One-pot relay catalysis: Divergent synthesis of furo[3,4-b]indoles and cyclopenta[b]indoles

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A dissertation submitted for the partial fulfilment of BS-MS dual degree in science

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Certificate of Examination

This is to certify that the dissertation titled "*One pot relay catalysis: Divergent synthesis of furo[3,4-b]indoles and cyclopenta[b]indoles*" submitted by Ms. Manisha (Reg. No. MS11036) for the partial fulfilment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

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Dated: April 22, 2016

Declaration

The work presented in this dissertation has been carried out by me under the guidance of **Dr. S. S. V. Ramasastry** at the Indian Institute of Science Education and Research Mohali.

This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussion. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

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

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Acknowledgement

It is my privilege to express my sincere gratitude to my supervisor, **Dr. S. S. V. Ramasastry** for his guidance and invaluable discussion throughout the work. Additionally, I am very thankful to him for exposing me to this interesting field of research.

I am extremely thankful to all my lab-mates for their help in learning the experimental techniques, which benefited me during the course of the project. I am thankful to DST, New Delhi for inspire fellowship. Also, I would like to acknowledge all the faculties of Department of chemical sciences for their constant support. I am thankful to library, IR, NMR and HRMS facilities of IISER-Mohali.

Last but not the least; I would like to acknowledge my family for always standing behind me with their love and support.

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Notations and Abbreviations

NMR	Nuclear magnetic resonance
IR	Infra-red
HRMS	High resolution mass spectroscopy
TLC	Thin layer chromatography
δ	Chemical shift in ppm
ppm	Parts per million
EtOAc	Ethyl acetate
s	Singlet
d	Doublet
t	Triplet
q	Quartet
m	Multiplet
dd	Doublet of doublet
dt	Doublet of triplet
td	Triplet of doublet
ddd	Doublet of doublet of doublet
M. P.	Melting point

Contents

Abstract

An efficient divergent strategy for the synthesis of furo[3,4-*b*]indoles via a sequential Ag(I)/Bi(III)/Pd(II) catalysis and cyclopenta[*b*]indoles via a one-pot Ag(I)/Brønsted acid relay catalysis from 3-(2-aminophenyl)-4-pentenyn-3-ols, accessible in three simple steps from 2-aminobenzaldehydes, is investigated.

Introduction

Cyclic compounds having one or more of the ring carbons replaced by another atom are known as Heterocyclic compounds. Among them, Indole is an important heterocyclic system, which is assembled into proteins in the form of amino acid tryptophan and thus provides the skeleton to a vast number of biologically active natural and unnatural compounds.[1a-b] In addition, the indole ring-containing molecules have been associated with multiple biological activities such as anticancer, anti-leukamic, analgesic, antiviral, anti-HIV, schizophrenia etc.[1c-d] Therefore, indoles and indolines are appraised to be privileged scaffolds from drug discovery standpoint.[1a-d]

Among profuse indole derivatives, cyclopenta[*b*]indoles are especially charismatic to synthetic chemists due to their presence in several biologically active natural products such as spiroindimicins,[2] fischerindoles,[3] yeuhchukene,[4] paspalines,[5] emindoles,[6] polyveolines,[7] terpendoles,[5] etc., and in medicinally important compounds for instance MK-0524[8] (Fig. 1). Therefore, cyclopenta[*b*]indoles with impressive pharmacological properties and complex molecular architectures inspired several research groups to contribute significantly to their synthesis (see for example, Scheme-1a, 1b and 1c).[9a-c]

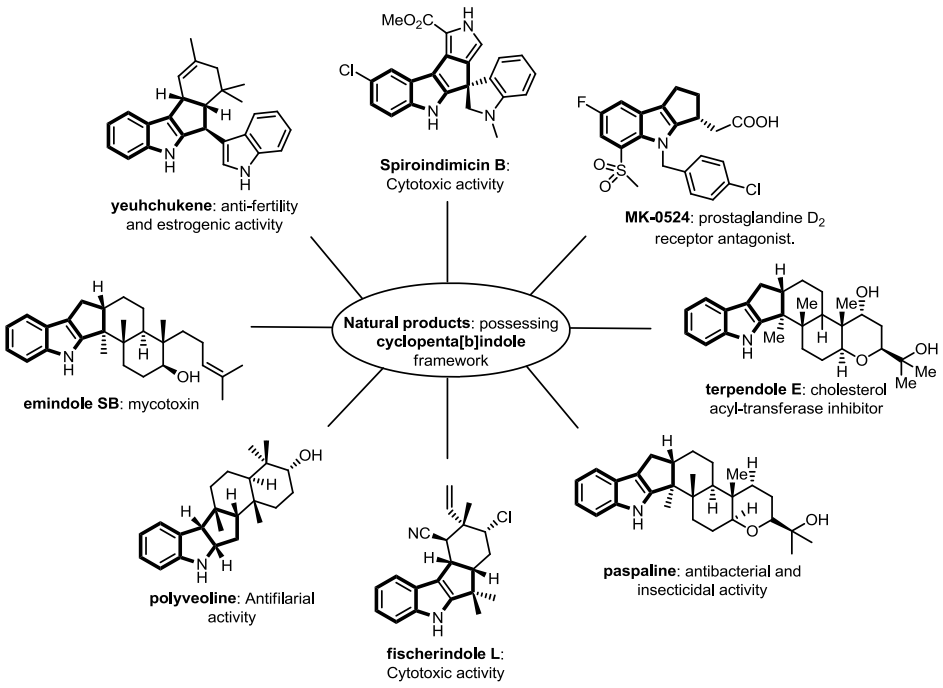
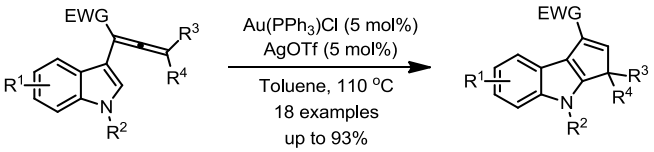
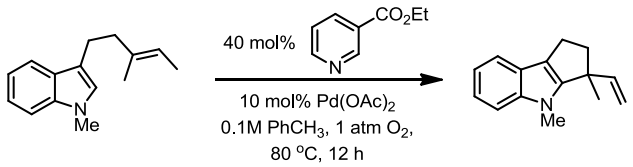


Fig. 1. Few examples of natural products and medicinally important compounds possessing cyclopenta[*b*]indole framework.

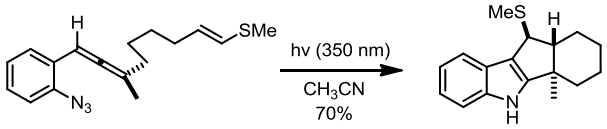
a) Electronic effect directed Au(I) catalyzed cyclic C2-H bond functionalization of 3-allenylindoles.[9a]



b) Catalytic C-H bond functionalization with Palladium(II): Aerobic oxidative annulations of indoles.[9b]



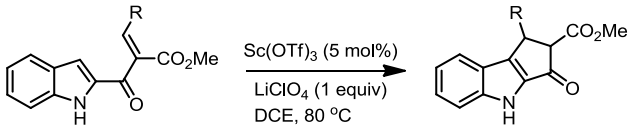
c) Synthesis of cyclopenta[*b*]indoles via indolines and indolidenium intermediates through photochemical pathway.[9c]



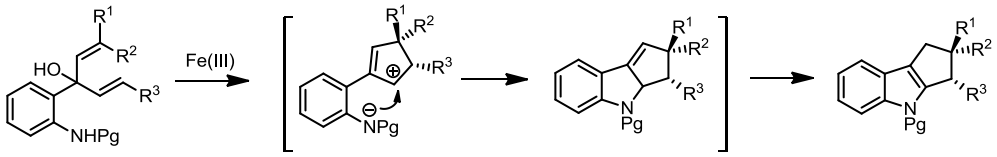
Scheme 1. Synthesis of cyclopenta[*b*]indoles through various strategies.

Among many traditionally used strategies for the construction of cyclopenta[*b*]indoles, Nazarov reaction-based approaches are popular (see for example, Scheme-2a and 2b). In particular, a well ordered generation of 4π-electron system designates a Nazarov cyclization effectively.[10a-g] But the drawbacks associated with this approach, includes harsh reaction conditions, lack of availability of starting materials, multi-step synthetic sequence, infuriating purification and low enantioselectivity.[10h] Therefore, due to environmental concerns, the quest to explore new sustainable catalytic approaches still remains an area of active research. Over the years, metal catalysis has emerged as one of the most powerful means for the activation of C-C multiple bonds towards a number of complexity-oriented transformations.[9a-b] For this purpose, precious metal catalysis (Ag, Au, Pd and Ru) due to their higher reactivity and selectivity has been proven to be a potent tool for the assemblage of cyclopenta[*b*]indoles in a highly selective, atom and step economical manner.[9a-b]

a) Frontier's Nazarov cyclization strategy for the pentannulation of indoles.[10f]



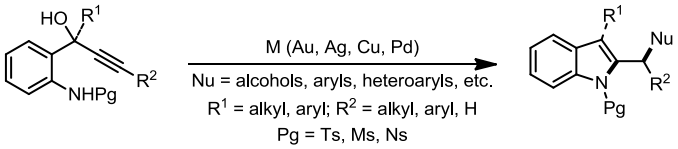
b) Kwon's Nazarov-cyclization based approach for cyclopenta[*b*]indoles.[10g]



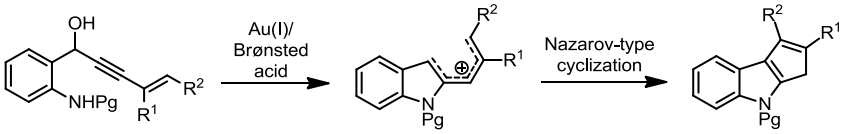
Scheme 2. Synthesis of cyclopenta[*b*]indoles via Nazarov cyclization strategy.

In literature, it is well known that amino propargyl alcohols under the influence of metal catalysis generate indolyl cation equivalents, which can be captured by nucleophiles to assemble a variety of products, Scheme-3a.[11] In this context, our group has recently published a one-pot relay gold(I)/Brønsted acid relay catalytic methodology for the synthesis of a variety of 1,2-disubstitued cyclopenta[*b*]indoles, Scheme-3b.[12]

a) Generation of indolyl cation equivalents.[11]



b) Our earlier work: Au(I)/Brønsted acid relay catalytic approach for the synthesis of 1,2-disubstituted cyclopenta[*b*]indoles.[12]



Scheme 3. Synthesis of cyclopenta[*b*]indoles via Au(I)/Brønsted acid relay catalysis.

Now-a-days, an escalated emphasis has been placed on the advancement of Relay catalysis for organic transformations that enable assemblage of complex molecules from simple and easily accessible starting materials in a short and competent manner.[13] The reaction catalyzed by two diverse catalysts at the same time circumvents yield losses, time and labour associated with isolation and purification of the intermediates. Moreover, it favours the enantioselectivity, which is otherwise less feasible by the use of a single catalyst. Undoubtedly, such a strategy can provide a

potent mean to synthesize complex molecular architectures via preserving resources and energy. But the expansion of such processes is not always straightforward. The main obstacle, mostly encountered during these reactions is to find the catalyst of choice, which should not only be compatible with other employed catalysts but also bears all reagents and intermediates generated during the course of the reaction. Hence, these compatibility issues and control over the selectivity aspects complicate the development of such methods. Among a variety of existing classes, novel relay processes promoted by two specific metal catalysts or metal/organocatalyst or organocatalyst/organocatalyst binary systems are well investigated.[14] Regardless, to the best of our knowledge, reactions promoted by three orthogonal metal relay catalytic systems are not reported until now.

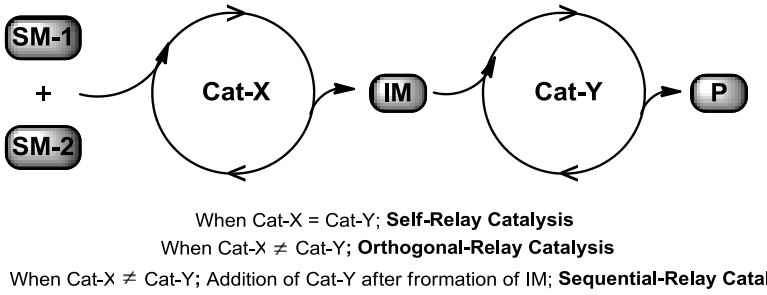
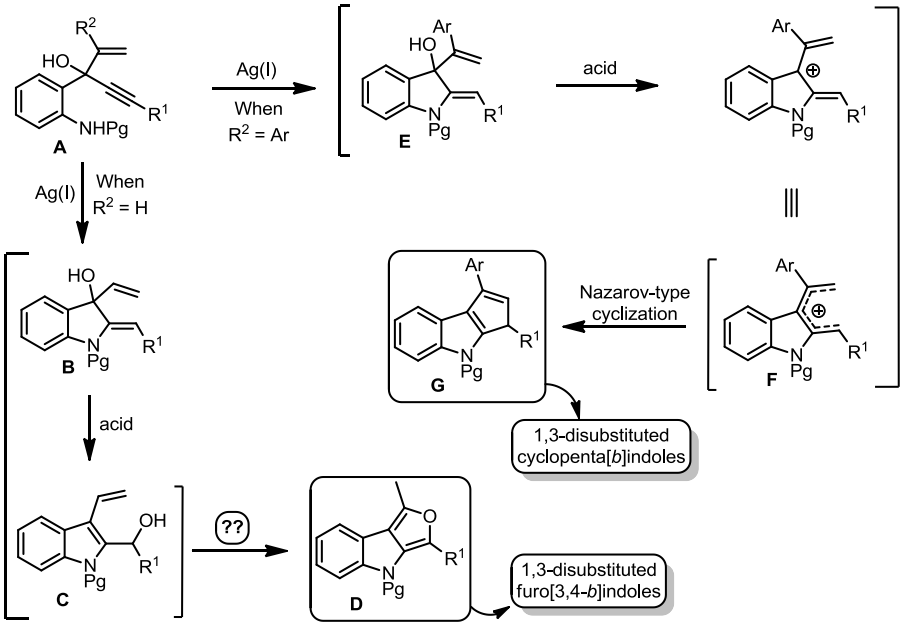


Fig.2. General representation of relay catalysis.

Furoindoles have attracted enormous attention of many researchers and considered as valuable tools in the area of organic chemistry. The fused heterocycle furo[3,4-*b*]indole has served as an indole-2,3-quinodimethane synthetic analogue in diverse inter- and intramolecular cycloaddition reactions, over the past 30 years. In general, these interesting molecules are short-lived. These furo[3,4-*b*]indoles acted as dienes, when subjected to various dienophiles in Diels-Alder pathway, hence offer rapid access to the synthesis of novel classes of heterocycles such as pyridocarbazoles, benzocarbazoles, and the antitumor alkaloid ellipticine.[15] Therefore, motivated by the literature reports and our lab work, we have designed enynol **A** as our potential substrate for the preparation of cyclopenta[*b*]indoles and furo[3,4-*b*]indoles. It was envisioned that indoline alcohol **B** can be generated from designer substrate **A** via Ag(I)-catalyzed 5-*exo*-dig cyclization (intramolecular hydroamination). Then, the treatment with acids lead to the formation of **C**, via 1,3-allylic alcohol isomerization (1,3-AAl). Further, intramolecular etherification of **C** through a 5-*exo*-trig cyclization, especially under oxidative conditions, could afford

the furo[3,4-*b*]indoles **D**, Scheme 4. These furo[3,4-*b*]indoles **D** can act as dienes, thus generates a possibility of being captured by dienophiles via Diels- Alder pathway, which may leads to the formation of respective carbazole motifs.



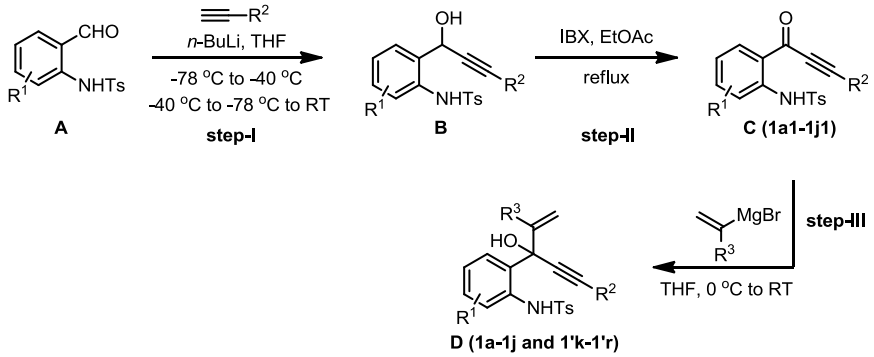
Scheme 4. Divergent approach for the synthesis of furo[3,4-*b*]indoles and cyclopenta[*b*]indoles.

On the other hand, indoline alcohol **E** can be generated from substrate **A** via Ag(I)-catalyzed 5-*exo*-dig cyclization (intramolecular hydroamination). Further, indoline alcohol **E** under the influence of appropriate Brønsted acid give rise to 4π-electon system **F**, which can undergo Nazarov-type cyclization yielding cyclopenta[*b*]indoles **G**, Scheme-4.

Herein, we delineate our efforts toward developing a new synthetic approach for furo[3,4-*b*]indoles via Ag(I)/Bi(III)/Pd(II)-promoted relay catalytic system. In addition, we also report a Ag(I)/Brønsted acid relay system that facilitates the synthesis of cyclopenta[*b*]indoles.

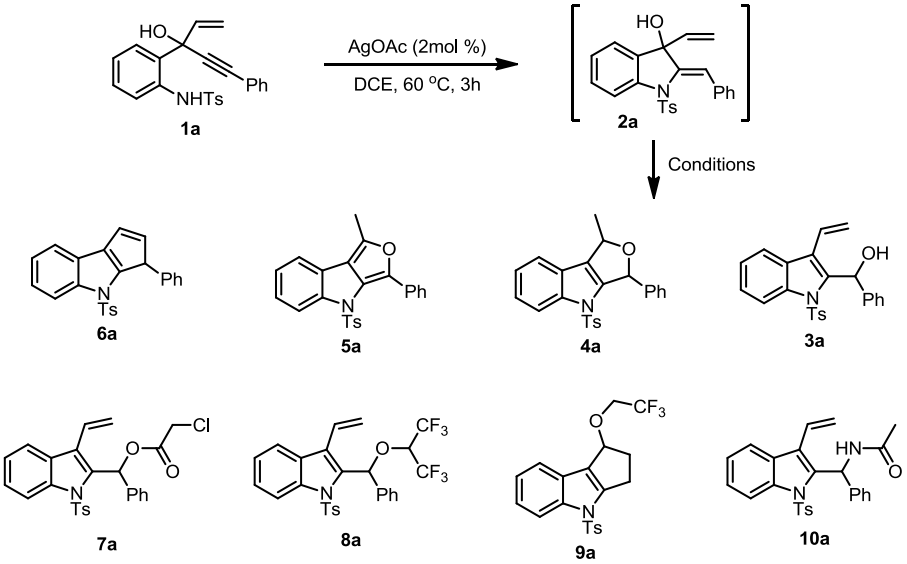
Results and Discussion

At the outset, the enynols **D** (**1a-1j** and **1'k-1'r**) were synthesized from the corresponding ynones **C** (**1a1-1j1**) in good to excellent yields (Scheme-5).



Scheme 5. General approach for the synthesis of 3-(2-aminophenyl)pent-4-en-1-yn-3-ols **1a-1j** and **1'k-1'r**.

We have initiated screening of various catalyst and solvent combinations with **1a** as the model substrate, with the intention to obtain the pentannulated indole **6a**, Scheme 6. To start with, the Au(I)-catalyzed intramolecular hydroamination conditions, reported earlier by our group have been tried for formation of **2a**.[12] However, the desired product formation was not observed. Among few other variations attempted for the 5-*exo*-dig product **2a**, to our delight, AgOAc successfully delivered **2a** in excellent regio- and chemoselectivity.[16]



Scheme 6. Different products formed from **1a** under the reaction conditions.

Table 1. Screening of different catalysts.

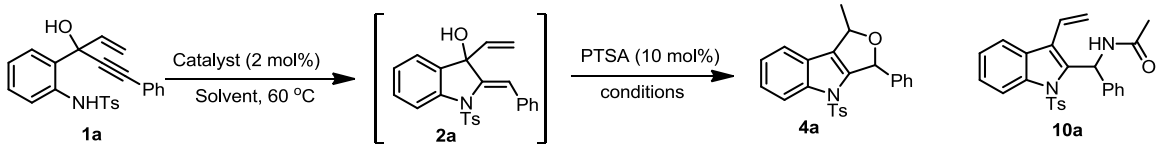
S. No.	Catalyst (10 mol%)	Solvent	Temp (^oC)	Time (h)	Observation
1	**$Bi(OTf)_3$**	**DCE**	**0**	**2**	**3a (85% yield)**
2	$La(OTf)_3$	DCE	0	24	**3a** (68% yield)
3	$Yb(OTf)_3$	DCE	0	24	**3a** (64% yield)
4	$Sc(OTf)_3$	DCE	0	20	**3a**
5	$EtAlCl_2$	DCE	0	15	**3a**
6	PPTS	DCE	0	20	**3a**
7	Amberlyst-15	DCE	0	28	**3a**
8	Dowex	DCE	0	20	**3a**
9	Montmorillonite	DCE	0	24	**3a**
10	PTSA	DCE	0	12	**4a** (40% yield)
11	CSA	DCE	0	48	**4a** (35% yield)
12	$ClCH_2COOH$	DCE	0	15	**7a**
13	$FeCl_3$	DCE	0	5	Complex mixture
14	TMSOTf	DCE	0	4	Complex mixture
15	TfOH	DCE	0	4	Complex mixture
16	$BF_3.Et_2O$	DCE	0	4	Complex mixture

The reaction of **2a** catalysed by different Lewis acids such as $Bi(OTf)_3$, $La(OTf)_3$, $Yb(OTf)_3$, $Sc(OTf)_3$ and ethylaluminum dichloride ($EtAlCl_2$) generated only the indolyl alcohol **3a** (Table 1, entries 1-5). Further, various Brønsted acids, for example, Amberlyst-15, Dowex, Montmorillonite and pyridinium *p*-toluenesulfonate (PPTS) led to the formation of the indolyl alcohol **3a** (Table 1, entries 6-9). Interestingly, under the influence of *p*-toluenesulfonic acid (PTSA) and camphorsulfonic acid (CSA), formation of the dihydrofuro[3,4-*b*]indole **4a** was observed, which presumably formed via the 5-*exo*-trig cyclization of **3a** (Table 1, entries 10-11). Surprisingly, reaction of **2a** in presence of chloroacetic acid ($ClCH_2COOH$) led to the formation of product **7a** (Table 1, entry 12). Subsequent evaluation with Lewis acids such as TMSOTf, TfOH, $BF_3.Et_2O$ and $FeCl_3$ resulted in formation of only a complex mixture (Table 1, entries 13-16).

Further, screenings have been attempted to improve the yields of dihydrofuro[3,4-*b*]indole **4a** (Table 2). During screening, for first step different Ag(I) catalysts like Ag_2O, Ag_2CO_3, $AgNO_3$, AgOTf, $AgBF_4$ etc have been screened, in order to improve the yield of **4a**, but the efforts were futile (Table 2, entries 4-5, 9-11). Despite realizing **4a** in moderate yields, we were pleased to establish a new one-

pot approach for the synthesis of 1,3-disubstituted 3,4-dihydro-1*H*-furo[3,4-*b*]indoles, since to best of our knowledge, there is no general method known for synthesis of **4a**.

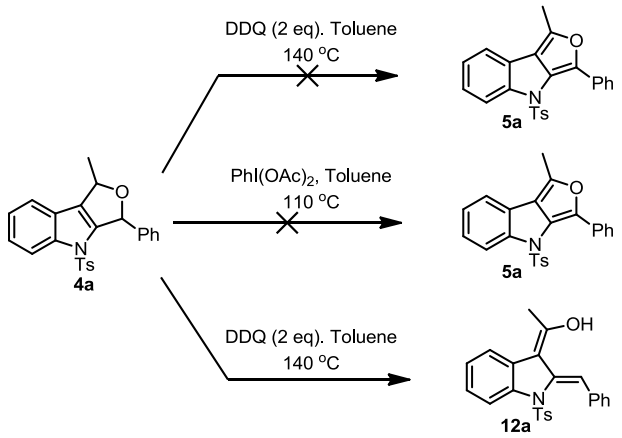
Table 2. Optimization of reaction parameters for **4a**.



S. No.	Catalyst	Solvent	Temp (^{o}C)	Time (h)	Yield of **4a** (%)
1	AgOAc	DCM	RT	13	35
2	**AgOAc**	**DCE**	**RT**	**12**	**40**
3	AgOAc	Toluene	RT	15	12
4	Ag_2O	DCE	RT	15	28
5	Ag_2CO_3	DCE	RT	21	25
6	AgOAc	DCE	60	3	35
7	AgOAc	Acetonitrile	RT	12	Formation of **10a**
8	AgOAc	Nitromethane	RT	48	-
9	$AgNO_3$	DCE	RT	48	-
10	AgOTf	DCE	RT	48	-
11	$AgBF_4$	DCE	RT	48	-
12	AgOAc	DCE	-20	72	-
13	AgOAc	DCE	-10	72	-
14	AgOAc	DCE	10	72	-

Several subsequent efforts directed to improve the yields of **4a** were met with no considerable success (Table 2, entries 1, 3-6), except that a marginal yield increment in case when the PTSA reaction was performed with the purified sample of **3a** (Table 3, entry 2). Interestingly, when reaction was tried in presence of acetonitrile solvent, product **10a** was obtained (Table 2, entry 7). Subsequent attempts to improve the yield of 3a were unsuccessful (Table 2, entries 8-14).

At this stage, attempts were made to aromatize the product **4a** to obtain furo[3,4-*b*]indoles **5a** as the potential product.

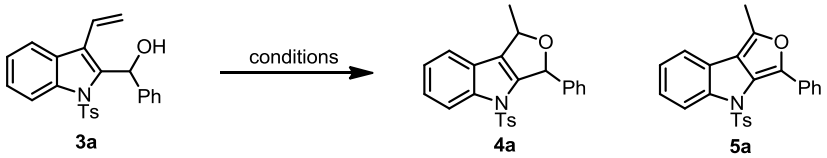


Scheme 7. Attempts for aromatization of dihydrofuro[3,4-*b*]indole **4a**.

For aromatization of 1,3-disubstituted 3,4-dihydro-1*H*-furo[3,4-*b*]indole **4a** to furo[3,4-*b*]indole **5a**, oxidation by 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) and (diacetoxyiodo)benzene ($PhI(OAc)_2$) were attempted.[17] But, these attempts were unsuccessful, and instead we obtained the ring opened product **12a**.

Therefore, as part of our attempts to improve the efficiency of the formation of **4a** from **2a**, we tried few more modifications, and performed the reaction with indolyl alcohol **3a** (instead of **2a**) in presence of different catalysts.

