Electronic Supplementary Material (ESI) for ChemComm.

AgOTf-Catalyzed dehydrative [3+2] annulation of aziridines with 2-naphthols

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Supporting Information

1. General Information

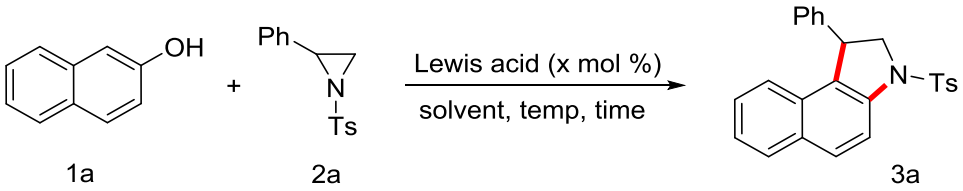
Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. 30 °C corresponds to the room temperature of the lab when the experiments were carried out. Dry DCE was purchased from commercial sources. The Lewis acid AgOTf used in this work were purchased from either Sigma Aldrich, or Alfa Aesar and stored in argon filled glove box. All the aziridines were synthesized following literature procedure.[1] Chiral aziridine **(*R*)-2a** was prepared in one step according to followed literature procedure.[2] The 2-naphthol **1a** and derivatives **1p, 1q, 1r** were purchased from Sigma Aldrich, other naphthols **1s,**[3] **1t,**[3] **1v,**[4] and **1w**[4] were prepared following the literature procedure.

Analytical thin layer chromatography was performed on TLC Silica gel 60 F254. Visualization was accomplished with short wave UV light. Chromatography was performed on silica gel (230-400 mesh) by standard techniques eluting with solvents as indicated.

All compounds were fully characterized. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV 400, 500 in solvents as indicated. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm). Infrared spectra were recorded on a Bruker Alpha-E Infrared Spectrophotometer. The wave numbers (n) of recorded IR-signals are quoted in cm^{-1}. HRMS data were recorded on either Thermo Scientific Q-Exactive, Accela 1250 pump or Waters SYNAPT G2 High Definition Mass Spectroscopy System. X-ray intensity data measurements of compound **3a** was carried out on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (MoK_α= 0.71073Å) radiation at room temperatute.

[1] K. Kiyokawa, T. Kosaka and Minakata, S. *Org. Lett.,* 2013,**15**, 4858.
[2] R. A. II Craig, N. R. O'Connor, A. F. G. Goldberg and B. M. Stoltz, *Chem. - Eur. J.*, 2014, **20**, 4806.
[3] M. Frotscher, E. Ziegler, S. Marchais-Oberwinkler, P. Kruchten, A. Neugebauer, L. Fetzer, C. Scherer, U. Muller-Vieira, J. Messinger, H. Thole and R. W. Hartmann, *J. Med. Chem.,* 2008, **51**, 2158.
[4] H. Y. Kim and K. Oh, *Org. Lett*., 2014, **16**, 5934.

2. Optimization of Reaction Conditions[a]



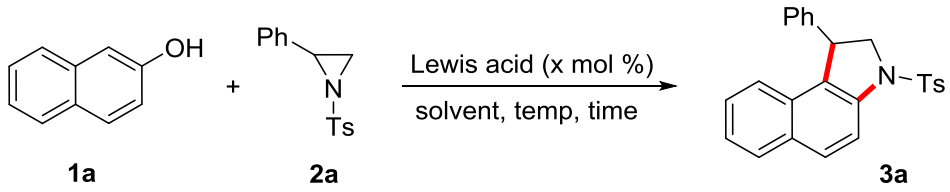
1a 2a 3a

entry	Lewis acid (x mol %)	solvent	temp (°C)	yield of **3a** (%)[b]
1	$Bi(OTf)_3$ (20)	DCE	80	62
2	$Bi(OTf)_3$+ KPF_6	DCE	80	66
3	$Cu(OTf)_2$ (20)	DCE	80	67
4	$Sc(OTf)_3$ (20)	DCM	80	<5
5	$Yb(OTf)_3$ (20)	DCE	80	<5
6	$Fe(OTf)_3$ (20)	DCE	80	27
7	$AgSbF_6$ (20)	DCE	80	31
8	$BF_3.OEt_2$ (20)	DCE	80	24
9	TfOH (20)	DCE	80	44
10	AgOTf (20)	DCE	80	72
11	AgOTf (20)	DCE	60	64
12	AgOTf (20)	DCE	100	74
13	AgOTf (10)	THF	70	<5
14	AgOTf (10)	DME	80	<5
15	AgOTf (20)	DCM	45	58
16	AgOTf (10)	toluene	80	62
17	AgOTf (10)	DCE	80	78 (74)

[a] All reactions were carried out in 0.25 mmol of **1a** and 0.3 mmol of **2a** in 1.0 mL solvent unless otherwise specified. [b] The yields were determined by 1H NMR analysis of crude products using CH_2Br_2 as the internal standard, yield of isolated product in 0.5 mmol scale is given parentheses.

Optimization of reaction with various silver salts[a]

We have carried out the screening of Ag salts, which revealed that Ag salts such as AgOAc, $AgBF_4$, $(CH_3CN)_4AgBF_4$, $AgNTf_2$, and $AgSbF_6$ afforded the desired product **3a** in reduced yield.

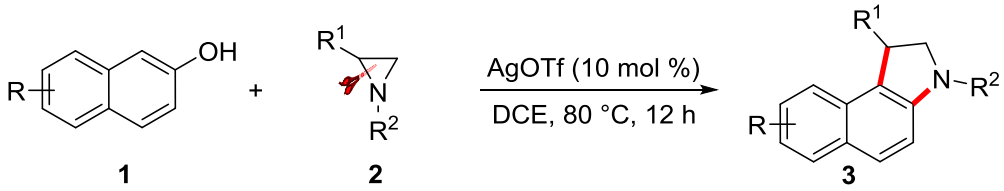


1a **2a** **3a**

entry	Lewis acid (x mol %)	solvent	temp (°C)	yield of **3a**[b] (%)
1	AgOAc (20)	DCE	80	32
2	$AgBF_4$ (20)	DCE	80	11
3	$[(CH_3CN)_4Ag]BF_4$ (20)	DCE	80	<5
4	$AgNTf_2$ (20)	DCE	80	60
5	$AgSbF_6$ (20)	DCE	80	31

[a] All reactions were carried out in 0.25 mmol of **1a** and 0.3 mmol of 2a in 1.0 mL solvent unless otherwise specified. [b] The yields were determined by ^1H NMR analysis of crude products using CH_2Br_2 as the internal standard, yield of isolated product in 0.5 mmol scale is given parentheses.

3. General Procedure for the AgOTf-Catalyzed Dehydrative [3+2] Annulation



1 **2** **3**

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added Ag OTf (0.006 g, 0.025 mmol) Naphthol **1** (0.25 mmol) and aziridine **2** (0.3 mmol) followed by the addition of DCE (1.0 mL) under argon atmosphere. Then the reaction mixture was placed in a preheated oil bath at 80 °C for 12 h under argon conditions. Then the reaction was stopped, and the reaction mixture cooled, the solvent was evaporated and the crude residue was pre-adsorbed on silica gel and purified by flash column chromatography (Pet. ether /EtOAc = 90/10) on silica gel to afford the corresponding benzoindoline derivatives **3** in moderate to good yields.

4. X-Ray Data of 3a

An X-ray intensity data measurement of compound **3a** was carried out on a Bruker D8 VENTURE Kappa Duo PHOTON II CPAD diffractometer equipped with Incoatech multilayer mirrors optics. The intensity measurements were carried out with Cu micro-focus sealed tube diffraction source (MoK_α= 0.71073Å) at 100(2) K temperature. The X-ray generator was operated at 50 kV and 1.4 mA. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 36 frames. Data were collected with ω scan width of 0.5° at different settings of φ and 2θ with a frame time of 10 secs keeping the sample-to-detector distance fixed at 4.00 cm. The X-ray data collection was monitored by APEX3 program (Bruker, 2016).[5] All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2016). ShelX-97 was used for structure solution and full matrix least-squares refinement on F^2.[6] All the hydrogen atoms were placed in a geomerically idalized position (C-H = 0.95 Å for the phenyl H atoms, C-H = 0.98 for the methyl H atoms, C-H = 1.00 Å for the methine H atoms and C-H = 0.99 Å of the methylene H atoms) and constrained to ride on its parent atoms [Uiso(H) = 1.2Ueq(C) for phenyl, methine and methylene H atoms and Uiso(H) = 1.5Ueq(C) for methyl H atoms]. An *ORTEP* III[7] view of compound was drawn with 30% probability displacement ellipsoids and H atoms are shown as small spheres of arbitrary radii. *Crystallographic data for **3a** have been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 1545103.*

[5] Bruker (2016). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc. Madison, Wisconsin, USA.
[6] G. M. Sheldrick, *Acta Crystallogr*., 2008, **A64**, 112.
[7] L. J. Farrugia, *J. Appl. Cryst.* 1997, **30**, 565.

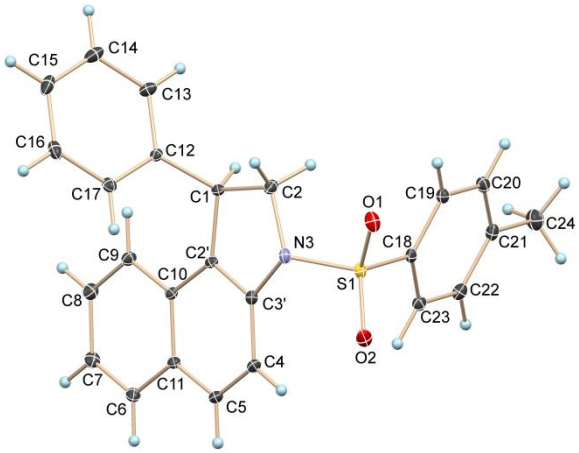
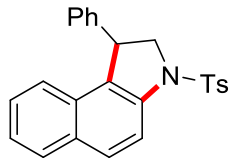


Figure S1. Crystal structure of **3a** (thermal ellipsoids are shown with 30% probability).

Crystal data of **3a**: $C_{25}H_{21}NO_2S$, M = 399.49, colorless block, 0.49 x 0.37 x 0.21 mm^3, monoclinic, space group *P*n, a = 9.131(2) Å, b = 11.420(2) Å, c = 9.833(2) Å, β = 107.26(3)°, V = 979.2(4) $Å^3$, Z = 2, T = 100(2) K, $2\theta_{max}$= 61.065°, D_{calc} (g cm^{-3}) = 1.355, $F(000)$ = 420, μ (mm^{-1}) = 0.187, 14847 reflections collected, 4803 unique reflections (R_{int}=0.0275), 4785 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.914, T_{max} = 0.961, 264 refined parameters, number of restraints = 2, Good of Fit = S = 1.041, $R1$ = 0.0275, $wR2$ = 0.0740 (all data R = 0.0275, $wR2$ = 0.0740), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.350, $\Delta\rho_{min}$= -0.215 ($eÅ^{-3}$).

5. Synthesis and Characterization of Benzoindoline Derivatives

1-Phenyl-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3a)

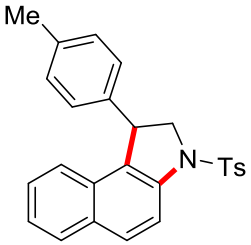


3a

Following the general procedure, treatment of 2-naphthol **1a** (0.072 g, 0.5 mmol) with 2-phenyl-1-tosylaziridine **2a** (0.164 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05 mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 1-phenyl-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole **3a** as a white solid (0.148 g, 74%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.42; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.13 (d, *J* = 9.0 Hz, 1H), 7.88 (dd, J_1 = 8.9 Hz, J_2 = 15.7 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.22 (m, 3H), 7.20 – 7.03 (m, 5H), 6.77 (d, *J* = 7.3 Hz, 2H), 4.75 (dd, J_1 = 4.3 Hz, J_2 =10.2 Hz, 1H), 4.49 (t, *J* = 10.8 Hz, 1H), 4.00 (dd, J_1 = 4.5 Hz, J_2 = 11.1 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 144.20, 143.42, 140.37, 133.67, 131.40, 130.31, 130.02, 129.83, 128.86, 128.72, 127.52, 127.42, 127.29, 126.96, 126.90, 124.58, 123.68, 115.65, 59.54, 45.62, 21.62. **HRMS** calculated $[M+H]^+$ for $C_{25}H_{22}O_2NS$: 400.1366, found: 400.1363. **FTIR(cm^{-1}):** 3020, 2401, 1599, 1521, 1371, 1216, 1176, 1139, 1096, 773, 669.

1-(p-Tolyl)-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole (3b)



3b

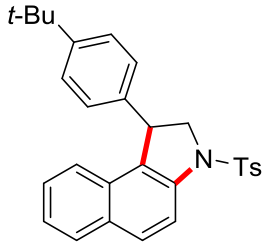
Following the general procedure, treatment of 2-naphthol **1a** (0.072 g, 0.5 mmol) with 2-(p-tolyl)-1-tosylaziridine **2b** (0.172 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05 mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 1-(*p*-tolyl)-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole **3b** as a white solid (0.160 g, 77%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.46; **^{1}H NMR (400 MHz, CDCl$_3$)** δ8.10 (d, *J* = 9.0 Hz, 1H), 7.83 (dd, J_1 = 8.7 Hz, J_2 = 12.7 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.32 - 7.24 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 7.6 Hz, 2H), 6.65 (d, *J* = 7.7 Hz, 2H), 4.70 (dd, J_1 = 4.2 Hz, J_2 = 10.1 Hz, 1H), 4.45 (t, *J* = 10.6 Hz, 1H), 3.96 (dd, J_1 = 4.5 Hz, J_2 = 11.0 Hz, 1H), 2.36 (s, 3H), 2.27 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 144.17, 140.43, 140.25, 136.47, 133.67, 131.38, 130.33, 129.91, 129.78, 129.51, 128.69, 127.51, 127.29, 126.91, 124.54, 123.70, 115.63, 59.66, 45.24,

21.62, 21.15. **HRMS** calculated $[M+H]^+$ for $C_{26}H_{24}O_2NS$: 414.1522, found: 414.1519. **FTIR(cm^{-1}):** 3020, 2400, 1597, 1514, 1356, 1216, 1166, 1093, 817, 772, 669.

1-(4-(*t*ert-butyl)phenyl)-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3c)

Following the general procedure, treatment of 2-naphthol **1a** (0.072 g, 0.5 mmol) with 2-(4-(tert-butyl)phenyl)-1-tosylaziridine **2c** (0.198 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 1-(4-(tert-butyl)phenyl)-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole **3c** as a white solid (0.155 g, 68%).

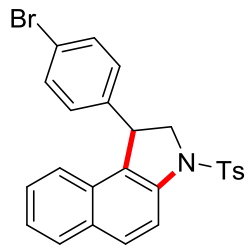


3c

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.43; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.09 (d, *J* = 9.0 Hz, 1H), 7.81 (dd, J_1 = 8.4 Hz, J_2 = 16.5 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.21 (m, 3H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.65 (d, *J* = 8.2 Hz, 2H), 4.69 (dd, J_1 = 4.3 Hz, J_2 = 10.2 Hz, 1H), 4.41 (t, *J* = 10.7 Hz, 1H), 3.96 (dd, J_1 = 4.3 Hz, J_2 = 11.0 Hz, 1H), 2.35 (s, 3H), 1.24 (s, 9H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 149.68, 144.07, 140.31, 140.24, 133.79, 131.36, 130.36, 129.88, 129.80, 128.68, 127.57, 126.96, 126.89, 125.68, 124.52, 123.80, 115.59, 59.59, 45.09, 34.47, 31.42, 21.67. **HRMS** calculated $[M+H]^+$ for $C_{29}H_{30}O_2NS$: 456.1992, found: 456.1938. **FTIR(cm^{-1}):** 3020, 2967, 2401, 1515, 1357, 1216, 1166, 1093, 758, 669.

1-(4-Bromophenyl)-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole (3d)

Following the general procedure, treatment of 2-naphthol **1a** (0.072 g, 0.5 mmol) with 2-(4-bromophenyl)-1-tosylaziridine **2d** (0.211 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 1-(4-bromophenyl)-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole **3d** as a white solid (0.171 g, 72%).

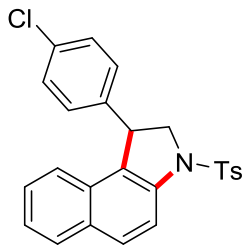


3d

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.37; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.01 (d, *J* = 8.9 Hz, 1H), 7.76 (dd, J_1 = 8.5 Hz, J_2 = 14.6 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.10(t, 3H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.49 (d, *J* = 7.8 Hz, 2H), 4.60 (dd, J_1 = 3.1 Hz, J_2 = 9.8 Hz, 1H), 4.38 (t, *J* = 10.7 Hz, 1H), 3.86 (dd, J_1 = 3.4 Hz, J_2 = 11.2 Hz, 1H), 2.27

(s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.42, 142.34, 140.44, 133.67, 131.89, 131.42, 130.29, 129.81, 129.04, 128.83, 127.41, 127.17, 126.68, 124.77, 123.52, 120.73, 115.84, 59.34, 44.89, 21.64. **HRMS** calculated $[M+H]^+$ for $C_{25}H_{21}O_2NBrS$: 478.0471, found: 478.0471. **FTIR(cm^{-1}):** 3020, 2401, 1596, 1516, 1487, 1357, 1216, 1166, 1093, 817, 773, 669.

1-(4-Chlorophenyl)-3-tosyl-2,3-dihydro-1H-benzo[e]indole (3e)

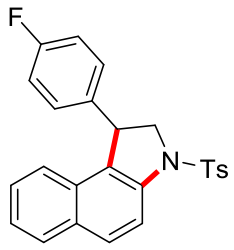


3e

Following the general procedure, treatment of 2-naphthol **1a** (0.072 g, 0.5 mmol) with 2-(4-chlorophenyl)-1-tosylaziridine **2e** (0.185 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 1-(4-chlorophenyl)-3-tosyl-2,3-dihydro-1*H*-benzo[e]indole **3e** as a white solid (0.148 g, 68%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.42; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 8.9 Hz, 1H), 7.74 (dd, J_1 = 8.5 Hz, J_2 = 15.5 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.3 Hz, 2H), 6.53 (d, *J* = 8.2 Hz, 2H), 4.59 (dd, J_1 = 3.7 Hz, J_2 = 10.1 Hz, 1H), 4.35 (t, *J* = 10.7 Hz, 1H), 3.84 (dd, J_1 = 3.9 Hz, J_2 = 11.3 Hz, 1H), 2.24 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ144.37, 141.82, 140.35, 133.61, 132.58, 131.37, 130.23, 130.11, 129.78, 128.90, 128.79, 128.65, 127.38, 127.12, 126.74, 124.72, 123.48, 115.76, 59.36, 44.77, 21.57. **HRMS** calculated $[M+H]^+$ for $C_{25}H_{21}O_2NClS$: 434.0976, found: 434.0974. **FTIR (cm^{-1}):** 3022, 2403, 1629, 1515, 1468, 1354, 1217, 1166, 1090, 767, 670.

1-(4-Fluorophenyl)-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole (3f)



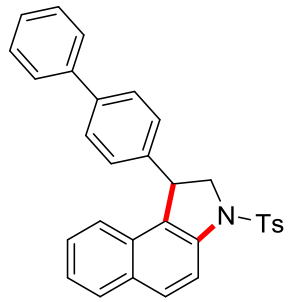
3f

Following the general procedure, treatment of 2-naphthol **1a** (0.072 g, 0.5 mmol) with 2-(4-fluorophenyl)-1-tosylaziridine **2f** (0.178 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05 mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 1-(4-fluorophenyl)-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole **3f** as a white solid (0.146 g, 70%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.42; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.12 (d, *J* = 8.9 Hz, 1H), 7.92 – 7.80 (m, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.29 (m, 3H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.78 (t, *J* =

8.5 Hz, 2H), 6.73 – 6.67 (m, 2H), 4.74 (dd, J_1 = 4.0 Hz, J_2 = 10.1 Hz, 1H), 4.47 (t, J = 10.7 Hz, 1H), 3.96 (dd, J_1 = 4.1 Hz, J_2 = 11.2 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.69 (d, J = 245.6 Hz), 144.32, 140.32, 139.17, 133.67, 131.42, 130.20, 129.83, 128.92, 128.83 (d, J = 2.58 Hz), 127.48, 127.08, 124.69, 123.52, 115.74 (d, J = 5.70 Hz), 59.50, 44.76, 21.59. **HRMS** calculated $[M+H]^+$ for $C_{25}H_{21}O_2NFS$: 418.1272, found: 418.1270. **FTIR (cm^{-1}):** 3020, 2400, 1599, 1509, 1357, 1216, 1167, 1094, 761, 669.

1-([1,1'-Biphenyl]-4-yl)-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3g)

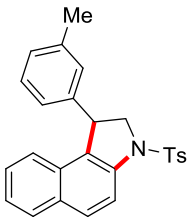


3g

Following the general procedure, treatment of 2-naphthol **1a** (0.072 g, 0.5 mmol) with 2-([1,1'-biphenyl]-4-yl)-1-tosylaziridine **2g** (0.210 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05 mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 1-([1,1'-Biphenyl]-4-yl)-3-tosyl-2,3-dihydro-1H-benzo[e]indole **3g** as a white solid (0.152 g, 64%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.40; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.14 (d, J = 8.9 Hz, 1H), 7.87 (dd, J_1 = 8.6 Hz, J_2 = 15.4 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 7.6 Hz, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.40 – 7.26 (m, 6H), 7.16 (d, J = 8.0 Hz, 2H), 6.84 (d, J = 7.9 Hz, 2H), 4.80 (dd, J_1 = 4.2 Hz, J_2 = 10.1 Hz, 1H), 4.51 (t, J = 10.7 Hz, 1H), 4.05 (dd, J_1 = 4.3 Hz, J_2 = 11.1, 1H), 2.32 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.25, 142.44, 140.69, 140.40, 139.78, 133.79, 131.43, 130.35, 130.08, 129.81, 128.91, 128.76, 127.83, 127.53, 127.43, 127.23, 127.01, 124.64, 123.73, 115.71, 59.58, 45.26, 21.60. **HRMS** calculated $[M+H]^+$ for $C_{31}H_{26}O_2NS$: 476.1679, found: 476.1675. **FTIR(cm^{-1}):** 3424, 3020, 2400, 1629, 1597, 1356, 1254, 1166, 1073, 772, 699.

1-(m-Tolyl)-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole (3h)



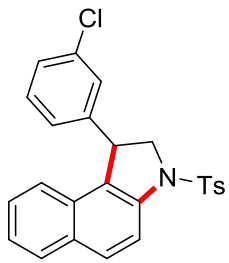
3h

Following the general procedure, treatment of 2-naphthol **1a** (0.072 g, 0.5 mmol) with 2-(m-tolyl)-1-tosylaziridine **2h** (0.172 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 1-(m-tolyl)-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole **3h**

as a white solid (0.143 g, 69%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.46; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.15 (d, *J* = 9.0 Hz, 1H), 7.86 (dd, J_1 = 8.5 Hz, J_2 = 15.7 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.26 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.03 – 6.98 (m, 2H), 6.64 (s, 1H), 6.58 (d, *J* = 6.8 Hz, 1H), 4.72 (dd, J_1 = 4.7 Hz, J_2 = 10.3 Hz, 1H), 4.49 (t, *J* = 10.7 Hz, 1H), 3.99 (dd, J_1 = 4.8 Hz, J_2 = 11.0 Hz, 1H), 2.36 (s, 3H), 2.19 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 144.18, 143.44, 140.21, 138.48, 133.56, 131.33, 130.33, 129.92, 129.77, 128.64, 128.04, 127.75, 127.51, 127.33, 126.89, 126.44, 124.52, 123.67, 123.47, 118.03, 115.47, 109.56, 59.53, 45.56, 21.59, 21.46. **HRMS** calculated $[M+H]^+$ for $C_{26}H_{24}O_2NS$: 414.1522, found: 414.1520. **FTIR(cm^{-1}):** 3021, 2925, 2404, 1629, 1598, 1463, 1353, 1255, 1217, 1166, 1093, 814, 762, 670.

1-(3-Chlorophenyl)-3-tosyl-2,3-dihydro-1*H*-benzo[e]indole (3i)

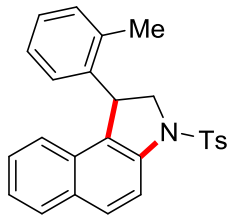


3i

Following the general procedure, treatment of 2-naphthol **1a** (0.072 g, 0.5 mmol) with 2-(3-chlorophenyl)-1-tosylaziridine **2i** (0.185 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05 mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 1-(3-chlorophenyl)-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole **3i** as a white solid (0.154 g, 71%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.37; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.01 (d, *J* = 8.9 Hz, 1H), 7.76 (dd, J_1 = 8.5 Hz J_2 = 16.4 Hz , 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 1H), 7.07 – 7.02 (m, 3H), 6.94 (t, *J* = 7.8 Hz, 1H), 6.59 – 6.56 (m, 2H), 4.61 (dd, J_1 = 4.0 Hz, J_2 = 10.3 Hz, 1H), 4.38 (t, *J* = 10.9 Hz, 1H), 3.86 (dd, J_1 = 4.2 Hz, J_2 = 11.3 Hz, 1H), 2.25 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 145.48, 144.50, 140.50, 134.72, 133.46, 131.40, 130.37, 130.13, 129.88, 128.82, 127.43, 127.27, 127.20, 126.34, 125.69, 124.73, 123.45, 115.69, 59.22, 45.19, 21.71. **HRMS** calculated $[M+H]^+$ for $C_{25}H_{21}O_2NClS$: 434.0976, found: 434.0976. **FTIR(cm^{-1}):** 3020, 1629, 1596, 1516, 1471, 1357, 1216, 1167, 1093, 815, 771, 669.

1-(o-Tolyl)-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3j)

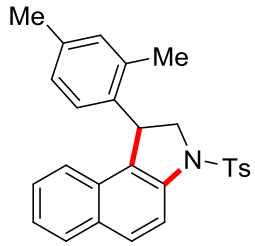


3j

Following the general procedure, treatment of 2-naphthol **1a** (0.072 g, 0.5 mmol) with 2-(o-tolyl)-1-tosylaziridine **2j** (0.172 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05 mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 1-(o-tolyl)-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole **3j** as a white solid (0.142 g, 69%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.46; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.01 (d, *J* = 8.9 Hz, 1H), 7.76 (dd, J_1 = 9.0 Hz, J_2 = 11.5 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 7.9 Hz, 3H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.55 (s, 1H), 5.85 (s, 1H), 4.82 (dd, J_1 = 4.6 Hz, J_2 = 10.3 Hz, 1H), 4.44 (t, *J* = 10.7 Hz, 1H), 3.77 (dd, J_1 = 4.6 Hz, J_2 = 11.0 Hz, 1H), 2.35 (s, 3H), 2.24 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 144.16, 140.74, 133.75, 131.40, 130.47, 130.32, 129.88, 129.78, 128.74, 127.42, 126.97, 126.62, 126.46, 124.64, 123.77, 115.86, 58.62, 21.61, 20.02**. HRMS** calculated $[M+H]^+$ for $C_{26}H_{24}O_2NS$: 414.1522, found: 414.1519. **FTIR(cm^{-1}):** 3021, 1629, 1597, 1356, 1216, 1166, 1093, 816, 757, 669.

1-(2,4-Dimethylphenyl)-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole (3k)



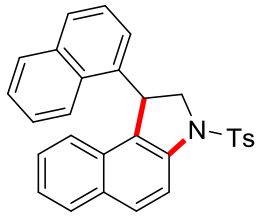
3k

Following the general procedure, treatment of 2-naphthol **1a** (0.072 g, 0.5 mmol) with 2-(2,4-dimethylphenyl)-1-tosylaziridine **2k** (0.181 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05 mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 1-(2,4-dimethylphenyl)-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole **3k** as a white solid (0.154 g, 72%)

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.35; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.09 (d, *J* = 8.9 Hz, 1H), 7.84 (t, *J* = 9.65 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.7 Hz, 3H), 6.99 (s, 1H), 6.45 (d, *J* = 5.7 Hz, 1H), 5.86 (s, 1H), 4.87 (dd, J_1 = 4.8 Hz, J_2 = 10.2 Hz, 1H), 4.50 (t, *J* = 10.6 Hz, 1H), 3.84 (dd, J_1 = 4.8 Hz, J_2 = 11.0 Hz, 1H), 2.39 (s, 3H), 2.33 (s, 3H), 2.23 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 144.12, 140.65, 138.20, 136.11, 134.53, 133.82, 131.37, 131.26, 130.36, 129.78, 129.72, 128.70, 127.53, 127.41, 127.11,

126.93, 124.59, 123.80, 115.83, 58.77, 41.50, 21.60, 21.03, 19.90. **HRMS** calculated $[M+H]^+$ for $C_{27}H_{26}O_2NS$: 428.1679, found: 428.1678. **FTIR(cm^{-1}):** 3021, 2926, 2404, 1597, 1353, 1217, 1166, 1093, 816, 762, 671.

1-(Naphthalen-1-yl)-3-tosyl-2,3-dihydro-1H-benzo[e]indole (3l)

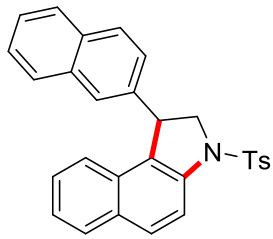


3l

Following the general procedure, treatment of 2-naphthol **1a** (0.072 g, 0.5 mmol) with 2-(naphthalen-1-yl)-1-tosylaziridine **2l** (0.194 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05 mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 1-(naphthalen-1-yl)-3-tosyl-2,3-dihydro-1H-benzo[e]indole **3l** as a white solid (0.154 g, 68%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.38; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.13 (dd, J_1 = 8.6 Hz, J_1 = 24.1 Hz, 2H), 8.02 – 7.85 (m, 3H), 7.70-7.58 (m, 3H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.24 – 7.12 (m, 2H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.82 (t, *J* = 7.5 Hz, 1H), 5.99 (d, *J* = 6.9 Hz, 1H), 5.46 (d, *J* = 8.9 Hz, 1H), 4.74 (t, *J* = 10.7 Hz, 1H), 4.23 – 3.94 (m, 1H), 2.34 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 144.02, 141.00, 138.41, 134.08, 133.92, 131.46, 130.82, 130.57, 130.08, 129.68, 129.26, 128.77, 127.30, 127.01, 126.77, 125.93, 125.53, 124.92, 124.75, 124.15, 122.97, 116.32, 59.13, 40.85, 21.60. **HRMS** calculated $[M+H]^+$ for $C_{29}H_{24}O_2NS$: 450.1522, found: 450.1513. **FTIR (cm^{-1}):** 3619, 3021, 2977, 2402, 1595, 1519, 1426, 1216, 1167, 768, 671.

1-(Naphthalen-2-yl)-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole (3m)



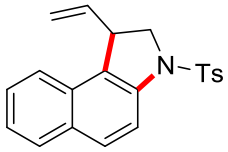
3m

Following the general procedure, treatment of 2-naphthol **1a** (0.072 g, 0.5 mmol) with 2-(naphthalen-2-yl)-1-tosylaziridine **2m** (0.194 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05 mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 1-(naphthalen-2-yl)-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole **3m** as a white solid (0.141 g, 63%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.37; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.05 (d, *J* = 8.9 Hz, 1H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.65 - 7.64 (m, 1H), 7.58 – 7.47 (m, 3H), 7.43

– 7.41 (m, 1H), 7.33 – 7.31 (m, 2H), 7.20 - 7.16 (m, 2H), 7.10 - 7.07 (m , 2H), 6.95 (d, *J* = 7.8 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 1H), 4.80 (dd, J_1 = 4.0 Hz, J_2 = 10.0 Hz, 1H), 4.47 (t, *J* = 10.8 Hz, 1H), 3.97 (dd, J_1 = 4.1 Hz, J_2 = 11.2 Hz, 1H), 2.15 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.27, 140.82, 140.46, 133.69, 133.38, 132.43, 131.43, 130.42, 130.15, 129.76, 128.85, 128.71, 127.94, 127.69, 127.46, 127.12, 127.03, 126.22, 126.16, 125.90, 125.47, 124.64, 123.73, 117.92, 115.80, 59.42, 45.76, 21.57. **HRMS** calculated $[M+H]^+$ for $C_{29}H_{24}O_2NS$: 450.1522, found: 450.1517. **FTIR(cm^{-1}):** 3021, 2403, 1597, 1512, 1354, 1216, 1166, 1093, 814, 764, 671.

3-Tosyl-1-vinyl-2,3-dihydro-1*H*-benzo[*e*]indole (3n)

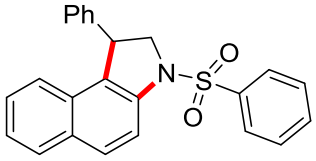


3n

Following the general procedure, treatment of 2-naphthol **1a** (0.072 g, 0.5 mmol) with 1-tosyl-2-vinylaziridine **2n** (0.134 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05 mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 3-tosyl-1-vinyl-2,3-dihydro-1H-benzo[e]indole **3n** as a white solid (0.074 g, 42%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.45; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 8.9 Hz, 1H), 7.81 (t, *J* = 9.0 Hz, 2H), 7.67 (t, *J* = 8.4 Hz, 3H), 7.47 – 7.31 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.67 – 5.29 (m, 1H), 4.98 (dd, J_1 = 13.5 Hz, J_2 = 27.4 Hz, 2H), 4.23 – 4.09 (m, 2H), 3.89 (d, *J* = 7.0 Hz, 1H), 2.33 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.25, 139.67, 138.54, 133.75, 131.28, 130.54, 129.77, 128.78, 127.55, 126.88, 126.70, 124.65, 123.37, 116.33, 115.83, 56.62, 44.06, 21.61. **HRMS** calculated $[M+H]^+$ for $C_{21}H_{20}O_2NS$: 350.1209, found: 350.1208. **FTIR(cm^{-1}):** 3349, 2926, 2256, 1593, 1355, 1257, 1167, 1000, 910, 738, 655.

