

Supporting Information

One-pot relay catalysis: Divergent synthesis of furo[3,4-*b*]indoles and cyclopenta[*b*]indoles from 3-(2-aminophenyl)-1,4-enynols

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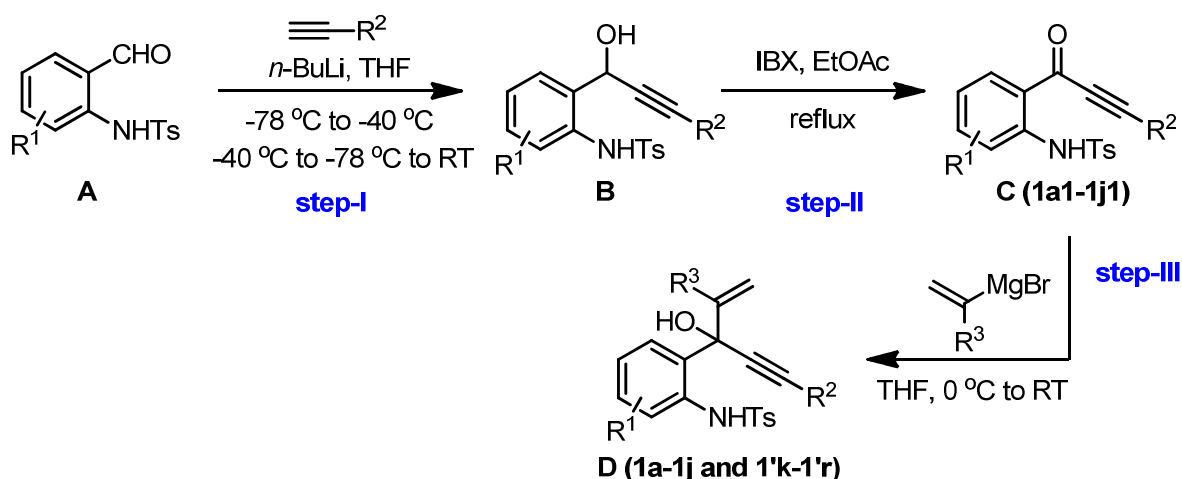
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General experimental methods: All the starting compounds and catalysts employed in this study were procured from Sigma-Aldrich and were used without further purification. For thin layer chromatography (TLC), silica aluminium foils with fluorescent 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. H₂SO₄ (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. ¹H NMR and ¹³C NMR spectra were recorded on a 400 MHz Bruker Biospin Avance III FT-NMR spectrometer. NMR shifts are reported as delta (δ) units in parts per million (ppm) and coupling constants (*J*) are reported in Hertz (Hz). The following abbreviations are utilized to describe peak patterns when appropriate: br=broad, s=singlet, d=doublet, t=triplet, q=quartet and m=multiplet. Proton chemical shifts are given in δ relative to tetramethylsilane (δ 0.00 ppm) in CDCl₃. Carbon chemical shifts are internally referenced to the deuterated solvent signals in CDCl₃ (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.

General procedure for the 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**.¹ *n*-Butyllithium mediated addition of alkynes to amino benzaldehydes **A** afforded ynols **B** which upon IBX oxidation generated the ynones **C**. Further addition of vinylmagnesium bromides to ynones **C** furnished 3-(2-aminophenyl)pent-4-en-1-yn-3-ols **D**.



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

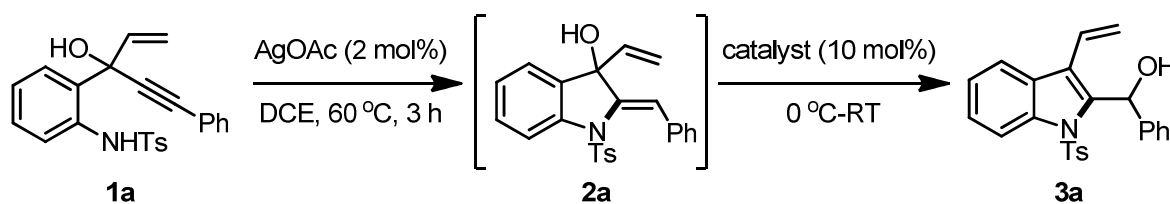
Representative procedure for step-I (Scheme 1S): To a stirred solution of the alkyne (2.2 equiv.) in anhydrous THF at $-78\text{ }^{\circ}\text{C}$, was added *n*-butyllithium (2.0 M in cyclohexane solution, 2.2 equiv.) drop wise, and the resulting solution was allowed to stir at the same temperature for 10 min. The reaction was warmed to $-40\text{ }^{\circ}\text{C}$. The resulting mixture was stirred at the same temperature for 1 h. After 1 h, reaction mixture was cooled to $-78\text{ }^{\circ}\text{C}$. N-(2-formylphenyl)-4-methylbenzenesulfonamide **A** (1 mmol) was dissolved in THF (2 mL) and added to the reaction mixture drop wise at $-78\text{ }^{\circ}\text{C}$ 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.

¹S. Dhiman, S. S. V. Ramasastry, *Chem. Commun.* **2015**, 51, 557.

Representative procedure for step-II (Scheme 1S): 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. NaHCO₃ solution to remove excess iodobenzoic acid. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, 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.

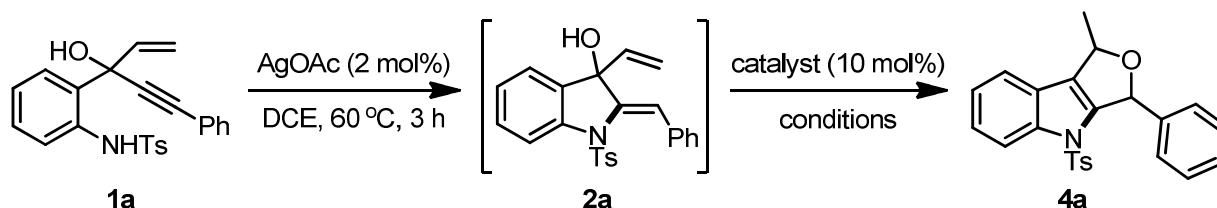
Representative procedure for step-III (Scheme 1S): An oven dried round bottom flask was charged with ynones **C** (1.0 mmol), 5 mL dry THF and placed at 0°C. Vinylmagnesium bromide (2.0 M in THF, 3.5 mmol) was added drop wise at the same temperature and stirred for 1h. Upon completion, the reaction mixture was quenched by adding saturated aq. NH₄Cl (1 mL) and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, 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.

Optimization of the reaction parameters (Table 1).



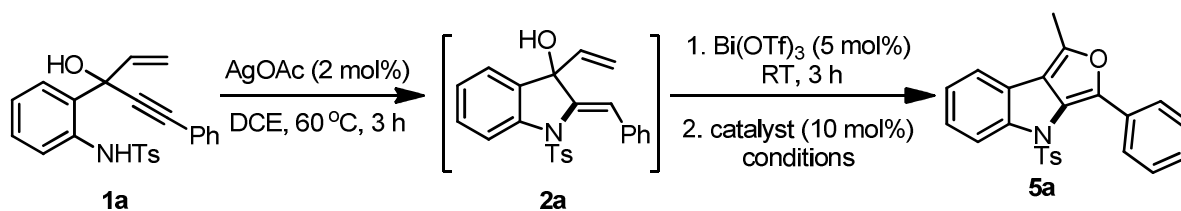
Scheme 2S. Optimization of reaction parameters.

Representative procedure for 3a (Table 1, entries 1-3): A 5 mL glass vial was charged with 3-(2-aminophenyl)-pent-4-en-1-yn-3-ol (0.1 mmol), AgOAc (2 mol%) in DCE solvent (1 mL) stirred at 60 °C. Upon disappearance of **1a**, catalyst (10 mol%) was introduced and continued stirring at 0°C to RT until intermediate **2a** disappeared. On complete formation of **3a**, the reaction mixture was quenched by adding saturated aq. NaHCO₃ (1 mL) and extracted with EtOAc (2 x 2 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (10-20% EtOAc/hexane) to afford **3a**.



Scheme 3S. Optimization of reaction parameters.

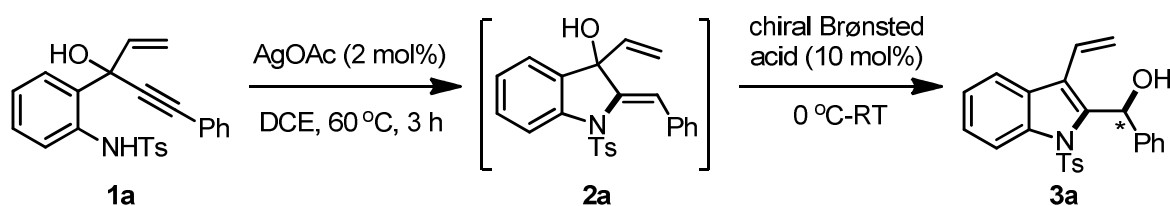
Representative procedure for 4a (Table 1, entries 4-12): A 5 mL glass vial was charged with 3-(2-aminophenyl)-pent-4-en-1-yn-3-ol (0.1 mmol), AgOAc (2 mol%) in DCE solvent (1 mL) stirred at 60 °C. Upon disappearance of **1a**, catalyst (10 mol%) in an appropriate solvent was introduced and continued stirring at appropriate temperature until intermediate **2a** disappeared. On complete formation of **4a**, the reaction mixture was quenched by adding saturated aq. NaHCO₃ (1 mL) and extracted with EtOAc (2 x 2 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (10-20% EtOAc/hexane) to afford **4a**.



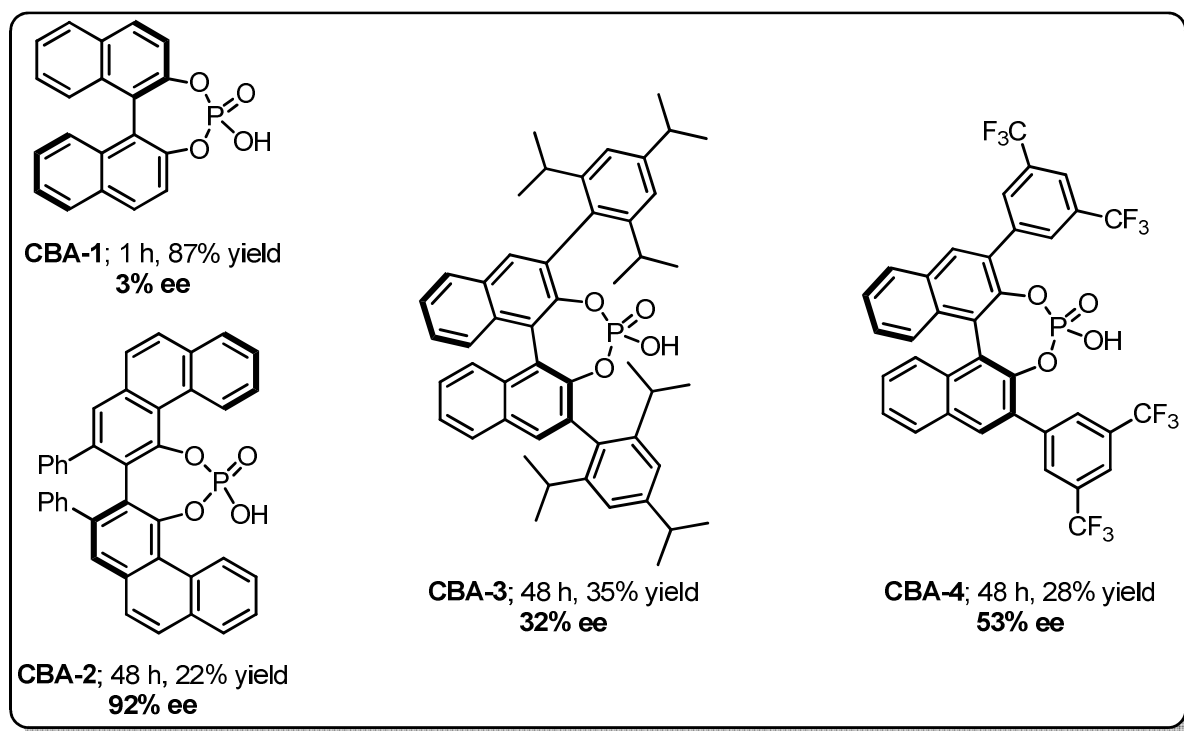
Scheme 4S. Optimization of reaction parameters.

Representative procedure for 5a (Table 1, entries 13-19): 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 °C. Upon disappearance of **1a**, Bi(OTf)₃ (5 mol%) was introduced and continued stirring at room temperature (see Table 1) until intermediate **2a** disappeared. Then, reaction mixture was quenched by adding saturated aq. NaHCO₃ (1 mL) and extracted with EtOAc (2 x 2 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, 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. 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**.

General procedure for Scheme 2.



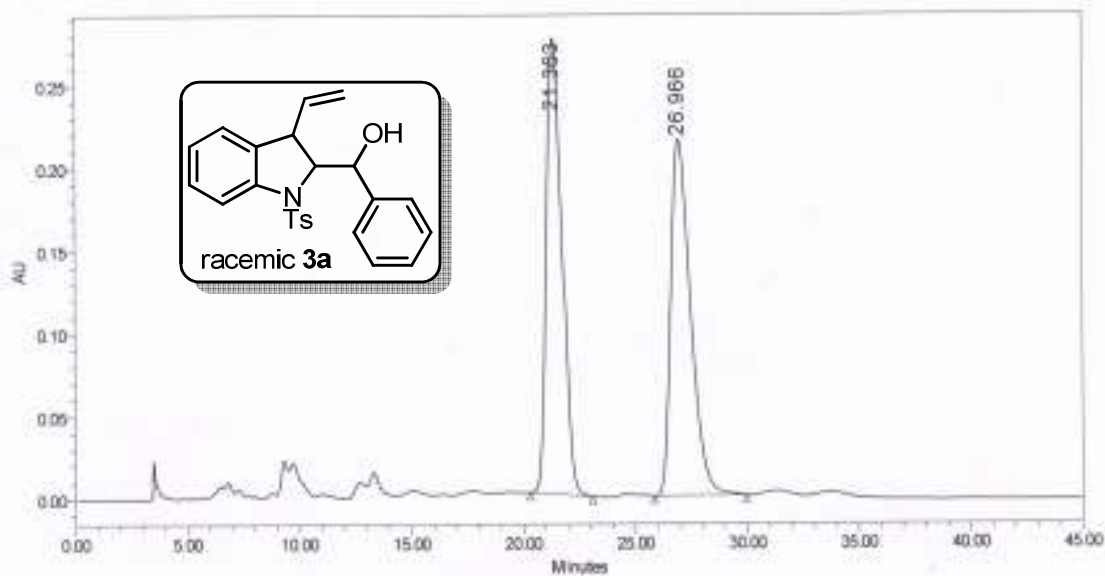
Scheme 5S. Optimization of reaction parameters.



Representative procedure for chiral 3a (Scheme 2): A 5 mL glass vial was charged with 3-(2-aminophenyl)-pent-4-en-1-yn-3-ol (0.1 mmol), AgOAc (2 mol%) in DCE solvent (1 mL) stirred at 60 °C. Upon disappearance of **1a**, chiral catalyst (10 mol%) was introduced and continued stirring at 0 °C-RT until the intermediate **2a** disappeared. Upon complete formation of **3a**, the reaction mixture was quenched by adding saturated aq. NaHCO₃ (1 mL) and extracted with EtOAc (2 x 2 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, 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 using chiral HPLC.