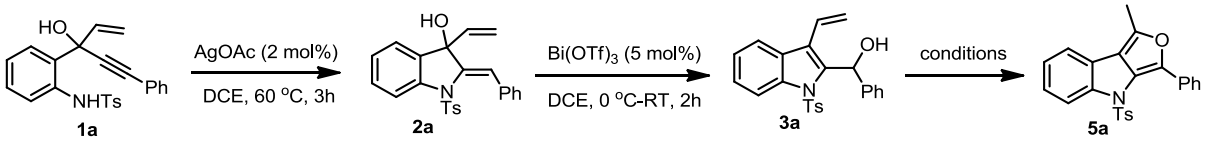
Table 3. Screenings with purified indolyl alcohol **3a**.



S. No.	Catalyst (10 mol%)	Solvent	Temp (^oC)	Time (h)	Observation
1	PTSA	DCE	RT	11	**4a** (45% yield)
2	**$Pd(OAc)_2$**	**DCE**	**RT**	**20**	**5a (45% yield)**
3	CuI	DCE	RT	4	-
4	$AgNO_3$	DCE	RT	4	-

Surprisingly, to our delight, the reaction of **3a**, in the presence of catalytic amount of $Pd(OAc)_2$ delivered the furo[3,4-*b*]indoles **5a** in 45% yield (Table 3, entry 2), which is the same product we tried to obtain via aromatization of 1,3-disubstituted 3,4-dihydro-1*H*-furo[3,4-*b*]indole **4a**. Further, attempts were made to find out the optimization condition for furo[3,4-*b*]indole **5a** (Table 4).

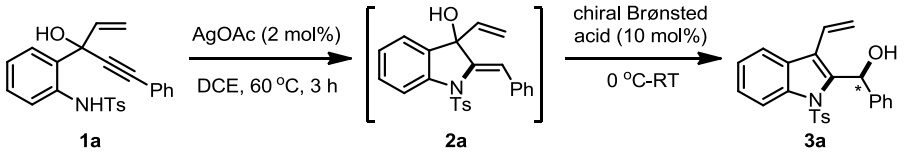
Table 4. Optimization of reaction parameters for furo[3,4-*b*]indole **5a** from **3a**.

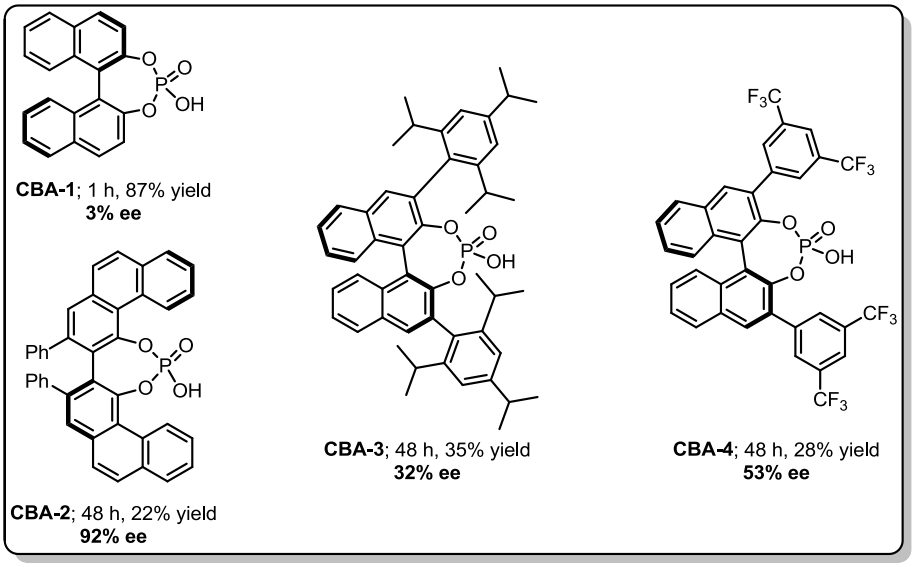


S. No.	Catalyst (10 mol%)	Solvent	Temp (^{o}C)	Time (h)	Yield of **5a** (%)
1	$Pd(OAc)_2$	DCE	0	30	43
2	$Pd(OAc)_2$	DCE	RT	20	45
3	**$Pd(OAc)_2$**	**DCE**	**60**	**10**	**50**
4	$Pd(PPh_3)_4$	DCE	60	20	20
5	$PdCl_2$	DCE	60	48	-
6	$Pd(dppf)Cl_2$	DCE	60	48	-
7	$Pd_2(dba)_3$	DCE	60	48	-

Therefore, among few other variations undertaken to increase the efficiency of the reaction, only the reaction of **3a** at an elevated temperature provided **5a** with a slight increase in the yield (Table 4, entry 3). Employing a few other Pd(II) salts proven to be unsuccessful (Table 4, entry 5-7). Thus, low yields of **4a** or **5a**, in general, are attributed to their inherent instability, which is well documented in the literature.[18]

A brief screening of chiral Brønsted acids was undertaken for the one-pot enantioselective synthesis of **3a**, Scheme 8.[19]





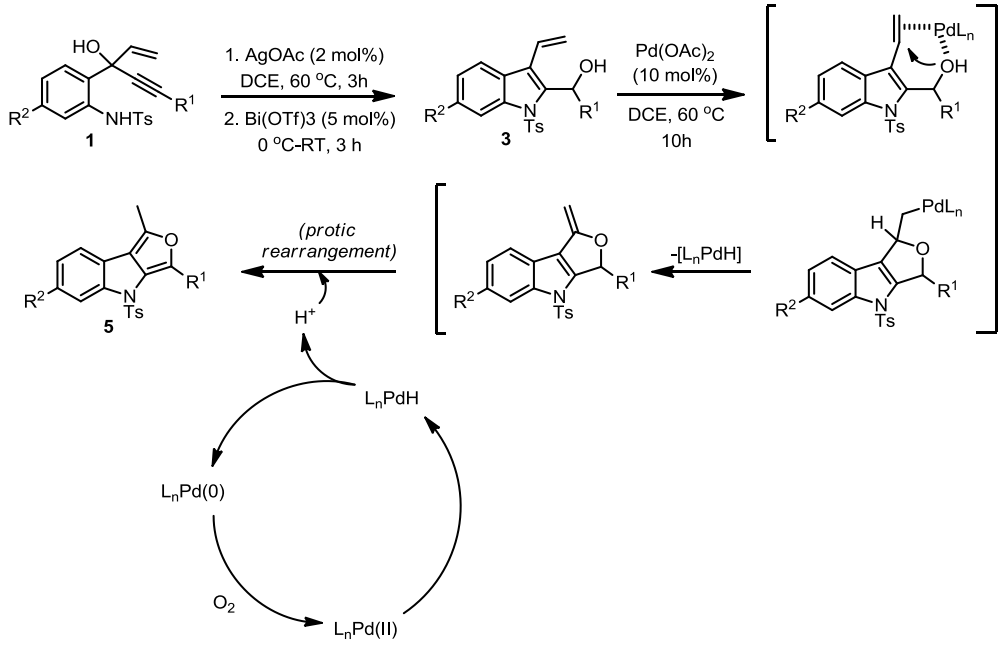
Scheme 8. Brief screening of chiral Brønsted acids for the enantioselective synthesis of **3a**.

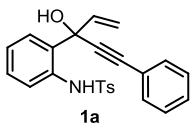
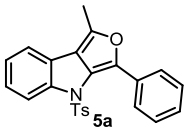
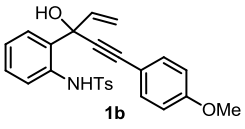
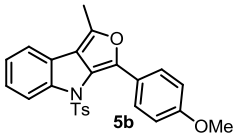
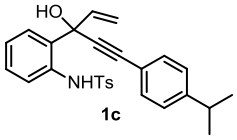
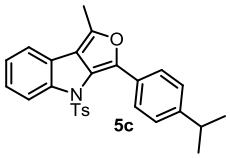
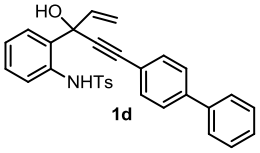
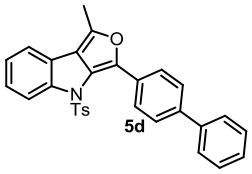
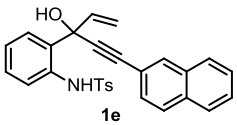
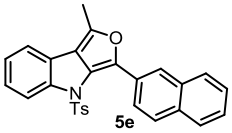
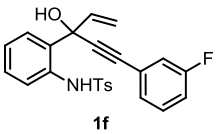
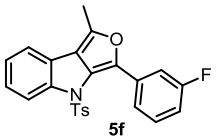
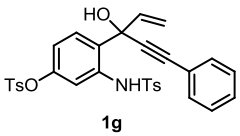
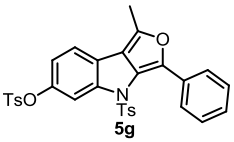
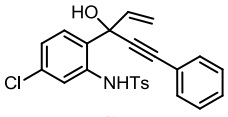
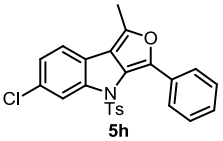
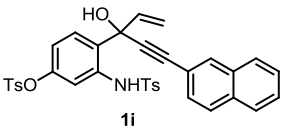
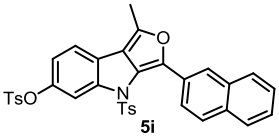
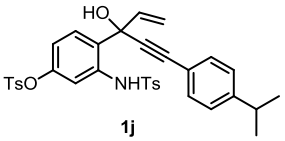
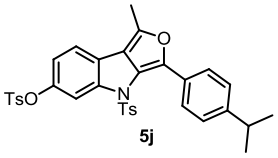
During this screening, chiral phosphoric acids CBA-1 to CBA-4 were evaluated for the transformations of **2a** to **3a**. With the (*R*)-VAPOL hydrogen phosphate CBA-2, **3a** was realized in 92% ee, however the reaction was found to be stalling after a certain extent of conversion. On the other hand, **3a** was obtained in 87% yield with (*R*)-BINOL phosphoric acid (CBA-1), but almost as a racemic mixture. To improve the enantioselectivity and yield, fluorinating solvents such as hexafluoroisopropanol and trifluoroethanol were introduced. But instead, product **8a** and **9a** was obtained respectively. Therefore, our attempts to achieve a better result were futile. Nevertheless, a new one-pot relay Ag(I)/chiral Brønsted acid system was established for the enantioselective synthesis of **3a**.

With the optimized conditions for furo[3,4-*b*]indoles in hand, we proceeded to evaluate the substrate scope, Table 5. Clearly, a wide range of electronically and structurally diverse substituents across the alkyne (R^1) and the aryl ring (R^2) were well-tolerated and generated the furoindoles **5a-5j** in moderate to good yields. Also, a narrow yield range (50-56%) indicates the robustness of the method which in turn highlights the least dependence of the relay catalytic system on the electron-donating/withdrawing contributions of the substituents. Interestingly, the furoindoles **5** were isolated in poor yields when the reaction was carried out in a one-pot trimetallic relay mode [Ag(I)/Bi(III)/Pd(II)], better yields were observed by performing the reaction initially under a one-pot bimetallic Ag(I)/Bi(III) system followed by subjecting the purified Indolyl alcohols **3** to Pd(II) catalysis. Regardless,

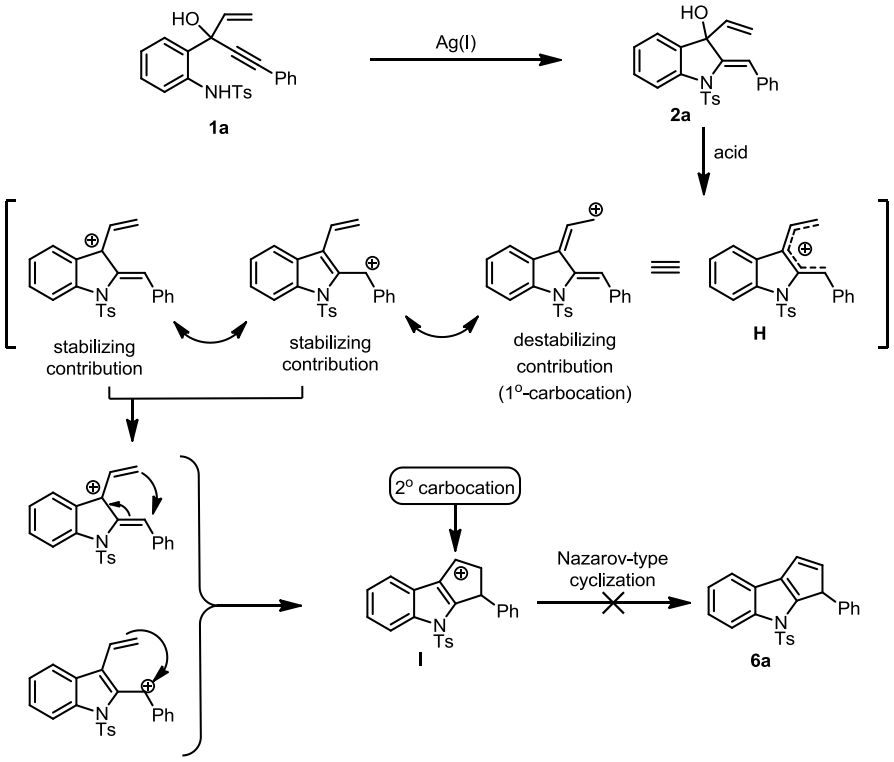
this method can serve as a prospective substitute to the existing approaches describing the synthesis of the interesting and short-lived furo[3,4-*b*]indoles.

Table 5. Mechanism and Substrate scope for furo[3,4-*b*]indoles.



Entry	Enynol	Product	Time	Yield(%)
1.	 **1a**	 **5a**	10 h	50%
2.	 **1b**	 **5b**	9 h	54%
3.	 **1c**	 **5c**	9 h	54%
4.	 **1d**	 **5d**	10 h	57%
5.	 **1e**	 **5e**	9 h	50%
6.	 **1f**	 **5f**	9 h	56%
7.	 **1g**	 **5g**	8 h	53%
8.	 **1h**	 **5h**	10 h	54%
9.	 **1i**	 **5i**	9 h	51%
10.	 **1j**	 **5j**	10 h	56%

After successfully establishing a new method for the synthesis of furo[3,4-*b*]indoles, we turned our attention to rationalize the non-formation of **6a** from **1a**. A mechanistic hypothesis for this observation is proposed in scheme 9.



Scheme 9. Plausible explanation for the non-formation of **6a** from **1a**.

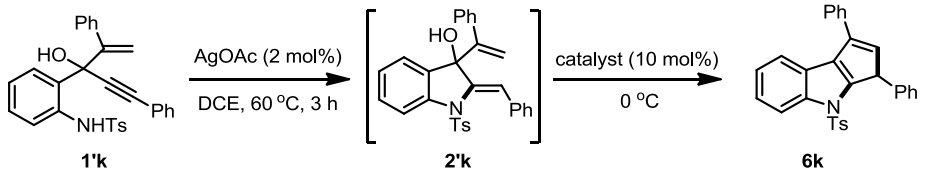
The indoline **2a** under the influence of an acid generates the 4π-electron system **H**, which during the process of undergoing a Nazarov-type cyclization builds up the potentially destabilizing 2^{o}-carbocation intermediate **I**. So, an additional substitution at this position creates a more stabilized 3^{o}-carbocationic intermediates that can make the way for the formation of the desired Nazarov cyclized product.

Based on this hypothesis, we have synthesized the enynol **1'k** which now possesses a phenyl group at vinylic position. The phenyl group at this position can also play a crucial role in shifting the system from *s*-trans to *s*-cis in the pentadienylcation intermediate **H**.[20a-c] Further, we have initiated a brief screening of Lewis and Brønsted acids, in order to evaluate the formation of Nazarov product **6k**.

Among few Brønsted and Lewis acids evaluated for the conversion of indoline 1**'k** to the Nazarov product **6k**, CSA, PTSA and TfOH were found to be optimum. So,

the initial reactions were performed with all three Brønsted acids in order to access their consistency.

Table 6. Optimization of reaction parameters for cyclopenta[*b*]indoles.

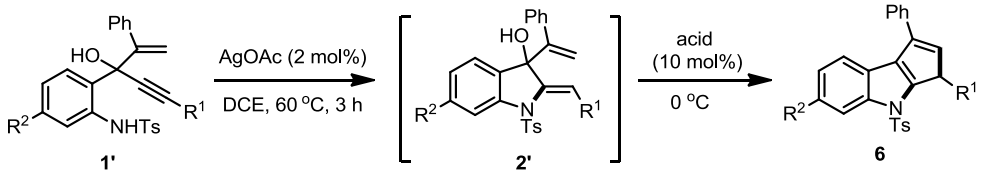


1'k **2'k** **6k**

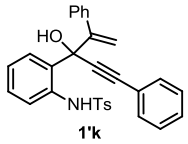
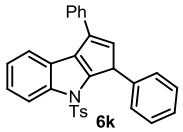
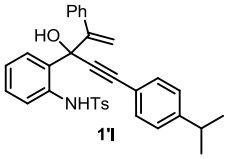
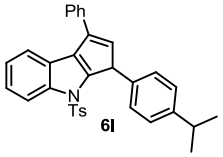
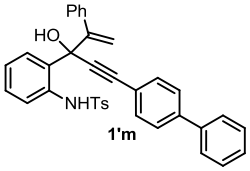
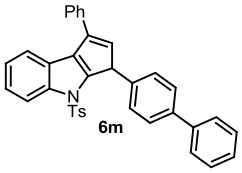
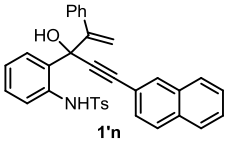
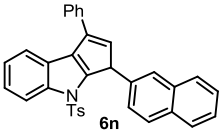
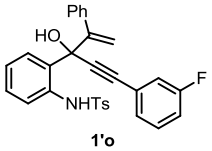
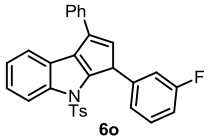
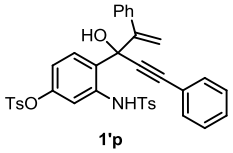
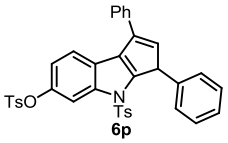
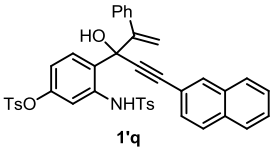
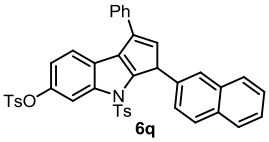
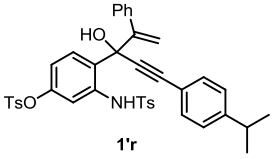
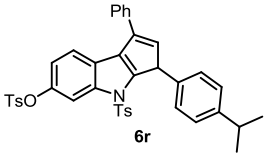
S. No.	Catalyst (10 mol%)	Time (min)	Yield (%)
1	$Sc(OTf)_3$	15	42
2	**CSA**	**30**	**80**
3	**PTSA**	**30**	**70**
4	$FeCl_3$	45	42
5	$AlCl_3$	35	65
6	AgOTf	40	55
7	**TfOH**	**20**	**68**
8	CF_3COOH	20	28
9	Amberlyst-15	180	56
10	$ClCH_2COOH$	360	-

Therefore, from Table-7 it is clear that the pentannulated indoles **6k**, **6l** and **6m** formed consistently in excellent yields under the CSA catalysis. Thus, CSA was chosen as the catalyst of choice for further deliberations. Subsequent evaluation of the substrate scope under the optimized conditions furnished a variety of 1,3-disubstituted cyclopenta[*b*]indoles **6n-6r** in very good yields. Hence, this methodology can provide an efficient and robust synthetic access to several medicinally important compounds and biologically active natural products possessing cyclopenta[*b*]indole scaffold.

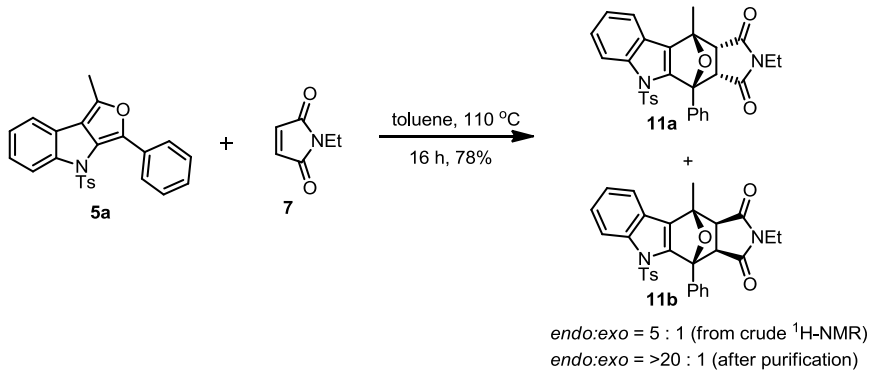
Table 7. Substrate scope for cyclopenta[*b*]indoles.



1' **2'** **6**

Entry	Enynol	Product	acid	Time	Yield(%)
1.	 **1'k**	 **6k**	CSA PTSA TfOH	30 min 30 min 20 min	78% 70% 68%
2.	 **1'l**	 **6l**	CSA PTSA TfOH	20 min 25 min 20 min	88% 83% 57%
3.	 **1'm**	 **6m**	CSA PTSA	20 min 25 min	68% 56%
4.	 **1'n**	 **6n**	CSA	50 min	69%
5.	 **1'o**	 **6o**	CSA	20 min	60%
6.	 **1'p**	 **6p**	CSA	45 min	74%
7.	 **1'q**	 **6q**	CSA	1 h	65%
8.	 **1'r**	 **6r**	CSA	50 min	83%

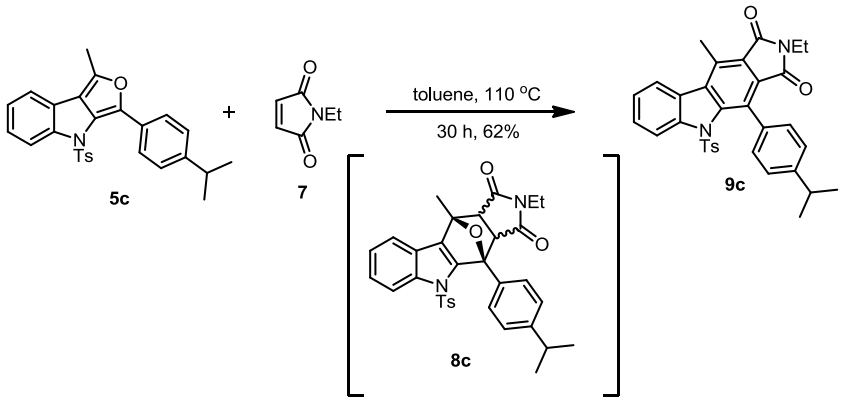
After establishing a new one-pot relay catalytic approach for construction of furo[3,4-*b*]indoles and cyclopenta[*b*]indoles, we planned an elaboration with furo[3,4-*b*]indoles. In literature, it is well demonstrated by Gribble and co-workers that furo[3,4-*b*]indoles behave as dienes in the Diels-Alder reaction, and thus served widely for the construction of several complex molecular architecture.[18] Towards this, furoindole **5a** and N-ethylmaleimide **7** were refluxed in toluene to produce a mixture of *endo/exo* Diels-Alder adducts (**11a** and **11b**) in 78% yield, Scheme 10.



Scheme 10. Diels-Alder reaction of the furoindole **5a** and maleimide **7** for the formation of **11a** and **11b**.

The isomeric structures (**11a** and **11b**) were assigned from the ^{1}H and ^{13}C-NMR data and further verified from the reported data of similar structures.[18b] This result indirectly confirms the structure of furoindole **5a** and other analogues as well.

Interestingly, the reaction of furoindole **5c** with N-ethylmaleimide **7** under reflux conditions furnished the carbazole **9c** in good yields via the [4+2] adduct **8c**, Scheme 11.[18]



Scheme 11. Formation of the carbazole **9c** via the Diels-Alder reaction of the furoindole **5c** and maleimide **7**.

Therefore, through this strategy we can successfully elaborate furoindoles to carbazoles, which are considered privileged scaffolds from medicinal chemistry standpoint. Since the first isolation of carbazoles, it has captured the interest of biologists and chemists due to promising biological activities and the intriguing structural features exhibited by a large number of carbazole alkaloids.[15a-g] Now-a-days, carbazoles have attracted enormous attention, mostly due to their material properties, which is used in polymer solar cells, organic light-emitting diodes etc.[15h] This method therefore can provide an access to highly functionalized carbazoles as well.

Summary

In summary, for the first time, a divergent one-pot relay catalytic approach for the synthesis of 1,3-disubstituted furo[3,4-*b*]indoles and cyclopenta[*b*]indoles accessible easily from 3-(2-aminophenyl)-4-pentenyn-3-ols is presented. Based on the mechanistic considerations, interesting substitution dependence on the product distribution was realized; hence this phenomenon was efficiently crafted to yield the product of choice. Therefore, these methodologies have demonstrated great potential for the synthesis of new heterocycles, thus will stimulate further research in this area.

Experimental methods

General experimental methods: All the starting compounds and catalysts employed in this study were procured from Sigma-Aldrich and were used without further purification. For thin layer chromatography (TLC), silica aluminium foils with fluorescent indicator 254 nm (from Aldrich) were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), and acetic acid (10 mL) in ethanol (900 mL) followed by heating. Column chromatography was performed using SD Fine silica gel 100-200 mesh (approximately 15–20 g per 1 g of the crude product). Dry THF was obtained by distillation over sodium and stored over sodium wire. IR spectra were recorded on a Perkin–Elmer FT IR spectrometer as thin films or KBr pellet, as indicated, with ν_{max} in inverse centimetres. Melting points were recorded on a digital melting point apparatus Stuart SMP30 and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz BrukerBiospinAvance 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 $CDCl_3$.Carbon chemical shifts are internally referenced to the deuterated solvent signals in $CDCl_3$ (δ 77.1 ppm). High-resolution mass spectra were recorded on a Waters QTOF mass spectrometer. Enantiomeric excess was determined by using Waters Chiral HPLC.

Procedure A: Preparation of 3-(2-aminophenyl)pent-4-en-1-yn-3-ols (1a-1j and 1'k-1'r).

All the 3-(2-aminophenyl)pent-4-en-1-yn-3-ols (**1a-1j and 1'k-1'r**) employed in this study were prepared following a three-step protocol starting from 2-aminobenzaldehydes **A**. *n*-Butyl lithium mediated addition of alkynes to amino benzaldehydes **A** afforded ynols **B** which upon IBX oxidation generated the ynones **C**. Further addition of vinyl magnesium bromides to ynones **C** furnished 3-(2-aminophenyl)pent-4-en-1-yn-3-ols **D** (Scheme 5).

