, for the first time, Shi *et al.*[24] utilized 2-methylenebut-3-enoates **13a** as a C_2 synthon in [3+2] cycloaddition reaction with allenoates **13b**, Scheme 13. The bifunctional chiral phosphine **13d** induced moderate enantioselectivity and delivered the cyclopentenes **13c** bearing an all-carbon quaternary stereogenic center in good yields.



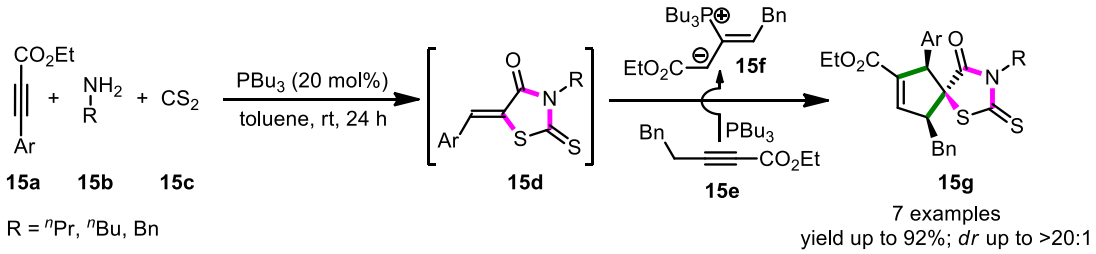
Scheme 13: Shi's asymmetric cycloaddition of 2-methylenebut-3-enoates

In 2015, Voituriez and Marinetti *et al.*[25] designed a novel class of phosphine possessing helical chirality. They have synthesized a library of chiral phosphahelicene and demonstrated their utilization in different cycloaddition reaction. Various γ-substituted allenoates **14a** with alkylidenemalononitriles **14b** undergo [3+2] cycloaddition reaction smoothly in the presence of phosphahelicene **14d**, leading to densely functionalized cyclopentenes **14c** in excellent diastereo- and enantioselectivities, Scheme 14.



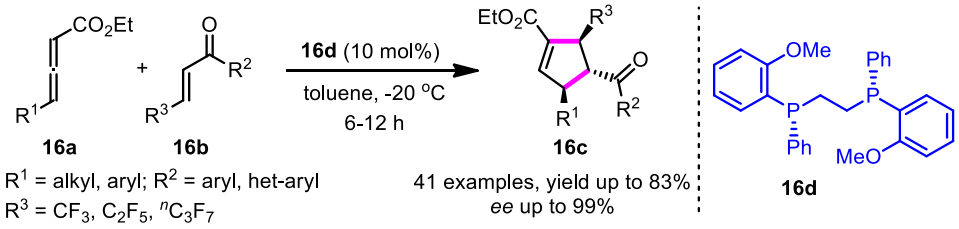
Scheme 14: Marinetti's phosphahelicene mediated asymmetric [3+2] reaction

In 2016, Miao *et al.*[26] explored a phosphine mediated one-pot sequential multicomponent [3+2]/[3+2] cycloaddition reaction of ethyl 5-phenylpent-2-ynoate **15e**, substituted aryl ethyl propiolates **15a**, amines **15b**, and carbon disulfide **15c**, Scheme 15. The reaction involves an initial PBu_3 mediated three-component reaction to form rhodanines **15d,** and subsequent cycloaddition reaction with allenoate **15f** (generated from 5-phenylpent-2-ynoate **15e**). A variety of substituted 5-spiro cyclopentene-rhodanines **15g** were synthesized in excellent yields and diastereoselectivities.



Scheme 15: Miao's one-pot multicomponent cycloaddition reaction

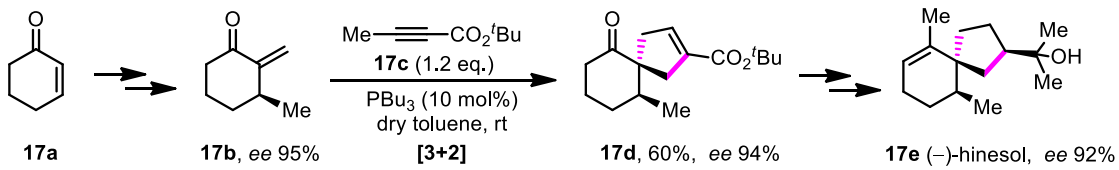
In 2017, Zhang *et al.*[27] reported a facile asymmetric synthesis of trifluoromethylated cyclopentenes **16c** bearing three contiguous chiral centers by utilizing the bidentate chiral phosphine **16d** *via* [3+2] cycloaddition reaction, Scheme 16. A wide variety of γ-alleonates **16a** and fluoroalkylated enones **16b** were well tolerated under the mild conditions to deliver the desired products **16c** in excellent enantioselectivities and yields.



Scheme 16: Zhang's asymmetric cycloaddition of γ-substituted allenoates

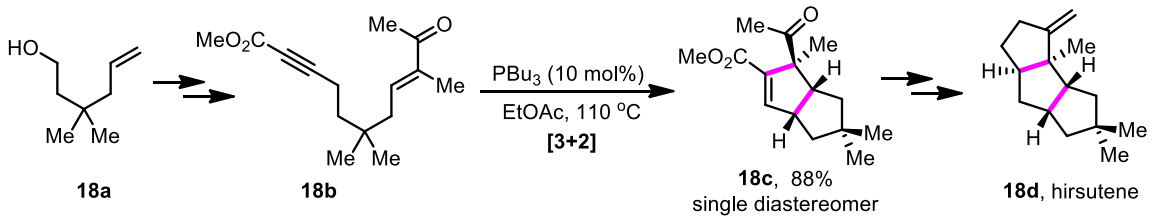
1.1.1: Application of [3+2] cycloaddition reaction in total synthesis

In 2003, Lu *et al.*[28] achieved the first total synthesis of (–)-hinesol **17e** by utilizing [3+2] cycloaddition reaction as the key step, Scheme 17. Enantiomerically pure cyclohexenone **17b**, obtained from commercially available cyclohexenone **17a**, was reacted with the *tert*-butyl 2-butynoate **17c** in the presence of tributylphosphine to construct the spirocyclic skeleton **17d**. The natural product (–)-hinesol was accomplished after a few synthetic transformations of **17d**, an overall 22% yield and excellent enantioselectivity were realized.



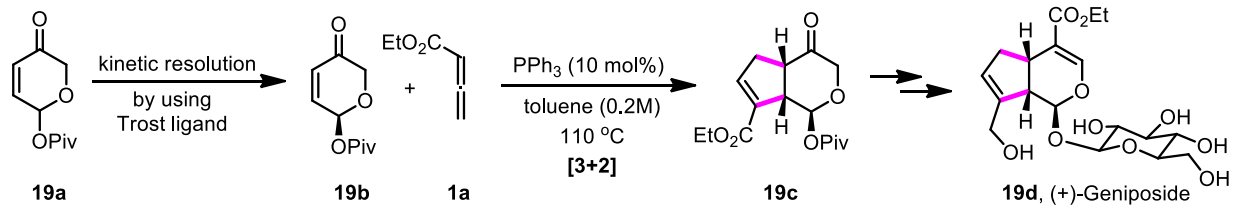
Scheme 17: Lu's total synthesis of (–)-hinesol

In 2003, Krische *et al.*[29] developed an intramolecular [3+2] cycloaddition reaction of a tethered enone-ynone system and applied to the total synthesis of triquinane natural product hirsutene **18d**, Scheme 18. The starting alcohol **18a** was converted to the enone-ynoate **18b** and subjected to the phosphine catalysis to furnish the diquinane **18c** as a single diastereomer. Further synthetic manipulations of **18c** afforded the efficient access of hirsutene **18d**.



Scheme 18: Krische's total synthesis of hirsutene

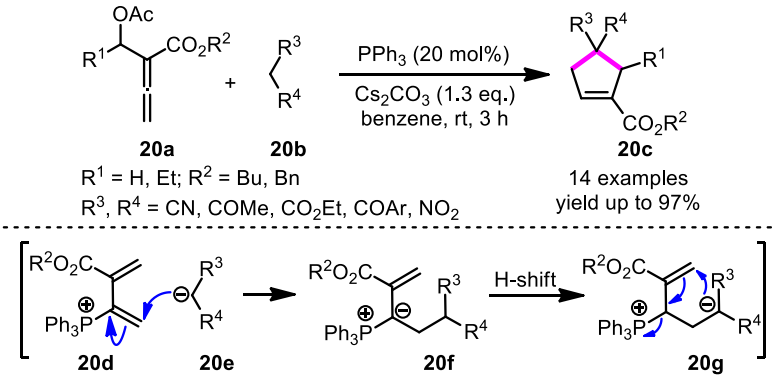
In 2009, Krische *et al.*[30] adopted the Lu's [3+2] cycloaddition reaction for the total synthesis of (+)-geniposide **19d**, Scheme 19. Kinetic resolution of pyranone **19a** using Trost's ligand resulted in the enantiopure pivolate **19b**. The phosphine catalyzed annulation with allenoate **1a** provided the advance intermediate **19c** and was further elaborated to complete the total synthesis of (+)-geniposide **19d**.



Scheme 19: Krische's total synthesis of (+)-geniposide

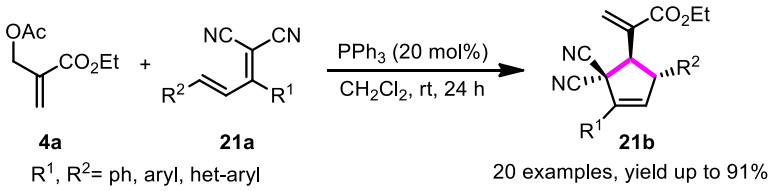
1.2: [4+1] cyclization based approaches for the synthesis of cyclopentanes

In 2010, Tong *et al.*[31] demonstrated a novel [4+1] cycloaddition reaction for the synthesis of cyclopentenes, Scheme 20. 2-(Acetoxymethyl)-buta-2,3-dienoates **20a** generate the species **20d** in the presence of triphenylphosphine and serve as a 1,4-bisnucleophilic system. The base mediated generation of **20e** followed a γ-umpolung addition to the diene **20d**. An intramolecular proton shift of ylide **20f** and subsequent cyclization lead to desired cyclopentenes **20c**.



Scheme 20: Tong's [4+1] cycloaddition of 2-(Acetoxymethyl)-buta-2,3-dienoates

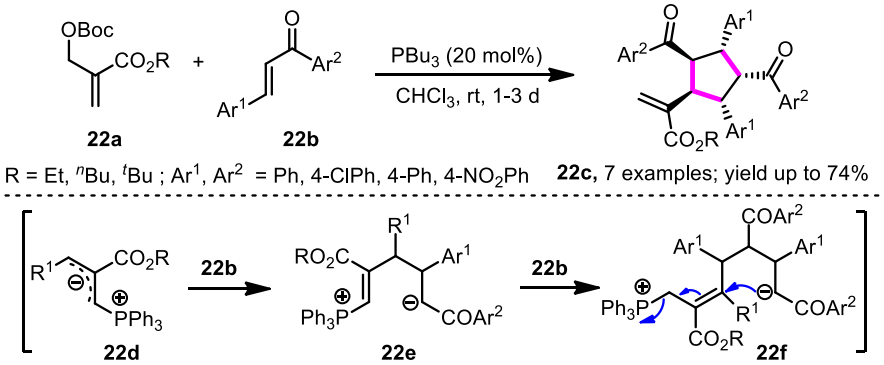
In 2013, He *et al.*[32] reported another variant of [4+1] cycloaddition by employing activated diene **21a** as a C_4 synthon and Morita-Baylis-Hillman acetate **4a** as a C_1 synthon to generate the functionalized cyclopentenes **21b** in good yields, Scheme 21.



Scheme 21: He's [4+1] cycloaddition of MBHADs

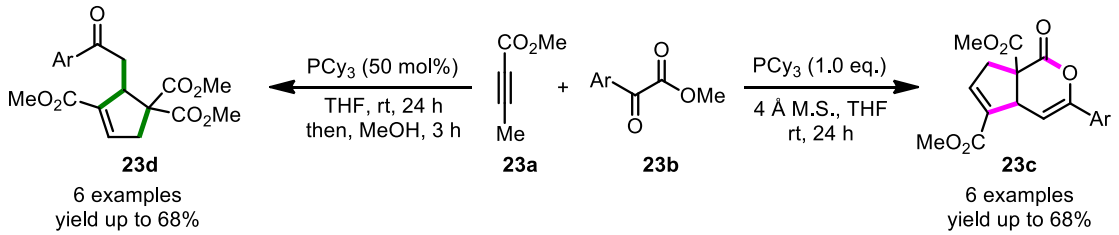
1.3: [2+2+1] cyclization based approaches for the synthesis of cyclopentanes

In 2011, He *et al.*[33] documented an unusual dimerization of chalcones **22b** *via* [2+2+1] cycloaddition reaction, Scheme 22. The initially formed ylide **22d** undergoes sequential Michael addition with two molecules of chalcone to form **22f**, and cyclizes to produce fully substituted cyclopentanes **22c**.



Scheme 22: He's [2+2+1] cycloaddition for fully substituted cyclopentane

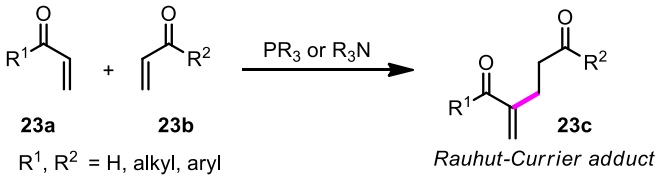
In 2014, Miller *et al.*[34] presented a phosphine catalyzed cyclization of butynoates and aroylformates, Scheme 23. PCy_3 mediated dimerization of **23a** followed by nucleophilic addition to the aroylformates **23b,** and subsequent rearrangements furnished the cyclopentene fused pyranones **23c**. However, in the presence of methanol, the in situ methanolysis delivered the substituted cyclopentenes **23d** in moderate to good yields.



Scheme 23: Miller's cycloaddition of 2-butynoate and α-keto esters

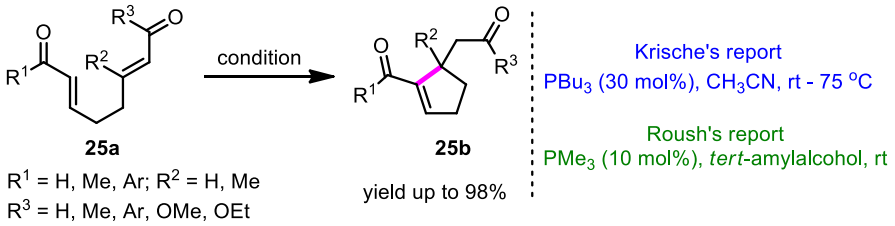
1.4: Rauhut-Currier (RC) reaction based strategy for cyclopentane synthesis

Rauhut-Currier reaction is a phosphine catalyzed dimerization of acrylonitrile disclosed in 1963.[35] This reaction proceeds *via* initial conjugate addition of phosphine to form an enolate and subsequent Michael addition to another activated alkene. Later, McClure reported the first cross-coupling reaction of acrylonitrile with ethyl acrylate albeit in low yields.[36] Though few other research groups introduced RC reaction mediated by tert-amines, this was not studied well owing to its inherent lack of stereo- and regioselectivity until 2002. A general representation of the RC reaction is depicted in Scheme 24.



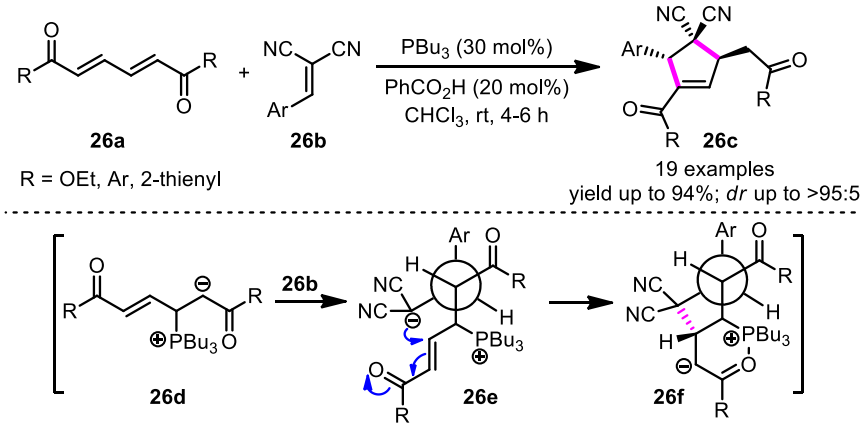
Scheme 24: General representation of RC reaction

In 2002, Krische[37] and Roush[38] independently described an intramolecular variant of Rauhut-Currier reaction to address the regioselectivity by designing an enone-enone tethered substrate **25a**, Scheme 25. The reaction underwent phosphine mediated chemo- and stereoselective cyclization for both symmetric and unsymmetric bis-enones to generate the desired cyclopentenes **25b** in excellent yields.



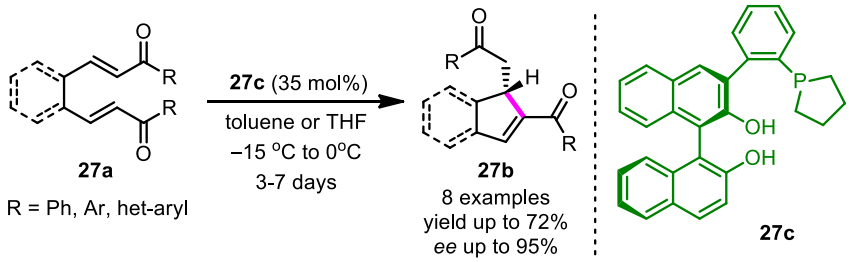
Scheme 25: Intramolecular Rauhut-Currier reaction of bis-enones

In 2012, Huang *et al.*[39] constructed highly functionalized cyclopentenes **26c** *via* an unconventional Rauhut-Currier domino reaction, Scheme 26. Initial 1,4-phospha Michael addition of dienone **26a** led to intermediate **26d**. Subsequently, **26d** underwent another Michael addition with activated nitrile **26b** to form the 1,5-zwitterionic species **26e**, followed by cyclization to furnish **26c** in excellent diastereoselectivities.



Scheme 26: Huang's Rauhut-Currier domino reaction of dienones

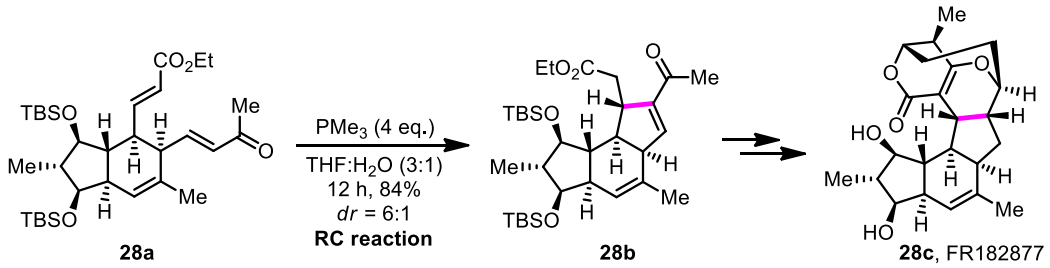
In 2012, Shi *et al.*[40] presented an intramolecular enantioselective Rauhut-Currier reaction. A multifunctional chiral phosphine **27c** was employed to synthesize the functionalized cyclopentenes and indenes **27b** in excellent enantiopurities from dienones **27a**, Scheme 27.



Scheme 27: Shi's asymmetric cyclopentannulation

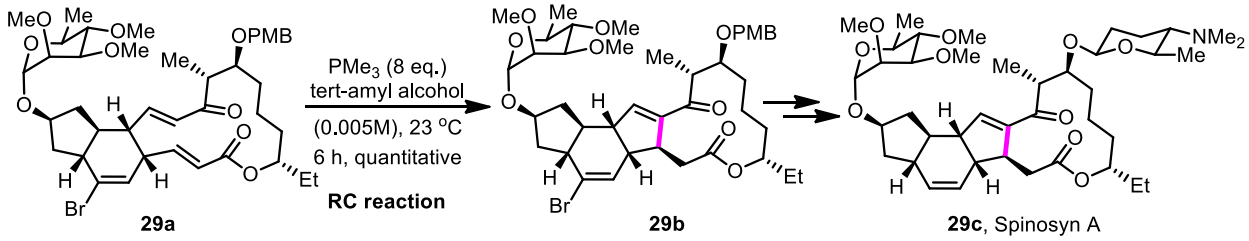
1.4.1: Application of Rauhut-Currier reaction in total synthesis

In 2003, a year after the first report on intramolecular Rauhut-Currier reaction, Roush *et al.*[41] exploited this strategy for the total synthesis of antimitotic agent FR182877 **28c**, Scheme 28. An advanced intermediate enone-enoate **28a** was subjected to the phosphine catalysis in a binary medium to deliver the key tricyclic core **28b**, which was further elaborated to **28c**.



Scheme 28: Roush's total synthesis of FR182877

In 2004, Roush *et al.*[42] described another application of the RC reaction in the stereoselective total synthesis of spinosin A **29c**, Scheme 29. The late-stage cyclopentannulation of **29a** *via* trimethylphosphine mediated RC reaction, and subsequent synthetic maneuvers led to the **29c**.

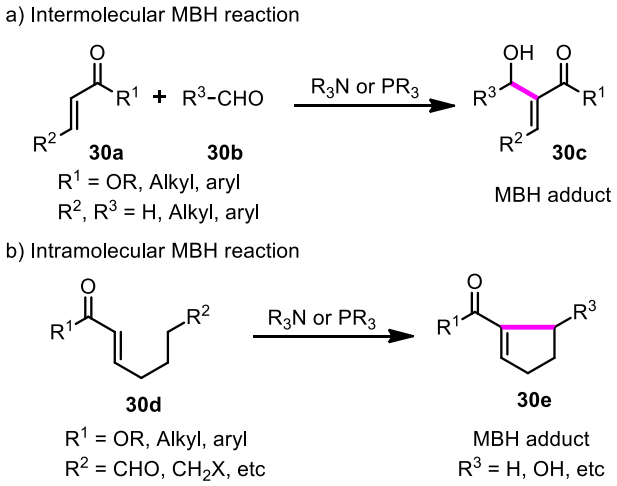


Scheme 29: Roush's total synthesis of spinosyn A

1.5: Morita-Baylis-Hillman (MBH) reaction based synthesis of cyclopentane

Morita-Baylis-Hillman (MBH) reaction is one of the most synthetically useful carbon-carbon bond forming reactions, which involves a reaction between an activated double bond and a carbon electrophile, Scheme 30. In the year 1968, Morita and co-workers[43] have reported the reaction between acrylates and various aldehydes in the presence of trialkylphosphine, then in 1972 Baylis and Hillman[44] described a similar reaction influenced by tertiary amine. In the last few decades, this reaction has received remarkable attention due to its operational simplicity, atom economic, and organocatalytic nature. This method also provides access to a large number

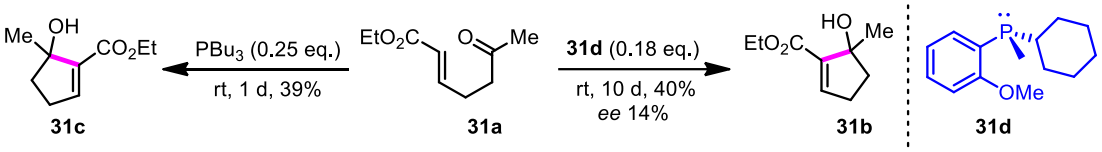
of natural products and biologically active molecules.[45] Several intramolecular MBH reactions are developed for the synthesis of cyclopentanes, Scheme 30.[46]



Scheme 30: General representation of MBH reaction

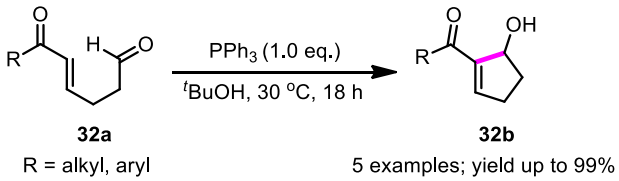
1.5.1 Conventional MBH reaction based synthesis of cyclopentanes

In 1992, Frater *et al.*[47] reported the first phosphine mediated intramolecular Morita-Baylis-Hillman reaction (IMBH) of α,β-unsaturated ester-ketone **31a** to access functionalized cyclopentenes **31c**, Scheme 31. An effort to develop the enantioselective IMBH of the substrate **31a** using (–)-CAMP **31d** was successful, albeit in low enantiomeric excess.



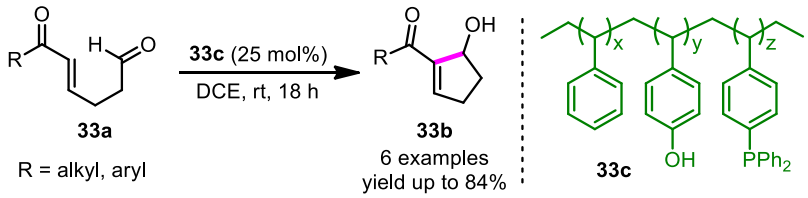
Scheme 31: Frater's intramolecular MBH reaction

In 2003, Koo *et al.*[48] designed ω-formyl-α,β-unsaturated carbonyl compounds **32a** and employed in PPh_3 mediated IMBH reaction to synthesize five-membered carbocycles **32b**, Scheme 32.



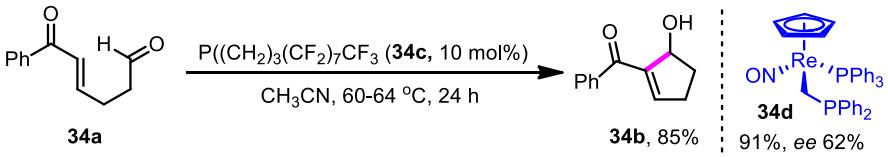
Scheme 32: Koo's cyclopentene synthesis *via* IMBH reaction

In 2007, Shi *et al.*[49] synthesized a library of polystyrene supported bi-functional phosphines **33c**. The application of these phosphines was further investigated by adopting Koo's substrate design **33a**, to achieve cyclopentenes **33b**, Scheme 33.



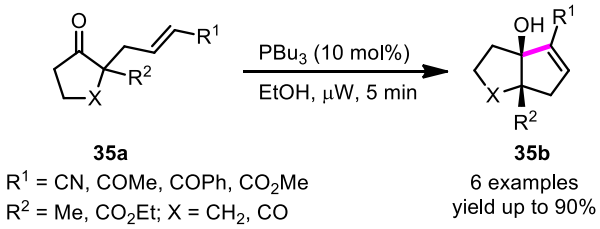
Scheme 33: Shi's IMBH reaction using polymer-supported phosphine

In 2008, Gladysz *et al.*[50] developed thermomorphic fluorous phosphine **34c** for IMBH reaction, Scheme 34. The easy recoverability of the catalyst makes this method advantageous over other existing methods. Eventually, an asymmetric version was also developed by using the chiral Rhenium-containing phosphine **34d** and synthesized cyclopentenes **34b** in excellent yields and moderate enantiopurities.[51]



Scheme 34: Gladysz's rhenium-phosphine mediated IMBH reaction

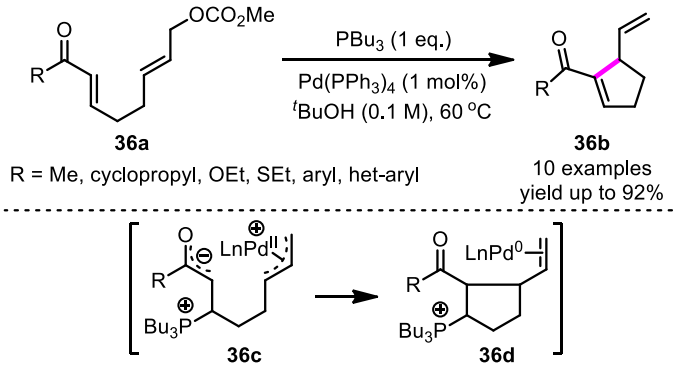
In 2013, Miesch *et al.*[52] described a solvent dependent IMBH reaction of activated olefins tethered to cycloalkanones **35a**, Scheme 35. Under microwave condition, wide varieties of bisquinanes **35b** were synthesized by using PBu_3 in excellent yields and diastereoselectivities in very short reaction times.



Scheme 35: Miesch's synthesis diquinanes

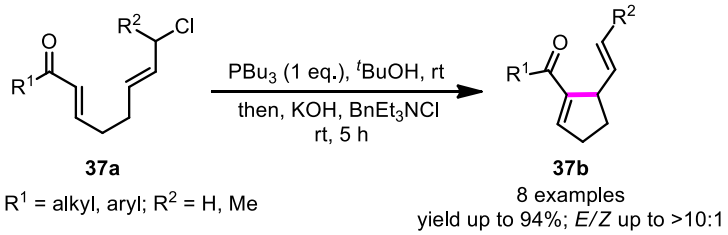
1.5.2 MBH alkylation based synthesis of cyclopentanes

In 2003, Krische *et al*.[53] demonstrated phosphine-palladium co-operative catalysis for carbocycles generation from the allyl carbonate **36a**, Scheme 36. The reaction involves an initial phosphine mediated enolate formation and subsequent reaction with electrophilic allyl-palladium species *via* the intermediate **36c**. This reaction represents the first example of a unique electrophilic system (generated from allyl carbonate *via* Tsuji-Trost reaction) employed in Morita-Baylis-Hillman reaction.



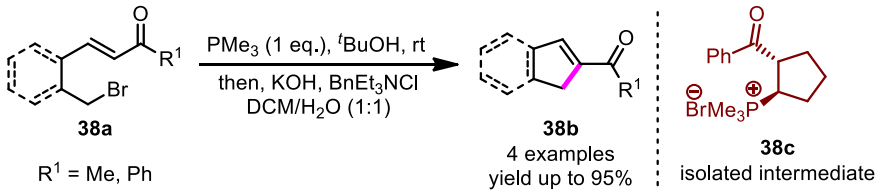
Scheme 36: Krische's intramolecular co-operative catalysis

In 2005, Krafft[54] modified the Krische's carbonate **36a** (Scheme 36) by installing allylic leaving groups (such as, -Cl, -OH, -OMs, -OTs) to develop an entirely organophosphine mediated cyclization, Scheme 37. However, only allyl chloride tethered enone **37a** was successful under the optimized condition to generate the cycloalkenes **37b**.



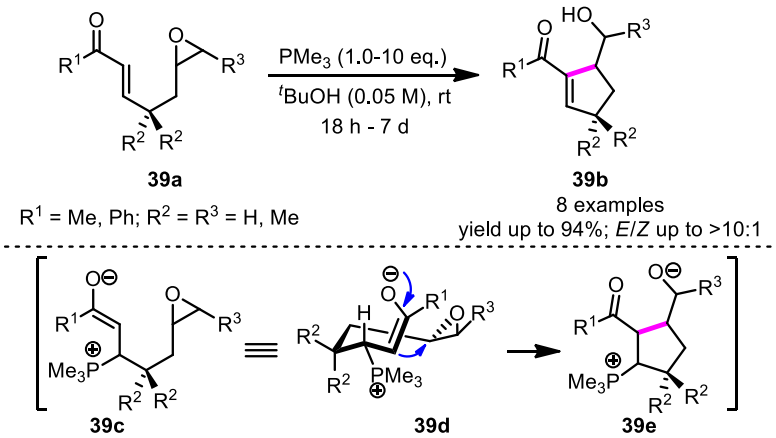
Scheme 37: Krafft's organocatalytic IMBH alkylation

In 2005, Krafft *et al*.[55] further developed an unprecedented sp^3 hybridized electrophilic system for MBH type alkylation, Scheme 38. A wide range of alkyl halides and enones **38a** were tolerated under the optimized condition to furnish cyclopentenes and indenes **38b**. The isolation of the intermediate **38c** further corroborates the MBH reaction pathway.



Scheme 38: Kraft's IMBH alkylation of alkyl halides

In 2006, Krafft *et al.*[56] introduced epoxide as an electrophile in IMBH reaction, Scheme 39. The enone-epoxide **39a** under phosphine catalysis resulted in homologous IMBH product **39b** in excellent yields through a chair-type transition state **39d**.



Scheme 39: Krafft's IMBH reaction of enone-epoxide

Despite tremendous advancements in organophosphine catalysis, these strategies described above and brief literature survey revealed that most of the methods are limited to the synthesis of cyclopentane analogs. The lack of efficient processes for the synthesis of cyclopentannulated arenes and heteroarenes has encouraged us to envision new advancement in organophosphine chemistry.

Section 2

Synthesis of Cyclopenta[b]annulated Arenes and Heteroarenes via an Enantioselective Intramolecular MBH Reaction of Enones

During the past few decades, the increasing health and environmental issues have raised tremendous global concerns and evolved into the consideration of "Green and Sustainable development" in the chemical synthesis. Towards this, the utmost importance of synthetic organic chemistry is to accomplish the desired complex molecules in short, stereoselective, eco-compatible, and atom-economic manner. This goal could be achieved one way by designing the reactions to perform under organocatalysis instead of toxic metals, as nature utilizes this strategy to synthesize the complex architectures for billions of years. The organocatalysis is often referred to as catalysis with organic molecules, and has received tremendous attention from the synthetic community due to easy handling, simple storage and most often moisture insensitive

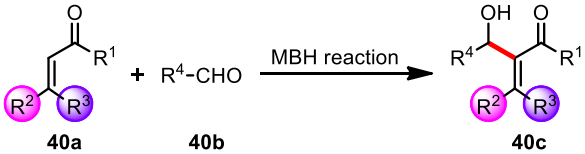
conditions.[57] In recent years, organocatalysis has widened in many different directions. Among them, N-heterocyclic carbenes (NHCs),[58] amines,[59] chiral Brønsted acids,[60] and organo-phosphines are most often employed in catalysis.[61]

Organophosphines have attracted considerable attention from the synthetic community. While the phosphine ligands have found wide applications in transition metal catalysis, the use of nucleophilic phosphines as organocatalysis was limited. The history of nucleophilic organophosphine catalysis can be traced back to Price's report of the triphenylphosphine catalyzed hexamerization of acrylonitrile in 1962,[62] and tributylphosphine mediated dimerization of acrylates by Rauhut and Currier in 1963.[35] A few years later, Morita and co-workers have reported trialkylphosphine mediated reaction of activated olefins with various aldehydes to generate β-hydroxy carbonyls, now known as Morita-Baylis-Hillman (MBH) reaction.[43] The nucleophilic phosphine has numerous features such as (i) substitution based reactivity, steric and electronic properties, (ii) easily tuneable properties of chiral phosphines and, (iii) highly atom-economical and metal free. Consequently, in the last two decades, a myriad of fascinating methodologies have been developed for the synthesis of fused carbocycles.[63]

The MBH reaction is one of the important C-C bond-forming reactions, leading to the formation of densely functionalized molecules in an atom economic and metal-free manner. The Morita-Baylis-Hillman adducts (MBHADs) bearing different functional groups nearby are often manipulated and utilized in the synthesis of natural products and pharmaceutically active compounds.[64] Surprisingly, this reaction gained momentum only after the landmark report of Frater's intramolecular asymmetric version to synthesize five- and six-membered carbocycles, though in poor enantioselectivities.[47] Subsequently, several research groups have designed numerous substrates for the IMBH reaction to access various carbocycles and heterocycles in high enantiopurities by employing chiral amines and phosphines.[65] More than three thousand publications in the last three decades signify the broad applicability of this reaction in organic synthesis.

Despite tremendous advancements in the area of MBH reaction, there remain few unresolved challenges such as (i) reactivity depends on the steric and electronic nature of the reactants, Lewis bases and eventually results in low yields, and (ii) in several instances the reaction proceeds sluggishly due to the presence of β-substitution to afford the desired product. In most of the MBH reactions, β-unsubstituted electron deficient olefins were employed,

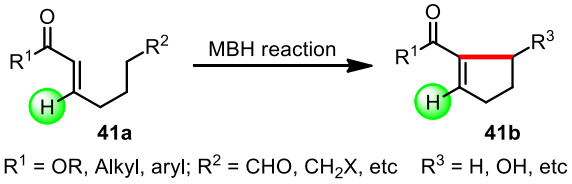
whereas only a few β-monosubstituted systems have been achieved successfully. The significant obstruction associated with the β,β-disubstituted-α,β-unsaturated electron-withdrawing systems are highly sterically and electronically demanding. As a result, no successful general method was established even with entropically beneficial intramolecular MBH reaction, Scheme 40.



$R^2 = R^3 = H$	- Commonly emplyed substrates - Numerous reports
R^2 = alkyl, aryl; $R^3 = H$	- Underexplored substrate - Only few reports
$R^2 = R^3$ = alkyl, aryl	- Unexplored substrate - No general methods

Scheme 40: General representation of intermolecular MBH reaction

The development of general and efficient protocols to synthesize the highly functionalized annulated cyclopentanes remains challenging. Most often, they are assembled in a multi-step manner due to lack of efficient annulation strategy. As our current research focuses on the efficient synthesis of fused cyclopentanes owing to their importance in natural products and pharmaceuticals, we intended to develop an organocatalytic annulation strategy. The absence of an intramolecular Morita-Baylis-Hillman (IMBH) reaction based approach to access highly enantioselective cyclopent[*b*]annulated arenes or heteroarenes prompted us to design a substrate amenable to IMBH reaction. Only limited strategies are available for the synthesis of cyclopentanes, Scheme 41.[46]



Scheme 41: IMBH based strategies to access cyclopentanes

To address the above challenges, substrate **42** was designed as depicted in Scheme 42.[66] Few crucial aspects were considered regarding the substrate design before performing the IMBH reaction. It was envisioned that (i) an intramolecular variant could overcome the high energy activation associated with sterically and electronically demanding β,β-substituents, and (ii)

placing the electron withdrawing enone and carbonyl *ortho* to each other could assert mutually beneficial driving force to facilitate the Michael addition of Lewis base.

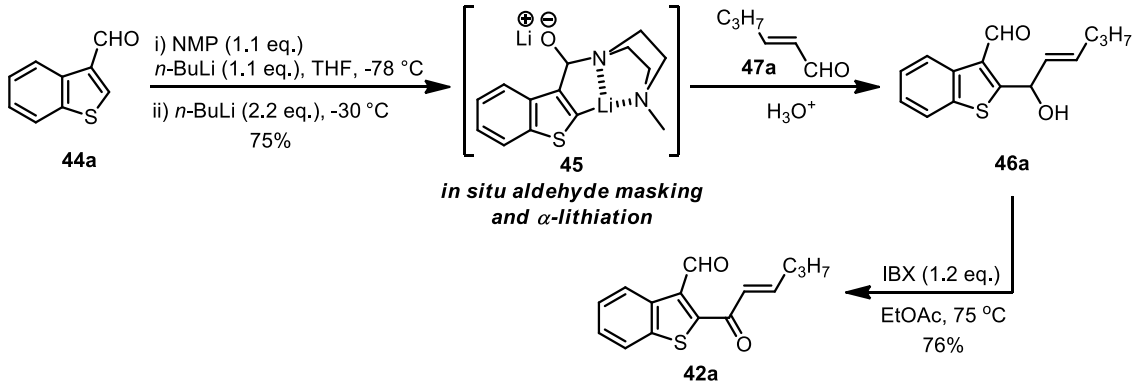
R^1 = alkyl, aryl, heteroaryl; R^2 = R^3 = H, alkyl, aryl

Scheme 42: Our design for the synthesis of cyclopenta[*b*]annulated arenes or heteroarenes

2.1: Results and Discussion

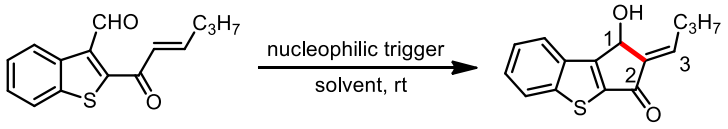
With the desire to access the cyclopent[*b*]annulated arenes and heteroarenes *via* IMBH reaction, we have initiated studies to synthesize the proposed starting material **42** bearing enone and aldehyde moiety *ortho* to each other, Scheme 42. Modular access of the enone-aldehyde **42a** can be easily achieved from the 3-benzothiophene carboxaldehyde **44a**, following a two steps method developed by our research group.[67]

The in situ masking of aldehyde functionality in 3-benzothiophene carboxaldehyde **44a** by lithium N-methylpiperazide (generated from NMP and *n*-BuLi) and subsequent C-2 (α-lithiation) alkylation with commercially available 2-hexenal **47a** led to the formation of enol **46a**, Scheme 43. Further, IBX mediated oxidation of alcohol **46a** furnished the desired enone-aldehyde **42a** in good yield.



Scheme 43: Synthesis of enone-aldehyde **42a** by following our earlier report

Table 1: Optimization of the reaction parameters for the IMBH reaction of **42a**



42a **43a**

Entry	Nucleophilic trigger (mol%)	Solvent	Time	Yield[a] (%)/(*E*/*Z*)[b]
1	DBU (20)	toluene	6 h	63 (6:1)
2	DABCO (20)	toluene	3 h	69 (8:1)
3	DABCO (20)	DMF	1.5 h	71 (7:1)
4	DMAP (20)	DCM	5 h	63 (7:1)
5	Imidazole (20)	toluene	7 h	79 (6:1)
6	PPh_3 (10)	DCM	48 h	–
7	PPh_2Et (10)	DCM	10 min	90 (8:1)
8	$PPhMe_2$ (10)	DCM	10 min	92 (11:1)
9	PCy_3 (10)	DCM	30 min	86 (8:1)
10	PMe_3 (10)	DCM	5 min	93 (10:1)
11	PMe_3 (10)	DMF	5 min	91 (9:1)
12	**PMe_3 (10)**	**toluene**	**5 min**	**93 (10:1)**
13	PMe_3 (10)	NMF	20 min	85 (10:1)
14	PMe_3 (10)	formamide	20 min	79 (9:1)
15	PMe_3 (10)	CH_3CN	10 min	89 (8:1)

All reactions were done on 0.1 mmol scales in 1 mL of solvent. [a] Isolated yields after silica gel column chromatography. [b] Determined by ^{1}H-NMR analysis of the crude reaction mixture.

We have commenced the optimization study by choosing 2-hexenoyl benzothiophene-3-carboxaldehyde **42a** as a model substrate. A wide variety of nucleophilic triggers and solvents combinations were tested, and the results are compiled in Table 1. The commonly employed amine based Lewis bases (DBU, DABCO, DMAP, and Imidazole) found to be effective to deliver the desired product **43a** in good yields (Table 1, entries 1-5).

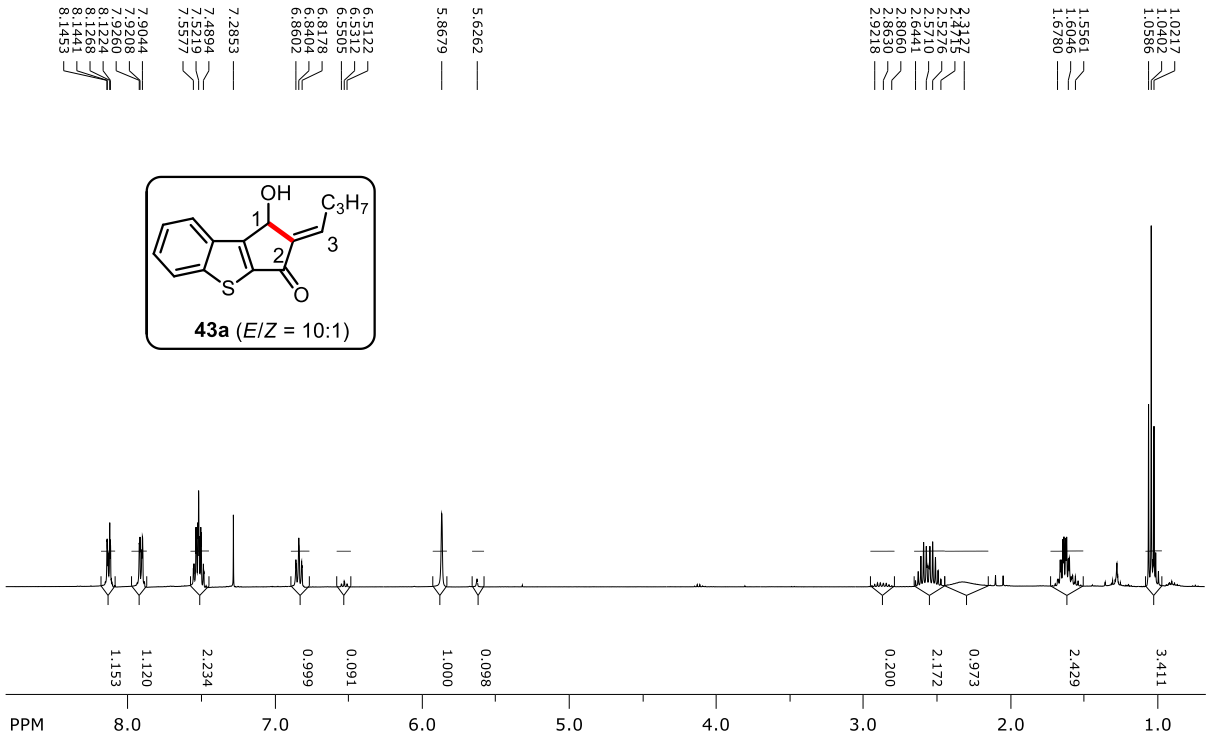


Figure 3: ^{1}H-NMR spectrum of the IMBH product **43a**

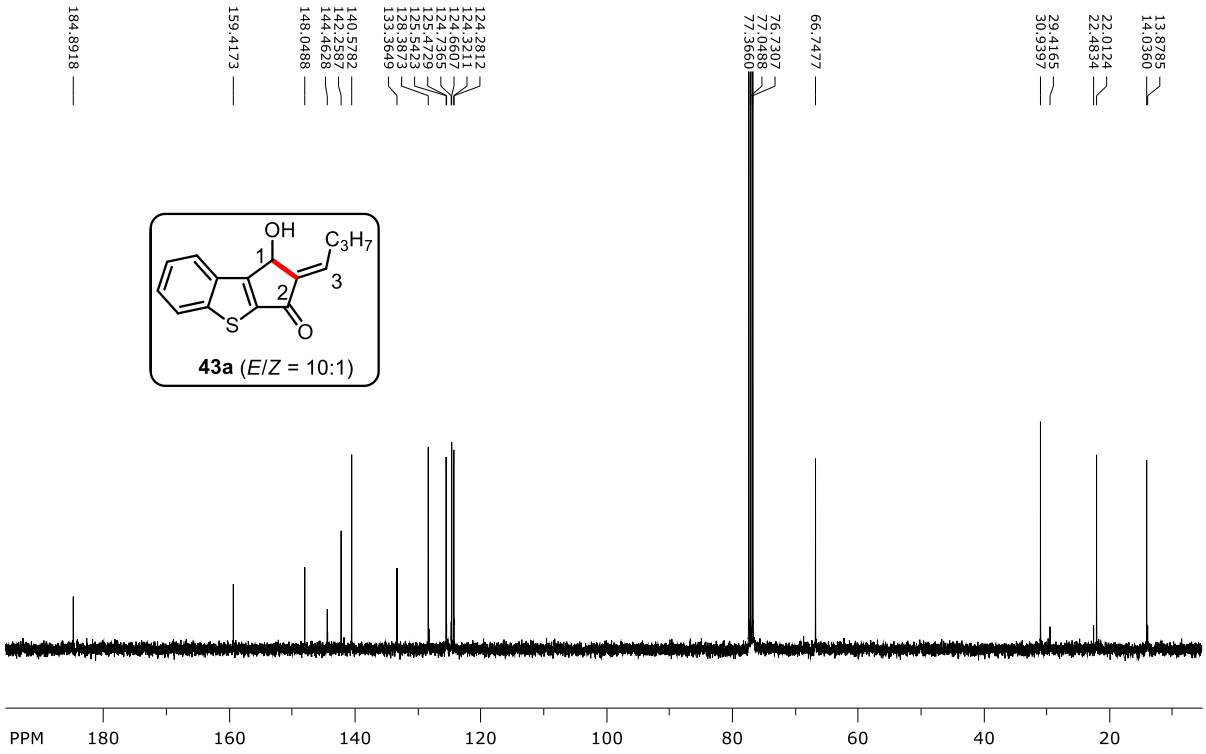
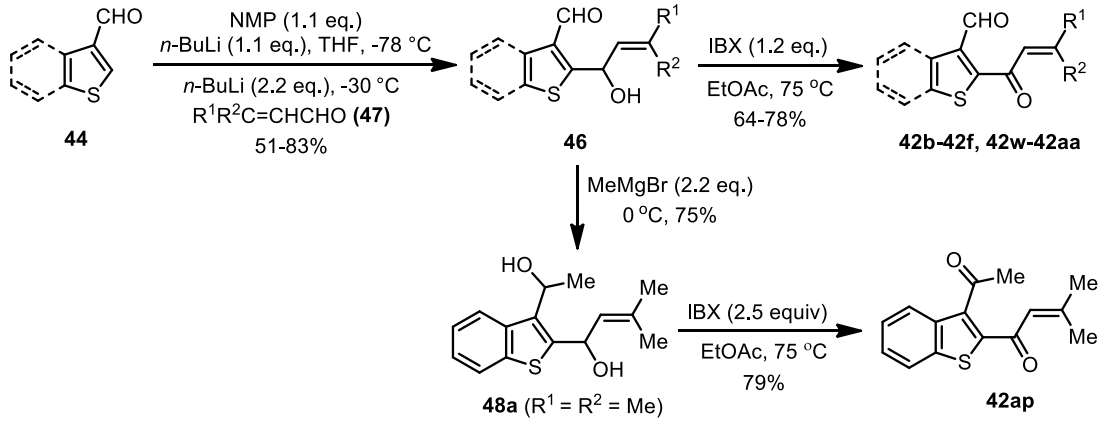


Figure 4: ^{13}C-NMR spectrum of the IMBH product **43a**

The structure of annulated benzothiophene **43a** was carefully deduced from the IR, NMR, and HRMS data. The presence of a broad absorption band at 3386 cm^{-1} due to secondary alcohol and a sharp band at 1688 cm^{-1} due to the unsaturated cyclic ketone in the IR spectrum indicated the formation of IMBH product **43a**. In the ^{1}H-NMR spectrum (see Fig. 3) presence of a singlet a δ 5.87 ppm due to the C-1 methine proton, a triplet at δ 6.84 ppm due to the β-proton (C-3), and in ^{13}C-NMR spectrum (see Fig. 4), presence of a peak at δ 184.8 ppm due to unsaturated ketone (C-2) and a peak at δ 66.7 ppm due to methine carbon (C-1), confirmed the formation of **43a**. The presence of a dehydroxylated molecular ion peak at *m/z* 241.0657 $(M\text{-}OH)^{+}$ further supports the product formation.

To further improve the efficiency of the reaction, organophosphines were investigated. Gratifyingly, phosphines bearing an alkyl group (PPh_2Et, $PPhMe_2$, and PCy_3) displayed a pronounced improvement in the yield and reaction time, whereas triphenylphosphine was not successful in delivering the desired product even after a prolonged reaction time (Table 1, entries 6-9). To our delight, trimethylphosphine requires only a few minutes for generating the product **43a** in excellent yield and stereoselectivity (Table 1, entry 10). Though a brief solvent screening was undertaken, no significant increment was observed concerning yield and reaction time (Table 1, entries 11-15). However, this prompted us to replace volatile dichloromethane with toluene for further studies (Table 1, entry 11).

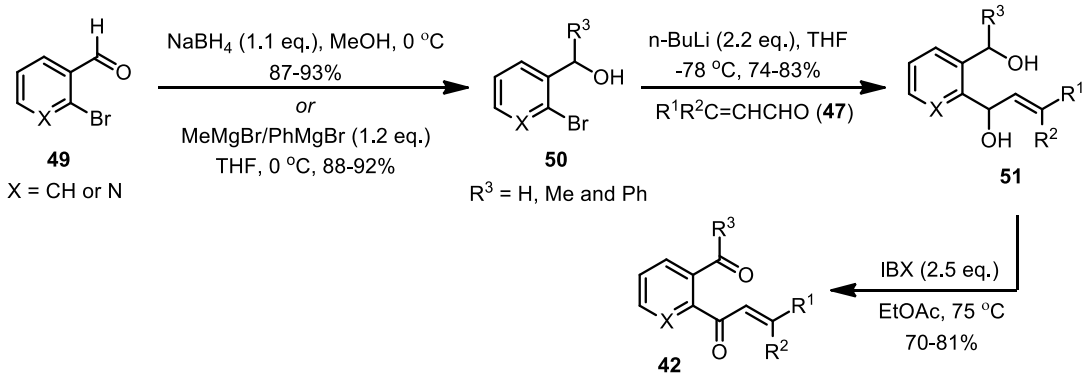


Scheme 44: Synthesis of thiophene and benzothiophene based enones **42**

With the optimal reaction condition in hand, we next focused on evaluating the substrate scope. Towards this, a diverse range of β-monosubstituted and β,β-disubstituted enones appended to aryl, and heteroaryl backbones were synthesized. Thiophene and benzothiophene

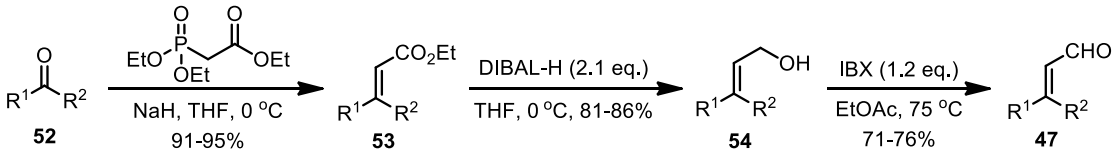
based substrates were accessed by following two-step protocol, Scheme 44. Direct α-alkylation of thiophene- and benzothiophene-3-carboxaldehydes **44** with different enals **47** afforded the enols **46** which upon IBX oxidation delivered the enone-aldehydes **42b-42f** and **42w-42aa**. On the other hand, the enone-ketones **42ap** can be synthesized from alcohols **46** *via* Grignard reaction and oxidation sequence, Scheme 44.

On the other hand, substrates bearing different aryl and pyridyl backbones could be achieved in a three-step protocol, Scheme 45. The commercially available 2-bromo-aldehydes **49** were treated with sodium borohydride or an appropriate Grignard reagent to obtain the 2-bromo alcohols **50**. Direct *n*-butyllithium mediated metal-halogen exchange of alcohol **50** followed by alkylation with an appropriate enal **47** generated the diols **51**.[68] IBX oxidation of the diols **51** led to the formation of the enone-aldehydes **42**.



Scheme 45: Synthesis of aryl and pyridyl based substrates **42**

Enals are valuable synthons often utilized in the organic synthesis for generating the complex and diverse molecular architectures. Enals **47** can be obtained from commercially available aldehydes or ketones **52**, Scheme 46. The reaction follows an initial Horner-Wadsworth-Emmons reaction, DIBAL-H reduction and IBX mediated oxidation sequence.[69]



Scheme 46: Synthesis of enals **47**

A wide range of β-monosubstituted enone-aldehydes was subjected to the optimized condition, Table 2. The intramolecular MBH reaction was realized to be general and efficient, and a diverse range of cyclopent[*b*]annulated arenes and heteroarenes could be accessed in excellent yields and stereoselectivities. The β-alkyl and β-aryl substituted enones appended to benzothiophene **42b-42c**, and thiophene-3-carboxaldehydes **42d-42f** delivered the annulated cyclopentanes **43b-43f** in excellent yields and short reaction time, Table 2. To our delight, functionalized pyrindanone **42g** also was achieved in excellent yields. To further extend our strategy, substituted indanone derivatives **43h-43s** also were assembled successfully in excellent yields within few minutes, Table 2. Regarding the β-substitution, substrates with alkyl, aryl, and heteroaryl substitutions are well tolerated under the optimized condition. The presence of an electron donating group (such as -Me, -OMe) either at β-position of enones **42l** or on aryl backbones **42n-42r** has no significant influence on the reaction efficiency, Table 2. The fluorinated compounds are known to exhibit unique biological properties. Therefore, fluorinated indanone **43s** also was accessed by this method in excellent yield, Table 2. Predicted *E*-geometry of the major isomer was confirmed by the single crystal X-ray diffraction analysis of indanone **43k** and assigned to other products in analogy, Fig. 5.

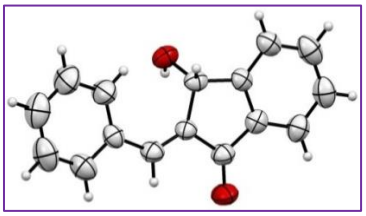
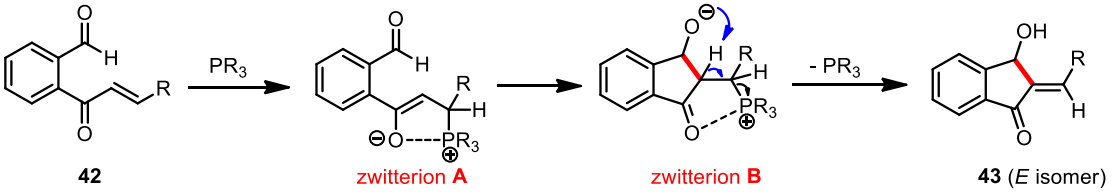


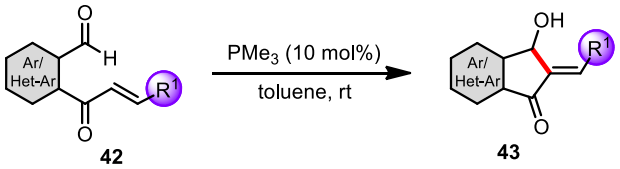
Figure 5: ORTEP diagram of racemic indanone **43k**

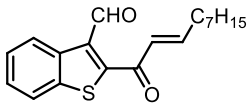
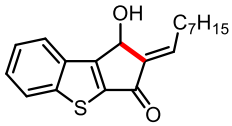
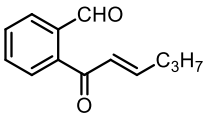
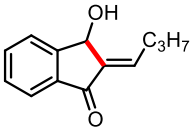
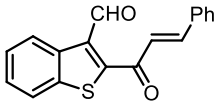
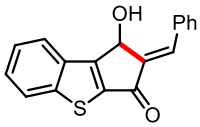
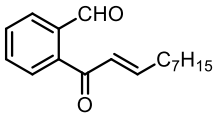
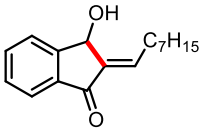
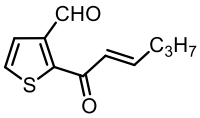
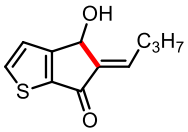
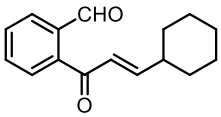
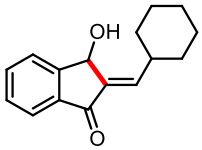
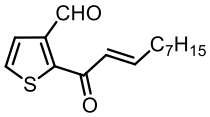
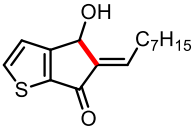
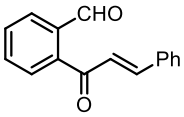
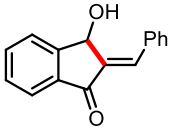
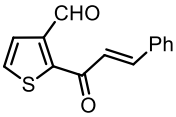
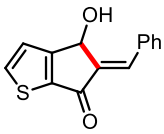
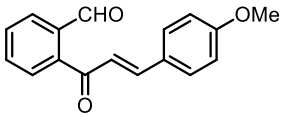
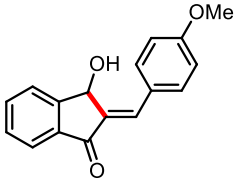
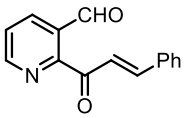
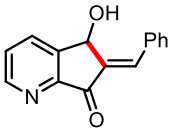
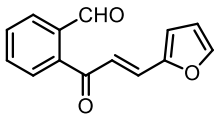
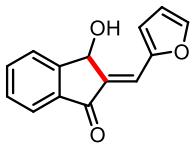
The stereoselective formation of *E* isomer of the intramolecular Morita-Baylis-Hillman reaction can be explained *via* the formation of zwitterionic intermediate **A**, generated by the conjugate addition of phosphine to the enone-aldehyde **42** (Scheme 47). Subsequent intramolecular aldol reaction and dephosphorylation delivered **43** as a major product.

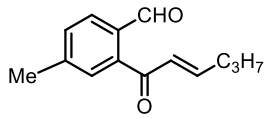
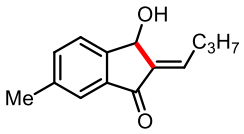
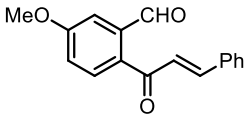
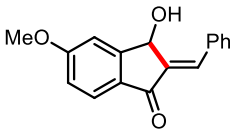
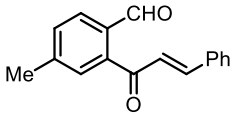
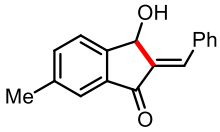
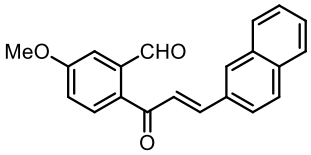
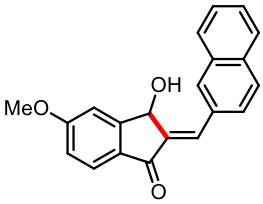
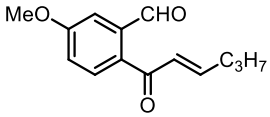
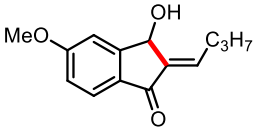
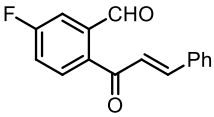
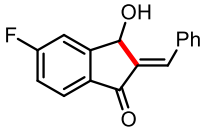


Scheme 47: Origin of stereoselectivity

Table 2: Substrate Scope: β-monosubstituted enone-aldehydes



Entry	Substrate	Product	Entry	Substrate	Product
1	 **42b**	 **43b**, 10 min, 93% (*E*/*Z* = 7:1)	7	 **42h**	 **43h**, 10 min, 94% (*E*/*Z* = 11:1)
2	 **42c**	 **43c**, 15 min, 93% (*E*/*Z* = 10:1)	8	 **42i**	 **43i**, 10 min, 93% (*E*/*Z* = 10:1)
3	 **42d**	 **43d**, 10 min, 94% (*E*/*Z* = 11:1)	9	 **42j**	 **43j**, 5 min, 94% (*E*/*Z* = 6:1)
4	 **42e**	 **43e**, 10 min, 87% (*E*/*Z* = 10:1)	10	 **42k**	 **43k**, 20 min, 93% (*E*/*Z* = 15:1)
5	 **42f**	 **43f**, 20 min, 90% (*E*/*Z* = 12:1)	11	 **42l**	 **43l**, 15 min, 92% (*E*/*Z* = 9:1)
6	 **42g**	 **43g**, 5 min, 91% (*E*/*Z* = 10:1)	12	 **42m**	 **43m**, 20 min, 90% (*E*/*Z* = 11:1)

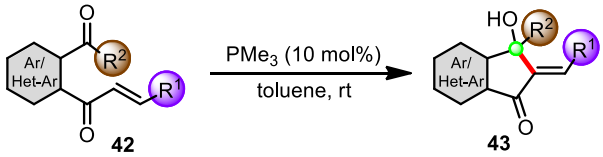
Entry	Substrate	Product	Entry	Substrate	Product
13	 **42n**	 **43n**, 15 min, 92% (*E*/*Z* = 11:1)	16	 **42q**	 **43q**, 30 min, 89% (*E*/*Z* = 11:1)
14	 **42o**	 **43o**, 25 min, 89% (*E*/*Z* = 13:1)	17	 **42r**	 **43r**, 10 min, 94% (*E*/*Z* = 9:1)
15	 **42p**	 **43p**, 15 min, 94% (*E*/*Z* = 10:1)	18	 **42s**	 **43s**, 5 min, 96% (*E*/*Z* = 10:1)

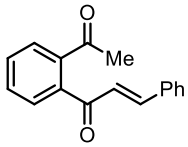
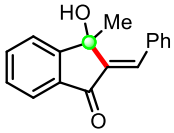
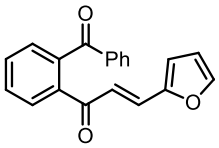
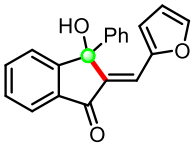
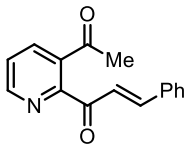
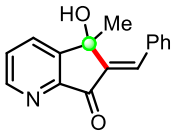
All reactions were done on 0.1 mmol scales. Yields were calculated after silica gel column chromatography. *E*/*Z* ratio was determined by ^{1}H-NMR analysis of the crude reaction mixture.

While aldehydes are well documented as electrophiles in the MBH reaction, the use of ketones is limited due to their very poor electrophilic nature. Towards that, we have synthesized few substrates **42t-42v** by tethering the β-monosubstituted enone and ketones in *ortho* to each other and treated under the optimized condition, Table 3. To our delight, the reaction efficiently generated the indanones **43t, 43u** and pyrindanone **43v** bearing a tetrasubstituted carbon in excellent yields and in very short reaction times, Table 3. Thus, compounds with poor electrophiles such as ketones proved to be excellent substrates under the reaction condition.

After realizing the efficient and facile transformation of β-monosubstituted enones appended to aryl and heteroaryl aldehydes or ketones, we considered investigating the previously unexplored β,β-disubstituted enone substrates. Accordingly, various electronically diverse enones-aldehydes **42w-am** were synthesized and subjected to the optimized reaction condition Table 4.

Table 3: Substrate scope: β-monosubstituted enone-ketones

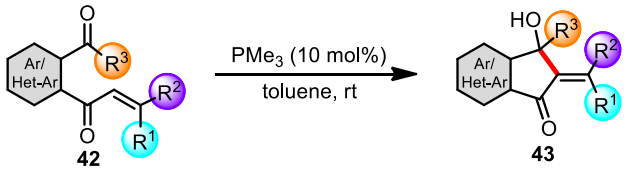


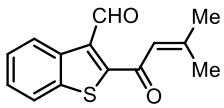
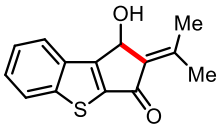
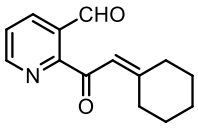
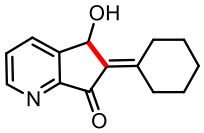
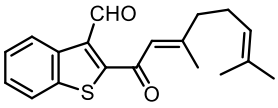
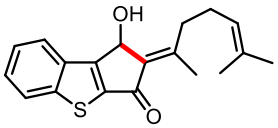
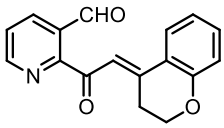
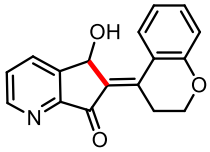
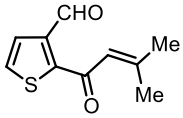
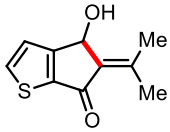
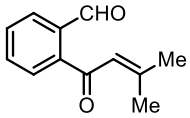
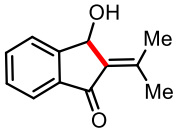
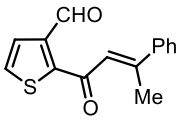
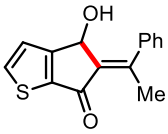
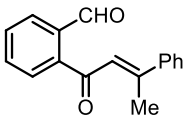
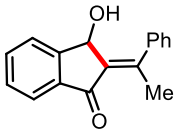
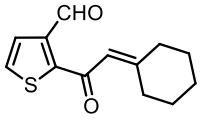
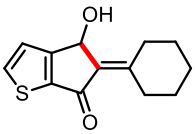
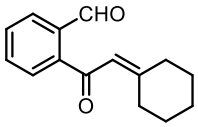
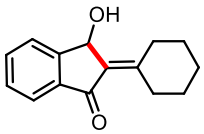
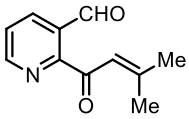
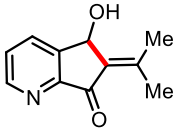
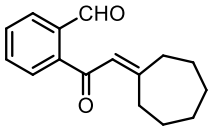
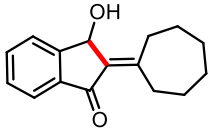
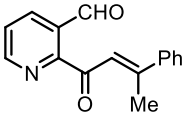
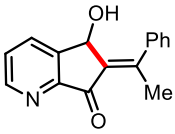
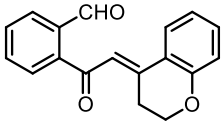
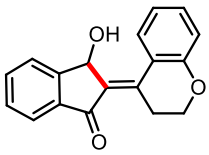
Entry	Substrate	Product
1	 **42t**	 **43t**, 15 min, 90% (*E*/*Z* = 13:1)
2	 **42u**	 **43u**, 30 min, 95% (*E*/*Z* = 9:1)
3	 **42v**	 **43v**, 10 min, 92% (*E*/*Z* = 10:1)

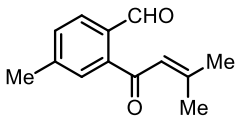
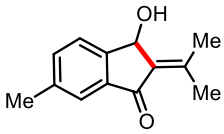
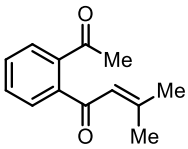
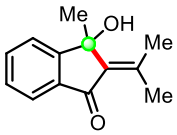
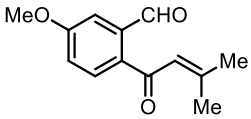
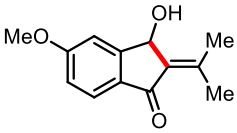
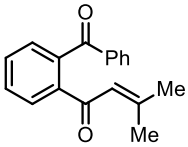
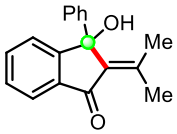
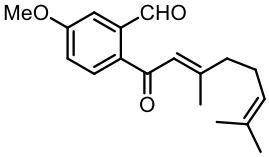
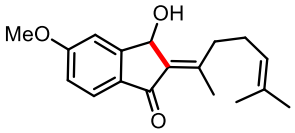
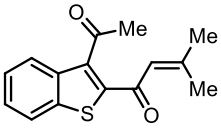
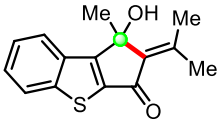
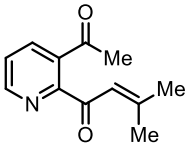
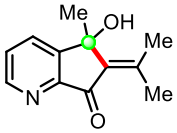
Yields were calculated after silica gel column chromatography.
E/*Z* ratio was calculated by ^{1}H-NMR analysis of the crude reaction mixture.

The results are summarized in Table 4. Thiophene and benzothiophene based substrates **42w-42aa** efficiently generated the cyclopent[*b*]annulated products **43w-43aa** in short turnaround time and excellent yields. The β,β-disubstituted pyrindanones **43ab-43ae** were also accessed in significantly short reaction time and high stereoselectivity, Table 4. These results highlight the role of an electron deficient pyridine backbone on the reaction rate enhancement. Difficult to access substituted cycloalkylidene, alkylidene, and arylidene indanones **43af-43am** could also be readily assembled by this method, Table 4. Interestingly, the presence of electron donating groups (such as –Me, –OMe) on aryl backbone **42ak-42al** does not have a significant influence on the reaction efficiency and delivered respective indanones **43ak-43al** in excellent yields, Table 4.

Table 4: Substrate Scope: β,β-disubstituted enone-aldehydes/ketones



Entry	Substrate	Product	Entry	Substrate	Product
1	 **42w**	 **43w**, 30 min, 92%	8	 **42ad**	 **43ad**, 30 min, 91%
2	 **42x**	 **43x**, 45 min, 82%, (*E*/*Z* = 9:1)	9	 **42ae**	 **43ae**, 30 min, 81% (*E*/*Z* = 9:1)
3	 **42y**	 **43y**, 30 min, 90%	10	 **42af**	 **43af**, 30 min, 93%
4	 **42z**	 **43z**, 45 min, 94%, (*E*/*Z* = 8:1)	11	 **42ag**	 **43ag**, 1 h, 89% (*E*/*Z* = 6:1)
5	 **42aa**	 **43aa**, 35 min, 90%	12	 **42ah**	 **43ah**, 40 min, 91%
6	 **42ab**	 **43ab**, 5 min, 92%	13	 **42ai**	 **43ai**, 45 min, 90%
7	 **42ac**	 **43ac**, 30 min, 84% (*E*/*Z* = 7:1)	14	 **42aj**	 **43aj**, 1 h, 93% (*E*/*Z* = 12:1)

Entry	Substrate	Product	Entry	Substrate	Product
15	 **42ak**	 **43ak**, 30 min, 95%	18	 **42an**	 **43an**, 30 min, 92%
16	 **42al**	 **43al**, 30 min, 92%	19	 **42ao**	 **43ao**, 1 h, 96%
17	 **42am**	 **43am**, 45 min, 88% (*E*/*Z* = 7/1)	20	 **42ap**	 **43ap**, 1 h, 93%
			21	 **42aq**	 **43aq**, 15 min, 90%

All reactions were done on 0.1 mmol scales. Yields were calculated after silica gel column chromatography. *E*/*Z* ratio was calculated by ^{1}H-NMR analysis of the crude reaction mixture.

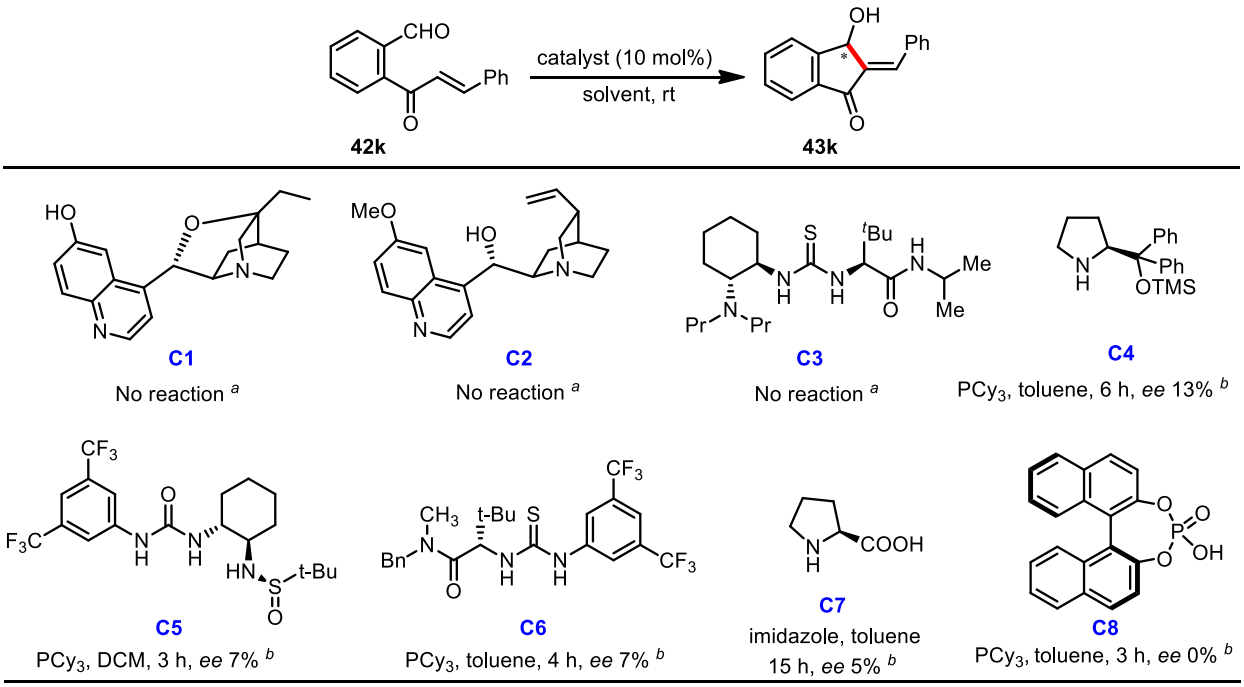
The versatility of this method was further demonstrated by utilizing the substrates possessing poor electrophiles such as ketones. A diverse range of synthetically challenging alkylidene indanones **43an-43ao**, pyrindanones **43aq** and cyclopent[*b*]annulated benzothiophene **43ap** bearing a tetrasubstituted carbon were achieved efficiently in excellent yields under these conditions, Table 4.

2.2: Development of an enantioselective IMBH reaction

After achieving a practical, general and highly efficient IMBH reaction for the synthesis of unprecedented cyclopenta[*b*]annulated arenes and heteroarenes from β-mono- and β,β disubstituted enones, we focused on developing an asymmetric organocatalytic version. Despite significant advancements in the area of asymmetric nucleophilic organocatalysis, only a handful of enantioselective IMBH reactions are reported so far.[70] Towards this, we have initiated the study with **42k** as a model substrate, Table 5. Various catalyst, ligand and solvent combinations were evaluated. The initial trials with cinchona alkaloids such as β-isocupreidine **C1** (β-ICD)[71]

and quinidine **C2** were failed to promote the IMBH reaction. Further, Jacobsen's bifunctional amine-thiourea catalyst **C3** also was unsuccessful.[72] However, a combination of chiral amine ligands **C4-C7** with different nucleophiles successfully delivered the desired product **43k** but in very poor enantioselectivities. A similar effort with chiral phosphoric acid **C8** was also discouraging as it led to no enantioinduction.

Table 5: Screening of chiral catalysts



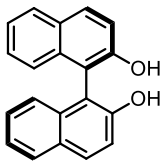
All reactions were performed on 0.1 mmol scales at room temperature by using 1.0 mL solvent. [a] Reactions were done using toluene and DCM as a solvent. [b] Nucleophile (10 mol%) and chiral ligand (12 mol%) were used.