SAMPLE INFORMATION

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Injection Volume:	10.00 ul	Channel Name:	254.0nm
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		



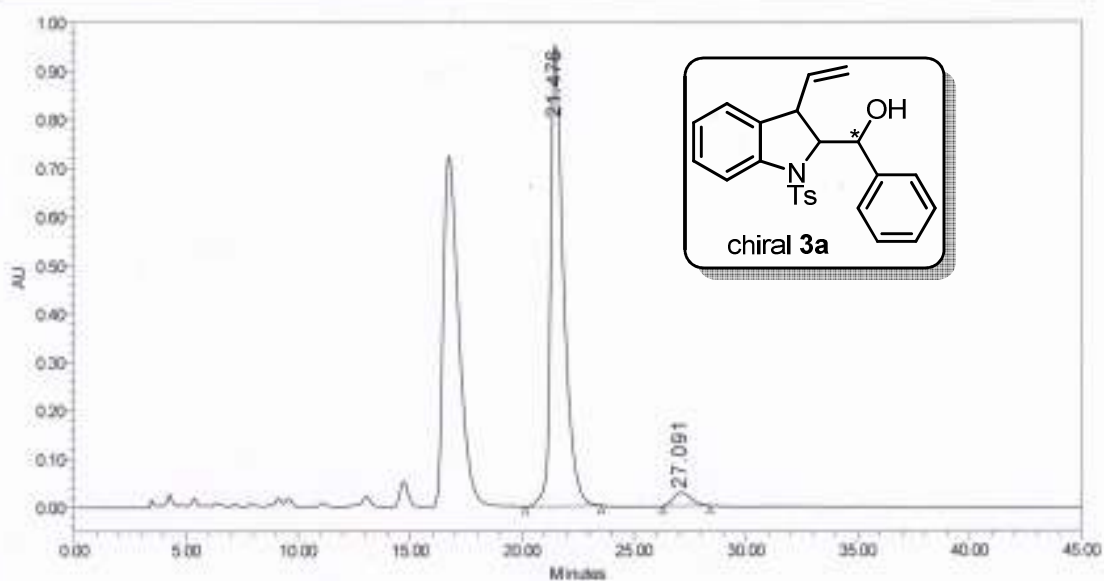
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Reported by User: System
Report Method: Vishnu
Report Method ID: 5245
Page: 1 of 1

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

SAMPLE INFORMATION

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Vial:	1	Acq. Method Set:	manisha
Injection #:	1	Processing Method:	ms0301vapp
Injection Volume:	10.00 ul	Channel Name:	254.0nm
Run Time:	60.0 Minutes	Prod. Chnl. Descr.:	PDA 254.0 nm
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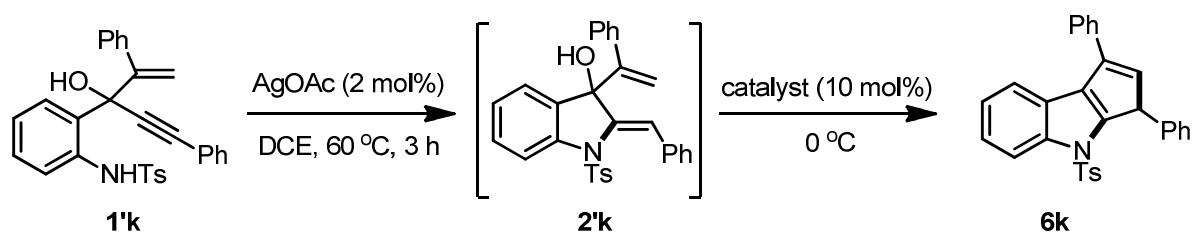
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Report Method ID: 6245
Page: 1 of 1

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Analysis with CBA-2 (92% ee)

General procedure for Table 3.



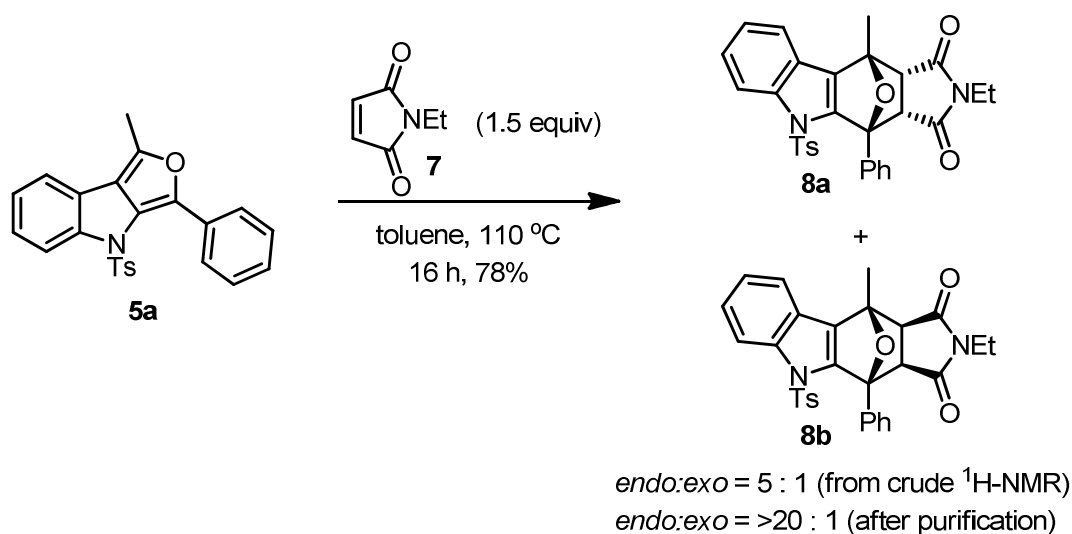
Scheme 6S. Optimization of reaction parameters.

Screening Table for compound 6k (Table 3).

Entry	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	Pd(OAc) ₂	360	-
7	Co(acac) ₂	360	-
8	AgOTf	40	55
9	TfOH	20	68
10	CF ₃ COOH	20	28
11	ClCH ₂ COOH	360	-
12	Amberlyst-15	180	56

Representative procedure for 6k (Scheme 6S, Table 3): 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 °C. Upon disappearance of **1'k**, catalyst (10 mol%) was introduced and continued stirring at 0 °C until intermediate **2'k** disappeared. On complete formation of **6a**, the reaction mixture was quenched by adding saturated aq. NaHCO₃ (1 mL) and extracted with EtOAc (2 x 2 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (10-20% EtOAc/hexane) to afford **6k**.

General procedure for the Diels-Alder reaction (Scheme 4).²

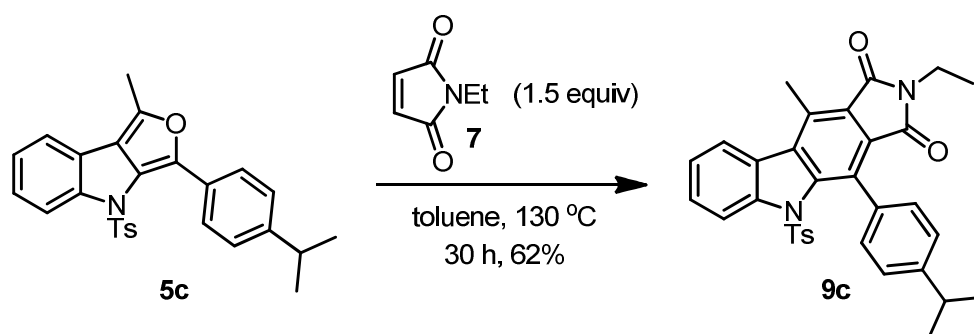


Scheme 7S. Diels-Alder reaction of the furoindole **5a** and N-ethyl maleimide **7**.

Representative procedure for **8a (Scheme 7S):** An oven dried 10 mL round bottom flask was charged with furo[3,4-*b*]indole **5a** (0.1 mmol), N-ethyl maleimide (0.15 mmol) in toluene (1.5 mL) and stirred at 110 °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 **8a** in 78% yield.

² (a) G. W. Gribble, M. G. Saulnier, M. P. Sibi and J. A. Obaza-Nutaitis, *J. Org. Chem.*, 1984, **49**, 4518; (b) G. W. Gribble, D. J. Keavy, D. A. Davis, M. G. Saulnier, B. Pelcman, T. C. Barden, M. P. Sibi, E. R. Olson and J. J. BelBruno, *J. Org. Chem.*, 1992, **57**, 5878;

General procedure for the Diels-Alder reaction (Scheme 5).²

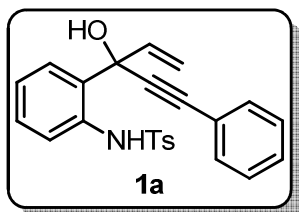


Scheme 8S. Diels-Alder reaction of the furoindole **5c** and N-ethyl maleimide **7**.

Representative procedure for **9c (Scheme 8S):** An oven dried 5 mL round bottom flask was charged with furo[3,4-*b*]indole **5c** (0.1 mmol), N-ethyl maleimide (0.15 mmol) in toluene (1.5 mL) and stirred at 130 °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.

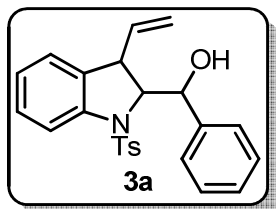
Spectroscopic data of all new compounds reported in this study

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



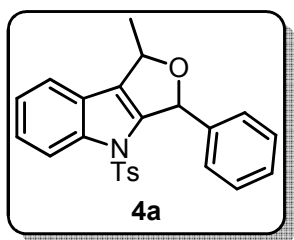
This compound was isolated as pale yellow oil. Following the general procedure (Scheme 1S), 80 mg of **1a** afforded 76 mg of **1a** (88% yield). $R_f = 0.5$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$ 3432, 3250, 2226, 1599, 1493, 1336, 1159, 1092, 757. **^1H NMR (400 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 $\text{C}_{24}\text{H}_{21}\text{NO}_3\text{SNa}$ ($\text{M}+\text{Na}$) $^+$: 426.1140. Found: 426.1115.

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



This compound was isolated as light brown oil. Following the general procedure (Scheme 2S), 50 mg of **1a** afforded 46 mg of **3a** (85% yield). $R_f = 0.5$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$ 3472, 3061, 2925, 1597, 1449, 1365, 1171, 1088, 748. **^1H 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 $\text{C}_{24}\text{H}_{21}\text{NO}_3\text{SNa}$ ($\text{M}+\text{Na}$) $^+$: 426.1140. Found: 426.1125.

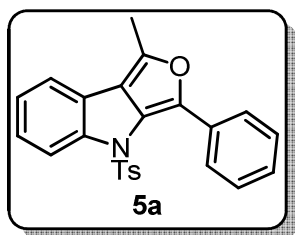
1-Methyl-3-phenyl-4-tosyl-3,4-dihydro-1H-furo[3,4-*b*]indole (4a).



This compound was isolated as light yellow oil. Following the general procedure (Scheme 3S), 40 mg of **1a** afforded 14 mg of **4a** (35% yield). $R_f = 0.6$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):**

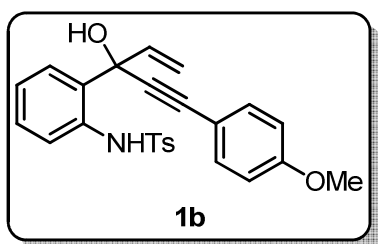
$\nu_{\max}/\text{cm}^{-1}$ 3066, 2924, 2857, 1597, 1448, 1371, 1176, 1040, 758. **^1H NMR (400 MHz, CDCl_3):** δ 7.97-8.01 (m, 2H), 7.29-7.40 (m, 7H), 7.07-7.12 (m, 2H), 6.99-7.03 (m, 2H), 6.35 (d, $J = 2.8$ Hz, 1H), 5.44-5.49 (m, 1H), 2.32 (s, 3H), 1.70 (d, $J = 6.4$ Hz, 3H). **^{13}C NMR (100 MHz, 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 $\text{C}_{24}\text{H}_{22}\text{NO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 404.1320. Found: 404.1306.

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



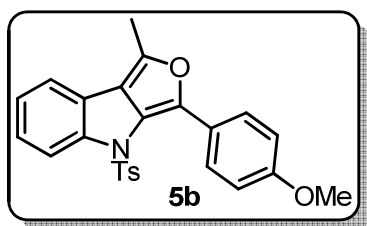
This compound was isolated as light brown oil. Following the general procedure (Scheme 4S), 30 mg of **1a** afforded 15 mg of **5a** (50% yield). $R_f = 0.8$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$ 2928, 2850, 1740, 1375, 750. **^1H NMR (400 MHz, CDCl_3):** δ 8.12 (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 $\text{C}_{24}\text{H}_{20}\text{NO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 402.1163. Found: 402.1150.

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



This compound was isolated as light brown oil. Following the general procedure (Scheme 1S), 80 mg of **1b1** afforded 77 mg of **1b** (97% yield). $R_f = 0.1$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$ 3441, 3252, 2932, 2225, 1742, 1605, 1510, 1251, 1160, 1091, 756. **^1H 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 $\text{C}_{25}\text{H}_{23}\text{NO}_4\text{SNa}$ ($\text{M}+\text{Na}$) $^+$: 456.1245. Found: 456.1228.

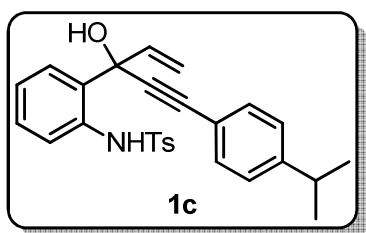
3-(4-Methoxyphenyl)-1-methyl-4-tosyl-4H-furo[3,4-b]indole (5b).



This compound was isolated as pale brown oil. Following the general procedure (Scheme 4S), 20 mg of **1b** afforded 11 mg of **5b** (54% yield). $R_f = 0.4$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$ 2924, 2855, 1669, 1599, 1371, 1258, 1176, 1090, 751. **^1H 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 $\text{C}_{25}\text{H}_{22}\text{NO}_4\text{S}$ ($\text{M}+\text{H}$) $^+$: 432.1270. Found: 432.1254.

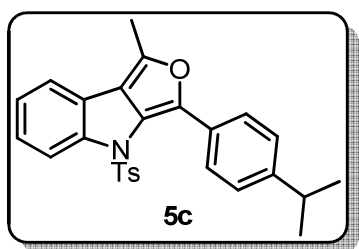
N-(2-(3-Hydroxy-5-(4-isopropylphenyl)pent-1-en-4-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (1c).



This compound was isolated as pale yellow oil. Following the general procedure (Scheme 1S), 70 mg of **1c1** afforded 63 mg of **1c** (84% yield). $R_f = 0.3$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$ 3446, 3243, 2962, 2928, 2225, 1672, 1495, 1336, 1160, 1092, 757. **^1H 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 $\text{C}_{27}\text{H}_{27}\text{NO}_3\text{SNa}$ ($\text{M}+\text{Na}$) $^+$: 468.1609. Found: 468.1592.

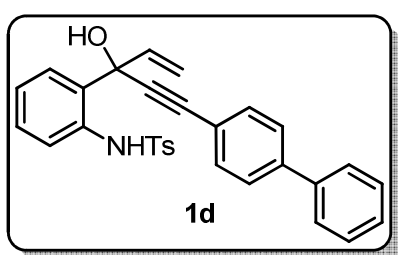
3-(4-Isopropylphenyl)-1-methyl-4-tosyl-4H-furo[3,4-b]indole (5c).



This compound was isolated as light brown oil. Following the general procedure (Scheme 4S), 30 mg of **1c** afforded 16 mg of **5c** (54% yield). $R_f = 0.7$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$ 2960, 2927, 1742, 1672, 1371, 1176, 1090, 752. **^1H 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 $\text{C}_{27}\text{H}_{26}\text{NO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 444.1633. Found: 444.1618.

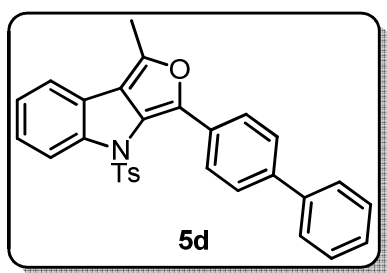
***N*-(2-(5-([1,1'-Biphenyl]-4-yl)-3-hydroxypent-1-en-4-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (1d).**



This compound was isolated as light brown oil. Following the general procedure (Scheme 1S), 75 mg of **1d1** afforded 68 mg of **1d** (85% yield). $R_f = 0.4$ (Hexane/EtOAc = 4/1).

IR (thin film, neat): $\nu_{\text{max}}/\text{cm}^{-1}$ 3432, 3272, 2231, 1599, 1490, 1337, 1161, 1091, 764. **^1H 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, $J = 8.3$ Hz, 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 $\text{C}_{30}\text{H}_{25}\text{NO}_3\text{SNa}$ ($\text{M}+\text{Na}$) $^+$: 259.0793. Found: 259.0778.

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



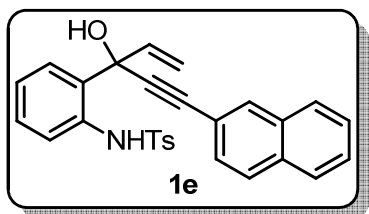
This compound was isolated as colourless solid. Following the general procedure (Scheme 4S), 20 mg of **1d** afforded 11 mg of **5d** (57% yield). M. P. = 175-176 °C. $R_f = 0.7$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\text{max}}/\text{cm}^{-1}$ 2919, 2859, 1763, 1375, 1260, 750.