Representative procedure for step-I (Scheme 5): To a stirred solution of the alkyne (2.2 equiv.) in anhydrous THF at −78 °C, was added *n*-butyllithium (2.0 M in

cyclohexane solution, 2.2 equiv.) drop wise, and the resulting solution was allowed to stir at the same temperature for 10 min. The reaction was warmed to −40 °C. The resulting mixture was stirred at the same temperature for 1 h. After 1 h, reaction mixture was cooled to −78 °C. N-(2-formylphenyl)-4-methylbenzenesulfonamide **A** (1 mmol) was dissolved in THF (2 mL) and added to the reaction mixture drop wise at −78 °C and allowed to stir for 1 h at the same temperature. The reaction mixture was slowly warmed up to room temperature and stirred for a further 1 h. Upon completion, the reaction mixture was quenched by adding saturated aq. NH_4Cl (1 mL) and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (20-30% EtOAc/hexane) to afford **B** in 80-90% yields.

Representative procedure for step-II (Scheme 5): Ynol **B** (1 mmol) was dissolved in EtOAc (5 mL), and IBX (1.5 mmol) was added. The resulting suspension was stirred at 75 °C until alcohol **B** disappeared as monitored by TLC. The reaction mixture was cooled to room temperature and filtered through celite pad. The residue was washed with ethyl acetate (3×2 mL). Organic extracts were combined and washed with saturated aq. $NaHCO_3$ solution to remove excess iodobenzoic acid. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (20-30% EtOAc/hexane) to afford **C** in 75-85% yields.

Representative procedure for step-III (Scheme 5): An oven dried round bottom flask was charged with ynones **C** (1.0 mmol), 5 mL dry THF and placed at 0^oC. Vinyl magnesium bromide (2.0 M in THF, 3.5mmol) was added drop wise at the same temperature and stirred for 1h. Upon completion, the reaction mixture was quenched by adding saturated aq. NH_4Cl (1 mL) and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (10-20% EtOAc/hexane) to afford **D** in 84-97% yields.

Procedure B: Synthesis of indolyl alcohol 3a: A 5 mL glass vial was charged with 3-(2-aminophenyl)-pent-4-en-1-yn-3-ol **1a** (0.1 mmol), AgOAc (2 mol%) in DCE solvent (1 mL) stirred at 60 ^oC. Upon disappearance of **1a**, catalyst (10 mol%) [See,

table-1] was introduced and continued stirring at 0^{o}C to RT until intermediate **2a** disappeared. On complete formation of **3a,** the reaction mixture was quenched by adding saturated aq. $NaHCO_3$ (1 mL) and extracted with EtOAc (2 x 2 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (10-20% EtOAc/hexane) to afford **3a**.

Procedure C: Synthesis of 1,3-disubstituted 3,4-dihydro-1*H*-furo[3,4-*b*]indole 4a: A 5 mL glass vial was charged with 3-(2-aminophenyl)-pent-4-en-1-yn-3-ol **1a** (0.1 mmol), AgOAc (2 mol%) in DCE solvent (1 mL) stirred at 60 ^{o}C. Upon disappearance of **1a**, catalyst (10 mol%) in an appropriate solvent [See, table-2] was introduced and continued stirring at appropriate temperature until intermediate **2a** disappeared. On complete formation of **4a**, the reaction mixture was quenched by adding saturated aq. $NaHCO_3$ (1 mL) and extracted with EtOAc (2 x 2 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (10-20% EtOAc/hexane) to afford **4a**.

Procedure D: synthesis of furo[3,4-*b*]indole 5a-5j: A 5 mL glass vial was charged with 3-(2-aminophenyl)-pent-4-en-1-yn-3-ol **1a** (0.1 mmol), AgOAc (2 mol%) in DCE solvent (1 mL) stirred at 60 ^{o}C. Upon disappearance of **1a**, $Bi(OTf)_3$ (5mol%) was introduced and continued stirring at room temperature (see Table 1) until intermediate **2a** disappeared. Then, reaction mixture was quenched by adding saturated aq. $NaHCO_3$ (1 mL) and extracted with EtOAc (2 x 2 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude residue (crude **3a**) was further subjected to a palladium catalyst (10 mol%) in 1,2-dichloroethane with continuous stirring at an appropriate temperature [see, table-4]. Upon disappearance of starting material (monitored by TLC), the volatiles were removed under reduced pressure and crude residue was purified by silica gel column chromatography (10-20% EtOAc/hexane) to afford **5a**.

Procedure E: synthesis of chiral indolyl alcohol 3a: A 5 mL glass vial was charged with 3-(2-aminophenyl)-pent-4-en-1-yn-3-ol **1a** (0.1 mmol), AgOAc (2 mol%) in

DCE solvent (1 mL) stirred at 60 ^{o}C. Upon disappearance of **1a**, chiral catalyst (10 mol%) [See, Scheme-15] was introduced and continued stirring at 0^{o}C-RT until the intermediate **2a** disappeared. Upon complete formation of **3a,** the reaction mixture was quenched by adding saturated aq. $NaHCO_3$ (1 mL) and extracted with EtOAc (2 x 2 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (10-20% EtOAc/hexane) to afford **3a**. The enantiomeric excess was determined by HPLC analysis using Chiralpak AD-H column (90:10 n-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 21.4 min, τ_{minor} = 27.0 min).

Empower 3 SOFTWARE

Vishnu

SAMPLE INFORMATION

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Injection #:	1	Processing Method	ms0301
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Run Time:	80.0 Minutes	Proc. Chnl. Descr.:	PDA 254.0 nm
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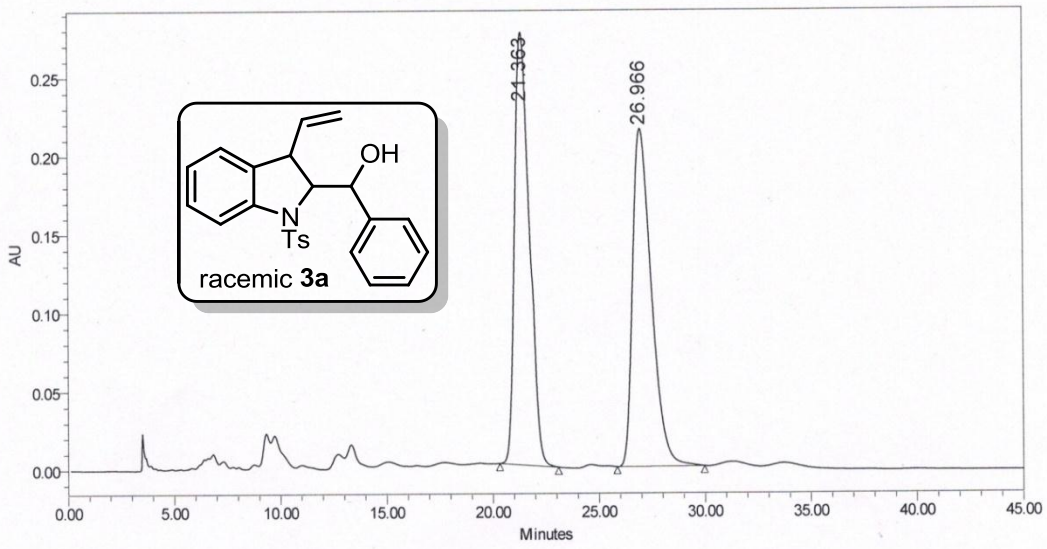
Date Processed:	05-02-2016 23:31:12 IST		



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Reported by User: System
Report Method: Vishnu
Report Method ID: 5245
Page: 1 of 1

Project Name: YR_01
Date Printed:
05-02-2016
23:34:59 Asia/Calcutta

Empower 3 SOFTWARE

Vishnu

SAMPLE INFORMATION

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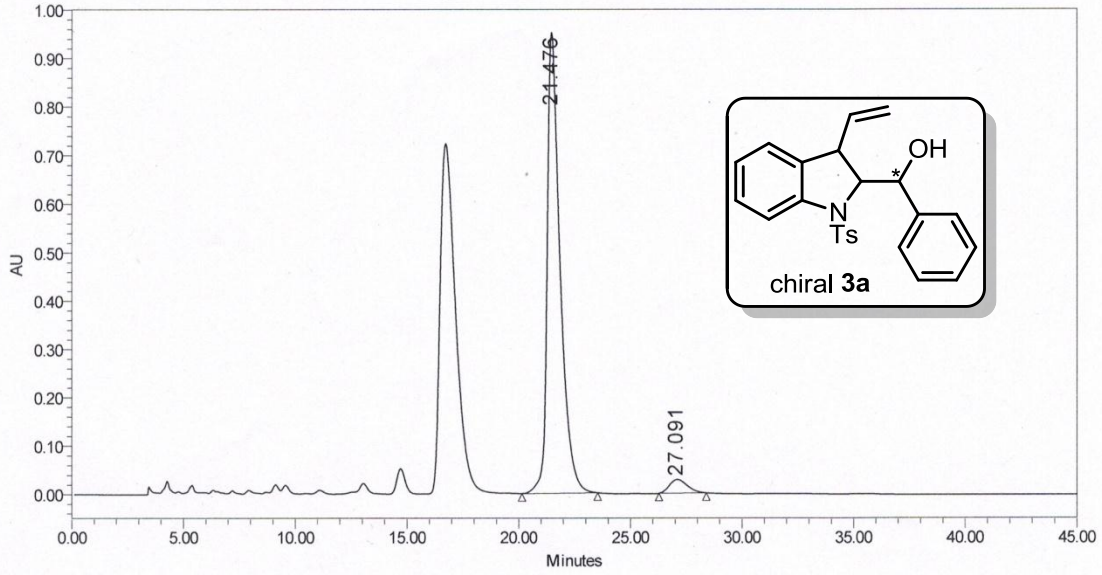

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Report Method ID: 5245
Page: 1 of 1

Project Name: YR_01
Date Printed:
05-02-2016
23:35:22 Asia/Calcutta

Analysis with CBA-2 (92% ee)

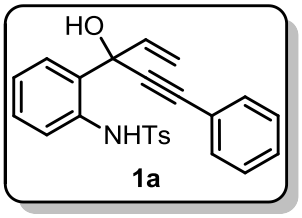
Procedure F: synthesis of cyclopenta[*b*]indole 6k-6r: A 5 mL glass vial was charged with 3-(2-aminophenyl)-pent-4-en-1-yn-3-ol **1'k** (0.1 mmol), AgOAc (2 mol%) in DCE solvent (1 mL) stirred at 60 ^{o}C. Upon disappearance of **1'k**, catalyst (10 mol%) [See, table-6] was introduced and continued stirring at 0^{o}C until intermediate **2'k** disappeared. On complete formation of **6a**, the reaction mixture was quenched by adding saturated aq. $NaHCO_3$ (1 mL) and extracted with EtOAc (2 x 2 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (10-20% EtOAc/hexane) to afford **6k**.

Procedure G: Synthesis of 11a and 11b: An oven dried 10 mL round bottom flask was charged with furo[3,4-*b*]indole **5a** (0.1 mmol), N-ethylmaleimide (0.15mmol) in toluene (1.5 mL) and stirred at 110 ^{o}C for 16 h. Upon disappearance of **5a** (monitored by TLC), the organic volatiles were removed under reduced pressure and crude residue was purified by silica gel column chromatography (10-20% EtOAc/hexane) to afford **11a** in 78% yield.

Procedure H: Synthesis of 9c: An oven dried 5 mL round bottom flask was charged with furo[3,4-*b*]indole **5c** (0.1 mmol), N-ethylmaleimide (0.15mmol) in toluene (1.5 ml) and stirred at 130 ^{o}C for 30 h. Upon disappearance of **5c** (monitored by TLC), the organic volatiles were removed under reduced pressure and crude residue was purified by silica gel column chromatography (10-20% EtOAc/hexane) to afford **9c** in 62% yield.

Spectroscopic data of all new compounds reported in this study

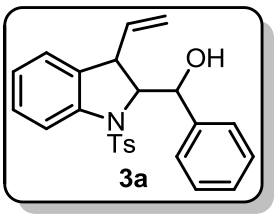
***N*-(2-(3-Hydroxy-5-phenylpent-1-en-4-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (1a).**



1a

This compound was isolated as pale yellow oil. Following the general procedure (Procedure A), 80 mg of **1a1** afforded 76 mg of **1a** (88% yield). R_f = 0.5 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3432, 3250, 2226, 1599, 1493, 1336, 1159, 1092, 757. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.97 (s, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.64-7.62 (m, 2H), 7.51-7.49 (m, 2H), 7.41-7.33 (m, 3H), 7.28-7.24 (m, 1H), 7.17 (dd, *J* = 8.9 and 2.8 Hz, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.02 (dd, *J* = 17.0 and 6.8 Hz, 1H),5.56 (d, *J* = 17.0 Hz, 1H), 5.20 (d, *J* = 10.2 Hz, 1H), 3.40 (s, 1H), 2.35 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.7, 139.0, 136.9, 136.1, 131.8(2C), 129.5(2C), 129.4, 129.2, 129.0, 128.4(2C), 128.3, 127.4(2C), 123.4, 121.8, 119.6, 115.7, 89.0, 87.9, 74.6, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{21}NO_3SNa$ $(M+Na)^+$: 426.1140. Found: 426.1115.

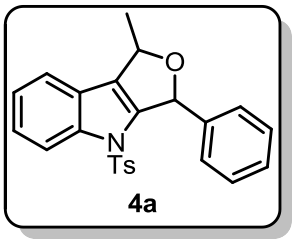
Phenyl(1-tosyl-3-vinylindolin-2-yl)methanol (3a).



3a

This compound was isolated as light brown oil. Following the general procedure (Procedure B), 50 mg of **1a** afforded 46 mg of **3a** (85% yield). R_f = 0.5 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3472, 3061, 2925, 1597, 1449, 1365, 1171, 1088, 748. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.11 (d, *J* = 8.0 Hz, 1H), 7.78-7.76 (m, 1H), 7.40-7.30 (m, 9H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.84 (dd, *J* = 17.8 and 11.5 Hz, 1H), 6.59 (d, *J* = 10.6 Hz, 1H), 5.77 (dd, *J* = 17.8 and 1.4 Hz, 1H), 5.56 (dd, *J* = 11.5 and 1.4 Hz, 1H), 4.45 (d, *J* = 10.6 Hz, 1H), 2.32 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 145.0, 142.0, 137.8, 136.6, 135.1, 129.6(2C), 128.4, 128.3(2C), 127.4, 127.1, 126.8(2C), 125.8(2C), 125.5, 124.0, 122.6, 120.5, 120.1, 115.0, 68.2, 21.6. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{21}NO_3SNa$ $(M+Na)^+$: 426.1140. Found: 426.1125.

1-Methyl-3-phenyl-4-tosyl-3,4-dihydro-1*H*-furo[3,4-*b*]indole (4a).

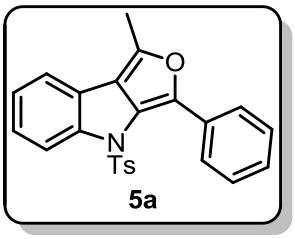


4a

This compound was isolated as light yellow oil. Following the general procedure (Procedure C), 40 mg of **1a** afforded 14 mg of **4a** (35% yield). R_f = 0.6 (Hexane/EtOAc = 4/1).

IR (thin film, neat): ν_{max}/cm^{-1} 3066, 2924, 2857, 1597, 1448, 1371, 1176, 1040, 758. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.97-8.01 (m, 2H), 7.29-7.40 (m, 7H), 7.07-7.12 (m, 2H), 6.99-7.03 (m, 2H), 6.35 (d, *J* = 2.8 Hz, 1H), 5.44-5.49 (m, 1H), 2.32 (s, 3H), 1.70 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.8, 140.8, 135.0, 129.6(2C), 129.0(2C), 128.6, 128.4(2C), 128.2, 128.1, 127.0(2C), 126.9, 124.4, 123.9, 123.6, 119.2, 114.6, 81.9, 75.7, 22.8, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{22}NO_3S$ $(M+H)^+$: 404.1320. Found: 404.1306.

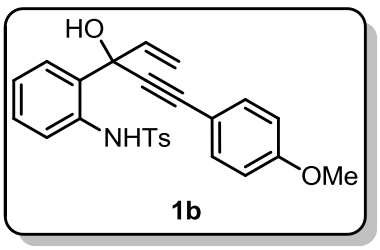
1-Methyl-3-phenyl-4-tosyl-4*H*-furo[3,4-*b*]indole (5a).



5a

This compound was isolated as light brown oil. Following the general procedure (Procedure D), 30 mg of **1a** afforded 15 mg of **5a** (50% yield). R_f = 0.8 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2928, 2850, 1740, 1375, 750. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.12 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 7.2 Hz, 2H), 7.50-7.33 (m, 6H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 2.53 (s, 3H), 2.27 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 145.9, 144.4, 140.3, 136.8, 132.3, 130.2, 129.0(2C), 128.5, 128.0(2C), 127.9, 127.8(2C), 127.4(2C), 126.6, 125.3, 124.3, 120.9, 120.3, 118.5, 21.6, 13.7. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{20}NO_3S$ $(M+H)^+$: 402.1163. Found: 402.1150.

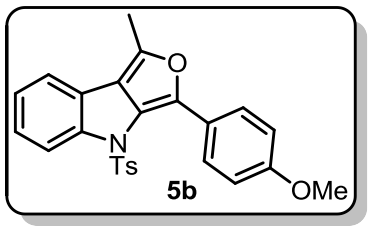
***N*-(2-(3-Hydroxy-5-(4-methoxyphenyl)pent-1-en-4-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (1b).**



1b

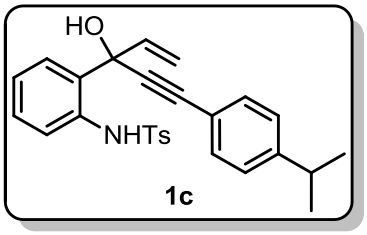
This compound was isolated as light brown oil. Following the general procedure (Procedure A), 80 mg of **1b1** afforded 77 mg of **1b** (97% yield). R_f = 0.1 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3441, 3252, 2932, 2225, 1742, 1605, 1510, 1251, 1160, 1091, 756. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.84 (s, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.64-7.59 (m, 2H), 7.44 (d, *J* = 9.1 Hz, 2H), 7.27-7.23 (m, 1H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.04 (td, *J* = 7.6 and 1.0 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 2H), 6.00 (dd, *J* = 17.0 and 10.1 Hz, 1H), 5.54 (d, *J* = 16.9 Hz, 1H), 5.20 (d, *J* = 10.2 Hz, 1H), 3.84 (s, 3H), 3.00 (s, 1H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.1, 143.6, 139.0, 137.0, 136.0, 133.3(2C), 129.5(2C), 129.3, 129.2, 128.1, 127.4(2C), 123.3, 119.6, 115.5, 114.0(2C), 113.6, 89.1, 86.5, 74.6, 55.3, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{23}NO_4SNa$ $(M+Na)^+$: 456.1245. Found: 456.1228.

3-(4-Methoxyphenyl)-1-methyl-4-tosyl-4*H*-furo[3,4-*b*]indole (5b).



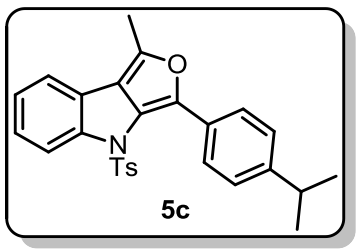
This compound was isolated as pale brown oil. Following the general procedure (Procedure D), 20 mg of **1b** afforded 11 mg of **5b** (54% yield). R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2924, 2855, 1669, 1599, 1371, 1258, 1176, 1090, 751. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.12 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.37-7.32 (m, 1H), 7.26 (d, *J* = 8.2 Hz, 3H), 7.03-6.99 (m, 4H), 3.90 (s, 3H), 2.51 (s, 3H), 2.27 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.3, 145.9, 144.3, 139.6, 136.7, 132.4, 129.4(2C), 129.0(2C), 127.8, 127.4(2C), 126.5, 125.3, 124.4, 123.0, 120.9, 120.1, 118.4, 113.3(2C), 55.3, 21.6, 13.6. **HRMS (ESI):** *m/z* calcd for $C_{25}H_{22}NO_4S$ $(M+H)^+$: 432.1270. Found: 432.1254.

***N*-(2-(3-Hydroxy-5-(4-isopropylphenyl)pent-1-en-4-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (1c).**



This compound was isolated as pale yellow oil. Following the general procedure (Procedure A), 70 mg of **1c1** afforded 63 mg of **1c** (84% yield). R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3446, 3243, 2962, 2928, 2225, 1672, 1495, 1336, 1160, 1092, 757. **^{1}H NMR (400 MHz, $CDCl_3$):**δ 8.85 (s, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.63 (d,*J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.27-7.21 (m, 3H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.06-7.01 (m, 1H), 6.01 (dd, *J* = 17.0 and 10.2 Hz, 1H), 5.55 (d, *J* = 17.0 Hz, 1H), 5.20 (d, *J* = 10.2 Hz, 1H), 3.01 (s, 1H), 2.97-2.90 (m, 1H), 2.36 (s, 3H), 1.27 (s, 3H), 1.26 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 150.2, 143.6, 138.9, 136.9, 136.0, 131.8(2C), 129.5(2C), 129.4, 129.1, 128.2, 127.4(2C), 126.5(2C), 123.3, 119.6, 118.9, 115.6, 89.3, 87.1, 74.6, 34.1, 23.8(2C), 21.5. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{27}NO_3SNa$ $(M+Na)^+$: 468.1609. Found: 468.1592.

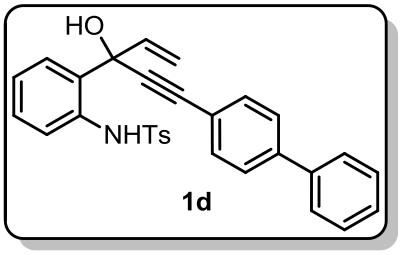
3-(4-Isopropylphenyl)-1-methyl-4-tosyl-4*H*-furo[3,4-*b*]indole (5c).



This compound was isolated as light brown oil. Following the general procedure (Procedure D), 30 mg of **1c** afforded 16 mg of **5c** (54% yield). R_f = 0.7 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2960, 2927, 1742, 1672, 1371, 1176, 1090, 752. **^{1}H**

NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.36-7.33 (m, 3H), 7.29-7.23 (m, 3H), 6.99 (d, *J* = 8.2 Hz, 2H), 3.03-2.94 (m, 1H), 2.51 (s, 3H), 2.27 (s, 3H), 1.33 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 148.5, 146.0, 144.3, 139.9, 137.1, 132.4, 129.0(2C), 128.1, 127.8(2C), 127.5(2C), 126.5, 125.9(2C), 125.3, 125.2, 124.4, 120.9, 120.2, 118.5, 34.0, 23.9(2C), 21.6, 13.7. **HRMS (ESI):** *m/z* calcd for $C_{27}H_{26}NO_3S$ $(M+H)^+$: 444.1633. Found: 444.1618.

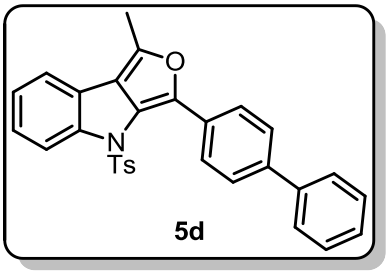
***N*-(2-(5-([1,1'-Biphenyl]-4-yl)-3-hydroxypent-1-en-4-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (1d).**



1d

This compound was isolated as light brown oil. Following the general procedure (Procedure A), 75 mg of **1d1** afforded 68 mg of **1d** (85% yield). R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3432, 3272, 2231, 1599, 1490, 1337, 1161, 1091, 764. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.95 (s, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.66-7.55 (m, 7H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.41-7.38 (m, 1H), 7.29-7.25 (m, 1H), 7.19 (d, *J* = 8.3Hz, 2H), 7.08-7.04 (m, 1H), 6.04 (dd, *J* = 17.0 and 10.2 Hz, 1H), 5.58 (d, *J* = 17.0 Hz, 1H), 5.22 (d, *J* = 10.2 Hz, 1H), 3.01 (s, 1H), 3.39 (d,*J* = 5.3 Hz, 1H), 2.35 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.6, 141.7, 140.1, 138.9, 136.9, 136.0, 132.2(2C), 129.5(2C), 129.4, 129.1, 128.9(2C), 128.2, 127.8, 127.4(2C), 127.0(4C), 123.4, 120.6, 119.5, 115.7, 88.8, 88.5, 74.6, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{30}H_{25}NO_3SNa$ $(M+Na)^+$: 259.0793. Found: 259.0778.

3-([1,1'-Biphenyl]-4-yl)-1-methyl-4-tosyl-4*H*-furo[3,4-*b*]indole (5d).

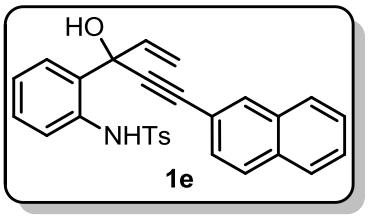


5d

This compound was isolated as colourless solid. Following the general procedure (Procedure D), 20 mg of **1d** afforded 11 mg of **5d** (57% yield). M. P. = 175-176 ^oC. R_f = 0.7 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2919, 2859, 1763, 1375, 1260, 750. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.13 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.75-7.70 (m, 4H), 7.51-7.47 (m, 2H), 7.44 (d, *J* = 7.3 Hz, 1H), 7.40-7.34 (m, 2H), 7.30-7.28 (m, 3H), 7.01 (d, *J* = 8.2 Hz, 2H), 2.55 (s, 3H), 2.28 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 146.0, 144.4, 140.9, 140.4, 140.3, 136.8, 132.3, 129.2, 129.1(2C), 128.8(2C), 128.7, 128.1(2C), 127.5(2C),

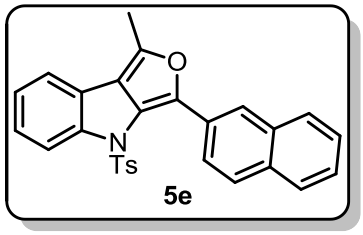
127.3, 127.1(2C), 126.6, 126.5(2C), 125.4, 124.4, 121.0, 120.5, 118.6, 21.6, 13.7. **HRMS (ESI):** *m/z* calcd for $C_{30}H_{24}NO_3S$ $(M+H)^+$: 478.1476. Found: 478.1459.

***N*-(2-(3-Hydroxy-5-(naphthalen-2-yl)pent-1-en-4-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (1e).**



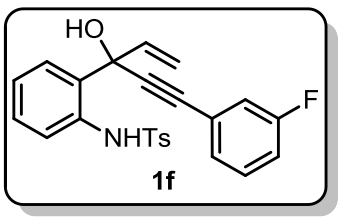
This compound was isolated as light brown oil. Following the general procedure (Procedure A), 60 mg of **1e1** afforded 60 mg of **1e** (94% yield). R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3430, 3244, 2923, 2231, 1598, 1497, 1337, 1159, 1091, 757. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.98 (s, 1H), 8.02 (s, 1H), 7.86-7.78 (m, 5H), 7.68 (dd, *J* = 7.9 and 1.4 Hz, 1H), 7.65 (dd, *J* = 8.2 and 0.8 Hz, 1H), 7.54-7.51 (m, 3H), 7.30-7.28 (m, 1H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.09-7.05 (m, 1H),6.06 (dd, *J* = 17.0 and 10.2 Hz, 1H),5.60 (d, *J* = 17.0 Hz, 1H), 5.24 (d, *J* = 10.2 Hz, 1H), 3.40 (s, 1H), 2.31 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.7, 139.0, 137.0, 136.1, 133.1, 132.8, 132.0, 129.5(2C), 129.4, 129.2, 128.3, 128.2, 128.1, 127.86, 127.83, 127.47(2C), 127.1, 126.8, 123.4, 119.6, 119.0, 115.8, 89.3, 88.2, 74.7, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{28}H_{23}NO_3SNa$ $(M+Na)^+$: 476.1296. Found: 476.1278.

