Supplementary Information

Rhodium(III)-catalyzed oxidative [3+2] annulation of aryl boron reagents and 7-azabenzonorbornadienes via transmetalation-initiated C-H activation

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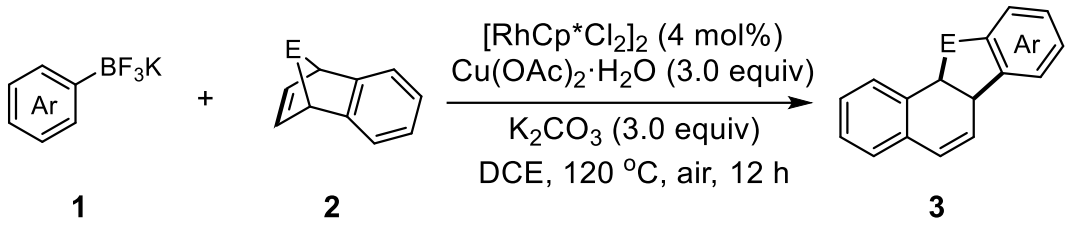
1. General Information

Commercially available chemicals were obtained from Adamas, Acros Organics, Aldrich Chemical Co., Alfa Aesar. and TCI, and they were used as received unless otherwise stated. Anhydrous solvent, purchased from Bide, Adamas, Acros Organics, and *J&K* Chemical, were used as received. NMR Spectra were recorded on 400 MHz NMR or 600 MHz NMR spectrometer in the deuterated solvent indicated. The chemical shift is given in dimensionless δ values and is frequency referenced to TMS in ^{1}H and ^{13}C NMR spectroscopy. HRMS data were obtained on a Thermo Scientific LTQ Orbitrap Discovery spectrometer (Bremen, Germany). Column chromatography was performed on silica gel (200-300 mesh) using ethyl acetate/hexanes.

Azabicyclic olefins **2a**-**2g**,[1] **2h**-**2j**,[2] and **2k**[3] were prepared according to published procedures.

2. Experimental Section

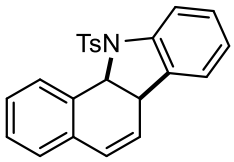
2.1 Synthesis of 3



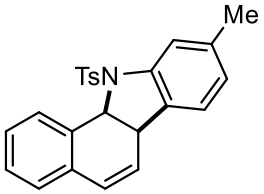
1 **2** **3**

A screw-cap vial (8 mL) was charged with **1** (0.3 mmol, 3.0 equiv), **2** (0.1 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (2.5 mg, 4 mol%), $Cu(OAc)_2·H_2O$ (59.9 mg, 0.3 mmol, 3.0 equiv), K_2CO_3 (41.4 mg, 0.3 mmol, 3.0 equiv) and DCE (1 mL). The reaction mixture in the vial was stirred at 120 °C on a heating mantle for 12 h. The reaction mixture was evaporated under vacuum and the residue was purified by preparative TLC to give the corresponding product.

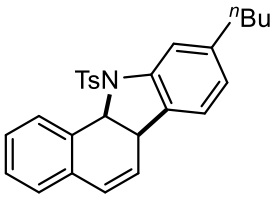
2.2 Characterization Data (NMR and HRMS)



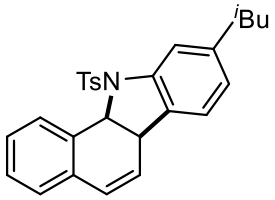
11-tosyl-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3aa**) White solid (29.2 mg, 78%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.7 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 8.3 Hz, 2H), 7.29 (t, J = 7.5 Hz, 1H), 7.24 – 7.14 (m, 4H), 7.07 (t, J = 7.4 Hz, 1H), 7.02 – 6.89 (m, 2H), 6.39 (d, J = 9.7 Hz, 1H), 6.08 – 5.96 (m, 1H), 5.64 (d, J = 10.1 Hz, 1H), 3.41 – 3.29 (m, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0, 140.9, 136.9, 135.1, 131.7, 131.6, 129.7, 128.6, 128.1, 127.9, 127.5, 127.0, 126.7, 126.1, 123.4, 122.5, 119.7, 63.6, 39.8, 21.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{23}H_{20}O_2NS^+$, ($[M + H]^+$), 374.1206, found 374.1204.



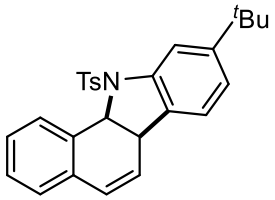
9-methyl-11-tosyl-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3ba**) White solid (25.9 mg, 67%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.8 Hz, 1H), 7.49 – 7.38 (m, 3H), 7.28 – 7.04 (m, 4H), 6.86 – 6.73 (m, 3H), 6.28 (d, J = 9.6 Hz, 1H), 5.89 (m, 1H), 5.53 (d, J = 9.9 Hz, 1H), 3.20 (m, 1H), 2.27 (d, J = 16.9 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 141.2, 138.2, 135.4, 134.1, 131.9, 131.8, 129.8, 128.7, 128.2, 127.4, 127.2, 127.1, 127.0, 126.8, 123.1, 123.0, 120.4, 64.0, 39.7, 21.7, 21.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{24}H_{22}O_2NS^+$, ($[M + H]^+$), 388.1366, found 388.1359.



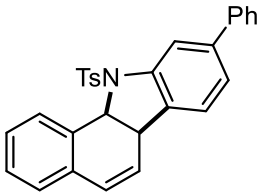
9-butyl-11-tosyl-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3ca**) White solid (28.3 mg, 66%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 6.4 Hz, 3H), 7.34 – 7.24 (m, 1H), 7.16 (d, J = 8.4 Hz, 3H), 6.97 – 6.81 (m, 3H), 6.37 (d, J = 9.9 Hz, 1H), 6.03 – 5.93 (m, 1H), 5.64 (d, J = 10.1 Hz, 1H), 3.39 – 3.26 (m, 1H), 2.64 – 2.55 (m, 2H), 2.37 (s, 3H), 1.63 – 1.54 (m, 2H), 1.39 – 1.30 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.9, 143.2, 140.9, 135.2, 134.1, 131.8, 131.6, 129.6, 128.6, 128.5, 128.0, 127.2, 127.0, 126.6, 126.3, 122.9, 122.8, 119.6, 63.8, 39.6, 35.6, 33.7, 22.3, 21.6, 13.9. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{27}H_{28}O_2NS^+$, ([M + H]$^+$), 430.1835, found 430.1835.



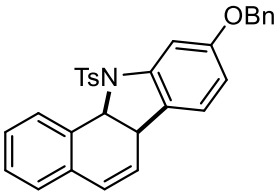
9-isobutyl-11-tosyl-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3da**) White solid (28.4 mg, 66%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.8 Hz, 1H), 7.51 – 7.38 (m, 3H), 7.28 – 7.16 (m, 1H), 7.15 – 7.04 (m, 3H), 6.92 – 6.71 (m, 3H), 6.29 (d, J = 9.9 Hz, 1H), 5.97 – 5.86 (m, 1H), 5.58 (d, J = 10.1 Hz, 1H), 3.30 – 3.22 (m, 1H), 2.45 – 2.33 (m, 5H), 1.87 – 1.73 (m, 1H), 0.83 (d, J = 6.6 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.9, 142.0, 140.8, 135.2, 134.2, 131.9, 131.6, 129.6, 128.7, 128.6, 128.0, 127.3, 127.1, 127.04, 126.96, 126.6, 122.82, 122.78, 120.1, 63.9, 45.3, 39.6, 30.3, 22.3, 22.3, 21.5. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{27}H_{28}O_2NS^+$, ([M + H]$^+$), 430.1835, found 430.1836.



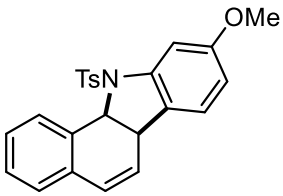
9-(tert-butyl)-11-tosyl-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3ea**) White solid (32.0 mg, 75%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.8 Hz, 1H), 7.71 (d, J = 1.9 Hz, 1H), 7.47 (d, J = 8.4 Hz, 2H), 7.34 – 7.03 (m, 5H), 6.96 – 6.84 (m, 2H), 6.37 (d, J = 9.9 Hz, 1H), 6.03 – 5.95 (m, 1H), 5.67 (d, J = 10.1 Hz, 1H), 3.39 – 3.30 (m, 1H), 2.37 (s, 3H), 1.32 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.6, 143.9, 140.9, 135.2, 133.9, 132.0, 131.7, 129.6, 128.8, 128.6, 128.0, 127.2, 127.1, 126.7, 123.0, 122.9, 122.6, 117.0, 63.9, 39.6, 34.9, 31.5, 21.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{27}H_{28}O_2NS^+$, ([M + H]$^+$), 430.1835, found 430.1832.



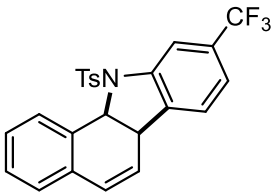
9-phenyl-11-tosyl-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3fa**) White solid (21.2 mg, 47%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, J = 7.6 Hz, 1H), 7.93 (d, J = 1.7 Hz, 1H), 7.29 – 7.64 (m, 9H), 7.15 – 7.24 (m, 3H), 7.04 (d, J = 7.6 Hz, 1H), 6.96 (d, J = 7.5 Hz, 1H), 6.42 (d, J = 9.7 Hz, 1H), 6.07 – 5.99 (m, 1H), 5.70 (d, J = 9.9 Hz, 1H), 3.44 – 3.36 (m, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 141.6, 141.4, 140.4, 135.9, 135.1, 131.64, 131.56, 129.7, 128.7, 128.64, 128.61, 128.1, 127.6, 127.5, 127.1, 127.0, 126.7, 125.1, 123.6, 122.5, 118.2, 63.9, 39.6, 21.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{29}H_{24}O_2NS^+$, ([M + H]$^+$), 450.1922, found 450.1929.



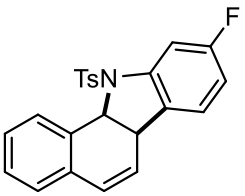
9-(benzyloxy)-11-tosyl-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3ga**) White solid (30.1 mg, 63%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.7 Hz, 1H), 7.48 – 7.23 (m, 9H), 7.20 – 7.10 (m, 3H), 6.92 (d, J = 7.5 Hz, 1H), 6.83 (d, J = 8.3 Hz, 1H), 6.72 – 6.64 (m, 1H), 6.35 (d, J = 9.8 Hz, 1H), 5.98 – 5.90 (m, 1H), 5.63 (d, J = 9.9 Hz, 1H), 5.11 – 5.00 (m, 2H), 3.31 – 3.23 (m, 1H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.7, 144.0, 142.0, 136.7, 135.1, 131.7, 131.6, 129.6, 128.9, 128.6, 128.5, 128.04, 127.96, 127.6, 127.2, 127.0, 126.6, 123.7, 122.8, 113.6, 106.1, 70.2, 64.2, 39.2, 21.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{30}H_{26}O_3NS^+$, ([M + H]$^+$), 480.1628, found 480.1637.



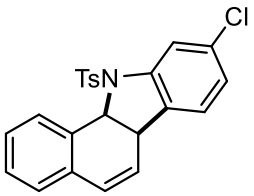
9-methoxy-11-tosyl-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3ha**) White solid (20.5mg , 51%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.8 Hz, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.26 – 7.06 (m, 5H), 6.85 (d, J = 7.5 Hz, 1H), 6.77 (d, J = 9.5 Hz, 1H), 6.58 – 6.51 (m, 1H), 6.29 (d, J = 9.8 Hz, 1H), 5.92 – 5.84 (m, 1H), 5.55 (d, J = 9.9 Hz, 1H), 3.73 (s, 3H), 3.24 – 3.16 (m, 1H), 2.31 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.9, 144.2, 142.3, 135.3, 131.9, 131.8, 129.8, 128.8, 128.74, 128.71, 128.2, 127.4, 127.2, 126.8, 123.8, 123.0, 112.8, 105.3, 64.4, 55.8, 39.3, 21.7. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{24}H_{22}O_3NS^+$, ([M + H]$^+$), 404.1315, found 404.1314.



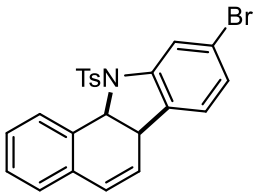
11-tosyl-9-(trifluoromethyl)-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3ia**) White solid (16.0 mg, 36%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.7 Hz, 1H), 7.92 (s, 1H), 7.52 (d, J = 8.3 Hz, 2H), 7.37 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 7.08 (d, J = 7.8 Hz, 1H), 6.96 (d, J = 7.5 Hz, 1H), 6.43 (d, J = 9.7 Hz, 1H), 6.04 – 5.94 (m, 1H), 5.71 (d, J = 10.1 Hz, 1H), 3.46 – 3.36 (m, 1H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.5, 141.6, 140.9, 134.9, 131.4, 131.1, 130.6 (q, J = 32.8 Hz), 129.9, 128.9, 128.5, 128.4, 128.2, 126.91, 126.89, 123.9, 123.8 (q, J = 274.7 Hz), 123.1 (q, J = 4.0 Hz), 121.4, 116.5 (q, J = 4.0 Hz), 63.9, 39.9, 21.6. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.12. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{24}H_{19}O_2F_3NS^+$, ($[M + H]^+$), 442.1083, found 442.1082.



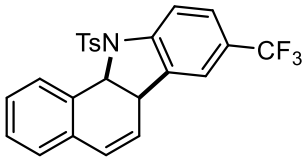
9-fluoro-11-tosyl-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3ja**) White solid (24.5 mg, 63%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.7 Hz, 1H), 7.54 (d, J = 8.2 Hz, 2H), 7.45 – 7.37 (m, 1H), 7.34 – 7.26 (m, 1H), 7.23 – 7.16 (m, 3H), 6.98 – 6.87 (m, 2H), 6.80 – 6.73 (m, 1H), 6.39 (d, J = 9.7 Hz, 1H), 6.00 – 5.91 (m, 1H), 5.66 (d, J = 9.9 Hz, 1H), 3.37 – 3.28 (m, 1H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.5 (d, J = 245.8 Hz), 144.3, 142.3 (d, J = 11.8 Hz), 135.0, 132.2 (d, J = 2.6 Hz), 131.5, 131.3, 129.8, 128.7, 128.6, 128.2, 127.7, 127.0, 126.8, 124.0 (d, J = 9.7 Hz), 122.2, 112.8 (d, J = 23.0 Hz), 107.6 (d, J = 27.3 Hz), 64.3, 39.3, 21.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.24. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{23}H_{19}FO_2NS^+$, ($[M + H]^+$), 392.1115, found 392.1115.



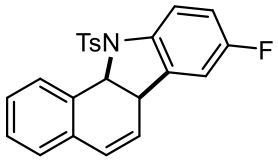
9-chloro-11-tosyl-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3ka**) White solid (25.6 mg, 63%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.8 Hz, 1H), 7.68 (s, 1H), 7.54 (d, J = 8.3 Hz, 2H), 7.37 – 7.12 (m, 4H), 7.07 – 7.00 (m, 1H), 6.98 – 6.85 (m, 2H), 6.40 (d, J = 9.7 Hz, 1H), 5.99 – 5.91 (m, 1H), 5.64 (d, J = 10.0 Hz, 1H), 3.35 – 3.26 (m, 1H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.4, 142.2, 135.4, 135.0, 133.5, 131.5, 131.3, 129.8, 128.8, 128.5, 128.3, 127.9, 127.0, 126.8, 126.2, 124.2, 121.9, 119.8, 64.1, 39.4, 21.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{23}H_{19}ClO_2NS^+$, ($[M + H]^+$), 408.0820, found 408.0824.



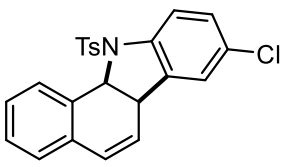
9-bromo-11-tosyl-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3la**) White solid (34.1 mg, 76%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.8 Hz, 1H), 7.83 (s, 1H), 7.54 (d, J = 7.9 Hz, 2H), 7.37 – 7.15 (m, 5H), 6.94 (d, J = 7.6 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.40 (d, J = 9.6 Hz, 1H), 5.99 – 5.90 (m, 1H), 5.63 (d, J = 9.9 Hz, 1H), 3.32 – 3.23 (m, 1H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.4, 142.4, 136.0, 135.0, 131.5, 131.2, 129.8, 129.1, 128.8, 128.5, 128.3, 127.9, 127.0, 126.8, 124.6, 122.6, 121.8, 121.2, 64.0, 39.5, 21.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{23}H_{19}BrO_2NS^+$, ([M + H]$^+$), 452.0314, found 452.0315.



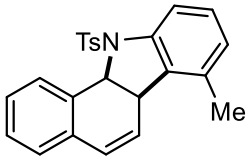
11-tosyl-8-(trifluoromethyl)-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3ma**) White solid (27.3 mg, 62%),**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.7 Hz, 1H), 7.76 (d, J = 8.3 Hz, 1H), 7.56 – 7.45 (m, 3H), 7.38 – 7.15 (m, 5H), 6.97 (d, J = 7.5 Hz, 1H), 6.45 (d, J = 9.7 Hz, 1H), 6.04 – 5.96 (m, 1H), 5.70 (d, J = 10.0 Hz, 1H), 3.46 – 3.37 (m, 1H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.5, 144.1, 137.6, 135.1, 131.5, 131.1, 129.9, 128.9, 128.6, 128.4, 128.3, 128.2 (q, J = 32.3 Hz), 126.90, 126.86, 125.60 (q, J = 4.0 Hz), 124.0 (q, J = 273.7 Hz), 121.4, 120.8 (q, J = 4.0 Hz), 119.20, 64.03, 39.71, 21.58. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -61.85. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{24}H_{19}O_2F_3NS^+$, ([M + H]$^+$), 442.1083, found 442.1083.



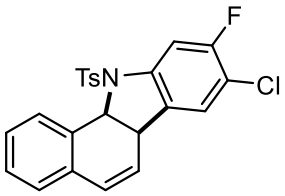
8-fluoro-11-tosyl-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3na**) White solid (8.7 mg, 22%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.8 Hz, 1H), 7.64 – 7.57 (m, 1H), 7.49 (d, J = 8.3 Hz, 2H), 7.34 – 7.28 (m, 1H), 7.22 – 7.16 (m, 3H), 6.97 – 6.85 (m, 2H), 6.69 – 6.63 (m, 1H), 6.41 (d, J = 9.7 Hz, 1H), 5.95 – 5.86 (m, 1H), 5.65 (d, J = 10.0 Hz, 1H), 3.34 – 3.24 (m, 1H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.2 (d, J = 245.4 Hz), 144.2, 139.1 (d, J = 8.3 Hz), 136.9 (d, J = 2.3 Hz), 134.8, 131.4, 129.8, 128.8, 128.5, 128.2, 128.1, 127.0, 126.8, 121.6, 120.9, 120.8, 114.7 (d, J = 23.7 Hz), 110.8 (d, J = 24.5 Hz), 64.1, 39.8, 21.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.85. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{23}H_{19}FO_2NS^+$, ([M + H]$^+$), 392.1115, found 392.1117.



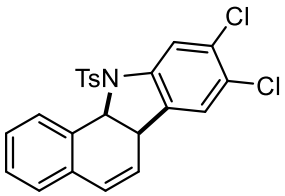
8-chloro-11-tosyl-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3oa**) White solid (23.2 mg, 57%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.8 Hz, 1H), 7.65 – 7.48 (m, 3H), 7.38 – 7.13 (m, 5H), 6.95 (d, J = 7.4 Hz, 2H), 6.41 (d, J = 9.7 Hz, 1H), 6.00 – 5.89 (m, 1H), 5.65 (d, J = 10.0 Hz, 1H), 3.36 – 3.28 (m, 1H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.3, 139.6, 138.8, 134.9, 131.4, 131.3, 129.8, 128.7, 128.5, 128.25, 128.1, 128.0, 126.9, 126.8, 123.8, 121.6, 120.5, 63.9, 39.7, 21.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{23}H_{19}ClO_2NS^+$, ([M + H]$^+$), 408.0820,found 408.0816.



7-methyl-11-tosyl-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3pa**) White solid (19.0 mg, 49%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.8 Hz, 1H), 7.59 – 7.41 (m, 3H), 7.35 – 7.06 (m, 5H), 6.97 – 6.80 (m, 2H), 6.36 (d, J = 9.9 Hz, 1H), 6.06 – 5.98 (m, 1H), 5.60 (d, J = 9.6 Hz, 1H), 3.48 – 3.40 (m, 1H), 2.38 (s, 3H), 2.20 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.9, 141.2, 135.4, 134.2, 133.8, 131.8, 131.7, 129.6, 128.7, 128.4, 128.1, 128.0, 127.8, 127.4, 127.0, 126.4, 123.0, 116.9, 63.4, 40.9, 21.5, 20.2. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{24}H_{22}O_2NS^+$, ([M + H]$^+$), 388.1366, found 388.1365.

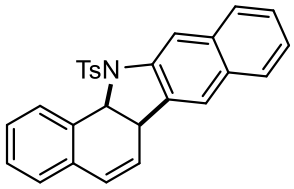


8-chloro-9-fluoro-11-tosyl-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3qa**) White solid (18.8 mg, 44%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.7 Hz, 1H), 7.58 – 7.46 (m, 3H), 7.35 – 7.21 (m, 4H), 7.02 – 6.93 (m, 2H), 6.42 (d, J = 9.6 Hz, 1H), 5.96 – 5.85 (m, 1H), 5.65 (d, J = 9.9 Hz, 1H), 3.35 – 3.27 (m, 1H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.8, 156.3, 144.6, 140.8 (d, J = 10.6 Hz), 134.9, 133.3 (d, J = 3.1 Hz), 131.4, 131.0, 130.0, 128.5, 128.4, 128.3, 127.9 (d, J = 201.0 Hz), 127.0, 125.0, 121.3, 118.1 (d, J = 19.1 Hz), 108.4 (d, J = 27.3 Hz), 64.3, 39.4, 21.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.90. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{23}H_{18}FClO_2NS^+$, ([M + H]$^+$), 426.0725, found 426.0726.

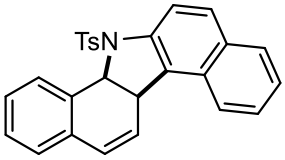


8,9-dichloro-11-tosyl-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3ra**) White solid (30.0 mg, 68%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.7 Hz, 1H), 7.77 (s, 1H), 7.55 (d, J = 8.3 Hz, 2H), 7.35 – 7.16 (m, 4H), 7.03 (s, 1H), 6.99 – 6.92 (m, 1H), 6.42 (d, J = 9.7 Hz, 1H), 5.95 – 5.87 (m, 1H), 5.64 (d, J = 9.9 Hz, 1H), 3.34 – 3.25 (m, 1H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.6, 140.6, 137.1, 134.9, 131.8 131.4, 131.0, 130.0, 129.6, 129.0, 128.5, 128.44, 128.40, 126.95, 126.93, 125.1, 121.1, 64.2, 39.5, 21.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{23}H_{18}Cl_2O_2NS^+$, ([M + H]$^+$),

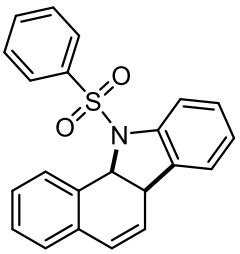
442.0430, found 442.0425.



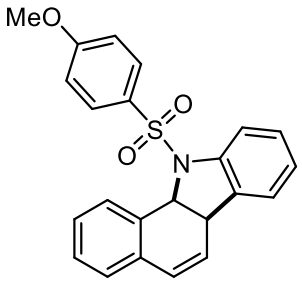
13-tosyl-6a,13a-dihydro-13*H*-dibenzo[a,h]carbazole (**3sa**) White solid (12.4 mg, 29%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 8.00 (d, J = 7.7 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.1 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.47 – 7.33 (m, 3H), 7.33 – 7.27 (m, 1H), 7.20 – 7.10 (m, 3H), 6.97 – 6.90 (m, 1H), 6.44 (d, J = 9.7 Hz, 1H), 6.19 – 6.10 (m, 1H), 5.73 (d, J = 9.9 Hz, 1H), 3.50 – 3.41 (m, 1H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 139.0, 136.9, 135.5, 133.5, 132.1, 131.72, 131.66, 129.8, 128.7, 128.5, 128.2, 128.1, 127.8, 127.4, 126.9, 126.7, 126.0, 125.4, 122.8, 122.3, 116.5, 64.0, 39.7, 21.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{27}H_{22}O_2NS^+$, ([M + H]$^+$), 424.1366, found 424.1366.



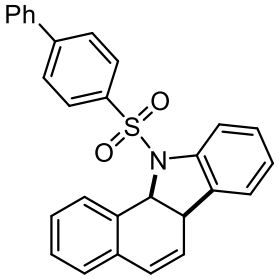
7-tosyl-7a,13a-dihydro-7*H*-dibenzo[a,g]carbazole (**3ta**) White solid (23.1 mg, 55%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.7 Hz, 1H), 7.94 (d, J = 8.8 Hz, 1H), 7.86 – 7.81 (m, 1H), 7.76 (d, J = 8.9 Hz, 2H), 7.48 – 7.36 (m, 4H), 7.33 – 7.27 (m, 1H), 7.21 – 7.14 (m, 1H), 7.09 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 7.4 Hz, 1H), 6.42 (d, J = 9.8 Hz, 1H), 6.35 – 6.26 (m, 1H), 5.73 (d, J = 9.4 Hz, 1H), 3.89 – 3.77 (m, 1H), 2.33 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0, 139.3, 135.1, 132.6, 131.7, 131.5, 129.7, 129.6, 129.5, 129.03, 129.00, 128.9, 128.4, 128.2, 127.7, 127.0, 126.5, 126.4, 124.8, 124.0, 123.2, 118.8, 64.0, 41.0, 21.5. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{27}H_{22}O_2NS^+$, ([M + H]$^+$), 424.1366, found 424.1369.



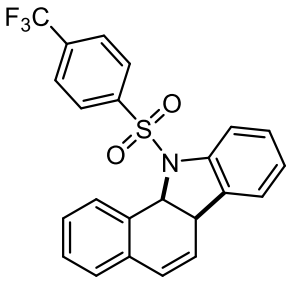
11-(phenylsulfonyl)-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3ab**) White solid (10.9 mg, 30%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.72 – 7.50 (m, 4H), 7.45 – 7.14 (m, 5H), 7.08 (t, J = 7.5 Hz, 1H), 7.02 – 6.90 (m, 2H), 6.39 (d, J = 9.8 Hz, 1H), 6.02 – 5.94 (m, 1H), 5.66 (d, J = 10.0 Hz, 1H), 3.35 – 3.26 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.8, 138.0, 136.8, 133.2, 131.6, 131.5, 129.0, 128.6, 128.6, 128.1, 128.0, 127.5, 127.0, 126.7, 126.2, 123.4, 122.5, 119.6, 63.7, 39.8. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{22}H_{18}O_2NS^+$, ([M + H]$^+$), 360.1053, found 360.1054.



11-((4-methoxyphenyl)sulfonyl)-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3ac**) White solid (22.6 mg, 58%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.8 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 8.5 Hz, 2H), 7.26 – 7.02 (m, 3H), 7.02 – 6.60 (m, 5H), 6.28 (d, J = 9.7 Hz, 1H), 5.94 – 5.86 (m, 1H), 5.53 (d, J = 10.1 Hz, 1H), 3.69 (s, 3H), 3.32 – 3.23 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.2, 140.9, 136.9, 131.7, 131.5, 129.5, 129.0, 128.51, 128.49, 128.0, 127.8, 127.4, 126.6, 126.1, 123.4, 122.6, 119.6, 114.1, 63.5, 55.5, 39.8. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{23}H_{20}O_3NS^+$, ([M + H]$^+$), 390.1158, found 390.1163.

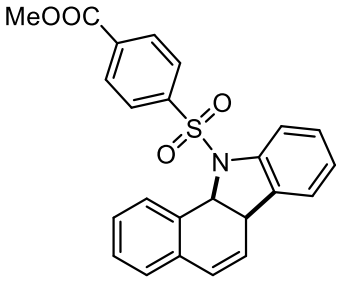


11-([1,1'-biphenyl]-4-ylsulfonyl)-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3ad**) White solid (17.9 mg, 41%), **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.92 (d, J = 7.8 Hz, 1H), 7.67 – 7.57 (m, 3H), 7.55 – 7.46 (m, 4H), 7.41 – 7.28 (m, 3H), 7.24 – 7.06 (m, 3H), 7.03 – 6.97 (m, 1H), 6.92 – 6.81 (m, 2H), 6.31 (d, J = 9.8 Hz, 1H), 5.94 – 5.88 (m, 1H), 5.62 (d, J = 10.0 Hz, 1H), 3.36 – 3.30 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 145.9, 140.9, 138.9, 136.9, 136.7, 131.7, 131.6, 129.1, 128.69, 128.67, 128.2, 128.1, 127.59, 127.55, 127.3, 126.8, 126.3, 123.6, 122.6, 119.7, 63.8, 39.9. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{28}H_{22}O_2NS^+$, ([M + H]$^+$), 436.1366, found 436.1364.

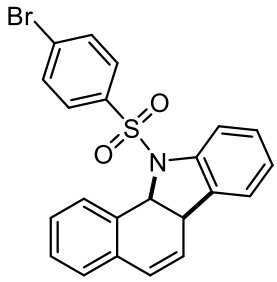


11-((4-(trifluoromethyl)phenyl)sulfonyl)-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3ae**) White solid (17.1 mg, 40%), **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.97 (d, J = 7.8 Hz, 1H), 7.76 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.2 Hz, 2H), 7.41 – 7.17 (m, 3H), 7.11 (t, J = 7.5 Hz, 1H), 7.02 (d, J = 7.5 Hz, 1H), 6.95 (d, J = 7.5 Hz, 1H), 6.41 (d, J = 9.7 Hz, 1H), 6.03 – 5.98 (m, 1H), 5.69 (d, J = 9.9 Hz, 1H), 3.40 – 3.34 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.7, 140.3, 136.5, 134.72 (q, J = 33.2 Hz), 131.6, 131.0, 128.7, 128.5, 128.3, 128.2, 127.6, 127.5, 126.8, 126.5, 126.2 (q, J = 4.5 Hz), 123.1 (q, J = 273.3 Hz), 123.8, 122.3, 119.3, 63.9, 39.9. **^{19}F NMR** (376 MHz, $CDCl_3$)

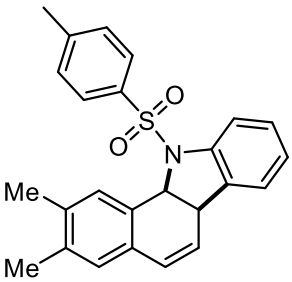
δ -63.04. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{23}H_{17}F_3O_2NS^+$, ([M + H]$^+$), 428.0927, found 428.0910.



methyl 4-((6a,11a-dihydro-11H-benzo[a]carbazol-11-yl)sulfonyl)benzoate (**3af**) White solid (16.8 mg, 40%), **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (d, J = 8.7 Hz, 2H), 7.96 (d, J = 7.7 Hz, 1H), 7.71 – 7.66 (m, 3H), 7.33 – 7.14 (m, 3H), 7.12 – 7.04 (m, 1H), 7.00 – 6.91 (m, 2H), 6.38 (d, J = 10.1 Hz, 1H), 6.00 – 5.94 (m, 1H), 5.67 (d, J = 10.0 Hz, 1H), 3.93 (s, 3H), 3.34 – 3.28 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.5, 141.9, 140.4, 136.6, 134.2, 131.6, 131.1, 130.1, 128.6, 128.5, 128.2, 128.1, 127.6, 127.0, 126.8, 126.5, 123.6, 122.3, 119.4, 63.9, 52.6, 39.8. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{24}H_{20}O_4NS^+$, ([M + H]$^+$), 418.1108, found 418.1110.

