Supporting Information

Efficient and General Synthesis of 3-Aminoindolines and 3-Aminoindoles via Copper-Catalyzed Three Component Coupling Reaction

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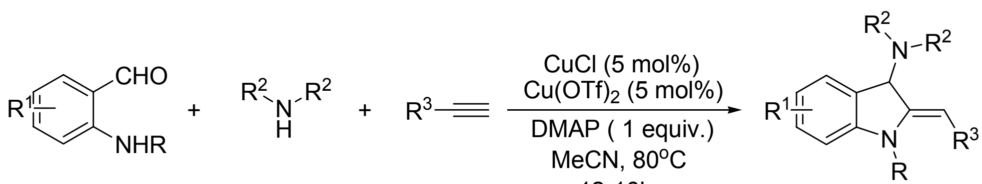
Content

General Information

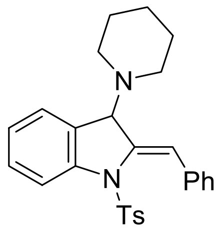
NMR spectra were recorded on a Bruker Avance DRX-500 (500 MHz). HRMS analysis was performed on Micromass 70 VSE high resolution mass spectrometer[1]. GC/MS analysis was performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m x 0.25 mm capillary column, HP-5MS). Chiral HPLC analysis was performed on a Gilson 321 Pump interfaced to a Hitachi L-4000 UV detector (0.46 cm x 25 cm, CHIRALCEL OD-H). Optical rotations were measured on JASCO digital polarimeter (DIP-370) using a 10 cm quartz cell.
Column chromatography was carried out employing Silicycle Silica-P Flash silica gel (40-63 μm). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography. Anhydrous solvents were purchased from Aldrich and stored over calcium hydride. Alkynes were commercially available and purchased from Aldrich, Strem Chemicals Inc. or Acros Organics. All manipulations with air sensitive materials were conducted under argon atmosphere using a combination of glovebox and standard Schlenk techniques. *N*-(2-formylphenyl)-4-methylbenzenesulfonamide and *N*-(2-formylphenyl)-4-nitrobenzenesulfonamide were prepared according to the known procedure[2].

Scheme S1. TCC Synthesis of 3-Aminoindolines (5).

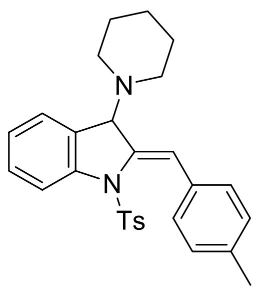


General Procedure: In a dry and argon flushed Wheaton 1mL V-vial, equipped with a magnetic stirring bar and a screw cap, CuCl (1.5 mg, 0.015 mmol, 5 mol%), $Cu(OTf)_2$ (5.4 mg, 0.015 mmol, 5 mol%), DMAP (36.7 mg, 0.3 mmol, 1 equiv.) and aldehyde **1** (0.3 mmol, 1 equiv.) were suspended in dry acetonitrile (0.3 mL). Secondary amine **2** (0.3 mmol, 1 equiv.) and alkyne **3** (0.45 mmol, 1.5 equiv.) were added and the reaction mixture was stirred at 80^{o}C until TLC analysis showed full conversion of the aldehyde. The reaction mixture was then filtered through Celite and washed with dichloromethane. The crude product **5** was concentrated *in vacuo* and purified by column chromatography on silica gel to afford desired 3-aminoindoline product.

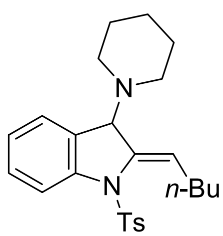
[1] The 70-VSE mass spectrometer was purchased in part with a grant from the Division of Research Resources, National Institutes of Health (RR 04648).
[2] Hechavarría Fonseca, M; Eibler, E.; Zabel, M.; König, B. *Tetrahedron: Asymmetry* **2003**, *14*, 1989.



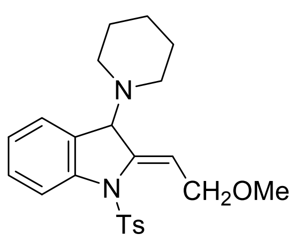
5a: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm δ ppm 7.77 - 7.83 (m, 3 H), 7.38 (t, *J*=7.61 Hz, 2 H), 7.28 - 7.34 (m, 3 H), 7.23 - 7.28 (m, 1 H), 7.19 - 7.23 (m, 1 H), 7.08 - 7.13 (m, 1 H), 7.06 (d, *J*=8.07 Hz, 2 H), 6.62 (d, *J*=2.02 Hz, 1 H), 4.01 (br. s., 1 H), 2.65 - 2.73 (m, 2 H), 2.36 - 2.43 (m, 2 H), 2.33 (s, 3 H), 1.32 - 1.54 (m, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 144.0, 142.4, 138.9, 136.2, 133.9, 133.9, 129.4, 128.9, 128.1, 128.0, 127.9, 127.2, 125.5, 125.1, 121.3, 120.4, 69.3, 50.4, 26.8, 24.6, 21.6; HRMS (EI+) calculated for $C_{27}H_{28}N_2O_2S$ (M^+): 444.18715, Found: 444.18858.



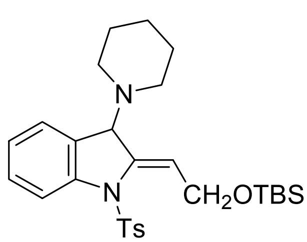
5b: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.79 (d, *J*=7.89 Hz, 1 H), 7.72 (d, *J*=8.07 Hz, 2 H), 7.28 - 7.34 (m, 3 H), 7.17 - 7.23 (m, 3 H), 7.10 (ddd, *J*=7.47, 1.01 Hz, 1 H), 7.05 (d, *J*=7.89 Hz, 2 H), 6.59 (d, *J*=2.38 Hz, 1 H), 3.98 (d, *J*=1.47 Hz, 1 H), 2.62 - 2.72 (m, 2 H), 2.34 - 2.42 (m, 5 H), 2.33 (s, 3 H), 1.37 - 1.50 (m, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 144.0, 142.5, 138.0, 137.1, 134.1, 133.9, 133.2, 129.4, 128.9, 128.6, 128.0, 125.5, 125.0, 121.3, 120.4, 69.3, 50.4, 26.8, 24.6, 21.6, 21.4; HRMS (EI+) calculated for $C_{28}H_{30}N_2O_2S$ (M^+): 458.20280, Found: 458.20386.



5c: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.68 (d, *J*=7.89 Hz, 1 H), 7.34 (d, *J*=8.25 Hz, 2 H), 7.22 - 7.27 (m, 1 H), 7.12 - 7.17 (m, 1 H), 7.03 - 7.09 (m, 3 H), 5.65 - 5.72 (m, 1 H), 3.77 (br. s., 1 H), 2.60 - 2.71 (m, 1 H), 2.46 - 2.59 (m, 3 H), 2.32 (s, 5 H), 1.32 - 1.53 (m, 10 H), 0.91 (t, *J*=7.15 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 143.8, 142.6, 137.6, 134.3, 134.2, 128.9, 127.9, 125.3, 125.1, 125.1, 120.1, 68.3, 50.2, 31.8, 28.5, 26.6, 24.6, 22.4, 21.5, 13.9; HRMS (ESI+) calculated for $C_{25}H_{33}N_2O_2S$ (M^++H): 425.2263, Found: 425.2272.

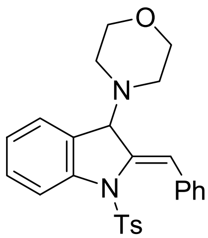


5d: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.68 (d, *J*=8.07 Hz, 1 H), 7.32 (d, *J*=8.44 Hz, 2 H), 7.23 - 7.28 (m, 1 H), 7.15 (d, *J*=7.34 Hz, 1 H), 7.04 - 7.10 (m, 3 H), 5.84 - 5.89 (m, 1 H), 4.48 - 4.54 (m, 1 H), 4.39 - 4.46 (m, 1 H), 3.86 (br. s., 1 H), 3.35 (s, 3 H), 2.52 - 2.60 (m, 2 H), 2.33 - 2.38 (m, 2 H), 2.32 (s, 3 H), 1.41 - 1.46 (m, 4 H), 1.36 - 1.40 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 144.2, 142.1, 140.1, 133.9, 133.4, 129.0, 128.1, 127.8, 125.4, 125.2, 121.3, 119.9, 69.9, 68.4, 58.0, 50.3, 26.6, 24.5, 21.5; HRMS (ESI+) calculated for $C_{23}H_{29}N_2O_3S$ (M^++H): 413.1899, Found: 413.1901.

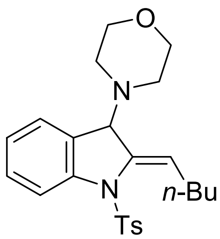


5e: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.66 - 7.70 (m, 1 H), 7.30 - 7.35 (m, 2 H), 7.23 - 7.28 (m, 1 H), 7.14 - 7.18 (m, 1 H), 7.04 - 7.09 (m, 3 H), 5.80 - 5.86 (m, 1 H), 4.76 (ddd, *J*=14.40, 8.16, 1.10 Hz, 1 H), 4.52 - 4.59 (m, 1 H), 3.84 (br. s., 1 H), 2.55 - 2.62 (m, 2 H), 2.29 - 2.37 (m, 5 H), 1.35 - 1.47 (m, 6 H), 0.89

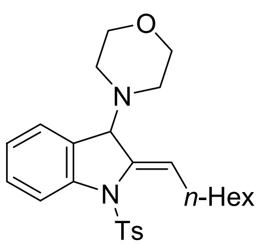
(s, 9 H), 0.09 (s, 3 H), 0.06 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 144.1, 142.2, 137.8, 134.1, 133.5, 129.0, 128.1, 127.9, 125.3, 125.2, 124.3, 119.9, 68.2, 60.9, 50.3, 26.6, 25.9, 24.6, 21.5, 18.2, -5.1; HRMS (ESI+) calculated for $C_{28}H_{41}N_2O_3SSi$ (M^++H): 513.2607, Found: 513.2596.



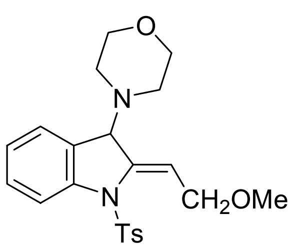
5f: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.76 - 7.88 (m, 3 H), 7.31 - 7.43 (m, 5 H), 7.21 - 7.31 (m, 2 H), 7.10 - 7.17 (m, 1 H), 7.07 (d, *J*=8.07 Hz, 2 H), 6.62 (d, *J*=1.28 Hz, 1 H), 3.97 - 4.04 (m, 1 H), 3.51 - 3.68 (m, 4 H), 2.65 - 2.81 (m, 2 H), 2.45 - 2.58 (m, 2 H), 2.34 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 144.1, 142.7, 137.9, 135.8, 134.0, 132.6, 129.4, 129.0, 128.6, 128.0, 127.9, 127.5, 125.6, 125.3, 122.3, 120.3, 68.8, 67.4, 49.4, 21.5; HRMS (ESI+) calculated for $C_{26}H_{27}N_2O_3S$ (M^++H): 447.1742, Found: 447.1748



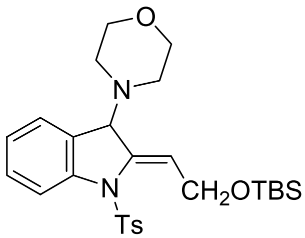
5g: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.71 (d, *J*=8.07 Hz, 1 H), 7.34 - 7.40 (m, 2 H), 7.26 - 7.31 (m, 1 H), 7.15 (d, *J*=7.52 Hz, 1 H), 7.04 - 7.10 (m, 3 H), 5.63 (ddd, *J*=8.12, 6.37, 1.83 Hz, 1 H), 3.70 (br. s., 1 H), 3.44 - 3.58 (m, 4 H), 2.49 - 2.68 (m, 4 H), 2.39 - 2.47 (m, 2 H), 2.32 (s, 3 H), 1.31 - 1.50 (m, 4 H), 0.91 (t, *J*=7.15 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 143.8, 143.0, 136.8, 134.4, 132.7, 128.9, 128.4, 128.0, 126.7, 125.5, 125.1, 120.0, 68.0, 67.2, 49.4, 31.7, 28.6, 22.4, 21.5, 13.9; HRMS (ESI+) calculated for $C_{24}H_{31}N_2O_3S$ (M^++H): 427.2055, Found: 427.2063.



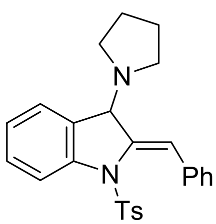
5h: ^{1}H NMR (5000 MHz, $CDCl_3$) δ ppm 7.71 (d, *J*=8.07 Hz, 1 H), 7.34 - 7.41 (m, 2 H), 7.27 - 7.32 (m, 1 H), 7.16 (d, *J*=7.52 Hz, 1 H), 7.03 - 7.11 (m, 3 H), 5.59 - 5.67 (m, 1 H), 3.70 (br. s., 1 H), 3.45 - 3.58 (m, 4 H), 2.48 - 2.66 (m, 4 H), 2.40 - 2.47 (m, 2 H), 2.33 (s, 3 H), 1.23 - 1.52 (m, 8 H), 0.82 - 0.92 (m, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 143.8, 143.0, 136.8, 134.5, 132.8, 129.0, 128.5, 128.0, 126.8, 125.5, 125.2, 120.1, 68.0, 67.3, 49.5, 31.7, 29.6, 29.1, 28.9, 22.6, 21.5, 14.1; HRMS (ESI+) calculated for $C_{26}H_{35}N_2O_3S$ (M^++H): 455.2368, Found: 455.2375.



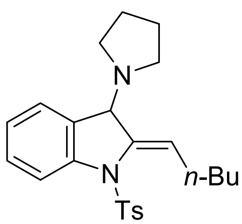
5i: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.71 (d, *J*=7.89 Hz, 1 H), 7.34 (d, *J*=8.25 Hz, 2 H), 7.27 - 7.32 (m, 1 H), 7.17 (d, *J*=7.52 Hz, 1 H), 7.04 - 7.12 (m, 3 H), 5.80 - 5.86 (m, 1 H), 4.46 - 4.53 (m, 1 H), 4.39 - 4.46 (m, 1 H), 3.81 (br. s., 1 H), 3.46 - 3.61 (m, 4 H), 3.36 (s, 3 H), 2.51 - 2.66 (m, 2 H), 2.38 - 2.51 (m, 2 H), 2.32 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 144.2, 142.4, 139.0, 134.0, 132.0, 129.1, 128.6, 127.9, 125.5, 125.4, 122.4, 119.8, 69.9, 68.0, 67.2, 58.3, 49.4, 21.5; HRMS (ESI+) calculated for $C_{22}H_{27}N_2O_4S$ (M^++H): 415.1692, Found: 415.1689.



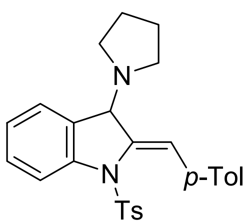
5j: [1]H NMR (500 MHz, $CDCl_3$) δ ppm 7.71 (d, *J*=8.07 Hz, 1 H), 7.34 (d, *J*=8.44 Hz, 2 H), 7.29 (t, *J*=7.43 Hz, 1 H), 7.17 (d, *J*=7.52 Hz, 1 H), 7.04 - 7.11 (m, 3 H), 4.68 - 4.75 (m, 1 H), 4.56 - 4.63 (m, 1 H), 3.79 (br. s., 1 H), 3.47 - 3.57 (m, 4 H), 2.55 - 2.62 (m, 2 H), 2.39 - 2.46 (m, 2 H), 2.32 (s, 3 H), 0.88 (s, 9 H), 0.09 (s, 3 H), 0.06 (s, 3 H); [13]C NMR (126 MHz, $CDCl_3$) δ ppm 144.1, 142.5, 137.0, 134.2, 132.1, 129.0, 128.6, 127.9, 125.6, 125.4, 125.3, 119.8, 67.9, 67.2, 60.8, 49.4, 25.8, 21.5, 18.2, -5.1, -5.2; HRMS (ESI+) calculated for $C_{27}H_{39}N_2O_4SSi$ (M^++H): 515.2400, Found: 515.2408.



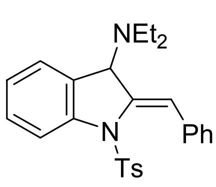
5k: [1]H NMR (500 MHz, $CDCl_3$) δ ppm 7.83 (d, *J*=8.07 Hz, 1 H), 7.80 (d, *J*=7.52 Hz, 2 H), 7.30 - 7.44 (m, 4 H), 7.23 - 7.29 (m, 1 H), 7.16 - 7.20 (m, 1 H), 7.10 (t, *J*=6.97 Hz, 1 H), 7.04 (d, *J*=8.07 Hz, 2 H), 6.41 (d, *J*=1.28 Hz, 1 H), 4.02 (br. s., 1 H), 2.48 - 2.63 (m, 4 H), 2.32 (s, 3 H), 1.53 - 1.70 (m, 4 H); [13]C NMR (126 MHz, $CDCl_3$) δ ppm 143.7, 143.2, 139.1, 135.7, 134.3, 133.5, 129.4, 128.6, 128.4, 128.2, 127.9, 127.4, 125.4, 125.2, 122.5, 119.8, 66.2, 49.5, 23.6, 21.5; HRMS (ESI+) calculated for $C_{26}H_{27}N_2O_2S$ (M^++H): 431.1793, Found: 431.1795.



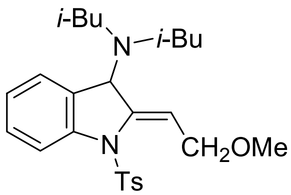
5l: [1]H NMR (500 MHz, $CDCl_3$) δ ppm 7.73 (d, *J*=8.07 Hz, 1 H), 7.41 (d, *J*=8.44 Hz, 2 H), 7.09 - 7.15 (m, 1 H), 6.98 - 7.09 (m, 3 H), 5.40 - 5.48 (m, 1 H), 3.67 (br. s., 3 H), 2.53 - 2.60 (m, 2 H), 2.40 - 2.49 (m, 2 H), 2.31 - 2.38 (m, 2 H), 2.31 (s, 3 H), 1.32 - 1.61 (m, 8 H), 0.92 (t, *J*=7.06 Hz, 3 H); [13]C NMR (126 MHz, $CDCl_3$) δ ppm 143.6, 143.4, 138.4, 134.8, 133.8, 128.6, 128.3, 128.1, 126.7, 125.6, 124.8, 119.6, 66.3, 50.0, 31.8, 28.4, 23.4, 22.5, 21.5, 14.0; HRMS (ESI+) calculated for $C_{24}H_{31}N_2O_2S$ (M^++H): 411.2106, Found: 411.2101.



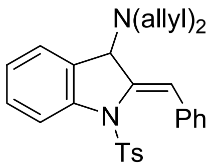
5m: [1]H NMR (500 MHz, $CDCl_3$) δ ppm 7.82 (d, *J*=7.89 Hz, 1 H), 7.70 (d, *J*=8.07 Hz, 2 H), 7.38 - 7.42 (m, 2 H), 7.30 - 7.36 (m, 1 H), 7.15 - 7.21 (m, 3 H), 7.07 - 7.12 (m, 1 H), 7.03 (d, *J*=8.07 Hz, 2 H), 6.36 (d, *J*=0.92 Hz, 1 H), 3.99 (br. s., 1 H), 2.48 - 2.60 (m, 4 H), 2.36 (s, 3 H), 2.31 (s, 3 H), 1.50 - 1.70 (m, 4 H); [13]C NMR (126 MHz, $CDCl_3$) δ ppm 143.6, 143.3, 138.3, 137.2, 134.4, 133.7, 132.8, 129.4, 128.6, 128.6, 128.4, 128.2, 125.4, 125.1, 122.6, 119.8, 66.3, 49.6, 23.6, 21.5, 21.4; HRMS (EI+) calculated for $C_{27}H_{28}N_2O_2S$ (M^+): 444.18715, Found: 444.18858.



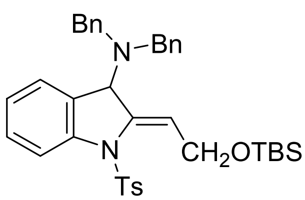
5n: [1]H NMR (500 MHz, $CDCl_3$) δ ppm 7.81 (d, *J*=7.70 Hz, 2 H), 7.77 (d, *J*=7.89 Hz, 1 H), 7.37 (t, *J*=7.70 Hz, 2 H), 7.27 - 7.35 (m, 3 H), 7.22 - 7.27 (m, 1 H), 7.04 - 7.16 (m, 4 H), 6.60 (d, *J*=2.38 Hz, 1 H), 4.08 - 4.15 (m, 1 H), 2.48 - 2.63 (m, 4 H), 2.34 (s, 3 H), 0.93 (t, *J*=7.06 Hz, 6 H); [13]C NMR (126 MHz, $CDCl_3$) δ ppm 144.2, 142.4, 140.6, 135.9, 135.0, 133.9, 129.4, 128.9, 128.0, 127.9, 127.3, 125.8, 124.3, 121.0, 120.7, 64.9, 45.0, 21.5, 14.8; HRMS (ESI+) calculated for $C_{26}H_{29}N_2O_2S$ (M^++H): 433.1950, Found: 433.1958.