1-Methyl-3-(naphthalen-2-yl)-4-tosyl-4*H*-furo[3,4-*b*]indole (5e).



This compound was isolated as pale yellow solid. Following the general procedure (Procedure D), 20 mg of **1e** afforded 11 mg of **5e** (54% yield). M. P. = 139-140^{o}C. R_f = 0.7 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2927, 1740, 1601, 1370, 1176, 796, 755. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.31 (s, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 8.02 (dd, *J* = 8.6 and 1.6 Hz, 1H), 7.98-7.92 (m, 2H), 7.53-7.50 (m, 2H), 7.46-7.44 (m, 1H), 7.40-7.35 (m, 2H), 7.30-7.28 (m, 1H), 7.24 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.1 Hz, 2H), 2.57 (s, 3H), 2.26 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 146.1, 144.4, 140.6, 137.1, 133.1, 133.0, 132.3, 129.0(2C), 128.3, 127.9, 127.8, 127.7, 127.5(2C), 127.1, 126.3, 126.12(2C), 126.07, 125.4, 125.2, 124.5, 121.0, 120.6, 118.7, 21.6, 13.8. **HRMS (ESI):** *m/z* calcd for $C_{28}H_{22}NO_3S$ $(M+H)^+$: 452.1320. Found: 452.1304.

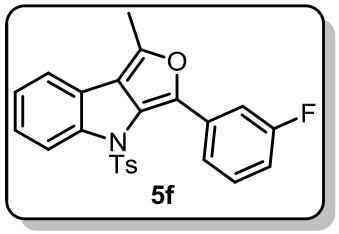
***N*-(2-(5-(3-Fluorophenyl)-3-hydroxypent-1-en-4-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (1f).**



1f

This compound was isolated as pale yellow oil. Following the general procedure (Procedure A), 60 mg of **1f1** afforded 61 mg of **1f** (95% yield). R_f = 0.5 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3434, 3235, 3070, 2927, 1709, 1582, 1494, 1373, 1159, 1091, 751. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.85 (s, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.62-7.57 (m, 2H), 7.33-7.24 (m, 3H), 7.20-7.16 (m, 3H), 7.12-7.03 (m, 2H), 6.02 (dd, *J* = 17.0 and 10.2 Hz, 1H), 5.55 (d, *J* = 16.9 Hz, 1H), 5.23 (d, *J* = 10.2 Hz, 1H), 3.22 (s, 1H), 2.36 (s, 3H). **^{19}F NMR (400 MHz, $CDCl_3$):** δ–112.47. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.2 (d, *J* = 245.7 Hz, 1C), 143.7, 138.6, 137.0, 136.0, 130.0 (d, *J* = 8.1 Hz, 1C), 129.5(2C), 128.8, 128.1, 127.8, 127.6, 127.4(2C), 123.5 (d, *J* = 9.5 Hz, 1C), 123.4, 119.7, 118.6 (d, *J* = 22.6 Hz, 1C), 116.4, 115.9, 88.7, 87.6 (d, *J* = 3.7 Hz, 1C), 74.5, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{20}FNO_3SNa$ $(M+Na)^+$: 444.1045. Found: 444.1028.

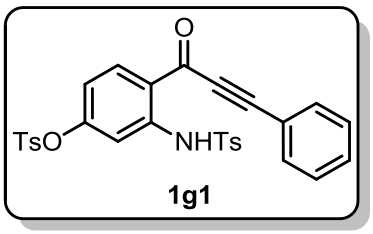
3-(3-Fluorophenyl)-1-methyl-4-tosyl-4*H*-furo[3,4-*b*]indole (5f).



5f

This compound was isolated as pale yellow oil. Following the general procedure (Procedure D), 20 mg of **1f** afforded 11 mg of **5f** (56% yield). R_f = 0.8 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3057, 2941, 1595, 1490, 1159, 756.**^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.12 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.55 (dt, *J* = 10.1 and 1.7 Hz, 1H), 7.46-7.40 (m, 2H), 7.38-7.34 (m, 1H), 7.29 (s, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.06 (dt, *J* = 8.5 and 2.5 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 2H), 2.53 (s, 3H), 2.28 (s, 3H). **^{19}F NMR (400 MHz, $CDCl_3$):** δ–113.90. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.3 (d, *J* = 242.8 Hz, 1C), 145.9, 144.5, 140.7, 135.7, 135.5, 132.2, 132.1 (d, *J* = 8.8 Hz, 1C), 129.1 (d, *J* = 8.2 Hz, 1C), 129.0(2C), 127.4(2C), 126.6, 125.4, 124.2, 123.6, 120.9, 120.5, 118.6, 114.5 (d, *J* = 10.1 Hz, 1C), 114.4 (d, *J* = 12.0 Hz, 1C), 21.5, 13.6. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{19}FNO_3S$ $(M+H)^+$: 420.1069. Found: 420.1055.

3-(4-Methylphenylsulfonamido)-4-(3-phenylpropioloyl)phenyl 4-methylbenzenesulfonate (1g1).

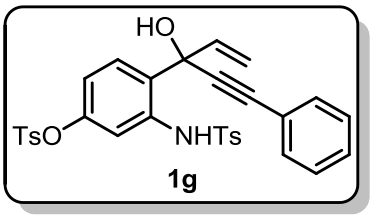


1g1

This compound was isolated as pale yellow solid. M. P. = 150-151 ^oC. R_f = 0.2 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2923, 2194, 1621, 1597,

1491, 1377, 1165, 1090, 795. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 11.16 (s, 1H), 7.94 (d, *J* = 2.8 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.69-7.63 (m, 6H), 7.58-7.55 (m, 1H), 7.50-7.47 (m, 2H), 7.29- 7.27 (m, 3H), 7.10 (dd, *J* = 9.1 and 2.8 Hz, 1H), 2.40 (s, 3H), 2.33 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 179.2, 146.0, 144.5, 144.0, 139.6, 136.1, 133.4(2C), 131.7, 131.6, 129.94(2C), 129.90(2C), 129.8, 128.9(2C), 128.6(2C), 128.0, 127.3(2C), 122.8, 119.6, 119.1, 96.4, 86.0, 21.64, 21.61. **HRMS (ESI):** *m/z* calcd for $C_{29}H_{23}NO_6S_2Na$ $(M+Na)^+$: 568.0864. Found: 568.0844.

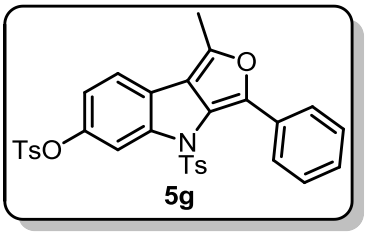
4-(3-Hydroxy-5-phenylpent-1-en-4-yn-3-yl)-3-(4-methylphenylsulfonamido)phenyl4-methylbenzenesulfonate (1g).



1g

This compound was isolated as light brown oil. Following the general procedure (Procedure A), 70 mg of **1g1** afforded 66 mg of **1g** (90% yield). R_f = 0.1 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3437, 3244, 2931, 2231, 1596, 1492, 1374, 1164, 1091, 757. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.88 (s, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 9.0 Hz, 1H), 7.46-7.35 (m, 5H), 7.22-7.20 (m, 4H), 7.18 (s, 1H), 6.87 (dd, *J* = 8.9 and 2.8 Hz, 1H), 5.84 (dd, *J* = 16.9 and 10.1 Hz, 1H),5.44 (d, *J* = 17.0 Hz, 1H), 5.15 (d, *J* = 10.2 Hz, 1H), 3.39 (s, 1H), 2.37 (s, 3H), 2.36 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 145.5, 144.8, 144.0, 138.2, 136.6, 135.0, 132.0, 131.8(2C), 130.6, 129.7(2C), 129.6(2C), 129.3, 128.54(2C), 128.48(2C), 127.4(2C), 123.2, 122.6, 121.4, 120.4, 116.2, 89.3, 86.9, 74.1, 21.7, 21.6. **HRMS (ESI):** *m/z* calcd for $C_{31}H_{27}NO_6S_2Na$ $(M+Na)^+$: 596.1177. Found: 596.1154.

1-Methyl-3-phenyl-4-tosyl-4*H*-furo[3,4-*b*]indol-6-yl 4-methylbenzenesulfonate (5g).

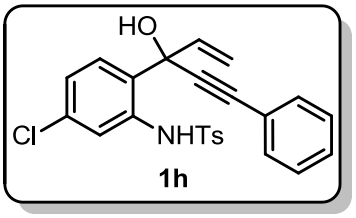


5g

This compound was isolated as pale yellow solid. Following the general procedure (Procedure D), 20 mg of **3g** afforded 10 mg of **5g** (53% yield). M. P. = 152-153^{o}C. R_f= 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2924, 2856, 1673, 1596, 1373, 1178, 763. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.96 (d, *J* = 9.0 Hz, 1H), 7.83-7.81 (m, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.50-7.46 (m, 2H), 7.40-7.36 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 2.4 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.75 (dd, *J* = 9.0 and 2.4 Hz, 1H), 2.50 (s, 3H), 2.48 (s, 3H), 2.31 (s, 3H). **^{13}C NMR**

(100 MHz, $CDCl_3$): δ 147.0, 145.7, 144.8, 144.3, 141.1, 137.1, 132.0(2C), 129.9, 129.8(2C), 129.2(2C), 128.7, 128.6(2C), 128.1, 127.9(2C), 127.8(2C), 127.3(2C), 125.6, 120.2, 119.5, 119.0, 115.4, 21.8, 21.6, 13.7. **HRMS (ESI):** *m/z* calcd for $C_{31}H_{26}NO_6S_2$ $(M+H)^+$: 572.1202. Found: 572.1180.

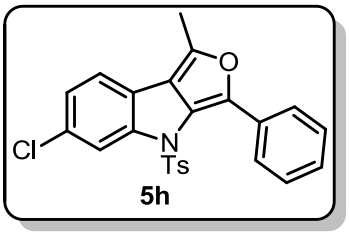
***N*-(5-Chloro-2-(3-hydroxy-5-phenylpent-1-en-4-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (1h).**



1h

This compound was isolated as pale yellow oil. Following the general procedure (Procedure A), 60 mg of **1h1** afforded 54 mg of **1h** (85% yield). R_f = 0.4 (Hexane/EtOAc = 4/1).**IR (thin film, neat):** ν_{max}/cm^{-1} 3441, 3272, 2199, 1599, 1491, 1336, 1159, 1091, 757. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.92 (s, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 2.0 Hz, 1H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.50-7.48 (m, 2H), 7.41-7.37 (m, 3H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.00 (dd, *J* = 8.4 and 2.0 Hz, 1H), 5.99 (dd, *J* = 17.0 and 10.2 Hz, 1H),5.55 (d, *J* = 17.0 Hz, 1H), 5.23 (d, *J* = 10.2 Hz, 1H), 3.15 (s, 1H), 2.38 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.0, 138.6, 137.2, 136.5, 135.3, 131.8(2C), 129.7(2C), 129.3, 129.2, 128.5(2C), 127.5(2C), 127.4, 123.2, 121.5, 119.3, 116.2, 89.3, 87.4, 74.3, 21.6. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{20}ClNO_3SNa$ $(M+Na)^+$: 460.0750. Found: 259.0730.

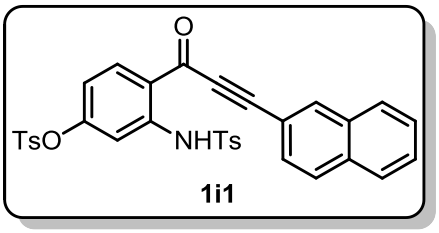
6-Chloro-1-methyl-3-phenyl-4-tosyl-4*H*-furo[3,4-*b*]indole (5h).



5h

This compound was isolated as light brown oil. Following the general procedure (Procedure D), 20 mg of **1h** afforded 11 mg of **5h** (54% yield). R_f = 0.7 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3056, 2939, 1595, 1491, 1160, 757. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.15 (d, *J* = 1.8 Hz, 1H), 7.82 (d, *J* = 7.2 Hz, 2H), 7.50-7.47 (m, 2H), 7.41-7.37 (m, 1H), 7.34 (d, *J* = 8.2 Hz, 1H) 7.27 (d, *J* = 8.4 Hz, 2H), 7.24 (dd, *J* = 8.2 and 1.8 Hz, 1H), 7.04 (d,*J* = 8.0 Hz, 2H), 2.51 (s, 3H), 2.30 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 146.6, 144.7, 140.5, 136.8, 132.23, 132.19, 130.0, 129.3(2C), 128.09(2C), 128.08, 127.8(2C), 127.45, 127.4(2C), 125.6, 122.8, 121.4, 119.4, 118.7, 21.6, 13.7. **HRMS (ESI):** *m/z* calcd for $C_{24}H_{19}ClNO_3S$ $(M+H)^+$: 436.0774. Found: 436.0774.

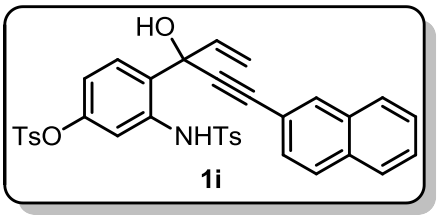
3-(4-Methylphenylsulfonamido)-4-(3-(naphthalen -2-yl)propioloyl)phenyl 4-methylbenz- enesulfonate (1i1).



1i1

This compound was isolated as pale yellow solid. M. P. = 145-146 ^{o}C. R_f = 0.2 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3061, 2924, 2190, 1698, 1619, 1489, 1377, 1176, 1090, 795. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 11.20 (s, 1H), 8.23 (s, 1H), 8.02 (s, 1H), 7.94-7.92 (m, 3H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.72-7.60 (m, 7H), 7.28 (t, *J* = 9.1 Hz, 3H), 7.13-7.11 (m, 1H), 2.40 (s, 3H), 2.26 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 179.11, 146.0, 144.5, 144.0, 139.6, 136.1, 135.2, 134.3, 132.6, 131.7, 129.93(2C), 129.90(2C), 129.7, 128.8, 128.6, 128.57(2C), 128.4, 128.2, 128.0, 127.96, 127.4, 127.3(2C), 123.0, 119.7, 116.2, 97.0, 86.4, 21.59(2C). **HRMS (ESI):** *m/z* calcd for $C_{33}H_{26}NO_6S_2$ $(M+H)^+$: 596.1202. Found: 596.1178.

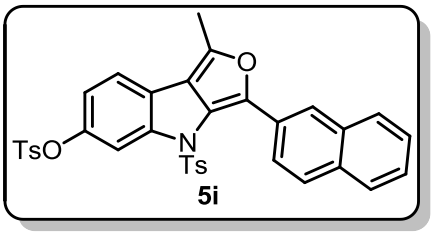
4-(3-Hydroxy-5-(naphthalen-2-yl)pent-1-en-4-yn-3-yl)-3-(4-methylphenylsulfonamido)phenyl 4-methylbenzenesulfonate (1i).



1i

This compound was isolated as pale yellow oil. Following the general procedure (Procedure A), 70 mg of **1i1** afforded 67 mg of **1i** (92% yield). R_f= 0.2 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3449, 3233, 2923, 2231, 1598, 1491, 1376, 1163, 795. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.87 (s, 1H), 7.99 (s, 1H), 7.88-7.83 (m, 3H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.57-7.54 (m, 3H), 7.48 (dd, *J* = 8.5 and 1.5 Hz, 1H), 7.28 (s, 1H), 7.19 (t, *J* = 8.6 Hz, 4H),6.89 (dd, *J* = 9.0 and 2.8 Hz, 1H), 5.88 (dd, *J* = 17.0 and 10.2 Hz, 1H), 5.50 (d, *J* = 17.0 Hz, 1H), 5.19 (d, *J* = 10.2 Hz, 1H), 3.24 (s, 1H), 2.34 (s, 3H), 2.31 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 145.5, 144.9, 144.0, 138.2, 136.6, 135.0, 133.2, 132.8, 132.1, 132.0, 130.5, 129.7(2C), 129.6(2C), 128.5(2C), 128.2, 128.0, 127.89, 127.86, 127.4(2C), 127.3, 126.9, 123.2, 122.6, 120.4, 118.6, 116.3, 89.8, 87.1, 74.2, 21.6, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{35}H_{29}NO_6S_2Na$ $(M+Na)^+$: 646.1334. Found: 646.1308.

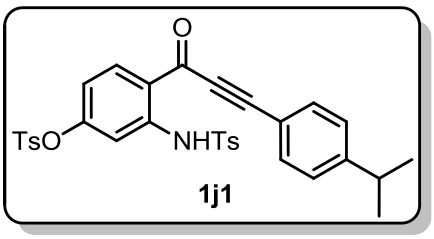
1-Methyl-3-(naphthalen-2-yl)-4-tosyl-4*H*-furo[3,4-*b*]indol-6-yl 4-methylbenzenesulfonate (5i).



5i

This compound was isolated as pale yellow solid. M. P. = 178-179 ^{o}C. Following the general procedure (Procedure D), 30 mg of **3i** afforded 15 mg of **5i** (51% yield). R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2927, 2856, 1673, 1596, 1373, 1179, 756. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.29 (s. 1H), 8.00-7.94 (m, 4H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.54-7.51 (m, 2H), 7.36 (d, *J* = 8.2 Hz, 3H), 7.19-7.17 (m, 3H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.76 (dd, *J* = 8.9 and 2.4 Hz, 1H), 2.52 (s, 3H), 2.51 (s, 3H), 2.30 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 147.1, 145.7, 144.8, 144.4, 141.4, 137.3, 133.0, 132.0, 131.9, 129.8(2C), 129.1(2C), 128.7(2C), 128.6, 128.3, 127.9, 127.8, 127.4(2C), 127.3, 127.2, 126.5, 126.24, 126.23, 126.0, 125.7, 120.3, 119.7, 119.2, 115.5, 21.8, 21.6, 13.8. **HRMS (ESI):** *m/z* calcd for $C_{35}H_{28}NO_6S_2$ $(M+H)^+$: 622.1358. Found: 622.1332.

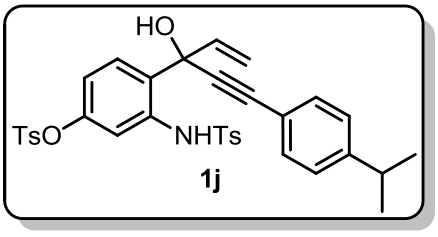
4-(3-(4-Isopropylphenyl)propioloyl)-3-(4-methylphenylsulfonamido)phenyl 4-methylbenzenesulfonate (1j1).



1j1

This compound was isolated as pale yellow oil. R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2964, 2923, 2190, 1620, 1599, 1490, 1377, 1151, 1091, 795. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 11.21 (s, 1H), 7.91 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.69-7.65 (m, 4H), 7.55 (d, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 3H), 7.26-7.24 (m, 2H), 7.13-7.09 (m, 1H), 3.02-2.95 (m, 1H), 2.37 (s, 3H), 2.28 (s, 3H), 1.29 (d, *J* = 7.2 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 179.3, 153.4, 146.0, 144.4, 143.9, 139.5, 136.2, 133.7(2C), 131.6, 129.94(2C), 129.87(2C), 129.6, 128.6(2C), 127.9, 127.3(2C), 127.1(2C), 123.0, 119.6, 116.3, 97.3, 86.0, 34.4, 23.7(2C), 21.62, 21.59. **HRMS (ESI):** *m/z* calcd for $C_{32}H_{30}NO_6S_2$ $(M+H)^+$: 588.1515. Found: 588.1485.

4-(3-Hydroxy-5-(4-isopropylphenyl)pent-1-en-4-yn-3-yl)-3-(4-methylphenylsulfonamido)phenyl 4-methylbenzenesulfonate (1j).

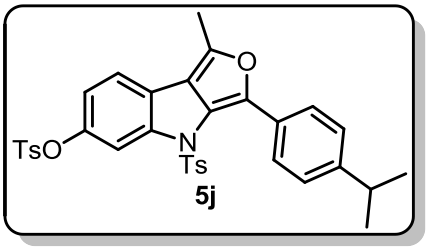


1j

This compound was isolated as light brown oil. Following the general procedure (Procedure A), 70 mg of **1j1** afforded 62 mg of **1j** (84% yield). R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film,**

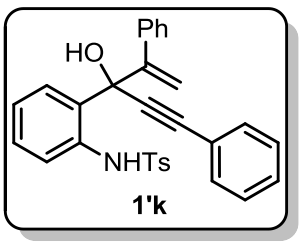
neat): ν_{max}/cm^{-1} 3449, 3251, 2961, 2227, 1598, 1493, 1375, 1164, 1091, 758. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.83 (s, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.9 Hz, 2H), 7.53 (d, *J* = 8.9 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.25-7.18 (m, 7H), 6.87 (dd, *J* = 9.0 and 2.8 Hz, 1H), 5.83(dd, *J* = 17.0 and 10.1 Hz, 1H),5.44 (d, *J* = 17.0 Hz, 1H), 5.15 (d, *J* = 10.2 Hz, 1H), 3.11 (s, 1H), 2.99-2.92 (m, 1H), 2.38 (s, 3H), 2.36 (s, 3H), 1.28 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 150.5, 145.5, 144.8, 143.9, 138.2, 136.6, 134.9, 132.0, 131.9(2C), 130.6, 129.7(2C), 129.6(2C), 128.5(2C), 127.4(2C), 126.6(2C), 123.2, 122.5, 120.0, 118.6, 116.1, 89.7, 86.1, 74.2, 34.2, 23.8(2C), 21.64, 21.55. **HRMS (ESI):** *m/z* calcd for $C_{34}H_{33}NO_6S_2Na$ $(M+Na)^+$: 638.1647. Found: 638.1620.

3-(4-Isopropylphenyl)-1-methyl-4-tosyl-4*H*-furo[3,4-*b*]indol-6-yl 4-methylbenzenesulfonate (5j).



This compound was isolated as light brown oil. Following the general procedure (Procedure D), 20 mg of **1j** afforded 11 mg of **5j** (56% yield). R_f = 0.2 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2960, 2926, 1597, 1463, 1375, 1179, 1091, 788. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.94 (d, *J* = 9.0 Hz, 1H), 7.73 (dd, *J* = 16.1 and 8.3 Hz, 4H), 7.36-7.33 (m, 4H), 7.21(d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 2.4 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.74 (dd, *J* = 9.0 and 2.5 Hz, 1H), 3.03-2.96 (m, 1H), 2.50 (s, 3H), 2.46 (s, 3H), 2.31 (s, 3H), 1.33 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 148.8, 147.0, 145.7, 144.7, 144.3, 140.8, 137.4, 132.04, 132.02, 129.79, 129.77(2C), 129.1(2C), 128.7(2C), 127.8(2C), 127.43(2C), 127.39, 126.0(2C), 125.7, 120.1, 119.4, 119.0, 115.4, 34.0, 24.0(2C), 21.8, 21.6, 13.7. **HRMS (ESI):** *m/z* calcd for $C_{34}H_{32}NO_6S_2$ $(M+H)^+$: 614.1671. Found: 614.1646.

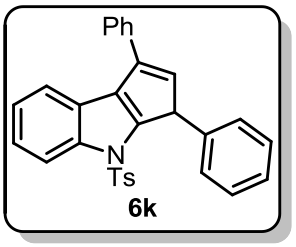
***N*-(2-(3-Hydroxy-2,5-diphenylpent-1-en-4-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (1'k).**



This compound was isolated as pale yellow oil. Following the general procedure (Procedure A), 70 mg of **1a1** afforded 79 mg of **1'k** (88% yield). R_f= 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3431, 3271, 3059, 2199, 1599, 1492, 1337, 1159, 1091, 757. **^{1}H NMR (400 MHz,**

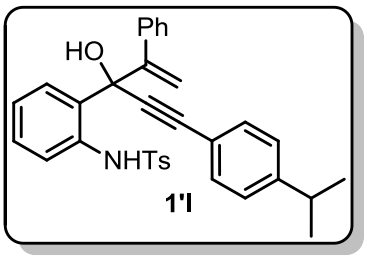
$CDCl_3$): δ 8.81 (s, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.65-7.60 (m, 2H), 7.47-7.45 (m, 2H), 7.40-7.34 (m, 4H), 7.28-7.22 (m, 4H), 7.18 (s, 1H), 7.11(d, *J* = 7.2Hz, 2H), 6.98-6.94 (m, 1H), 5.54 (s,1H), 5.26 (s,1H), 3.32 (s, 1H), 2.35 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 149.6, 143.7, 138.4, 137.1, 136.2, 133.1, 131.7(2C), 129.8, 129.6, 129.5(2C), 129.1(2C), 128.5(2C), 128.3, 127.7, 127.68(2C), 127.6(2C), 122.9, 121.8, 119.2, 116.6, 89.6, 88.9, 76.7, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{30}H_{25}NO_3SNa$ $(M+Na)^+$: 502.1453. Found: 502.1433.

1,3-Diphenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indole (6k).



This compound was isolated as light brown oil. Following the general procedure (Procedure F), 30 mg of **1'k** afforded 23 mg of **6k** (78% yield). R_f = 0.8 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3058, 2923, 2854, 1597, 1493, 1448, 1374, 1175, 1089, 750. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.08 (d, *J* = 8.3 Hz, 1H), 7.74-7.71 (m, 3H), 7.51-7.41 (m, 5H), 7.32-7.29 (m, 3H), 7.21-7.17 (m, 4H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.36 (d, *J* = 1.6 Hz, 1H), 5.09 (d, *J* = 1.4 Hz, 1H), 2.31 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 150.0, 144.6, 140.0, 139.7, 136.2, 135.7, 135.3, 134.0, 129.6(2C), 129.0, 128.8(2C), 128.68, 128.62(2C), 128.5, 128.0, 127.4(2C), 127.03(2C), 127.0, 124.2, 123.8, 123.3, 120.4, 114.6, 52.5, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{30}H_{24}NO_2S$ $(M+H)^+$: 462.1528. Found: 462.1511.