Schaus' pioneering report[73] on intermolecular asymmetric MBH reaction with chiral Brønsted acids inspired us to employ the BINOL derivatives. The reaction of **42k** in the presence of tricyclohexylphosphine and BINOL **C9** afforded the MBH product in 21% enantiomeric excess (Table 6, entry 1). Unfortunately, no further improvement in enantioselectivity was realized by varying the solvent and nucleophile (DABCO, Me_2PPh) combinations (Table 6, entries 2-3). Prompted by Aggarwal's study[74] on Lewis acid accelerated MBH reaction, we have evaluated a variety of metal triflates. The use of Lewis acids with (*R*)-BINOL **C9** and (*R*)-BINAP **C10** in the presence of nucleophilic phosphines (PCy_3, PMe_3, Me_2PPh and $EtPPh_2$) also failed to enhance the enantioselectivity (Table 6, entries 4-11).

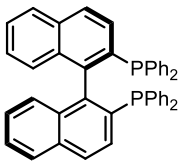
In recent years, functionalized amino acids are utilized widely as catalysts in enantioselective reactions.[75] Miller and co-workers have reported an intramolecular asymmetric Rauhut-Currier reaction by using protected cysteine.[76] Herein, we have synthesized two cysteine derivatives **C11** and **C12** by following the Miller's protocol. Under Miller's prototypical condition, the IMBH product was obtained in good yields in few minutes but with poor enantiopurities (Table 6, entries 12-14).

Table 6: Screening of chiral catalysts

Schaus and Aggarwal's strategy [a]



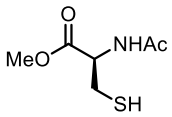
C9



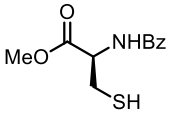
C10

1. **C9**, PCy_3, Toluene, 3.5 h, *ee* 21%
2. **C9**, DABCO, DMF, 7 h, *ee* 10%
3. **C9**, Me_2PPh, DCM, *ee* 7%
4. **C9**, PCy_3, $Yb(OTf)_3$, DCM, 3 h, *ee* 22%
5. **C9**, PMe_3, $Sc(OTf)_3$, DCM, 20 min, *ee* 4%
6. **C9**, $EtPPh_2$, $Sc(OTf)_3$, DCM, *ee* 6%
7. **C10**, PCy_3, $Yb(OTf)_3$, Toluene, 3 h, *ee* 5%
8. **C10**, PCy_3, $Sc(OTf)_3$, DCM, 3.5 h, *ee* 2%
9. **C10**, PCy_3, $Yb(OTf)_3$, THF, 3 h, *ee* 7%
10. **C10**, Me_2PPh, $La(OTf)_3$, Toluene, 10 min, *ee* 6%
11. **C10**, PMe_3, $Yb(OTf)_3$, DCM, *ee* 5%

Miller's strategy [b]



C11



C12

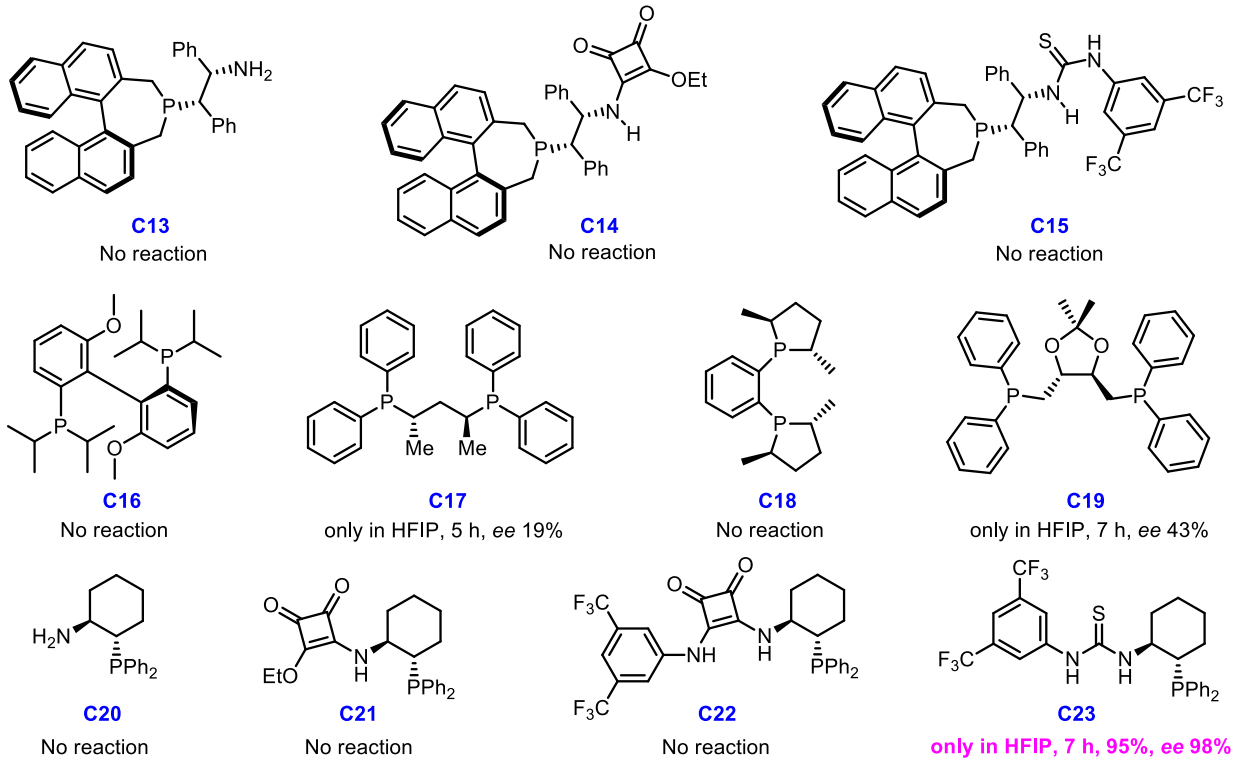
12. **C11**, *t*-BuOK, H_2O, CH_3CN, 5 min, –40 °C, *ee* 17%
13. **C11**, *t*-BuOK, H_2O, CH_3CN, 5 min, –30 °C, *ee* 4%
14. **C12**, *t*-BuOK, H_2O, CH_3CN, 40 min, –25 °C, *ee* 28%

All reactions were performed on 0.1 mmol scales at room temperature by using 1.0 mL solvent. [a] Lewis acid (12 mol%), BINAP or BINOL (12 mol%) and substrate were stirred at rt for 1 h in an appropriate solvent, then a nucleophile (10 mol%) was introduced.

Further, phosphepine[77] based bifunctional catalysts **C13-C15** have been tested in different solvents, but no product was observed even after prolonged reaction time, Table 7. Bidentate phosphines **C16-C19** also failed to deliver a trace of the product in dichloromethane and toluene. Recent advancements in the dramatic influence of fluorinated alcohols in co-operative catalysis by enhancing the H-bonding stimulated us to consider the fluorinated solvents.[78] Therefore, phosphines **C13-C19** were investigated using 2,2,2-trifluoroethanol (TFE), trifluorotoluene (TFT) and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP). Surprisingly, bidentate phosphine **C17** and **C19** afforded the desired product **43k** only in HFIP with 19% and 43% *ee* respectively, Table 7. With the initial success in HFIP, we have verified the outcome of a different class of bifunctional catalysts **C20-C23**. Interestingly, no product could be observed

with any of the phosphines **C20-C23** in toluene, dichloromethane or even in the fluorinated solvents such as TFE or TFT. To our delight, the bifunctional thiourea **C23** offered the desired IMBH product **43k** in 98% enantiomeric excess and 95% yield *only* in HFIP solvent, Table 7. This result suggests an extraordinary synergism between the substrate **42k**, HFIP and bifunctional catalyst **C23**.

Table 7: Screening of chiral phosphine catalysts



All reactions were performed on 0.1 mmol scales by using toluene (1.0 mL), DCM (1.0 mL), trifluorotoluene (TFT, 1.0 mL), trifluoroethanol (TFE, 1.0 mL) and hexafluoroisopropanol (HFIP, 0.5 mL) as solvent at room temperature and isolated by using silica gel column chromatography.

With the optimized reaction condition in hand, various β-monosubstituted enone-aldehydes have been evaluated, Table 8. The β-alkyl and aryl substituted thiophene and benzothiophene-3-carboxaldehydes **42c-42f** generated respective cyclopentannulated products **43c-43f** in excellent yields and enantioselectivities. Pyrindanone **43g** and indanones (**43i-j**, **43l-43m**, **43q-43s**) could also be accessed in high enantiopurities and near quantitative yields. This protocol found to be efficient even with the substrates **43l**, **43q** and **43r** bearing electron donating

groups (such as -Me, -OMe) either at the β-position of the enones or on aryl backbone. The β,β-disubstituted enones were also very promising under the optimized condition. For example, cyclopenta[*b*]thiophene **43y** and indanone **43af** were achieved in good yields and enantiopurities. Strikingly, electron deficient pyridine **42ab** delivered the pyrindanone **43ab** only in six hours in 91% yield and 85% enantioselectivity.

The absolute stereochemistry of **43k** was realized to be (*S*) by comparing the optical rotation with literature data[79] and was further supported by X-ray diffraction analysis (see Fig. 7). The absolute stereochemistry was assigned to other products by analogy. Accordingly, a proposed transition state is depicted in Fig. 6, which explains the experimental observation.

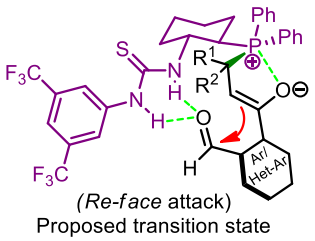


Figure 6: Proposed transition state for the asymmetric IMBH reaction

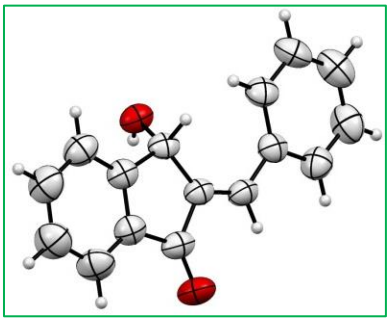
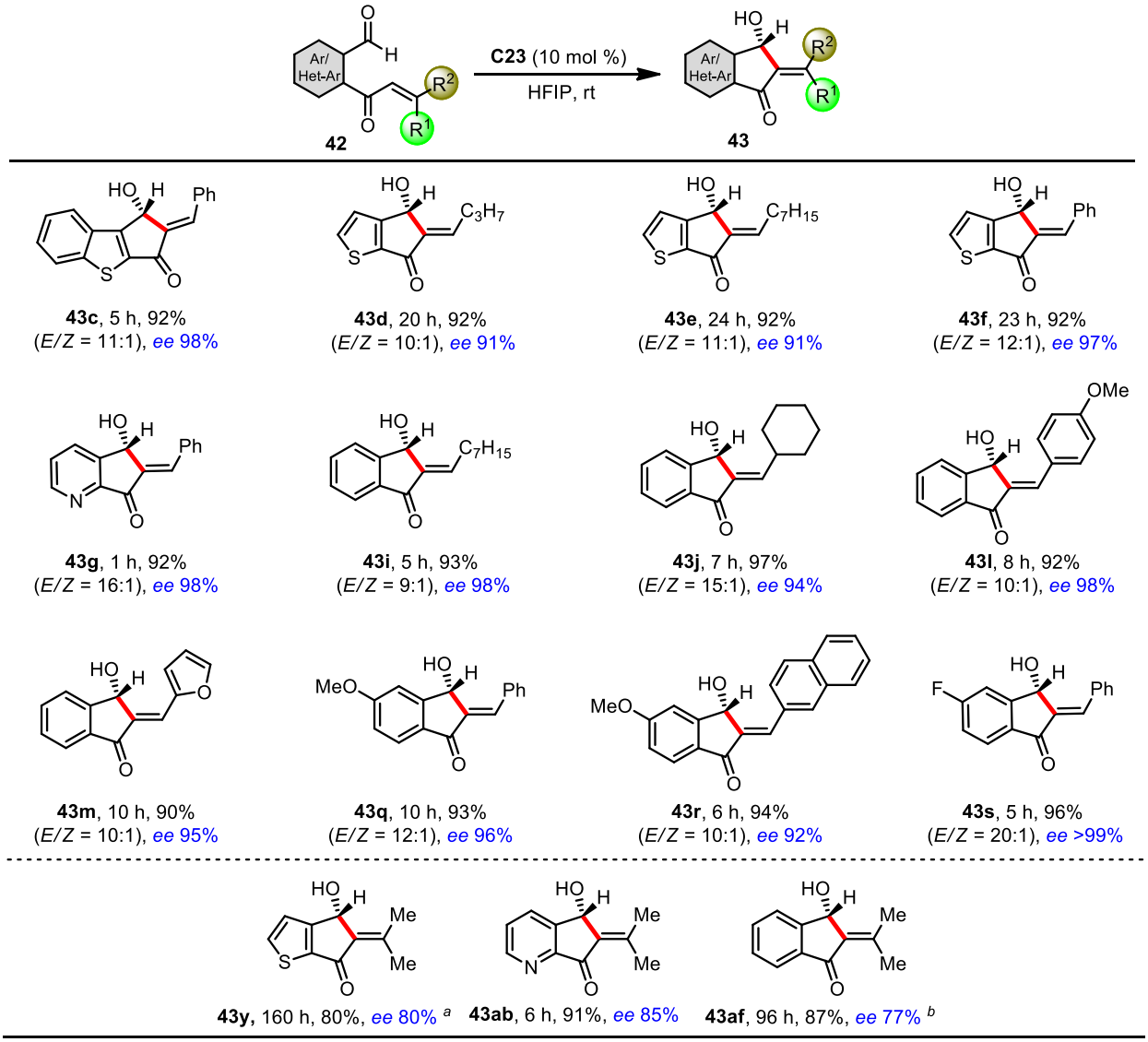


Figure 7: ORTEP diagram of chiral indanone **43k**

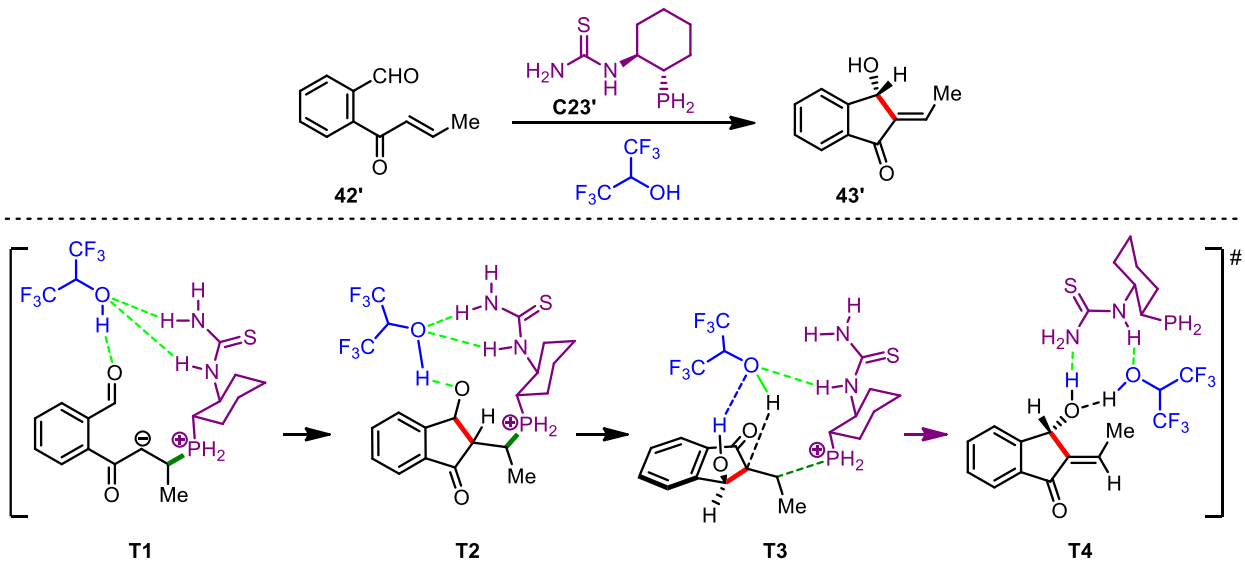
Table 8: Substrate scope: Enantioselective IMBH reaction



All reactions were performed on 0.1 mmol scales. *E/Z* ratio was determined by analyzing the ^{1}H-NMR of the crude reaction mixture. *ee* was determined by HPLC using chiral column. [a] Yield based on starting material recovery. [b] Reaction was performed at 10 ^{o}C.

Though the exact role of the hexafluoroisopropanol was not clearly understood at this stage, it could be attributed to its acidity (PK_a ca. 9.3) in the enhancement of hydrogen bonding. A brief DFT calculation by using B3LYP/6-31+G* basis set further supported our hypothesis.[80] The catalyst **C23** has been modified to fit within the optimum computational time, without the loss of relevant physical effects. The modification was such that the two phenyl groups of phosphorus and 3,5-trifluoromethyl-benzene of thiourea in **C23** are replaced with hydrogen

atoms. The reactant was chosen to be one with R^1 = Me and R^2 = R^3 = H, Scheme 47. The supramolecular assembly between the substrate **42'** and thiourea phosphine **C23'** in the presence of hexafluoroisopropanol *via* hydrogen bonding (as shown in Scheme 48; T1, T2, T3, and T4) could be the crucial driving force for the extremely facile transformation and excellent enantioinduction.



Scheme 48: Proposed transition state on the basis of DFT calculations

In conclusion, we have demonstrated the first asymmetric organocatalytic MBH reaction of β-mono- and β,β-disubstituted enones. A diverse range of enantiomerically enriched cyclopenta[*b*]annulated arenes and heteroarenes were synthesized from easily accessible starting materials in excellent yields and short reaction time. An extraordinary level of synergism was observed among the substrate, catalyst and fluorinated solvent in the MBH reaction.

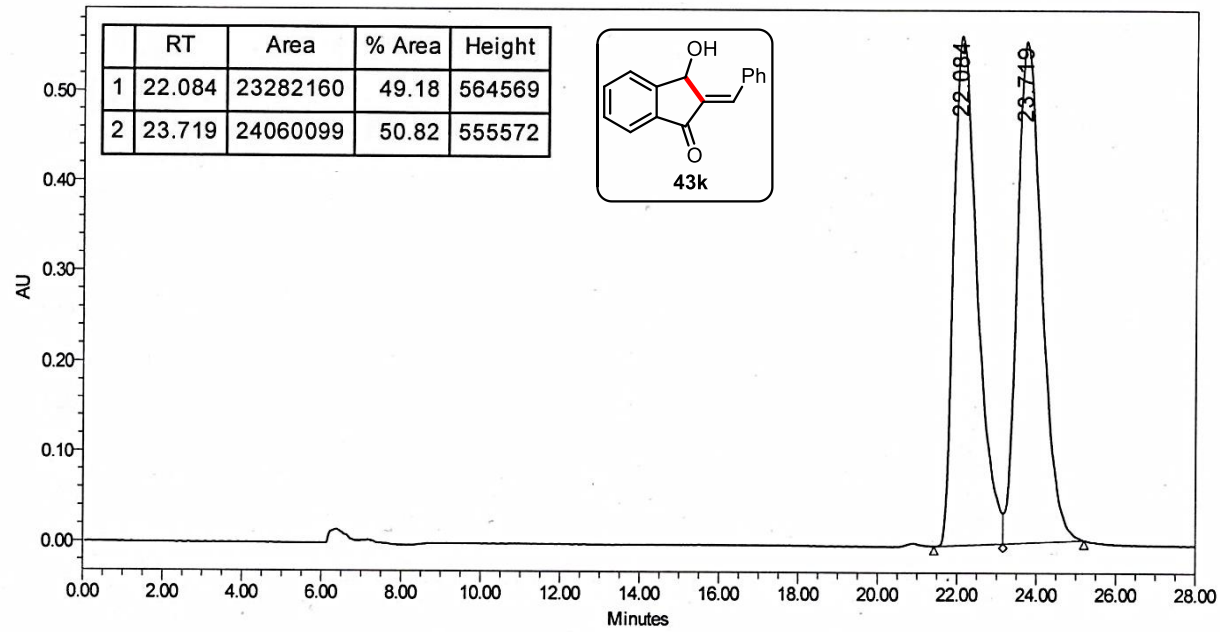


Figure 8: HPLC chromatogram of racemic **43k**

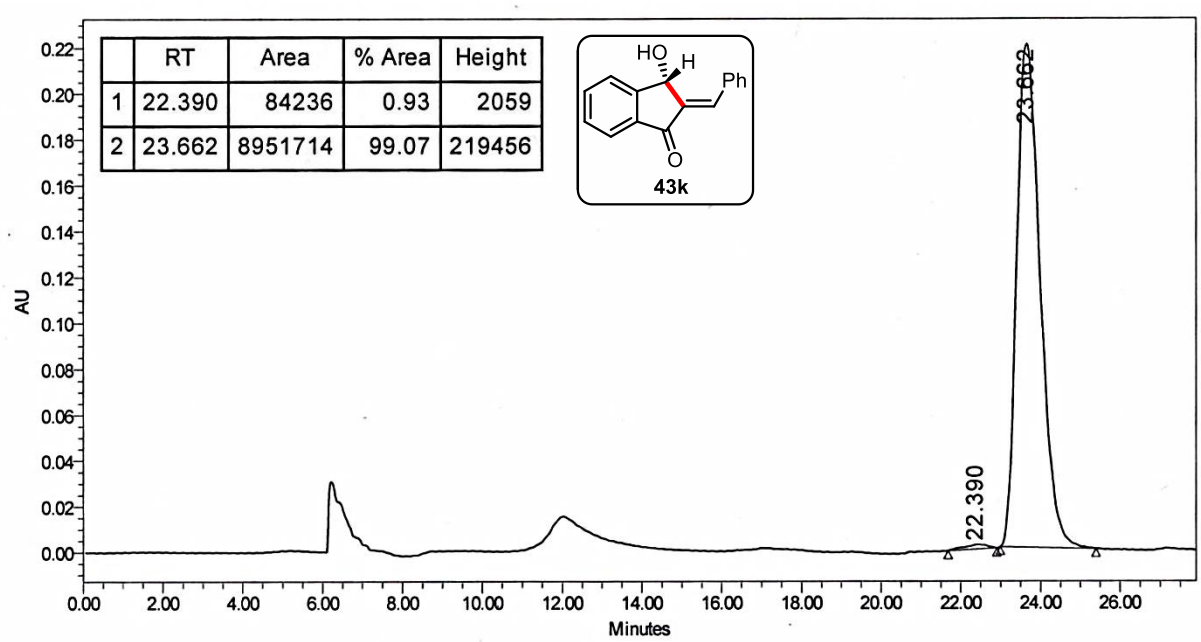


Figure 9: HPLC chromatogram of chiral **43k**

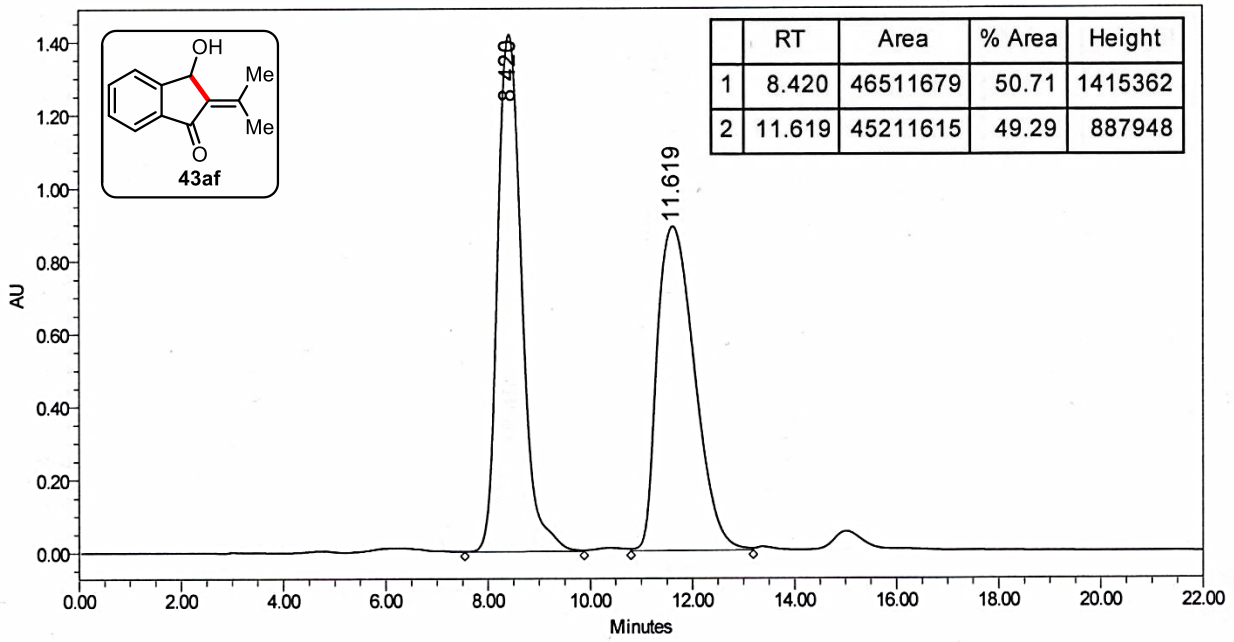


Figure 10: HPLC Chromatogram of racemic **43af**

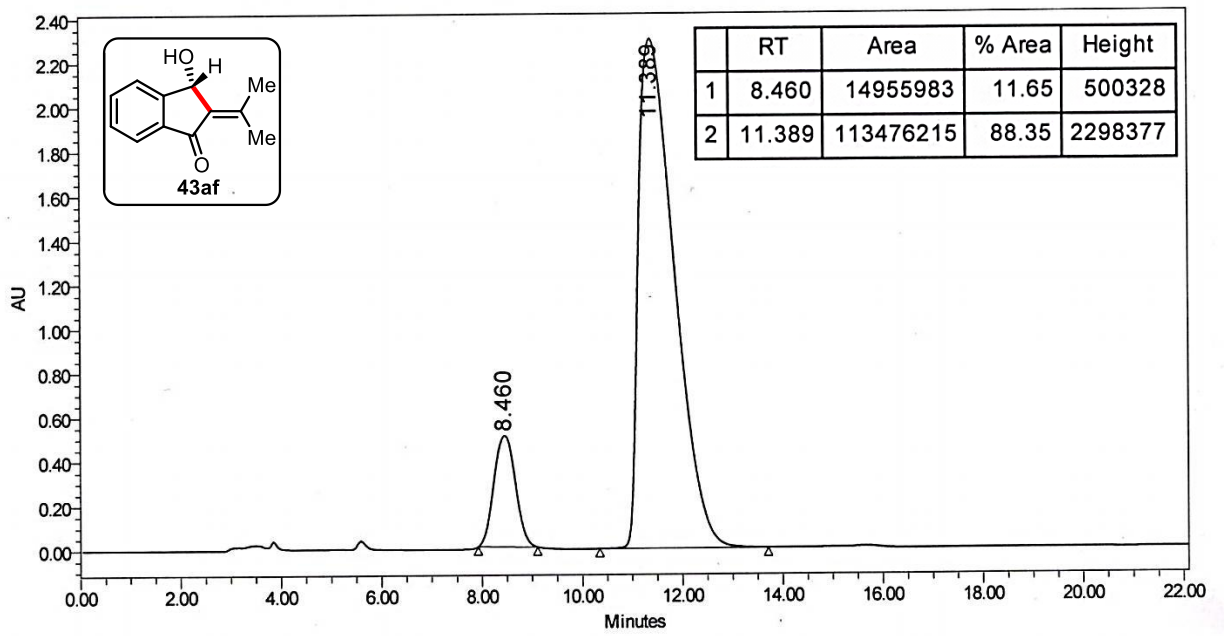


Figure 11: HPLC chromatogram of chiral **43af**

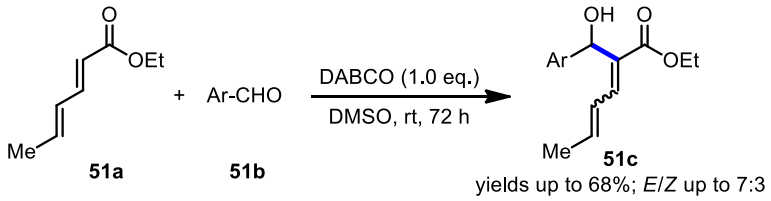
Section 3

An Enantioselective Intramolecular MBH Reaction of Dienones

The successful development of an efficient and practical enantioselective intramolecular Morita-Baylis-Hillman reaction of (described in section 2) inspired us to envision the reaction of dienones **58**, Scheme 54. Despite significant advancements in the area of MBH reaction, only a handful of successful studies have been realized with activated dienes.

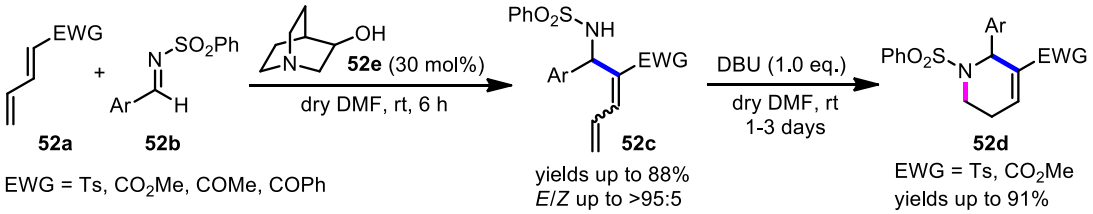
Towards this, in 2005, Radha Krishna *et al.*[81] described a novel protocol for the generation of β-branched MBH adducts by employing commercially available ethyl sorbate **51a** as a Michael acceptor in the presence of DABCO, Scheme 49. The scope of the reaction was further expanded with a variety of aromatic aldehydes under the optimized condition, and adducts **51c** were accessed in good yields and stereoselectivities. Though the reaction is limited

to the use of only electron-deficient aromatic aldehydes and a stoichiometric amount of nucleophilic trigger, it opened a new avenue in the area of MBH reaction of activated dienes.



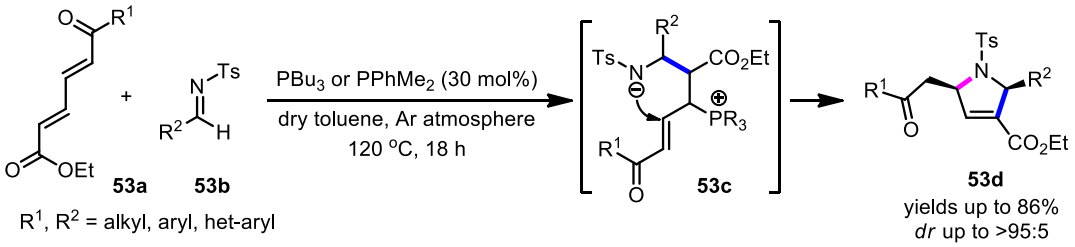
Scheme 49: Intermolecular MBH reaction of ethyl sorbate

In 2007, Back *et al.*[82] have reported an *aza*-MBH reaction of activated 1,3-dienes 52a, Scheme 50. Several dienes proceeded smoothly in the presence of 3-hydroxyquinuclidine **52e** to efficiently deliver the functionalized allylic amines **52c**. The MBH adducts obtained from the dienyl sulfone and dienoates were further elaborated to corresponding piperidine derivatives **52d** in excellent yields *via* a base mediated intramolecular 1,6-addition reaction.



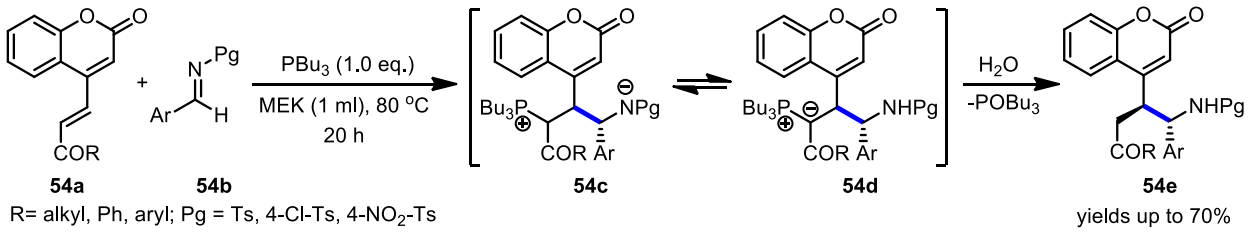
Scheme 50: Back's intermolecular *aza*-MBH reaction of activated dienes

In 2009, Marinetti *et al.*[83] developed an efficient method for the practical and scalable synthesis 2,3,5-trisubstituted 3-pyrrolines **53d**, Scheme 51. In the presence of nucleophilic phosphine, the doubly activated dienes **53a** underwent intermolecular *aza*-MBH reaction with a variety of aldimines **53b** to generate the zwitterionic intermediate **53c**. The subsequent *aza*-Michael addition afforded 3-pyrrolines **53d** in excellent yields and diastereoselectivities.



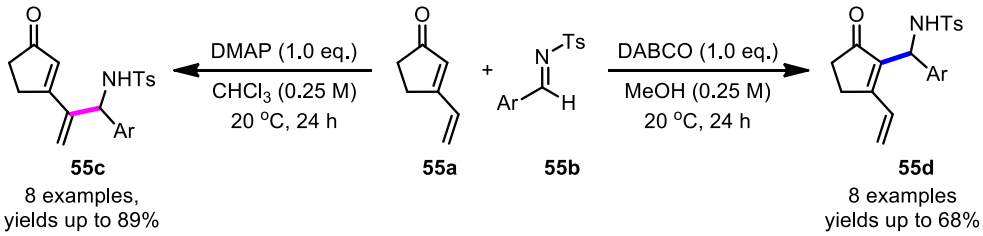
Scheme 51: Marinetti's synthesis of 3-pyrrolines

In 2012, Marinetti *et al.*[84] reported a tributylphosphine and water-mediated domino *aza*-MBH/reduction process of conjugated dienes, Scheme 52. This reaction involves in an initial vinylogous *aza*-MBH reaction of the vinyl substituted coumarins **54a** with aldimines **54b** and lead to the formation of zwitterion **54c**. Subsequently, zwitterion **54c** undergoes water-mediated hydrolysis either directly, or *via* the corresponding phosphorus ylide **54d** by eliminating phosphine oxide to afford the reduced product **54e** in good yields. The highly stereoselective generation of the reductive products bearing two contiguous stereogenic carbon centers signifies the potential utility of the reductive *aza*-MBH reaction.



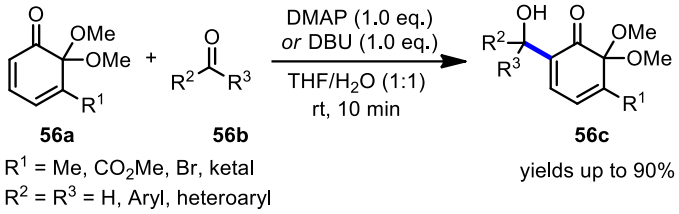
Scheme 52: Marinetti's intermolecular reductive *aza*-MBH reaction

In 2016, Kawabata *et al.*[85] disclosed a catalyst and solvent controlled regiodivergent *aza*-MBH reaction, Scheme 53. The 3-vinylcyclopent-2-en-1-one **55a** was found to deliver the γ-adduct **55c** preferentially in the presence of stoichiometric DMAP in chloroform. Whereas in the presence of a polar solvent such as methanol, DABCO promoted reaction exclusively to afford the α- adduct **55d** in excellent yields.



Scheme 53: Kawabata's regiodivergent *aza*-MBH reaction

In 2016, Chittimalla *et al.*[86] employed masked *ortho*-benzoquinone derivatives as activated diene partner in the MBH reaction, Scheme 54. A diverse range of *o*-quinones **56a**, aldehydes and ketones **56b** were well-tolerated under amine catalysis (DABCO or DBU), and furnished the MBH adducts **56c** in excellent yields.



Scheme 54: Intermolecular MBH reaction of *o*-benzoquinones

The aforementioned literature survey revealed few unaddressed challenges associated with the MBH reaction of activated dienes: (i) no intramolecular reaction was established, (ii) no report on an asymmetric variant of either inter- or intramolecular reaction, and (iii) activated dienes possessing δ,δ- or β,δ-substitutions (Fig. 12) are unexplored.

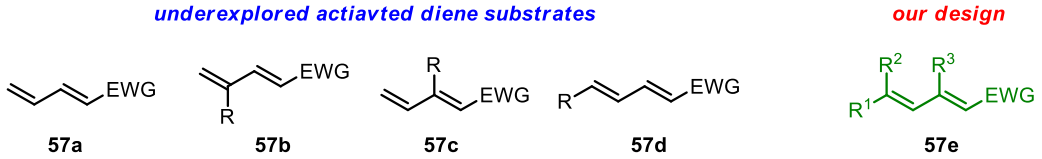
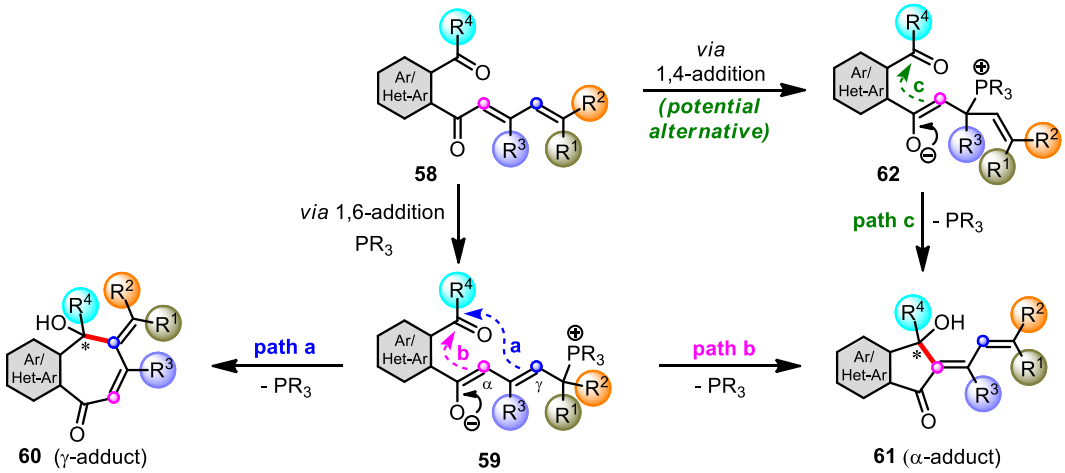


Figure 12: Substrate designs for intermolecular MBH reaction of activated dienes

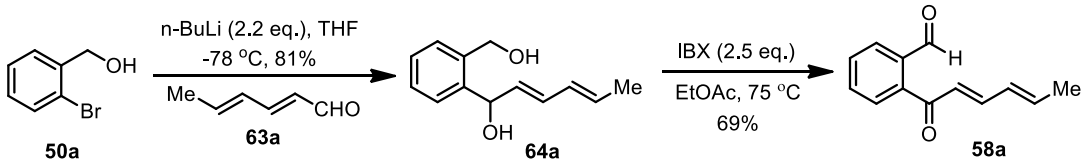
It was envisaged that the dienone **58** could undergo 1,6-conjugate addition of phosphine to generate the zwitterionic intermediate **59**. A Subsequent intramolecular aldol reaction of **59** can either lead to the formation of fused-cycloheptenones **60** *via* path a (γ-adduct) or fused-cyclopentenones **61** *via* path b (α-adduct), Scheme 55. Alternatively, the zwitterion **62** formed *via* an initial 1,4-phosphine addition can also lead to fused-cyclopentenones **61** *via* path c.



Scheme 55: Our hypothesis for the IMBH reaction of dienones **58**

3.1: Results and Discussion

In order to validate the hypothesis presented in the Scheme 54, we commenced synthesizing the substrate **58a**, Scheme 56. The substituted dienone-aldehyde **58a** can be achieved readily in a two-step protocol starting from 2-bromo benzyl alcohol **50a**. Direct *n*-butyllithium mediated alkylation of **50a** with commercially available 2,4-hexadienal **63a** generated the diol **64a**, and subsequent IBX oxidation furnished the enone-aldehyde **58a**.



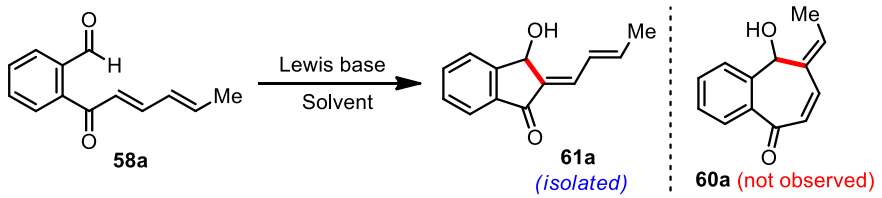
Scheme 56: Synthesis of dienone-aldehyde **58a**

Accordingly, we have initiated the optimization study with dienone-aldehyde **58a** as the model substrate. Prompted by our earlier success on intramolecular MBH reaction of enones (described in section 2), we have applied the prototypical condition during the initial screening. Strikingly, the dienone **58a** exclusively delivered the indanone **61a** in excellent yield in a 3:1 stereoisomeric ratio within 15 minutes (Table 9, entry 1).[87] However, even a trace of the expected arene fused-cycloheptenone **60a** was not observed. The other P-centered nucleophiles, except triphenylphosphine, were able to furnish the desired product, but were not encouraging (Table 9, entries 2-6). Typical amine-based Lewis bases also deliver discouring results (Table 9, entries 7-9).

The structure of indanone **61a** was deduced from the spectral data. The presence of two absorption bands in the IR spectrum at 3382 cm^{-1} due to secondary alcohol and at 1687 cm^{-1} due to the α,β-unsaturated ketone indicated the formation of **61a**. In the ^{1}H-NMR spectrum (see Fig. 14), the presence of a doublet at δ 5.73 ppm (J = 9.5 Hz) due to the methine proton (C-1), a doublet at δ 2.25 ppm (J = 9.6 Hz) due to -OH proton, and a doublet of doublet at δ 2.00 ppm (J = 7.0 and 0.8 Hz) due to methyl group confirmed the formation of **61a**. In the ^{13}C-NMR spectrum (see Fig 15), a signal at δ 192.1 ppm due to the unsaturated carbonyl (C-2), and a signal at δ 69.0 ppm due to the methine carbon (C-1) further established the structure **61a**. In the high-resolution mass spectrum presence of a dehydroxylated molecular ion peak at *m*/*z* 183.0821 $(M\text{-}OH)^{+}$ further supported the product formation. The X-ray diffraction analysis of **61a** (Fig.

13) confirmed the predicted *E*-geometry of the major isomer across the diene of the IMBH adducts.

Table 9: Optimization of the reaction parameters



Entry	Lewis Base (10 mol%)	Solvent	Temperature	Time	Yield (%)[a]/(*E*/*Z*)[b]
1	**PMe_3**	**Toluene**	**rt**	**15 min**	**95 (3:1)**
2	PPh_3	Toluene	50 °C	48 h	NR
3	PPh_2Et	Toluene	rt	30 min	89 (4:1)
4	PPh_2Et	DCM	rt	30 min	88 (4:1)
5	PCy_3	Toluene	rt	1 h	91 (4:1)
6	PCy_3	DCE	rt	1 h	90 (4:1)
7[c]	DBU	DCM	45 °C	24 h	86 (5:1)
8[c]	DABCO	DCM	rt	24 h	81 (3:1)
9[c]	DMAP	Toluene	rt	24 h	85 (3:1)

All reactions were performed on a 0.1 mmol scale. [a] Yield was calculated after silica gel column chromatography. [b] *E/Z* ratio was determined by ^{1}H-NMR analysis of the crude reaction mixture. [c] Yield was calculated based on the recovered starting material.
NR = no reaction.

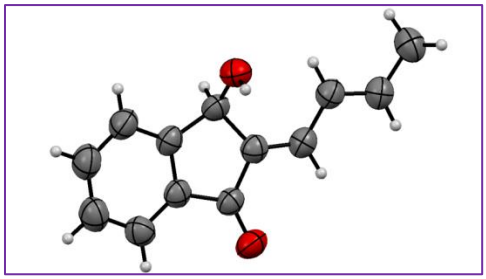


Figure 13: ORTEP diagram of indanone **61a**

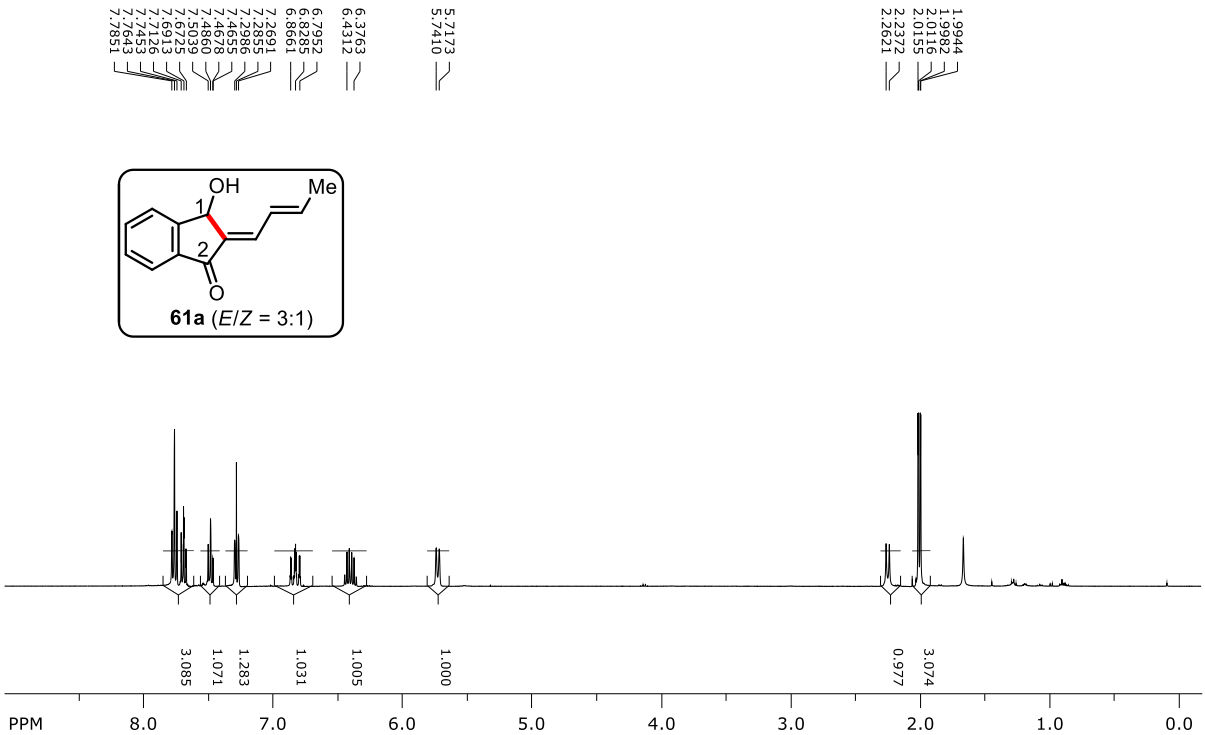


Figure 14: ^{1}H-NMR spectrum of indanone **61a**

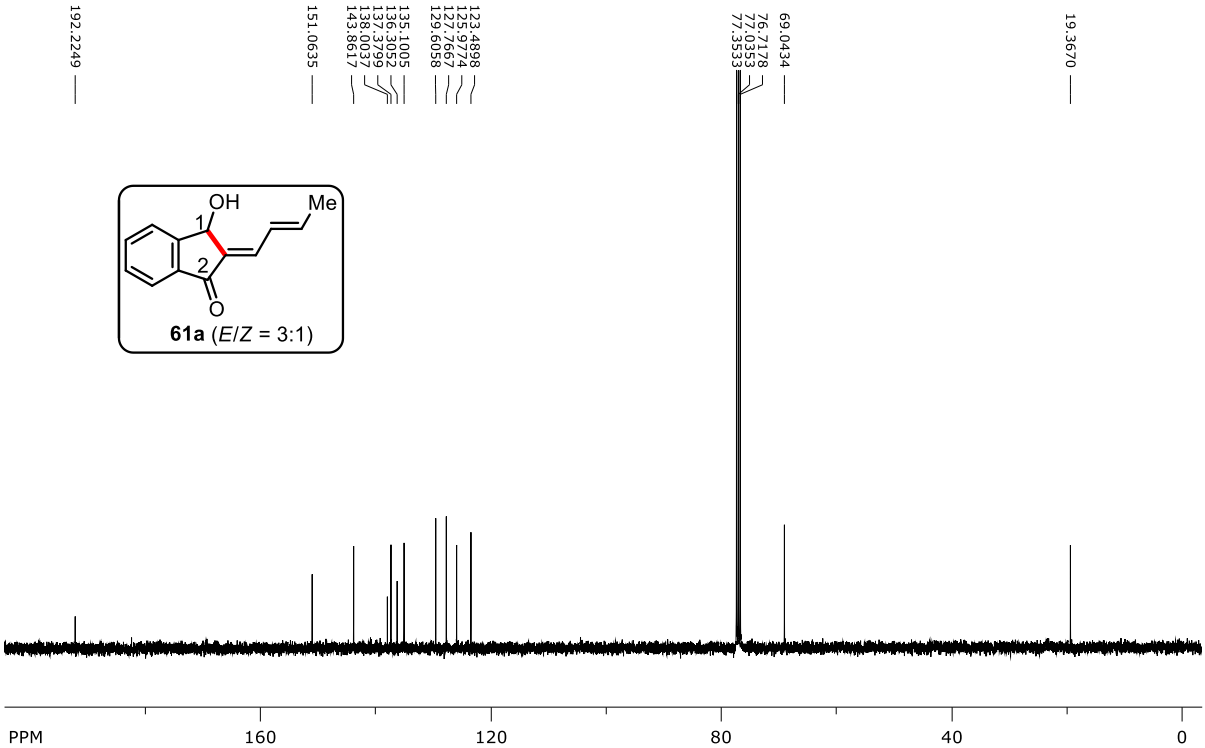
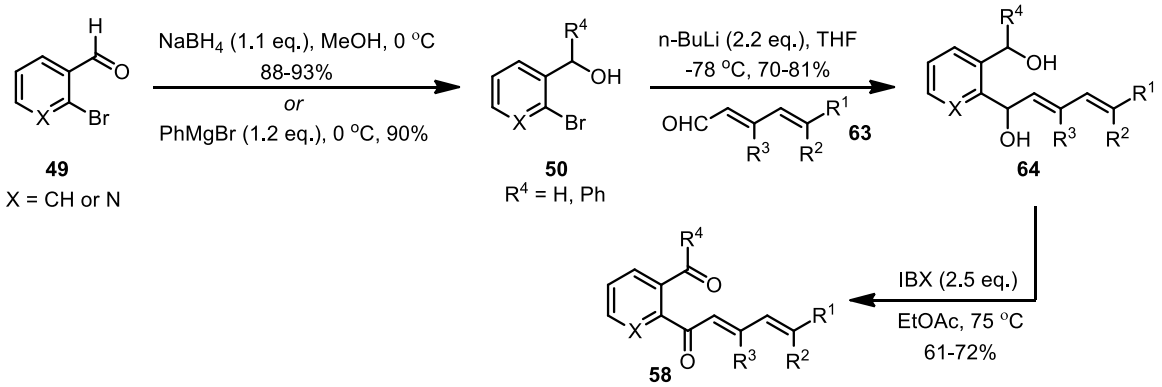


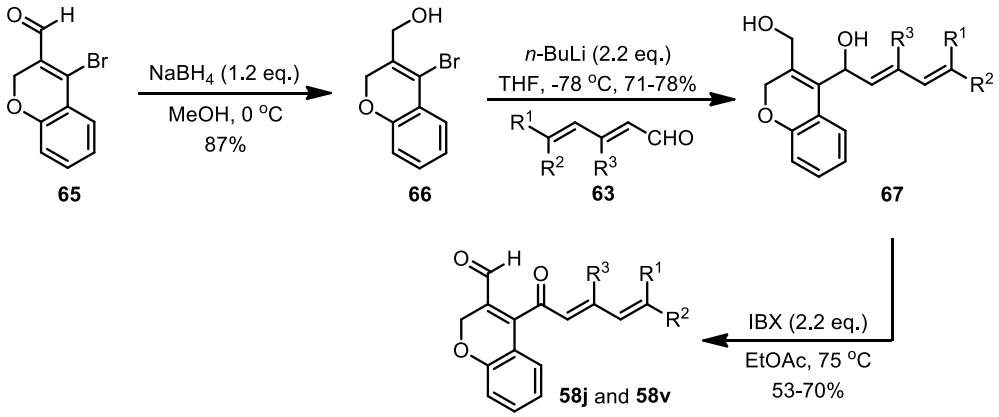
Figure 15: ^{13}C-NMR spectrum of indanone **61a**

After realizing a facile transformation of the dienone-aldehyde **58a** under the optimized condition, we sought to expand the substrate scope. Towards this, electronically diverse dienones were synthesized. Substrates bearing different aryl and pyridyl backbones can be synthesized in a three-step protocol, Scheme 57. The commercially available 2-bromo-aldehydes **49** were converted to the alcohol **50** by treating with either sodium borohydride or phenyl magnesium bromide reagent. Direct *n*-butyllithium mediated metal-halogen exchange of alcohol **50** followed by alkylation with an appropriate dienal **63** generated the diols **64**. IBX oxidation of the diols **64** led to the formation of the dienones **58**.



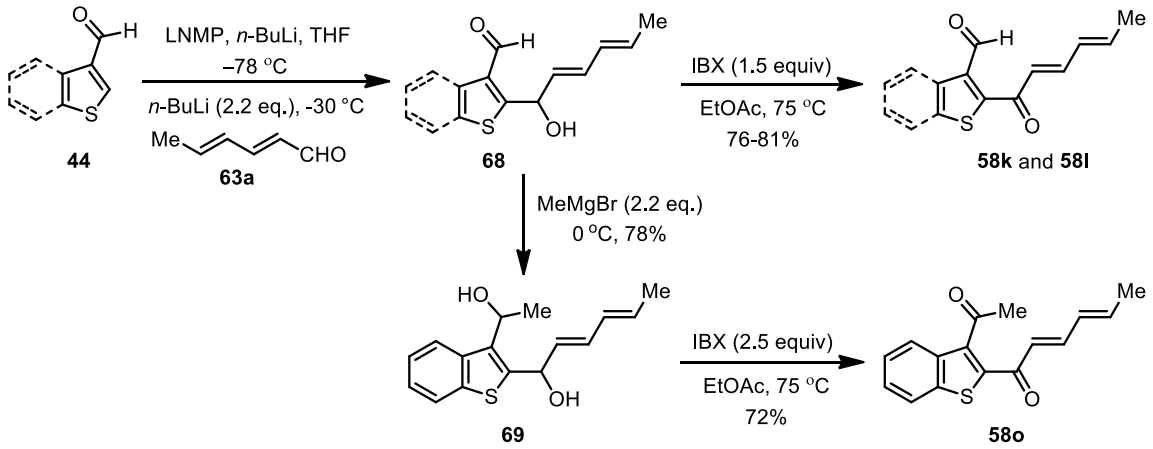
Scheme 57: Synthesis of substituted dienone-aldehydes **58**

Substrates bearing a non-aromatic backbone **58j** and **58v** also can be readily synthesized, Scheme 58. The bromo-aldehyde **65** was synthesized based on literature procedure from 4-chromanone,[88] and subjected to the borohydride reduction. The desired dienones were achieved *via n*-butyllithium mediated alkylation and IBX oxidation sequences of the bromo-alcohol **66**.



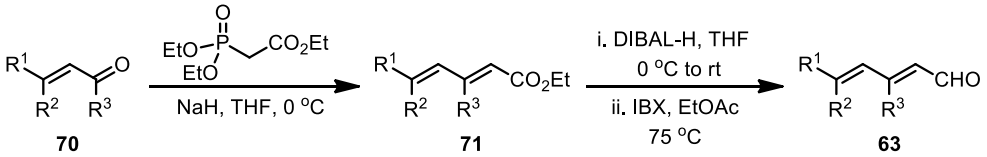
Scheme 58: Synthesis of chromene based dienone-aldehydes **58j** and **58v**

Thiophene and benzothiophene based dienone-aldehydes **58k** and **58l** can be accessed in a two-step protocol, Scheme 59. Directed α-alkylation of thiophene- and benzothiophene-3-carboxaldehydes **44** with 2,4-hexa-dienal **63a** afforded the dienols **69**, which upon IBX oxidation generates the dienone-aldehydes **58k** and **58l**. Alternatively, the dienone-ketone **58o** can be accessed from **69** *via* methyl magnesium bromide addition and oxidation sequence.



Scheme 59: Synthesis of thiophene and benzothiophene based dienones **58k**, **58l** and **58o**

The substituted dienals **63** employed in this study can be synthesized in a three-step protocol starting from enals or enones **70** *via* Horner-Wadsworth-Emmons (HWE) reaction, DIBAL-H reduction and IBX oxidation sequence, Scheme 60.[89]

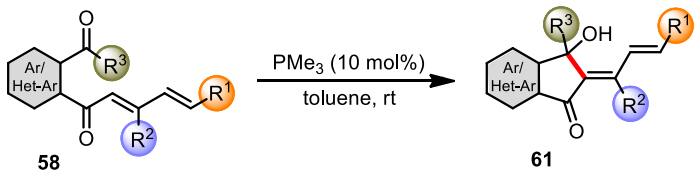


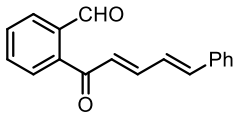
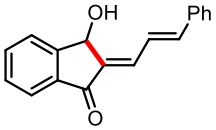
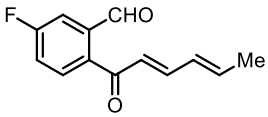
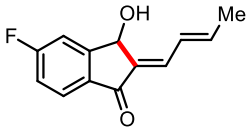
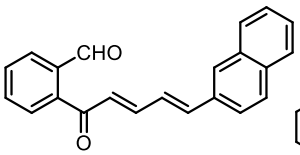
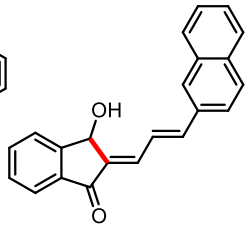
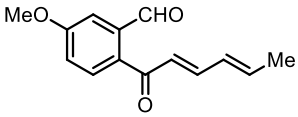
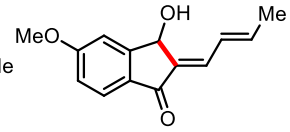
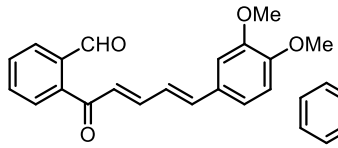
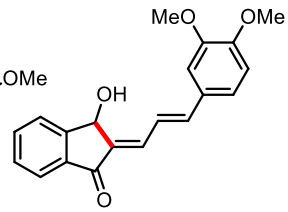
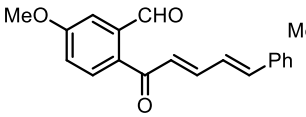
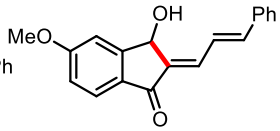
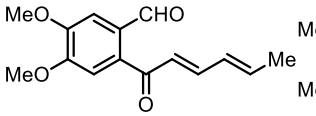
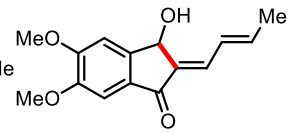
Scheme 60: Synthesis of substituted dienals **63**

To validate the generality of this method, the optimized reaction conditions were applied to a diverse range of substrates **58b-58p** bearing δ-monosubstituted dienones, Table 10. The reaction was realized to be general and proceeded smoothly to afford the annulated arenes and heteroarenes in excellent yields and stereoselectivities. In general, consistent reaction times were observed irrespective of the electronics and steric factors associated. A variety of indanones **61b-61i** bearing δ-aryl or alkyl substituents were assembled in excellent yields, Table 10. The presence of electron donating groups (such as -OMe) either on δ-substitutions **58d** or on aryl

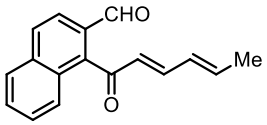
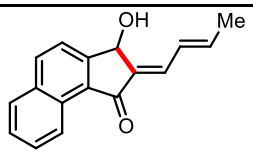
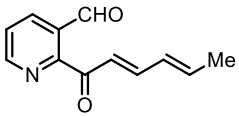
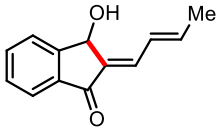
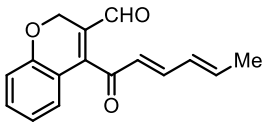
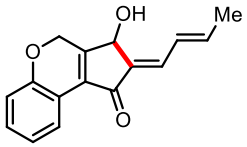
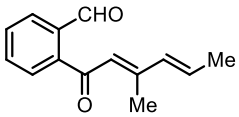
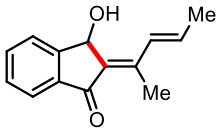
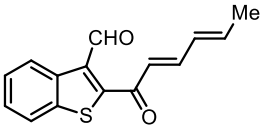
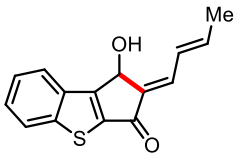
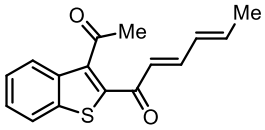
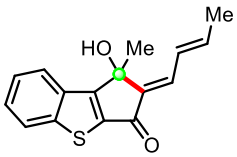
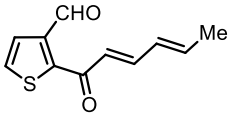
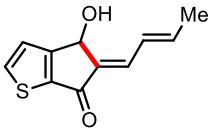
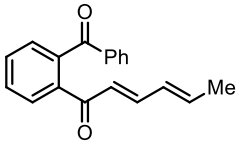
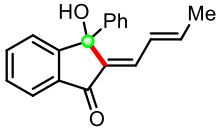
rings **58f-58h** was well tolerated under the optimized condition (Table 10, **61d**, **61f-61h**). Dienone appended to 2-naphthaldehyde moiety **58i** also delivered the cyclized product **61i**. The synthesis of cyclopenta-fused chromene **61j** in excellent yield and short reaction time further signified the tolerance of substrate with non-aromatic backbone, Table 10. Pleasingly, our further efforts to extend this method for the synthesis of cyclopenta-fused benzothiophene **61k**, thiophene **61l**, and pyridine **61m** also were successful, Table 10. The β-substituted dienone **58n** also was realized to be very effective under the optimized condition and afforded the indanone **61n** in excellent yield and stereoselectivity, Table 10.

Table 10: Substrate scope: δ-and δ,β-disubstituted dienones



Entry	Substrate	Product	Entry	Substrate	Product
1	 **58b**	 **61b**, 15 min, 91% (*E*/*Z* = 3:1)	4	 **58e**	 **61e**, 15 min, 97% (*E*/*Z* = 3:1)
2	 **58c**	 **61c**, 20 min, 95% (*E*/*Z* = 5:1)	5	 **58f**	 **61f**, 15 min, 92% (*E*/*Z* = 4:1)
3	 **58d**	 **61d**, 30 min, 90% (*E*/*Z* = 3:1)	6	 **58g**	 **61g**, 15 min, 92% (*E*/*Z* = 4:1)
			7	 **58h**	 **61h**, 15 min, 91% (*E*/*Z* = 5:1)

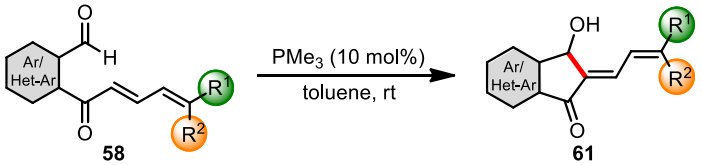
All reactions were done on 0.1 mmol scales. Yields were calculated after silica gel column chromatography. *E*/*Z* ratio was determined by ^{1}H-NMR analysis of the crude reaction mixture.

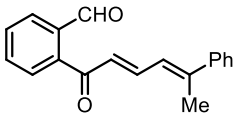
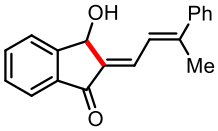
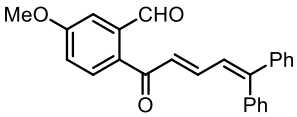
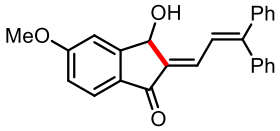
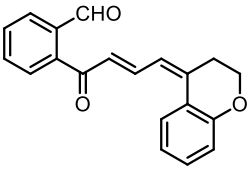
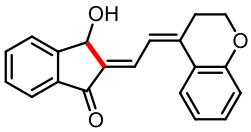
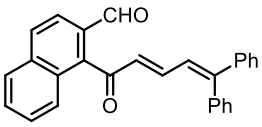
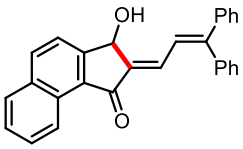
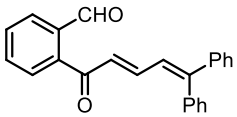
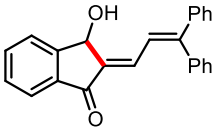
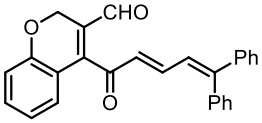
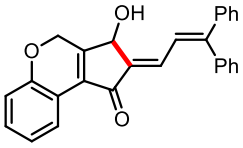
Entry	Substrate	Product	Entry	Substrate	Product
8	 **58i**	 **61i**, 15 min, 90% (*E*/*Z* = 5:1)	12	 **58m**	 **61m**, 10 min, 87% (*E*/*Z* = 5:1)
9	 **58j**	 **61j**, 15 min, 93% (*E*/*Z* = 6/1)	13	 **58n**	 **61n**, 25 min, 91% (*E*/*Z*= 3:2)
10	 **58k**	 **61k**, 15 min, 93% (*E*/*Z* = 4:1)	14	 **58o**	 **61o**, 30 min, 89% (*E*/*Z*= 5:2)
11	 **58l**	 **61l**, 10 min, 94% (*E*/*Z* = 4:1)	15	 **58p**	 **61p**, 20 min, 92% (*E*/*Z*= 3:1)

It is noteworthy that the compounds **58o** and **58p** possessing poor electrophile such as ketone were also demonstrated to be excellent substrate under the optimized condition. The cyclopenta[*b*]- annulated benzothiophene **61o** and indanone **61p** bearing a tetrasubstituted carbon atom could be efficiently accessed in excellent yields and diastereoselectivities in short reaction time, Table 10.

After realizing the extremely facile transformation of δ-monosubstituted dienones, we intended to explore the δ,δ-disubstituted dienone substrates. A diverse range of δ,δ-disubstituted dienones **58q-58u** tethered to aryl carboxaldehydes were evaluated under the optimized condition, Table 11. To our delight, the reaction proceeded smoothly to deliver the cyclopenta-fused arenes **61q-61u** in excellent yields and consistently short reaction time, Table 11. Of significance, the substrate with a non-aromatic backbone **58v** was also realized to be equally efficient under the optimized condition and resulted in the cylopentannulated chromene **61v**, Table 11. The table 11 further outlines the tolerability of the substitutions at δ-position across the diene and remarkably broad substrate scope of this protocol.

Table 11: Substrate scope: δ,δ-disubstituted dienone-aldehydes



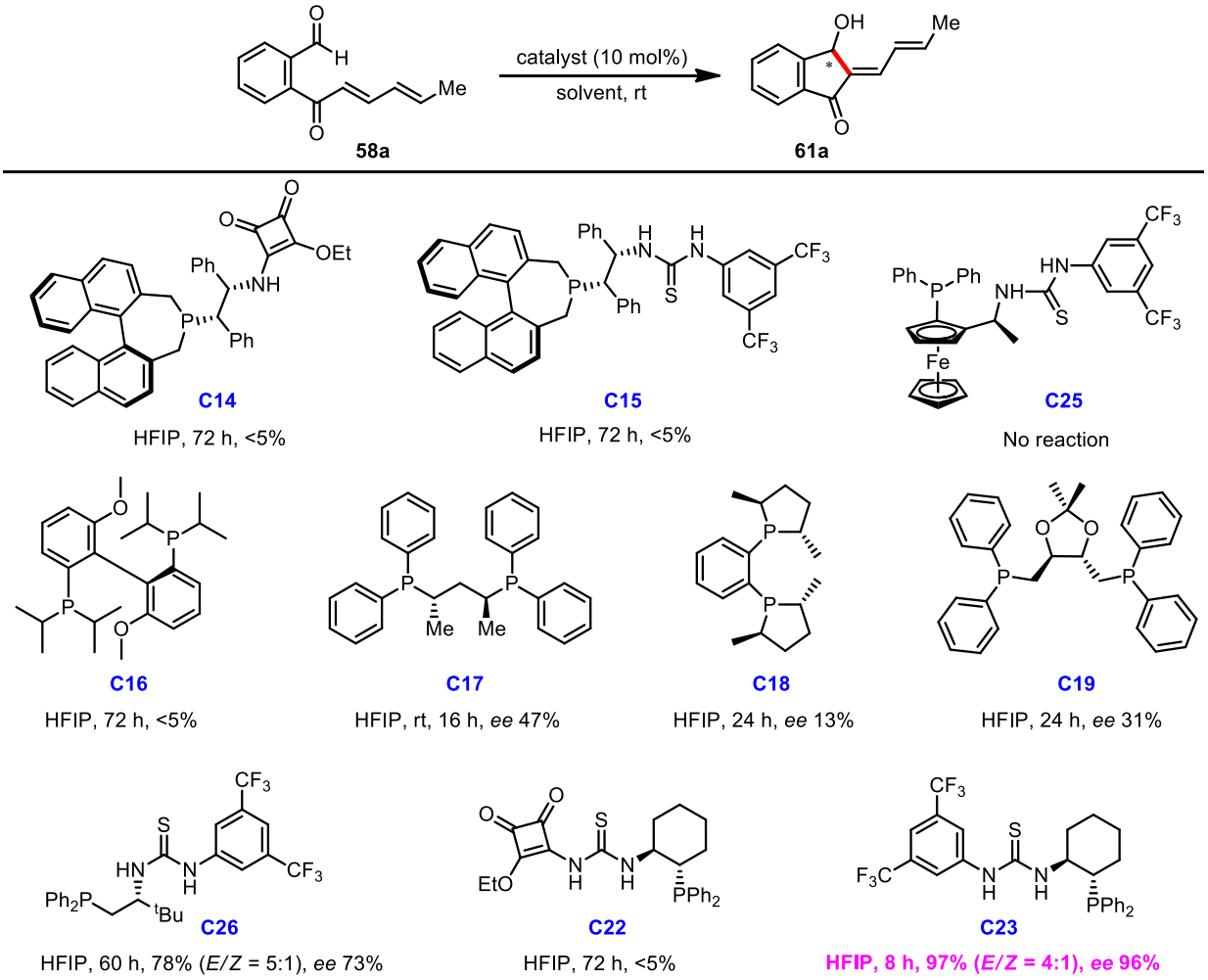
Entry	Substrate	Product	Entry	Substrate	Product
1	 **58q**	 **61q**, 30 min, 87% (*E*/*Z* = 4:1)	4	 **58t**	 **61t**, 15 min, 92 % (*E*/*Z* = 4:1)
2	 **58r**	 **61r**, 35 min, 89% (*E*/*Z* = 5:1)	5	 **58u**	 **61u**, 20 min, 89% (*E*/*Z* = 6:1)
3	 **58s**	 **61s**, 20 min, 93% (*E*/*Z* = 6:1)	6	 **58v**	 **61v**, 25 min, 96% (*E*/*Z* = 8:1)

All reactions were done on 0.1 mmol scales. Yields were calculated after silica gel column chromatography. *E*/*Z* ratio was calculated by ^{1}H-NMR analysis of the crude reaction mixture.

3.2: Development of an enantioselective IMBH reaction

Next, we focused on the development of an enantioselective organocatalytic IMBH reaction of dienones. Towards this, we have initiated the study by investigating the nucleophilic chiral phosphines in various solvent combinations with dienone **58a** as the model substrate, Table 12. The initial screening with bifunctional phosphines **C14, C15** and **C25** was unsuccessful even in fluorinated solvents. The bisnucleophilic phosphines **C16-C19** delivered the desired product in poor to moderate enantioselectivities only in hexafluoroisopropanol (HFIP). However, in HFIP solvent, the amino acid derived bifunctional phosphine **C26** afforded the IMBH adduct **61a** in good yield and enantioselectivity was encouraging. With the initial success in HFIP solvent, we investigated the catalysts **C22** and **C23** in fluorinated solvents. Interestingly, catalyst **C23** furnished the product **61a** in 97% yield and 96% enantioselectivity *only* in HFIP solvent.

Table 12: Screening of chiral catalysts

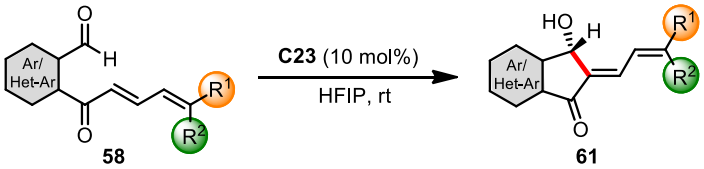


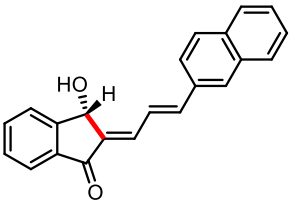
All reactions were performed on a 0.1 mmol scale using DCM, toluene, TFT, TFE, and HFIP. Yields were calculated after silica gel column chromatography. *E*/*Z* ratio was calculated from the ^{1}H-NMR spectrum of the crude reaction mixture.

With the optimized reaction condition in hand, we have evaluated various δ-mono and δ,δ-disubstituted dienone-aldehydes, Table 13. All the δ-monosubstituted dienones **58c-58i** possessing aryl backbones generated the respective products **61c-61i** in excellent enantiopurities and near quantitative yields with an improved *E*/*Z* ratio compared to racemic variants. The versatility of this protocol is furthered with the synthesis of cyclopentannulated chromene **61j** in excellent enantioselectivities. Cyclopenta-fused benzothiophene **61k,** thiophene **61l**, and pyridine **61m** could also be achieved efficiently in high enantiopurities. Substrates bearing δ,δ-disubstituted dienones **58q** and **58t-58v** also proceeded smoothly and efficiently to deliver the

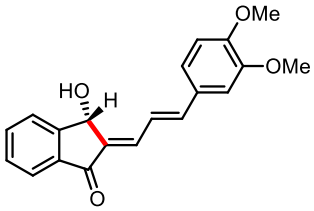
respective annulated products **61q** and **61t-61v** in excellent enantioselectivities and yields. This protocol was found to be efficient even in the presence of electron donating groups (such as –OMe) on the aryl backbone **61f-61h**. However, a moderate enantioinduction was realized with the substrate **61d** where electron rich δ-substitution was present. The absolute stereochemistry was determined to be (*S*) from the X-ray crystal structure of **61t** (Fig. 16) and assigned to other products in analogy.

Table 13: Substrate scope: δ-mono and δ,δ-disubstituted dienone-aldehydes

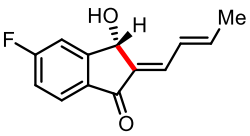




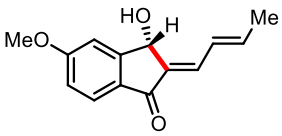
61c, 13 h, 97% (*E*/*Z* = 5:1)
ee 90%



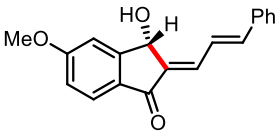
61d, 14 h, 87% (*E*/*Z* = 5:1)
ee 78%



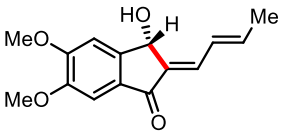
61e, 8 h, 93% (*E*/*Z* = 3:1)
ee 99%



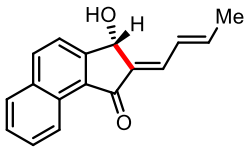
61f, 10 h, 94% (*E*/*Z* =5:1)
ee 94%



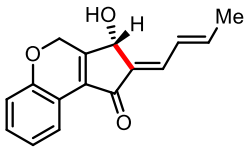
61g, 11 h, 95% (*E*/*Z* = 4:1)
ee 94%



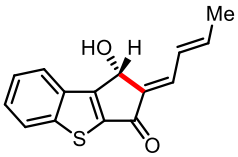
61h, 13 h, 93% (*E*/*Z* = 4:1)
ee 93%



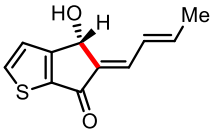
61i, 15 h, 93% (*E*/*Z* = 5:1)
ee 99%



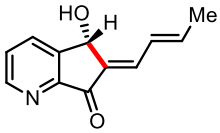
61j, 13 h, 97% (*E*/*Z* = 6:1)
ee 95%



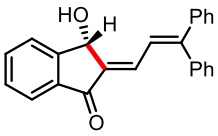
61k, 8 h, 91% (*E*/*Z* = 4:1)
ee 94%



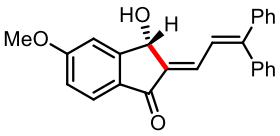
61l, 9 h, 89% (*E*/*Z* = 5:1)
ee 92%



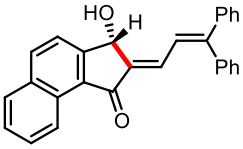
61m, 5 h, 88% (*E*/*Z* = 4:1)
ee 96%



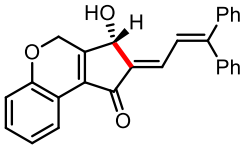
61q, 17 h, 92% (*E*/*Z* = 6:1)
ee 94%



61t, 16 h, 88% (*E*/*Z* = 7:1)
ee 97%



61u, 17 h, 95% (*E*/*Z* = 7:1)
ee 91%



61v, 18 h, 91% (*E*/*Z* = 6:1)
ee 98%

Yields were calculated after silica gel column chromatography. *E*/*Z* ratio was calculated from the ^{1}H-NMR spectrum of the crude reaction mixture.