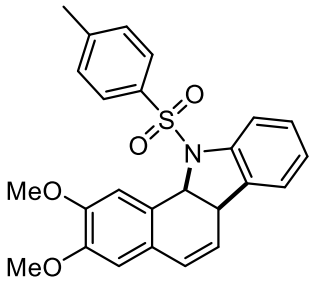


11-((4-bromophenyl)sulfonyl)-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3ag**) White solid (30.1 mg, 69%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.7 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.57 – 7.43 (m, 4H), 7.34 – 7.14 (m, 3H), 7.10 (t, J = 7.5 Hz, 1H), 7.04 – 6.86 (m, 2H), 6.40 (d, J = 9.7 Hz, 1H), 6.05 – 5.97 (m, 1H), 5.64 (d, J = 10.0 Hz, 1H), 3.43 – 3.35 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.5, 137.1, 136.7, 132.3, 131.6, 131.2, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.6, 126.8, 126.4, 123.7, 122.4, 119.5, 63.8, 39.9. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{22}H_{17}BrO_2NS^+$, ([M + H]$^+$),438.0158 , found 438.0148.

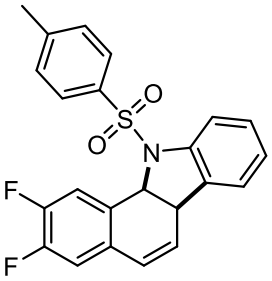


2,3-dimethyl-11-tosyl-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3ah**) White solid (15.3 mg, 38%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.64 (m, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.26 – 7.13 (m, 3H), 7.06 (t, J = 7.4 Hz, 1H), 6.96 (d, J = 7.5 Hz, 1H), 6.71 (s, 1H), 6.34 (d, J = 9.6 Hz, 1H), 5.92 (m, 1H), 5.60 (d, J = 9.9 Hz, 1H), 3.30 (m, 1H), 2.38 (s, 3H), 2.29 (s, 3H), 2.17 (s, 3H). **^{13}C NMR** (101

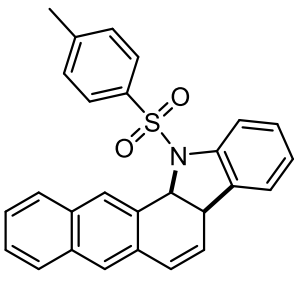
MHz, $CDCl_3$) δ 143.9, 140.9, 137.19, 137.16, 136.3, 135.2, 129.6, 129.3, 128.9, 128.0, 127.8, 127.4, 127.0, 126.0, 123.4, 121.5, 119.7 , 63.6, 39.9, 21.5, 19.7, 19.2. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{25}H_{24}O_2NS^+$, ($[M + H]^+$), 402.1522, found 402.1529.



2,3-dimethoxy-11-tosyl-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3ai**) White solid (17.3 mg, 40%) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.0 Hz, 1H), 7.54 (s, 1H), 7.49 (d, J = 8.0 Hz, 2H), 7.28 – 7.13 (m, 3H), 7.08 (t, J = 7.4 Hz, 1H), 6.98 (d, J = 7.5 Hz, 1H), 6.45 (s, 1H), 6.29 (d, J = 9.7 Hz, 1H), 5.95 – 5.86 (m, 1H), 5.59 (d, J = 10.2 Hz, 1H), 3.99 (s, 3H), 3.81 (s, 3H), 3.36 – 3.27 (m, 1H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.1, 148.5, 144.0, 140.7, 137.1, 135.1, 129.6, 127.9, 127.0, 126.8, 126.1, 124.6, 124.1, 123.4, 120.8, 119.6, 111.6, 109.8, 63.7, 56.1, 55.9, 39.6, 21.5. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{25}H_{24}O_4NS^+$, ($[M + H]^+$), 434.1421, found 434.1420.

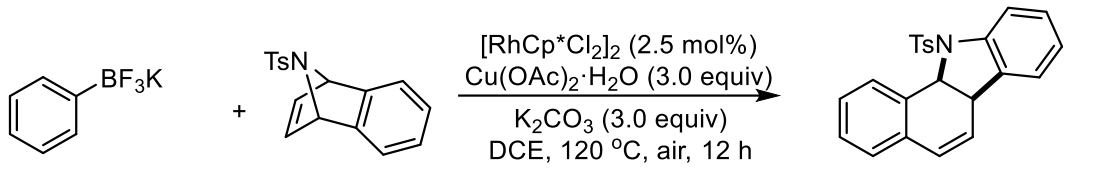


2,3-difluoro-11-tosyl-6a,11a-dihydro-11*H*-benzo[a]carbazole (**3aj**) White solid (22.5 mg, 55%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 – 7.69 (m, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 8.2 Hz, 2H), 7.21 – 6.97 (m, 4H), 6.88 (d, J = 7.6 Hz, 1H), 6.68 – 6.59 (m, 1H), 6.18 (d, J = 9.7 Hz, 1H), 5.99 – 5.90 (m, 1H), 5.45 (d, J = 10.1 Hz, 1H), 3.30 – 3.21 (m, 1H), 2.29 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.1 (dd, J = 13.0, 3.7 Hz), 148.6 (dd, J = 13.1, 2.3 Hz), 144.3, 140.5, 136.2, 134.7, 129.7, 128.7, 128.6, 128.5, 128.2, 126.9, 126.4, 125.5, 123.5, 119.5, 118.01 (d, J = 19.0 Hz), 115.04 (d, J = 17.8 Hz), 62.8, 39.3, 21.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -136.65 (d, J = 21.3 Hz), -139.30 (d, J = 21.3 Hz). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{23}H_{18}F_2O_2NS^+$, ($[M + H]^+$), 410.1021, found 410.1027.



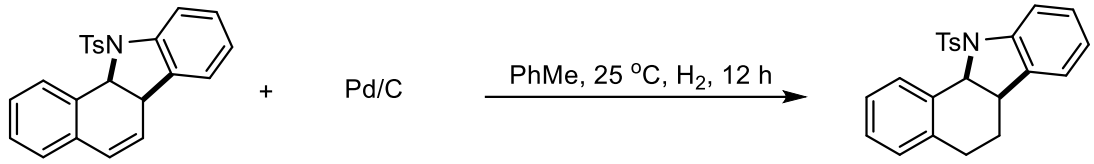
12-tosyl-7a,12a-dihydro-12*H*-naphtho[2,3-a]carbazole (**3ak**) White solid (17.4 mg, 41%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.94 – 7.85 (m, 1H), 7.73 – 7.64 (m, 2H), 7.54 (d, J = 8.0 Hz, 2H), 7.47 – 7.35 (m, 3H), 7.24 – 7.15 (m, 3H), 7.07 (t, J = 7.4 Hz, 1H), 6.99 (d, J = 7.4 Hz, 1H), 6.60 (d, J = 9.7 Hz, 1H), 6.11 – 6.03 (m, 1H), 5.74 (d, J = 9.3 Hz, 1H), 3.45 – 3.37 (m, 1H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 141.1, 137.0, 135.4, 133.6, 133.1, 130.1, 129.9, 129.7, 128.3, 128.1, 128.0, 127.9, 127.4, 127.0, 126.4, 126.1, 126.1, 125.5, 123.4, 123.1, 119.8, 63.6, 40.2, 21.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{27}H_{22}O_2NS^+$, ($[M + H]^+$), 424.1366, found 424.1373.

3. Synthetic Applications



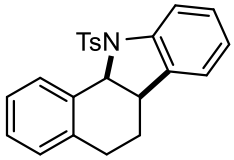
1a **2a** **3aa**, 60% yield (1 mmol scale)

A screw-cap vial (10 mL) was charged with **1a** (552.0 mg, 3.0 mmol, 3.0 equiv), **2a** (297.1 mg, 1.0 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (15.6 mg, 2.5 mol%), $Cu(OAc)_2·H_2O$ (599.0 mg, 3.0 mmol, 3.0 equiv), K_2CO_3 (414.6 mg, 0.3 mmol, 3.0 equiv) and DCE (5 mL). The reaction mixture in the vial was stirred at 120 °C on a heating mantle for 12 h. The reaction mixture was evaporated under vacuum and the residue was purified by preparative TLC to give the corresponding product **3aa** (223.5 mg, 60%). Eluent: 5:1 petroleum ether/ethyl acetate.



3aa **5**, 85% yield

To a stirred solution of compound **3aa** (37.3 mg, 0.1 mmol) in toluene (4 mL) was added 10 mg Pd/C (10 wt%) at room temperature and a hydrogen balloon was attached. After being stirred for 12h at 25 °C, the mixture was filtered. After the removal of the solvent, the crude solid was purified by silica-gel column chromatography to give **5** as a white solid (31.8 mg, 85%).

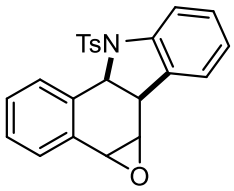


11-tosyl-6,6a,11,11a-tetrahydro-5*H*-benzo[a]carbazole (**5**) White solid (31.8 mg, 85%), **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.99 (d, J = 7.8 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.3 Hz, 2H), 7.33 – 7.09 (m, 6H), 7.04 (d, J = 7.5 Hz, 1H), 6.93 (d, J = 7.6 Hz, 1H), 5.41 (d, J = 8.5 Hz, 1H), 3.14 – 3.08 (m, 1H), 2.66 – 2.40 (m, 2H), 2.37 (s, 3H), 2.16 – 1.90 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.8, 142.1, 137.5, 136.2, 135.6, 134.3, 130.5, 129.5, 128.0, 127.94, 127.85, 127.3, 127.1, 126.8, 125.7, 123.4, 120.0, 64.0, 39.4, 24.8, 23.6, 21.5. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{23}H_{22}O_2NS^+$, ($[M + H]^+$), 376.1366, found 376.1365.

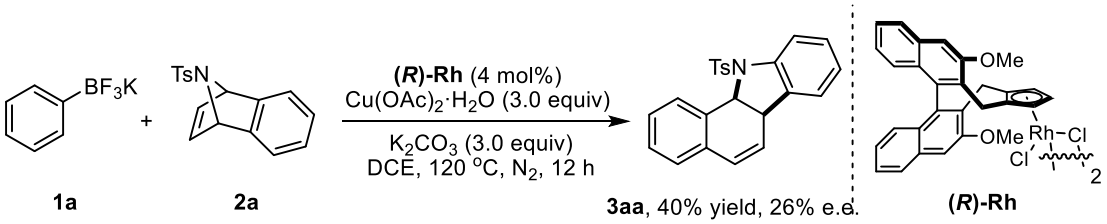
3aa **6**, 78% yield

A screw-cap vial (8 mL) was charged with **3aa** (37.3 mg, 0.1 mmol, 1.0 equiv), *m*-CPBA (51.8 mg, 0.3 mmol, 3.0 equiv) and DCM (1 mL). The reaction mixture in the vial was stirred at 0 °C for 4 h. The reaction mixture was evaporated under vacuum and the residue was purified by preparative

TLC to give the corresponding product **6** (30.4 mg, 78%).

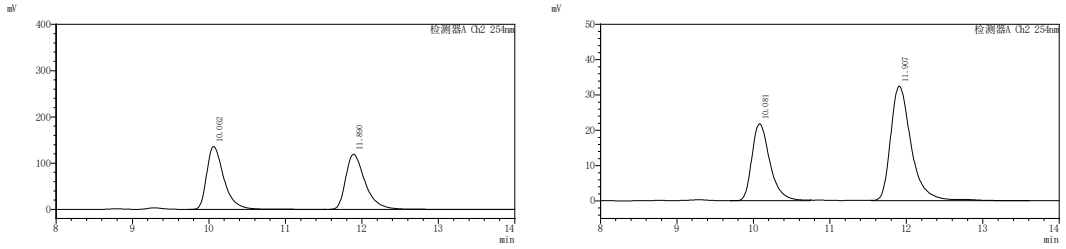


6-tosyl-1a,5b,10b,10c-tetrahydro-6*H*-benzo[a]oxireno[2,3-c]carbazole (**6**) White solid (30.4 mg, 78%), **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.06 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.3 Hz, 2H), 7.45 – 7.39 (m, 1H), 7.32 – 7.17 (m, 5H), 7.13 – 7.06 (m, 2H), 5.23 (d, J = 8.6 Hz, 1H), 3.91 – 3.84 (m, 2H), 3.57 – 3.51 (m, 1H), 2.39 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.3, 141.5, 135.4, 133.1, 132.9, 131.3, 129.8, 129.7, 129.33, 129.30, 128.6, 127.8, 126.9, 126.0, 123.4, 120.2, 61.3, 52.4, 52.3, 40.0, 21.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{23}H_{20}O_3NS^+$, ([M + H]$^+$), 390.1158 , found 390.1154.



A screw-cap vial (8 mL) was charged with **1a** (55.2 mg, 0.3 mmol, 3.0 equiv), **2a** (29.7 mg, 0.1 mmol, 1.0 equiv), **(*R*)-Rh** (4.6 mg, 4 mol%), $Cu(OAc)_2·H_2O$ (59.9 mg, 0.3 mmol, 3.0 equiv), K_2CO_3 (41.4 mg, 0.3 mmol, 3.0 equiv) and DCE (1 mL). The reaction mixture in the vial was stirred at 120 °C on a heating mantle for 12 h. The reaction mixture was evaporated under vacuum and the residue was purified by preparative TLC to give the corresponding product **3aa** (15.0 mg, 40%, 26% e.e.).

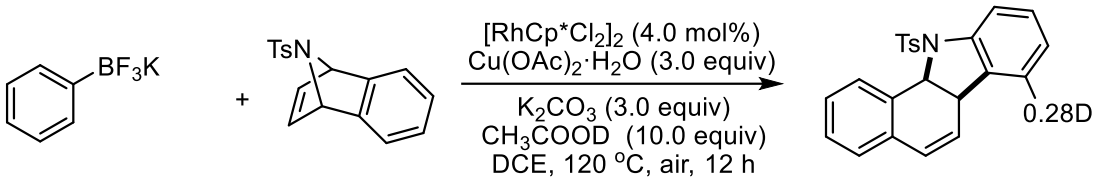
HPLC conditions: Daicel Chiralpak OD-3 column (95:5 hexane: 2-propanol, 0.8 mL/min, 40 °C, 254 nm); tr (major) = 11.9 min, tr (minor) = 10.1 min, 26% e.e..



No.	Time	Area	Area (%)	No.	Time	Area	Area (%)
1	10.062	2130852	50.294	1	10.081	358999	37.091
2	11.890	2105948	49.706	2	11.907	608877	62.909

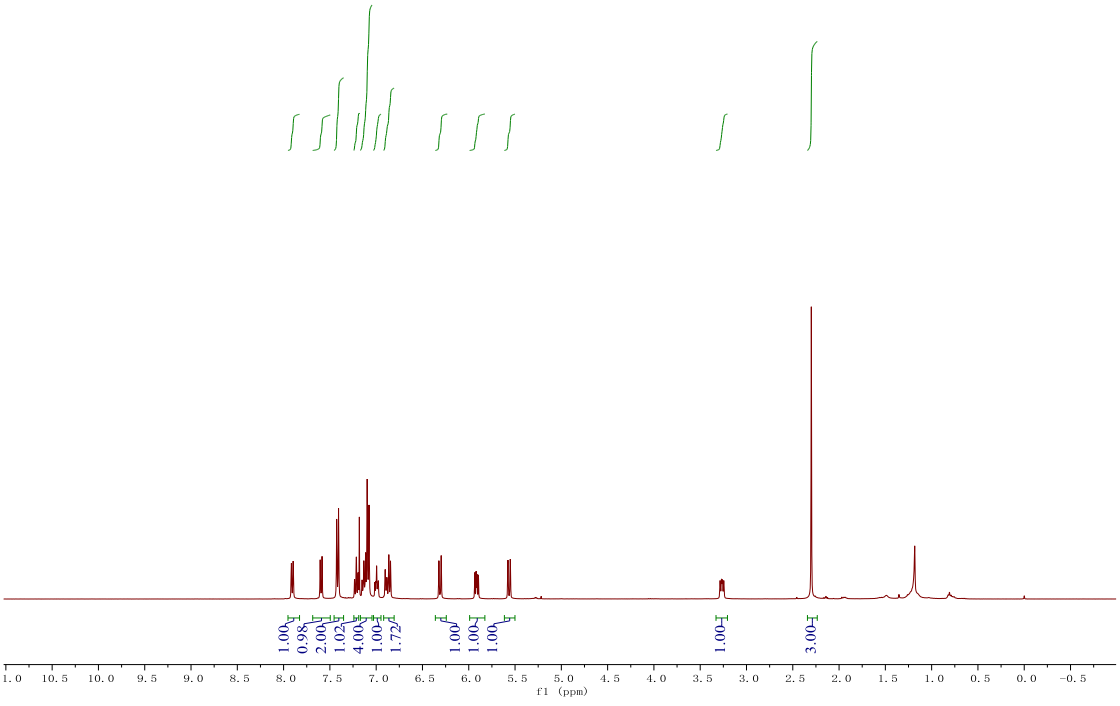
4. Mechanistic Studies

4.1 H/D Exchange Experiments

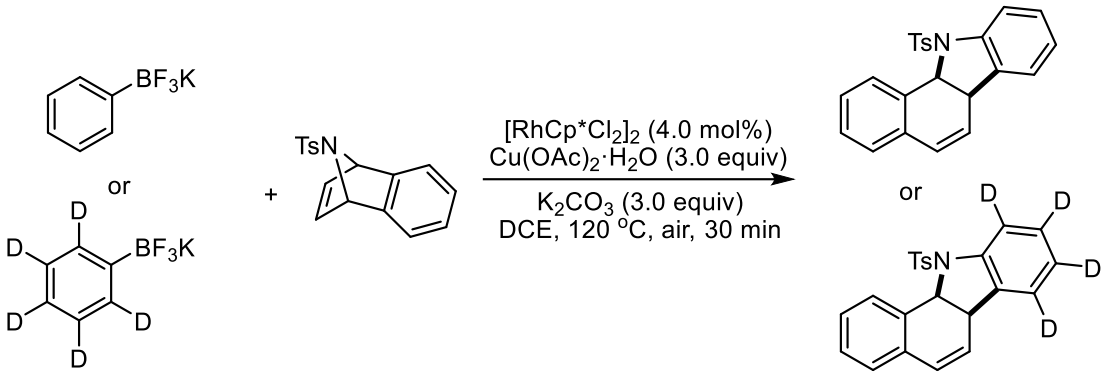


1a **2a** **3aa**, 45% yield

A screw-cap vial (8 mL) was charged with **1a** (55.2 mg, 0.3 mmol, 3.0 equiv), **2a** (29.7 mg, 0.1 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (2.5 mg, 4 mol%), $Cu(OAc)_2·H_2O$ (59.9 mg, 0.3 mmol, 3.0 equiv), K_2CO_3 (41.4 mg, 0.3 mmol, 3.0 equiv), CH_3COOD (64.0 mg, 1.0 mmol, 10.0 equiv) and DCE (1 mL). The reaction mixture in the vial was stirred at 120 °C on a heating mantle for 12 h. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using (petroleum ether/ethyl acetate 5:1) to give the corresponding product, and the extent of deuteration was obtained by ^1H NMR analysis.

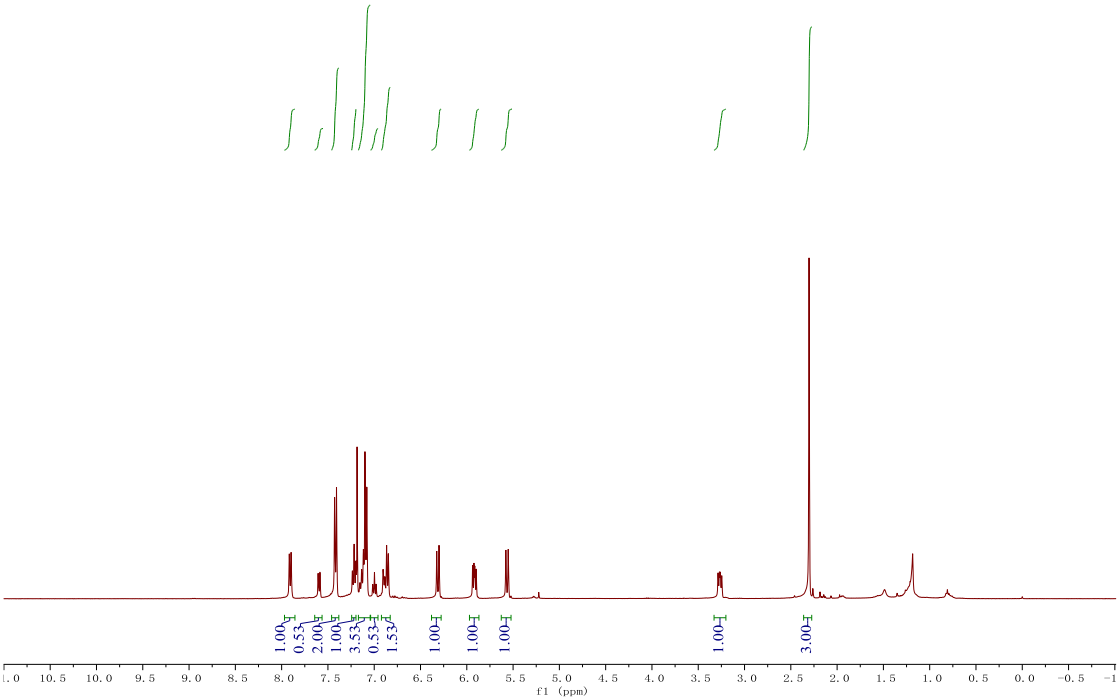


4.2 KIE Experiments

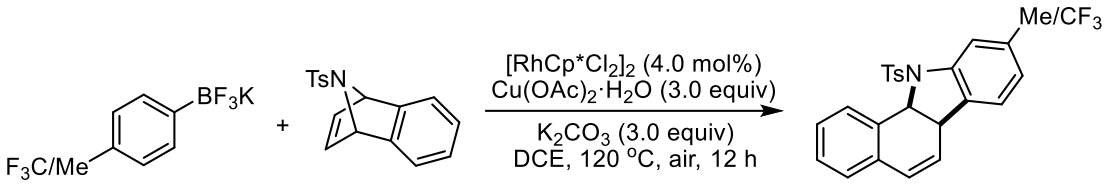


1a or **1a-*d*$_5$** **2a** **3aa** or **3aa-*d*$_4$**
KIE = 1.1:1

Two screw-cap vials (8 mL) each was charged with **1a** (55.2 mg, 0.3 mmol, 3 equiv) or **1a-*d*$_5$** (56.7 mg, 0.3 mmol, 3 equiv). To each vial was added **2a** (29.7 mg, 0.1 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (2.5 mg, 4.0 mol%), $Cu(OAc)_2·H_2O$ (59.9 mg, 0.3 mmol, 3.0 equiv), K_2CO_3 (41.4 mg, 0.3 mmol, 3.0 equiv) and DCE (1 mL). The reaction mixtures were stirred side-by-side at 120 °C on a heating mantle for 30 min. The reaction tubes were quenched by cooling in ice-water. The two mixtures were combined and were rapidly evaporated under reduced pressure separately. The purification was performed by flash column chromatography on silica gel (eluent: PE/EA = 5:1) to afford the product(s). The KIE value was determined to be k_H/k_D = 1.1:1 on the basis of ^{1}H NMR analysis.

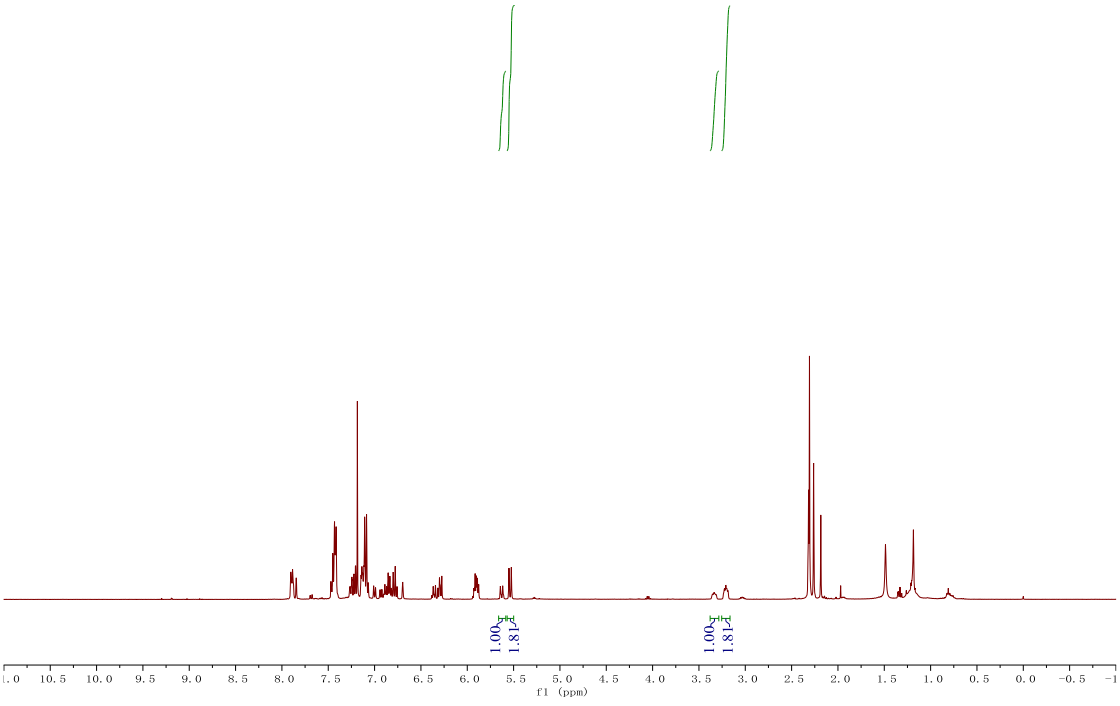


4.3 Competition experiment



1b/1i **2a** **3ba:3ia** = 1.8:1

A screw-cap vial (8 mL) was charged with **1b** (29.7 mg, 0.15 mmol, 1.5 equiv), **1i** (37.8 mg, 0.15 mmol, 1.5 equiv), **2a** (29.7 mg, 0.1 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (2.5 mg, 4.0 mol%), $Cu(OAc)_2·H_2O$ (59.9 mg, 0.3 mmol, 3.0 equiv), K_2CO_3 (41.4 mg, 0.3 mmol, 3.0 equiv) and DCE (1 mL). The reaction mixture in the vial was stirred at 120 ℃ on a heating mantle for 12 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using (petroleum ether/ethyl acetate 5:1) to afford product **3ba** and **3ia**. The ratio of **3ba**:**3ia** = 1.8:1 was determined on the basis of ^1H NMR analysis.



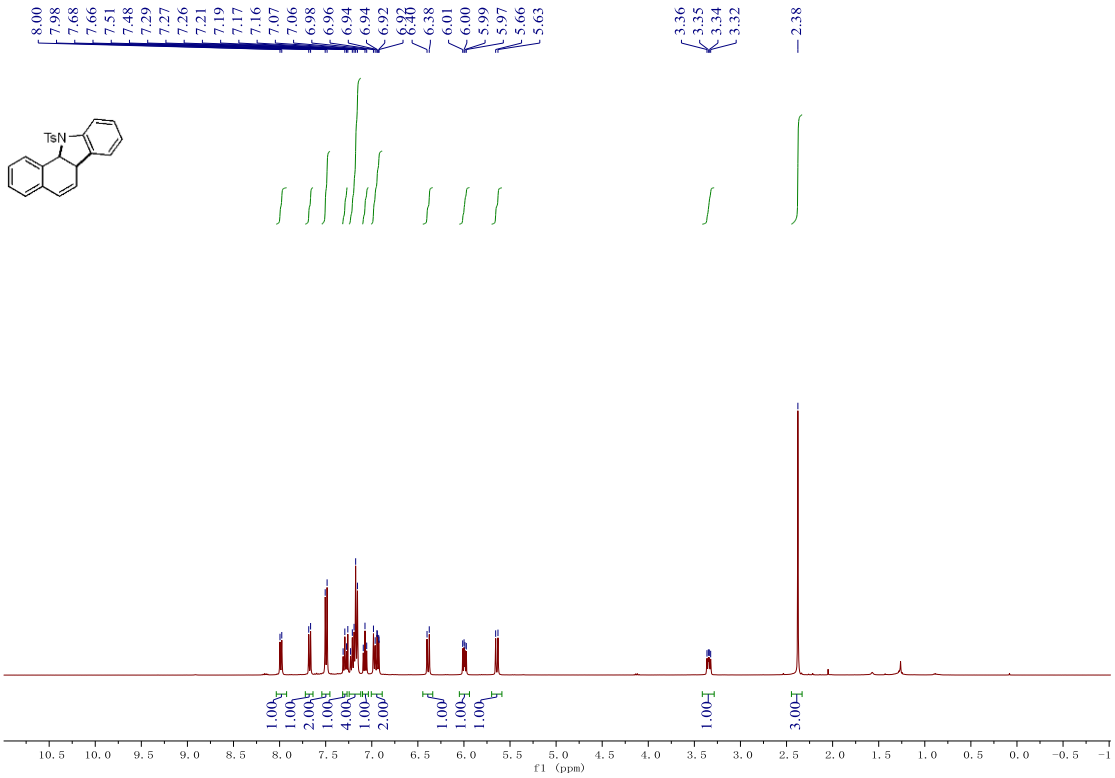
5. References

[1] (a) G. Kaupp. *Chem. Ber.* 1970, 2288−2301. (b) M. Lautens, K. Fagnou and V. Zunic. *Org. Lett.* 2002, **4**, 3465−3468.

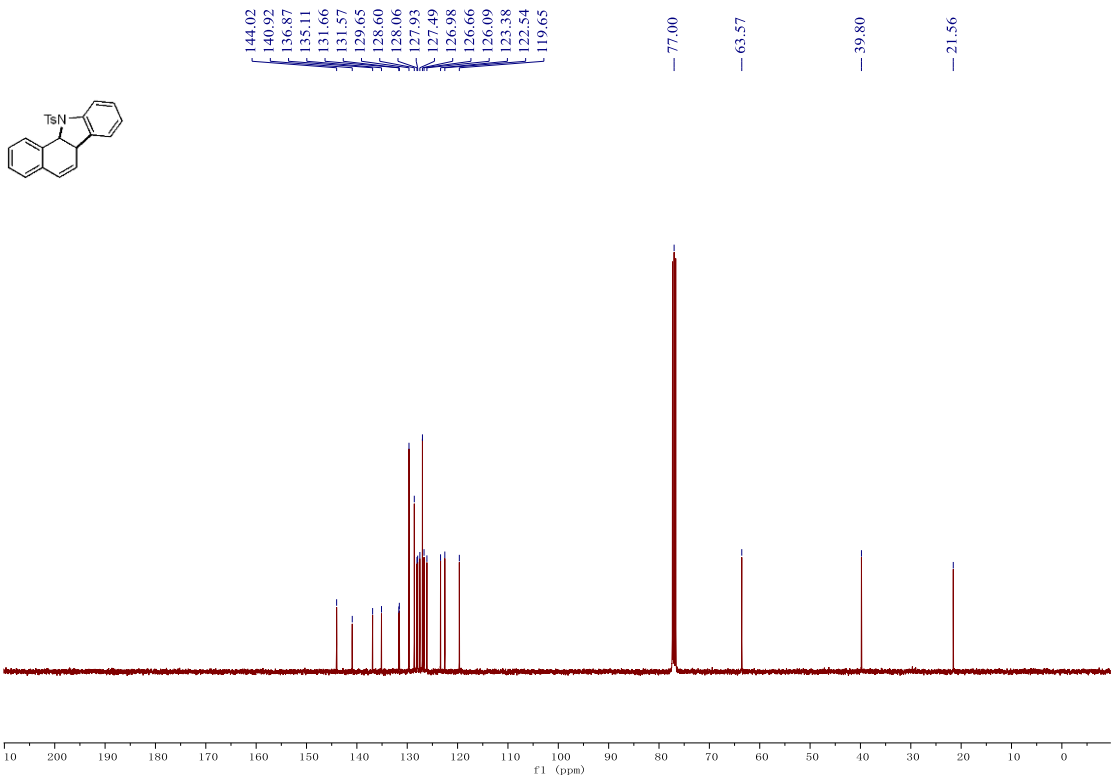
[2] (a) D. M. Hodgson, P. Willis and M. W. Bebbington, P. *Org. Lett.* 2002, **4**, 4353−4356. (b) M. Lautens and C. Dockendorff. *Org. Lett.* 2003, **5**, 3695−3698.