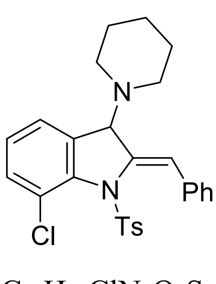
5o: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.66 (d, *J*=8.07 Hz, 1 H), 7.23 - 7.30 (m, 3 H), 7.04 - 7.14 (m, 4 H), 5.87 (dt, *J*=8.89, 2.89 Hz, 1 H), 4.53 (ddd, *J*=13.85, 8.99, 1.19 Hz, 1 H), 4.38 (dt, *J*=13.80, 3.37 Hz, 1 H), 3.83 (br. s., 1 H), 3.36 (s, 3 H), 2.34 (s, 3 H), 2.15 - 2.27 (m, 4 H), 1.47 - 1.57 (m, 2 H), 0.82 (d, *J*=6.60 Hz, 6 H), 0.76 (d, *J*=6.60 Hz, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 144.3, 142.0, 140.6, 134.5, 133.6, 128.9, 127.9, 127.8, 125.7, 124.4, 120.8, 120.5, 69.8, 65.2, 59.7, 58.2, 27.4, 21.4, 20.8, 20.5; HRMS (ESI+) calculated for $C_{26}H_{37}N_2O_3S$ (M^++H): 457.2525, Found: 457.2524.



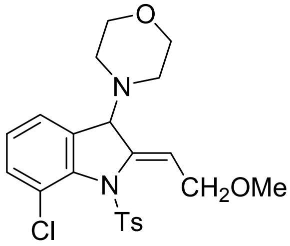
5p: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.83 (d, *J*=7.34 Hz, 2 H), 7.78 (d, *J*=8.07 Hz, 1 H), 7.37 - 7.41 (m, 2 H), 7.30 - 7.34 (m, 1 H), 7.26 - 7.30 (m, 3 H), 7.11 - 7.18 (m, 2 H), 7.05 (d, *J*=7.89 Hz, 2 H), 6.64 (d, *J*=2.57 Hz, 1 H), 5.64 - 5.75 (m, 2 H), 5.00 - 5.10 (m, 4 H), 4.19 (d, *J*=2.38 Hz, 1 H), 3.22 (dd, *J*=14.40, 4.68 Hz, 2 H), 3.05 (dd, *J*=14.31, 7.70 Hz, 2 H), 2.33 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 144.1, 142.5, 140.1, 136.6, 135.7, 134.6, 133.6, 129.5, 128.9, 128.1, 127.9, 127.4, 125.9, 124.1, 121.1, 120.8, 116.7, 63.5, 53.5, 21.5; HRMS (ESI+) calculated for $C_{28}H_{29}N_2O_2S$ (M^++H): 457.1950, Found: 457.1938.



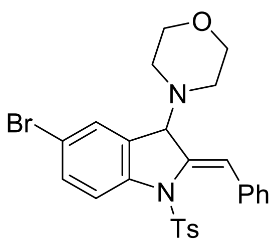
5q: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.71 (d, *J*=7.89 Hz, 1 H), 7.22 - 7.34 (m, 13 H), 7.13 - 7.18 (m, 1 H), 7.03 - 7.08 (m, 2 H), 6.68 - 6.73 (m, 2 H), 6.19 (dt, *J*=8.80, 2.66 Hz, 1 H), 4.85 (ddd, *J*=14.49, 8.99, 1.28 Hz, 1 H), 4.60 (dt, *J*=14.40, 3.07 Hz, 1 H), 3.89 (br. s., 1 H), 3.72 (d, *J*=13.57 Hz, 2 H), 3.49 (d, *J*=13.57 Hz, 2 H), 2.18 (s, 3 H), 0.91 (s, 9 H), 0.12 (s, 3 H), 0.05 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 143.9, 142.3, 139.0, 138.8, 134.2, 133.1, 128.7, 128.6, 128.2, 128.1, 127.3, 127.0, 125.9, 124.2, 124.2, 120.8, 61.5, 60.9, 54.2, 25.9, 21.5, 18.2, -5.1, -5.3; HRMS (EI+) calculated for $C_{37}H_{44}N_2O_3SSi$ (M^+): 624.28420, Found: 624.28396.



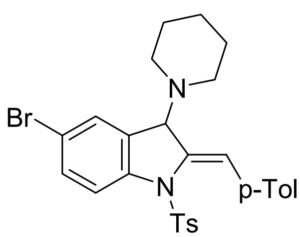
5r: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.70 - 7.74 (m, 2 H), 7.67 (dd, *J*=7.89, 0.73 Hz, 1 H), 7.39 - 7.43 (m, 2 H), 7.33 - 7.39 (m, 2 H), 7.23 - 7.29 (m, 2 H), 7.07 - 7.13 (m, 3 H), 6.54 (d, *J*=1.65 Hz, 1 H), 4.05 (d, *J*=1.65 Hz, 1 H), 2.46 - 2.60 (m, 4 H), 2.35 (s, 3 H), 1.31 - 1.50 (m, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 144.8, 144.2, 138.7, 135.9, 134.4, 131.5, 131.4, 129.6, 129.4, 129.0, 128.1, 127.9, 127.4, 126.6, 122.5, 117.5, 70.0, 50.1, 26.6, 24.3, 21.5. HRMS (ESI+) calculated for $C_{27}H_{28}ClN_2O_2S$ (M^++H): 479.1560, Found: 479.1553.



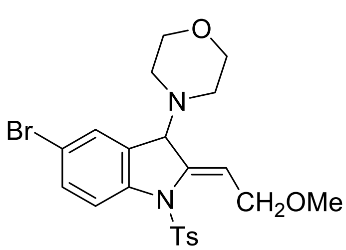
5s: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.61 (d, *J*=8.07 Hz, 1 H), 7.52 (d, *J*=8.25 Hz, 2 H), 7.25 (t, *J*=8.07 Hz, 1 H), 7.15 (d, *J*=8.44 Hz, 2 H), 7.05 - 7.10 (m, 1 H), 5.65 (t, *J*=5.69 Hz, 1 H), 4.35 - 4.46 (m, 2 H), 3.90 (br. s., 1 H), 3.42 - 3.49 (m, 2 H), 3.37 (s, 3 H), 3.29 - 3.35 (m, 2 H), 2.48 - 2.55 (m, 2 H), 2.29 - 2.38 (m, 5 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 144.7, 144.5, 138.3, 134.9, 132.1, 130.2, 129.3, 129.3, 128.1, 126.2, 123.1, 116.8, 69.8, 68.2, 66.9, 58.4, 49.4, 21.5; HRMS (EI+) calculated for $C_{22}H_{26}ClN_2O_4S$ (M^++H): 449.13018, Found: 449.13007.



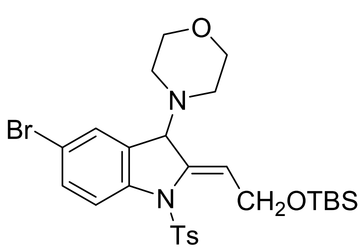
5t: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.53 (d, *J*=8.62 Hz, 1 H), 7.37 - 7.42 (m, 3 H), 7.33 (dd, *J*=8.44, 2.38 Hz, 1 H), 7.24 - 7.28 (m, 2 H), 7.16 - 7.23 (m, 3 H), 7.13 (d, *J*=8.07 Hz, 2 H), 6.05 (d, *J*=6.60 Hz, 1 H), 5.19 (d, *J*=6.60 Hz, 1 H), 3.74 - 3.81 (m, 2 H), 3.64 - 3.70 (m, 2 H), 2.56 - 2.64 (m, 2 H), 2.36 (s, 3 H), 1.94 - 2.21 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 145.1, 143.6, 138.5, 136.4, 133.3, 131.3, 130.4, 129.1, 128.8, 128.2, 127.8, 127.5, 127.4, 126.7, 120.2, 107.9, 66.7, 56.9, 50.7, 21.4; HRMS (EI+) calculated for $C_{26}H_{25}BrN_2O_3S$ (M^+): 524.07693, Found: 524.07677.



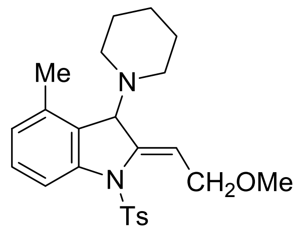
5u: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.48 (d, *J*=8.62 Hz, 1 H), 7.35 - 7.44 (m, 3 H), 7.30 (dd, *J*=8.44, 2.20 Hz, 1 H), 7.09 - 7.18 (m, 4 H), 7.01 (d, *J*=7.89 Hz, 2 H), 5.98 (d, *J*=6.42 Hz, 1 H), 5.11 (dd, *J*=6.42, 1.83 Hz, 1 H), 2.44 - 2.53 (m, 2 H), 2.35 (s, 3 H), 2.25 (s, 3 H), 1.87 - 2.19 (m, 2 H), 1.59 - 1.70 (m, 2 H), 1.40 - 1.58 (m, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 146.0, 143.4, 137.4, 136.5, 135.8, 133.1, 130.9, 130.2, 129.8, 129.1, 128.9, 127.5, 127.5, 126.9, 120.1, 107.4, 56.9, 51.7, 25.9, 24.3, 21.4, 21.0; HRMS (EI+) calculated for $C_{28}H_{29}N_2O_2S^{81}Br$ (M^+): 538.11127, Found: 538.11208.



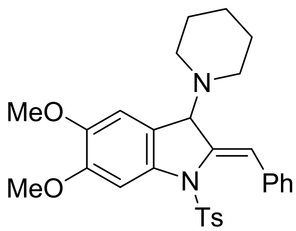
5v: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.58 (d, *J*=8.62 Hz, 1 H), 7.39 - 7.44 (m, 1 H), 7.33 - 7.37 (m, 2 H), 7.29 - 7.32 (m, 1 H), 7.09 - 7.14 (m, 2 H), 5.83 (ddd, *J*=7.15, 4.68, 2.11 Hz, 1 H), 4.44 - 4.50 (m, 1 H), 4.36 - 4.43 (m, 1 H), 3.81 (br. s., 1 H), 3.49 - 3.59 (m, 4 H), 3.36 (s, 3 H), 2.53 - 2.60 (m, 2 H), 2.39 - 2.45 (m, 2 H), 2.35 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 144.6, 141.6, 138.3, 134.4, 133.8, 131.7, 129.3, 128.4, 127.9, 122.7, 121.3, 118.7, 69.8, 67.9, 67.2, 58.3, 49.3, 21.5; HRMS (EI+) calculated for $C_{22}H_{25}N_2O_4S^{81}Br$ (M^+): 494.06980, Found: 494.06873.



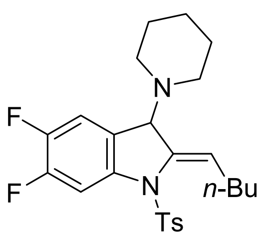
5w: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.58 (d, *J*=8.62 Hz, 1 H), 7.39 - 7.43 (m, 1 H), 7.33 - 7.37 (m, 2 H), 7.30 - 7.32 (m, 1 H), 7.09 - 7.13 (m, 2 H), 5.79 (ddd, *J*=7.29, 4.45, 2.02 Hz, 1 H), 4.66 - 4.72 (m, 1 H), 4.56 (ddd, *J*=14.63, 4.45, 2.57 Hz, 1 H), 3.79 (br. s., 1 H), 3.48 - 3.58 (m, 4 H), 2.55 - 2.61 (m, 2 H), 2.38 - 2.44 (m, 2 H), 2.34 (s, 3 H), 0.88 (s, 9 H), 0.08 (s, 3 H), 0.05 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 144.5, 141.6, 136.3, 134.4, 133.9, 131.7, 129.3, 128.4, 127.9, 125.7, 121.2, 118.6, 67.7, 67.2, 60.7, 49.3, 26.0, 25.8, 21.5, 18.2, -5.2, -5.2; HRMS (EI+) calculated for $C_{27}H_{37}BrN_2O_4SSi$ (M^+): 592.14267, Found: 592.14311.



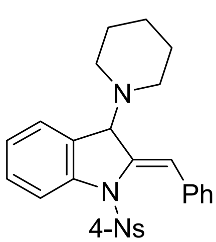
5x: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.19 - 7.24 (m, 2 H), 7.08 - 7.16 (m, 3 H), 7.04 (t, *J*=7.43 Hz, 1 H), 6.96 (d, *J*=7.34 Hz, 1 H), 5.86 - 5.92 (m, 1 H), 4.57 - 4.66 (m, 1 H), 4.35 - 4.42 (m, 1 H), 3.41 (br. s., 1 H), 3.37 (s, 3 H), 2.57 (s, 3 H), 2.46 - 2.56 (m, 2 H), 2.38 (s, 3 H), 2.05 - 2.32 (m, 2 H), 1.30 - 1.51 (m, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 144.3, 142.2, 141.6, 136.0, 133.1, 132.5, 130.7, 128.9, 128.6, 126.0, 121.7, 121.4, 69.6, 67.8, 58.1, 26.8, 24.5, 21.6, 19.5; HRMS (ESI+) calculated for $C_{24}H_{31}N_2O_3S$ (M^++H): 427.2055, Found: 427.2044.



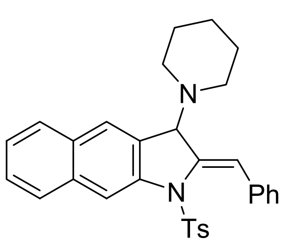
5y: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.81 (d, *J*=7.52 Hz, 2 H), 7.35 - 7.42 (m, 3 H), 7.33 (d, *J*=8.25 Hz, 2 H), 7.22 - 7.29 (m, 1 H), 7.07 (d, *J*=8.07 Hz, 2 H), 6.70 (s, 1 H), 6.60 (d, *J*=2.20 Hz, 1 H), 4.00 (s, 3 H), 3.95 (d, *J*=2.02 Hz, 1 H), 3.85 (s, 3 H), 2.60 - 2.71 (m, 2 H), 2.37 - 2.44 (m, 2 H), 2.35 (s, 3 H), 1.36 - 1.56 (m, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 149.1, 147.2, 144.0, 139.6, 136.1, 135.6, 133.6, 129.4, 128.9, 128.1, 127.8, 127.2, 125.5, 121.4, 107.7, 104.5, 69.3, 56.3, 50.3, 26.8, 24.6, 21.6; HRMS (ESI+) calculated for $C_{29}H_{33}N_2O_4S$ (M^++H): 505.2161, Found: 505.2163.



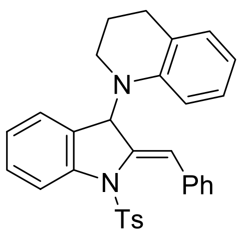
5z: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.54 (dd, *J*=10.64, 6.97 Hz, 1 H), 7.36 (d, *J*=8.25 Hz, 2 H), 7.12 (d, *J*=8.07 Hz, 2 H), 6.93 (t, *J*=8.53 Hz, 1 H), 5.68 (td, *J*=5.96, 2.75 Hz, 1 H), 3.72 (br. s., 1 H), 2.57 - 2.67 (m, 1 H), 2.43 - 2.55 (m, 3 H), 2.36 (s, 3 H), 2.26 - 2.34 (m, 2 H), 1.31 - 1.52 (m, 10 H), 0.92 (t, *J*=7.15 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 150.8 (d, *J*=12.9 Hz), 149.2 (d, *J*=12.9 Hz), 148.8 (d, *J*=13.9 Hz), 147.3 (d, *J*=13.9 Hz), 144.3, 138.5 (d, *J*=8.3 Hz), 137.2, 133.9, 130.4, 129.2, 127.9, 126.0, 113.4 (d, *J*=19.4 Hz), 110.0 (d, *J*=22.2 Hz), 68.1, 50.2, 31.8, 28.5, 26.6, 24.5, 22.4, 21.6, 14.0; HRMS (ESI+) calculated for $C_{25}H_{31}F_2N_2O_2S$ (M^++H): 461.2074, Found: 461.2083.



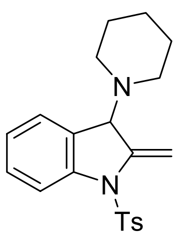
5aa: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.07 - 8.15 (m, 2 H), 7.80 (d, *J*=7.89 Hz, 1 H), 7.76 (d, *J*=7.52 Hz, 2 H), 7.66 (d, *J*=8.62 Hz, 2 H), 7.33 - 7.45 (m, 3 H), 7.21 - 7.32 (m, 2 H), 7.12 - 7.19 (m, 1 H), 6.66 (d, *J*=1.10 Hz, 1 H), 3.99 (s, 1 H), 2.58 - 2.75 (m, 2 H), 2.34 - 2.51 (m, 2 H), 1.34 - 1.54 (m, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 150.3, 142.5, 141.6, 137.9, 135.6, 133.3, 129.4, 129.3, 128.6, 128.1, 127.7, 126.1, 125.8, 123.4, 122.8, 120.0, 69.1, 50.5, 26.6, 24.4; HRMS (ESI+) calculated for $C_{26}H_{26}N_3O_4S$ (M^++H): 476.1644, Found: 476.1634.



5ab: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.10 (s, 1 H), 7.75 - 7.84 (m, 2 H), 7.74 (s, 1 H), 7.40 - 7.47 (m, 2 H), 7.34 - 7.40 (m, 2 H), 7.29 - 7.34 (m, 2 H), 7.09 - 7.21 (m, 3 H), 7.05 (d, *J*=8.07 Hz, 2 H), 6.11 (d, *J*=6.60 Hz, 1 H), 5.27 (d, *J*=6.60 Hz, 1 H), 2.56 - 2.69 (m, 2 H), 2.32 (s, 3 H), 1.99 - 2.27 (m, 1 H), 1.68 - 1.78 (m, 2 H), 1.43 - 1.67 (m, 5 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 147.2, 143.1, 139.4, 136.8, 132.9, 131.9, 131.6, 129.1, 128.2, 128.0, 127.7, 127.5, 127.5, 127.0, 126.2, 126.0, 126.0, 123.2, 107.6, 57.4, 51.9, 26.1, 24.5, 21.3; HRMS (ESI+) calculated for $C_{31}H_{31}N_2O_2S$ (M^++H): 495.2106, Found: 495.2097.

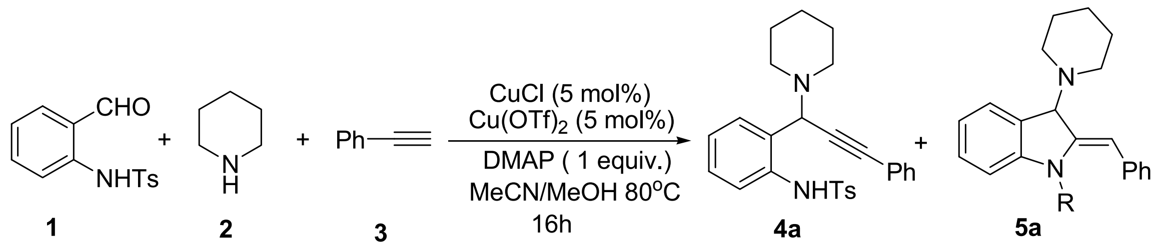


5ac: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.25 (d, *J*=8.44 Hz, 1 H), 7.39 - 7.43 (m, 2 H), 7.30 - 7.35 (m, 1 H), 7.15 - 7.23 (m, 5 H), 7.08 - 7.14 (m, 4 H), 7.00 (dd, *J*=7.52, 0.73 Hz, 1 H), 6.72 - 6.77 (m, 1 H), 6.61 (ddd, *J*=7.34, 1.10 Hz, 1 H), 5.88 - 5.92 (m, 1 H), 4.50 (d, *J*=15.96 Hz, 1 H), 4.19 (d, *J*=15.96 Hz, 1 H), 3.52 - 3.59 (m, 1 H), 3.21 - 3.28 (m, 1 H), 2.84 - 2.92 (m, 1 H), 2.74 - 2.83 (m, 1 H), 2.35 (s, 3 H), 1.92 - 2.07 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 144.6, 144.0, 138.9, 136.7, 136.3, 135.6, 129.6, 129.3, 128.6, 128.2, 127.4, 126.7, 126.5, 126.1, 124.8, 123.6, 122.0, 118.9, 117.1, 115.9, 113.0, 50.3, 31.5, 27.8, 22.4, 21.5. HRMS (ESI+) calculated for $C_{31}H_{29}N_2O_2S$ (M^++H): 493.1950, Found: 493.1933.