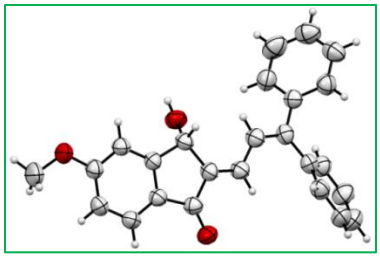


Figure 16: ORTEP diagram of chiral indanone **61t**

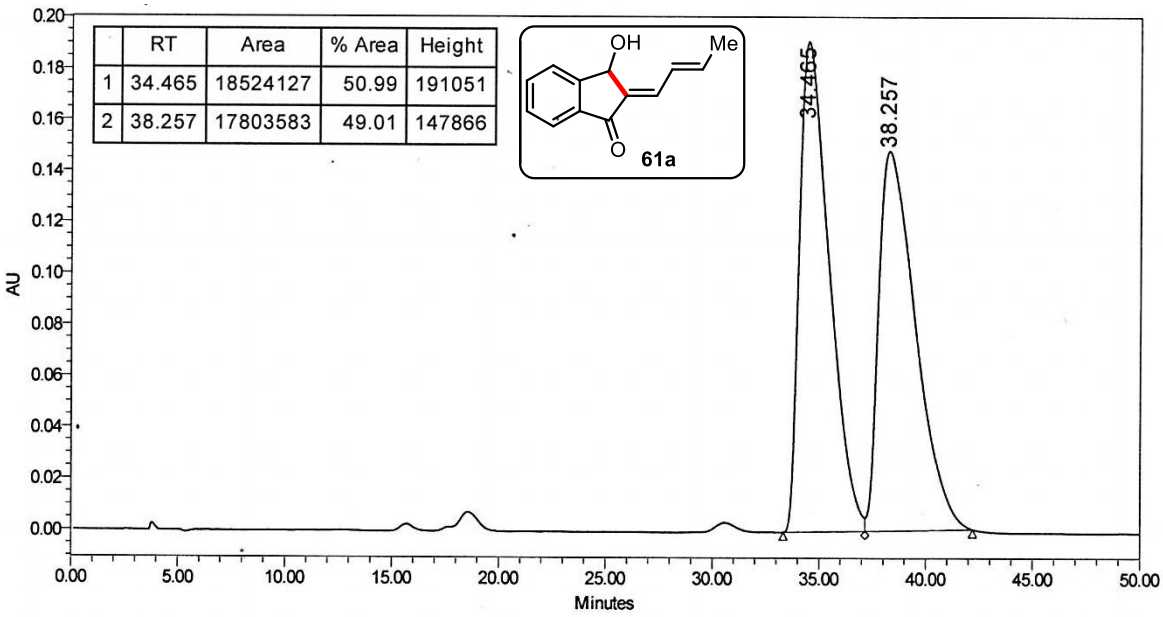


Figure 17: HPLC chromatogram of racemic **61a**

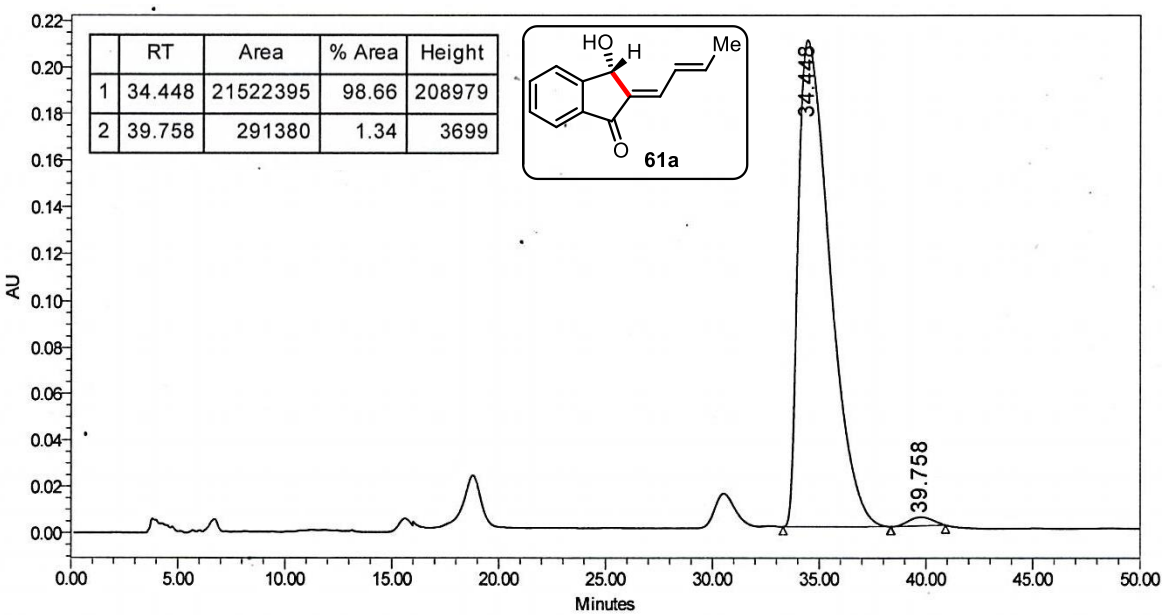
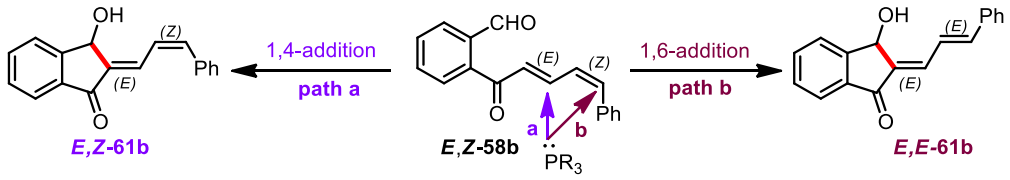


Figure 18: HPLC chromatogram of chiral **61a**

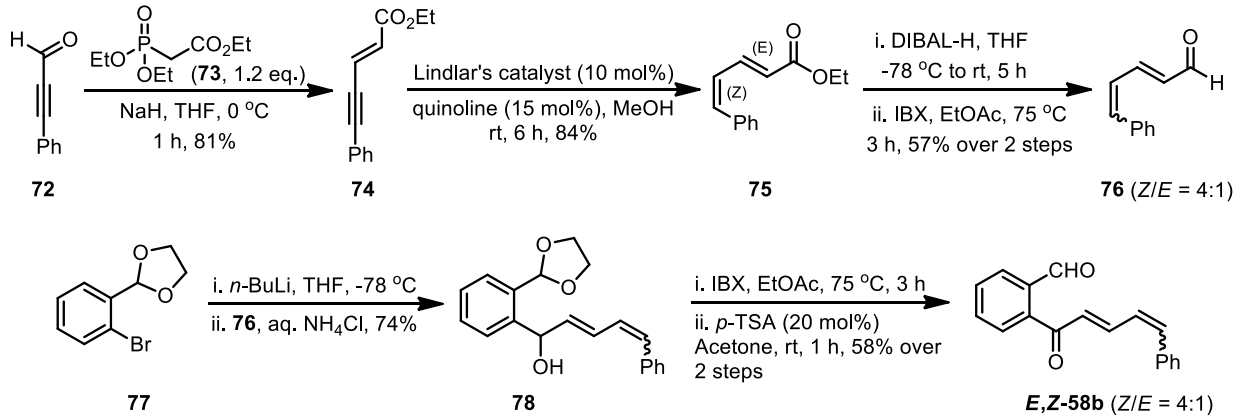
3.3: Efforts to gain evidence for 1,4- vs. 1,6-phosphine addition

In principle, the dienones **58** can undergo an initial 1,4- or 1,6-phosphine addition. In an attempt to address this concern, we have designed a substrate ***E*,*Z*-58b**, where two double bonds across the dienenone are disposed *E* and *Z*, Scheme 61. It is presumed that in the case of 1,4-addition of phosphine (path a) the stereochemical integrity of *Z*-alkene should remain unchanged leading to the indanone ***E*,*Z*-61b**. But in the case of 1,6-addition (path b), the *Z*-alkene should be equilibrated to thermodynamically stable *E*-alkene leading to the indanone ***E*,*E*-61b**, Scheme 60.



Scheme 61: Our hypothesis towards 1,4-vs. 1,6-addition

Accordingly, a synthetic route was proposed to access the dienone ***E*,*Z*-58b**, Scheme 62. The stereospecific ester **75** was obtained from commercially available phenylpropiolaldehyde **72** *via* Horner-Wadsworth-Emmons reaction using **73** and subsequent Lindlar's hydrogenation. Ester **75** was converted to corresponding primary alcohol and oxidized to obtain the dienal **76**. Further, *n*-butyllithium mediated alkylation of **77** with dienal **76** furnished the alcohol **78**. Subsequent IBX oxidation of alcohol **78** and acetal deprotection delivered the desired dienone-aldehyde ***E*,*Z*-58b** in 4:1 ratio.



Scheme 62: Synthesis of dienone-aldehyde ***E*,*Z*-58b**

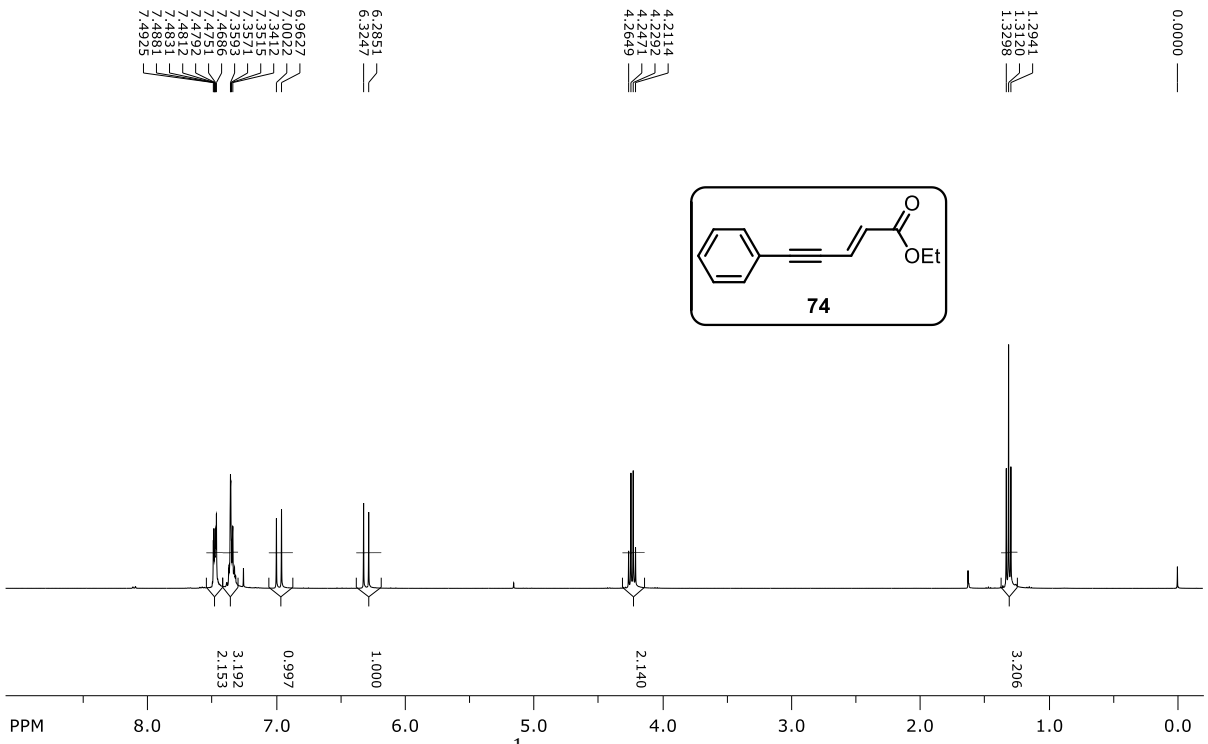


Figure 19: ^{1}H-NMR spectrum of **74**

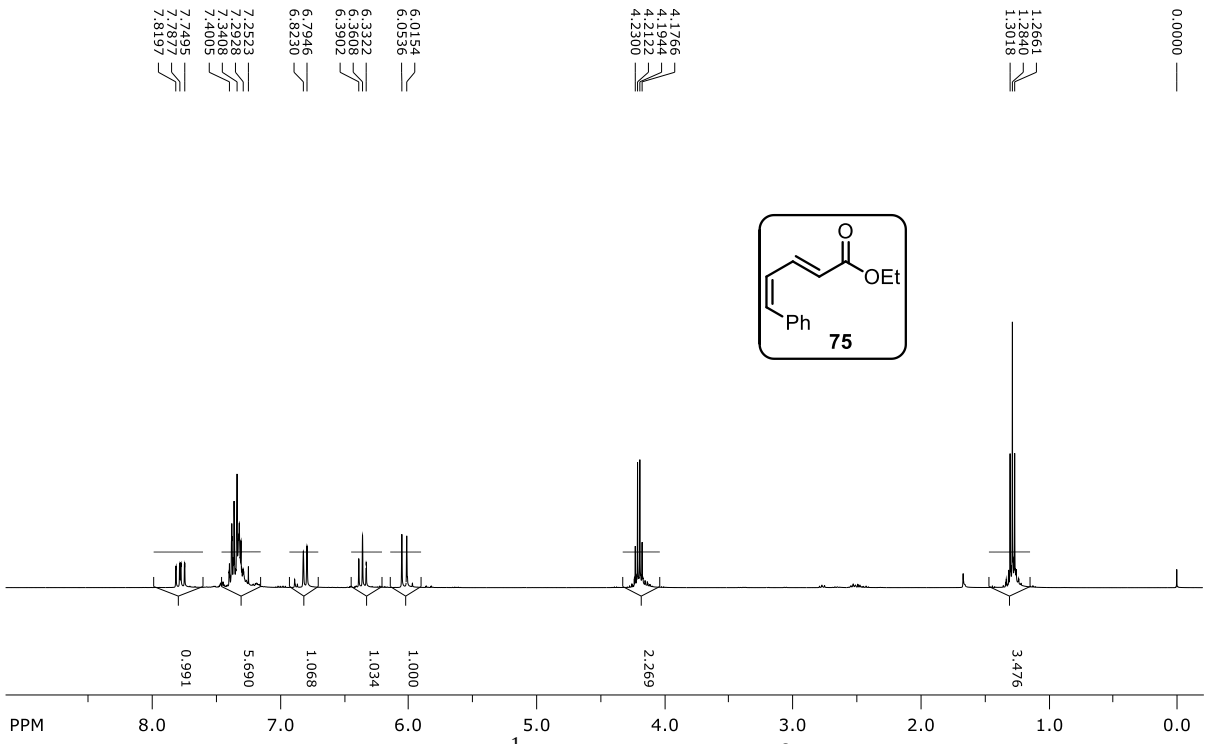


Figure 20: ^{1}H-NMR spectrum of **75**

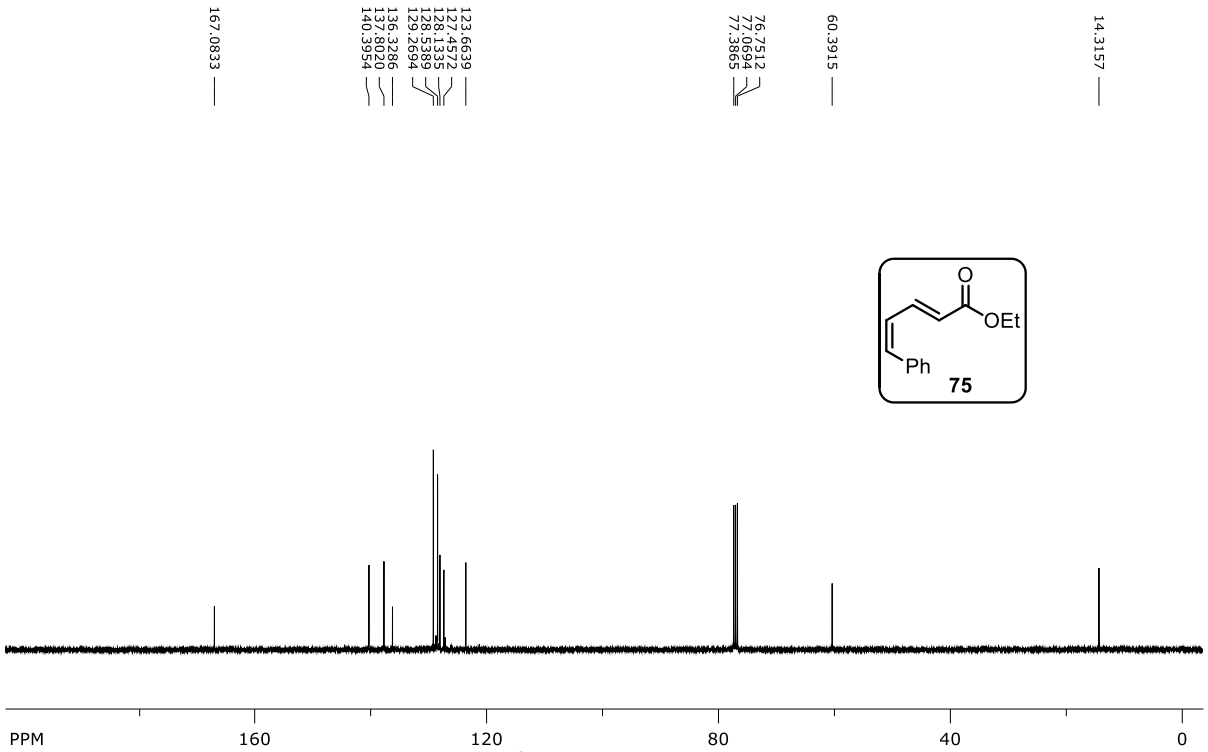


Figure 21: ^{13}C-NMR spectrum of **75**

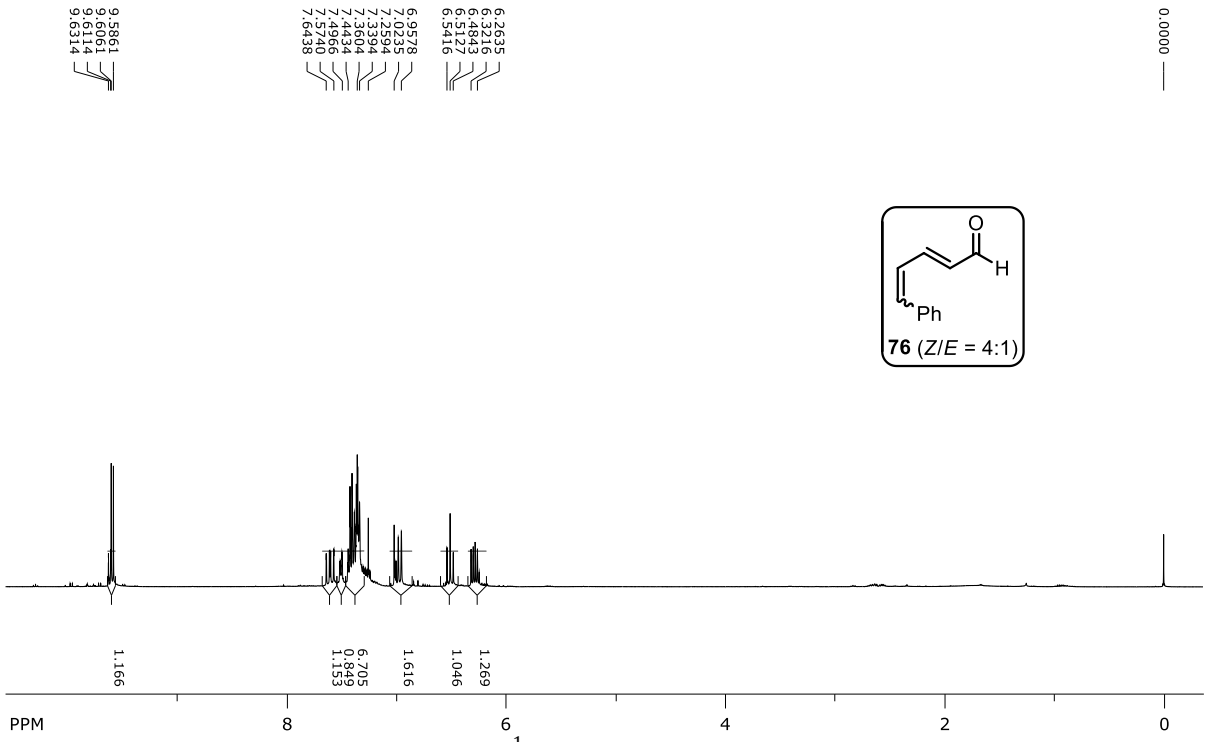


Figure 22: ^{1}H-NMR spectrum of **76**

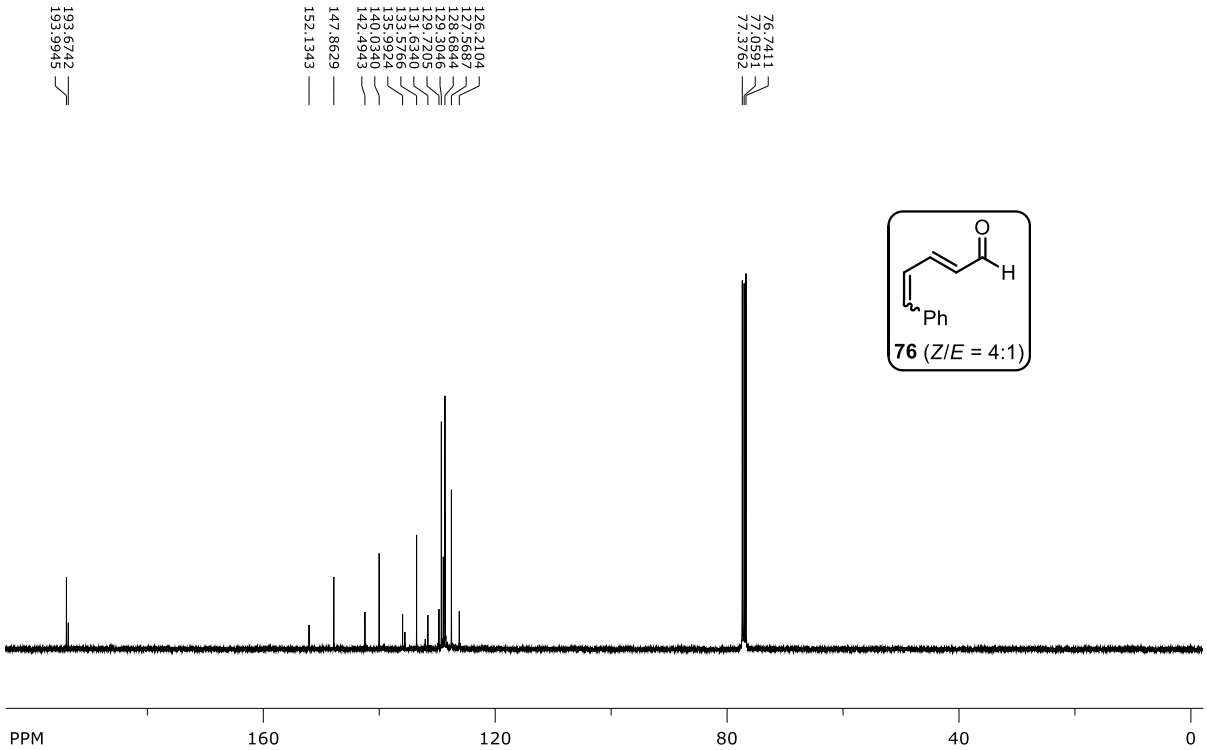


Figure 23: ^{13}C-NMR spectrum of **76**

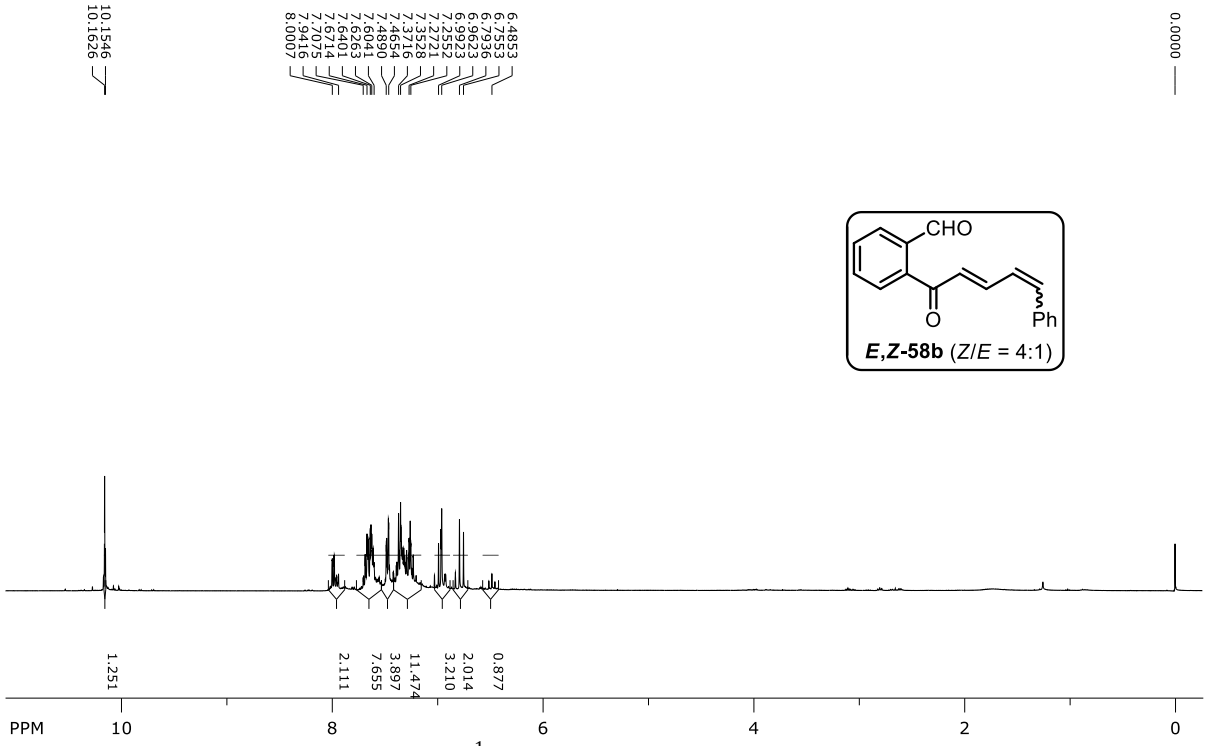
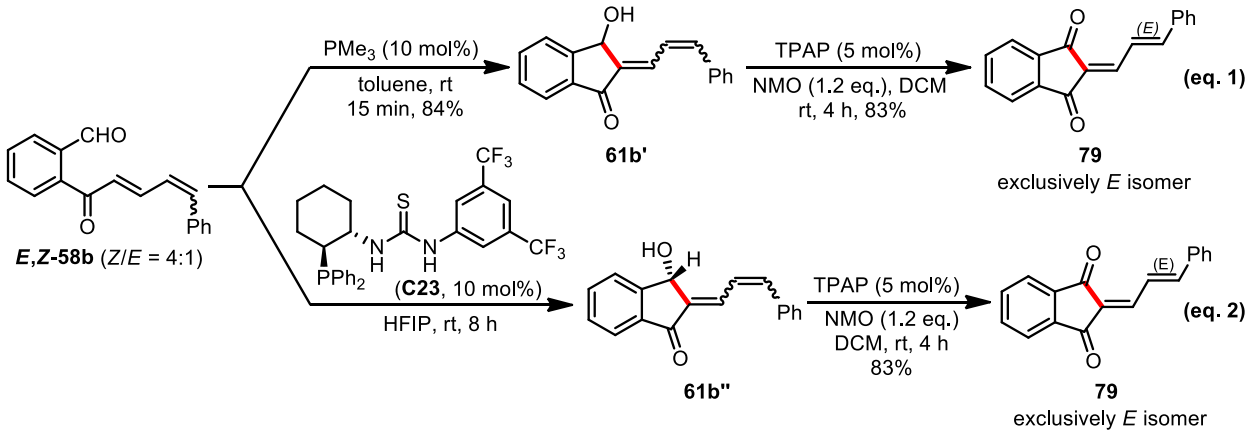


Figure 24: ^{1}H-NMR spectrum of ***E*,*Z*-58b**

The IMBH reaction was performed on dienone ***E*,*Z*-58b** under the optimized condition to obtain the indanone **61b'** (eq. 1, Scheme 63). At this stage, we could not realize the stereochemical information across the double bond. Thus, **61b'** was oxidized using tetrapropyl-ammonium perruthenate (TPAP) to indanedione **79**. A careful analysis of the ^{1}H-NMR spectrum of **79** revealed the presence of *E*-configured double bond across the diene. The IMBH reaction also was performed in the presence of phosphine **C23** (eq. 2, Scheme 63), and the ^{1}H-NMR of indandione **79** indicated the exclusive formation of the *E*-isomer.[90]



Scheme 63: IMBH reaction of dienone-aldehyde ***E*,*Z*-58b**

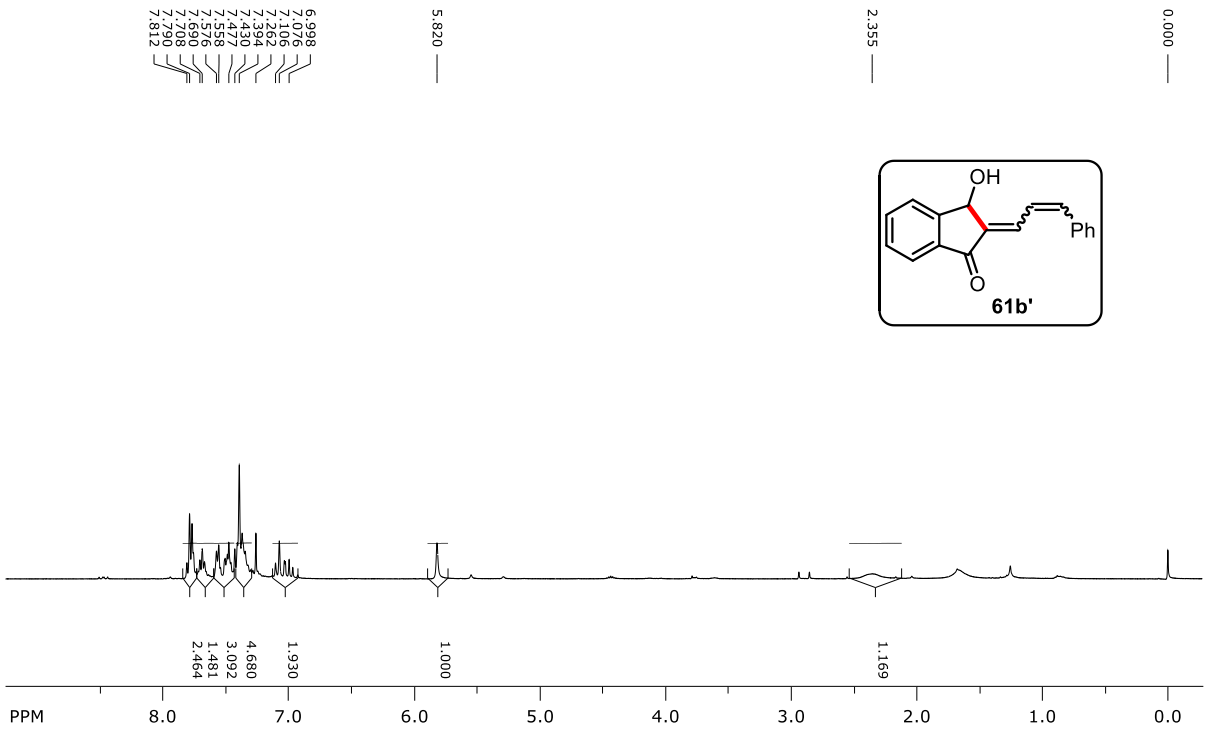


Figure 25: ^{1}H-NMR spectrum of **61b'**

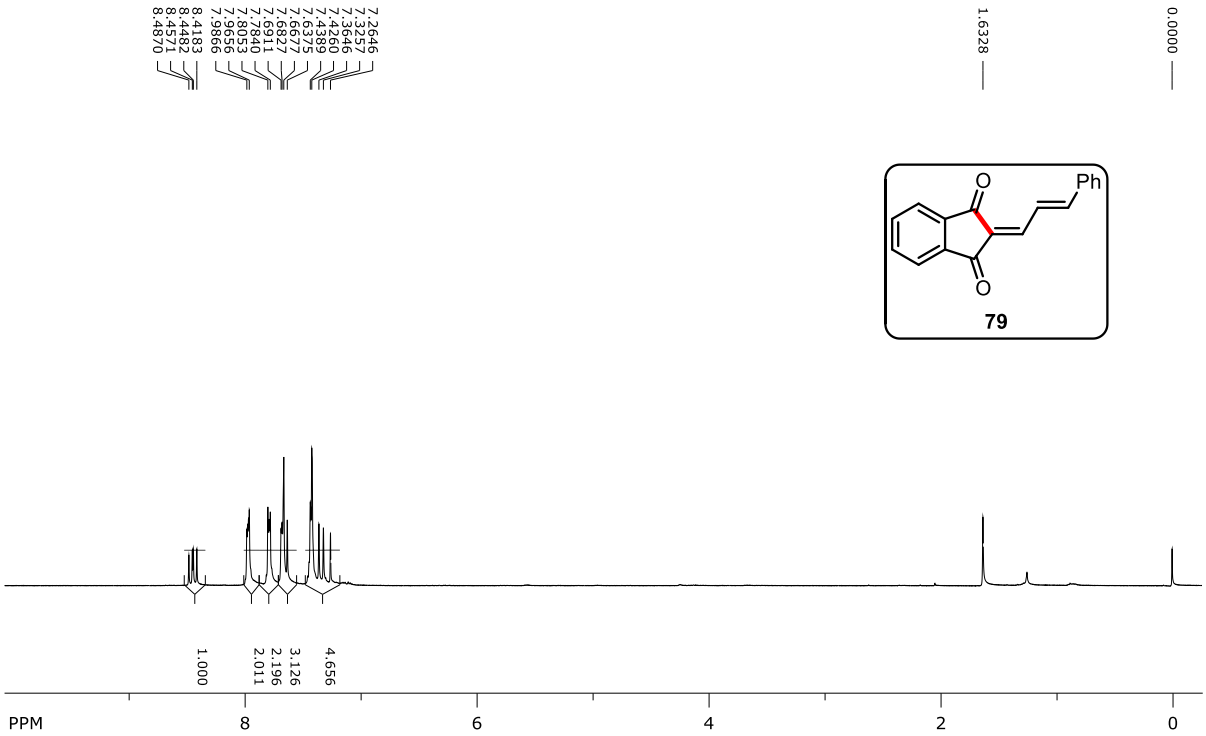


Figure 26: ^{1}H-NMR spectrum of **79 (Scheme 63, eq. 1)**

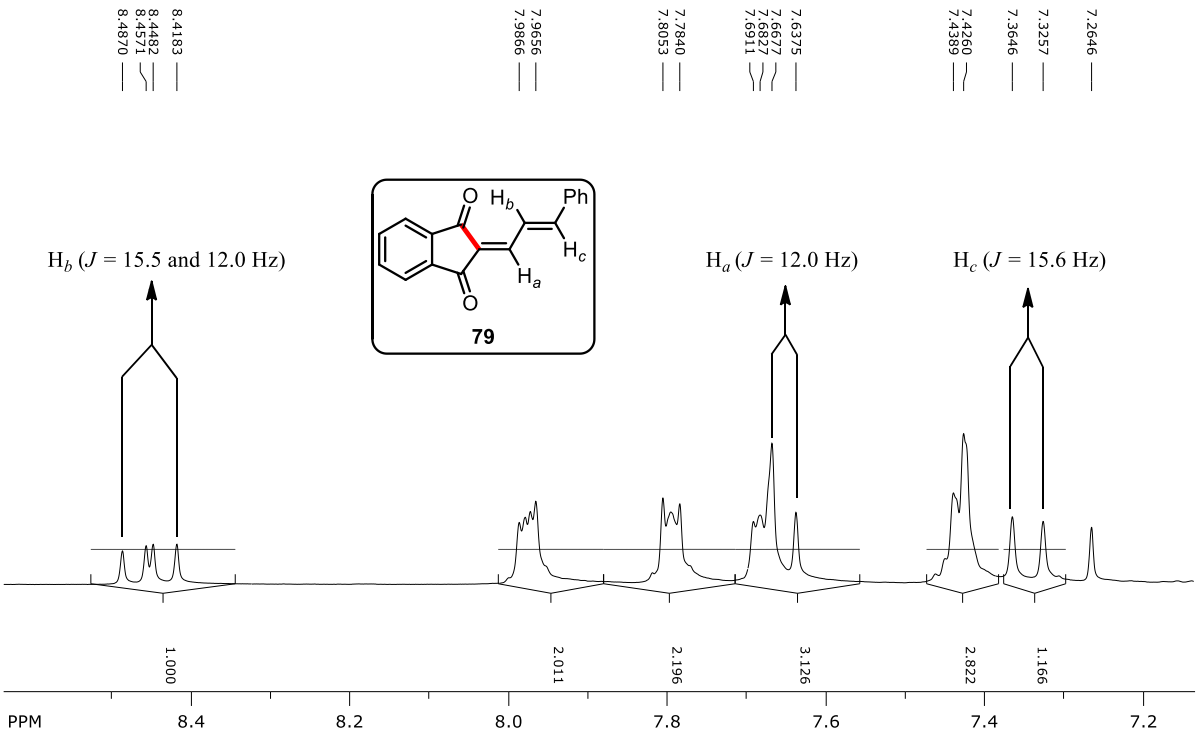


Figure 27: Expanded ^{1}H-NMR spectrum of **79 (Scheme 63, eq. 1)**

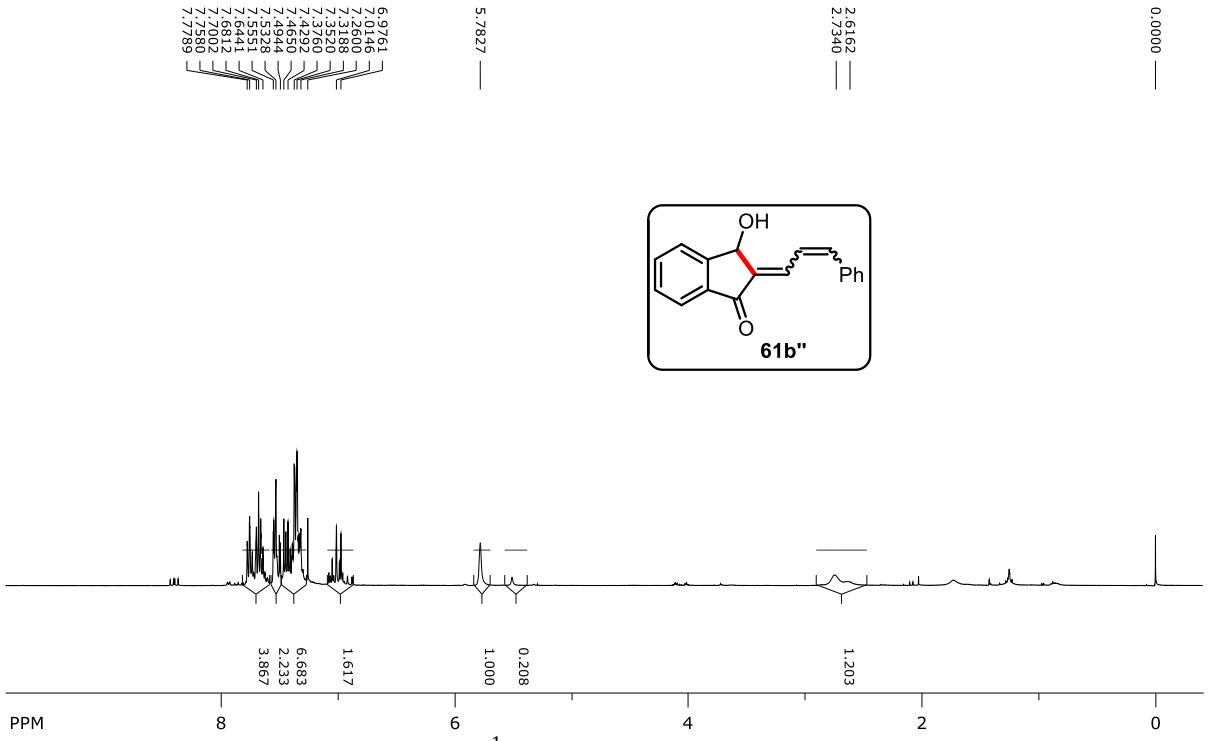


Figure 28: ^{1}H-NMR spectrum of **61b''**

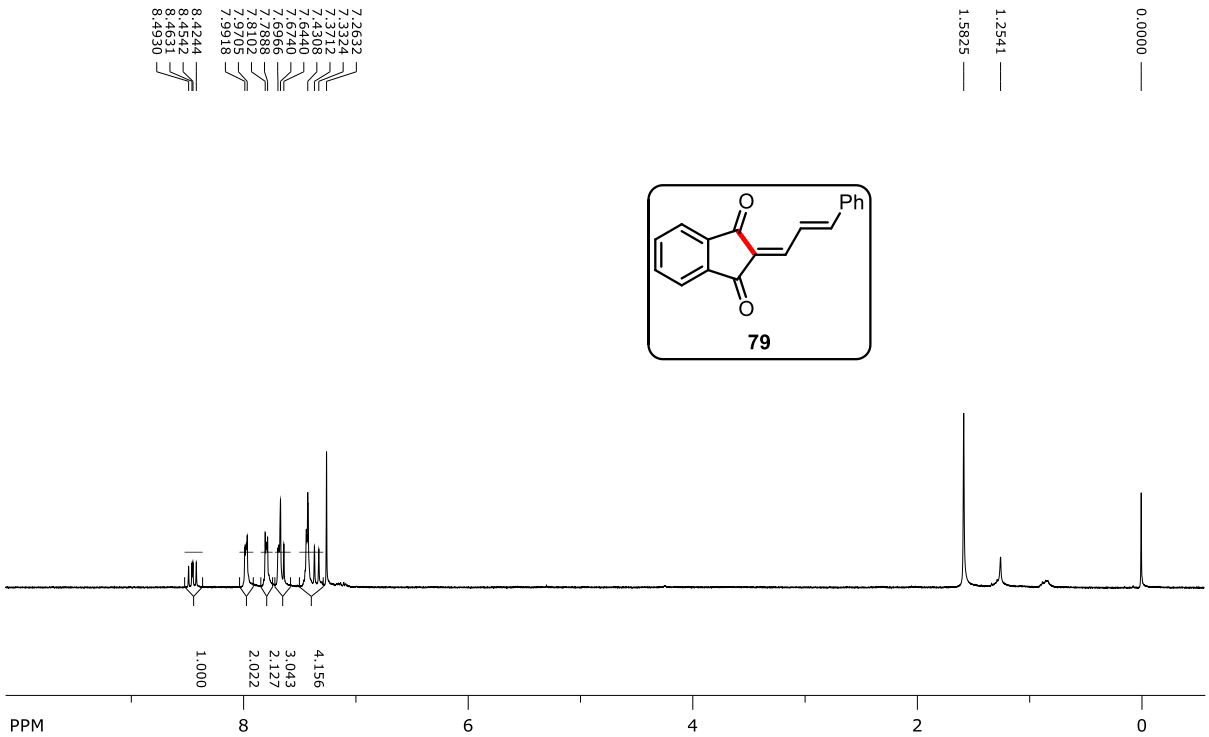


Figure 29: ^{1}H-NMR spectrum of **79 (Scheme 63**, **eq. 2)**

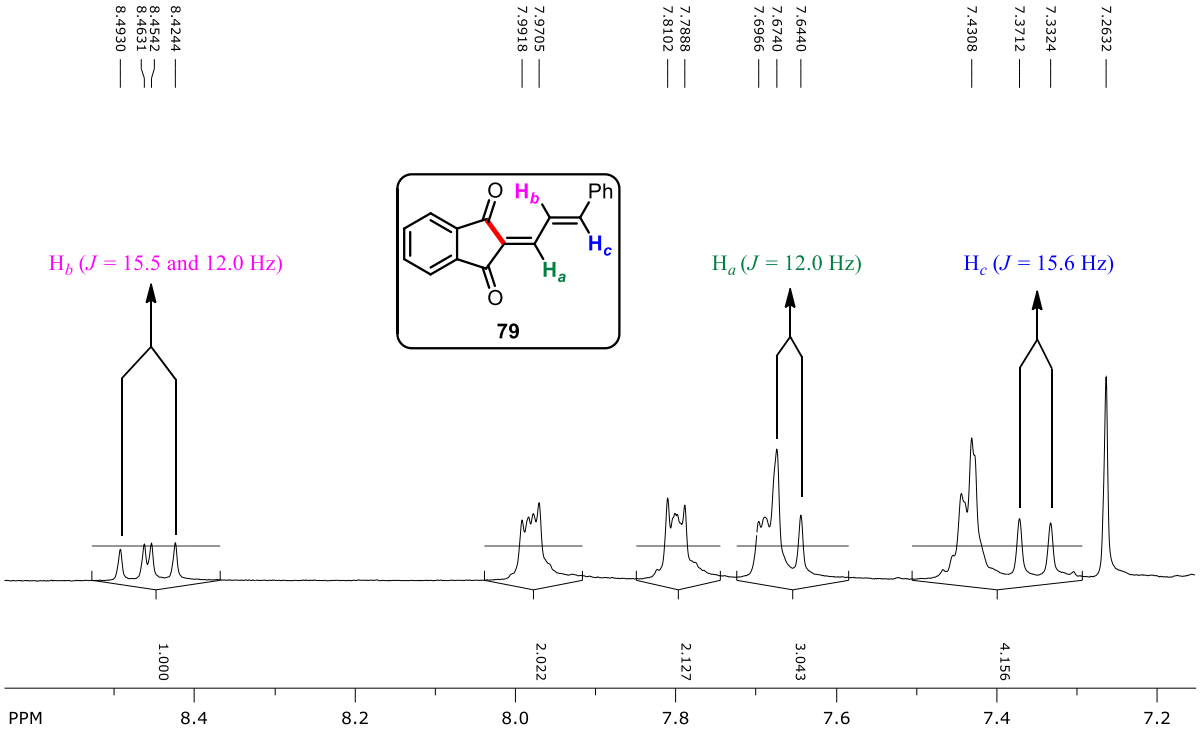
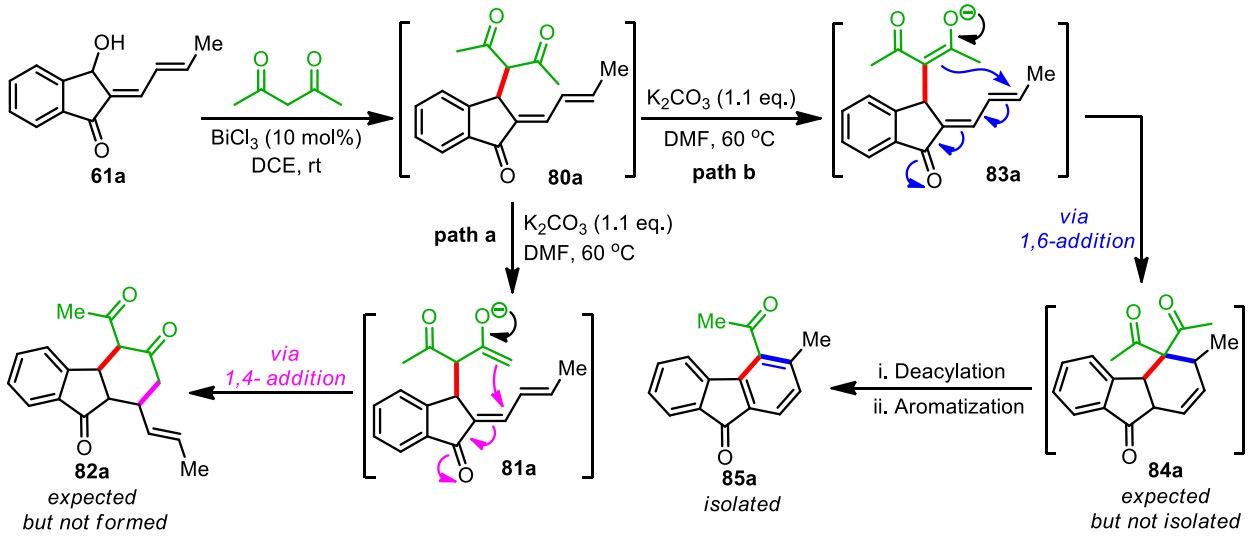


Figure 30: Expanded ^{1}H-NMR spectrum of **79 (Scheme 63**, **eq. 2)**

3.4: Elaboration towards the synthesis of substituted fluorenones

After successfully synthesizing an array of enantioenriched cyclopenta[*b*]annulated arenes and heteroarenes, we intended to illustrate the synthetic utility of the MBH adducts **61**. A synthetic elaboration was devised to exploit the doubly activated benzylic alcohol functionality and the dienone moiety present in **61a**, Scheme 64. Prompted by our earlier report,[91] it was anticipated that, the acid-mediated generation of the 1,3-dicarbonyl adduct **80a** could undergo a base-mediated cyclization reaction to furnish the hydrofluorenone **82a** (*via* path-a) and/or **84a** (*via* path-b) as depicted in the Scheme 64. Accordingly, indanone **58a** was subjected to a dehydrative nucleophilic substitution reaction in the presence of catalytic bismuth(III)chloride to achieve the acetylacetone adduct **80a**. For the further cyclization of **80a**, a variety of inorganic bases ($NaCO_3$, $NaHCO_3$, and K_2CO_3) were evaluated in DMF. Interestingly, the formation of an unexpected product 3-methyl-4-acetyl fluorenone **85a** was realized in a potassium carbonate-mediated reaction at an elevated temperature. It was assumed that the initially formed hydrofluorenone **84a** *via* path-b underwent base mediated deacylation and aromatization sequence to afford the fluorenone **85a**. To further make it interesting, the isolation of the

intermediate **80a** was avoided by optimizing the reaction in a way that the conversion of indanone **61a** to **85a** could be performed in a one-pot telescopic manner.



Scheme 64: Serendipitous formation of 4-acetyl-3-methyl fluorenone **85a**

The structure of the 4-acetyl-3-methyl fluorenone **85a** was deduced by careful analysis of IR, NMR, and HRMS data. The presence of two carbonyls at 1714 cm^{-1} and 1695 cm^{-1} in the IR absorption spectrum indicated the formation of **85a**. In the ^{1}H-NMR spectrum (see Fig. 31) the presence of two singlet at δ 2.67 ppm and δ 2.35 ppm due to acetyl methyl and aromatic methyl respectively, and in ^{13}C-NMR spectrum (see Fig. 32), the presence of a quaternary carbon at δ 206.7 ppm due to unsaturated acetyl carbonyl (C-2), a signal at δ 192.5 ppm due to fluorenone carbonyl (C-1), and presence of two methyl carbons at δ 32.3 ppm and δ 19.3 ppm due to acetyl methyl and aromatic methyl group respectively established the structure of the fluorenone **85a**. The presence of a deprotonated molecular ion peak at *m/z* 235.0750 $(M-H)^{+}$ in the HRMS spectrum further confirmed the product formation.

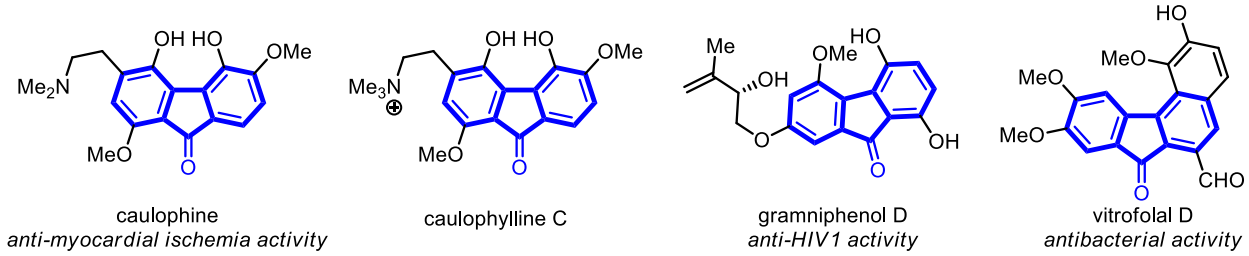


Figure 33: Representative natural products possessing the fluoren-9-one framework

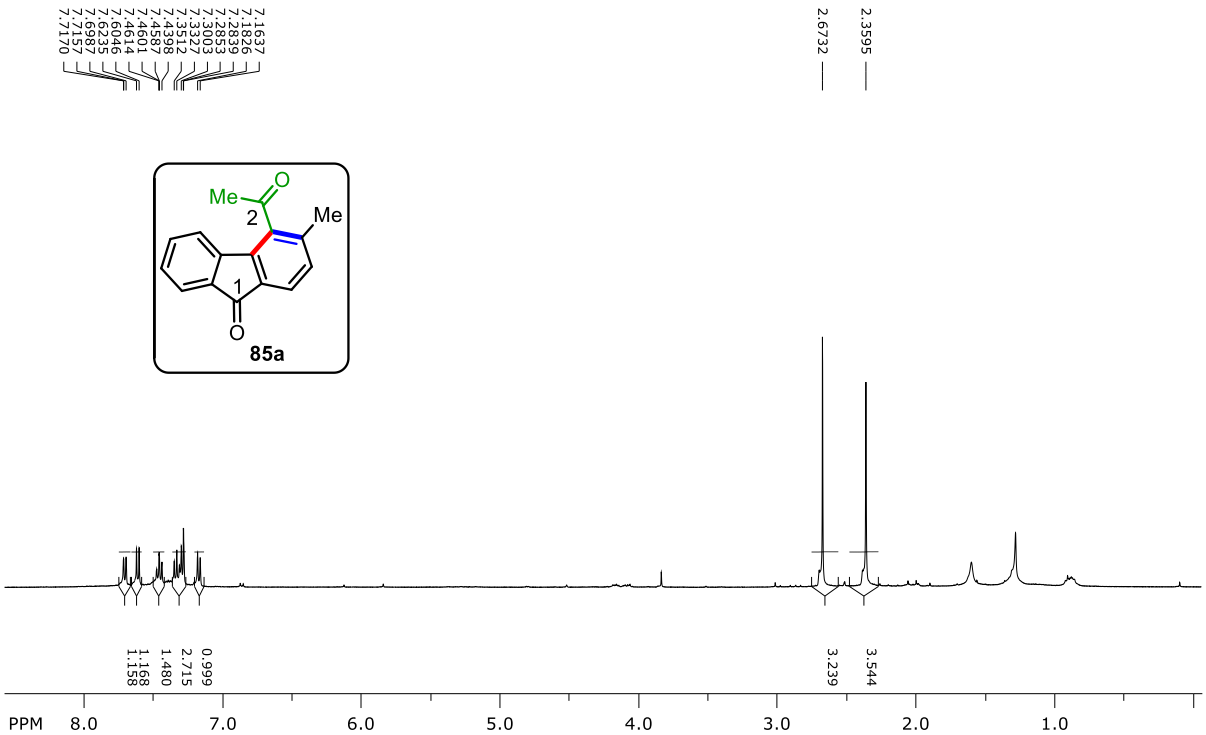


Figure 31: ^{1}H-NMR spectrum of the fluorenone **85a**

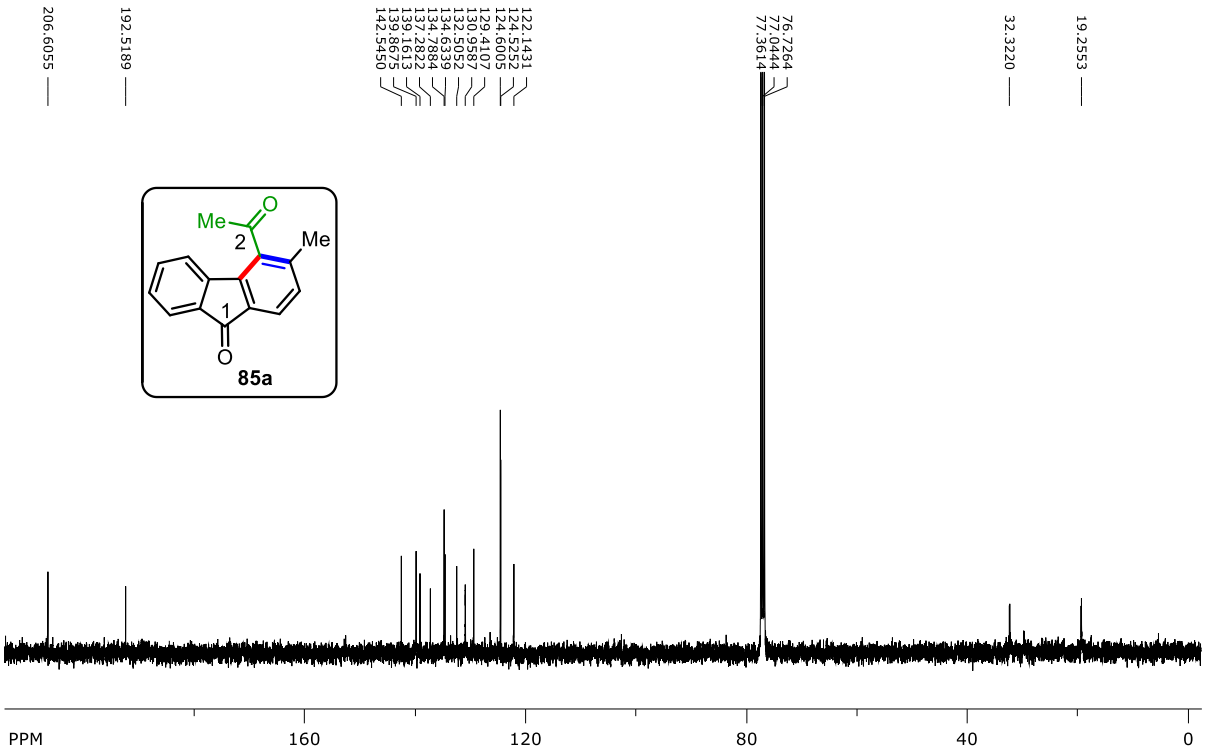
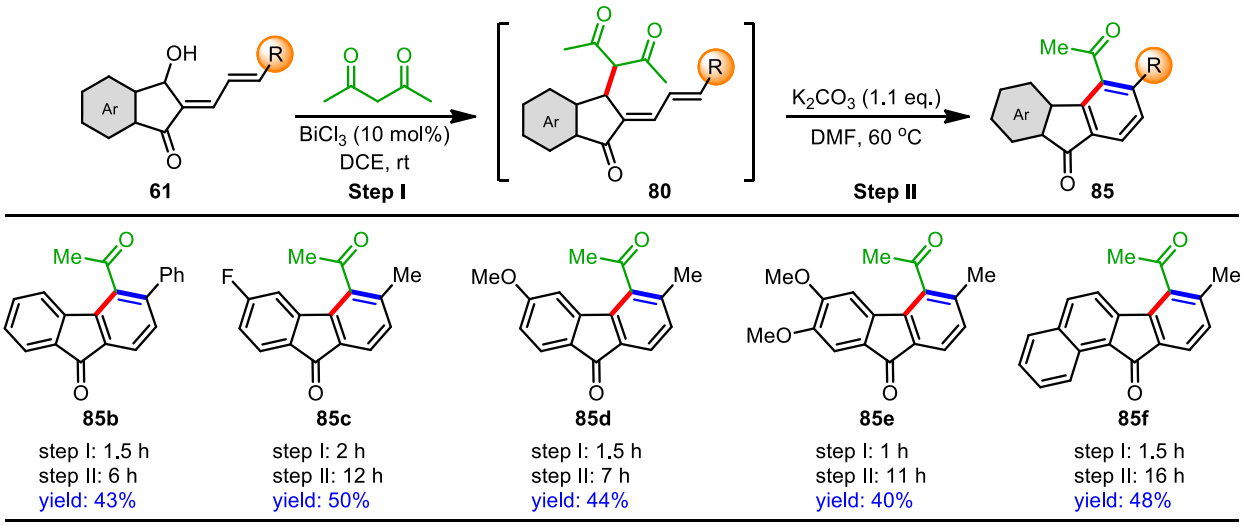


Figure 32: ^{13}C-NMR spectrum of the fluorenone **85a**

The fluoren-9-one derivatives are often encountered as privileged substructures in a diverse range of natural products exhibiting biological and pharmaceutical activities, Fig. 33. To name a few, caulophine a fluorenone alkaloid isolated from the radix of *Caulophyllum robustum* Maxim shows anti-myocardial ischemia activity. Similarly, gramniphenol analogs isolated from the whole plant extract of *Arundina gramnifolia* displayed promising anti-HIV1 activity. Vitrofolal D natural product possessing a benzo fluorenone skeleton also showed antibacterial activity against methicillin-resistant *Staphylococcus aureus* isolated from the subterranean part of *Vitex rotundifolia*.[92] Furthermore, functionalized fluorenones have found wide application, especially in organic semiconducting materials, optics and photoelectronics, owing to their unique liquid crystalline, blue photo- and electroluminescence properties.[93]

Table 14: Telescopic synthesis of 3,4-disubstituted-9-fluorenones



Yields were calculated over two steps after silica gel column chromatography.

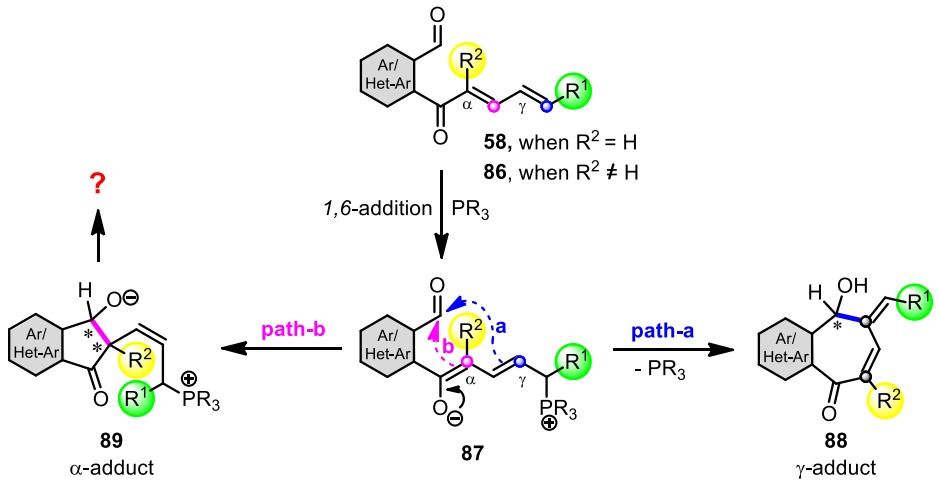
To validate the generality of this unprecedented observation few other electronically diverse IMBH adducts **61b, 61e-61f** and **61h-61i** were subjected to the optimized condition, Table 14. The one–pot telescopic process was realized to be general, effective and a wide range of 3-substituted-4-acetyl fluorenones **85b-85f** were assembled albeit in moderate yields. However, our attempts with other 1,3-dicarbonyls were unsuccessful. This two-step telescopic strategy represents a unique way to access 3-substituted-4-acetyl fluorenones.

In Conclusion, we have demonstrated the first enantioselective intramolecular Morita-Baylis-Hillman reaction of substituted dienones. Highly enantioenriched cyclopenta-fused arenes and heteroarenes were assembled in excellent yields and stereoselectivities. An efficient one-pot telescopic method to convert the IMBH adducts to substituted fluorenones was established.

Section 4

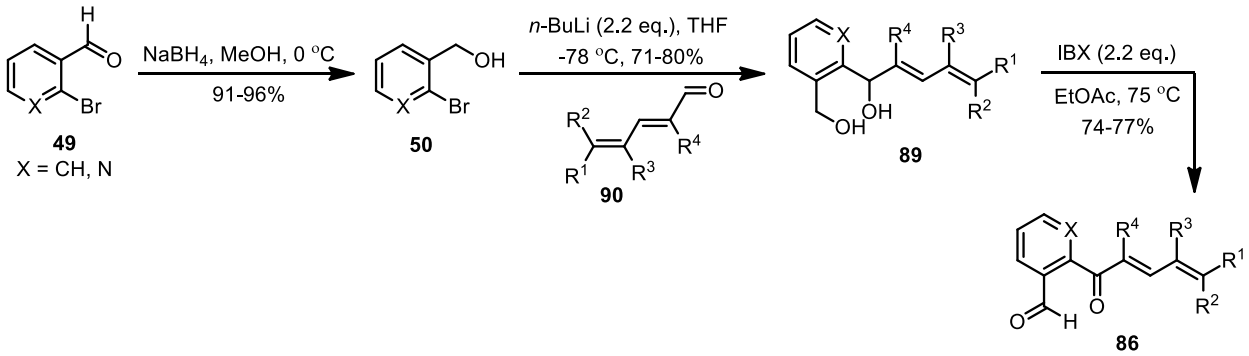
Metal- and Hydride-Free Pentannulative Reductive Aldol Reaction

After accomplishing a mild and highly efficient asymmetric protocol for the synthesis of a diverse range of cyclopentannulated arenes and heteroarenes (as described in section 3), we have conceived that sheer incorporation of α-substitution in **58** would lead to a completely different reactive substrate **86**, as depicted in Scheme 65. It was envisioned that the phosphine could activate the substrate **86** *via* 1,6-addition to furnish the dienolate species **87**, which can undergo intramolecular aldol reaction *via* path-a (γ-addition) leading to fused cycloheptenoids **88** by phosphine elimination.[94] Alternatively, an intramolecular aldol reaction of the dienolate **87** *via* path-b (α-adduct) would lead to a zwitterion **89**, though the subsequent fate is not realized at this time.



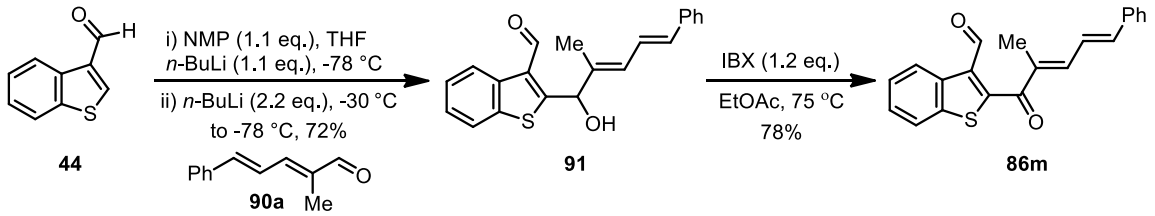
Scheme 65: Our hypothesis towards the synthesis of cycloheptannulated arenes and heteroarenes

In order validate the hypothesis presented in Scheme 65, a model substrate **86** was considered. The α-substituted dienone-aldehyde **86** can be accessed easily in three steps starting from commercially available 2-bromo aldehydes **49**, Scheme 66. The bromo aldehydes were converted to 2-bromo alcohol **50** *via* a straightforward sodium borohydride reduction. Direct *n*-butyllithium mediated alkylation of **50** with α-substituted dienal **90** generated the diol **89.** Subsequent IBX oxidation of **89** furnished the α-substituted dienone-aldehydes **86**.



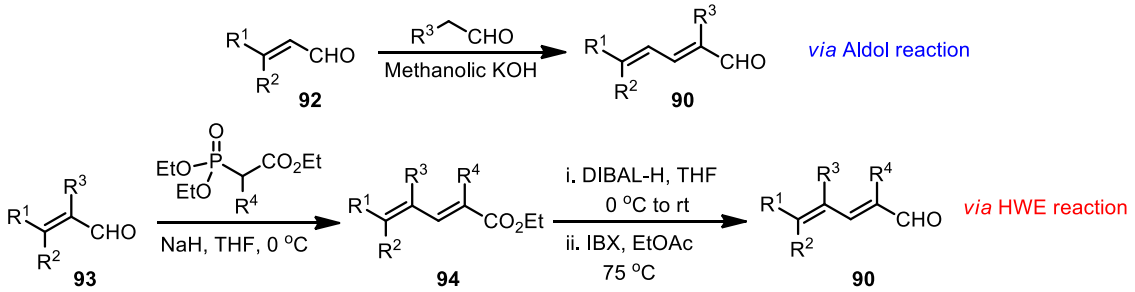
Scheme 66: Synthesis of α-substituted dienone-aldehydes **86**

Benzothiophene based substrate **86m** also can be accessed readily in a two-step protocol, Scheme 67. In situ masking of aldehyde functionality in benzothiophene-3-carboxaldehyde **44** and direct α-alkylation afforded the dienol **91**, which upon IBX oxidation generated the dienone-aldehyde **86m**.



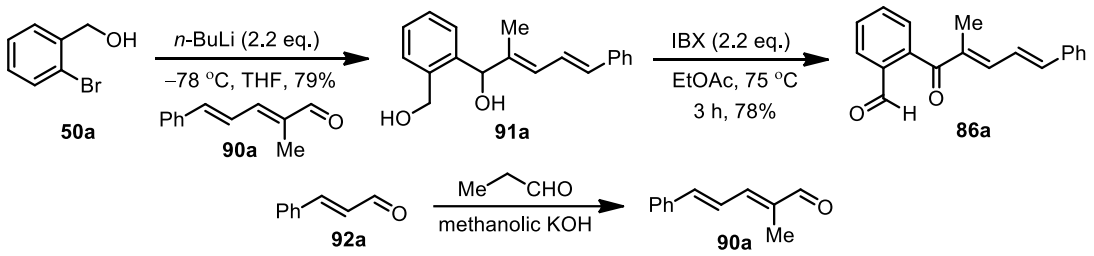
Scheme 67: Synthesis of benzothiophene based α-substituted dienone-aldehyde **86m**

α-Substituted dienals **90** employed in this study can be synthesized from enals **92** by employing classical aldol reaction or from **93** *via* Horner-Wadsworth-Emmons (HWE) reaction, DIBAL-H reduction, and oxidation sequence, Scheme 68.[95]



Scheme 68: Synthesis of α-substituted dienals **90**

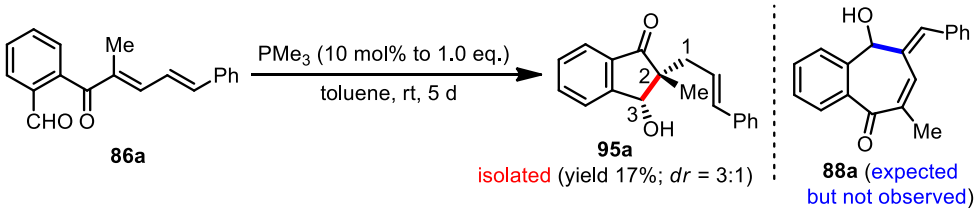
We initiated our study to validate the mechanistic hypothesis proposed in Scheme 65, towards the synthesis of fused-cycloheptenes **88**. The α-methyl dienone-aldehyde **86a** was synthesized by following the procedure shown in Scheme 69. Dienal **90a** was prepared from the commercially available *trans*-cinnamaldehyde **92a** by following the synthetic strategy described in Scheme 68.



Scheme 69: Synthesis of α-substituted dienal-aldehyde **86a**

Our earlier success with trimethylphosphine catalyzed cyclopentannulation of dienone-aldehydes (section 3) inspired us to apply the prototypical condition during the initial evaluation.

However, the substrate **86a** failed to generate any product with catalytic trimethylphosphine in toluene at room temperature. The use of stoichiometric phosphine with a prolonged reaction time furnished a polar compound albeit in low yield, Scheme 70. To our surprise, a careful analysis of the spectral data revealed the exclusive formation of reductive aldol product (α-adduct) **95a** in a 3:1 diastereomeric ratio, without a trace of expected fused-cycloheptenes (γ-adduct) **88a**, Scheme 70.[96] In the ^{1}H-NMR spectrum (see Fig. 34), the presence of a multiplet at δ 2.75-2.54 ppm due to allylic protons (C-1 protons), a singlet at δ 5.01 ppm due to the benzylic proton (C-3 proton), a doublet at δ 6.44 ppm (J = 15.9 Hz), a triplet of doublet at δ 6.09 ppm (J_{major} = 15.9 Hz) due to the presence of a *trans*-olefin, and in ^{13}C-NMR spectrum (see Fig. 35), the presence of a downfielded benzylic carbon (C-3) at δ 78.5 ppm, an all-carbon quaternary (C-2) at δ 54.8 ppm, a methylene carbon (C-1) at δ 37.8 ppm asserted the formation of fused-cyclopentane **95a**. In the IR spectrum, a broad absorption band at 3427 cm^{-1} due to the secondary alcohol and a strong band at 1705 cm^{-1}due to the presence of carbonyl further supported the product formation. In the high-resolution mass spectrum, the presence of protonated molecular ion peak at *m*/*z* 279.1394 $(M+H)^{+}$ corroborated the structure of **95a**.



Scheme 70: Reaction of α-substituted dienone-aldehyde **86a**

The aldol reaction is one of the most useful synthetic transformations leading to β-hydroxy carbonyl compounds in presence catalytic amount of base or acid. This reaction has been utilized widely for the synthesis of complex molecules due to its atom economical nature.[97] But, when nonsymmetrical carbonyls are employed, the traditionally used base or acid lead to multiple products *via* the formation of non-regiospecific enolates. These undesired side reactions can be prevented by preforming the enolate prior to the aldol reaction. For example, Mukaiyama described an aldol reaction of preformed silyl enol ether with a carbonyl compound in the presence of Lewis acid.[98]

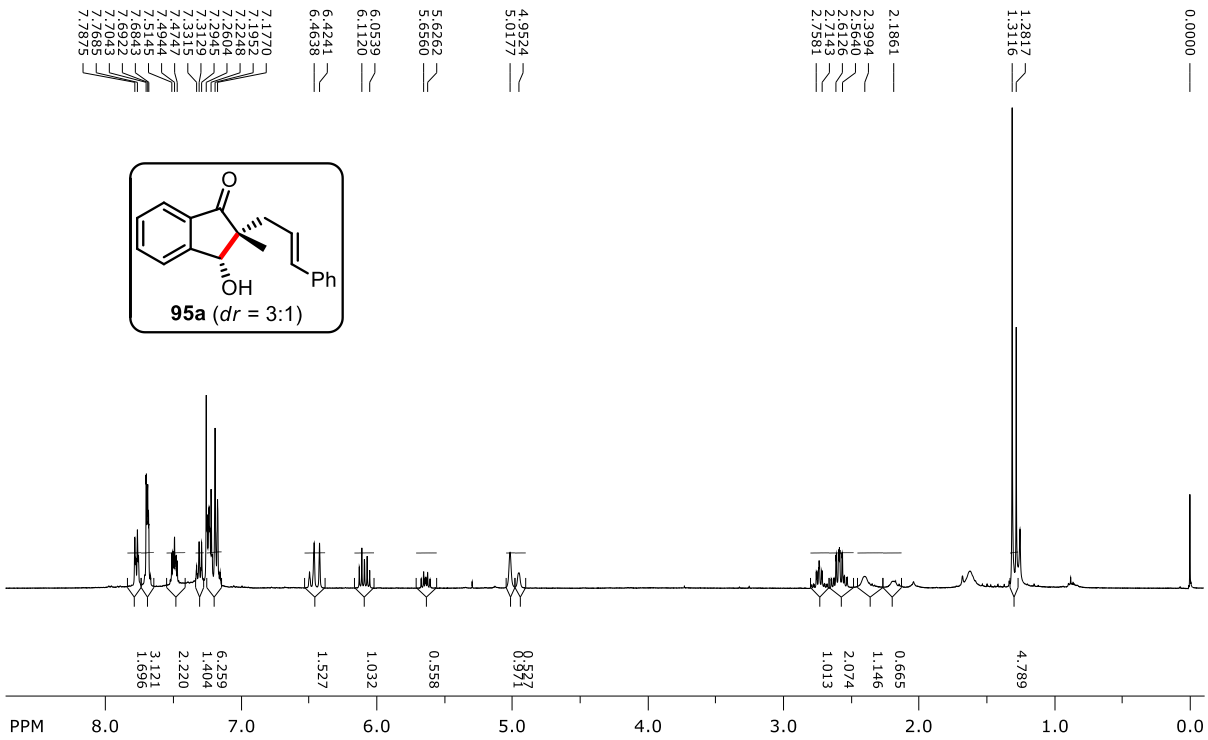


Figure 34: ^{1}H-NMR spectrum of **95a**

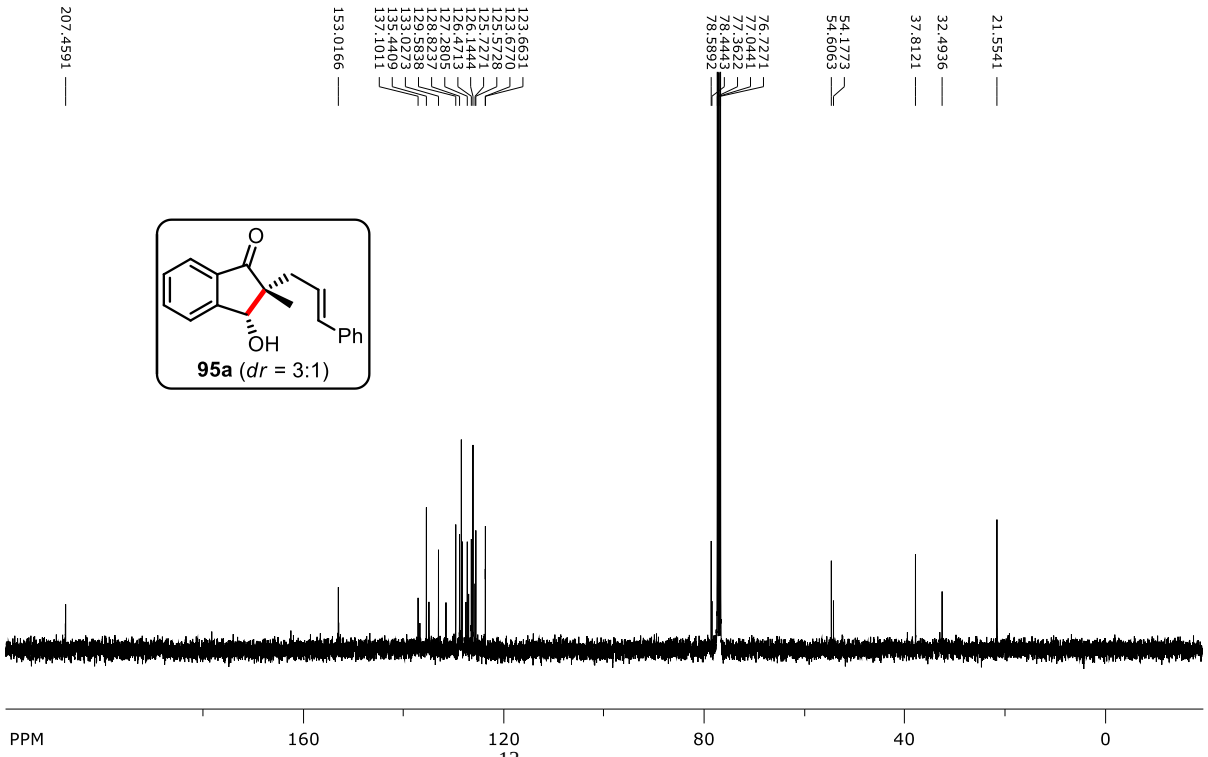
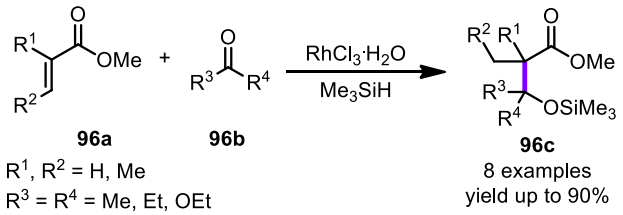


Figure 35: ^{13}C-NMR spectrum of **95a**

On the other hand, the reductive aldol reaction (RAR) typically involves a metal catalyzed coupling of an aldehyde with *in situ* formed regioselective enolate in the presence of a hydride source from a α,β-unsaturated carbonyl compound. This reaction is advantageous as the presynthesis of the enolate species is not necessary.[99]

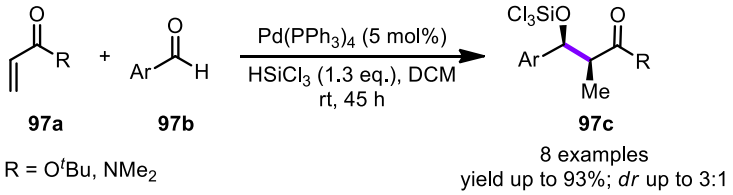
The pioneering concept of the regiospecific generation of enolates from α,β-unsaturated carbonyls *via* dissolving metal reductions and subsequent reaction was introduced by Stork in 1961,[100] paved the way for further advancements in the area of reductive aldol reaction. Consequently, numerous impressive contributions are made by several researchers by manifesting the above concept.