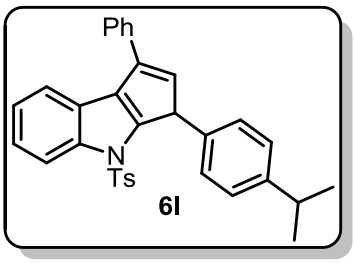
***N*-(2-(3-Hydroxy-5-(4-isopropylphenyl)-2-phenylpent-1-en-4-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (1'l).**



This compound was isolated as pale yellow oil. Following the general procedure (Procedure A), 80 mg of **1c1** afforded 91 mg of **1'l** (91% yield). R_f = 0.5 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3441, 3266, 2959, 2924, 2226, 1600, 1493, 1338, 1160, 1092, 758. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.77 (s, 1H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.65-7.60 (m, 2H), 7.40-7.38 (m, 2H), 7.28-7.24 (m, 3H), 7.22-7.18 (m, 5H), 7.13-7.10 (m, 2H), 6.95(dt, *J* = 7.7 and 1.2 Hz, 1H), 5.50 (s,1H), 5.24 (s,1H), 3.13 (d, *J* = 3.6 Hz, 1H), 2.97-2.90 (m, 1H), 2.35 (s, 3H), 1.28 (s, 3H), 1.26 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 150.3, 149.7, 143.7, 138.4, 137.1, 136.2, 131.7(2C), 129.8, 129.52, 129.50(2C), 129.1(2C), 128.4, 127.7, 127.68(2C),

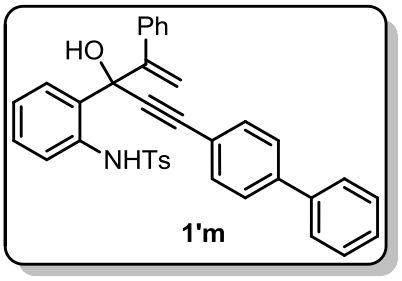
127.6(2C), 126.6(2C), 122.9, 119.2, 119.0, 116.5, 89.9, 88.1, 82.6, 34.1, 23.8(2C), 21.5. **HRMS (ESI):** *m/z* calcd for $C_{33}H_{31}NO_3SNa$ $(M+Na)^+$: 544.1922. Found: 544.1904.

3-(4-Isopropylphenyl)-1-phenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indole (6l).



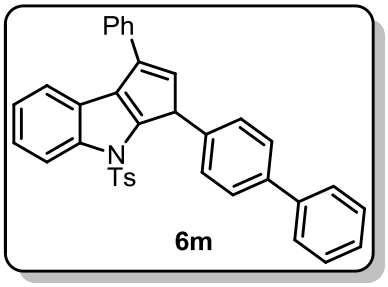
This compound was isolated as light brown oil. Following the general procedure (Procedure F), 30 mg of **1'l** afforded 25 mg of **6l** (88% yield). R_f = 0.9 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3459, 2970, 1740, 1369, 1217, 1160, 756. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.07(d, *J* = 8.3 Hz, 1H), 7.75-7.71 (m, 3H), 7.50-7.49 (m, 2H), 7.42-7.30 (m, 3H), 7.20-7.14(m, 6H), 7.01(d, *J* = 8.2 Hz, 2H),6.36 (d, *J* = 1.9 Hz, 1H), 5.08 (d, *J* = 1.9 Hz, 1H), 2.99-2.92 (m, 1H), 2.30 (s, 3H), 1.32 (s, 3H), 1.30 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 150.1, 147.7, 144.5, 139.7, 139.6, 135.7, 135.4, 134.2, 133.2, 129.5(2C), 128.7(2C), 128.6(2C), 128.3, 127.9, 127.4(2C), 127.1(2C), 126.6(2C), 124.2, 123.6, 123.2, 120.3, 114.5, 52.2, 33.8, 24.2(2C), 21.5. **HRMS (ESI):** *m/z* calcd for $C_{33}H_{30}NO_2S$ $(M+H)^+$: 504.1997. Found: 504.1977.

***N*-(2-(5-([1,1'-Biphenyl]-4-yl)-3-hydroxy-2-phenylpent-1-en-4-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (1'm).**



This compound was isolated as pale yellow oil. Following the general procedure (Procedure A), 70 mg of **1d1** afforded 76 mg of **1'm** (88% yield). R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3429, 3293, 3062, 2925, 2198, 1708, 1599, 1491, 1337, 1160, 1091, 764. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.80 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.66-7.59 (m, 7H), 7.54-7.47 (m, 4H), 7.42-7.39 (m, 1H), 7.26-7.19 (m, 5H), 7.13 (d, *J* = 7.2 Hz, 2H), 6.98 (t, *J* = 7.6 Hz, 1H), 5.54 (s, 1H), 5.28 (s, 1H), 3.23 (s, 1H), 2.36 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 149.6, 143.7, 141.9, 140.1,138.3, 137.1, 136.2, 132.1(2C), 129.8, 129.6, 129.5(2C), 129.1(2C), 128.9(2C), 128.3, 127.9, 127.8, 127.7(2C), 127.6(2C), 127.13(2C), 127.06(2C), 123.0, 120.6, 119.2, 116.7, 89.53, 89.46, 76.6, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{36}H_{29}NO_3SNa$ $(M+Na)^+$: 578.1766. Found: 578.1743.

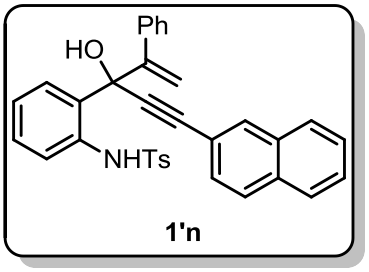
3-([1,1'-Biphenyl]-4-yl)-1-phenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indole (6m).



6m

This compound was isolated as light brown oil. Following the general procedure (Procedure F), 30 mg of **1'm** afforded 20 mg of **6m** (68% yield). R_f = 0.8 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3059, 3029, 2924, 1598, 1486, 1449, 1372, 1174, 1009, 755. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.14 (d, *J* = 8.2 Hz, 1H), 7.77-7.75 (m, 3H), 7.64-7.62 (m, 2H), 7.53-7.47 (m, 7H), 7.43-7.36 (m, 4H), 7.25-7.23 (m, 3H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.40 (d, *J* = 2.0 Hz, 1H), 5.15 (d, *J* = 1.9 Hz, 1H), 2.24 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 149.9, 144.5, 140.8, 140.1, 140.0, 139.8, 135.6, 135.5, 135.2, 133.8, 129.5(2C), 129.2(2C), 128.9(2C), 128.7(2C), 128.5, 128.0, 127.4(2C), 127.3, 127.2(2C), 127.0(2C), 126.9(2C), 124.2, 123.8, 123.4, 120.4, 114.6, 52.1, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{36}H_{28}NO_2S$ $(M+H)^+$: 538.1841. Found: 538.1819.

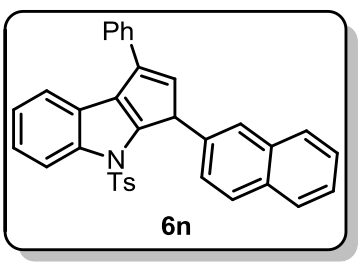
***N*-(2-(3-Hydroxy-5-(naphthalen-2-yl)-2-phenylpent-1-en-4-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (1'n).**



1'n

This compound was isolated as pale yellow oil. Following the general procedure (Procedure A), 70 mg of **1e1** afforded 80 mg of **1'n** (92% yield). R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3437, 3291, 3058, 2925, 2229, 1598, 1583, 1493, 1337, 1160, 1091, 815, 749. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.82 (s, 1H), 7.99 (s, 1H), 7.87-7.82 (m, 5H), 7.67-7.65 (m, 2H), 7.55-7.53 (m, 2H), 7.49 (dd, *J* = 8.5 and 1.2 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 2H), 7.22-7.14 (m, 6H), 7.01-6.97 (m, 1H), 5.57 (s, 1H), 5.30 (s, 1H), 3.26 (s, 1H), 2.33 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 149.6, 143.7, 138.3, 137.1, 136.2, 133.1, 132.8, 131.9, 129.8, 129.6, 129.5(2C), 129.1(2C), 128.3, 128.2, 128.0, 127.78(2C), 127.82, 127.7(2C), 127.6(2C), 127.1, 126.8, 123.0, 119.2, 119.0, 116.8, 90.0, 89.1, 76.8, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{34}H_{27}NO_3SNa$ $(M+Na)^+$: 552.1609. Found: 552.1593.

3-(Naphthalen-2-yl)-1-phenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indole (6n).

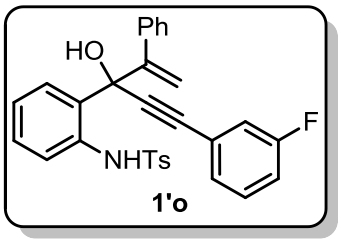


6n

This compound was isolated as light brown oil. Following the general procedure (Procedure F), 30 mg of **1'n** afforded 20 mg of **6n** (69% yield). R_f = 0.8 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1}

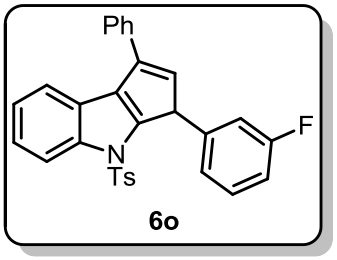
3054, 2924, 1735, 1598, 1448, 1372, 1175, 913, 747. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.16 (d, *J* = 8.2 Hz, 1H), 7.79-7.71 (m, 6H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.52-7.47 (m, 5H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.10-7.02 (m, 4H), 6.62 (d, *J* = 8.1 Hz, 2H), 6.40 (d, *J* = 2.0 Hz, 1H), 5.25 (d, *J* = 1.9 Hz, 1H), 2.15 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 150.0, 144.3, 140.1, 140.0, 135.4, 133.8, 133.7, 133.4, 132.8, 129.3(2C), 129.0, 128.7(2C), 128.5, 128.1, 128.0, 127.8, 127.7, 127.5, 127.4(2C), 126.6(2C), 126.4, 126.0, 125.7, 124.1, 123.8, 123.3, 120.4, 114.6, 52.5, 21.4. **HRMS (ESI):** *m/z* calcd for $C_{34}H_{26}NO_2S$ $(M+H)^+$: 512.1684. Found: 512.1663.

***N*-(2-(5-(3-Fluorophenyl)-3-hydroxy-2-phenylpent-1-en-4-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (1'o).**



This compound was isolated as pale yellow oil. Following the general procedure (Procedure A), 70 mg of **1f1** afforded 78 mg of **1'o** (88% yield). R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3432, 3281, 3066, 2928, 2203, 1737, 1582, 1492, 1338, 1159, 757. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.74 (s, 1H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.64 (dd, *J* = 8.2 and 1.0 Hz, 1H), 7.57 (dd, *J* = 7.8 and 1.4 Hz, 1H), 7.36-7.30 (m, 2H), 7.26-7.19 (m, 6H), 7.15-7.08 (m, 4H), 6.97(dt, *J* = 7.7 and 1.1 Hz, 1H), 5.53 (s,1H), 5.28 (s,1H), 3.20(s, 1H), 2.35 (s, 3H). **^{19}F NMR (400 MHz, $CDCl_3$):** δ–112.36. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.3 (d, *J* = 245.5 Hz, 1C), 149.4, 143.8, 138.2, 137.1, 136.2, 130.1 (d, *J* = 8.5 Hz, 1C), 129.7(2C), 129.6(2C), 129.1(2C), 128.4, 128.1, 127.84, 127.76(2C), 127.61, 127.57(2C), 123.5 (d, *J* = 7.4 Hz, 1C), 123.0, 119.4, 118.5 (d, *J* = 22.7 Hz, 1C), 116.9, 116.5 (d, *J* = 20.9 Hz, 1C), 89.7, 88.2, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{30}H_{24}FNO_3SNa$ $(M+Na)^+$: 520.1358. Found: 520.1337.

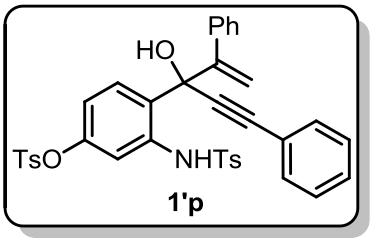
3-(3-Fluorophenyl)-1-phenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indole (6o).



This compound was isolated as light brown oil. Following the general procedure (Procedure F), 30 mg of **1'o** afforded 17 mg of **6o** (60% yield). R_f = 0.8 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3062, 2955, 2925, 1613, 1596, 1487, 1373, 1175, 793, 758. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.13 (d, *J* = 8.3 Hz, 1H), 7.74-7.72 (m, 3H), 7.52-7.48 (m, 3H), 7.44-7.34 (m, 4H), 7.27-7.26 (m, 1H),

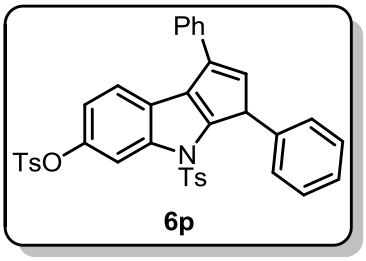
7.08-7.05 (m, 3H), 7.00-6.96 (m, 1H), 6.79-6.76 (m, 1H), 6.33 (d, *J* = 2.0 Hz, 1H), 5.08 (d, *J* = 1.8 Hz, 1H), 2.33 (s, 3H). **^{19}F NMR (400 MHz, $CDCl_3$):** δ–113.2. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.9 (d, *J* = 244.5 Hz, 1C), 149.1, 144.8, 140.3, 139.9, 138.9 (d, *J* = 7.3 Hz, 1C), 135.4 (d, *J* = 5.8 Hz, 1C), 133.3, 130.0 (d, *J* = 8.3 Hz, 1C), 129.6(2C), 129.0 (d, *J* = 6.4 Hz, 1C), 128.8, 128.7(2C), 128.1, 127.4(2C), 127.0, 126.8(2C), 124.7, 124.1 (d, *J* = 9.8 Hz, 1C), 123.5, 120.5, 115.1 (d, *J* = 21.6 Hz, 1C), 114.7, 113.9 (d, *J* = 21.1 Hz, 1C), 52.1, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{30}H_{23}FNO_2S$ $(M+H)^+$: 480.1433. Found: 480.1415.

4-(3-Hydroxy-2,5-diphenylpent-1-en-4-yn-3-yl)-3-(4-methylphenylsulfonamido)phenyl 4-methylbenzenesulfonate(1'p).



This compound was isolated as pale yellow oil. Following the general procedure (Procedure A), 70 mg of **1g1** afforded 73 mg of **1'p** (87% yield). R_f = 0.1 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3445, 3291, 3056, 2923, 2229, 1734, 1598, 1492, 1375, 1338, 1195, 1091, 914, 758. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.74 (s, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 3H), 7.43-7.38 (m, 6H), 7.25-7.19 (m, 5H), 7.13-7.07 (m, 4H), 6.83 (dd, *J* = 9.0and 2.8 Hz, 1H), 5.46 (s,1H), 5.24 (s,1H), 3.32 (s, 1H), 2.36 (s, 3H), 2.30 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 149.0, 145.3, 144.6, 144.1, 137.9, 136.7, 135.0, 132.0, 131.7(2C), 129.8, 129.7(2C), 129.6(2C), 129.3, 129.0(2C), 128.5(2C), 128.4(2C), 127.9, 127.8(2C), 127.5(2C), 123.8, 123.4,121.4, 119.9, 117.0, 90.0, 87.9, 76.1, 21.6, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{37}H_{31}NO_6S_2Na$ $(M+Na)^+$: 672.1490. Found: 672.1462.

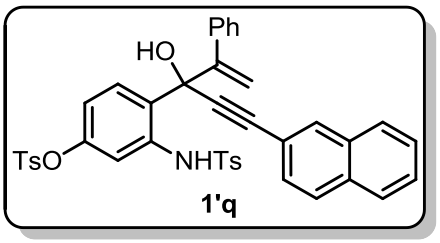
1,3-Diphenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indol-6-yl 4-methylbenzenesulfonate (6p).



This compound was isolated as light brown oil. Following the general procedure (Procedure F), 30 mg of **1'p** afforded 22 mg of **6p** (74% yield). R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3062, 2925, 1735, 1597, 1493, 1448, 1373, 1192, 1178, 1091, 909, 735. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.99 (d, *J* = 9.1 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.52-7.50 (m, 2H), 7.42-7.40 (m, 3H), 7.33-7.29 (m, 4H), 7.22-7.17 (m, 4H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.03-7.00 (m, 3H), 6.34 (d, *J* = 1.9 Hz, 1H),

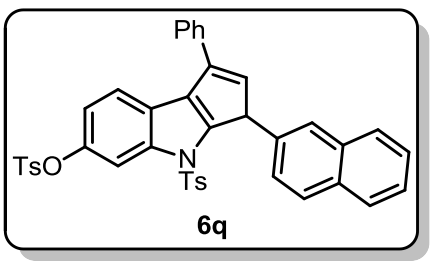
5.07 (d, *J* = 1.9 Hz, 1H), 2.46 (s, 3H), 2.33 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 151.6, 145.7, 145.4, 145.0, 139.4, 137.7, 135.6, 135.1, 135.0, 134.0, 132.3, 129.8, 129.7(2C), 128.8(2C), 128.73(2C), 128.71(2C), 128.7(2C), 128.6, 128.5, 128.1, 128.0, 127.6, 127.2, 127.1(2C), 124.4, 118.2, 115.1, 114.0, 52.5, 21.8, 21.6. **HRMS (ESI):** *m/z* calcd for $C_{37}H_{30}NO_5S_2$ $(M+H)^+$: 632.1565. Found: 632.1575.

4-(3-Hydroxy-5-(naphthalen-2-yl)-2-phenylpent-1-en-4-yn-3-yl)-3-(4-methylphenylsulfonamido)phenyl 4-methylbenzenesulfonate (1'q).



This compound was isolated as pale yellow oil. Following the general procedure (Procedure A), 70 mg of **1i1** afforded 74 mg of **1'q** (90% yield). R_f = 0.1 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3437, 3273, 3062, 2926, 2194, 1735, 1597, 1493, 1374, 1194, 1091, 913, 748. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.74 (s, 1H), 7.95 (s, 1H), 7.86-7.84 (m, 3H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.58-7.56 (m, 1H), 7.55-7.52 (m, 4H), 7.44 (dd, *J* = 8.4 and 1.5 Hz, 1H), 7.36 (d, *J* = 2.8 Hz, 1H),7.25-7.18 (m, 5H), 7.14-7.09 (m, 4H), 6.85 (dd, *J* = 8.9 and 2.8 Hz, 1H), 5.50 (s,1H), 5.28 (s,1H), 3.28 (s, 1H), 2.35 (s, 3H), 2.22 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 149.1, 145.3, 144.7, 144.1, 137.9, 136.7, 135.0, 133.2, 132.8, 132.1, 132.0, 129.9, 129.7, 129.66(2C), 129.6(2C), 129.0(2C), 128.6, 128.4(2C), 128.3, 128.0, 127.9(2C), 127.89, 127.87, 127.5(2C), 127.3, 126.9, 123.8, 123.4, 120.0, 118.5, 117.1, 90.4, 88.1, 31.0, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{41}H_{33}NO_6S_2Na$ $(M+Na)^+$: 722.1647. Found: 722.1617.

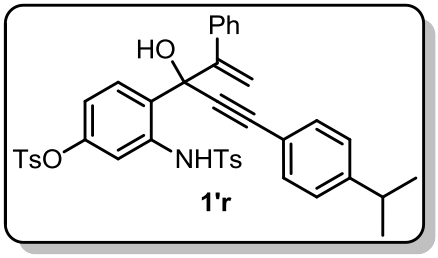
3-(Naphthalen-2-yl)-1-phenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indol-6-yl 4-methylbenzenesulfonate (6q).



This compound was isolated as light brown oil. Following the general procedure (Procedure F), 30 mg of **1'q** afforded 19 mg of **6q** (65% yield). R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3059, 2925, 2852, 1597, 1448, 1373, 1192, 1177, 1092, 745. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.05 (d, *J* = 9.1 Hz, 1H), 7.84-7.82 (m, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.69 (s, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.56-7.49 (m, 5H), 7.43-7.42 (m, 3H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.06-7.00 (m, 3H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.60 (d, *J* = 8.2

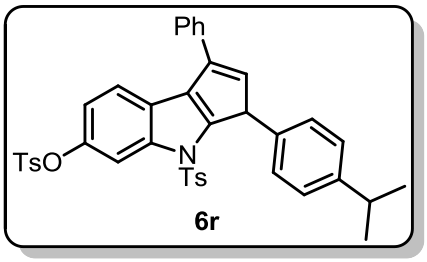
Hz, 2H), 6.37 (d, *J* = 1.5 Hz, 1H), 5.22 (d, *J* = 1.3 Hz, 1H), 2.47 (s, 3H), 2.15 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 151.6, 145.7, 145.4, 144.7, 139.6, 138.1, 135.09, 135.07, 133.82, 133.67, 132.81, 132.79, 132.3, 129.8(2C), 129.3(2C), 128.73(2C), 128.66(2C), 128.6, 128.2, 128.1, 128.0, 127.9, 127.5, 127.1(2C), 126.6(2C), 126.3, 126.2, 125.9, 124.3, 118.2, 115.2, 114.0, 52.5, 21.8, 21.4. **HRMS (ESI):** *m/z* calcd for $C_{41}H_{32}NO_5S_2$ $(M+H)^+$: 682.1722. Found: 682.1693.

4-(3-Hydroxy-5-(4-isopropylphenyl)-2-phenylpent-1-en-4-yn-3-yl)-3-(4-methylphenylsulfonamido)phenyl 4-methylbenzenesulfonate (1'r).



This compound was isolated as pale yellow oil. Following the general procedure (Procedure A), 70 mg of **1j1** afforded 70 mg of **1'r** (85% yield). R_f = 0.2 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3451, 3276, 2961, 2923, 2227, 1598, 1493, 1376, 1165, 1091, 793. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.73 (s, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 4H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.25-7.18 (m, 7H), 7.13-7.08 (m, 4H), 6.82 (dd, *J* = 8.9 and 2.8 Hz, 1H), 5.44 (s, 1H), 5.23 (s, 1H), 3.24 (s, 1H), 2.99-2.92 (m, 1H), 2.36 (s, 3H), 2.30 (s, 3H), 1.29 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 150.5, 149.1, 145.3, 144.6, 144.0, 138.0, 136.7, 135.0, 132.0, 131.8(2C), 130.0, 129.7(2C), 129.6(2C), 129.0(2C), 128.4(2C), 127.9, 127.87(2C), 127.5(2C), 126.7(2C), 123.8, 123.3, 119.9, 118.6, 116.9, 90.3, 87.2, 76.1, 34.2, 23.8(2C), 21.6, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{40}H_{37}NO_6S_2Na$ $(M+Na)^+$: 714.1960. Found: 714.1930.

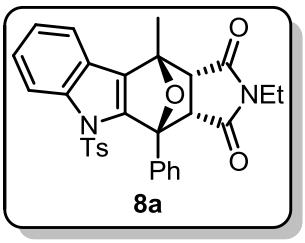
3-(4-Isopropylphenyl)-1-phenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indol-6-yl 4-methylbenzenesulfonate (6r).



This compound was isolated as light brown oil. Following the general procedure (Procedure F), 30 mg of **1'r** afforded 24 mg of **6r** (83% yield). R_f= 0.5 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2960, 2929, 1738, 1597, 1448, 1374, 1192, 1178, 1094, 741. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.96 (d, *J* = 9.0 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.52-7.49 (m, 2H), 7.42-7.40 (m, 3H), 7.32-7.30 (m, 2H), 7.20-7.14 (m, 3H), 7.10(d, *J* = 7.4 Hz, 4H), 7.02-6.98 (m, 3H), 6.33 (d, *J* = 1.9 Hz, 1H), 5.05(d, *J* = 1.9 Hz, 1H), 2.99-2.92

(m, 1H), 2.45 (s, 3H), 2.32 (s, 3H), 1.32 (s, 3H), 1.30 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 151.7, 147.9, 145.6, 145.3, 144.9, 139.2, 137.7, 135.2, 135.0, 134.2, 132.7, 132.3, 129.8, 129.7(2C), 129.6(2C), 128.8(2C), 128.72, 128.67(2C), 128.0, 127.8, 127.2(2C), 127.1(2C), 126.7(2C), 124.4, 118.1, 115.1, 113.9, 52.2, 33.8, 24.2(2C), 21.8, 21.6. **HRMS (ESI):** *m/z* calcd for $C_{40}H_{36}NO_5S_2$ $(M+H)^+$: 674.2038. Found: 674.2008.

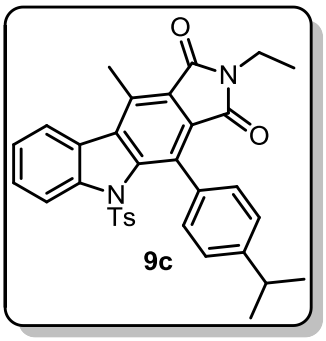
2-Ethyl-10-methyl-4-phenyl-5-tosyl-3a,4,10,10a-tetrahydro-4,10-epoxypyrrolo[3,4-*b*]carbazole-1,3(2*H*,5*H*)-dione (8a).



8a

This compound was isolated as colourless solid. M. P. = 160-161^{o}C. Following the general procedure (Procedure G), 20 mg of **5a** afforded 20 mg of **8a** (78% yield). R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2916, 1769, 1701, 1385, 1351, 1180, 1091, 795, 669. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.09-8.03 (m, 3H), 7.58-7.52 (m, 4H), 7.36-7.30 (m, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 4.15 (d, *J* = 7.6 Hz, 1H), 3.58 (d, *J* = 7.5 Hz, 1H), 2.90 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 2.23 (s, 3H), 0.17 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.9, 171.1, 144.1, 144.0, 140.0, 135.1, 133.8, 132.0, 128.5(2C), 128.0(2C), 126.8(2C), 125.9(2C), 124.3, 123.1, 121.8, 119.0, 114.4, 91.7, 84.4, 54.43, 54.41, 32.3, 28.7, 20.5, 17.7, 10.4. **HRMS (ESI):** *m/z* calcd for $C_{30}H_{26}N_2O_5SNa$ $(M+Na)^+$: 549.1460. Found: 549.1440.

2-Ethyl-4-(4-isopropylphenyl)-10-methyl-5-tosylpyrrolo[3,4-*b*]carbazole-1,3(2*H*,5*H*)-dione (9c).