[3] D. M. Hodgson, M. W. Bebbington and P. Willis. *Org. Biomol. Chem.* 2003, **1**, 3787−3798.

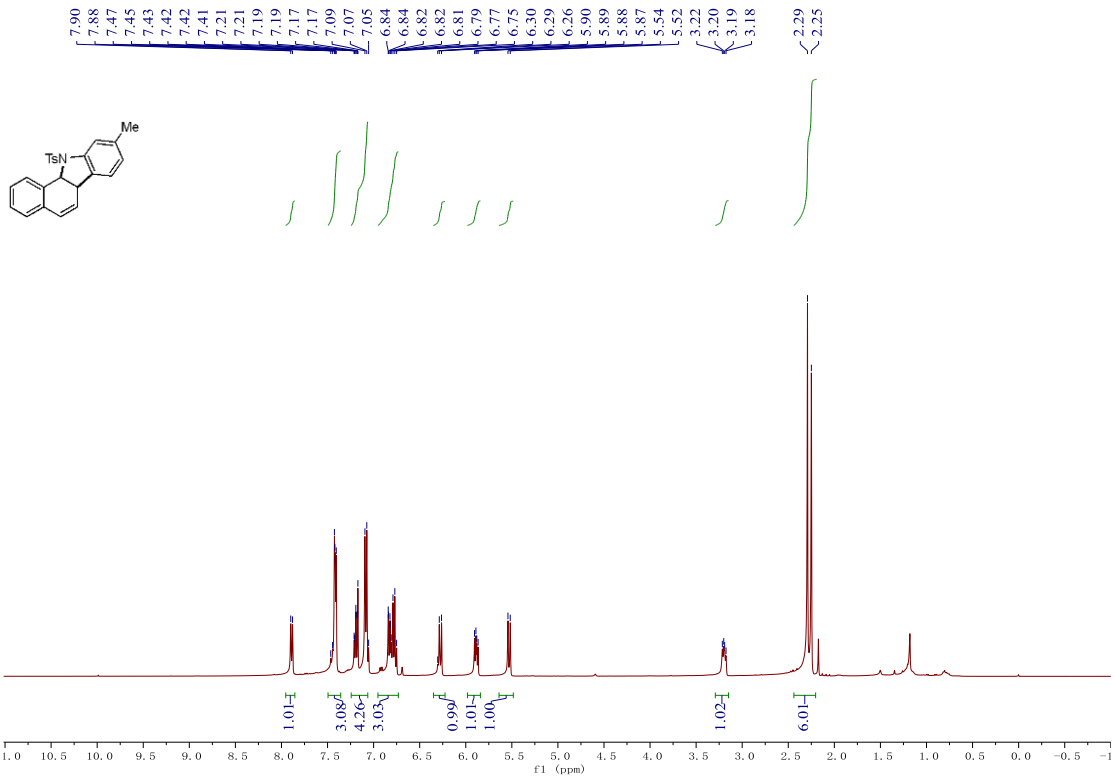
6. NMR Spectra



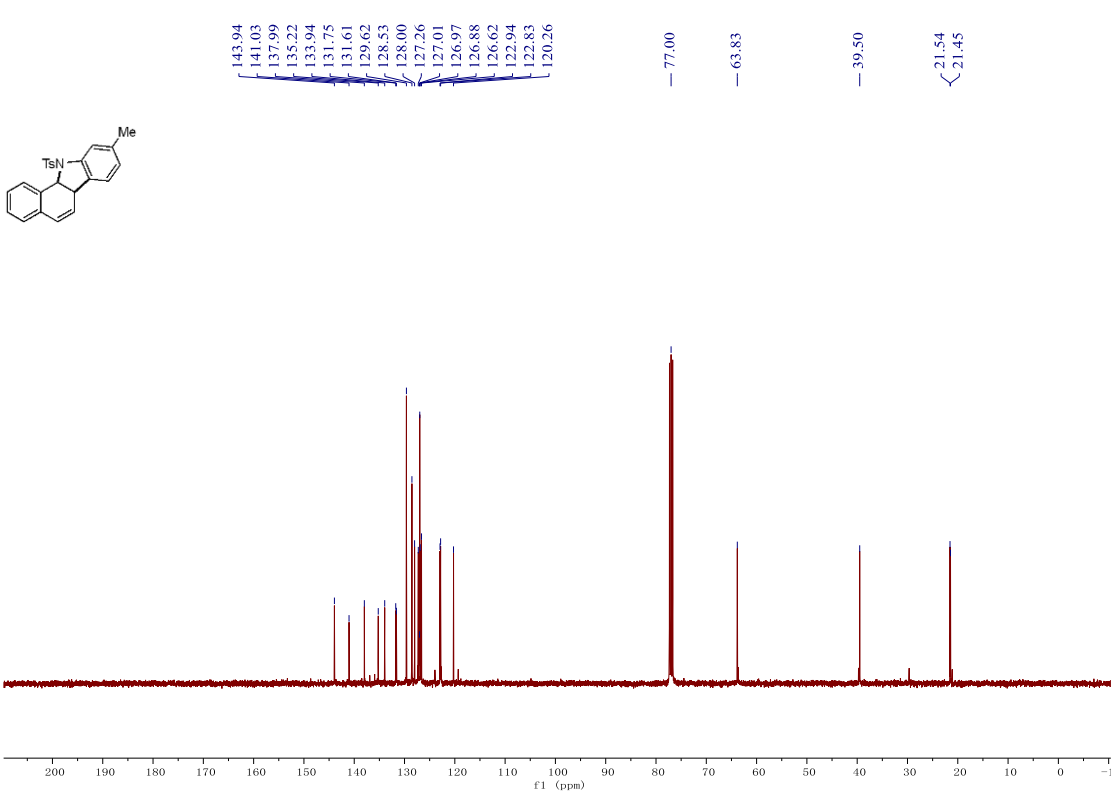
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3aa.



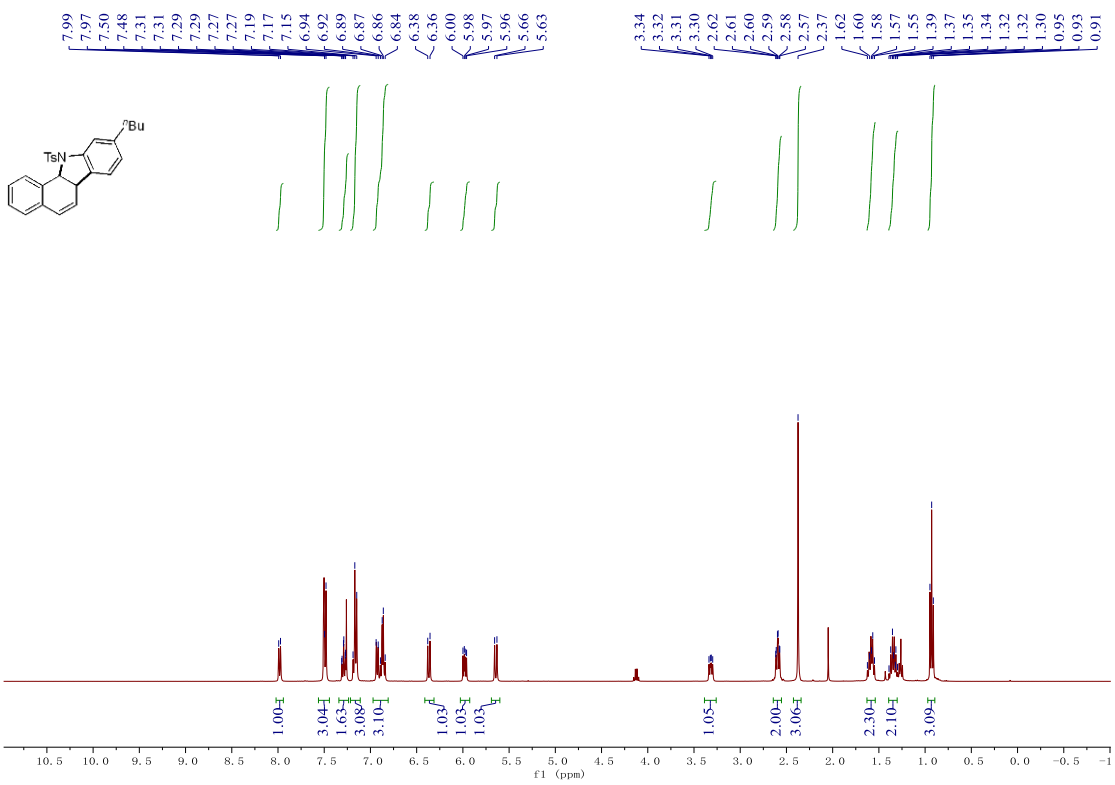
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3aa.



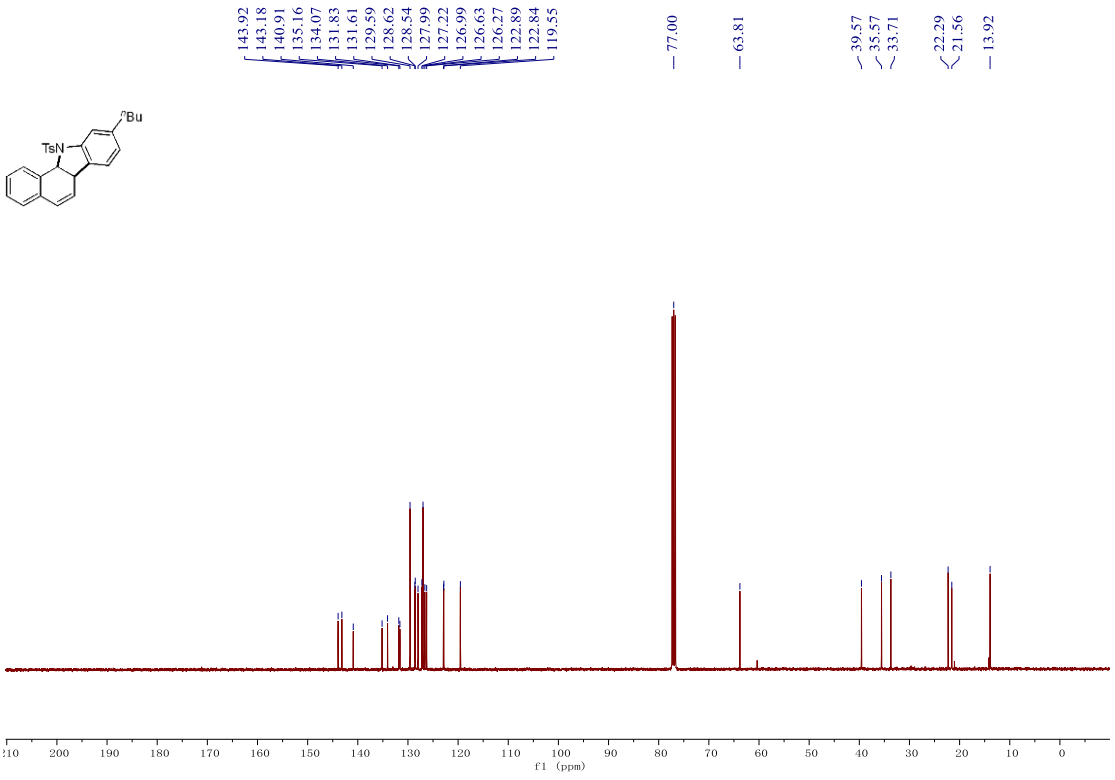
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ba.



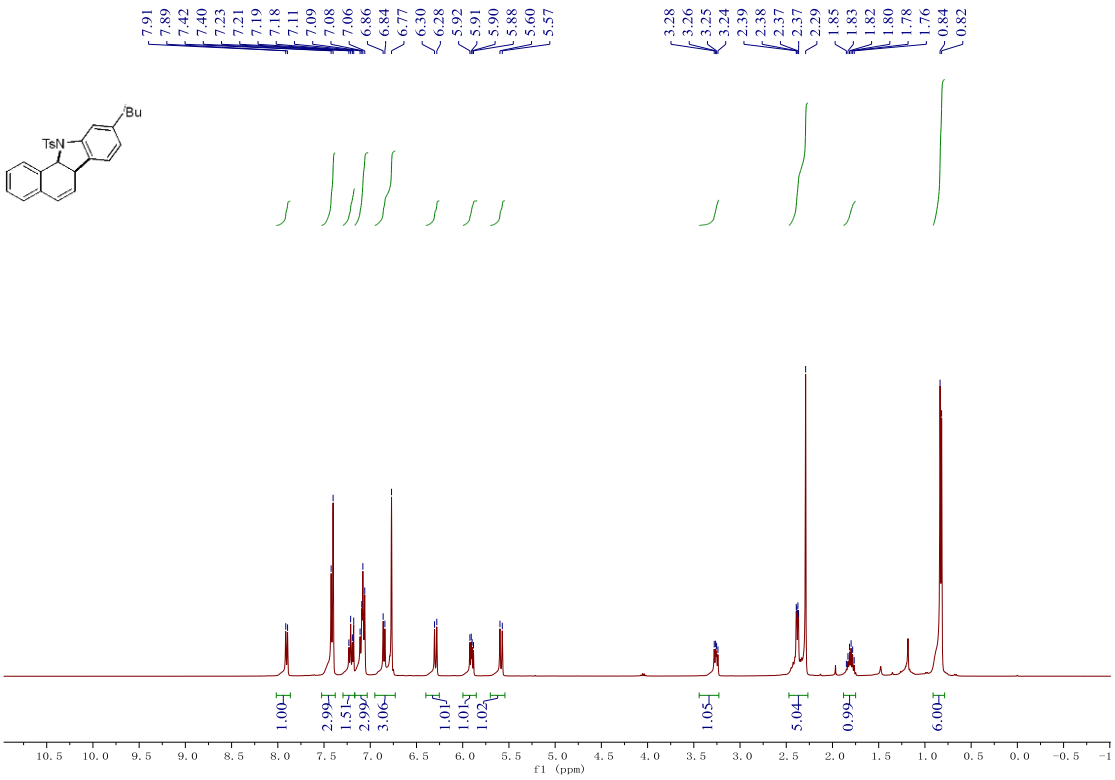
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3ba.



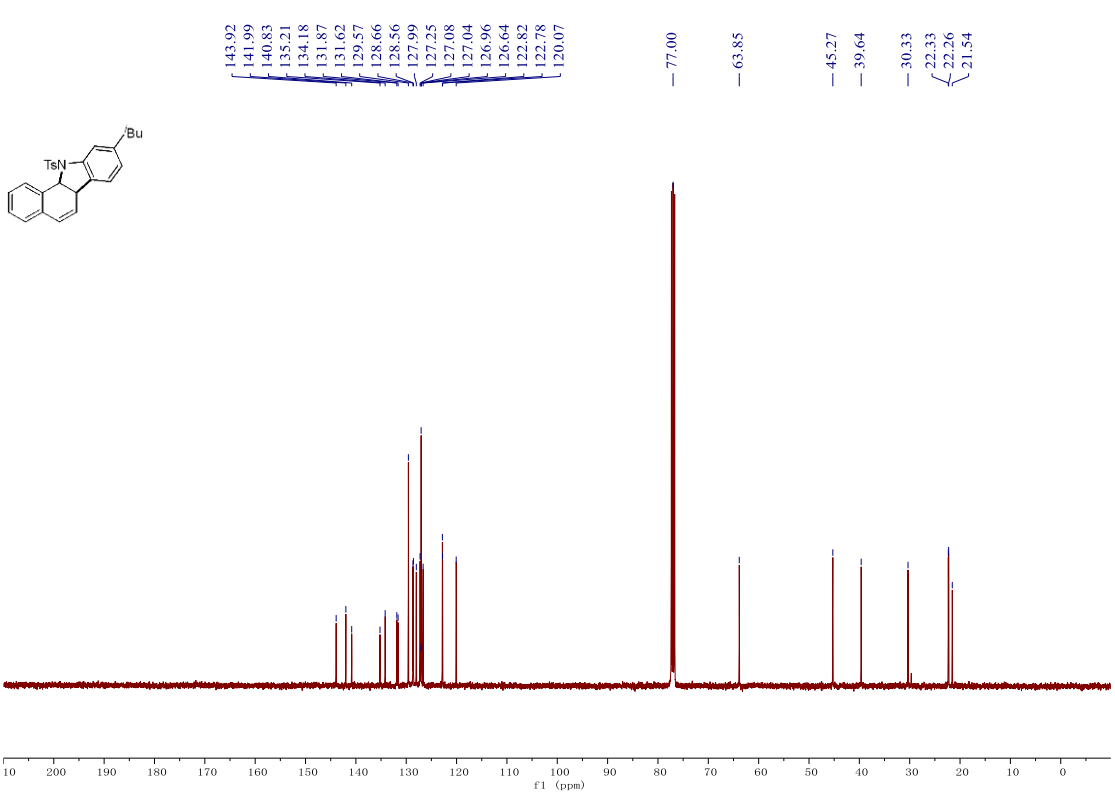
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ca.



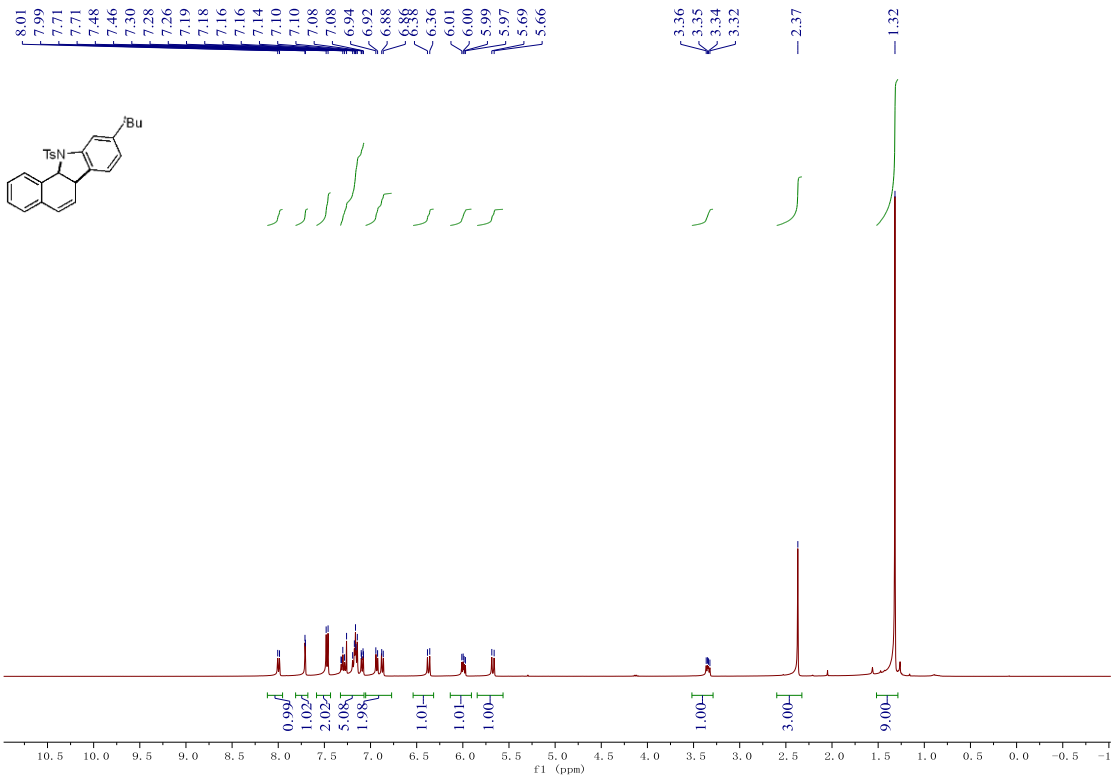
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3ca.



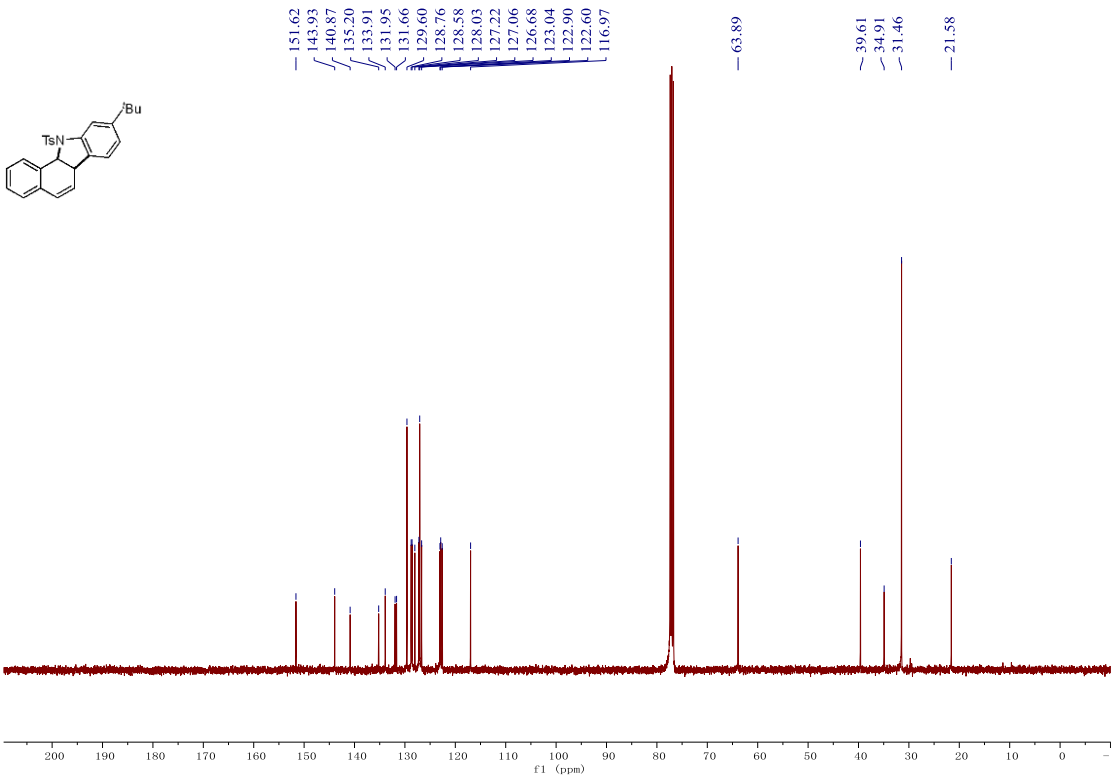
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3da.



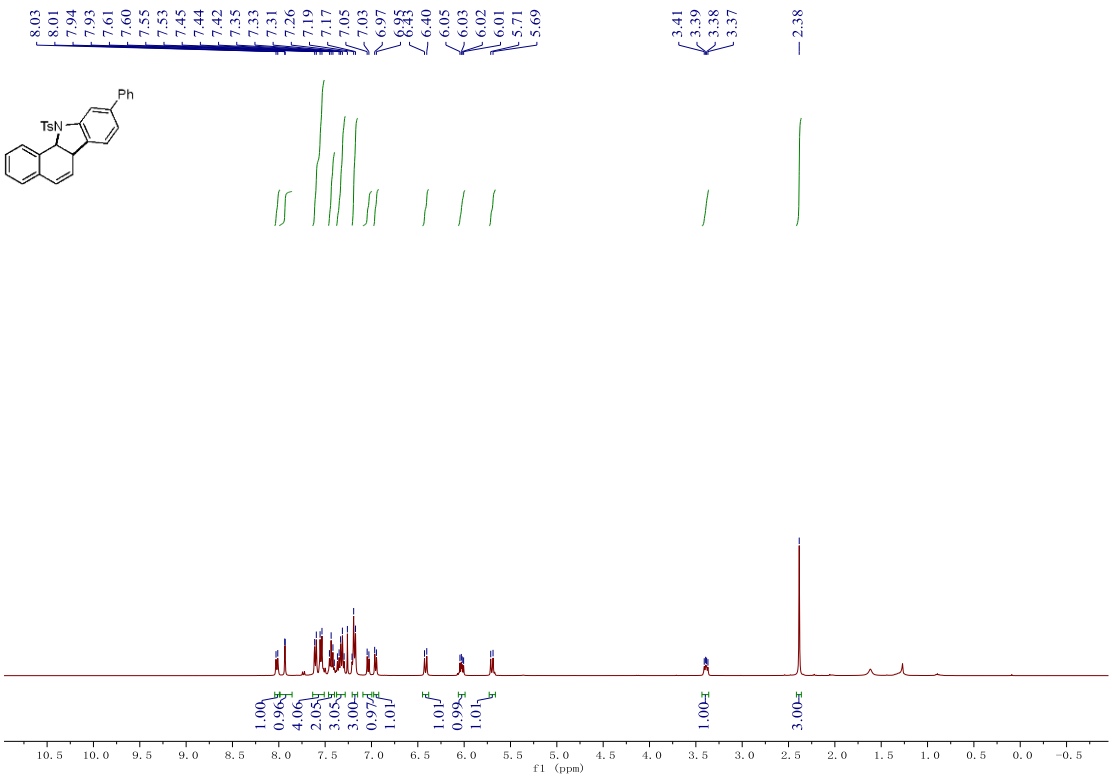
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3da.



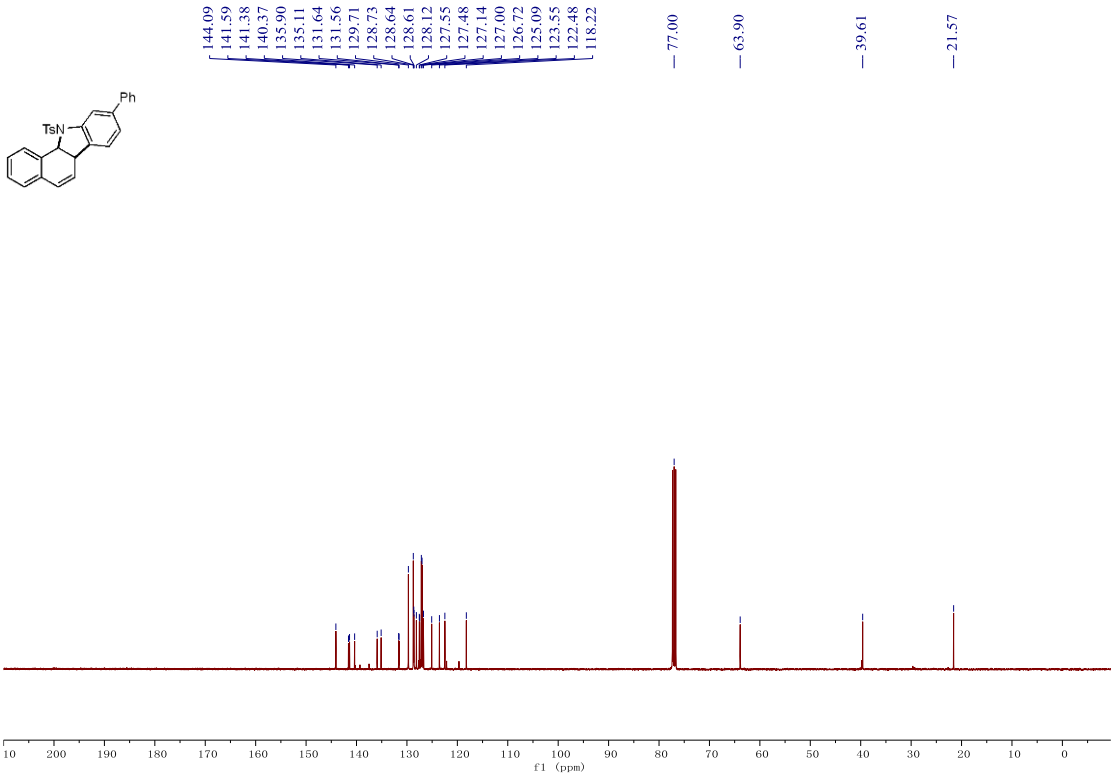
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ea.



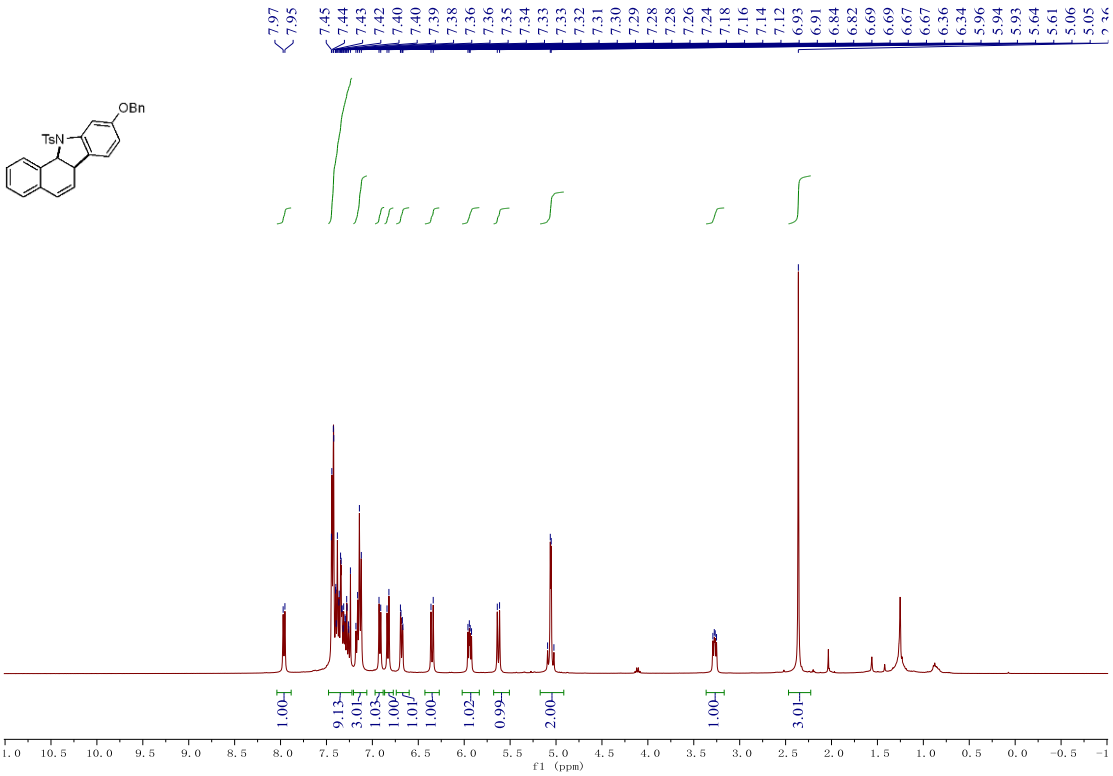
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3ea.