1-Phenyl-3-(phenylsulfonyl)-2,3-dihydro-1H-benzo[e]indole (3o)

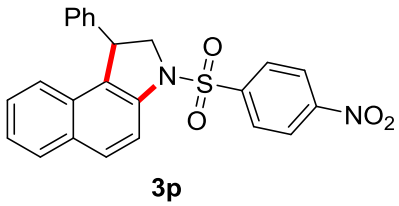


3o

Following the general procedure, treatment of 2-naphthol **1a** (0.072 g, 0.5 mmol) with 2-phenyl-1-(phenylsulfonyl)aziridine **2o** (0.155 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05mmol)in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 1-phenyl-3-(phenylsulfonyl)-2,3-dihydro-1*H*-benzo[*e*]indole **3o** as a white solid (0.110 g, 57%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.38; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.14 (d, *J* = 8.9 Hz, 1H), 7.94 – 7.73 (m, 4H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 6.9 Hz, 1H), 7.27 - 7.22 (m, 2H), 7.17 – 7.09 (m, 3H), 6.76 (d, *J* = 7.1 Hz, 2H), 4.75 (dd, J_1= 4.5 Hz, J_2=10.2, 1H), 4.50 (t, *J* = 10.7 Hz, 1H), 4.00 (dd, J_1 = 4.6 Hz , J_2= 11.1 Hz, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 143.34, 140.16, 136.63, 133.34, 131.40, 130.26, 130.07, 129.21, 128.93, 128.70, 127.45, 127.33, 126.99, 124.62, 123.65, 115.46, 59.53, 45.59. **HRMS** calculated $[M+H]^+$ for $C_{24}H_{20}O_2NS$: 386.1209, found: 386.1205. **FTIR(cm^{-1}):** 3022, 2403, 1595, 1518, 1357, 1216, 1170, 1095, 1038, 765, 671.

3-((4-Nitrophenyl)sulfonyl)-1-phenyl-2,3-dihydro-1H-benzo[*e*]indole (3p)

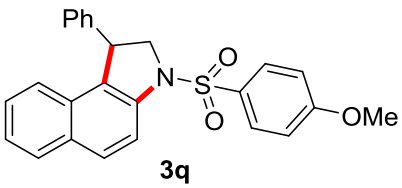


3p

Following the general procedure, treatment of 2-naphthol **1a** (0.072 g, 0.5 mmol) with 1-((4-nitrophenyl)sulfonyl)-2-phenylaziridine **2p** (0.183 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05 mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 3-((4-nitrophenyl)sulfonyl)-1-phenyl-2,3-dihydro-1H-benzo[*e*]indole **3p** as a white solid (0.110 g, 49%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.32; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.97 (dd, J_1 = 5.7 Hz, J_2 = 8.5 Hz, 3H), 7.82 – 7.71 (m, 4H), 7.26 (t, *J* = 6.5 Hz, 1H), 7.21 – 7.15 (m, 2H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 2H), 6.53 (d, *J* = 7.5 Hz, 2H), 4.66 (dd, J_1 = 3.2 Hz, J_2 = 9.8 Hz, 1H), 4.47 (t, *J* = 10.7 Hz, 1H), 3.98 (dd, J_1 = 3.4 Hz, J_2 = 11.5 Hz, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 150.44, 142.78, 142.36, 139.30, 131.69, 130.47, 130.35, 128.83, 128.34, 127.66, 127.40, 127.12, 127.05, 125.24, 124.26, 123.91, 115.55, 60.07, 45.20. **HRMS** calculated $[M+H]^+$ for $C_{24}H_{19}N_2O_4S$: 431.1060, found: 431.1031. **FTIR(cm^{-1}):** 3022, 2403, 1599, 1530, 1358, 1216, 1171, 1096, 1037, 764, 672.

3-((4-Methoxyphenyl)sulfonyl)-1-phenyl-2,3-dihydro-1H-benzo[*e*]indole (3q)



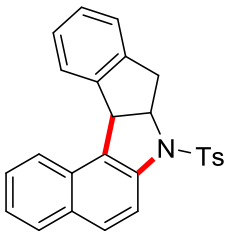
3q

Following the general procedure, treatment of 2-naphthol **1a** (0.072 g, 0.5 mmol) with 1-((4-methoxyphenyl)sulfonyl)-2-phenylaziridine **2q** (0.174 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05 mmol) in 1,2-dichloroethane (2.0 mL) at

80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 3-((4-Methoxyphenyl)sulfonyl)-1-phenyl-2,3-dihydro-1H-benzo[*e*]indole **3q** as a white solid (0.156 g, 75%).

***R*$_f$** (Pet. ether/EtOAc =80/20): 0.36; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.01 (d, *J* = 8.9 Hz, 1H), 7.74 (dd, J_1 = 8.6 Hz, J_2 = 14.0 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.23 – 7.19 (m, 1H), 7.17 - 7.14 (m, 2H), 7.05 – 6.99 (m, 3H), 6.71 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 6.8 Hz, 2H), 4.64 (dd, J_1 = 4.4 Hz, J_2 = 10.2 Hz, 1H), 4.37 (t, *J* = 10.7 Hz, 1H), 3.87 (dd, J_1 = 4.5 Hz, J_2 = 11.1 Hz, 1H), 3.70 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 163.49, 143.46, 140.46, 131.39, 130.31, 130.00, 129.59, 128.87, 128.71, 128.25, 127.40, 127.33, 126.96, 126.91, 124.58, 123.70, 115.74, 114.36, 59.54, 55.66, 45.62. **HRMS** calculated $[M+H]^+$ for $C_{25}H_{22}O_3NS$: 416.1315, found: 416.1311. **FTIR(cm^{-1}):** 3022, 2403, 1593, 1501, 1464, 1353, 1259, 1217, 1162, 1093, 1031, 767, 672.

7-Tosyl-7,7a,8,12b-tetrahydrobenzo[*e*]indeno[2,1-b]indole (3r)

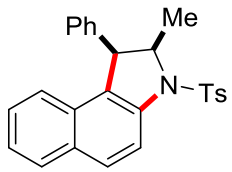


3r

Following the general procedure, treatment of 2-naphthol **1a** (0.072 g, 0.5 mmol) with 1-tosyl-1,1a,6,6a-tetrahydroindeno[1,2-b]azirine **2r** (0.171 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 7-tosyl-7,7a,8,12b-tetrahydrobenzo[*e*]indeno[2,1-b]indole **3r** as a white solid (0.033 g, 32%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.37; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.08 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 8.9 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.71 (t, *J* = 8.5 Hz, 3H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.39 (dd, J_1= 7.7 Hz, J_2 = 18.4 Hz, 2H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 3H), 7.04 (t, *J* = 7.2 Hz, 1H), 5.22 (d, *J* = 8.0 Hz, 1H), 4.94 (t, *J* = 7.1 Hz, 1H), 3.98 (d, *J* = 17.7 Hz, 1H), 3.65 (dd, J_1 = 6.2 Hz, J_2 = 17.7 Hz, 1H), 2.32 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 144.40, 142.56, 141.15, 139.70, 133.36, 131.41, 129.99, 129.82, 129.10, 128.92, 127.86, 127.78, 127.08, 126.99, 125.36, 124.88, 124.53, 124.07, 115.72, 68.56, 51.17, 40.86, 21.63. **HRMS** calculated $[M+H]^+$ for $C_{26}H_{22}O_2NS$: 412.1366, found: 412.1364. **FTIR(cm^{-1}):** 3022, 2402, 1596, 1520, 1356, 1216, 1169, 1041, 928, 770, 671.

1-Phenyl-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3s)



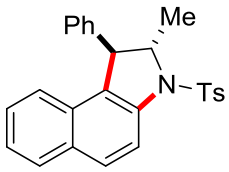
3s

Following the general procedure, treatment of 2-naphthol **1a** (0.072 g, 0.5 mmol) with 2-methyl-3-phenyl-1-tosylaziridine **2s** (0.172 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05 mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 1-phenyl-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole **3s** as a white solid (0.066 g, 32%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.46; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.14 (d, *J* = 9.0 Hz, 1H), 7.87 (dd, *J* = 17.4, 8.6 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.28-7.20 (m, 2H), 7.12 – 7.02 (m, 3H), 6.94 (t, *J* = 7.5 Hz, 2H), 6.34 (d, *J* = 7.5 Hz, 2H), 4.25 (d, *J* = 3.0 Hz, 1H), 4.14 (dd, J_1 = 3.4 Hz, J_1 = 6.4, Hz, 1H), 2.35 (s, 3H), 1.71 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 143.88, 143.30, 139.62, 134.37, 131.69, 130.11, 129.75, 128.74, 128.65, 127.46, 127.38, 127.02, 126.93, 126.47, 126.05, 124.67, 123.88, 116.87, 68.81, 54.63, 24.36, 21.57. **HRMS** calculated $[M+H]^+$ for $C_{26}H_{24}O_2NS$: 414.1522, found: 414.1514. **FTIR (cm^{-1}):** 3424, 3020, 2400, 1629, 1597, 1356, 1254, 1166, 1074, 772, 699.

2-Methyl-1-phenyl-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3s')

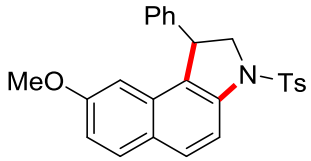


3s'

Following the general procedure, treatment of 2-naphthol **1a** (0.072 g, 0.5 mmol) with 2-methyl-3-phenyl-1-tosylaziridine **2s** (0.172 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05 mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 2-methyl-1-phenyl-3-tosyl-2,3-dihydro-1H-benzo[e]indole **3s'** as a white solid (0.070 g, 34%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.40; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.15 (d, *J* = 8.9 Hz, 1H), 8.01 – 7.78 (m, 2H), 7.65 (d, *J* = 7.7 Hz, 2H), 7.35 – 7.10 (m, 8H), 7.09 – 6.86 (m, 2H), 4.78 (d, *J* = 9.8 Hz, 1H), 4.69 – 4.43 (m, 1H), 2.35 (s, 3H), 1.20 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 144.14, 140.34, 138.58, 134.08, 131.81, 130.02, 129.79, 129.68, 129.51, 128.66, 128.44, 127.49, 127.34, 126.51, 124.49, 124.21, 116.65, 63.21, 51.08, 21.62, 19.72. **HRMS** calculated $[M+H]^+$ for $C_{26}H_{24}O_2NS$: 414.1522, found: 414.1512. **FTIR(cm^{-1}):** 3777, 2975, 2403, 1597, 1454, 1217, 1167, 1044, 766, 670.

8-Methoxy-1-phenyl-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3t)

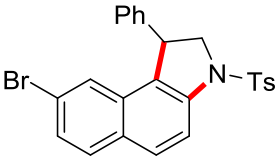


3t

Following the general procedure, treatment of 7-methoxynaphthalen-2-ol **1t** (0.087 g, 0.5 mmol) with 2-phenyl-1-tosylaziridine **2a** (0.164 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 8-methoxy-1-phenyl-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole **3t** as a white solid (0.112 g, 52%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.30; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.85 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 3H), 7.05 (dd, J_1 = 7.7 Hz, J_2 = 16.1 Hz, 5H), 6.84 (dd, J_1 = 1.6 Hz, J_2 = 9.0 Hz, 1H), 6.71 (d, *J* = 7.0 Hz, 2H), 6.37 (s, 1H), 4.57 (dd, J_1 = 5.1 Hz, J_2 = 10.2 Hz, 1H), 4.39 (t, *J* = 10.7 Hz, 1H), 3.86 (dd, J_1 = 4.9 Hz, J_2 = 11.2 Hz, 1H), 3.42 (s, 3H), 2.27 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 158.23, 144.19, 143.26, 140.75, 133.63, 131.50, 130.18, 129.82, 129.61, 128.85, 127.58, 127.54, 126.97, 126.74, 126.27, 117.16, 113.03, 102.11, 59.41, 55.02, 45.84, 21.62. **HRMS** calculated $[M+H]^+$ for $C_{26}H_{24}O_3NS$: 430.1471, found: 430.1469. **FTIR(cm^{-1}):** 3022, 2403,1628, 1513, 1465, 1357, 1217, 1167, 1093, 1033, 763, 669.

8-Bromo-1-phenyl-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole (3u)



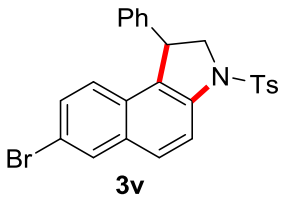
3u

Following the general procedure, treatment of 7-bromonaphthalen-2-ol **1u** (0.112 g, 0.5 mmol) with 2-phenyl-1-tosylaziridine **2a** (0.164 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 8-bromo-1-phenyl-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole **3u** as a white solid (0.166 g, 70%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.30; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.10 (d, *J* = 8.9 Hz, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.65 (t, *J* = 8.1 Hz, 3H), 7.38 (s, 1H), 7.35 (d, *J* = 8.7 Hz, 1H), 7.16 – 7.09 (m, 5H), 6.74 (d, *J* = 7.2 Hz, 2H), 4.66 (dd, J_1 = 4.3 Hz, J_2 = 10.2 Hz, 1H), 4.44 (t, *J* = 10.7 Hz, 1H), 3.98 (dd, J_1 = 4.4 Hz, J_2 = 11.1 Hz, 1H), 2.35 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 144.39, 142.84, 141.24, 133.60, 131.50, 130.34, 129.99, 129.90, 129.68, 129.01, 128.00, 127.46, 127.30, 127.17, 126.48, 125.80, 121.40, 115.89, 59.56, 45.38, 21.65. **HRMS** calculated $[M+H]^+$

for $C_{25}H_{21}O_2NBrS$: 478.0471, found: 478.0471. **FTIR(cm^{-1}):** 3020, 2977, 2401, 1619, 1502, 1434, 1351, 1256, 1165, 842, 771, 668.

7-Bromo-1-phenyl-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3v)

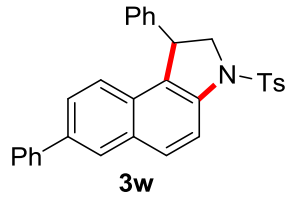


3v

Following the general procedure, treatment of 6-bromonaphthalen-2-ol **1v** (0.111 g, 0.5 mmol) with 2-phenyl-1-tosylaziridine **2a** (0.164 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05 mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 7-bromo-1-phenyl-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole **3v** as a white solid (0.171 g, 71%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.30; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.12 (d, *J* = 8.9 Hz, 1H), 7.92 – 7.78 (m, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.35-7.22 (m, 3H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.78 (t, *J* = 8.5 Hz, 2H), 6.73 – 6.63 (m, 2H), 4.74 (dd, J_1 = 4.0 Hz, J_2 = 10.1 Hz, 1H), 4.47 (t, *J* = 10.7 Hz, 1H), 3.96 (dd, J_1 = 4.1 Hz, J_2 = 11.2 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 144.38, 143.09, 140.76, 133.56, 132.49, 130.69, 130.28, 129.90, 129.13, 128.96, 128.77, 127.55, 127.48, 127.35, 127.10, 125.33, 118.36, 116.67, 59.46, 45.53, 21.64. **HRMS** calculated $[M+H]^+$ for $C_{25}H_{21}O_2NBrS$: 478.0471, found: 478.0471. **FTIR (cm^{-1}):** 3020, 1584, 1500, 1354, 1216, 1166, 1092, 882, 772, 703, 668.

1,7-Diphenyl-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole (3w)



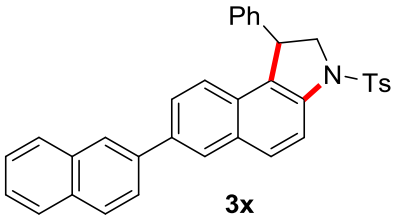
3w

Following the general procedure, treatment of 6-phenylnaphthalen-2-ol **1w** (0.110 g, 0.5 mmol) with 2-phenyl-1-tosylaziridine **2a** (0.164 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 1,7-diphenyl-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole **3w** as a white solid (0.180 g, 76%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.37; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.15 (d, *J* = 8.9 Hz, 1H), 8.02 (s, 1H), 7.92 (d, *J* = 8.9 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.51 (dd, J_1 = 0.9 Hz, J_2 = 8.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.34 (dd, J_1 = 8.0 Hz, J_2 = 17.8 Hz, 2H), 7.17 – 7.10 (m, 5H), 6.79 (d, *J* = 7.0 Hz, 2H), 4.76 (dd, J_1 = 4.5 Hz, J_2 = 10.2 Hz, 1H), 4.50

(t, J = 10.7 Hz, 1H), 4.00 (dd, J_1 = 4.6 Hz, J_2 = 11.1 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.24, 143.39, 140.84, 140.43, 137.30, 133.61, 131.69, 130.33, 129.85, 129.42, 128.97, 128.89, 127.52, 127.44, 127.28, 126.96, 126.67, 126.54, 124.18, 116.08, 59.56, 45.61, 21.62. **HRMS** calculated $[M+H]^+$ for $C_{31}H_{26}O_2NS$: 476.1679, found: 476.1678. **FTIR(cm^{-1}):** 3020, 2400, 1597, 1494, 1355, 1216, 1167, 1093, 813, 771, 700, 667.

7-(Naphthalen-2-yl)-1-phenyl-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3x)

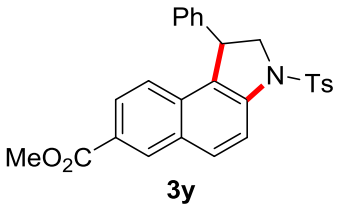


3x

Following the general procedure, treatment of [2,2'-binaphthalen]-6-ol **1x** (0.135 g, 0.5 mmol) with 2-phenyl-1-tosylaziridine **2a** (0.164 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 7-(naphthalen-2-yl)-1-phenyl-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole **3x** as a white solid (0.176 g, 67%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.32; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.15– 8.11 (m, 2H), 8.03 (s, 1H), 7.93 – 7.83 (m, 4H), 7.74 (d, J = 8.5 Hz, 1H), 7.65 (d, J = 8.1 Hz, 2H), 7.61 (d, J = 8.7 Hz, 1H), 7.49 – 7.46 (m, 2H), 7.32 (d, J = 8.7 Hz, 1H), 7.11 (dd, J_1 = 7.7 Hz, J_2 = 16.8 Hz, 5H), 6.76 (d, J = 7.1 Hz, 2H), 4.74 (dd, J_1 = 4.5 Hz, J_2 = 10.2 Hz, 1H), 4.48 (t, J = 10.7 Hz, 1H), 3.97 (dd, J_1 = 4.6 Hz, J_2 = 11.1 Hz, 1H), 2.33 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.25, 143.41, 140.51, 138.13, 137.15, 133.80, 133.64, 132.72, 131.77, 130.38, 129.87, 129.49, 128.92, 128.66, 128.29, 127.77, 127.53, 127.47, 127.34, 126.98, 126.84, 126.81, 126.51, 126.15, 125.97, 125.56, 124.30, 116.16, 59.58, 45.64, 21.63. **HRMS** calculated $[M+H]^+$ for $C_{35}H_{28}O_2NS$: 526.1835, found: 526.1838. **FTIR(cm^{-1}):** 3020, 2400, 11597, 1356, 1216, 1167, 1092, 817, 757, 669.

Methyl-1-phenyl-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole-7-carboxylate (3y)



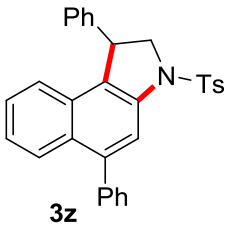
3y

Following the general procedure, treatment of methyl 6-hydroxy-2-naphthoate **1y** (0.101 g, 0.5 mmol) with 2-phenyl-1-tosylaziridine **2a** (0.164 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05 mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the

crude mixture afforded methyl-1-phenyl-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole-7-carboxylate **3y** as a white solid (0.197 g, 86%).

***R*$_f$** (Pet. ether/EtOAc =80/20): 0.34; **^{1}H NMR (400 MHz, CDCl$_3$** δ 8.56 (s, 1H), 8.16 (d, *J* = 8.9 Hz, 1H), 7.96 (d, *J* = 8.9 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.24 (m, 1H), 7.23 – 7.04 (m, 5H), 6.75 (d, *J* = 7.1 Hz, 2H), 4.76 (dd, J_1 = 4.5 Hz, J_2 = 10.3 Hz, 1H), 4.50 (t, *J* = 10.7 Hz, 1H), 4.03 – 3.97 (m, 1H), 3.94 (d, *J* = 8.7 Hz, 3H), 2.36 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 167.14, 144.47, 143.05, 142.43, 133.67, 132.56, 131.79, 131.62, 130.32, 129.94, 128.96, 127.44, 127.35, 127.26, 127.12, 126.42, 125.97, 123.75, 116.15, 59.55, 52.31, 45.38, 21.63. **HRMS** calculated $[M+H]^+$ for $C_{27}H_{24}O_4NS$: 458.1421, found: 458.1421. **FTIR (cm^{-1}):** 3023, 2403, 1714, 1627, 1468, 1355, 1215, 1167, 1096, 763, 668.

1,5-Diphenyl-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole (3z)



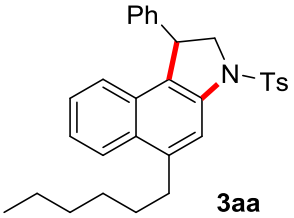
3z

Following the general procedure, treatment of 4-phenylnaphthalen-2-ol **1z** (0.110 g, 0.5 mmol) with 2-phenyl-1-tosylaziridine **2a** (0.164 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05 mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 1,5-diphenyl-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole **3z** as a yellow solid (0.166g, 70%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.34; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.06 (s, 1H), 7.83 – 7.78 (m, 1H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.53 - 7.52 (m, 4H), 7.47 (dd, J_1 = 4.1 Hz, J_2 = 8.4 Hz, 1H), 7.32 – 7.29 (m, 1H), 7.22 - 7.20 (m, 2H), 7.16 – 7.09 (m, 5H), 6.80 (d, *J* = 7.1 Hz, 2H), 4.76 (dd, J_1 = 4.1 Hz, J_2 = 10.2 Hz, 1H), 4.48 (t, *J* = 10.7 Hz, 1H), 4.00 (dd, J_1 = 4.2 Hz, J_2 = 11.0 Hz, 1H), 2.34 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 144.25, 143.45, 142.62, 140.52, 139.84, 133.68, 130.61, 130.24, 129.85, 129.69, 128.89, 128.47, 127.72, 127.54, 127.45, 127.20, 126.94, 126.83, 126.60, 124.59, 123.95, 116.39, 59.60, 45.67, 21.62. **HRMS** calculated $[M+H]^+$ for $C_{31}H_{26}O_2NS$: 476.1679, found: 476.1679. **FTIR(cm^{-1}):** 3021, 1597, 1470, 1355, 1216, 1167, 1093, 813, 768, 700, 669.

5-Hexyl-1-phenyl-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3aa)

Following the general procedure, treatment of 4-hexylnaphthalen-2-ol **1aa** (0.114 g, 0.5 mmol) with 2-phenyl-1-tosylaziridine **2a** (0.164 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05

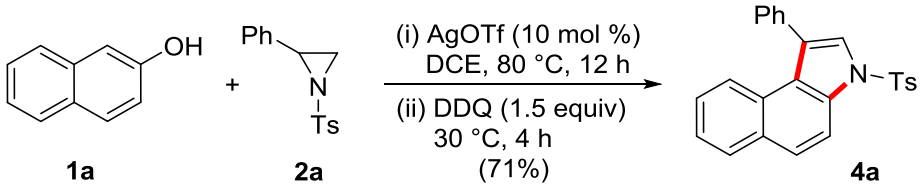


3aa

mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 5-hexyl-1-phenyl-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole **3aa** as a white solid (0.165 g, 68%).

R_f (Pet. ether/EtOAc =90/10): 0.4; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.04 (d, *J* = 9.7 Hz, 2H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.37 – 7.25 (m, 3H), 7.17 – 7.09 (m, 5H), 6.76 (d, *J* = 7.0 Hz, 2H), 4.73 (dd, J_1 = 3.5 Hz, J_2 = 9.8 Hz , 1H), 4.47 (t, *J* = 10.7 Hz, 1H), 3.99 (dd, J_1 = 3.8 Hz, J_2 = 11.0 Hz, 1H), 3.18 (t, *J* = 7.5 Hz, 2H), 2.38 (s, 3H), 1.85 (dd, J_1 = 7.2 Hz, J_2 = 14.4 Hz, 2H), 1.55 – 1.44 (m, 6H), 0.99 (t, *J* = 6.46 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 144.10, 143.62, 141.72, 139.95, 133.65, 130.69, 129.81, 129.75, 128.77, 127.49, 127.37, 126.76, 126.45, 125.30, 124.89, 124.43, 124.28, 115.59, 59.56, 45.56, 33.86, 31.93, 31.24, 29.62, 22.83, 21.57, 14.28. **HRMS** calculated $[M+H]^+$ for $C_{31}H_{34}O_2NS$: 484.2305, found: 484.2307. **FTIR(cm^{-1}):** 3027, 2929, 2857, 1596, 1466, 1357, 1165, 1092, 1033, 878, 812, 757, 702, 667.

1-Phenyl-3-tosyl-3*H*-benzo[*e*]indole (4a)



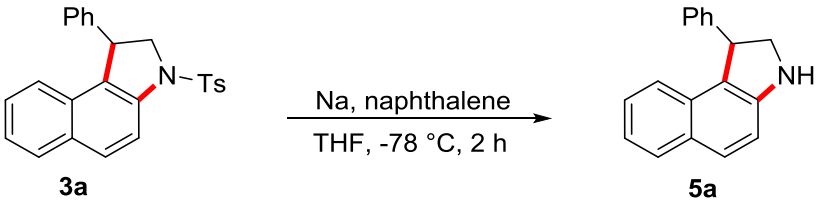
1a **2a** **4a**

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added Ag OTf (0.013 g, 0.05 mmol) 2-naphthol **1a** (0.072 g, 0.5 mmol) and 2-phenyl-1-tosylaziridine **2a** (0.164 g, 0.6 mmol) followed by DCE (2.0 mL) was added under argon atmosphere. Then the reaction mixture was placed in a preheated oil bath at 80 °C for 12 h under argon conditions. To this reaction mixture 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (227 mg, 1.0 mmol) was added at 30 °C. The reaction mixture stirred for 4 h. Then the reaction stopped and the crude reaction mixture was purified by column chromatography on silica gel to afford 1-phenyl-3-tosyl-3*H*-benzo[e]indole **4a** as a white solid (0.141 g, 71%).

R_f (Pet. ether/EtOAc =90/10): 0.6; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.23 (d, *J* = 9.1 Hz, 1H), 7.92 - 7.87 (t, *J* = 9.41 Hz, 2H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 9.1 Hz, 1H), 7.60 (s, 1H), 7.55 –

7.48 (m, 5H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 2.33 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 145.28, 135.51, 135.06, 132.41, 130.93, 130.11, 130.05, 128.81, 128.66, 128.15, 128.00, 127.00, 126.27, 126.15, 126.04, 124.84, 123.97, 123.73, 113.61, 21.70. **HRMS** calculated $[M+H]^+$ for $C_{25}H_{20}O_2NS$: 398.1209, found: 398.1209. **FTIR(cm^{-1}):** 3020, 1599, 1520, 1446, 1371, 1216, 1175, 1155, 1139, 1096, 772, 702, 669.

1-phenyl-2,3-dihydro-1*H*-benzo[e]indole (5a)



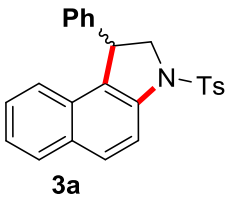
3a **5a**

Following the related procedure by Ghorai and co-workers,[8] to a flame-dried screw-capped test tube equipped with a magnetic stir bar was added **3a** (0.100 g, 0.25 mmol), in 2.0 mL THF under argon atmosphere at -78 °C. Then added sodium naphthalide (Sodium naphthalide Solution: To the vigorously stirred suspension of sodium in THF, added naphthalene (0.320 g, 2.5 mmol) in one portion (0.043 g, 1.875 mmol) under argon atmosphere at 30 °C, the resulted dark blue colour solution was further stirred for 2h) in portion wise. The dark-brown solution was stirred at -78 °C for 2 h. The reaction mixture was quenched with saturated aqueous ammonium chloride solution and the afforded the suspension was extracted with ethyl acetate (3 × 10 mL). Then the organic layer was washed with brine, dried over Na_2SO_4, concentrated and the crude reaction mixture was purified by flash column chromatography to afford the 1-phenyl-2,3-dihydro-1*H*-benzo[e]indole **5a** as a sticky liquid (0.044 g, 72%).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.36; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.36-7.22 (m, 8H), 7.16 (d, *J* = 8.5 Hz, 1H), 4.93 (dd, J_1 = 5.5, J_2 =9.7 Hz, 1H), 4.20 (t, *J* = 9.6 Hz, 1H), 4.04 (bs, 1H), 3.65 (dd, J_1 = 5.6, J_2 = 9.2 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.39, 144.63, 131.10, 129.48, 129.38, 128.80, 127.81, 126.69, 126.54, 123.02, 122.78, 122.15, 113.35, 57.31, 48.10. **HRMS** calculated $[M+H]^+$ for $C_{18}H_{16}N$: 246.1277, found: 246.1280. **FTIR (cm^{-1}):** 3394, 3062, 2867, 2251, 1626, 1593, 1486, 1304, 1254, 1028, 909, 735.

[8] A. Mal, M. Sayyad, I. A. Wani and M. K. Ghorai, *J. Org. Chem*., 2017, **82**, 4.