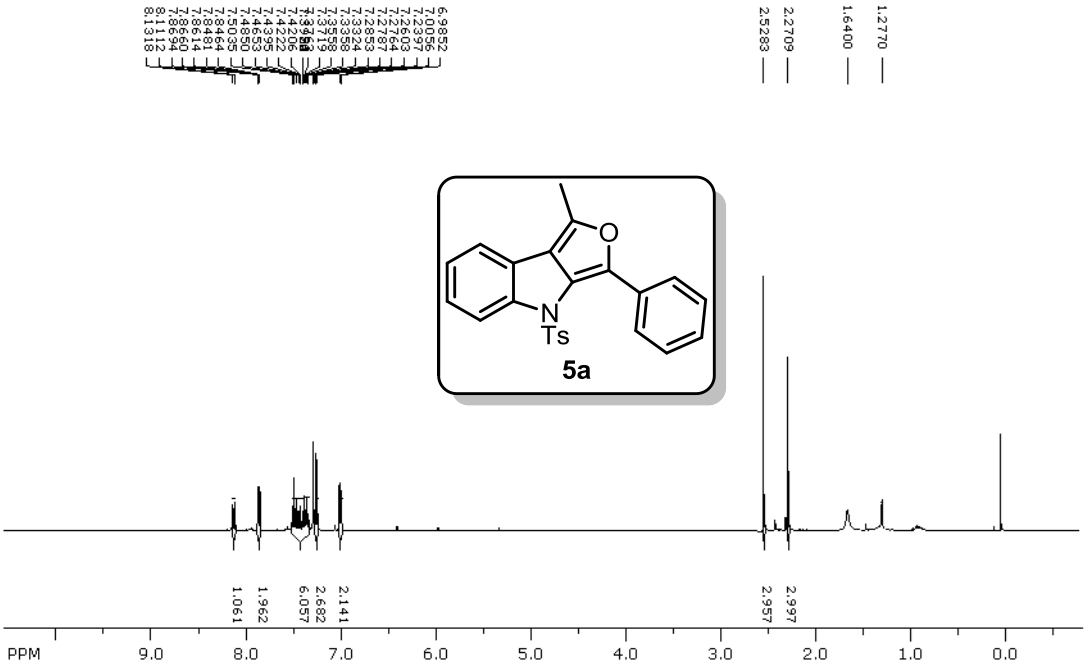


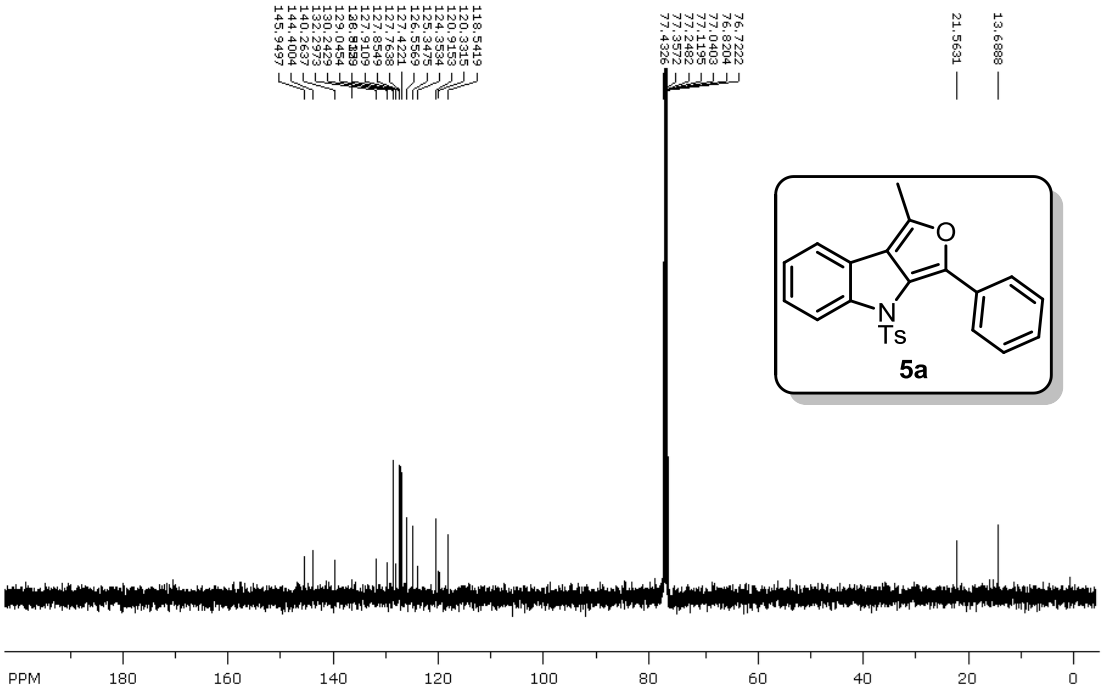
9c

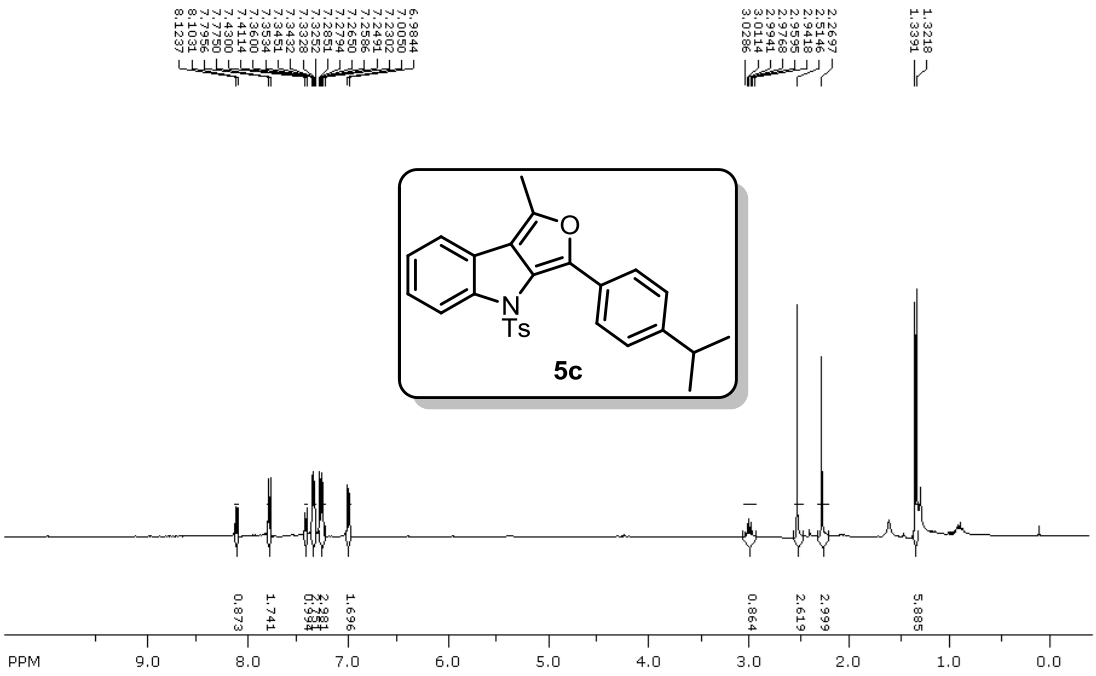
This compound was isolated as colourless solid. Following the general procedure (Procedure H), 40 mg of **5c** afforded 31 mg of **9c** (62% yield). M. P. = 228-229 ^{o}C. R_f = 0.6 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2961, 2870, 1762, 1704, 1450, 1400, 1362, 1176, 1093, 1051, 734. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.19 (d, *J* = 8.2 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.58-7.54 (m, 1H), 7.47-7.44 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 3.71 (q, *J* = 7.1 Hz, 2H), 3.17 (s, 3H), 2.99 (hep, *J* = 6.7 Hz, 1H), 2.30 (s, 3H), 1.35 (d, *J* = 6.9 Hz, 6H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 168.7, 166.9, 148.4, 144.2, 142.9, 142.8, 134.6, 134.0, 132.5, 131.7,

131.4, 130.6(2C), 129.0(2C), 128.4, 128.1, 127.6, 126.8, 126.2(2C), 125.5, 125.2(2C), 123.2, 119.1, 33.8, 32.8, 23.9(2C), 21.5, 14.8, 13.9. **HRMS (ESI):** *m/z* calcd for $C_{33}H_{30}N_2O_4SNa$ $(M+Na)^+$: 573.1824. Found: 573.1811.

NMR Spectra



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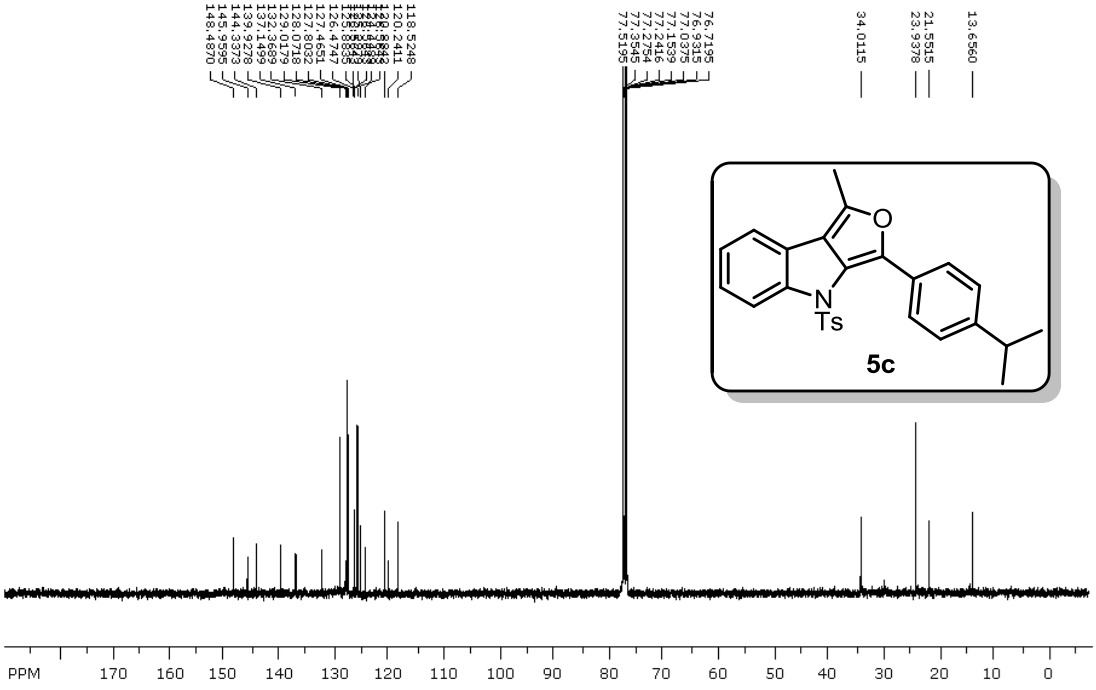
PPM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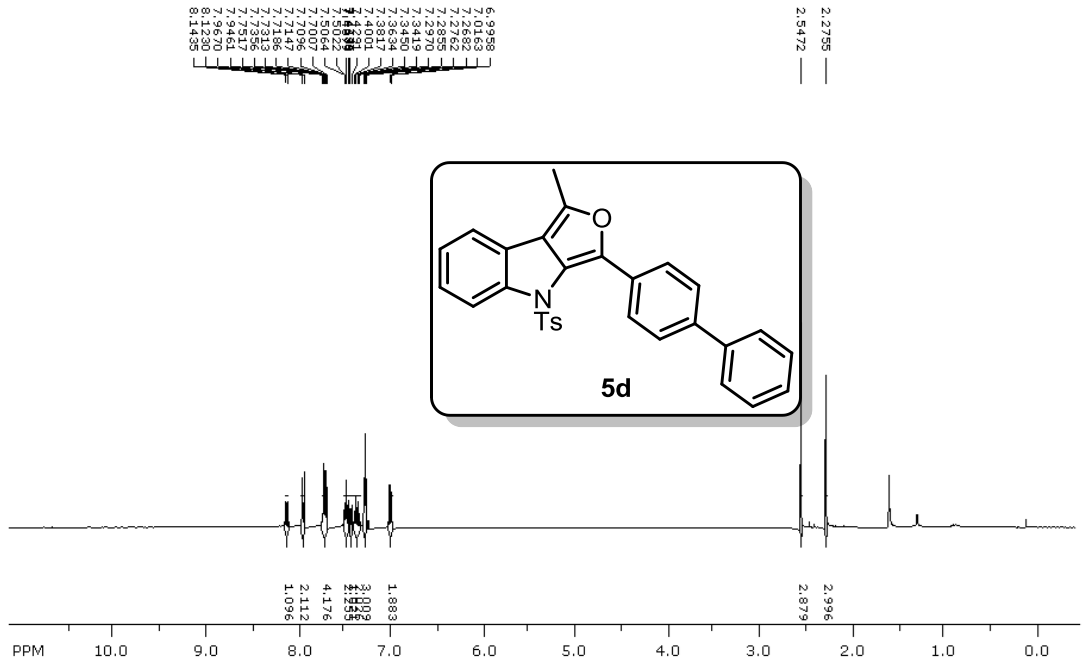
PPM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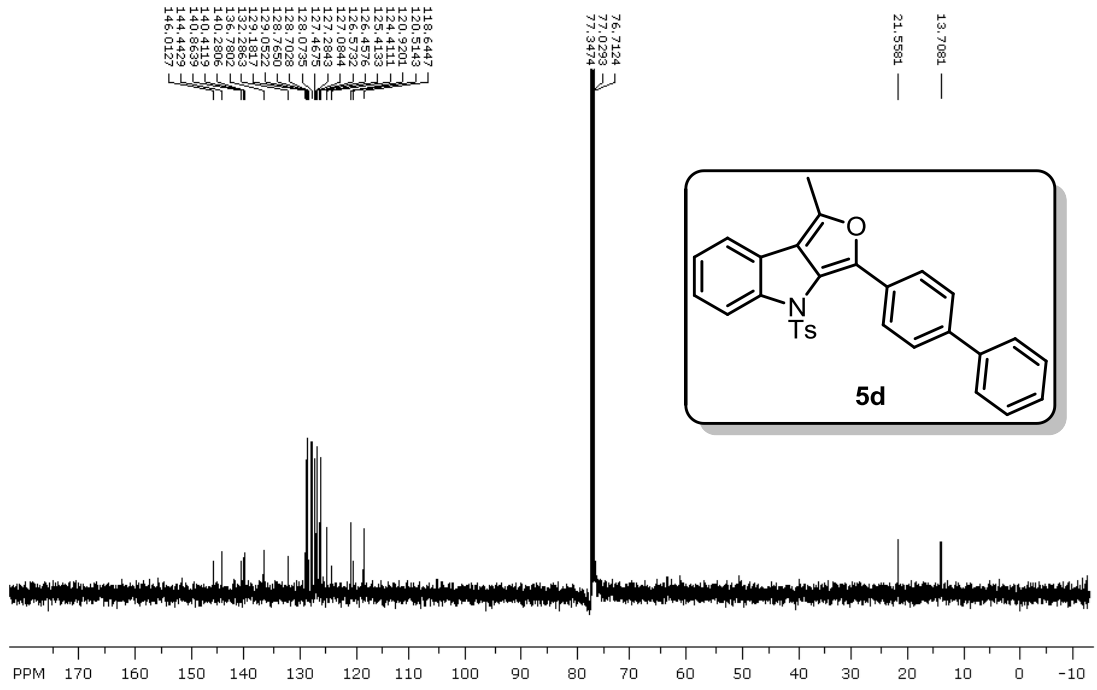
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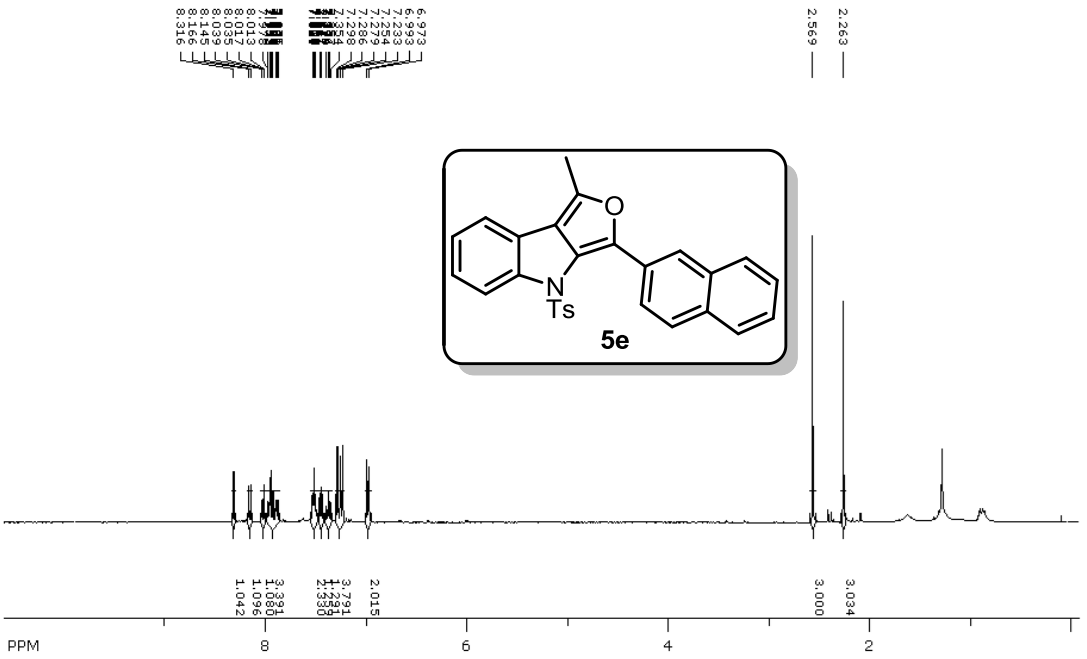
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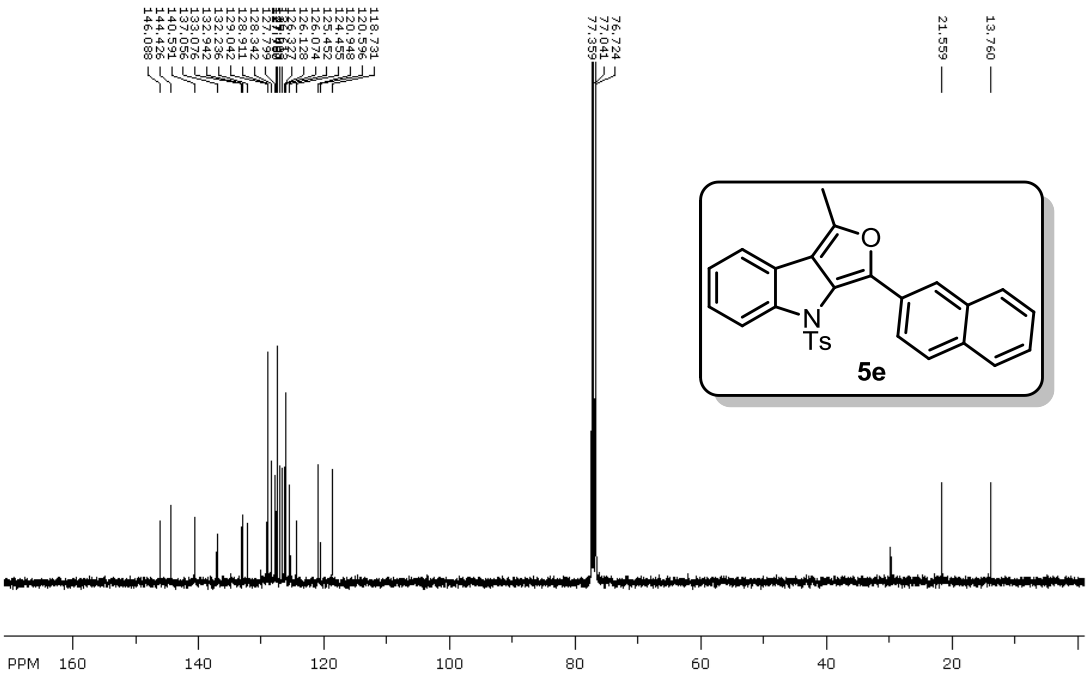
5e
PPM
8
6
4
2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PPM
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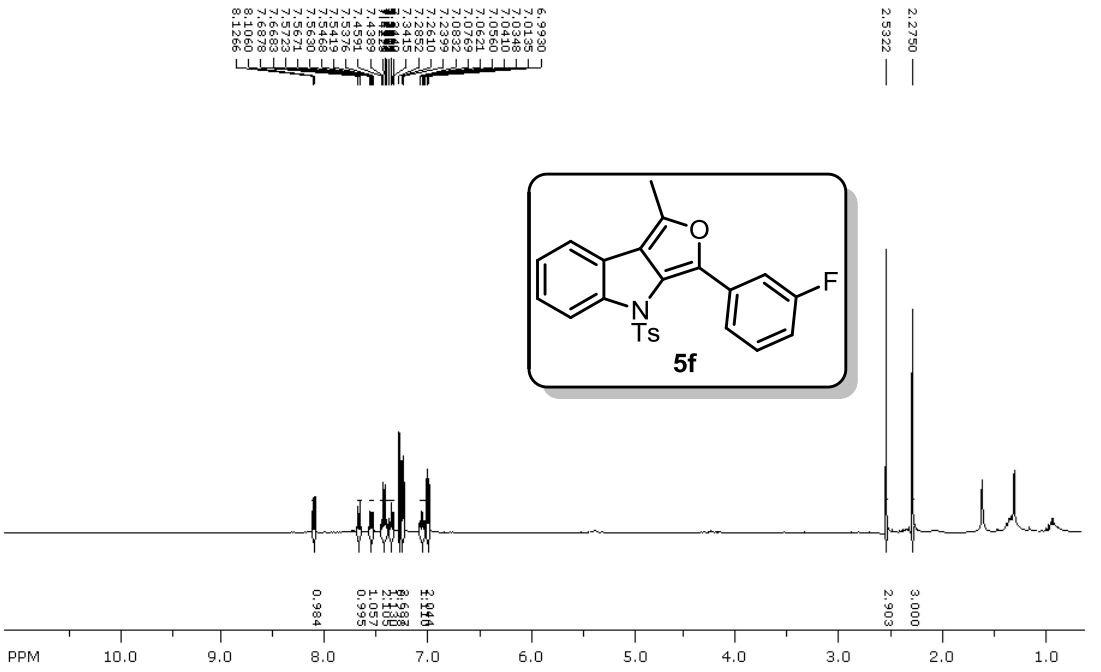
80
60
40
20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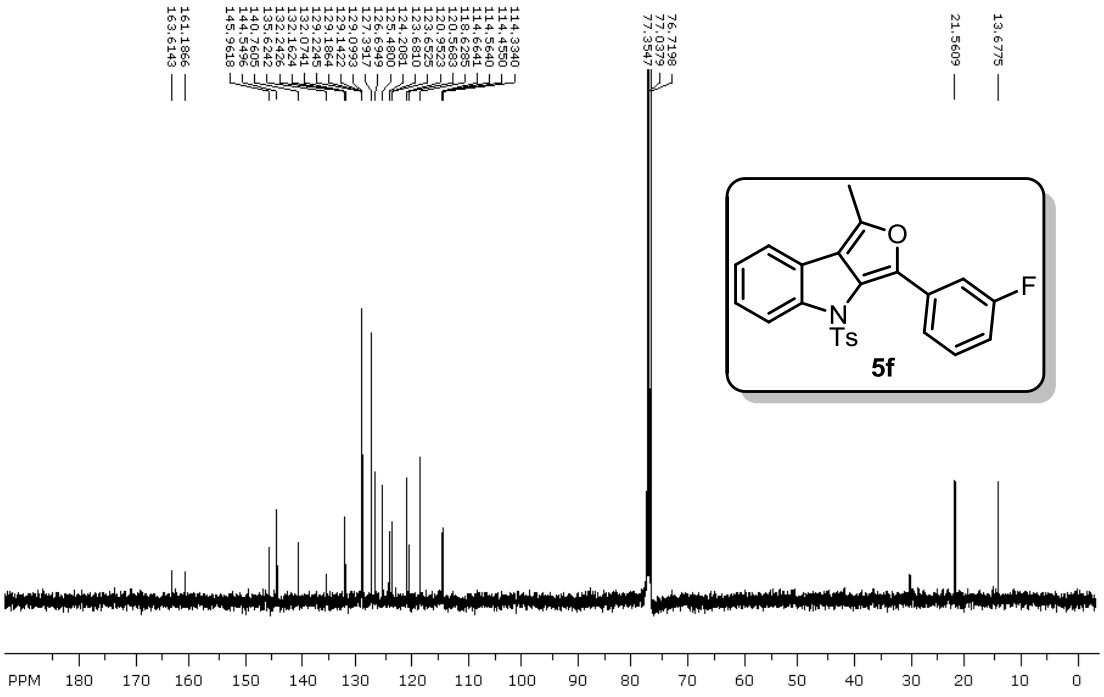
PPM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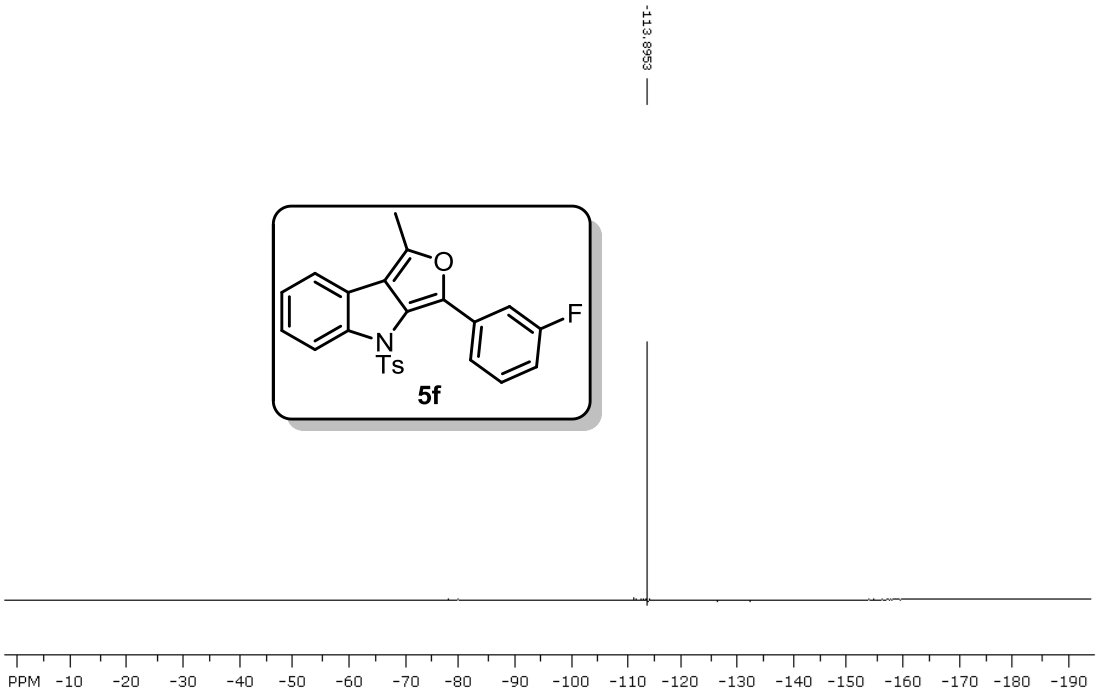
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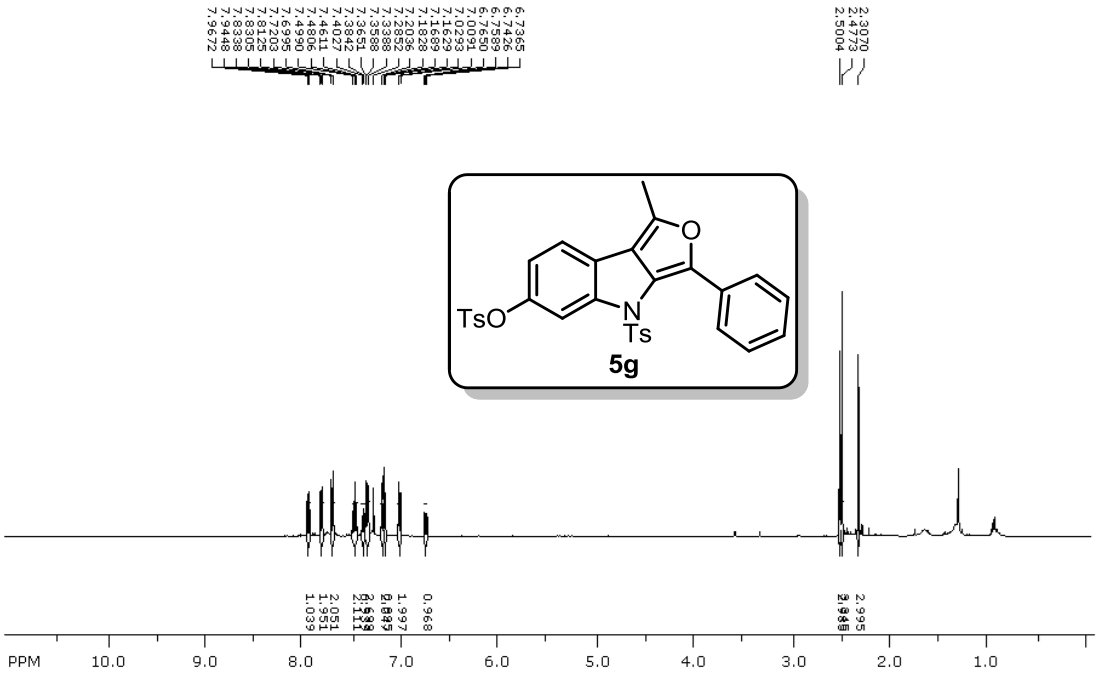
O
F
N
Ts
5f
PPM -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190