For example, among the metal catalyzed RARs, a seminal contribution was reported by Revis in 1987.[101] Revis *et al*. disclosed a Rhodium-catalyzed intermolecular reductive aldol reaction of acrylate **96a** in the presence of trimethylsilane, Scheme 71. This mild and efficient protocol furnished a wide variety of β-siloxy esters **96c** in excellent yields.



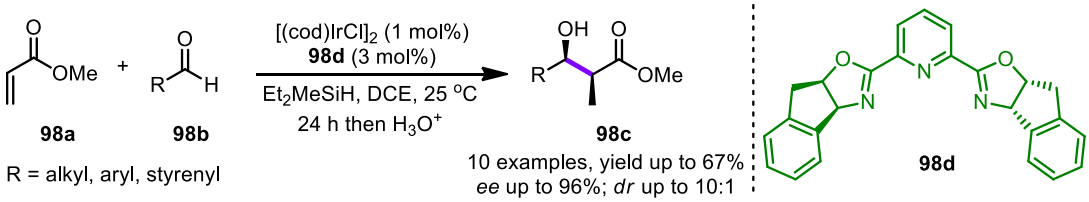
Scheme 71: Revis' Rhodium-catalyzed intermolecular RAR

In 1998, Kiyooka *et al*.[102] have documented a palladium catalyzed intermolecular hydrosilylation of unsaturated carbonyls, Scheme 72. The reaction of acrylamides/acrylates **97a** and aldehydes **97b** in the presence of tetrakis(triphenylphosphine)palladium(0) and trichlorosilane generated the β-siloxy carbonyls **97c** in excellent yields and moderate diastereoselectivities.



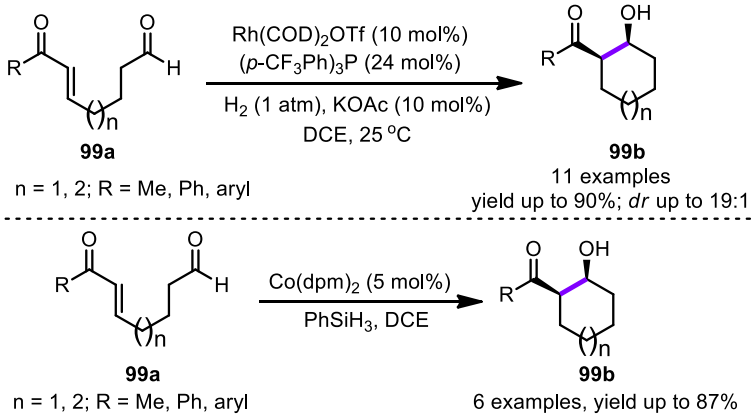
Scheme 72: Kiyooka's Palladium catalyzed intermolecular RAR

In 2001, Morken *et al.*[103] reported iridium catalyzed asymmetric intermolecular RAR of acrylates, Scheme 73. Highly diastereo- and enantioselective aldol products **98c** were obtained in good yields in the presence $[(cod)IrCl]_2$, indane-Pybox **98d** and silane.



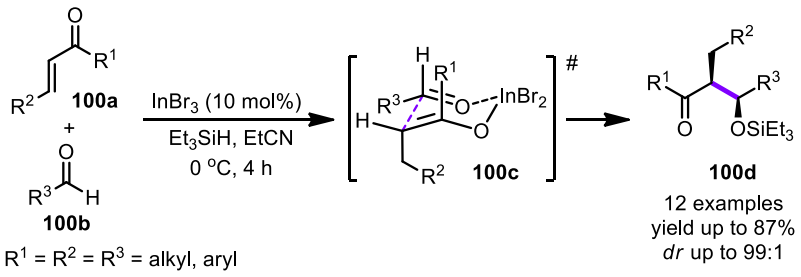
Scheme 73: Copper-catalyzed enantioselective intermolecular RAR

In 2002, Krische *et al.*[104] developed an intramolecular hydrogenative coupling reaction, Scheme 74. Under the rhodium catalysis, an intramolecularly tethered enone and aldehydes **99a** led to the formation of five and six-membered carbocycles **99b** in excellent diastereoselectivities. They have employed hydrogen gas as a reducing agent. In another parallel approach, Krische[105] has utilized a cobalt complex to perform a similar transformation in the presence of phenyl silane as a reductant, Scheme 74.



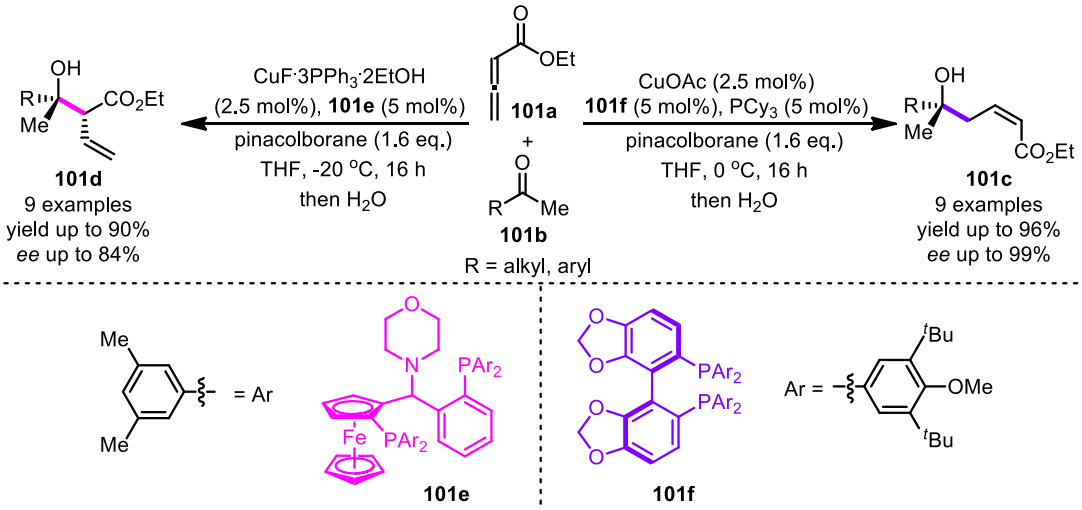
Scheme 74: Krische's intramolecular hydrogenative coupling

In 2004, Baba *et al.*[106] established a Lewis acid catalyzed RAR, Scheme 75. The *in situ* generated $HInBr_2$ from $InBr_2$ and triethylsilane undergoes reductive 1,4-addition with the enone **100a** to generate the indium enolate and subsequently reacts with the aldehydes **100b** *via* a Zimmerman-Traxler type six-membered chair transition state **100c** to afford the highly diastereoselective β-siloxy ketones **100d**.



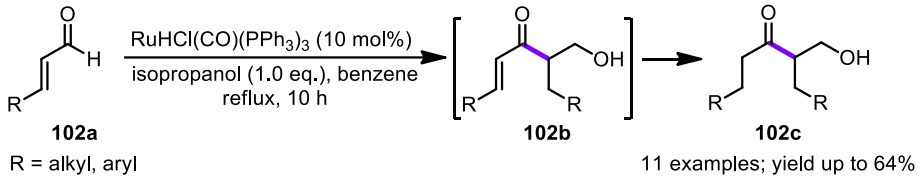
Scheme 75: Baba's Lewis acid mediated intermolecular RAR

In 2006, Kanai and Shibasaki[107] have utilized allenoates **101a** as a latent enolate and exploited in the Copper(I) catalyzed enantioselective reductive aldol reaction, Scheme 76. Pinacolborane was used as a reducing agent. The authors have demonstrated the switch of product selectivity depending on the use of chiral phosphine ligand and copper salt. The DTBM-SEGPHOS **101f** in the presence of CuOAc furnished the γ-addition adducts **101c.** Whereas, the CuF and Taniaphos **101e** exclusively led to the formation of α-adducts **101d** in excellent enantiopurities.



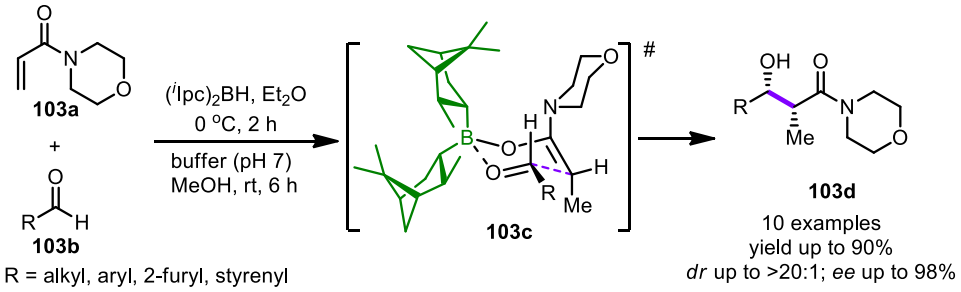
Scheme 76: Enantioselective RAR of allenoates

In 2006, Ryu *et al.*[108] have shown Ruthenium catalyzed reductive dimerization of α,β-unsaturated aldehydes, Scheme 77. The $RuHCl(CO)(PPh_3)_3$ mediated formation of reductive aldol product **102b** further undergoes transfer hydrogenation in the presence of isopropanol to give the α-hydroxymethyl ketones **102c** in moderate yields.



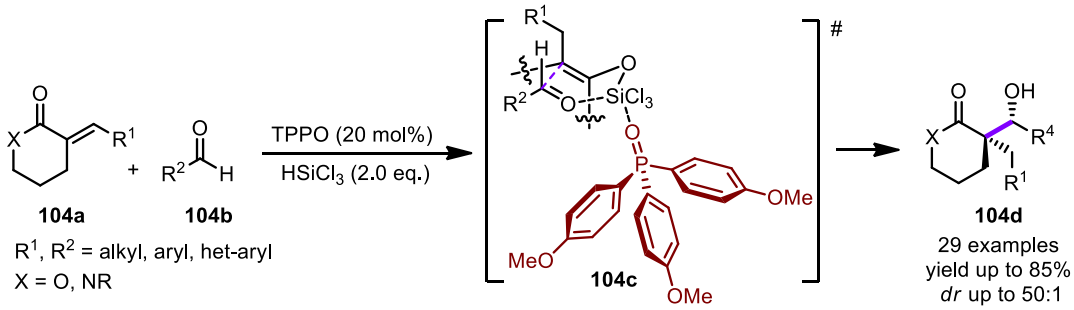
Scheme 77: Ryu's reductive dimerization

In 2013, Roush *et al.*[109] described a highly diastereo- and enantioselective reductive *syn*-aldol reaction by employing diisopinocampheylborane, Scheme 78. The generation of stereospecific (*Z*)-boron enolate through the hydroboration of 4-acryloylmorpholine **103a** and subsequent reaction with the aldehyde **103b** is believed to be proceeding *via* a chair like transition state **103c**. Wide varieties of *syn*-α-methyl-β-hydroxymorpholine amides **103d** were accessed in high enantiopurities.



Scheme 78: Roush's enantioselective reductive *syn*-aldol reaction

In 2018, Schindler *et al.*[110] demonstrated a Lewis base promoted the construction of β-hydroxy lactones and lactams, Scheme 79. The tris(*p*-methoxyphenyl)phosphine oxide (TPPO) with trichlorosilane as reductant resulted in the formation of aldol product through a boat like transition state **104c**. This method provides access to highly diastereoselective lactones and lactams **104d** possessing an all-carbon quaternary center.



Scheme 79: Lewis base mediated intermolecular RAR

As showcased above, the literature survey unfolded a few important aspects of reductive aldol reaction: (i) the reaction required stoichiometric amount of reducing agent (hydrogen gas, silane, borane or metal hydride), (ii) most of the protocols rely on the use of transition metal catalysts (Pd, Rh, Ru, In, Co, Cu, Ir), (iii) no other Michael acceptors are known other than enone, (iv) enones possessing α- or α,β- substitutions (Fig. 36) are less explored.

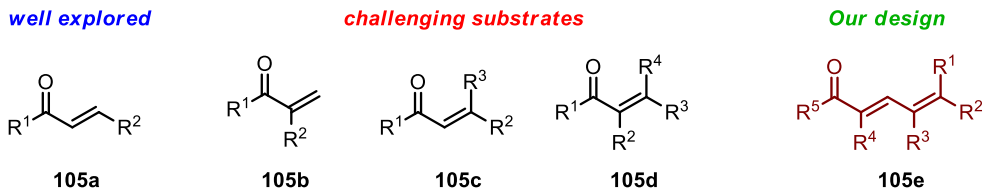
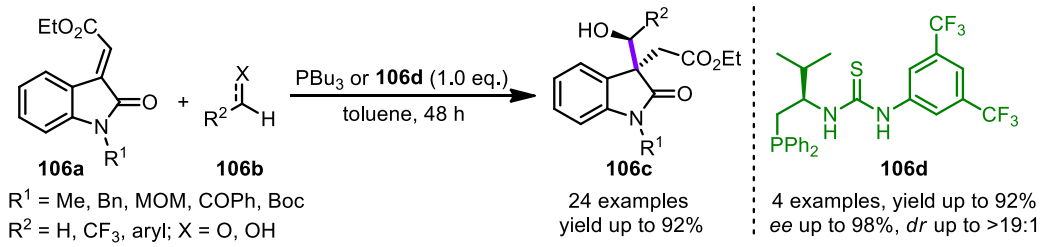


Figure 36: Substrate designs for the intermolecular reductive aldol reaction

Recently, Ouyang and Chen[111] disclosed an organophosphine mediated interrupted Morita-Baylis-Hillman type reaction, Scheme 80. In the presence of stoichiometric tributylphosphine, oxindole **106a** undergoes a formal reductive aldol reaction with various electrophiles **106b** to afford **106c** bearing an all carbon quaternary center. The reaction involves an initial formation of zwitterionic enolate species, subsequent aldol reaction, and a dephosphoration process. Excellent enantioselectivities were achieved by employing the chiral bifunctional thiourea catalyst **106d** in stoichiometric amount. This reaction represents the first example of metal- and hydride free intermolecular reductive aldol reaction of enones.



Scheme 80: Chen's interrupted Morita-Baylis-Hillman reaction

Interestingly, our observation described in Scheme 70 represents an unprecedented metal- and hydride free organophosphine-mediated intramolecular reductive aldol reaction of α-substituted dienone-aldehydes.

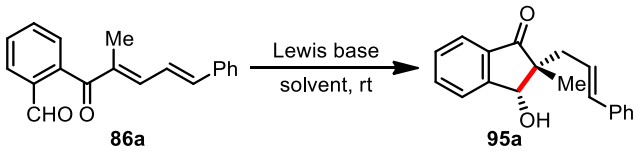
4.1: Results and Discussion

After the initial result with the trimethylphosphine, further efforts were made to find out the optimized condition as depicted in Table 15. The substantial increment of PMe_3 loading improved the yield but was not practically encouraging (Table 15, entry 1). An optimization with catalytic tributylphosphine was unsuccessful (Table 15, entry 2), whereas a sub-stoichiometric loading delivered the desired product **95a** in low yield (Table 15, entry 3). To our surprise, the water additive showed a dramatical effect to the reaction yield (Table 15, entries 4-6).[112] Our intentions to improve the yield and time succeeded while optimizing the quantity of water (Table 15, entries 6-8). The use of 30 equivalent of water found to be the optimal beyond which no further improvement was observed in the yield or reaction time (Table 15, entries 9 and 10). Further efforts with optimizing the quantity of phosphine in the presence of 30 equivalent of water revealed the use of 1.2 eq. PBu_3 is optimal (Table 15, entries 11-14). The brief solvents screening did not offer any promising result (Table 15, entries 15-17). Other *P*-centered or *N*-centered Lewis bases failed to produce even a trace of the desired product (Table 15, entries 18-21).

To expand the substrate scope of this method, the optimized condition was employed to a wide variety of α-substituted dienone-aldehydes **86b-86m** bearing different steric and electric features, Table 16. A diverse range of cyclopentannulated arenes and heteroarenes **95b-95m** could be assembled in good to excellent yields, and moderate to good diastereoselectivities possessing two contiguous stereogenic centers, one of them being an all-carbon quaternary center, Table 16.[113] Regarding the α-substitution (R^2) both alkyl **86b**, **86d-86m** and aryl groups **86c** were well tolerated under the reaction condition, Table 16. The presence of an electron-donating group (such as -OMe) either on an aryl **95j-95g** or at δ-position of the dienone moiety **95d** has no considerable impact on the reaction time and yield, Table 16. Contrary to our expectation, the presence of an electron withdrawing (such as -F) group on aryl moiety **86f** showed a significant drop of yield and afforded indanone **95f**, Table 16. Substrate bearing naphthalene backbone **86k** efficiently generated the reductive aldol product **95k** in excellent yield, Table 16. A dramatic influence on reaction efficiency was realized with the electron deficient pyridine substrate **86l** under the optimized condition and delivered the pyrindanone **95l** in excellent yield and diastereoselectivity. Pleasingly, the α-methyl dienone appended to the benzothiophene carboxaldehyde moiety **86m** also proceeded smoothly to afford the

cyclopent[*b*]annulated benzothiophene **95m**, Table 16. The method appears to be robust and general on a wide range of substrates.

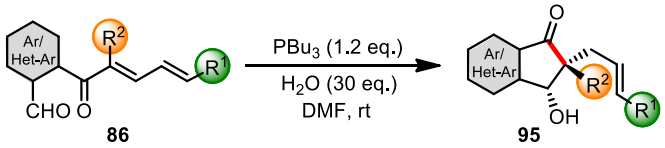
Table 15: Optimization of reaction parameters

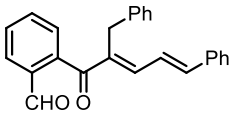
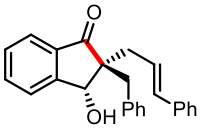
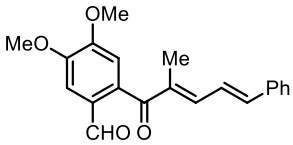
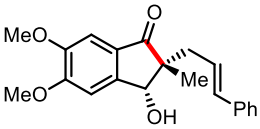
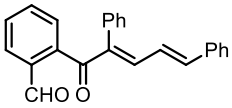
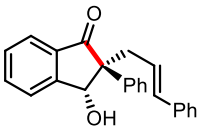
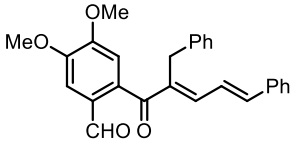
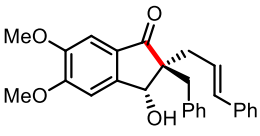
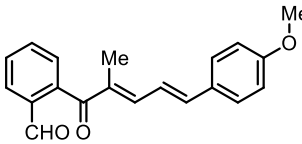
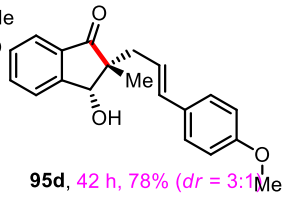
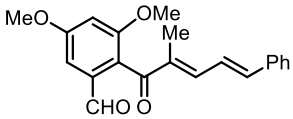
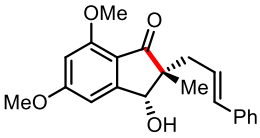
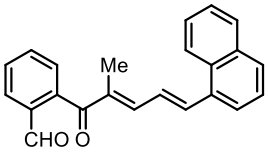
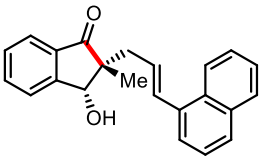
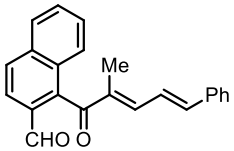
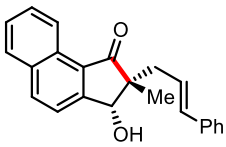
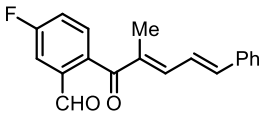
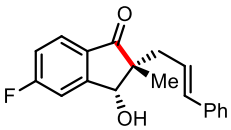
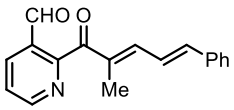
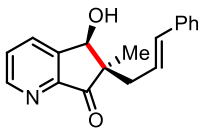
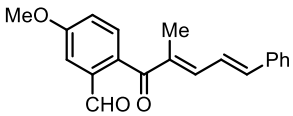
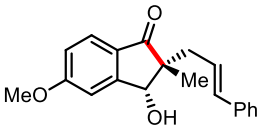
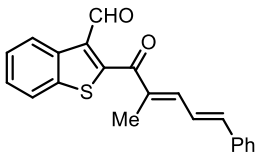
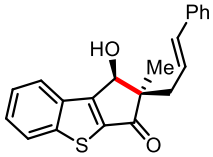


Entry	Lewis Base (eq.)	Water (eq.)	Solvent	Time (h)	Yield (%)[a]
1	PMe_3 (4.0)	-	toluene	120	51
2	PBu_3 (0.25)	-	toluene	96	trace
3	PBu_3 (0.5)	-	toluene	96	12
4	PBu_3 (1.0)	-	toluene	96	33
5	PBu_3 (1.0)	5	toluene	96	47
6	PBu_3 (1.0)	5	DMF	96	51
7	PBu_3 (1.0)	10	DMF	96	58
8	PBu_3 (1.0)	30	DMF	40	77
9	PBu_3 (1.0)	50	DMF	48	75
10	PBu_3 (1.0)	75	DMF	48	74
11	**PBu_3 (1.2)**	**30**	**DMF**	**34**	**87**
12	PBu_3 (0.25)	30	DMF	160	8
13	PBu_3 (0.5)	30	DMF	120	39
14	PBu_3 (0.75)	30	DMF	96	50
15	PBu_3 (1.2)	30	DMSO	96	21
16	PBu_3 (1.2)	30	CH_3CN	96	38
17	PBu_3 (1.2)	30	1,2-DCE	96	6
18	PPh_3 (1.2)	30	DMF	120	-
19	PCy_3 (1.2)	30	DMF	120	-
20	DABCO (1.2)	30	DMF	120	-
21	β-ICD	30	DMF	120	-

All reactions were performed on 0.1 mmol scales. [a] Yields were calculated after silica gel column chromatography.

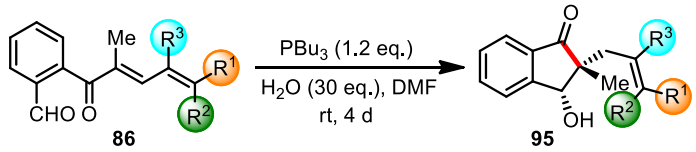
Table 16: Substrate Scope: Annulated cyclopentanoids *via* an intramolecular RAR

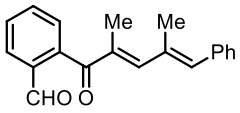
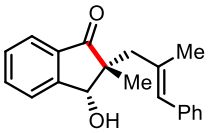
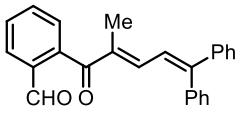
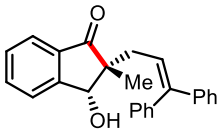


Entry	Substrate	Product	Entry	Substrate	Product
1	 **86b**	 **95b**, 40 h, 83% (*dr* = 3:1)	7	 **86h**	 **95h**, 36 h, 83% (*dr* = 2:1)
2	 **86c**	 **95c**, 40 h, 81% (*dr* = 5:3)	8	 **86i**	 **95i**, 40 h, 82% (*dr* = 3:1)
3	 **86d**	 **95d**, 42 h, 78% (*dr* = 3:1)	9	 **86j**	 **95j**, 43 h, 82% (*dr* = 2:1)
4	 **86e**	 **95e**, 36 h, 87% (*dr* = 4:1)	10	 **86k**	 **95k**, 26 h, 92% (*dr* = 3:1)
5	 **86f**	 **95f**, 40 h, 77% (*dr* = 5:1)	11	 **86l**	 **95l**, 18 h, 87% (*dr* = 10:1)
6	 **86g**	 **95g**, 34 h, 86% (*dr* = 2:1)	12	 **86m**	 **95m**, 34 h, 80% (*dr* = 3:2)

However, this method is not without limitations. While studying the role of substitutions across the diene in the reductive aldol process, the dienone having a γ-substitution **86n** and dienone with δ,δ-disubstitution **86o** failed to undergo reductive aldol reaction, Table 17.

Table 17: Substrates failed to deliver intramolecular reductive aldol product



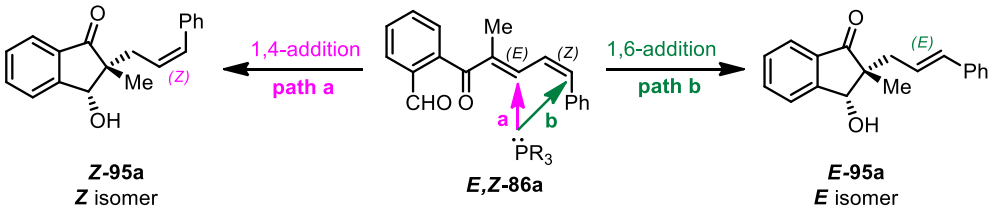
Entry	Substrate	Product
1	 **86n**	 **95n**, 0%
2	 **86o**	 **95o**, 0%

4.2: Mechanistic Insights

Based on the optimization result presented in Table 15, it can be perceived that the reaction is proceeding through a stoichiometric pathway with respect to phosphine. Few other aspects were considered to gain mechanistic insights, (i) 1,4- *vs* 1,6-phosphine addition (ii) the role of water, and (iii) the fate of the phosphine after the reaction. To address the above, we have performed a few control experiments as described below.

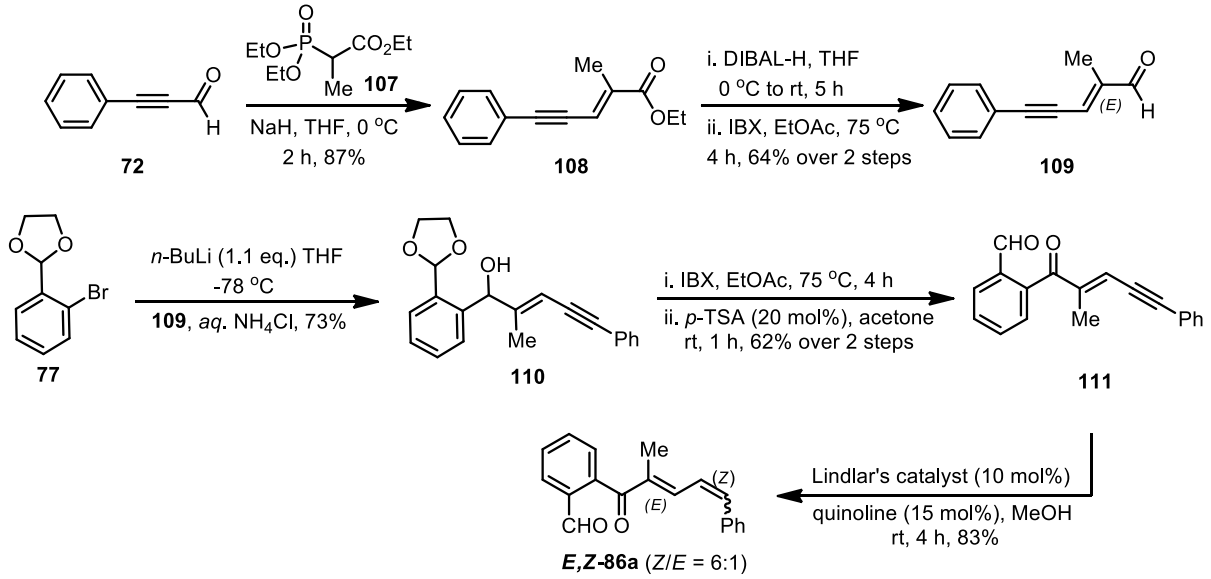
4.2.1: 1,4- vs. 1,6- phosphine addition

We have hypothesized a substrate design ***E,Z*-86a** in order to gain evidence for an initial phosphine addition (1,4- *vs.* 1,6), as shown in Scheme 81. Presumably, in the case of 1,4-phospha Michael, the configuration of the *Z*-alkene should remain unchanged and lead to the formation of ***Z*-95a** (path a). Whereas, in the case of the 1,6-addition, the *Z*-alkene across the diene should lead to the thermodynamically preferred ***E*-95a** (path-b).



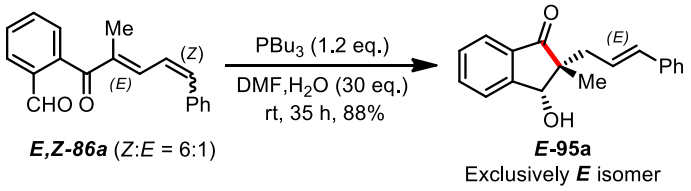
Scheme 81: Hypothesis for 1,4- *vs.* 1,6-phosphine addition

Accordingly, a synthetic route was proposed for ***E,Z*-86a**, as depicted in Scheme 82. The ynenal **109** was procured starting from commercially available phenylpropiolaldehyde **72** *via* a sequential Wittig-Horner-Emmons reaction using **107**, DIBAL-H reduction, and IBX oxidation. Further *n*-butyllithium mediated alkylation of 2-(2-bromophenyl)-1,3-dioxolane **77** with ynenal **109** delivered the alcohol **110**. Finally, alcohol **110** was converted to the desired dienone ***E,Z*-86a** (*Z/E* = 6:1) by following an IBX oxidation, acetal deprotection, and Lindlar's hydrogenation sequence (see Fig. 37-42).



Scheme 82: Synthesis of dienone-aldehyde ***E*,*Z*-86a**

The dienone-aldehyde ***E*,*Z*-86a** was subjected to the optimized condition, Scheme 83. The presence of a doublet at δ 6.25 ppm (J = 15.9 Hz) and a triplet of a doublet at 6.13 ppm (J_{major} = 15.9 Hz) in the ^{1}H-NMR spectrum of the isolated reductive aldol product ***E*-95a** revealed the exclusive formation of *E*-isomer (see Fig. 43 and Fig. 44). This result indicates that the initial phosphine addition occurs in a 1,6-conjugate manner.



Scheme 83: Reductive Aldol reaction of dienone-aldehyde ***E*,*Z*-86a**

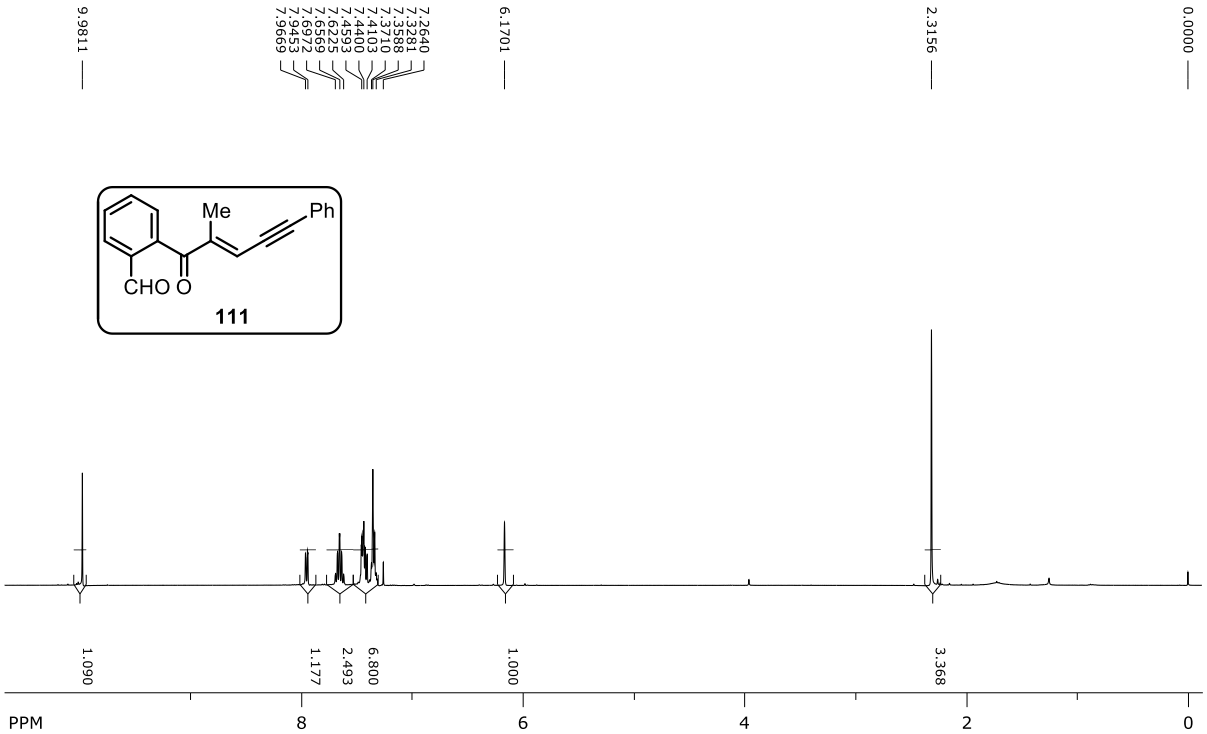


Figure 37: ^{1}H-NMR spectrum of **111**

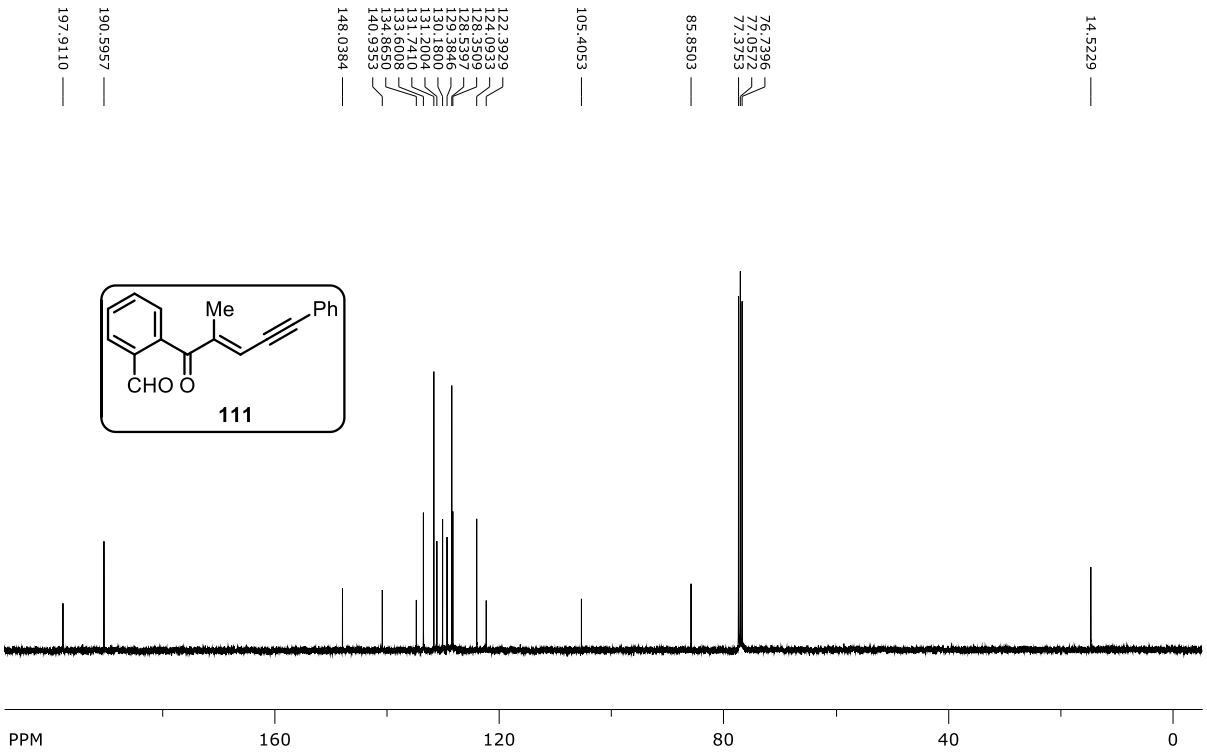


Figure 38: ^{13}C-NMR spectrum of **111**

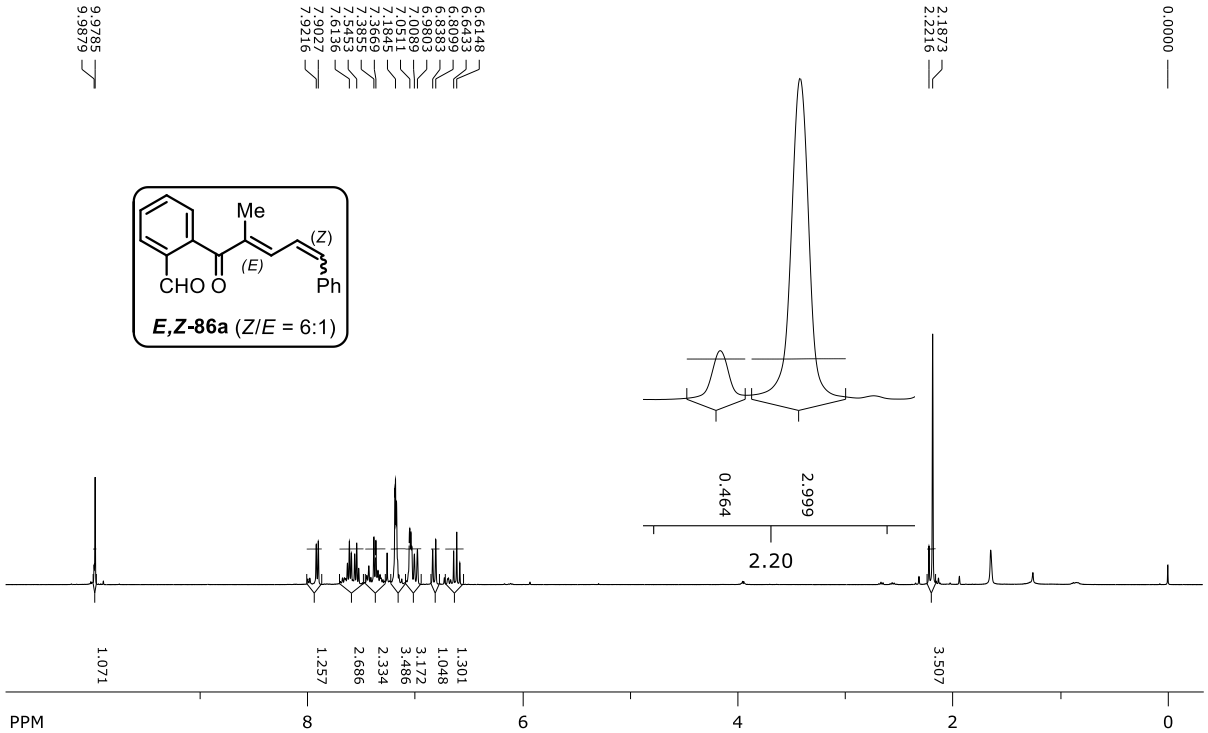


Figure 39: ^{1}H-NMR spectrum of ***E*,*Z*-86a**

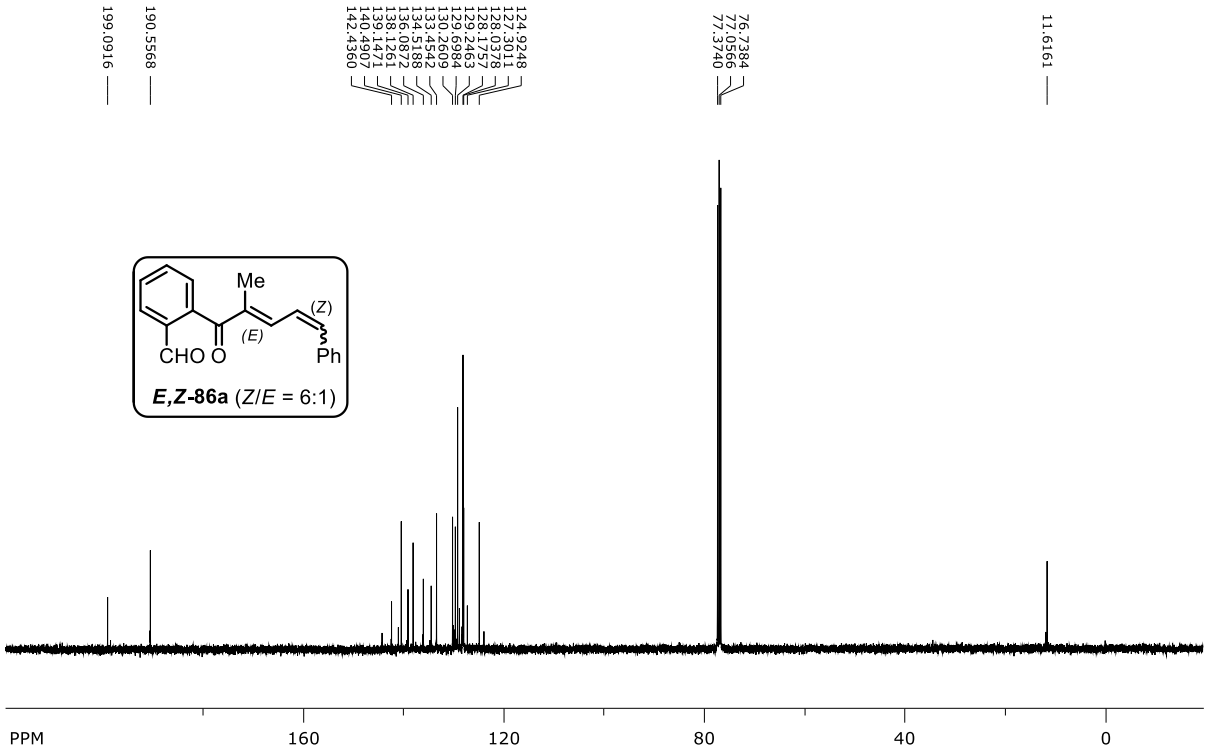


Figure 40: ^{13}C-NMR spectrum of ***E*,*Z*-86a**

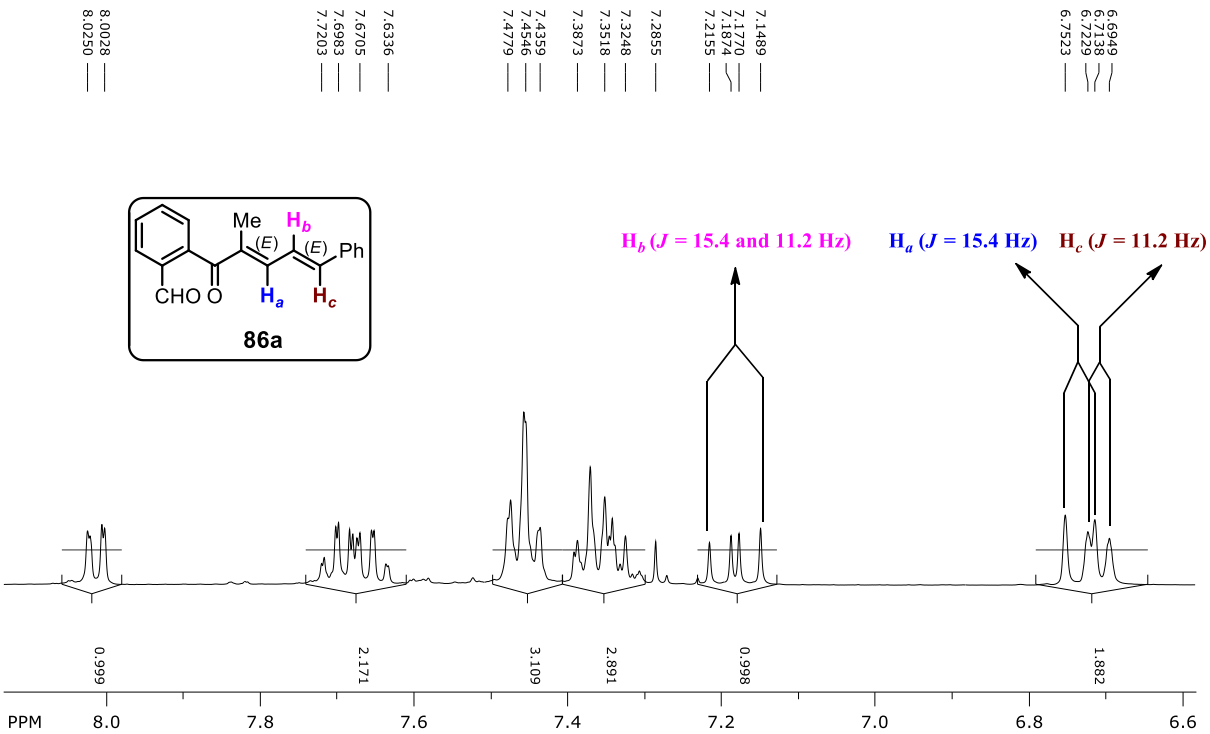


Figure 41: Expanded ^{1}H-NMR spectrum of **86a**

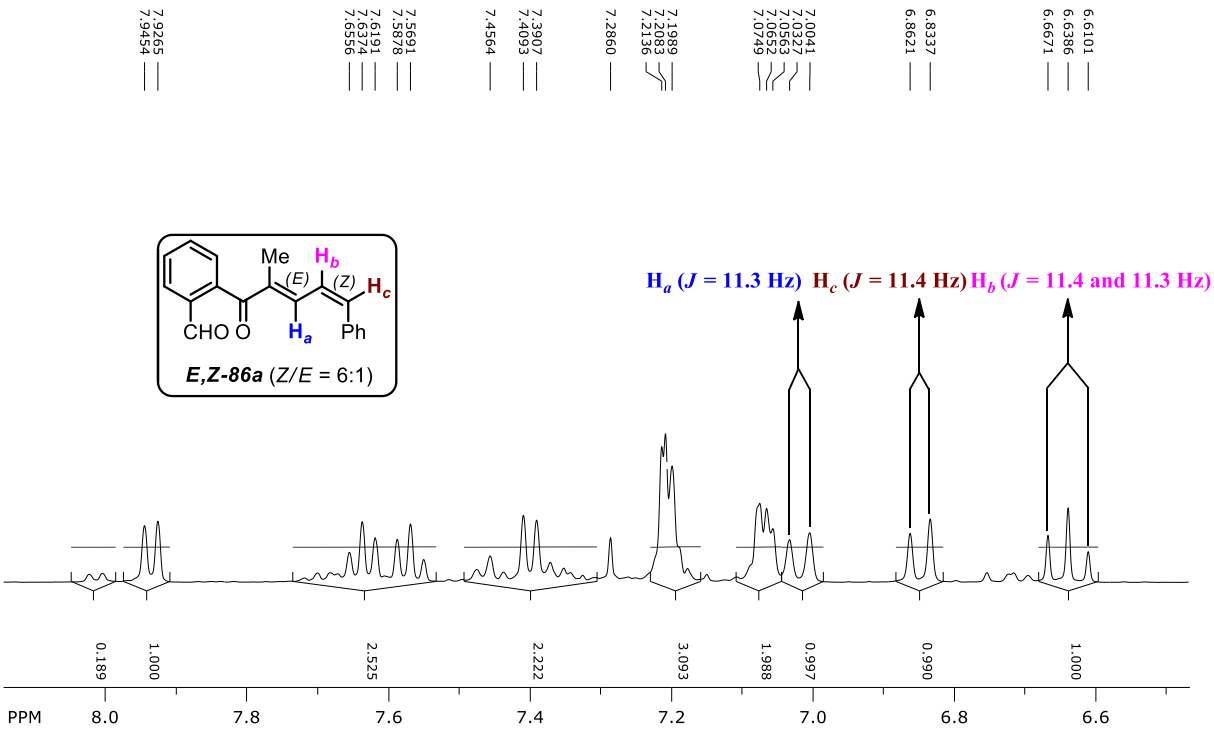


Figure 42: Expanded ^{1}H-NMR spectrum of ***E*,*Z*-86a**

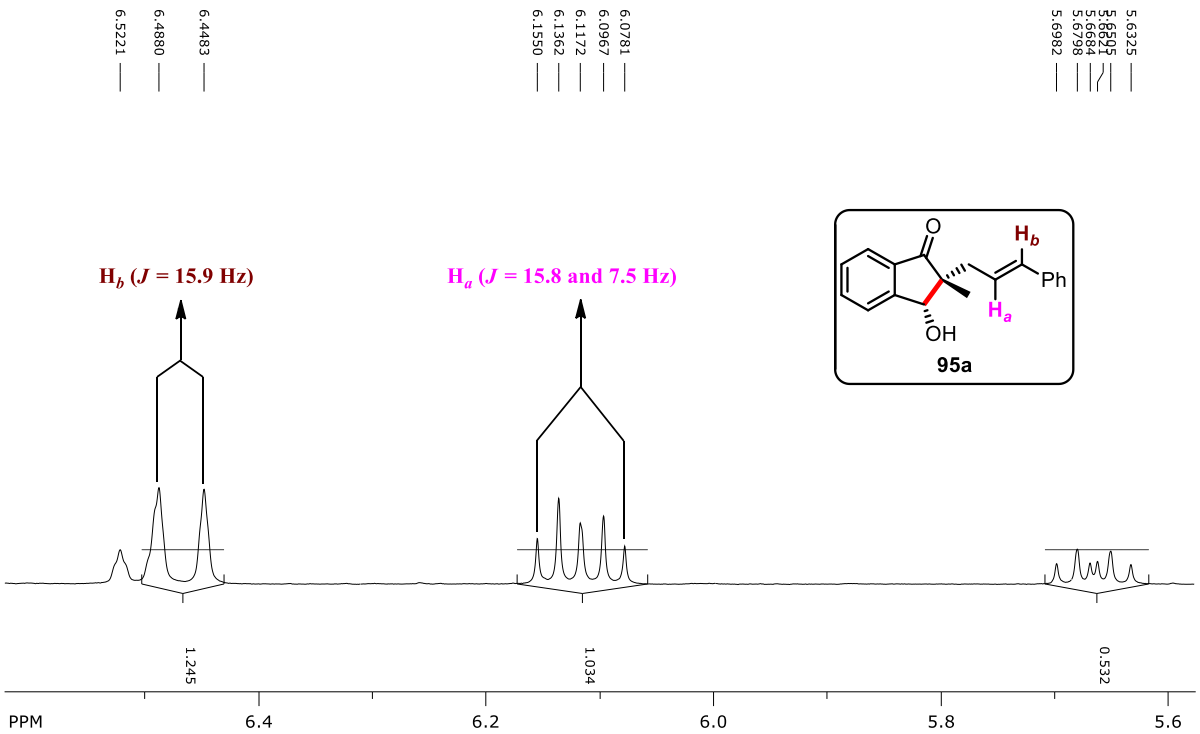


Figure 43: Expanded ^{1}H-NMR spectrum of **95a** (in $CDCl_3$)

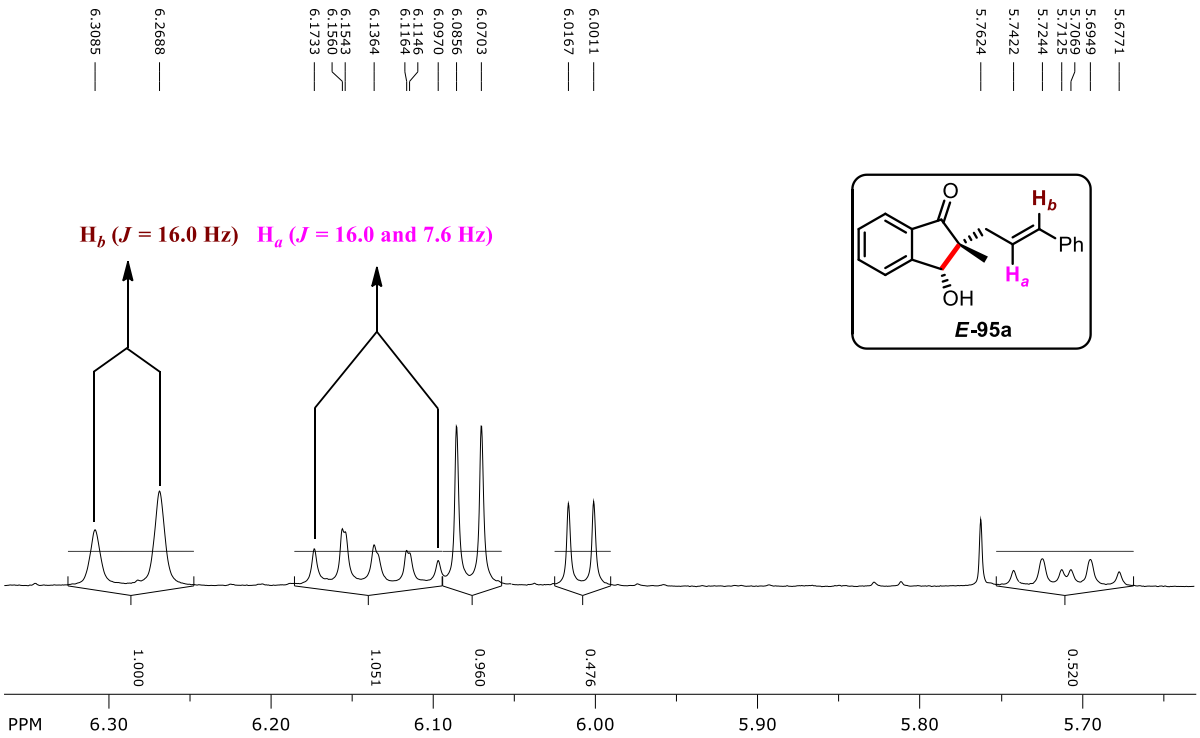
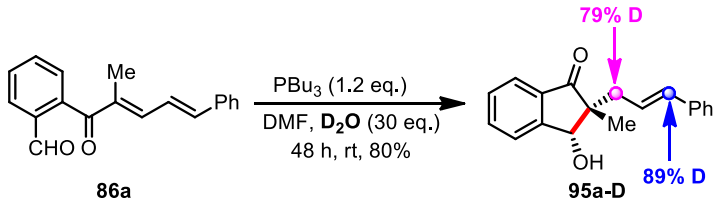


Figure 44: Expanded ^{1}H-NMR spectrum of ***E*-95a** (in DMSO-d_6)

4.2.2: Reductive aldol reaction of 86a in the presence of D_2O

The reductive aldol reaction (RAR) of **86a** was carried out in the presence of D_2O, Scheme 84. Dienone **86a**, dissolved in DMF (1 mL) was treated with tributylphosphine (1.2 eq.) in the presence of 30 equivalent of D_2O at room temperature and continued stirring for 48 h before commencing the purification. The reaction resulted in the formation of **95a-D** in 80% yield. The *D*-incorporation was realized to be 89% at δ-position and 79% at the β-position in **95a-D** from the ^{1}H-NMR spectrum (see Fig. 45-48). The *D*-incorporation indicates that the β- and δ-carbons experience an anionic character at a certain stage during the product formation.



Scheme 84: Reductive aldol reaction of **86a** in the presence of D_2O

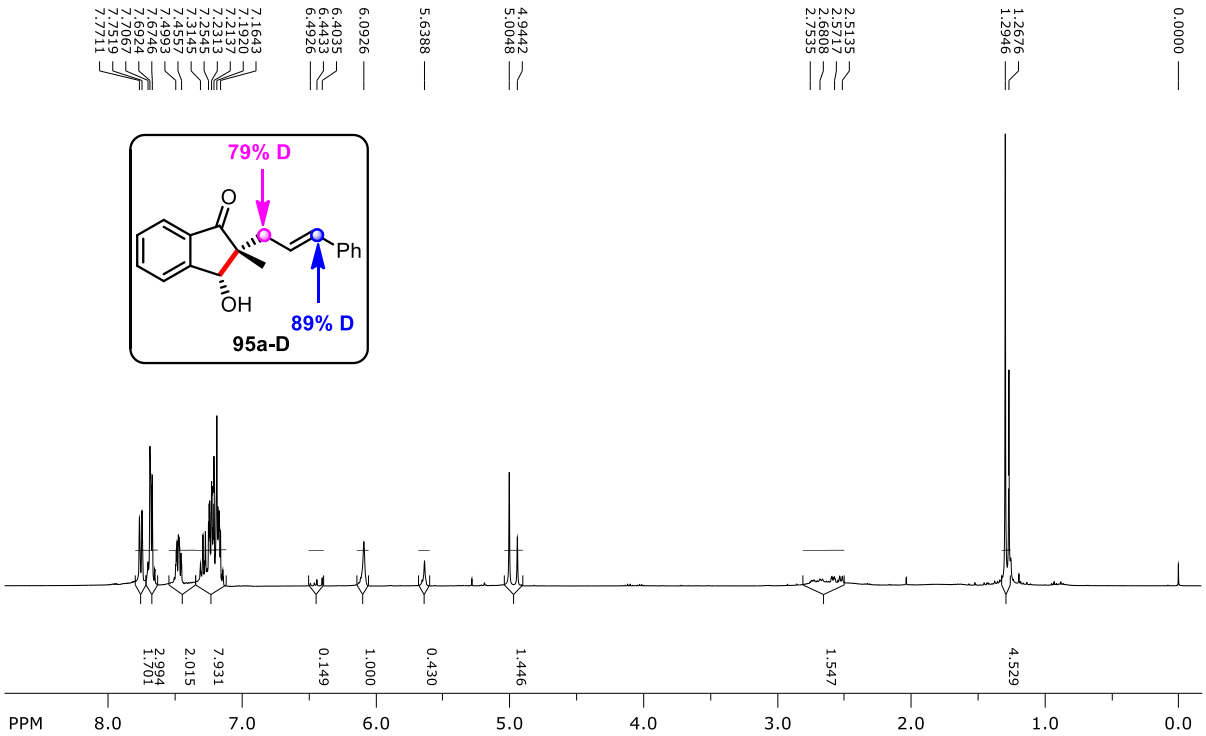


Figure 45: ^{1}H-NMR spectrum of **95a-D**

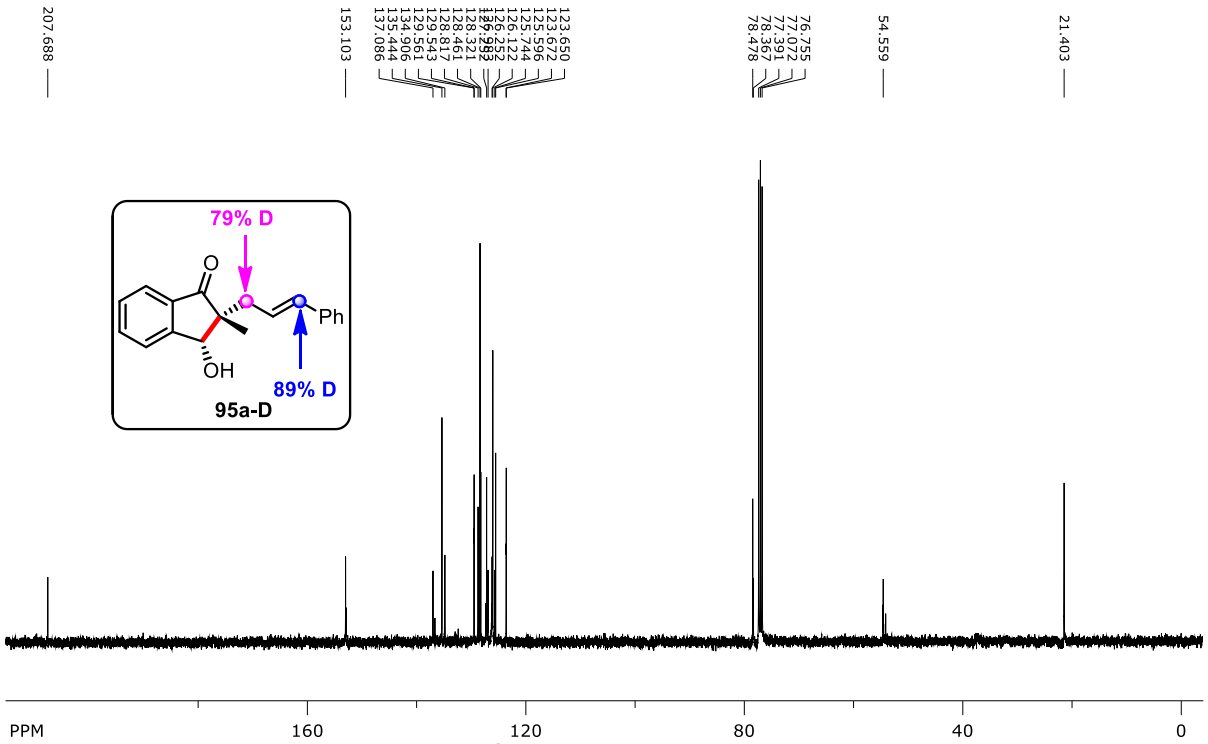


Figure 46: ^{13}C-NMR spectrum of **95a-D**

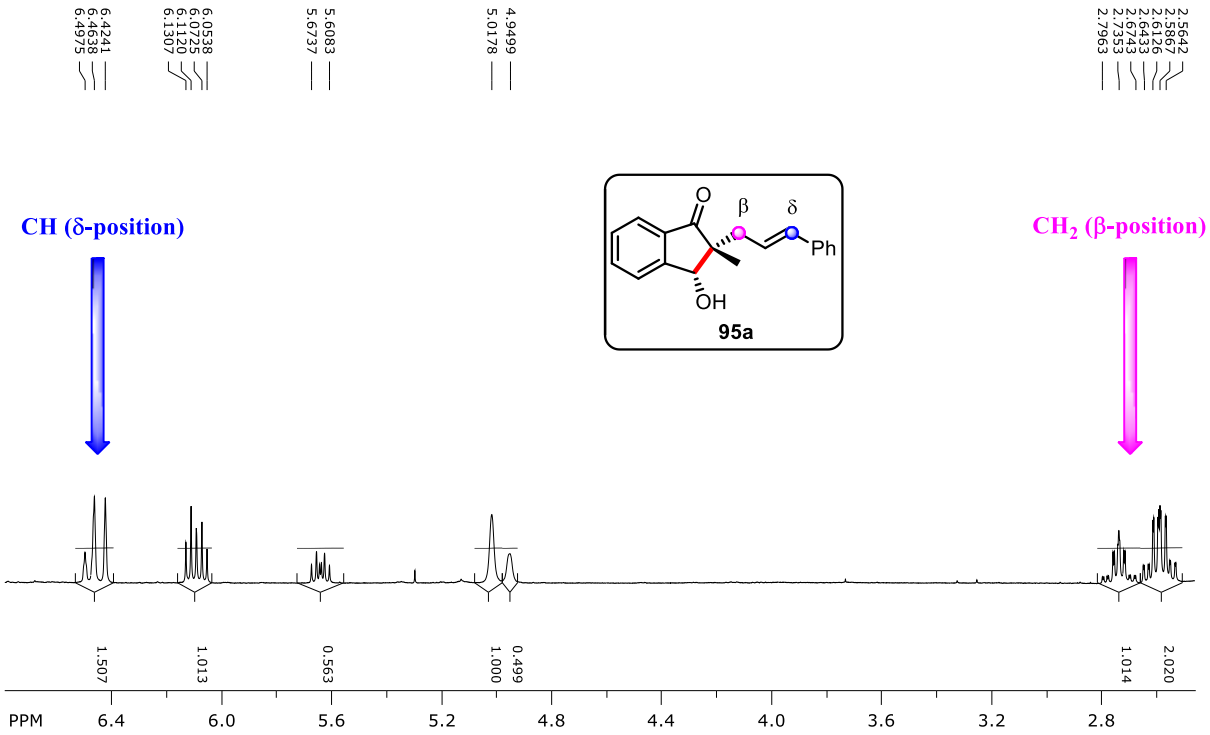


Figure 47: Expanded ^{1}H-NMR spectrum of **95a** (in $CDCl_3$)

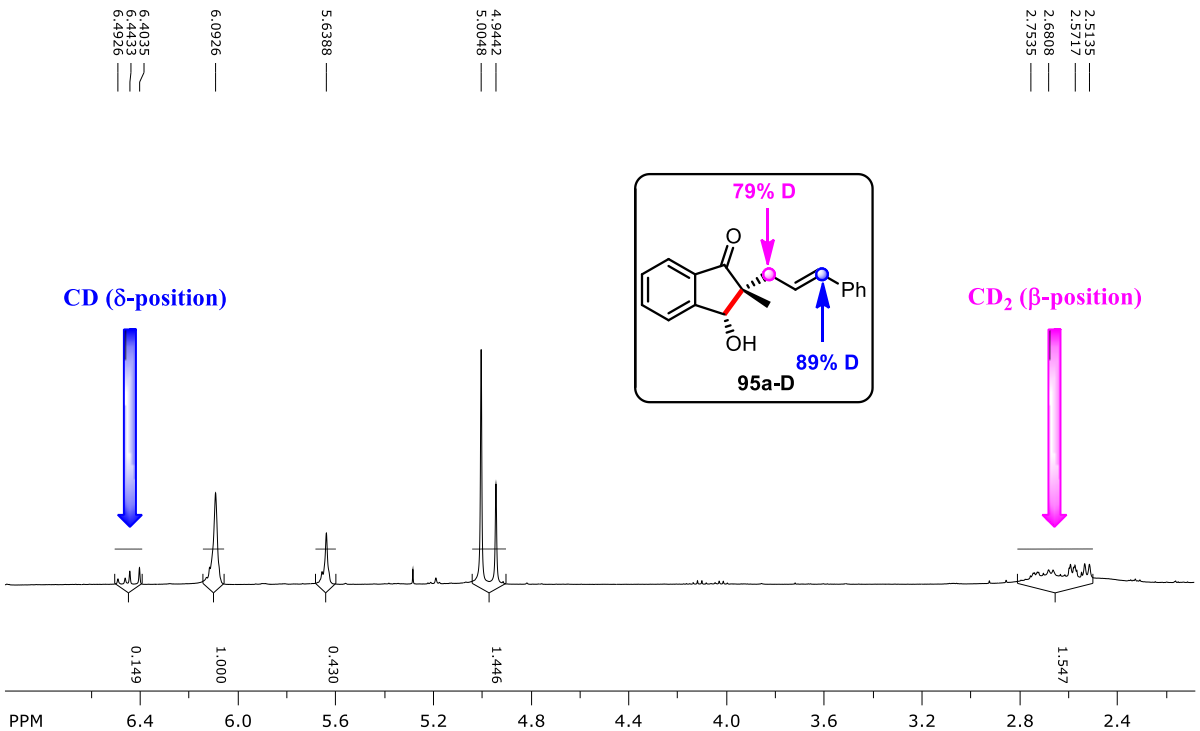
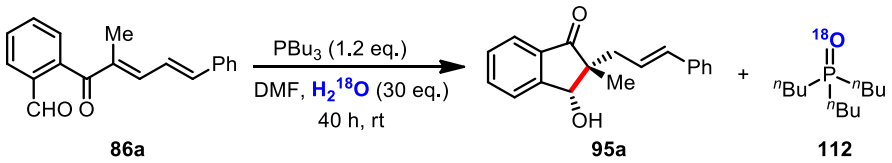


Figure 48: Expanded ^{1}H-NMR spectrum of **95a-D** (in DMSO-d_6)

4.2.3: Reductive aldol reaction of 86a in the presence of $H_2{}^{18}O$

The role of water during the transformation was investigated by using the ^{18}O-labelled water, Scheme 85. The dienone-aldehyde **86a** dissolved in DMF (1.0 mL) was treated with tributylphosphine (1.2 eq.) in the presence of $H_2{}^{18}O$ (30 eq.). Once the starting material **86a** disappeared (as monitored by TLC), the crude reaction mixture was subjected to high-resolution mass spectrometry (HRMS) analysis. The abundance of the peak at **221.1916** [calculated $(M+H)^+$: **221.1920**] for $P(^{18}O)Bu_3$ in $H_2{}^{18}O$ reaction (see Fig. 49) was found to be significantly increased than the respective abundance of $P(^{18}O)Bu_3$ peak at **221.1905** [calculated $(M+H)^+$: **221.1920**] obtained from water reaction (see Fig. 50). This result confirms that water is responsible in the elimination of phosphine as phosphine oxide.[114]



Scheme 85: Reductive aldol reaction of **86a** in the presence of $H_2{}^{18}O$

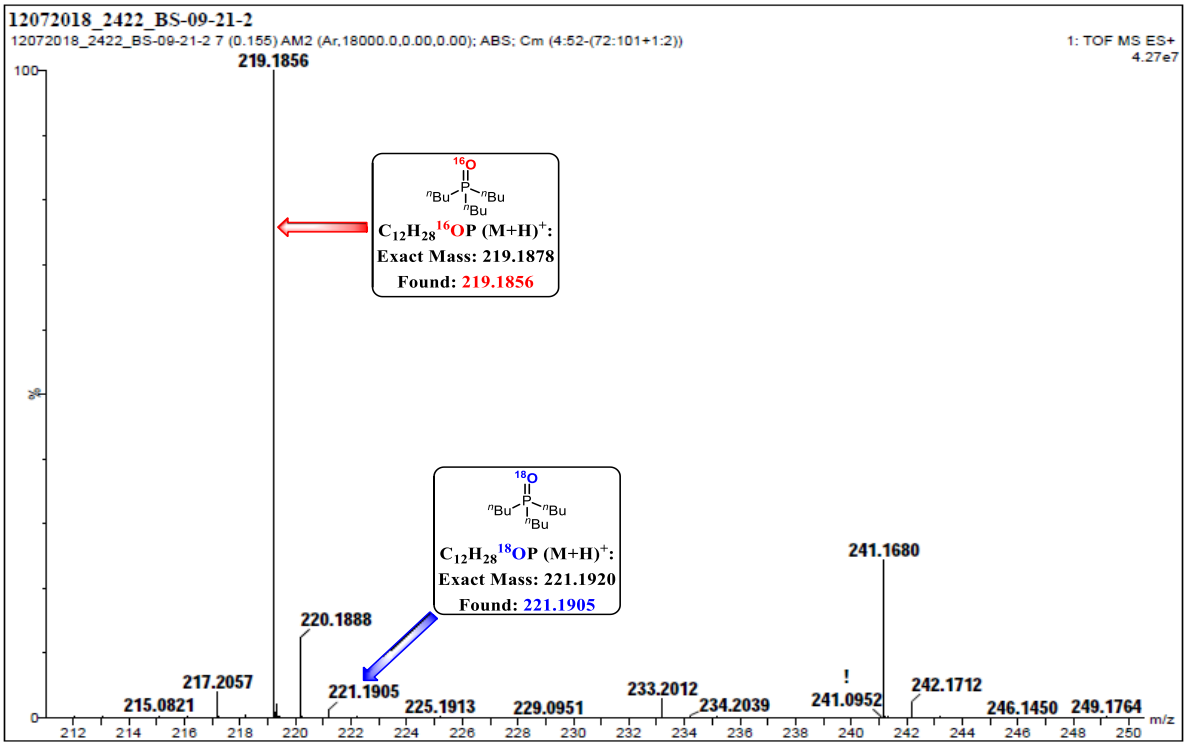


Figure 49: HRMS spectrum of the crude reaction mixture obtained from RAR of **86a** in the presence of **H_2O**

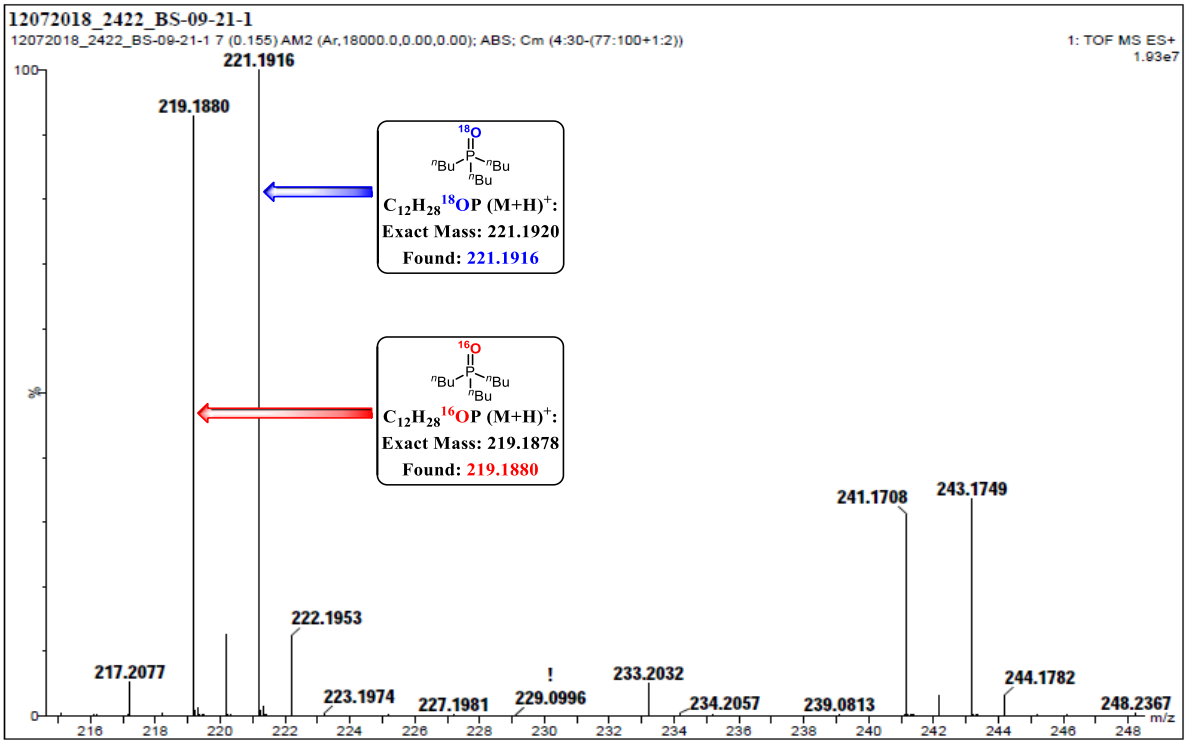
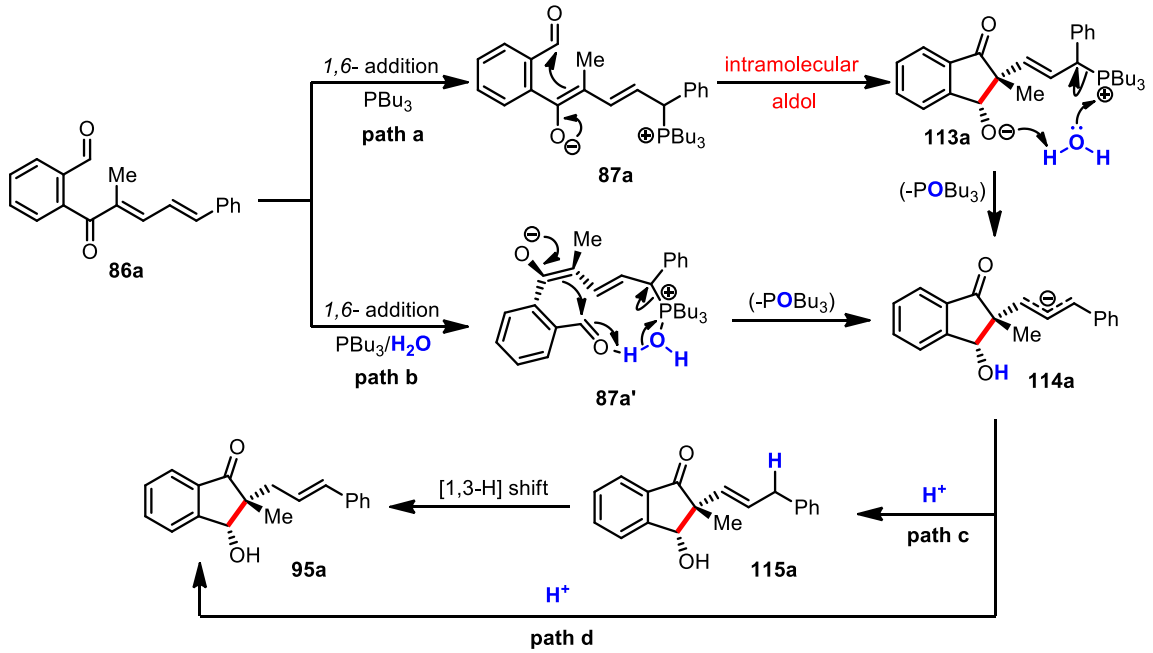


Figure 50: HRMS spectrum of the crude reaction mixture obtained from RAR of **86a** in the presence of **$H_2{}^{18}O$**

Based on the evidence obtained from the control experiments, a plausible mechanism is outlined in Scheme 86.[115] The initial 1,6-phosphine addition to **86a** leads to the formation of dienolate **87a** *via* path a, and undergoes intramolecular aldol reaction to form the zwitterion **113a**. The water-mediated protonation of alkoxide and phosphine oxide elimination generates the anionic species **114a**. The subsequent protonation of **114a** can proceed either *via* formation of **115a** followed by 1,3-proton shift (path c) or *via* direct protonation (path d) to afford the desired product **95a**. The origin of diastereoselectivity could be attributed to the hydrogen bonding ability of water, where the water promoted 1,6-phosphine addition to **86a**, and subsequent intramolecular aldol reaction *via* path b (intermediate **87a'**) can directly lead to the formation of **114a**, possessing *syn* stereochemistry, which explains the stereochemical outcome.