1-Phenyl-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3a)



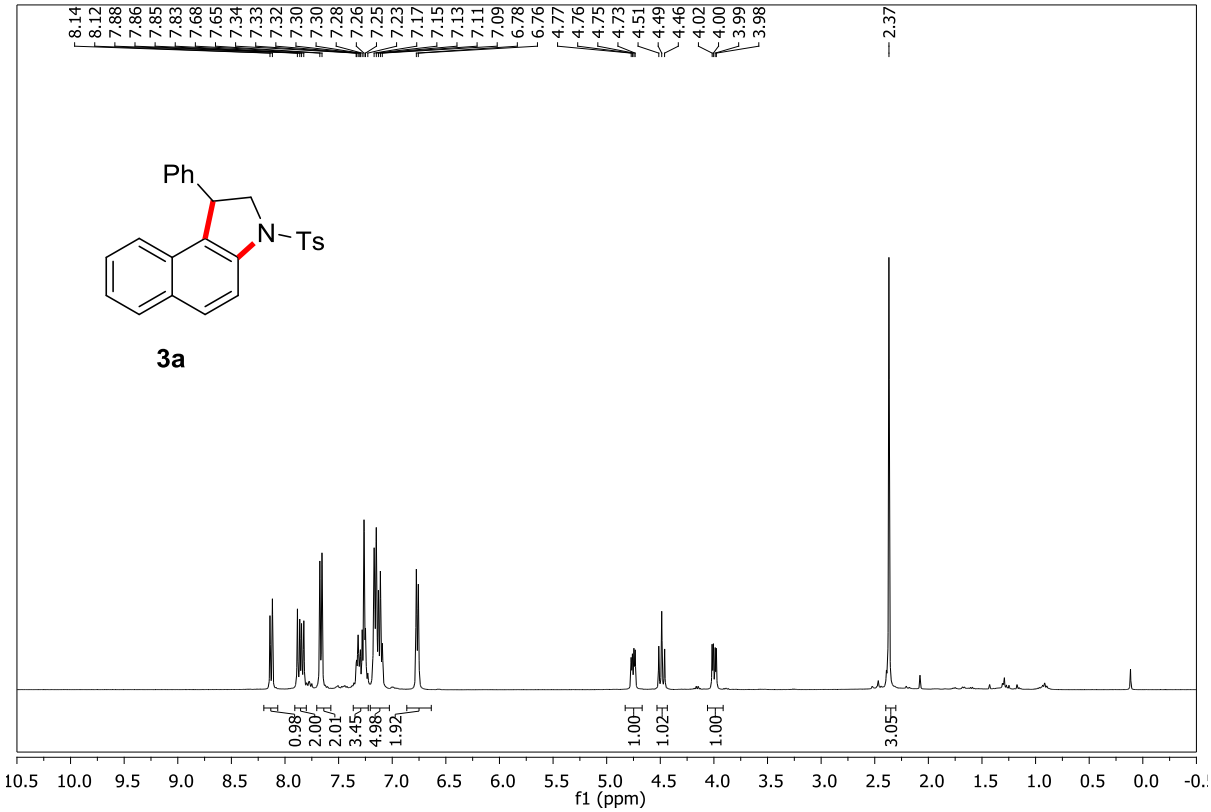
3a

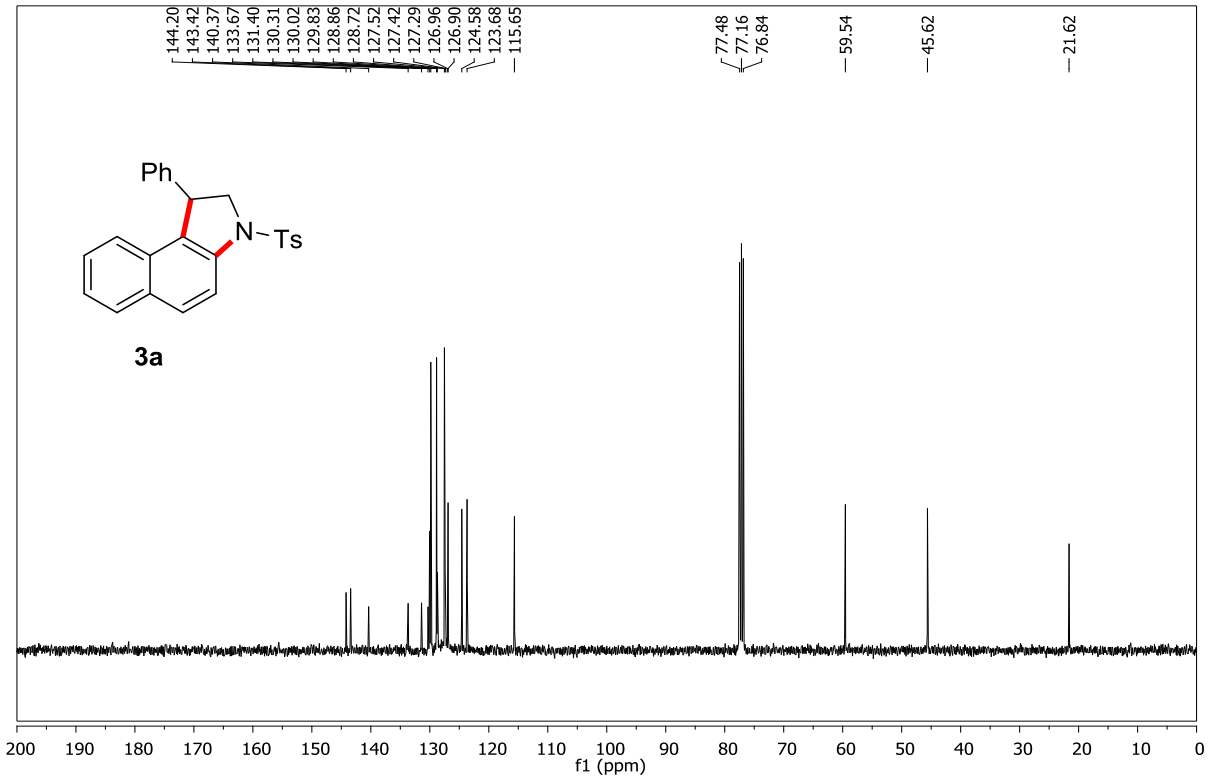
Following the general procedure, treatment of 2-naphthol **1a** (0.072 g, 0.5 mmol) with (*R*)-2-phenyl-1-tosylaziridine **(*R*)-2a** (0.164 g, 0.6 mmol) in the presence of AgOTf (0.013 g, 0.05 mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude mixture afforded 1-phenyl-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole **3a** as a white solid (0.144 g, 72%, 53:47 er).

***R*$_f$** (Pet. ether/EtOAc =90/10): 0.42; 53:47 er, HPLC (Chiralcel OD-H, 80:20 Hexane / IPA, 0.5 mL/min.) Major: 13.4 min, Minor: 19.6 min. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.12 (d, *J* = 9.0 Hz, 1H), 7.88 (dd, J_1 = 8.9 Hz, J_2 = 15.7 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.26 (m, 3H), 7.17 – 7.09 (m, 5H), 6.76 (d, *J* = 7.3 Hz, 2H), 4.77 (dd, J_1 = 4.4 Hz, J_2 =10.3 Hz, 1H), 4.48 (t, *J* = 10.8 Hz, 1H), 4.01 (dd, J_1 = 4.5 Hz, J_2 = 11.1 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 144.20, 143.41, 140.34, 133.62, 131.39, 130.29, 130.01, 129.83, 128.84, 128.71, 127.51, 127.41, 127.29, 126.95, 126.89, 124.57, 123.67, 115.63, 59.53, 45.59, 21.61. **HRMS** calculated $[M+H]^+$ for $C_{25}H_{22}O_2NS$: 400.1366, found: 400.1360. **FTIR(cm^{-1}):** 3025, 2408,1912, 1629, 1594, 1469, 1371, 1216, 1176, 1166, 1090, 767, 670.

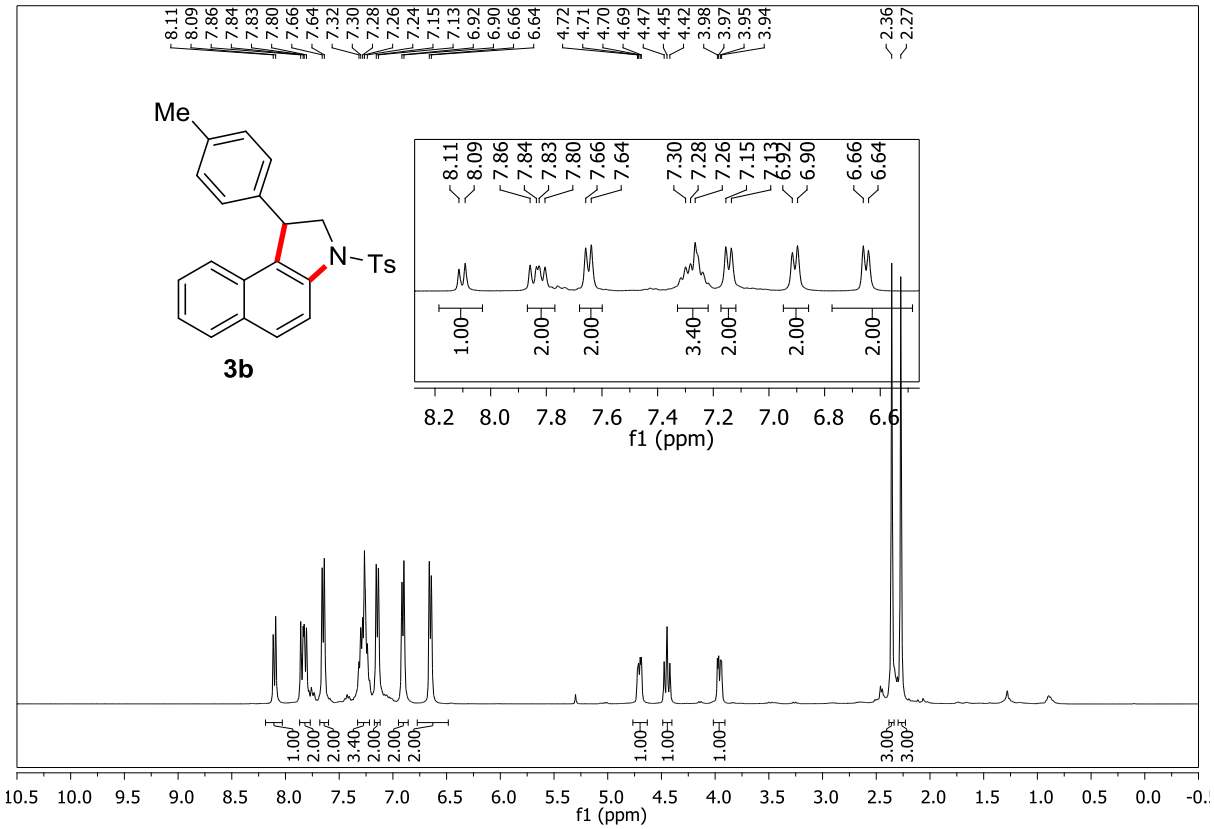
6. ^{1}H and ^{13}C NMR Spectra of Benzoindoline Derivatives

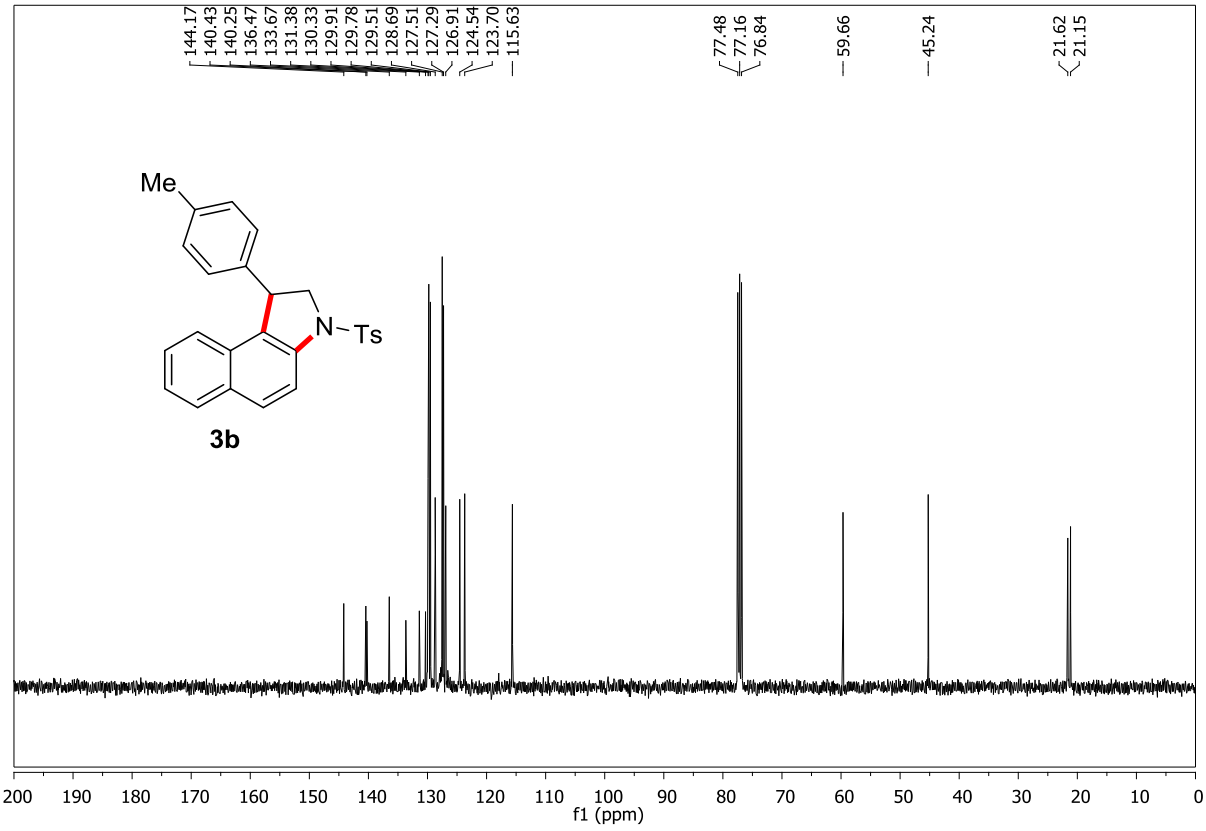
1-Phenyl-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3a)



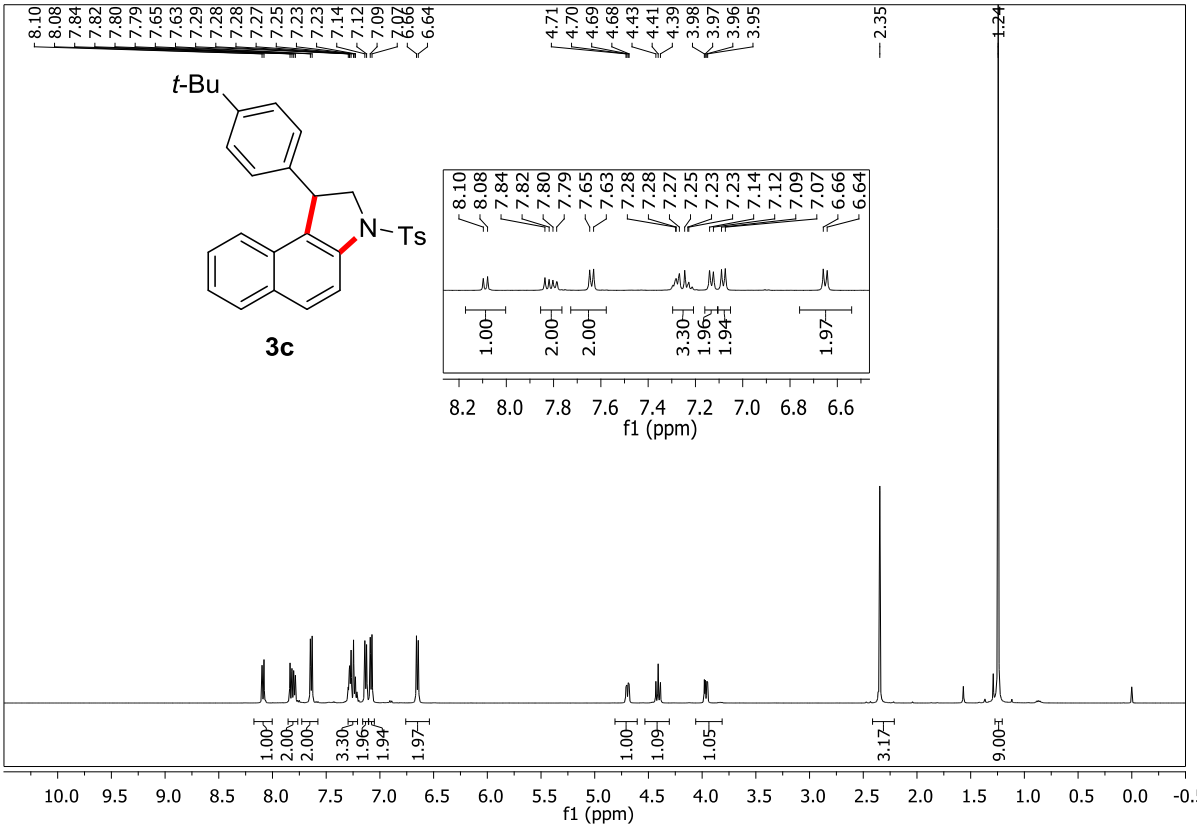


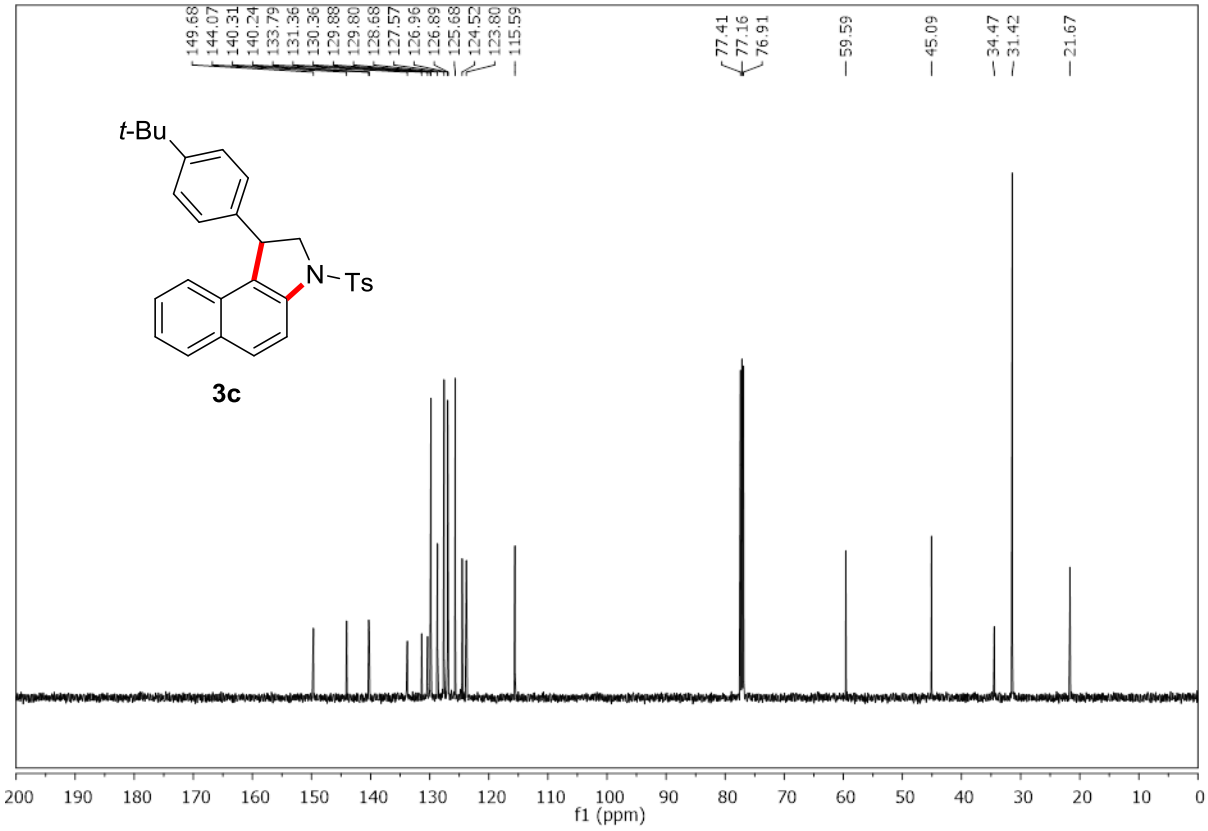
1-(*p*-Tolyl)-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3b)



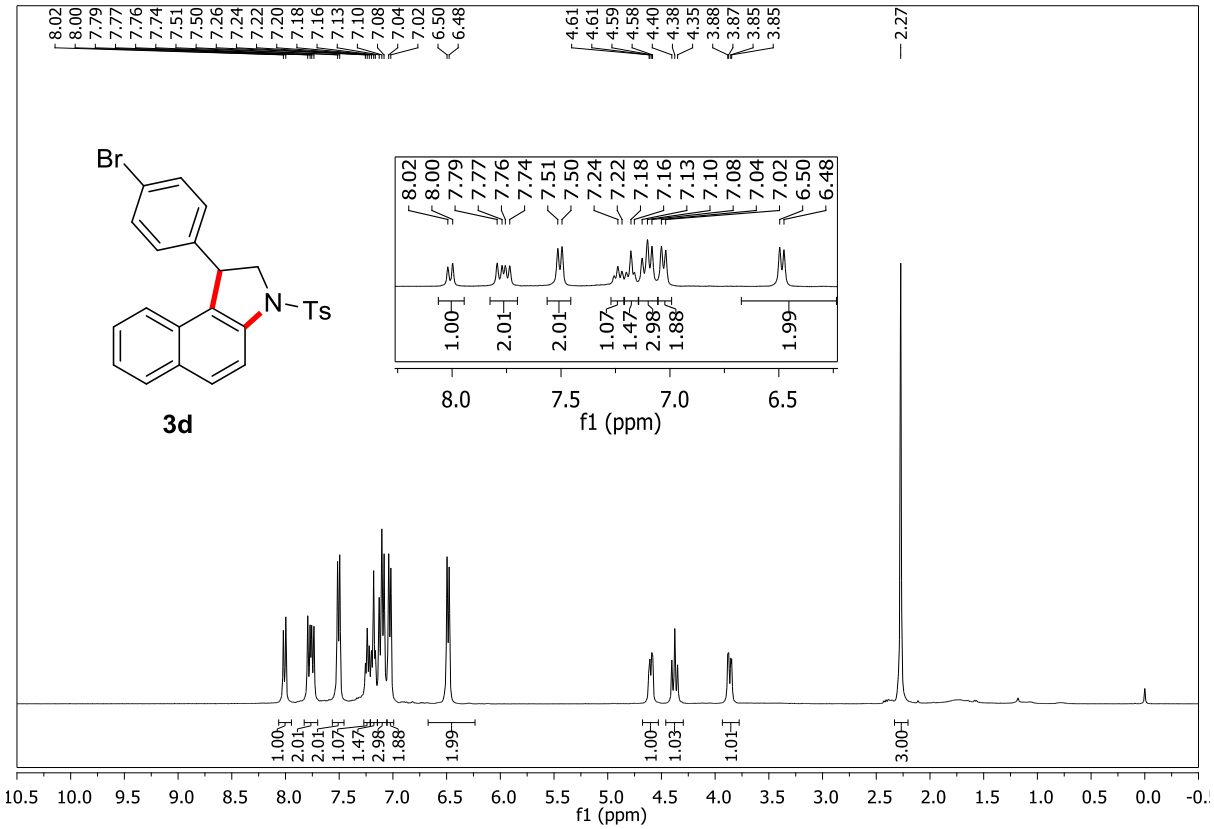


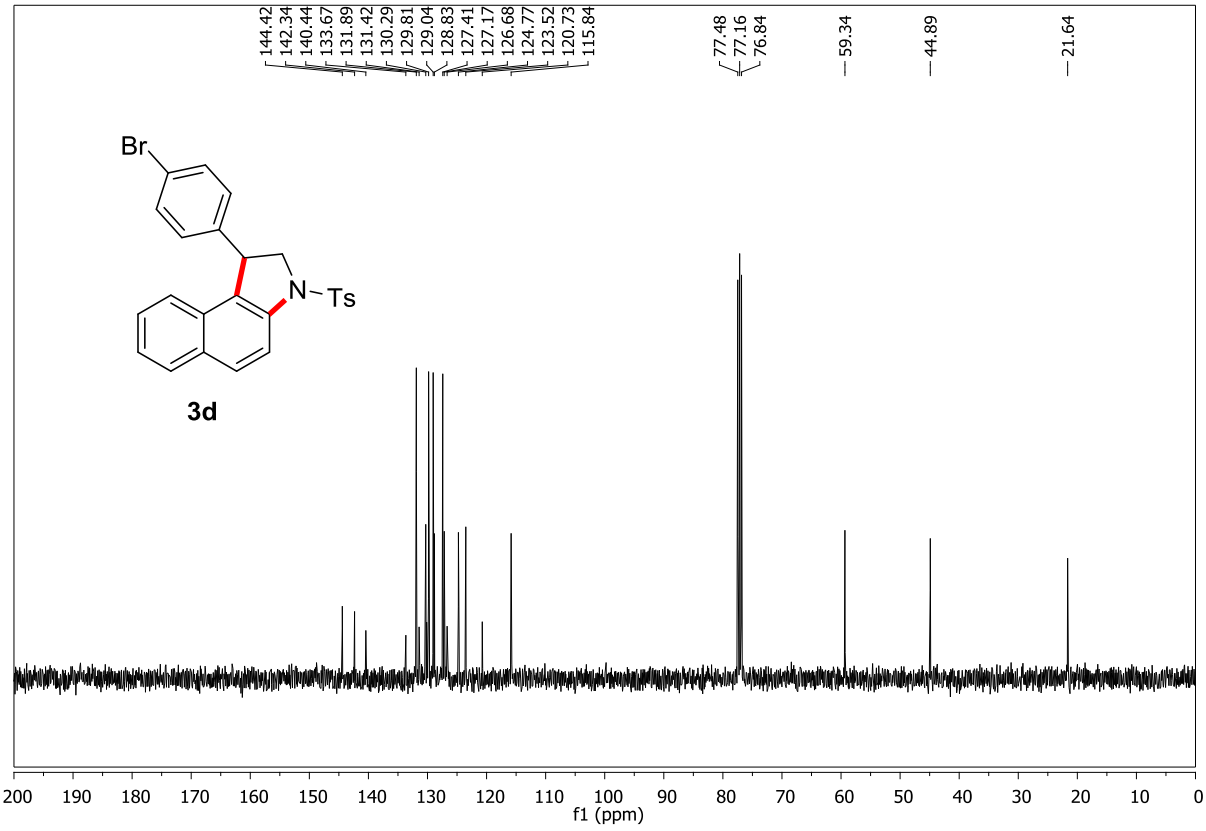
1-(4-(Tert-butyl)phenyl)-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3c)



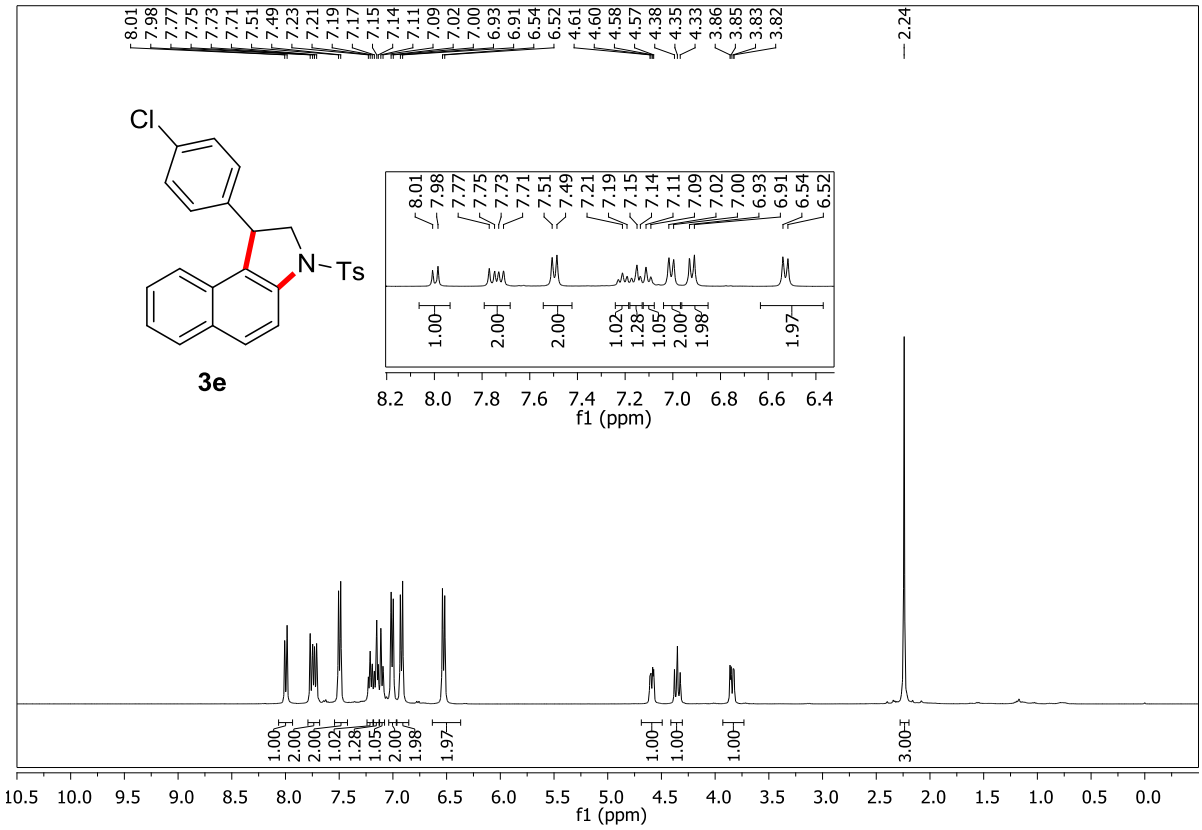


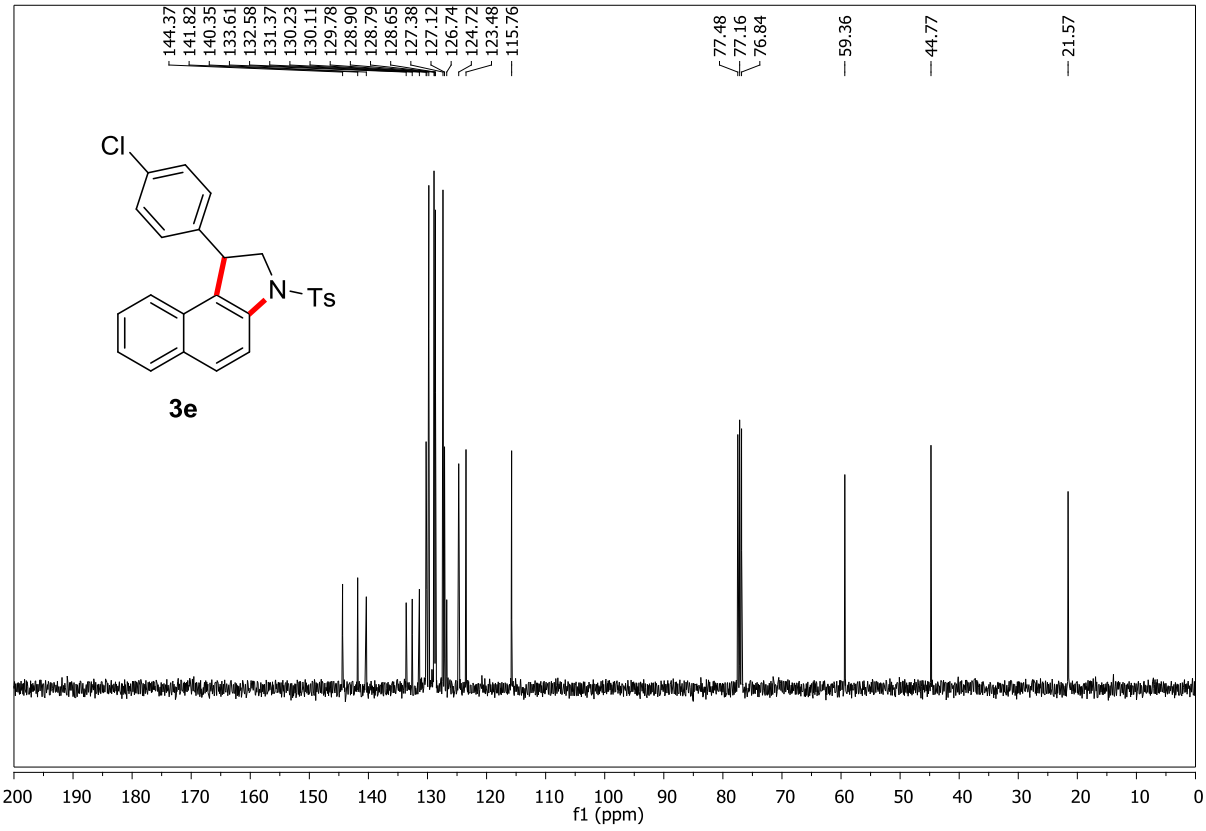
1-(4-Bromophenyl)-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3d)