^{19}F-NMR of **5f**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7.3842
7.3651
7.3588
7.3386
7.2036
7.1828
7.1689
7.1629
7.0293
7.0091
6.7589
6.7426
6.7365
2.5004
2.4773
2.3070
O
TsO
N
Ts
5g
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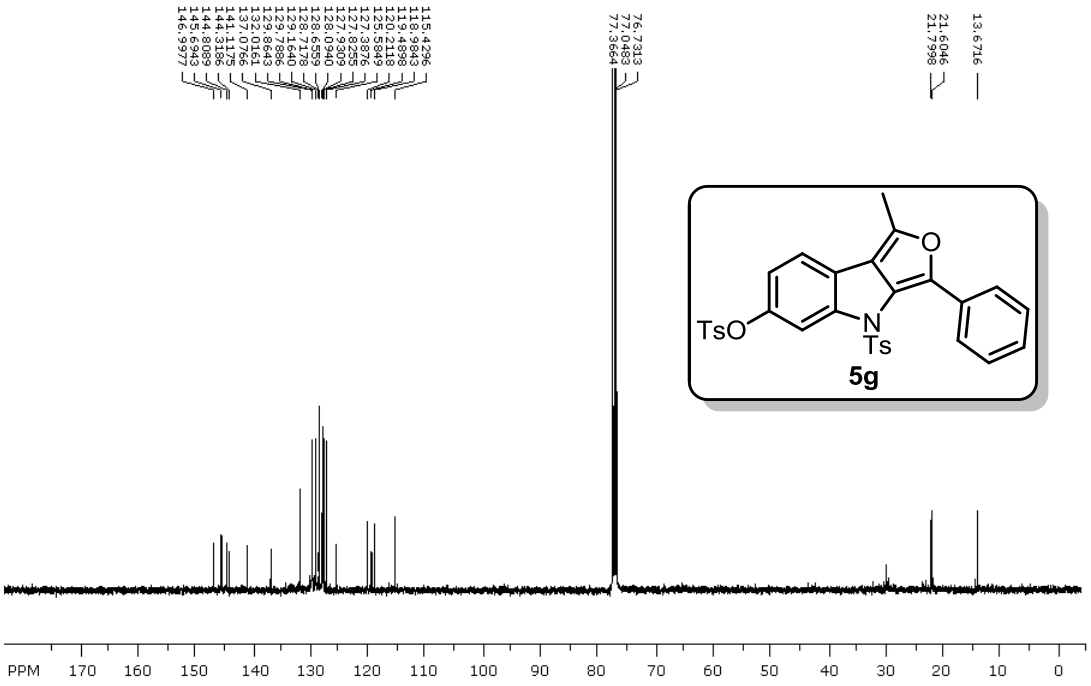
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Ts
O
5g
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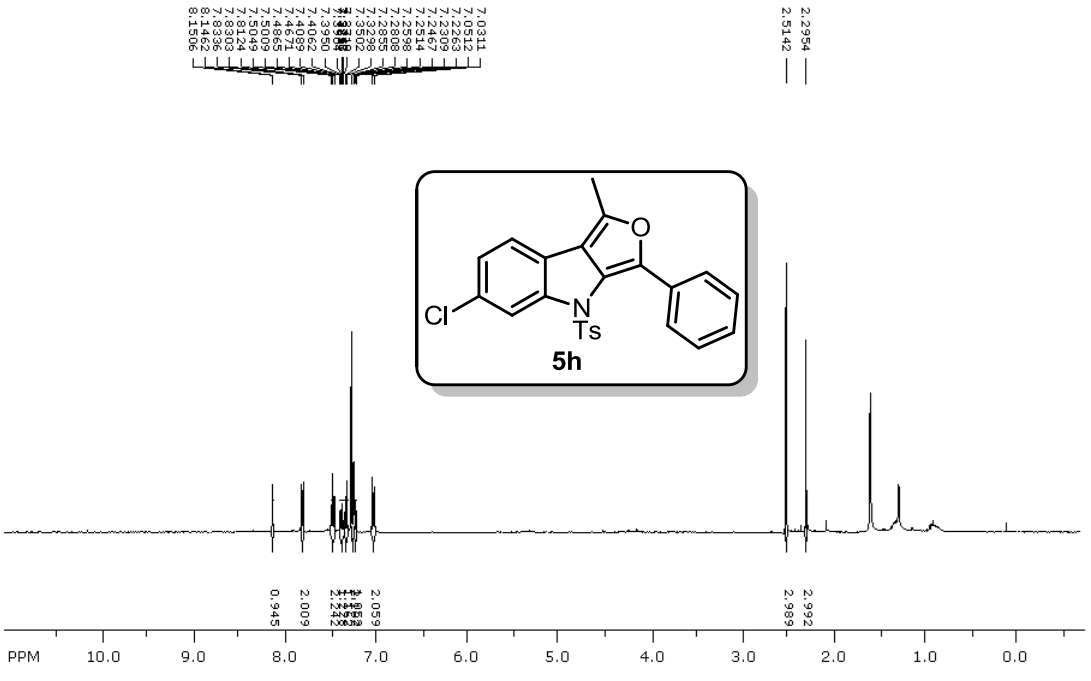
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Ts
O
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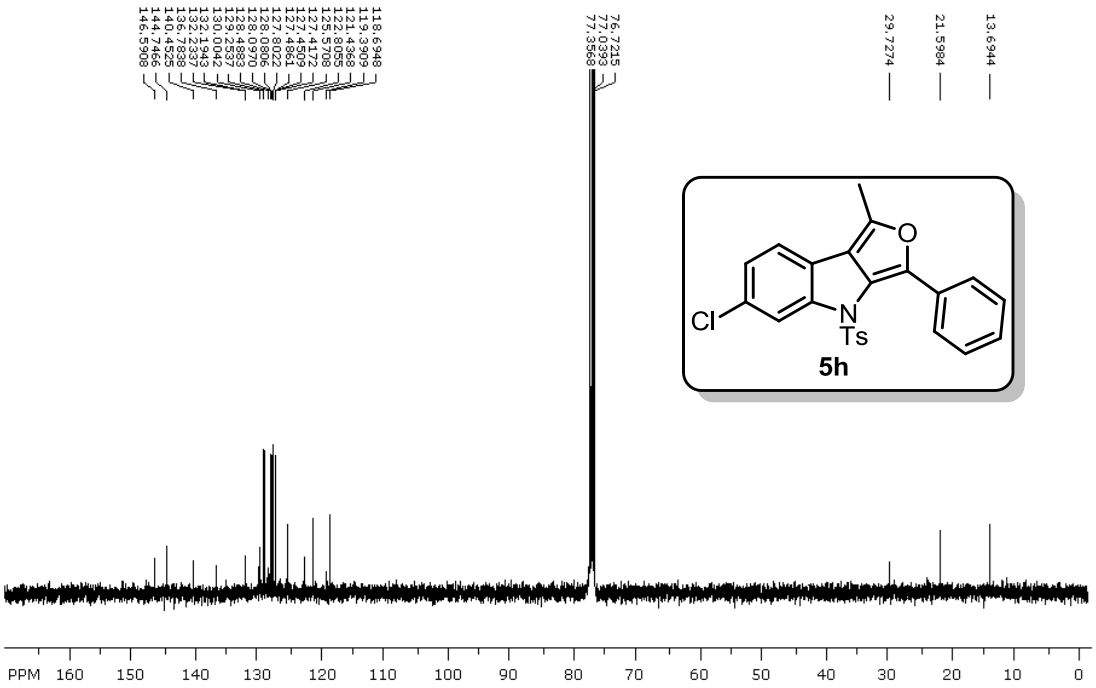
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Ts
O
5h
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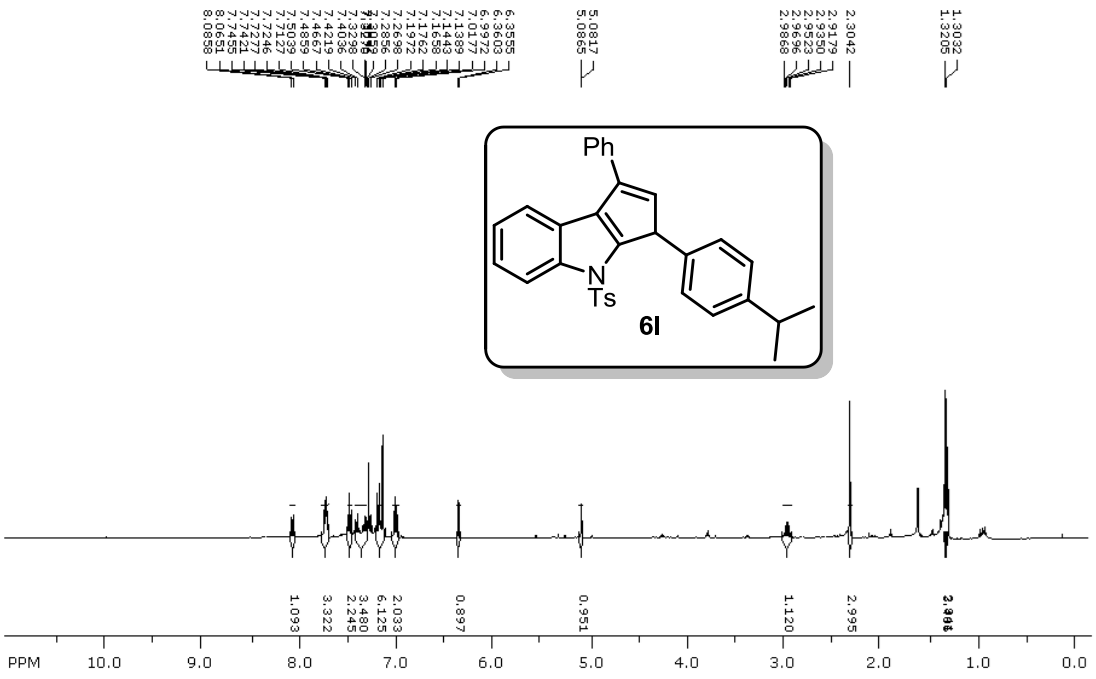
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7.1389
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2.9350
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1.3205
1.3032
Ph
N
Ts
6l
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2.245
6.125
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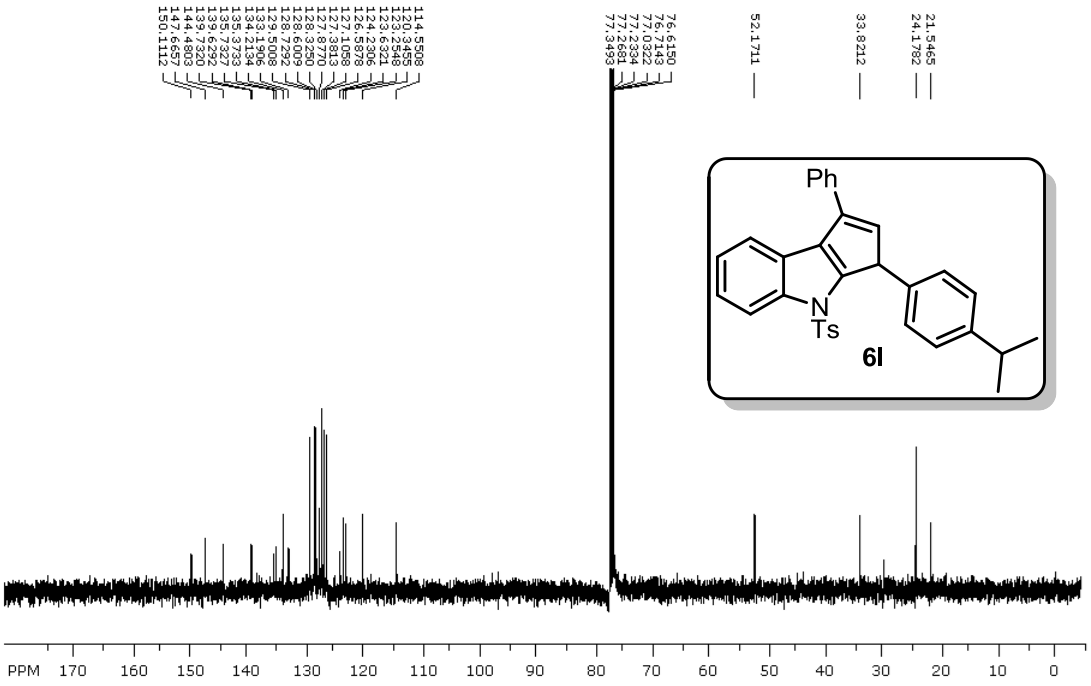
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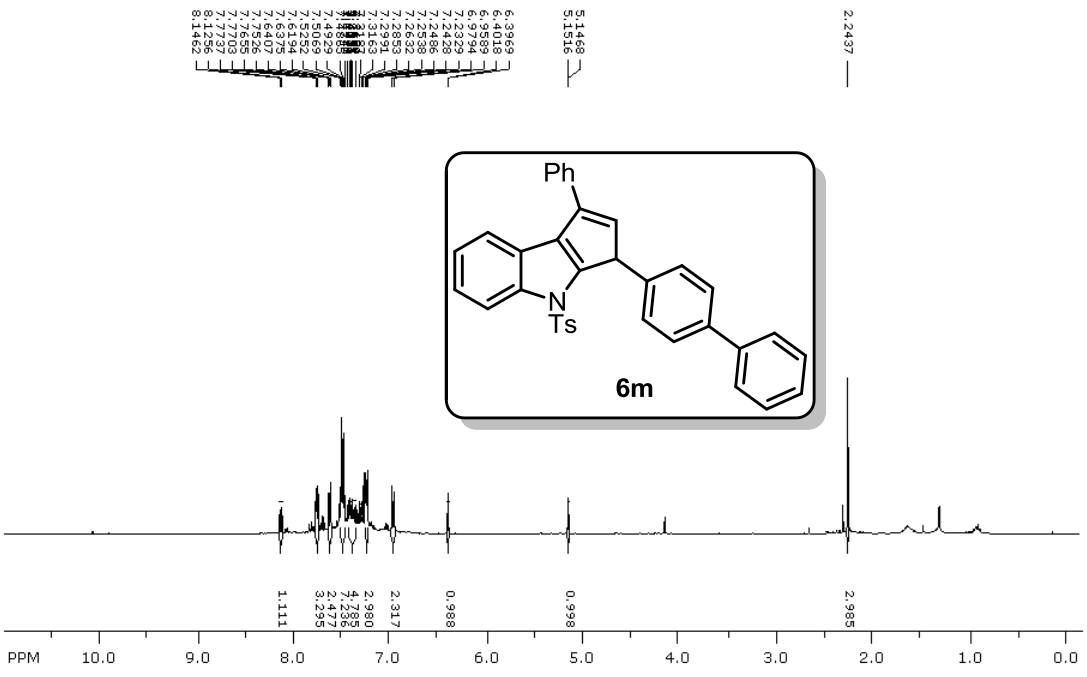
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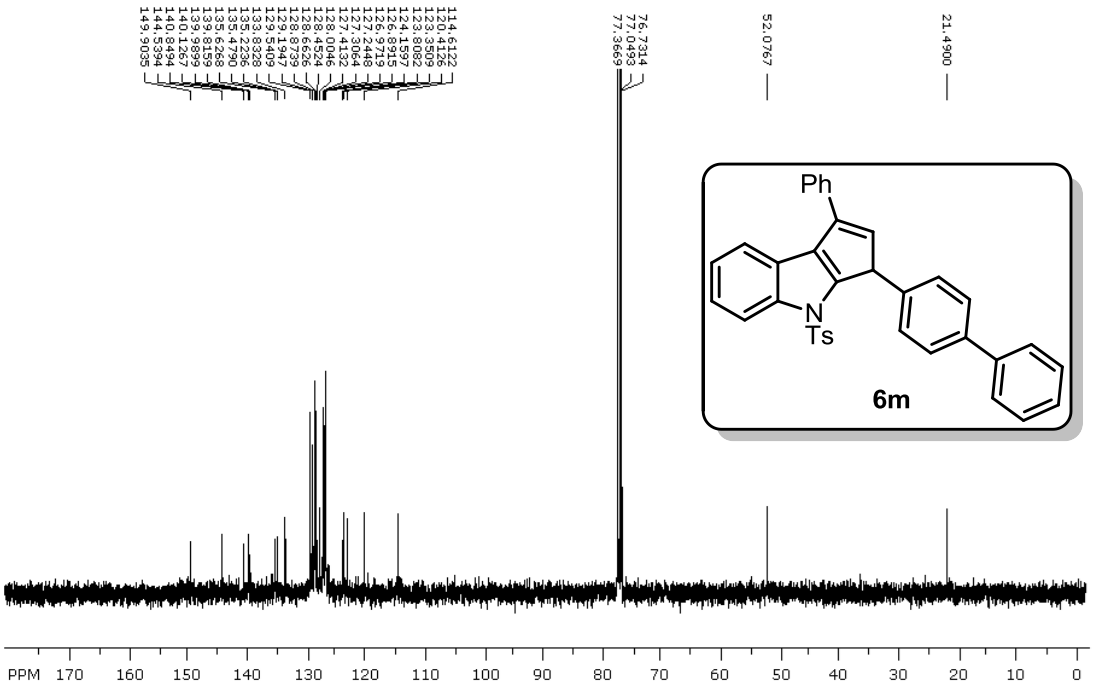
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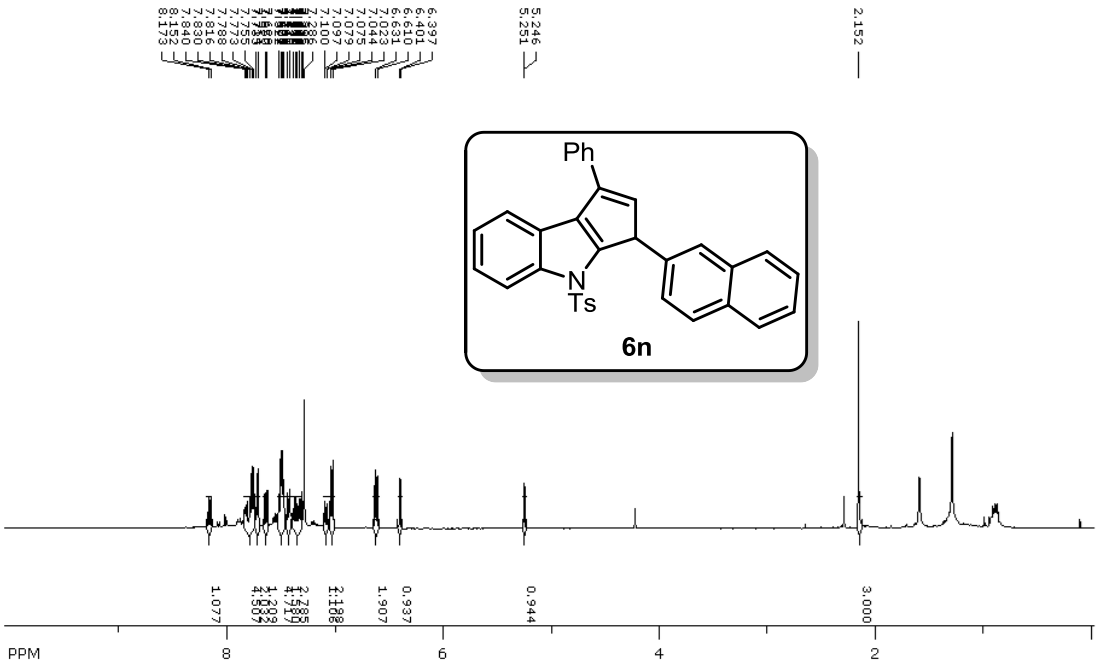
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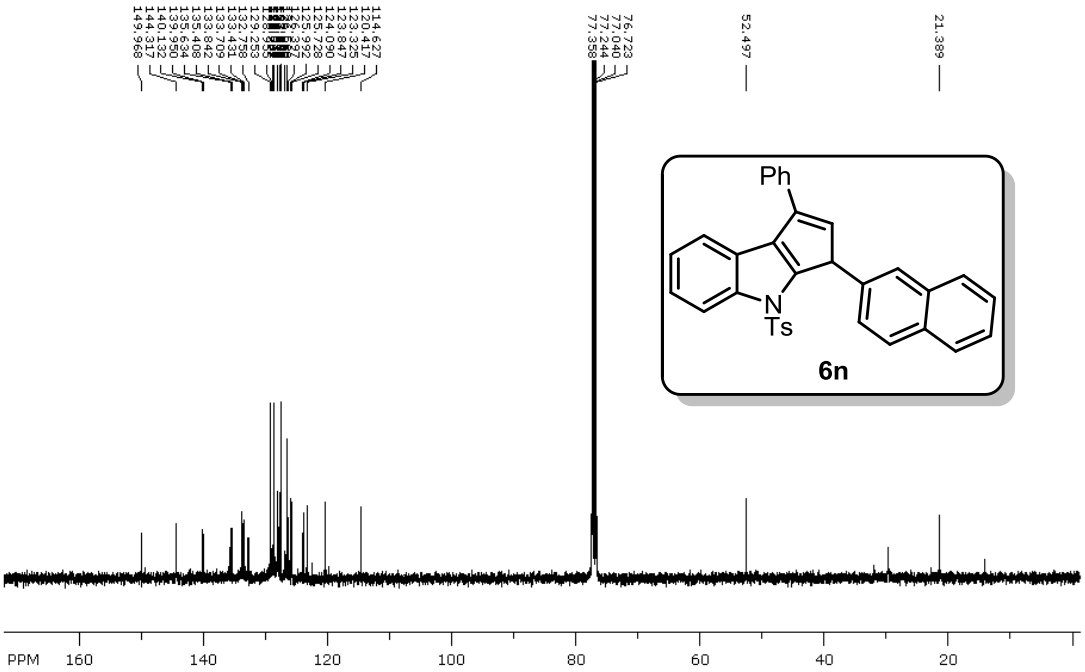
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N
Ts
6n
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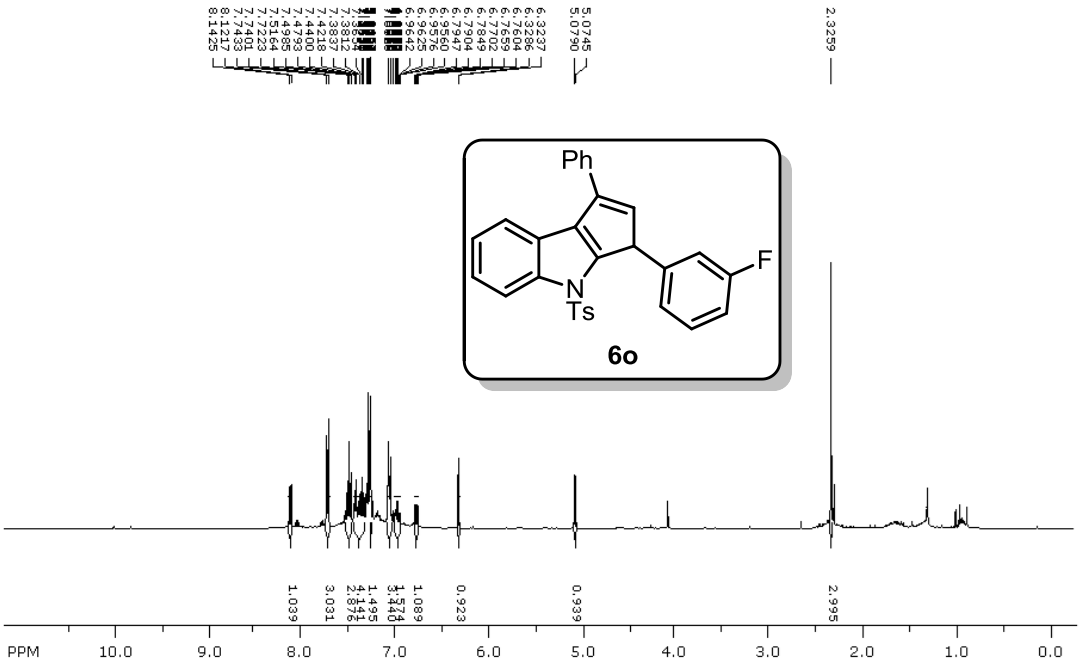
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Ts