5ad: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.86 - 7.91 (m, 1 H), 7.64 - 7.69 (m, 2 H), 7.26 - 7.33 (m, 2 H), 7.15 - 7.21 (m, 2 H), 7.07 (td, *J*=7.43, 0.92 Hz, 1 H), 5.79 (dd, *J*=2.11, 1.38 Hz, 1 H), 4.91 - 4.95 (m, 1 H), 4.46 (br. s., 1 H), 2.34 (s, 3 H), 2.06 - 2.16 (m, 4 H), 1.23 - 1.39 (m, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 144.5, 144.4, 142.1, 134.9, 129.6, 129.3, 129.0, 127.4, 125.8, 124.1, 115.3, 98.9, 68.3, 49.3, 26.5, 24.4, 21.5; HRMS (ESI+) calculated for $C_{21}H_{25}N_2O_2S$ (M^++H): 369.1637, Found: 369.1632.

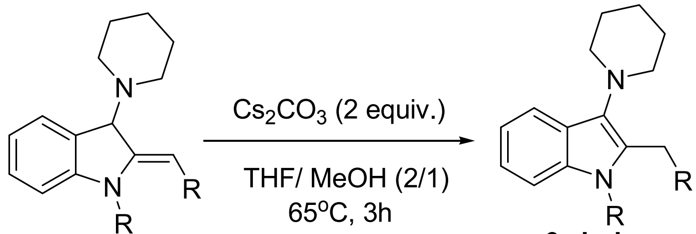
Scheme S2. TCC Synthesis of 3-Aminoindoline (5a) employing protic solvent



	4a	5a
20% MeOH in MeCN (v/v)	**1%**	**70%**
50% MeOH in MeCN (v/v)	**3%**	**67%**
100% MeOH (v/v)	**9%**	**66%**

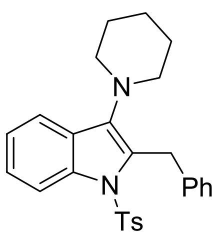
General Procedure: In a dry and argon flushed Wheaton 1mL V-vial, equipped with a magnetic stirring bar and a screw cap, CuCl (1.5 mg, 0.015 mmol, 5 mol%), $Cu(OTf)_2$ (5.4 mg, 0.015 mmol, 5 mol%), DMAP (36.7 mg, 0.3 mmol, 1 equiv.) and aldehyde (0.3 mmol, 1 equiv.) were suspended in dry acetonitrile-methanol mixture (0.3 mL). Secondary amine (0.3 mmol, 1 equiv.) and alkyne (0.45 mmol, 1.5 equiv.) were added and the reaction mixture was stirred at 80^{o}C until TLC analysis showed full conversion of the aldehyde. The reaction mixture was then filtered through Celite and washed with dichloromethane. The crude product was concentrated *in vacuo* and purified by column chromatography on silica gel. Reaction yields employing different amounts of MeOH are shown in the Scheme S2. No formation of indole product was observed.

Scheme S3. Isomerization of 3-Aminoindolines (5).

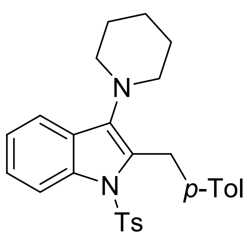


5 a,b,d → **6a,b,d**

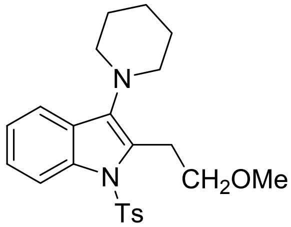
General Procedure: Indoline **5** (0.2 mmol) was dissolved in 1.5 mL THF/MeOH mixture (2/1). Cs_2CO_3 (130 mg, 0.4 mmol) was added and the reaction mixture was stirred at 65°C until TLC analysis showed full conversion of the indoline **5** (3 hours). The reaction mixture was then filtered through Celite and washed with ethyl acetate. The crude product **6** was concentrated *in vacuo* and purified by column chromatography on silica gel.



6a: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.18 (d, *J*=8.25 Hz, 1 H), 7.69 (d, *J*=7.52 Hz, 1 H), 7.31 (d, *J*=8.44 Hz, 2 H), 7.16 - 7.29 (m, 7 H), 6.98 - 7.05 (m, 2 H), 4.55 (s, 2 H), 3.08 - 3.16 (m, 4 H), 2.26 - 2.32 (m, 3 H), 1.63 - 1.71 (m, 4 H), 1.54 - 1.62 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 144.1, 139.9, 135.8, 135.6, 135.4, 133.6, 129.3, 128.6, 128.1, 128.1, 126.4, 125.8, 123.8, 122.8, 119.9, 115.5, 53.3, 30.9, 26.9, 24.3, 21.4; HRMS (EI+) calculated for $C_{27}H_{28}N_2O_2S$ (M^+): 444.18715, Found: 444.18603.

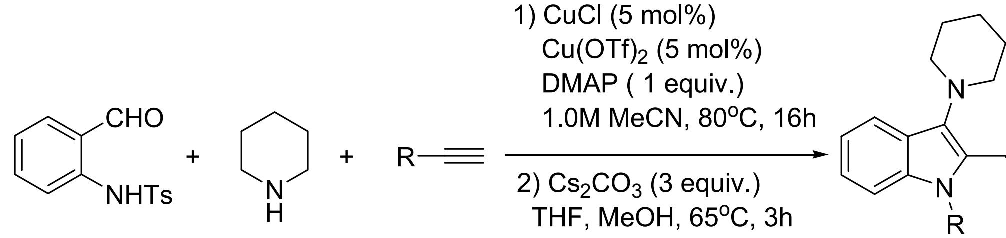


6b: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.17 (d, *J*=8.25 Hz, 1 H), 7.67 (d, *J*=7.52 Hz, 1 H), 7.30 (d, *J*=8.25 Hz, 2 H), 7.16 - 7.26 (m, 2 H), 7.05 - 7.10 (m, 2 H), 6.98 - 7.03 (m, 4 H), 4.48 (s, 2 H), 3.10 (s, 4 H), 2.31 (s, 3 H), 2.29 (s, 3 H), 1.52 - 1.68 (m, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 144.0, 136.8, 135.9, 135.8, 135.4, 135.2, 133.8, 129.3, 128.8, 128.5, 128.1, 126.4, 123.8, 122.8, 119.8, 115.5, 53.4, 30.5, 26.9, 24.3, 21.5, 21.0; HRMS (EI+) calculated for $C_{28}H_{30}N_2O_2S$ (M^+): 458.20280, Found: 458.20373.



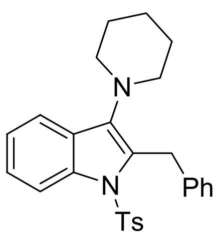
6d: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.19 (d, *J*=8.25 Hz, 1 H), 7.53 - 7.60 (m, 3 H), 7.21 - 7.26 (m, 1 H), 7.12 - 7.20 (m, 3 H), 3.68 (t, *J*=7.24 Hz, 2 H), 3.34 - 3.40 (m, 5 H), 3.03 - 3.07 (m, 4 H), 2.32 (s, 3 H), 1.63 - 1.72 (m, 4 H), 1.53 - 1.62 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 144.4, 136.2, 136.1, 135.6, 131.4, 129.6, 128.4, 126.2, 123.9, 123.0, 119.7, 115.7, 72.4, 58.5, 53.3, 26.9, 26.4, 24.3, 21.5; HRMS (EI+) calculated for $C_{23}H_{28}N_2O_3S$ (M^+): 412.18207, Found: 412.18114.

Scheme S4. **One-pot TCC Synthesis of Indoles (6).**

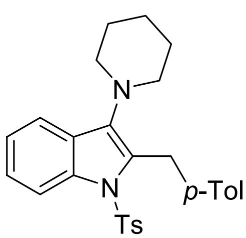


1a **2a** **3** **6a, b, d**

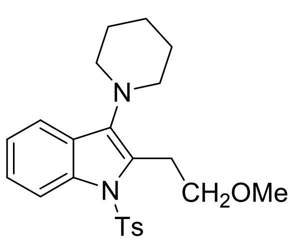
General Procedure: In a dry and argon flushed Wheaton 3mL V-vial, equipped with a magnetic stirring bar and a screw cap, CuCl (0.015 mmol, 5 mol%), $Cu(OTf)_2$ (0.015 mmol, 5 mol%), DMAP (0.3 mmol, 1 equiv.) and aldehyde **1a** (0.3 mmol, 1 equiv.) were suspended in dry acetonitrile (0.3 mL). Secondary amine **2a** (0.3 mmol, 1 equiv.) and alkyne **3** (0.45 mmol, 1.5 equiv.) were added and the reaction mixture was stirred at 80°C until TLC analysis showed full conversion of the aldehyde **1a**. The reaction mixture was then filtered through Celite and washed with dichloromethane. Solvent was evaporated under reduced pressure. The resulting crude product was dissolved in 1.5 mL THF/MeOH mixture (2/1). Cs_2CO_3 (293 mg, 0.9 mmol) was added and the reaction mixture was stirred at 65°C for 3 hours. The reaction mixture then was filtered through Celite and washed with ethyl acetate. The crude product **6** was concentrated *in vacuo* and purified by column chromatography on silica gel to afford desired 3-aminoindole product **6**.



6a: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.18 (d, *J*=8.25 Hz, 1 H), 7.69 (d, *J*=7.52 Hz, 1 H), 7.31 (d, *J*=8.44 Hz, 2 H), 7.16 - 7.29 (m, 7 H), 6.98 - 7.05 (m, 2 H), 4.55 (s, 2 H), 3.08 - 3.16 (m, 4 H), 2.26 - 2.32 (m, 3 H), 1.63 - 1.71 (m, 4 H), 1.54 - 1.62 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 144.1, 139.9, 135.8, 135.6, 135.4, 133.6, 129.3, 128.6, 128.1, 128.1, 126.4, 125.8, 123.8, 122.8, 119.9, 115.5, 53.3, 30.9, 26.9, 24.3, 21.4; HRMS (EI+) calculated for $C_{27}H_{28}N_2O_2S$ (M^+): 444.18715, Found: 444.18603.



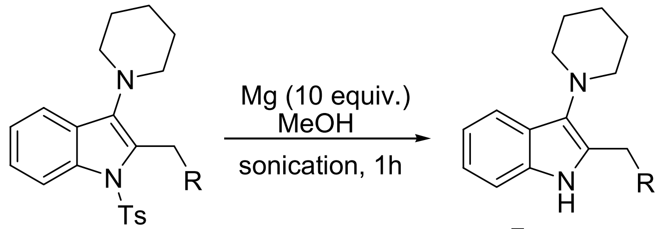
6b: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.17 (d, *J*=8.25 Hz, 1 H), 7.67 (d, *J*=7.52 Hz, 1 H), 7.30 (d, *J*=8.25 Hz, 2 H), 7.16 - 7.26 (m, 2 H), 7.05 - 7.10 (m, 2 H), 6.98 - 7.03 (m, 4 H), 4.48 (s, 2 H), 3.10 (s, 4 H), 2.31 (s, 3 H), 2.29 (s, 3 H), 1.52 - 1.68 (m, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 144.0, 136.8, 135.9, 135.8, 135.4, 135.2, 133.8, 129.3, 128.8, 128.5, 128.1, 126.4, 123.8, 122.8, 119.8, 115.5, 53.4, 30.5, 26.9, 24.3, 21.5, 21.0; HRMS (EI+) calculated for $C_{28}H_{30}N_2O_2S$ (M^+): 458.20280, Found: 458.20373.



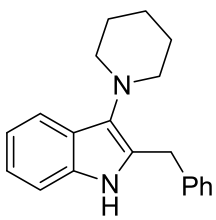
6d: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.19 (d, *J*=8.25 Hz, 1 H), 7.53 - 7.60 (m, 3 H), 7.21 - 7.26 (m, 1 H), 7.12 - 7.20 (m, 3 H), 3.68 (t, *J*=7.24 Hz, 2 H), 3.34 - 3.40 (m, 5 H), 3.03 - 3.07 (m, 4 H), 2.32 (s, 3 H), 1.63 - 1.72 (m, 4 H), 1.53 - 1.62 (m, 2

H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 144.4, 136.2, 136.1, 135.6, 131.4, 129.6, 128.4, 126.2, 123.9, 123.0, 119.7, 115.7, 72.4, 58.5, 53.3, 26.9, 26.4, 24.3, 21.5; HRMS (EI+) calculated for $C_{23}H_{28}N_2O_3S$ (M^+): 412.18207, Found: 412.18114.

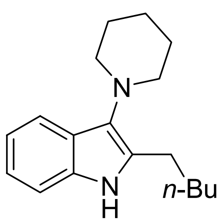
Scheme S5. Isomerization/Deprotection of 3-Aminoindoles (6).



General Procedure: In a dry and argon flushed 3 mL V-vial, magnesium granules (24.3 mg, 1 mmol, 10 equiv.) and indole **6** (0.1 mmol, 1 equiv.) were added followed by dry MeOH (2 mL). Bubbles were observed as the reaction mixture warmed. The reaction mixture was sonicated for 1 hour at rt. The resulting slurry was filtered through Celite and washed with ethyl acetate (10 mL). The filtrate was washed with water (10 mL) and brine (10 mL). The organic phase was dried (Na_2SO_4) and concentrated under reduced pressure. Indole **7** was purified by column chromatography on silica gel.

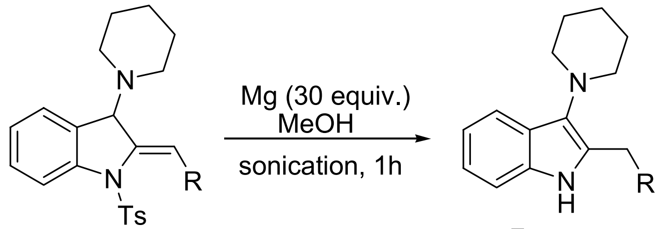


7a: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.74 - 7.82 (m, 1 H), 7.42 (br. s., 1 H), 7.29 - 7.34 (m, 2 H), 7.21 - 7.26 (m, 3 H), 7.17 - 7.21 (m, 1 H), 7.02 - 7.12 (m, 2 H), 4.19 (s, 2 H), 3.17 - 3.28 (m, 4 H), 1.68 - 1.79 (m, 4 H), 1.58 - 1.66 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 139.5, 134.4, 131.1, 128.7, 128.6, 127.9, 126.4, 125.3, 120.9, 119.7, 118.7, 111.0, 54.5, 31.7, 27.3, 24.5; HRMS (EI+) calculated for $C_{20}H_{22}N_2$ (M^+): 290.17830, Found: 290.17744.



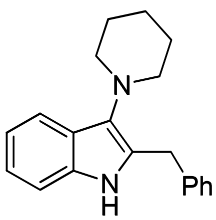
7c: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.76 (dd, *J*=7.43, 0.83 Hz, 1 H), 7.53 (br. s., 1 H), 7.24 - 7.29 (m, 1 H), 7.04 - 7.15 (m, 2 H), 3.15 - 3.21 (m, 4 H), 2.80 (t, *J*=7.61 Hz, 2 H), 1.70 - 1.79 (m, 4 H), 1.59 - 1.70 (m, 4 H), 1.33 - 1.46 (m, 4 H), 0.94 (t, *J*=7.06 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 134.0, 133.2, 127.1, 125.6, 120.4, 119.4, 118.6, 110.7, 54.3, 31.4, 29.3, 27.2, 25.4, 24.6, 22.4, 14.0; HRMS (EI+) calculated for $C_{18}H_{26}N_2$ (M^+): 270.20960, Found: 270.20947.

Scheme S6. Isomerization/Deprotection of 3-Aminoindolines (5).

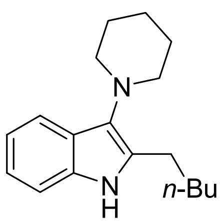


5a,c **7a, c**

General Procedure: In a dry and argon flushed 5 mL V-vial, magnesium granules (145 mg, 6 mmol, 30 equiv.) and indoline **5** (0.2 mmol, 1 equiv.) were added followed by dry MeOH (4 mL). Bubbles were observed as the reaction mixture warmed. The reaction mixture was sonicated for 1 hour at rt. The resulting slurry was filtered through Celite and washed with ethyl acetate (25 mL). The filtrate was washed with water (20 mL) and brine (20 mL). The organic phase was dried (Na_2SO_4) and concentrated under reduced pressure. Indole product **7** was purified by column chromatography on silica gel.

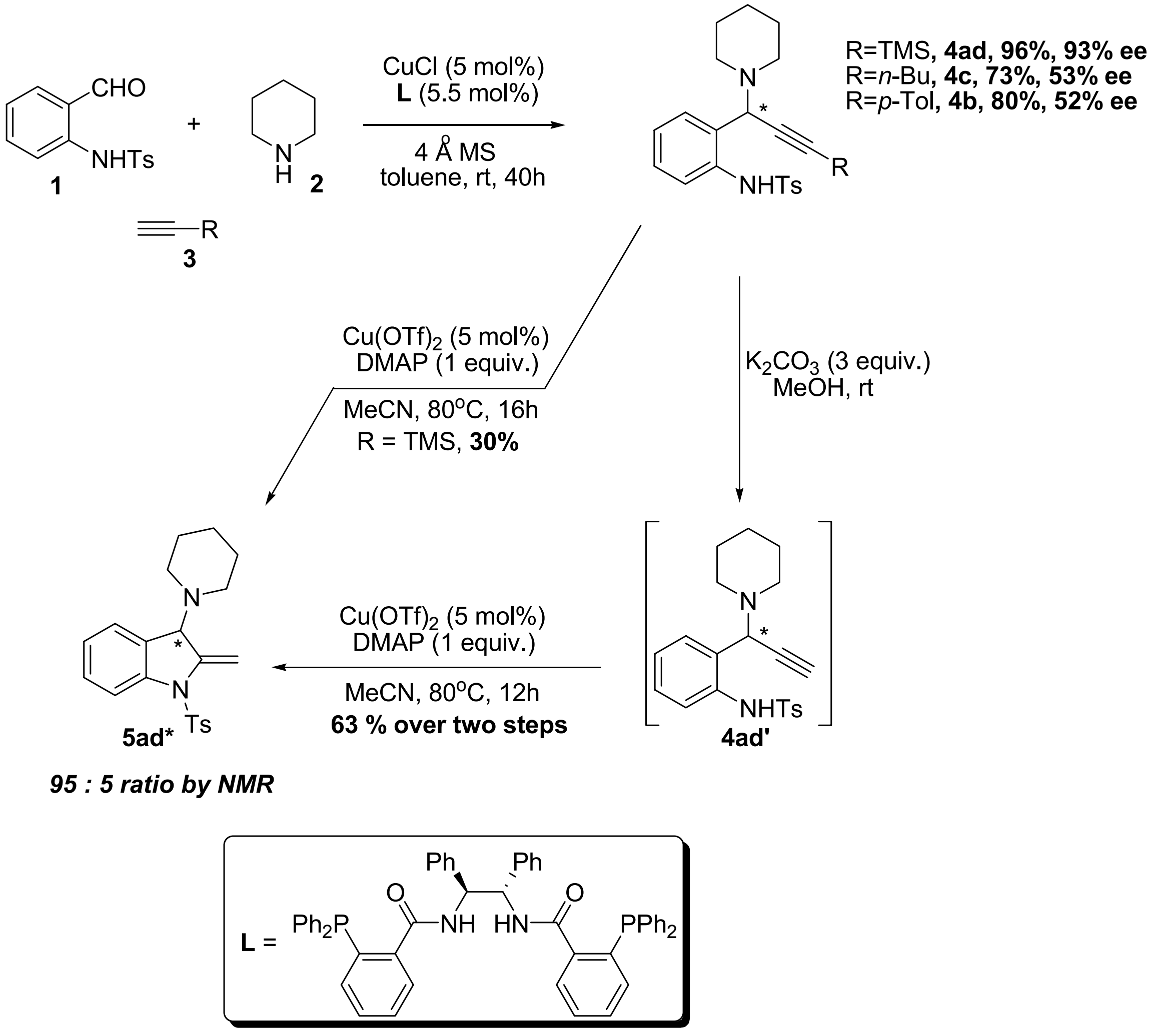


7a: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.74 - 7.82 (m, 1 H), 7.42 (br. s., 1 H), 7.29 - 7.34 (m, 2 H), 7.21 - 7.26 (m, 3 H), 7.17 - 7.21 (m, 1 H), 7.02 - 7.12 (m, 2 H), 4.19 (s, 2 H), 3.17 - 3.28 (m, 4 H), 1.68 - 1.79 (m, 4 H), 1.58 - 1.66 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 139.5, 134.4, 131.1, 128.7, 128.6, 127.9, 126.4, 125.3, 120.9, 119.7, 118.7, 111.0, 54.5, 31.7, 27.3, 24.5; HRMS (EI+) calculated for $C_{20}H_{22}N_2$ (M^+): 290.17830, Found: 290.17744.

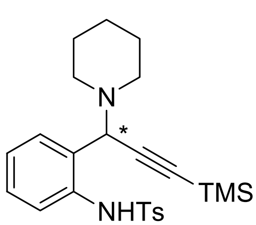


7c: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.76 (dd, *J*=7.43, 0.83 Hz, 1 H), 7.53 (br. s., 1 H), 7.24 - 7.29 (m, 1 H), 7.04 - 7.15 (m, 2 H), 3.15 - 3.21 (m, 4 H), 2.80 (t, *J*=7.61 Hz, 2 H), 1.70 - 1.79 (m, 4 H), 1.59 - 1.70 (m, 4 H), 1.33 - 1.46 (m, 4 H), 0.94 (t, *J*=7.06 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 134.0, 133.2, 127.1, 125.6, 120.4, 119.4, 118.6, 110.7, 54.3, 31.4, 29.3, 27.2, 25.4, 24.6, 22.4, 14.0; HRMS (EI+) calculated for $C_{18}H_{26}N_2$ (M^+): 270.20960, Found: 270.20947.