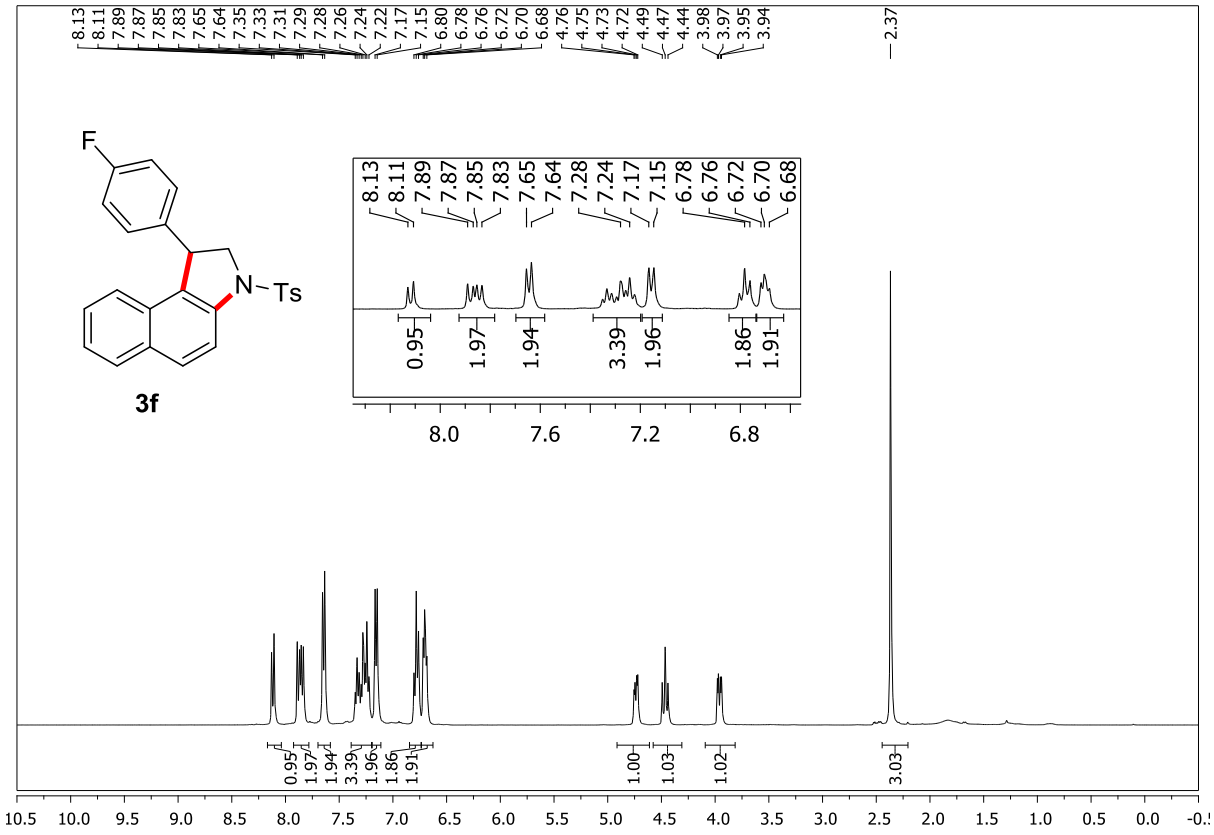


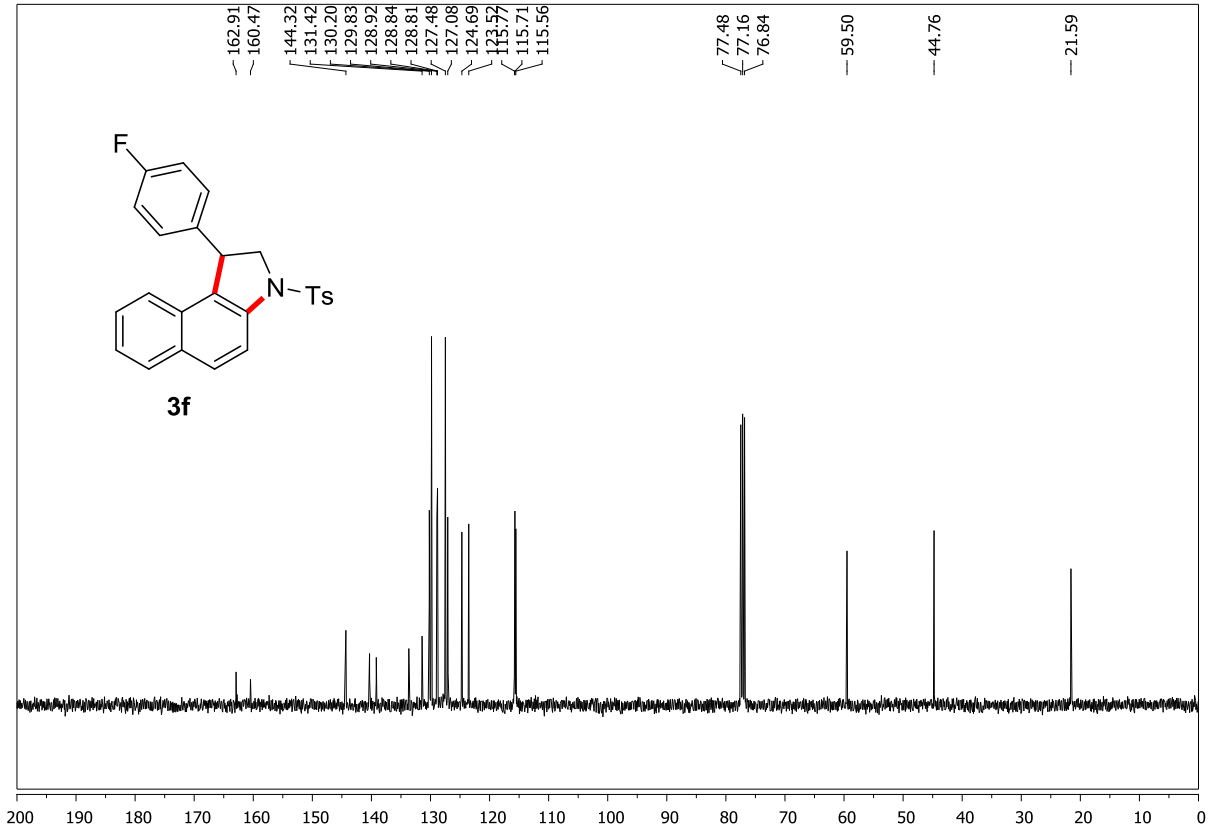
1-(4-Chlorophenyl)-3-tosyl-2,3-dihydro-1*H*-benzo[e]indole (3e)



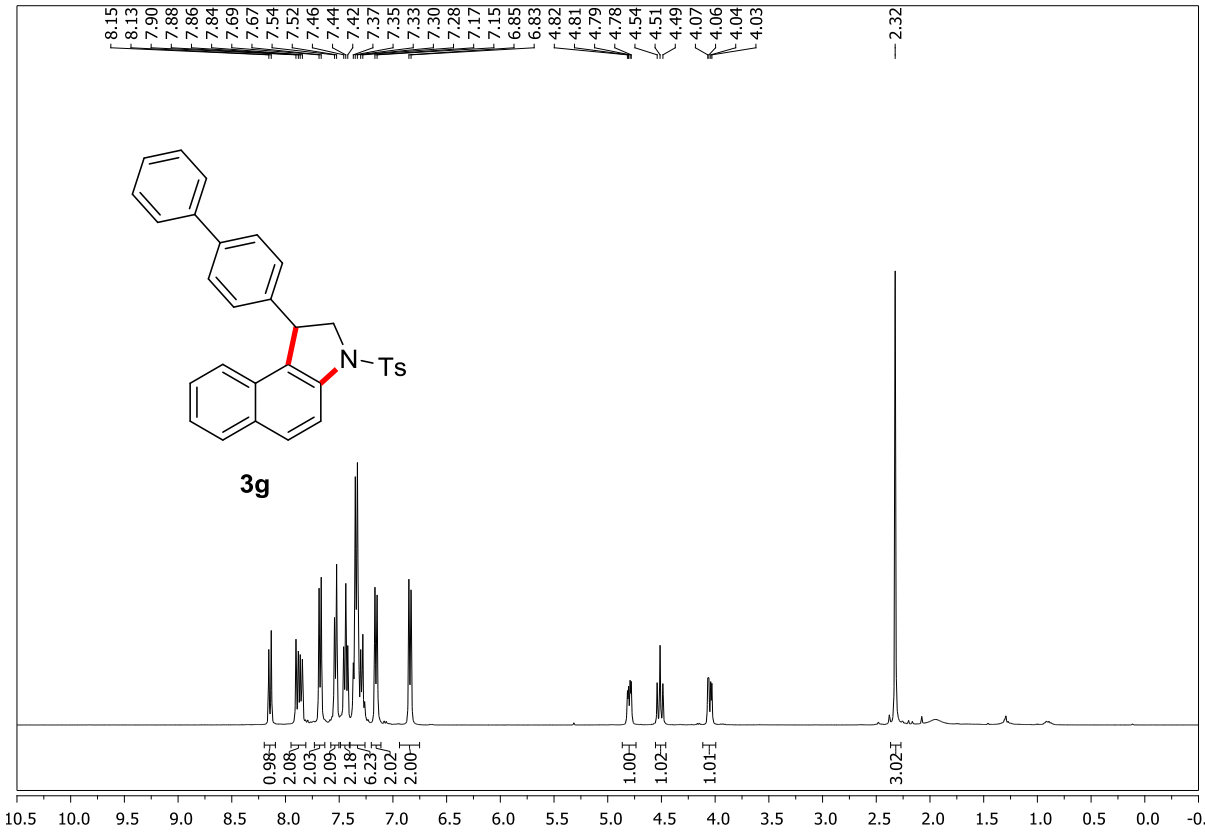


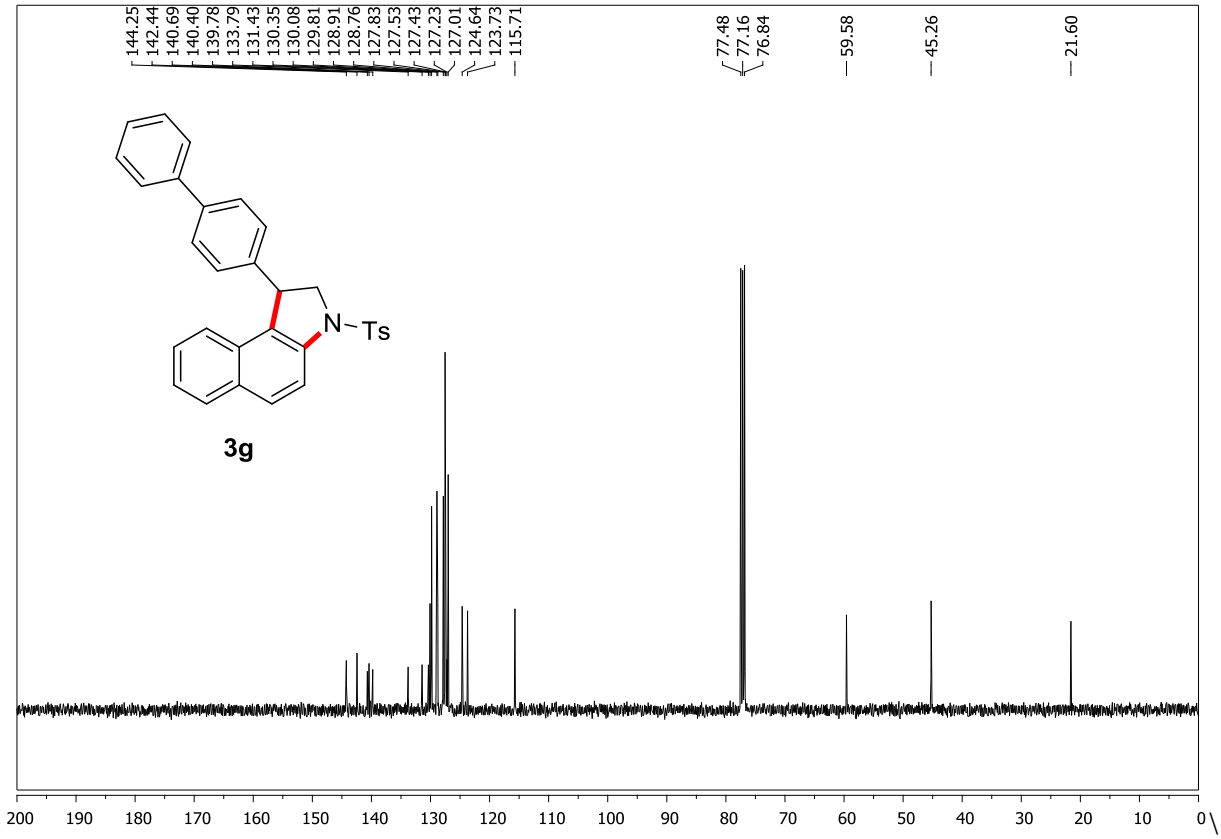
1-(4-Fluorophenyl)-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3f)



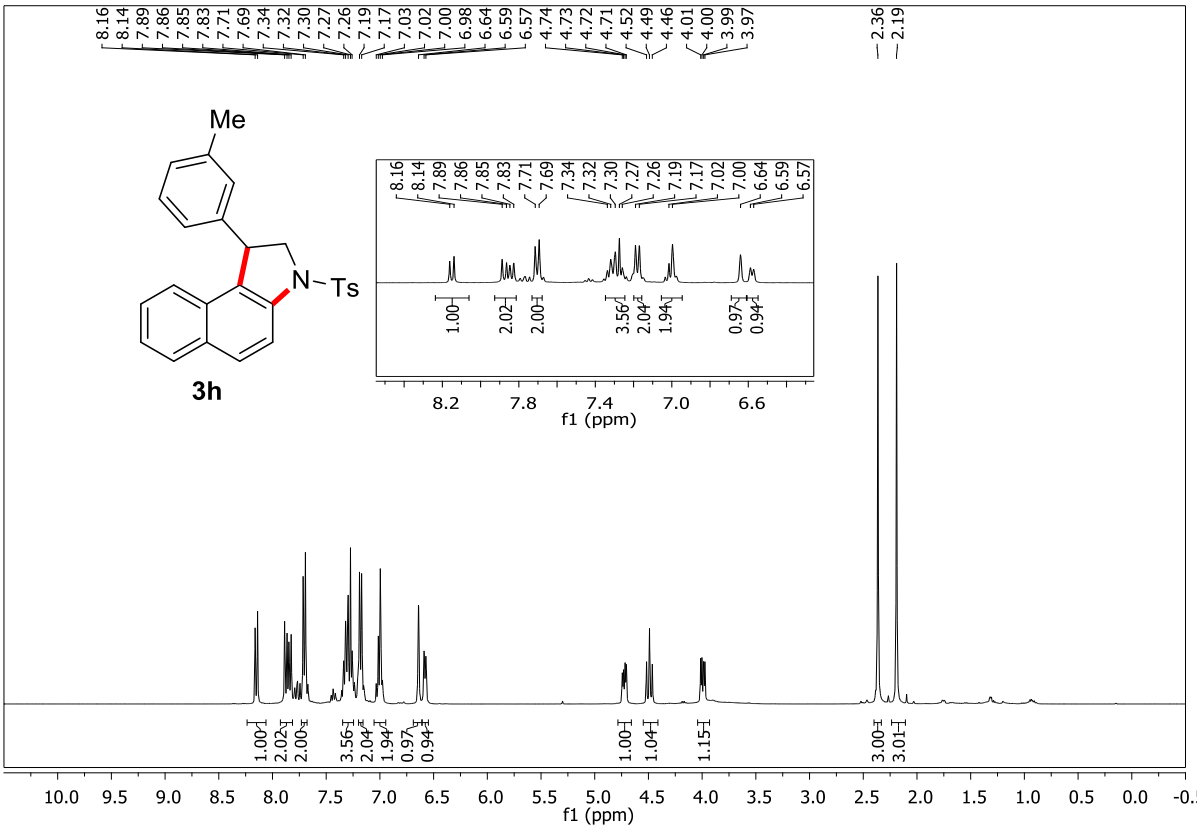


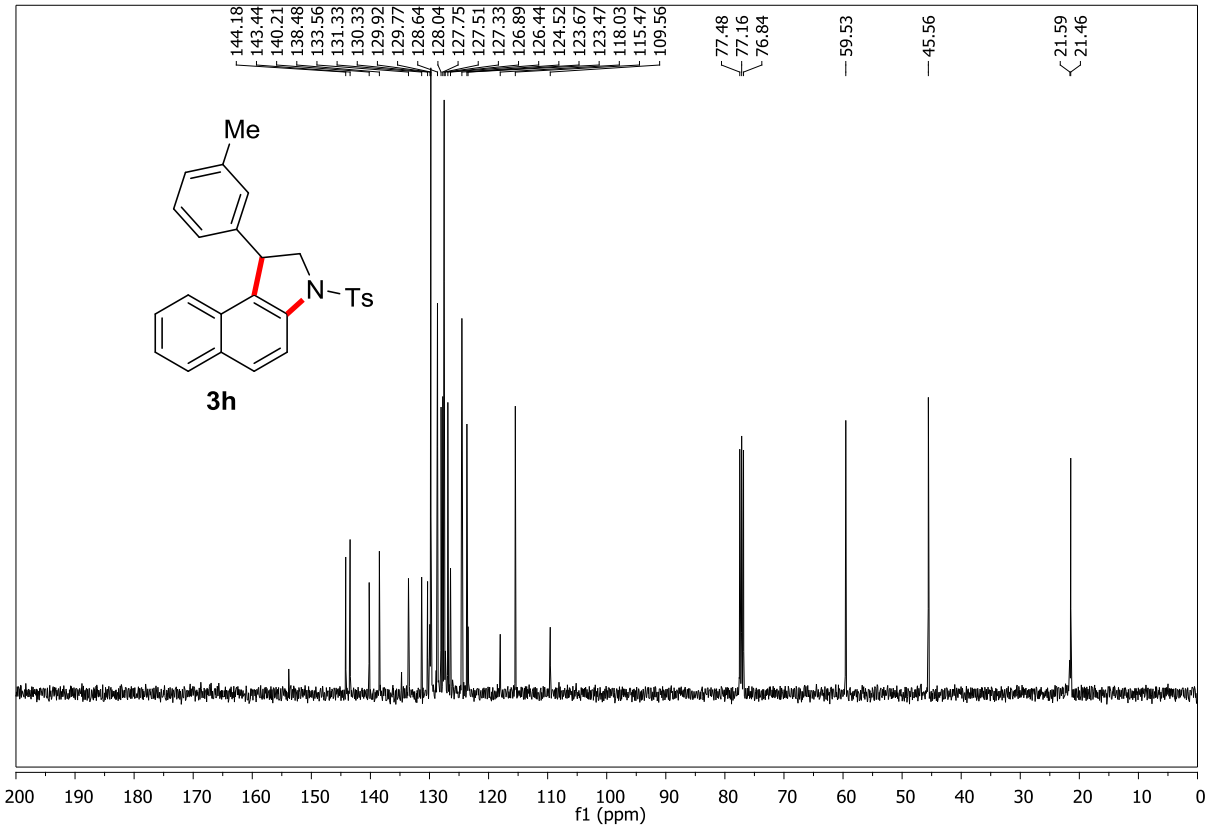
1-([1,1'-Biphenyl]-4-yl)-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3g)



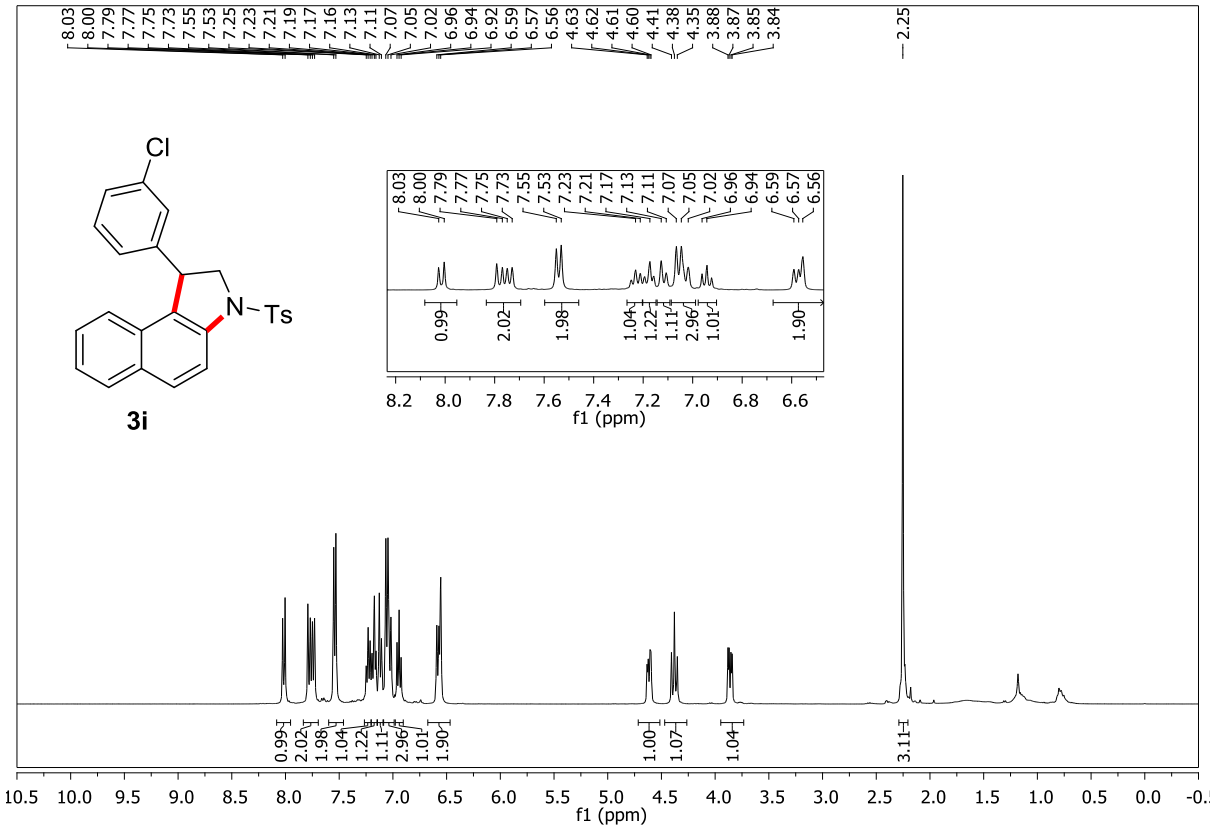


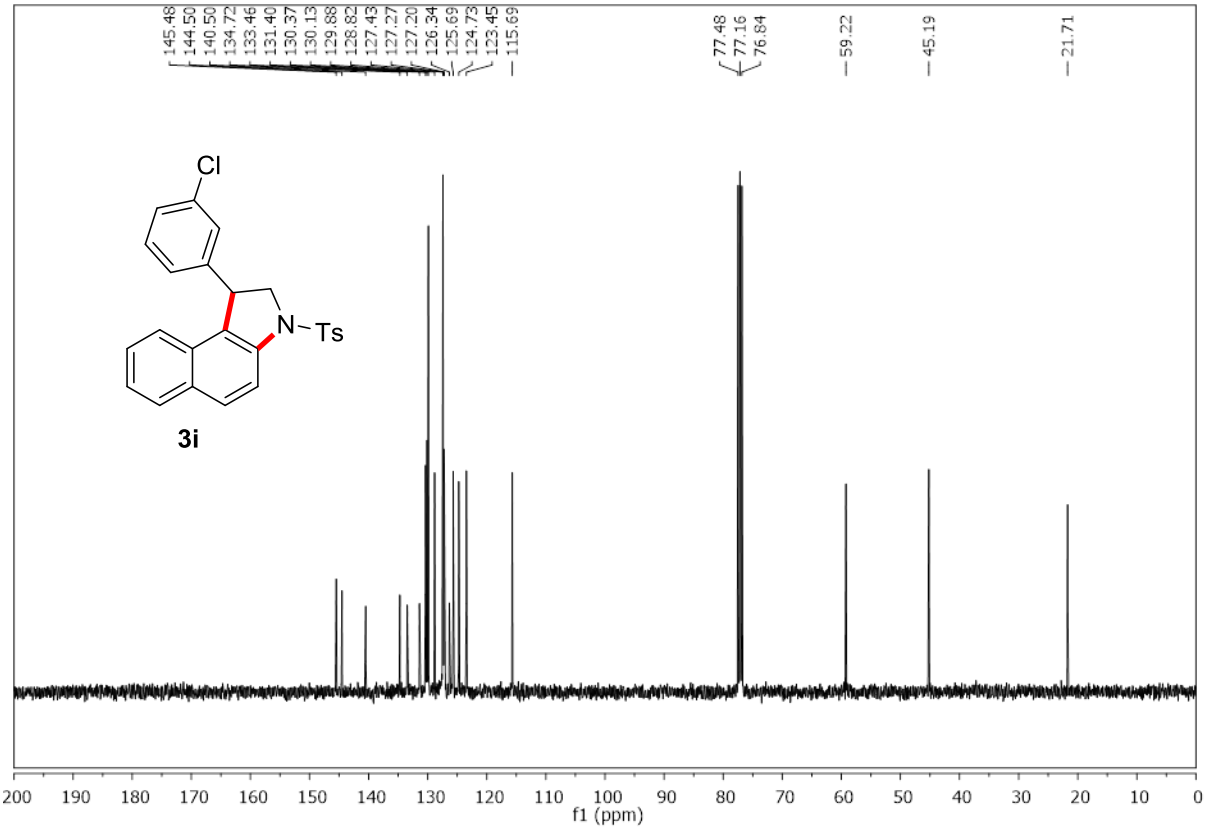
1-(*m*-Tolyl)-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole (3h)



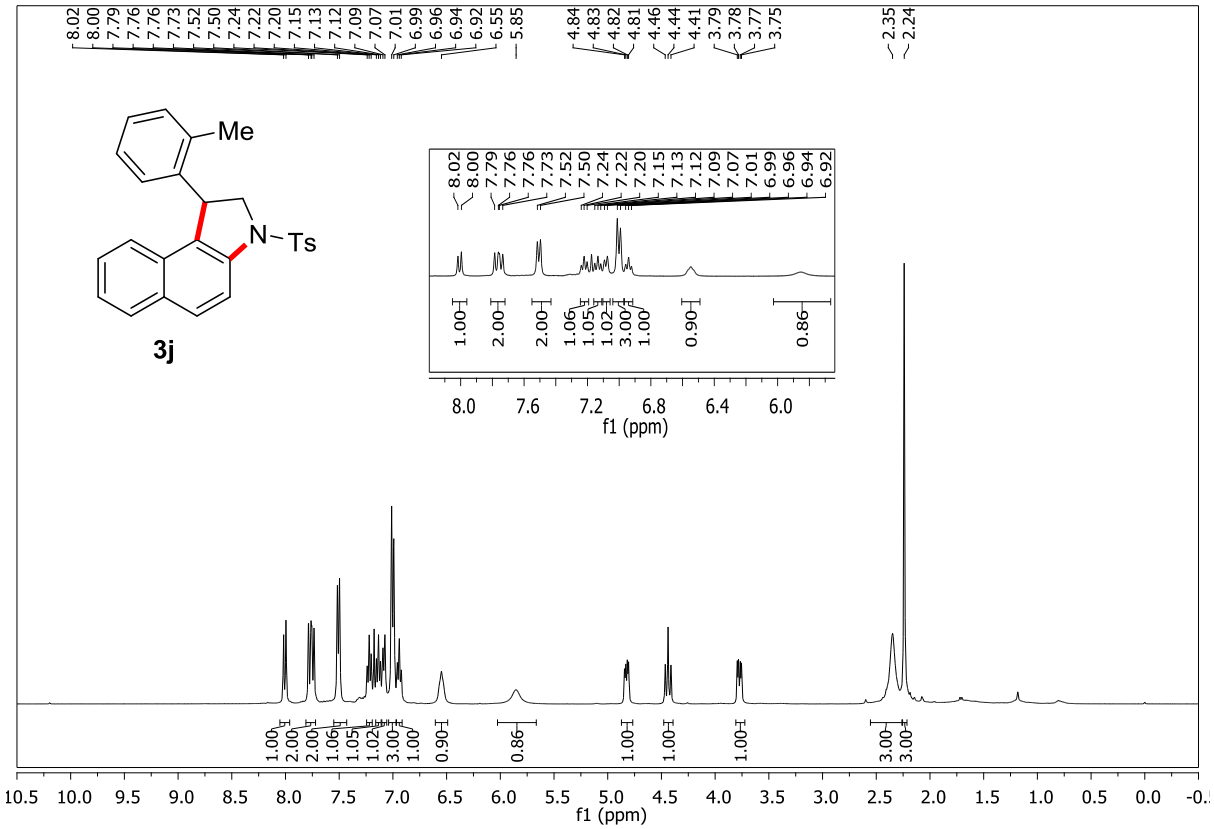


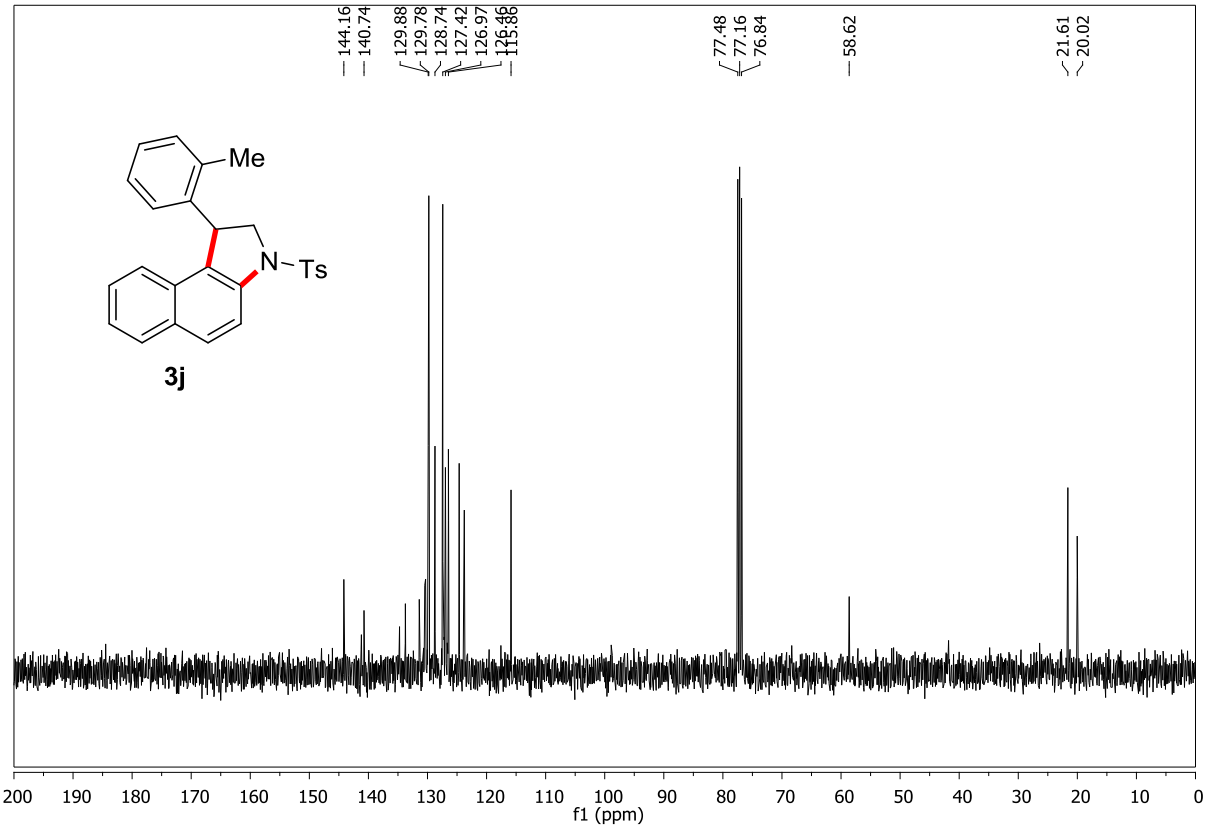
1-(3-Chlorophenyl)-3-tosyl-2,3-dihydro-1H-benzo[*e*]indole (3i)



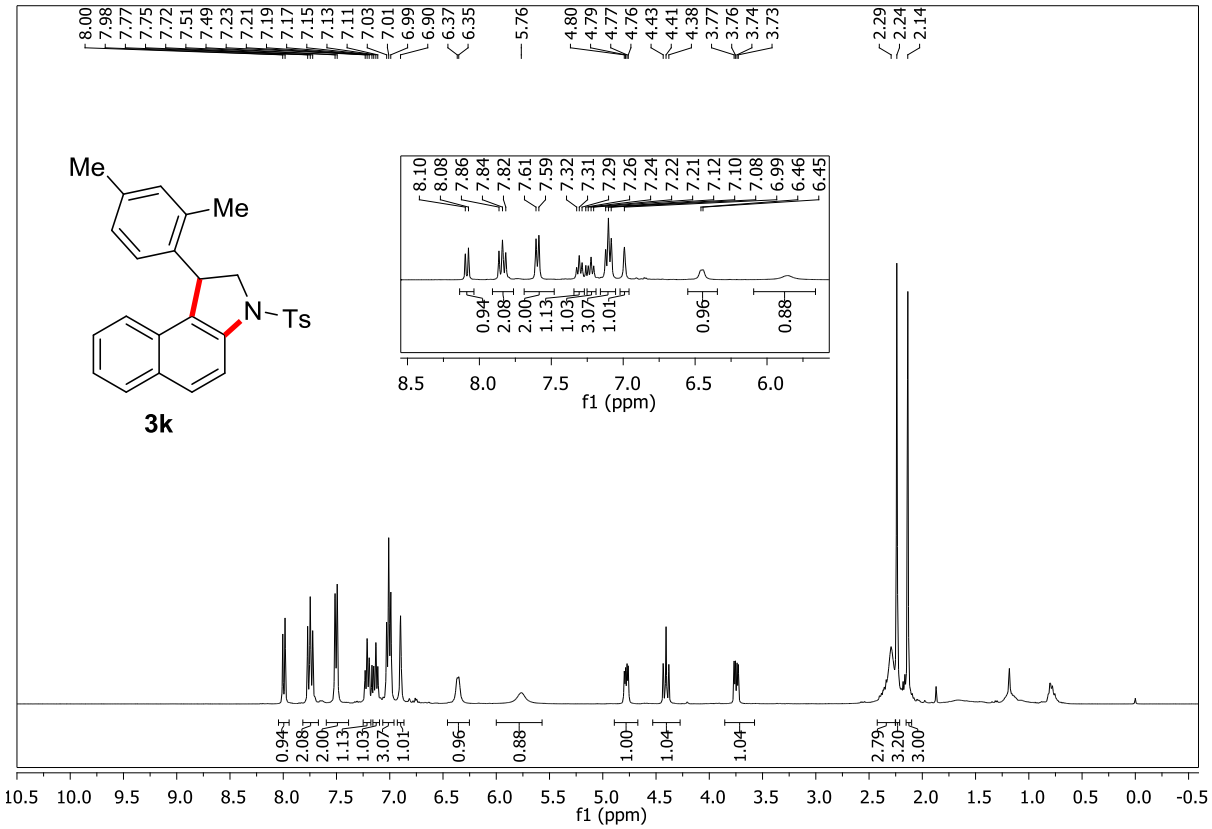


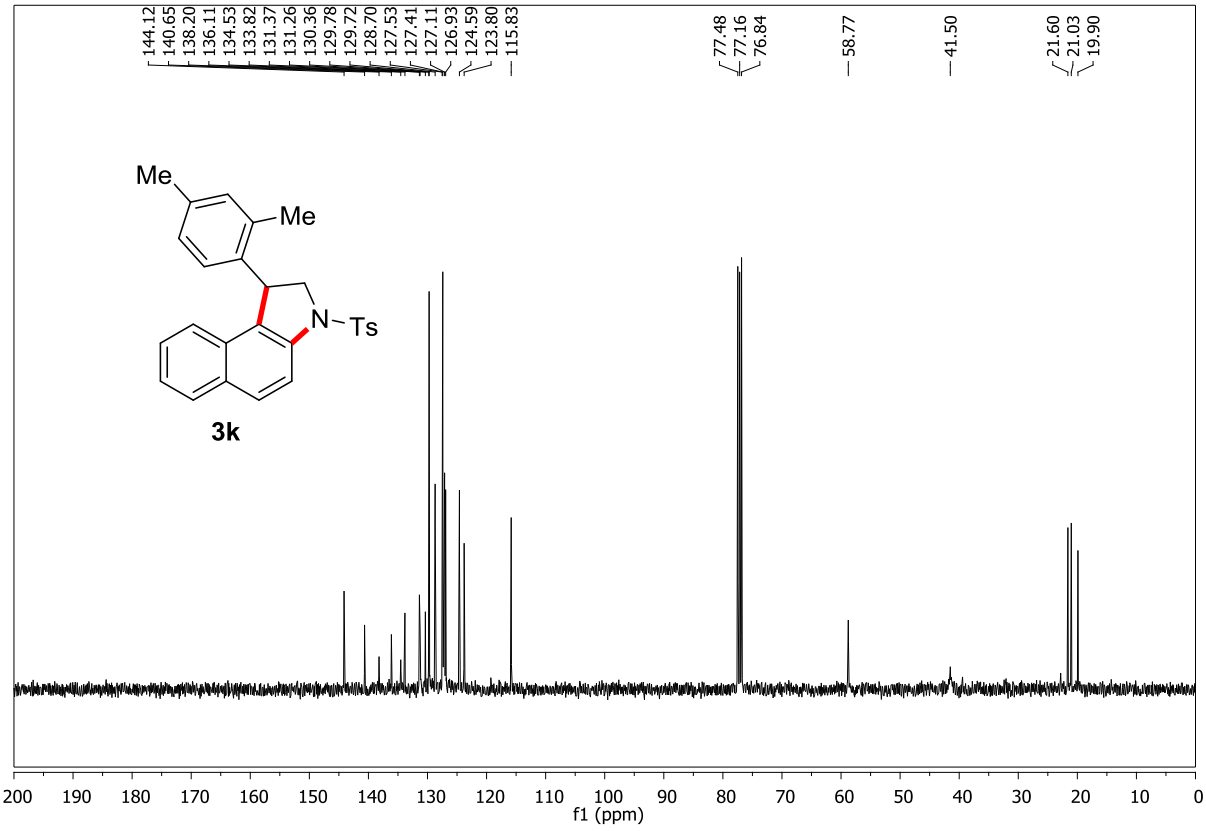
1-(o-Tolyl)-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3j)