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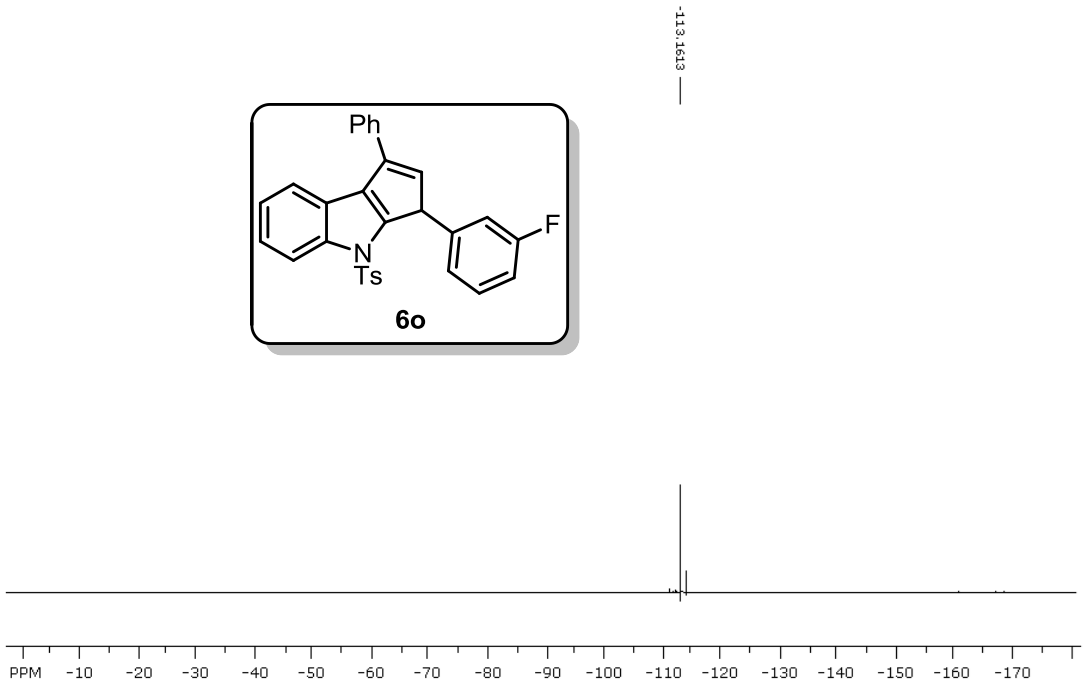
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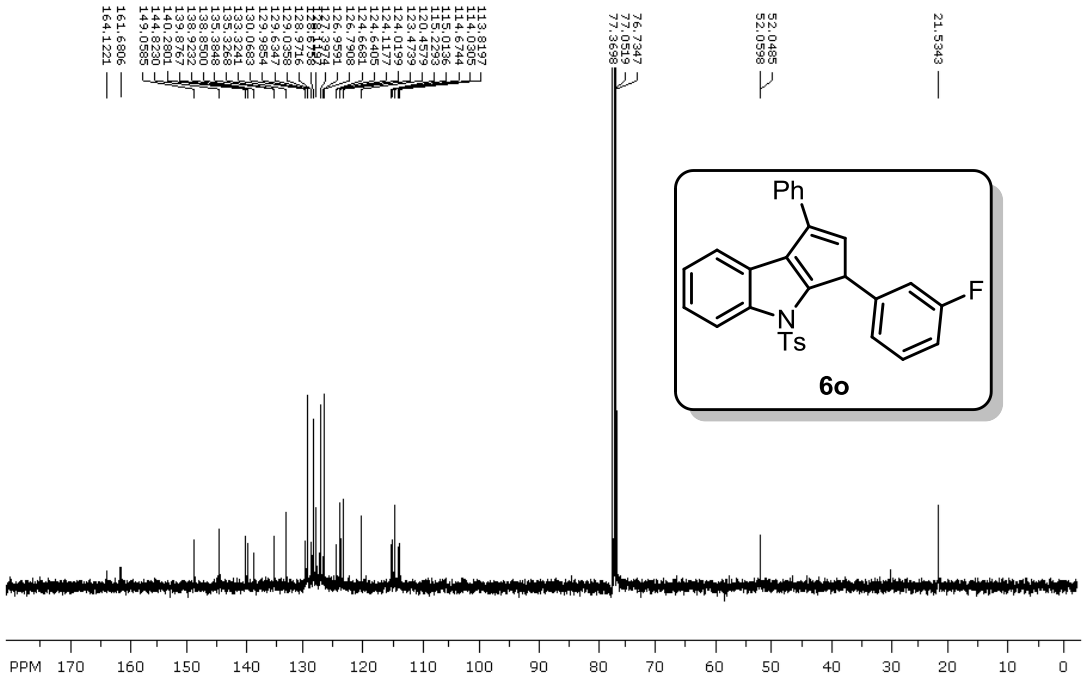
^{19}F-NMR of **6o**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6o
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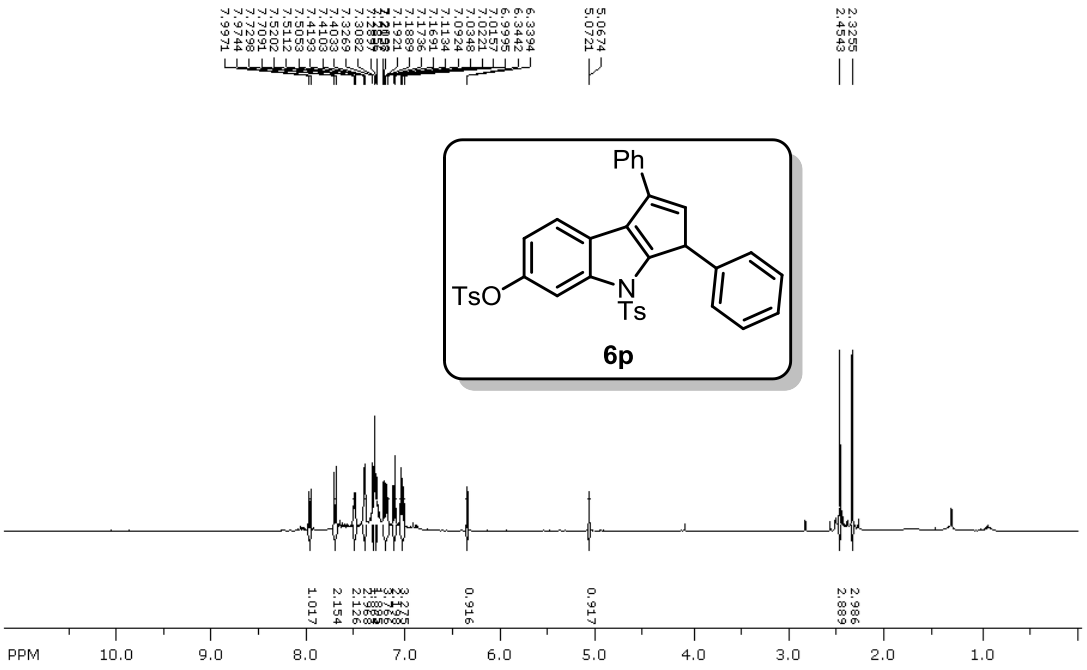
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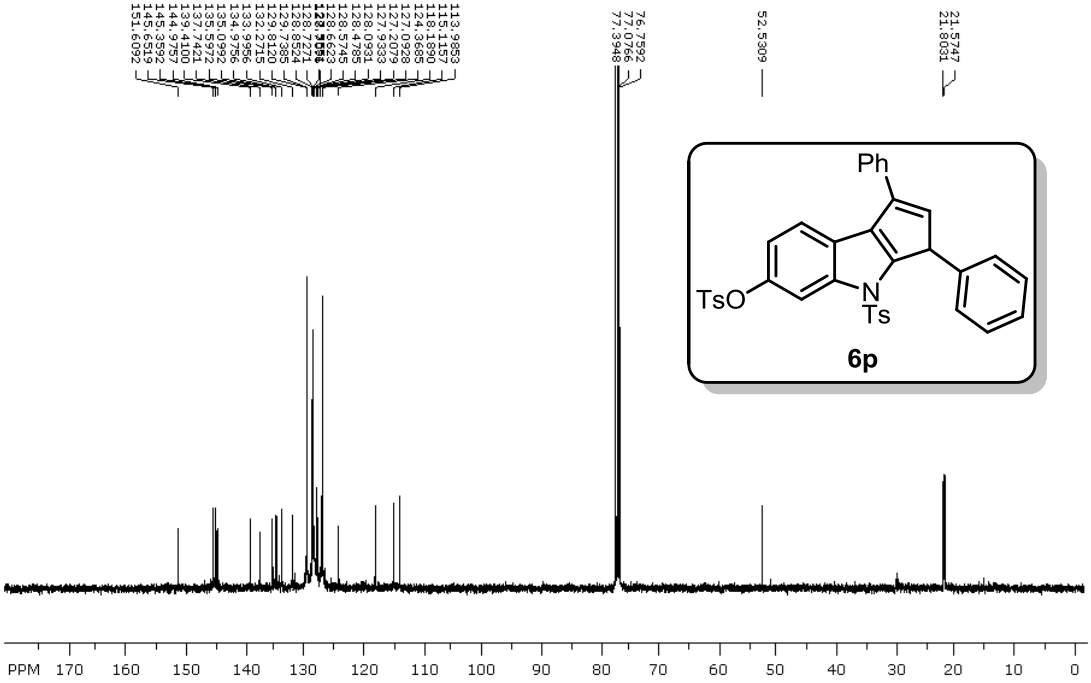
1.0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TsO
N
Ts
6p
PPM
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160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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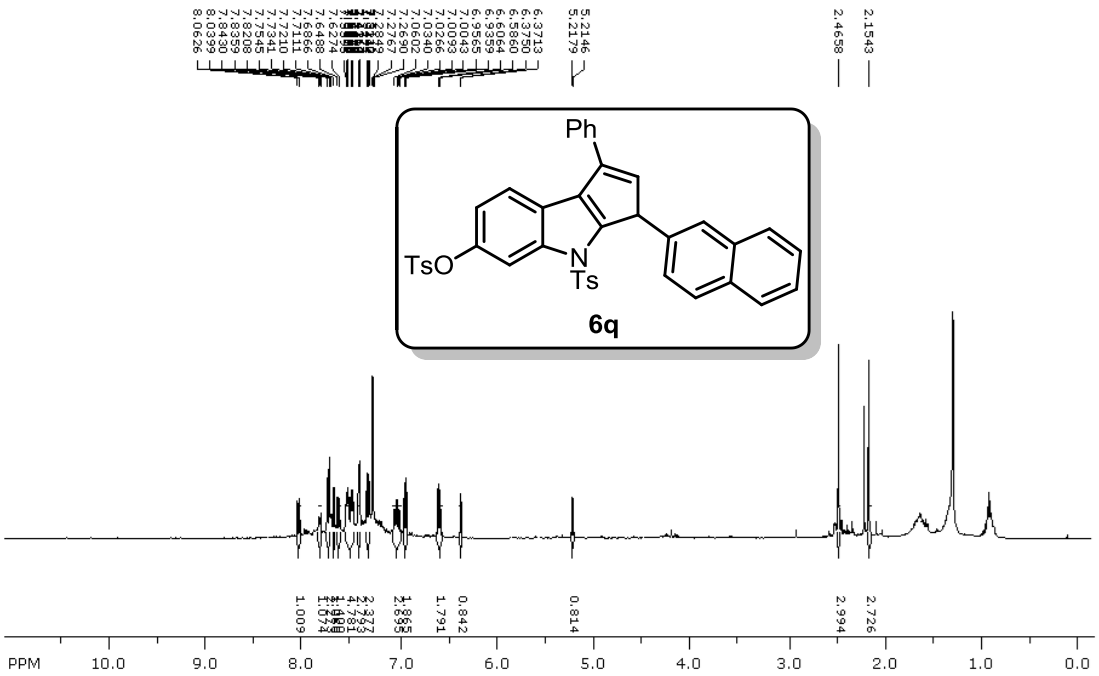
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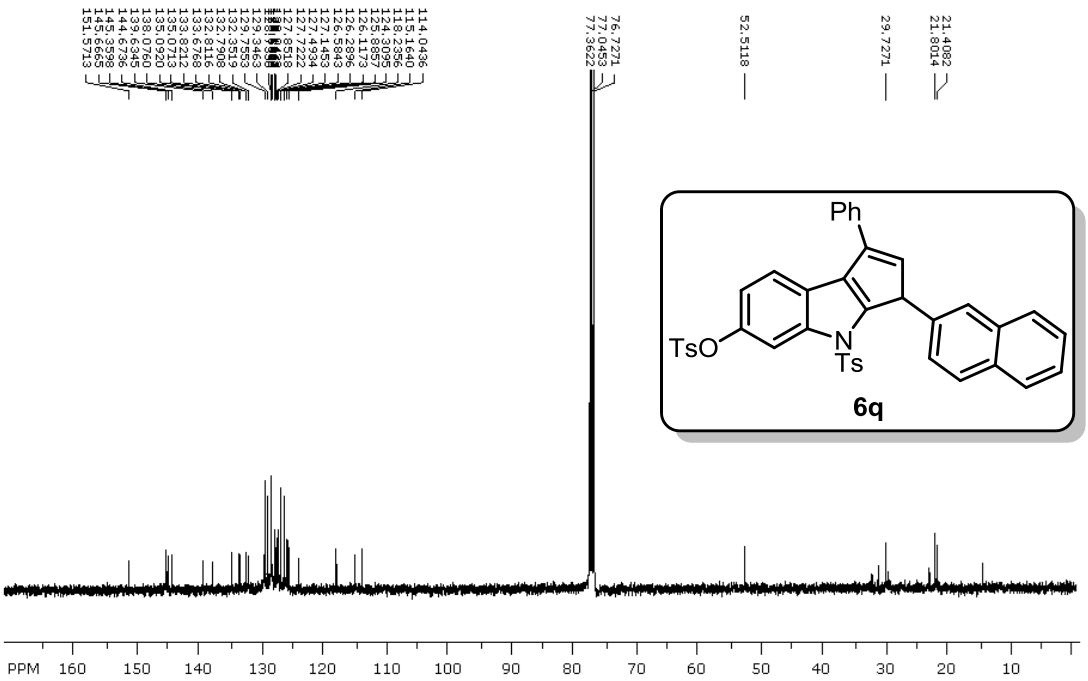
N
Ts
6q
PPM 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0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Ts
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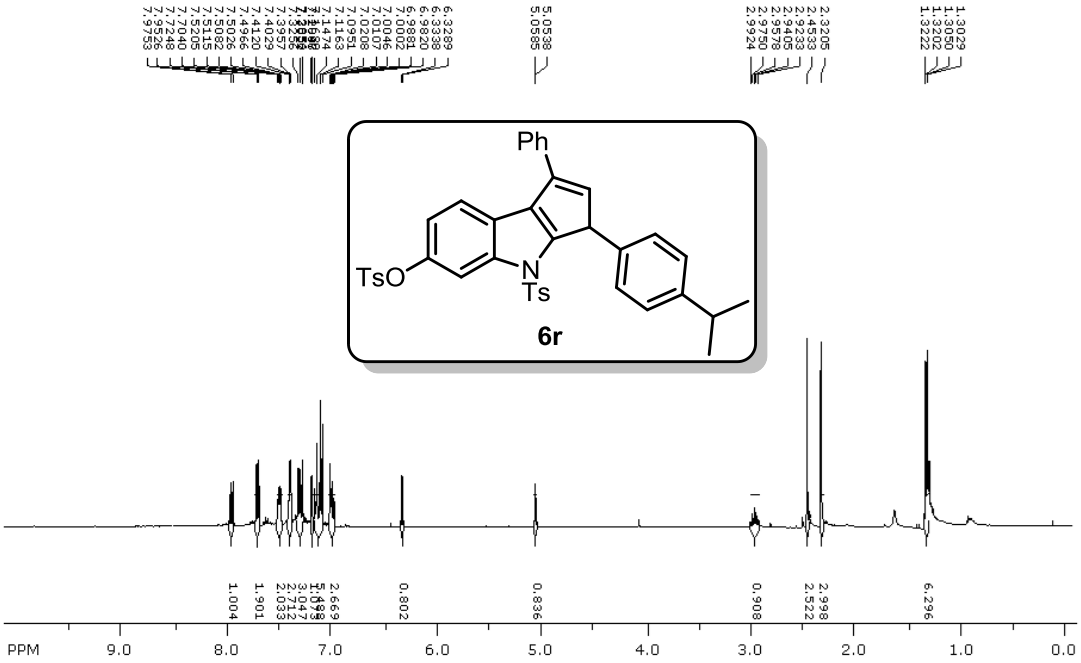
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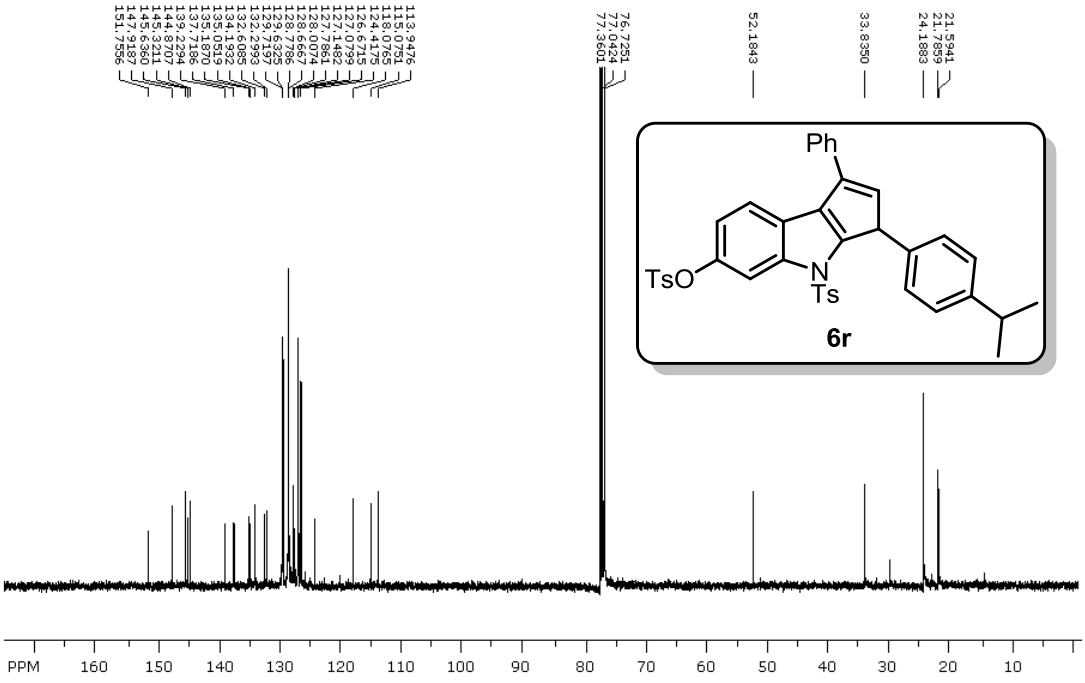
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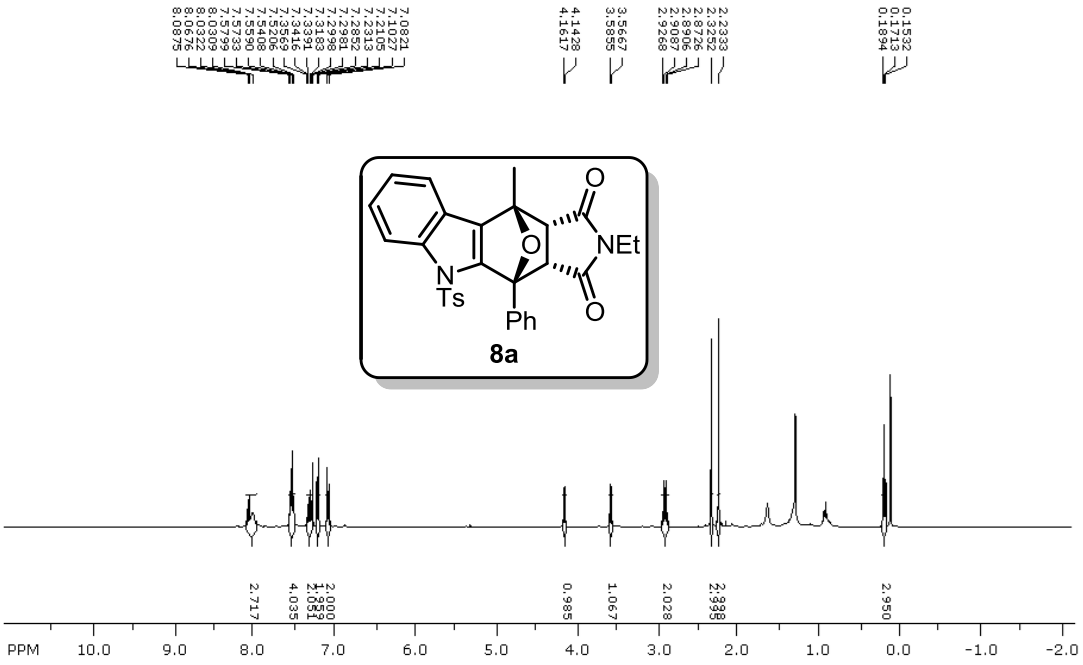
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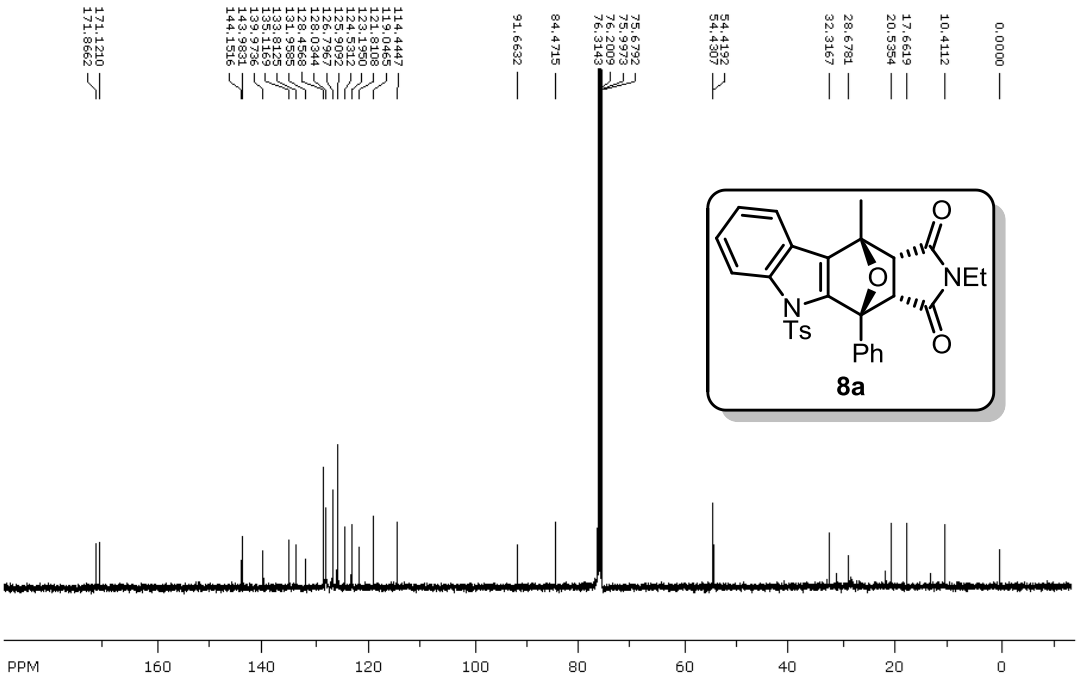
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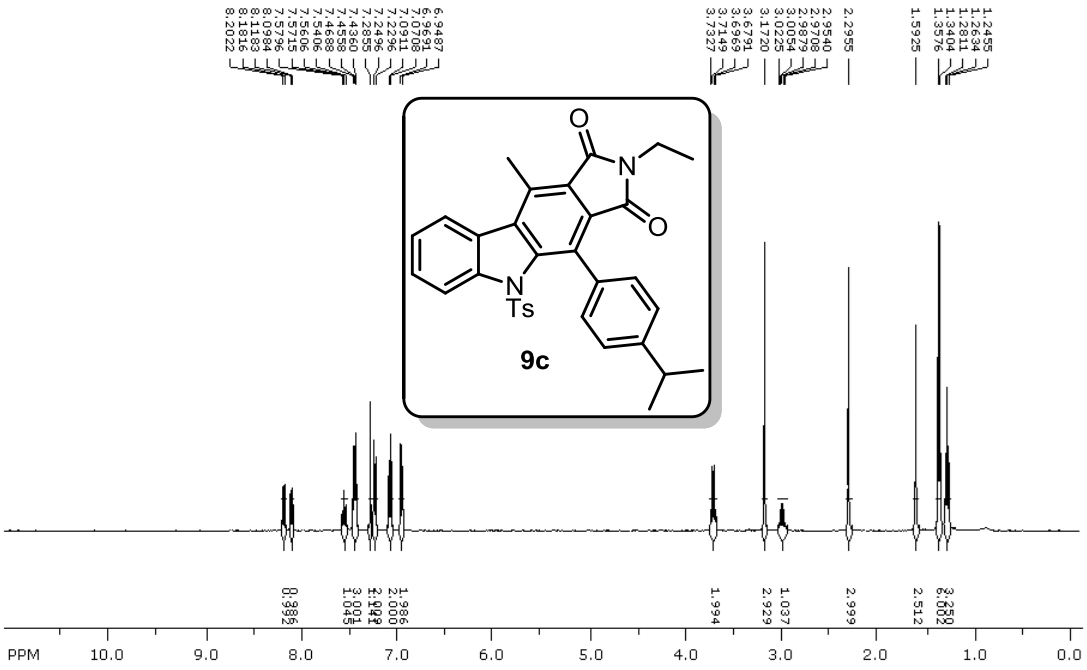
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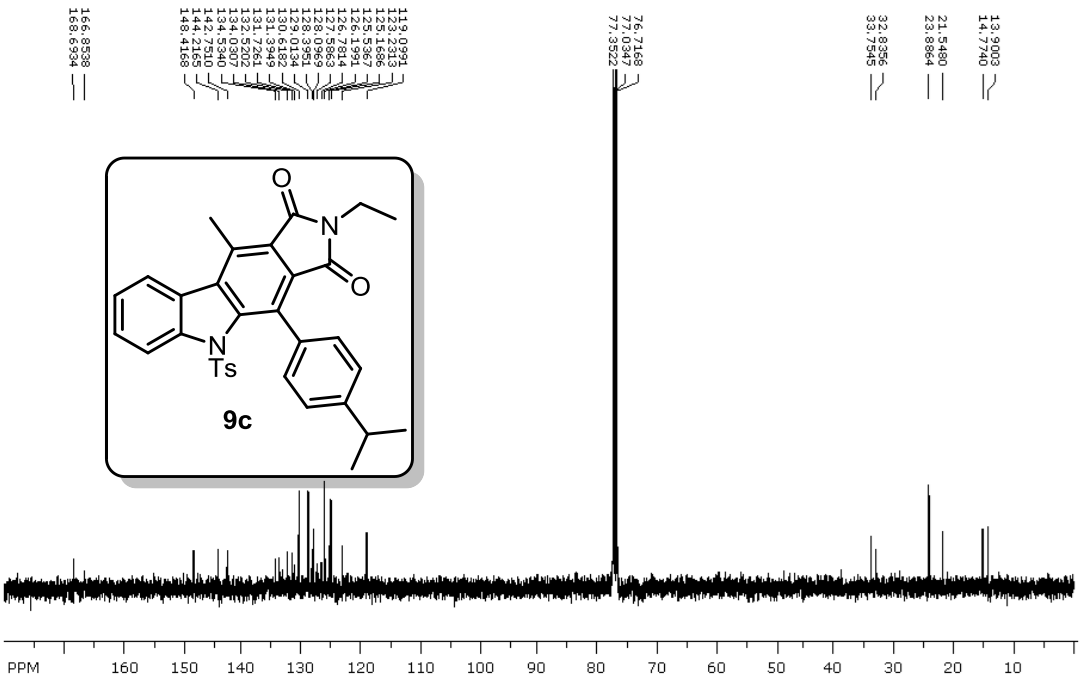
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Publications resulted out of the present research:

21. Manisha; Dhiman, S.; Mathew, J.; Ramasastry, S. S. V. *Org. Bimol. Chem.* **2016**, DOI: 10.1039/C6OB00319B. [*Invited article towards the thematic issue 'New Talent'*]