Scheme S7. Enantioselective TCC Synthesis of Indoline (5ad*).

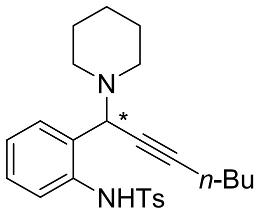


Experimental Procedure (4ad, 4c, 4b): In a dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, CuCl (0.025 mmol, 5 mol %) and ligand (0.027 mmol, 5.5 mol %) were suspended in dry toluene (2 mL) and stirred for 30 min. MS 4Å (0.3 g) were added, followed by the alkyne **3** (0.5 mmol), the aldehyde **1** (0.5 mmol) and the secondary amine **2** (0.5 mmol). The reaction mixture was stirred at rt until GC and TLC analysis showed full conversion. The crude reaction mixture was filtered through Celite and then washed with Et_2O. The crude product was concentrated under reduced pressure and purified by column chromatography on silica gel to give propargylamine **4**.

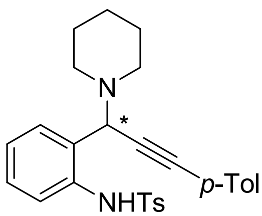


4ad: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.66 - 7.70 (m, 2 H), 7.52 - 7.56 (m, 1 H), 7.46 (dd, *J*=8.07, 1.10 Hz, 1 H), 7.20 - 7.25 (m, 3 H), 7.01 - 7.07 (m, 1 H), 4.23 (s, 1 H), 2.40 - 2.46 (m, 2 H), 2.37 (s, 3 H), 1.56 - 1.74 (m, 4 H), 1.39 - 1.55 (m, 2 H), 0.24 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 143.3, 138.0, 137.6, 129.6, 129.0, 128.8, 126.6, 125.7, 123.6, 120.7, 98.0, 95.0, 60.6, 25.9,

24.0, 21.4, 0.1. HPLC: (CHIRALCEL OD-H, 1% i-PrOH in hexanes, 1 mL/min, t(min)=7.845 3.5% and t(min)=8.271 96.5%; $[\alpha]^{25}_{D}$ = +20.2° (c=1, $CHCl_3$).



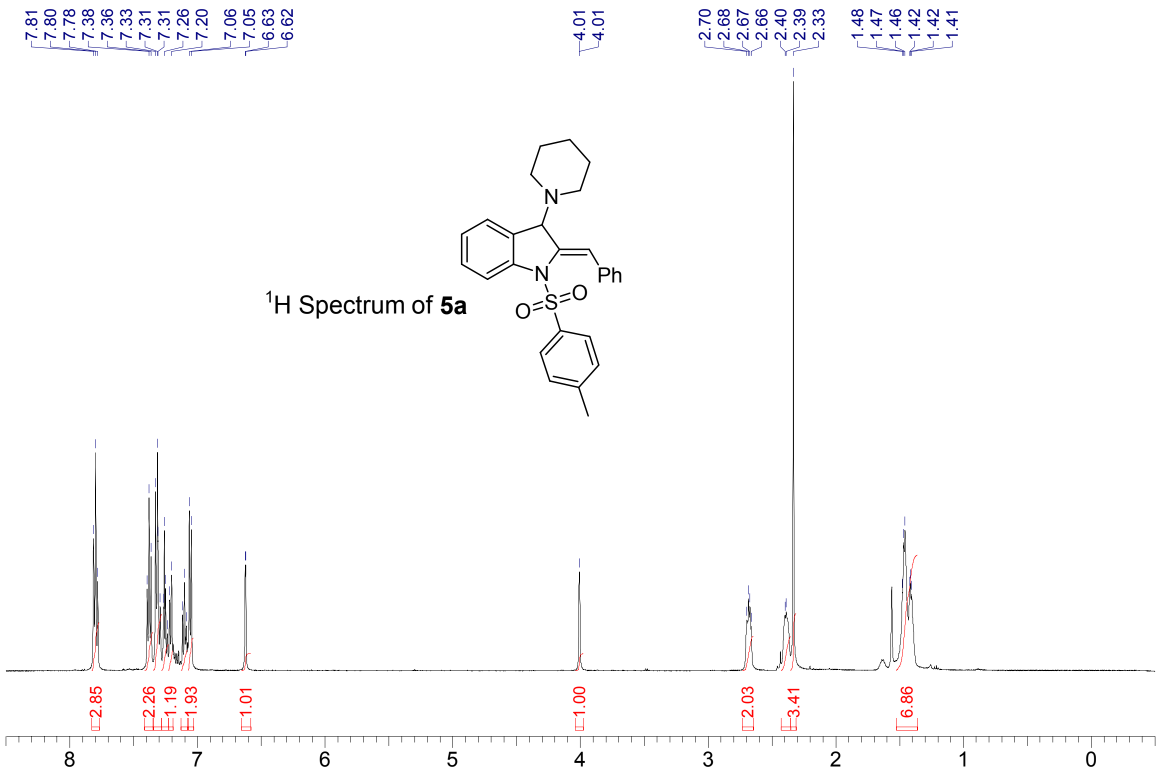
4c: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 11.41 (br. s., 1 H), 7.65 - 7.72 (m, 2 H), 7.54 (d, *J*=7.79 Hz, 1 H), 7.46 (d, *J*=8.02 Hz, 1 H), 7.18 - 7.24 (m, 3 H), 6.99 - 7.05 (m, 1 H), 4.21 (s, 1 H), 2.39 - 2.54 (m, 4 H), 2.36 (s, 3 H), 2.26 - 2.34 (m, 2 H), 1.61 - 1.74 (m, 4 H), 1.52 - 1.60 (m, 2 H), 1.40 - 1.52 (m, 4 H), 0.94 (t, *J*=7.22 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 143.16, 138.10, 137.54, 129.47, 129.04, 128.54, 126.57, 123.43, 120.50, 90.47, 72.40, 60.12, 30.91, 25.87, 24.02, 21.91, 21.35, 18.31, 13.44. HPLC: (CHIRALCEL OD, 0.5% i-PrOH in hexanes, 0.7 mL/min, t(min)=16.410 23.5% and t(min)=16.877 76.5%.

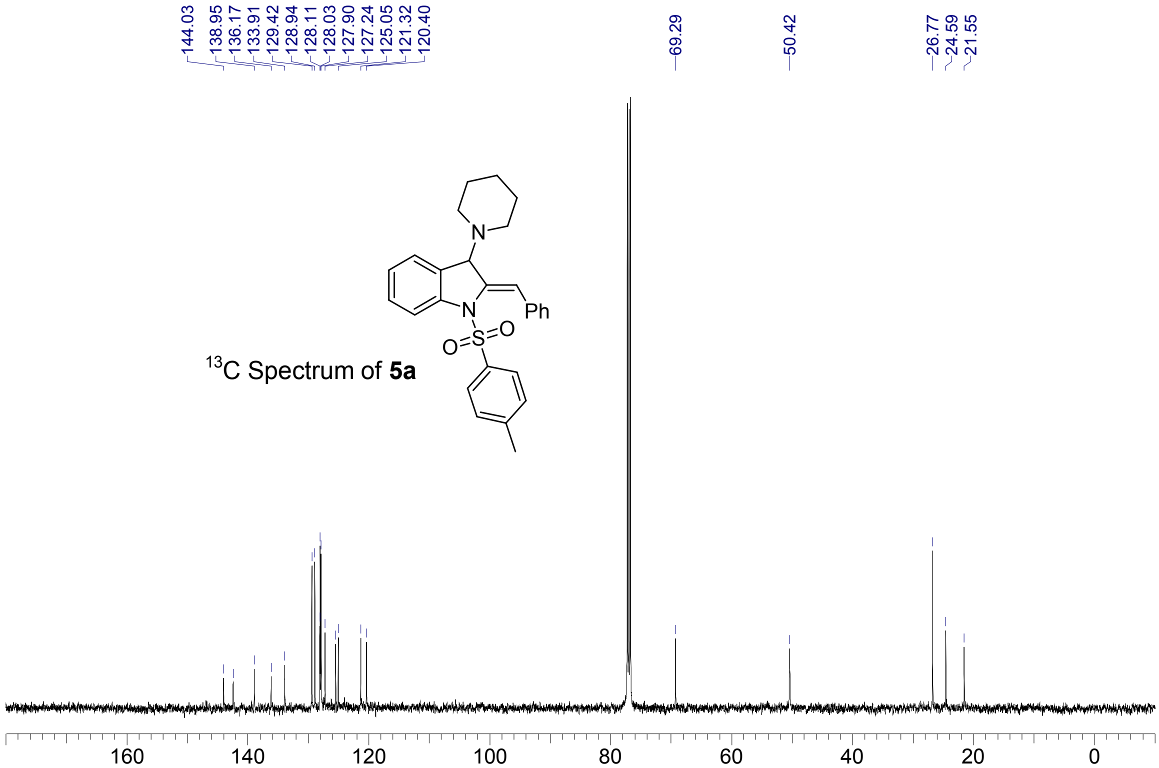


4b: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 11.43 (br. s., 1 H), 7.72 (d, *J*=8.02 Hz, 2 H), 7.60 - 7.65 (m, 1 H), 7.49 - 7.53 (m, 1 H), 7.40 (d, *J*=8.02 Hz, 2 H), 7.20 - 7.30 (m, 3 H), 7.16 (d, *J*=7.79 Hz, 2 H), 7.06 (t, *J*=7.45 Hz, 1 H), 4.44 (s, 1 H), 2.49 - 2.66 (m, 4 H), 2.38 (s, 3 H), 2.38 (s, 3 H), 1.61 - 1.80 (m, 4 H), 1.43 - 1.58 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 143.32, 138.71, 138.10, 137.59, 131.65, 129.61, 129.10, 128.84, 126.69, 126.23, 123.67, 120.78, 119.40, 90.14, 81.46, 60.65, 25.99, 24.05, 21.47. HPLC: (CHIRALCEL OD, 2% i-PrOH in hexanes, 1 mL/min, t(min)=9.222 76% and t(min)=10.835 24%.

Experimental Procedure (4ad'): Propargylamine **4ad** (132 mg, 0.3 mmol) was dissolved in 10 mL of MeOH. Potassium carbonate (124 mg, 0.9 mmol) was added and resulting suspension was stirred at room temperature for 30 minutes. The reaction mixture was diluted with 10 mL of distilled water and the mixture was extracted with hexanes (3 X 10 mL). The combined organic extracts were dried over sodium sulfate and concentrated under reduced pressure. The resulting propargylamine **4ad'** was obtained in 110 mg yield and was used without further purification.

Experimental Procedure (5ad*): Propargylamine **4ad'** (110 mg, 0.3 mmol) was dissolved in 0.3 mL of MeCN. $Cu(OTf)_2$ (5.4 mg, 0.015 mmol) and DMAP (36.7 mg 0.3 mmol) resulting suspension was stirred at 80°C for 12 hours. The reaction mixture was then filtered through Celite and washed with dichloromethane. Solvent was evaporated under reduced pressure. The resulting crude material was purified by column chromatography. Chiral indoline **5ad*** was obtaned in 63% (69 mg) isolated yield. Enantiomeric purity was determined by ^{1}H-NMR spectra of (*S*)-Mosher's acid salt of chiral indoline **5ad*** in deuterated benzene. Enatiomeric purity of **5ad*** was determined to be 95:5 (See pages S53 and S54); $[\alpha]^{25}_{D}$ = +139.6° (c=1.62, $CHCl_3$).


7.81
7.80
7.78
7.38
7.36
7.33
7.31
7.31
7.26
7.20
7.06
7.05
6.63
6.62
4.01
4.01
2.70
2.68
2.67
2.66
2.40
2.39
2.33
1.48
1.47
1.46
1.42
1.42
1.41
N
N
Ph
O=S=O
[1]H Spectrum of **5a**
2.85
2.26
1.19
1.93
1.01
1.00
2.03
3.41
6.86
8
7
6
5
4
3
2
1
0


144.03
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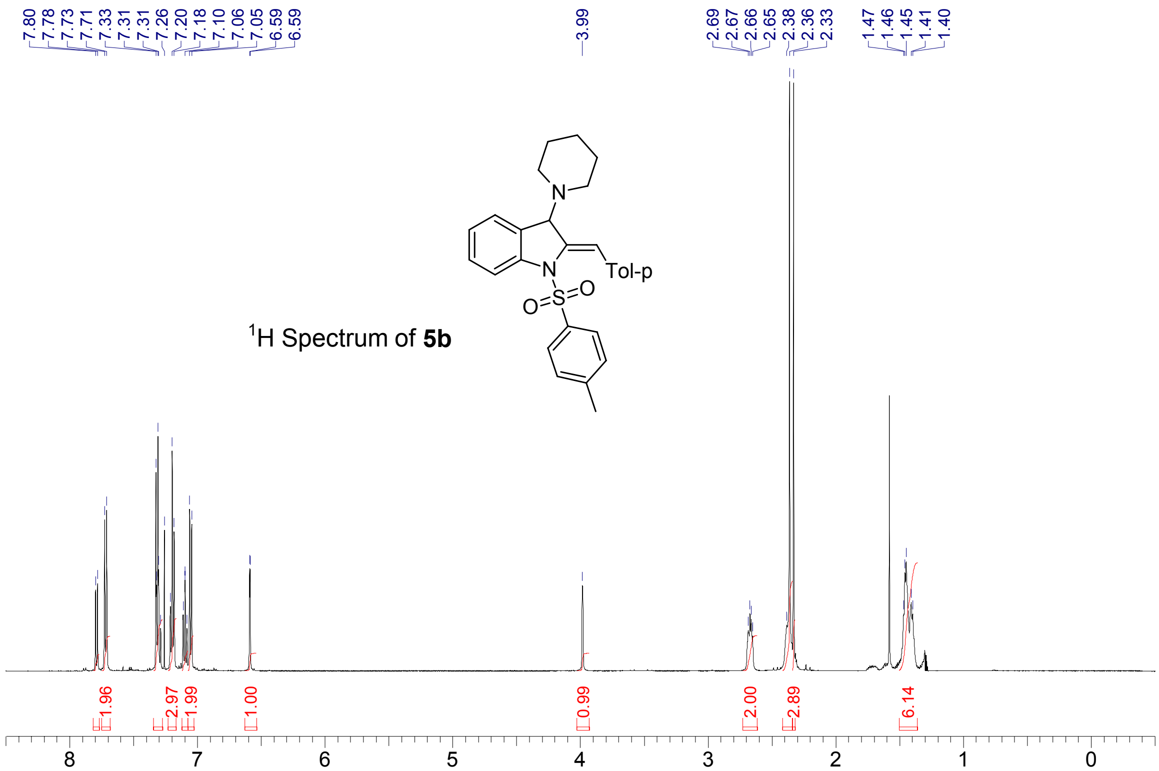
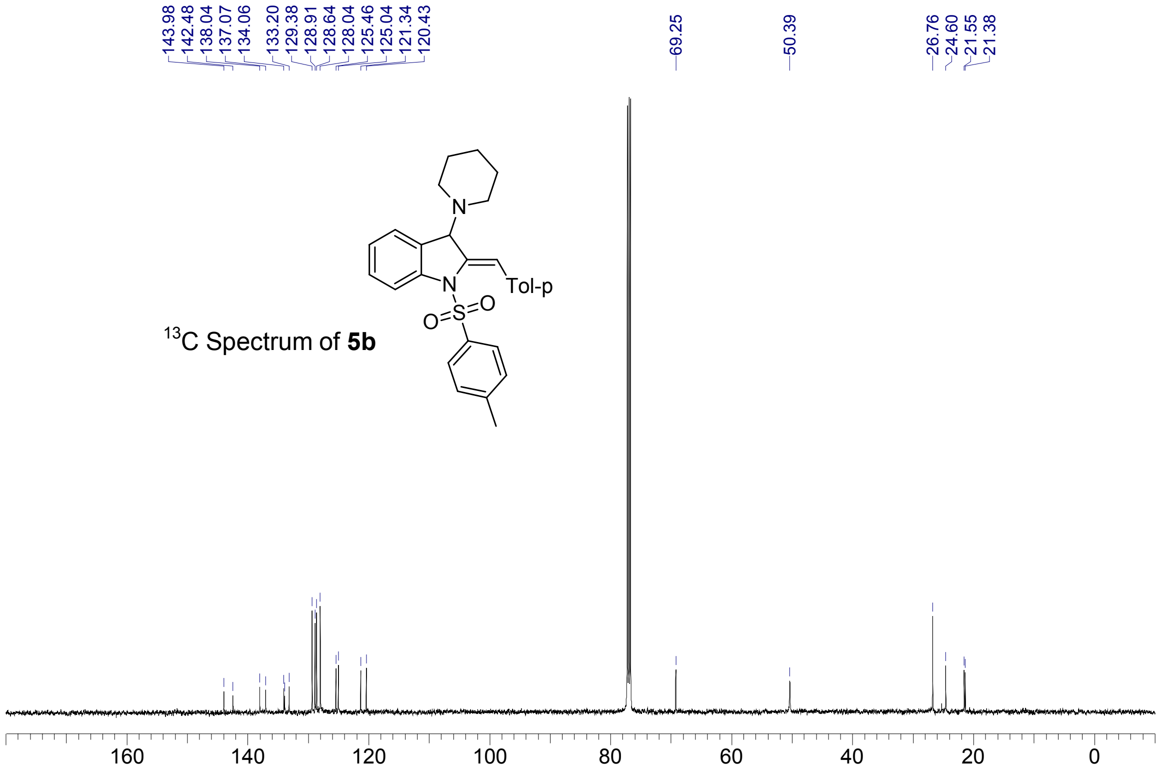
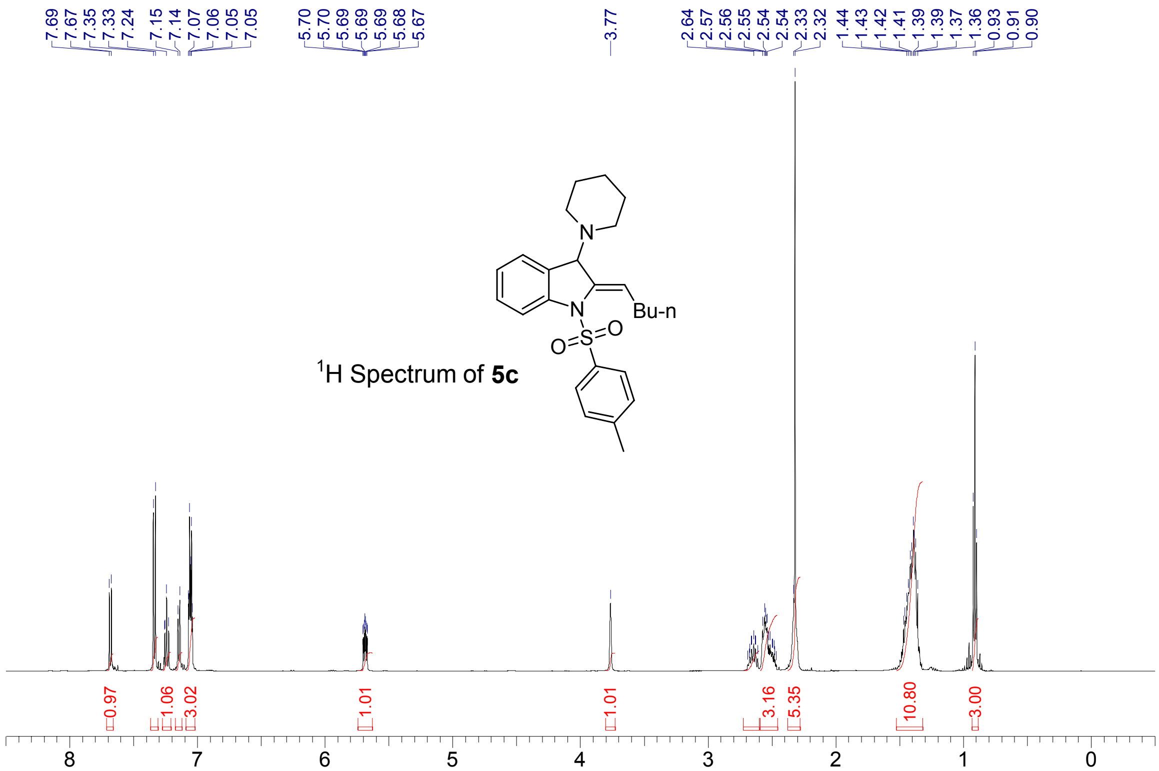
133.91
129.42
128.94
128.11
128.03
127.90
127.24
125.05
121.32
120.40
69.29
50.42
26.77
24.59
21.55
N
N
Ph
O=S=O
[13]C Spectrum of **5a**
160
140
120
100
80
60
40
20
0