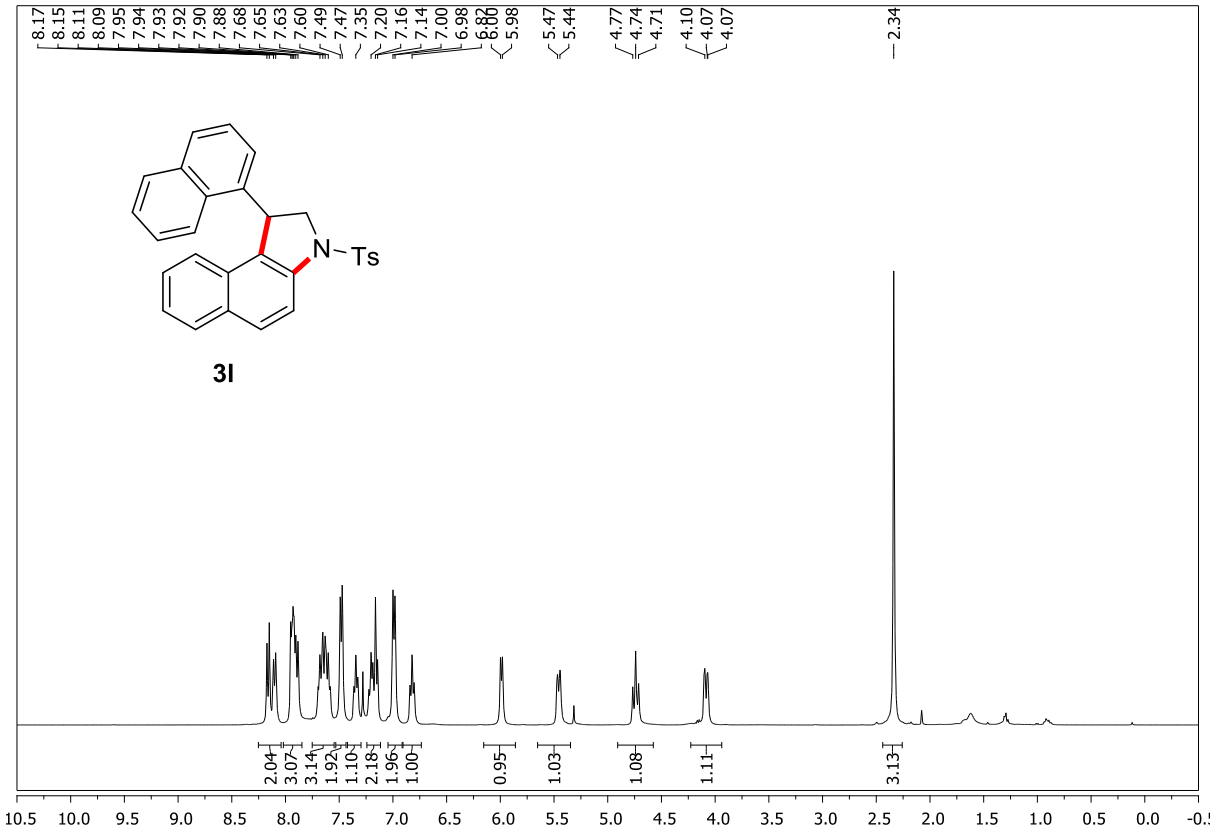


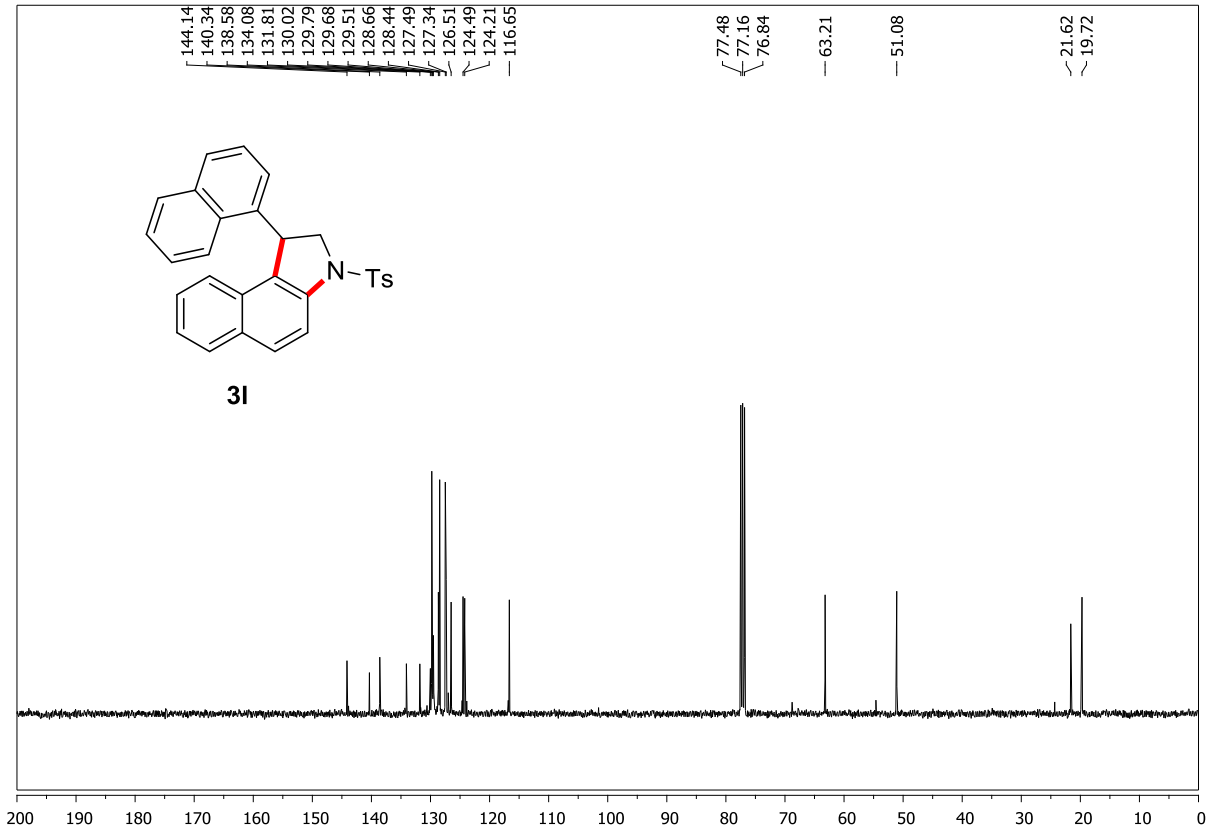
1-(2,4-Dimethylphenyl)-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3k)



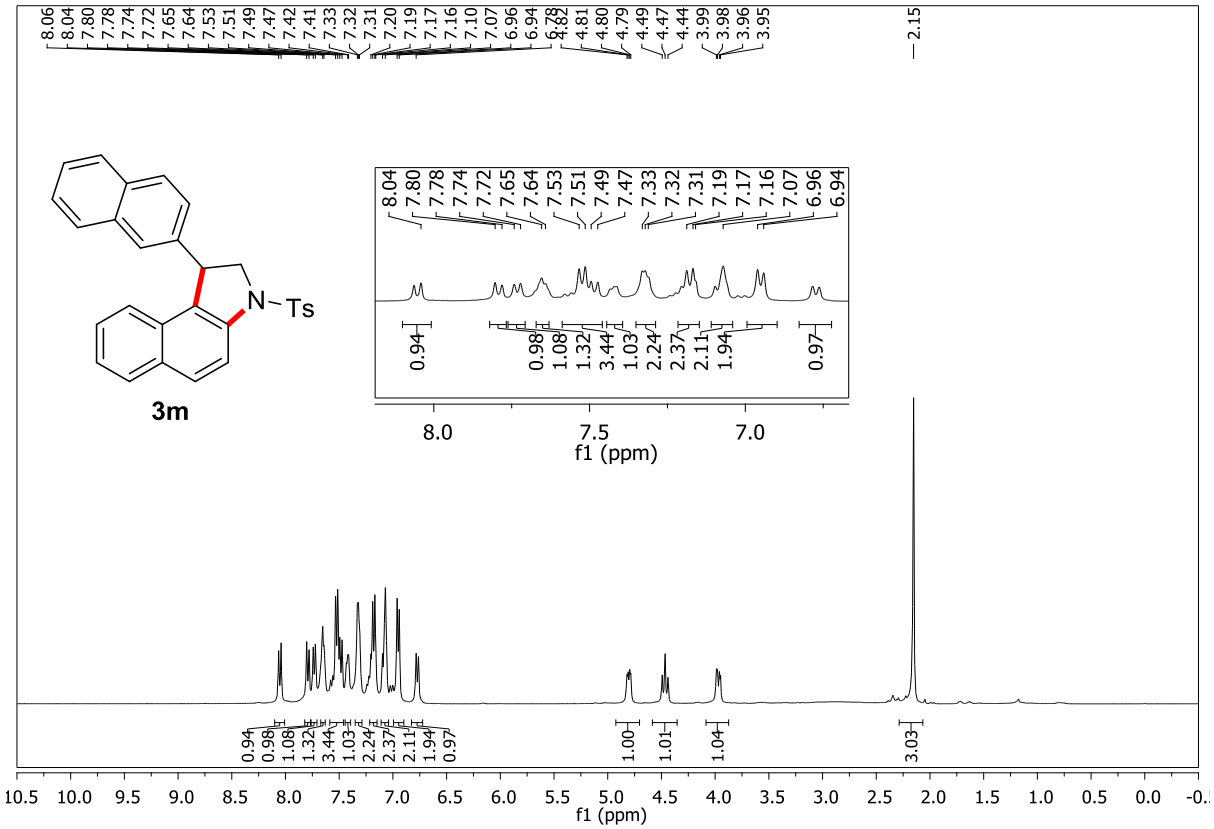


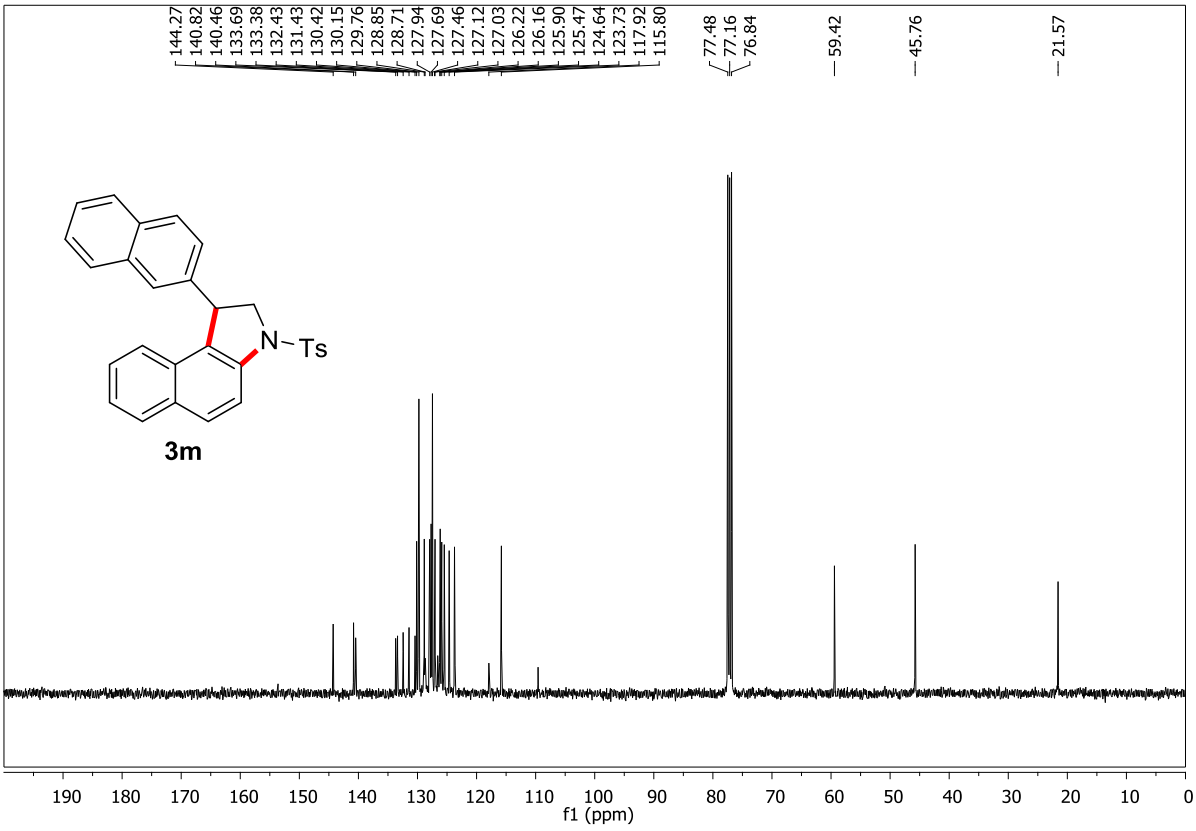
1-(Naphthalen-1-yl)-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3l)



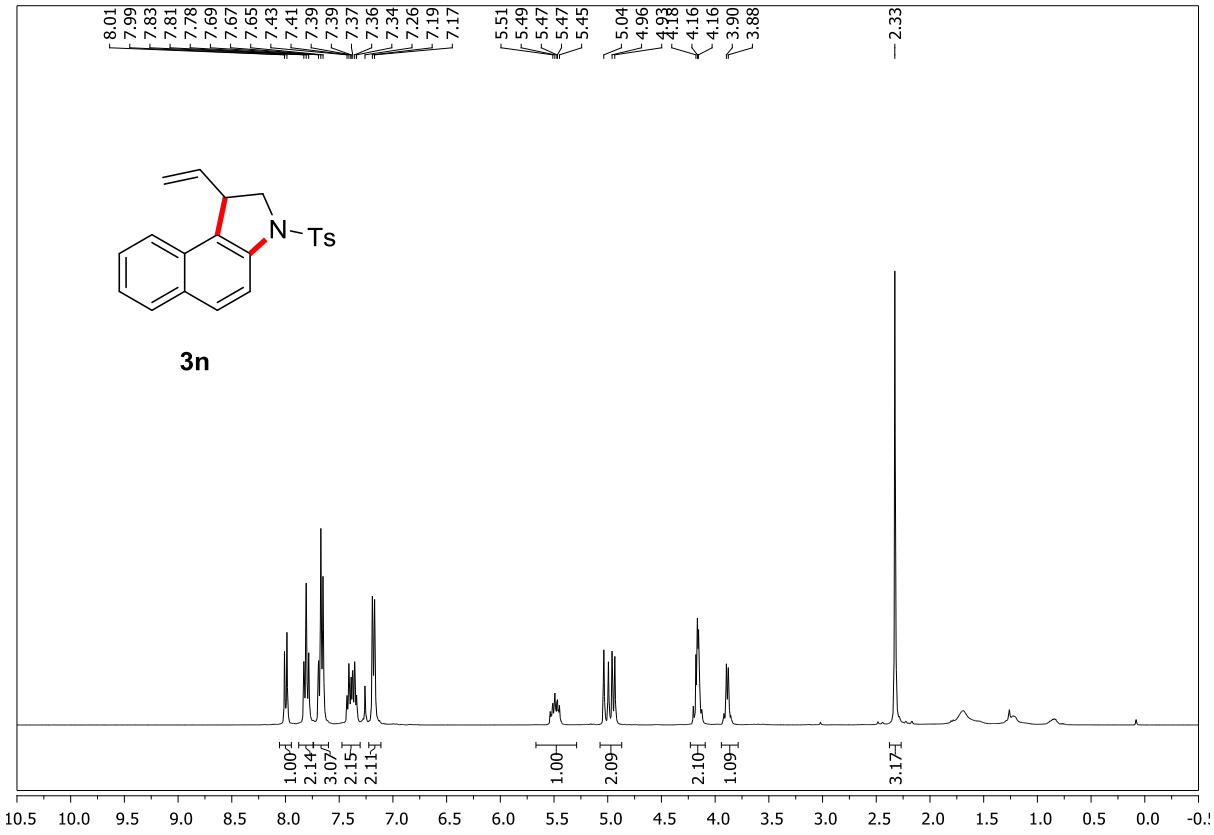


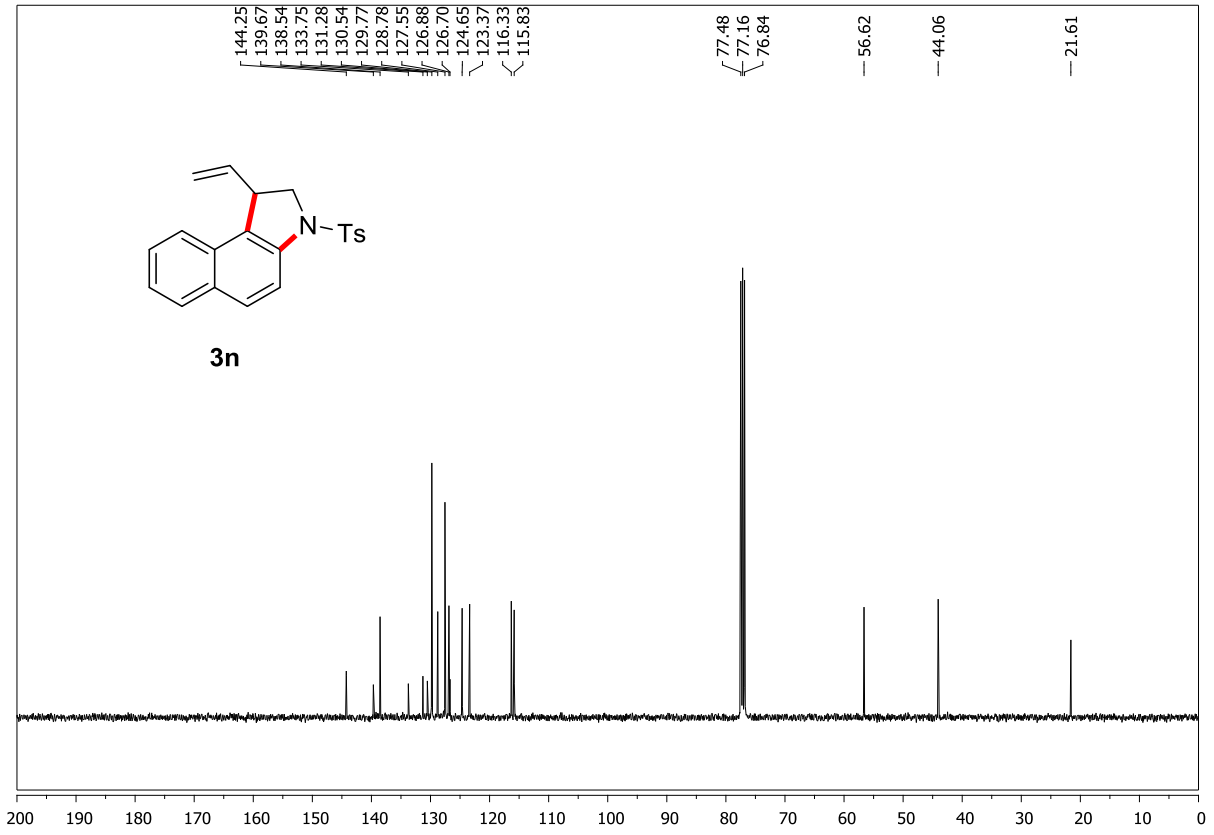
1-(Naphthalen-2-yl)-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3m)



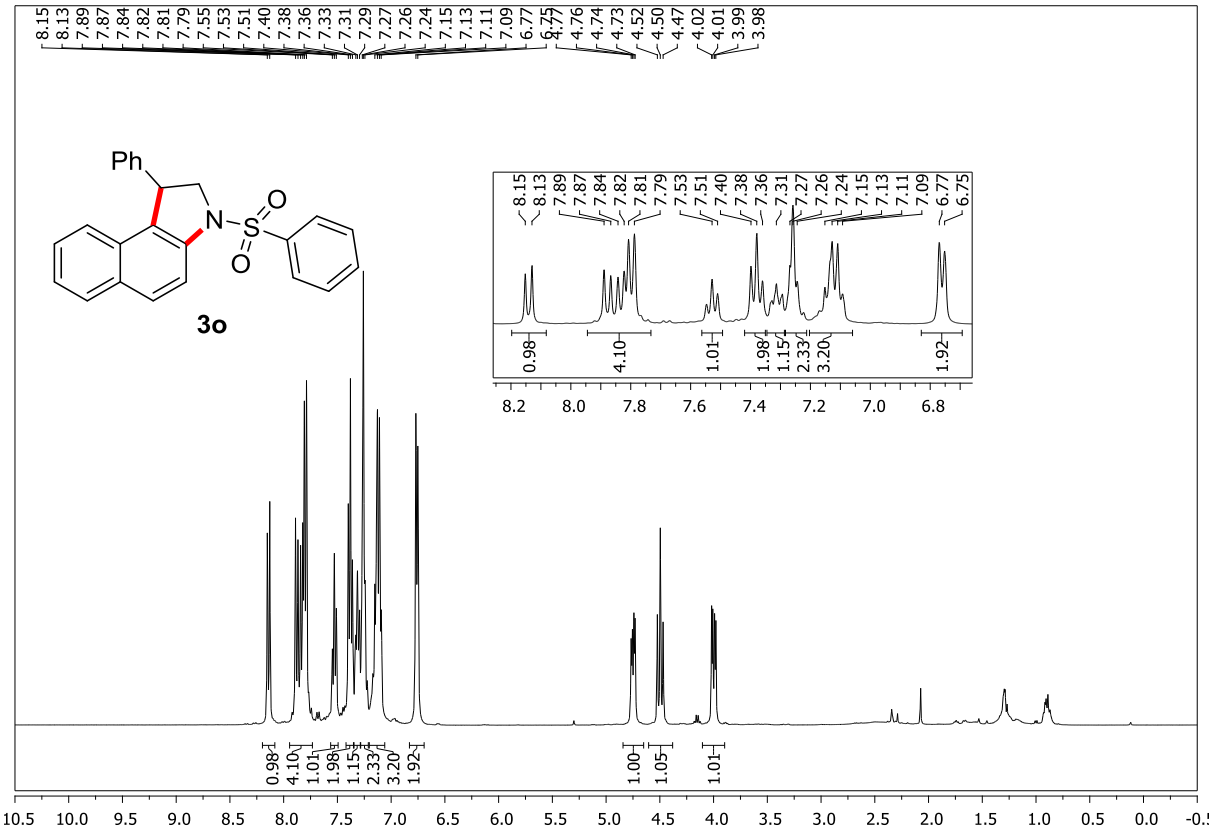


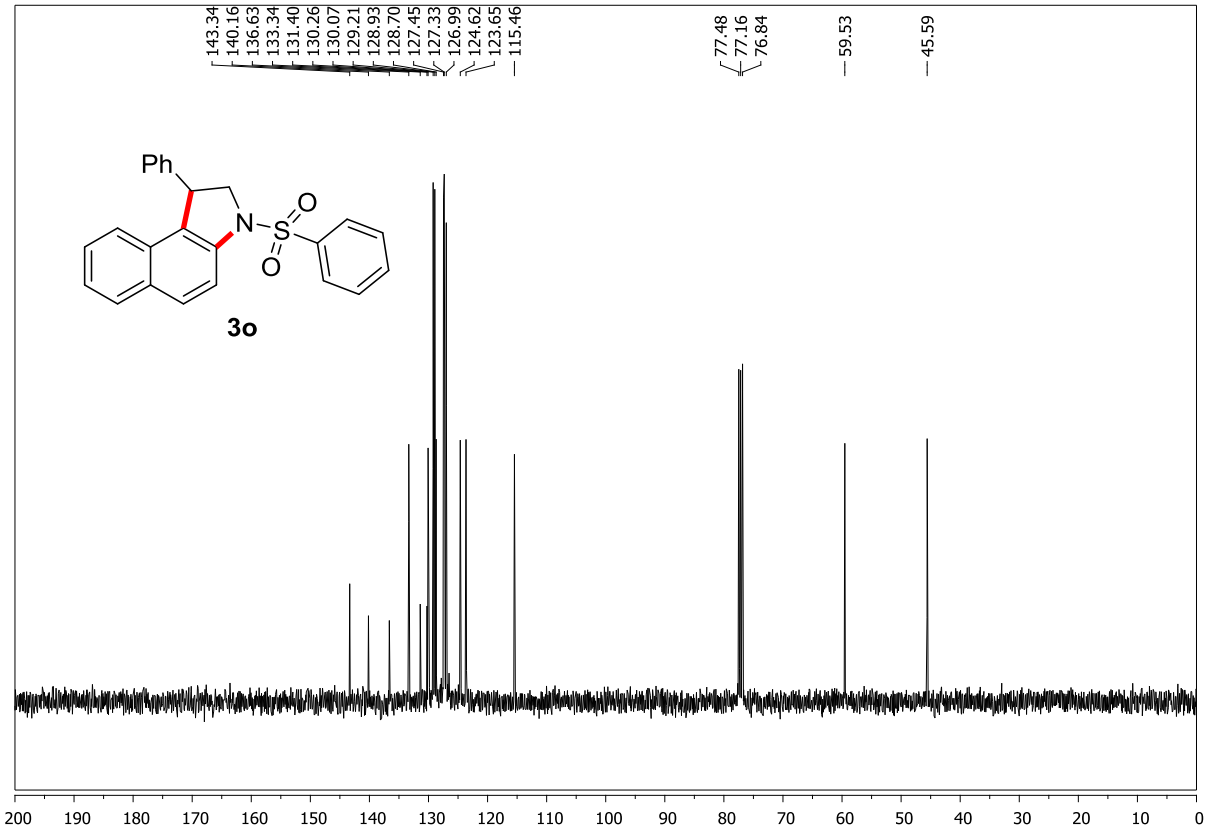
3-Tosyl-1-vinyl-2,3-dihydro-1*H*-benzo[*e*]indole (3n)



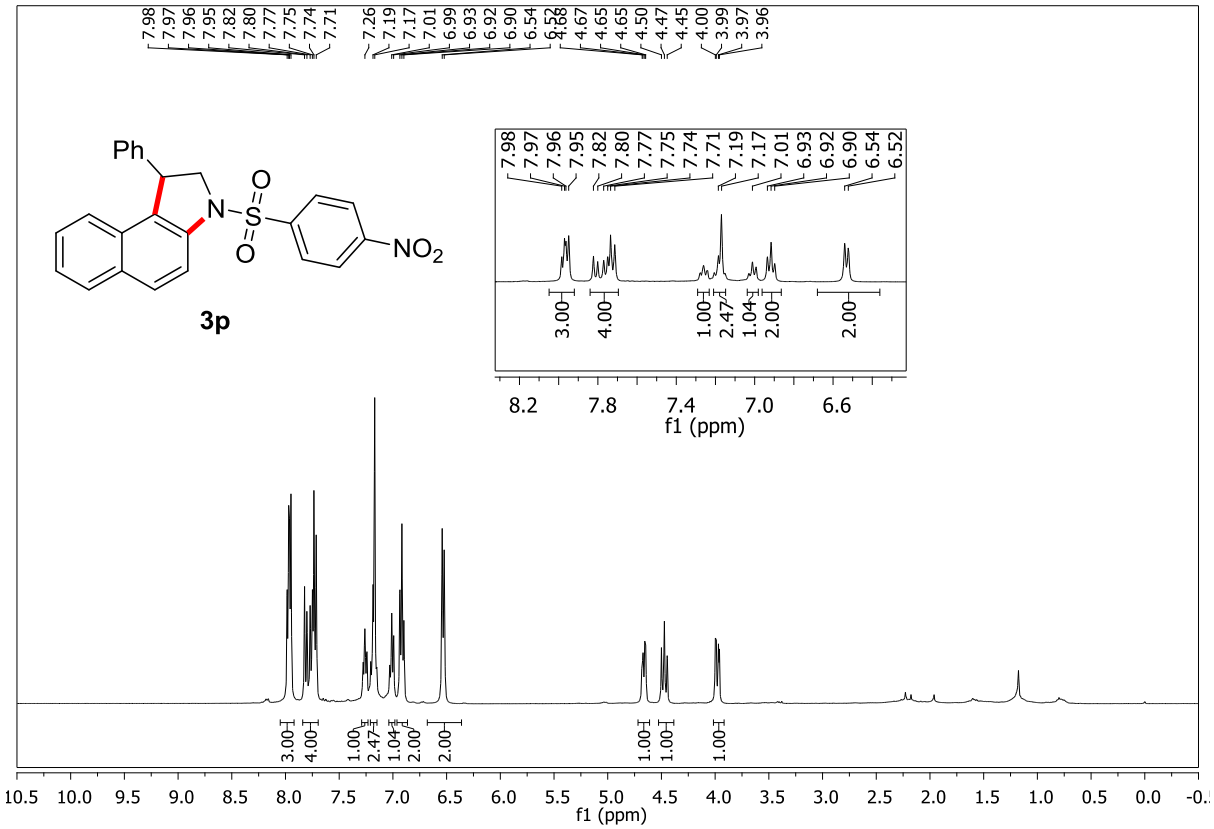


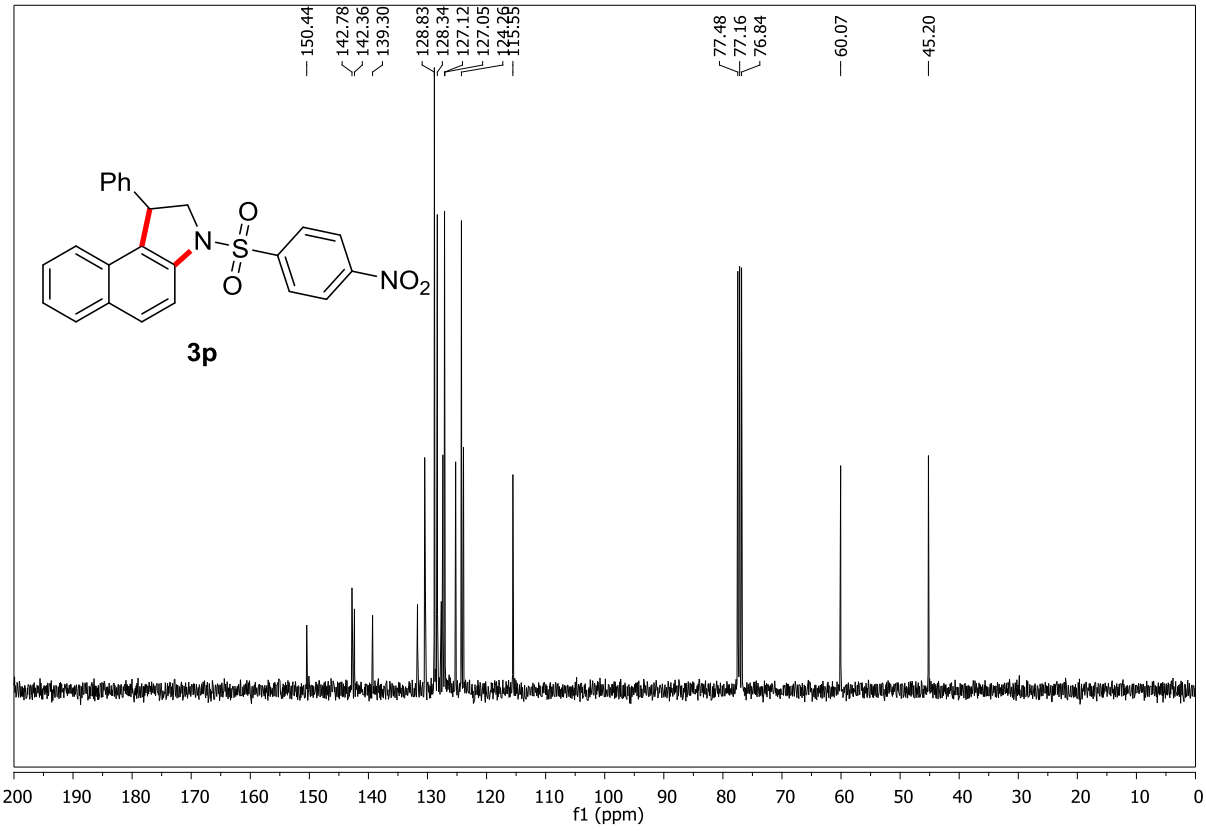
1-Phenyl-3-(phenylsulfonyl)-2,3-dihydro-1*H*-benzo[*e*]indole (3o)