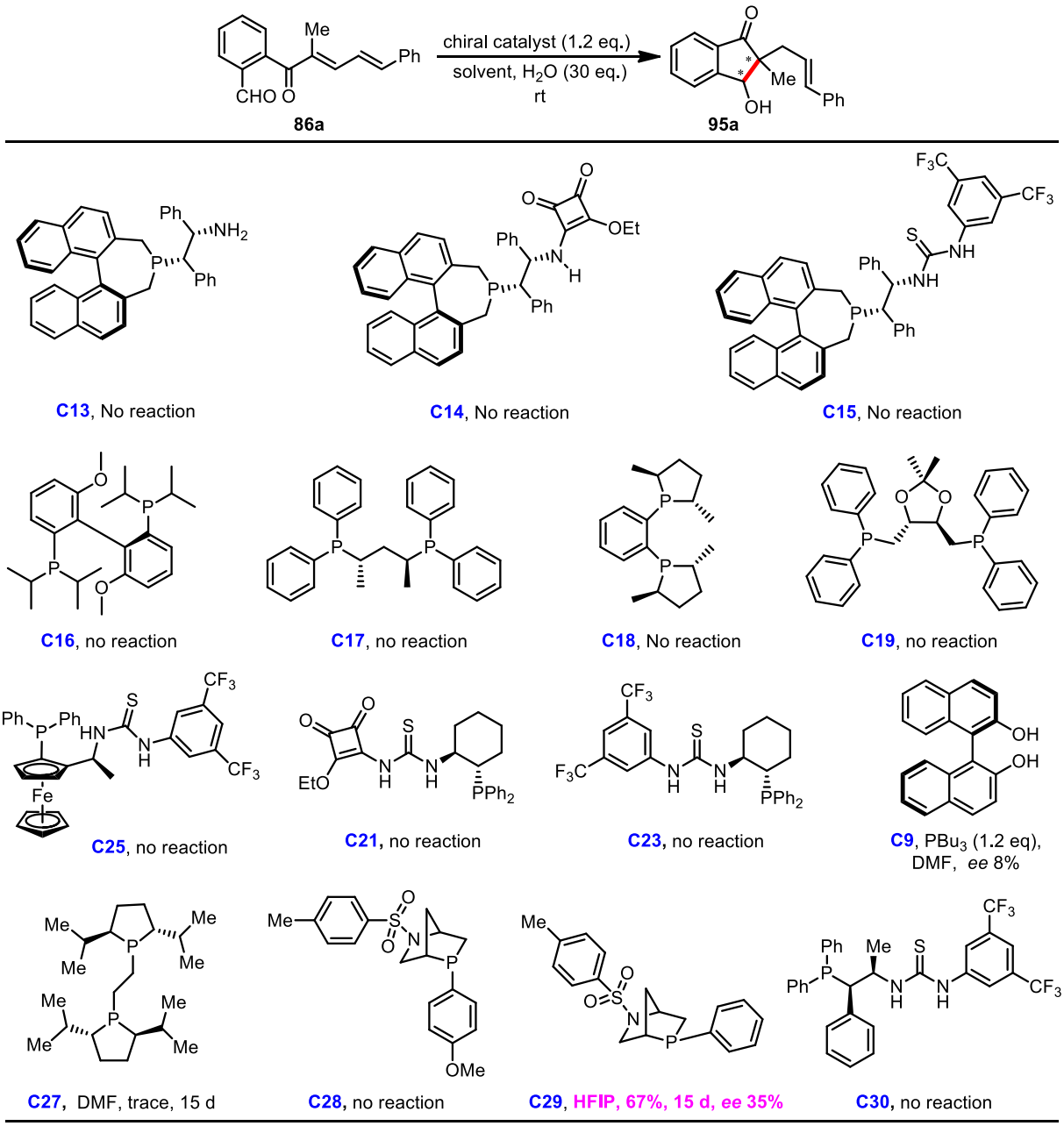
Scheme 86: Plausible mechanism of the intramolecular RAR

4.3: Efforts towards an enantioselective intramolecular RAR

As the reductive aldol products possess two contagious stereogenic centers, we have focused on developing an asymmetric RAR. Based on our earlier success on asymmetric IMBH reaction of enone/dienone-aldehydes (as described in section 2 and 3), a variety of chiral phosphines and solvent combinations were tested, Table 18. Surprisingly, the bifunctional catalysts **C13-C15**, **C21**, **C23**, **C25**, **C30**, and bis-nucleophilic chiral phosphines **C16-C19**, **C27** were unsuccessful. A combination of (*R*)-BINOL **C9** and Lewis base led to poor

enantioinduction. Gratifyingly, the *exo*-Kwon catalyst[116] **C29** delivered the desired product in good yield and moderate enantioselectivity only in HFIP. Several of our efforts to further improve the enantioselectivity failed.

Table 18: Screening of chiral catalysts



All reactions were performed on 0.05 mmol scales using DCM, toluene, hexafluoroisopropanol (HFIP), and trifluorotoluene (TFT) as solvent at room temperature in the presence of 30 eq. of water additive.

4.4: Synthetic utility of RAR products

4.4.1: Synthesis of fused γ-lactones

The γ-lactones are privileged substructure present in many natural products and biologically active molecules. Fused γ-lactones are widely used in the perfume industry due to their pleasant odor. Strigolactones, a class of fused γ-lactone derivatives isolated from root exudates of mono- and dicotyledonous plants, play an important role in plant-plant or plant-fungi communications and plant growth, Fig. 51. In the last few decades, (+)-GR24, a synthetic strigolactone mimic, has been used extensively in plant positive assay as they are more potent than their parent molecules. The only aromatic ring-containing natural strigolactone, (–)-Solanacol was isolated from *Nicotiana tabacum* L, which is highly active to seed germination process, Fig. 51.[117]

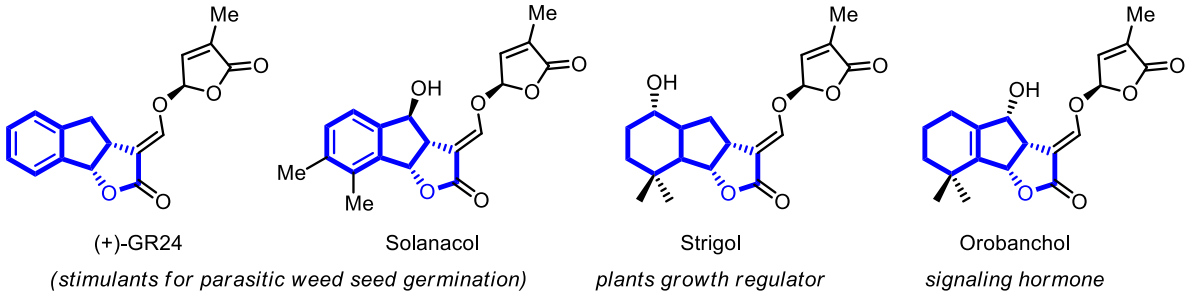
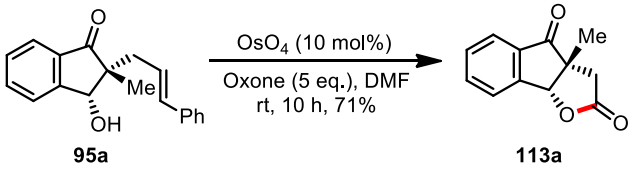


Figure 51: Representative examples of γ-lactone fused bioactive molecules

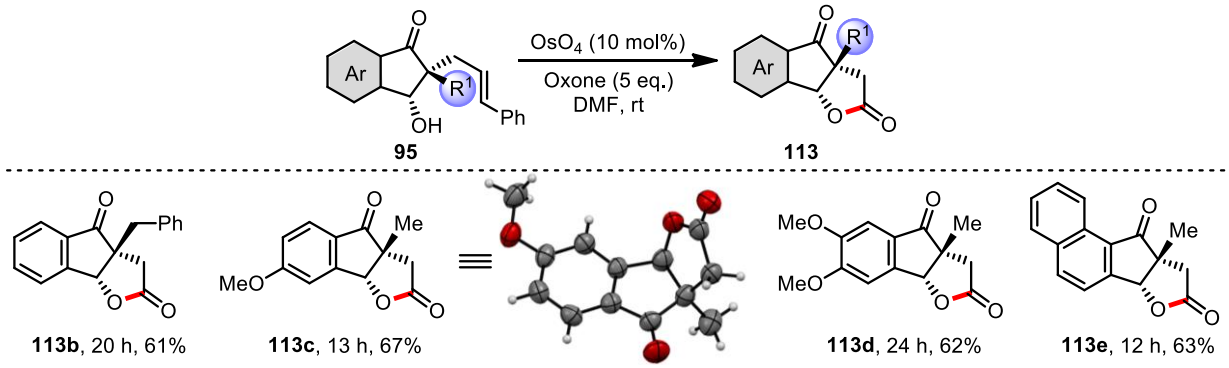
Because of the significance of indanone-fused γ-lactones described above, the developments of new methodologies to access them are of great importance. Accordingly, we have applied Borhan's lactonization protocol[118] to the reductive aldol product **95a**, Scheme 87. Indanone **95a** upon reaction with catalytic osmium tetroxide and excess of oxone as co-oxidant in dimethylformamide underwent smooth lactonization to afford **113a** in 71% yield. The presence of an $AB_{quartet}$ at δ 2.85 ppm (J = 19.2 Hz) and δ 2.85 ppm (J = 19.2 Hz) in the ^{1}H-NMR spectrum (see Fig. 52) and a lactone carbonyl at δ 174.5 ppm in ^{13}C-NMR (see Fig. 53) confirmed the product formation.



Scheme 87: Lactonization of reductive aldol product **95**

Few other indanone-fused γ-lactone analogs **113b-113e** were synthesized by employing the same protocol, Table 19. Interestingly, the complete molecular framework of (+)-GR24 or (–)-Solanacol can be achieved in one step from lactone **113** by following the literature method.[119] The *cis*-stereochemistry along the ring junction of fused γ-lactones was confirmed from the crystal structure of **113c**, Table 19.

Table 19: Synthesis of indanone-fused γ-lactone analogs **113**



Reactions were done on 0.1 mmol scales. Yields based on silica gel column chromatography

4.4.2: Synthesis of dihydroindeno[1,2-b]-pyrans and dibenzo[a,h]-azulen-8-ones

Cyclic ethers are considered as basic building blocks in organic chemistry. They are often encountered as important structural motifs in marine natural products, Fig. 54. Among the cyclic ethers, tetrahydropyrans are used widely as they find applications in pharmaceuticals, cosmetics, and foodstuff.[120] Numerous methods are known to synthesize tetrahydropyrans such as Prins cyclization, Diels-alder reaction, and intramolecular Michael reaction.[121] An intramolecular addition of alcohol across the pendant olefin in the presence of Lewis acids also often utilized to access the tetrahydropyrans in an atom economic manner.[122]

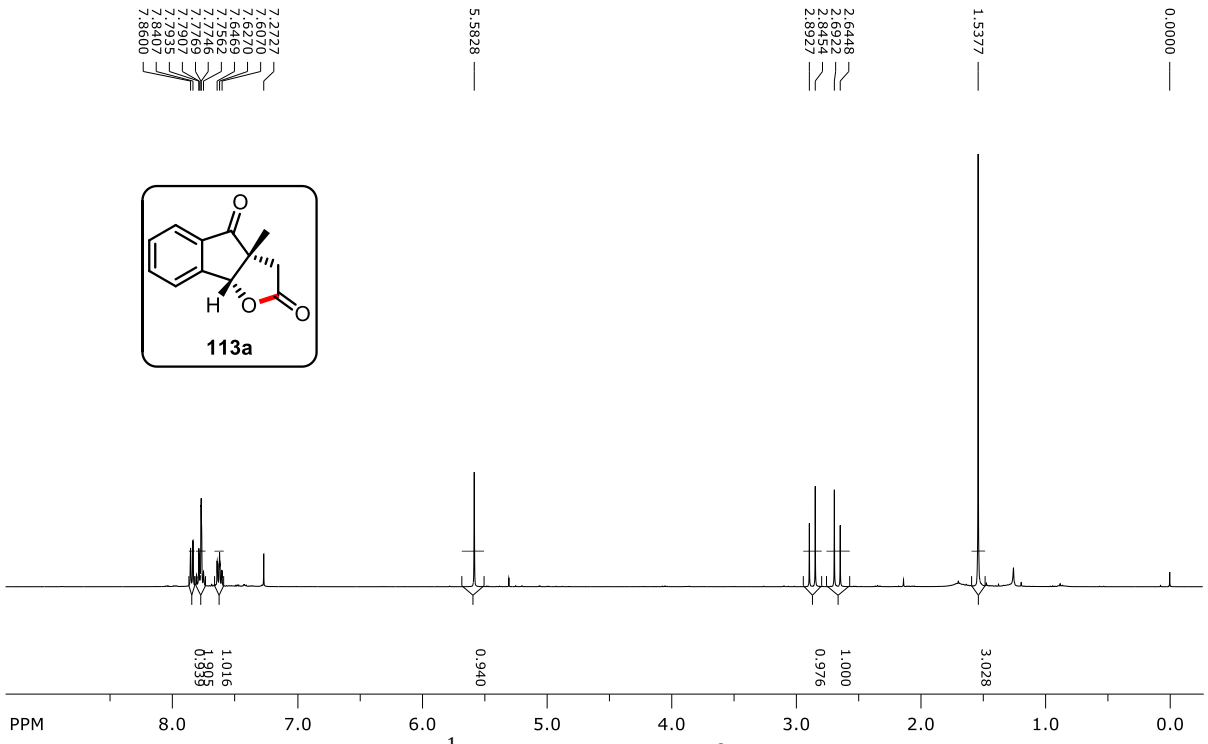


Figure 52: ^{1}H-NMR spectrum of lactone **113a**

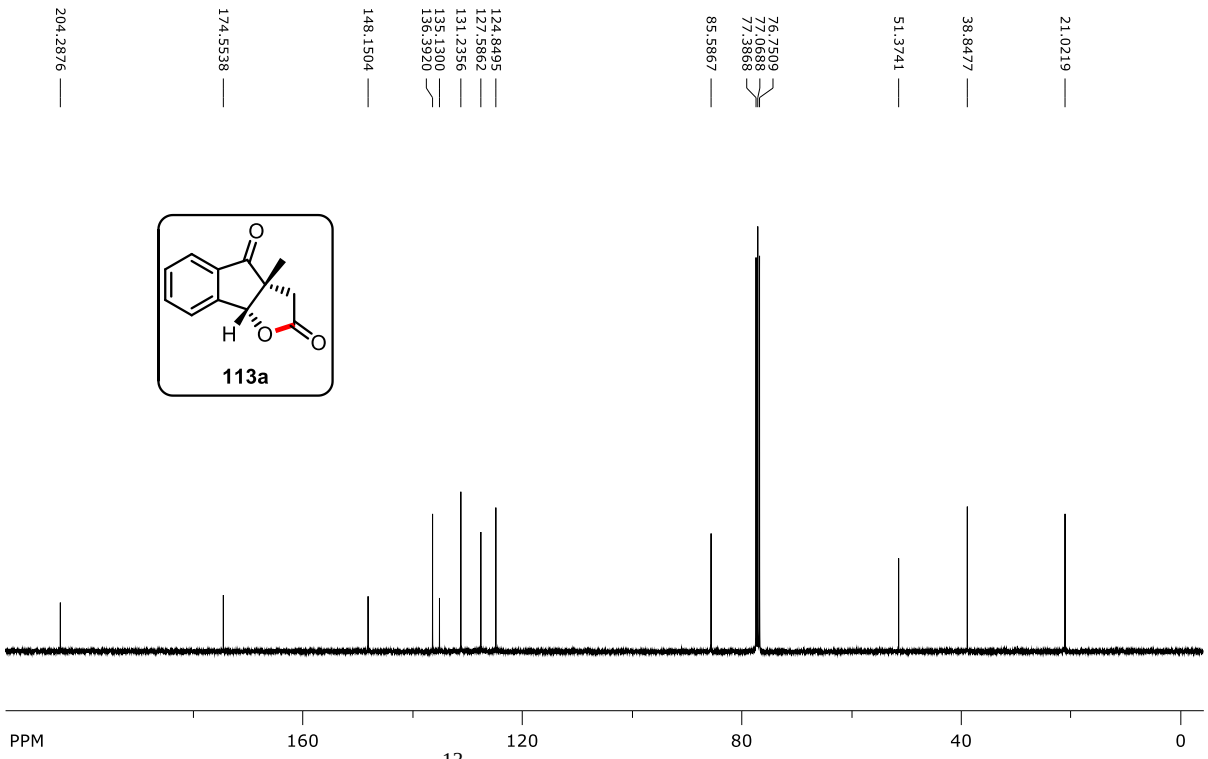


Figure 53: ^{13}C-NMR spectrum of lactone **113a**

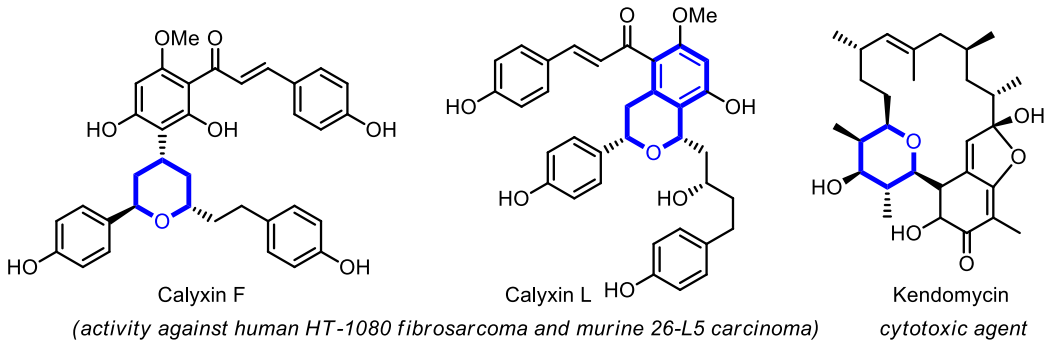
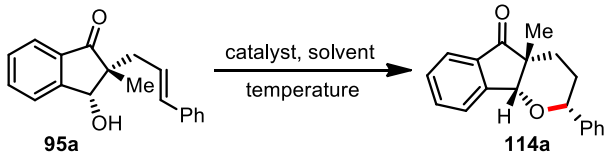


Figure 54: Representative natural products containing functionalized tetrahydropyran moiety

Table 20: Optimization of reaction parameters to synthesize dihydroindeno[1,2-*b*]pyarns **114**



Entry	Lewis/Brønsted acid	Solvent	Temperature	Time/Yield
1	$BF_3.OEt_2$ (30 mol%)	DCM	0 ^oC to rt	48 h/23%
2	$FeCl_3$ (20 mol%)	DCM	rt	48 h/ND
3	$FeCl_3$ (1.2 eq.)	DCM	rt	48 h/32%
4	$BiCl_3$ (20 mol%)	DCM	rt	48 h/ND
5	$BiCl_3$ (1.2 eq.)	DCM	rt	48 h/41%
6	*p*-TSA (1.2 eq.)	Toluene	rt to 80 ^oC	36 h/76%
7	**$BF_3.OEt_2$ (1.2 eq.)**	**DCM**	**0 ^oC to rt**	**8 h/83%**

Reactions were performed on 0.1 mmol scales. ND = not determined

Herein, we have adopted a protocol to access the fused tetrahydropyrans by exploiting the benzylic alcohol and pendant styrenyl groups present in the reductive aldol products **95**. Accordingly, the indanone **95a** was subjected to catalytic $BF_3{\cdot}OEt_2$ in dichloromethane. Desired dihydroindeno-pyran **114a** was isolated in 23% yield after 48 h (Table 20, entry 1). To further improve the reaction yield, a brief screening was performed, Table 20. The stoichiometric amount of the Lewis acids such as $FeCl_3$, $BiCl_3$ were able to afford the pyran **114a** only in moderate yields (Table 20, entries 2-5). Brønsted acid was effective only at elevated temperature (Table 20, entry 6). Stoichiometric $BF_3{\cdot}OEt_2$ displayed the best result in dichloromethane (Table

20, entry 7). The structure of pyran **114a** was confirmed by-NMR analysis (see Fig 56 and Fig 57). The stereochemistry was assigned based on the crystal structure **115** obtained from the hydrazone derivative of **114a**, Fig. 55.

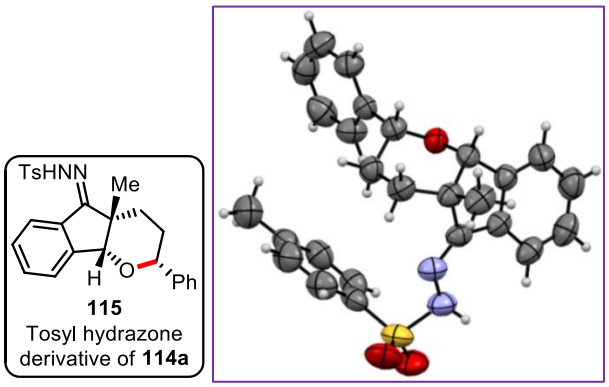
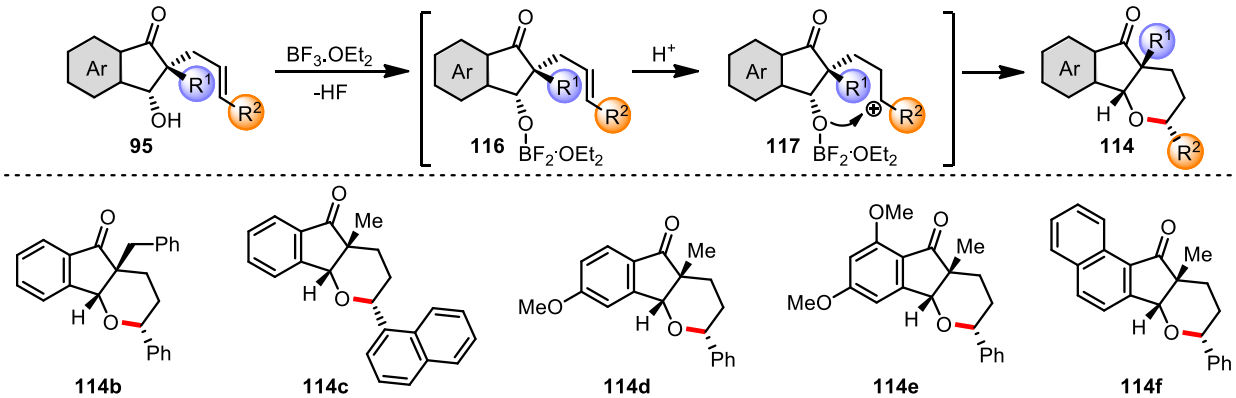


Figure 55: ORTEP diagram of pyran **115**

The optimized condition provided general access to the other dihydroindeno[1,2-*b*]pyran analogs **114b-114f** in excellent yields and moderate diastereoselectivities, Table 21. A plausible mechanism is proposed based on the literature evidence; Table 21.[122b] $BF_3{\cdot}OEt_2$ initially activates the benzylic alcohol of **95** to form **116** by releasing hydrogen fluoride. The proton (generated from HF) further adds to the less hindered side of the olefin to give more stable carbocation **117** and subsequent cyclization by the alkoxide forms the tetrahydropyran **114**.

Table 21: Synthesis of dihydroindeno[1,2-*b*]pyarns **114**



Reactions were performed on a 0.1 mmol scale. Yields were calculated after silica gel column chromatography. *dr* ratio was calculated from the ^{1}H-NMR spectrum of the crude reaction mixture.

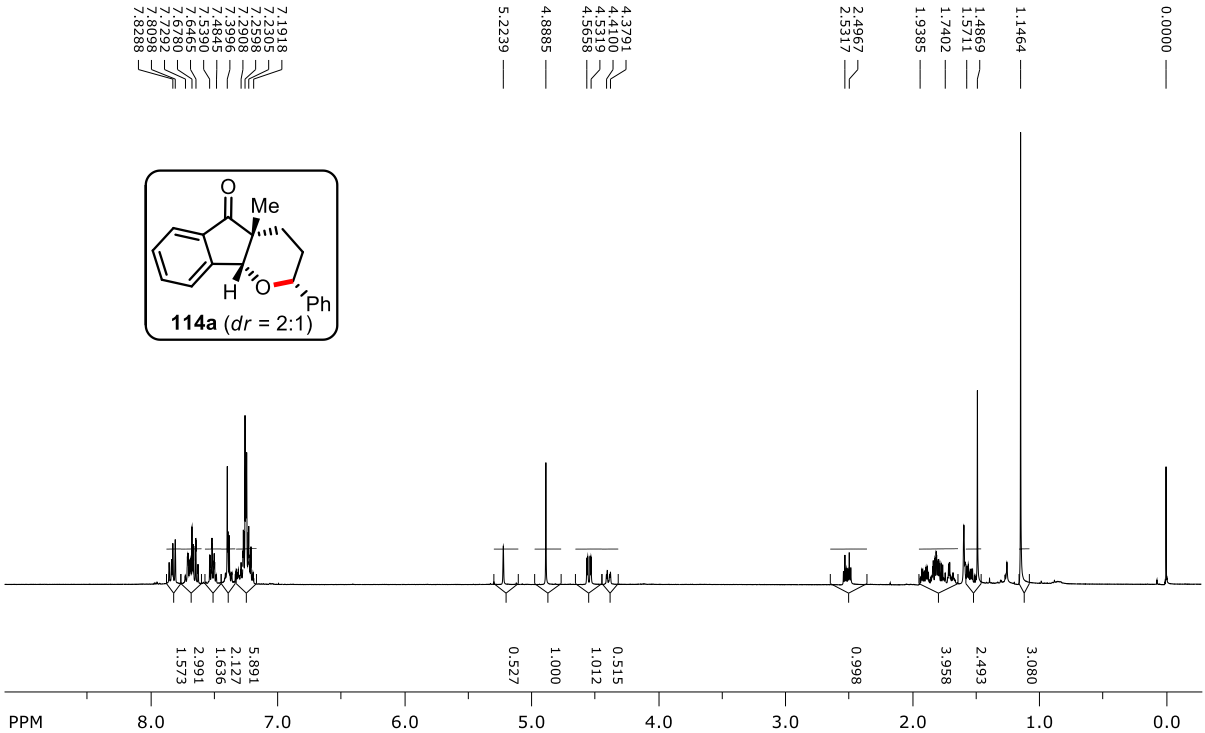


Figure 56: ^{1}H-NMR spectrum of **114a**

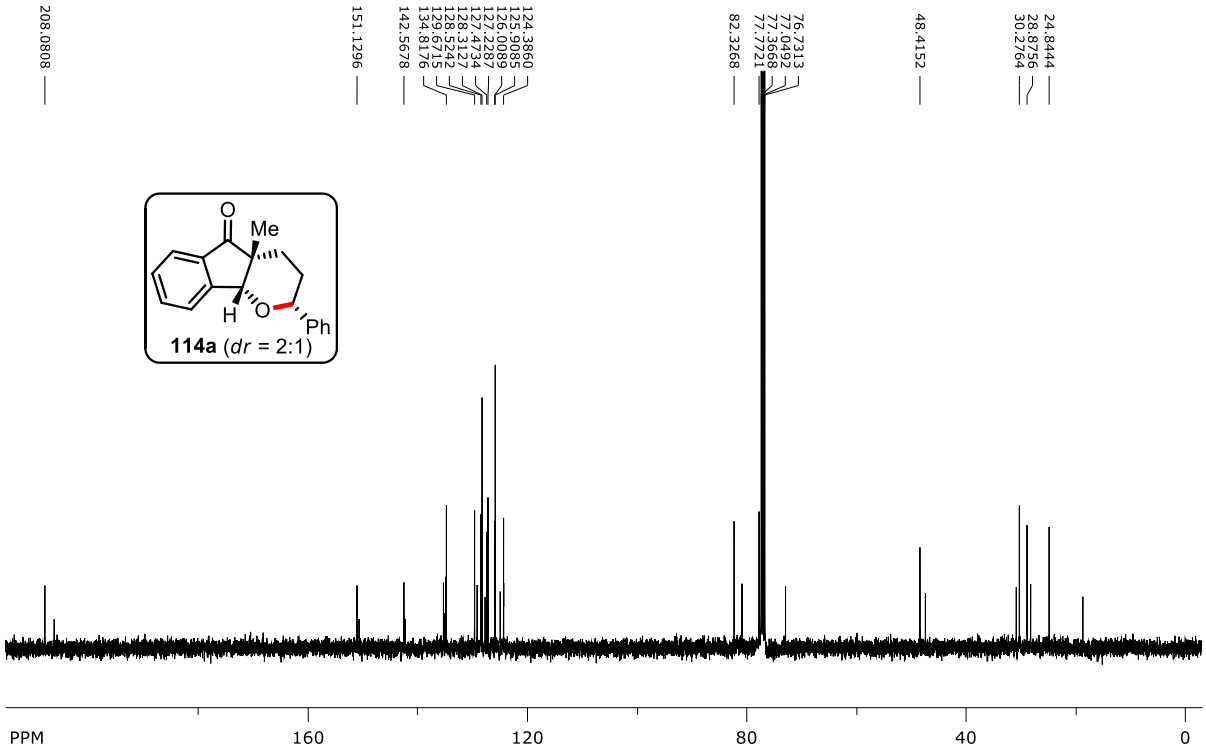
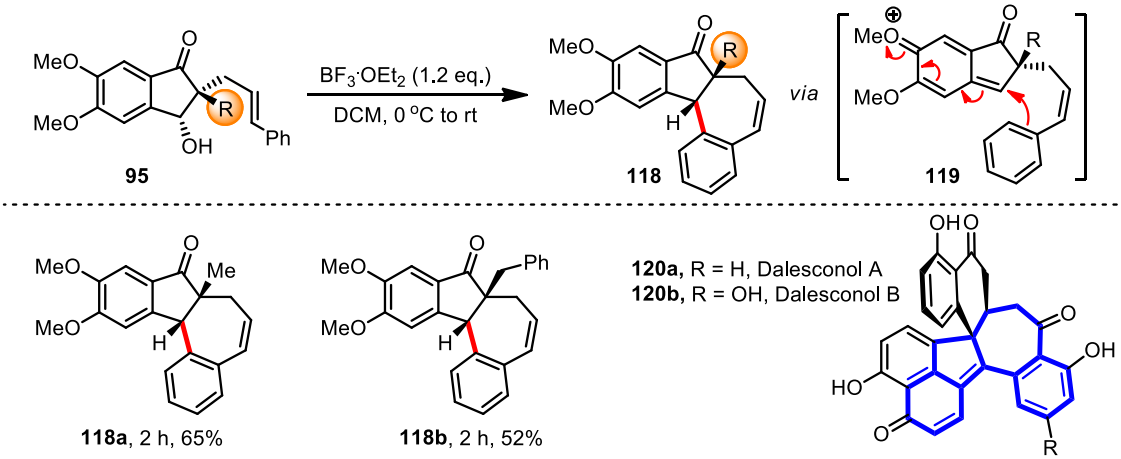


Figure 57: ^{13}C-NMR spectrum of **114a**

Surprisingly, indanones **95h** and **95i** up on treatment with $BF_3{\cdot}OEt_2$ afforded dibenzo[*a*,*h*]- azulen-8-ones **118a** and **118b**, Scheme 88. It was assumed that the presence of a *para*-methoxy group to the benzylic alcohols **95h** and **95i** facilitates the *para*-quinone methide formation **119** and eventually cyclizes to form **118a** and **118b**. In the case of indanone **95g** and **95j**, the similar reactivity pattern was not observed where the methoxy groups were situated *meta* to the benzylic alcohol and afforded fused pyran **114d** and **114e** respectively, Table 21. The tetracyclic dibenzo[*a*,*h*]- azulen-8-one moiety of **118** represents a part structure of the immune-suppressive natural products dalesconol A (**120a)** and B (**120b**), Scheme 88.[123]



Scheme 88: Synthesis of dibenzo[*a*,*h*]-azulen-8-ones **118**

In conclusion, we have disclosed the first metal- and hydride/hydrogen free intramolecular reductive aldol reaction of dienones. Highly functionalized cyclopenta[*b*]nnulated arenes and heteroarenes were accessed under extremely mild and moisture insensitive condition in excellent regio- and diastereoselectivities. The unusual role of water as terminal oxidant was also discovered. Control experiments thoroughly elucidated the mechanistic details. To illustrate the general utility of the reductive aldol products, we have demonstrated a series of serendipitous one-step elaborations. These strategies provide efficient access to indeno-[1,2-*b*]furanones, indeno[1,2-*b*]pyrans, and dibenzo[*a*,*h*]-azulen-8-ones.

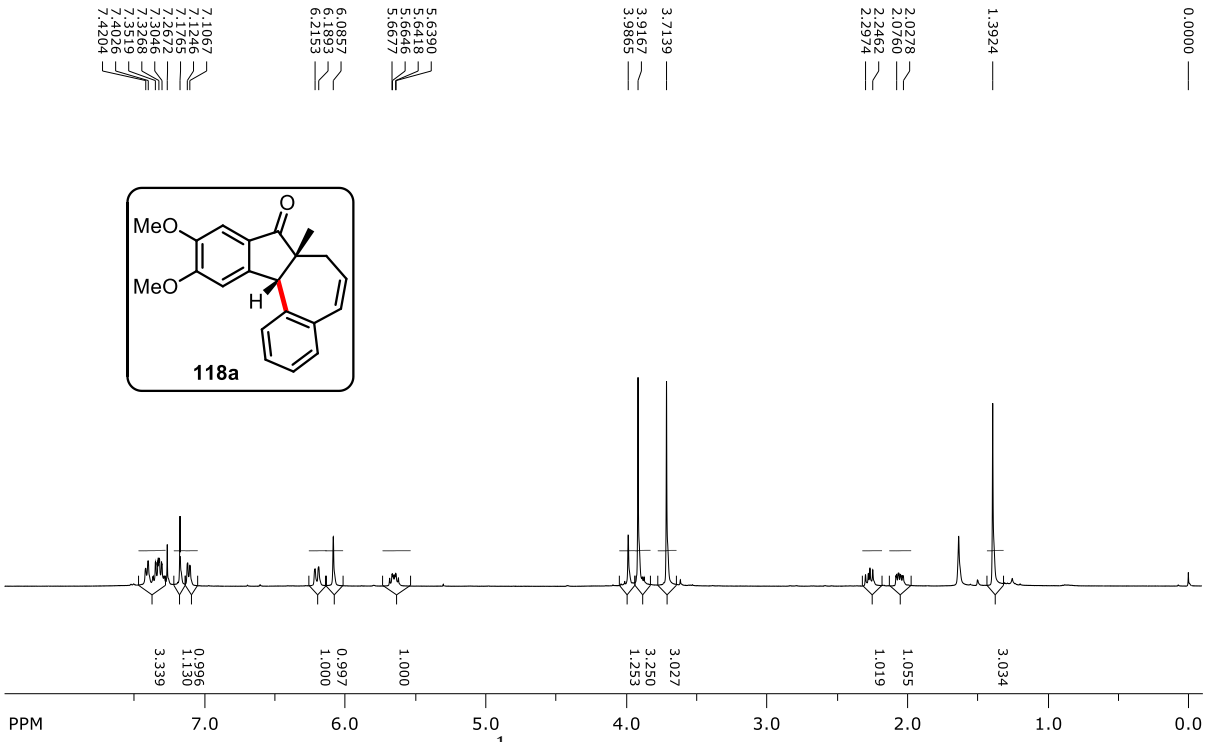


Figure 58: ^{1}H-NMR spectrum of **118a**

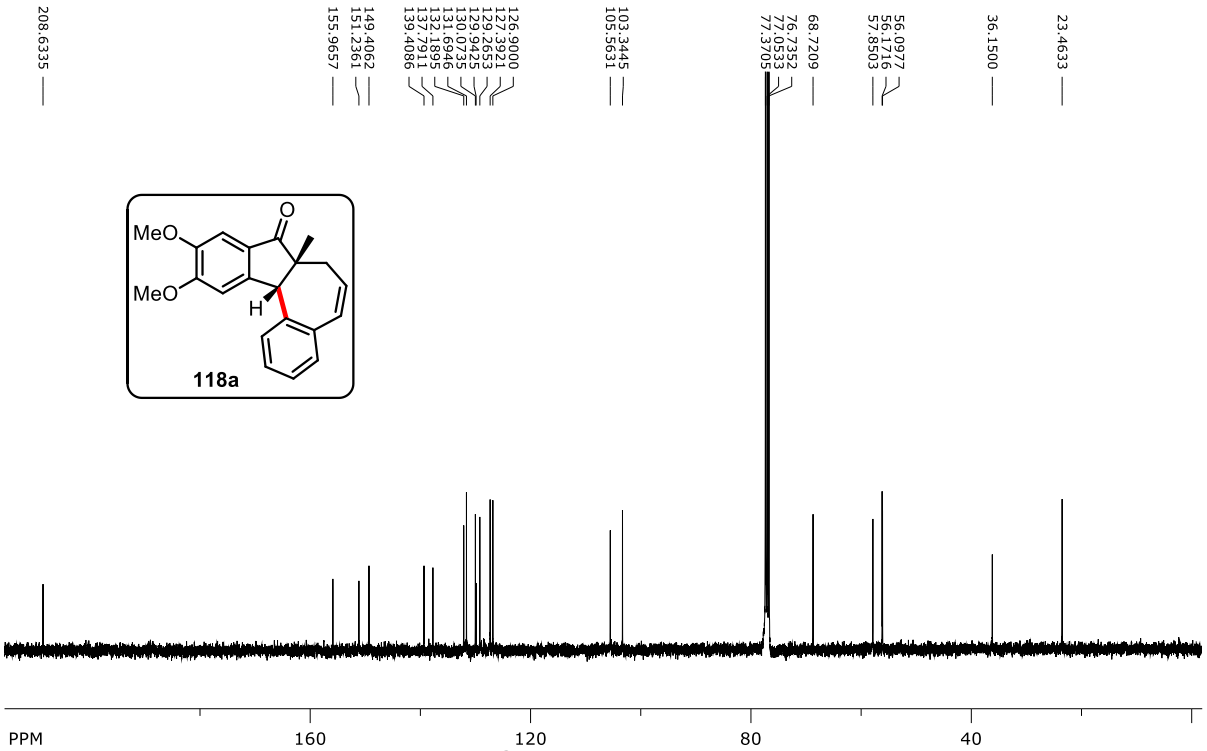


Figure 59: ^{13}C-NMR spectrum of **118a**

Conclusions

In conclusion, we have demonstrated an intramolecular Morita-Baylis-Hillman (IMBH) reaction of previous unexplored β-mono and β,β-disubstituted enones to access cyclopenta-fused arenes and heteroarenes in excellent yields. Further, an enantioselective version also was developed by employing bifunctional thiourea catalyst in hexafluoroisopropanol. This strategy was extended to design another IMBH substrate possessing dienones. Toward this, we have described an efficient enantioselective IMBH reaction of δ-mono and δ,δ-disubstituted dienones to afford highly enantioenriched fused-cyclopentanes in nearly quantitative yields. The IMBH adducts were successfully elaborated to substituted fluorenones in a one-pot telescopic manner.

Continued research interest in developing new strategies to achieve fused-cyclopentanes led us to develop an intramolecular reductive aldol reaction. We have described a phosphine and water-mediated intramolecular reductive cyclization of α-substituted dienone-aldehydes to synthesize a diverse range of cyclopenta[*b*]nnulated arenes and heteroarenes bearing two contagious stereogenic centers, one of them being an all-carbon quaternary center, in good yields and diastereoselectivities. Further, a series of serendipitous one-step elaborations of reductive aldol products were established. These strategies describe efficient access to indeno-[1,2-*b*]furanones, indeno[1,2-*b*]pyrans, and dibenzo[*a*,*h*]-azulen-8-ones.

General experimental methods: All the starting compounds and catalysts employed in this study were procured from Sigma-Aldrich, TCI chemicals, Avra Synthesis 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 Merck silica gel 60-120 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} in inverse centimetres. 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 Avance 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 Bruker AXS KAPPA APEX II system or Rigaku XtaLAB mini X-ray diffractometer. High-resolution mass spectra were recorded on a Waters QTOF mass spectrometer. Optical rotations were recorded on Rudolph APIII/2W. HPLC data was acquired from a Waters 515 using normal phase chiral columns.

General procedure 1: Synthesis of enones 42a-42f and 42w-42aa

Step-I: To a solution of *N*-methylpiperazine (NMP, 0.18 mL, 1.6 mmol) in THF (5 mL) at –78 ^oC was added *n*-BuLi (1.6 *M* in hexane, 1.0 mL, 1.6 mmol). After 15 min, thiophene- or benzothiophene 3-carboxaldehyde **44** (200 mg, 1.2 mmol) was added and then the reaction mixture was stirred for an additional 30 min. A hexane solution of *n*-BuLi (2.0 mL, 3.2 mmol) was added and the mixture was stirred for an additional 15 min and then the mixture was warmed to –30 ^oC in 2 h. The solution was again cooled to –78 ^oC and an enal **47** (1.5 mmol) was added drop wise over 5 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 as eluent to afford enol **46**.

Step-II: Alcohol **46** (1 mmol) was dissolved in ethyl acetate (10 mL), and IBX (1.5 mmol) was added. The resulting suspension was immersed in an oil bath set to 75 °C and stirred until alcohol **46** 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 (3×2 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 vacuum. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate as eluent to afford the enones **42a-42f** and **42w-42aa**.

General procedure 2: Synthesis of enone-ketone 42ap

In to solution of Alcohol **46** in dry THF, methyl magnesium bromide (1.2 eq.) was added at 0 ^{o}C. The reaction was continued until the starting alcohol **46** disappeared as monitored by TLC. The reaction mixture was quenched by saturated aqueous ammonium chloride and extracted using ethyl acetate. Organic extracts were combined, dried over anhydrous sodium sulphate, and concentrated to afford the diol **48a** and proceeded to the next step without purification. Subsequent IBX oxidation of diol **48a** delivered the desired enone-ketone **42ap**.

General procedure 3: Synthesis of arene and pyridine based enone-aldehydes 42

Step-I: An oven dried 25 mL RB flask was charged with 2-bromo aldehydes **49** (2.0 mmol), 10 mL dry MeOH and placed at 0 ^{o}C. Sodium borohydride (2.1 mmol) was added portion wise under nitrogen atmosphere and stirred at room temperature until **49** disappeared (monitored by TLC) and quenched by saturated aqueous ammonium chloride. Methanol was removed under vacuum and extracted using ethyl acetate. Organic extracts were combined and dried over anhydrous sodium sulphate and concentrated to afford crude 2-bromo alcohol **50** and proceeded

to the next step without further purification. Alternatively, aldehyde **49** was treated with an appropriate Grignard reagent in dry THF to access the secondary alcohol **50**.

Step-II: An oven dried 25 mL long neck RB flask was charged with 2-bromo alcohol **50** (1.0 mmol), 5 mL dry THF and placed at –78 ^{o}C. *n*-BuLi (1.6 *M* in hexanes, 2.2 mmol) was added drop wise at same temperature and stirred for 2 hours. An enal **47** (1.3 mmol) dissolved in 1 mL of dry THF, was added drop wise over 2 mins and stirred at room temperature for 30 mins. The reaction mixture was quenched with saturated aq. ammonium chloride solution and extracted using 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 to afford diol **51**.

Step-III: The diols **51** were oxidized using IBX following the general procedure 1, step II to afford enones **42**.

General procedure-4: Intramolecular MBH reaction of enones 42

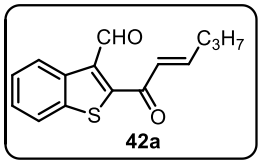
An oven dried 5 mL glass vial was charged with **42** (30 mg, 0.1 mmol). Toluene (1 mL) and PMe_3 (1 M solution in toluene, 0.1 mL, 0.01 mmol) were introduced at room temperature (rt) under nitrogen atmosphere and stirring continued at rt until **42** disappeared as monitored by TLC. All the volatiles were removed under reduced pressure. The crude product was purified by silica gel flash chromatography using hexane/ethyl acetate as eluent, to afford **43**.

General Procedure-5: Enantioselective IMBH reaction of enones 42

An oven dried 5 mL glass vial was charged with **42** (30 mg, 0.1 mmol) in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP, 0.6 mL), catalyst **C23** was introduced at room temperature (rt) under nitrogen atmosphere and stirring continued at rt until **42** disappeared as monitored by TLC. Volatiles were removed under reduced pressure. The crude product was purified by silica gel flash chromatography using hexane/ethyl acetate as eluent, to afford **43**.

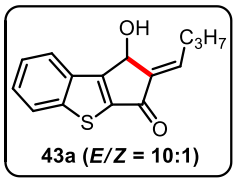
(*E*)-2-(Hex-2-enoyl)benzo[*b*]thiophene-3-carbaldehyde (42a).

This compound was prepared by following the general procedure **1** and isolated as pale yellow oil. R_f = 0.5 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2962, 2873, 1674, 1663, 1614, 1501, 1178, 1087, 758. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.63 (s, 1H), 8.81-8.79 (m, 1H),



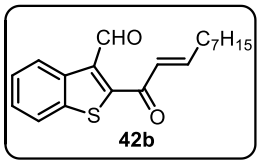
7.93-7.90 (m, 1H), 7.59-7.55 (m, 2H), 7.23 (dt, *J* = 15.3 and 1.5 Hz, 1H), 6.81 (dt, *J* = 15.3 and 1.5 Hz, 1H), 2.38 (dq, *J* = 7.2 and 1.5 Hz, 2H), 1.61 (qd, *J* = 14.8 and 7.4 Hz, 2H), 1.02 (t, *J* = 7.4 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 187.9, 184.8, 153.3, 150.2, 139.1, 136.6, 136.5, 128.6, 127.9, 126.9, 126.7, 122.2, 34.9, 21.3, 13.7. **HRMS (ESI):** *m/z* calcd for $C_{15}H_{15}O_2S$ $(M+H)^+$: 259.0793. Found: 259.0778.

(*E*)-2-Butylidene-1-hydroxy-1*H*-benzo[*b*]cyclopenta[*d*]thiophen-3(2*H*)-one (43a).



This compound was isolated as a pale yellow solid. Following the general procedure **4**, 30 mg of **42a** afforded 28 mg of **43a** (93% yield). M.P = 100-101 °C. R_f = 0.2 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3386, 2960, 2873, 1688, 1650, 1514, 1425, 1096, 743. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.14-8.12 (m, 1H), 7.92-7.90 (m, 1H), 7.55-7.48 (m, 2H), 6.84 (td, *J* = 7.8 and 1.4 Hz, 1H), 5.87 (s, 1H), 2.64-2.47 (m, 2H), 2.30 (br s, 1H), 1.67-1.57 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 184.8, 159.3, 148.0, 144.4, 142.2, 140.5, 133.3, 128.3, 125.5, 124.6, 124.3, 66.7, 30.9, 22.0, 14.0. **HRMS (ESI):** *m/z* calcd for $C_{15}H_{13}OS$ $(M-OH)^+$: 241.0687. Found: 241.0657.

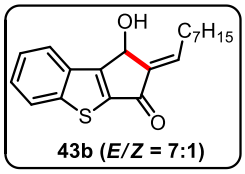
(*E*)-2-(Dec-2-enoyl)benzo[*b*]thiophene-3-carbaldehyde (42b).



This compound was prepared by following the general procedure **1** and isolated as pale yellow oil. R_f = 0.6 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2964, 2871, 1672, 1665, 1614, 1505, 1090, 743. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.67 (s, 1H), 8.79-8.77 (m, 1H), 7.91-7.89 (m, 1H), 7.57-7.54 (m, 2H), 7.22 (td, *J* = 15.2 and 6.9 Hz, 1H), 6.80 (td, *J* = 15.3 and 1.3 Hz, 2H), 1.65-1.52 (m, 2H), 1.40-1.31 (m, 9H), 0.91 (t, *J* = 7.3 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 187.9, 184.9, 153.6, 139.1, 136.63, 136.60, 128.4, 127.8, 126.9, 126.7, 122.2, 122.1, 32.9, 31.7, 29.2, 29.0, 27.9, 22.6, 14.1. **HRMS (ESI):** *m/z* calcd for C19H23O2S $(M+H)^+$: 315.1418. Found: 315.1409.

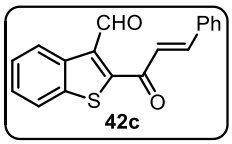
(*E*)-1-Hydroxy-2-octylidene-1*H*-benzo[*b*]cyclopenta[*d*]thiophen-3(2*H*)-one (43b).

This compound was isolated as pale yellow oil. Following the general procedure **4**, 30 mg of **42b** afforded 27.5 mg of **43b** (92% yield). R_f = 0.3 (Hexane/EtOAc = 5/1). **IR (thin film, neat):**



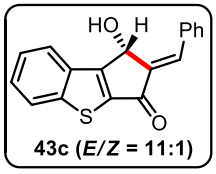
ν_{max}/cm^{-1} 3423, 2930, 2856, 1689, 1599, 1285, 1239, 1024. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.17-8.13 (m, 1H), 7.97-7.93 (m, 1H), 7.58-7.52 (m, 2H), 6.88 (td, *J* = 7.8 and 1.4 Hz, 1H), 5.90 (d, *J* = 9.3 Hz, 1H), 2.67-2.50 (m, 2H), 2.03 (d, *J* = 10.4 Hz, 1H), 1.63-1.54 (m, 3H), 1.45-1.26 (m, 7H), 0.91 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 184.7, 159.2, 148.0, 144.6, 142.0, 140.8, 133.3, 128.3, 125.5, 124.6, 124.3, 66.8, 31.7, 29.4, 29.1, 29.0, 28.7, 22.6, 14.1. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{23}O_2S$ $(M+H)^+$: 315.1418. Found: 315.1410.

2-Cinnamoylbenzo[*b*]thiophene-3-carbaldehyde (42c).



This compound was prepared by following the general procedure **1** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2924, 2854, 1673, 1652, 1593, 1498, 1087, 758. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.77 (s, 1H), 8.84-8.81 (m, 1H), 7.96-7.94 (m, 1H), 7.93 (d, *J* = 15.6 Hz, 1H), 7.70-7.68 (m, 2H), 7.61-7.58 (m, 2H), 7.51-7.47 (m, 3H), 7.43 (d, *J* = 15.6 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 188.0, 184.4, 150.3, 147.4, 139.1, 138.8, 136.6, 133.9, 131.5, 129.1(2C), 128.9(2C), 128.0, 127.0, 126.8, 124.0, 122.3. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{13}O_2S$ $(M+H)^+$: 293.0636. Found: 293.0659.

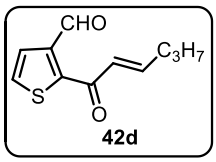
(*R*,*E*)-2-Benzylidene-1-hydroxy-1*H*-benzo[*b*]cyclopenta[*d*]thiophen-3(2*H*)-one (43c).



This compound was isolated as pale yellow solid. Following the general procedure **5**, 30 mg of **42c** afforded 27.6 mg of **43c** (92% yield). M.P = 121-122 ^{o}C. R_f = 0.2 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3333, 2926, 1673, 1620, 1017, 919, 742. **^{1}H-NMR (400 MHz, $(CD_3)_2SO$):** δ 8.25-8.20 (m, 2H), 8.06 (d, *J* = 7.2 Hz, 2H), 7.66-7.59 (m, 2H), 7.55-7.46 (m, 3H), 7.45 (s, 1H), 6.24 (d, *J* = 9.8 Hz, 1H), 6.17-6.13 (m, 1H). **^{13}C-NMR (100 MHz, $(CD_3)_2SO$):** δ 186.0, 162.4, 147.4, 142.8, 141.7, 134.1, 133.8, 133.7, 132.3(2C), 130.4, 129.2(2C), 129.1, 126.2, 125.4, 125.2, 65.8. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{13}O_2S$ $(M+H)^+$: 293.0636. Found: 293.0621.

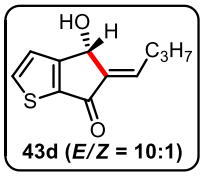
Optical rotation: $[\alpha]_D^{22}$ +37.9 (*c* 0.10, $CHCl_3$) for a sample with *ee* 98%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AS Column (96:4 *n*-Hexane/2-Propanol, 0.8 mL/min, 254 nm, τ_{major} = 39.2 min, τ_{minor} = 45.1 min).

(*E*)-2-(Hex-2-enoyl)thiophene-3-carbaldehyde (42d).



This compound was prepared by following the general procedure **1** and isolated as pale yellow oil. R_f = 0.5 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2921, 2854, 1673, 1648, 1611, 1366, 733. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.57 (s, 1H), 7.67 (d, *J* = 5,1 Hz, 1H), 7.50 (dd, *J* = 5.1 and 0.8 Hz, 1H), 7.20 (dt, *J* = 15.2 and 7.0 Hz, 1H), 6.73 (dt, *J* = 15.2 and 1.5 Hz, 1H), 2.34 (dq, *J* = 7.3 and 1.5 Hz, 2H), 1.59 (sextet, *J* = 7.3 Hz, 2H), 1.00 (t, *J* = 7.3 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 187.3, 182.7, 151.9, 146.6, 144.5, 129.4, 128.5, 127.6, 34.7, 21.3, 13.7. **HRMS (ESI):** *m/z* calcd for $C_{11}H_{13}O_2S$ $(M+H)^+$: 209.0636. Found: 209.0618.

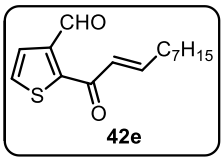
(*R*,*E*)-5-Butylidene-4-hydroxy-4*H*-cyclopenta[*b*]thiophen-6(5*H*)-one (43d).



This compound was isolated as Pale yellow oil. Following the general procedure **5**, 20 mg of **42d** afforded 18.4 mg of **43d** (92% yield). R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3370, 2913, 1673, 1629, 1445, 1300, 1024, 786. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.89 (d, *J* = 4.8 Hz, 1H), 7.28 (d, *J* = 4.8 Hz, 1H), 6.78 (t, *J* = 7.8 Hz, 1H), 5.60 (s, 1H), 2.57-2.40 (m, 2H), 1.77-1.52 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 183.6, 164.2, 144.0, 143.1, 140.6, 140.2, 123.3, 66.4, 30.8, 21.9, 14.0. **HRMS (ESI):** *m/z* calcd for $C_{11}H_{13}O_2S$ $(M+H)^+$: 209.0636. Found: 209.0625.

Optical rotation: $[\alpha]_D^{22}$ +24.1 (*c* 0.07, $CHCl_3$) for a sample with *ee* 91%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H Column (95:5 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 17.8 min, τ_{minor} = 13.1 min).

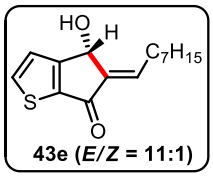
(*E*)-2-(Dec-2-enoyl)thiophene-3-carbaldehyde (42e).



This compound was prepared by following the general procedure **1** and isolated as pale yellow oil. R_f = 0.5 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2943, 2879, 1677, 1654, 1621, 1429, 1024, 733. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.56 (s, 1H), 7.67 (d, *J* = 5.1 Hz, 1H), 7.50 (dd, *J* = 5.1 and 0.8 Hz, 1H), 7.20 (dt, *J* = 15.2 and 7.0 Hz, 1H), 6.73 (dt, *J* = 15.2 and 1.5 Hz, 1H), 2.35 (qd, *J* = 7.3 and 1.5 Hz, 2H), 1.56-1.54 (m, 2H), 1.38-1.29 (m, 8H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C-NMR (100 MHz,**

$CDCl_3$): δ 187.3, 182.7, 152.2, 146.6, 144.5, 129.4, 128.4, 127.4, 32.8, 31.7, 29.2, 29.0, 28.0, 22.6, 14.0. **HRMS (ESI)**: *m/z* calcd for $C_{15}H_{21}O_2S$ $(M+H)^+$: 265.1262. Found: 265.1259.

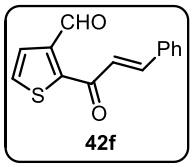
(*R*,*E*)-4-Hydroxy-5-octylidene-4*H*-cyclopenta[*b*]thiophen-6(5*H*)-one (43e).



This compound was isolated as pale yellow oil. Following the general procedure **5**, 20 mg of **42e** afforded 18.4 mg of **43e** (92% yield). R_f = 0.2 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3380, 2927, 1670, 1629, 1423, 934, 786. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.90 (d, *J* = 4.8 Hz, 1H), 7.29 (d, *J* = 4.8 Hz, 1H), 6.81-6.77 (m, 1H), 5.61 (d, *J* = 6.9 Hz, 1H), 2.59-2.43 (m, 2H), 2.33 (d, *J* = 7.4 Hz, 1H), 1.61-1.50 (m, 2H), 1.46-1.25 (m, 8H), 0.89 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 183.6, 164.1, 144.1, 142.9, 140.9, 140.2, 123.3, 66.5, 31.7, 29.4, 29.1, 28.9, 28.6, 22.6, 14.1. **HRMS (ESI):** *m/z* calcd for $C_{15}H_{21}O_2S$ $(M+H)^+$: 265.1262. Found: 265.1262.

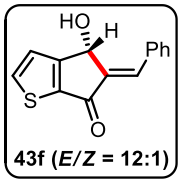
Optical rotation: $[\alpha]_D^{22}$ +57.5 (*c* 0.10, $CHCl_3$) for a sample with *ee* 91%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H Column (95:5 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 18.0 min, τ_{minor} = 12.3 min).

2-Cinnamoylthiophene-3-carbaldehyde (42f).



This compound was prepared by following the general procedure **1** and isolated as pale yellow solid. M.P = 91-92 °C. R_f = 0.4 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2927, 2855, 1679, 1652, 1593, 1423, 1190, 762. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.65 (s, 1H), 7.92 (d, *J* = 15.4 Hz, 1H), 7.72 (d, *J* = 5.1 Hz, 1H), 7.69-7.65 (m, 2H), 7.55 (dd, *J* = 5.1 and 0.8 Hz, 1H), 7.48-7.47 (m, 3H), 7.36 (d, *J* = 15.4 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 187.4, 182.4, 146.9, 146.3, 144.6, 134.1, 131.3, 129.5, 129.1(2C), 128.8(2C), 128.7, 123.2. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{11}O_2S$ $(M+H)^+$: 243.0480. Found: 243.0456.

(*R*,*E*)-5-Benzylidene-4-hydroxy-4*H*-cyclopenta[*b*]thiophen-6(5*H*)-one (43f).

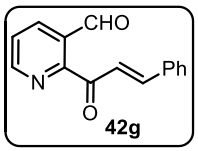


This compound was isolated as Pale yellow solid. Following the general procedure **5**, 20 mg of **42f** afforded 18.4 mg of **43f** (92% yield). M.P = 147-148 °C. R_f = 0.2 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3372, 2920, 1682, 1624, 1430, 1127, 922, 778. **^{1}H-NMR (400 MHz, $(CD_3)_2CO$):** δ 8.22 (d, *J* = 4.7 Hz, 1H),

8.06 (d, *J* = 7.3 Hz, 2H), 7.53-7.44 (m, 4H), 7.43 (d, *J* = 4.8 Hz, 1H), 5.92 (d, *J* = 8.8 Hz, 1H), 5.13 (d, *J* = 8.9 Hz, 1H). **^{13}C-NMR (100 MHz, $(CD_3)_2CO$):** δ 183.8, 165.9, 143.0, 142.1, 140.3, 134.2, 133.8, 131.7(2C), 129.7, 128.6(2C), 123.8, 65.9. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{11}O_2S$ $(M+H)^+$: 243.0479. Found: 243.0468.

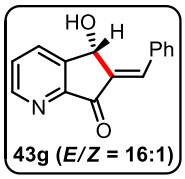
Optical rotation: $[\alpha]_D^{22}$ +124.3 (*c* 0.23, $CHCl_3$) for a sample with *ee* 97%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H Column (95:5 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 36.0 min, τ_{minor} = 28.6 min).

2-Cinnamoylnicotinaldehyde (42g).



This compound was prepared by following the general procedure **3** and isolated as a colorless solid. M.P = 78-79 °C. R_f = 0.3 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2926, 2852, 1696, 1671, 1600, 1575, 1333, 1033, 749. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.58 (d, *J* = 0.6 Hz, 1H), 8.92 (dd, *J* = 4.7 and 1.7 Hz, 1H), 8.30 (dd, *J* = 7.8 and 1.8 Hz, 1H), 8.11 (d, *J* = 16.0 Hz, 1H), 7.96 (d, *J* = 16.0 Hz, 1H), 7.75 (dd, *J* = 6.9 and 2.9 Hz, 2H), 7.65 (ddd, *J* = 7.8, 4.7 and 0.6 Hz, 1H), 748-7.45 (m, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 190.9, 165.6, 156.5, 139.4, 134.6, 134.5, 132.2, 130.3, 130.1, 129.1, 125.3, 117.5, 110.1, 67.6, 56.3. **HRMS (ESI):** *m/z* calcd for $C_{15}H_{12}NO_2$ $(M+H)^+$: 238.0868. Found: 243.0873.

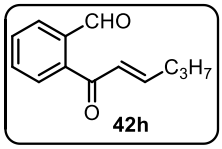
(*S*,*E*)-6-Benzylidene-5-hydroxy-5*H*-cyclopenta[*b*]pyridin-7(6*H*)-one (43g).



This compound was isolated as pale yellow solid. Following the general procedure **5**, 15 mg of **42g** afforded 13.8 mg of **43g** (92% yield). M.P = 176-177 °C. R_f = 0.2 (Hexane/EtOAc = 1/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3395, 2925, 2853, 1712, 1627, 1546, 1405, 1298, 947, 750. **^{1}H-NMR (400 MHz, $(CD_3)_2SO$):** δ 8.86 (dd, *J* = 4.5 and 1.3 Hz, 1H), 8.27 (dd, *J* = 7.8 and 1.1 Hz, 1H), 8.10-8.08 (m, 2H), 7.74 (dd, *J* = 7.8 and 4.6 Hz, 1H), 7.65 (d, *J* = 1.3 Hz, 1H), 7.56-7.50 (m, 3H), 6.14 (d, *J* = 9.0 Hz, 1H), 5.90 (d, *J* = 9.0 Hz, 1H). **^{13}C-NMR (100 MHz, $(CD_3)_2SO$):** δ 192.0, 153.8, 152.5, 148.7, 137.6, 137.3, 135.6, 134.1, 132.6(2C), 130.9, 129.2(2C), 128.9, 65.9. **HRMS (ESI):** *m/z* calcd for $C_{15}H_{12}NO_2$ $(M+H)^+$: 238.0868. Found: 238.0862.

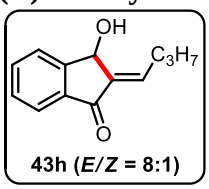
Optical rotation: $[\alpha]_D^{22}$ +136.0 (*c* 0.17, DMSO) for a sample with *ee* 99%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AS Column (85:15 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 47.9 min, τ_{minor} = 37.5 min).

(*E*)-2-(Hex-2-enoyl)benzaldehyde (42h).



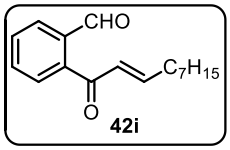
This compound was prepared by following the general procedure **3** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2950, 2937, 2855, 1697, 1657, 1623, 1449, 737. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.12 (s, 1H), 7.98 (dd, *J* = 7.5 and 1.4 Hz, 1H), 7.69-7.61 (m, 2H), 7.57-7.55 (m, 1H), 6.74 (td, *J* = 15.8 and 6.8 Hz, 1H), 6.60 (td, *J* = 15.8 and 1.3 Hz, 1H), 2.31-2.25 (m, 2H), 1.57-1.47 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.8, 191.0, 152.9, 141.7, 135.4, 133.1, 130.7, 130.4, 129.3, 128.4, 34.8, 21.2, 13.7. **HRMS (ESI):** *m/z* calcd for $C_{13}H_{15}O_2$ $(M+H)^+$: 203.1072. Found: 203.1083.

(*E*)-2-Butylidene-3-hydroxy-2,3-dihydro-1*H*-inden-1-one (43h).



This compound was isolated as pale yellow oil. Following the general procedure **4**, 25 mg of **42h** afforded 24 mg of **43h** (94% yield). R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3398, 2923, 2850, 1694, 1643, 1606, 1445, 1105, 937. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.77-7.74 (m, 1H), 7.72-7.65 (m, 1H), 7.52-7.48 (m, 1H), 7.00-6.96 (m, 1H), 5.68 (s, 1H), 2.64-2.47 (m, 2H), 2.25 (s, 1H), 1.67-1.53 (m, 2H), 1.02 (t, *J* = 7.3 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 191.6, 151.3, 143.0, 139.6, 137.5, 135.2, 129.6, 126.0, 123.7, 68.7, 31.3, 21.9, 14.0. **HRMS (ESI):** *m/z* calcd for $C_{13}H_{13}O$ $(M-OH)^+$: 185.0966. Found: 185.0982.

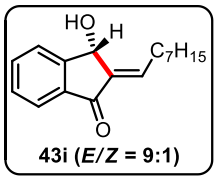
(*E*)-2-(dec-2-enoyl)benzaldehyde (42i).



This compound was prepared by following the general procedure **3** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2947, 2930, 2859, 1695, 1660, 1623, 1443, 737. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.12 (s, 1H), 7.98 (dd, *J* = 7.4 and 1.5 Hz, 1H), 7.69-7.60 (m, 2H), 7.57-7.55 (m, 1H), 6.74 (td, *J* = 15.8 and 6.8 Hz, 1H), 6.59 (td, *J* = 15.8 and 1.2 Hz, 1H), 2.32-2.26 (m, 2H), 1.51-1.44 (m, 2H), 1.30-1.28 (m, 8H), 0.89 (t, *J* = 6.8 Hz, 3H). **^{13}C-NMR (100 MHz,**

$CDCl_3$): δ 194.8, 191.0, 153.3, 141.7, 135.4, 133.1, 130.7, 130.2, 129.3, 128.3, 32.8, 31.6, 29.1, 29.0, 27.9, 22.6, 14.1. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{23}O_2$ $(M+H)^+$: 259.1698. Found: 259.1714.

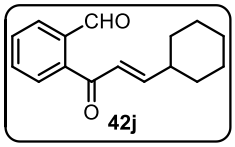
(*S*,*E*)-3-Hydroxy-2-octylidene-2,3-dihydro-1*H*-inden-1-one (43i).



This compound was isolated as pale yellow oil. Following the general procedure **5**, 23 mg of **42i** afforded 21.4 mg of **43i** (93% yield). R_f = 0.3 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3402, 2922, 2854, 1689, 1643, 1603, 1258, 753. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.79-7.73 (m, 2H), 7.71-7.65 (m, 1H), 7.51-7.47 (m, 1H), 6.98 (td, *J* = 7.8 and 1.7 Hz, 1H), 5.68 (d, *J* = 7.6 Hz, 1H), 2.64-2.48 (m, 2H), 2.28 (d, *J* = 8.3 Hz, 1H), 1.63-1.48 (m, 2H), 1.43-1.27 (m, 8H), 0.90 (t, *J* = 7.0 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 191.6, 151.3, 143.4, 139.4, 137.5, 135.2, 129.6, 126.0, 123.7, 68.7, 31.7, 29.5, 29.4, 29.1, 28.6, 22.6, 14.1. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{23}O_2$ $(M+H)^+$: 259.1698. Found: 259.1698.

Optical rotation: $[\alpha]_D^{22}$ +18.0 (*c* 0.17, $CHCl_3$) for a sample with *ee* 98%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AS Column (95:5 *n*-Hexane/2-Propanol, 0.9 mL/min, 254 nm, τ_{major} = 36.0 min, τ_{minor} = 28.6 min).

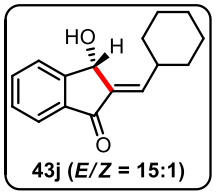
(*E*)-2-(3-Cyclohexylacryloyl)benzaldehyde (42j).



This compound was prepared by following the general procedure **3** and isolated as colorless oil. R_f = 0.5 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2942, 2927, 2872, 1696, 1662, 1620, 1427, 972, 737. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.12 (s, 1H), 7.99-7.97 (m, 1H), 7.68-7.61 (m, 2H), 7.57-7.55 (m, 1H), 6.70 (dd, *J* = 16.0 and 6.4 Hz, 1H), 6.55 (dd, *J* = 16.0 and 1.0 Hz, 1H), 2.25-2.20 (m, 1H), 1.81-1.71 (m, 5H), 1.34-1.12 (m, 5H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 195.1, 191.1, 157.9, 141.8, 135.4, 133.1, 130.7, 129.2, 128.4, 127.8, 41.0, 31.5(2C), 25.8, 25.6(2C). **HRMS (ESI):** *m/z* calcd for $C_{16}H_{19}O_2$ $(M+H)^+$: 243.1385. Found: 243.1372.

(*S*,*E*)-2-(Cyclohexylmethylene)-3-hydroxy-2,3-dihydro-1*H*-inden-1-one (43j).

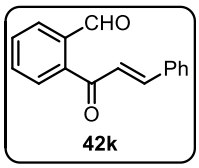
This compound was isolated as colorless solid. Following the general procedure **5**, 25 mg of **42j** afforded 24.3 mg of **43j** (97% yield). M.P = 110-111 ^oC. R_f = 0.3 (Hexane/EtOAc = 5/1). **IR**



(thin film, neat): ν_{max}/cm^{-1} 3400, 2926, 2851, 1698, 1650, 1606, 1448, 1258, 1105, 926, 747. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.74 (t, *J* = 7.2 Hz, 2H), 7.70-7.65 (m, 1H), 7.48-7.45 (m, 1H), 6.81 (dd, *J* = 10.5 and 1.6 Hz, 1H), 5.68 (s, 1H), 2.86-2.78 (m, 1H), 2.24 (br s, 1H), 1.82-1.73 (m, 5H), 1.42-1.18 (m, 5H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.3, 151.3, 147.8, 137.6, 137.5, 135.2, 129.6, 126.0, 123.6, 68.6, 38.4, 32.1, 31.8, 25.8, 25.4, 25.3. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{17}O$ $(M\text{-}OH)^+$: 225.1279. Found: 225.1268.

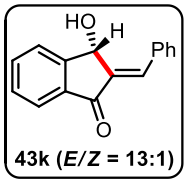
Optical rotation: $[\alpha]_D^{22}$ +15.5 (*c* 0.33, $CHCl_3$) for a sample with *ee* 94%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AS Column (95:5 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 23.1 min, τ_{minor} = 31.9 min).

2-Cinnamoylbenzaldehyde (42k).



This compound was prepared by following the general procedure **3** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2927, 2851, 1698, 1660, 1621, 1574, 1340, 1118, 737. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.19 (s, 1H), 8.04-8.01 (m, 1H), 7.72-7.67 (m, 3H), 7.59-7.57 (m, 2H), 7.50 (d, *J* = 16.1 Hz, 1H), 7.44-7.41 (m, 3H), 7.25 (d, *J* = 16.1 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.3, 191.1, 147.0, 141.7, 135.5, 134.1, 133.3, 131.1, 131.0, 129.6, 129.0(2C), 128.6(2C), 128.4, 125.9. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{13}O_2$ $(M+H)^+$: 235.0759. Found: 235.0750.

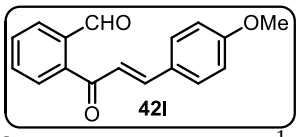
(*S*,*E*)-2-Benzylidene-3-hydroxy-2,3-dihydro-1*H*-inden-1-one (43k).



This compound was isolated as colorless solid. Following the general procedure **5**, 25 mg of **42k** afforded 24 mg of **43k** (95% yield). M.P = 187-188 ^{o}C. R_f = 0.2 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3425, 2922, 2880, 1696, 1626, 1275, 1092, 750. **^{1}H-NMR (400 MHz, $(CD_3)_2CO$):** δ 8.14-8.11 (m, 2H), 7.89-7.86 (m, 1H), 7.81-7.77 (m, 2H), 7.62-7.59 (m, 2H), 7.55-7.46 (m, 3H), 5.96 (dd, *J* = 9.0 and 1.4 Hz, 1H), 5.03 (d, *J* = 9.1 Hz, 1H). **^{13}C-NMR (100 MHz, $(CD_3)_2CO$):** δ. 191.9, 152.8, 138.4, 136.9, 135.8, 135.1, 134.5, 132.0(2C), 129.9, 129.3, 128.7(2C), 126.4, 122.8, 68.0. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{11}O$ $(M\text{-}OH)^+$: 219.0809. Found: 219.0804.

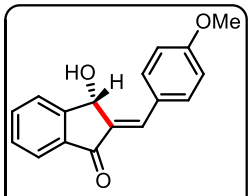
Optical rotation: $[\alpha]_D^{22}$ +130.3 (*c* 0.1, $CHCl_3$) for a sample with *ee* 98%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H Column (95:5 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 23.6 min, τ_{minor} = 22.3 min).

(*E*)-2-(3-(4-Methoxyphenyl)acryloyl)benzaldehyde (42l).



This compound was prepared by following the general procedure **3** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2948, 2852, 1689, 1650, 1604, 1574, 1442, 1142, 766. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.20 (s, 1H), 8.04-8.02 (m, 1H), 7.71-7.67 (m, 3H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 16.0 Hz, 1H), 7.13 (d, *J* = 16.0 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.3, 191.2, 162.1, 147.2, 142.2, 135.4, 133.2, 130.8(2C), 130.5, 129.2, 128.3, 126.8, 123.7, 114.5(2C), 55.4. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{15}O_3$ $(M+H)^+$: 267.1021. Found: 267.1054.

(*S*,*E*)-3-Hydroxy-2-(4-methoxybenzylidene)-2,3-dihydro-1*H*-inden-1-one (43l).



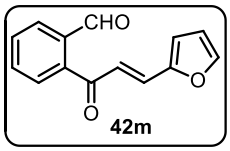
43l (*E*/*Z* = 10:1)

This compound was isolated as pale yellow solid. Following the general procedure **5**, 20 mg of **42l** afforded 18.4 mg of **43l** (92% yield). M.P = 164-166 °C. R_f = 0.2 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3389, 2930, 2850, 1685, 1634, 1600, 1434, 1258, 1105, 786. **^{1}H-NMR (400 MHz, $(CD_3)_2CO$):** δ 8.10 (d, *J* = 8.8 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.79-7.75 (m, 2H), 7.59-7.55 (m, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 5.91 (d, *J* = 8.8 Hz, 1H), 4.91 (d, *J* = 9.2 Hz, 1H), 3.91 (s, 3H). **^{13}C-NMR (100 MHz, $(CD_3)_2CO$):** δ 191.8, 161.4, 152.7, 137.2, 135.9, 135.8, 134.8, 134.0(2C), 129.2, 127.1, 126.3, 122.7, 114.2(2C), 68.1, 54.9. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{14}O_3$ $(M)^+$: 266.0942. Found: 266.0936.

Optical rotation: $[\alpha]_D^{22}$ +145.0 (*c* 0.08, $CHCl_3$) for a sample with *ee* 98%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AD-H Column (90:10 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 28.9 min, τ_{minor} = 30.7 min).

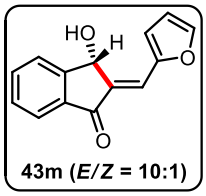
(*E*)-2-(3-(Furan-2-yl)acryloyl)benzaldehyde (42m).

This compound was prepared by following the general procedure **3** and isolated as pale brown solid. M.P = 91-92 °C. R_f = 0.2 (Hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2925,



2855, 1695, 1596, 1466, 1285, 1015, 737. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.21 (s, 1H), 8.01-7.99 (m, 1H), 7.71-7.65 (m, 3H), 7.57 (d, *J* = 1.4 Hz, 1H), 7.33 (d, *J* = 15.6 Hz, 1H), 7.16 (d, *J* = 15.6 Hz, 1H), 6.75 (d, *J* = 3.5 Hz, 1H), 6.54 (dd, *J* = 3.5 and 1.8 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 193.3, 191.3, 150.9, 145.6, 141.7, 135.7, 133.2, 132.4, 131.0, 129.3, 128.4, 122.7, 117.2, 112.9. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{11}O_3$ $(M+H)^+$: 227.0708. Found: 227.0709.