^{1}H Spectrum of **5b**



^{13}C Spectrum of **5b**


7.69
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7.07
7.06
7.05
7.05
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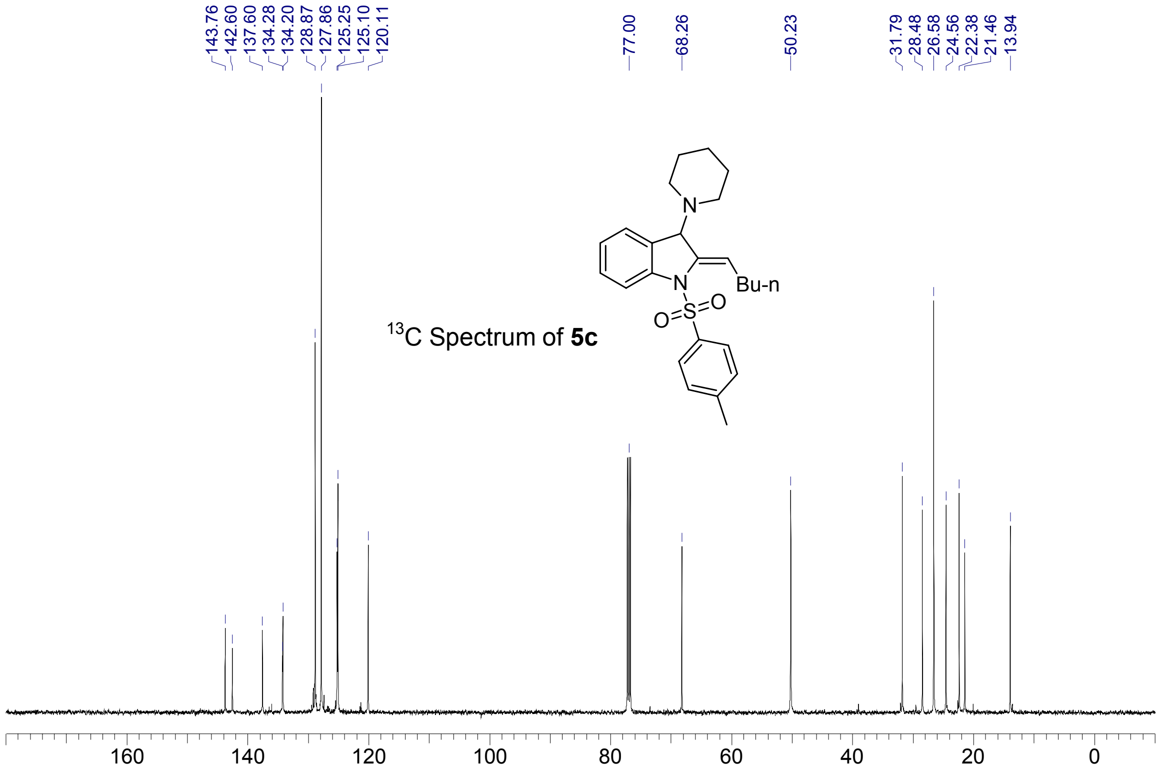
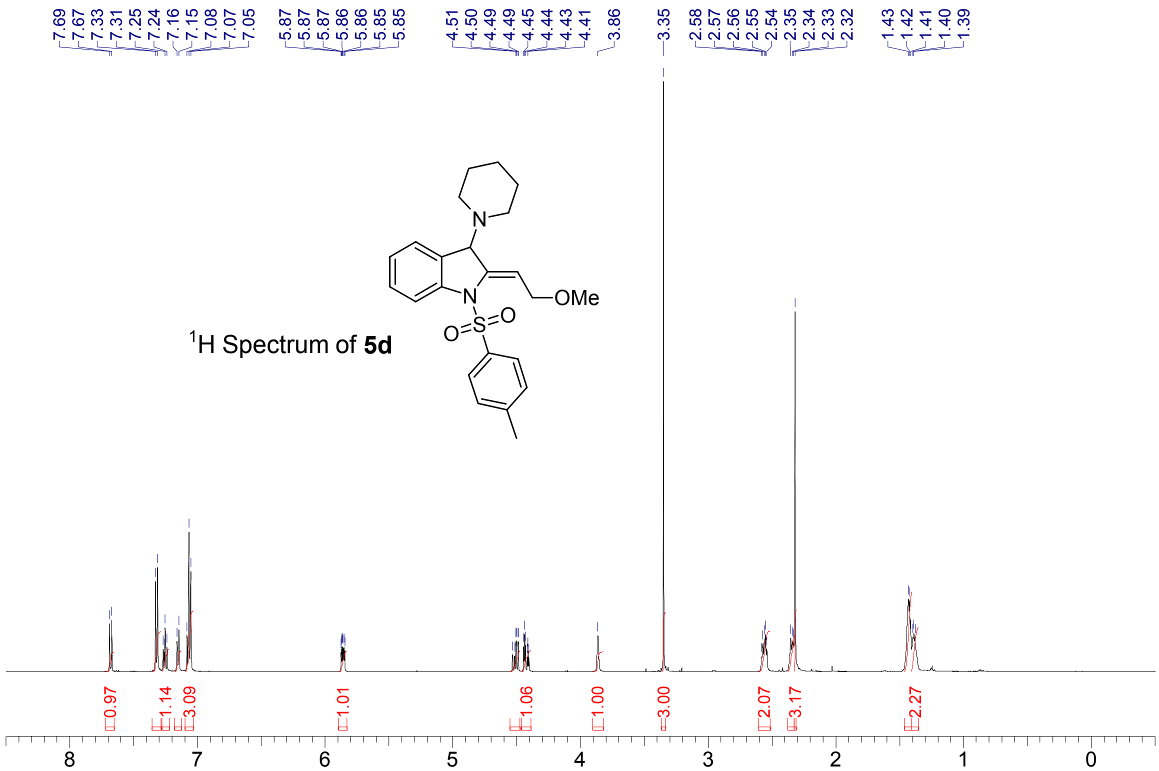
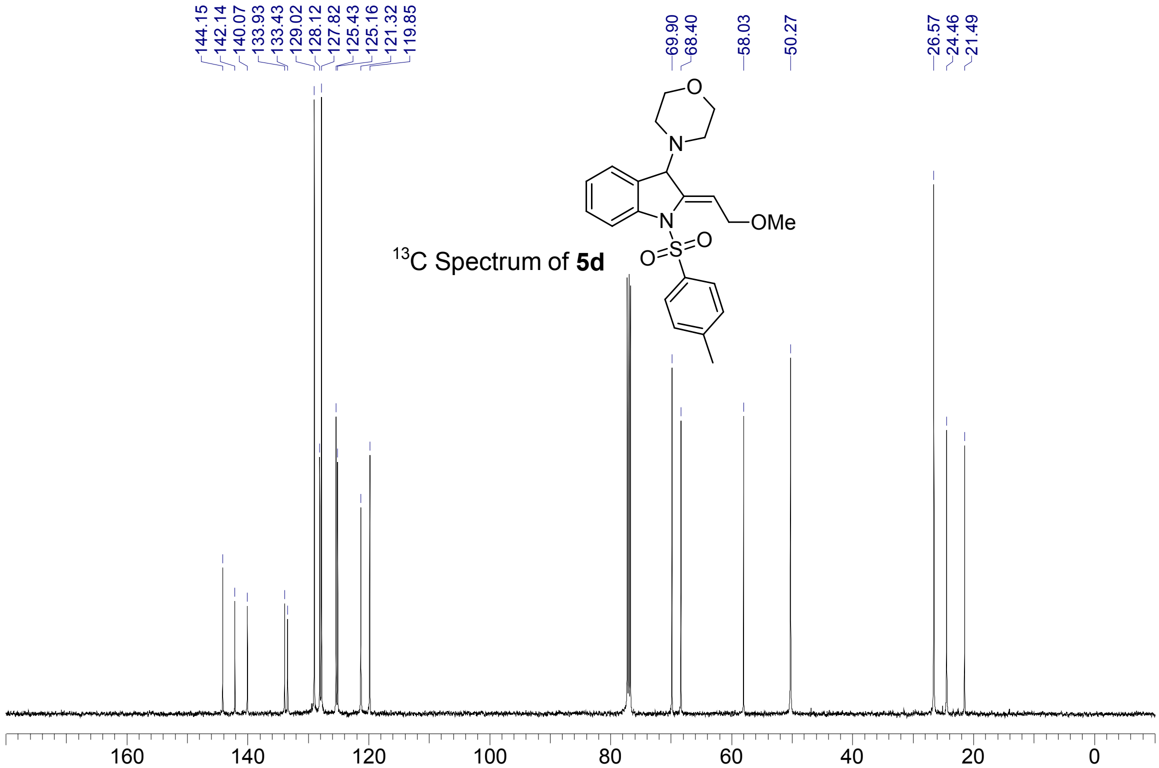
5.70
5.69
5.69
5.69
5.68
5.67
3.77
2.64
2.57
2.56
2.55
2.54
2.54
2.33
2.32
2.32
1.44
1.43
1.42
1.41
1.39
1.39
1.37
1.36
0.93
0.91
0.90
N
Bu-n
O=S=O
1H Spectrum of 5c
0.97
1.06
3.02
1.01
1.01
3.16
5.35
10.80
3.00
8
7
6
5
4
3
2
1
0

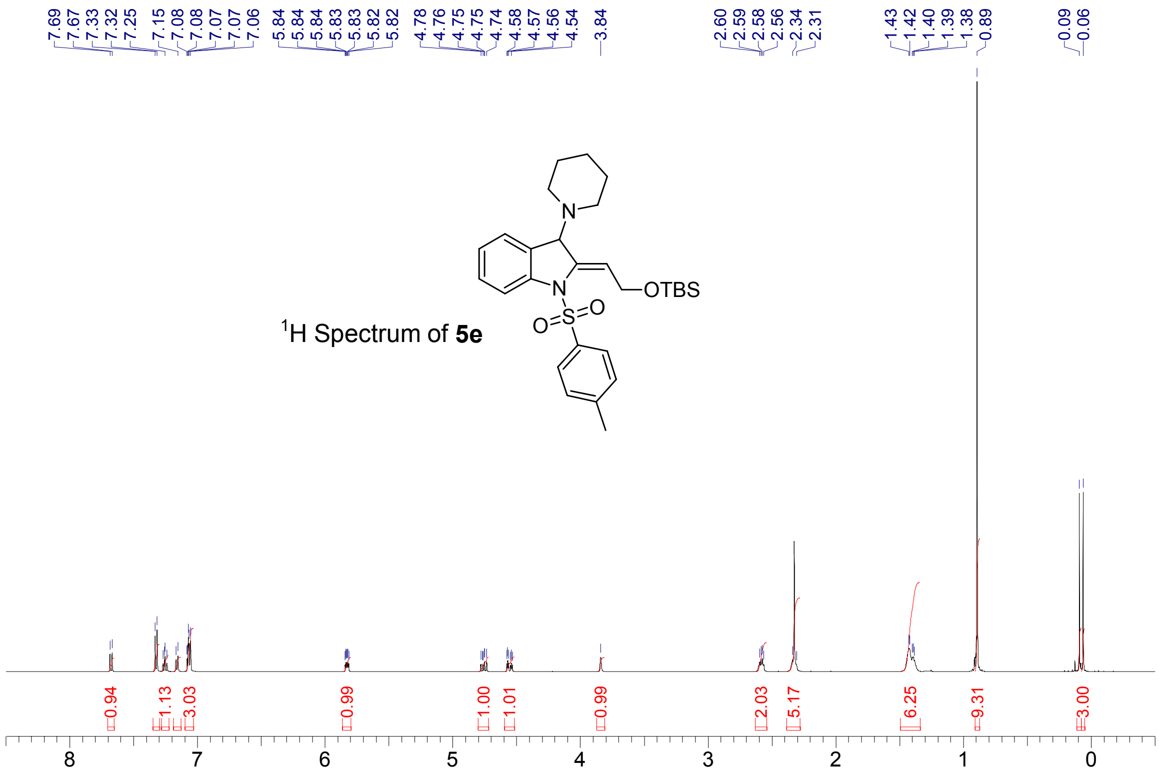

143.76
142.60
137.60
134.28
134.20
128.87
127.86
125.25
125.10
120.11
77.00
68.26
50.23
31.79
28.48
26.58
24.56
22.38
21.46
13.94
N
Bu-n
O=S=O
13C Spectrum of 5c
160
140
120
100
80
60
40
20
0