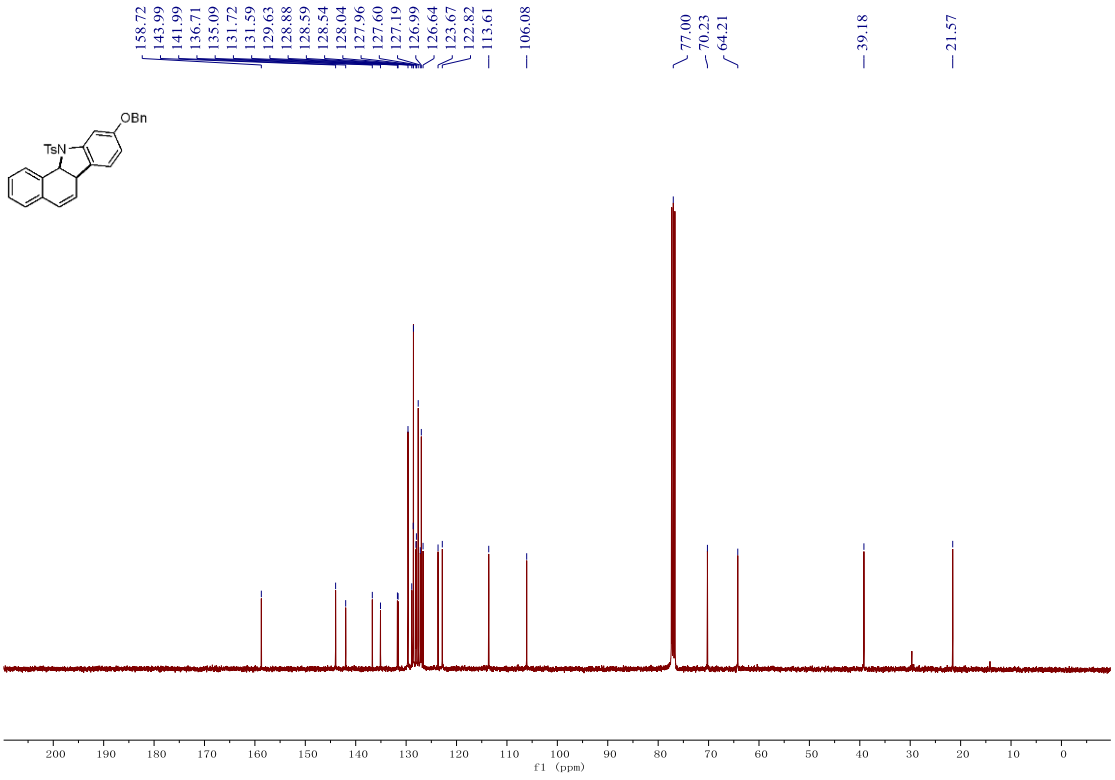
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3fa.



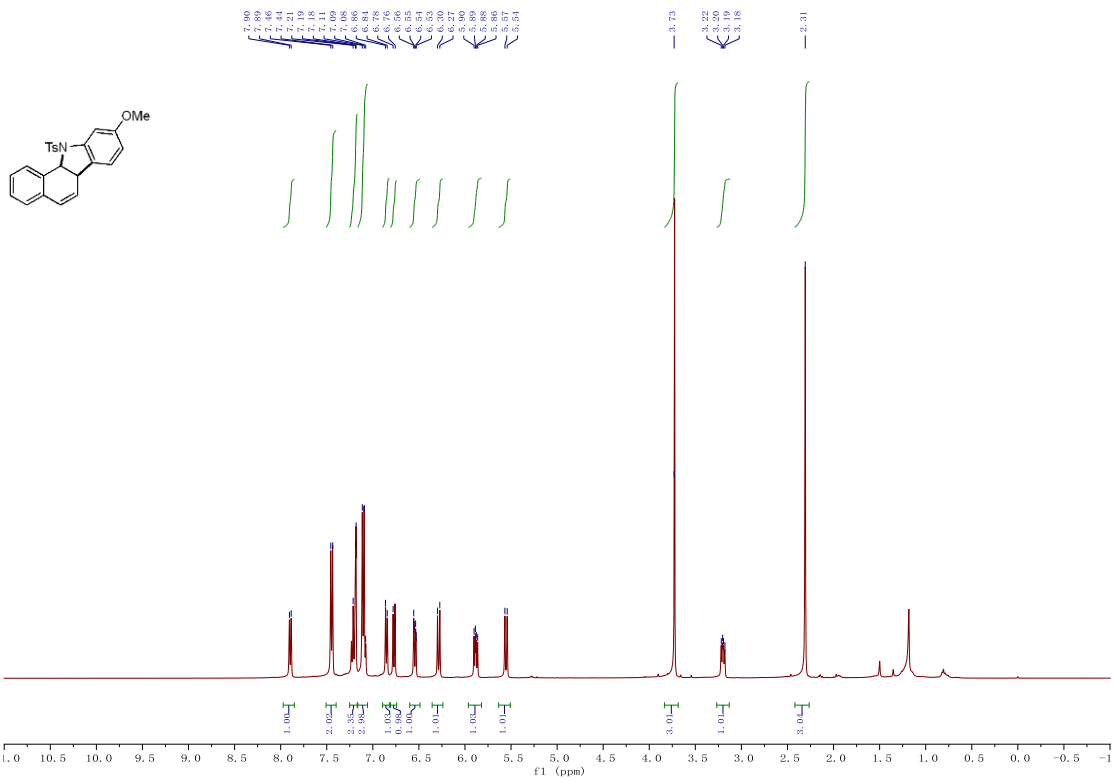
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3fa.



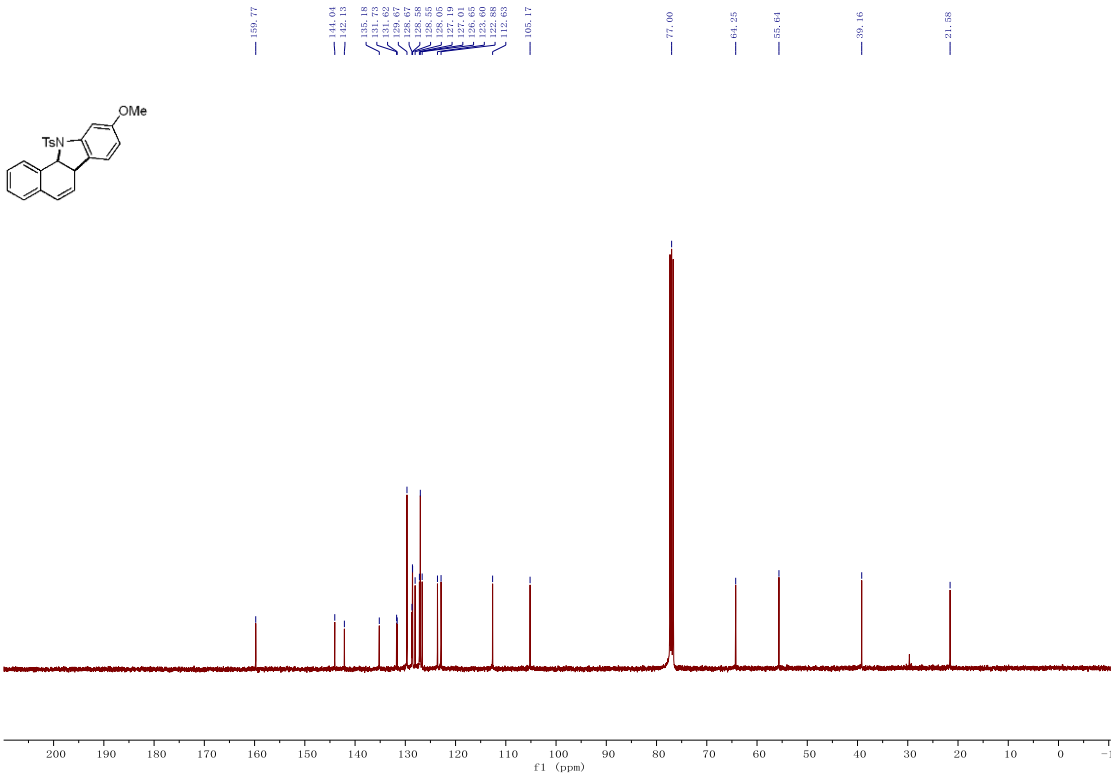
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ga.



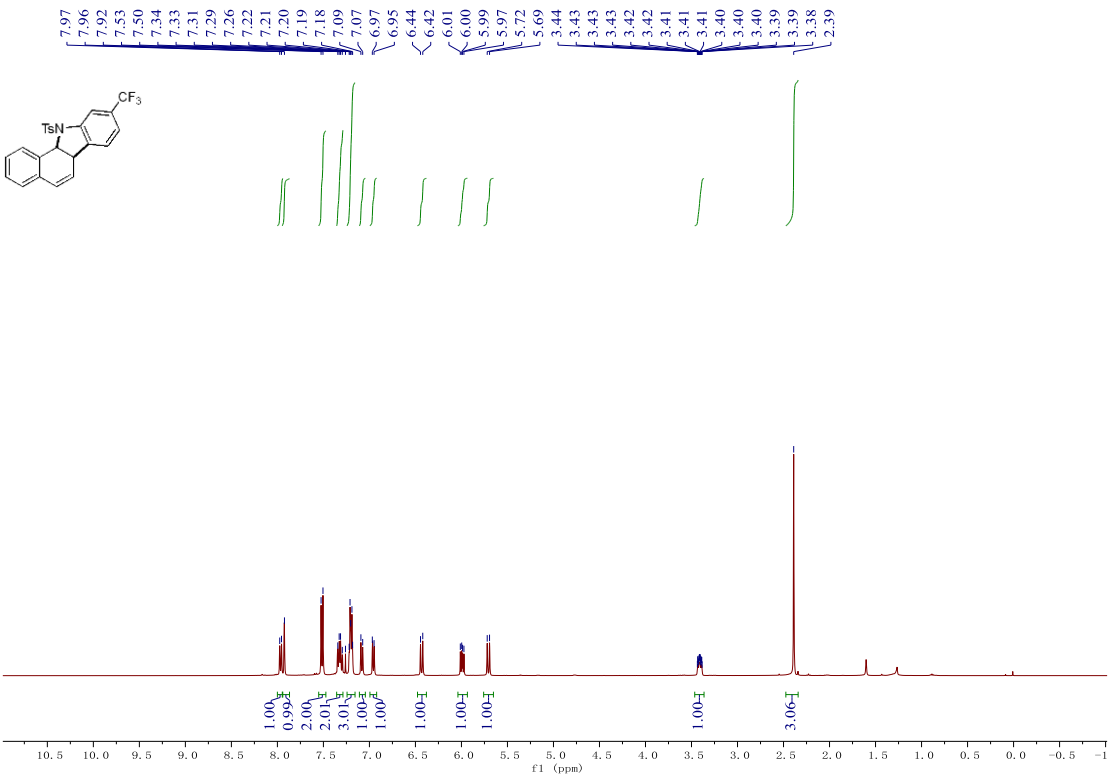
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3ga.



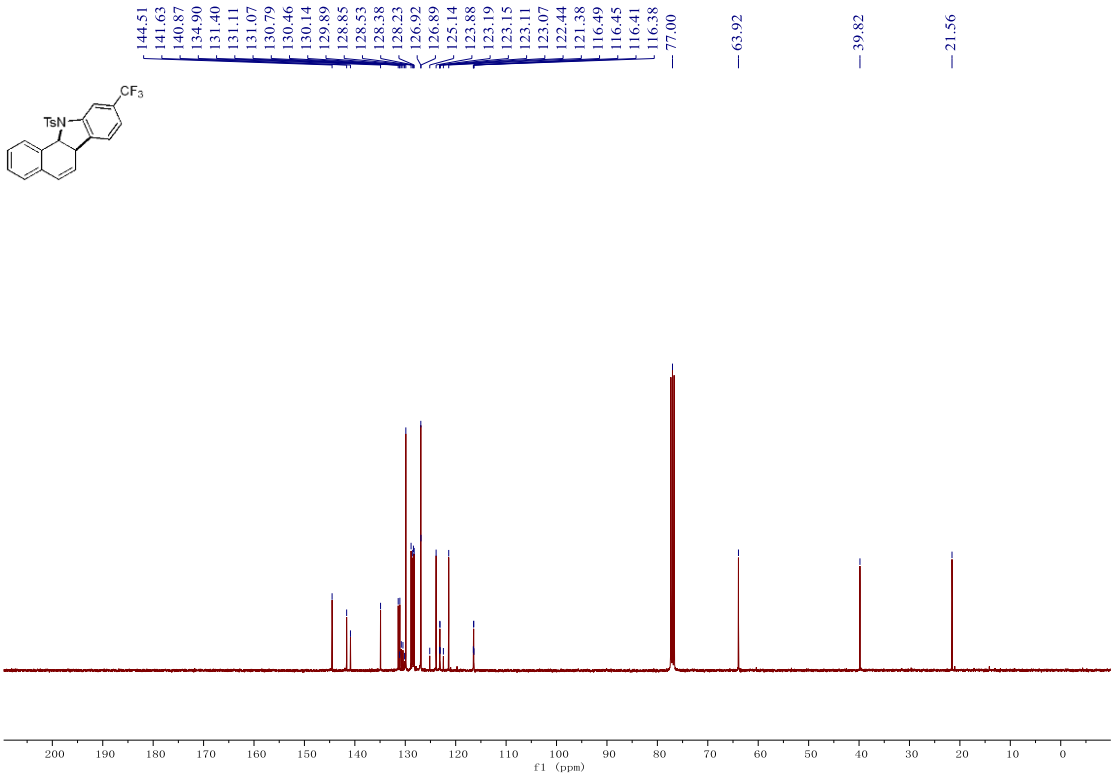
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ha.



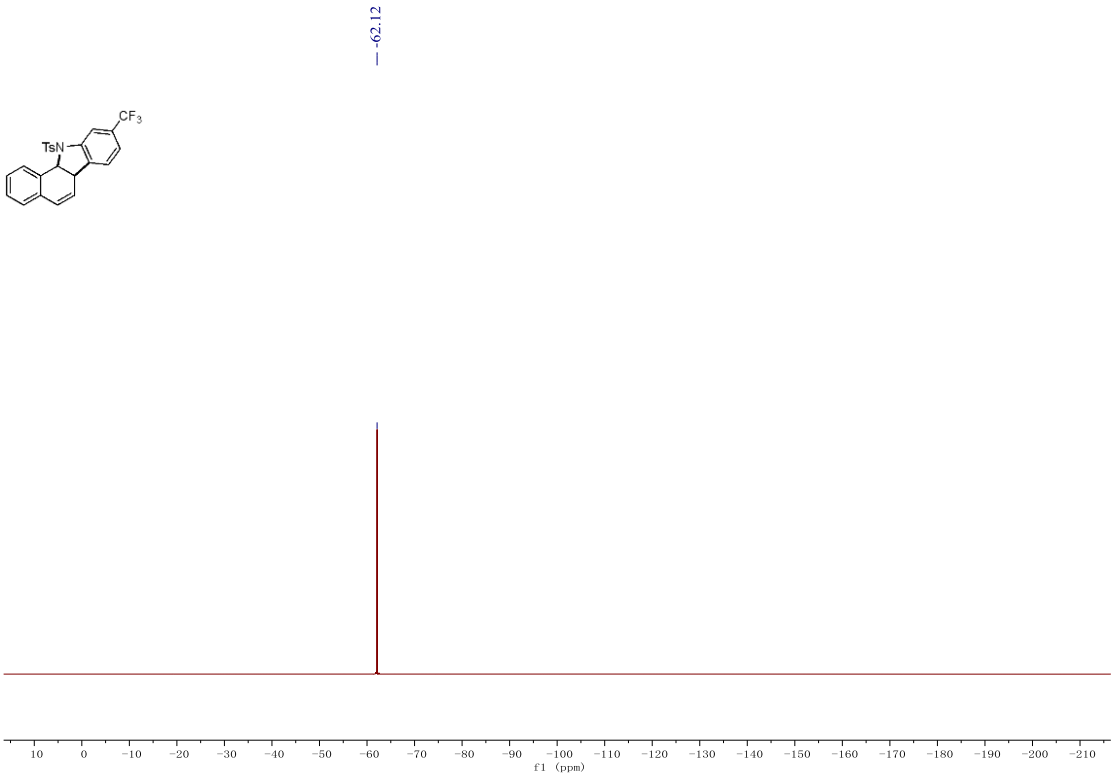
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3ha.



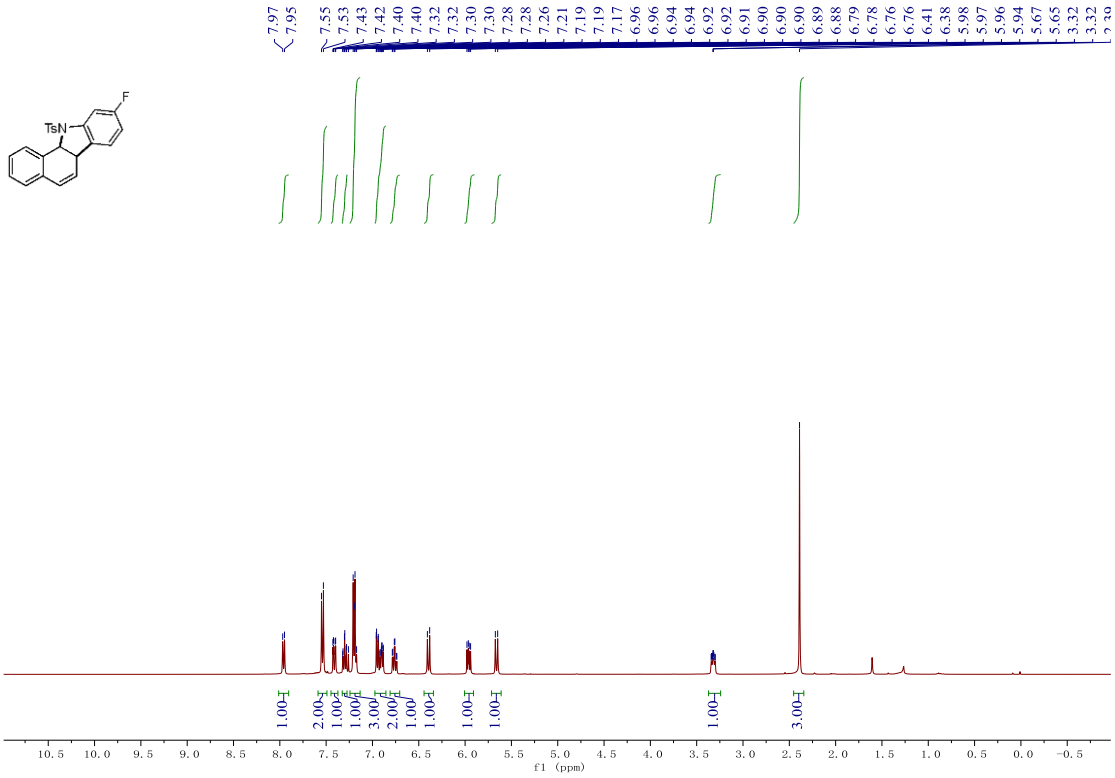
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ia.



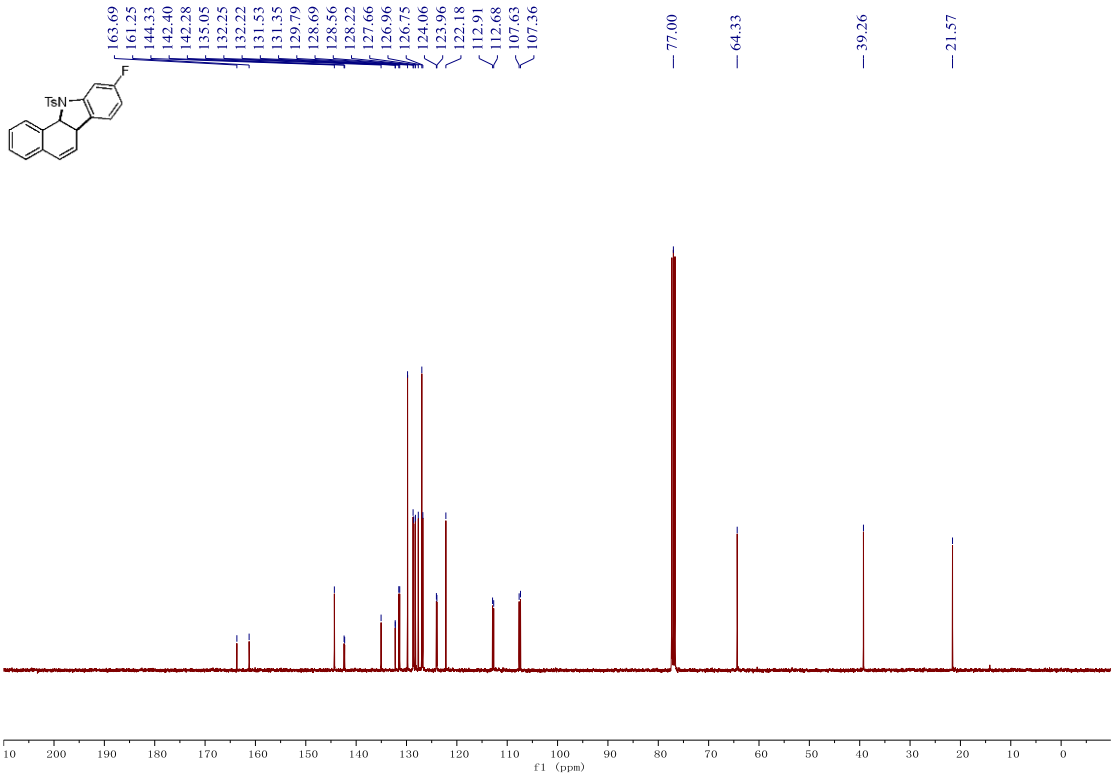
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3ia.



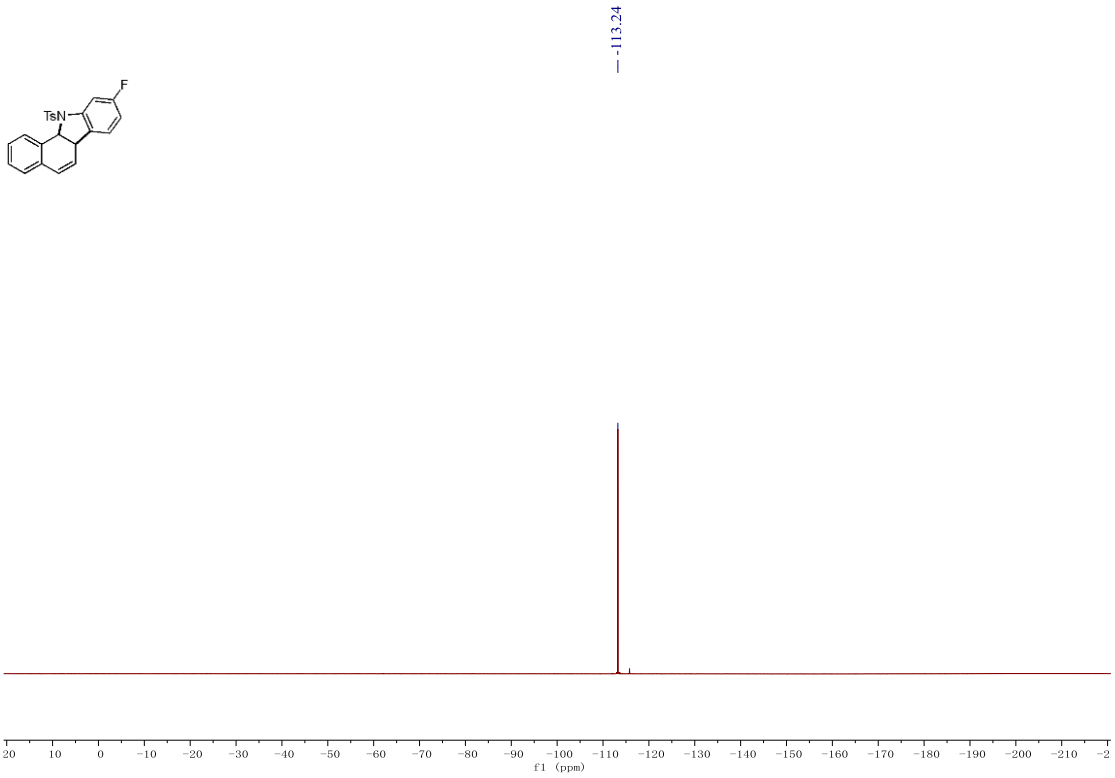
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 3ia.



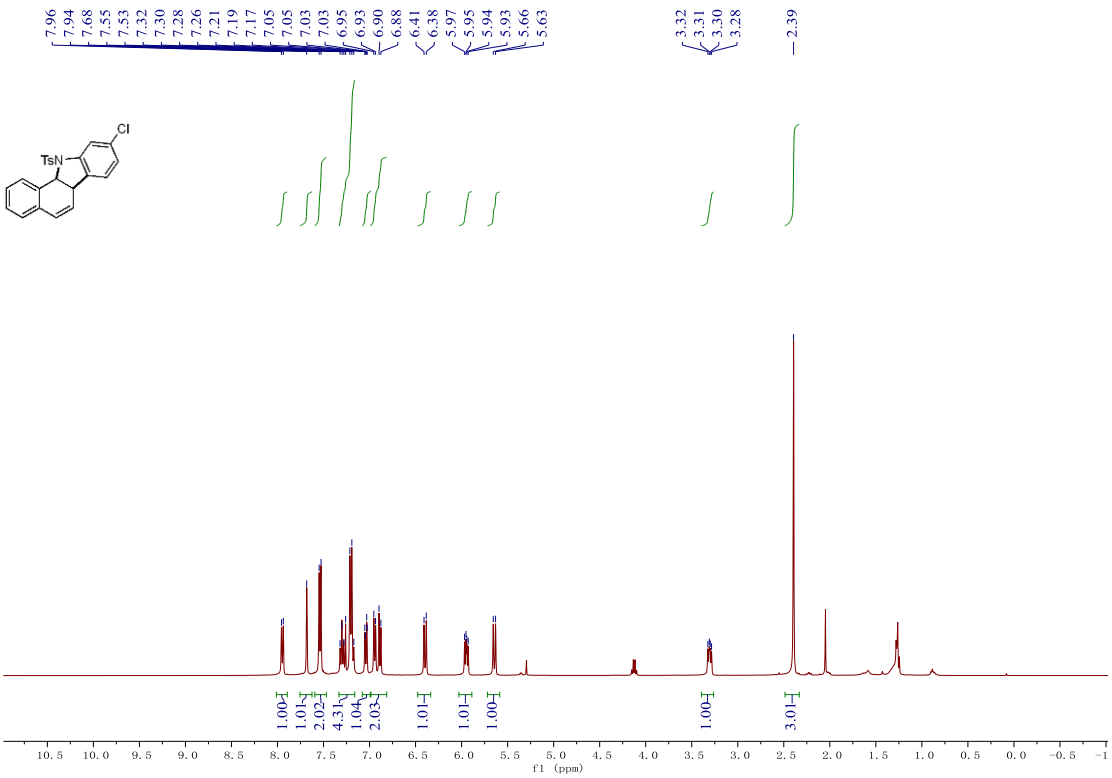
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ja.



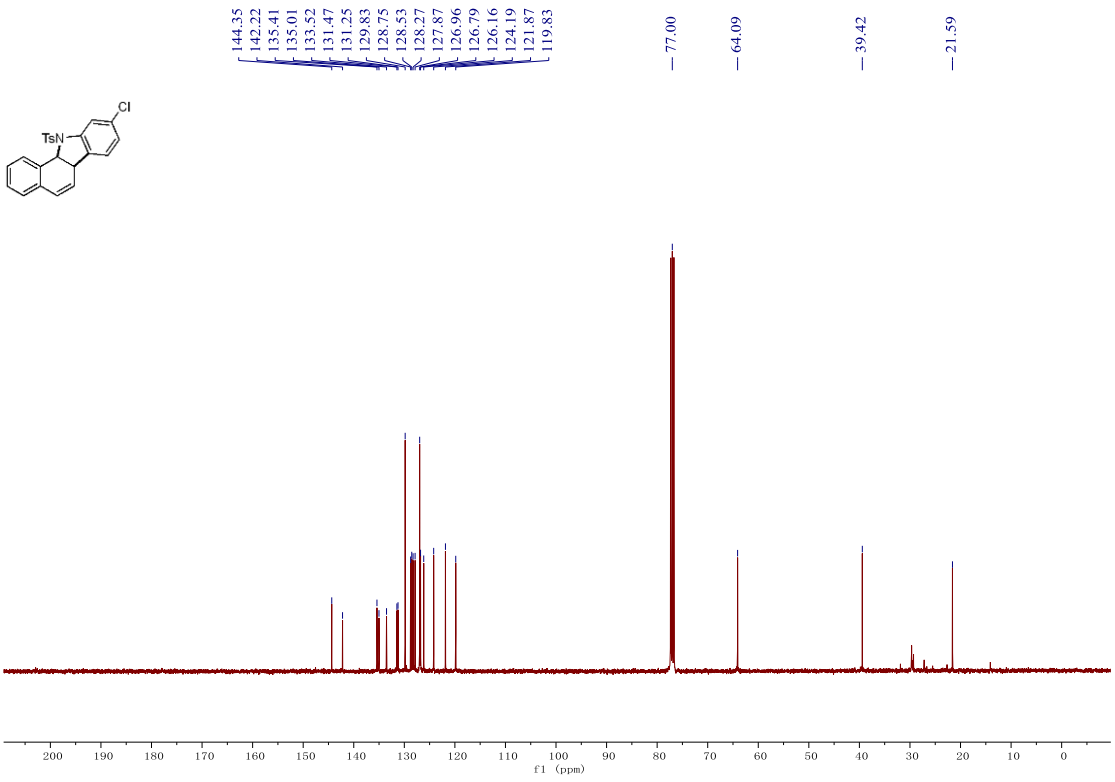
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3ja.



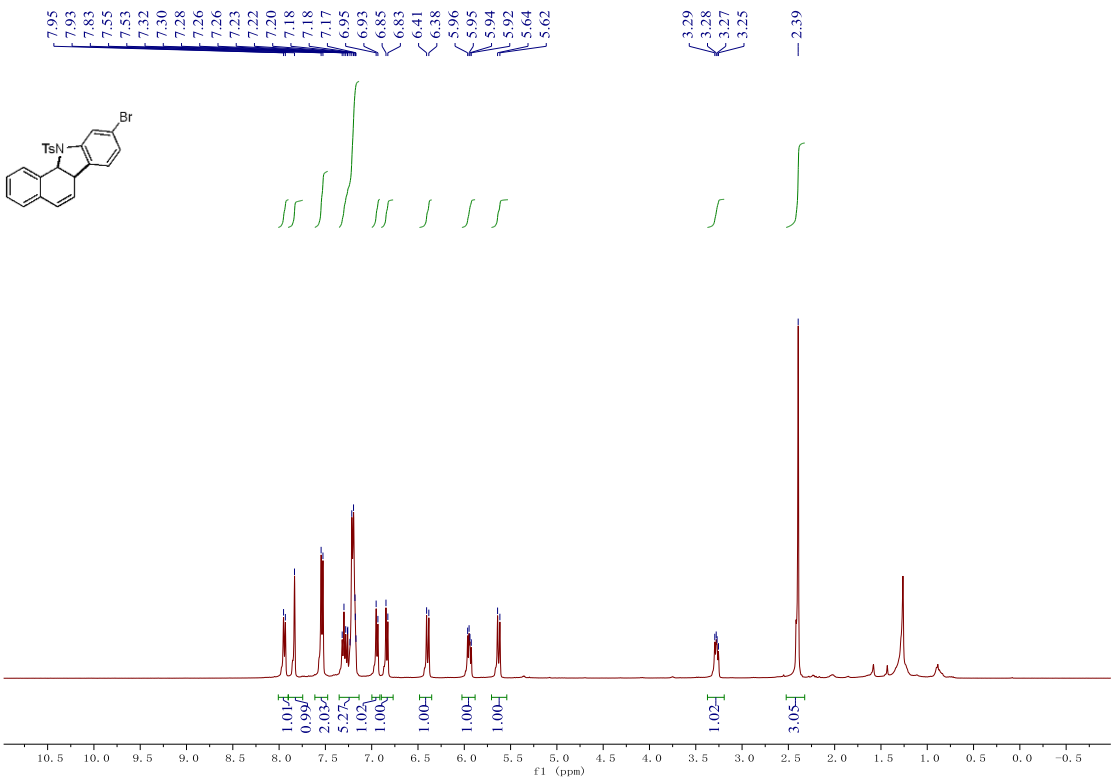
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3ja.