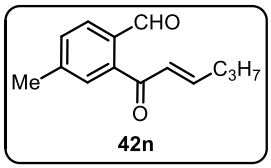
(*S*,*E*)-2-(Furan-2-ylmethylene)-3-hydroxy-2,3-dihydro-1*H*-inden-1-one (43m).



This compound was isolated as pale brown solid. Following the general procedure **5**, 20 mg of **42m** afforded 18 mg of **43m** (90% yield). M.P = 150-151 °C. R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3378, 2923, 2852, 1693, 1626, 1467, 1021, 752. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.90 (d, *J* = 7.7 Hz, 1H), 7.84 (dq, *J* = 7.6 and 0.8 Hz, 1H), 7.76-7.72 (m, 2H), 7.58-7.53 (m, 1H), 7.50 (d, *J* = 1.5 Hz, 1H), 6.98 (d, *J* = 3.5 Hz, 1H), 6.66 (dd, *J* = 3.5 Hz, 1H), 6.05 (d, *J* = 3.7 Hz, 1H), 3.38 (d, *J* = 4.6 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.0, 157.2, 150.4, 146.1, 137.9, 135.7, 135.2, 129.6, 126.3, 123.6, 121.2, 118.9, 113.3, 68.8. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{11}O_3$ $(M+H)^+$: 227.0708. Found: 227.0695.

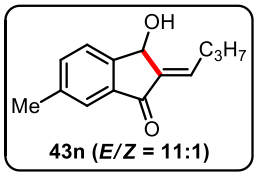
Optical rotation: $[\alpha]_D^{22}$ +189.0 (*c* 0.07, $CHCl_3$) for a sample with *ee* 95%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H Column (97:3 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 28.7 min, τ_{minor} = 32.5 min).

(*E*)-2-(Hex-2-enoyl)-4-methylbenzaldehyde (42n).



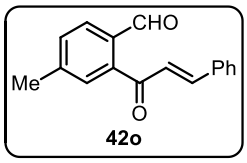
This compound was prepared by following the general procedure **3** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2961, 2931, 2872, 1694, 1660, 1616, 1305, 979, 825. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.04 (s, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.46-7.40 (m, 1H), 7.31-7.30 (m, 1H), 6.70 (td, *J* = 16.0 and 6.8 Hz, 1H), 6.55 (td, *J* = 16.0 and 1.4 Hz, 1H), 2.46 (s, 3H), 2.29-2.23 (m, 2H), 1.54-1.47 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 195.4, 190.6, 152.7, 144.5, 142.0, 132.8, 131.2, 130.7, 129.6, 128.8, 34.7, 21.7, 21.2, 13.7. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{17}O_2$ $(M+H)^+$: 217.1228. Found: 217.1221.

(*E*)-2-Butylidene-3-hydroxy-6-methyl-2,3-dihydro-1*H*-inden-1-one (43n).



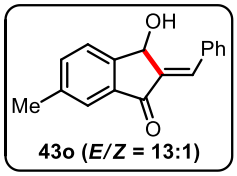
This compound was isolated as colorless oil. Following the general procedure **4**, 20 mg of **42n** afforded 18.4 mg of **43n** (92% yield). R_f = 0.2 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3405, 2960, 2929, 2872, 1700, 1651, 1489, 1285, 1153, 783. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.64 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 4.5 Hz, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 6.97-6.92 (m, 1H), 5.64 (s, 1H), 2.62-2.47 (m, 2H), 2,43 (s, 3H), 2.26 (br s, 1H), 1.61-1.58 (m, 2H), 1.01 (t, *J* = 7.3 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 191.8, 148.8, 142.6, 140.1, 139.8, 137.7, 136.4, 125.7, 123.7, 68.5, 31.2, 21.9, 21.3, 14.0. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{15}O$ $(M\text{-}OH)^+$: 199.1122. Found: 199.1113.

2-Cinnamoyl-4-methylbenzaldehyde (42o).



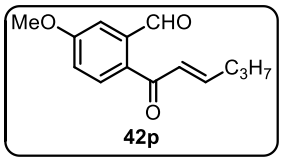
This compound was prepared by following the general procedure **3** and isolated as pale yellow solid. M.P = 190-191 ^{o}C. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3059, 2955, 2858, 1693, 1652, 1598, 1574, 1332, 1168, 1031, 772. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.12 (s, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.59-7.58 (m, 1H), 7.48-7.46 (m, 2H), 7.44-7.41 (m, 4H), 7.21 (d, *J* = 16.1 Hz, 1H), 2.51 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.9, 190.7, 146.8, 144.6, 141.9, 134.2, 132.9, 131.5, 131.0, 129.9, 129.0(2C), 128.9, 128.6(2C), 126.3, 21.8. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{15}O_2$ $(M+H)^+$: 251.1072. Found: 251.1066.

(*E*)-2-Benzylidene-3-hydroxy-6-methyl-2,3-dihydro-1*H*-inden-1-one (43o).



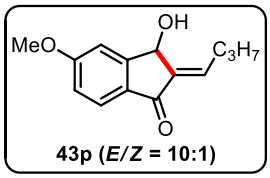
This compound was isolated as colorless solid. Following the general procedure **4**, 22 mg of **42o** afforded 19.5 mg of **43o** (89% yield). M.P = 189-190 ^{o}C. R_f = 0.3 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3484, 2925, 1686, 1620, 1287, 1158, 1014, 785. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.96-7.93 (m, 2H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.58-7.55 (m, 2H), 7.54-7.43 (m, 4H), 5.91 (d, *J* = 6.5 Hz, 1H), 2.62 (d, *J* = 9.0 Hz, 1H), 2.42 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.9, 149.1, 140.0, 137.6, 137.5, 137.1, 136.6, 133.9, 131.9(2C), 130.4, 128.9(2C), 125.7, 123.7, 68.5, 21.3. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{13}O$ $(M\text{-}OH)^+$: 233.0966. Found: 233.0957.

(*E*)-2-(Hex-2-enoyl)-5-methoxybenzaldehyde (42p).



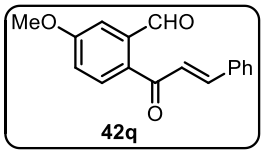
This compound was prepared by following the general procedure **3** and isolated as pale yellow oil. R_f = 0.5 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2961, 2929, 2872, 1695, 1660, 1613, 1463, 1281, 1114, 978. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.18 (s, 1H), 7.65 (dd, *J* = 8.5 and 2.0 Hz, 1H), 7.43-7.42 (m, 1H), 7.122 (dt, *J* = 8.5 and 2.8 Hz, 1H), 6.92-6.84 (m, 1H), 6.68 (dd, *J* = 15.7 and 1.1 Hz, 1H), 3.91 (d, *J* = 3.0 Hz, 3H), 2.29 (q, *J* = 7.4 Hz, 2H), 1.54 (qd, *J* = 7.4 and 2.5 Hz, 2H), 0.96 (td, *J* = 7.4 and 2.8 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.3, 191.5, 161.8, 151.8, 138.7, 133.9, 131.0, 129.0, 118.8, 112.4, 55.7, 34.8, 21.3, 13.7. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{17}O_3$ $(M+H)^+$: 233.1177. Found: 233.1159.

(*S*,*E*)-2-Butylidene-3-hydroxy-5-methoxy-2,3-dihydro-1*H*-inden-1-one (43p).



This compound was isolated as colorless solid. Following the general procedure **4**, 20 mg of **42p** afforded 18.8 mg of **43p** (94% yield). M.P = 97-99 ^{o}C. R_f = 0.2 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3385, 2961, 2932, 2872, 1693, 1649, 1599, 1341, 1289, 1095, 797. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.74-7.72 (m, 1H), 7.18 (d, *J* = 2.1 Hz, 1H), 7.02-6.99 (m, 1H), 6.92-6.87 (m, 1H), 5.60 (s, 1H), 3.93 (s, 3H), 2.62-2.45 (m, 2H), 2.20 (br s, 1H), 1.69-1.59 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 190.1, 165.6, 154.3, 141.5, 140.0, 130.8, 125.6, 117.6, 108.9, 68.7, 55.8, 31.1, 22.0, 14.0. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{17}O_3$ $(M+H)^+$: 233.1177. Found: 233.1184.

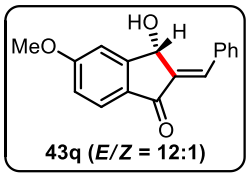
2-Cinnamoyl-5-methoxybenzaldehyde (42q).



This compound was prepared by following the general procedure **3** and isolated as pale yellow solid. M.P = 129-130 ^{o}C. R_f = 0.5 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2976, 2934, 1693, 1661, 1601, 1334, 1238, 1015, 769. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.27 (d, *J* = 0.6 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.66 (d, *J* = 15.9 Hz, 1H), 7.63-7.61 (m, 2H), 7.49 (dd, *J* = 2.6 and 1.1 Hz, 1H), 7.45-7.43 (m, 3H), 7.34 (d, *J* = 15.9 Hz, 1H), 7.18 (ddd, *J* = 8.5, 2.7 and 0.8 Hz, 1H), 3.95 (d, *J* = 1.0 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 191.7, 191.5, 162.0, 138.9, 134.3, 134.0, 131.0,

130.9, 129.0(2C), 128.5(2C), 124.6, 118.9, 112.6, 55.8. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{15}O_3$ $(M+H)^+$: 267.1021. Found: 267.1032.

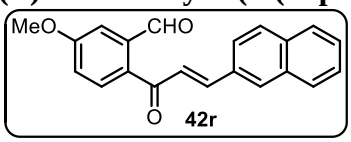
(*S*,*E*)-2-Benzylidene-3-hydroxy-5-methoxy-2,3-dihydro-1*H*-inden-1-one (43q).



This compound was isolated as pale yellow solid. Following the general procedure **5**, 20 mg of **42q** afforded 18.6 mg of **43q** (93% yield). M.P = 164-165 ^oC. R_f = 0.2 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2955, 2858, 1685, 1611, 1369, 767, 733. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.05-8.03 (m, 2H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.50-7.46 (m, 4H), 7.30 (d, *J* = 2.3 Hz, 1H), 7.12 (dd, *J* = 8.5 and 2.3 Hz, 1H), 6.03 (d, *J* = 8.7 Hz, 1H), 5.78 (d, *J* = 8.5 Hz, 1H), 3.92 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 190.9, 165.6, 156.5, 139.4, 134.6, 134.5, 132.2(2C), 130.3, 130.1, 129.1(2C), 125.3, 117.5, 110.1, 67.6, 56.3. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{15}O_3$ $(M+H)^+$: 267.1021. Found: 267.1025.

Optical rotation: $[\alpha]_D^{22}$ +100.1 (*c* 0.27, $CHCl_3$) for a sample with *ee* 96%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AS Column (85:15 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 39.1 min, τ_{minor} = 22.9 min).

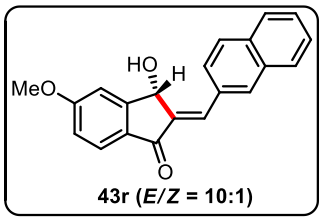
(*E*)-5-Methoxy-2-(3-(naphthalen-2-yl)acryloyl)benzaldehyde (42r).



This compound was prepared by following the general procedure **3** and isolated as pale brown solid. M.P = 135-136 ^oC. R_f = 0.4 (Hexane/ EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3056, 2980, 1689, 1651, 1595, 1361, 1237, 1017, 815. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.30 (s, 1H), 8.01 (s, 1H), 7.90-7.77 (m, 6H), 7.58-7.54 (m, 2H), 7.52 (d, *J* = 2.6 Hz, 1H), 7.46 (d, *J* = 15.9 Hz, 1H), 7.22-7.19 (dd, *J* = 8.5 and 2.7 Hz, 1H), 3.96 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 191.7, 191.6, 162.1, 146.3, 138.9, 134.3, 134.2, 133.2, 131.8, 131.1, 131.0, 128.8, 128.7, 127.8, 127.6, 126.9, 124.7, 123.5, 118.9, 112.6, 55.8. **HRMS (ESI):** *m/z* calcd for $C_{21}H_{17}O_3$ $(M+H)^+$: 317.1177. Found: 317.1172.

(*S*,*E*)-3-Hydroxy-5-methoxy-2-(naphthalen-2-ylmethylene)-2,3-dihydro-1*H*-inden-1-one (43r).

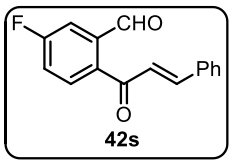
This compound was isolated as pale yellow solid. Following the general procedure **5**, 20 mg of **42r** afforded 18.8 mg of **43r** (94% yield). M.P = 56-57 ^oC. R_f = 0.2 (Hexane/ EtOAc = 5/1). **IR**



(thin film, neat): ν_{max}/cm^{-1} 2962, 2878, 1683, 1610, 1454, 1322, 737. **^{1}H-NMR (400 MHz, $(CD_3)_2SO$):** δ 8.55 (s, 1H), 8.23 (dd, *J* = 8.7 and 1.6 Hz, 1H), 8.02-7.96 (m, 3H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.63-7.58 (m, 3H), 7.34 (d, *J* = 2.3 Hz, 1H), 7.14 (dd, *J* = 8.5 and 2.3 Hz, 1H), 6.13 (d, *J* = 8.7 Hz, 1H), 5.92 (d, *J* = 8.6 Hz, 1H), 3.93 (s, 3H). **^{13}C-NMR (100 MHz, $(CD_3)_2SO$):** δ 190.9, 165.6, 156.5, 139.7, 134.7, 133.7, 133.3, 133.1, 132.3, 130.2, 129.1, 128.55, 128.5, 128.0, 127.9, 127.1, 125.3, 117.5, 110.1, 67.7, 56.3. **HRMS (ESI):** *m/z* calcd for $C_{21}H_{15}O_2$ $(M\text{-}OH)^+$: 299.1072. Found: 299.1089.

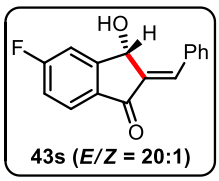
Optical rotation: $[\alpha]_D^{22}$ +14.2 (*c* 0.20, DMSO) for a sample with *ee* 92%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AS Column (85:15 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 51.3 min, τ_{minor} = 27.8 min).

2-Cinnamoyl-5-fluorobenzaldehyde (42s).



This compound was prepared by following the general procedure **3** and isolated as a colorless solid. M.P = 147-149 °C. R_f = 0.4 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2950, 2858, 1694, 1657, 1600, 1574, 1168, 737. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.20 (d, *J* = 2.6 Hz, 1H), 7.79 (dd, *J* = 8.5 and 5.0 Hz, 1H), 7.71 (dd, *J* = 8.7 and 2.7 Hz, 1H), 7.63-7.60 (m, 2H), 7.60 (d, *J* = 16.0 Hz, 1H), 7.48-7.37 (m, 3H), 7.40 (td, *J* = 8.7 and 2.6 Hz, 1H), 7.28 (d, *J* = 16.0 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.6, 189.9, 165.3, 162.8, 147.4, 138.7 (d, *J* = 7.3 Hz, 1C), 137.8 (d, *J* = 3.7 Hz, 1C), 134.0, 131.3, 131.1 (d, *J* = 8.1 Hz, 1C), 129.1(2C), 128.6(2C), 124.9, 120.0 (d, *J* = 87.5 Hz, 1C), 115.8 (d, *J* = 90.4 Hz, 1C). **^{19}F-NMR (400 MHz, $CDCl_3$):** δ -106.1. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{12}FO_2$ $(M+H)^+$: 255.0821. Found: 255.0842.

(*S*,*E*)-2-Benzylidene-5-fluoro-3-hydroxy-2,3-dihydro-1*H*-inden-1-one (43s).

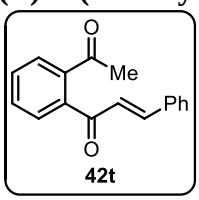


This compound was isolated as colorless solid. Following the general procedure **5**, 20 mg of **42s** afforded 18.8 mg of **43s** (96% yield). M.P = 146-147 °C. R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3438, 3064, 3028, 1686, 1619, 1592, 1480, 1282, 1089, 767. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.91 (dd, *J* = 7.4 and 2.0 Hz, 2H), 7.71 (dd, *J* = 8.4 and 5.1 Hz, 1H), 7.59 (d, *J* = 1.5 Hz, 1H), 7.50-7.45 (m, 4H), 7.15 (td, *J* = 8.6 and 2.3 Hz, 1H), 5.90 (d, *J* = 9.6 Hz, 1H), 2.93 (d, *J* = 10.0 Hz, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 191.2, 168.6, 166.0, 154.6 (d, *J* = 9.5 Hz, 1C), 138.2, 136.7, 133.4 (d, *J* = 131.2 Hz, 1C), 132.0(2C), 130.6, 129.0(2C), 126.1 (d, *J* = 10.3 Hz, 1C), 117.8 (d, *J* = 92.8 Hz, 1C), 112.9 (d, *J* = 90.4 Hz, 1C), 68.4. **^{19}F-NMR (400 MHz, $CDCl_3$):** δ -100.3. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{10}FO$ $(M\text{-}OH)^+$: 237.0715. Found: 237.0723.

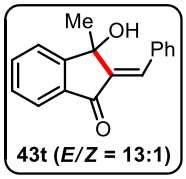
Optical rotation: $[\alpha]_D^{22}$ +121.1 (*c* 0.30, $CHCl_3$) for a sample with *ee* >99%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AS Column (85:15 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 13.4 min, τ_{minor} = 10.6 min).

(*E*)-1-(2-Acetylphenyl)-3-phenylprop-2-en-1-one (42t).



This compound was prepared by following the general procedure **3** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc =5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3062, 1682, 1650, 1597, 1490, 1263, 1019, 761. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.78-7.76 (m, 1H), 7.61-7.60 (m, 2H), 7.55-7.52 (m, 3H), 7.39-7.37 (m, 3H), 7.34 (d, *J* = 16.2 Hz, 1H), 7.13 (d, *J* = 16.4 Hz, 1H), 2.57 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 200.1, 195.9, 145.0, 140.1, 138.8, 134.4, 131.6, 130.6, 130.3, 128.9(2C), 128.7, 128.4(2C), 128.1, 126.2, 28.3. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{15}O_2$ $(M+H)^+$: 251.1072. Found: 251.1065.

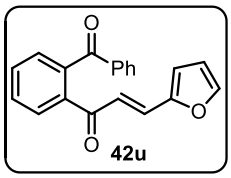
(*E*)-2-Benzylidene-3-hydroxy-3-methyl-2,3-dihydro-1*H*-inden-1-one (43t).



This compound was isolated as pale yellow solid. Following the general procedure **4**, 20 mg of **42s** afforded 18 mg of **43s** (90% yield). M.P = 147-148 ^oC. R_f = 0.3 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3376, 2923, 2853, 1693, 1621, 1465, 1232, 737. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.13 (dd, *J* = 7.9 and 1.3 Hz, 2H), 7.84-7.79 (m, 1H), 7.78-7.71 (m, 2H), 7.63 (s, 1H), 7.50-7.44 (m, 4H), 2.80 (s, 1H), 1.78 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.4, 156.7, 141.1, 137.5, 135.6, 135.2, 133.6, 132.7(2C), 130.0, 129.4, 128.6(2C), 123.7, 123.5, 74.9, 24.5. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{13}O$ $(M\text{-}OH)^+$: 233.0966. Found: 233.0968.

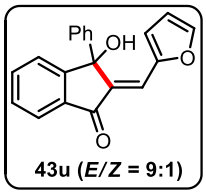
(*E*)-1-(2-Benzoylphenyl)-3-(furan-2-yl)prop-2-en-1-one (42u).

This compound was prepared by following the general procedure **3** and isolated as pale yellow solid. M.P = 177-178 ^oC. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3043, 2958, 1676, 1663, 1609, 1492, 1024, 763. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.92-7.90 (m, 1H),



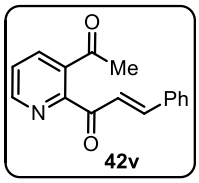
7.80-7.78 (m, 2H), 7.64-7.62 (m, 2H), 7.54-7.51 (m, 3H), 7.49-7.44 (m, 2H), 7.34 (d, *J* = 15.6 Hz, 1H), 7.20 (d, *J* = 15.6 Hz, 1H), 6.65 (*J* = 3.4 Hz, 1H), 6.49 (dd, *J* = 3.4 and 1.8 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 197.5, 190.9, 151.2, 145.2, 140.9, 138.9, 137.2, 132.9, 131.6, 131.4, 129.8, 129.5(2C), 128.7, 128.6, 128.4(2C), 120.5, 116.7, 112.7. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{15}O_3$ $(M+H)^+$: 303.1021. Found: 303.1015.

(*E*)-2-(Furan-2-ylmethylene)-3-hydroxy-3-phenyl-2,3-dihydro-1*H*-inden-1-one (43u).



This compound was isolated as pale yellow semi solid. Following the general procedure **4**, 20 mg of **42u** afforded 19 mg of **43u** (95% yield). R_f = 0.4 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3353, 2919, 2851, 1682, 1616, 1465, 1237, 752. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.63-7.52 (m, 5H), 7.46 (td, *J* = 7.2 and 1.3 Hz, 1H), 7.41 (d, *J* = 1.8 Hz, 1H), 7.30-7.26 (m, 2H), 7.22-7.18 (m, 1H), 6.82 (d, *J* = 3.5 Hz, 1H), 6.45 (dd, *J* = 3.5 and 1.8 Hz, 1H), 4.02 (s, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.4, 155.2, 150.2, 145.9, 144.5, 139.7, 135.77, 135.7, 129.2, 128.4(2C), 127.1, 125.1, 124.8(2C), 123.5, 120.6, 119.5, 113.1, 78.7. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{13}O_2$ $(M-OH)^+$: 285.0915. Found: 285.0910.

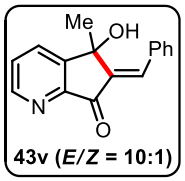
(*E*)-1-(3-Acetylpyridin-2-yl)-3-phenylprop-2-en-1-one (42v).



This compound was prepared by following the general procedure **3** and isolated as a colorless solid. M.P = 102-104 °C. R_f = 0.3 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2927, 2859, 1712, 1667, 1621, 1365, 1216, 757. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.80 (dd, *J* = 4.8 and 1.6 Hz, 1H), 8.10 (d, *J* = 16.1 Hz, 1H), 7.78 (dd, *J* = 7.8 and 1.6 Hz, 1H), 7.73-7.69 (m, 2H), 7.56 (dd, *J* = 7.7 and 4.7 H, 3H), 2.58 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 202.3, 189.9, 151.8, 149.6, 146.0, 138.9, 134.7(2C), 130.9, 129.0(2C), 128.9(2C), 126.1, 121.2, 30.4. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{14}NO_2$ $(M+H)^+$: 252.1024. Found: 252.1016.

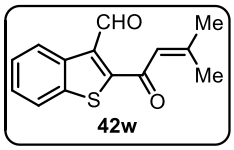
(*E*)-6-Benzylidene-5-hydroxy-5-methyl-5*H*-cyclopenta[*b*]pyridin-7(6*H*)-one (43v).

This compound was isolated as colorless solid. Following the general procedure **4**, 20 mg of **42v** afforded 18.5 mg of **43v** (92% yield) M.P = 219-220 °C. R_f = 0.2 (Hexane/EtOAc = 1/2). **IR**



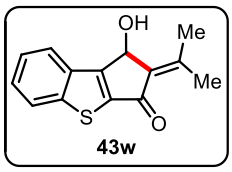
(thin film, neat): ν_{max}/cm^{-1} 3367, 2924, 2851, 1713, 1621, 1311, 764. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 8.73-8.72 (m, 1H), 8.20 (dd, *J* = 7.6 and 1.7 Hz, 2H), 7.70 (s, 1H), 7.56 (dd, *J* = 7.8 and 4.6 Hz, 1H), 7.50-7.47 (m, 3H), 3.42 (brs, 1H), 1.78 (s, 3H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 191.2, 152.4, 152.0, 151.6, 139.5, 139.3, 133.2, 133.0(2C), 132.8, 130.6, 128.7(2C), 128.6, 73.3, 24.2. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{12}NO$ (M-OH)$^+$: 234.0918. Found: 234.0903.

2-(3-Methylbut-2-enoyl)benzo[*b*]thiophene-3-carbaldehyde (42w).



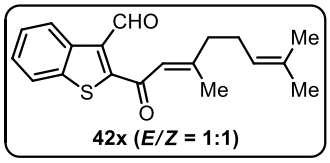
This compound was prepared by following the general procedure **1** and isolated as colorless oil. R_f = 0.5 (Hexane/EtOAc = 5/1). IR (thin film, neat): ν_{max}/cm^{-1} 2965, 2913, 1672, 1660, 1615. 1421, 1155, 733. **^{1}H-NMR** (400 MHz, CDCl$_3$): δ 10.67 (s, 1H), 8.76-8.73 (m, 1H), 7.87-7.85 (m, 1H), 7.53-7.51 (m, 2H), 6.70-6.69 (m, 1H), 2.33 (d, *J* = 0.8 Hz, 3H), 2.09 (d, *J* = 0.9 Hz, 3H). **^{13}C-NMR** (100 MHz, CDCl$_3$): δ 188.3, 184.5, 162.0, 151.9, 138.7, 136.6, 136.2, 127.7, 126.6, 122.8, 122.1, 28.4, 21.7. HRMS (ESI): *m/z* calcd for $C_{14}H_{13}O_2S$ (M+H)$^+$: 245.0636. Found: 245.0642.

1-Hydroxy-2-(propan-2-ylidene)-1*H*-benzo[*b*]cyclopenta[*d*]thiophen-3(2*H*)-one (43w).



This compound was isolated as colorless solid. Following the general procedure **4**, 20 mg of **42w** afforded 18.8 mg of **43w** (94% yield). M.P = 168-169 ^{o}C. R_f = 0.2 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3400, 2917, 1678, 1633, 1427, 1267, 1110, 743. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 8.11-8.08 (m, 1H), 7.89-7.87 (m, 1H), 7.51-7.45 (m, 2H), 5.75 (d, *J* = 8.5 Hz, 1H), 2.40 (d, *J* = 9.6 Hz, 1H), 2.34 (s, 3H), 2.21 (s, 3H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 186.2, 157.1, 153.1, 147.4, 145.7, 136.3, 133.4, 127.9, 125.3, 124.5, 124.2, 67.8, 23.8, 20.5. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{11}OS$ (M-OH)$^+$: 227.0530. Found: 227.0517.

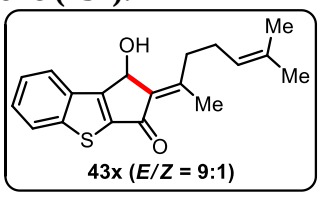
(*E*)-2-(3,7-Dimethylocta-2,6-dienoyl)benzo[*b*]thiophene-3-carbaldehyde (42x).



This compound was prepared by following the general procedure **1** and isolated as colorless oil. R_f = 0.5 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2968, 2873, 1678, 1661, 1614, 1204, 1085, 760. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 10.68 (s, 1H), 8.77-8.74 (m, 1H), 7.88-7.86 (m, 1H),

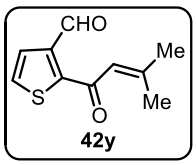
7.55-7.51 (m, 2H), 6.95-6.68 (m, 1H), 5.22-5.18 (m,1H), 2.75 (t, *J* = 8.0 Hz, 2H), 2.32 (d, *J* = 0.8 Hz, 3H), 2.37-2.24 (m, 2H), 1.74 (s, 3H), 1.66 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 188.3, 184.7, 165.6, 152.1, 138.8, 136.7, 136.1, 133.1, 127.7, 126.8, 127.7, 123.2, 122.6, 122.1, 41.7, 28.8, 25.8, 20.5, 17.8. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{21}O_2S$ $(M+H)^+$: 313.1262. Found: 313.1280.

(*E*)-1-Hydroxy-2-(6-methylhept-5-en-2-ylidene)-1*H*-benzo[*b*]cyclopenta[*d*]thiophen-3(2*H*)-one (43x).



This compound was isolated as colorless solid. Following the general procedure **4**, 30 mg of **42x** afforded 24.6 mg of **43x** (82% yield). M.P = 103-104 °C. R_f = 0.4 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3401, 2967, 2919, 2855, 1682, 1629, 1523, 1375, 1266, 1111, 743. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.10-8.07 (m, 1H), 7.88-7.85 (m, 1H), 7.50-7.46 (m, 2H), 5.75 (s, 1H), 5.23-5.11 (m, 1H), 2.95-2.88 (m, 1H), 2.78-2.50 (m, 2H), 2.20 (s, 3H), 1.69 (s, 3H), 1.65 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 185.6, 157.1, 156.1, 147.3, 145.8, 136.4, 133.4, 132.4, 127.9, 125.3, 124.4, 124.2, 123.5, 67.8, 33.6, 27.1, 25.7, 21.8, 17.6. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{19}OS$ $(M+H)^+$: 295.1156. Found: 295.1143.

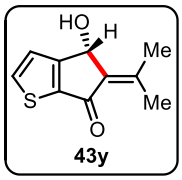
2-(3-Methylbut-2-enoyl)thiophene-3-carbaldehyde (42y).



This compound was prepared by following the general procedure **1** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2965, 2888, 1678, 1653, 1622, 1342, 1267, 737. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.58 (s, 1H), 7.61 (d, *J* = 5.1 Hz, 1H), 7.42 (dd, *J* = 5.1 and 0.8 Hz, 1H), 6.61-6.59 (m, 1H), 2.29 (d, *J* = 1.3 Hz, 3H), 2.05 (d, *J* = 1.3 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 187.6, 183.2, 160.7, 148.3, 144.0, 128.6, 128.2, 122.3, 28.5, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{10}H_{11}O_2S$ $(M+H)^+$: 195.0479. Found: 195.0481.

(*R*)-4-Hydroxy-5-(propan-2-ylidene)-4*H*-cyclopenta[*b*]thiophen-6(5*H*)-one (43y).

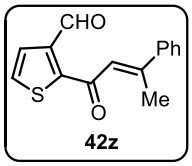
This compound was isolated as colorless solid. Following the general procedure **5**, 25 mg of **42y** afforded 22 mg of **43y** (80% yield). M.P = 138-140 °C. R_f = 0.5 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3377, 2917, 1676, 1634, 1435, 1299, 1118, 786. **^{1}H-NMR (400 MHz,**



CDCl$_3$): δ 7.80 (d, *J* = 4.8 Hz, 1H), 7.23 (d, *J* = 4.8 Hz, 1H), 5.50 (d, *J* = 7.0 Hz, 1H), 2.49 (d, *J* = 8.0 Hz, 1H), 2.30 (s, 3H), 2.14 (s, 3H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 185.1, 162.1, 153.0, 145.4, 138.8, 137.1, 123.1, 67.6, 23.8, 20.4. **HRMS (ESI):** *m/z* calcd for $C_{10}H_9OS$ $(M\text{-}OH)^+$: 177.0374. Found: 177.0372.

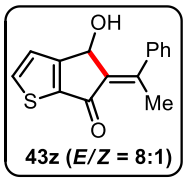
Optical rotation: $[\alpha]_D^{22}$ +8.7 (*c* 0.10, $CDCl_3$) for a sample with *ee* 80%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H Column (90:10 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 13.3 min, τ_{minor} = 9.5 min).

(*E*)-2-(3-Phenylbut-2-enoyl)thiophene-3-carbaldehyde (42z).



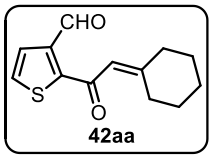
This compound was prepared by following the general procedure **1** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2930, 2856, 1680, 1657, 1594, 1433, 1196, 737. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 10.66 (s, 1H), 7.67 (d, *J* = 5.1 Hz, 1H), 7.60-7.56 (m, 2H), 7.48-7.43 (m, 4H), 7.05-7.04 (m, 1H), 2.71 (d, *J* = 1.3 Hz, 3H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 191.3, 187.5, 158.7, 144.1, 142.0, 129.8, 128.9, 128.8(2C), 128.7, 126.6(2C), 126.2, 122.7, 19.2. **HRMS (ESI):** *m/z* calcd for $C_{15}H_{13}O_2S$ $(M+H)^+$: 257.0636. Found: 257.0644.

(*E*)-4-Hydroxy-5-(1-phenylethylidene)-4*H*-cyclopenta[*b*]thiophen-6(5*H*)-one (43z).



This compound was isolated as pale yellow oil solid. Following the general procedure **4**, 15 mg of **42z** afforded 14 mg of **43z** (94% yield). R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3370, 2922, 2855 1685, 1622, 1429, 1130, 1024, 776. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 8.12 (d, *J* = 7.2 Hz, 1H), 7.85-7.83 (m, 1H), 7.51-7.47 (m, 2H), 7.42-7.37 (m, 3H), 5.65 (s, 1H), 2.71 (s, 3H) 2.05 (brs, 1H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 185.1, 161.8, 151.6, 139.2, 130.1, 129.1(2C), 128.4, 127.9, 127.2, 126.7(2C), 123.2, 65.4, 20.7. **HRMS (ESI):** *m/z* calcd for $C_{15}H_{11}OS$ $(M\text{-}OH)^+$: 239.0530. Found: 239.0543.

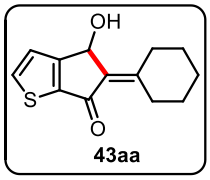
2-(2-Cyclohexylideneacetyl)thiophene-3-carbaldehyde (42aa).



This compound was prepared by following the general procedure **1** and isolated as pale yellow oil. R_f = 0.5 (Hexane/EtOAc = 4/1). **IR (thin film,**

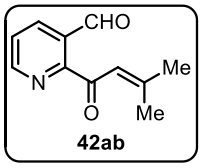
neat): ν_{max}/cm^{-1} 2943, 2876, 1670, 1656, 1619, 1119, 760. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.59 (s, 1H), 7.62 (d, *J* = 5.1 Hz, 1H), 7.43 (dd, *J* = 5.1 and 0.8 Hz, 1H), 6.51 (t, *J* = 1.0 Hz, 1H), 2.89 (t, *J* = 6.1 Hz, 2H), 2.33 (td, *J* = 6.2 and 0.9 Hz, 2H), 1.76-1.65 (m, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 187.6, 183.9, 167.2, 148.4, 143.9, 128.8, 128.2, 119.7, 38.5, 30.8, 28.8, 28.0, 26.1. **HRMS (ESI):** *m/z* calcd for $C_{13}H_{15}O_2S$ $(M+H)^+$: 235.0792. Found: 235.0801.

5-Cyclohexylidene-4-hydroxy-4*H*-cyclopenta[*b*]thiophen-6(5*H*)-one (43aa).



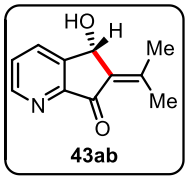
This compound was isolated as colorless solid. Following the general procedure **4**, 20 mg of **42aa** afforded 18 mg of **43aa** (90% yield). M.P = 85-87 ^{o}C. R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3372, 2923, 1679, 1630, 1449, 1298, 786. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.81 (d, *J* = 4.8 Hz, 1H), 7.24 (d, 4.8 Hz, 1H), 5.58 (d, *J* = 6.8 Hz, 1Hz), 3.14-3.09 (m, 2H), 2.63-2.57 (m, 1H), 2.54-2.47 (m, 1H), 2.02 (br s, 1H), 1.82-1.65 (m, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 185.3, 161.6, 160.8, 145.9, 138.7, 134.4, 123.1, 67.3, 33.4, 28.9, 28.6, 28.4, 26.2. **HRMS (ESI):** *m/z* calcd for $C_{13}H_{13}OS$ $(M-OH)^+$: 217.0687. Found: 217.0678.

2-(3-Methylbut-2-enoyl)nicotinaldehyde (42ab).



This compound was prepared by following the general procedure **3** and isolated as colorless oil. R_f = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2925, 2854, 1697, 1664, 1609, 1442, 1274, 1015, 750. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.46 (s, 1H), 8.84 (dd, *J* = 4.7 and 1.7 Hz, 1H), 8.24 (dd, *J* = 7.8 and 1.7 Hz, 1H), 7.58 (dd, *J* = 7.6 and 4.9 Hz, 1H), 7.29-7.27 (m, 1H), 2.37 (d, *J* = 1.0 Hz, 3H), 2.13 (d, *J* = 1.0 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 191.3, 190.7, 162.0, 157.2, 151.7, 136.3, 133.0, 126.0, 120.7, 28.6, 21.6. **HRMS (ESI):** *m/z* calcd for $C_{11}H_{12}NO_2$ $(M+H)^+$: 190.0868 Found: 190.0859.

(*S*)-5-Hydroxy-6-(propan-2-ylidene)-5*H*-cyclopenta[*b*]pyridin-7(6*H*)-one (43ab).

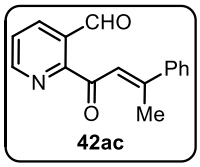


This compound was isolated as colorless solid. Following the general procedure **5**, 15 mg of **42ab** afforded 13.7 mg of **43ab** (91% yield). M.P = 178-179 ^{o}C. R_f = 0.2 (Hexane/EtOAc = 1/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3313, 2921, 2854, 1698, 1634, 1425, 1313, 1165, 1029, 768. **^{1}H-NMR (400 MHz, ($CDCl_3$):** δ 8.74 (dd, *J* = 4.6 and

1.2 Hz, 1H), 8.12 (dd, *J* = 7.8 and 0.8 Hz, 1H), 7.49 (dd, *J* = 7.8 and 4.6 Hz, 1H), 5.64 (s, 1H), 2.50 (s, 3H), 2.27 (s, 3H). **^{13}C-NMR (100 MHz, ($CDCl_3$):** δ 190.8, 158.7, 155.0, 152.2, 144.5, 134.8, 132.8, 127.7, 68.0, 24.2, 21.6. **HRMS (ESI):** *m/z* calcd for $C_{11}H_{10}NO$ $(M\text{-}OH)^+$: 172.0762. Found: 172.0761.

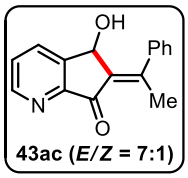
Optical rotation: $[\alpha]_D^{22}$ +8.6 (*c* 0.17, $CHCl_3$) for a sample with *ee* 85%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AS Column (85:15 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 22.7 min, τ_{minor} = 17.4 min).

(*E*)-2-(3-Phenylbut-2-enoyl)nicotinaldehyde (42ac).



This compound was prepared by following the general procedure **3** and isolated as pale yellow oil. R_f = 0.5 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2923, 2852, 1697, 1665, 1588, 1446, 1107, 758. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.55 (d, *J* = 3.1 Hz, 1H), 8.86-8.84 (m, 1H), 8.27-8.24 (m, 1H), 7.83-7.82 (m, 1H), 7.68-7.66 (m, 2H), 7.62-7.58 (m, 1H), 7.46-7.44 (m, 3H), 2.77 (d, *J* =2.4 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 191.3, 191.1, 159.2, 157.0, 151.7, 142.4, 136.3, 133.1, 129.7, 128.6(2C), 126.8(2C), 126.1, 121.0, 19.1. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{14}NO_2$ $(M+H)^+$: 252.1024. Found: 252.1018.

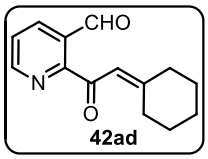
(*E*)-5-Hydroxy-6-(1-phenylethylidene)-5*H*-cyclopenta[*b*]pyridin-7(6*H*)-one (43ac).



This compound was isolated as pale yellow solid. Following the general procedure **4**, 15 mg of **42ac** afforded 12.5 mg of **43ac** (84% yield).. M.P = 199-201 °C. R_f = 0.2 (Hexane/EtOAc = 1/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3456, 2923, 2856, 1738, 1617, 1365, 1216, 757. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.84 (d, *J* = 4.5 Hz, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.54-7.49 (m, 2H), 7.47-7.40 (m, 3H), 7.33-7.31 (m, 1H), 5.75 (s, 1H), 2.80 (d, *J* = 0.8 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 191.7, 156.2, 155.1, 152.4, 144.4, 141.8, 134.8, 129.2(2C), 128.8, 128.0, 127.4, 126.6(2C), 67.5, 21.7. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{12}NO$ $(M\text{-}OH)^+$: 234.0918. Found: 234.0900.

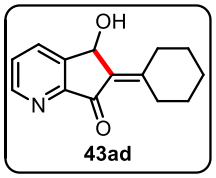
2-(2-Cyclohexylideneacetyl)nicotinaldehyde (42ad).

This compound was prepared by following the general procedure **3** and isolated as colorless oil. R_f = 0.2 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2969, 2854, 1698, 1667, 1615,



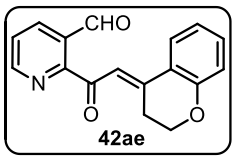
1133, 1024, 767. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.55 (d, *J* = 3.1 Hz, 1H), 8.86-8.84 (m, 1H), 8.27-8.24 (m, 1H), 7.83-7.82 (m, 1H), 7.68-7.66 (m, 1H), 2.92 (t, *J* = 5.6 Hz, 2H), 2.43-2.40 (m, 2H), 1.81-1.76 (m, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 191.3, 191.1, 159.2, 157.0, 151.7, 142.4, 136.5, 132.3, 120.5, 38.5, 30.6, 28.8, 28.1, 28.0. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{16}NO_2$ $(M+H)^+$: 230.1181. Found: 230.1179.

6-Cyclohexylidene-5-hydroxy-5*H*-cyclopenta[*b*]pyridin-7(6*H*)-one (43ad).



This compound was isolated as colorless solid. Following the general procedure **4**, 20 mg of **42ad** afforded 18.2 mg of **43ad** (91% yield). M.P = 199-201 ^{o}C. R_f = 0.2 (Hexane/EtOAc = 1/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3367, 2924, 2851, 1713, 1621, 1311, 764. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.85 (d, *J* = 4.6 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.57-7.55 (m, 1H), 5.81 (s, 1H), 3.45-3.40 (m, 2H), 2.75-2.67 (m, 2H), 2.01 (s, 1H), 1.81-1.65 (m, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 190.9, 158.1, 154.5, 151.2, 144.5, 134.8, 131.8, 127.6, 68.7, 38.9, 31.1, 28.3, 28.0, 27.9. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{14}NO$ $(M-OH)^+$: 212.1075. Found: 212.1067.

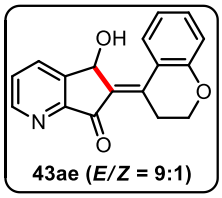
(*E*)-2-(2-(Chroman-4-ylidene)acetyl)nicotinaldehyde (42ae).



This compound was prepared by following the general procedure **3** and isolated as a pale yellow solid. M.P = 100-101 ^{o}C. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2929, 2857, 1697, 1674, 1601, 1570, 1426, 1033, 743. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.53 (d, *J* = 0.5 Hz, 1H), 8.88 (dd, *J* = 4.7 and 1.7 Hz, 1H), 8.25 (dd, *J* = 7.8 and 1.7 Hz, 1H), 8.08 (t, *J* = 1.7 Hz, 1H), 7.92 (dd, *J* = 8.1 and 1.5 Hz, 1H), 7.62 (ddd, *J* = 7.8, 4.7 and 0.6 Hz, 1H), 7.37 (ddd, *J* = 8.4, 7.1 and 1.6 Hz, 1H), 7.01 (ddd, *J* = 8.2, 7.4 and 1.2 Hz, 1H), 6.95 (dd, *J* = 8.3 and 1.2 Hz, 1H), 4.32 (t, *J* = 6.2 Hz, 2H), 3.57 (td, *J* = 6.2 and 1.8 Hz, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 191.3, 190.7, 157.9, 156.9, 151.6, 151.1, 136.4, 133.2, 132.9, 126.2, 125.2, 121.2, 121.1, 118.4, 113.4, 65.6, 27.8. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{14}NO_3$ $(M+H)^+$: 280.0973. Found: 280.0962.

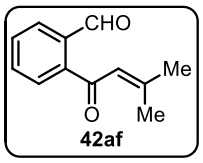
(*E*)-6-(Chroman-4-ylidene)-5-hydroxy-5*H*-cyclopenta[*b*]pyridin-7(6*H*)-one (43ae).

This compound was isolated as pale yellow solid. Following the general procedure **4**, 15 mg of **42ae** afforded 12.1 mg of **43ae** (81% yield). M.P = 121-122 ^{o}C. R_f = 0.2 (Hexane/EtOAc = 1/2).



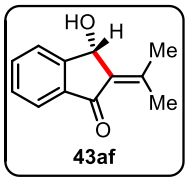
IR (thin film, neat): ν_{max}/cm^{-1} 3360, 2924, 2857, 1711, 1625, 1333, 756. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.84 (d, *J* = 4.2 Hz, 1H), 8.17 (ddd, *J* = 12.0, 8.0 and 1.3 Hz, 2H), 7.56 (dd, *J* = 7.8 and 4.7 Hz, 1H), 7.40 (ddd, *J* = 8.4, 7.1 and 1.5 Hz, 1H), 7.10-7.08 (m, 1H), 6.95 (dd, *J* = 8.3 and 1.2 Hz, 1H), 6.05 (s, 1H), 4.35-4.28 (m, 2H), 3.83-3.81 (m, 1H), 3.85-3.61 (m, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.1, 157.9, 154.5, 152.4, 147.6, 144.7, 134.5, 133.0, 130.2, 129.2, 127.9, 121.0, 120.5, 118.1, 68.1, 66.0, 26.1. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{12}NO_2$ $(M\text{-}OH)^+$: 262.0868. Found: 262.0882.

2-(3-Methylbut-2-enoyl)benzaldehyde (42af).



This compound was prepared by following the general procedure **3** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2914, 2849, 1695, 1650, 1439, 1367, 767. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.23 (s, 1H), 7.94-7.92 (m, 1H), 7.68-7.60 (m, 3H), 6.59 (pentet, *J* = 1.2 Hz, 1H), 2.26 (d, *J* = 0.9 Hz, 3H), 2.04 (d, *J* = 1.1 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.1, 191.7, 159.4, 143.6, 135.8, 132.9, 130.9, 128.7, 128.1, 123.0, 28.1, 21.3. **HRMS (ESI):** *m/z* calcd for $C_{12}H_{13}O_2$ $(M+H)^+$: 189.0915. Found: 189.0909.

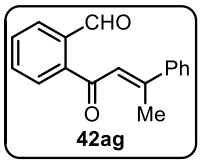
(*S*)-3-Hydroxy-2-(propan-2-ylidene)-2,3-dihydro-1*H*-inden-1-one (43af).



This compound was isolated as colorless solid. Following the general procedure **5**, 20 mg of **42af** afforded 18.6 mg of **43af** (93% yield). M. P = 107-108 °C. R_f = 0.2 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3453, 2919, 1680, 1632, 1276, 749. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.72-7.70 (m, 2H), 7.66-7.63 (m, 1H), 7.48-7.43 (m, 1H), 5.59 (s, 1H), 2.35 (s, 3H), 2.26 (br s, 1H), 2.20 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.6, 156.0, 149.9, 138.7, 134.6, 134.0, 129.4, 125.8, 123.3, 70.0, 24.2, 21.0. **HRMS (ESI):** *m/z* calcd for $C_{12}H_{11}O$ $(M\text{-}OH)^+$: 171.0809. Found: 171.0804.

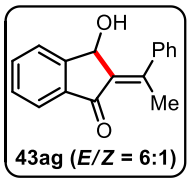
Optical rotation: $[\alpha]_D^{22}$ +7.4 (*c* 0.17, $CHCl_3$) for a sample with *ee* 71%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AS Column (96:4 *n*-Hexane/2-Propanol, 0.8 mL/min, 254 nm, τ_{major} = 11.3 min, τ_{minor} = 8.4 min).

(*E*)-2-(3-phenylbut-2-enoyl)benzaldehyde (42ag).



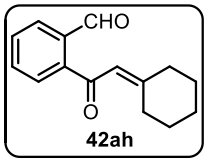
This compound was prepared by following the general procedure **3** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2957, 2922, 1695, 1661, 1592, 1446, 1377, 1215, 757. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.31 (s, 1H), 7.98 (dd, *J* = 7.3 and 1.6 Hz, 1H), 7.77-7.75 (m, 1H), 7.70-7.64 (m, 2H), 7.59-7.57 (m, 2H), 7.44-7.43 (m, 3H), 7.02 (d, *J* = 1.0 Hz, 1H), 2.69 (d, *J* = 0.7 Hz, 3H).**^{13}C-NMR (100 MHz, $CDCl_3$):** δ 193.2, 191.8, 157.5, 143.6, 142.1, 135.9, 133.0, 131.2, 129.6, 129.0, 128.7(2C), 128.6, 126.6(2C), 123.3, 19.0. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{15}O_2$ $(M+H)^+$: 251.1072. Found: 251.1068.

(*E*)-3-Hydroxy-2-(1-phenylethylidene)-2,3-dihydro-1*H*-inden-1-one (43ag).



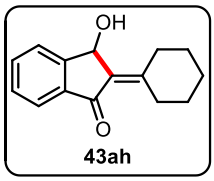
This compound was isolated as pale yellow oil. Following the general procedure **4**, 20 mg of **42ag** afforded 18 mg of **43ag** (89% yield). R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3397, 2924, 1688, 1623, 1606, 1369, 1155, 1008, 748. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.85 (d, *J* = 7.7 Hz, 1H), 7.65-7.60 (m, 2H), 7.53-7.50 (m, 3H), 7.46-7.41 (m, 3H), 5.71 (s, 1H), 2.76 (d, *J* = 0.8 Hz, 3H), 1.89 (br s, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 193.2, 153.9, 149.6, 142.3, 138.8, 136.2, 134.7, 129.5, 129.0(2C), 128.5, 126.7(2C), 125.9, 123.5, 69.4, 21.2. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{13}O$ $(M-OH)^+$: 233.0966. Found: 233.0949.

2-(2-Cyclohexylideneacetyl)benzaldehyde (42ah).



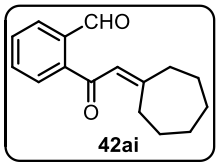
This compound was prepared by following the general procedure **3** and isolated as pale yellow oil. R_f = 0.5 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2918, 2851, 1694, 1648, 1441, 1363, 733. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.26 (s, 1H), 7.94-7.93 (m, 1H), 7.72-7.69 (m, 1H), 7.66-7.58 (m, 2H), 6.47 (s, 1H), 2.81 (t, *J* = 5.6 Hz, 2H), 2.33-2.30 (m, 2H), 1.76-1.66 (m, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 193.8, 191.8, 165.8, 143.6, 135.9, 132.9, 131.0, 128.6, 128.3, 120.5, 38.5, 30.6, 28.8, 28.1, 28.0. **HRMS (ESI):** *m/z* calcd for $C_{15}H_{17}O_2$ $(M+H)^+$: 229.1228. Found: 229.1243.

2-Cyclohexylidene-3-hydroxy-2,3-dihydro-1*H*-inden-1-one (43ah).



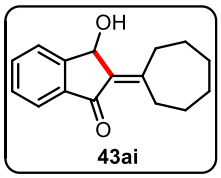
This compound was isolated as colorless solid. Following the general procedure **4**, 20 mg of **42ah** afforded 18.8 mg of **43ah** (91% yield). M.P = 116-117 ^{o}C. R_f = 0.2 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3389, 2919, 2851, 1682, 1616, 1465, 1247, 1005, 747. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.72-7.70 (m, 1H), 7.66 (dt, *J* = 7.6 and 1.2 Hz, 1H), 7.50-7.46 (m, 1H), 5.66 (d, *J* = 5.7 Hz, 1H), 3.23-3.12 (m, 2H), 2.70-2.54 (m, 2H), 1.98 (d, *J* = 8.2 Hz, 1H), 1.81-1.65 (m, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 193.0, 163.8, 149.6, 139.0, 134.6, 131.3, 129.4, 125.7, 123.4, 69.7, 33.9, 29.5, 28.7, 28.5, 26.2. **HRMS (ESI):** *m/z* calcd for $C_{15}H_{15}O$ $(M\text{-}OH)^+$: 211.1122. Found: 211.1145.

2-(2-Cycloheptylideneacetyl)benzaldehyde (42ai).



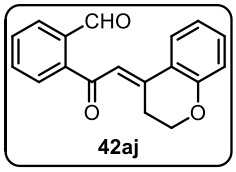
This compound was prepared by following the general procedure **3** and isolated as pale yellow oil. R_f = 0.5 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2924, 2853, 1696, 1653, 1594, 1445, 1247, 954, 758. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.23 (s, 1H), 7.93-7.91 (m, 1H), 7.69-7.67 (m, 1H), 7.65-7.61 (m, 1H), 7.60-7.54 (m, 1H), 6.59 (s, 1H), 2.98 (t, *J* = 6.0 Hz, 2H), 2.50 (t, *J* = 6.1 Hz, 2H), 1.75-1.71 (m, 4H), 1.59-1.57 (m, 4H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.7, 191.8, 170.5, 144.0, 135.8, 132.9, 130.8, 128.5, 128.0, 122.3, 39.6, 33.6, 29.8, 29.3, 28.1, 26.4. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{19}O_2$ $(M+H)^+$: 243.1385. Found: 243.1375.

2-Cycloheptylidene-3-hydroxy-2,3-dihydro-1*H*-inden-1-one (43ai).



This compound was isolated as colorless solid. Following the general procedure **4**, 20 mg of **42ah** afforded 18.8 mg of **43ah** (90% yield). M.P = 125-126 ^{o}C. R_f = 0.3 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3385, 2923, 2853, 1681, 1615, 1465, 1337, 1249, 1005, 749. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.71-7.68 (m, 2H), 7.65-7.61 (m, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 5.59 (s, 1H), 3.28-3.21 (m, 1H), 3.02-2.96 (m, 1H), 2.82-2.78 (m, 2H), 2.32 (s, 1H), 1.81-1.50 (m, 8H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.6, 166.5, 149.9, 138.9, 134.4, 13.3, 129.3, 125.7, 123.2, 69.9, 34.8, 32.1, 29.9, 29.1, 26.9, 26.8. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{17}O$ $(M\text{-}OH)^+$: 225.1279. Found: 225.1259.

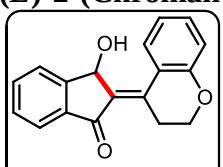
(*E*)-2-(2-(Chroman-4-ylidene)acetyl)benzaldehyde (42aj).



42aj

This compound was prepared by following the general procedure **3** and isolated as pale yellow solid. M.P = 77-79 ^{o}C. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3066, 2875, 1695, 1647, 1576, 1482, 1259, 1016, 756. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 10.26 (s, 1H), 7.98 (dd, *J* = 7.5 and 1.4 Hz, 1H), 7.79-7.75 (m, 1H), 7.71-7.69 (m, 1H), 7.68-7.64 (m, 2H), 7.35 (ddd, *J* = 8.3, 7.2 and 1.5 Hz, 1H), 7.23 (t, *J* = 1.6 Hz, 1H), 6.98-6.93 (m, 2H), 4.31 (t, *J* = 6.1 Hz, 2H), 3.51-347 (m, 2H). **^{13}C-NMR (100 MHz, CDCl$_3$)**: δ 192.8, 191.7, 157.8, 149.5, 143.7, 135.8, 133.1, 132.8, 131.1, 129.1, 128.0, 124.6, 121.1, 120.6, 118.4, 115.5, 65.6, 27.6. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{15}O_3$ $(M+H)^+$: 279.1021. Found: 279.1044.

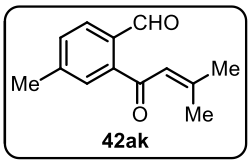
(*E*)-2-(Chroman-4-ylidene)-3-hydroxy-2,3-dihydro-1*H*-inden-1-one (43aj).



43aj (*E*/*Z* = 12:1)

This compound was isolated as yellow solid. Following the general procedure **4**, 20 mg of **42aj** afforded 18.8 mg of **43aj** (93% yield). M.P = 143-145 ^{o}C. R_f = 0.3 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3392, 2923, 1677, 1603, 1581, 1482, 1221, 1046, 749. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 8.25 (dd, *J* = 8.1 and 1.4 Hz, 1H), 7.75 (t, *J* = 7.0 Hz, 2H), 7.69-7.65 (m, 1H), 7.49-7.46 (m, 1H), 7.36 (ddd, *J* = 8.3, 7.1 and 1.5 Hz, 1H), 7.09-7.04 (m, 1H), 6.91 (dd, *J* = 8.3 and 1.1 Hz, 1H), 5.96 (s, 1H), 4.31-4.21 (m, 2H), 3.61 (t, *J* = 6.1 Hz, 2H), 2.86 (br s, 1H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 194.1, 157.6, 150.2, 145.6, 138.1, 134.9, 132.4, 131.6, 129.6, 129.6, 129.5, 125.6, 123.4, 120.9, 120.8, 117.8, 70.0, 66.1, 25.8. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{13}O_2$ $(M-OH)^+$: 261.0915. Found: 261.0903.

4-Methyl-2-(3-methylbut-2-enoyl)benzaldehyde (42ak).

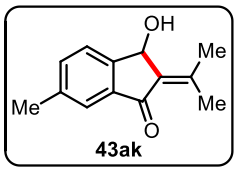


42ak

This compound was prepared by following the general procedure **3** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 5/1). IR (thin film, neat): ν_{max}/cm^{-1} 2965, 2918, 1696, 1655, 1621, 1421, 758. **^{1}H-NMR** (400 MHz, CDCl$_3$): δ 10.17 (d, *J* = 0.4 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 0.4 Hz, 1H), 7.39 (dd, *J* = 7.9 and 0.7 Hz, 1H), 6.54-6.53 (m, 1H), 2.47 (s, 3H), 2.25 (d, *J* = 1.1 Hz, 3H), 2.04 (d, *J* = 1.1 Hz, 3H). **^{13}C-NMR** (100 MHz, CDCl$_3$): δ 193.5, 191.4, 159.0, 144.2, 144.0, 133.0,

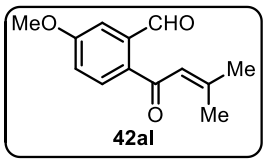
131.4, 129.0, 128.6, 123.4, 28.1, 21.7, 21.3. HRMS (ESI): *m/z* calcd for $C_{13}H_{15}O_2$ $(M+H)^+$: 203.1072. Found: 203.1052.

3-Hydroxy-6-methyl-2-(propan-2-ylidene)-2,3-dihydro-1*H*-inden-1-one (43ak).



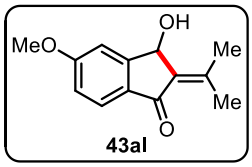
This compound was isolated as colorless solid. Following the general procedure **4**, 20 mg of **42ak** afforded 19 mg of **43ak** (95% yield). M.P = 162-163 °C. R_f = 0.2 (Hexane/EtOAc = 5/1). IR (thin film, neat): ν_{max}/cm^{-1} 3449, 2922, 1680, 1621, 1366, 1287, 1110, 1022, 784. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.8 Hz, 1H), 7.52 (s, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 5.57 (d, *J* = 7.5 Hz, 1H), 2.44 (s, 3H), 2.40 (s, 3H), 2.20 (s, 3H), 2.11 (d, *J* = 8.4 Hz, 1H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 192.7, 155.4, 147.3, 139.6, 139.0, 135.7, 134.5, 125.5, 123.3, 69.8, 24.2, 21.4, 21.0. HRMS (ESI): *m/z* calcd for $C_{13}H_{13}O$ $(M-OH)^+$: 185.0966. Found: 185.0957.

5-Methoxy-2-(3-methylbut-2-enoyl)benzaldehyde (42al).



This compound was prepared by following the general procedure **3** and isolated as colorless oil. R_f = 0.5 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2940, 2913, 2872, 1695, 1651, 1602, 1567, 1426, 1236, 1010, 820. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.27 (s, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.39 (d, *J* = 2.5 Hz, 1H), 7.10 (dd, *J* = 8.5 and 2.7 Hz, 1H), 6.63 (s, 1H), 3.90 (s, 3H), 2.22 (s, 3H), 2.03 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.0, 191.5, 161.8, 158.4, 139.1, 135.6, 130.8, 122.6, 118.6, 112.1, 28.1, 21.2. **HRMS (ESI):** *m/z* calcd for $C_{13}H_{15}O_3$ $(M+H)^+$: 219.1021. Found: 219.1013.

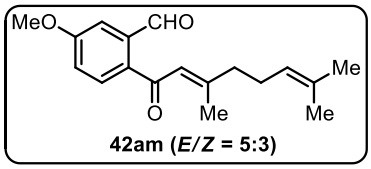
3-Hydroxy-5-methoxy-2-(propan-2-ylidene)-2,3-dihydro-1*H*-inden-1-one (43al).



This compound was isolated as colorless solid. Following the general procedure **4**, 20 mg of **42al** afforded 18.4 mg of **43al** (92% yield). M.P = 167-168 °C. R_f = 0.2 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3333, 2920, 2857, 1673, 1622, 1599, 1264, 1090, 797. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.63 (d, *J* = 8.5 Hz, 1H), 7.14 (d, *J* = 2.2 Hz, 1H), 6.96 (dd, *J* = 8.5 and 2.1 Hz, 1H), 5.51 (d, *J* = 7.0 Hz, 1H), 3.92 (s, 3H), 2.35 (s, 3H), 2.32 (d, *J* = 7.0 Hz, 1H), 2.18 (s, 3H). **^{13}C-NMR (100 MHz,**

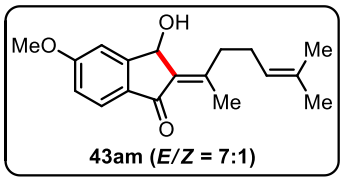
$CDCl_3$): δ 191.4, 165.1, 154.2, 152.8, 134.3, 132.2, 125.1, 117.3, 108.6, 69.9, 55.7, 24.1, 20.7. **HRMS (ESI):** *m/z* calcd for $C_{13}H_{13}O_2$ $(M\text{-}OH)^+$: 201.0915. Found: 201.0889.

(*E*)-2-(3,7-Dimethylocta-2,6-dienoyl)-5-methoxybenzaldehyde (42am).



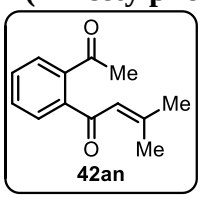
This compound was prepared by following the general procedure **3** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2967, 2921, 2857, 1694, 1651, 1600, 1567, 1284, 1112. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.28 (s, 1H), 7.77-7.70 (m, 1H), 7.40 (d, *J* = 2.6 Hz, 1H), 7.11-7.08 (m, 1H), 6.60 (s, 1H), 5.15-5.13 (m, 1H), 3.91 (s, 3H), 2.67 (t, *J* = 7.7 Hz, 1H), 2.29-2.24 (m, 3H), 2.21 (d, *J* = 1.2 Hz, 3H), 1.76 (s, 3H), 1.63 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.0, 191.7, 161.8, 161.4, 139.1, 135.8, 132.7, 130.8, 122.9, 122.2, 118.6, 112.0, 55.7, 41.4, 26.1, 25.7, 19.9, 17.7. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{23}O_3$ $(M+H)^+$: 287.1647. Found: 287.1651.

(*E*)-2-(3,7-Dimethylocta-2,6-dienoyl)-5-methoxybenzaldehyde (43am).



This compound was isolated as colorless oil. Following the general procedure **4**, 20 mg of **42am** afforded 18.8 mg of **43am** (88% yield). R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3382, 2967, 2919, 2854, 1681, 1627, 1599, 1490, 1256, 1094. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.67-7.63 (m, 1H), 7.13-7.12 (m, 1H), 6.98-6.94 (m, 1H), 5.53-5.50 (m, 1H), 5.22-5.19 (m, 1H), 3.91 (s, 3H), 2.98-2.80 (m, 1H), 2.57-2.50 (m, 1H), 2.38-2.37 (m, 1H), 2.32-2.28 (m, 1H), 2.17 (s, 3H), 1.69 (s, 3H), 1.64 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 190.7, 165.05, 158.2, 152.7, 134.4, 132.3, 132.2, 125.2, 123.7, 117.3, 108.6, 70.0, 55.7, 33.9, 27.1, 25.7, 22.2, 17.6. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{21}O_2$ $(M\text{-}OH)^+$: 269.1541. Found: 269.1529.

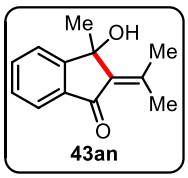
1-(2-Acetylphenyl)-3-methylbut-2-en-1-one (42an).



This compound was prepared by following the general procedure **3** and isolated as pale yellow oil. R_f = 0.5 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3057, 2968, 2876, 1679, 1651, 1620, 1413, 1021, 763. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.75 (dd, *J* = 7.6 and 1.2 Hz, 1H), 7.53-7.51 (m, 2H), 7.18 (dd, *J* = 7.2 and 1.2 Hz, 1H), 6.48-6.47 (m, 1H), 2.55 (s, 3H), 2.21 (d, *J* = 1.0 Hz, 3H), 2.00 (d, *J* = 1.0

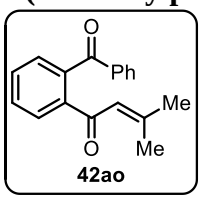
Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 201.7, 193.9, 157.5, 138.6, 131.0, 130.7, 130.4, 1128.6, 127.7, 127.6, 28.0, 21.1, 20.4. **HRMS (ESI):** *m/z* calcd for $C_{13}H_{15}O_2$ $(M+H)^+$: 203.1072. Found: 203.1079.

3-Hydroxy-3-methyl-2-(propan-2-ylidene)-2,3-dihydro-1*H*-inden-1-one (43an).



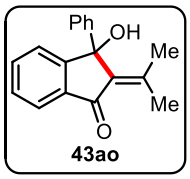
This compound was isolated as pale brown solid. Following the general procedure **4**, 20 mg of **42an** afforded 18.4 mg of **43an** (92% yield). M.P = 133-135 °C. R_f = 0.3 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3420, 2972, 2929, 1683, 1620, 1292, 1092, 756. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.77 (dt, *J* = 7.6 and 1.0 Hz, 1H), 7.72-7.70 (m, 1H), 7.69-7.65 (m, 1H), 7.49-7.45 (m, 1H), 2.46 (s, 3H), 2.29 (s, 3H), 2.01 (br s, 1H), 1.76 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.4, 155.4, 153.9, 137.6, 136.9, 134.7, 129.1, 123.3, 123.1, 76.0, 27.5, 23.3, 22.0. **HRMS (ESI):** *m/z* calcd for $C_{13}H_{13}O$ $(M-OH)^+$: 185.0966. Found: 185.0970.

1-(2-Benzoylphenyl)-3-methylbut-2-en-1-one (42ao).



This compound was prepared by following the general procedure **3** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 9/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3040, 2965, 2887, 1673, 1653, 1614, 1402, 1024, 767. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.87-7.77 (m, 3H), 7.59-7.53(m, 3H), 7.47-7.41 (m, 3H), 6.54-6.52 (m, 1H), 1.96 (d, *J* = 1.0 Hz, 3H), 1.92 (d, *J* = 1.1 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 197.7, 192.0, 158.1, 140.7, 140.4, 137.5, 132.8, 131.0, 129.7, 129.5(2C), 128.5, 128.32, 128.3(2C), 122.5, 27.8, 21.0. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{16}NaO_2$ $(M+Na)^+$: 287.1048. Found: 287.1057.

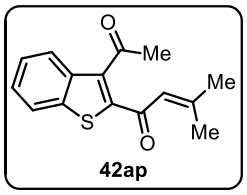
3-Hydroxy-3-phenyl-2-(propan-2-ylidene)-2,3-dihydro-1*H*-inden-1-one (43ao).



This compound was isolated as pale brown solid. Following the general procedure **4**, 25 mg of **42ao** afforded 24 mg of **43ao** (96% yield). M.P = 202-203 °C. R_f = 0.4 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3335, 2922, 1681, 1616, 1448, 1240, 1029, 768. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.77 (dt, *J* = 7.6 and 0.9 Hz, 1H), 7.56-7.52 (m, 1H), 7.47-7.54 (m, 2H), 7.43-7.40 (m, 1H), 7.37-7.36 (m, 1H), 7.35-7.31 (m, 2H), 7.28-7.21 (m, 1H), 2.68 (s, 1H), 2.43 (s, 3H), 1.81 (s, 3H). **^{13}C-NMR (100 MHz,**

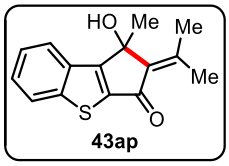
$CDCl_3$): δ 193.3, 156.2, 155.1, 144.3, 138.9, 136.9, 135.1, 129.0, 128.3(2C), 126.7, 125.1(2C), 124.8, 123.2, 79.2, 24.0, 21.9. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{15}O$ $(M\text{-}OH)^+$: 247.1122. Found: 247.1118.

1-(3-Acetylbenzo[*b*]thiophen-2-yl)-3-methylbut-2-en-1-one (42ap).



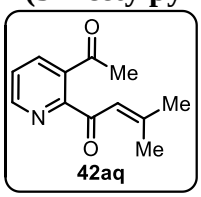
This compound was prepared by following the general procedure **2** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2965, 2887, 1671, 1650, 1619, 1428, 1208, 758. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.89-7.87 (m, 1H), 7.79-7.76 (m, 1H), 7.54-7.44 (m, 2H), 6.63-6.62 (m, 1H), 2.63 (s, 3H), 2.31 (d, *J* = 1.1 Hz, 3H), 2.07 (d, *J* = 1.1 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 201.7, 183.7, 161.1, 142.3, 140.6, 139.4, 136.7, 127.6, 125.7, 124.3, 122.8, 121.7, 31.5, 28.3, 21.6. **HRMS (ESI):** *m/z* calcd for $C_{15}H_{15}O_2S$ $(M+H)^+$: 259.0792. Found: 259.0788.

1-Hydroxy-1-methyl-2-(propan-2-ylidene)-1*H*-benzo[*b*]cyclopenta[*d*]thiophen-3(2*H*)-one (43ap).



This compound was isolated as colorless solid. Following the general procedure **4**, 20 mg of **42ap** afforded 18.6 mg of **43ap** (93% yield). M.P = 173-174 ^oC. R_f = 0.3 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3379, 2925, 1681, 1631, 1367, 1241, 1089, 763. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.16-8.13 (m, 1H), 7.94-7.92 (m, 1H), 7.52-7.49 (m, 2H), 2.42 (s, 3H), 2.28 (s, 3H), 2.24 (s, 1H), 1.93 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 185.8, 161.3, 151.0, 147.6, 143.4, 140.5, 132.3, 127.8, 125.2, 124.9, 124.5, 75.5, 25.6, 23.0, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{15}H_{15}O_2S$ $(M+H)^+$: 259.0792. Found: 259.0798.

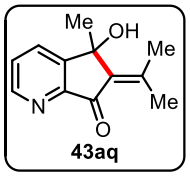
1-(3-Acetylpyridin-2-yl)-3-methylbut-2-en-1-one (42aq).



This compound was prepared by following the general procedure **3** and isolated as colorless oil. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2969, 1738, 1698, 1615, 1435, 1365, 1216, 748. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.72 (dd, *J* = 4.6 and 1.6 Hz, 1H), 7.72 (dd, *J* = 7.7 and 1.7 Hz, 1H), 7.49 (dd, *J* = 7.7 and 4.8 Hz, 1H), 7.31-7.28 (m, 1H), 2.54 (s, 3H), 2.31 (d, *J* = 0.9 Hz, 3H), 2.10 (d, *J* = 1.0 H, 3H). **^{13}C-**

NMR (100 MHz, $CDCl_3$): δ 202.6, 190.1, 161.3, 153.2, 149.3, 138.6, 134.6, 125.6, 120.0, 30.5, 28.5, 21.6. **HRMS (ESI):** *m/z* calcd for $C_{12}H_{14}NO_2$ $(M+H)^+$: 204.1024. Found: 204.1017.

5-Hydroxy-5-methyl-6-(propan-2-ylidene)-5*H*-cyclopenta[*b*]pyridin-7(6*H*)-one (43aq).



This compound was isolated as colorless solid. Following the general procedure **4**, 20 mg of **42aq** afforded 18 mg of **43aq** (90% yield). M.P = 195-197 °C. R_f = 0.2 (Hexane/EtOAc = 1/2). **IR (thin film, neat):** ν_{max}/cm^{-1} 3367, 2924, 2851, 1713, 1621, 1311, 764. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.72-8.67 (m, 1H), 8.09 (d, *J* = 7.9 Hz, 1H), 7.50-7.46 (m, 1H), 2.75 (brs, 1H), 2.44-2.42 (m, 3H), 2.31 (s, 3H), 1.75 (d, *J* = 3.0 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 190.9, 156.7, 153.1, 151.9, 149.9, 136.5, 132.5, 127.9, 74.1, 27.2, 23.6, 22.4. **HRMS (ESI):** *m/z* calcd for $C_{12}H_{14}NO_2$ $(M+H)^+$: 204.1024. Found: 204.1017.

General Procedure 6: Synthesis of dienones 58

Step-I: The alcohols **50** were synthesized from 2-bromo aldehydes **49** by following the general procedure **3**, Step I.

Step-II: An oven dried 25 mL long neck RB flask was charged with 2-bromo alcohol **50** (1.0 mmol), 5 mL dry THF and placed at –78 °C. *n*-BuLi (1.6 *M* in hexanes, 2.2 mmol) was added dropwise at the same temperature and stirred for 2 hours. An appropriate dienal **63** (1.3 mmol) dissolved in 1 mL of dry THF, was added dropwise over 2 mins and stirred at room temperature for 30 mins. The reaction mixture was quenched with saturated aq. ammonium chloride solution and extracted using 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 as eluent to afford the diol **64**.

Step-III: Alcohols **64** were oxidized using IBX following the general procedure **3**, Step III to afford dienones **58**.

General procedure 7: Synthesis of dienones 58j and 58v

The Substrates bearing chromene backbone **58j** and **58v** also can be readily synthesized from 4-bromo-2*H*-chromene-3-carbaldehyde **65** by following the general procedure **6**.

General Procedure 8: Synthesis of dienones 58k and 58l

Step-I: To a solution of *N*-methylpiperazine (NMP, 0.18 mL, 1.6 mmol) in THF (5 mL) at –78 ^{o}C was added *n*-BuLi (1.6 *M* in hexane, 1.0 mL, 1.6 mmol). After 15 min, thiophene- or benzothiophene-3-carboxaldehyde **44** (200 mg, 1.2 mmol) was added and then the reaction mixture was stirred for an additional 30 min. A hexane solution of *n*-BuLi (2.0 mL, 3.2 mmol) was added and the mixture was stirred for an additional 15 min and then the mixture was warmed to –30 ^{o}C in 2 h. The solution was again cooled to –78 ^{o}C and 2,4-hexa-dienal **63a** (1.5 mmol) was added dropwise over 5 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 as eluent to afford dienol **68**.

Step-II: Alcohol **68** (1 mmol) was dissolved in ethyl acetate (10 mL), and IBX (1.5 mmol) was added. The resulting suspension was immersed in an oil bath set to 75 °C and stirred until alcohol **68** disappeared as monitored by TLC. The reaction was cooled to room temperature and filtered through Buchner funnel. The filter cake was washed with 3×2 mL of ethyl acetate. 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 vacuum. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate as eluent to afford the dienone **58k** and **58l**.

General Procedure 9: Synthesis of dienone 58o

In to solution of Alcohol **68** in dry THF, methylmagnesium bromide (1.2 eq.) was added at 0 ^{o}C. The reaction was continued until the starting alcohol **68** disappeared as monitored by TLC. The reaction mixture was quenched by saturated aqueous ammonium chloride and extracted using ethyl acetate. Organic extracts were combined, dried over anhydrous sodium sulphate and concentrated to afford the diol **69** and proceeded to the next step without purification. Subsequent IBX oxidation of diol **69** delivered the desired enone-ketone **58o**.

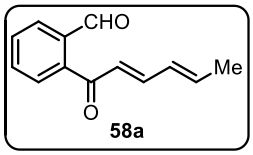
General procedure 10: Intramolecular MBH reaction of dienones

An oven dried 5 mL glass vial was charged with **58** (30 mg, 0.15 mmol). Toluene (1 mL) and PMe_3 (1 M solution in toluene, 0.1 mL, 0.015 mmol) were introduced at room temperature (rt) under nitrogen atmosphere and stirring continued at rt until **58** disappeared as monitored by TLC. All the volatiles were removed under reduced pressure. The crude product was purified by silica gel flash chromatography using hexane/ethyl acetate as eluent, to afford **58**.

General Procedure 11: Enantioselective intramolecular MBH of dienones

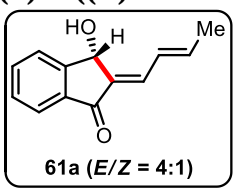
An oven dried 5 mL glass vial was charged with **58** (20 mg, 0.1 mmol) in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP, 0.5 mL), catalyst **C23** was introduced at room temperature (rt) under nitrogen atmosphere and stirring continued at rt until **58** disappeared as monitored by TLC. Volatiles were removed under reduced pressure. The crude product was purified by silica gel flash chromatography using hexane/ethyl acetate as eluent, to afford **58**.

2-((2*E*,4*E*)-Hexa-2,4-dienoyl)benzaldehyde (58a).



This compound was prepared by following the general procedure **6** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3447, 2910, 1701, 1663, 1586, 1199, 1002, 770. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.12 (s, 1H), 7.97-7.95 (m, 1H), 7.68-7.56 (m, 3H), 7.06 (dd, *J* = 15.3 and 10.8 Hz, 1H), 6.56 (d, *J* =15.3 Hz, 1H), 6.31-6.18 (m, 2H), 1.88 (d, *J* = 6.4 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.6, 191.2, 147.6, 142.6, 142.0, 135.4, 133.2, 130.7, 130.2, 129.2, 128.3, 127.3, 19.0. **HRMS (ESI):** *m/z* calcd for $C_{13}H_{13}O_2$ (M+H): 201.0916. Found: 201.0905.

(*S*)-2-((*E*)-But-2-en-1-ylidene)-3-hydroxy-2,3-dihydro-1*H*-inden-1-one (61a).