^1H 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,

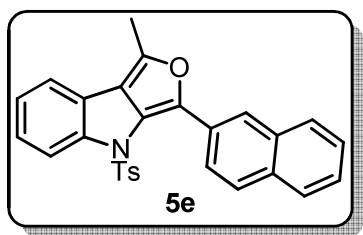
118.6, 21.6, 13.7. **HRMS (ESI):** m/z calcd for $C_{30}H_{24}NO_3S$ ($M+H$)⁺: 478.1476. Found: 478.1459.

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



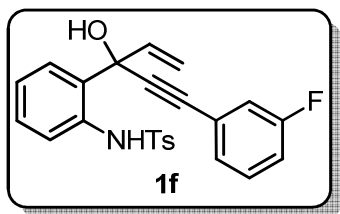
This compound was isolated as light brown oil. Following the general procedure (Scheme 1S), 60 mg of **1e1** afforded 60 mg of **1e** (94% yield). R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$ 3430, 3244, 2923, 2231, 1598, 1497, 1337, 1159, 1091, 757. **¹H NMR (400 MHz, CDCl₃):** 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). **¹³C NMR (100 MHz, CDCl₃):** 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-4H-furo[3,4-*b*]indole (5e).



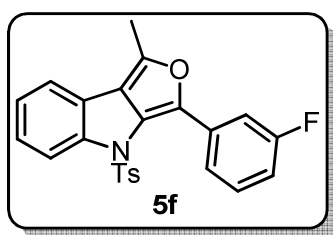
This compound was isolated as pale yellow solid. Following the general procedure (Scheme 4S), 20 mg of **1e** afforded 11 mg of **5e** (54% yield). M. P. = 139-140°C. R_f = 0.7 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$ 2927, 1740, 1601, 1370, 1176, 796, 755. **¹H NMR (400 MHz, CDCl₃):** 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). **¹³C NMR (100 MHz, CDCl₃):** 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).**



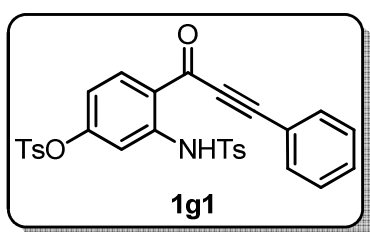
This compound was isolated as pale yellow oil. Following the general procedure (Scheme 1S), 60 mg of **1f** afforded 61 mg of **1f** (95% yield). $R_f = 0.5$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$ 3434, 3235, 3070, 2927, 1709, 1582, 1494, 1373, 1159, 1091, 751. **^1H 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 $\text{C}_{24}\text{H}_{20}\text{FNO}_3\text{SNa}$ ($\text{M}+\text{Na}$) $^+$: 444.1045. Found: 444.1028.

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



This compound was isolated as pale yellow oil. Following the general procedure (Scheme 4S), 20 mg of **1f** afforded 11 mg of **5f** (56% yield). $R_f = 0.8$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$ 3057, 2941, 1595, 1490, 1159, 756. **^1H 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 $\text{C}_{24}\text{H}_{19}\text{FNO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 420.1069. Found: 420.1055.

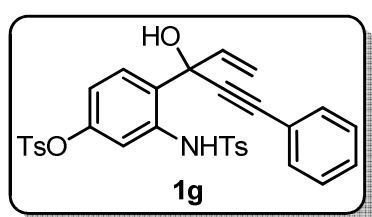
3-(4-Methylphenylsulfonamido)-4-(3-phenylpropioloyl)phenyl methylbenzenesulfonate (**1g1**).



This compound was isolated as pale yellow solid. M. P. = 150-151 °C. $R_f = 0.2$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$ 2923, 2194, 1621, 1597, 1491, 1377, 1165, 1090, 795. **^1H NMR (400 MHz, CDCl_3):** δ 11.16 (s, 1H),

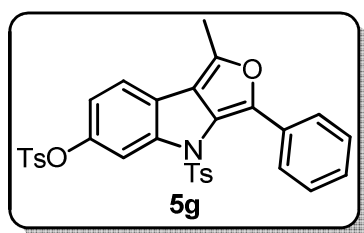
7.94 (d, $J = 2.8$ Hz, 1H), 7.76 (d, $J = 8.3$ Hz, 2H), 7.69-7.63 (m, 6H), 7.58-7.55 (m, 1H), 7.50-7.47 (m, 2H), 7.29- 7.27 (m, 3H), 7.10 (dd, $J = 9.1$ and 2.8 Hz, 1H), 2.40 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 179.2, 146.0, 144.5, 144.0, 139.6, 136.1, 133.4(2C), 131.7, 131.6, 129.94(2C), 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 $\text{C}_{29}\text{H}_{23}\text{NO}_6\text{S}_2\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 568.0864. Found: 568.0844.

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



This compound was isolated as light brown oil. Following the general procedure (Scheme 1S), 70 mg of **1g1** afforded 66 mg of **1g** (90% yield). $R_f = 0.1$ (Hexane/EtOAc = 4/1). IR (thin film, neat): $\nu_{\text{max}}/\text{cm}^{-1}$ 3437, 3244, 2931, 2231, 1596, 1492, 1374, 1164, 1091, 757. ^1H 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 $\text{C}_{31}\text{H}_{27}\text{NO}_6\text{S}_2\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 596.1177. Found: 596.1154.

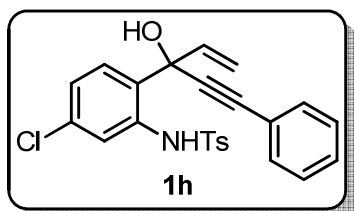
1-Methyl-3-phenyl-4-tosyl-4H-furo[3,4-b]indol-6-yl 4-methylbenzenesulfonate (5g).



This compound was isolated as pale yellow solid. Following the general procedure (Scheme 4S), 20 mg of **3g** afforded 10 mg of **5g** (53% yield). M. P. = 152-153 °C. $R_f = 0.4$ (Hexane/EtOAc = 4/1). IR (thin film, neat): $\nu_{\text{max}}/\text{cm}^{-1}$ 2924, 2856, 1673, 1596, 1373, 1178, 763. ^1H 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),

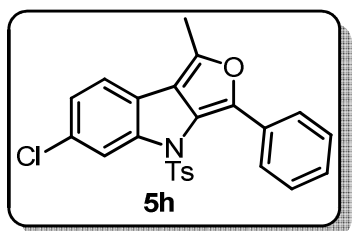
127.3(2C), 125.6, 120.2, 119.5, 119.0, 115.4, 21.8, 21.6, 13.7. **HRMS (ESI):** m/z calcd for $C_{31}H_{26}NO_6S_2$ (M+H)⁺: 572.1202. Found: 572.1180.

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



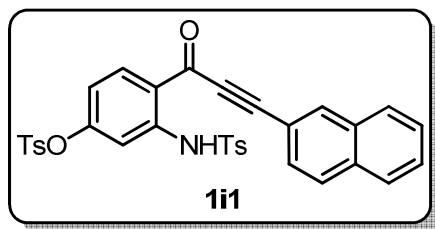
This compound was isolated as pale yellow oil. Following the general procedure (Scheme 1S), 60 mg of **1h1** afforded 54 mg of **1h** (85% yield). R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3441, 3272, 2199, 1599, 1491, 1336, 1159, 1091, 757. **¹H NMR (400 MHz, CDCl₃):** 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). **¹³C NMR (100 MHz, CDCl₃):** 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).



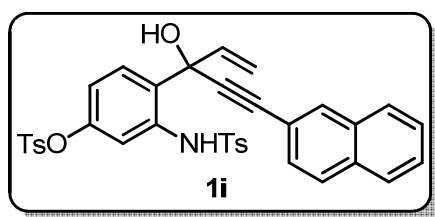
This compound was isolated as light brown oil. Following the general procedure (Scheme 4S), 20 mg of **1h** afforded 11 mg of **5h** (54% yield). R_f = 0.7 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 3056, 2939, 1595, 1491, 1160, 757. **¹H NMR (400 MHz, CDCl₃):** δ 8.15 (d, J = 1.8 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). **¹³C NMR (100 MHz, CDCl₃):** 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-methylbenzenesulfonate (1i1).



This compound was isolated as pale yellow solid. M. P. = 145-146 °C. R_f = 0.2 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$ 3061, 2924, 2190, 1698, 1619, 1489, 1377, 1176, 1090, 795. **^1H 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 $\text{C}_{33}\text{H}_{26}\text{NO}_6\text{S}_2$ ($\text{M}+\text{H}$) $^+$: 596.1202. Found: 596.1178.

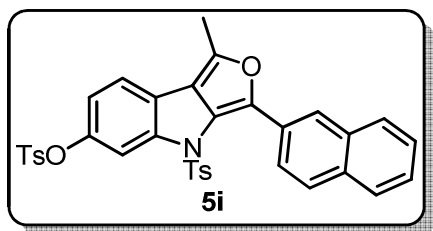
4-(3-Hydroxy-5-(naphthalen-2-yl)pent-1-en-4-yn-3-yl)-3-(4-methylphenylsulfonamido)phenyl 4-methylbenzenesulfonate (1i).



This compound was isolated as pale yellow oil. Following the general procedure (Scheme 1S), 70 mg of **1i1** afforded 67 mg of **1i** (92% yield). R_f = 0.2 (Hexane/EtOAc = 5/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$ 3449, 3233, 2923, 2231, 1598, 1491, 1376, 1163, 795. **^1H 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 $\text{C}_{35}\text{H}_{29}\text{NO}_6\text{S}_2\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 646.1334. Found: 646.1308.

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

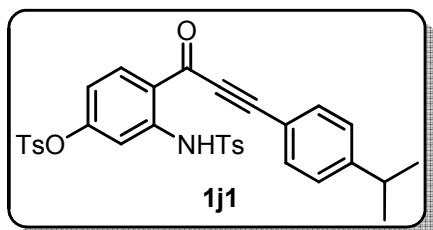
4-



This compound was isolated as pale yellow solid. M. P. = 178-179 °C. Following the general procedure (Scheme 4S), 30 mg of **3i** afforded 15 mg of **5i** (51% yield). R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$ 2927, 2856, 1673, 1596, 1373, 1179,

756. **^1H 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 $\text{C}_{35}\text{H}_{28}\text{NO}_6\text{S}_2$ ($\text{M}+\text{H}$) $^+$: 622.1358. Found: 622.1332.

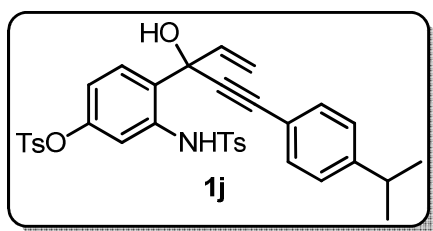
4-(3-(4-Isopropylphenyl)propioloyl)-3-(4-methylphenylsulfonamido)phenyl 4-methylbenzenesulfonate (**1j1**).



This compound was isolated as pale yellow oil. R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$ 2964, 2923, 2190, 1620, 1599, 1490, 1377, 1151, 1091, 795. **^1H 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 $\text{C}_{32}\text{H}_{30}\text{NO}_6\text{S}_2$ ($\text{M}+\text{H}$) $^+$: 588.1515. Found: 588.1485.

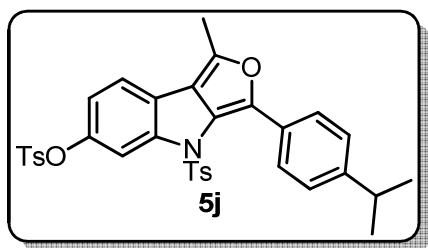
4-(3-Hydroxy-5-(4-isopropylphenyl)pent-1-en-4-yn-3-yl)-3-(4-methylphenylsulfonamido)phenyl 4-methylbenzenesulfonate (**1j**).



This compound was isolated as light brown oil. Following the general procedure (Scheme 1S), 70 mg of **1j1** afforded 62 mg of **1j** (84% yield). R_f = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$

3449, 3251, 2961, 2227, 1598, 1493, 1375, 1164, 1091, 758. **¹H NMR (400 MHz, CDCl₃):** 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). **¹³C NMR (100 MHz, CDCl₃):** 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 C₃₄H₃₃NO₆S₂Na (M+Na)⁺: 638.1647. Found: 638.1620.

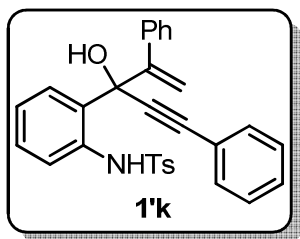
3-(4-Isopropylphenyl)-1-methyl-4-tosyl-4*H*-furo[3,4-*b*]indol-6-yl methylbenzenesulfonate (5j).



This compound was isolated as light brown oil. Following the general procedure (Scheme 4S), 20 mg of **1j** afforded 11 mg of **5j** (56% yield). *R_f* = 0.2 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** *v*_{max}/cm⁻¹ 2960, 2926, 1597, 1463, 1375, 1179, 1091, 788. **¹H**

NMR (400 MHz, CDCl₃): 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). **¹³C NMR (100 MHz, CDCl₃):** 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 C₃₄H₃₂NO₆S₂ (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).**

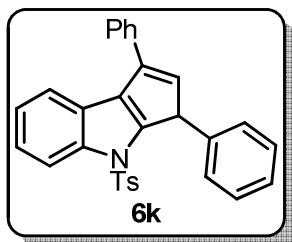


This compound was isolated as pale yellow oil. Following the general procedure (Scheme 1S), 70 mg of **1a1** afforded 79 mg of **1'k** (88% yield). *R_f* = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** *v*_{max}/cm⁻¹ 3431, 3271, 3059, 2199, 1599, 1492, 1337, 1159, 1091, 757. **¹H NMR (400 MHz, CDCl₃):** 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),

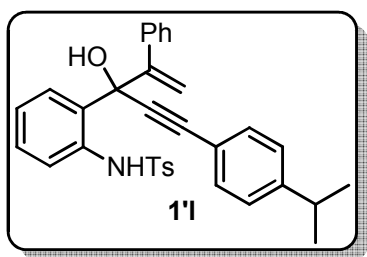
7.18 (s, 1H), 7.11(d, $J = 7.2$ Hz, 2H), 6.98-6.94 (m, 1H), 5.54 (s, 1H), 5.26 (s, 1H), 3.32 (s, 1H), 2.35 (s, 3H). **^{13}C NMR (100 MHz, CDCl_3):** δ 149.6, 143.7, 138.4, 137.1, 136.2, 133.1, 131.7(2C), 129.8, 129.6, 129.5(2C), 129.1(2C), 128.5(2C), 128.3, 127.7, 127.68(2C), 127.6(2C), 122.9, 121.8, 119.2, 116.6, 89.6, 88.9, 76.7, 21.5. **HRMS (ESI):** m/z calcd for $\text{C}_{30}\text{H}_{25}\text{NO}_3\text{SNa}$ ($\text{M}+\text{Na}$) $^+$: 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 (Scheme 6S), 30 mg of **1'k** afforded 23 mg of **6k** (78% yield). $R_f = 0.8$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\text{max}}/\text{cm}^{-1}$ 3058, 2923, 2854, 1597, 1493, 1448, 1374, 1175, 1089, 750. **^1H 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 $\text{C}_{30}\text{H}_{24}\text{NO}_2\text{S}$ ($\text{M}+\text{H}$) $^+$: 462.1528. Found: 462.1511.

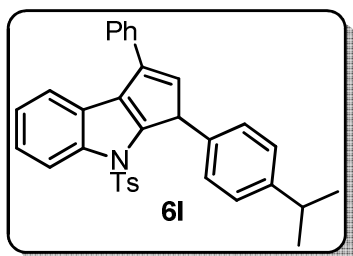
N-(2-(3-Hydroxy-5-(4-isopropylphenyl)-2-phenylpent-1-en-4-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (1'l).



This compound was isolated as pale yellow oil. Following the general procedure (Scheme 1S), 80 mg of **1c1** afforded 91 mg of **1'l** (91% yield). $R_f = 0.5$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\text{max}}/\text{cm}^{-1}$ 3441, 3266, 2959, 2924, 2226, 1600, 1493, 1338, 1160, 1092, 758. **^1H 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.

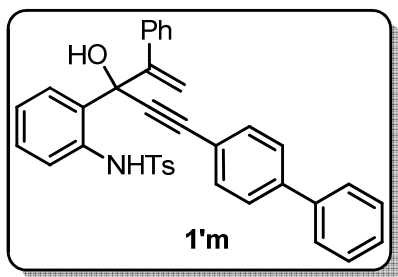
3-(4-Isopropylphenyl)-1-phenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indole (6l).



This compound was isolated as light brown oil. Following the general procedure (Scheme 6S), 30 mg of **1l** 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. **¹H NMR (400 MHz, CDCl₃):** 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). **¹³C NMR (100 MHz, CDCl₃):** 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.