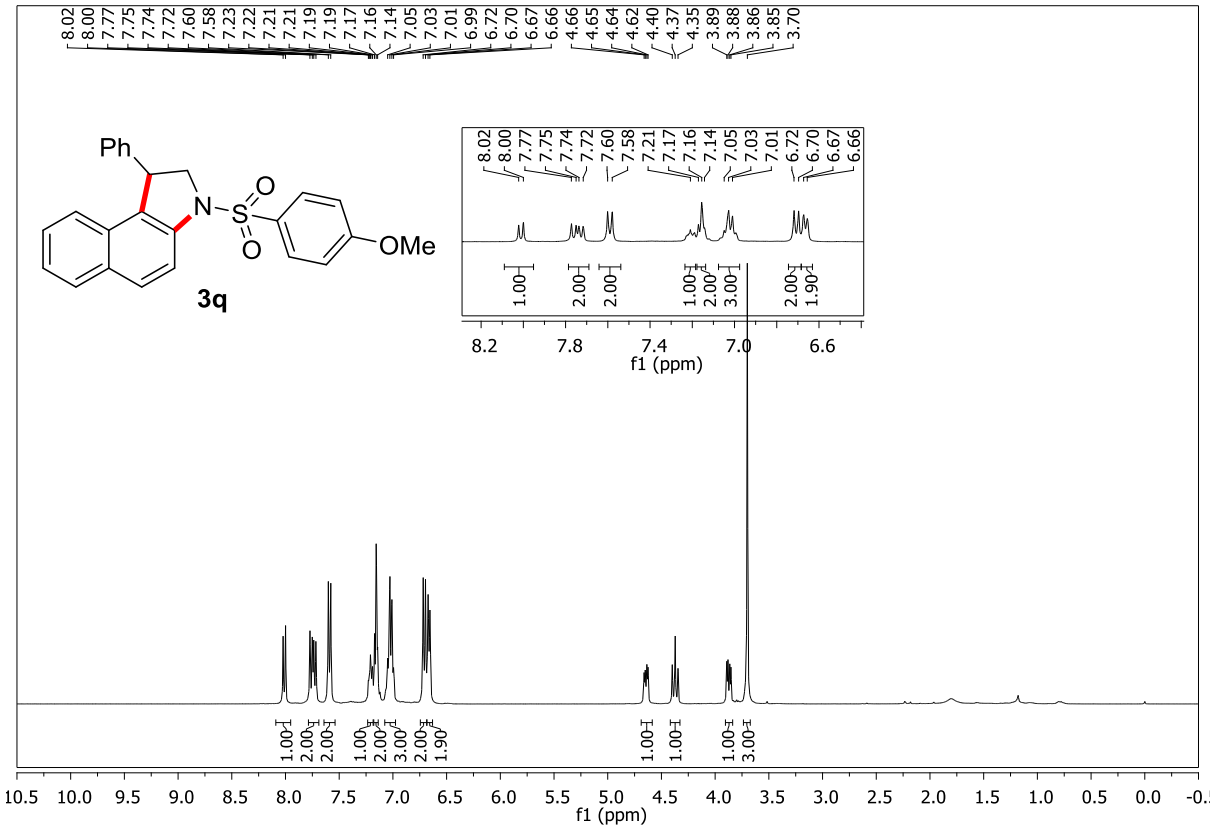


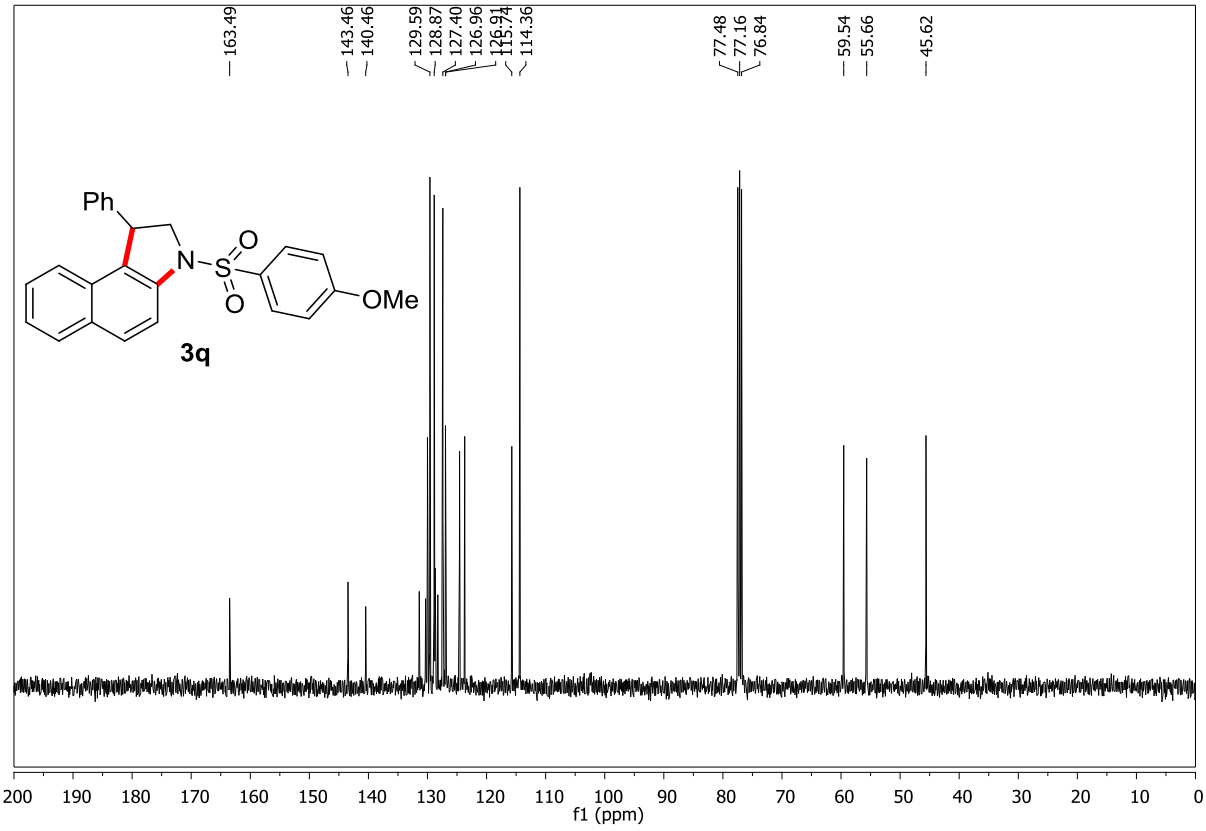
3-((4-Nitrophenyl)sulfonyl)-1-phenyl-2,3-dihydro-1*H*-benzo[*e*]indole (3p)



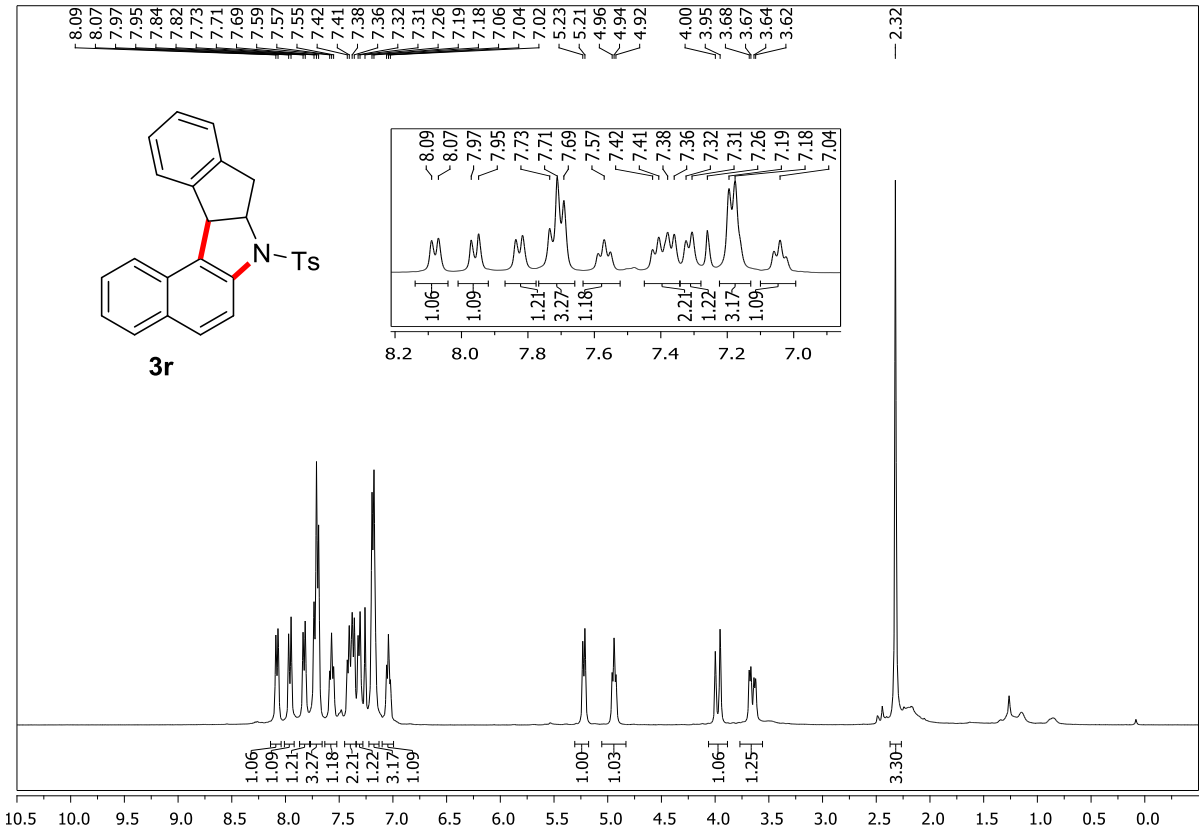


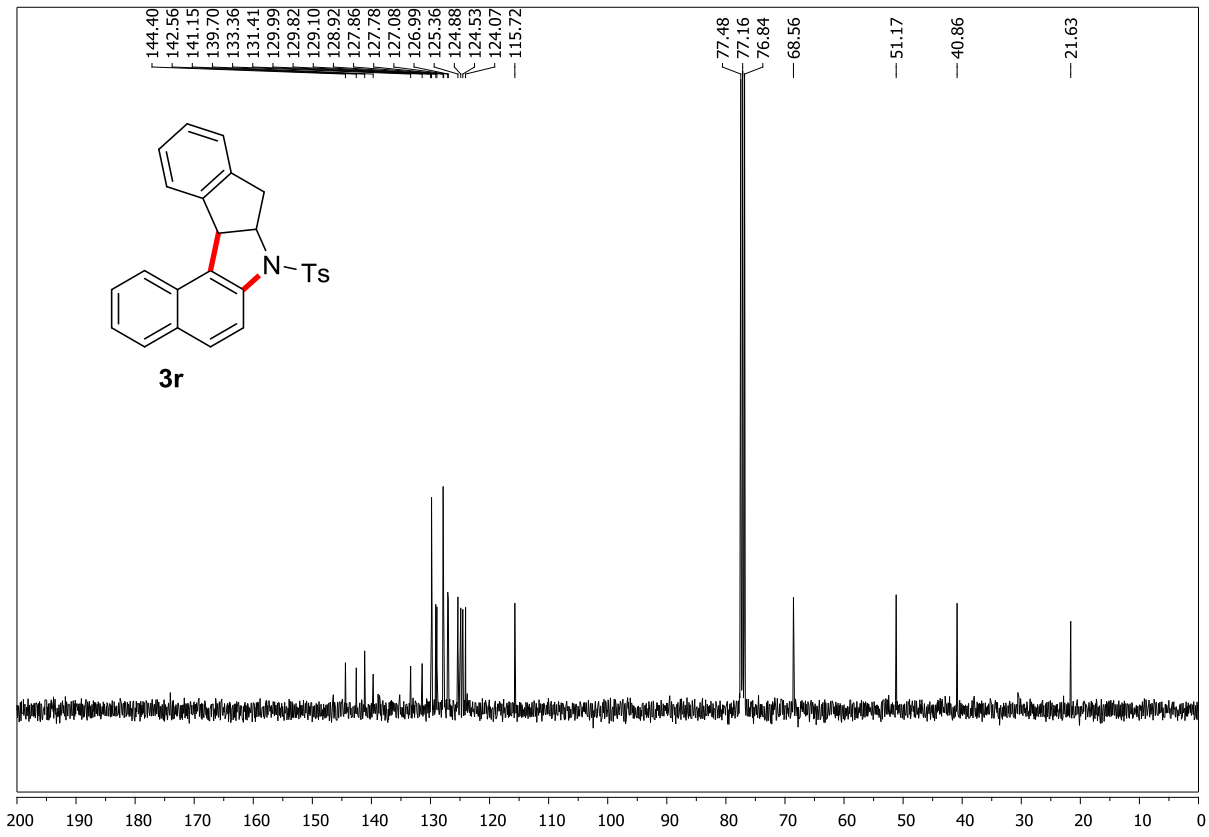
3-((4-Methoxyphenyl)sulfonyl)-1-phenyl-2,3-dihydro-1H-benzo[*e*]indole (3q)



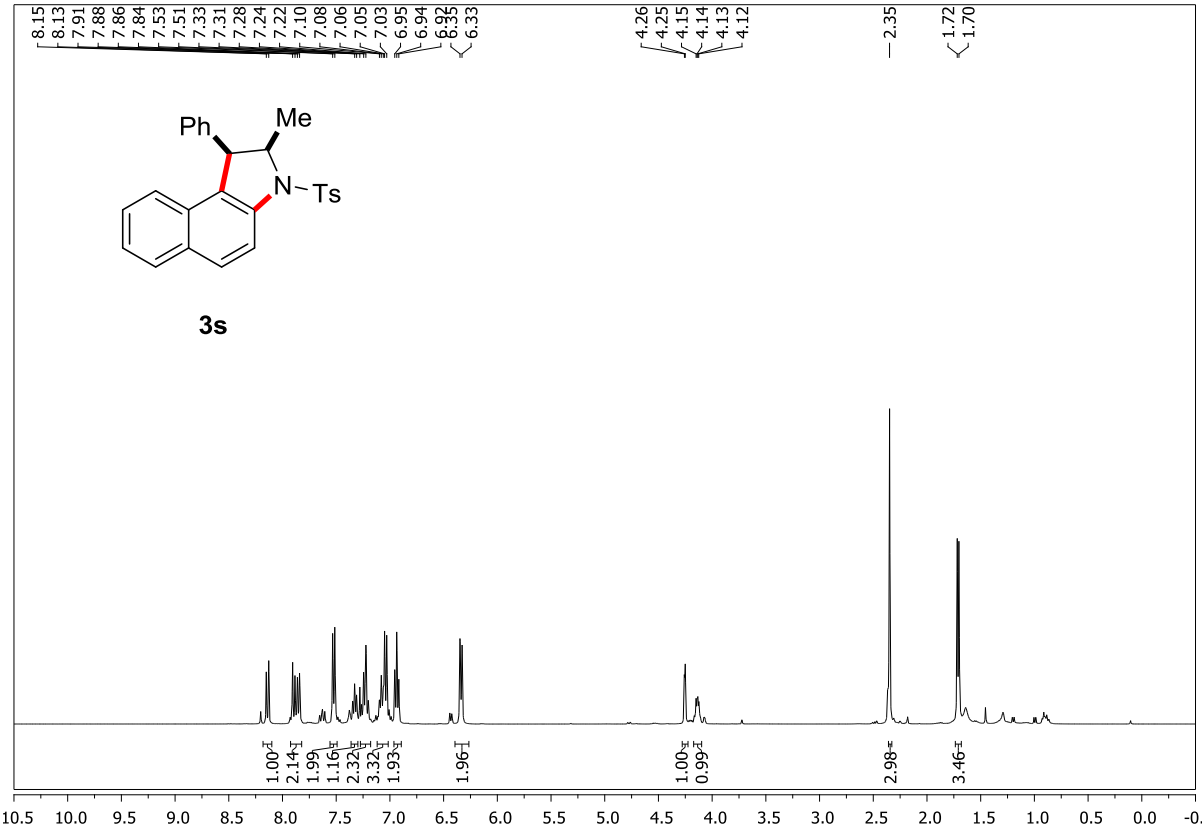


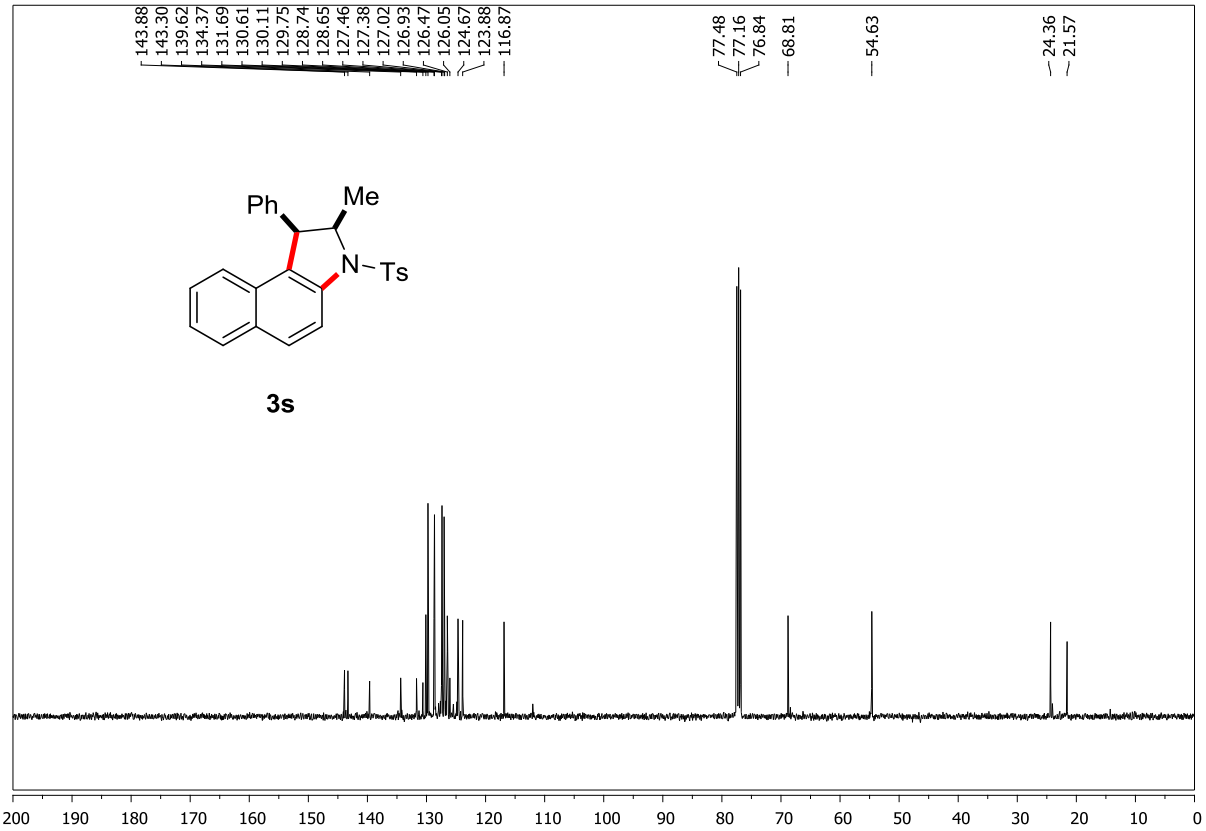
7-Tosyl-7,7a,8,12b-tetrahydrobenzo[*e*]indeno[2,1-*b*]indole (3r)



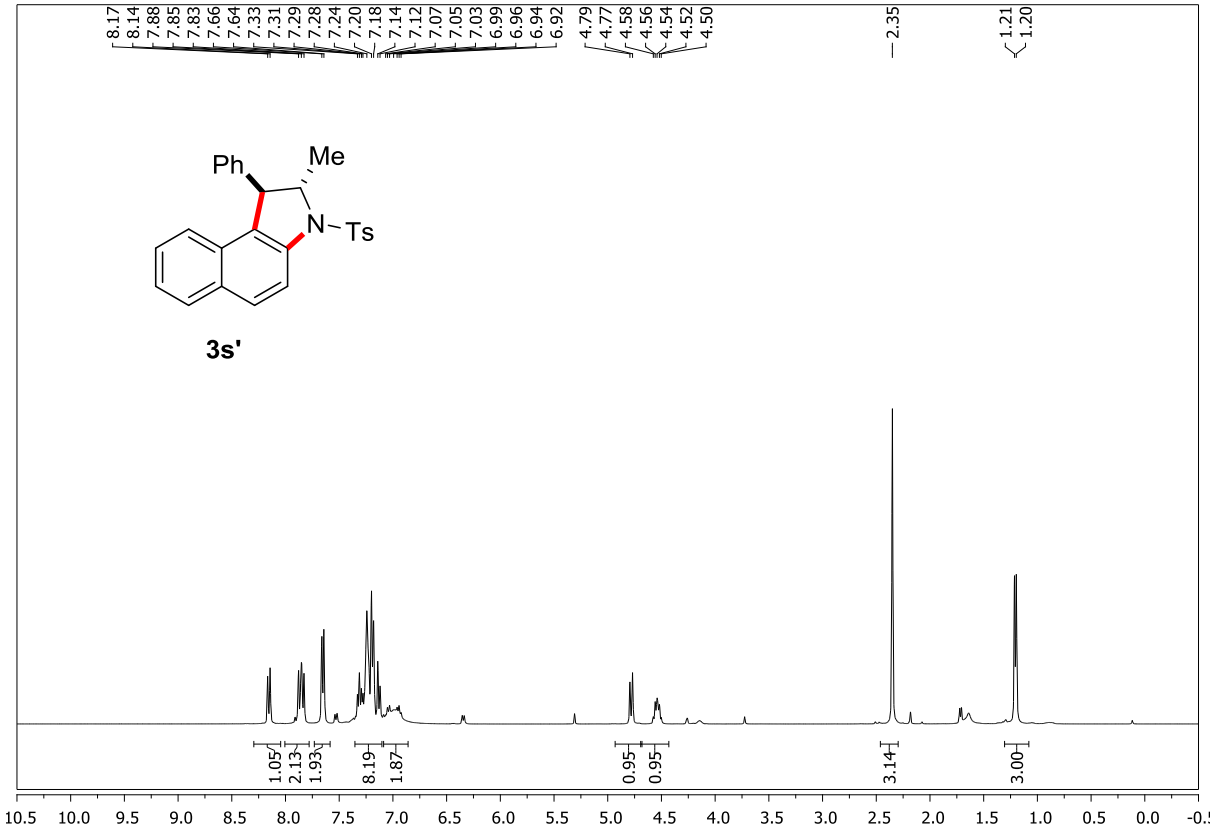


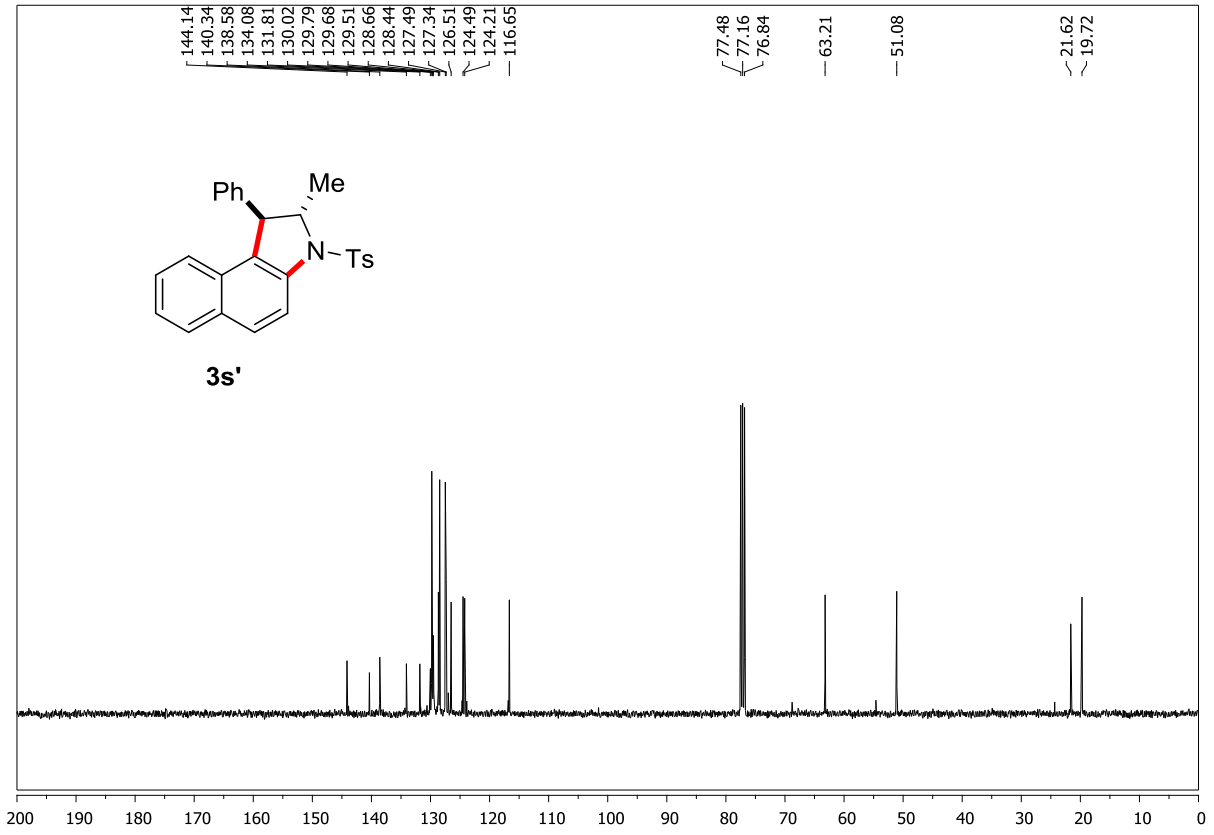
2-methyl-1-phenyl-3-tosyl-2,3-dihydro-1H-benzo[e]indole (3s)



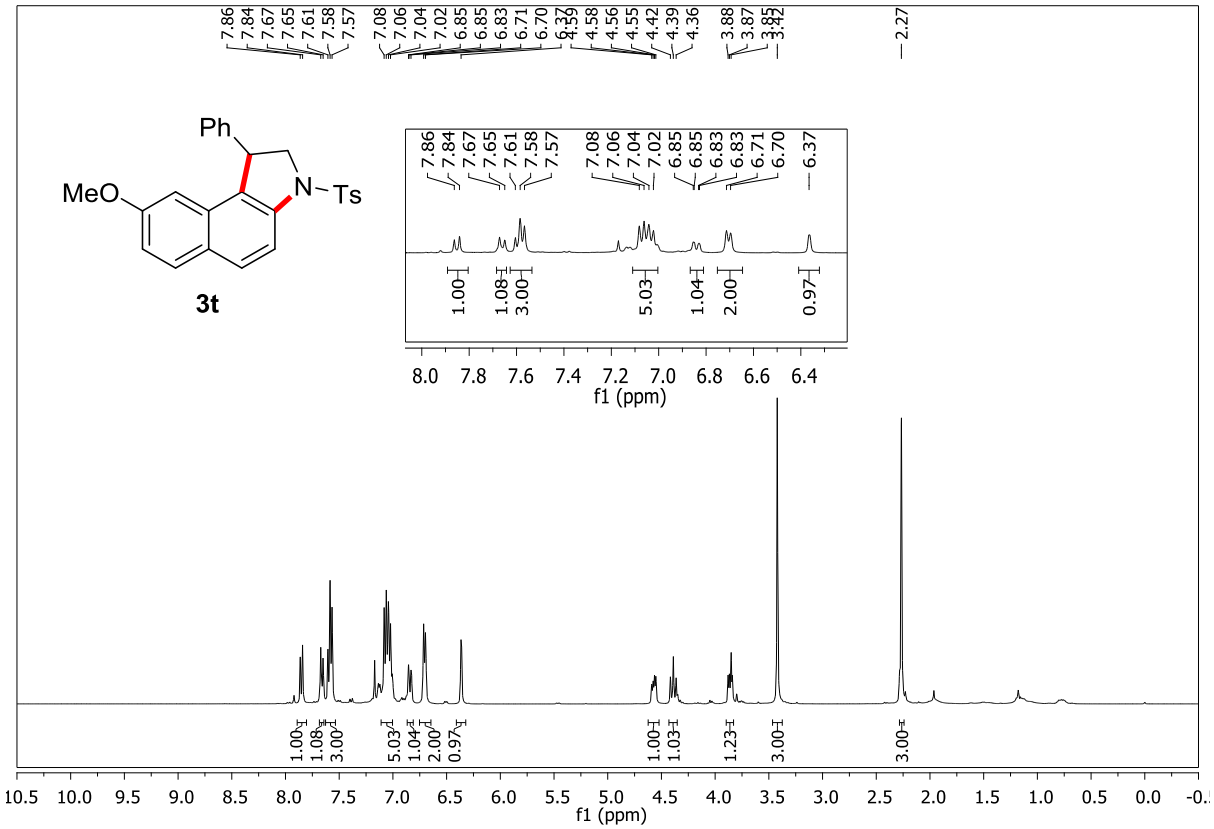


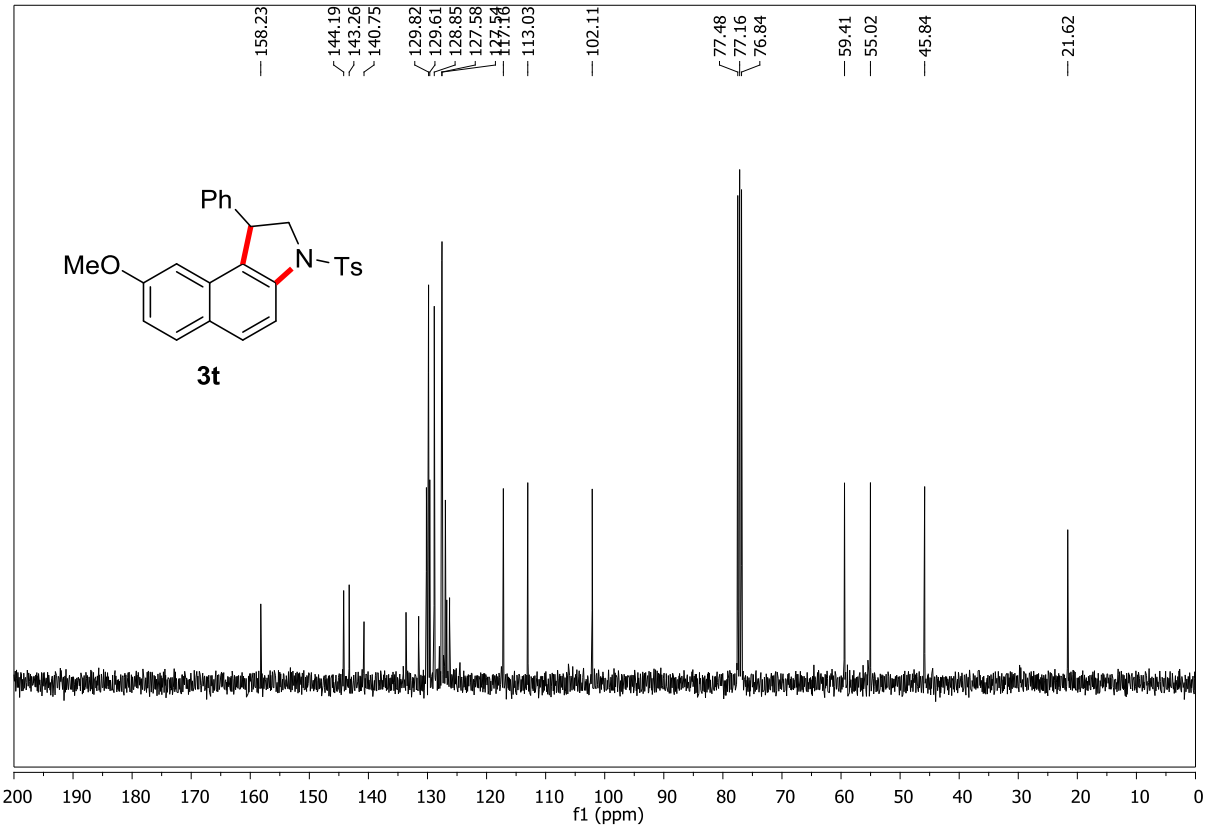
2-Methyl-1-phenyl-3-tosyl-2,3-dihydro-1*H*-benzo[e]indole (3s')