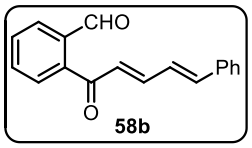


This compound was isolated as pale yellow solid. Following the general procedure **11**, 25 mg of **58a** afforded 24 mg of **61a** (97% yield). M.P = 117-119 °C. R_f = 0.2 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3382, 2910, 1687, 1632, 1030, 922, 754. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.76 (t, *J* = 7.6 Hz, 2H), 7.69 (dt, *J* = 7.6 and 1.2 Hz, 1H), 7.50-7.46 (m, 1H), 7.28-7.26 (m, 1H), 6.86-6.79 (m, 1H), 6.41 (sextet, 3.2 Hz, 1H), 5.73 (d, *J* = 9.6 Hz, 1H), 2.25 (d, *J* = 9.5 Hz, 1H), 2.00 (dd, *J* = 7.0 and

0.8 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.1, 151.0, 143.8, 138.0, 137.3, 136.3, 135.1, 129.6, 127.7, 125.9, 123.4, 69.0, 19.3. **HRMS (ESI):** *m/z* calcd for *m/z* calcd for $C_{13}H_{11}O$ (M-OH): 183.0810. Found: 183.0821.

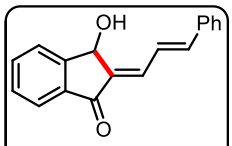
Optical rotation: $[\alpha]^{23}_{D}$ +31.7 (*c* 0.20, $CHCl_3$) for a sample with *ee* 97%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AS Column (92:8 *n*-Hexane/2-Propanol, 0.8 mL/min, 254 nm, τ_{major} = 34.4 min, τ_{minor} = 39.7 min).

2-((2*E*,4*E*)-5-Phenylpenta-2,4-dienoyl)benzaldehyde (58b).



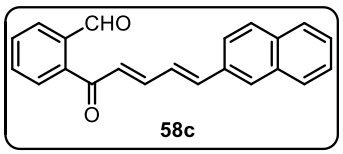
This compound was prepared by following the general procedure **6** and isolated as a pale yellow solid. M.P = 67-69 °C. R_f = 0.5 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3029, 2859, 1695, 1649, 1614, 1581, 1253, 1022, 775. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.18 (s, 1H), 8.02 (d, *J* = 7.2 Hz, 1H), 7.71-7.64 (m, 3H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.41-7.35 (m, 3H), 7.31-7.25 (m, 1H), 7.01-6.99 (m, 2H), 6.80 (d, *J* = 7.3 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.3, 191.2, 147.1, 143.0, 141.9, 135.7, 135.5, 133.2, 130.9, 129.6, 129.3, 129.1, 128.9(2C), 128.3, 127.4(2C), 126.4. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{15}O_2$ (M+H): 263.1072 Found: 263.1081.

(*E*)-3-Hydroxy-2-((*E*)-3-phenylallylidene)-2,3-dihydro-1*H*-inden-1-one (61b).



This compound was isolated as pale yellow solid. Following the general procedure **10**, 50 mg of **58b** afforded 46 mg of **61b** (91% yield). M.P = 162-164 °C. R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3395, 3064, 1691, 1614, 1293, 976, 765. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.80-7.78 (m, 1H), 7.70-7.51 (m, 5H), 7.43-7.34 (m, 5H), 7.02 (dd, *J* = 15.2 and 3.2 Hz, 1H), 5.97 (d, *J* = 4.8 Hz, 1H), 2.86 (d, *J* = 4.9 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.2, 151.2, 144.1, 138.3, 137.9, 137.3, 136.0, 135.2, 129.6, 129.5, 128.9(2C), 127.7(2C), 125.9, 124.0, 123.4, 69.1. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{13}O$ (M-OH): 245.0966. Found: 245.0970.

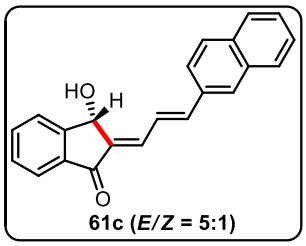
2-((2*E*,4*E*)-5-(Naphthalen-2-yl)penta-2,4-dienoyl)benzaldehyde (58c).



This compound was prepared by following the general procedure **6** and isolated as pale yellow solid. M.P = 107-109 °C. R_f = 0.4

(Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3056, 1695, 1650, 1579, 1326, 1274, 1022, 748. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.20 (s, 1H), 8.02 (d, *J* = 7.5 Hz, 1H), 7.85-7.83 (m, 4H), 7.72-7.65 (m, 4H), 7.53-7.50 (m, 2H), 7.36-7.33 (m, 1H), 7.13-7.12 (m, 2H), 6.83 (d, *J* = 15.2 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.2, 191.3, 147.1, 143.1, 141.9, 135.6, 133.8, 133.4, 133.3, 133.2, 130.9, 129.4, 129.0, 128.8, 128.7, 128.43, 128.4, 127.8, 127.0, 126.8, 126.7, 123.3. **HRMS (ESI):** *m/z* calcd for $C_{22}H_{16}NaO_2$ (M+Na): 335.1048. Found: 335.1051.

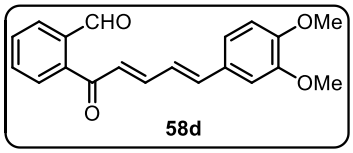
(*S*)-3-Hydroxy-2-((*E*)-3-(naphthalen-2-yl)allylidene)-2,3-dihydro-1*H*-inden-1-one (61c).



This compound was isolated as pale yellow solid. Following the general procedure **11**, 20 mg of **58c** afforded 19.4 mg of **61c** (97% yield). M.P = 169-171 ^{o}C. R_f = 0.2 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3660, 2937, 1697, 1604, 1072, 1022, 746. **^{1}H-NMR (400 MHz, $(CD_3)_2SO$):** δ 8.08 (s, 1H), 7.99-7.87 (m, 4H), 7.81-7.68 (m, 4H), 7.59-7.54 (m, 3H), 7.54-7.37 (m, 2H), 6.18 (d, *J* = 8.4 Hz, 1H), 5.85 (d, *J* = 8.4 Hz, 1H). **^{13}C-NMR (100 MHz, $(CD_3)_2SO$):** δ 192.0, 152.9, 142.8, 140.6, 138.0, 135.6, 135.3, 134.3, 133.7, 133.5, 129.7, 129.0, 128.8, 128.7, 128.1, 127.4, 127.2, 126.9, 125.7, 124.1, 123.0, 67.7. **HRMS (ESI):** *m/z* calcd for $C_{22}H_{15}O$ (M-OH): 295.1123. Found: 295.1129.

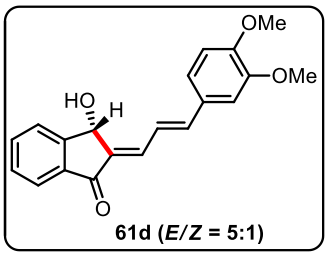
Optical rotation: $[\alpha]^{23}_{D}$ +78.9 (*c* 0.08, DMSO) for a sample with *ee* 92%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AS Column (88:12 *n*-Hexane/2-Propanol, 0.8 mL/min, 254 nm, τ_{major} = 22.1 min, τ_{minor} = 30.2 min).

2-((2*E*,4*E*)-5-(3,4-Dimethoxyphenyl)penta-2,4-dienoyl)benzaldehyde (58d).



This compound was prepared by following the general procedure **6** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2956, 2925, 1712, 1654, 1463, 1378, 1267, 1023, 745. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.17 (s, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.68-7.62 (m, 3H), 7.30-7.23 (m, 1H), 7.05-7.02 (m, 2H), 6.90-6.85 (m, 3H), 6.75 (d, *J* = 14.9 Hz, 1H), 3.93 (s, 3H), 3.91 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.2, 191.2, 150.6, 149.2, 147.6, 143.2, 142.1, 135.4, 133.2, 130.8, 129.2, 128.8, 128.3, 128.0, 124.5, 121.8, 111.1, 109.1, 56.0, 55.9. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{19}O_4$ (M+H): 323.1283. Found: 323.1290.

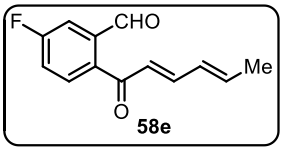
(*S*)-2-((*E*)-3-(3,4-dimethoxyphenyl)allylidene)-3-hydroxy-2,3-dihydro-1*H*-inden-1-one (61d).



This compound was isolated as pale brown solid. Following the general procedure **11**, 20 mg of **58d** afforded 17.5 mg of **61d** (87% yield). M.P = 144-146 ^{o}C. R_f = 0.2 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3456, 2932, 1694, 1608, 1517, 1269, 1023, 759. **^{1}H-NMR (400 MHz, $(CD_3)_2SO$):** δ 7.77-7.76 (m, 2H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.57-7.53 (m, 1H), 7.43 (dd, *J* = 15.4 and 12.1 Hz, 1H), 7.31-7.16 (m, 4H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.11 (d, *J* = 8.0 Hz, 1H), 5.80 (d, *J* = 8.0 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H). **^{13}C-NMR (100 MHz, $(CD_3)_2SO$):** δ 191.9, 152.8, 150.7, 149.4, 143.4, 139.2, 138.1, 135.8, 135.4, 129.6, 129.5, 126.8, 123.0, 122.9, 122.2, 112.2, 110.1, 67.7, 56.0, 55.9. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{17}O_3$ (M-OH): 305.1178. Found: 305.1180.

Optical rotation: $[\alpha]^{23}_{D}$ +135.8 (*c* 0.18, $CHCl_3$) for a sample with *ee* 78%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AD Column (85:15 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 20.3 min, τ_{minor} = 29.1 min).

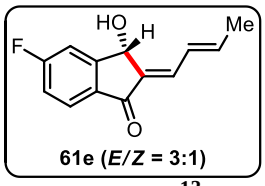
5-Fluoro-2-((2*E*,4*E*)-hexa-2,4-dienoyl)benzaldehyde (58e).



This compound was prepared by following the general procedure **6** and isolated as a pale yellow solid. M.P = 100-102 ^{o}C. R_f = 0.4 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2956, 1691, 1658, 1588, 1341, 1257, 1000, 836. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.14 (d, *J* = 2.8 Hz, 1H), 7.70-7.65 (m, 2H0, 7.35 (dt, *J* = 8.1 and 2.6 Hz, 1H), 7.20-7.13 (m, 1H), 6.61 (d, *J* = 15.2 Hz, 1H), 6.34-6.29 (m, 2H), 1.93 (d, *J* = 6.0 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.5, 189.9, 163.2 (d, *J* = 260.3 Hz), 147.9, 143.1, 138.5 (d, *J* = 6.2 Hz), 138.1 (d, *J* = 3.7 Hz), 131.0 (d, *J* = 8.2 Hz), 130.2, 126.4, 119.8 (d, *J* = 22.1 Hz), 115.5 (d, *J* = 23.0 Hz), 19.0. **^{19}F-NMR (376 MHz, $CDCl_3$):** δ -106.7. **HRMS (ESI):** *m/z* calcd for $C_{13}H_{12}FO_2$ (M+H): 219.0821. Found: 219.0821.

(*S*)-2-((*E*)-But-2-en-1-ylidene)-5-fluoro-3-hydroxy-2,3-dihydro-1*H*-inden-1-one (61e).

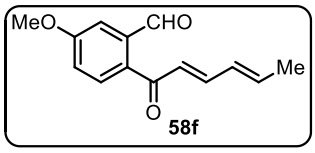
This compound was isolated as pale yellow solid. Following the general procedure **11**, 20 mg of **58e** afforded 18.5 mg of **61e** (93% yield). M.P = 159-161 ^{o}C. R_f = 0.3 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3442, 2927, 1703, 1634, 1266, 1015, 750. **^{1}H-NMR (400 MHz,**



$CDCl_3$): δ 7.75-7.72 (m, 1H), 7.42 (dd, *J* = 8.1 and 1.9 Hz, 1H), 7.24 (dd, *J* = 11.2 and 2.4 Hz, 1H), 7.18-7.13 (m, 1H), 6.84-6.77 (m, 1H), 6.40 (sextet, *J* = 3.2 Hz, 1H), 5.60 (s, 1H), 2.42 (br s, 1H), 2.01 (dd, *J* = 6.8 and 1.2 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 190.6, 163.3 (d, *J* = 253.1 Hz), 144.3, 137.5, 135.9, 134.2, 127.5, 125.8 (d, *J* = 10.3 Hz), 117.6 (d, *J* = 32.0 Hz), 117.5, 112.8 (d, *J* = 25.3 Hz), 68.7, 19.4. **^{19}F-NMR (376 MHz, $CDCl_3$):** δ -101.1. **HRMS (ESI):** *m/z* calcd for $C_{13}H_{10}FO$ (M-OH): 201.0716. Found: 201.0722.

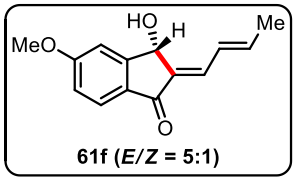
Optical rotation: $[\alpha]^{23}_{D}$ +69.1 (*c* 0.12, $CHCl_3$) for a sample with *ee* 99%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak IC Column (95:5 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 39.5 min, τ_{minor} = 27.7 min).

2-((2*E*,4*E*)-Hexa-2,4-dienoyl)-5-methoxybenzaldehyde (58f).



This compound was prepared by following the general procedure **6** and isolated as pale yellow solid. M.P = 82-85 °C. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3440, 2938, 1693, 1653, 1596, 1260, 1015, 750. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.20 (s, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.45 (d, *J* = 2.4 Hz, 1H), 7.25-7.12 (m, 2H), 6.65 (d, *J* = 15.2 Hz, 1H), 6.33-6.27 (m, 2H), 3.92 (s, 3H), 1.91 (d, *J* = 6.0 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.2, 191.6, 161.8, 146.7, 142.2, 138.6, 134.3, 130.8, 130.3, 126.1, 118.9, 112.3, 55.7, 18.9. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{14}NaO_3$ (M+Na): 253.0841. Found: 253.0836.

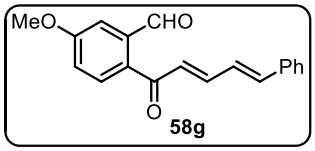
(*S*)-2-((*E*)-But-2-en-1-ylidene)-3-hydroxy-5-methoxy-2,3-dihydro-1*H*-inden-1-one (61f).



This compound was isolated as pale yellow solid. Following the general procedure **11**, 25 mg of **58f** afforded 23.5 mg of **61f** (94% yield). M.P = 129-131 °C. R_f = 0.2 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3374, 2926, 1681, 1631, 1597, 1290, 1018, 759. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.69-7.67 (m, 1H), 7.21-7.18 (m, 2H), 6.99-6.97 (m, 1H), 6.83-6.76 (m, 1H), 6.38-6.33 (m, 1H), 5.65 (s, 1H), 3.94 (s, 3H), 2.46 (br s, 1H), 1.98 (dd, *J* = 6.8 and 1.2 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 190.8, 165.5, 154.1, 143.0, 136.7, 136.2, 131.3, 127.6, 125.3, 117.5, 108.9, 68.9, 55.8, 19.3. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{15}O_3$ (M+H): 231.1021. Found: 231.1009.

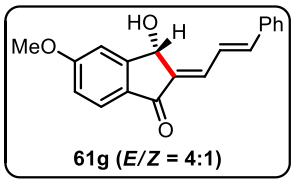
Optical rotation: $[\alpha]^{23}_{D}$ -2.7 (*c* 0.14, $CHCl_3$) for a sample with *ee* 94%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AS Column (90:10 *n*-Hexane/2-Propanol, 0.8 mL/min, 254 nm, τ_{major} = 18.2 min, τ_{minor} = 16.2 min).

5-Methoxy-2-((2*E*,4*E*)-5-phenylpenta-2,4-dienoyl)benzaldehyde (58g).



This compound was prepared by following the general procedure **6** and isolated as pale brown oil. R_f = 0.4 (Hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 3027, 1692, 1653, 1596, 1579, 1350, 1237, 1016, 736. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.25 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.51-7.34 (m, 7H), 7.16 (dd, *J* = 8.4 and 2.7 Hz, 1H), 7.02 (d, *J* = 4.8 Hz, 1H), 7.00 (s, 1H), 6.89 (d, *J* = 15.2 Hz, 1H), 3.93 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 191.6, 162.0, 146.2, 142.7, 138.9, 138.8, 135.8, 134.2, 130.9, 129.5, 128.9(2C), 127.9, 127.4(2C), 126.5, 118.9, 112.5, 55.8. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{17}O_3$ (M+H): 293.1178. Found: 293.1178.

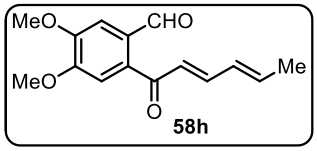
(*S*)-3-Hydroxy-5-methoxy-2-((*E*)-3-phenylallylidene)-2,3-dihydro-1*H*-inden-1-one (61g).



This compound was isolated as pale yellow solid. Following the general procedure **11**, 18 mg of **58g** afforded 17 mg of **61g** (95% yield). M.P = 170-172 ^oC. R_f = 0.2 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3308, 2928, 1667, 1601, 1275, 1260, 1020, 749. **^{1}H-NMR (400 MHz, $(CD_3)_2SO$):** δ 7.68 (d, *J* = 8.3 Hz, 1H), 7.64-7.62 (m, 2H), 7.55 (dd, *J* = 16.0 and 12.0 Hz, 1H), 7.45-7.42 (m, 2H), 7.38-7.35 (m, 1H), 7.24-7.18 (m, 3H), 7.09 (dd, *J* = 8.0 and 2.4 Hz, 1H), 6.12 (d, *J* = 8.4 Hz, 1H), 5.73 (d, *J* = 8.2 Hz, 1H), 3.91 (s, 3H). **^{13}C-NMR (100 MHz, $(CD_3)_2SO$):** δ 190.2, 165.5, 155.9, 141.9, 141.0, 136.7, 133.9, 131.3, 129.6, 129.4(2C), 127.8(2C), 125.2, 125.0, 117.4, 110.0, 67.7, 56.3. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{15}O_2$ (M-OH): 275.1072. Found: 275.1085.

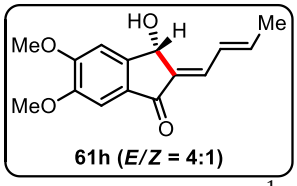
Optical rotation: $[\alpha]^{23}_{D}$ +125.2 (*c* 0.10, $CHCl_3$) for a sample with *ee* 96%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H Column (80:10 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 28.7 min, τ_{minor} = 22.0 min).

2-((2*E*,4*E*)-Hexa-2,4-dienoyl)-4,5-dimethoxybenzaldehyde (58h).



This compound was prepared by following the general procedure **6** and isolated as a pale yellow solid. M.P = 127-129 ^{o}C. R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3006, 2851, 1672, 1588, 1519, 1355, 1283, 1118, 871, 736. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 10.05 (s, 1H), 7.50 (s, 1H), 7.15-7.08 (m, 1H), 7.03 (s, 1H), 6.54 (d, *J* = 15.2 Hz, 1H), 6.32-6.25 (m, 2H), 3.98 (s, 6H), 1.89 (d, *J* = 6.2 Hz, 3H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 193.5, 189.8, 152.7, 150.7, 147.4, 142.7, 137.1, 130.2, 129.2, 127.5, 110.5, 109.5, 56.3, 56.2, 19.0. **HRMS (ESI):** *m/z* calcd for $C_{15}H_{16}NaO_4$ (M+H): 283.0946. Found: 283.0965.

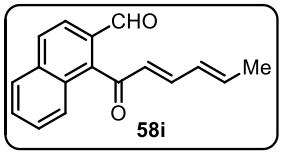
(*S*)-2-((*E*)-But-2-en-1-ylidene)-3-hydroxy-5,6-dimethoxy-2,3-dihydro-1*H*-inden-1-one (61h).



This compound was isolated as Pale yellow solid. Following the general procedure **11**, 25 mg of **58h** afforded 23 mg of **61h** (93% yield). M.P = 147-149 ^{o}C. R_f = 0.2 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3374, 2931, 1682, 1591, 1306, 1100, 760. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 7.17 (s, 1H), 7.05 (d, *J* = 12.1 Hz, 1H), 7.02 (s, 1H), 6.84-6.77 (m, 1H), 6.34-6.29 (m, 1H), 5.60 (s, 1H), 4.02 (s, 3H), 3.89 (s, 3H), 2.55 (br s, 1H), 1.98 (dd, *J* = 6.8 and 0.8 Hz, 3H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 191.3, 155.6, 150.8, 146.4, 142.7, 136.8, 135.6, 131.3, 127.7, 106.7, 103.8, 68.8, 56.4, 56.1, 19.2. **HRMS (ESI):** *m/z* calcd for $C_{15}H_{15}O_3$ (M-OH): 243.1021. Found: 243.1035.

Optical rotation: $[\alpha]^{23}_{D}$ -49.6 (*c* 0.15, $CHCl_3$) for a sample with *ee* 93%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AD Column (88:12 *n*-Hexane/2-Propanol, 0.7 mL/min, 254 nm, τ_{major} = 20.8 min, τ_{minor} = 25.6 min).

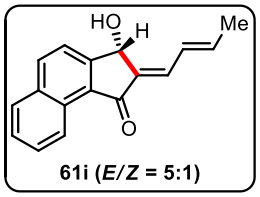
1-((2*E*,4*E*)-Hexa-2,4-dienoyl)-2-naphthaldehyde (58i).



This compound was prepared by following the general procedure **6** and isolated as pale brown solid. M.P = 85-87 ^{o}C. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3016, 1697, 1275, 1260, 764, 750. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 10.17 (s, 1H), 8.05-7.94 (m, 3H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.69-7.65 (m, 1H), 7.60-7.56 (m, 1H), 6.79-6.72 (m, 1H), 6.60 (d, *J* = 15.6 Hz, 1H), 6.31-6.28 (m, 1H), 6.09-6.03 (m, 1H), 1.85 (d, *J* = 6.8 Hz, 3H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 198.2, 190.4,

149.0, 143.3, 139.4, 136.1, 130.7, 130.4, 130.2, 129.9, 129.7, 129.3, 128.4, 127.8, 126.7, 123.0, 19.0. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{14}O_2$ $(M+H)^+$: 251.1072. Found: 251.1053.

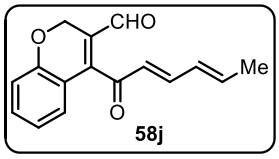
(*S*)-2-((*E*)-But-2-en-1-ylidene)-3-hydroxy-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1-one (61i).



This compound was isolated as pale yellow solid. Following the general procedure **11**, 20 mg of **58i** afforded 18.6 mg of **61i** (93% yield). M.P = 196-198 ^oC. R_f = 0.2 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3365, 2926, 1693, 1608, 1517, 1441, 1176, 834, 760. **^{1}H-NMR (400 MHz, $(CD_3)_2SO$):** δ 9.13 (d, *J* =8.4 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.77-7.73 (m, 1H), 7.68-7.64 (m, 1H), 7.11 (d, *J* = 11.9 Hz, 1H), 6.86-6.79 (m, 1H), 6.45-6.40 (m, 1H), 5.99 (d, *J* = 8.4 Hz, 1H), 5.71 (d, *J* = 8.3 Hz, 1H), 1.94 (dd, *J* = 6.8 and 1.1 Hz, 3H). **^{13}C-NMR (100 MHz, $(CD_3)_2SO$):** δ 193.0, 155.2, 141.9, 138.3, 136.5, 134.2, 133.5, 131.7, 129.5, 129.1, 128.6, 128.5, 127.6, 124.3, 123.7, 67.5, 19.5. HRMS (ESI): *m/z* calcd for $C_{17}H_{14}O_2$ $(M+H)^+$: 251.1072. Found: 251.1089.

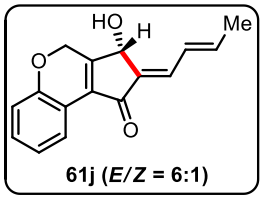
Optical rotation: $[\alpha]^{23}_D$ +44.9 (*c* 0.08, $CHCl_3$) for a sample with *ee* 99%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H Column (90:10 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 19.6 min, τ_{minor} = 13.7 min).

4-((2*E*,4*E*)-Hexa-2,4-dienoyl)-2*H*-chromene-3-carbaldehyde (58j).



This compound was prepared by following the general procedure **7** and isolated as light brown oil. R_f = 0.5 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3370, 3030, 2832, 2745, 1701, 1654, 1616, 1578, 1458, 1100, 752. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 9.65 (s, 1H), 7.36-7.32 (m, 1H), 7.16-7.09 (m, 2H), 6.97-6.94 (m, 2H), 6.37 (d, *J* = 15.2 Hz, 1H), 6.31-6.29 (m, 2H), 5.03 (s, 2H), 1.91 (d, *J* = 5.0 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.2, 187.8, 155.8, 149.8, 149.7, 149.3, 144.6, 133.6, 130.0, 128.6, 127.0, 122.3, 119.4, 117.2, 62.4, 19.1. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{15}O_3$ (M+H): 255.1021. Found: 255.1036.

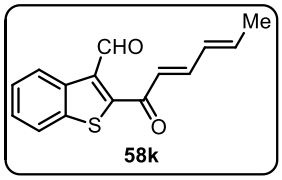
(*S*)-2-((*E*)-But-2-en-1-ylidene)-3-hydroxy-2,3-dihydrocyclopenta[*c*]chromen-1(4*H*)-one (61j).



This compound was isolated as pale brown solid. Following the general procedure **11**, 22 mg of **58j** afforded 21.3 mg of **61j** (97% yield). M.P = 167-169 ^{o}C. R_f = 0.3 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2929, 1696, 1608, 1459, 1277, 1072, 1019, 757. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.16-8.12 (m, 1H), 7.24-7.20 (m, 1H), 7.05 (d, *J* = 11.6 Hz, 1H), 6.98-6.94 (m, 1H), 6.85 (dd, *J* = 8.0 and 0.8 Hz, 1H), 6.69-6.28 (m, 1H), 6.37-6.30 (m, 1H), 5.41-5.35 (m, 1H), 5.26 (s, 2H), 5.25-5.19 (m, 1H), 1.98 (dd, *J* = 6.8 and 1.2 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 190.3, 156.9, 153.0, 143.2, 134.5, 134.1, 133.9, 130.8, 127.0, 125.2, 121.7, 116.5, 115.9, 68.5, 65.2, 19.2. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{15}O_3$ $(M+H)^+$: 255.1021. Found: 255.1043.

Optical rotation: $[\alpha]^{23}_{D}$ +3.1 (*c* 0.05, $CHCl_3$) for a sample with *ee* 95%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H Column (95:5 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 34.6 min, τ_{minor} = 23.4 min).

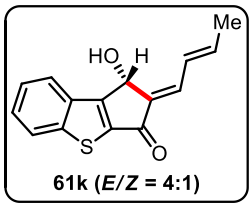
2-((2*E*,4*E*)-Hexa-2,4-dienoyl)benzo[b]thiophene-3-carbaldehyde (58k).



This compound was prepared by following the general procedure **8** and isolated as a pale yellow solid. M.P = 122-124 ^{o}C. R_f = 0.5 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3442, 3002, 1671, 1655, 1592, 1499, 1000, 751. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.65 (s, 1H), 8.80-8.78 (m, 1H), 7.92-7.90 (m, 1H), 7.58-7.54 (m, 2H), 7.53-7.47 (m, 1H), 6.70 (d, *J* = 14.8 Hz, 1H), 6.40-6.39 (m, 2H), 1.96 (d, *J* = 5.2 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 188.0, 184.7, 150.7, 147.7, 144.3, 138.9, 136.6, 136.4, 130.2, 127.8, 126.9, 126.7, 125.4, 122.2, 19.1. **HRMS (ESI):** *m/z* calcd for $C_{15}H_{13}O_2S$ (M+H): 257.0636. Found: 257.0654.

(*S*)-2-((*E*)-But-2-en-1-ylidene)-1-hydroxy-1*H*-benzo[*b*]cyclopenta[*d*]thiophen-3(2*H*)-one (61k).

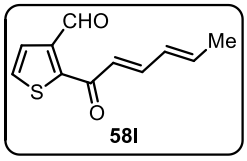
This compound was isolated as pale yellow solid. Following the general procedure **11**, 20 mg of **58k** afforded 18.3 mg of **61k** (91% yield). M.P = 127-129 ^{o}C. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3467, 2925, 1690, 1633, 1270, 1019, 760. **^{1}H-NMR (400 MHz,**



$CDCl_3$): δ 8.16-8.14 (m, 1H), 7.92-7.90 (m, 1H), 7.56-7.49 (m, 2H), 7.16 (d, *J* = 11.6 Hz, 1H), 6.85-6.78 (m, 1H), 6.36 (sextet, *J* = 7.2 Hz, 1H), 5.91 (d, *J* = 6.5 Hz, 1H), 2.35 (d, *J* = 6.4 Hz, 1H), 2.00 (dd, *J* = 6.9 and 1.3 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 185.4, 158.9, 148.1, 145.0, 143.2, 138.9, 135.3, 133.3, 128.3, 127.2, 125.5, 124.6, 124.3, 67.0, 19.3. HRMS (ESI): *m/z* calcd for $C_{15}H_{13}O_2S$ $(M+H)^+$: 257.0636. Found: 257.0644.

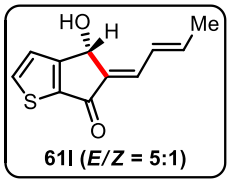
Optical rotation: $[\alpha]^{23}_D$ -36.3 (*c* 0.11, $CHCl_3$) for a sample with *ee* 94%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AS Column (98:2 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 13.2 min, τ_{minor} = 23.9 min).

2-((2*E*,4*E*)-Hexa-2,4-dienoyl)thiophene-3-carbaldehyde (58l).



This compound was prepared by following the general procedure **8** and isolated as pale yellow oil. R_f = 0.5 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2928, 1680, 1651, 1623, 1584, 1244, 1156, 732. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.50 (s, 1H), 7.65 (d, *J* = 4.9 Hz, 1H), 7.50-7.47 (m, 2H), 6.68 (d, *J* = 14.8 Hz, 1H), 6.36-6.34 (m, 2H), 1.43 (d, *J* = 5.3 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 187.5, 182.8, 147.1, 146.6, 144.3, 143.5, 130.1, 129.2, 128.4, 124.6, 19.0. **HRMS (ESI):** *m/z* calcd for $C_{11}H_{11}O_2S$ $(M+H)^+$: 207.0480. Found: 207.0467.

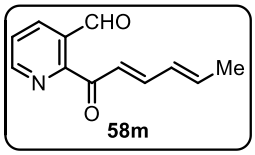
(*R*,*E*)-5-((*E*)-But-2-en-1-ylidene)-4-hydroxy-4*H*-cyclopenta[*b*]thiophen-6(5*H*)-one (61l).



This compound was isolated as Pale yellow oil. Following the general procedure **11**, 20 mg of **58l** afforded 19.4 mg of **61l** (89% yield). R_f = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3383, 2961, 2925, 1692, 1633, 1434, 1377, 1035, 732. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.89 (d, *J* = 4.8 Hz, 1H), 7.30 (d, *J* = 4.9 Hz, 1H), 7.09 (d, *J* = 12.0 Hz, 1H), 6.77-6.69 (m, 1H), 6.34-6.29 (m, 1H), 5.65 (s, 1H), 2.41 (brs, 1H), 1.97 (dd, *J* = 8.0 and 1.5 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 184.1, 163.7, 144.6, 142.7, 140.0, 139.8, 135.4, 127.1, 123.3, 66.7, 19.2. **HRMS (ESI):** *m/z* calcd for $C_{11}H_9OS$ $(M-OH)^+$: 189.0374. Found: 189.0389.

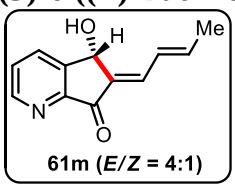
Optical rotation: $[\alpha]^{23}_D$ -6.6 (*c* 0.10, $CHCl_3$) for a sample with *ee* 92%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H Column (90:10 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 22.1 min, τ_{minor} = 33.2 min).

2-((2*E*,4*E*)-Hexa-2,4-dienoyl)nicotinaldehyde (58m).



This compound was prepared by following the general procedure **6** and isolated as pale brown solid. M.P = 114-116 ^{o}C. R_f = 0.4 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3009, 1700, 1662, 1574, 1275, 997, 750. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.49 (s, 1H), 8.86-8.85 (m, 1H), 8.23 (d, *J* = 7.6 Hz, 1H), 7.60 (dd, *J* = 7.6 and 4.8 Hz, 1H), 7.55-7.49 (m, 1H), 7.33 (d, *J* = 15.6 Hz, 1H), 6.41-6.37 (m, 2H), 1.94 (d, *J* = 5.6 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 191.2, 190.8, 156.0, 151.9, 147.0, 143.1, 136.3, 133.0, 130.8, 126.2, 123.5, 19.1. **HRMS (ESI):** *m/z* calcd for $C_{12}H_{12}NO_2$ (M+H): 202.0868. Found: 202.0881.

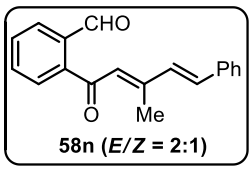
(*S*)-6-((*E*)-But-2-en-1-ylidene)-5-hydroxy-5*H*-cyclopenta[*b*]pyridin-7(6*H*)-one (61m).



This compound was isolated as Pale brown solid. Following the general procedure **11**, 20 mg of **58m** afforded 17.7 mg of **61m** (88% yield). M.P = 123-125 ^{o}C. R_f = 0.2 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3417, 2834, 1659, 1651, 1025, 999, 764. **^{1}H-NMR (400 MHz, $(CD_3)_2SO$):** δ 8.81-8.80 (m, 1H), 8.21-8.19 (m, 1H), 7.68 (dd, *J* = 8.0 and 6.9 Hz, 1H), 7.20 (d, *J* = 7.0 Hz, 1H), 6.84-6.76 (m, 1H), 6.53-6.47 (m, 1H), 6.00 (d, *J* = 8.4 Hz, 1H), 5.67 (d, J = 8.1 Hz, 1H), 1.94 (d, *J* = 6.8 Hz, 3H). **^{13}C-NMR (100 MHz, $(CD_3)_2SO$):** δ 191.5, 154.6, 152.2, 148.1, 144.0, 137.0, 136.8, 135.5, 128.6, 128.4, 65.9, 19.6. **HRMS (ESI):** *m/z* calcd for $C_{12}H_{10}NO$ (M-OH): 184.0762. Found: 184.0756.

Optical rotation: $[\alpha]^{23}_{D}$ +39.2 (*c* 0.05, DMSO) for a sample with *ee* 96%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AS Column (87:13 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 9.2 min, τ_{minor} = 11.8 min).

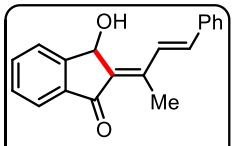
2-((2*E*,4*E*)-3-Methyl-5-phenylpenta-2,4-dienoyl)benzaldehyde (58n).



This compound was prepared by following the general procedure **6** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2922, 1694, 1654, 1575, 1246, 968, 725. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.28 (s, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.74-7.72 (m, 1H), 7.68-7.52 (m, 4H), 7.41-7.28 (m, 3H), 7.14 (d, *J* = 16.0 Hz, 1H), 6.93 (d, *J* = 16.0 Hz, 1H), 6.78 (s, 1H), 2.52 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.8, 191.8, 153.9, 143.8, 136.7, 136.1, 135.8, 133.0,

132.0, 129.1, 128.9(2C), 128.8, 128.1, 127.3(2C), 125.9, 124.0, 14.7. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{17}O_2$ $(M+H)^+$: 277.1229. Found: 277.1216.

(*E*)-3-Hydroxy-2-((*E*)-4-phenylbut-3-en-2-ylidene)-2,3-dihydro-1*H*-inden-1-one (61n).

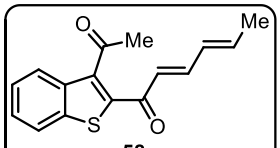


61n (*E*/*Z* = 3:2)

This compound was isolated as Pale yellow solid. Following the general procedure **10**, 40 mg of **58n** afforded 36.5 mg of **61n** (91% yield). M.P = 127-129 ^oC. R_f = 0.2 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3400, 2924, 1668, 1605, 1579, 1336, 1094, 751. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.74-7.70 (m, 2H), 7.65-7.53 (m, 4H), 7.42-7.28 (m, 4H), 7.12 (d, *J* = 16.0 Hz, 1H), 5.8 (s, 1H), 2.92 (brs, 2.50 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 193.7, 149.7, 149.3, 131.9, 137.6, 136.5, 135.3, 134.9, 129.2, 128.8(2C), 128.5, 127.6(2C), 125.8, 125.7, 123.2, 69.9, 13.3. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{17}O_2$ $(M+H)^+$: 277.1229. Found: 277.1215.

Data of the pure *E*-isomer of 61n: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.82 (dd, *J* = 16.1 and 3.2 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.57-7.51 (m, 4H), 7.41-7.31 (m, 4H), 7.00 (d, *J* = 16.1 Hz, 1H), 5.63 (s, 7.2 Hz, 1H), 2.89 (d, *J* = 7.1 Hz, 1H), 2.36 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 193.0, 150.3, 149.9, 138.9, 136.8, 136.7, 134.8, 134.7, 129.3, 128.9, 128.7(2C), 127.8(2C), 126.4, 125.6, 123.1, 70.5, 16.2.

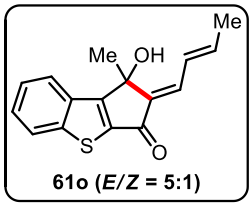
(2*E*,4*E*)-1-(3-Acetylbenzo[b]thiophen-2-yl)hexa-2,4-dien-1-one (58o).



58o

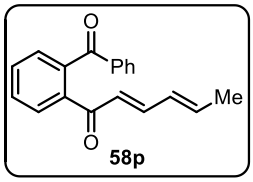
This compound was prepared by following the general procedure **9** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $_{max}/cm^{-1}$ 3444, 3064, 2918, 1699, 1652, 1585, 1510, 1140, 757. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.52-7.47 (m, 3H), 6.67 (d, *J* = 14.8 Hz, 1H), 6.37-6.35 (m, 2H), 2.62 (s, 3H), 1.94 (d, *J* = 4.8 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 200.9, 184.0, 146.9, 143.5, 142.1, 140.5, 136.7, 130.2, 127.6, 125.8, 125.2, 124.5, 124.3, 122.7, 31.5, 19.1. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{15}O_2S$ (M+H): 271.0793. Found: 271.0793.

(*E*)-2-((*E*)-But-2-en-1-ylidene)-1-hydroxy-1-methyl-1*H*-benzo[*b*]cyclopenta[*d*]thiophen-3(2*H*)-one (61o).



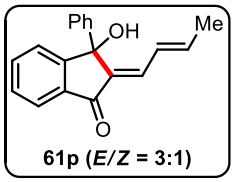
This compound was isolated as light yellow semi solid. Following the general procedure **10**, 20 mg of **58o** afforded 17.8 mg of **61o** (89% yield). R_f = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** $_{max}$/cm^{-1} 3387, 2929, 1681, 1632, 1267, 1041, 735. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 8.18-8.15 (m, 1H), 7.93-7.90 (m, 1H), 7.53-7.49 (m, 2H), 7.03 (d, *J* = 12.0 Hz, 1H), 6.97-6.93 (m, 1H), 6.34-6.28 (m, 1H), 2.61 (br s, 1H), 2.00 (dd, *J* = 6.7 and 1.6 Hz, 3H), 1.96 (s, 3H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 185.1, 162.8, 148.3, 143.0, 142.8, 133.4, 132.2, 128.8, 127.2, 126.5, 125.3, 125.0, 124.4, 74.7, 26.1, 19.3. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{15}O_2S$ $(M+H)^+$: 271.0793. Found: 271.0782.

(2*E*,4*E*)-1-(2-Benzoylphenyl)hexa-2,4-dien-1-one (58p).



This compound was prepared by following the general procedure **6** and isolated as pale brown oil. R_f = 0.5 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $_{max}$/cm^{-1} 3451, 3061, 2930, 1664, 1587, 1448, 1284, 704. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 7.79-7.77 (m, 3H), 7.61-7.56 (m, 2H), 7.55-7.48 (m, 2H), 7.44-7.40 (m, 2H), 7.16-7.10 (m, 1H), 6.56 (d, *J* = 15.1 Hz, 1H), 6.24-6.17 (m, 2H), 1.86 (d, *J* = 6.2 Hz, 3H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 197.4, 192.5, 146.5, 141.7, 140.6, 139.3, 137.2, 132.9, 131.0, 130.3, 129.9, 129.6(2C), 128.7, 128.6, 128.3(2C), 125.1, 18.9. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{17}O_2$ (M+H): 277.1229. Found: 277.1244.

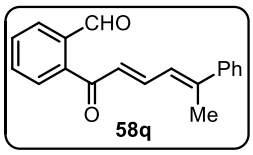
(*E*)-2-((*E*)-But-2-en-1-ylidene)-3-hydroxy-3-phenyl-2,3-dihydro-1*H*-inden-1-one (61p).



This compound was isolated as pale yellow sticky oil. Following the general procedure **10**, 25 mg of **58p** afforded 23 mg of **61p** (92% yield). R_f = 0.2 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $_{max}$/cm^{-1} 3413, 2929, 1687, 1624, 1288, 982, 699. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 7.75 (d, *J* = 8.4 Hz, 1H), 7.65 (dt, *J* = 11.6 and 1.2 Hz, 1H), 7.50 (dt, *J* = 7.7 and 0.9 Hz, 1H), 7.37-7.33 (m, 3H), 7.31-7.27 (m, 2H), 7.21-7.17 (m, 1H), 7.04 (d, *J* = 10.6 Hz, 1H), 6.56 (s, 1H), 6.36-6.29 (m, 2H), 1.72 (d, *J* = 5.8 Hz, 3H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 192.7, 157.3, 145.9, 143.1, 142.2, 136.4, 136.0, 134.6,

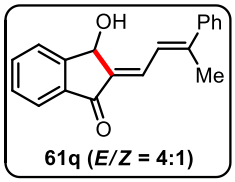
129.4, 128.6(2C), 127.8, 127.0, 125.7, 125.5(2C), 122.9, 77.6, 19.5. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{15}O$ (M-OH): 259.1123. Found: 259.1143.

2-((2*E*,4*E*)-5-Phenylhexa-2,4-dienoyl)benzaldehyde (58q).



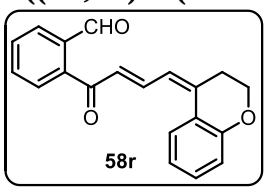
This compound was prepared by following the general procedure **6** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3379, 3058, 1695, 1651, 1578, 1445, 1291, 1022, 761. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.22 (s, 1H), 8.02 (d, *J* = 7.3 Hz, 1H), 7.74-7.66 (m, 3H), 7.55-7.53 (m, 2H), 7.42-7.35 (m, 4H), 6.82 (d, *J* = 15.4 Hz, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 2.30 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 193.9, 191.4, 148.7, 142.7, 142.2, 141.6, 135.7, 133.1, 131.0, 129.2, 128.8, 128.6(2C), 128.4, 128.3, 126.0(2C), 125.2, 16.8. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{17}O_2$ $(M+H)^+$: 277.1229. Found: 277.1223.

(*E*)-3-Hydroxy-2-((*E*)-3-phenylbut-2-en-1-ylidene)-2,3-dihydro-1*H*-inden-1-one (61q).



This compound was isolated as pale yellow solid. Following the general procedure **10**, 25 mg of **58q** afforded 22 mg of **61q** (87% yield). M.P = 158-160 ^oC. R_f = 0.4 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3416, 3006, 1681, 1610, 1275, 749. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.80-7.75 (m, 1H), 7.70 (t, *J* = 7.2 Hz, 1H), 7.62-7.60 (m, 2H), 7.50-7.37 (m, 6H), 7.29-7.25 (m, 1H), 5.83 (s, 1H), 2.48 (br s, 1H), 2.39 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.2, 151.0, 149.9, 141.9, 138.2, 138.0, 135.2, 132.8, 129.6, 128.8, 128.5(2C), 126.2(2C), 125.9, 123.5, 122.4, 69.1, 16.5. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{15}O$ (M-OH): 259.1123. Found: 259.1136.

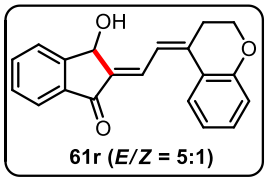
2-((2*E*,4*Z*)-4-(Chroman-4-ylidene)but-2-enoyl)benzaldehyde (58r).



This compound was prepared by following the general procedure **6** and isolated as pale brown oil. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2925, 1694, 1646, 1578, 1481, 1276, 750. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.22 (s, 1H), 8.01 (d, *J* = 7.2 Hz, 1H), 7.71-7.64 (m, 5H), 7.28-7.26 (m, 1H), 6.98-6.95 (m, 1H), 6.92-6.87 (m, 2H), 6.84 (d, *J* = 15.2 Hz, 1H), 4.27 (t, *J* = 6.0 Hz, 2H), 2.90 (t, *J* = 6.1 Hz, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 193.4, 191.4, 156.0, 142.2, 141.4, 141.2,

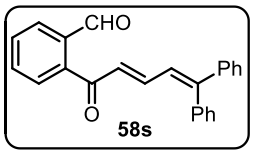
135.7, 133.2, 131.2, 131.0, 129.2, 128.3, 128.1, 124.4, 121.5, 121.2, 118.8, 118.0, 65.6, 26.5. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{17}O_3$ (M+H): 305.1178. Found: 305.1163.

(*E*)-2-((*Z*)-2-(Chroman-4-ylidene)ethylidene)-3-hydroxy-2,3-dihydro-1*H*-inden-1-one (61r).



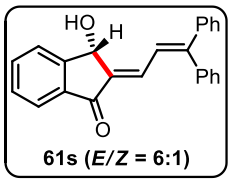
This compound was isolated as Pale brown solid. Following the general procedure **10**, 25 mg of **58r** afforded 22 mg of **61r** (89% yield). M.P = 166-168 ^{o}C. R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3400, 3002, 1683, 1609, 1260, 750. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 7.82-7.78 (m, 3H), 7.72-7.63 (m, 2H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.43-7.40 (m, 1H), 7.28-7.24 (m, 1H), 6.97 (dt, *J* = 6.9 and 1.2 Hz, 1H), 6.90 (dd, *J* = 8.0 and 1.1 Hz, 1H), 5.85 (s, 1H), 4.27 (t, *J* = 6.0 Hz, 2H), 3.01-2.97 (m, 2H), 2.62 (br s, 1H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 192.0, 156.0, 151.1, 142.0, 138.1, 137.9, 135.1, 131.6, 131.2, 129.6, 125.9, 124.9, 123.5, 121.9, 121.2, 117.9, 116.2, 69.1, 65.7, 26.3. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{15}O_2$ (M-OH): 287.1072. Found: 287.1099.

(*E*)-2-(5,5-Diphenylpenta-2,4-dienoyl)benzaldehyde (58s).



This compound was prepared by following the general procedure **6** and isolated as pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3378, 3057, 2854, 1696, 1647, 1577, 1445, 1278, 1023, 772, 700. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 10.15 (s, 1H), 7.95-7.93 (m, 1H), 7.64-7.58 (m, 2H), 7.40-7.17 (m, 12H), 6.93 (d, *J* = 11.2 Hz, 1H), 6.85 (dd, *J* = 15.2 and 0.6 Hz, 1H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 194.1, 191.2, 153.8, 145.1, 142.0, 141.0, 138.2, 135.5, 133.1, 130.8, 130.4(2C), 129.6, 129.2, 129.1, 128.6, 128.5(2C), 128.4(2C), 128.3(2C), 125.5. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{19}O_2$ (M+H): 339.1385. Found: 339.1392.

(*S*)-2-(3,3-Diphenylallylidene)-3-hydroxy-2,3-dihydro-1*H*-inden-1-one (61s).

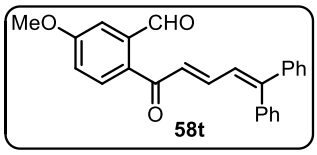


This compound was isolated as pale yellow solid. Following the general procedure **11**, 25 mg of **58s** afforded 23 mg of **61s** (92% yield). M.P = 162-164 ^{o}C. R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3395, 3056, 1681, 1610, 1275, 749. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 7.80 (d, *J* = 6.5 Hz, 2H), 7.70-7.66 (m, 1H), 7.50-7.34 (m, 11H), 7.28-7.25 (m, 2H), 5.88 (d, *J* = 7.2 Hz, 1H), 2.39 (d, *J* = 7.1 Hz, 1H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 191.7, 154.2, 150.8, 141.5, 139.2, 138.3, 138.2,

135.1, 134.5, 130.6(2C), 129.6, 129.1, 128.6, 128.5(2C), 128.4(2C), 128.3 (2C), 125.9, 123.5, 122.9, 69.2. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{17}O$ (M-OH): 321.1279. Found: 321.1283.

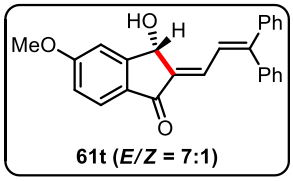
Optical rotation: $[\alpha]^{23}_{D}$ +20.5 (*c* 0.05, $CHCl_3$) for a sample with *ee* 97%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AS Column (90:10 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 44.5 min, τ_{minor} = 20.7 min).

(*E*)-2-(5,5-Diphenylpenta-2,4-dienoyl)-5-methoxybenzaldehyde (58t).



This compound was prepared by following the general procedure **6** and isolated as pale brown oil. R_f = 0.4 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3055, 1690, 1595, 1577, 1444, 1276, 1018, 765. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.22 (s, 1H), 7.75-7.70 (m, 1H), 7.44-7.36 (m, 11H), 7.24-7.21 (m, 1H), 7.15-7.11 (m, 1H), 7.01-6.95 (m, 2H), 3.98 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 191.7, 191.5, 161.9, 153.4, 144.0, 141.2, 138.9, 138.4, 134.3, 130.8, 130.4(2C), 129.1, 128.7, 128.6, 128.5(2C), 128.4(2C), 128.3(2C), 125.7, 118.8, 112.3, 55.8. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{21}O_3$ (M+H): 369.1491. Found: 369.1479.

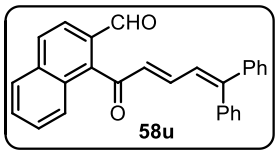
(*S*)-2-(3,3-Diphenylallylidene)-3-hydroxy-5-methoxy-2,3-dihydro-1*H*-inden-1-one (61t).



This compound was isolated as pale yellow solid. Following the general procedure **11**, 15 mg of **58t** afforded 13 mg of **61t** (88% yield). M.P = 191-193 ^oC. R_f = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3006, 2919, 1691, 1609, 1275, 1260, 750. **^{1}H-NMR (400 MHz, $(CD_3)_2SO$):** δ 7.63 (d, *J* = 8.8 Hz, 1H), 7.54-7.50 (m, 4H), 7.43-7.35 (m, 5H), 7.25-7.23 (m, 3H), 7.07 (dd, *J* = 8.6 and 2.2 Hz, 1H), 6.96 (dd, *J* = 8.1 and 1.4 Hz, 1H), 6.15 (d, *J* = 8.0 Hz, 1H), 5.78 (d, *J* = 7.9 Hz, 1H), 3.91 (s, 3H). **^{13}C-NMR (100 MHz, $(CD_3)_2SO$):** δ 190.1, 165.6, 156.0, 151.2, 141.9, 141.3, 138.5, 131.2, 130.7, 130.5(2C), 129.4, 129.1(2C), 129.0(2C), 128.9, 128.2(2C), 125.0, 123.7, 117.3, 169.9, 67.7, 56.3. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{19}O_2$ (M-OH): 351.1385. Found: 351.1399.

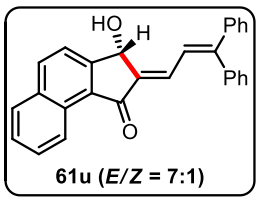
Optical rotation: $[\alpha]^{23}_{D}$ +20.2 (*c* 0.30, $CHCl_3$) for a sample with *ee* 97%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AD Column (94:6 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 39.8 min, τ_{minor} = 30.2 min).

(*E*)-1-(5,5-Diphenylpenta-2,4-dienoyl)-2-naphthaldehyde (58u).



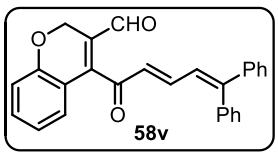
This compound was prepared by following the general procedure **6** and isolated as pale yellow solid. M.P = 122-124 ^{o}C. R_f = 0.4 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3007, 1695, 1641, 1604, 1275, 1260, 749. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.17 (s, 1H), 7.93-7.89 (m, 3H), 7.69-7.61 (m, 2H), 7.36-7.19 (m, 7H), 7.07 (t, *J* = 7.6 Hz, 2H), 6.92-6.84 (m, 5H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 197.9, 190.5, 154.3, 147.2, 147.1, 143.5, 140.8, 137.8, 136.0, 132.5, 130.4, 130.3, 129.7, 129.6, 129.3, 129.2(2C), 128.4(2C), 128.3(2C), 127.9, 127.6(2C), 126.7, 125.2, 122.9. **HRMS (ESI):** *m/z* calcd for $C_{28}H_{21}O_2$ (M+H): 389.1542. Found: 389.1546.

(*S*)-2-(3,3-Diphenylallylidene)-3-hydroxy-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1-one (61u).



This compound was isolated as pale yellow solid. Following the general procedure **11**, 24 mg of **58u** afforded 23 mg of **61u** (95% yield). M.P = 147-149 ^{o}C. R_f = 0.2 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3418, 3056, 1681, 1609, 1275, 1173, 749. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 9.19-9.17 (m, 1H), 8.14-8.10 (m, 1H), 7.93-7.89 (m, 1H), 7.83-7.78 (m, 1H), 7.71-7.57 (m, 2H), 7.54-7.21 (m, 12H), 5.91 (s, 1H), 2.40 (br s, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.5, 153.5, 152.73, 152.71, 141.5, 139.5, 138.3, 136.4, 139.5, 136.4, 133.1, 130.6(2C), 129.1, 129.0, 128.9, 128.5(2C), 128.4(4C), 128.3, 127.4, 125.0, 122.9, 122.4, 69.0. **HRMS (ESI):** *m/z* calcd for $C_{28}H_{19}O$ (M–OH): 371.1436. Found: 371.1453. **Optical rotation:** $[\alpha]^{23}_{D}$ +114.7 (*c* 0.18, $CHCl_3$) for a sample with *ee* 89%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H Column (95:5 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 59.6 min, τ_{minor} = 37.8 min).

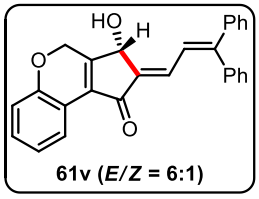
(*E*)-4-(5,5-Diphenylpenta-2,4-dienoyl)-2*H*-chromene-3-carbaldehyde (58v).



This compound was prepared by following the general procedure **7** and isolated as pale brown sticky oil. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3058, 2855, 1759, 1672, 1602, 1445, 1275, 751. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 9.66 (s, 1H), 7.40-7.35 (m, 4H), 7.34-7.28 (m, 4H), 7.27-7.25 (m, 2H), 7.12 (dd, *J* = 8.0 and 1.6 Hz, 1H), 7.01-6.98 (m, 3H), 6.93 (dd, *J* = 8.0 and 0.8 Hz,

1H), 6.89 (d, *J* = 11.6 Hz, 1H), 6.61 (d, *J* = 15.2 Hz, 1H), 4.90 (s, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.1, 187.8, 155.7, 155.5, 149.4, 148.1, 140.7, 137.8, 133.5, 130.5, 130.4(2C), 129.5, 128.9, 128.6(2C), 128.5(2C), 128.3(2C), 127.2, 126.9, 124.9, 122.1, 119.4, 117.1, 62.1. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{21}O_3$ $(M+H)^+$: 393.1491. Found: 393.1473.

(*S*,*E*)-2-(3,3-Diphenylallylidene)-3-hydroxy-2,3-dihydrocyclopenta[*c*]chromen-1(4*H*)-one (61v).



This compound was isolated as light yellow liquid. Following the general procedure **11**, 20 mg of **58v** afforded 18.3 mg of **61v** (91% yield, *E*/*Z* = 6:1). R_f = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3437, 2924, 1634, 1614, 1269, 760. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.11 (dd, *J* = 7.8 and 0.8 Hz, 1H),7.44-7.43 (m, 3H), 7.36-7.35 (m, 5H), 7.32-7.28 (m, 2H), 7.26-7.19 (m, 3H), 6.96-6.93 (m, 1H), 6.92-6.83 (m, 1H), 5.42-5.20 (m, 3H), 2.07 (br s, 1H) . **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 189.9, 156.7, 153.8, 153.0, 141.4, 138.1, 136.9, 134.1, 131.8, 130.6(2C), 129.0, 128.6, 128.4(6C), 125.2, 122.3, 121.7, 116.5, 115.9, 68.7, 65.2. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{21}O_3$ $(M+H)^+$: 393.1491. Found: 393.1474.

Optical rotation: $[\alpha]^{23}_D$ +49.9 (*c* 0.10, $CHCl_3$) for a sample with *ee* 98%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H Column (93:7 *n*-Hexane/2-Propanol, 0.8 mL/min, 254 nm, τ_{major} = 35.7 min, τ_{minor} = 32.3 min).

General procedure 12: Synthesis of *E*,*Z*-58b

Step I: An oven dried 25 mL RB flask was charged with sodium hydride (60% oil dispersion, 5.2 mmol), 10 mL dry THF and placed at 0 ^{o}C. To this suspension, triethyl phosphonoacetate **73** (5.1 mmol) was added dropwise under argon atmosphere at same temperature and stirred until the effervescence of hydrogen gas ceased. Phenyl propiolaldehyde **72** (5.0 mmol) dissolved in 1 mL of dry THF was added dropwise over 2 min and continued stirring for 30 min. The reaction mixture was quenched with saturated aq. NH_4Cl solution and extracted using 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 to afford **74** as colorless oil.

Step II: In an oven dried 10 mL RB flask the ester **74** (1 mmol) was dissolved in 1 mL dry methanol. Quinoline (0.15 mmol) and Lindlar's catalyst (0.1 mmol) were introduced to the reaction mixture. The reaction mixture was evacuated and refilled with hydrogen gas (3 times) and stirred at room temperature. The reaction mixture was followed carefully to avoid over-reduction. After completion of the reaction (by TLC), the reaction mixture was filtered through a celite pad and the filtrate was extracted using 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 to afford **75** as pale yellow oil.

Step III: An oven dried 50 mL RB flask was charged with **75** (4.0 mmol), 10 mL dry THF and placed at 0 ^{o}C. To the reaction mixture DIBAL-H (8.2 mmol) was added drop wise at the same temperature and allowed to stir at rt for 5 h. The reaction mixture was quenched with saturated aq. NH_4Cl solution and the resultant mixture was filtered through Buchner funnel, the filtrate was extracted using ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated to afford the crude alcohol as pale yellow oil. The crude alcohol was further subjected to IBX oxidation to afford the aldehyde **76** as yellow solid.

Step IV: An oven dried 25 mL long neck RB flask was charged with 2-(2-bromophenyl)-1,3-dioxolane **77** (1.0 mmol), 5 mL dry THF and placed at -78 ^{o}C. A hexane solution of *n*-BuLi (1.2 mL, 3.2 mmol) was added and the mixture was stirred for an additional 45 mins. The dienal **76** (1.1 mmol) dissolved in 1 mL dry THF, was added dropwise over 5 min. The mixture was warmed to room temperature. 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 as eluent to afford dienol **78**.

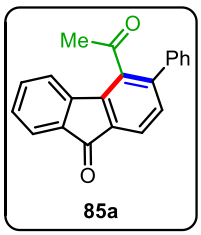
Step V: The IBX oxidation (as described in general procedure **1**, Step II) of alcohol **78** delivered the crude dienone and subsequently subjected to *p*-TSA (0.2 mmol) mediated acetal deprotection in acetone. The reaction mixture was quenched with saturated aq. Sodium bicarbonate and extracted using ethylacetate. The crude product was purified by flash chromatography using hexane/ethyl acetate to afford ***E,Z*-58b** as a pale yellow oil.

General Procedure 13: One-pot telescopic synthesis of 3,4-disubstituted fluorenones 85

Step-I: An oven dried 5 mL glass vial was charged with **61** (30 mg, 0.15 mmol), acetylacetone (0.2 mmol) in dichloroethane (DCE, 1 mL) and bismuth(III)chloride (10 mol%) was introduced at room temperature (rt). Stirring continued at RT until **61** disappeared as monitored by TLC. Reaction mixture was quenched with water and extracted using dichloromethane. Volatiles were removed under reduced pressure. The crude product **80** was subjected to next step without further purification.

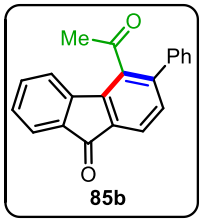
Step-II: An oven dried 5 mL glass vial was charged with **80** (0.1 mmol) in dimethylformamide (DMF, 1 mL) and potassium carbonate (0.11 mmol) was introduced at room temperature (rt) and stirring continued at 60 ^{o}C until **80** disappeared as monitored by TLC. The crude reaction mixture was purified by silica gel flash chromatography using hexanes/ethyl acetate as eluent, to afford **85**.

4-Acetyl-3-methyl-9*H*-fluoren-9-one (85a).



This compound was isolated as pale yellow solid. Following the general procedure **13**, 30 mg of **61a** afforded 16 mg of **85a** (46% yield, over two steps). M.P = 150-152 ^{o}C. R_f = 0.5 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2924, 2854, 1714, 1695, 1357, 1111, 752. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.70 (d, *J* = 7.3 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.46 (dt, *J* = 7.6 and 1.1 Hz, 1H), 7.35-7.28 (m, 2H), 7.71 (d, *J* = 7.6 Hz, 1H), 2.67 (s, 3H), 2.35 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 206.7, 192.5, 142.5, 139.8, 139.2, 137.2, 134.7, 134.6, 132.5, 130.9, 129.4, 124.6, 124.5, 122.1, 32.3, 19.3. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{11}O_2$ $(M-H)^+$: 235.0759. Found: 235.0750.

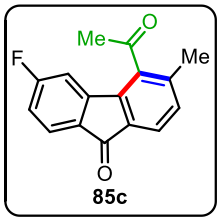
4-Acetyl-3-phenyl-9*H*-fluoren-9-one (85b).



This compound was isolated as pale yellow solid. Following the general procedure **13**, 25 mg of **61b** afforded 12 mg of **85b** (43% yield, over two steps). M.P = 115-117 ^{o}C. R_f = 0.5 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2993, 1715, 1698, 1606, 1576, 1412, 1275, 1259, 749. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.73 (dd, *J* = 7.4 and 0.8 Hz, 1H), 7.48-7.41 (m, 7H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.35 (dt, *J* = 7.6 and 1.3 Hz, 1H), 2.11 (s, 3H). **^{13}C-NMR**

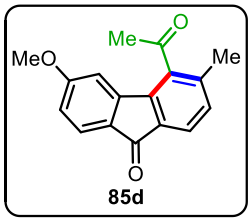
(100 MHz, $CDCl_3$): δ 206.3, 192.5, 144.8, 142.8, 142.6, 139.7, 138.9, 136.5, 135.0, 134.5, 133.6, 130.7, 129.5, 128.9(2C), 128.8(2C), 128.7, 124.7, 124.5, 122.6, 32.0. HRMS (ESI): *m/z* calcd for $C_{21}H_{13}O_2$ $(M-H)^+$: 297.0916. Found: 297.0903.

4-Acetyl-6-fluoro-3-methyl-9*H*-fluoren-9-one (85c).



This compound was isolated as off white solid. Following the general procedure **13**, 25 mg of **61e** afforded 15 mg of **85c** (50% yield). M.P = 110-112 °C. R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2990, 1714, 1690, 1612, 1584, 1275, 1260, 750. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.70 (dd, *J* = 8.0 and 2.8 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.21 (7.7 Hz, 1H), 7.01-6.96 (m, 2H), 2.67 (s, 3H), 2.37 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 206.1, 190.7, 165.7 (d, *J* = 254.1 Hz), 145.4 (d, *J* = 9.7 Hz), 139.9, 137.53, 137.51, 132.9, 131.6, 130.6 (d, *J* = 2.5 Hz), 126.5 (d, *J* = 10.2 Hz), 124.5, 115.8 (d, *J* = 23.2 Hz), 110.4 (d, *J* = 25.0 Hz), 32.2, 19.3. **^{19}F-NMR (376 MHz, $CDCl_3$):** δ -101.9. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{12}FO_2$ $(M+H)^+$: 255.0821. Found: 255.0819.

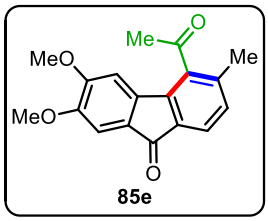
4-Acetyl-6-methoxy-3-methyl-9*H*-fluoren-9-one (85d).



This compound was isolated as pale yellow solid. Following the general procedure **13**, 30 mg of **61f** afforded 15 mg of **85d** (44% yield). M.P = 116-117 °C. R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2928, 1704, 1688, 1612, 1584, 1363, 1228, 782. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.67 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 6.81 (d, *J* = 2.0 Hz, 1H), 6.77 (dd, *J* = 8.2 and 2.0 Hz, 1H), 3.89 (s, 3H), 2.67 (s, 3H), 2.37 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 206.5, 191.1, 165.2, 144.9, 139.2, 138.0, 137.2, 133.7, 131.1, 129.6, 126.5, 124.1, 112.5, 109.7, 55.8, 32.3, 19.2. HRMS (ESI): *m/z* calcd for $C_{17}H_{15}O_3$ $(M+H)^+$: 267.1021. Found: 267.1009.

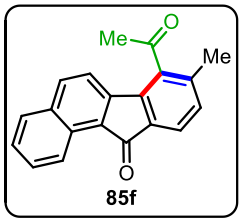
5-Acetyl-2,3-dimethoxy-6-methyl-9*H*-fluoren-9-one (85e).

This compound was isolated as pale yellow solid. Following the general procedure **13**, 35 mg of **61h** afforded 16 mg of **85e** (43% yield). M.P = 178-180 °C. R_f = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2926, 1704, 1681, 1609, 1480, 1276, 749. **^{1}H-NMR (400 MHz,**



$CDCl_3$): δ 7.50 (d, *J* = 7.6 Hz, 1H), 7.23 (s, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.78 (s, 1H), 3.96 (s, 3H), 3.95 (s, 3H), 2.67 (s, 3H), 2.33 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 206.8, 191.8, 154.2, 149.8, 139.3, 138.8, 137.4, 136.1, 133.2, 129.9, 127.7, 124.0, 107.2, 105.3, 56.29, 56.28, 32.3, 19.3. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{17}O_4$ $(M+H)^+$: 297.1127. Found: 297.1123.

7-Acetyl-8-methyl-11*H*-benzo[*a*]fluoren-11-one (85f).



This compound was isolated as pale yellow solid. Following the general procedure **13**, 40 mg of **61i** afforded 22 mg of **85f** (48% yield). M.P = 162-164 °C. R_f = 0.4 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2935, 1702, 1692, 1604, 1581, 1280, 1060, 761. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 9.02 (d, *J* = 8.5 Hz, 1H), 7.95 (*J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.64-7.62 (m, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.49-7.46 (m, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 2.71 (s, 3H), 2.34 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 206.8, 194.0, 144.3, 139.2, 138.6, 137.0, 135.8, 134.3, 132.9, 130.9, 130.2, 129.6, 128.3, 127.6, 126.8, 124.4, 123.9, 119.4, 32.6, 19.2. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{15}O_2$ $(M+H)^+$: 287.1072. Found: 287.1076.

General Procedure 14: Synthesis of α-substituted dienones 86

Step-I: The alcohol **50** was synthesized by following the general procedure **2**, Step I.

Step-II: An oven dried 25 mL long neck RB flask was charged with 2-bromo alcohol **50** (1.0 mmol), dry THF (5 mL) and placed at –78 °C. *n*-BuLi (1.6 *M* in hexanes, 2.2 mmol) was added drop wise at the same temperature and stirred for an hour. Then, α-substituted dienal **90** (1.3 mmol) dissolved in 1 mL of dry THF was added dropwise over 2 mins and stirred at room temperature for 30 mins. The reaction mixture was quenched with saturated aq. NH_4Cl solution and extracted using ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The product was purified by silica gel column chromatography using hexane/ethyl acetate (10:3) as eluent to afford the diol **89**.

Step-III: The diol **89** (1.0 mmol) was dissolved in ethyl acetate (10 mL) and IBX (2.2 mmol) was added. The resulting suspension was immersed in an oil bath set to 75 °C and stirred until diol **C** disappeared as monitored by TLC. The reaction mixture was cooled to room temperature and filtered through a Buchner funnel. The filter cake was washed with 3×5 mL of ethyl acetate.

Organic extracts were combined and washed with saturated sodium bicarbonate solution to remove excess iodobenzoic acid. The extract was dried over anhydrous sodium sulphate and concentrated under vacuum. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (1:10) as eluent to afford the a-substituted dienone-aldehydes **86**.

General procedure 15: Synthesis of benzothiophene based dienone 86m.

Step-I: To a solution of *N*-methylpiperazine (NMP, 0.18 mL, 1.6 mmol) in THF (5 mL) at –78 ^{o}C was added *n*-BuLi (1.6*M* in hexane, 1.0 mL, 1.6 mmol). After 15 min, benzothiophene-3-carboxaldehyde **44a** (200 mg, 1.2 mmol) was added, and then the reaction mixture was stirred for an additional 30 min. A hexane solution of *n*-BuLi (2.0 mL, 3.2 mmol) was added, and the mixture was stirred for an additional 15 min, and then the mixture was warmed to –30 ^{o}C in 2 h. The solution was again cooled to –78 ^{o}C, and dienal **90a** (1.5 mmol) was added dropwise over 5 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 as eluent to afford dienol **91**.

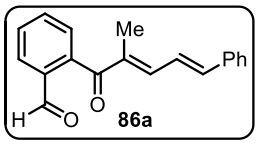
Steps-II: IBX oxidation of alcohol **91** was performed by following the general procedure 14, Step III to afford the dienone **86m**.

General Procedure 16: Synthesis of cyclopenta-fused arenes and heteroarenes *via* RAR

An oven dried 5 mL glass vial was charged with **86** (30 mg, 0.11 mmol). DMF (1 mL), water (3.3 mmol) and PBu_3 (1.3 mmol) were introduced at room temperature (rt) and stirring continued at rt until **86** disappeared as monitored by TLC. The reaction mixture was extracted using ethyl acetate and ice water. All the volatiles were removed under reduced pressure. The crude product was purified by silica gel chromatography using hexane/ethyl acetate as eluent, to afford **95**.

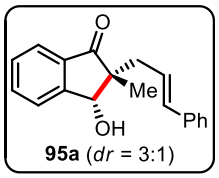
2-((2*E*,4*E*)-2-Methyl-5-phenylpenta-2,4-dienoyl)benzaldehyde (86a).

This compound was prepared by following the general procedure **14** and isolated as pale yellow solid. R_f = 0.5 (Hexane/EtOAc = 3/1). **IR (thin film, neat): ν_{max}/cm^{-1}** ν_{max}/cm^{-1} 3040, 2926,



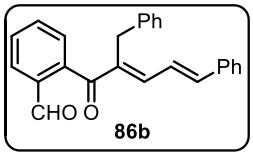
2854, 2743, 1700, 1645, 1612, 1390, 1287, 1241, 1012, 749. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.01 (s, 1H), 8.01 (dd, *J* = 7.6 and 1.6 Hz, 1H), 7.70-7.65 (m, 2H), 7.47-7.43 (m, 3H), 7.39-7.32 (m, 3H), 7.18 (dd, *J* = 15.3 and 11.5 Hz, 1H), 6.73 (d, *J* = 15.3 Hz, 1H), 6.71 (d, *J* = 11.4 Hz, 1H), 2.24 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 198.5, 190.6, 144.3, 142.4, 141.0, 137.6, 136.1, 134.7, 133.4, 130.1, 129.8, 129.2, 128.8(2C), 128.3, 127.3(2C), 123.9, 11.9. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{17}O_2$ $(M+H)^+$: 277.1229. Found: 277.1221.

2-Cinnamyl-3-hydroxy-2-methyl-2,3-dihydro-1*H*-inden-1-one (95a).



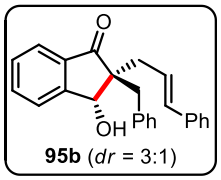
This compound was isolated as pale yellow oil. Following the general procedure **16**, 40 mg of **86a** afforded 34 mg of **95a** (85% yield). R_f = 0.2 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3427, 2927, 1705, 1605, 1062. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.71-7.67 (m, 2H), 7.51-7.47 (m, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.25-7.21 (m, 2H), 7.19-7.15 (m, 2H), 6.44 (d, *J* = 15.9 Hz, 1H), 6.09 (td, *J* = 15.9 and 11.5 Hz, 1H), 5.01 (s, 1H), 2.75-2.54 (m, 2H), 2.39 (s, 1H), 1.31 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.5, 153.0, 137.0, 135.4, 134.9, 133.0, 129.5, 128.4(2C), 127.2, 126.4, 126.1(2C), 125.5, 123.6, 78.5, 54.6, 37.8, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{19}O_2$ $(M+H)^+$: 279.1385. Found: 279.1394.

2-((2*E*,4*E*)-2-Benzyl-5-phenylpenta-2,4-dienoyl)benzaldehyde (86b).



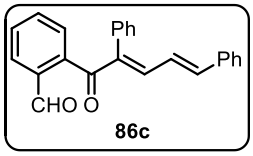
This compound was prepared by following the general procedure **14** and isolated as white solid. M.P = 135-137 ^oC. R_f = 0.5 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3029, 2849, 1701, 1643, 1609, 1492, 1449, 1372, 1287, 1241, 746. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 9.92 (s, 1H), 7.99 (d, *J* = 6.8 Hz, 1H), 7.66-7.59 (m, 2H), 7.41-30 (m, 11H), 7.25 (dd, *J* = 16.2 and 11.2 Hz, 1H), 6.87 (d, *J* = 16.4 Hz, 1H), 6.78 (d, *J* = 16.4 Hz, 1H), 4.08 (s, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 197.6, 190.5, 145.7, 142.5, 142.3, 140.2, 139.5, 135.9, 134.9, 133.3, 129.9, 129.6, 129.5, 128.9(2C), 128.6(2C), 128.4(2C), 128.3, 127.4(2C), 126.2, 123.7, 31.7. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{21}O_2$ $(M+H)^+$: 353.1542. Found: 353.1558.

2-Benzyl-2-cinnamyl-3-hydroxy-2,3-dihydro-1*H*-inden-1-one (95b).



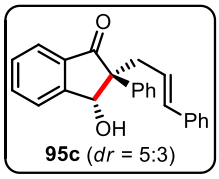
This compound was isolated as pale yellow oil. Following the general procedure **16**, 40 mg of **86b** afforded 33 mg of **95b** (83% yield). R_f = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3435, 3029, 2918, 1701, 1604, 1453, 1069, 701. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.72 (d, *J* = 7.5 Hz, 1H), 7.63-7.60 (m, 2H), 7.45-7.38 (m, 1H), 7.32-7.30 (m, 1H), 7.25-7.07 (m, 9H), 6.38 (d, *J* = 15.8 Hz, 1H), 5.96 (td, *J* = 15.8 and 7.5 Hz, 1H), 5.27 (d, *J* = 6.2 Hz, 1H), 3.24 (d, J_{AB} = 13.8 Hz, 1H), 3.01 (d, J_{AB} = 13.8 Hz, 1H), 2.70-2.64 (m, 1H), 2.59-2.53 (m, 1H), 2.23 (d, *J* = 7.1 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 206.3, 153.5, 137.5, 137.0, 135.3, 135.2, 132.9, 130.2(2C), 129.2, 128.8, 128.5(2C), 128.4(2C), 127.2, 126.7, 126.1(2C), 124.9, 123.3, 74.3, 59.9, 40.1, 38.1. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{21}O$ $(M-OH)^+$: 337.1592. Found: 337.1609.

2-((2*E*,4*E*)-2,5-Diphenylpenta-2,4-dienoyl)benzaldehyde (86c).



This compound was prepared by following the general procedure **14** and isolated as Pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3058, 2848, 2745, 1779, 1699, 1647, 1607, 1492, 1448, 1279, 1239, 1068, 753. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.09 (s, 1H), 7.97 (d, *J* = 7.2 Hz, 1H), 7.68-7.61 (m, 2H), 7.53-7.40 (m, 6H), 7.28-7.24 (m, 5H), 6.98-6.78 (m, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 197.1, 190.7, 144.4, 142.3, 142.1, 141.7, 135.9, 134.8, 134.7, 133.5, 130.7, 130.5(2C), 130.0, 129.3, 128.8(2C), 128.5, 128.3(2C), 128.1, 127.4(2C), 124.9. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{19}O_2$ $(M+H)^+$: 339.1385. Found: 339.1402.

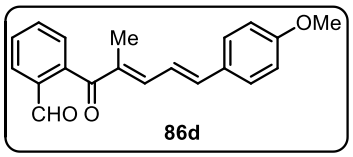
2-Cinnamyl-3-hydroxy-2-phenyl-2,3-dihydro-1*H*-inden-1-one (95c).