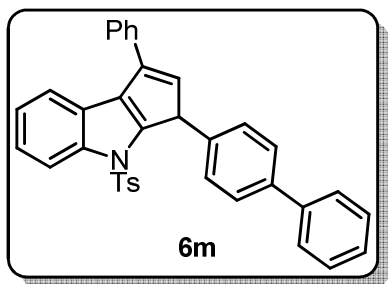
N-(2-(5-([1,1'-Biphenyl]-4-yl)-3-hydroxy-2-phenylpent-1-en-4-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (1'm).



This compound was isolated as pale yellow oil. Following the general procedure (Scheme 1S), 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. **¹H NMR (400 MHz, CDCl₃):** 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). **¹³C NMR (100 MHz, CDCl₃):** 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).

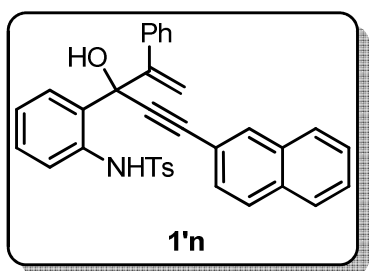


This compound was isolated as light brown oil. Following the general procedure (Scheme 6S), 30 mg of **1'm** afforded 20 mg of **6m** (68% yield). $R_f = 0.8$ (Hexane/EtOAc = 4/1).

IR (thin film, neat): $\nu_{\max}/\text{cm}^{-1}$ 3059, 3029, 2924, 1598, 1486, 1449, 1372, 1174, 1009, 755. **^1H 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 $\text{C}_{36}\text{H}_{28}\text{NO}_2\text{S} (\text{M}+\text{H})^+$: 538.1841. Found: 538.1819.

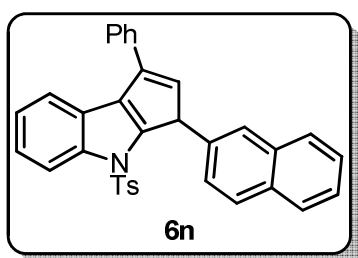
***N*-(2-(3-Hydroxy-5-(naphthalen-2-yl)-2-phenylpent-1-en-4-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (**1'n**).**



This compound was isolated as pale yellow oil. Following the general procedure (Scheme 1S), 70 mg of **1e1** afforded 80 mg of **1'n** (92% yield). $R_f = 0.3$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$ 3437, 3291, 3058, 2925, 2229, 1598, 1583, 1493, 1337, 1160, 1091, 815, 749. **^1H 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 $\text{C}_{34}\text{H}_{27}\text{NO}_3\text{SNa} (\text{M}+\text{Na})^+$: 552.1609. Found: 552.1593.

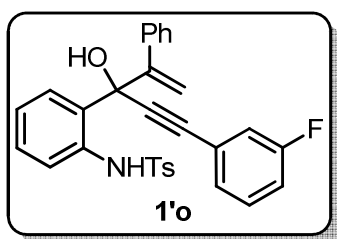
3-(Naphthalen-2-yl)-1-phenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indole (6n**).**



This compound was isolated as light brown oil. Following the general procedure (Scheme 6S), 30 mg of **1'n** afforded 20 mg of **6n** (69% yield). $R_f = 0.8$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$ 3054, 2924, 1735, 1598, 1448, 1372,

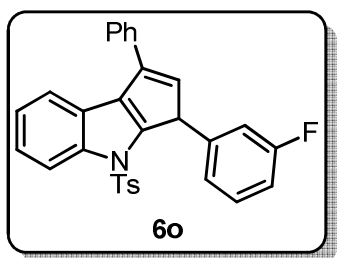
1175, 913, 747. **¹H NMR (400 MHz, CDCl₃):** δ 8.16 (d, *J* = 8.2 Hz, 1H), 7.79-7.71 (m, 6H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.52-7.47 (m, 5H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.10-7.02 (m, 4H), 6.62 (d, *J* = 8.1 Hz, 2H), 6.40 (d, *J* = 2.0 Hz, 1H), 5.25 (d, *J* = 1.9 Hz, 1H), 2.15 (s, 3H). **¹³C NMR (100 MHz, CDCl₃):** 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 C₃₄H₂₆NO₂S (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 (Scheme 1S), 70 mg of **1f1** afforded 78 mg of **1'o** (88% yield). *R_f* = 0.3 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** *v*_{max}/cm⁻¹ 3432, 3281, 3066, 2928, 2203, 1737, 1582, 1492, 1338, 1159, 757. **¹H NMR (400 MHz, CDCl₃):** 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). **¹⁹F NMR (400 MHz, CDCl₃):** δ -112.36. **¹³C NMR (100 MHz, CDCl₃):** 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 C₃₀H₂₄FNO₃SNa (M+Na)⁺: 520.1358. Found: 520.1337.

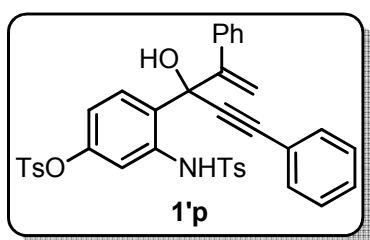
3-(3-Fluorophenyl)-1-phenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indole (6o).



This compound was isolated as light brown oil. Following the general procedure (Scheme 6S), 30 mg of **1'o** afforded 17 mg of **6o** (60% yield). *R_f* = 0.8 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** *v*_{max}/cm⁻¹ 3062, 2955, 2925, 1613, 1596, 1487, 1373, 1175, 793, 758. **¹H NMR (400 MHz, CDCl₃):** 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). **¹⁹F NMR (400 MHz, CDCl₃):** δ

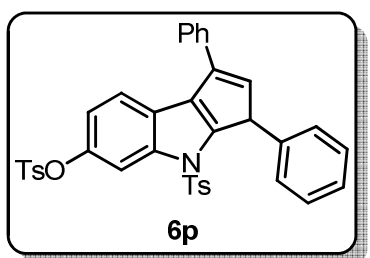
–113.2. ^{13}C NMR (100 MHz, CDCl_3): δ 162.9 (d, J = 244.5 Hz, 1C), 149.1, 144.8, 140.3, 139.9, 138.9 (d, J = 7.3 Hz, 1C), 135.4 (d, J = 5.8 Hz, 1C), 133.3, 130.0 (d, J = 8.3 Hz, 1C), 129.6(2C), 129.0 (d, J = 6.4 Hz, 1C), 128.8, 128.7(2C), 128.1, 127.4(2C), 127.0, 126.8(2C), 124.7, 124.1 (d, J = 9.8 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 $\text{C}_{30}\text{H}_{23}\text{FNO}_2\text{S}$ ($\text{M}+\text{H}$) $^+$: 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 (Scheme 1S), 70 mg of **1g1** afforded 73 mg of **1'p** (87% yield). R_f = 0.1 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\text{max}}/\text{cm}^{-1}$ 3445, 3291, 3056, 2923, 2229, 1734, 1598, 1492, 1375, 1338, 1195, 1091, 914, 758. **^1H 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 = 9.0 and 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 $\text{C}_{37}\text{H}_{31}\text{NO}_6\text{S}_2\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 672.1490. Found: 672.1462.

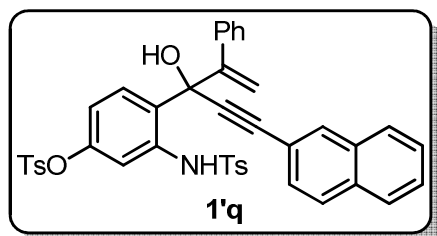
1,3-Diphenyl-4-tosyl-3,4-dihydrocyclopenta[b]indol-6-yl 4-methylbenzenesulfonate (6p).



This compound was isolated as light brown oil. Following the general procedure (Scheme 6S), 30 mg of **1'p** afforded 22 mg of **6p** (74% yield). R_f = 0.4 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\text{max}}/\text{cm}^{-1}$ 3062, 2925, 1735, 1597, 1493, 1448, 1373, 1192, 1178, 1091, 909, 735. **^1H 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,

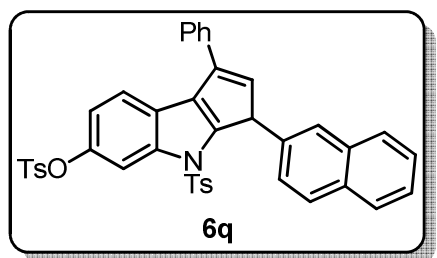
127.6, 127.2, 127.1(2C), 124.4, 118.2, 115.1, 114.0, 52.5, 21.8, 21.6. **HRMS (ESI):** m/z calcd for $C_{37}H_{30}NO_5S_2$ (M+H)⁺: 632.1565. Found: 632.1575.

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 (Scheme 1S), 70 mg of **1i1** afforded 74 mg of **1'q** (90% yield). $R_f = 0.1$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$ 3437, 3273, 3062, 2926, 2194, 1735, 1597, 1493, 1374, 1194, 1091, 913, 748. **¹H NMR (400 MHz, CDCl₃):** 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). **¹³C NMR (100 MHz, CDCl₃):** 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.

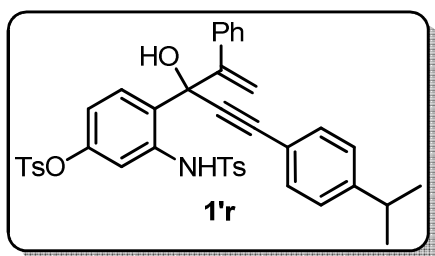
3-(Naphthalen-2-yl)-1-phenyl-4-tosyl-3,4-dihydrocyclopenta[b]indol-6-yl 4-methylbenzenesulfonate (6q).



This compound was isolated as light brown oil. Following the general procedure (Scheme 6S), 30 mg of **1'q** afforded 19 mg of **6q** (65% yield). $R_f = 0.4$ (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$ 3059, 2925, 2852, 1597, 1448, 1373, 1192, 1177, 1092, 745. **¹H NMR (400 MHz, CDCl₃):** 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). **¹³C NMR (100 MHz, CDCl₃):** 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),

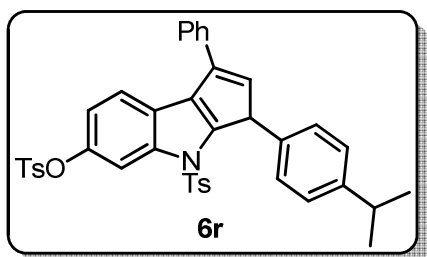
128.66(2C), 128.6, 128.2, 128.1, 128.0, 127.9, 127.5, 127.1(2C), 126.6(2C), 126.3, 126.2, 125.9, 124.3, 118.2, 115.2, 114.0, 52.5, 21.8, 21.4. **HRMS (ESI):** m/z calcd for $C_{41}H_{32}NO_5S_2$ ($M+H$)⁺: 682.1722. Found: 682.1693.

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 (Scheme 1S), 70 mg of **1j1** afforded 70 mg of **1'r** (85% yield). R_f = 0.2 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$ 3451, 3276, 2961, 2923, 2227, 1598, 1493, 1376, 1165, 1091, 793. **¹H NMR (400 MHz, CDCl₃):** 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). **¹³C NMR (100 MHz, CDCl₃):** 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.

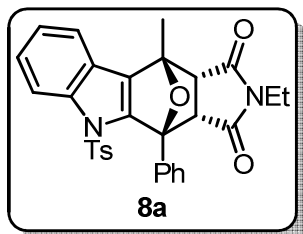
3-(4-Isopropylphenyl)-1-phenyl-4-tosyl-3,4-dihydrocyclopenta[b]indol-6-yl 4-methylbenzenesulfonate (6r).



This compound was isolated as light brown oil. Following the general procedure (Scheme 6S), 30 mg of **1'r** afforded 24 mg of **6r** (83% yield). R_f = 0.5 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** $\nu_{\max}/\text{cm}^{-1}$ 2960, 2929, 1738, 1597, 1448, 1374, 1192, 1178, 1094, 741. **¹H NMR (400 MHz, CDCl₃):** 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). **¹³C NMR (100 MHz, CDCl₃):** 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,

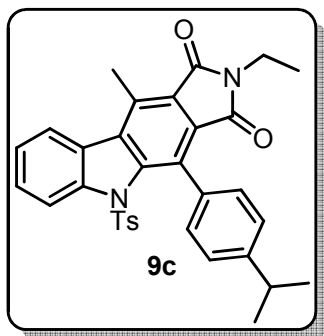
127.8, 127.2(2C), 127.1(2C), 126.7(2C), 124.4, 118.1, 115.1, 113.9, 52.2, 33.8, 24.2(2C), 21.8, 21.6. **HRMS (ESI):** m/z calcd for $C_{40}H_{36}NO_5S_2$ (M+H)⁺: 674.2038. Found: 674.2008.

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).



This compound was isolated as colourless solid. M. P. = 160-161°C. Following the general procedure (Scheme 7S), 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. **¹H NMR (400 MHz, CDCl₃):** 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). **¹³C NMR (100 MHz, CDCl₃):** 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.

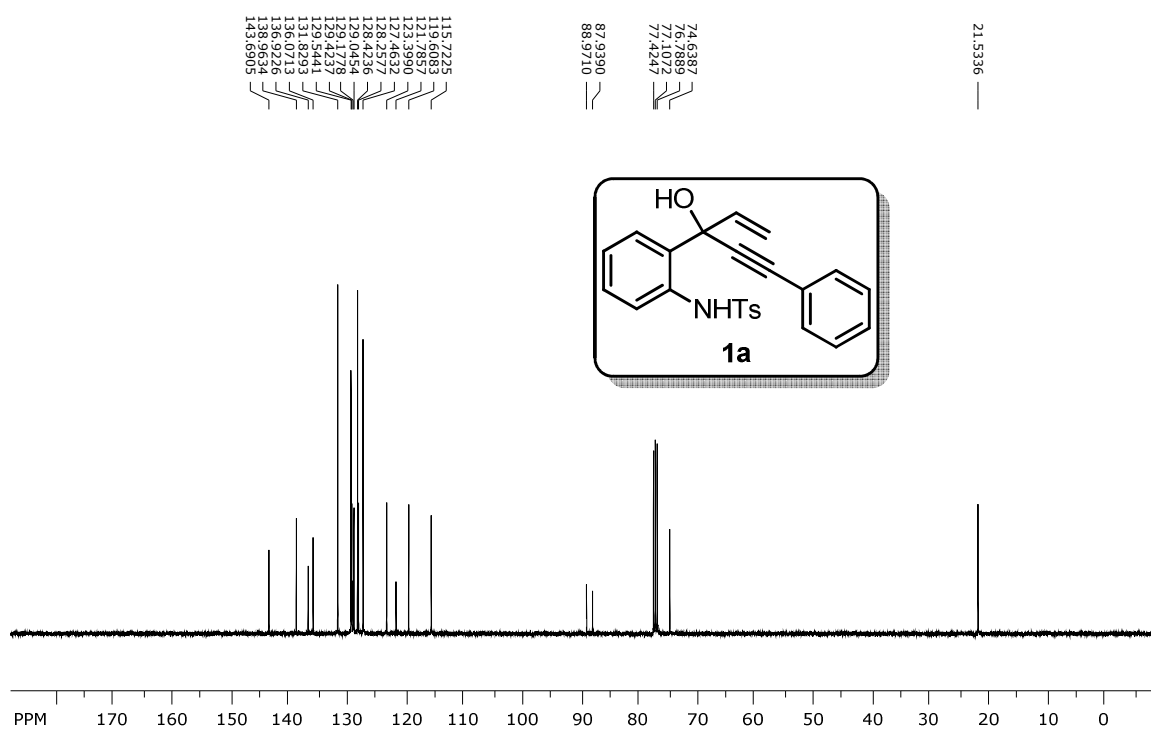
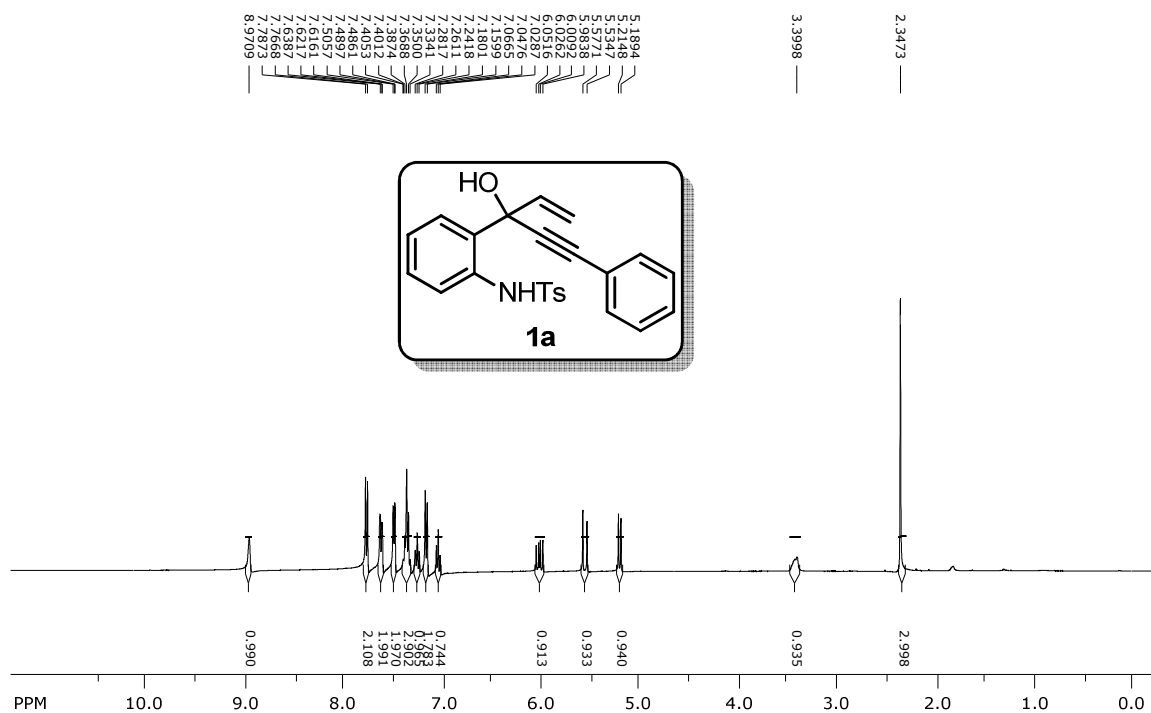
2-Ethyl-4-(4-isopropylphenyl)-10-methyl-5-tosylpyrrolo[3,4-*b*]carbazole-1,3(2*H*,5*H*)-dione (9c).