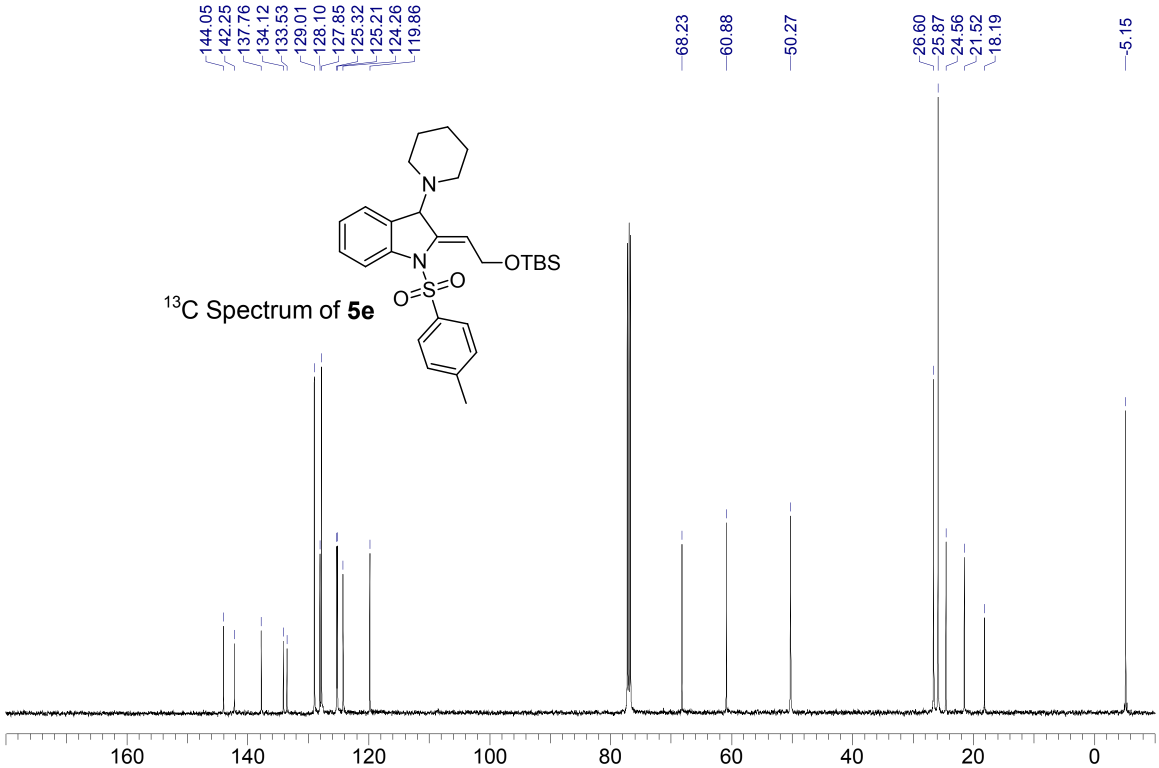


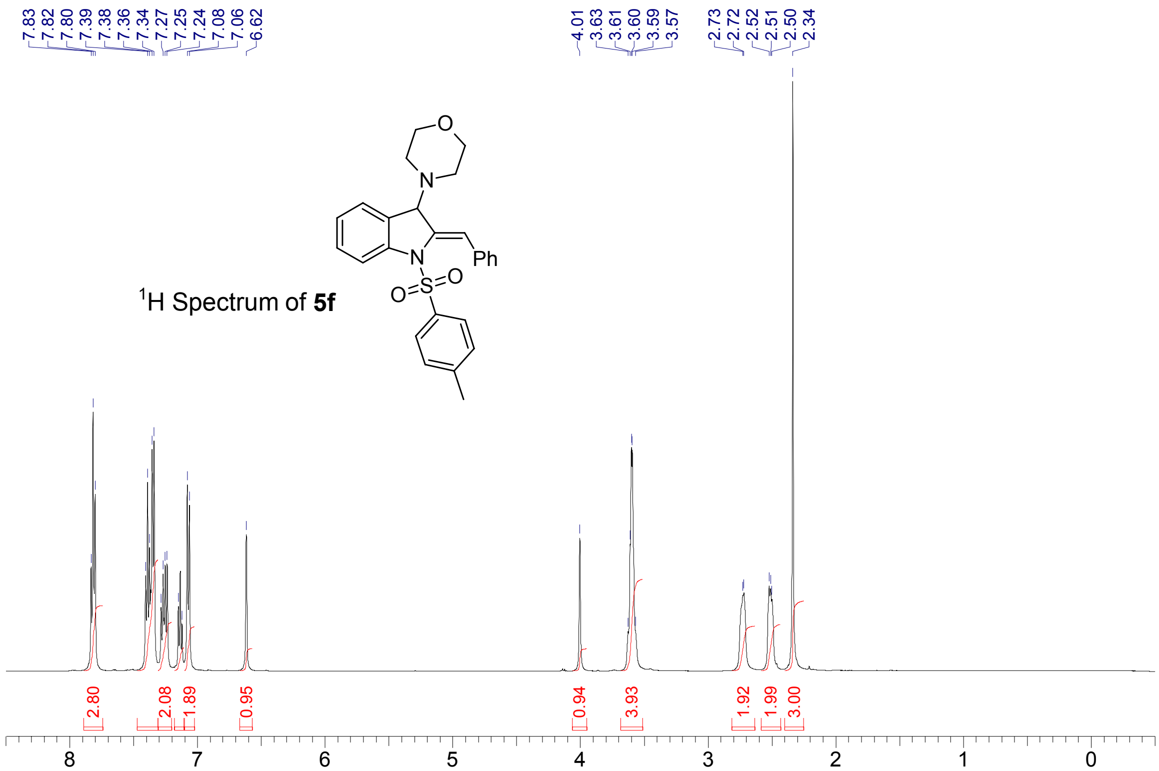
[1]H Spectrum of **5d**

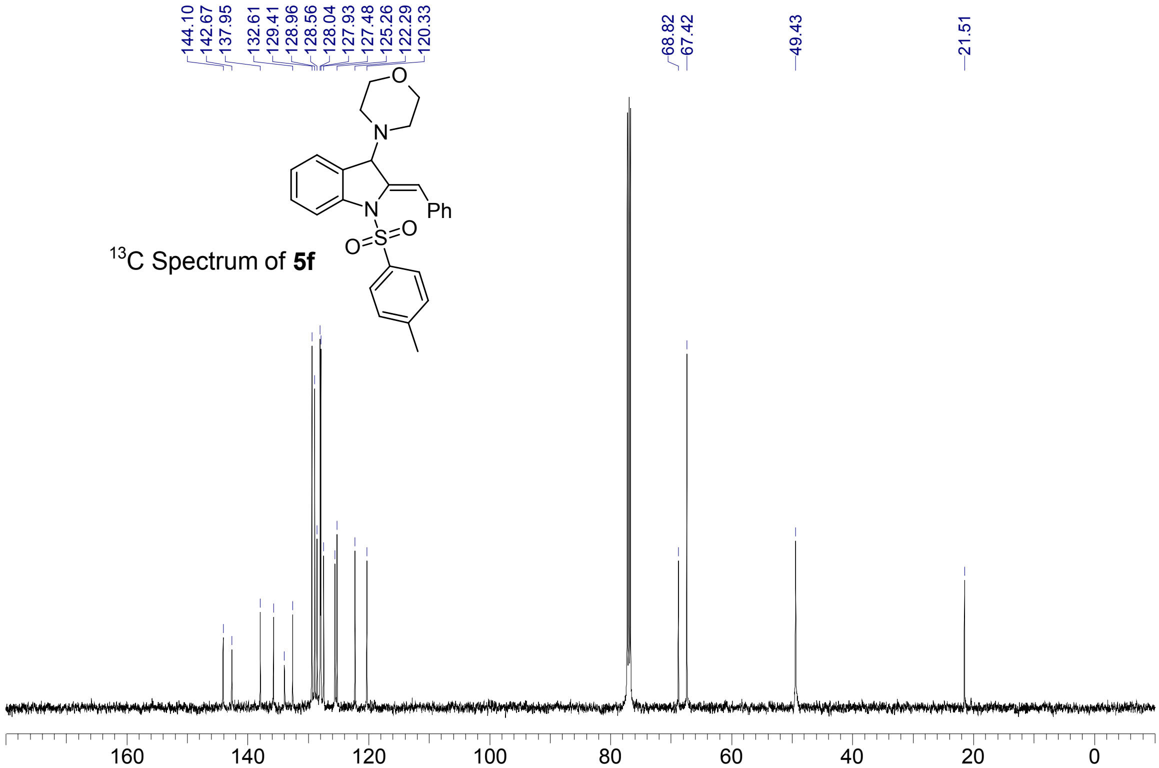


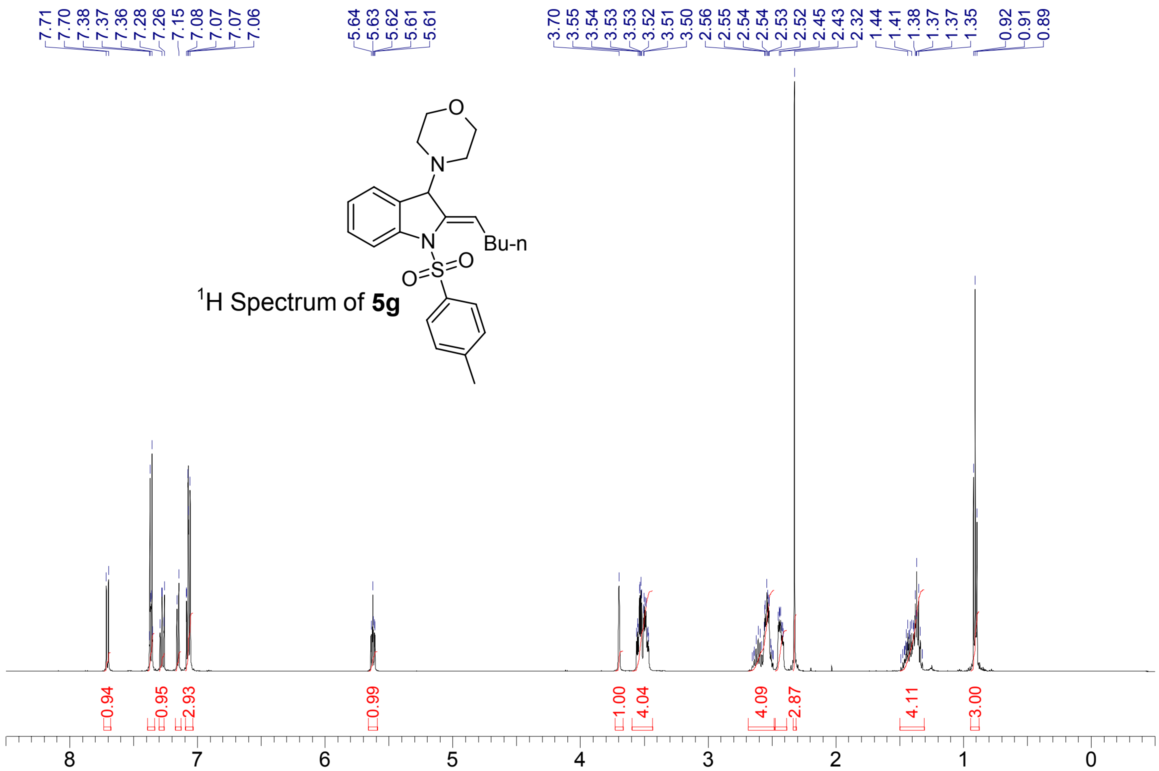
[13]C Spectrum of **5d**

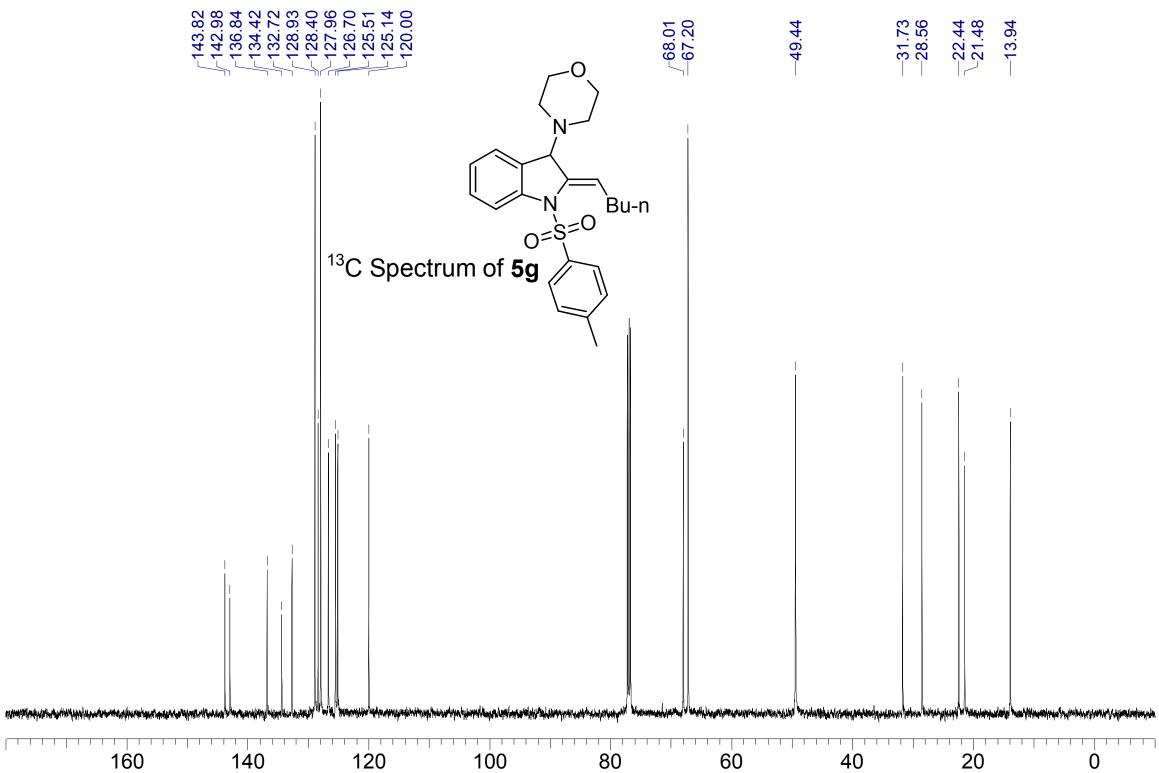

7.69
7.67
7.33
7.32
7.25
7.15
7.08
7.08
7.07
7.07
7.06
5.84
5.84
5.84
5.83
5.83
5.82
5.82
4.78
4.76
4.75
4.75
4.74
4.58
4.57
4.56
4.54
3.84
2.60
2.59
2.58
2.56
2.34
2.31
1.43
1.42
1.40
1.39
1.38
0.89
0.09
0.06
N
N
S
O
O
OTBS
^{1}H Spectrum of **5e**
0.94
1.13
3.03
0.99
1.00
1.01
0.99
2.03
5.17
6.25
9.31
3.00
8
7
6
5
4
3
2
1
0

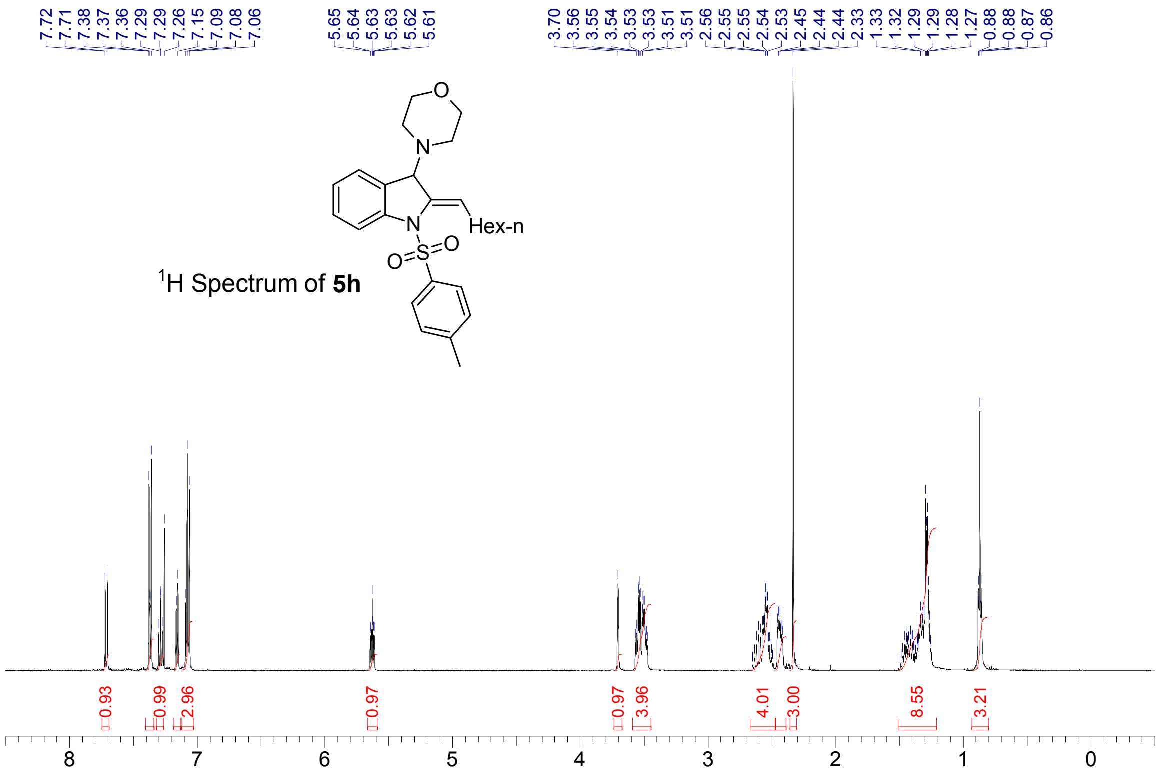

144.05
142.25
137.76
134.12
133.53
129.01
128.10
127.85
125.32
125.21
124.26
119.86
68.23
60.88
50.27
26.60
25.87
24.56
21.52
18.19
-5.15
N
N
S
O
O
OTBS
^{13}C Spectrum of **5e**
160
140
120
100
80
60
40
20
0

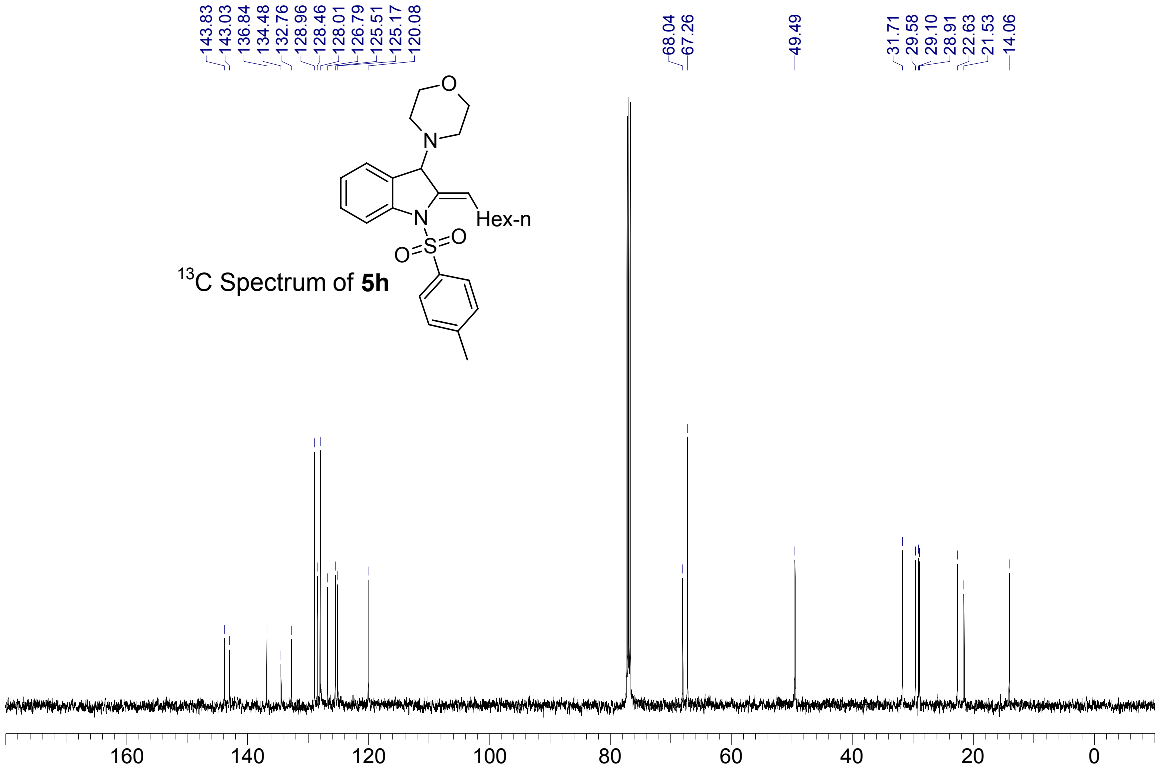

7.83
7.82
7.80
7.39
7.38
7.36
7.34
7.27
7.25
7.24
7.08
7.06
6.62
4.01
3.63
3.61
3.60
3.59
3.57
2.73
2.72
2.52
2.51
2.50
2.34
O
N
N
Ph
O=S=O
[1]H Spectrum of 5f
2.80
2.08
1.89
0.95
0.94
3.93
1.92
1.99
3.00
8
7
6
5
4
3
2
1
0

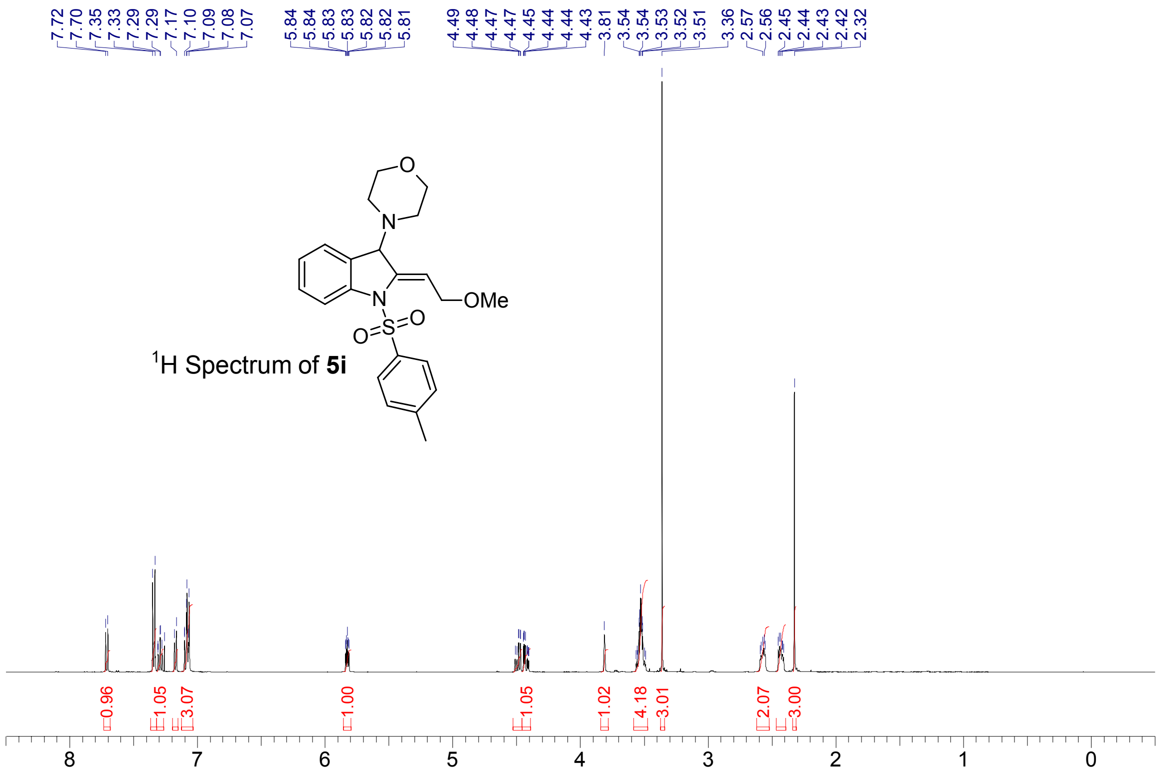

144.10
142.67
137.95
132.61
129.41
128.96
128.56
128.04
127.93
127.48
125.26
122.29
120.33
68.82
67.42
49.43
21.51
O
N
N
Ph
O=S=O
[13]C Spectrum of 5f
160
140
120
100
80
60
40
20
0

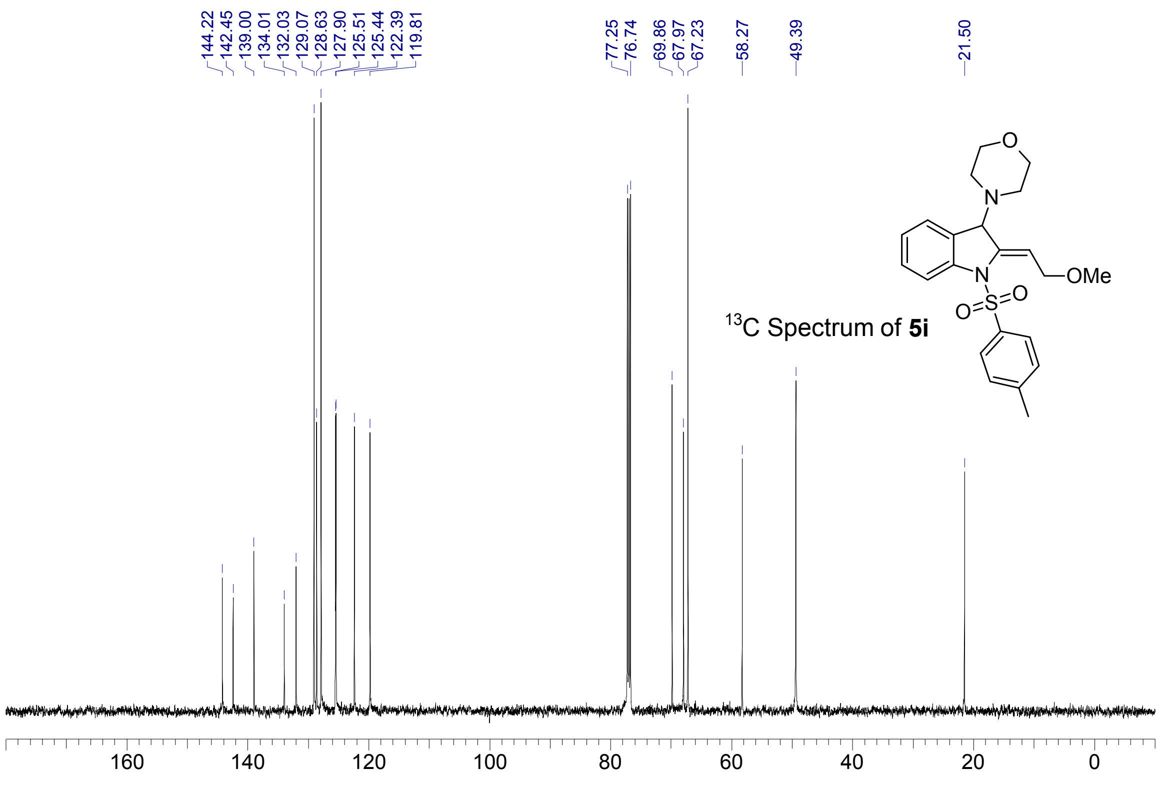

7.71
7.70
7.38
7.37
7.36
7.28
7.26
7.15
7.08
7.07
7.07
7.06
5.64
5.63
5.62
5.61
5.61
3.70
3.55
3.54
3.53
3.53
3.52
3.51
3.50
2.56
2.55
2.54
2.54
2.53
2.52
2.45
2.43
2.32
1.44
1.41
1.38
1.37
1.37
1.35
0.92
0.91
0.89
O
N
N
Bu-n
S
O
O
^{1}H Spectrum of **5g**
0.94
0.95
2.93
0.99
1.00
4.04
4.09
2.87
4.11
3.00
8
7
6
5
4
3
2
1
0