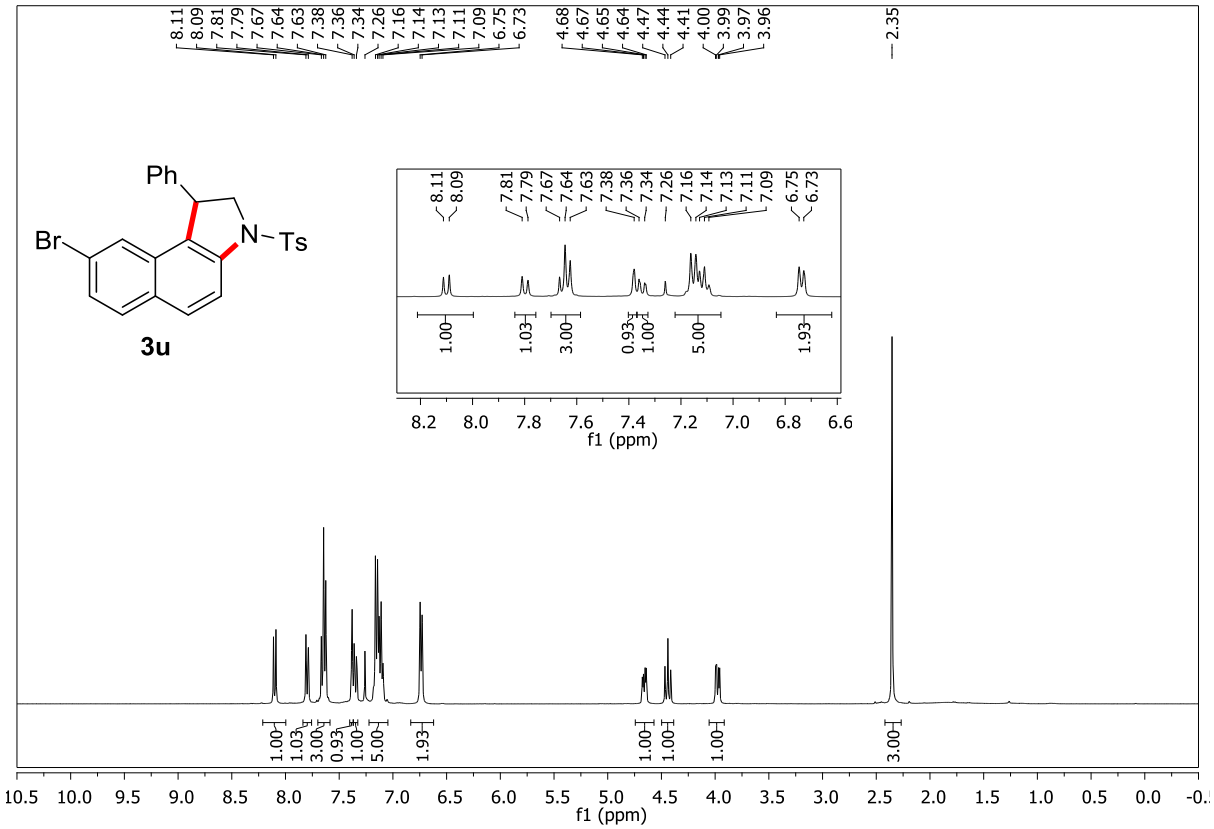


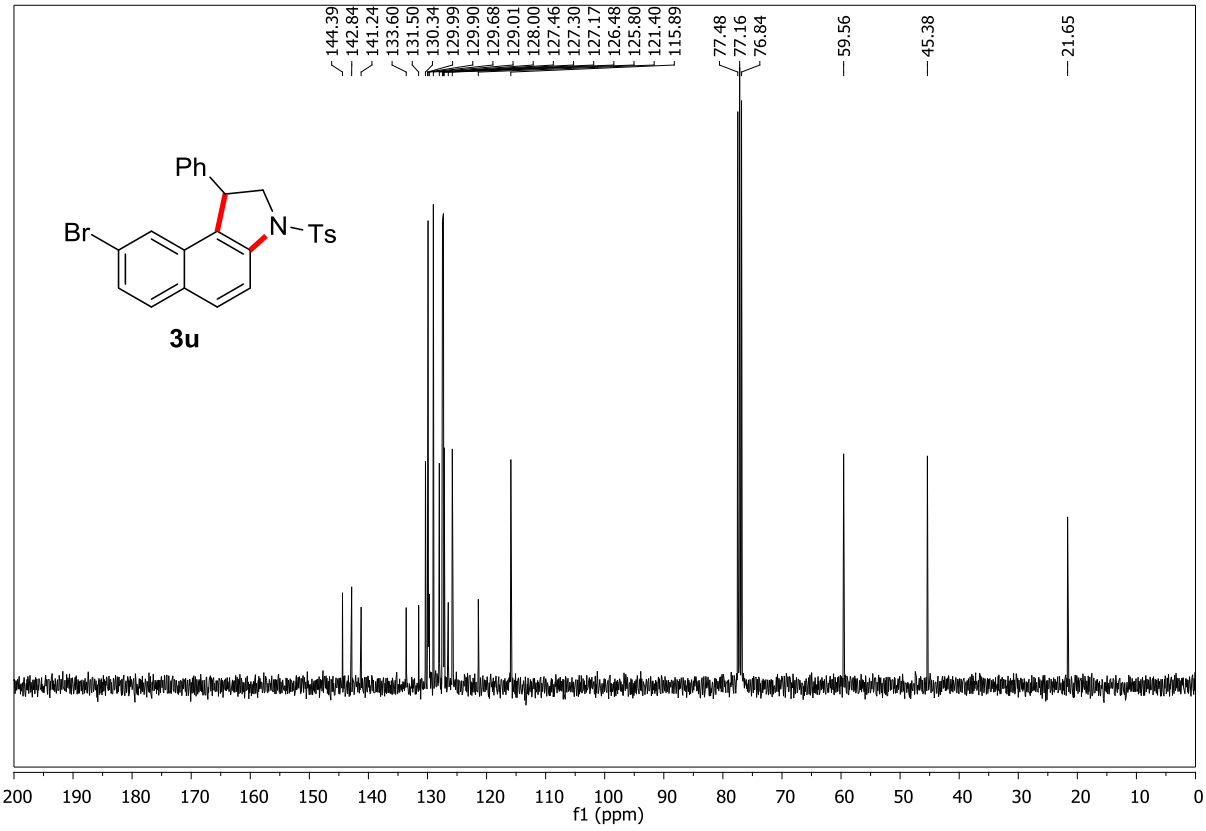
8-Methoxy-1-phenyl-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3t)



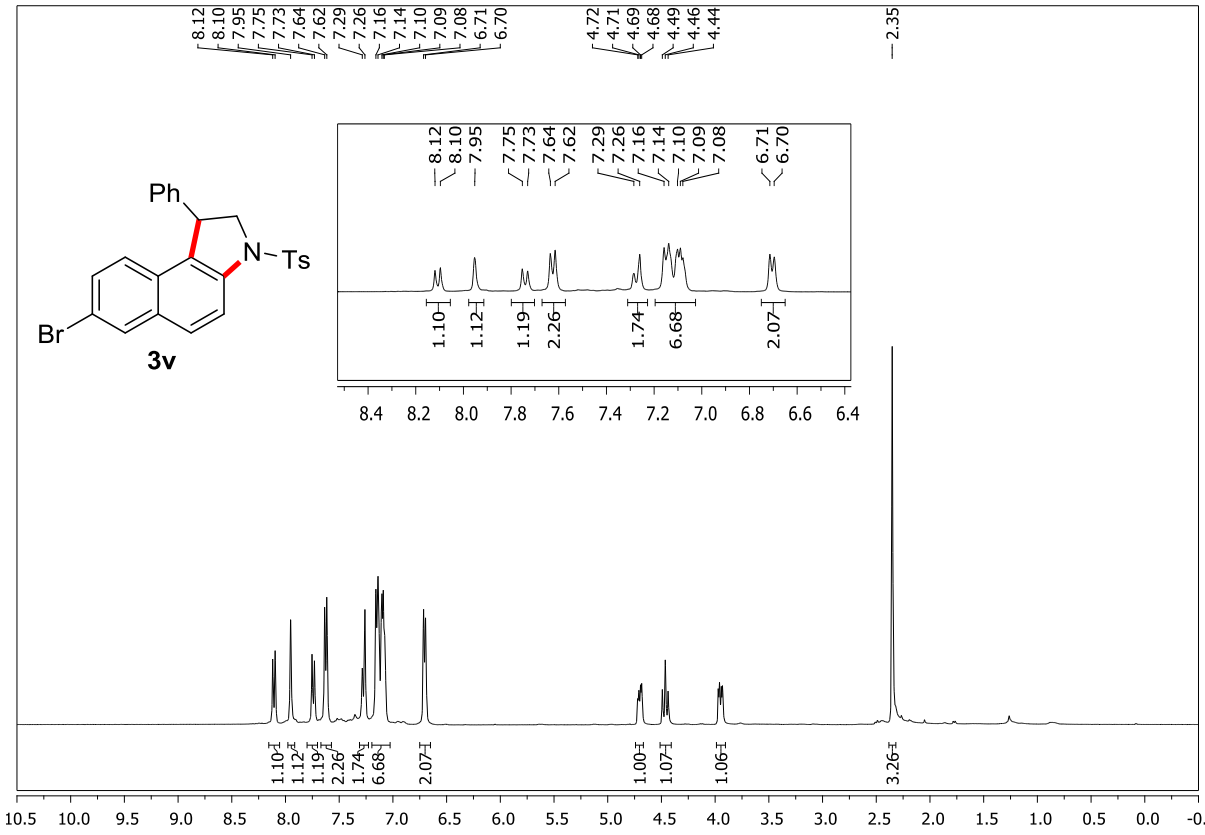


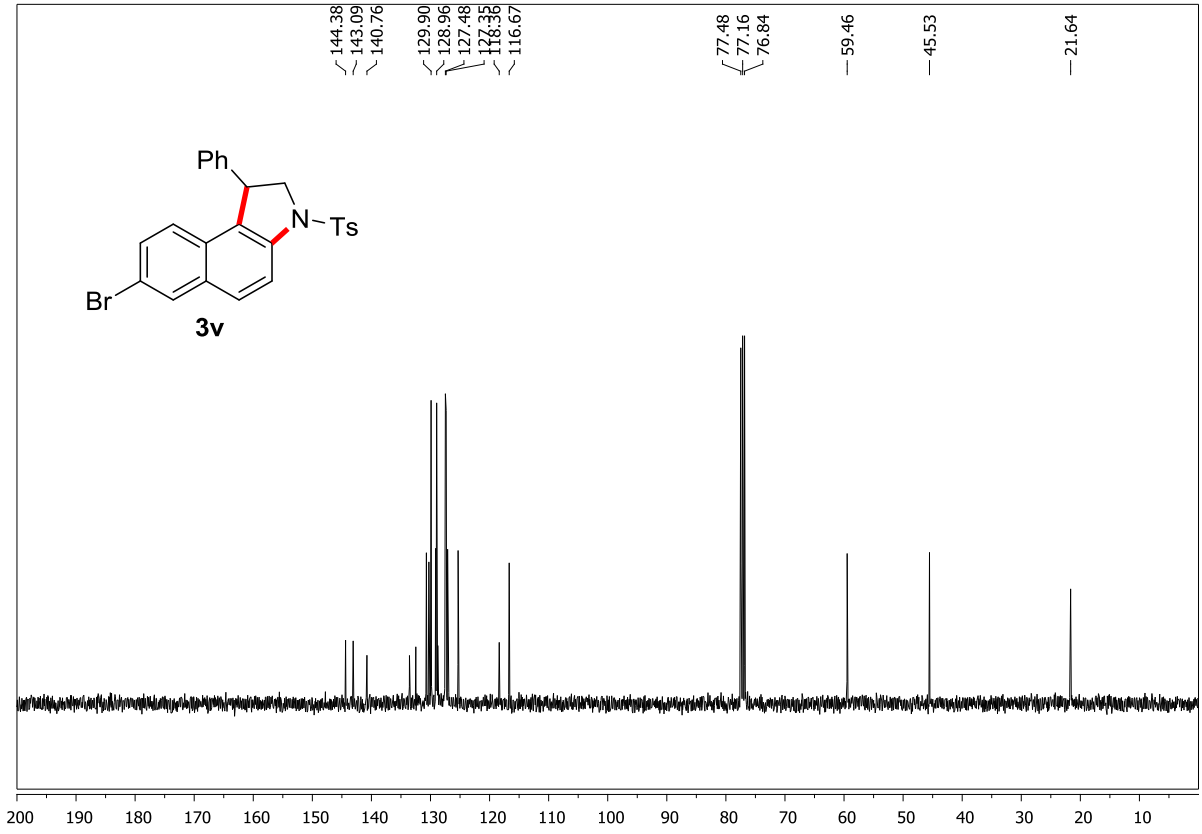
8-Bromo-1-phenyl-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3u)



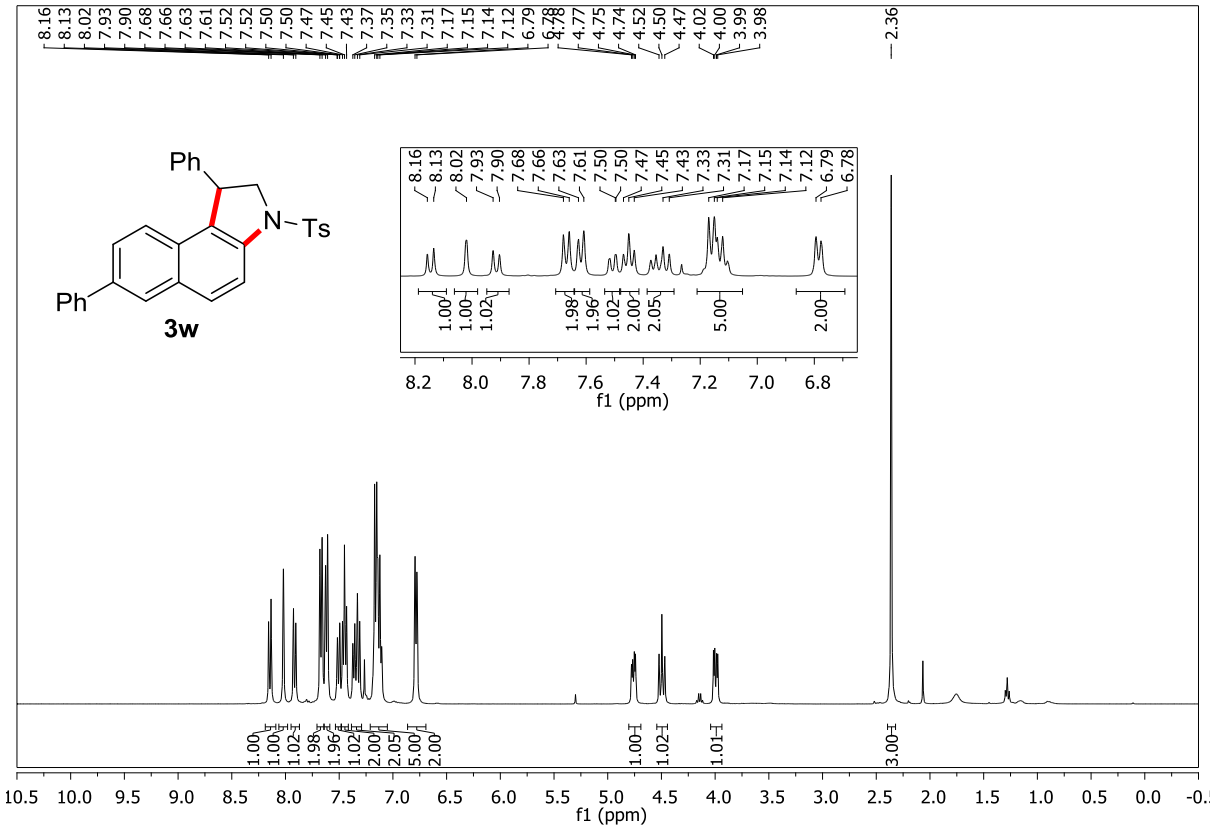


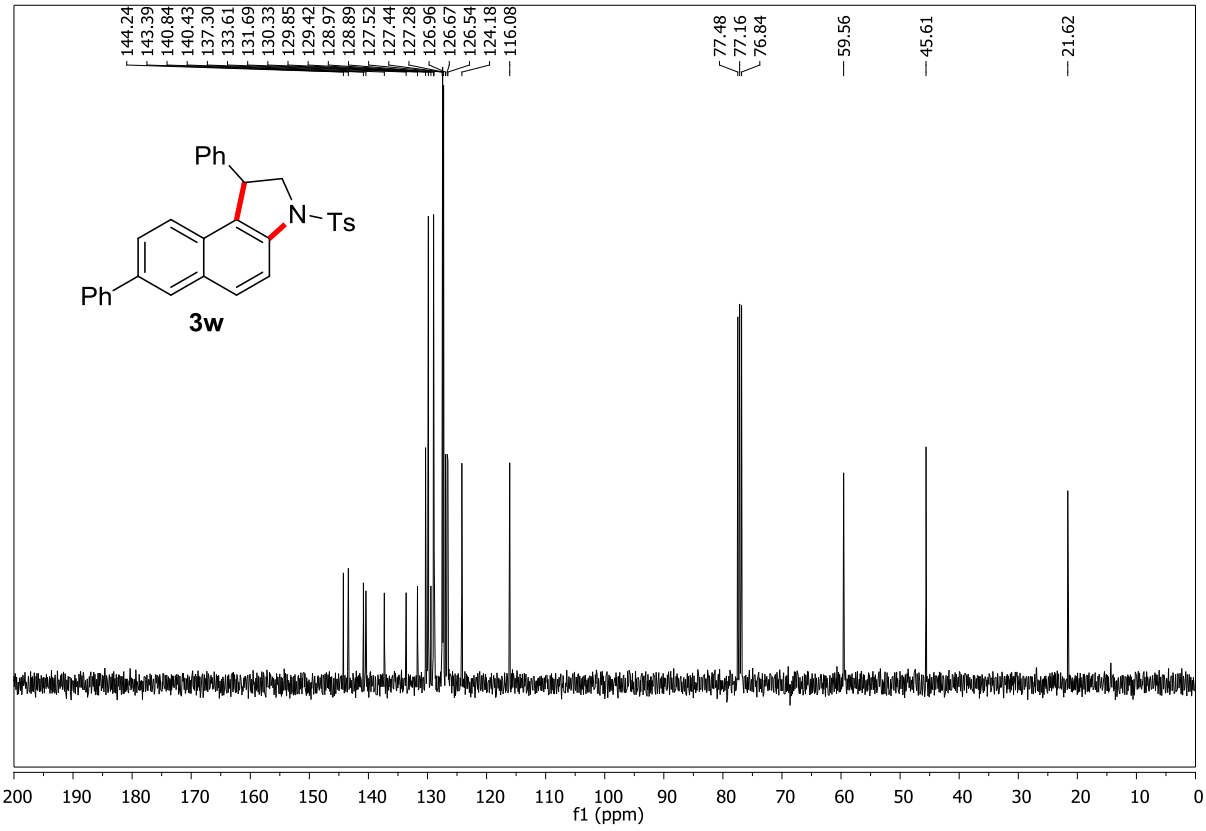
7-Bromo-1-phenyl-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3v)



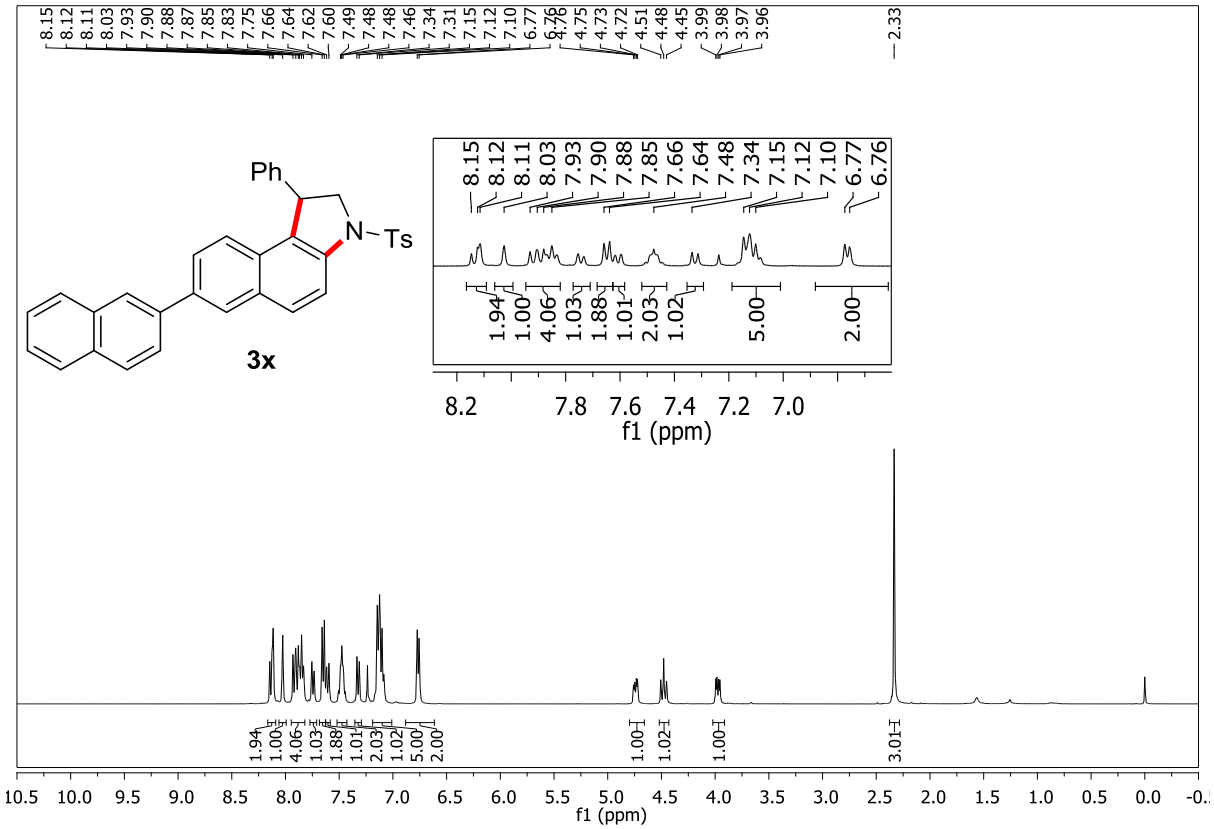


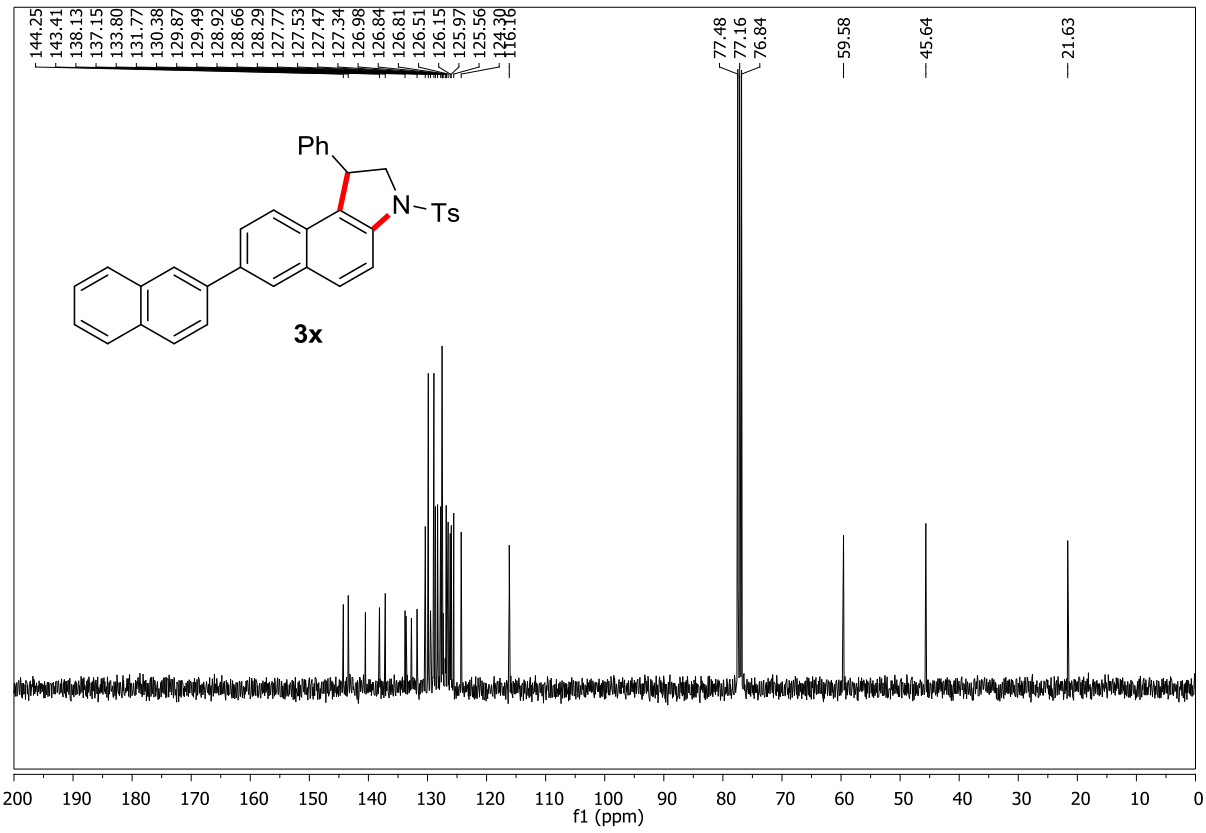
1,7-Diphenyl-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3w)



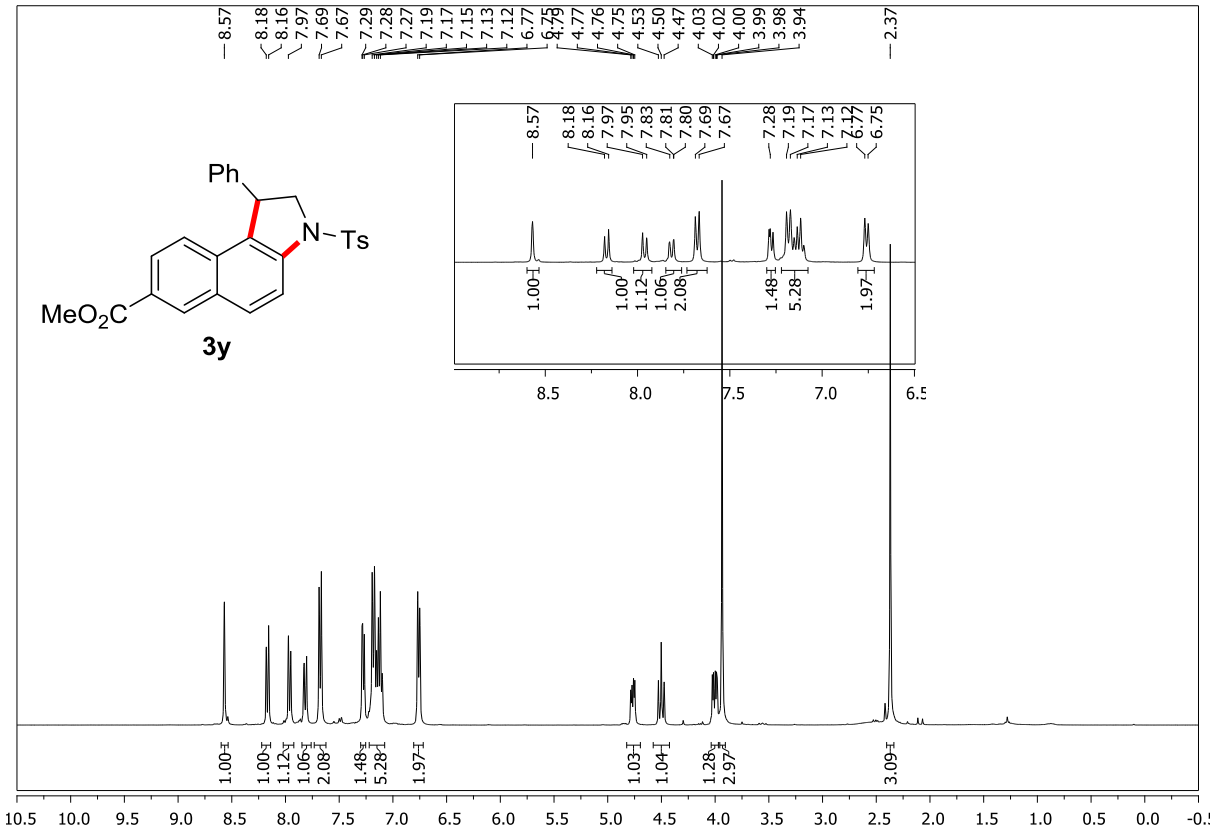


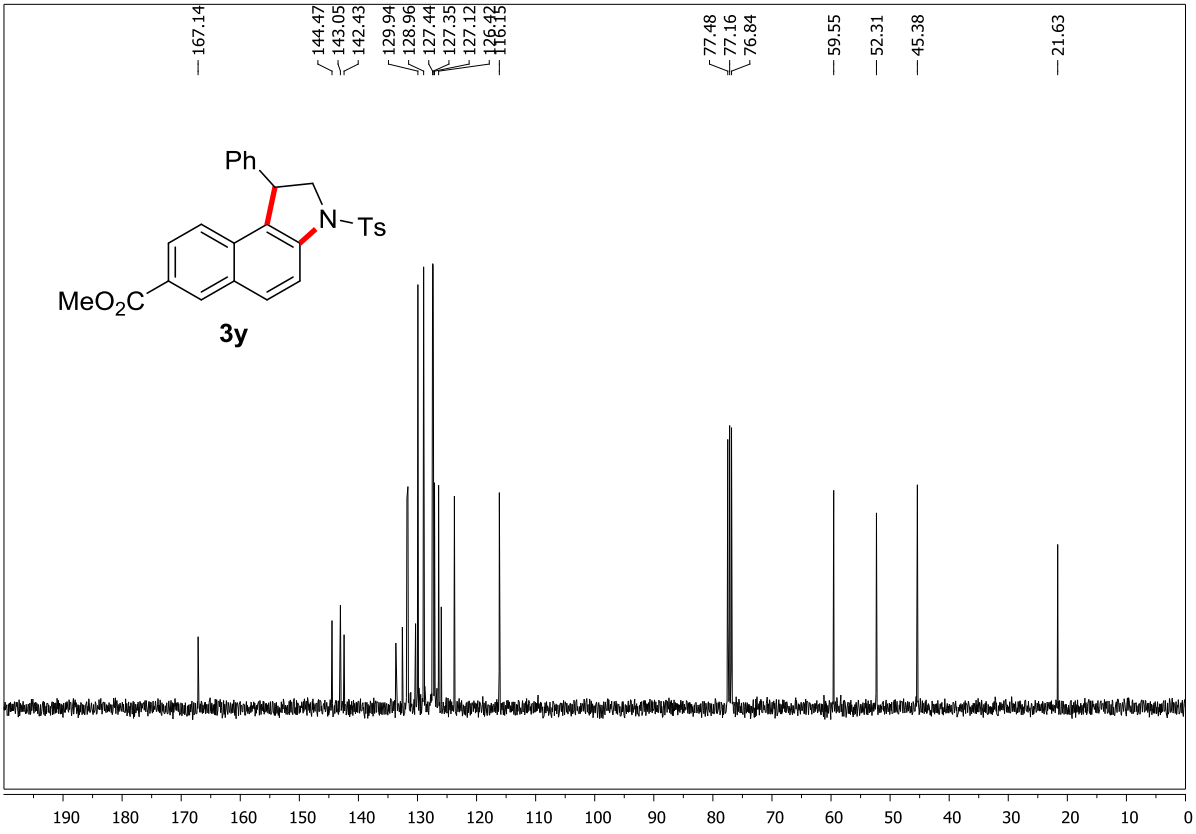
7-(Naphthalen-2-yl)-1-phenyl-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3x)