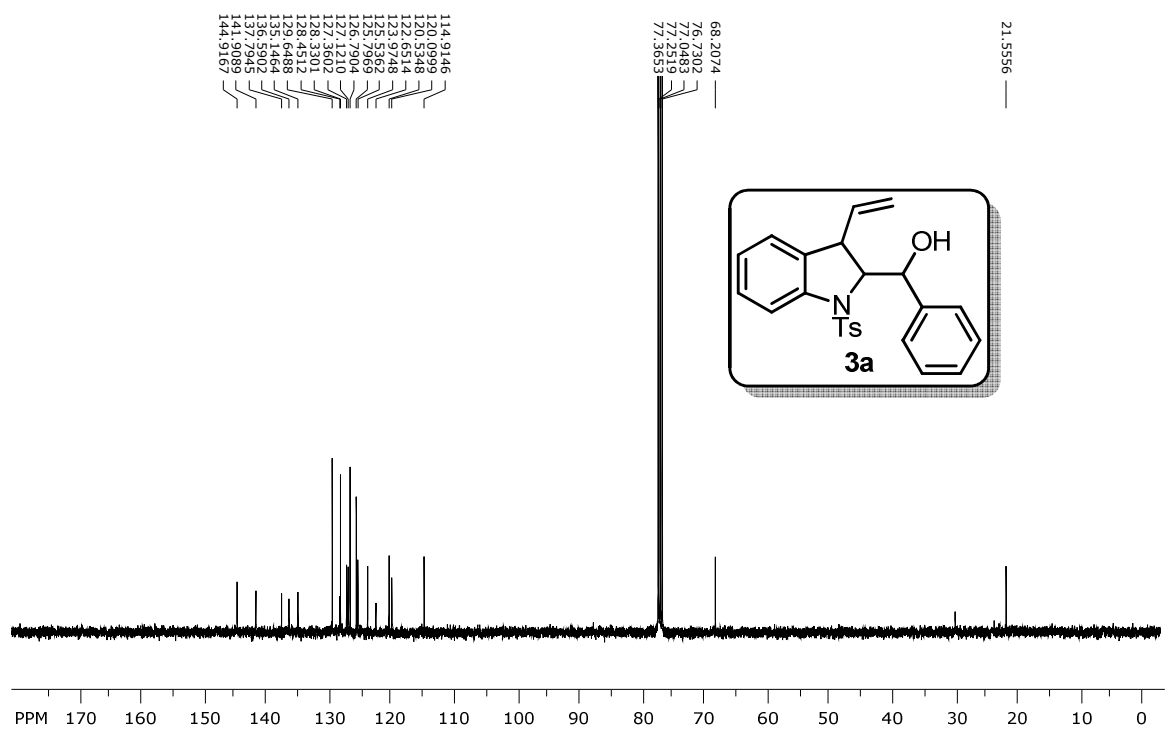
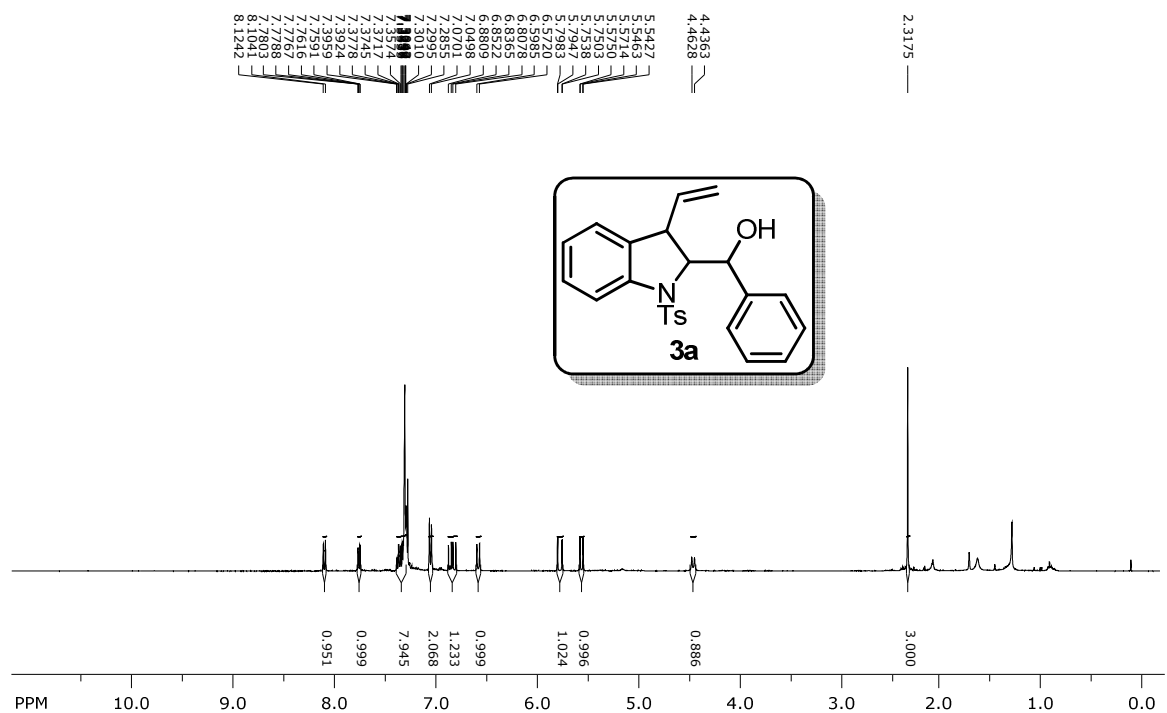


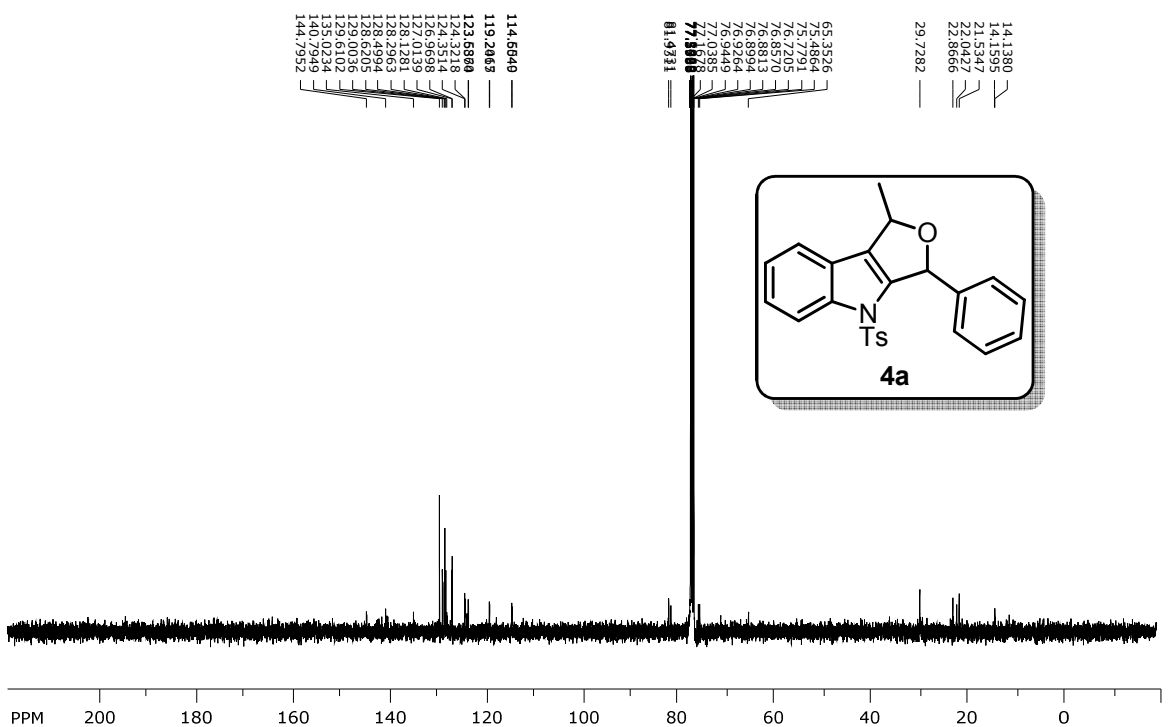
This compound was isolated as colourless solid. Following the general procedure (Scheme 8S), 40 mg of **5c** afforded 31 mg of **9c** (62% yield). M. P. = 228-229 °C. R_f = 0.6 (Hexane/EtOAc = 4/1). **IR (thin film, neat):** ν_{max}/cm^{-1} 2961, 2870, 1762, 1704, 1450, 1400, 1362, 1176, 1093, 1051, 734. **¹H NMR (400 MHz, CDCl₃):** 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). **¹³C NMR (100 MHz, CDCl₃):** 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.

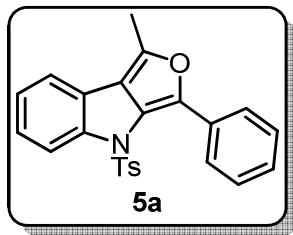
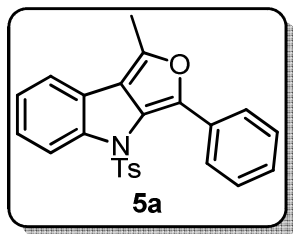
Copies of ^1H and ^{13}C -NMR spectra of all the new compounds reported in this study

(Note: In general, in a ^1H NMR spectrum recorded in CDCl_3 , a peak at around δ 1.6 refers to moisture in the solvent/sample and a peak at about δ 1.2 refers to oil/grease present in the sample. In a ^{13}C NMR spectrum recorded in CDCl_3 , a peak at about δ 29.7 usually represents oil/grease)