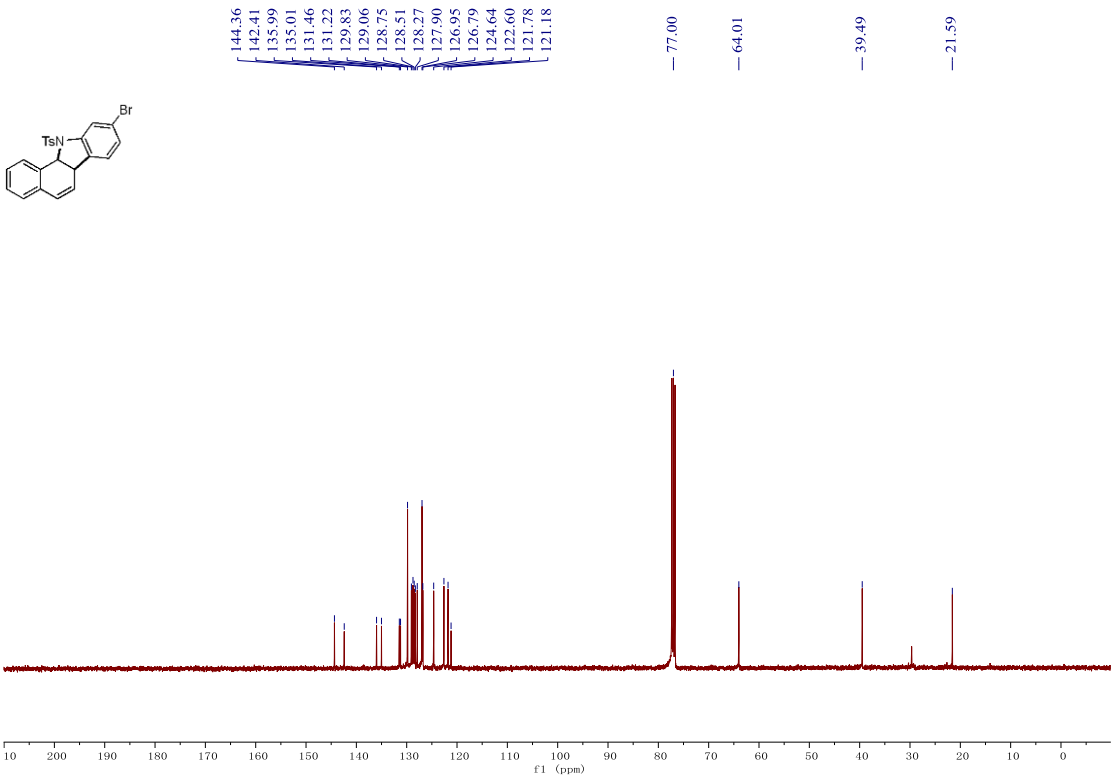
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ka.



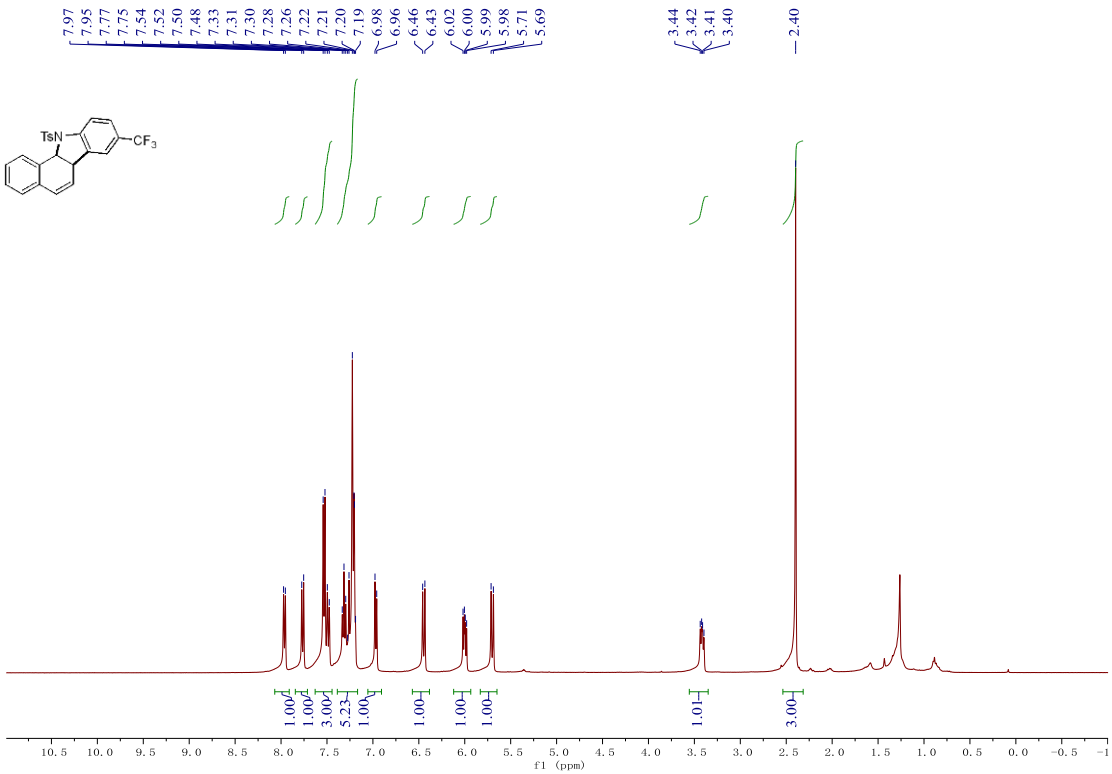
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3ka.



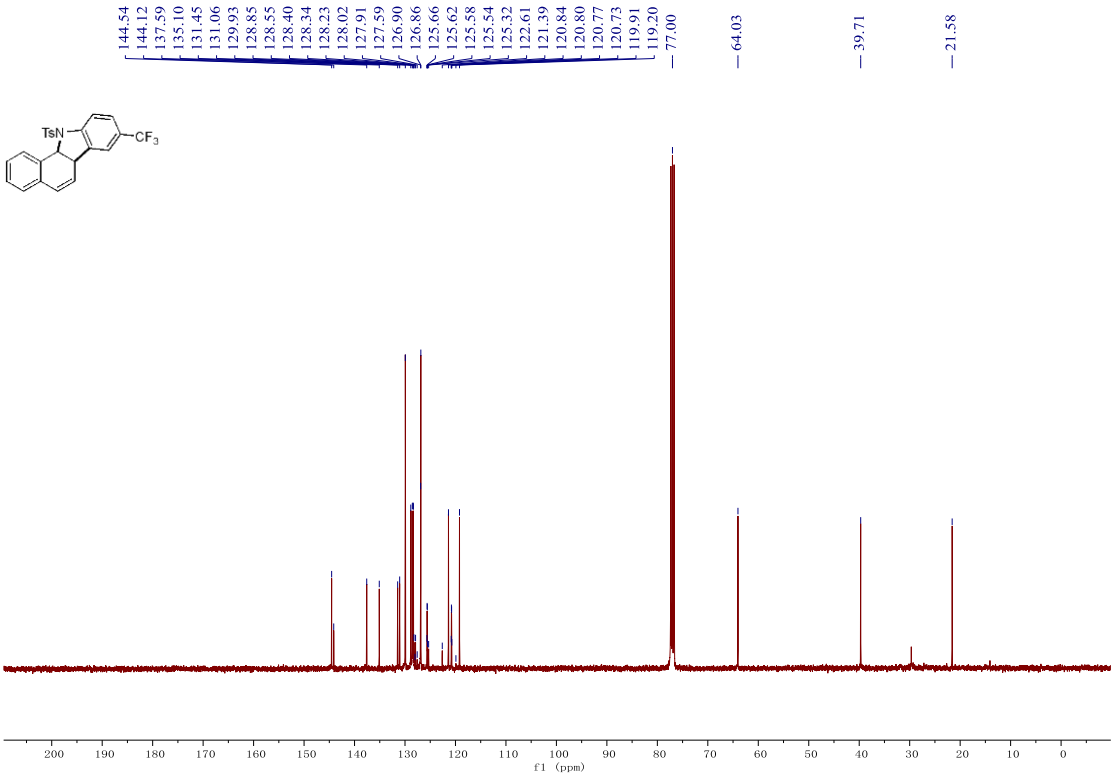
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3la.



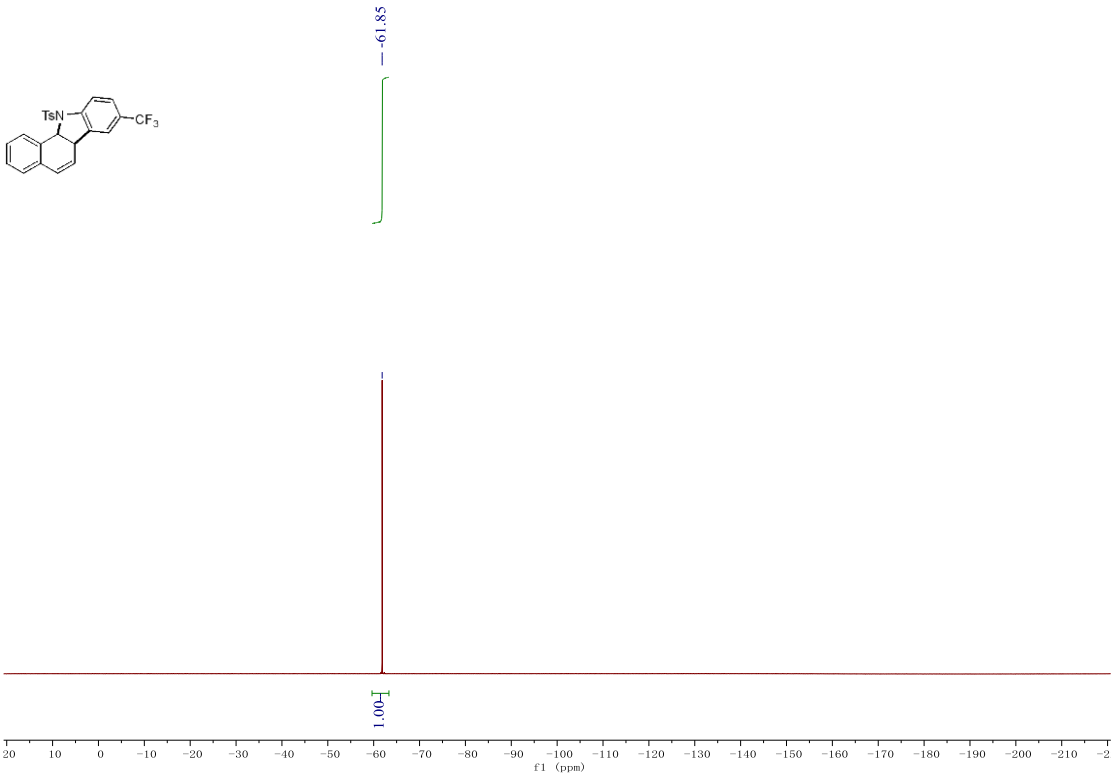
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3la.



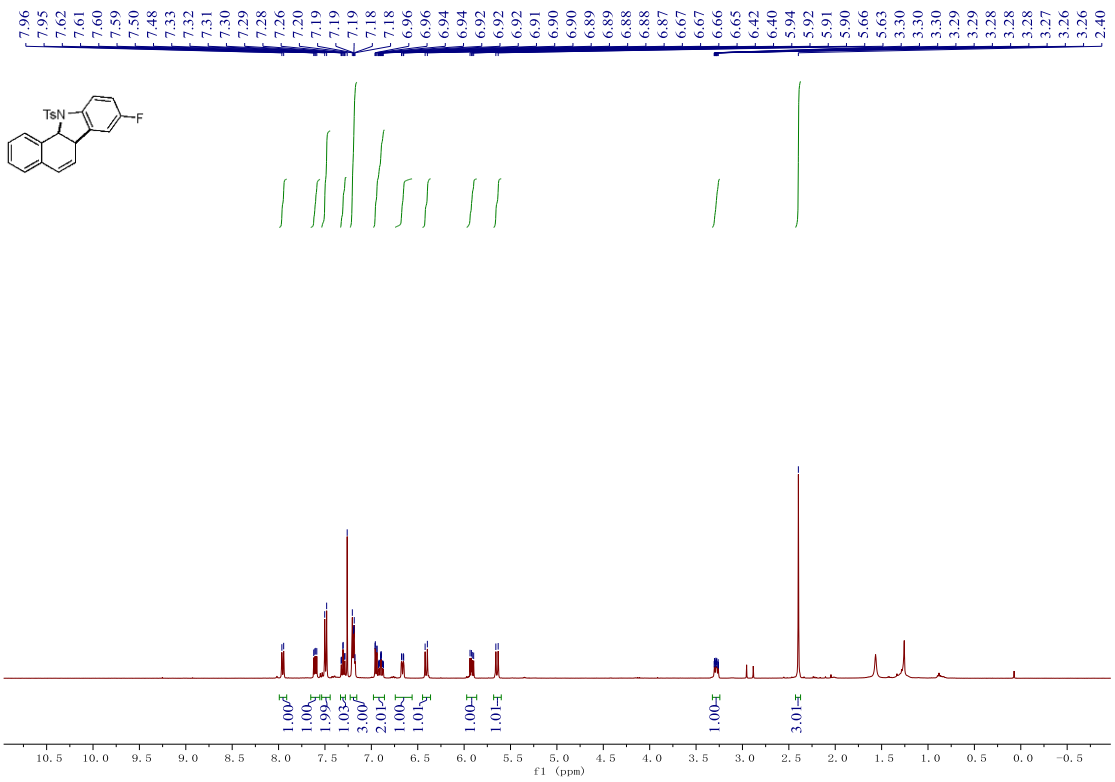
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ma.



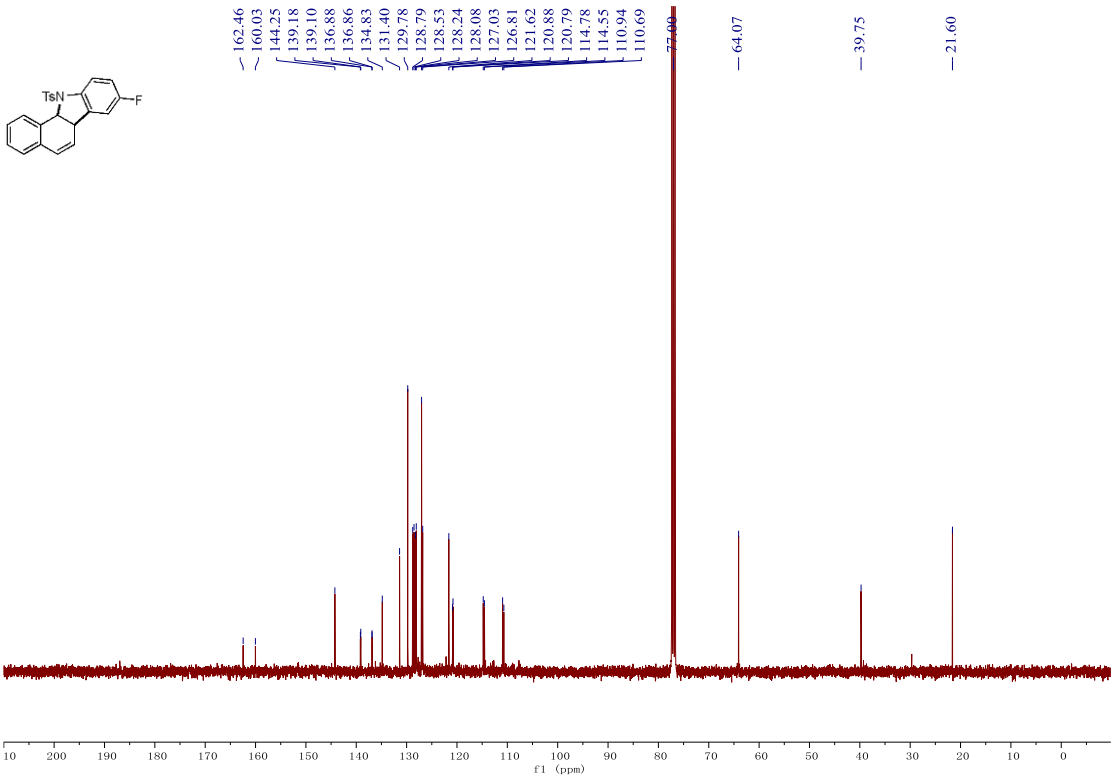
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3ma.



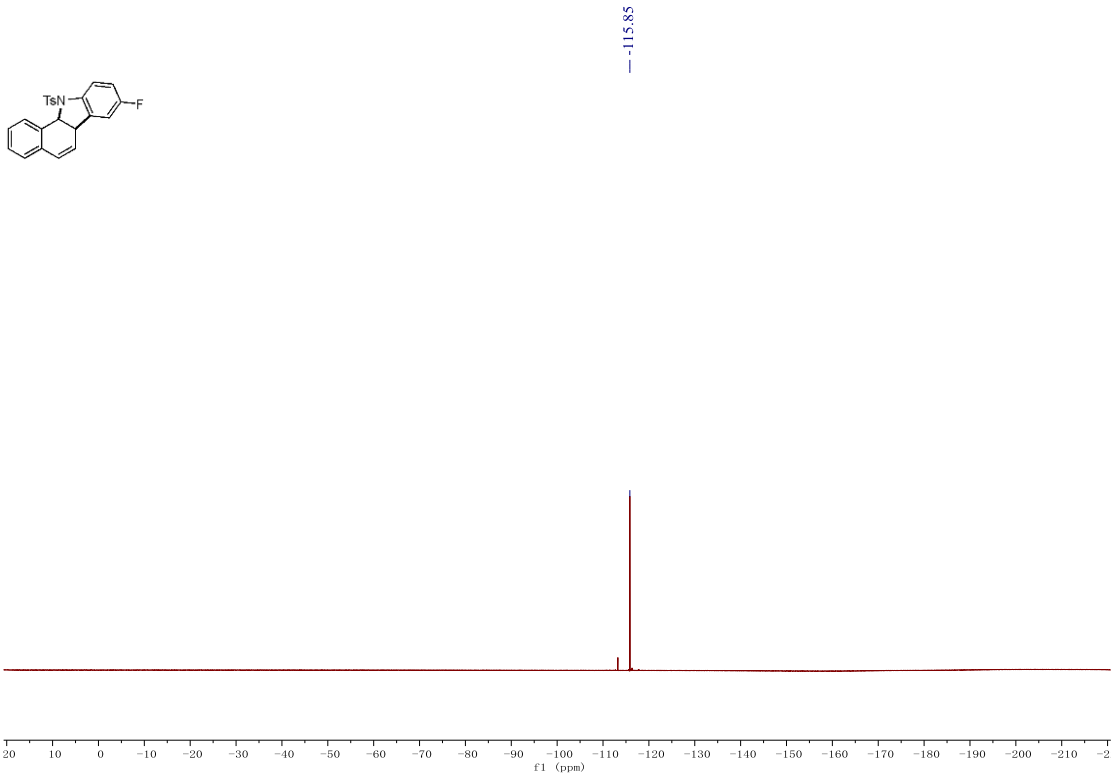
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3ma.



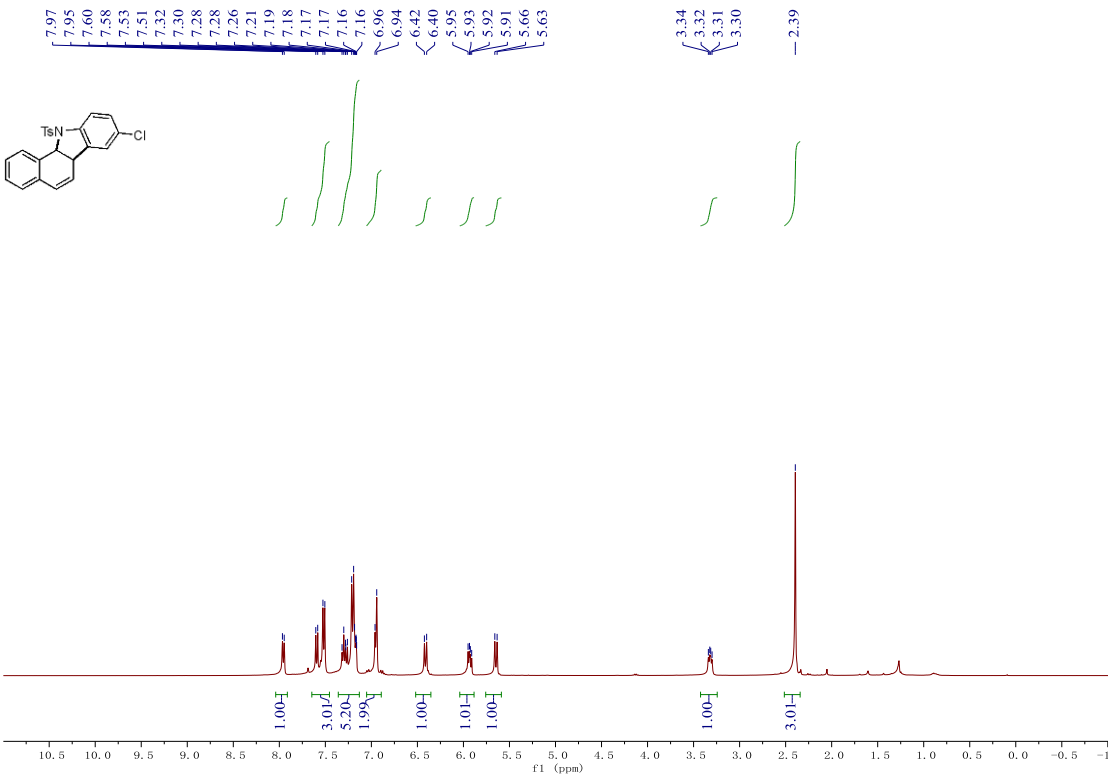
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3na.



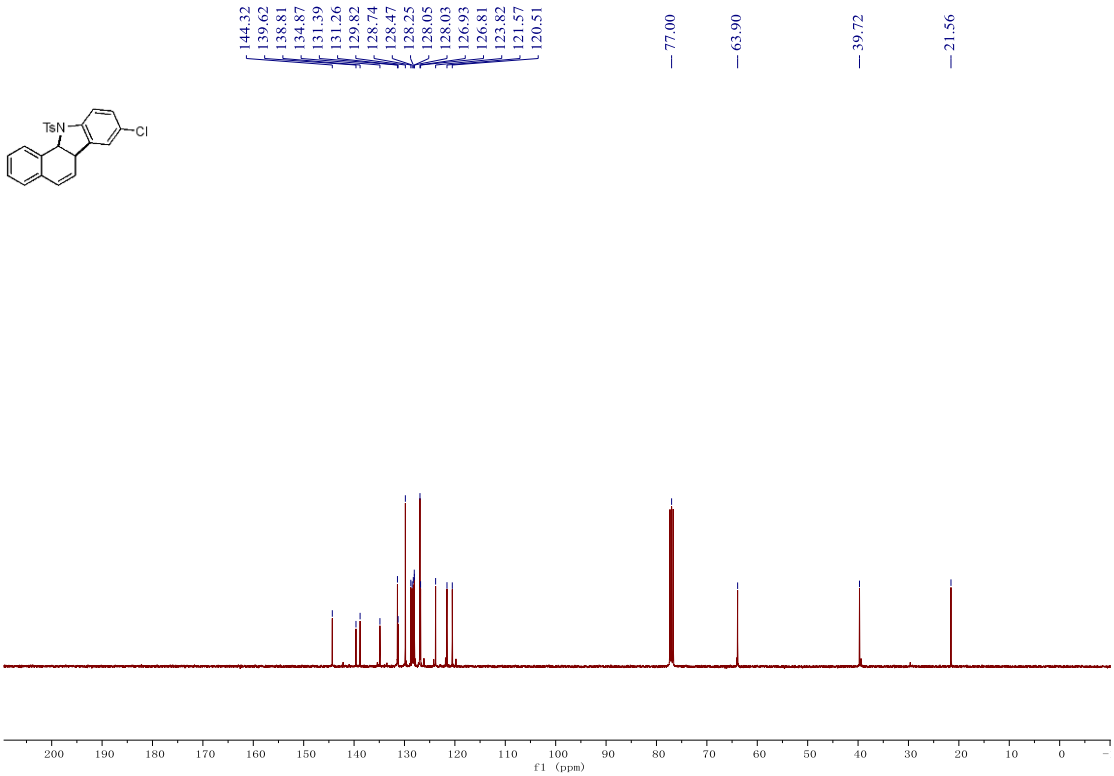
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3na.



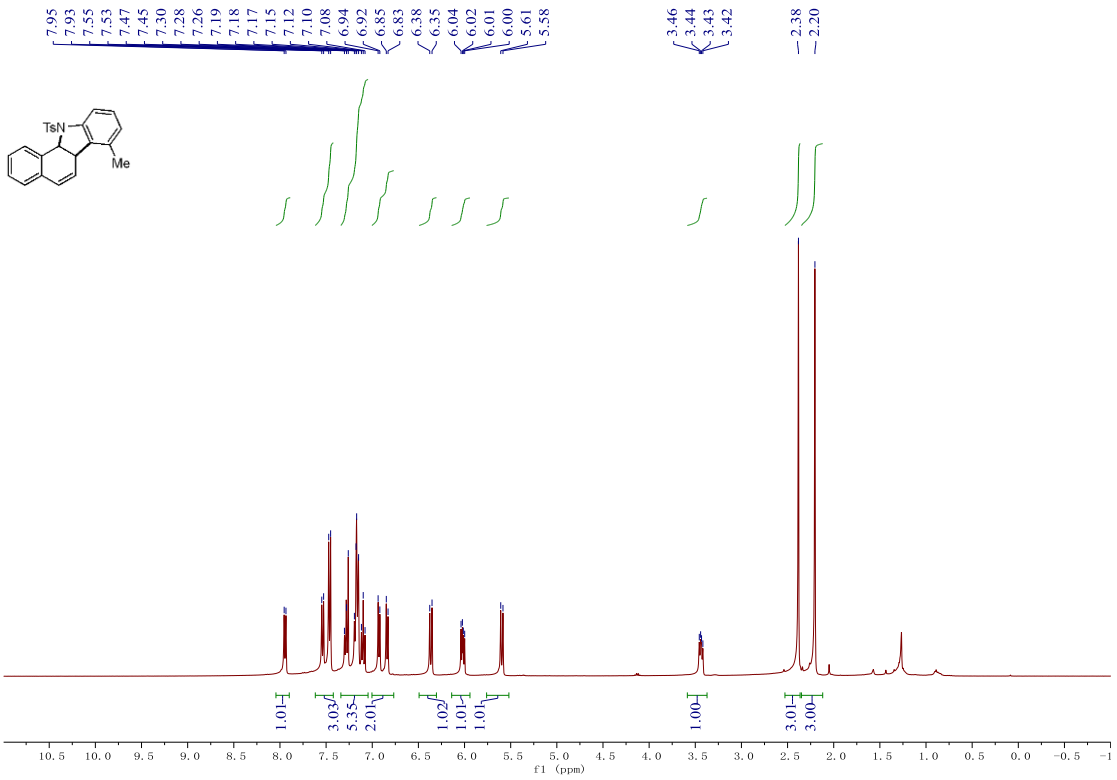
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3na.



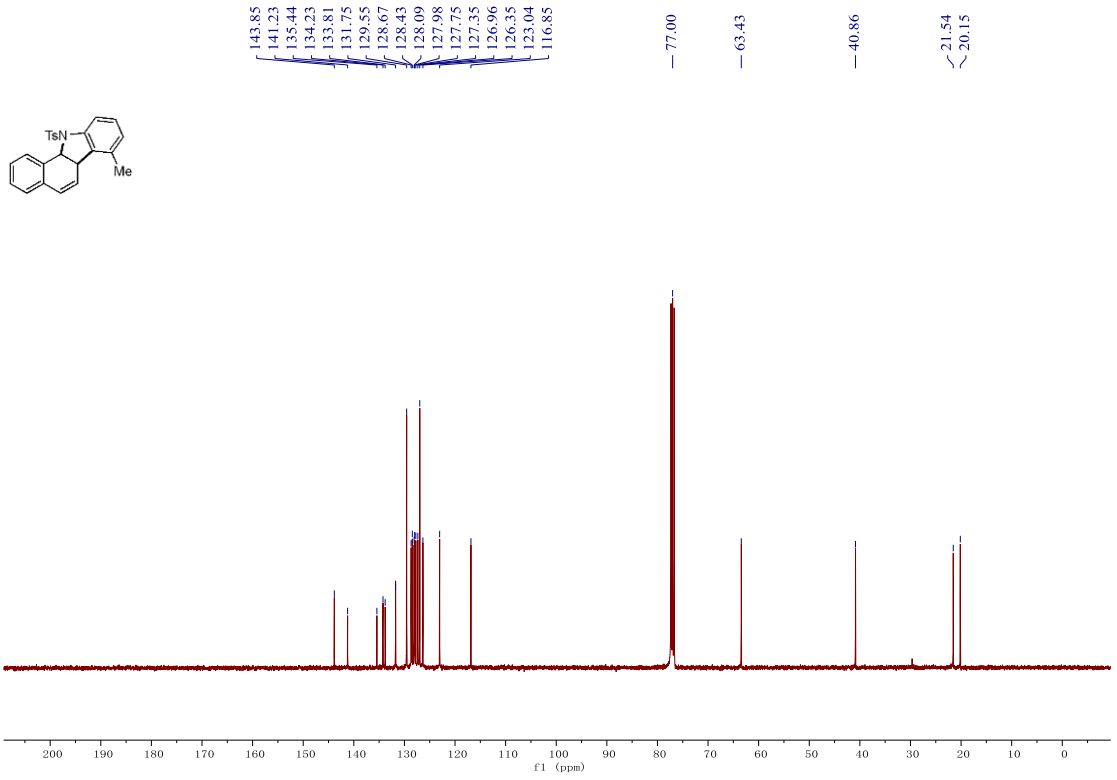
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3oa.