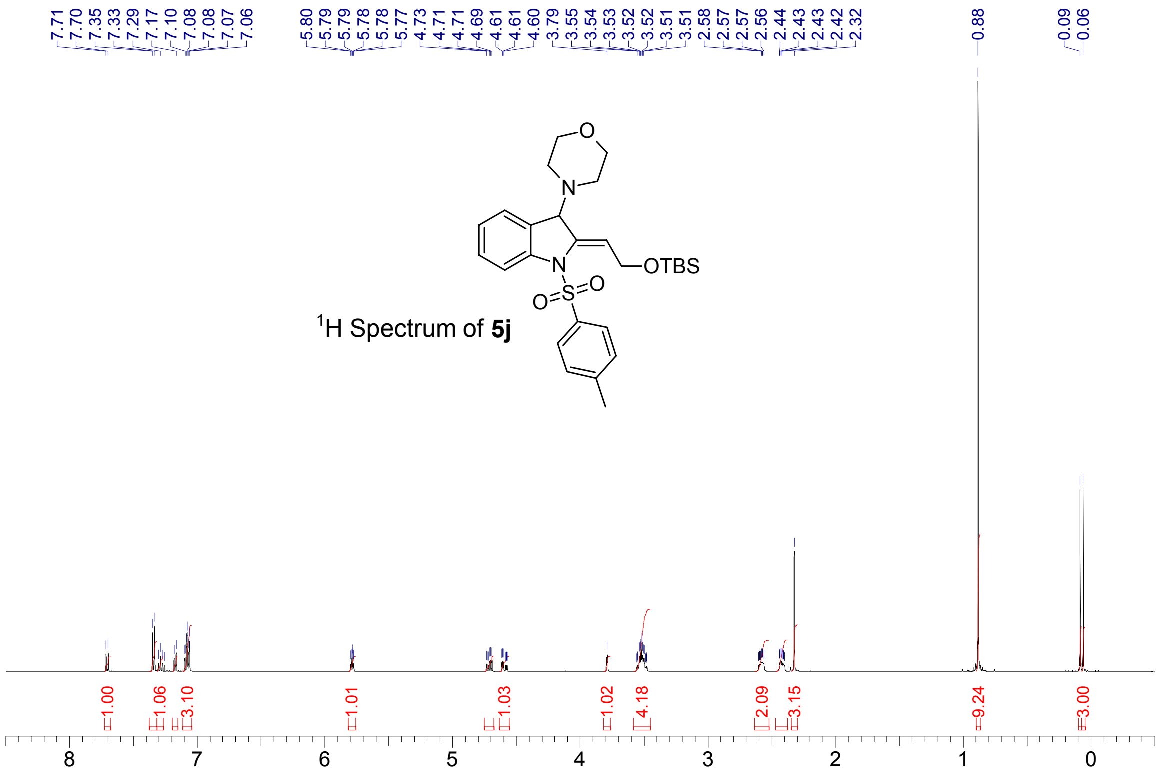

143.82
142.98
136.84
134.42
132.72
128.93
128.40
127.96
126.70
125.51
125.14
120.00
68.01
67.20
49.44
31.73
28.56
22.44
21.48
13.94
O
N
N
Bu-n
S
O
O
^{13}C Spectrum of **5g**
160
140
120
100
80
60
40
20
0

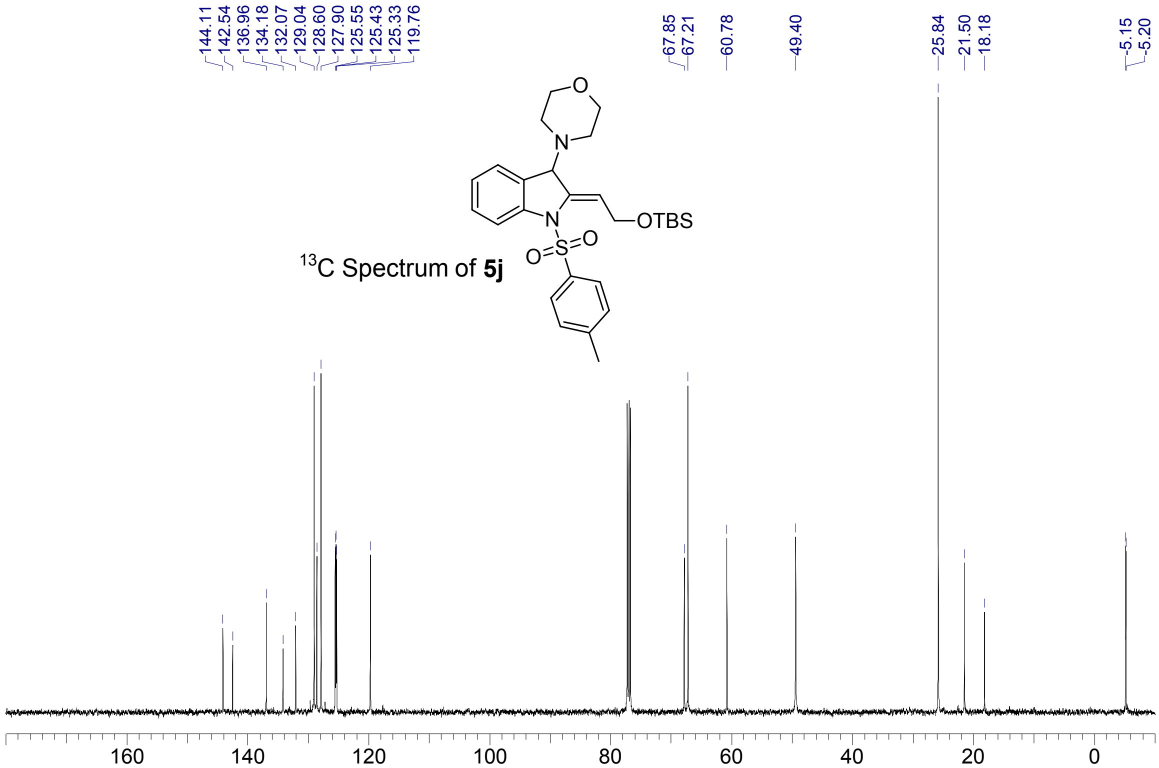

7.72
7.71
7.38
7.37
7.36
7.29
7.29
7.26
7.15
7.09
7.08
7.06
5.65
5.64
5.63
5.63
5.62
5.61
3.70
3.56
3.55
3.54
3.53
3.53
3.51
3.51
2.56
2.55
2.55
2.54
2.53
2.45
2.44
2.44
2.33
1.33
1.32
1.29
1.29
1.28
1.27
0.88
0.88
0.87
0.86
Hex-n
^{1}H Spectrum of **5h**
0.93
0.99
2.96
0.97
0.97
3.96
4.01
3.00
8.55
3.21
8
7
6
5
4
3
2
1
0

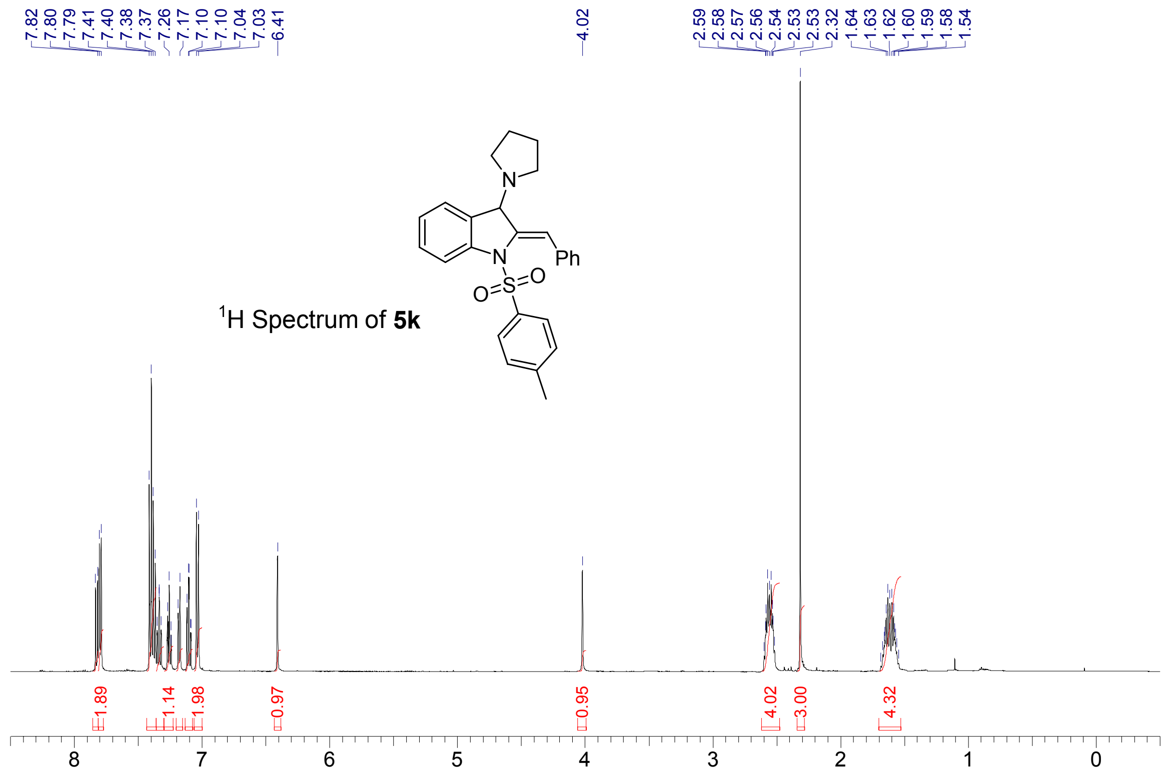

143.83
143.03
136.84
134.48
132.76
128.96
128.46
128.01
126.79
125.51
125.17
120.08
68.04
67.26
49.49
31.71
29.58
29.10
28.91
22.63
21.53
14.06
Hex-n
^{13}C Spectrum of **5h**
160
140
120
100
80
60
40
20
0

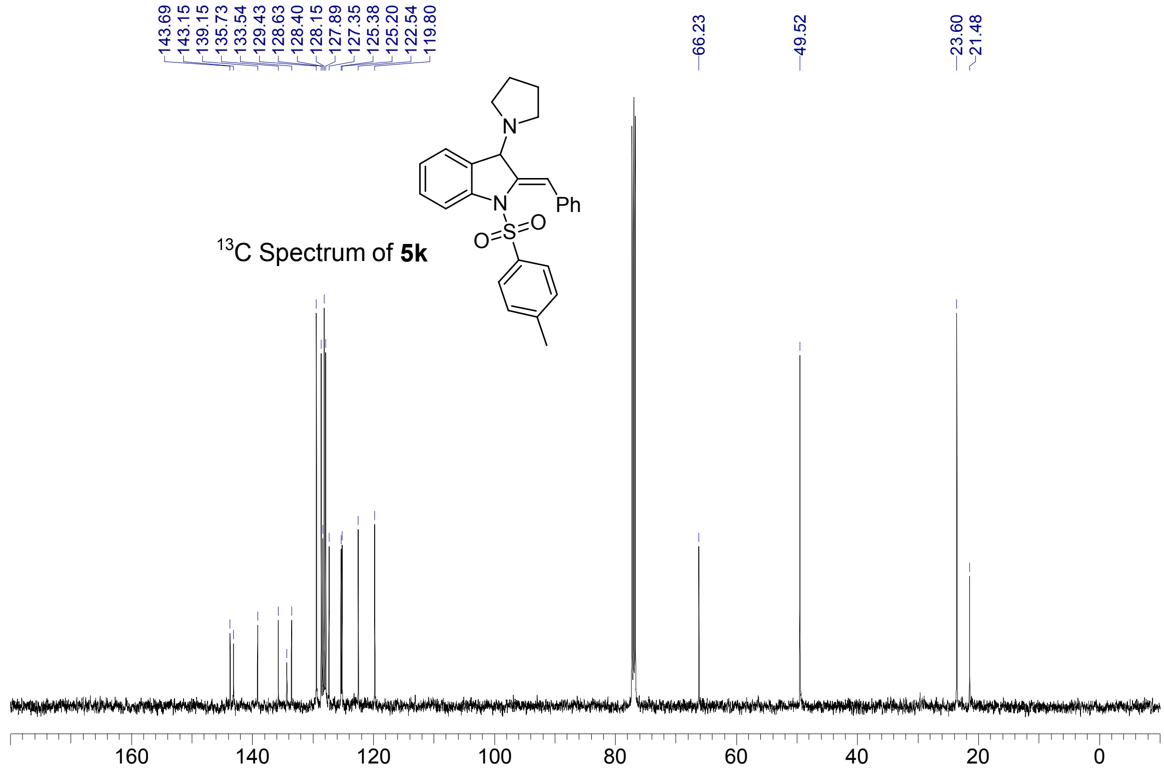

7.72
7.70
7.35
7.33
7.29
7.29
7.17
7.10
7.09
7.08
7.07
5.84
5.84
5.83
5.83
5.82
5.82
5.81
4.49
4.48
4.47
4.47
4.45
4.44
4.44
4.43
3.81
3.54
3.54
3.53
3.52
3.51
3.36
2.57
2.56
2.45
2.44
2.43
2.42
2.32
O
N
N
OMe
O=S=O
^{1}H Spectrum of **5i**
0.96
1.05
3.07
1.00
1.05
1.02
4.18
3.01
2.07
3.00
8
7
6
5
4
3
2
1
0

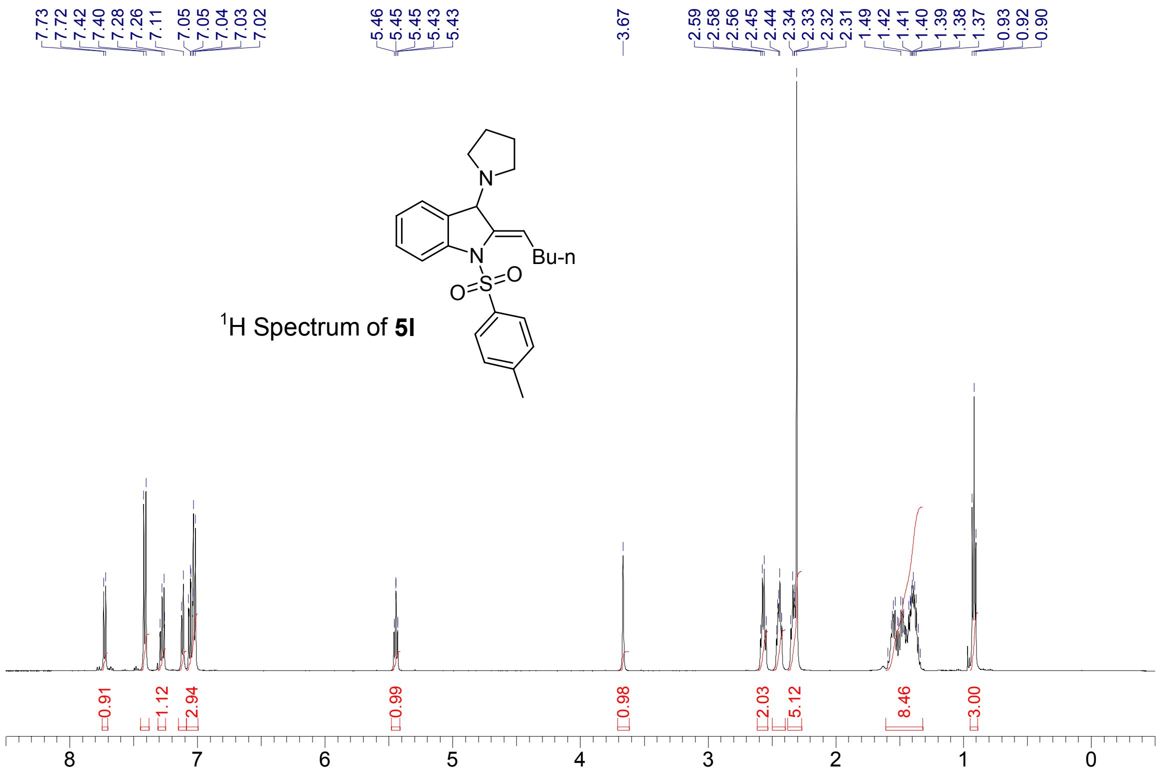

144.22
142.45
139.00
134.01
132.03
129.07
128.63
127.90
125.51
125.44
122.39
119.81
77.25
76.74
69.86
67.97
67.23
58.27
49.39
21.50
O
N
N
OMe
O=S=O
^{13}C Spectrum of **5i**
160
140
120
100
80
60
40
20
0

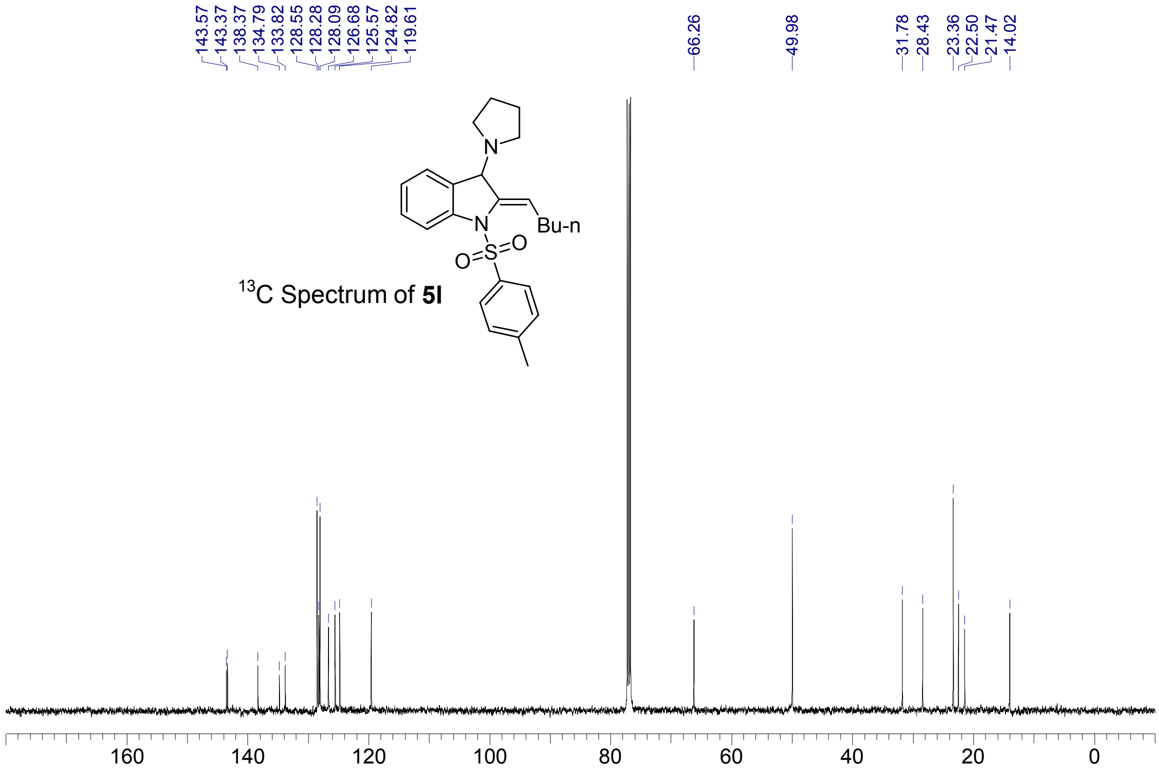

7.71
7.70
7.35
7.33
7.29
7.17
7.10
7.08
7.07
7.06
5.80
5.79
5.79
5.78
5.78
5.77
4.73
4.71
4.71
4.69
4.61
4.61
4.60
3.79
3.55
3.54
3.53
3.52
3.52
3.51
3.51
2.58
2.57
2.57
2.56
2.44
2.43
2.43
2.42
2.32
0.88
0.09
0.06
O
N
N
S
O
O
OTBS
^{1}H Spectrum of **5j**
1.00
1.06
3.10
1.01
1.03
1.02
4.18
2.09
3.15
9.24
3.00
8
7
6
5
4
3
2
1
0

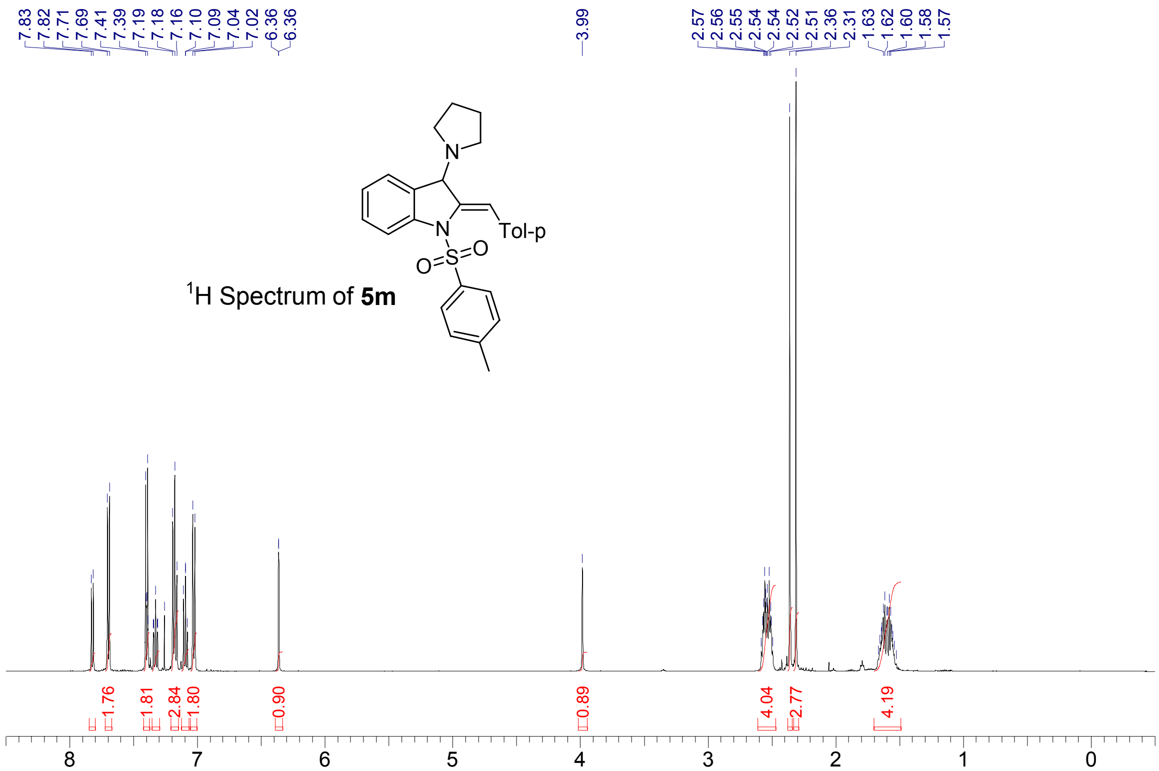

144.11
142.54
136.96
134.18
132.07
129.04
128.60
127.90
125.55
125.43
125.33
119.76
67.85
67.21
60.78
49.40
25.84
21.50
18.18
-5.15
-5.20
O
N
N
S
O
O
OTBS
^{13}C Spectrum of **5j**
160
140
120
100
80
60
40
20
0