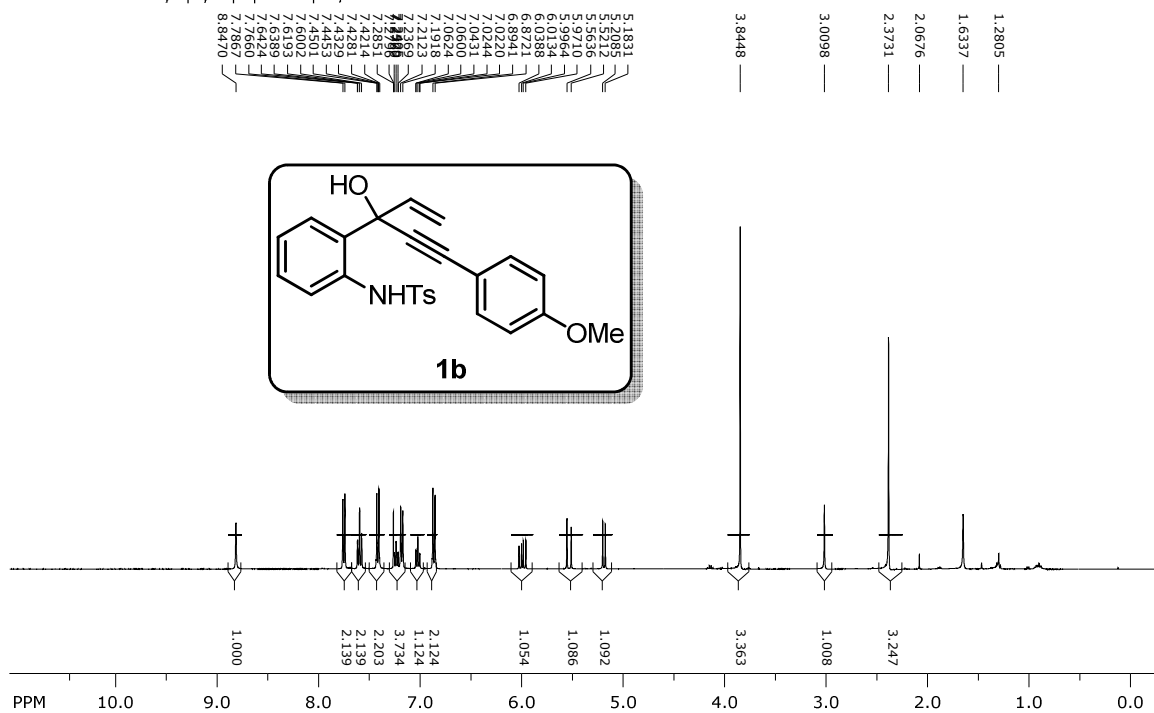




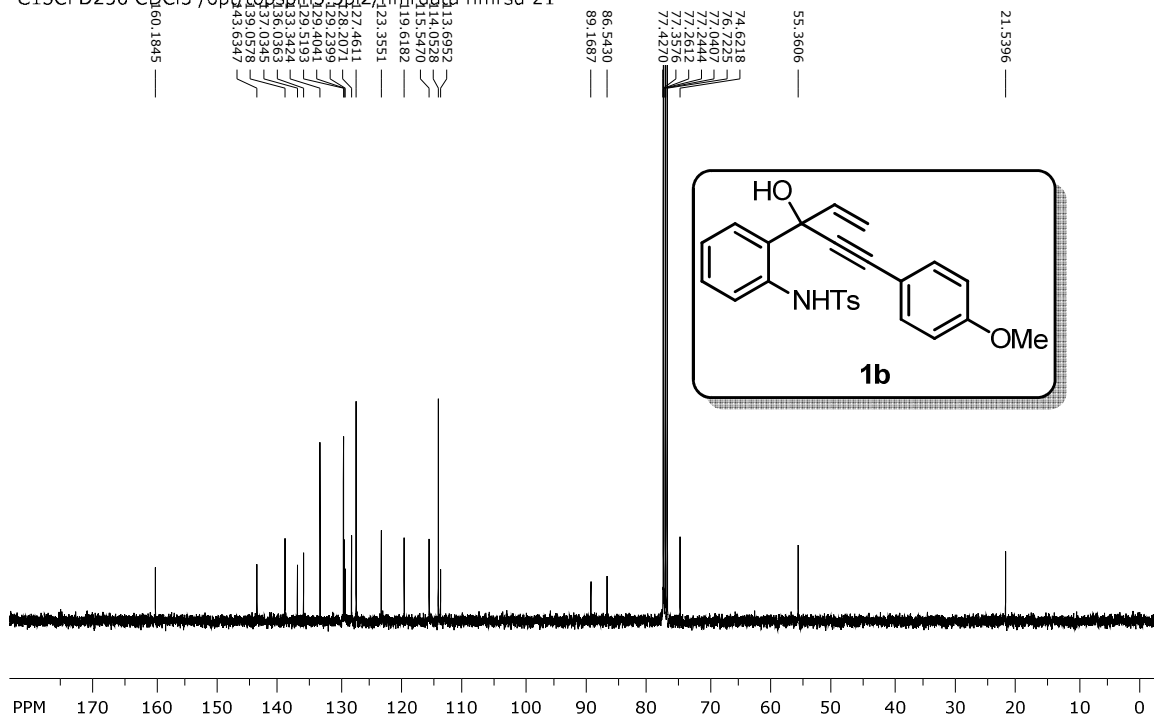
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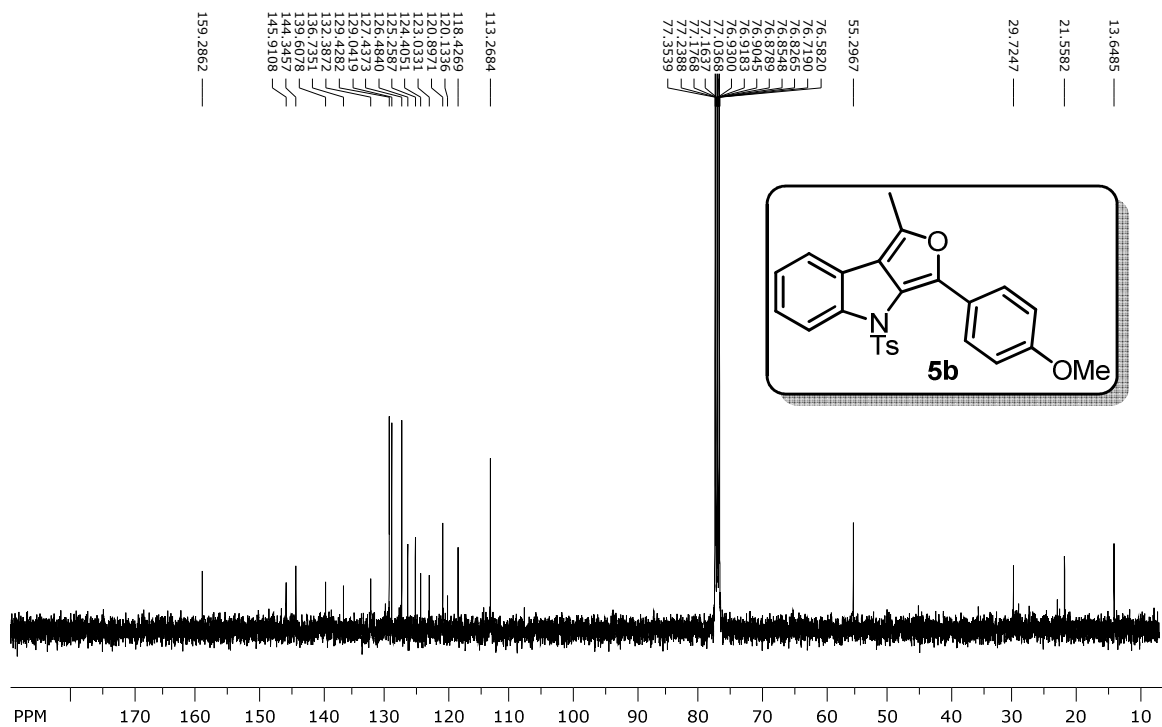
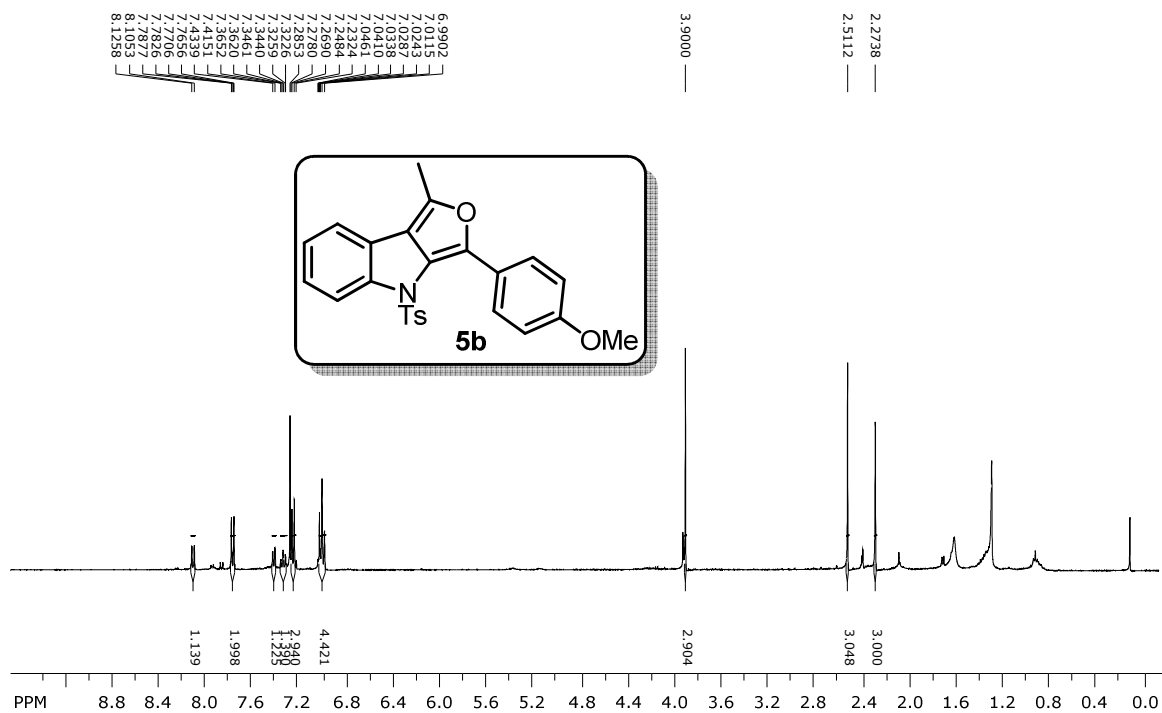


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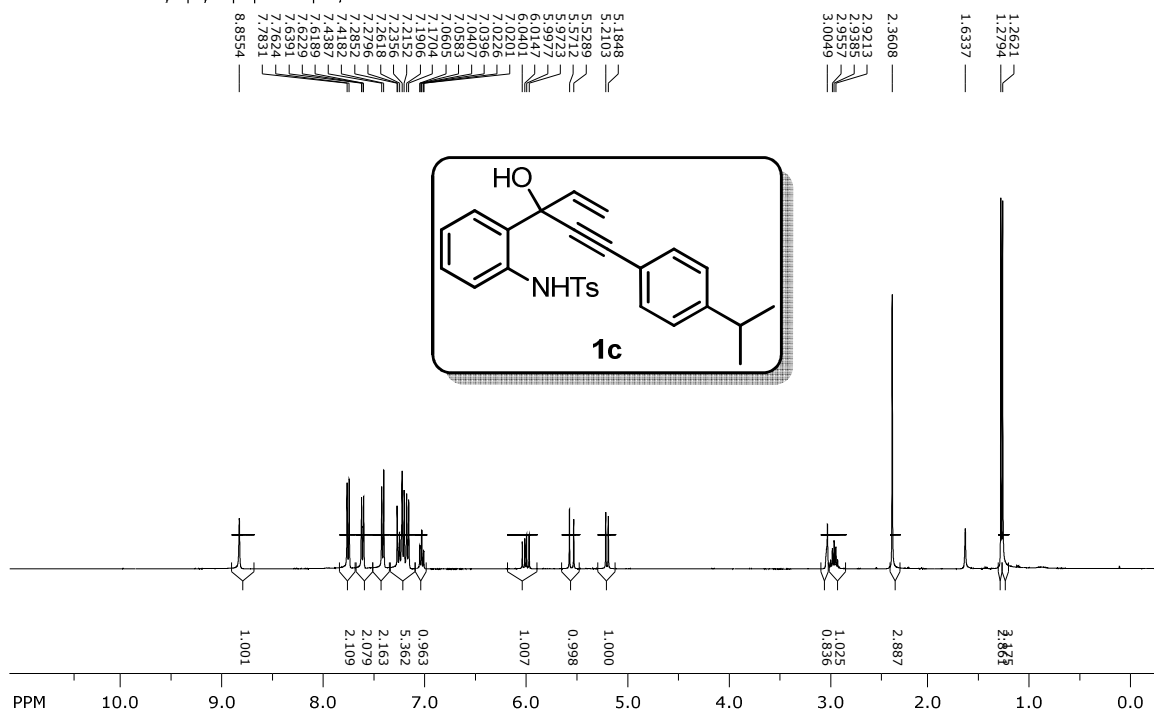


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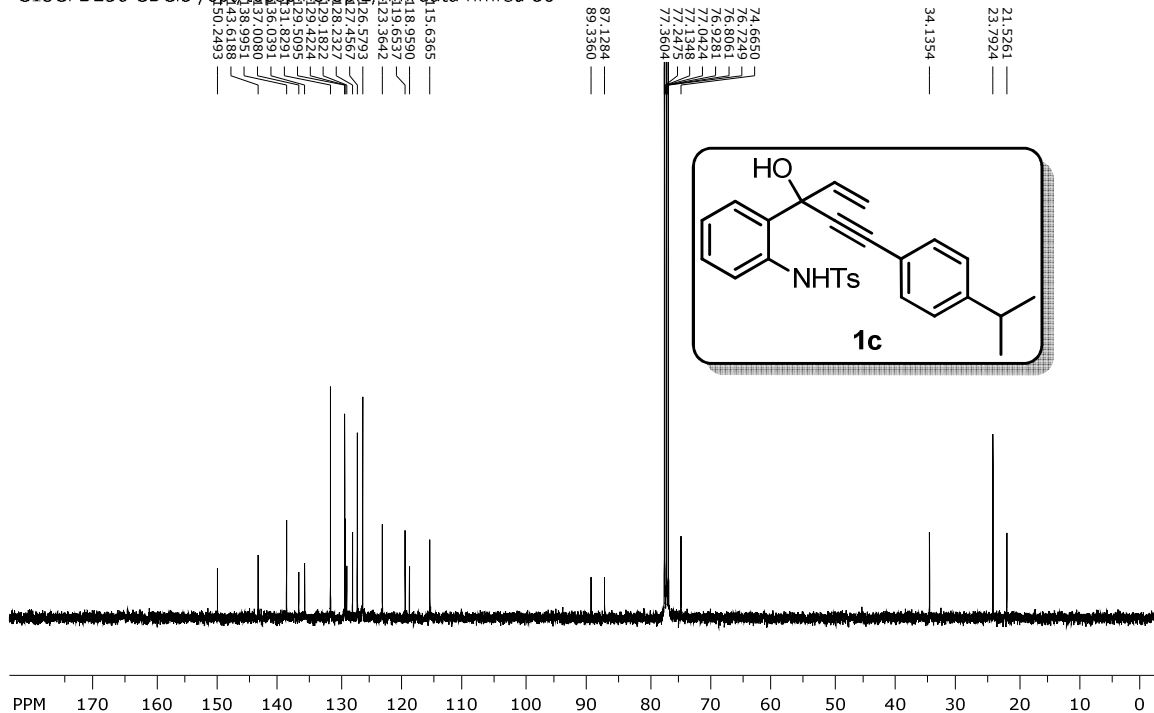


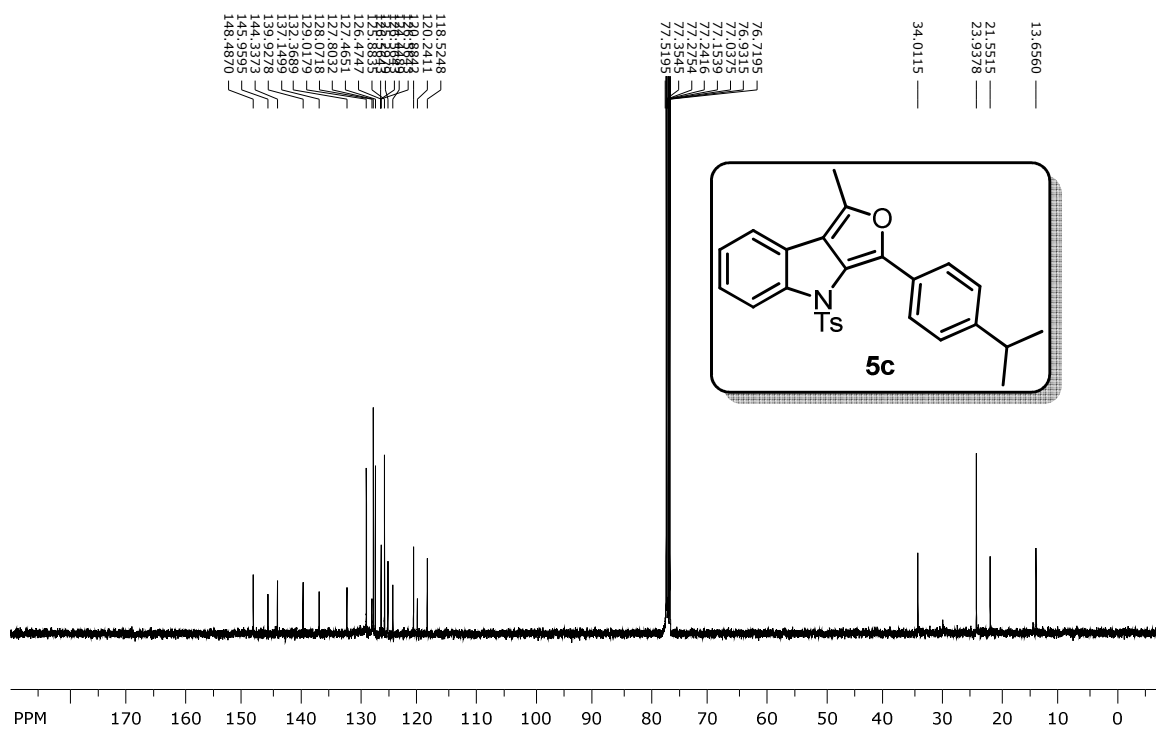
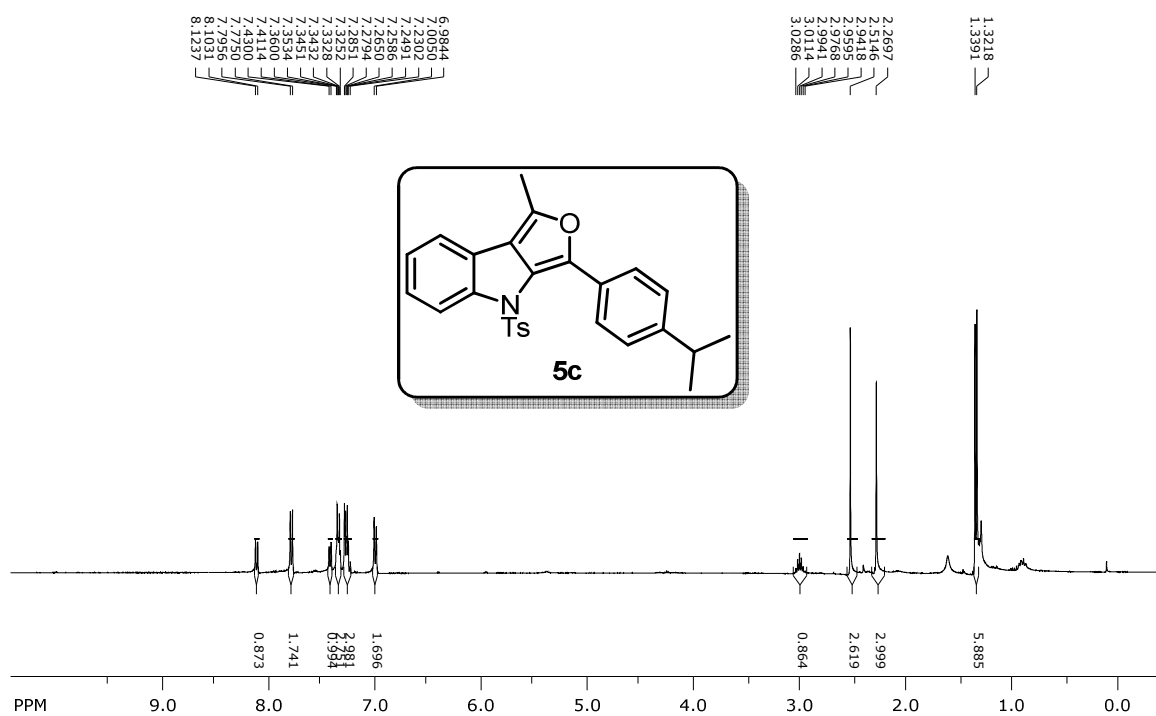