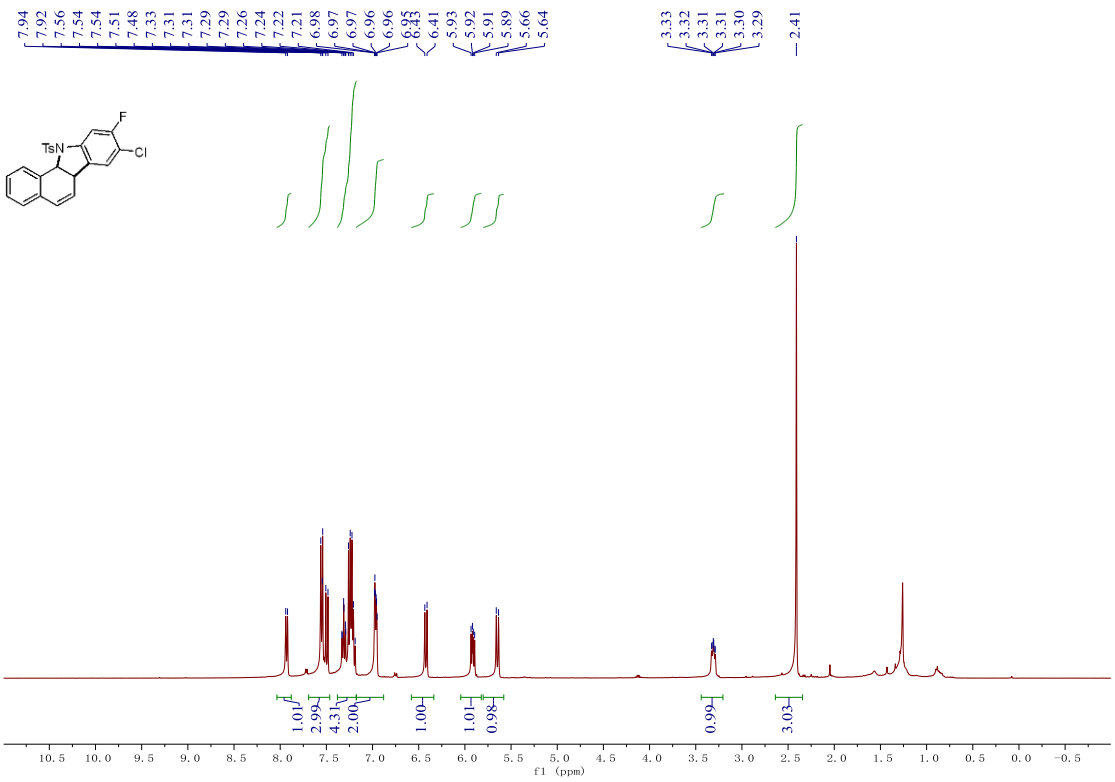
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3oa.



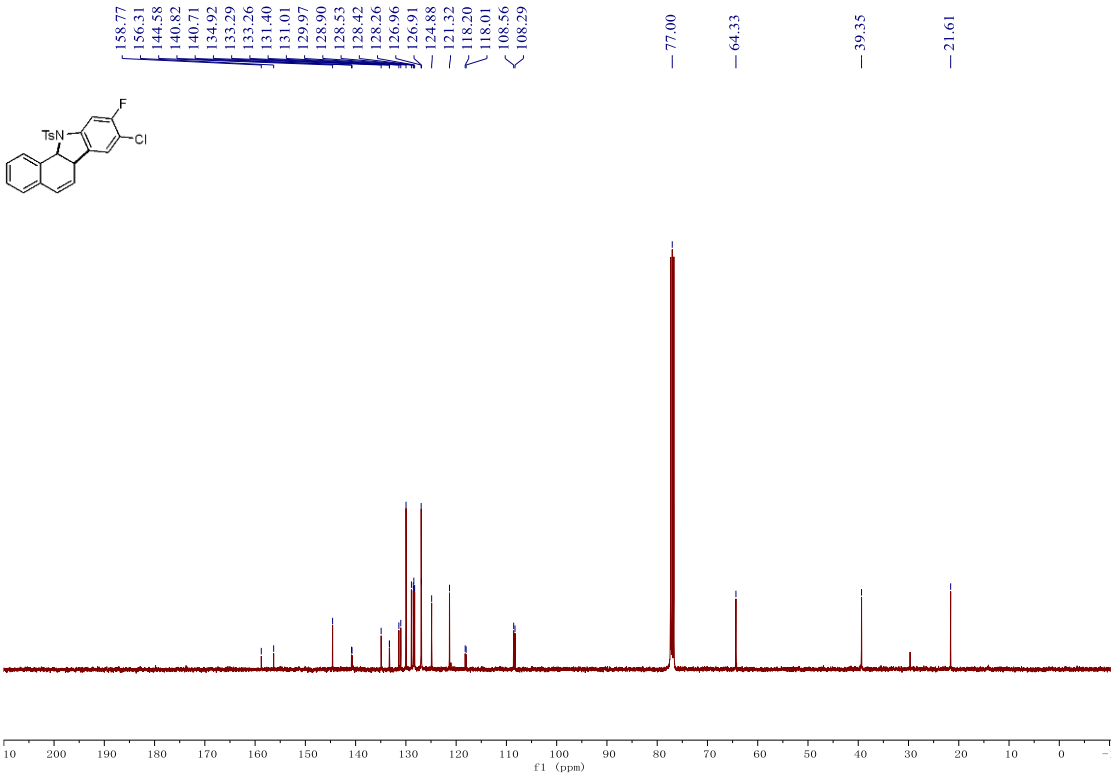
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3pa.



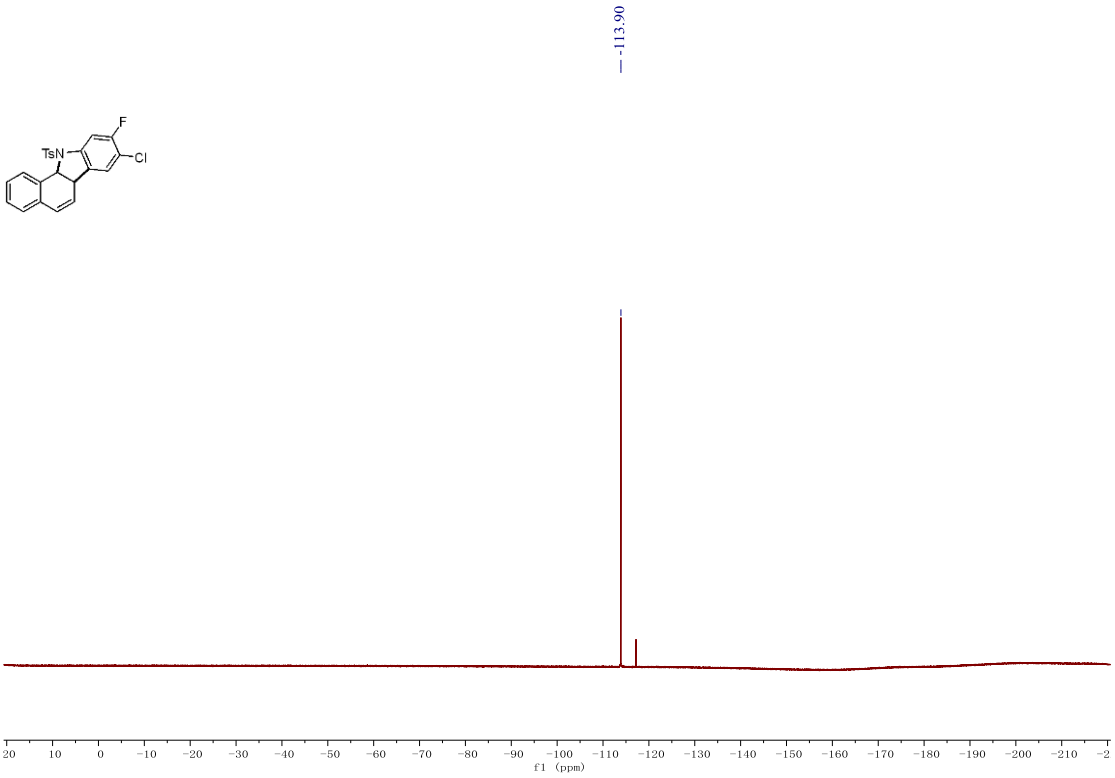
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3pa.



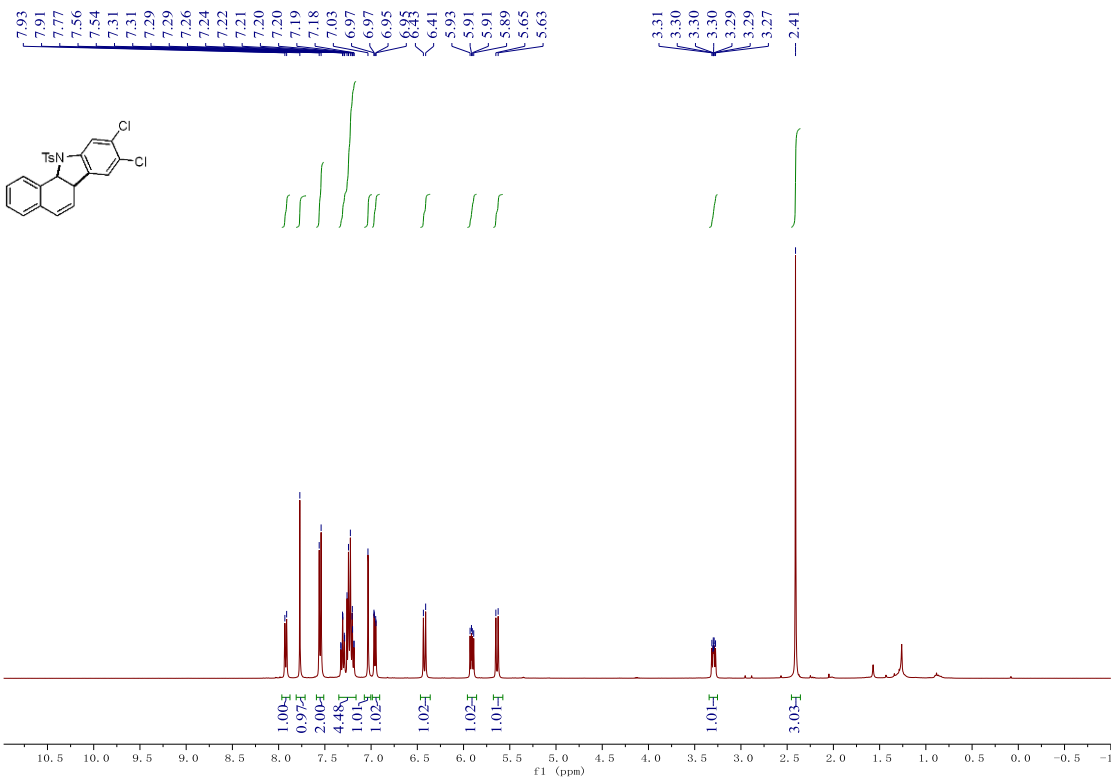
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3qa.



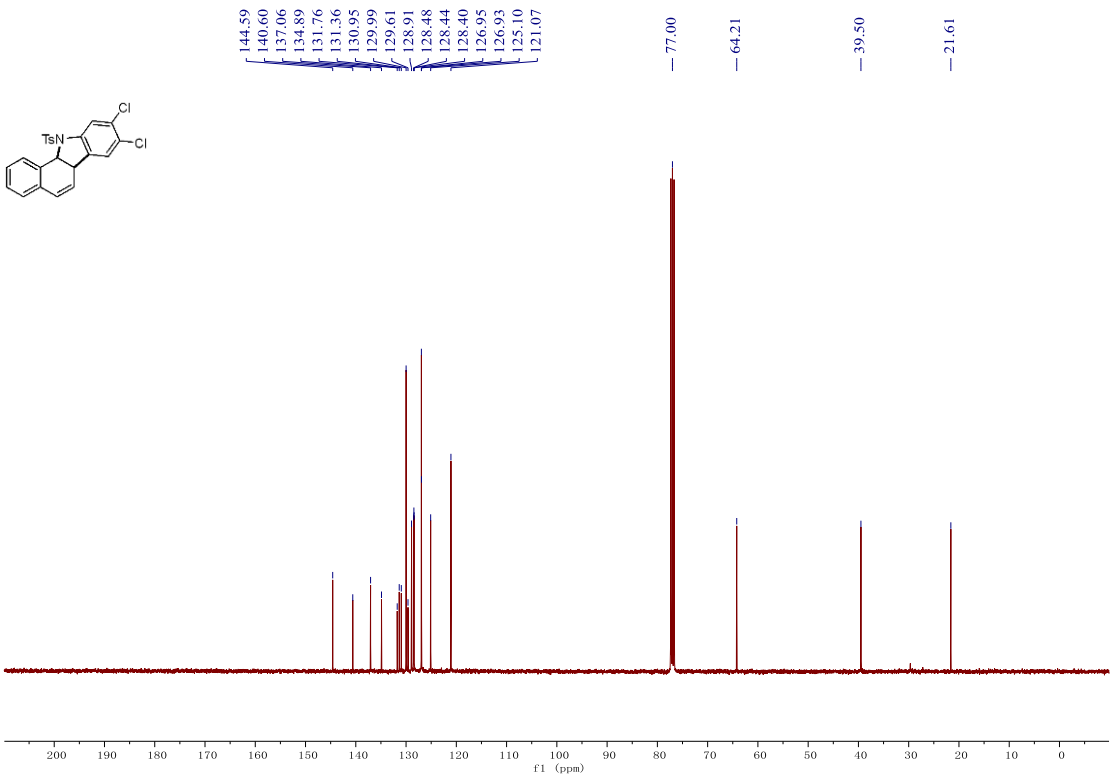
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3qa.



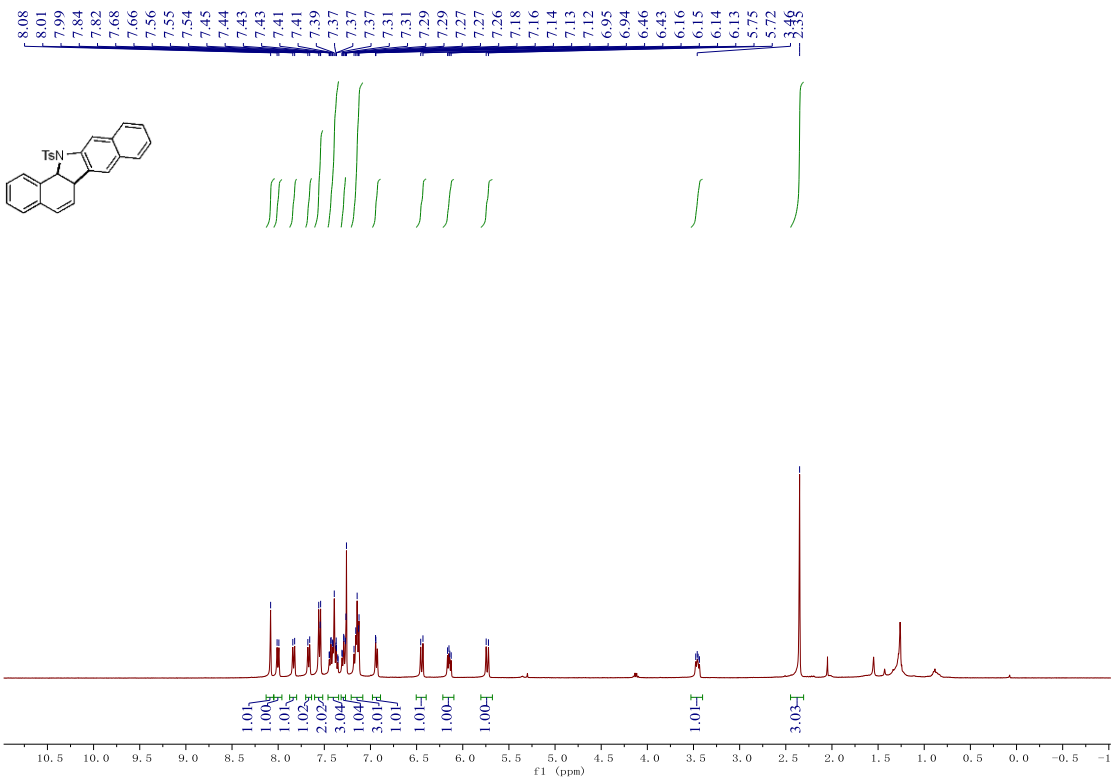
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3qa.



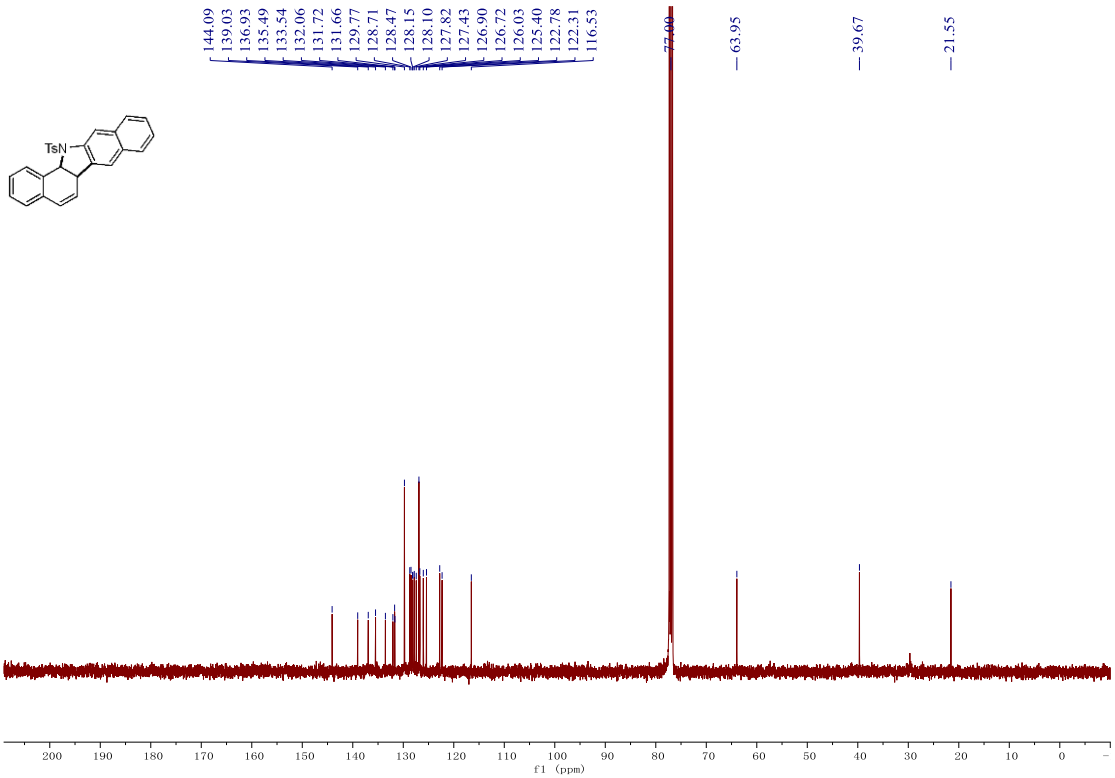
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ra.



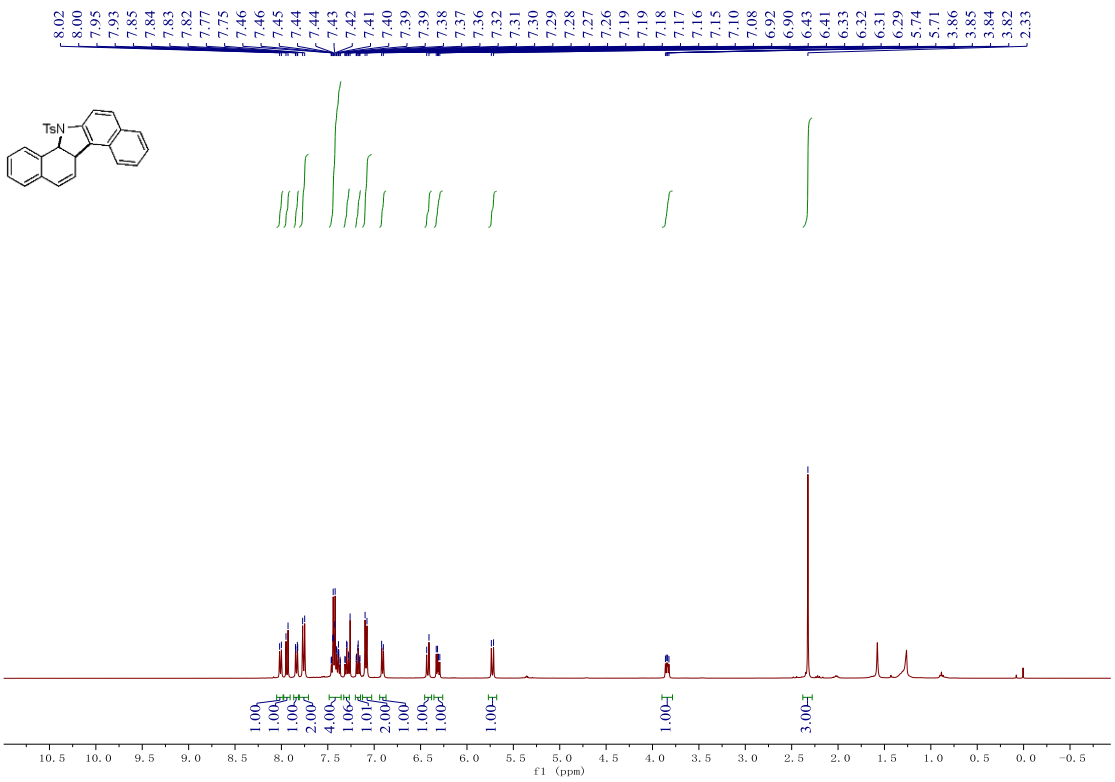
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3ra.



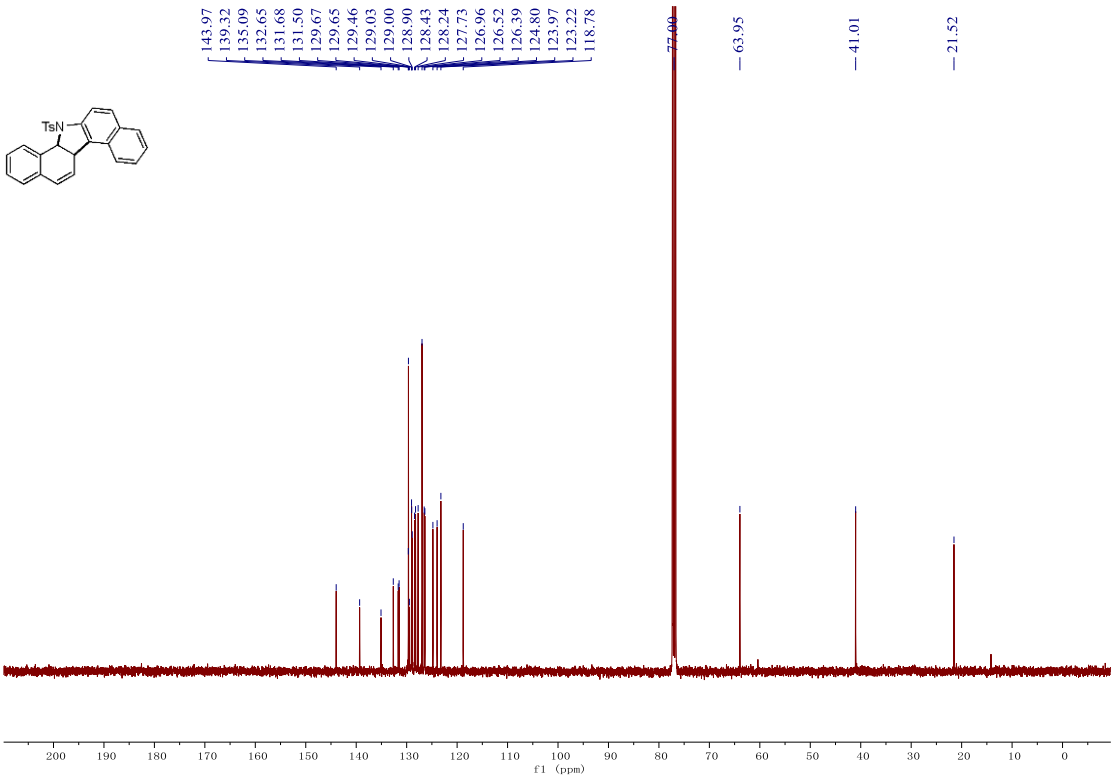
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3sa.



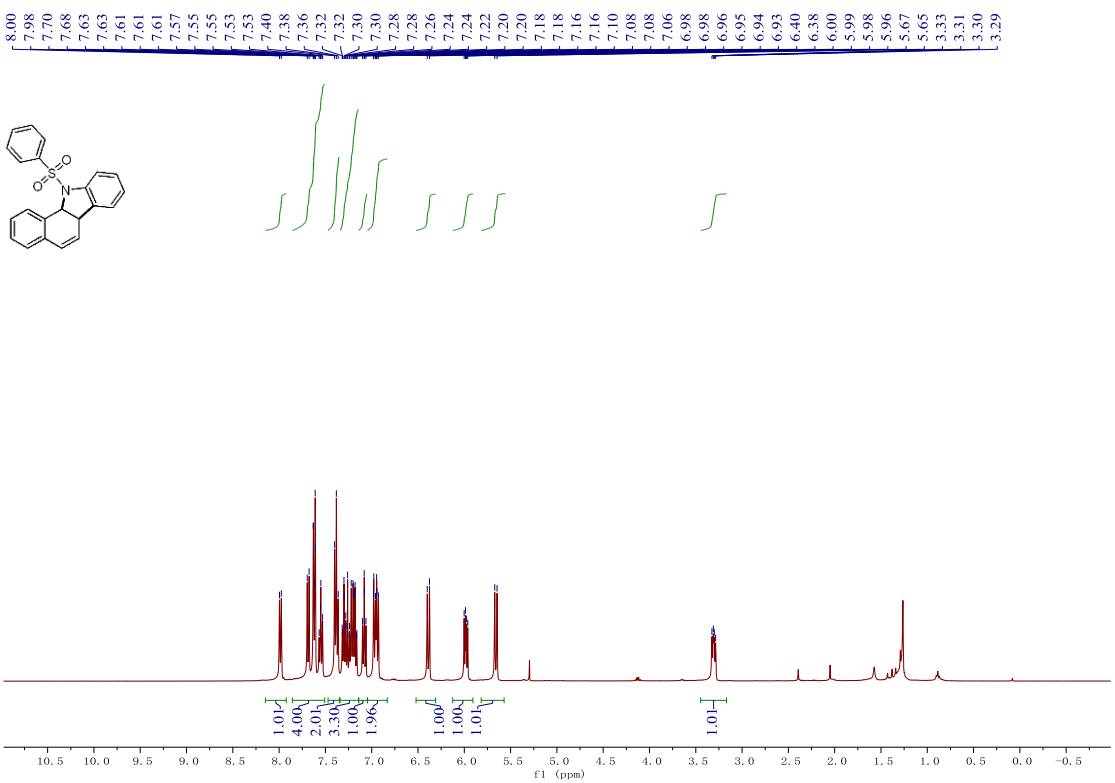
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3sa.



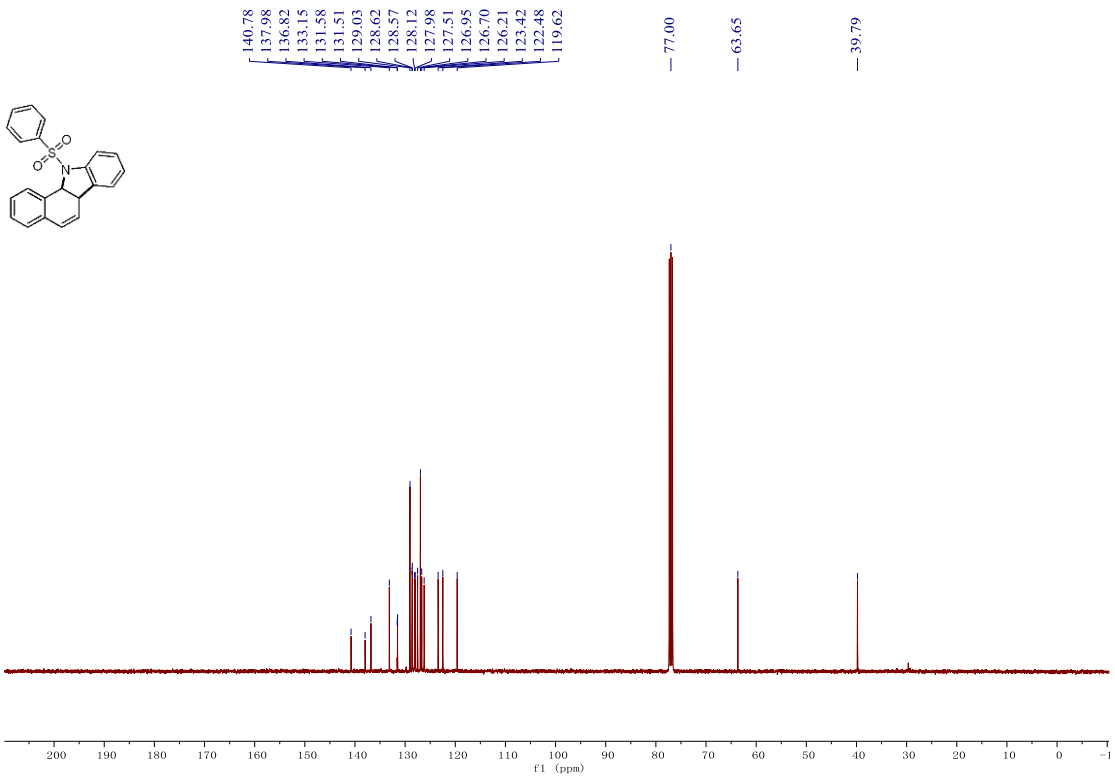
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ta.



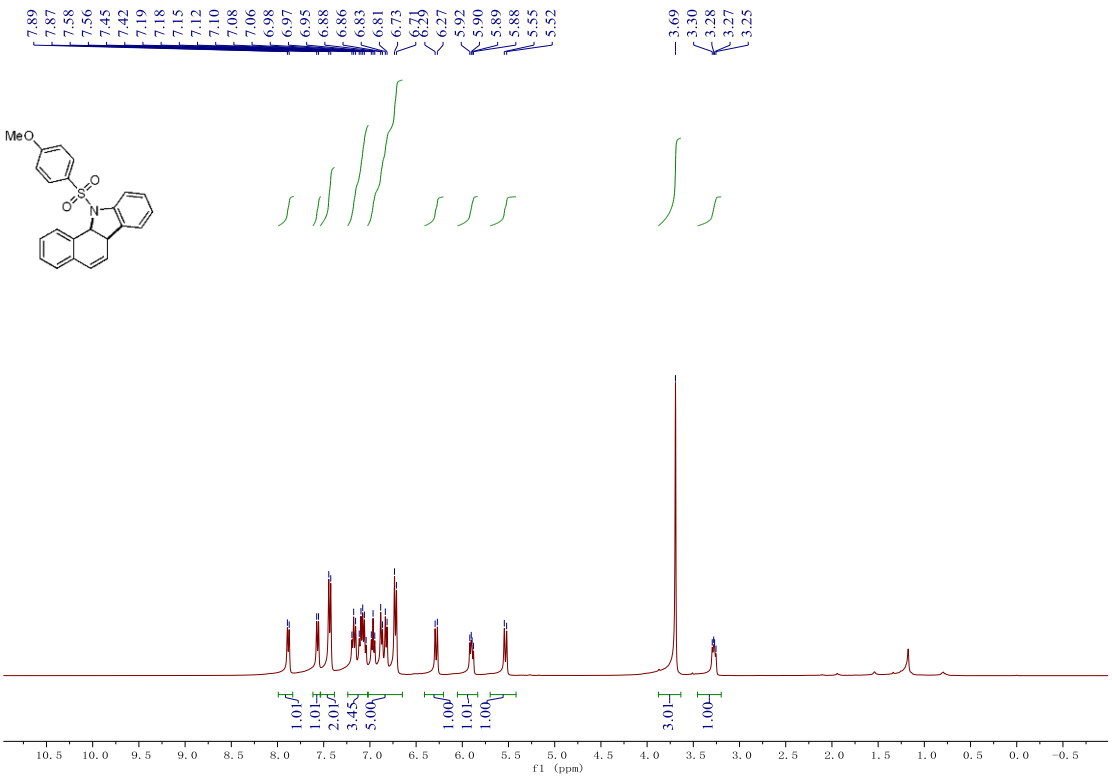
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3ta.