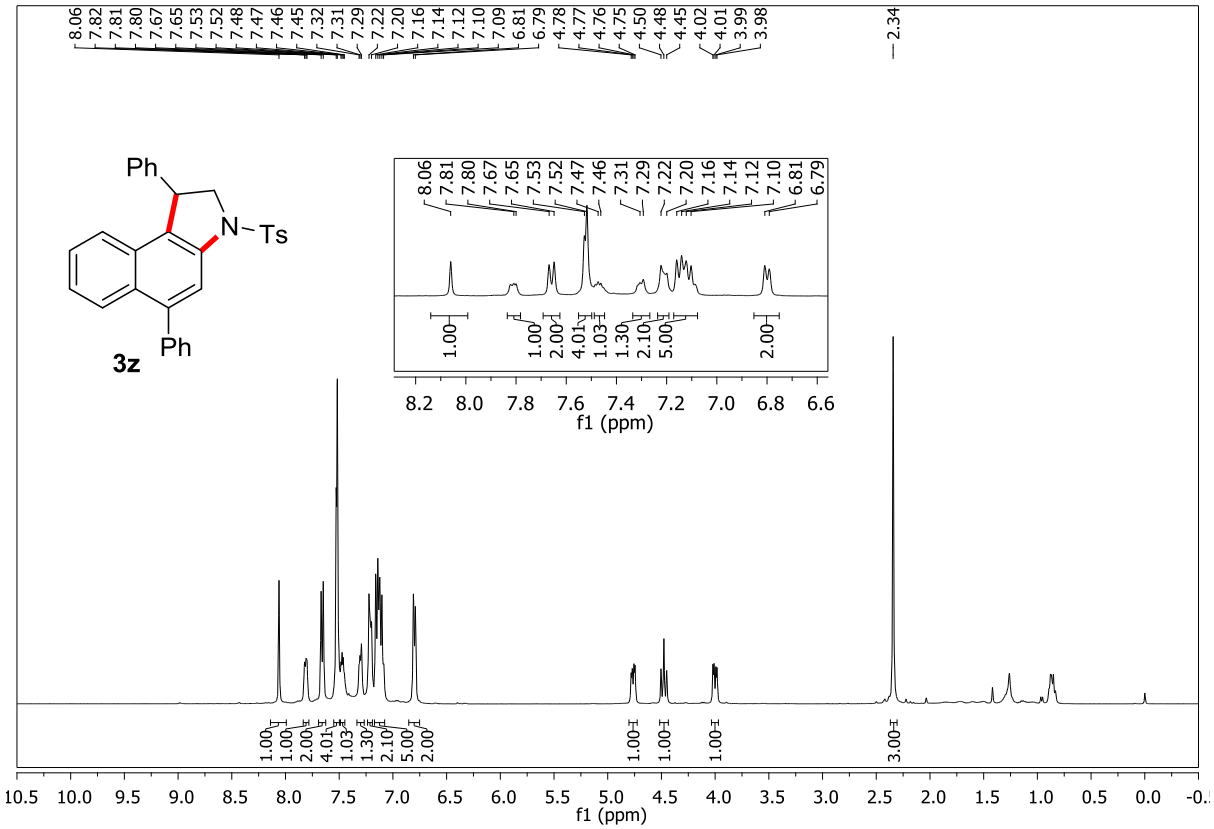


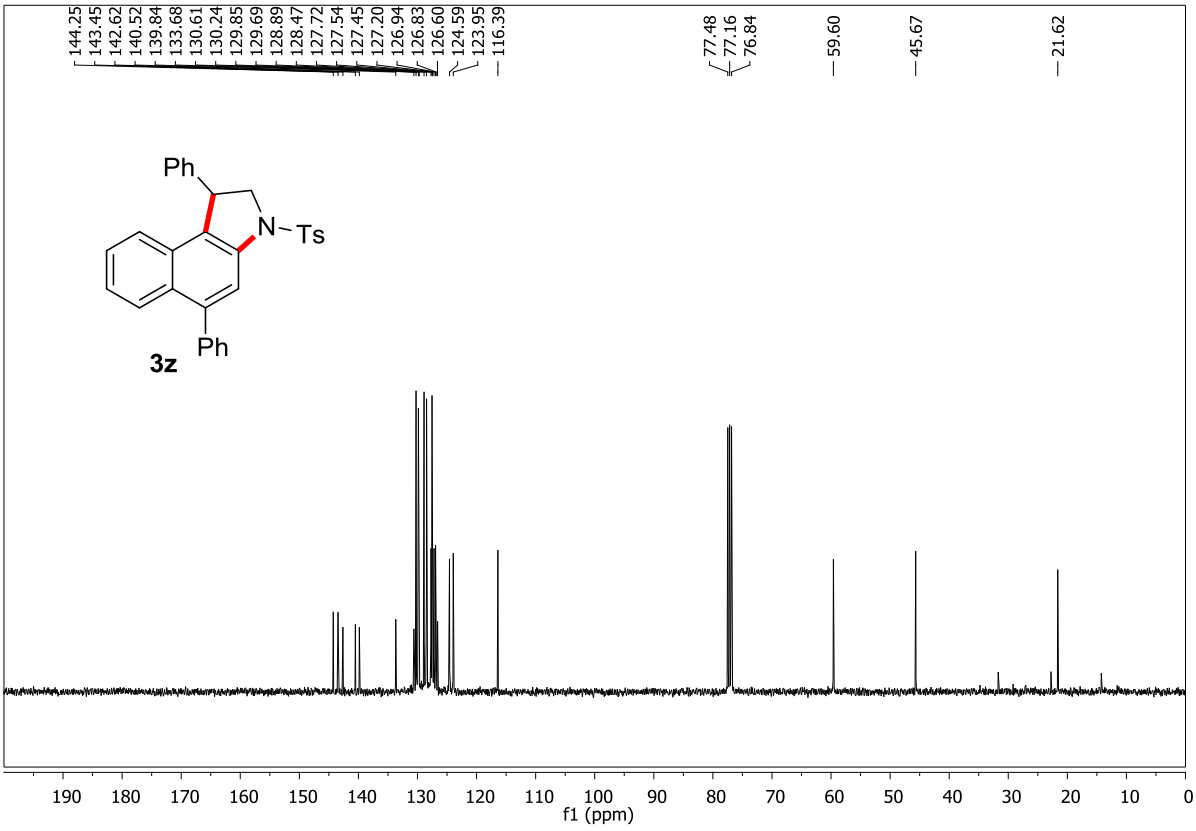
Methyl -1-phenyl-3-tosyl-2,3-dihydro-1*H*-benzo[e]indole-7-carboxylate (3y)



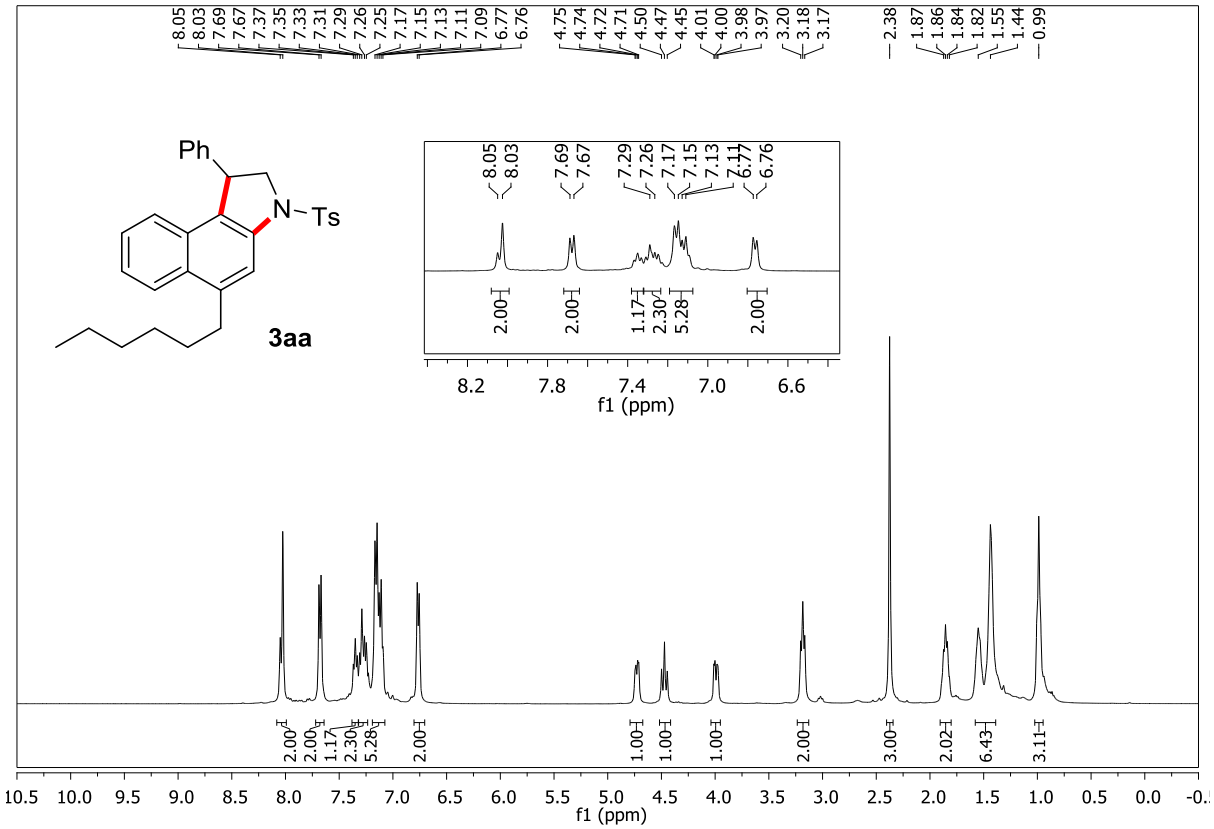


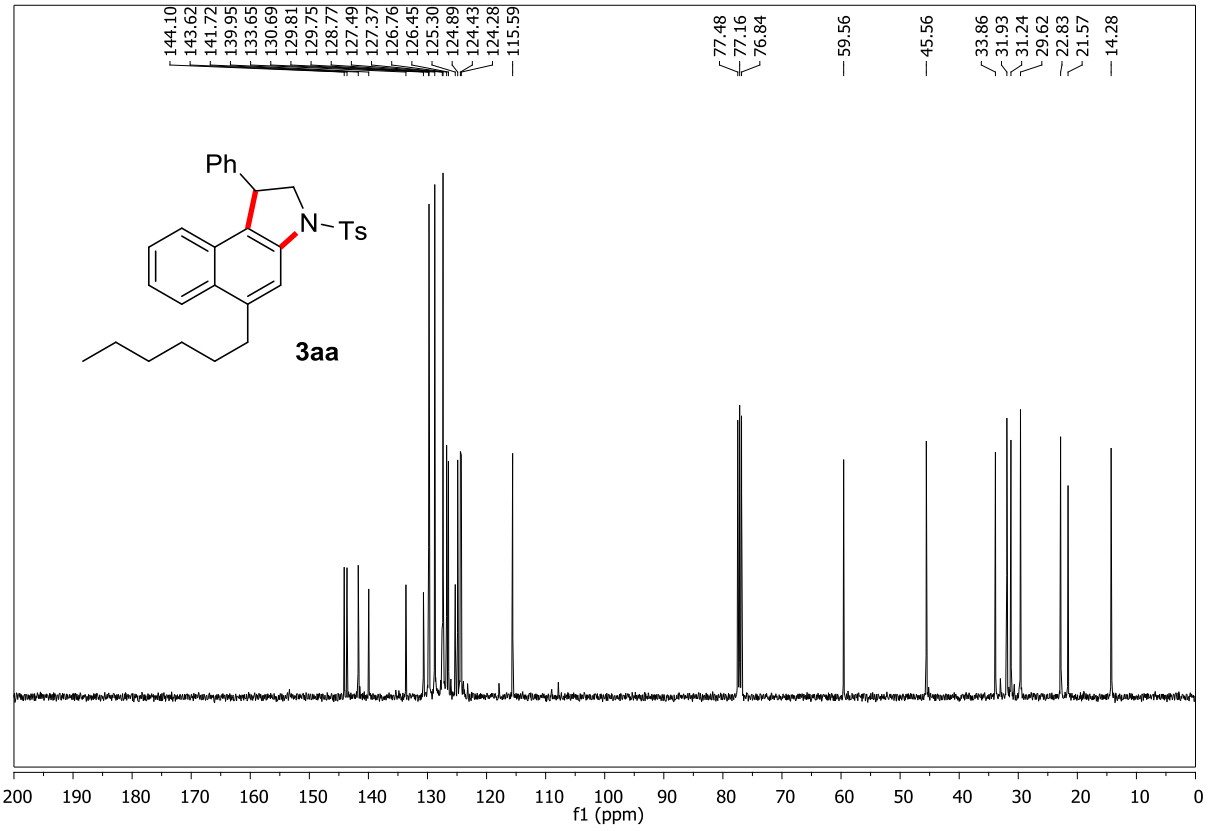
1,5-Diphenyl-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3z)



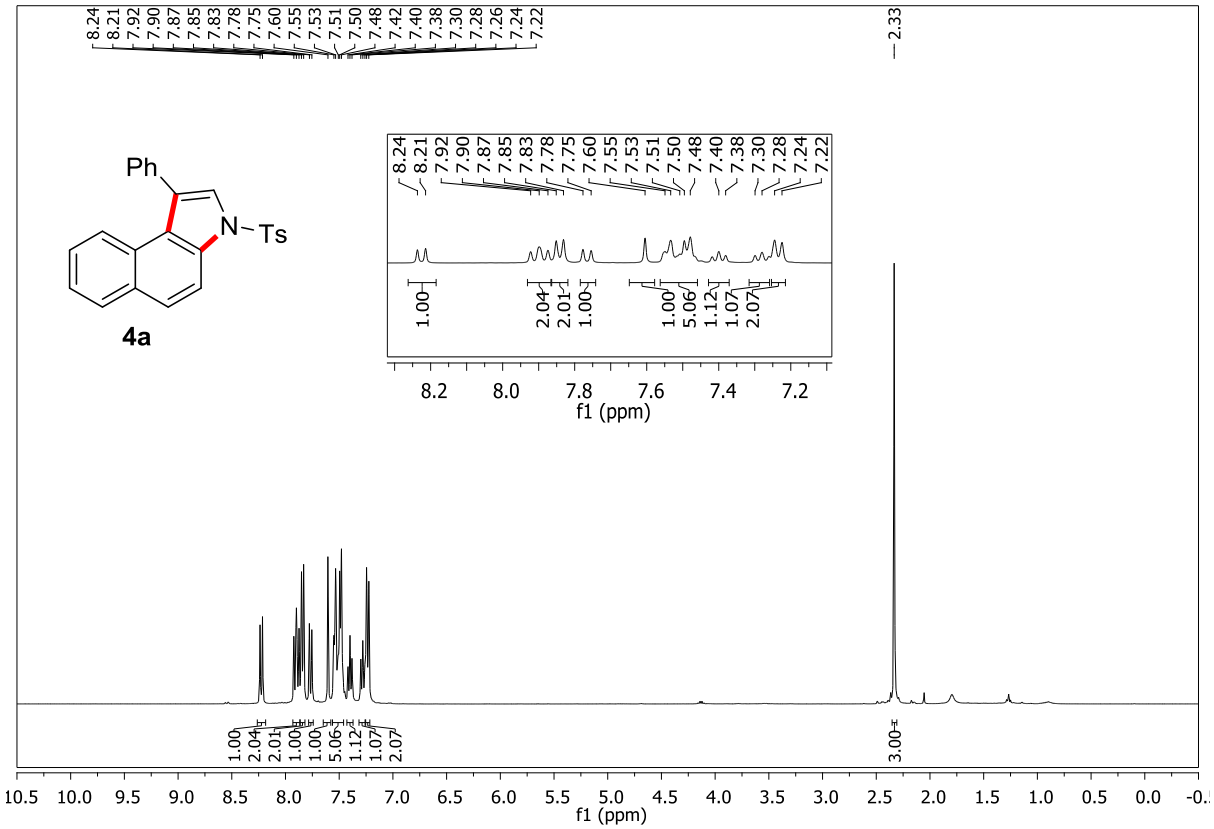


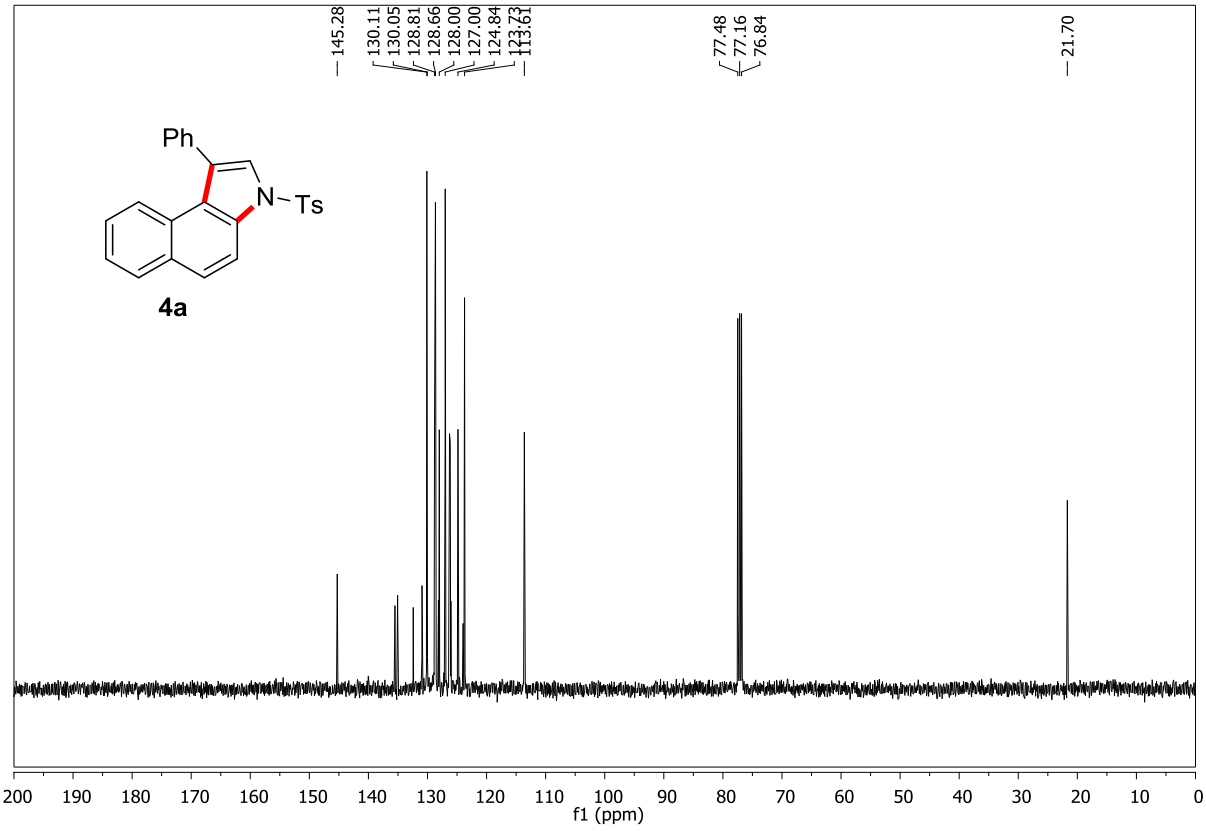
5-Hexyl-1-phenyl-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3aa)



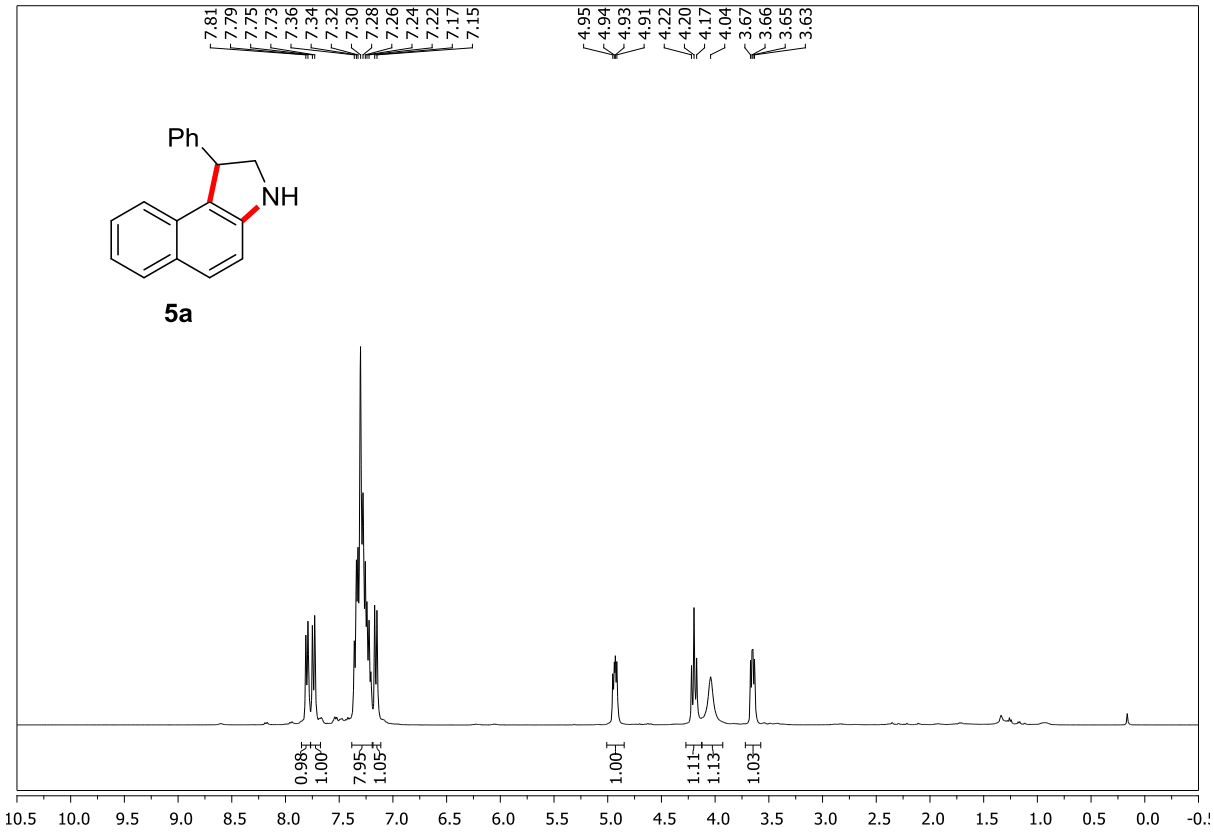


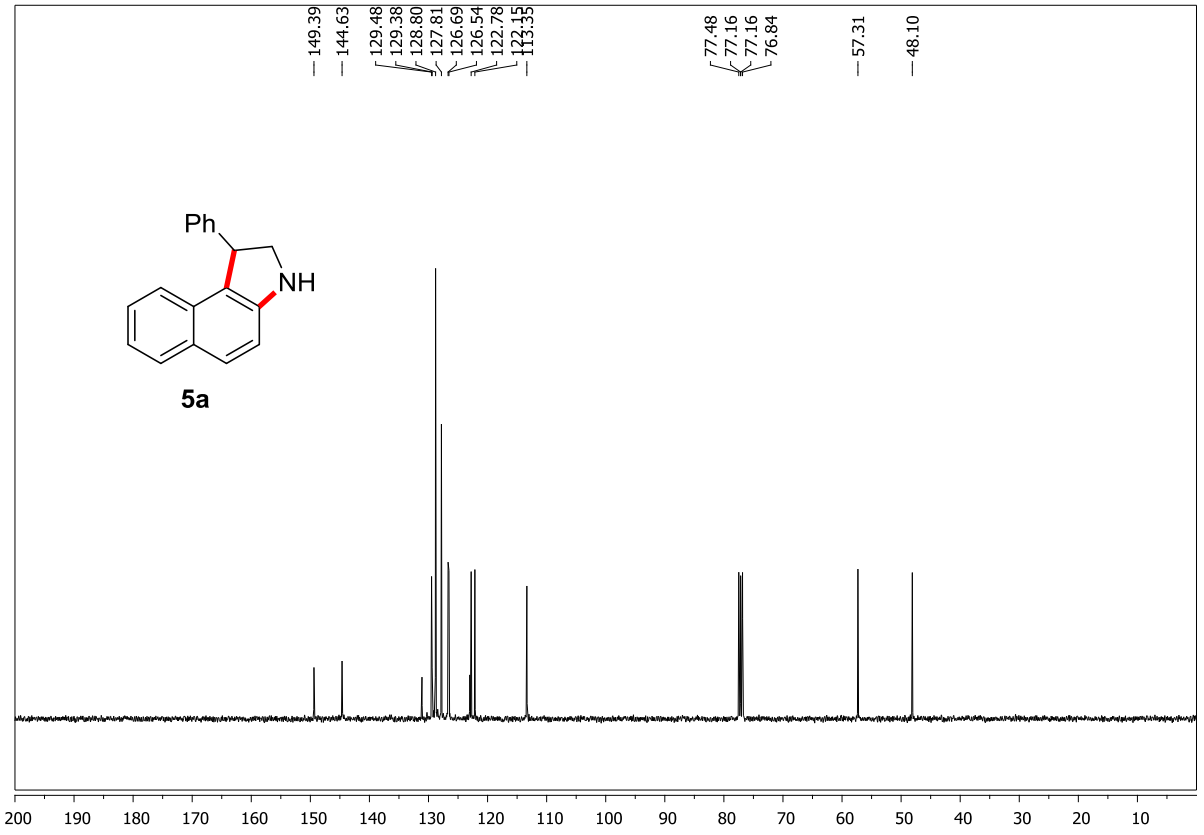
1-Phenyl-3-tosyl-3*H*-benzo[*e*]indole (4a)



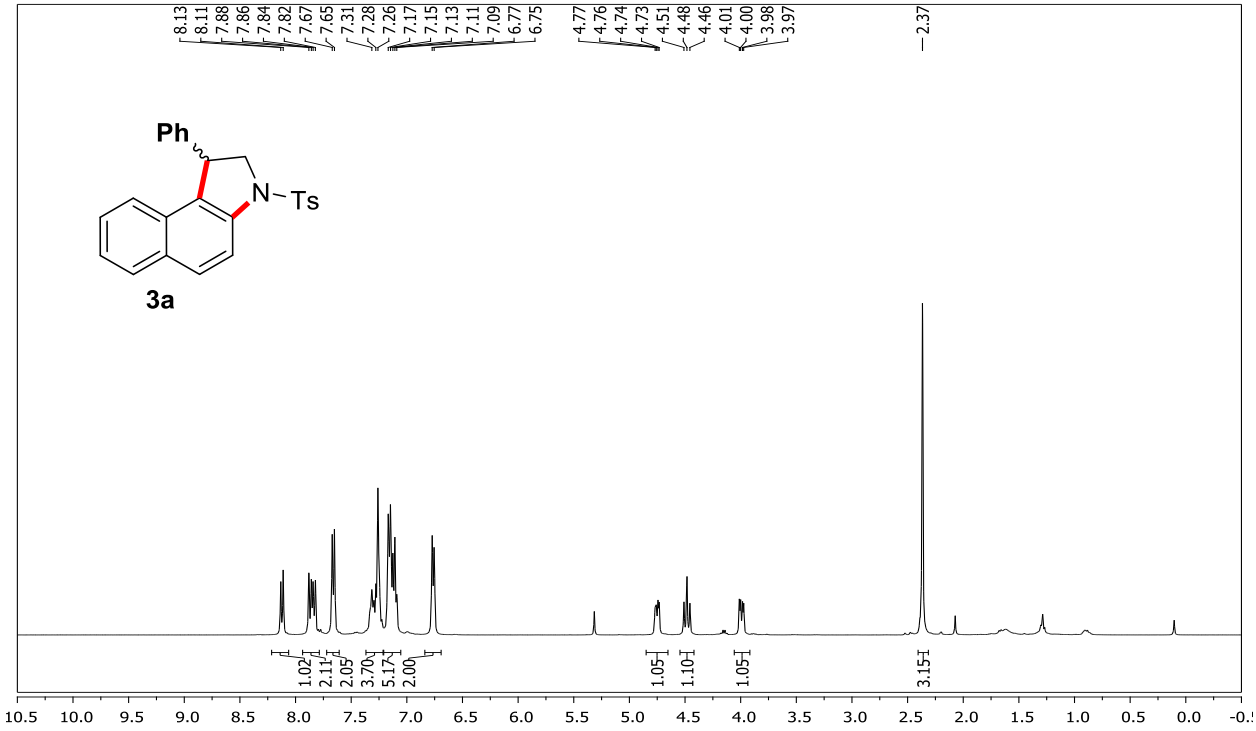


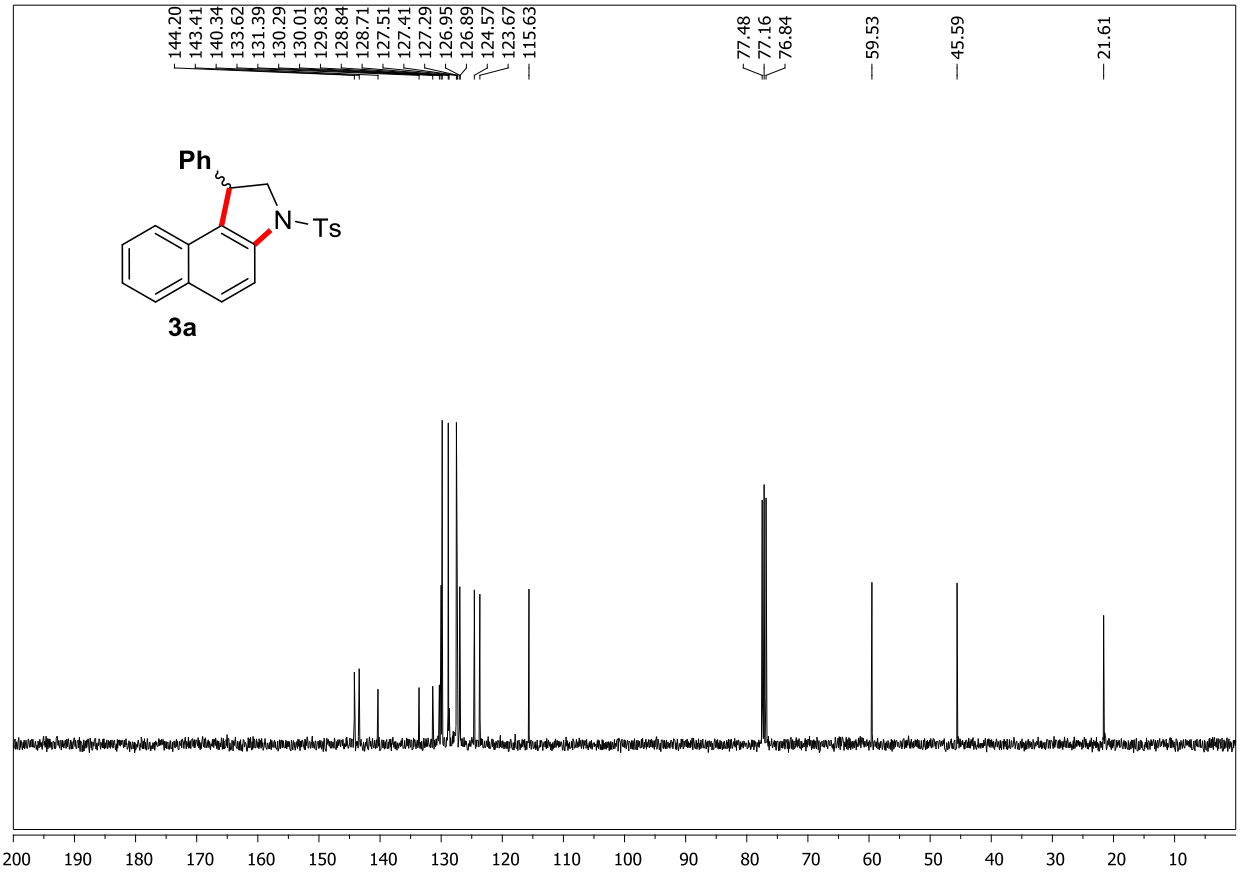
1-phenyl-2,3-dihydro-1*H*-benzo[e]indole (5a)





1-Phenyl-3-tosyl-2,3-dihydro-1*H*-benzo[*e*]indole (3a)

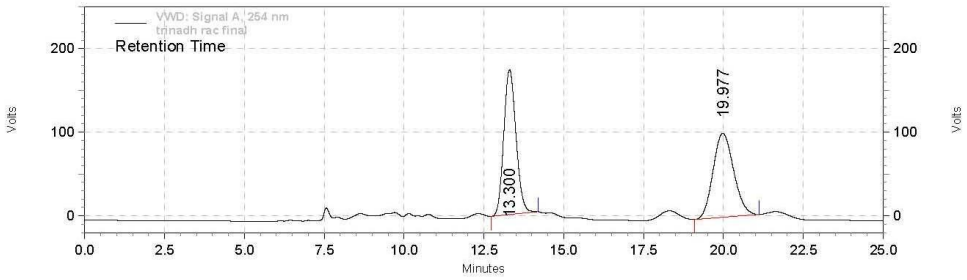




7. HPLC Data of Compound of 3a

Racemic

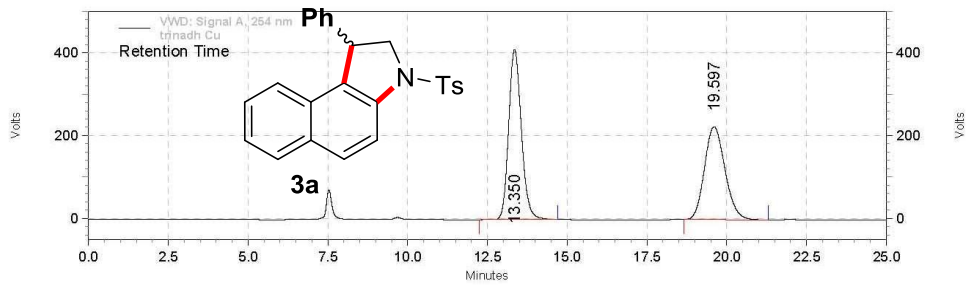
Data File: D:\BIJU\SBM\trinadh rac final.dat
Method: E:\cvr\106.met
Acquired: 3/1/2017 10:47:16 AM Printed: 4/17/2017 11:50:23 PM



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
13.300	77240404	50.57
19.977	75488500	49.43
Totals	152728904	100.00

Chiral



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
13.350	190878638	53.24
19.597	167653253	46.76
Totals	358531891	100.00

Column : Chiralcel OD-H
Eluent System : 80 : 20 (HEXANE:IPA)
Flow rate: 0.5 ml/min
Injection vol..: 10ul
Wavelength: 254 nm
Sample Conc.: 1 mg/ ml