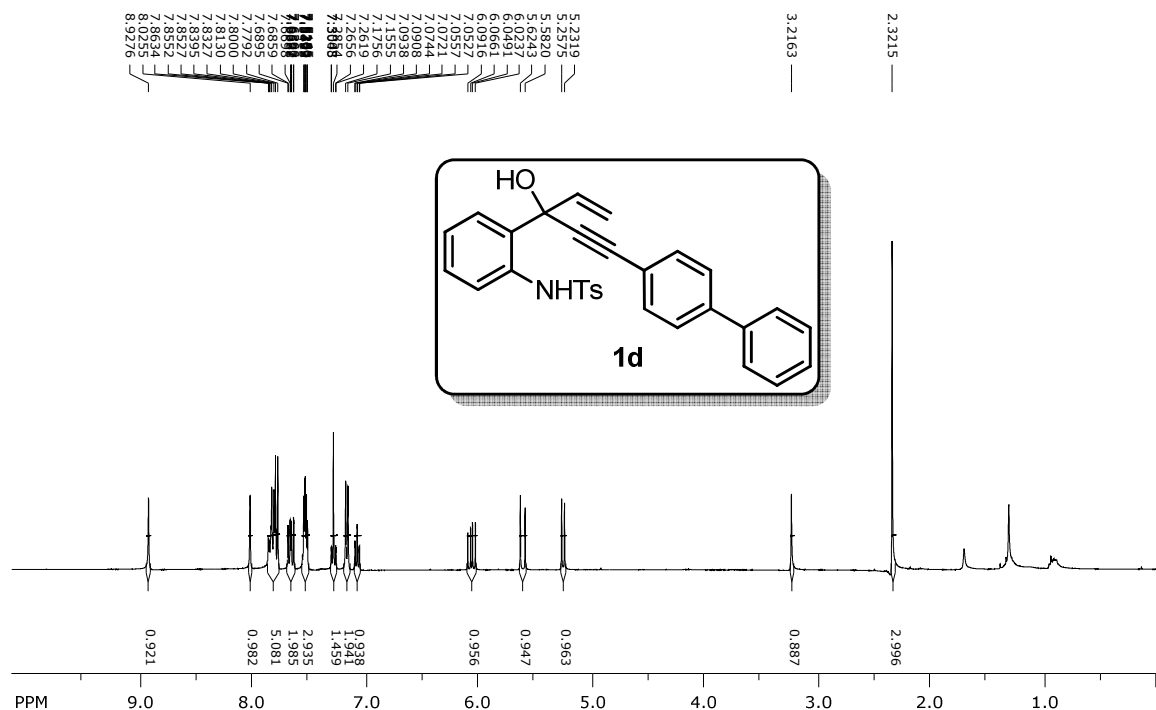
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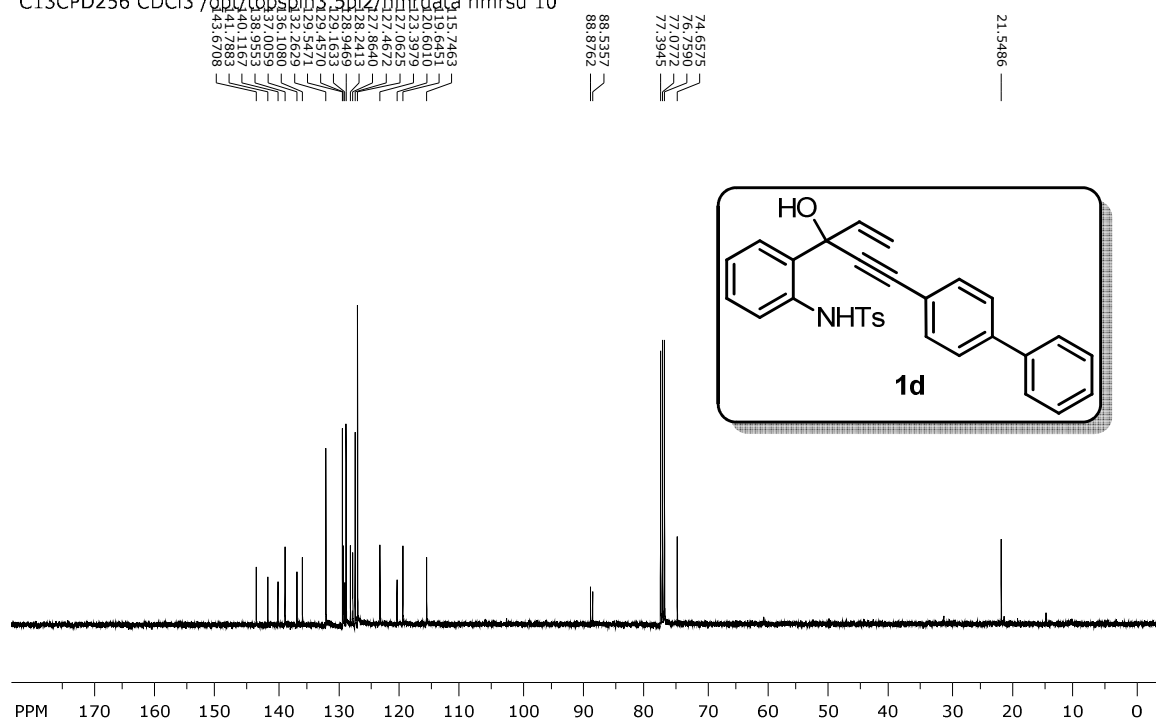
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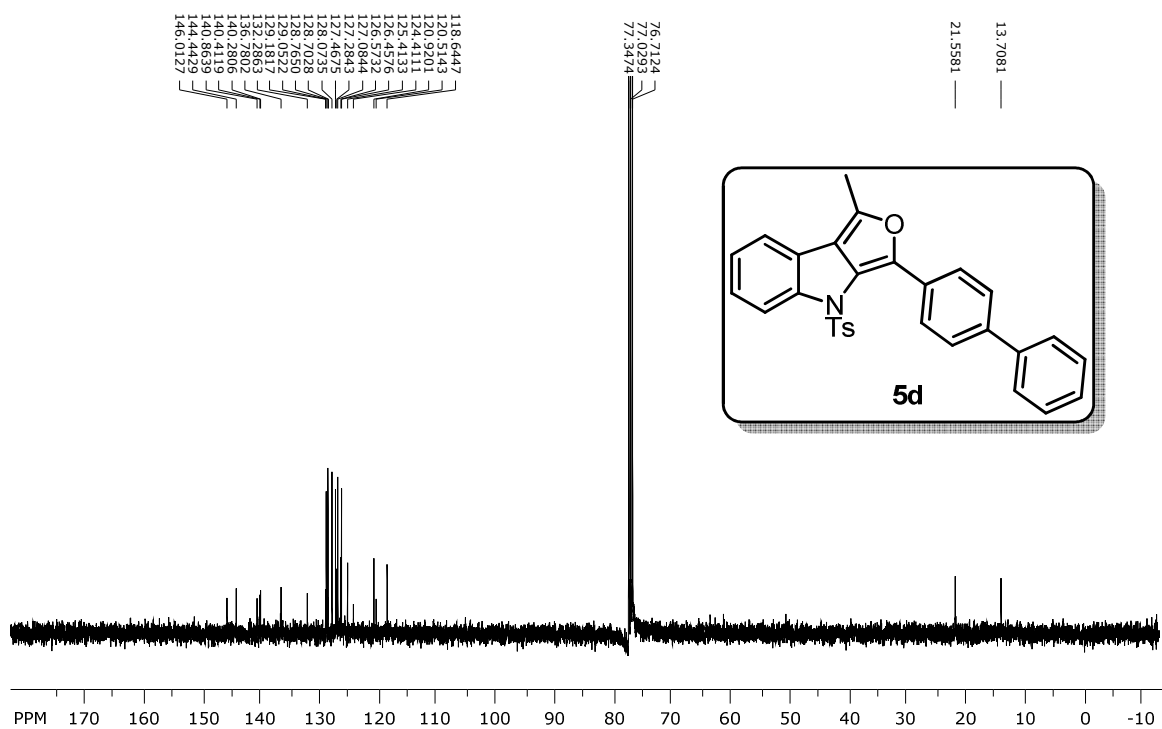
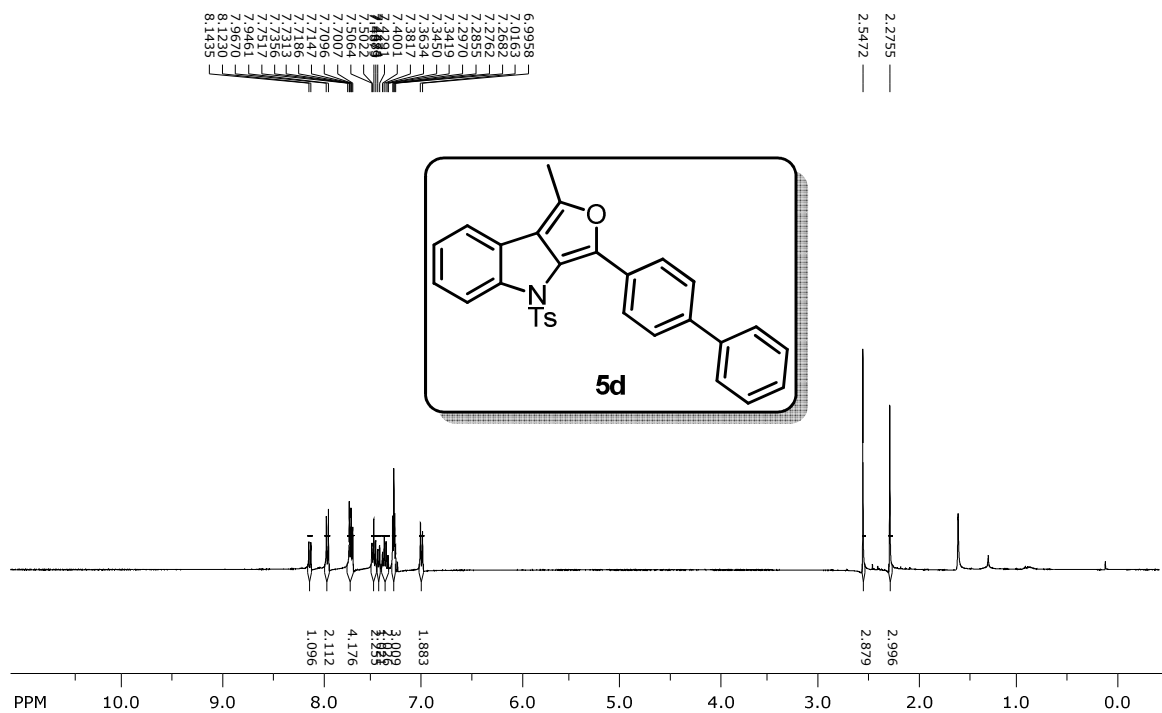


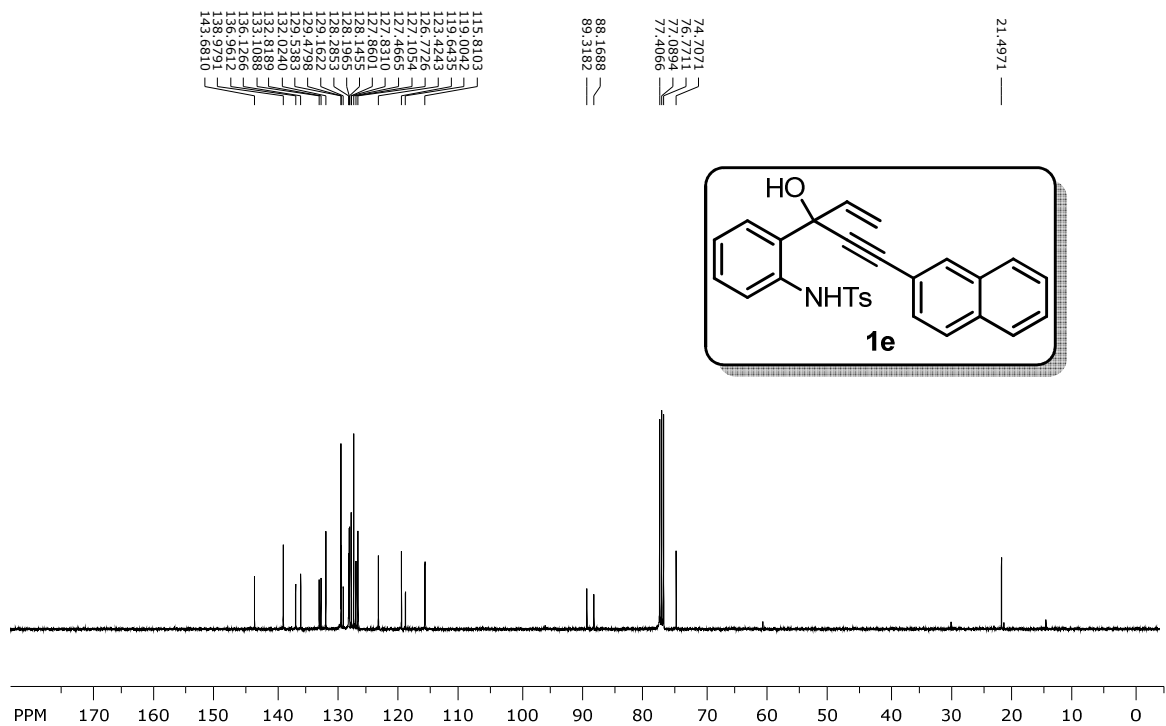
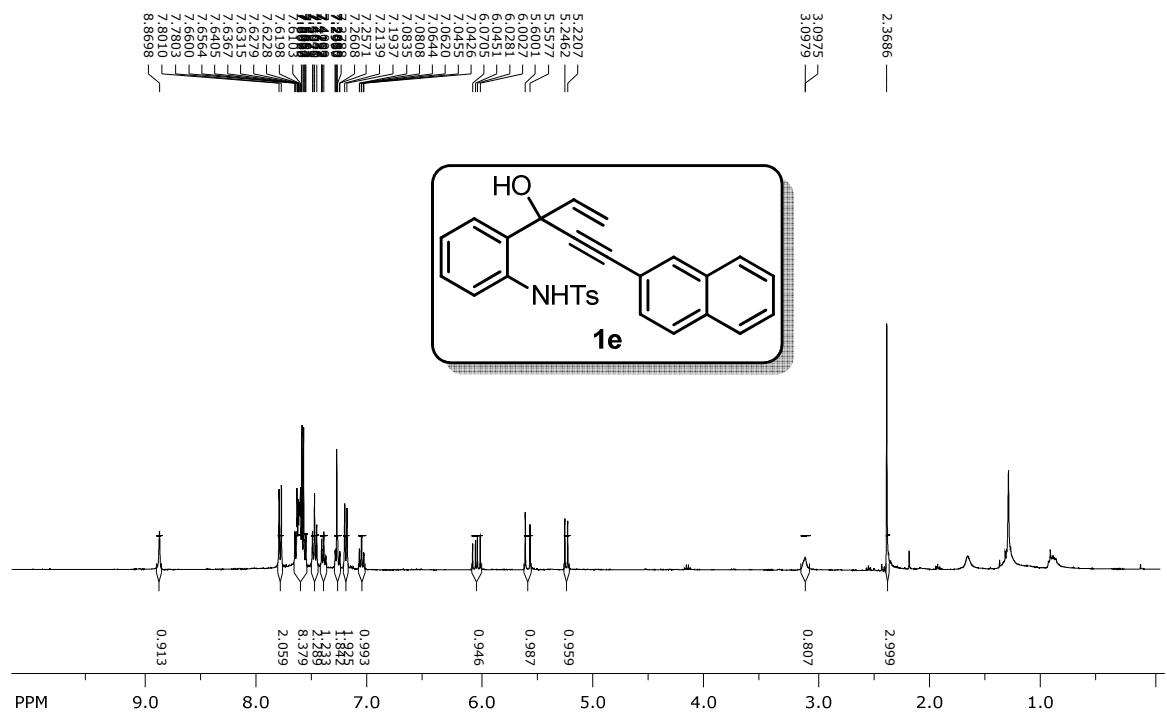