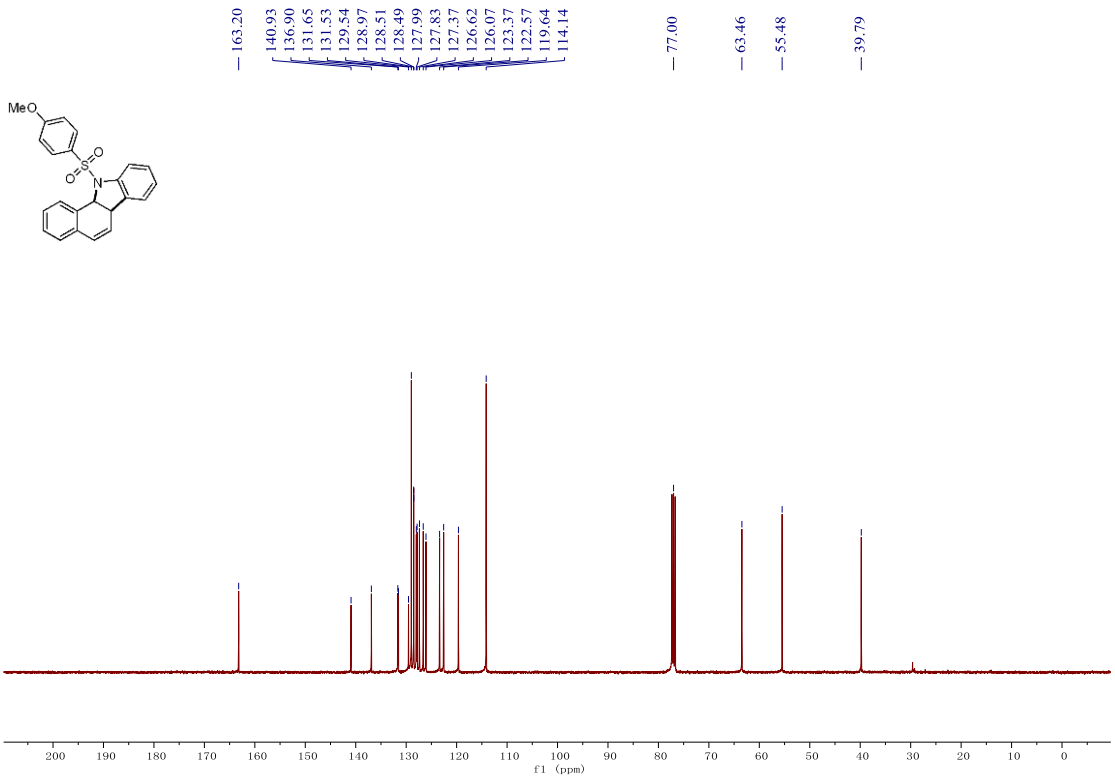
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ab.



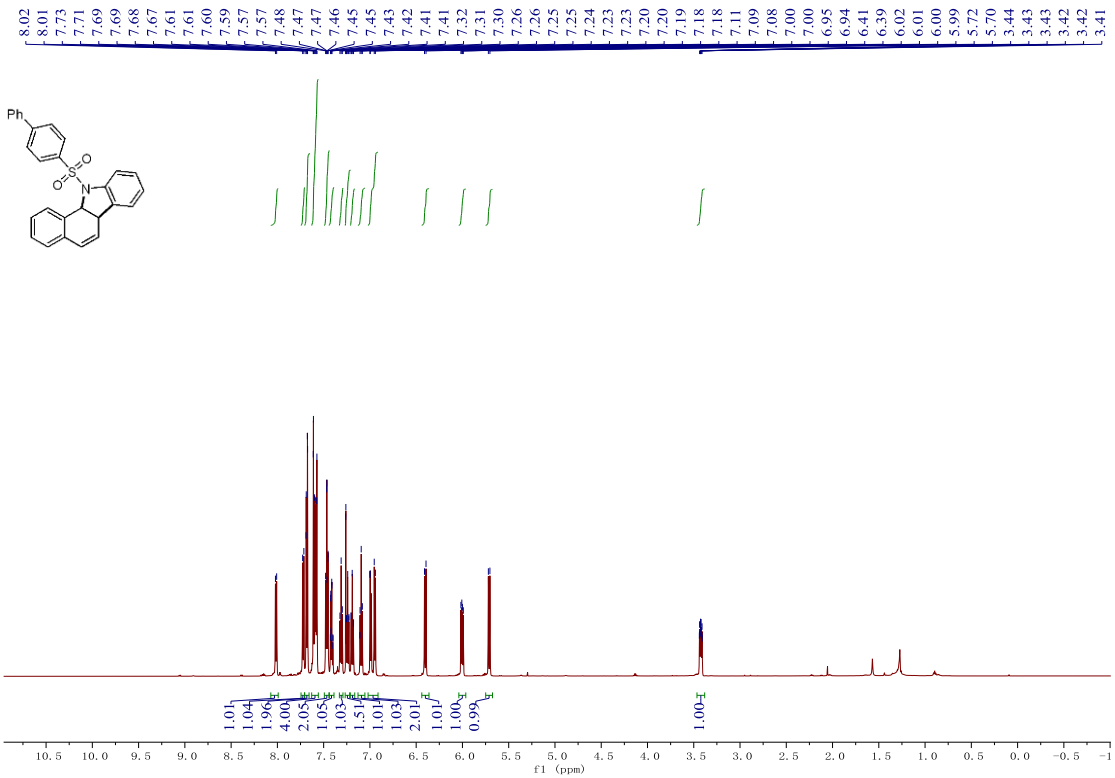
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3ab.



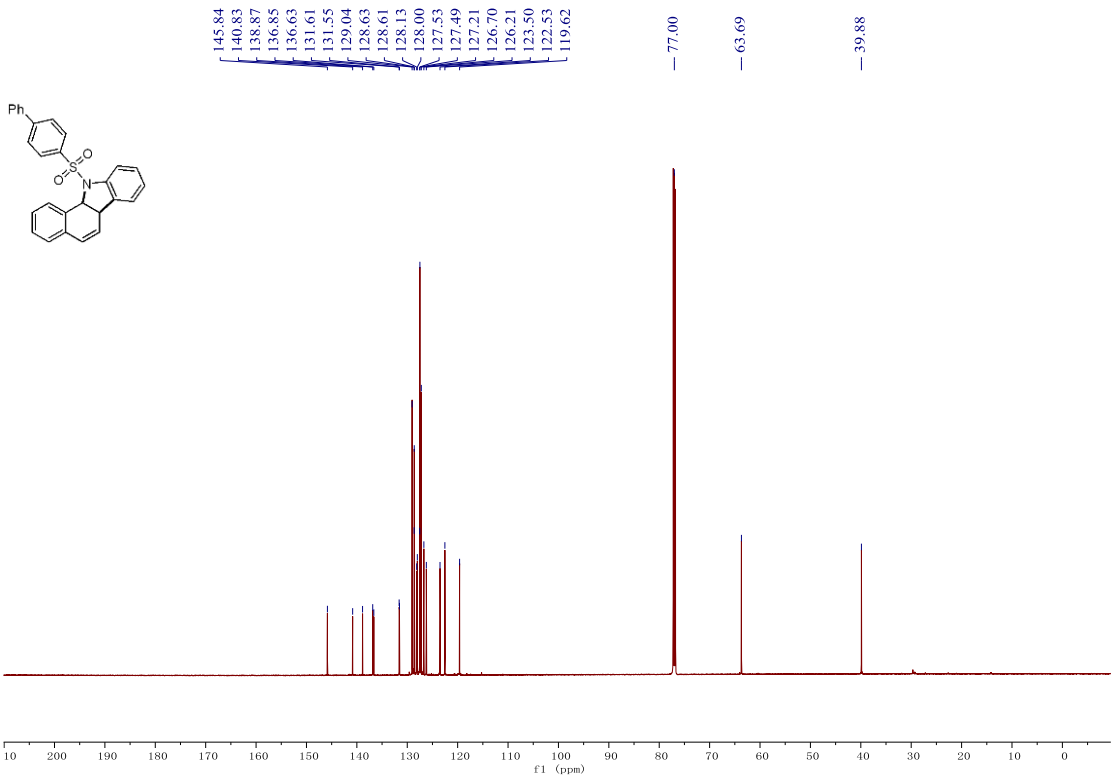
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ac.



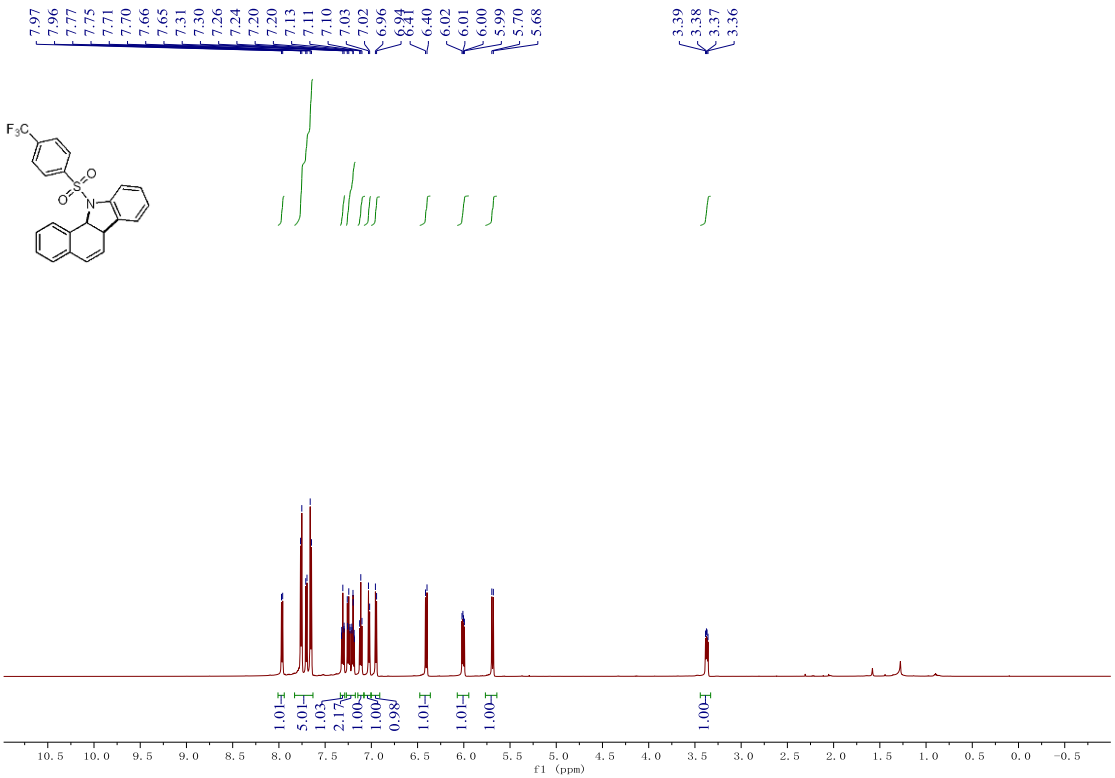
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3ac.



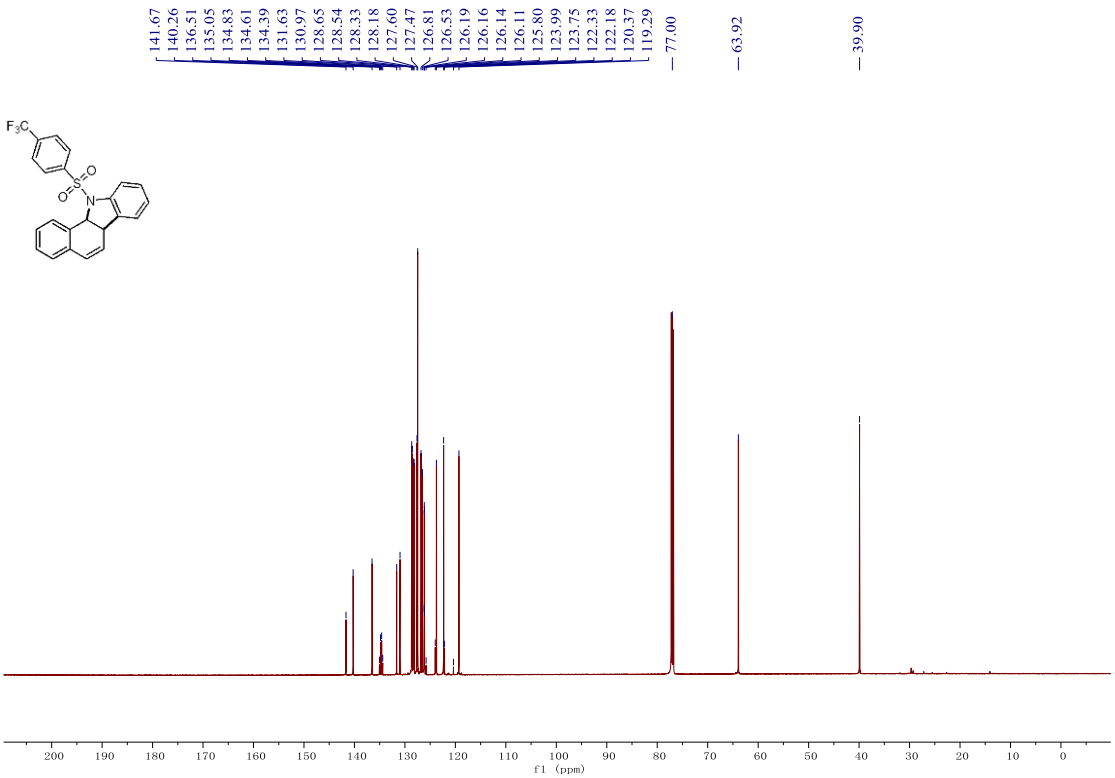
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ad.



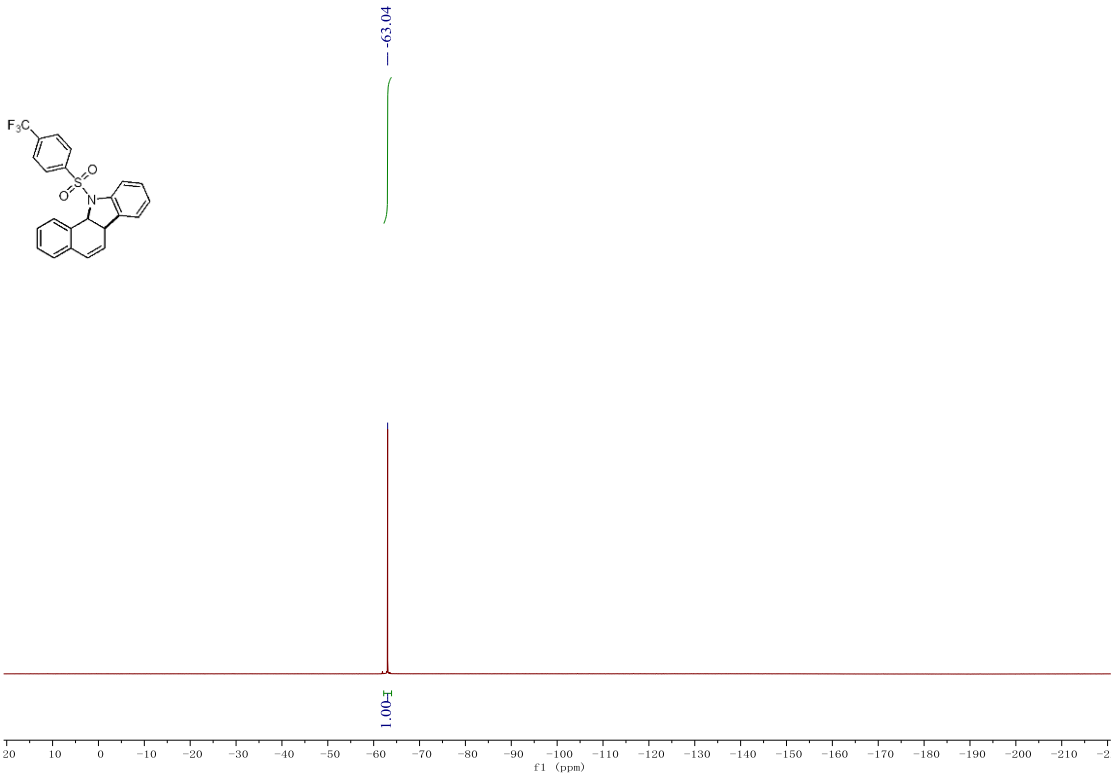
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3ad.



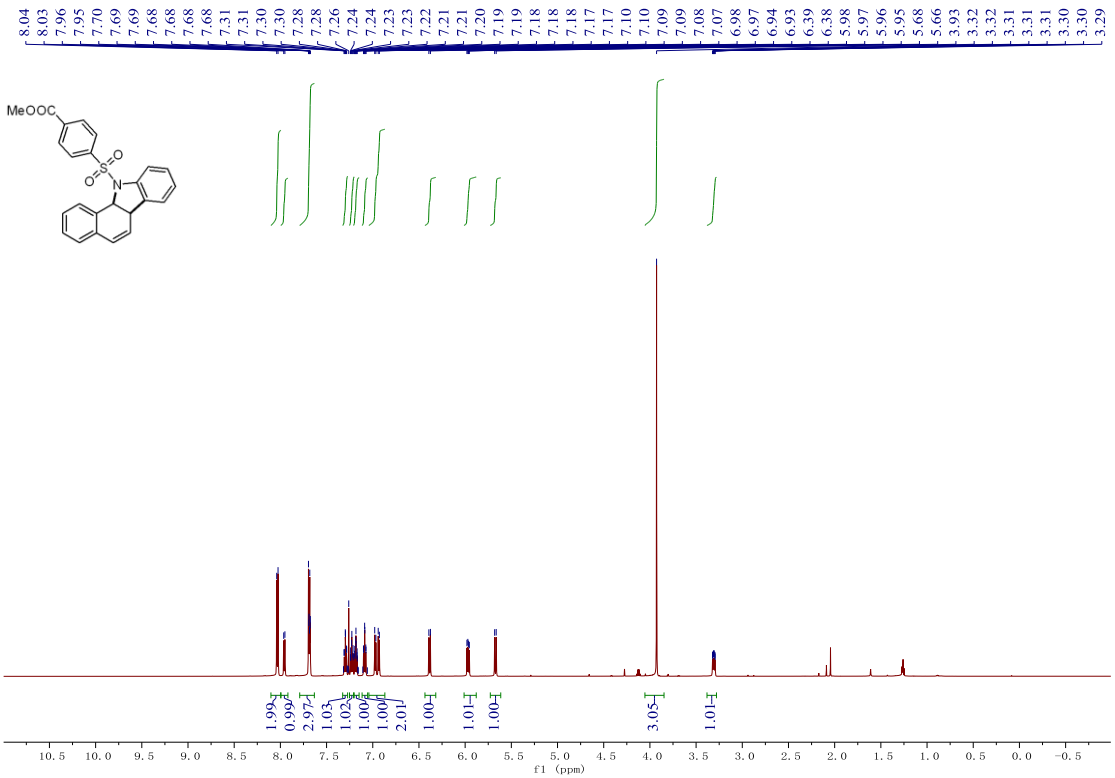
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ae.



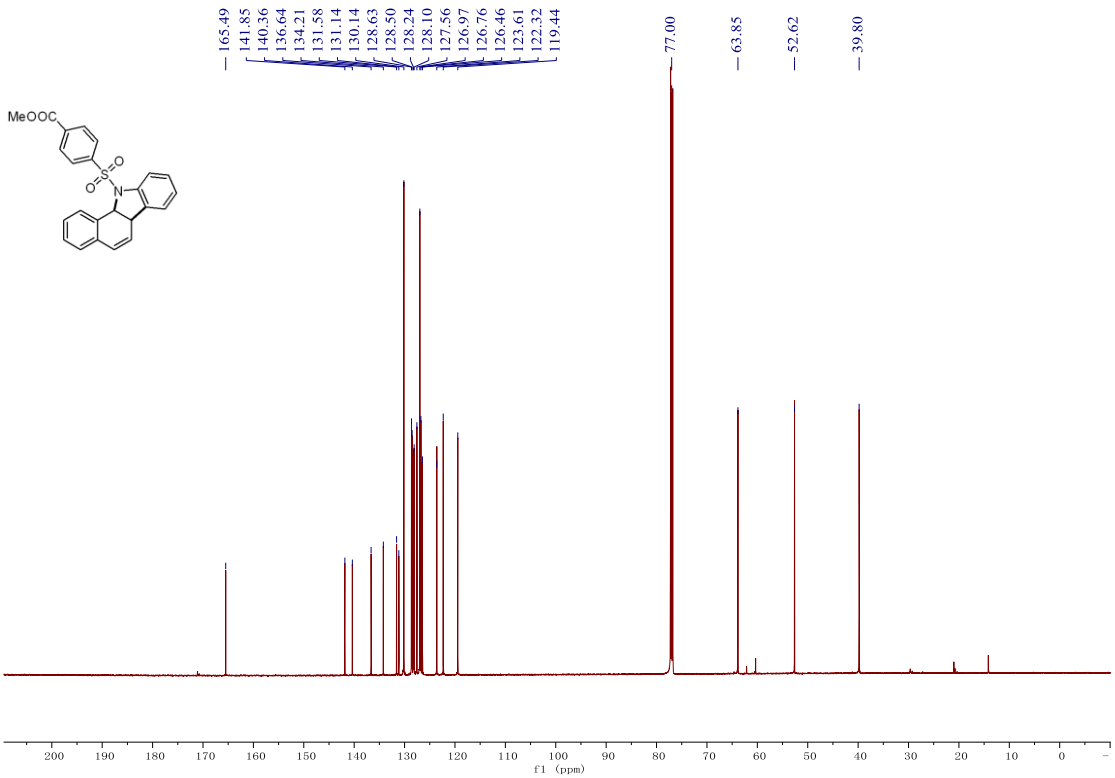
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3ae.



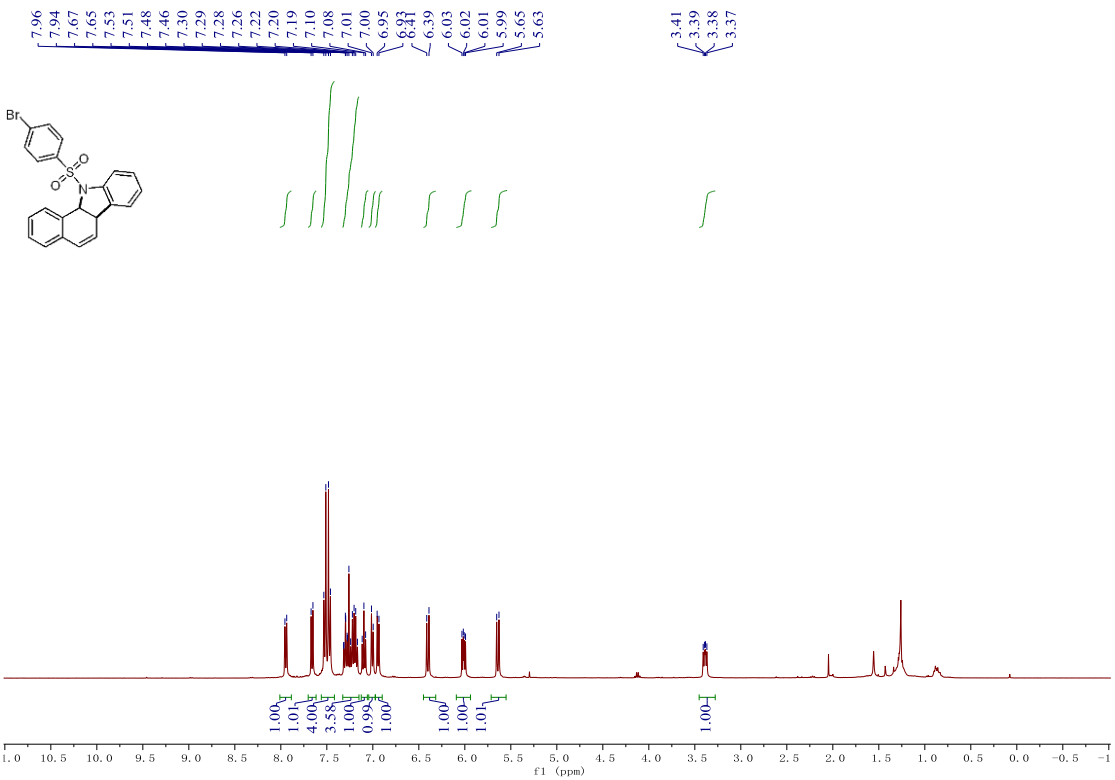
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3ae.



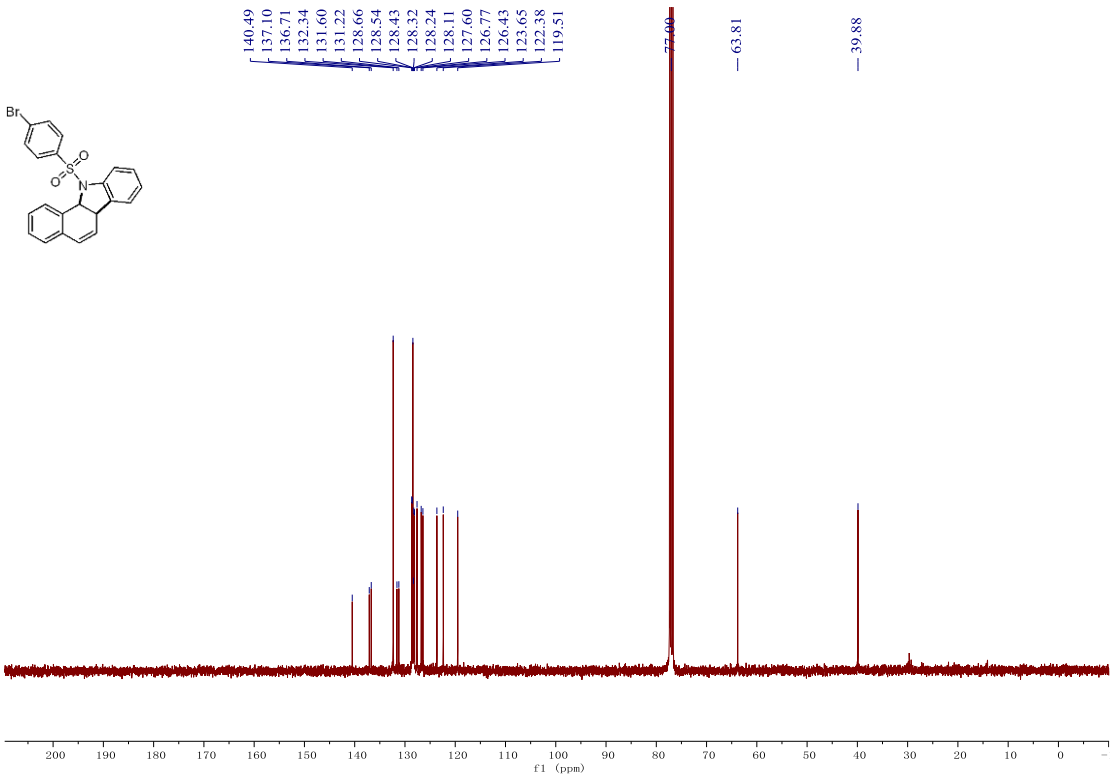
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3af.



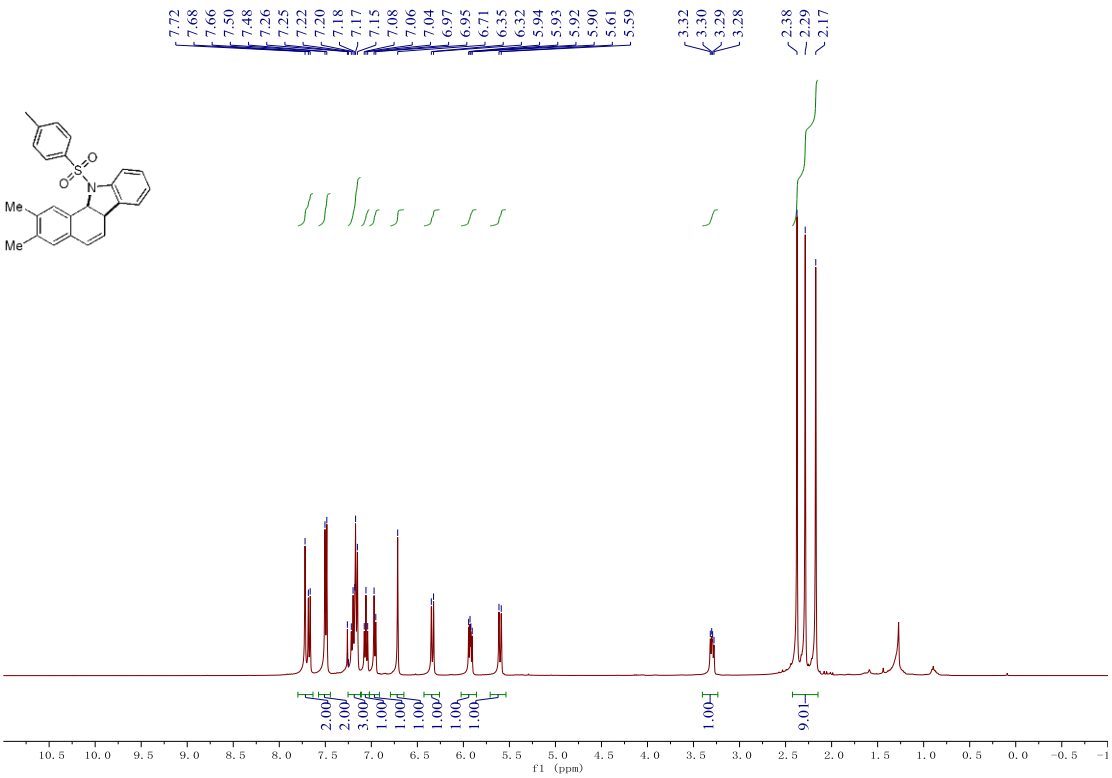
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3af.