This compound was isolated as pale yellow oil. Following the general procedure **16**, 40 mg of **86c** afforded 32.4 mg of **95c** (81% yield). R_f = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3444, 3055, 3028, 1702, 1604, 1494, 1222, 1068, 754. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.70-7.69 (m, 2H), 7.52-7.45 (m, 2H), 7.35-7.12 (m, 8H), 7.05-7.03 (m, 1H), 6.37 (d, *J* = 16.3 Hz, 1H), 5.95 (dd, *J* = 16.0 and 7.8 Hz, 1H), 5.49 (s, 1H), 3.11-2.99 (m, 2H), 2.83 (brs, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 205.0, 52.9, 141.4, 137.0, 135.6(2C), 135.4, 132.9(2C), 129.6,

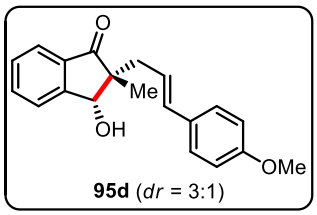
128.7(2C), 128.3(2C), 127.3, 128.4, 127.1(2C), 127.0, 126.1(2C), 125.2, 123.8, 79.4, 62.2, 37.9. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{21}O_2$ $(M+H)^+$: 341.1542. Found: 341.1531.

2-((2*E*,4*E*)-5-(4-Methoxyphenyl)-2-methylpenta-2,4-dienoyl)benzaldehyde (86d).



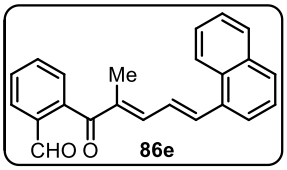
This compound was prepared by following the general procedure **14** and isolated as Pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2932, 2840, 2749, 1700, 1639, 1593, 1510, 1253, 1016, 749. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 9.98 (s, 1H), 7.89 (dd, *J* = 7.6 and 1.2 Hz, 1H), 7.66-7.60 (m, 2H), 7.40 (dd, *J* = 7.6 and 1.2 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.01 (dd, *J* = 15.4 and 11.3 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.69 (d, *J* = 11.3 Hz, 1H), 6.66 (d, *J* = 15.2 Hz, 1H), 3.89 (s, 3H), 2.19 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 198.3, 190.6, 160.6, 145.3, 142.7, 141.0, 136.3, 134.7, 133.4, 129.8, 129.7, 128.9, 128.8(2C), 128.3, 121.8, 114.3(2C), 55.3, 11.8. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{19}O_3$ $(M+H)^+$: 307.1334. Found: 307.1322.

3-Hydroxy-2-((*E*)-3-(4-methoxyphenyl)allyl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (95d).



This compound was isolated as pale yellow oil. Following the general procedure **16**, 40 mg of **86d** afforded 31 mg of **95d** (78% yield). R_f = 0.2 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3441, 3057, 3029, 2917, 1706, 1604, 1495, 1222, 1067, 743. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.78-7.76 (m, 1H), 7.70-7.68 (m, 2H), 7.51-7.47 (m, 1H), 7.23-7.18 (m, 1H), 7.11 (d, *J* = 8.7 Hz, 1H), 6.86-6.81 (m, 1H), 6.78 (d, *J* = 8.8 Hz, 1H), 6.39 (d, *J* = 15.9 Hz, 1H), 5.91 (td, *J* = 15.8 and 7.4 Hz, 1H), 5.01 (s, 1H), 3.77 (s, 3H), 2.62-2.51 (m, 2H), 2.40 (brs, 1H), 1.31 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.5, 158.9, 153.1, 135.4, 132.4, 130.1, 129.8, 129.5, 127.2(2C), 125.5, 124.2, 123.6, 113.8(2C), 78.6, 52.2, 54.5, 37.9, 21.6. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{19}O_3$ $(M-H)^+$: 307.1334. Found: 307.1323.

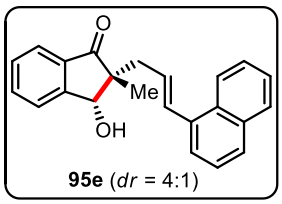
2-((2*E*,4*E*)-2-Methyl-5-(naphthalen-1-yl)penta-2,4-dienoyl)benzaldehyde (86e).



This compound was prepared by following the general procedure **14** and isolated as white solid. M.P = 174-176 °C. R_f = 0.3 (Hexane/EtOAc

= 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3054, 2933, 2337, 1699, 1643, 1606, 1391, 1292, 1266, 1011, 772. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.02 (s, 1H), 8.04-8.01 (m, 2H), 7.86-7.82 (m, 2H), 7.77 (d, *J* = 7.2 Hz, 1H), 7.72-7.65 (m, 2H), 7.53-7.45 (m, 5H), 7.25 (dd, *J* = 15.3 and 11.3 Hz, 1H), 6.83 (d, *J* = 11.3 Hz, 1H), 2.25 (d, *J* = 0.8 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 198.6, 190.6, 144.2, 142.5, 137.8, 137.6, 134.8, 133.7, 133.5, 133.4, 131.1, 130.2, 129.8, 129.6, 128.8, 128.4, 126.6, 126.5, 126.1, 125.5, 124.3, 123.2, 12.0. **HRMS (ESI):** *m/z* calcd for $C_{23}H_{19}O_2$ $(M+H)^+$: 327.1385. Found: 327.1397.

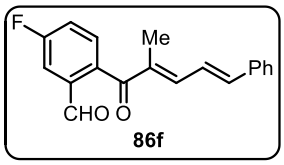
3-Hydroxy-2-methyl-2-((*E*)-3-(naphthalen-1-yl)allyl)-2,3-dihydro-1*H*-inden-1-one (95e).



95e (*dr* = 4:1)

This compound was isolated as pale yellow oil. Following the general procedure **16**, 40 mg of **86e** afforded 34.8 mg of **95e** (87% yield). R_f = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3424, 2962, 2926, 1702, 1606, 1059, 777. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.97-7.95 (m, 1H), 7.85-7.62 (m, 5H), 7.48-7.43 (m, 3H), 7.33-7.18 (m, 2H), 7.12 (d, *J* = 15.6 Hz, 1H), 6.09 (td, *J* = 15.6 and 7.5 Hz, 1H), 5.03 (s, 1H), 2.74-2.44 (m, 2H), 1.67 (s, 1H), 1.35 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.1, 153.1, 135.4, 135.1, 135.0, 133.5, 130.9, 130.4, 129.8, 129.5, 128.4, 127.6, 126.0, 125.7, 125.6, 125.5, 123.9, 13.8, 123.6, 78.5, 54.9, 38.3, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{23}H_{21}O_2$ $(M+H)^+$: 329.1542. Found: 329.1534.

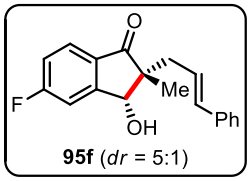
5-Fluoro-2-((2*E*,4*E*)-2-methyl-5-phenylpenta-2,4-dienoyl)benzaldehyde (86f).



86f

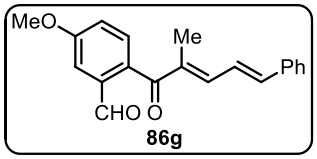
This compound was prepared by following the general procedure **14** and isolated as Pale yellow solid. M.P = 88-90 ^{o}C. R_f = 0.5 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3031, 2864, 2754, 1701, 1648, 1612, 1580, 1456, 1252, 1155, 999, 793. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 9.95 (d, *J* = 2.2 Hz, 1H), 7.68 (dd, *J* = 8.6 and 2.6 Hz, 1H), 7.48-7.44 (m, 3H), 7.37-7.31 (m, 4H), 7.15 (dd, *J* = 15.4 and 11.2 Hz, 1H), 6.76 (d, *J* = 15.4 Hz, 1H), 6.72 (d, *J* = 11.2 Hz, 1H), 2.21 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 197.0, 189.1, 163.3 (d, *J* = 251 Hz, 1C), 145.0, 141.6, 138.7 (d, *J* = 3.5 Hz, 1C), 137.5, 137.3 (d, *J* = 64.0 Hz, 1C), 135.9, 130.9 (d, *J* = 7.8 Hz, 1C), 129.4, 128.9(2C), 127.(2c), 123.8, 120.3 (d, *J* = 21.8 Hz, 1C), 115.7 (d, *J* = 22.4 Hz, 1C), 12.0. **^{19}F-NMR (374 MHz, $CDCl_3$):** δ -108.8. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{16}FO_2$ $(M+H)^+$: 295.1134. Found: 295.1100.

2-Cinnamyl-5-fluoro-3-hydroxy-2-methyl-2,3-dihydro-1*H*-inden-1-one (95f).



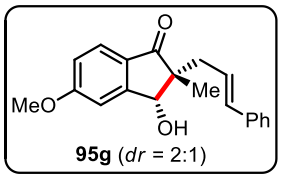
This compound was isolated as pale yellow oil. Following the general procedure **16**, 50 mg of **86f** afforded 38.4 mg of **95f** (77% yield). R_f = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3434, 3029, 2967, 2928, 1702, 1607, 1254, 1055, 744. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 7.77 (dd, *J* = 8.4 and 5.1 H, 1H), 7.36-7.28 (m, 2H), 7.25-7.13 (m, 5H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.07 (td, *J* = 15.8 and 7.5 Hz, 1H), 4.98 (s, 1H), 2.81 (s, 1H), 2.76-2.50 (m, 2H), 1.30 (s, 3H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 205.7, 167.6 (d, *J* = 255.9 Hz, 1C), 156.1 (d, *J* = 9.2 Hz, 1C), 137.0, 133.1, 131.2 (d, *J* = 1.6 Hz, 1C), 128.8, 128.4(2C), 127.3, 126.1(2C), 126.0, 117.7 (d, *J* = 23.5 Hz, 1C), 112.4 (d, *J* = 22.5 Hz, 1C), 78.0 (d, *J* = 1.7 Hz, 1C), 55.1, 37.9, 21.3. **^{19}F-NMR (374 MHz, CDCl$_3$):** δ -101.0. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{16}FO$ $(M-OH)^+$: 279.1185. Found: 279.1170.

5-Methoxy-2-((2*E*,4*E*)-2-methyl-5-phenylpenta-2,4-dienoyl)benzaldehyde (86g).



This compound was prepared by following the general procedure **14** and isolated as Pale yellow oil. R_f = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3039, 2938, 2846, 1697, 1606, 1491, 1448, 1361, 1281, 1009, 748. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 9.98 (s, 1H), 7.49 (d, *J* = 2.6 Hz, 1H), 7.46-7.41 (m, 3H), 7.37-7.30 (m, 3H), 7.19-7.13 (m, 2H), 6.78 (d, *J* = 11. Hz, 1H), 6.75 (d, *J* = 15.2 Hz, 1H), 3.92 (s, 3H), 2.20 (s, 3H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 197.7, 190.5, 160.9, 144.3, 140.9, 137.8, 137.1, 136.1, 135.1, 130.7, 129.2, 128.8(2C), 127.3(2C), 123.9, 119.5, 112.5, 55.7, 12.2. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{19}O_3$ $(M+H)^+$: 307.1334. Found: 307.1322.

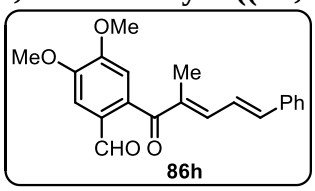
2-Cinnamyl-3-hydroxy-5-methoxy-2-methyl-2,3-dihydro-1*H*-inden-1-one (95g).



This compound was isolated as pale yellow oil. Following the general procedure **16**, 40 mg of **86g** afforded 34.4 mg of **95g** (86% yield). R_f = 0.2 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3409, 2963, 2929, 1690, 1600, 1490, 1260, 1060. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 7.70 (d, *J* = 4.5 Hz, 1H), 7.32-7.15 (m, 5H), 7.12-7.10 (m, 1H), 7.01-6.97 (m, 1H), 6.43 (d, *J* = 15.9 Hz, 1H), 6.11 (td, *J* = 15.8 and 7.5 Hz, 1H), 4.94 (s, 1H), 3.88 (s, 3H), 2.73-2.70 (m, 1H), 2.63-2.51 (m, 1H), 1.76 (s, 1H), 1.29 (s, 3H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 205.6, 165.9, 156.1, 137.1, 132.8, 128.8,

128.4(2C), 127.2, 126.7, 126.1(2C), 125.4, 117.6, 78.6, 55.7, 54.6, 38.0, 21.7. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{21}O_3$ $(M+H)^+$: 309.1491. Found: 309.1478.

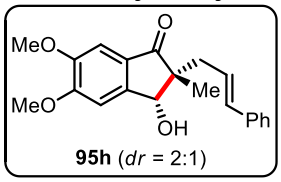
4,5-Dimethoxy-2-((2*E*,4*E*)-2-methyl-5-phenylpenta-2,4-dienoyl)benzaldehyde (86h).



86h

This compound was prepared by following the general procedure **14** and isolated as Pale yellow oil. R_f = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2932, 2851, 1770, 1774, 1685, 1640, 1461, 1249, 738. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 9.86 (s, 1H), 7.50 (s, 1H), 7.45 (dd, *J* = 7.5 and 1.0 Hz, 1H), 7.37-7.30 (m, 4H), 7.17 (dd, *J* = 15.3 and 11.2 Hz, 1H), 6.89 (s, 1H), 6.76 (d, *J* = 11.3 Hz, 1H), 6.75 (d, *J* = 15.4 Hz, 1h), 4.00 (s, 3H), 3.96 (s, 3H), 2.20 (d, *J* = 1.0 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 197.7, 189.0, 153.1, 150.1, 144.9, 141.4, 137.9, 137.7, 136.0, 129.3, 128.8(2C), 128.5, 127.3(2C), 123.9, 110.7, 109.6, 56.4, 56.2, 12.0. **HRMS (ESI):** *m/z* calcd for $C_{21}H_{21}O_4$ $(M+H)^+$: 337.1440. Found: 337.1425.

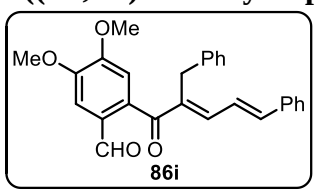
2-Cinnamyl-3-hydroxy-5,6-dimethoxy-2-methyl-2,3-dihydro-1*H*-inden-1-one (95h).



95h (*dr* = 2:1)

This compound was isolated as pale yellow oil. Following the general procedure **16**, 40 mg of **86h** afforded 33 mg of **95h** (83% yield). R_f = 0.3 (Hexane/EtOAc = 2/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3417, 3020, 2962, 1694, 1596, 1500, 1289, 1011, 742. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.32-7.18 (m, 5H), 7.17 (s, 1H), 7.11 (s, 1H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.14 (td, *J* = 15.8 and 7.3 Hz, 1H), 4.92 (s, 1H), 3.97 (s, 3H), 3.90 (s, 3H), 2.75-2.52 (m, 2H), 1.64 (brs, 1H), 1.28 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 206.2, 156.0, 150.9, 148.3, 137.1, 132.9, 128.8, 128.4(2C), 127.2, 126.7, 126.1(2C), 106.5, 103.8, 78.5, 56.3, 56.2, 54.2, 38.2, 21.9. **HRMS (ESI):** *m/z* calcd for $C_{21}H_{23}O_4$ $(M+H)^+$: 339.1596. Found: 339.1580.

2-((2*E*,4*E*)-2-Benzyl-5-phenylpenta-2,4-dienoyl)-4,5-dimethoxybenzaldehyde (86i).

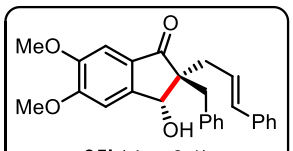


86i

This compound was prepared by following the general procedure **14** and isolated as Pale yellow oil. R_f = 0.2 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3060, 3026, 2937, 2851, 1768, 1687, 1590, 1459, 1348, 1282, 1079, 738. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 9.76 (s, 1H), 7.49 (s, 1H), 7.43 (dd, *J* = 7.6 and 1.2 Hz, 2H), 7.36-7.25 (m, 7H), 7.24-7.20 (m, 2H), 6.92 (d, *J* = 11.3 Hz,

1H), 6.80 (d, *J* = 15.3 Hz, 1H), 6.80 (s, 1H), 4.06 (s, 2H), 3.99 (s, 3H), 3.91 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 197.0, 189.0, 153.0, 150.2, 145.7, 142.5, 140.8, 139.3, 137.7, 135.8, 129.6, 128.9(2C), 128.7(2C), 128.6, 128.4(2C), 127.4(2C), 126.3, 123.6, 110.6, 109.3, 56.4, 56.2, 32.0. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{25}O_4$ $(M+H)^+$: 413.1753. Found: 413.1736.

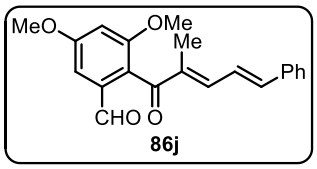
2-Benzyl-2-cinnamyl-3-hydroxy-5,6-dimethoxy-2,3-dihydro-1*H*-inden-1-one (95i).



95i (*dr* = 3:1)

This compound was isolated as pale yellow oil. Following the general procedure **16**, 40 mg of **86i** afforded 32 mg of **95i** (82% yield). R_f = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3418, 3025, 2930, 1695, 1595, 1499, 1286, 738. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.32-7.29 (m, 1H), 7.24-7.19 (m, 5H), 7.17-7.09 (m, 5H), 7.00 (s, 1H), 6.43 (d, *J* = 15.9 Hz, 1H), 6.02 (td, *J* = 15.9 and 7.8 Hz, 1H), 5.18 (s, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.23 (d, J_{AB} = 13.7 Hz, 1H), 2.98 (d, J_{AB} = 13.7 Hz, 1H), 2.73-2.68 (m, 1H), 2.61-2.56 (m, 1H), 2.37 (brs, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 204.8, 156.0, 150.7, 149.0, 137.5, 137.0, 132.9, 130.2(2C), 128.8, 128.4(2C), 128.3(2C), 127.3, 126.1(2C), 106.0, 103.5, 74.2, 59.2, 56.3, 56.1, 40.6, 38.7. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{27}O_4$ $(M+H)^+$: 415.1909. Found: 415.1913.

3,5-Dimethoxy-2-((2*E*,4*E*)-2-methyl-5-phenylpenta-2,4-dienoyl)benzaldehyde (86j).

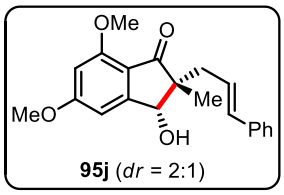


86j

This compound was prepared by following the general procedure **14** and isolated as Pale yellow solid. M.P = 114-116 ^oC. R_f = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2941, 2843, 1699, 1645, 1605, 1457, 1389, 1289, 1008, 748. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 9.81 (s, 1H), 7.44-7.42 (m, 2H), 7.35-7.28 (m, 3H), 7.6 (dd, *J* = 15.3 and 11.2 Hz, 1H), 7.05 (d, *J* = 2.3 Hz, 1H), 6.75-6.69 (m, 2H), 6.74 (d, *J* = 2.2 Hz, 1H), 3.90 (s, 3H), 3.78 (s, 3H), 2.18 (d, *J* = 0.9 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 197.1, 190.1, 161.3, 158.2, 143.1, 140.5, 138.6, 136.2, 135.9, 129.1, 128.8(2C), 127.2(2C), 125.6, 124.3, 104.6, 103.7, 56.2, 55.8, 11.5. **HRMS (ESI):** *m/z* calcd for $C_{21}H_{21}O_4$ $(M+H)^+$: 337.1440. Found: 337.1430.

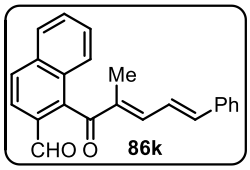
2-Cinnamyl-3-hydroxy-5,7-dimethoxy-2-methyl-2,3-dihydro-1*H*-inden-1-one (95j).

This compound was isolated as pale yellow oil. Following the general procedure **16**, 40 mg of **86j** afforded 32 mg of **95j** (82% yield). R_f = 0.3 (Hexane/EtOAc = 2/1). **IR (thin film, neat):**



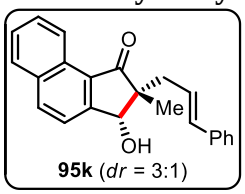
ν_{max}/cm^{-1} 3431, 2961, 1688, 1603, 1458, 1220, 1325, 1048. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 7.31-7.27 (m, 1H), 7.24-7.15 (m, 4H), 6.73-6.71 (m, 1H), 6.45 (d, *J* = 15.5 Hz, 1H), 6.39-6.38 (m, 1H), 6.18 (td, *J* = 15.8 and 7.6 Hz, 1H), 4.86 (s, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 2.72-2.50 (m, 2H), 1.64 (brs, 1H), 1.26 (s, 3H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 203.4, 167.5, 159.0, 158.2, 137.2, 132.7(2C), 128.4(2C), 128.2, 127.1, 126.1(2C), 116.8, 100.5, 99.3, 78.3, 55.9(2C), 54.6, 38.0, 21.9. **HRMS (ESI):** *m/z* calcd for $C_{21}H_{21}O_3$ (M-OH)$^+$: 321.1491. Found: 321.1457.

1-((2*E*,4*E*)-2-Methyl-5-phenylpenta-2,4-dienoyl)-2-naphthaldehyde (86k).



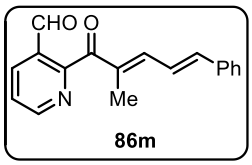
This compound was prepared by following the general procedure **14** and isolated as white solid. R_f = 0.5 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} ^{1} 3058, 2926, 2854, 2749, 1762, 1694, 1643, 1609, 1459, 1386, 1282, 1081, 745. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 10.13 (s, 1H), 8.04 (s, 2H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.41-7.28 (m, 5H), 7.19 (dd, *J* = 15.2 and 11.2 Hz, 1H), 6.69 (d, *J* = 11.2 Hz, 1H), 6.59 (d, *J* = 15.2 Hz, 1H), 2.36 (s, 3H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 199.5, 190.4, 145.3, 143.6, 141.8, 138.6, 136.0, 135.9, 130.7, 130.6, 129.5, 129.4, 129.3, 128.8(2C), 128.4, 127.8, 127.3(2C), 126.9, 123.8 123.5, 11.5. **HRMS (ESI):** *m/z* calcd for $C_{23}H_{17}O_2$ (M-H)$^+$: 325.1229. Found: 325.1246.

2-Cinnamyl-3-hydroxy-2-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1-one (95k).



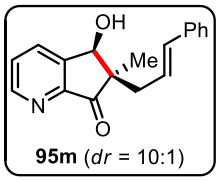
This compound was isolated as pale yellow oil. Following the general procedure **16**, 40 mg of **86k** afforded 36 mg of **95k** (92% yield). R_f = 0.3 (Hexane/EtOAc = 2/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3430, 3055, 3026, 2965, 1704, 1605, 1461, 1293, 1061, 764. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 9.12 (d, *J* = 8.1 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.75-7.68 (m, 2H), 7.62-7.58 (m, 1H), 7.30-713 (m, 5H), 6.47 (d, *J* = 15.6 Hz, 1H), 6.18 (td, *J* = 15.8 and 7.8 Hz, 1H), 5.09 (s, 1H), 2.81-2.79 9m, 1H), 2.71-2.55 (m, 1H), 2.16 (s, 1H), 1.37 (s, 3H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 207.9, 155.1, 137.0, 136.6, 133.8, 133.1, 129.2, 128.83, 128.81, 128.4(2C), 128.3(2C), 127.3, 127.2, 126.6, 122.3, 78.5, 54.6, 38.1, 33.1, 21.8. **HRMS (ESI):** *m/z* calcd for $C_{23}H_{19}O$ (M-OH)$^+$: 311.1436. Found: 311.1428.

2-((2*E*,4*E*)-2-Methyl-5-phenylpenta-2,4-dienoyl)nicotinaldehyde (86m).



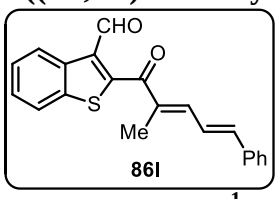
This compound was prepared by following the general procedure **14** and isolated as Pale yellow oil. R_f = 0.3 (Hexane/EtOAc = 2/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3050, 2922, 2860, 1702, 1650, 1610, 1445, 1291, 1191, 1022, 970, 741. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.07 (s, 1H), 8.85 (dd, *J* = 7.2 and 2.3 Hz, 1H), 8.34 (dd, *J* = 8.0 and 1.6 Hz, 1H), 7.58 (dd, *J* = 8.0 and 4.8 Hz, 1H), 7.48-7.45 (m, 2H), 7.37-7.32 (m, 3H), 7.21 (dd, *J* = 15.5 and 11.2 Hz, 1H), 6.89 (dd, *J* = 11.2 and 0.8 Hz, 1H), 6.79 (d, *J* = 15.5 Hz, 1H), 2.24 (d, *J* = 0.8 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 195.1, 189.4, 160.0, 152.6, 146.4, 142.0, 136.6, 136.0, 135.8, 130.8, 129.4, 128.9(2C), 127.4(2C), 124.6, 123.9, 11.8. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{18}NO_2$ $(M+H)^+$: 280.1338. Found: 280.1325.

6-Cinnamyl-5-hydroxy-6-methyl-5*H*-cyclopenta[*b*]pyridin-7(6*H*)-one (95m).



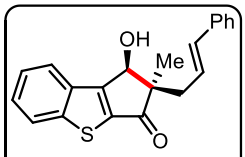
This compound was isolated as white solid. Following the general procedure **16**, 30 mg of **86m** afforded 26 mg of **95m** (87% yield). M.P = 197-199 ^oC. R_f = 0.2 (Hexane/EtOAc = 1/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3420, 2964, 1721, 1463, 1299, 1025, 763. **^{1}H-NMR (400 MHz, $(CD_3)_2SO$):** δ 8.77-8.76 (m, 1H), 8.20-8.18 (m, 1H), 7.68 (dd, *J* = 7.8 and 4.6 Hz, 1H), 7.28-7.24 (m, 2H), 7.19-7.17 (m, 3H), 6.29 (d, *J* = 15.9 Hz, 1H), 6.22 (d, *J* = 6.0 Hz, 1H), 6.10 (td, *J* = 15.9 and 7.8 Hz, 1H), 4.97 (d, *J* = 6.0 Hz, 1H), 2.45-2.39 (m, 1H), 2.34-2.29 (m, 1H), 1.22 (s, 3H). **^{13}C-NMR (100 MHz, $(CD_3)_2SO$):** δ 207.1, 152.2, 152.1, 150.0, 137.5, 134.8, 132.2, 128.9(2C), 128.7, 127.5, 126.9, 126.2(2C), 74.4, 54.8, 38.0, 20.6. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{18}NO_2$ $(M+H)^+$: 280.1338. Found: 280.1337.

2-((2*E*,4*E*)-2-Methyl-5-phenylpenta-2,4-dienoyl)benzo[*b*]thiophene-3-carbaldehyde (86l).



This compound was prepared by following the general procedure **15** and isolated as Pale yellow oil. R_f = 0.5 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3058, 2927, 2849, 1678, 1606, 1503, 1458, 1281, 1222, 1076, 756. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.17 (s, 1H), 8.78 (dd, *J* = 7.2 and 1.2 Hz, 1H), 7.90-7.88 (m, 1H), 7.59-7.46 (m, 4H), 7.38-7.33 (m, 3H), 7.21-7.18 (m, 2H), 6.90-6.85 (m, 1H), 2.24 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 190.5, 185.5, 153.7, 146.6, 142.8, 139.1, 137.8, 135.9, 135.8, 134.7, 129.7, 128.9(2C), 127.5(2C), 127.1, 126.7, 125.9, 123.5, 122.0, 12.3. **HRMS (ESI):** *m/z* calcd for $C_{21}H_{17}O_2S$ $(M+H)^+$: 333.0949. Found: 333.0935.

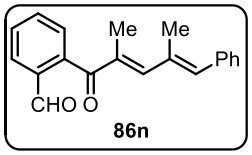
2-Cinnamyl-1-hydroxy-2-methyl-1*H*-benzo[*b*]cyclopenta[*d*]thiophen-3(2*H*)-one (95l).



95l (*dr* = 3:2)

This compound was isolated as pale yellow oil. Following the general procedure **16**, 35 mg of **86l** afforded 28 mg of **95l** (80% yield). R_f = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3425, 3026, 2925, 1689, 1595, 1426, 1268, 1084, 745. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.11-8.08 (m, 1H), 7.93-7.91 (m, 1H), 7.54-7.46 (m, 2H), 7.35-7.17 (m, 5H), 6.53 (d, *J* = 15.8 Hz, 1H), 6.24 (td, *J* = 15.8 and 7.0 Hz, 1H), 5.22 (d, *J* = 8.4 Hz, 1H), 2.95-2.67 (m, 2H), 2.50 (d, *J* = 8.8 Hz, 1H), 1.39 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 199.8, 161.4, 148.7, 140.6, 136, 133.5, 131.8, 128.5(2C), 128.4, 128.3(2C), 127.4, 126.3, 125.4, 124.7, 124.4, 76.4, 58.7, 38.2, 22.6. **HRMS (ESI):** *m/z* calcd for $C_{21}H_{19}O_2S$ $(M+H)^+$: 335.1106. Found: 335.1089.

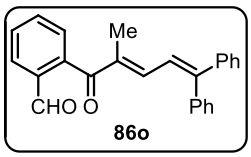
2-((2*E*,4*E*)-2,4-Dimethyl-5-phenylpenta-2,4-dienoyl)benzaldehyde (86n).



86n

This compound was prepared by following the general procedure **14** and isolated as Pale yellow oil. R_f = 0.6 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3035, 2931, 1706, 1458, 1285, 1075, 702. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.01 (s, 1H), 7.98 (dd, *J* = 7.3 and 1.2 Hz, 1H), 7.67-7.61 (m, 2H), 7.44 (dd, *J* = 7.4 and 1.4 Hz, 1H), 7.37-7.33 (m, 2H), 7.29-7.26 (m, 3H), 6.62 (s, 1H), 6.55 (s, 1H), 2.28 (d, *J* = 1.2 Hz, 3H), 2.10 (d, *J* = 1.2 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 199.6, 190.6, 149.6, 142.6, 137.2, 136.7, 136.6, 134.7, 134.2, 133.4, 130.3, 129.8, 129.3(2C), 128, 128.3(2C), 127.5, 18.2, 13.3. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{17}O_2$ $(M-H)^+$: 289.1229. Found: 289.1224.

(*E*)-2-(2-Methyl-5,5-diphenylpenta-2,4-dienoyl)benzaldehyde (86o).



86o

This compound was prepared by following the general procedure **14** and isolated as Pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3379, 3058, 1695, 1651, 1578, 1445, 1291, 1022, 761. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 9.94 (s, 1H), 7.83 (d, *J* = 7.3 Hz, 1H), 7.53-7.46 (m, 2H), 7.34-7.20 (m, 9H), 7.05-6.99 (m, 3H), 6.63 (d, *J* = 11.5 Hz, 1H), 2.24 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 198.8, 190.5, 151.7, 143.0, 142.5, 141.2, 138.4, 137.8, 134.3, 133.2, 130.3(2C), 129.7, 129.3, 128.9, 128.4(2C), 128.3(2C), 128.1, 128.0, 127.9(2C), 122.9, 11.6. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{21}O_2$ $(M+H)^+$: 353.1542. Found: 353.1524.

General procedure 17: Synthesis of *E,Z*-86a

Step I: An oven dried 25 mL RB flask was charged with sodium hydride (60% oil dispersion, 5.2 mmol), 10 mL dry THF and placed at 0 ^{o}C. To this suspension, triethyl 2-phosphonopropionate **107** (5.1 mmol) was added drop wise under argon atmosphere at same temperature and stirred until the effervescence of hydrogen gas ceased. Phenyl propiolaldehyde **72** (5.0 mmol) dissolved in 1 mL of dry THF was added dropwise over 2 min and continued stirring for 30 min. The reaction mixture was quenched with saturated aq. NH_4Cl solution and extracted using 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 to afford **108** as colorless oil.

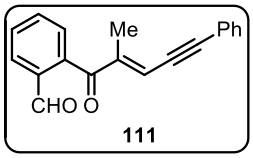
Step II: An oven dried 50 mL RB flask was charged with **108** (4.0 mmol), 10 mL dry THF and placed at 0 ^{o}C. To the reaction mixture DIBAL-H (8.2 mmol) was added drop wise at the same temperature and allowed to stir at rt for 5 h. The reaction mixture was quenched with saturated aq. NH_4Cl solution and the resultant mixture was filtered through Buchner funnel, the filtrate was extracted using ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated to afford the crude alcohol as pale yellow oil. The crude alcohol was further subjected to IBX oxidation to afford the aldehyde **109** as a pale yellow solid.

Step III: Alcohol **110** was synthesized by following the general procedure **12**, Step IV.

Step IV: The IBX oxidation of alcohol **110** and subsequent *p*-TSA mediated acetal deprotection (as described in general procedure **12**, Step IV) afforded the ynenone-aldehyde **111**.

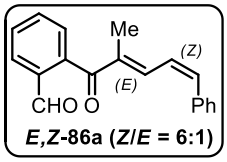
Step V: In an oven dried 10 mL RB flask the enynone **111** (1 mmol) was dissolved in 1 mL dry methanol. Quinoline (0.15 mmol) and Lindlar's catalyst (0.1 mmol) were introduced to the reaction mixture. The reaction mixture was evacuated and refilled with hydrogen gas (3 times) and stirred at room temperature. The reaction mixture was followed carefully to avoid over-reduction. After completion of the reaction (by TLC), the reaction mixture was filtered through a celite pad and the filtrate was extracted using 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 to afford ***E,Z*-86a** as pale yellow oil.

(*E*)-2-(2-Methyl-5-phenylpent-2-en-4-ynoyl)benzaldehyde (111).



This compound was isolated as pale yellow oil. Following the general procedure **17**, 150 mg of **110** afforded 93 mg of **111** (62% yield over two steps). R_f = 0.5 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3067, 2927, 2196, 1700, 1657, 1598, 1253, 1004. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 9.98 (s, 1H), 7.95 (dd, *J* = 7.3 and 1.4 Hz, 1H), 7.69-7.62 (m, 2H), 7.46-7.40 (m, 3H), 7.37-7.31 (m, 3H), 6.16 (s, 1H), 2.31 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 197.9, 190.9, 148.0, 140.9, 134.8, 133.6, 131.7(2C), 131.2, 130.1, 129.3, 128.5(2C), 128.3, 124.0, 122.3, 105.4, 85.8, 14.5. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{15}O_2$ $(M+H)^+$: 275.1072. Found: 275.1060.

2-((2*E*,4*Z*)-2-Methyl-5-phenylpenta-2,4-dienoyl)benzaldehyde (*E,Z*-86a).



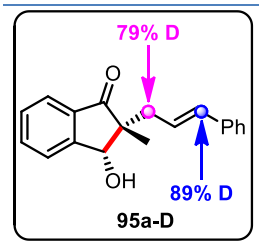
This compound was isolated as pale yellow oil. Following the general procedure **17** (step-IV), 80 mg of **111** afforded 66 mg of ***E,Z*-86a** (83% yield). R_f = 0.5 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3040, 2926, 2743, 1705, 1642, 1612, 1390, 1012, 749. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 9.97 (s, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.18-7.15 (m, 3H), 6.99 (d, *J* = 11.3 Hz, 1H), 6.85 (d, *J* = 11.4 Hz, 1H), 6.63 (dd, *J* = 11.4 and 11.3 Hz, 1H), 2.18 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 199.0, 190.5, 142.4, 140.5, 139.1, 138.1, 136.0, 134.5, 133.4, 130.2, 129.6, 129.2(2C), 128.1(2C), 128.0, 127.3, 124.9, 11.6.

General Procedure 18: Reductive aldol reaction of 86a in the presence of D_2O

An oven dried 5 mL glass vial was charged with **86a** (30 mg, 0.11 mmol). DMF (1 mL), D_2O (3.3 mmol) and PBu_3 (1.3 mmol) were introduced at room temperature (rt) and stirring continued at rt until **86a** disappeared as monitored by TLC. The reaction mixture was extracted using ethyl acetate. All the volatiles were removed under reduced pressure. The crude product was directly purified by silica gel chromatography using hexane/ethyl acetate as eluent, to afford **95a**.

2-Cinnamyl-3-hydroxy-2-methyl-2,3-dihydro-1*H*-inden-1-one (95a-D).

This compound was isolated as pale yellow oil. Following the general procedure **18**, 50 mg of **86a** afforded 41 mg of **95a-D** (80% yield). R_f = 0.2 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3424, 2926, 1703, 1605, 1461, 1293, 1061. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.75 (d, *J*



= 7.6 Hz, 1H), 7.70-7.65 (m, 2H), 7.48-7.44 (m, 1H), 7.30-7.27 (m, 1H), 7.25-7.21 (m, 2H), 6.42 (d, *J* = 15.8 Hz, 0.11H), 6.09 (s, 1H), 4.99 (s, 1H), 2.74-2.50 (m, 0.42H), 1.28 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.6, 153.1, 137.0, 135.4, 134.9, 132.9 (t, *J* = 10.8 Hz, CD), 129.5, 128.4(2C), 128.3, 127.2, 126.1(2C), 125.5, 123.6, 78.4, 54.5, 37.7-3.71 (m, CD_2), 21.4. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{15}D_2O_2$ $(M-D)^+$: 279.1354. Found: 279.1331.

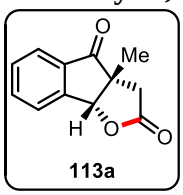
General Procedure 19: Reductive aldol reaction of 86a in the presence of ^{18}O-labelled water

An oven dried 5 mL glass vial was charged with **86a** (30 mg, 0.11 mmol). DMF (1 mL), $H_2{}^{18}O$ (3.3 mmol) and PBu_3 (1.3 mmol) were introduced at room temperature (rt) and stirring continued at rt until **86a** disappeared as monitored by TLC. The crude reaction mixture was directly subjected to the HRMS analysis.

General procedure 20: Synthesis of fused γ-lactones

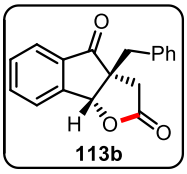
An oven dried 5 mL glass vial was charged with **95** (0.15 mmol) in 1.0 mL dimethylformamide. oxone (0.75 mmol) was added in one portion followed by the addition of 10 mol% OsO_4 (0.1 M solution in DMF) and stirring continued at rt until **95** disappeared as monitored by TLC. The reaction mixture was diluted with brine and extracted using ethyl acetate. All the volatiles were removed under reduced pressure. The crude product was purified by silica gel chromatography using hexane/ethyl acetate as eluent to afford **113**.

3*a*-Methyl-3,3*a*-dihydro-2*H*-indeno[1,2-*b*]furan-2,4(8*bH*)-dione (113a).



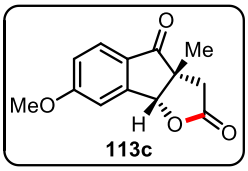
This compound was isolated as white solid. Following the general procedure **20**, 50 mg of **95a** afforded 25 mg of **113a** (71% yield). M.P = 116-117 °C. R_f = 0.2 (Hexane/EtOAc = 2/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2931, 1782, 1723, 1605, 1463, 1379, 1293, 1175, 1019, 748. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.85 (d, *J* = 7.9 Hz, 1H), 7.81-7.75 (m, 2H), 7.64-7.60 (m, 1H), 5.58 (s, 1H), 2.87 (d, J_{AB} = 18.9 Hz, 1H), 2.67 (d, J_{AB} = 18.9 Hz, 1H), 1.53 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 204.2, 174.5, 148.2, 136.3, 135.1, 131.2, 127.5, 124.8, 85.5, 51.3, 38.8, 21.0. **HRMS (ESI):** *m/z* calcd for $C_{12}H_{11}O_3$ $(M+H)^+$: 203.0708. Found: 203.0699.

3*a*-Benzyl-3,3*a*-dihydro-2*H*-indeno[1,2-*b*]furan-2,4(8*bH*)-dione (113b).



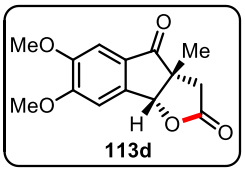
This compound was isolated as white solid. Following the general procedure **20**, 40 mg of **95b** afforded 19 mg of **113b** (60% yield). M.P = 98-100 ^{o}C. R_f = 0.3 (Hexane/EtOAc = 2/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3033, 2927, 2855, 1783, 1720, 1170, 1011, 704. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.71-7.63 (m, 2H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.25-7.14 (m, 5H), 5.78 (s, 1H), 3.41 (d, J_{AB} = 13.8 Hz, 1H), 3.04 (d, J_{AB} = 13.8 Hz, 1H), 2.84 (d, J_{AB} = 19.0 Hz, 1H), 2.78 (d, J_{AB} = 19.0 Hz, 1H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 203.8, 174.2, 148.4, 136.3, 135.7, 135.0, 131.0, 129.9(2C), 128.8(2C), 127.4, 127.3, 124.5, 82.1, 56.3, 39.7, 37.6. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{15}O_3$ $(M+H)^+$: 279.1021. Found: 279.1008.

7-Methoxy-3*a*-methyl-3,3*a*-dihydro-2*H*-indeno[1,2-*b*]furan-2,4(8*bH*)-dione (113c).



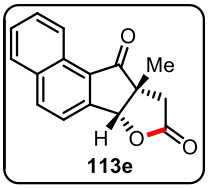
This compound was isolated as white solid. Following the general procedure **20**, 40 mg of 9**5g** afforded 20 mg of **113c** (67% yield). M.P = 113-114 ^{o}C. R_f = 0.4 (Hexane/EtOAc = 1/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3056, 1781, 1712, 1600, 1263, 1019. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 7.76 (d, *J* = 8.3 Hz, 1H), 7.13 (dt, *J* = 8.3 and 2.3 Hz, 2H), 5.50 (s, 1H), 3.93 (s, 3H), 2.85 (d, J_{AB} = 19.0 Hz, 1H), 2.64 (d, J_{AB} = 19.0 Hz, 1H), 1.52 (s, 3H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 202.3, 174.7, 166.4, 151.1, 127.9, 126.5, 119.5, 110.1, 85.4, 56.0, 51.5, 38.8, 21.1. **HRMS (ESI):** *m/z* calcd for $C_{13}H_{13}O_4$ $(M+H)^+$: 233.0814. Found: 233.0808.

6,7-Dimethoxy-3*a*-methyl-3,3*a*-dihydro-2*H*-indeno[1,2-*b*]furan-2,4(8*bH*)-dione (113d).



This compound was isolated as white solid. Following the general procedure **20**, 50 mg of **95h** afforded 24 mg of **113d** (62% yield). M.P = 165-167 ^{o}C. R_f = 0.3 (Hexane/EtOAc = 1/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3028, 2936, 2841, 1779, 1707, 1593, 1506, 1331, 1014. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 7.20 (s, 1H), 7.13 (s, 1H), 5.49 (s, 1H), 4.02 (s, 3H), 3.95 (s, 3H), 2.85 (d, J_{AB} = 19.1 Hz, 1H), 2.64 (d, J_{AB} = 191.1 Hz, 1H), 1.52 (s, 3H). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 198.8, 170.8, 152.6, 148.2, 139.5, 124.2, 103.9, 100.6, 81.6, 52.6, 52.4, 47.5, 35.0, 17.3. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{15}O_5$ $(M+H)^+$: 263.0919. Found: 263.0916.

9*a*-Methyl-9,9*a*-dihydro-6*bH*-benzo[4,5]indeno[1,2-*b*]furan-8,10-dione (113e).

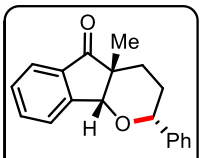


This compound was isolated as white solid. Following the general procedure **20**, 50 mg of **95k** afforded 24 mg of **113e** (63% yield). M.P = 154-156 ^{o}C. R_f = 0.2 (Hexane/EtOAc = 2/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3058, 1781, 1707, 1325, 1177, 1041. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 9.12 (d, *J* = 8.3 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.78-7.74 (m, 2H), 7.68 (t, *J* = 7.9 Hz, 1H), 5.66 (s, 1H), 2.95 (d, J_{AB} = 19.0 Hz, 1H), 2.72 (d, J_{AB} = 19.0 Hz, 1H), 1.61 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 204.7, 174.6, 150.4, 137.7, 134.3, 129.8, 129.0, 128.5, 128.2, 124.8, 123.2, 85.4, 51.4, 39.2, 21.3. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{13}O_3$ $(M+H)^+$: 253.0865. Found: 253.0854.

General Procedure 21: Synthesis of indane fused-pyrans 114 and dibenzo azulenones 118

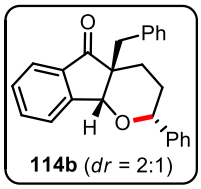
An oven dried 5 mL glass vial was charged with **95** (30 mg, 0.1 mmol) in an appropriate solvent (1.0 mL) and catalyst was introduced under nitrogen atmosphere and stirring continued at an appropriate temperature until **95** disappeared as monitored by TLC. The reaction mixture was quenched with saturated aq. $NaHCO_3$ and extracted using DCM. Volatiles were removed under reduced pressure. The crude product was purified by silica gel chromatography using hexane/ethyl acetate as eluent to afford **114** and **118**.

4*a*-Methyl-2-phenyl-2,3,4,4*a*-tetrahydroindeno[1,2-*b*]pyran-5(9*bH*)-one (114a).



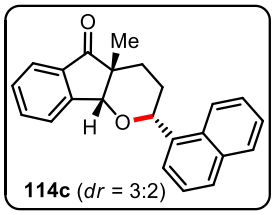
This compound was isolated as pale yellow oil. Following the general procedure **21**, 30 mg of **95a** afforded 25 mg of **114a** (83% yield). R_f = 0.6 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3033, 2930, 2865, 1720, 1605, 1455, 1284, 1068, 760. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.71-7.62 (m, 2H), 7.53-7.49 (m, 1H), 7.39-7.36 (m, 1H), 7.32-7.19 (m, 4H), 4.88 (s, 1H), 4.54 (dd, *J* = 10.3 and 3.0 Hz, 1H), 2.51 (td, *J* = 13.7 and 4.7 Hz, 1H), 1.92-1.70 (m, 3H), 1.14 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.0, 151.1, 142.5, 135.3, 134.8, 129.6, 128.3(2C), 127.4, 127.2, 125.9(2C), 124.3, 82.3, 77.7, 48.4, 30.2, 28.8, 24.8. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{19}O_2$ $(M+H)^+$: 279.1385. Found: 279.1371.

4*a*-Benzyl-2-phenyl-2,3,4,4*a*-tetrahydroindeno[1,2-*b*]pyran-5(9*bH*)-one (114b).



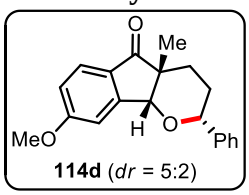
This compound was isolated as pale yellow oil. Following the general procedure **21**, 30 mg of **95b** afforded 24.4 mg of **114b** (81% yield). R_f = 0.6 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3061, 3031, 2924, 2857, 1717, 1605, 1451, 1344, 1217, 1066, 756, 702. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.62-7.57 (m, 2H), 7.49-7.41 (m, 1H), 7.38-7.36 (m, 1H), 7.33-7.29 (m, 1H), 7.26-7.13 (m, 7H), 7.00-6.99 (m, 1H), 5.06 (s, 1H), 4.47 (dd, *J* = 10.3 and 2.8 Hz, 1H), 2.90 (d, J_{AB} = 13.5 Hz, 1H), 2.75 (d, J_{AB} = 13.5 Hz, 1H), 2.36 (td, *J* = 14.1 and 4.0 Hz, 1H), 1.98-1.52 (m, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.0, 151.2, 142.5, 136.1, 134.8, 130.2(2C), 129.6, 128.3(2C), 128.1(2C), 127.4, 126.9, 126.7, 125.8(2C), 124.9, 124.1, 80.0, 77.5, 53.0, 43.7, 30.0, 27.3. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{23}O_2$ $(M+H)^+$: 355.1698. Found: 355.1715.

4*a*-Methyl-2-(naphthalen-1-yl)-2,3,4,4*a*-tetrahydroindeno[1,2-*b*]pyran-5(9*bH*)-one (114c).



This compound was isolated as pale yellow oil. Following the general procedure **21**, 25 mg of **95e** afforded 20.2 mg of **114c** (81% yield). R_f = 0.7 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3053, 2931, 2865, 1717, 1604, 1461, 1074, 777. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.90-7.79 (m, 3H), 7.73-7.62 (m, 3H), 7.54-7.49 (m, 2H), 7.46-7.42 (m, 2H), 5.28 (dd, *J* = 9.7 and 3.2 Hz, 1H), 5.00 (s, 1H), 2.52 (td, *J* = 13.9 and 4.9 Hz, 1H), 1.94-1.85 (m, 2H), 1.74-1.53 (m, 1H), 1.22 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 26.5, 151.0, 138.0, 135.4, 134.9, 133.7, 130.3, 129.7, 128.9, 127.2, 125.9, 125.5, 125.4, 124.4, 123.1, 122.9, 82.5, 74.5, 48.5, 29.1, 28.8, 24.5. **HRMS (ESI):** *m/z* calcd for $C_{23}H_{21}O_2$ $(M+H)^+$: 329.1542. Found: 329.1531.

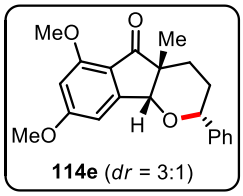
8-Methoxy-4*a*-methyl-2-phenyl-2,3,4,4*a*-tetrahydroindeno[1,2-*b*]pyran-5(9*bH*)-one (114d).



This compound was isolated as pale yellow oil. Following the general procedure **21**, 25 mg of **95g** afforded 21.8 mg of **114d** (87% yield). R_f = 0.6 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2934, 1709, 1601, 1489, 1455, 1337, 1067, 1022. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.74 (d, *J* = 8.4 Hz, 1H), 7.40-7.38 (m, 1H), 7.33-7.20 (m, 4H), 7.13-7.12 (m, 1H), 7.03-7.00 (m, 1H), 4.82 (s, 1H), 4.55 (dd, *J* = 10.1 and 3.4 Hz, 1H), 3.88 (s, 3H), 2.44 (td, *J* = 13.8 and 5.0 Hz, 1H), 1.89-1.54 (m, 3H), 1.16

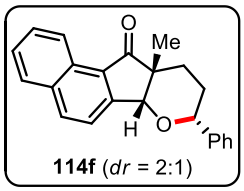
(s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 206.4, 165.3, 153.9, 142.6, 128.5, 128.3(2C), 127.5, 126.0, 125(2C), 117.3, 110.6, 82.1, 77.6, 55.7, 48.4, 30.0, 28.7, 24.8. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{21}O_3$ $(M+H)^+$: 309.1491. Found: 309.1475.

6,8-Dimethoxy-4*a*-methyl-2-phenyl-2,3,4,4*a*-tetrahydroindeno[1,2-*b*]pyran-5(9*bH*)-one (114e).



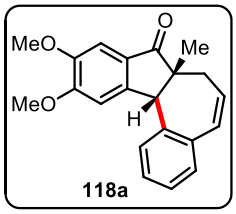
This compound was isolated as pale yellow oil. Following the general procedure **21**, 20 mg of **95j** afforded 16 mg of **114e** (80% yield). R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2934, 2852, 1706, 1604, 1459, 1327, 1215, 1060, 738. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.39-7.37 (m, 1H), 7.27-7.21 (m, 4H), 6.72 (d, *J* = 2.0 Hz, 1H), 6.44 (d, *J* = 2.0 Hz, 1H), 4.74 (s, 1H), 4.50 (dd, *J* = 10.2 and 3.1 Hz, 1H), 3.93 (s, 3H), 3.87 (s, 3H), 2.46 (td, *J* = 13.7 and 3.2 Hz, 1H), 1.89-1.51 (m, 3H), 1.15 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 204.0, 167.0, 159.4, 155.7, 142.7, 128.3(2C), 127.4, 126(2C), 116.7, 102.8, 99.6, 81.9, 77.7, 55.9, 55.8, 48.5, 30.2, 28.7, 25.1. **HRMS (ESI):** *m/z* calcd for $C_{21}H_{23}O_4$ $(M+H)^+$: 339.1596. Found: 339.1580.

10*a*-Methyl-8-phenyl-8,9,10,10*a*-tetrahydrobenzo[4,5]indeno[1,2-*b*]pyran-11(6*bH*)-one (114f).



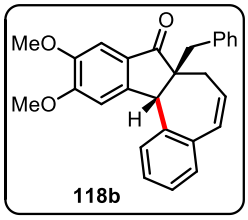
This compound was isolated as pale yellow solid. Following the general procedure **21**, 30 mg of **95k** afforded 24 mg of **114f** (80% yield). M.P = 118-120 ^{o}C. R_f = 0.5 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3061, 2928, 2858, 1705, 1450, 1324, 1077, 1023, 750, 699. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 9.12 (dd, *J* = 7.8 and 0.5 Hz, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.79-7.68 (m, 2H), 7.62-7.60 (m, 1H), 7.40-7.34 (m, 1H), 7.27-7.22 (m, 4H), 4.98 (s, 1H), 4.64 (dd, *J* = 10.0 and 2.1 Hz, 1H), 2.49 (td, *J* = 13.8 and 5.2 Hz, 1H), 2.01-1.56 (m, 3H), 1.26 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.7, 153.3, 142.8, 135.9, 134.1, 129.5, 128.9, 128.5, 128.3(2C), 127.4, 127.1, 126.0, 125.8(2C), 124.7, 124.0, 82.0, 77.6, 48.3, 30.0, 28.7, 24.7. **HRMS (ESI):** *m/z* calcd for $C_{23}H_{21}O_2$ $(M+H)^+$: 329.1542. Found: 329.1535.

10,11-Dimethoxy-7*a*-methyl-7,7*a*-dihydrodibenzo[a,*h*]azulen-8(12*bH*)-one (118a).



This compound was isolated as white solid. Following the general procedure **21**, 25 mg of **95h** afforded 15.4 mg of **118a** (65% yield). M.P = 169-171 ^{o}C. R_f = 0.2 (Hexane/EtOAc = 2/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2958, 1695, 1593, 1498, 1460, 1296, 1011, 756. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.41 (dd, *J* = 7.2 and 1.4 Hz, 1H), 7.37-7.28 (m, 2H), 7.17 (s, 1H), 7.11 (dd, *J* = 7.2 and 1.4 Hz, 1H), 6.20 (dd, *J* = 10.4 and 1.5 Hz, 1H), 6.08 (s, 1H), 5.68-5.62 (m, 1H), 3.98 (s, 1H), 3.91 (s, 3H), 3.71 (s, 3H), 2.27 (dd, *J* = 12.6 and 8.0 Hz, 1H), 2.08-2.02 (m, 1H), 1.39 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.6, 155.9, 151.1, 149.4, 139.4, 137.7, 132.1, 131.6, 130.0, 129.9, 129.2, 127.3, 126.9, 105.5, 103.3, 68.7, 57.8, 56.1, 56.0, 36.1, 23.4. **HRMS (ESI):** *m/z* calcd for $C_{21}H_{21}O_3$ $(M+H)^+$: 321.1491. Found: 321.1482.

7*a*-Benzyl-10,11-dimethoxy-7,7*a*-dihydrodibenzo[*a*,*h*]azulen-8(12*bH*)-one (118b).



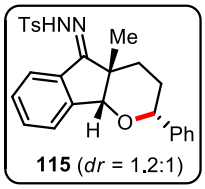
This compound was isolated as pale yellow solid. Following the general procedure **21**, 20 mg of **95i** afforded 10 mg of **118b** (52% yield). R_f = 0.3 (Hexane/EtOAc = 3/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3022, 2926, 2849, 1693, 1593, 1498, 1293. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.35-7.27 (m, 4H), 7.25 (s, 1H), 7.24-7.23 (m, 3H), 7.14 (s, 1H), 7.10-7.08 (m, 1H), 6.17 (dd, *J* = 10.4 and 1.5 Hz, 1H), 5.94 (s, 1H), 5.68-5.61 (m, 1H), 4.16 (s, 1H), 3.89 (s, 3H), 3.63 (s, 3H), 3.40 (d, *J* = 13.7 Hz, 1H), 2.89 (d, *J* = 13.7 Hz, 1H), 2.40 (dd, *J* = 12.4 and 8.0 Hz, 1H), 2.17-2.12 (m, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.8, 155.9, 152.1, 149.2, 139.5, 138.0, 137.9, 132.1, 131.8, 130.4(2C), 130.4, 130.0, 128.8, 128.3(2C), 127.3, 126.9, 126.4, 105.5, 103.1, 74.0, 56.1, 56.0, 51.9, 42.4, 36.3. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{25}O_3$ $(M+H)^+$: 397.1804. Found: 397.1806.

General Procedure 22: Derivatization of pyran 114a

An oven dried 5 mL glass vial was charged with pyran **114a** (30 mg, 0.1 mmol) in methanol solvent (1.0 mL) and *p*-tosylhydrazide was introduced under nitrogen atmosphere and stirring continued at 60 ^{o}C until **114a** disappeared as monitored by TLC. Methanol was removed under reduced pressure. The crude product was purified by silica gel chromatography using hexane/ethyl acetate as eluent, to afford **115** as colourless solid. The hydrazone **115** was

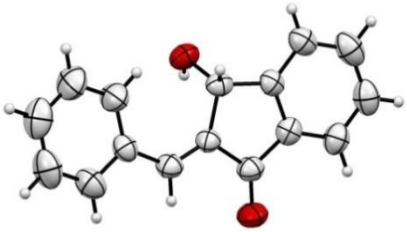
recrystallized using ethanol/hexane mixture at room temperature and its structure was confirmed by X-ray diffraction analysis.

4-Methyl-N'-(4*a*-methyl-2-phenyl-2,3,4,4*a*-tetrahydroindeno[1,2-*b*]pyran-5(9*bH*)ylidene)-benzenesulfonohydrazide (115).



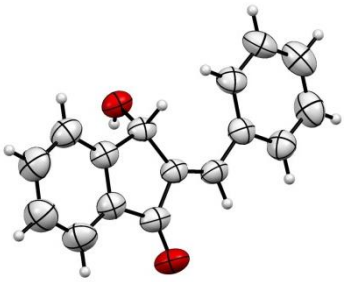
This compound was isolated as white solid. Following the general procedure **22**, 30 mg of **114a** afforded 39 mg of **115** (82% yield). M.P = 169-171 ^{o}C. R_f = 0.2 (Hexane/EtOAc = 2/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3204, 2930, 1599, 1382, 1167, 1019, 742. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.95-7.81 (m, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.66 (brs, 1H), 7.58-7.56 (m, 1H), 7.54-7.44 (m, 2H), 7.37-7.36 (m, 2H), 7.32-7.29 (m, 1H), 7.21-7.17 (m, 3H), 6.97-6.95 (m, 1H), 4.56 (s, 1H), 4.33 (dd, *J* = 11.3 and 1.6 Hz, 1H), 2.50 (td, *J* = 13.7 and 3.4 Hz, 1H), 2.14 (s, 3H), 1.83-1.66 (m, 3H), 1.00 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 159.8, 146.6, 144.3, 142.0, 134.4, 131.9, 131.7, 129.5(2C), 129.4, 128.5(2C), 128.1(2C), 127.7, 127.4, 126.3, 126.1(2C), 84.2, 77.7, 46.3, 32.3, 29.0, 26.3, 21.3. **HRMS (ESI):** *m/z* calcd for $C_{26}H_{27}N_2O_3S$ $(M+H)^+$: 447.1742. Found: 447.1720.

Table 22: General data and structure refinement parameters for racemic indanone 43k



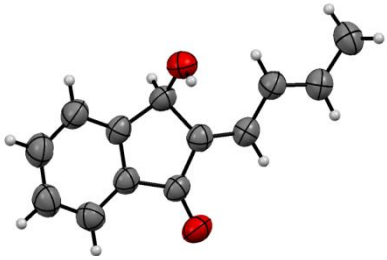
Empirical formula	$C_{16}H_{12}O_2$	
Formula weight	236.26	
Temperature	296.15K	
Crystal system	orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 11.261(3) Å	$\alpha = 90^o$
	b = 8.507(3) Å	$\beta = 90^o$
	c = 25.456(7) Å	$\gamma = 90^o$
Volume	2438.6(12) $Å^3$	
Z	8	
ρ_{calc}	1.287 g/cm^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	992.0	
Crystal size	0.2 × 0.1 × 0.1 mm^3	
Radiation	MoKα (λ = 0.71073)	
2θ range for data collection	4.83 to 50.266^o	
Index ranges	$-13 \leq h \leq 9$, $-10 \leq k \leq 10$, $-27 \leq l \leq 30$	
Reflections collected	8505	
Independent reflections	2162 [R_{int} = 0.0915, R_{sigma} = 0.0843]	
Data/restraints/parameters	2162/0/164	
Goodness-of-fit on F^2	0.856	
Final R indexes [I>=2σ (I)]	R_1 = 0.0552, wR_2 = 0.1315	
Final R indexes [all data]	R_1 = 0.1189, wR_2 = 0.1770	
Largest diff. peak/hole	0.16/-0.22 e $Å^{-3}$	
CCDC	1429346	

Table 23: General data and structure refinement parameters for chiral indanone 43k



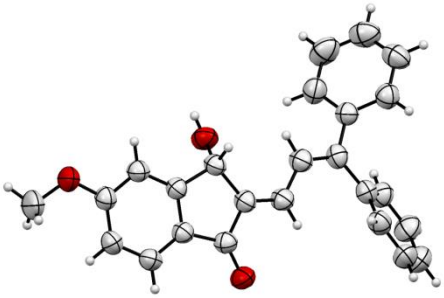
Empirical formula	$C_{16}H_{12}O_2$	
Formula weight	236.26	
Temperature	296.15K	
Crystal system	monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 5.413(7) Å	$\alpha = 90^o$
	b = 10.505(13) Å	$\beta = 90^o$
	c = 21.34(3) Å	$\gamma = 90^o$
Volume	1214(3) $Å^3$	
Z	2	
Density (calculated)	1.2902 g/cm^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	494.3	
Radiation	Mo Kα (λ = 0.71073)	
2θ range for data collection	1.9 to 50.18^o	
Index ranges	$-6 \leq h \leq 5$, $-12 \leq k \leq 12$, $-25 \leq l \leq 25$	
Reflections collected	11953	
Independent reflections	4233 [R_{int} = 0.2438, R_{sigma} = 0.1845]	
Data/restraints/parameters	4233/0/327	
Goodness-of-fit on F^2	0.882	
Final R indexes [I>=2σ (I)]	R_1 = 0.0746, wR_2 = 0.1780	
Final R indexes [all data]	R_1 = 0.1429, wR_2 = 0.2237	
Largest diff. peak/hole	0.27/-0.30 e $Å^{-3}$	
Flack parameter	-3.1(7)	
CCDC	1429345	

Table 24: General data and structure refinement parameters for racemic indanone 61a



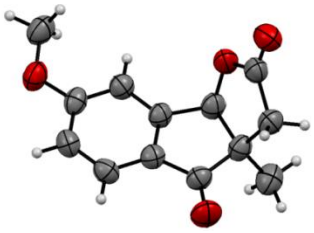
Empirical formula	$C_{13}H_{12}O_2$	
Formula weight	200.24	
Temperature	298K	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.8751(9) Å	α = 73.986(8)°
	b = 8.2320(4) Å	β = 73.564(11)°
	c = 8.8523(12) Å	γ = 83.983(8)°
Volume	528.84(10) $Å^3$	
Z	2	
Density (calculated)	1.2574 g/cm^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	212.1	
Radiation	Mo Kα (λ = 0.71073)	
2θ range for data collection	4.96 to 65.5°	
Index ranges	$-11 \leq h \leq 10$, $-11 \leq k \leq 12$, $-12 \leq l \leq 13$	
Reflections collected	11929	
Independent reflections	3626 [R_{int} = 0.0618, R_{sigma} = 0.0428]	
Data/restraints/parameters	3626/0/137	
Goodness-of-fit on F^2	1.467	
Final R indexes [I>=2σ (I)]	R_1 = 0.0969, wR_2 = 0.2396	
Final R indexes [all data]	R_1 = 0.1444, wR_2 = 0.2917	
Largest diff. peak/hole	0.72/-0.35 e $Å^{-3}$	
CCDC	1520613	

Table 25: General data and structure refinement parameters for chiral indanone 61t



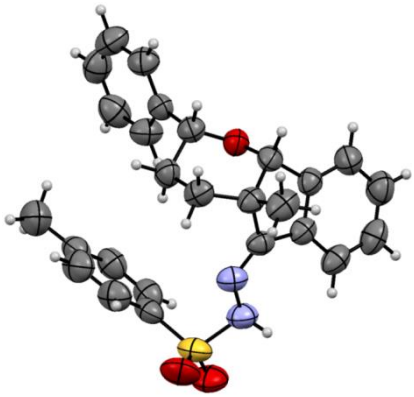
Empirical formula	$C_{25}H_{20}O_3$
Formula weight	368.42
Temperature	298K
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 10.1899(4) Å α = 90°
	b = 13.3377(5) Å β = 90°
	c = 14.4940(7) Å γ = 90°
Volume	1969.88(14) $Å^3$
Z	8
Density (calculated)	1.2422 g/cm^3
Absorption coefficient	0.081 mm^{-1}
F(000)	776.4
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection	5.62 to 65.52°
Index ranges	$-14 \leq h \leq 14$, $-16 \leq k \leq 19$, $-15 \leq l \leq 21$
Reflections collected	15325
Independent reflections	6671 [R_{int} = 0.0263, R_{sigma} = 0.0399]
Data/restraints/parameters	6671/0/254
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0593, wR_2 = 0.1576
Final R indexes [all data]	R_1 = 0.1099, wR_2 = 0.1979
Largest diff. peak/hole	0.28/-0.20 e $Å^{-3}$
Flack parameter	-0.6(9)
CCDC	1520308

Table 26: General data and structure refinement parameters for lactone 113c



Empirical formula	$C_{13}H_{12}O_4$	
Formula weight	232.23	
Temperature	298K	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 14.3583(8) Å	$\alpha = 90^o$
	b = 6.9961(5) Å	$\beta = 96.545(4)^o$
	c = 22.3157(10) Å	$\gamma = 90^o$
Volume	2227.0(2) $Å^3$	
Z	8	
Density (calculated)	1.385 g/cm^3	
Absorption coefficient	0.103 mm^{-1}	
F(000)	976.0	
Radiation	Mo Kα (λ = 0.71073)	
2θ range for data collection	5.712 to 65.642^o	
Index ranges	$-21 \leq h \leq 21$, $-10 \leq k \leq 9$, $-33 \leq l \leq 34$	
Reflections collected	33488	
Independent reflections	8005 [R_{int} = 0.0682, R_{sigma} = 0.0738]	
Data/restraints/parameters	8005/0/311	
Goodness-of-fit on F^2	1.034	
Final R indexes [I>=2σ (I)]	R_1 = 0.0758, wR_2 = 0.1814	
Final R indexes [all data]	R_1 = 0.2011, wR_2 = 0.2515	
Largest diff. peak/hole	0.35/-0.22 e $Å^{-3}$	
CCDC	1848427	

Table 27: General data and structure refinement parameters for hydrazone 115



Empirical formula	$C_{26}H_{26}N_2O_3S$	
Formula weight	446.56	
Temperature	293K	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.8584(4) Å	$\alpha = 90^o$
	b = 18.6348(7) Å	$\beta = 100.475(4)^o$
	c = 12.6465(5) Å	$\gamma = 90^o$
Volume	2284.56(16) $Å^3$	
Z	10	
Density (calculated)	1.2983 g/cm^3	
Absorption coefficient	0.172 mm^{-1}	
F(000)	944.9	
Radiation	Mo Kα (λ = 0.71073)	
2θ range for data collection	5.3 to 65.56^o	
Index ranges	$-14 \leq h \leq 14$, $-27 \leq k \leq 28$, $-13 \leq l \leq 18$	
Reflections collected	27062	
Independent reflections	8069 [R_{int} = 0.0283, R_{sigma} = 0.0336]	
Data/restraints/parameters	8069/0/291	
Goodness-of-fit on F^2	1.286	
Final R indexes [I>=2σ (I)]	R_1 = 0.0751, wR_2 = 0.2100	
Final R indexes [all data]	R_1 = 0.1407, wR_2 = 0.2601	
Largest diff. peak/hole	0.79/-0.50 e $Å^{-3}$	
CCDC	1848426	

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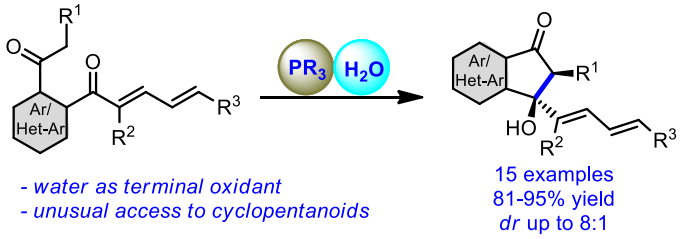
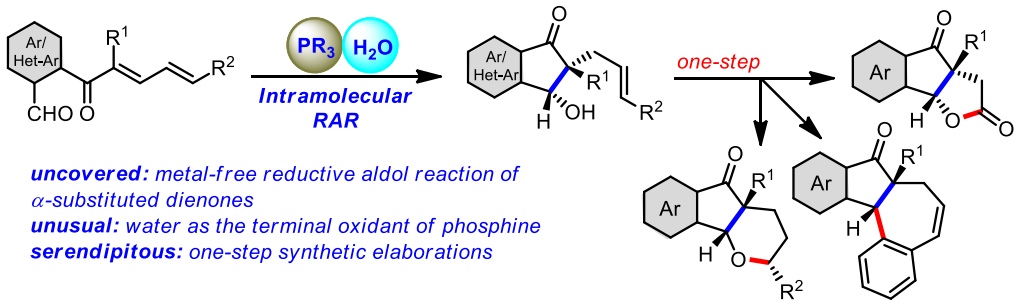
Satpathi, B.; Dutta, L.; Ramasastry, S. S. V. *Org. Biomol. Chem*. **2019**, *17*, 1547.



(2) *"Metal- and Hydride-Free Pentannulative Reductive Aldol Reaction"*

Satpathi, B.; Dutta, L.; Ramasastry, S. S. V. *Org. Lett*. **2019**, *21*, 170.

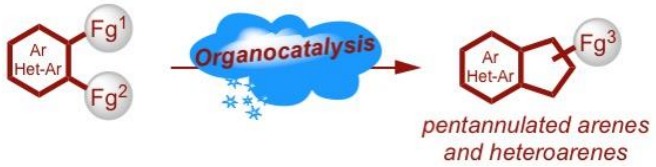


(3) *"Recent metal-catalysed approaches for the synthesis of cyclopenta[b]indoles"*

Vivekanand, T.; Satpathi, B.; Bankar, S. K.; Ramasastry, S. S. V. *RSC Adv*. **2018**, *8*, 18576. [*Invited for the RSC Advances special issue celebrating the decennial year of Chemical Frontiers Goa*]

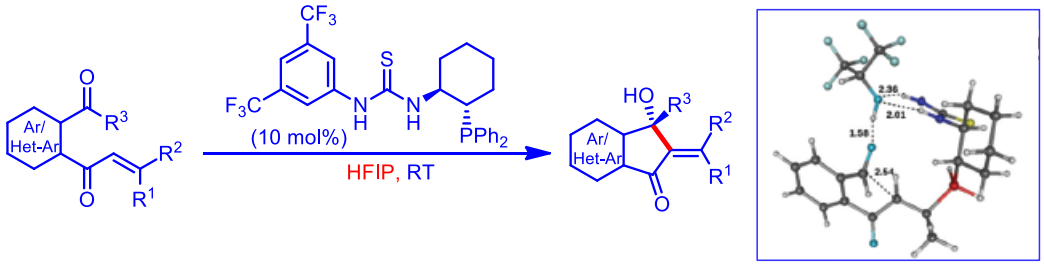
(4) *"Organocatalytic Strategies for the Synthesis of Cyclopenta-Fused Arenes and Heteroarenes"*

Satpathi, B.; Mondal, A.; Ramasastry, S. S. V. *Chem. – Asian. J.* **2018**, *13*, 1642. [*'Focus Review' invited by the Editor*]



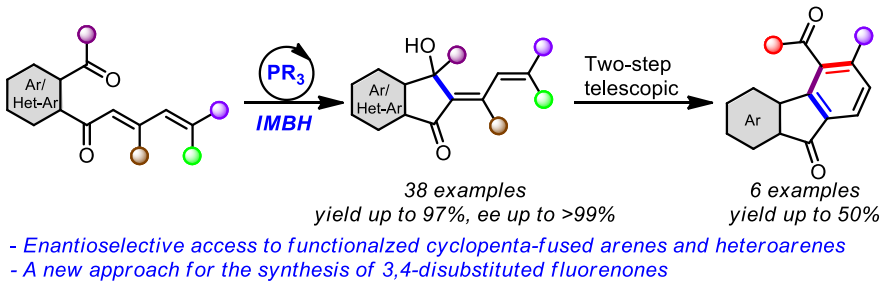
(5) *"A computational investigation of the solvent-dependent enantioselective intramolecular Morita-Baylis-Hillman Reaction of enones"*

Singh, N. K.; Satpathi, B.; Balanarayan, P.; Ramasastry, S. S. V. *Org. Biomol. Chem.* **2017**, *15*, 10212. [*Invited for the themed issue 'Mechanistic Aspects of Organic Synthesis'*]



(6) *"Enantioselective organocatalytic intramolecular Morita-Baylis-Hillman (IMBH) reaction of dienones, and elaboration of the IMBH adducts to fluorenones"*

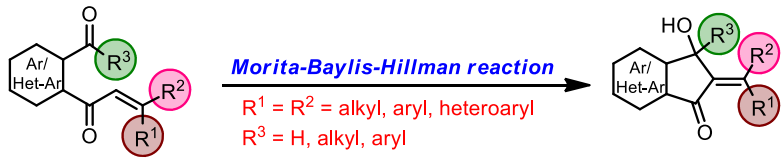
Satpathi, B.; Wagulde, S. V.; Ramasastry, S. S. V. *Chem. Commun.* **2017**, *53*, 8042.



- *Enantioselective access to functionalzed cyclopenta-fused arenes and heteroarenes*
- *A new approach for the synthesis of 3,4-disubstituted fluorenones*

(7) *"Enantioselective Organocatalytic Intramolecular Morita-Baylis-Hillman Reaction of Some Unusual Substrates"*

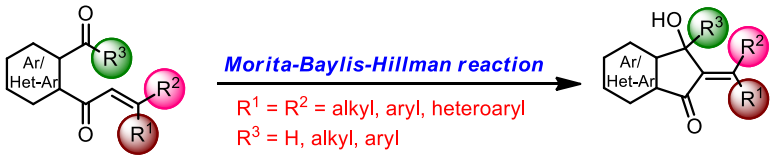
Satpathi, B.; Ramasastry, S. S. V. *Synlett* **2016**, *27*, 2178. [*Invited 'Synpacts' article*]



- *Orgaocatalytic intramolecularMBH reaction of the β,β-disubstituted enones*
- *Efficient access to cyclopenta[b]annulated arenes and heteroarennes*

(8) *"Morita-Baylis-Hillman Reaction of β,β-Disubstituted Enones: An Enantioselective Organocatalytic Approach for the Synthesis of Cyclopenta[b]annulated Arenes and Heteroarenes"*

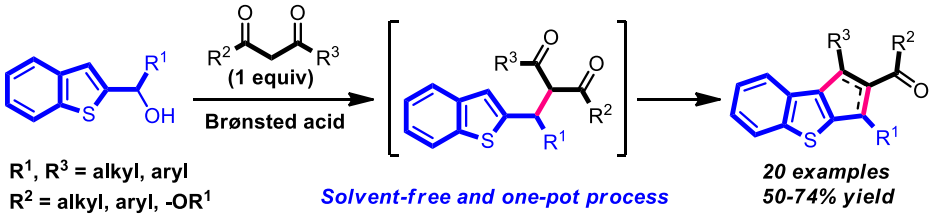
Satpathi, B.; Ramasastry, S. S. V. *Angew. Chem., Int. Ed.* **2016**, *55*, 1777.



- *First Morita-Baylis-Hillman reaction of the β,β-disubstituted-α,β-unsaturated ketones.*
- *Efficient access to cyclopenta[b]annulated thiophenes, indanones and pyrindanones.*
- *Excellent substrate scpe and short reaction times; yields up to 97% and ee up to >99%.*

(9) *"Synthesis of 1,2,3-Trisubstituted Cyclopentannulated Benzothiophenes through an Acid-Mediated, Solvent-Free, One-Pot Domino Process"*

Satpathi, B.; Dhiman, S.; Ramasastry, S. S. V. *Eur. J. Org. Chem.* **2014**, 2022.



The author, Mr. Bishnupada Satpathi was born at Egra, West Bengal. After his initial schooling at Egra, he received a B.Sc. degree in Chemistry from Bajkul Milani Mahavidyalaya, Vidyasagar University in 2011. After obtaining a Masters degree from the Indian Institute of Technology (IIT), Hyderabad, in 2013, he joined the research group of Dr. Ramasastry at the Indian Institute of Science Education and Research (IISER) Mohali, as a Ph.D. student in January 2014. He passed the comprehensive examination in January 2015. Presently, he is working as a Senior Research Fellow of IISER Mohali in the Department of Chemical Sciences.

CONFERENCES ATTENDED

- Delivered a talk at the **Emerging Trends in Drug Developments and Natural Products (ETDDNP-2018)** held at University of Delhi, India during January 2018 and received Elsevier award for one of the best oral presentations. Title of the presentation: *Organocatalytic Enantioselective Cyclopentannulation of Arenes and Heteroarenes.*
- Presented a poster at the **Thematic Conference in Chemical Sciences (TC_2S-2017)** held at IIT-Ropar, India during May 2017 and awarded for one of the best poster presentations. Title of the poster: *Cyclopentannulation of Arenes and Heteroarenes.*
- Presented a poster at the **International Conference on Organic Synthesis (ICOS 21)** held at IIT-Bombay, India during December 2016. Title of the poster: *Cyclopentannulation of Arenes and Heteroarenes.*
- Delivered a talk at the **XI JNOST-Organic Chemistry Conference (JNOST-OCC)** held at NISER-Bhubaneswar, India during December 2015. Title of the presentation: *Unusual Approaches for Cyclopentannulation of Arenes and Heteroarenes.*