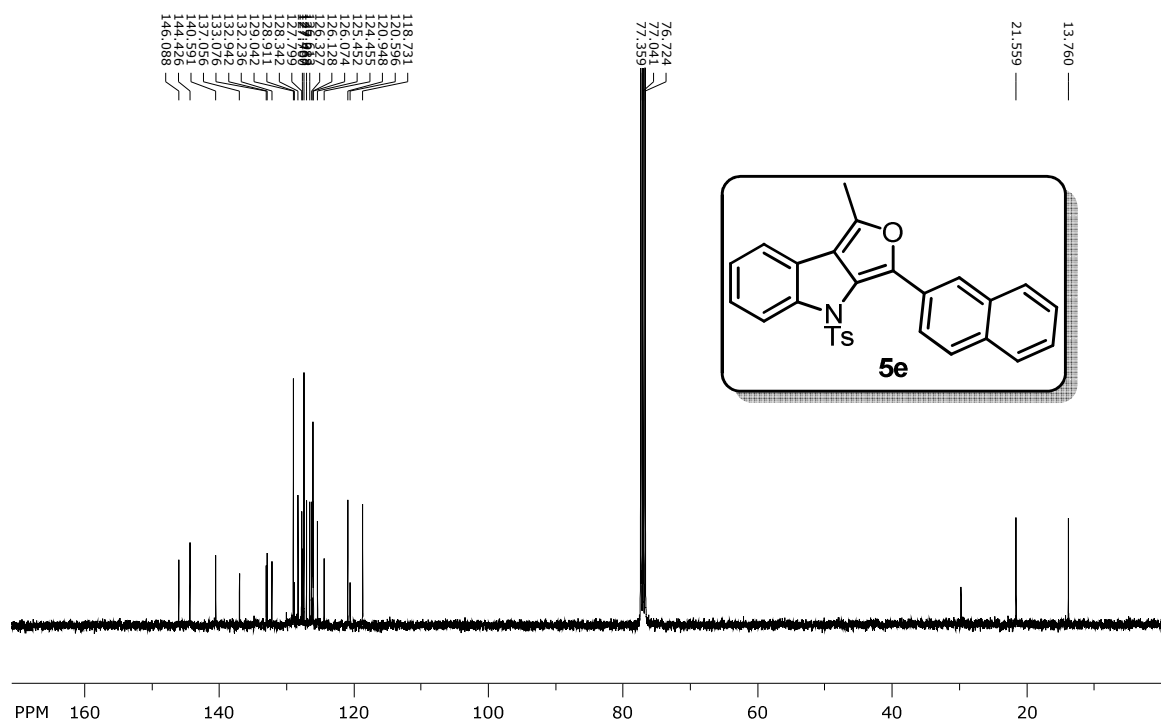
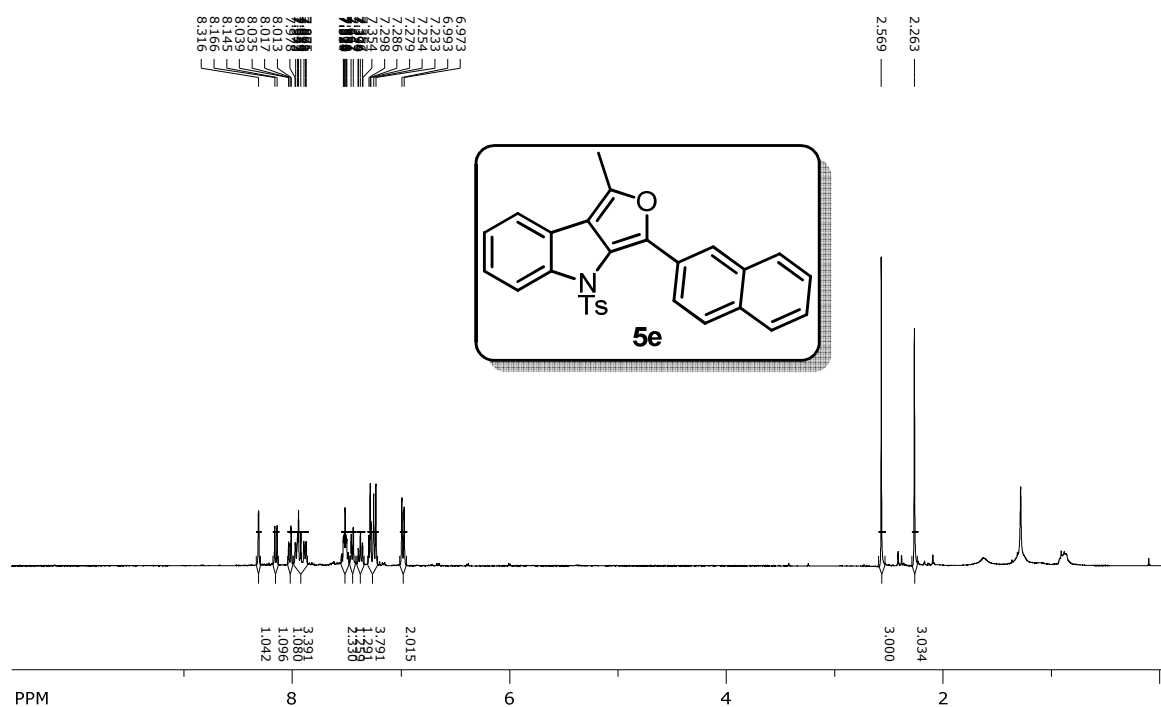


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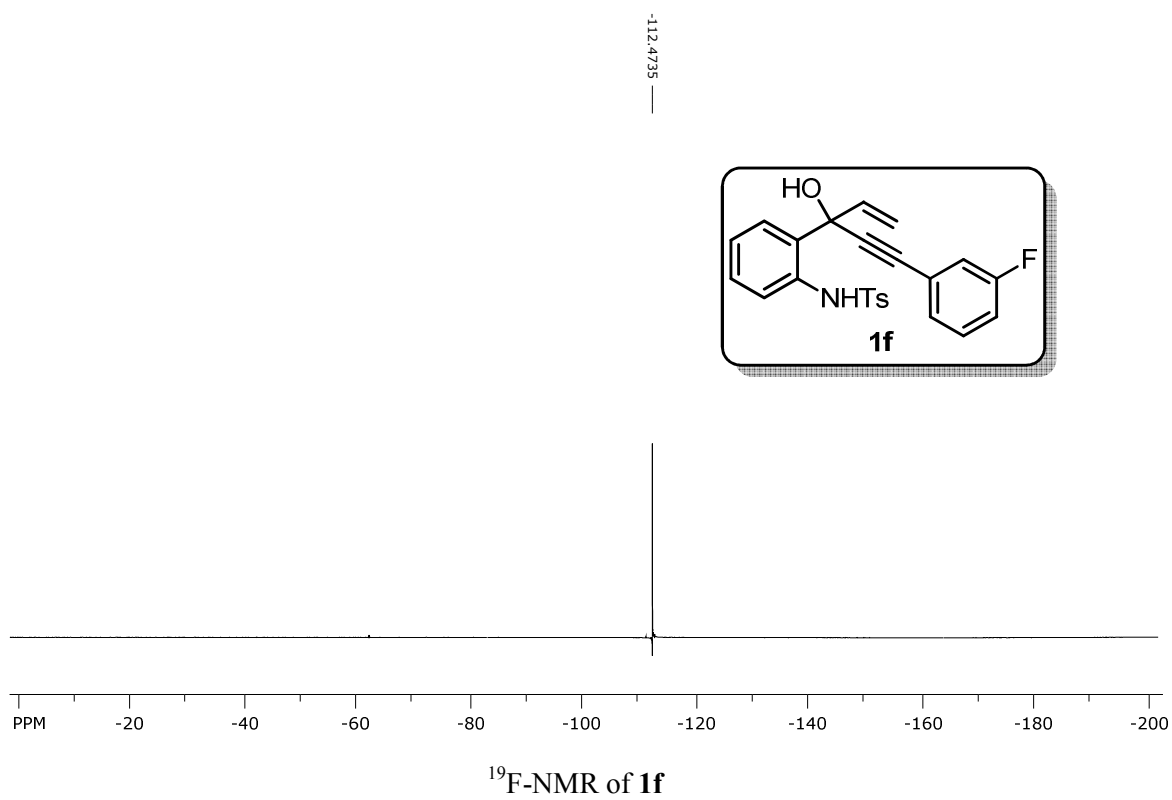
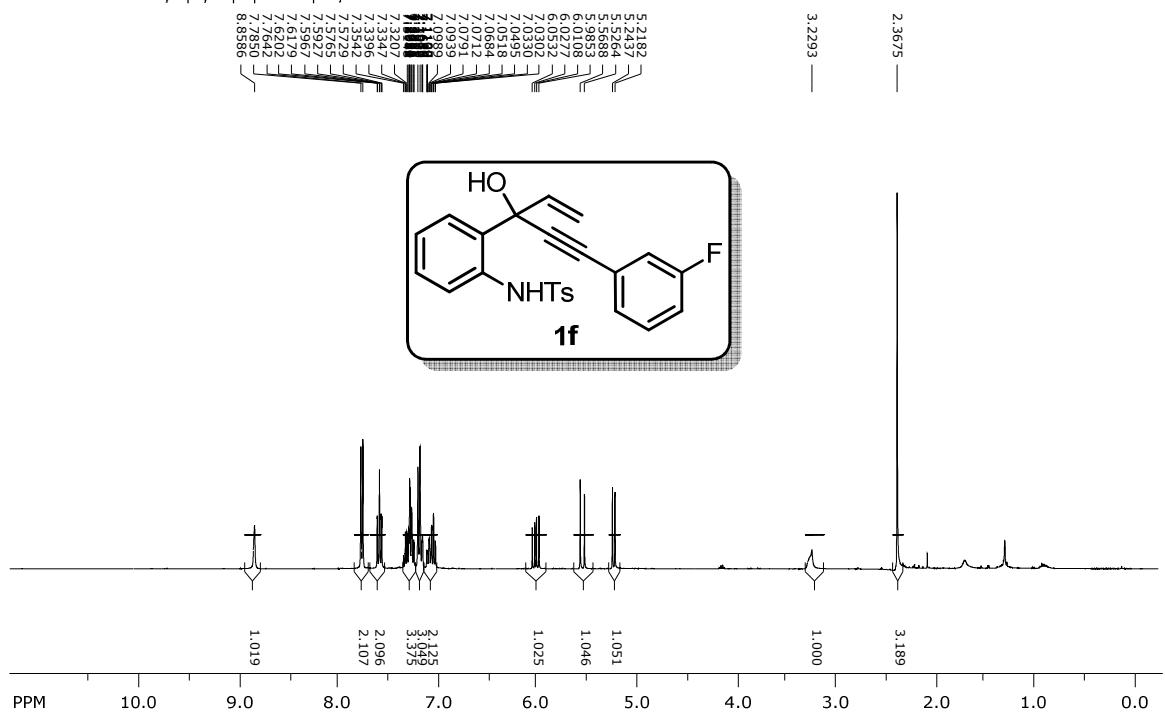








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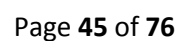


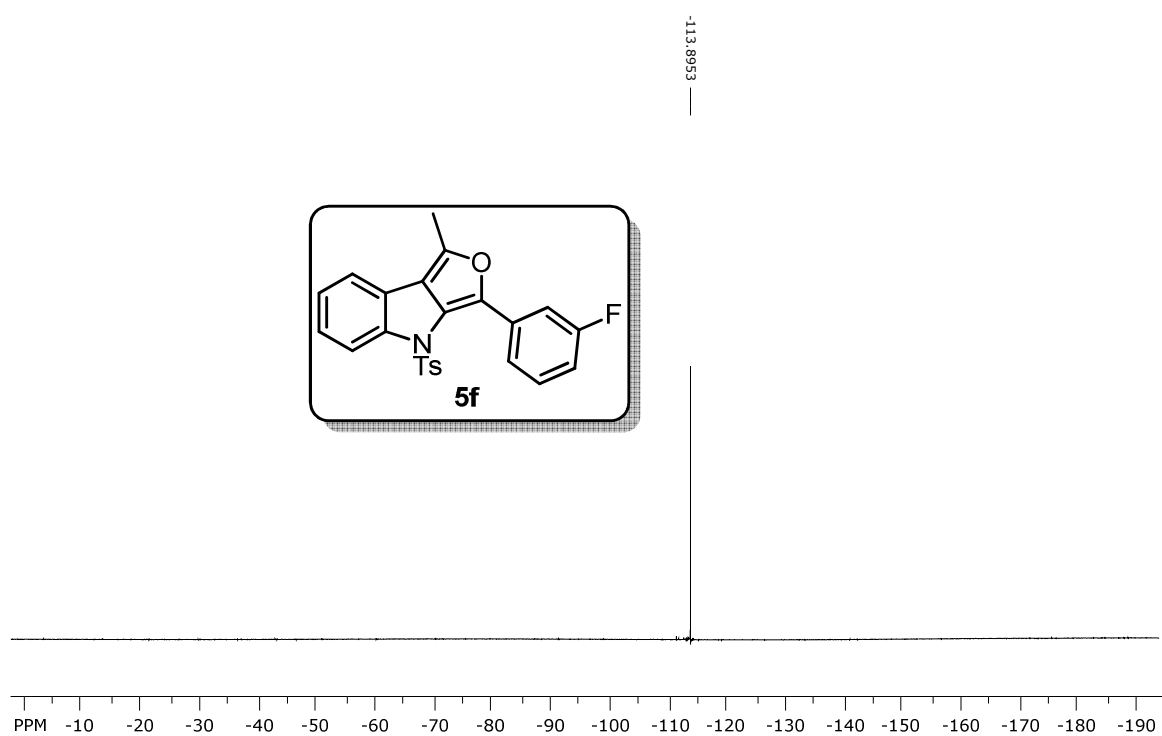
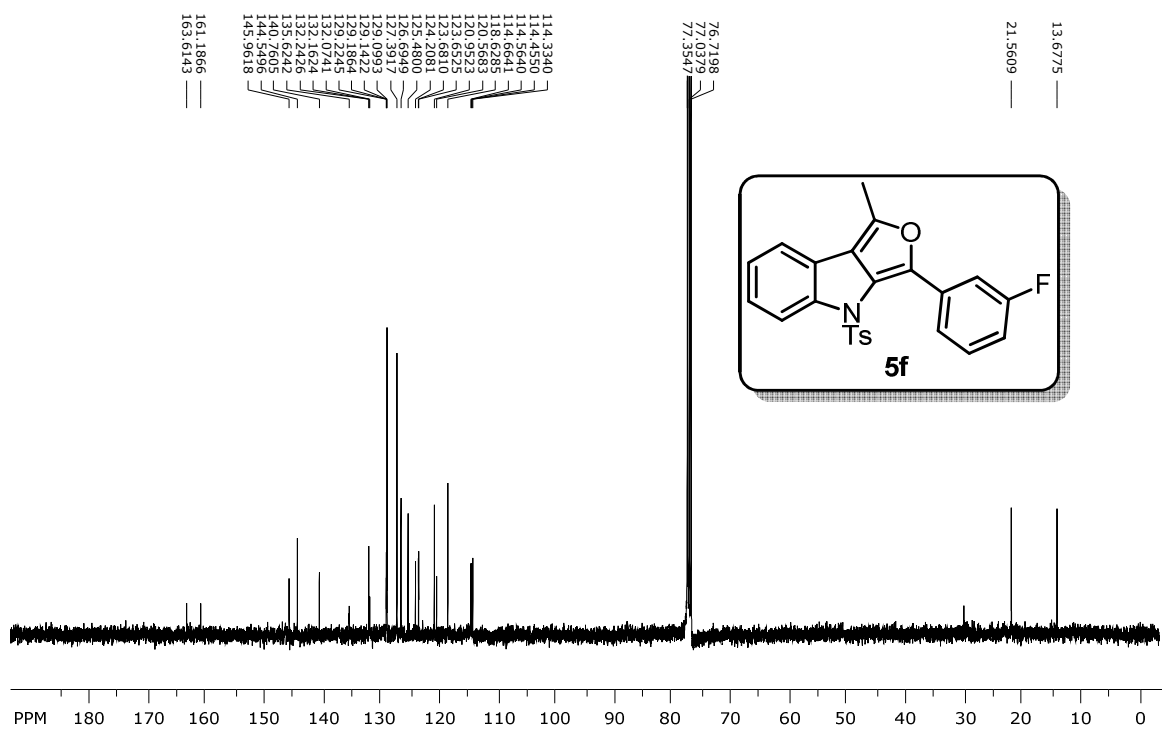
Chemical structure of **1f** is shown in the inset:

CC1=CC=C(C=C1)C(=O)C2=CC=CC=C2C2(O)C#CC#CC3=CC=C(C=C3)F

1f

¹³C NMR peaks (ppm): 161.0670, 163.5238, 143.7285, 136.0984, 135.1110, 130.0329, 130.1169, 128.9813, 128.1415, 127.7604, 127.7307, 127.4240, 123.5868, 123.4929, 123.4314, 118.7407, 118.5226, 116.5586, 116.3490, 116.0046, 88.7485, 87.6492, 87.6151, 77.3688, 77.2853, 77.2545, 77.0506, 76.7356, 76.7323, 74.5723, 21.5217.





¹⁹F-NMR of 5f