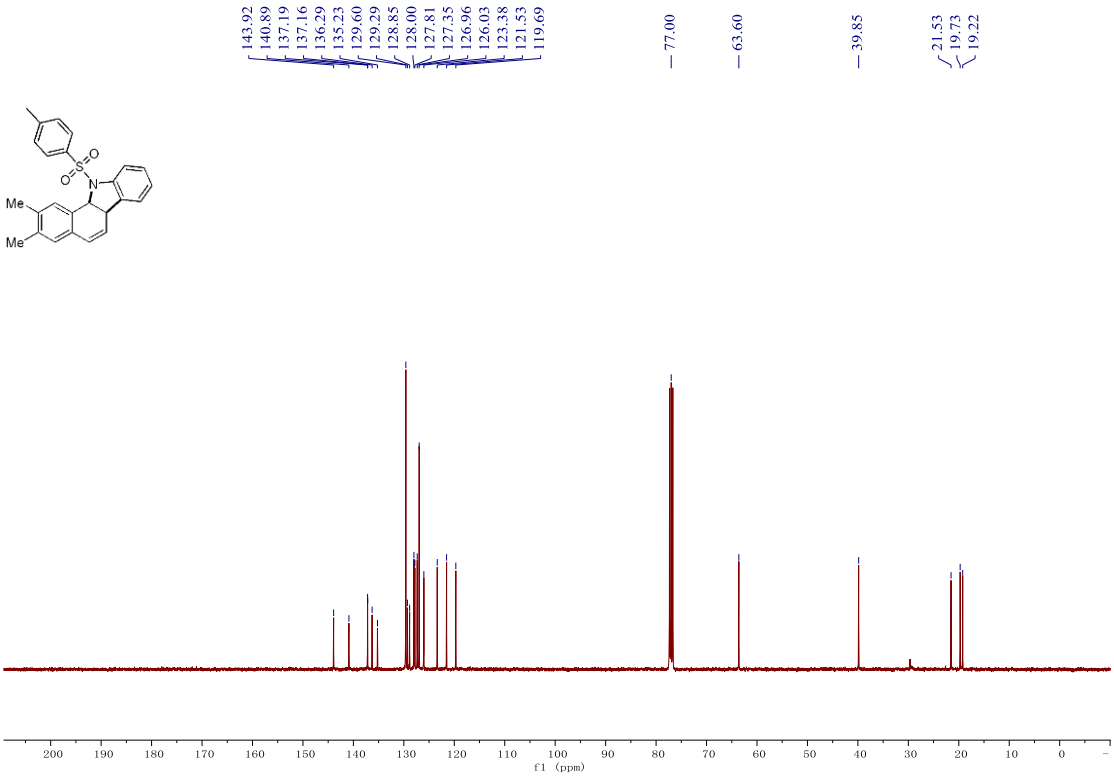
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ag.



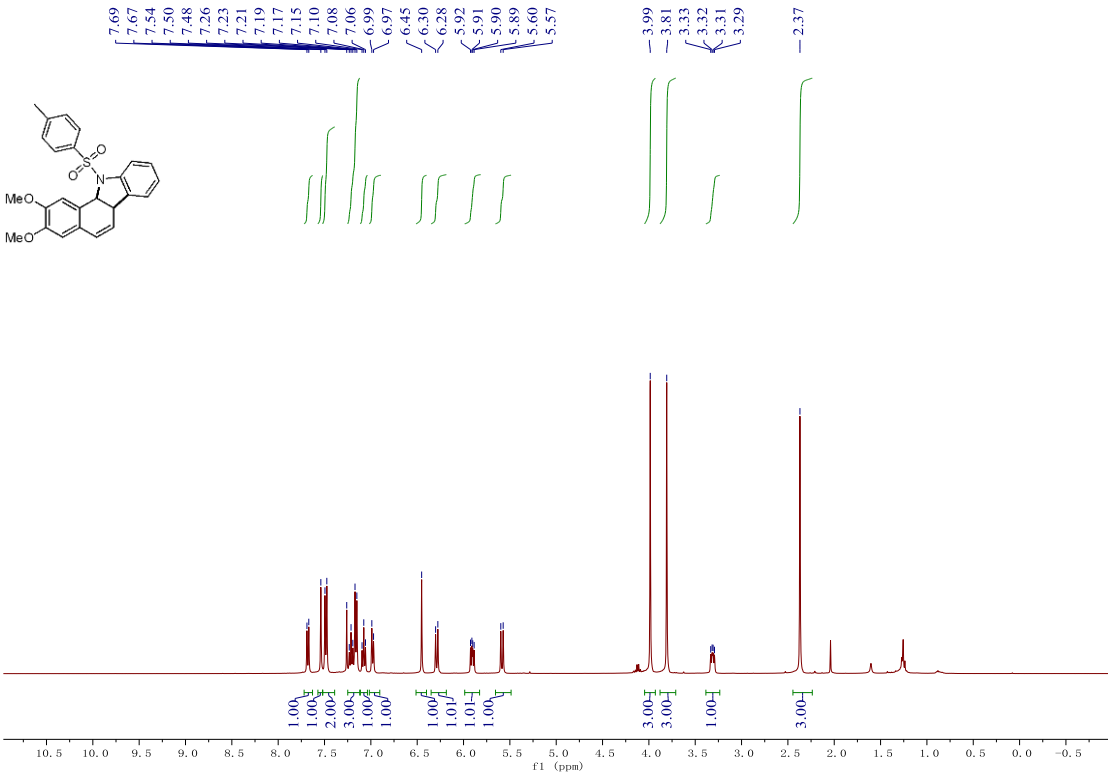
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3ag.



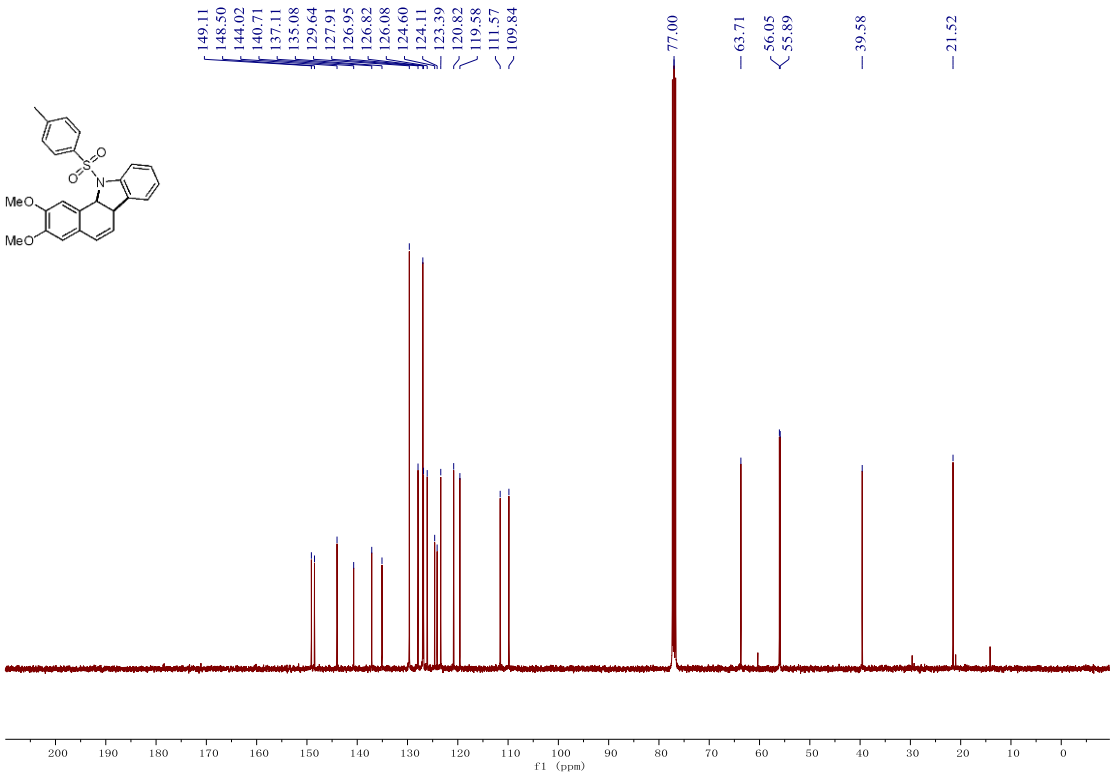
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ah.



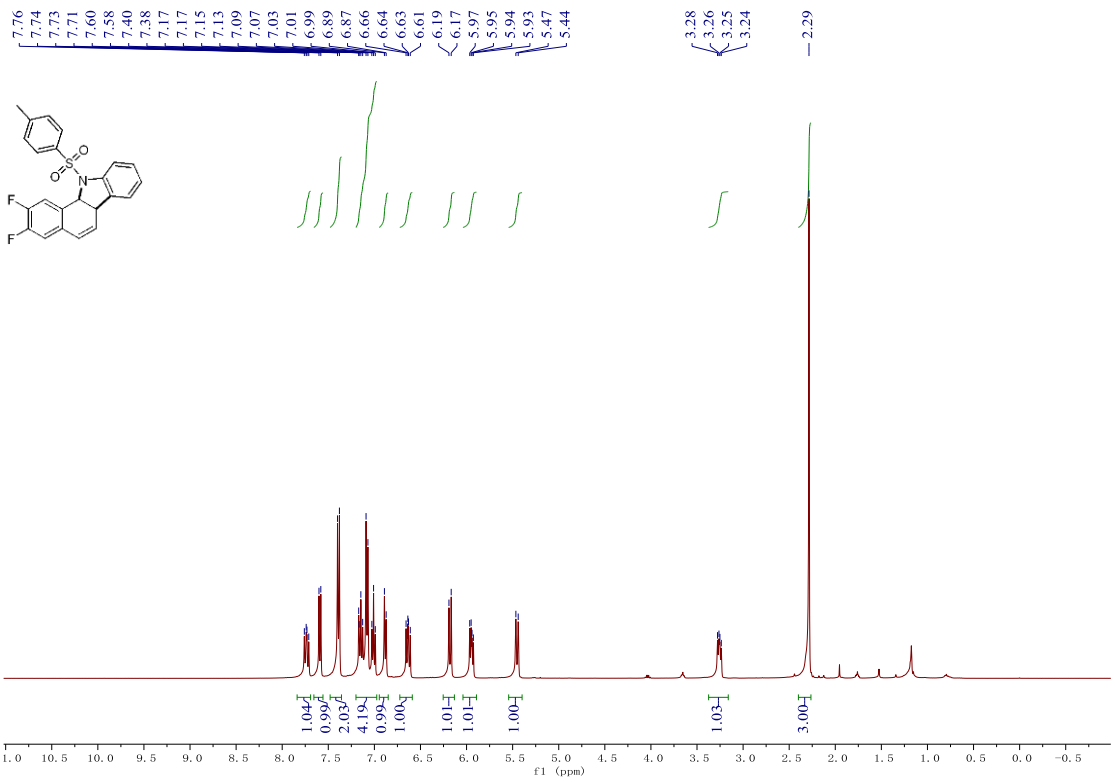
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3ah.



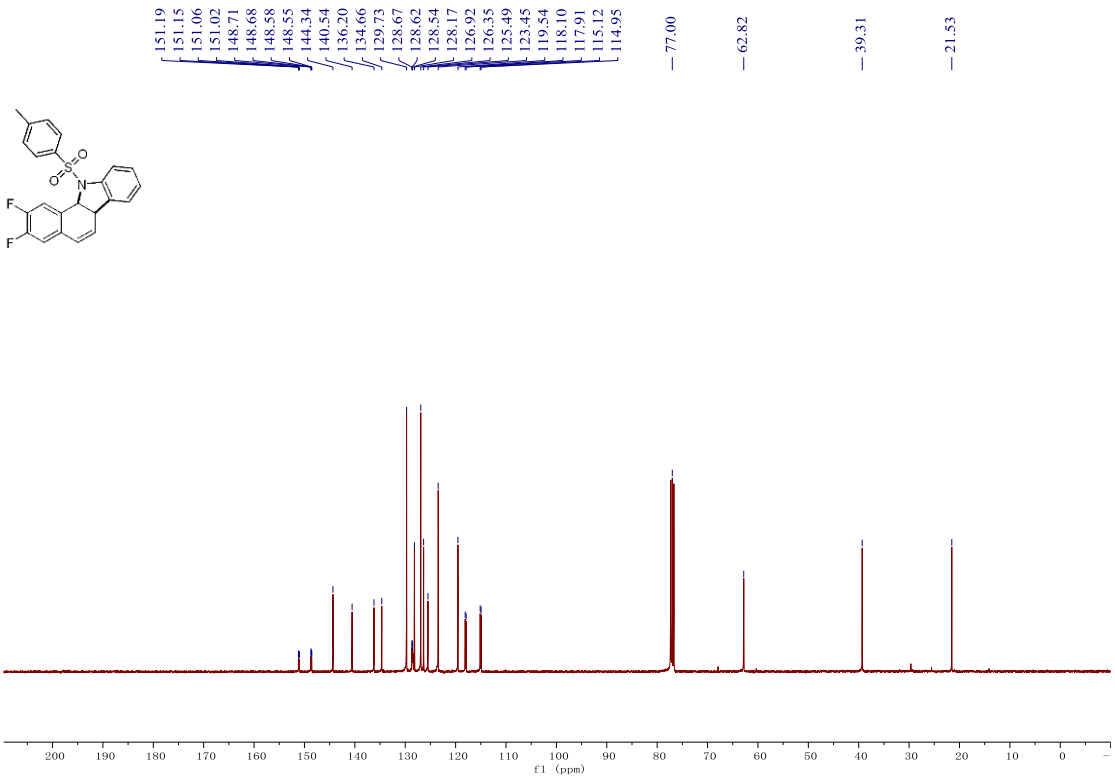
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ai.



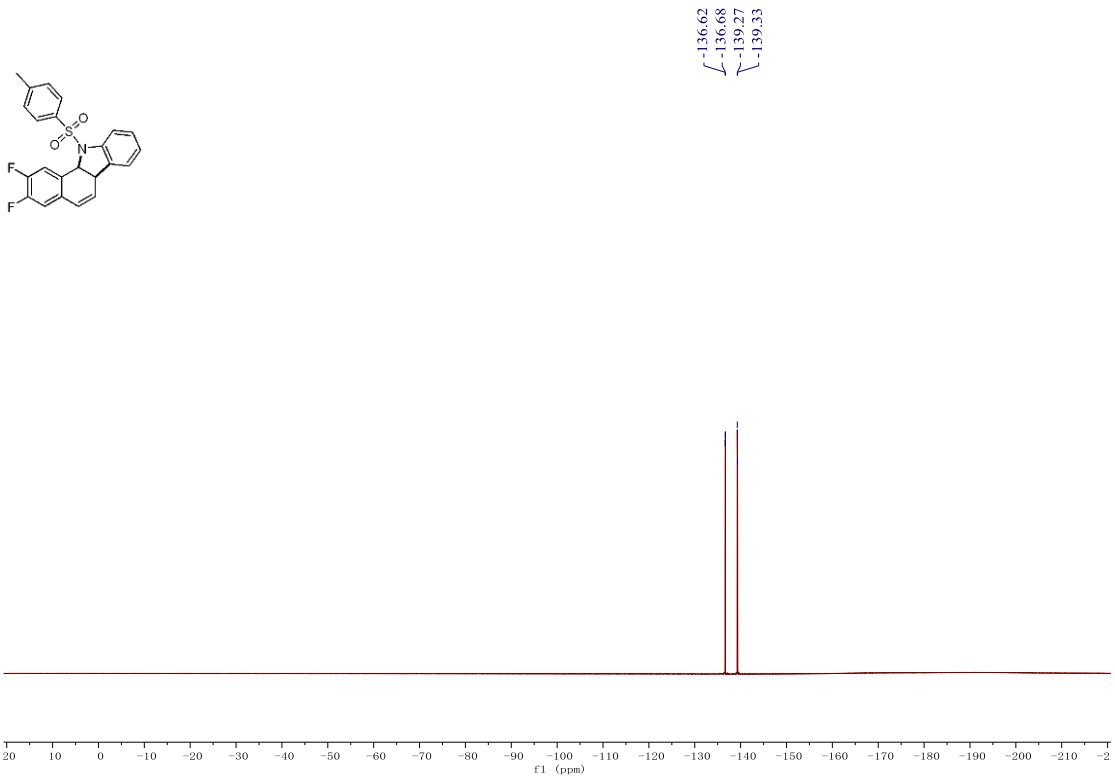
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3ai.



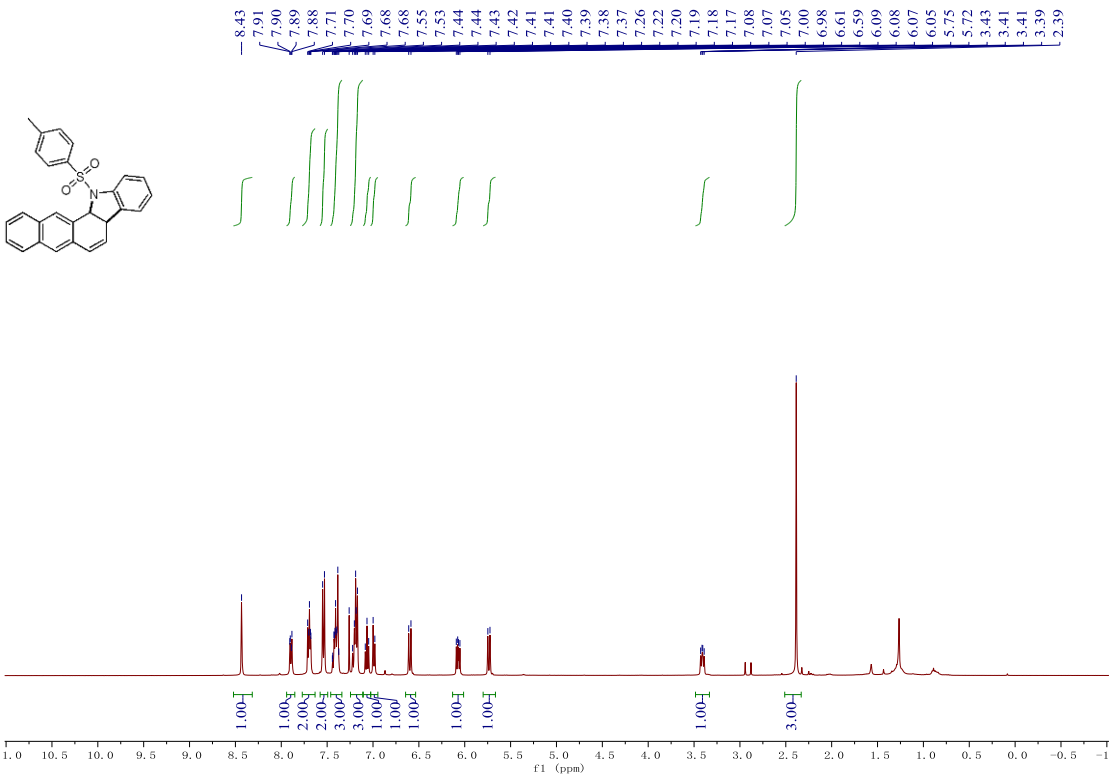
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3aj.



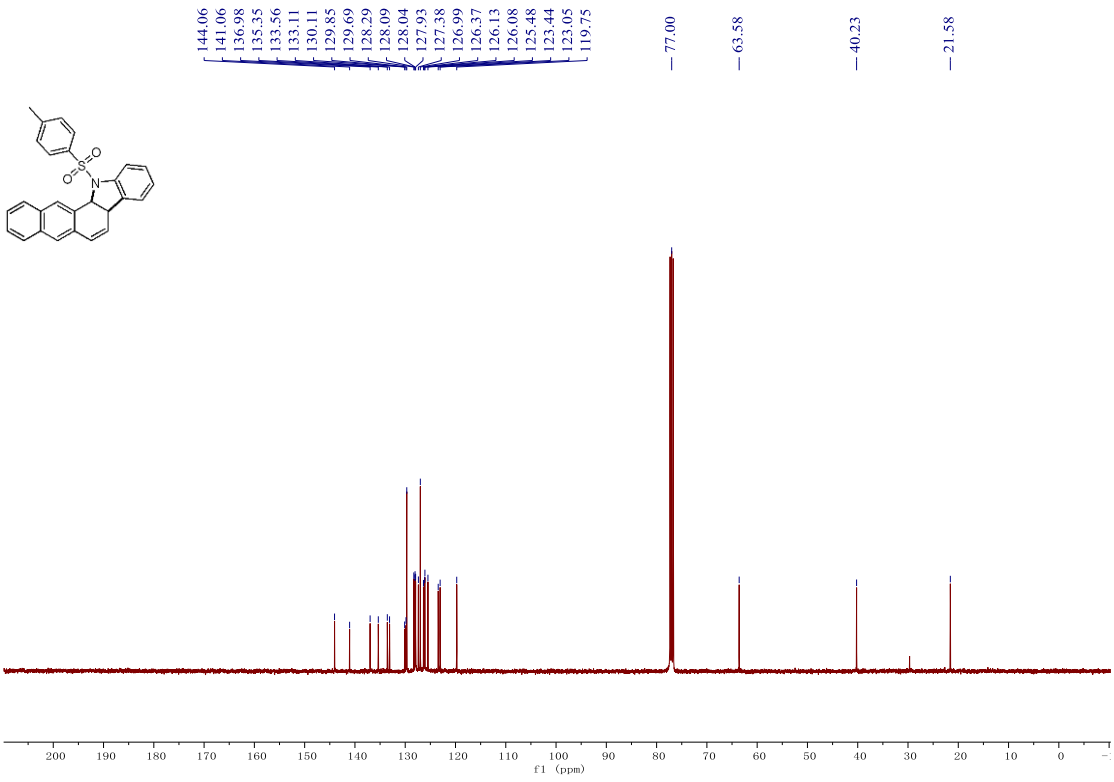
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3aj.



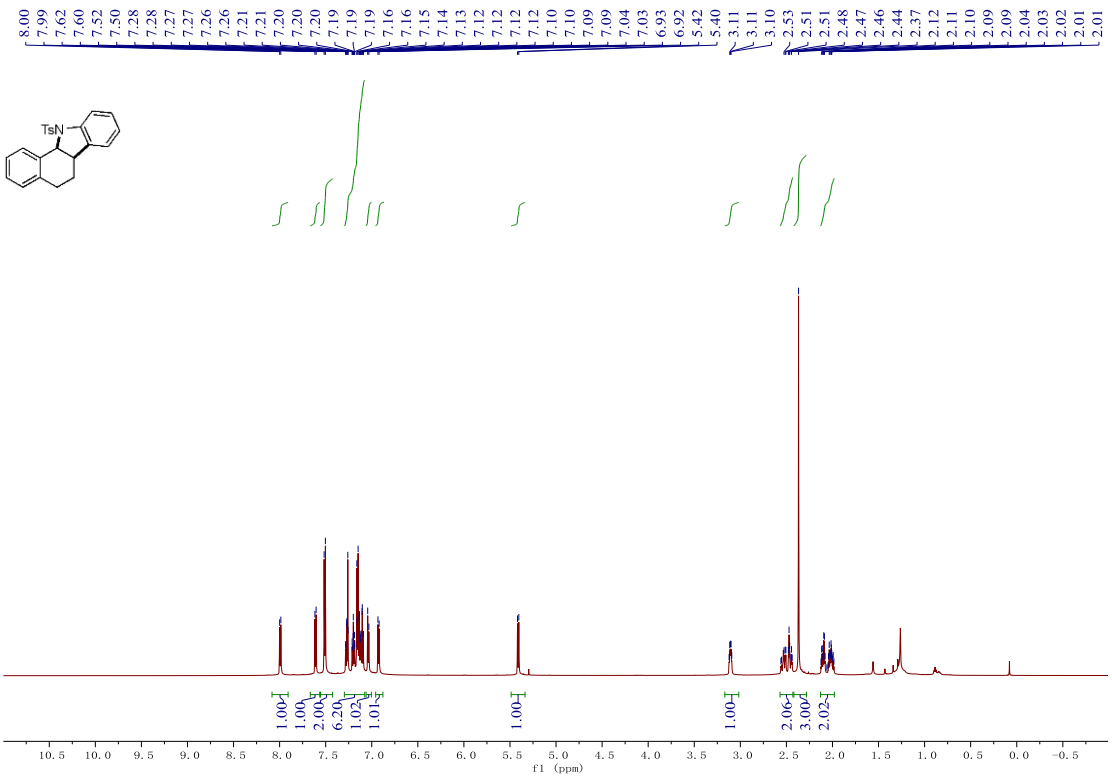
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3aj.



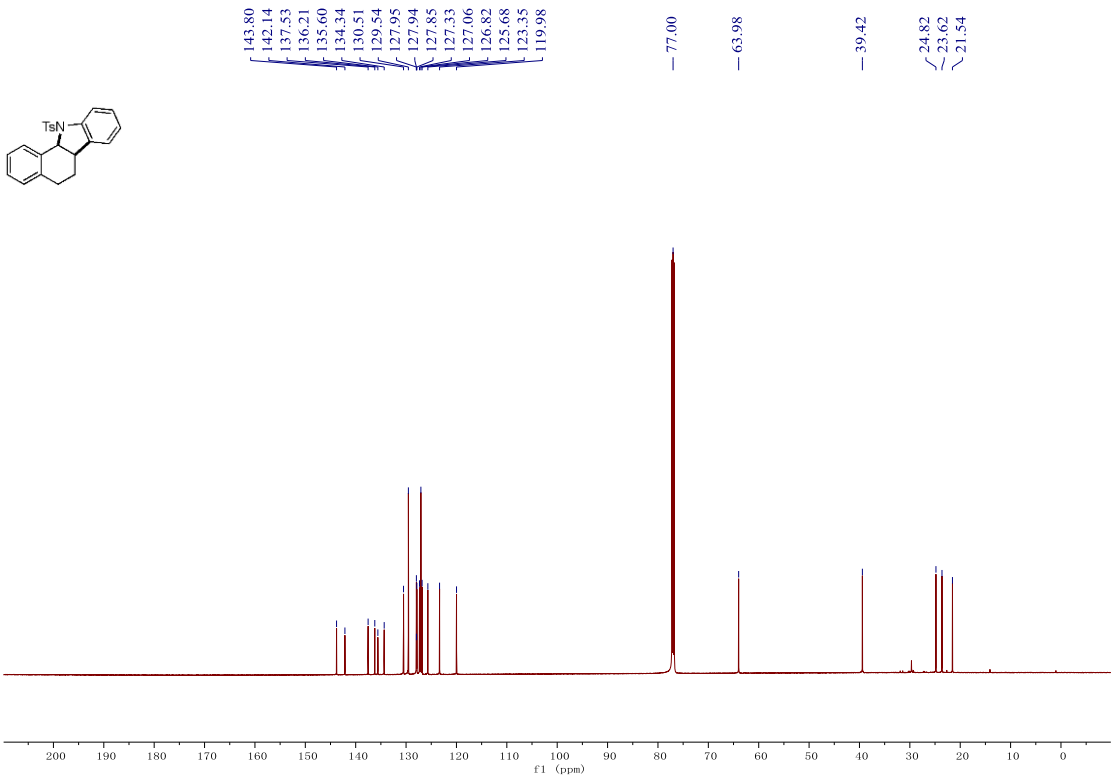
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ak.



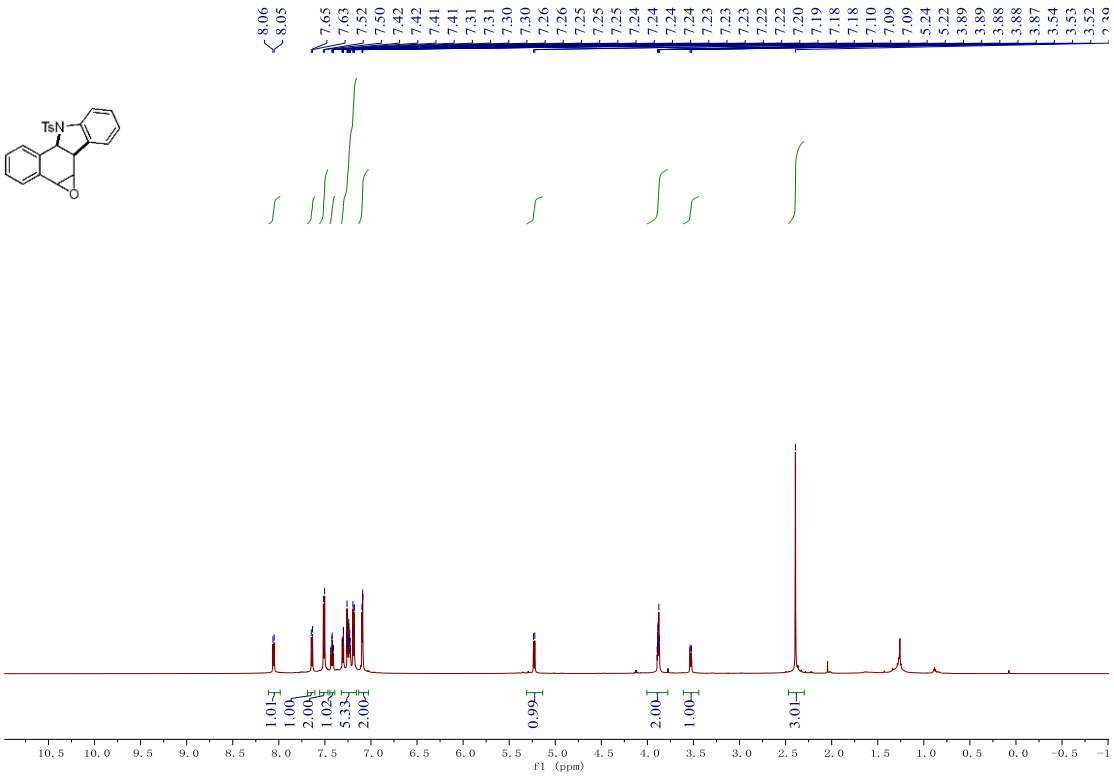
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3ak.



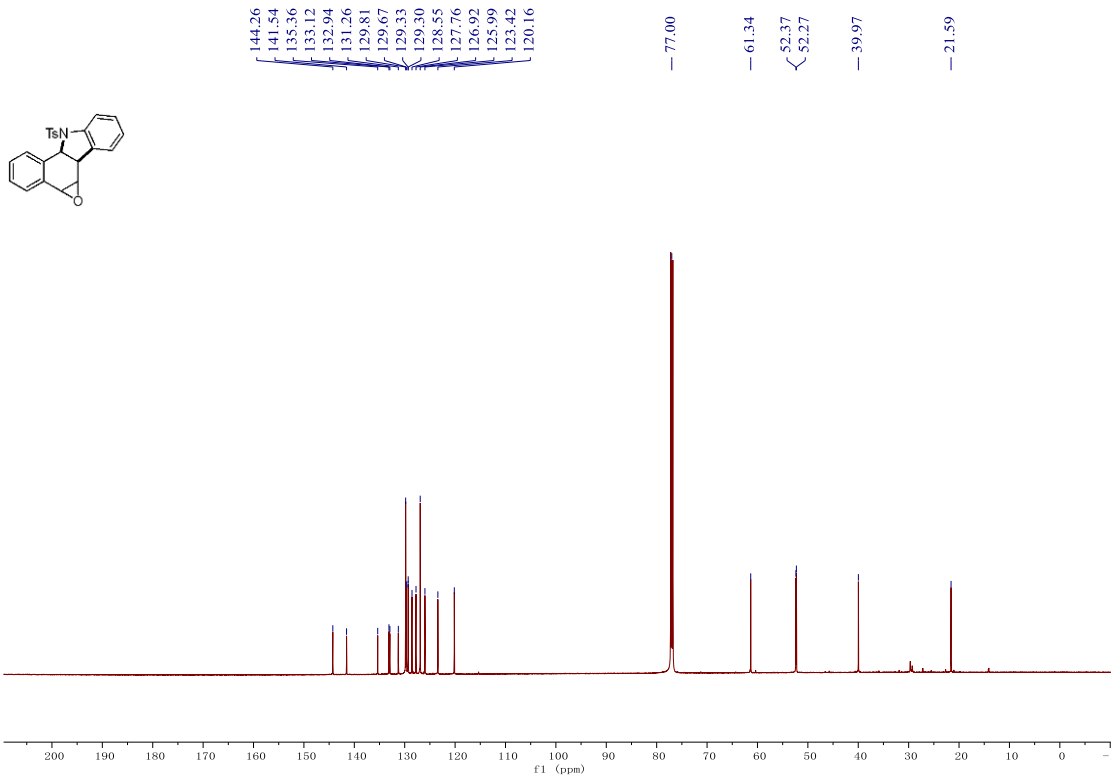
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 5.



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 5.



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 6.



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 6.