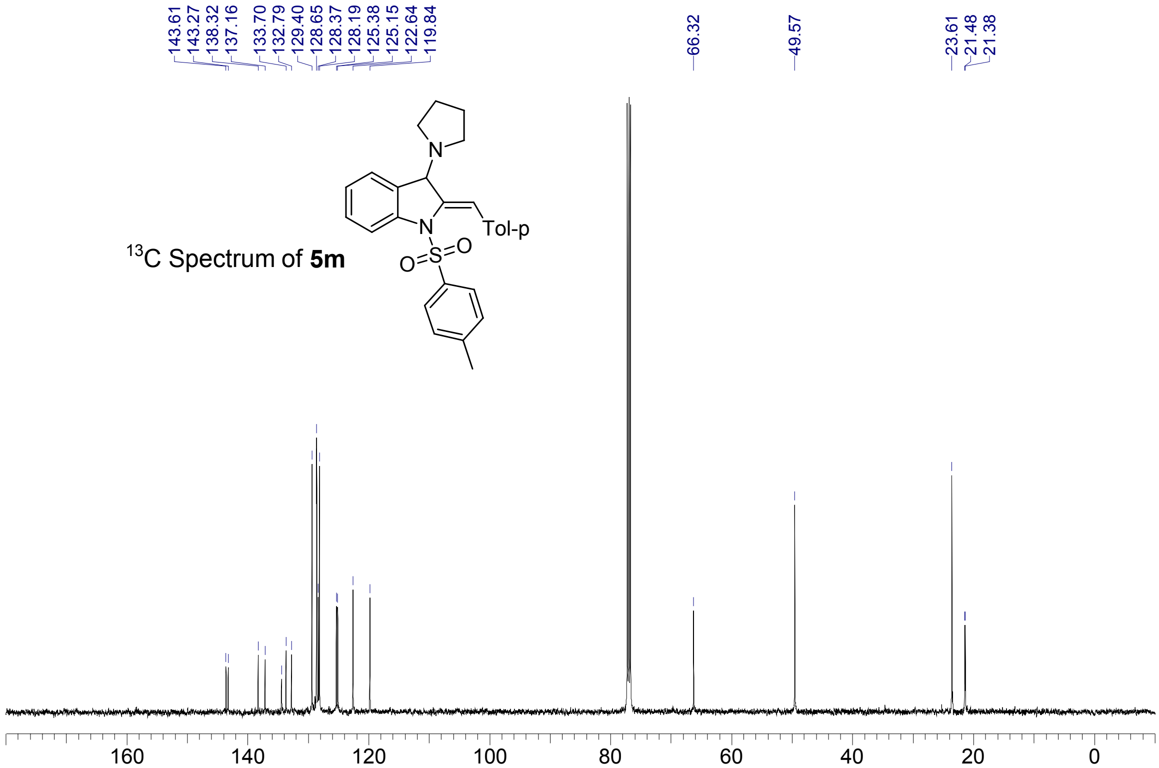

7.82
7.80
7.79
7.41
7.40
7.38
7.37
7.26
7.17
7.10
7.10
7.04
7.03
6.41
4.02
2.59
2.58
2.57
2.56
2.54
2.53
2.53
2.32
1.64
1.63
1.62
1.60
1.59
1.58
1.54
N
N
Ph
O=S=O
^{1}H Spectrum of **5k**
1.89
1.14
1.98
0.97
0.95
4.02
3.00
4.32
8
7
6
5
4
3
2
1
0

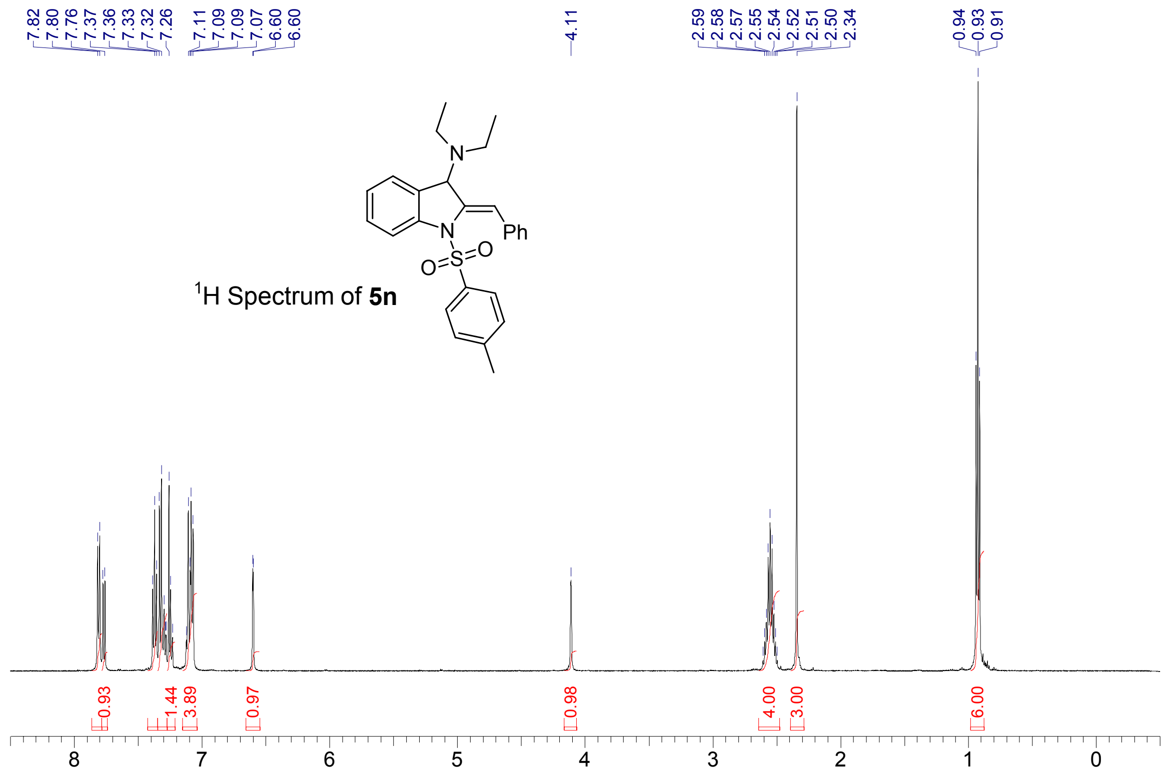

143.69
143.15
139.15
135.73
133.54
129.43
128.63
128.40
128.15
127.89
127.35
125.38
125.20
122.54
119.80
66.23
49.52
23.60
21.48
N
N
Ph
O=S=O
^{13}C Spectrum of **5k**
160
140
120
100
80
60
40
20
0

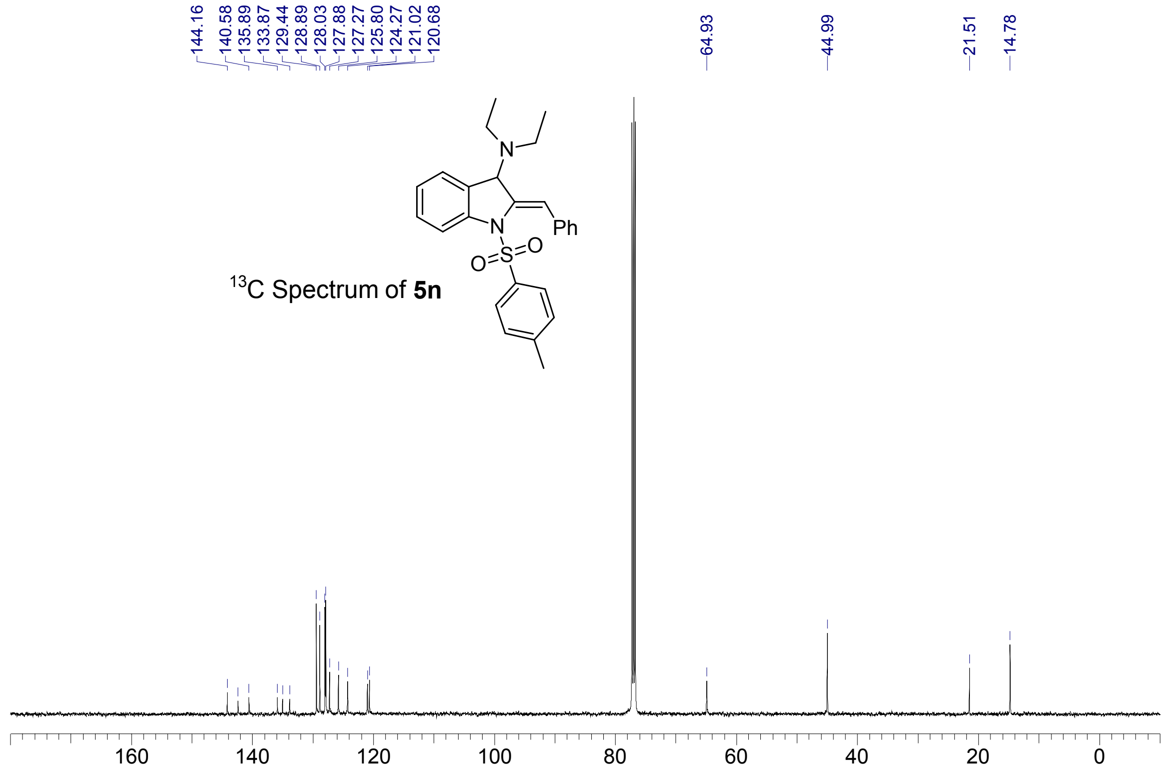

7.73
7.72
7.42
7.40
7.28
7.26
7.11
7.05
7.05
7.04
7.03
7.02
5.46
5.45
5.45
5.43
5.43
3.67
2.59
2.58
2.56
2.45
2.44
2.34
2.33
2.32
2.31
1.49
1.42
1.41
1.40
1.39
1.38
1.37
0.93
0.92
0.90
N
N
Bu-n
O=S=O
[1]H Spectrum of **5l**
0.91
1.12
2.94
0.99
0.98
2.03
5.12
8.46
3.00
8
7
6
5
4
3
2
1
0

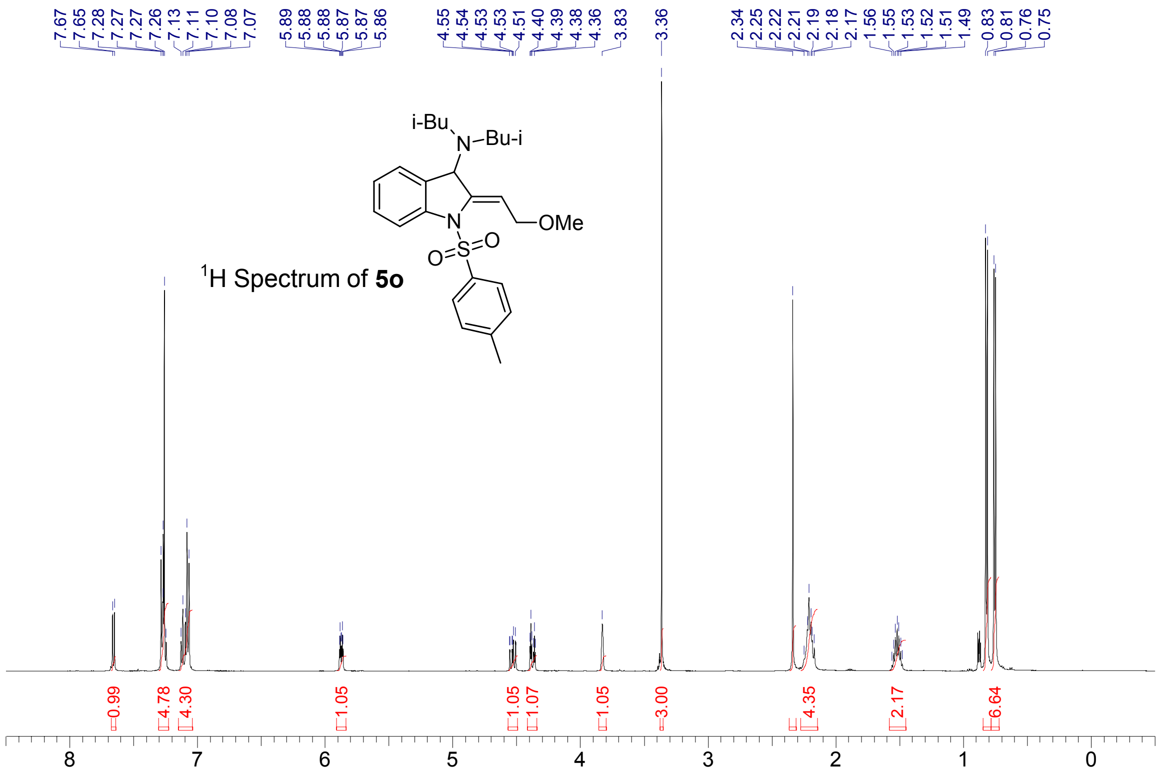

143.57
143.37
138.37
134.79
133.82
128.55
128.28
128.09
126.68
125.57
124.82
119.61
66.26
49.98
31.78
28.43
23.36
22.50
21.47
14.02
N
N
Bu-n
O=S=O
[13]C Spectrum of **5l**
160
140
120
100
80
60
40
20
0


7.83
7.82
7.71
7.69
7.41
7.39
7.19
7.18
7.16
7.10
7.09
7.04
7.02
6.36
6.36
3.99
2.57
2.56
2.55
2.54
2.54
2.52
2.51
2.36
2.31
1.63
1.62
1.60
1.58
1.57
N
N
Tol-p
O=S=O
[1]H Spectrum of 5m
1.76
1.81
2.84
1.80
0.90
0.89
4.04
2.77
4.19
8
7
6
5
4
3
2
1
0

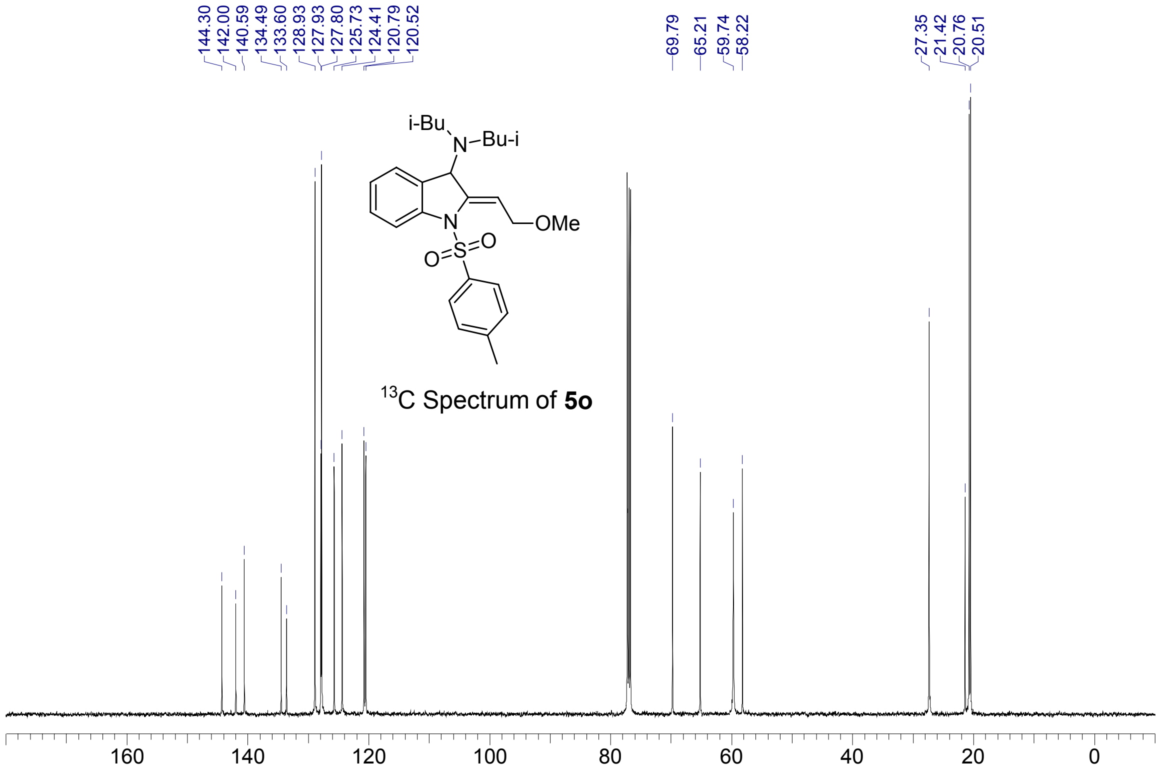

143.61
143.27
138.32
137.16
133.70
132.79
129.40
128.65
128.37
128.19
125.38
125.15
122.64
119.84
66.32
49.57
23.61
21.48
21.38
N
N
Tol-p
O=S=O
[13]C Spectrum of 5m
160
140
120
100
80
60
40
20
0


7.82
7.80
7.76
7.37
7.36
7.33
7.32
7.26
7.11
7.09
7.09
7.07
6.60
6.60
4.11
2.59
2.58
2.57
2.55
2.54
2.52
2.51
2.50
2.34
0.94
0.93
0.91
Ph
N
O=S=O
[1]H Spectrum of **5n**
0.93
1.44
3.89
0.97
0.98
4.00
3.00
6.00
8
7
6
5
4
3
2
1
0

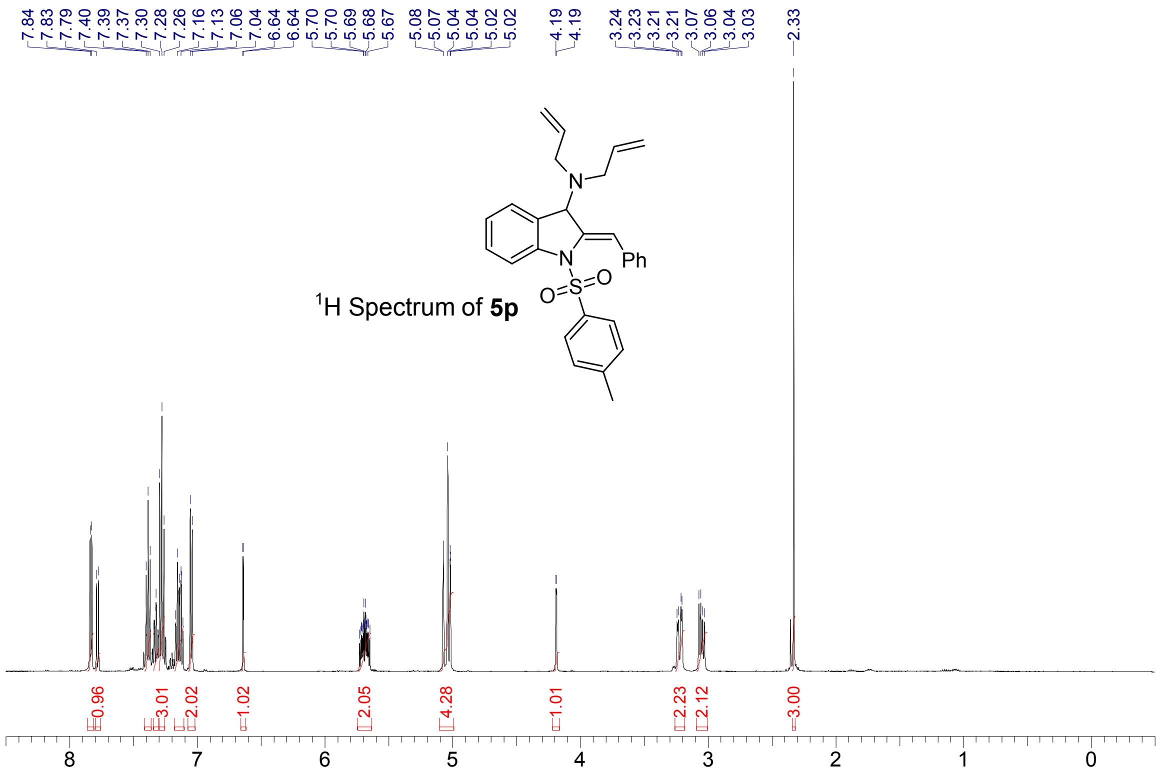

144.16
140.58
135.89
133.87
129.44
128.89
128.03
127.88
127.27
125.80
124.27
121.02
120.68
64.93
44.99
21.51
14.78
Ph
N
O=S=O
[13]C Spectrum of **5n**
160
140
120
100
80
60
40
20
0



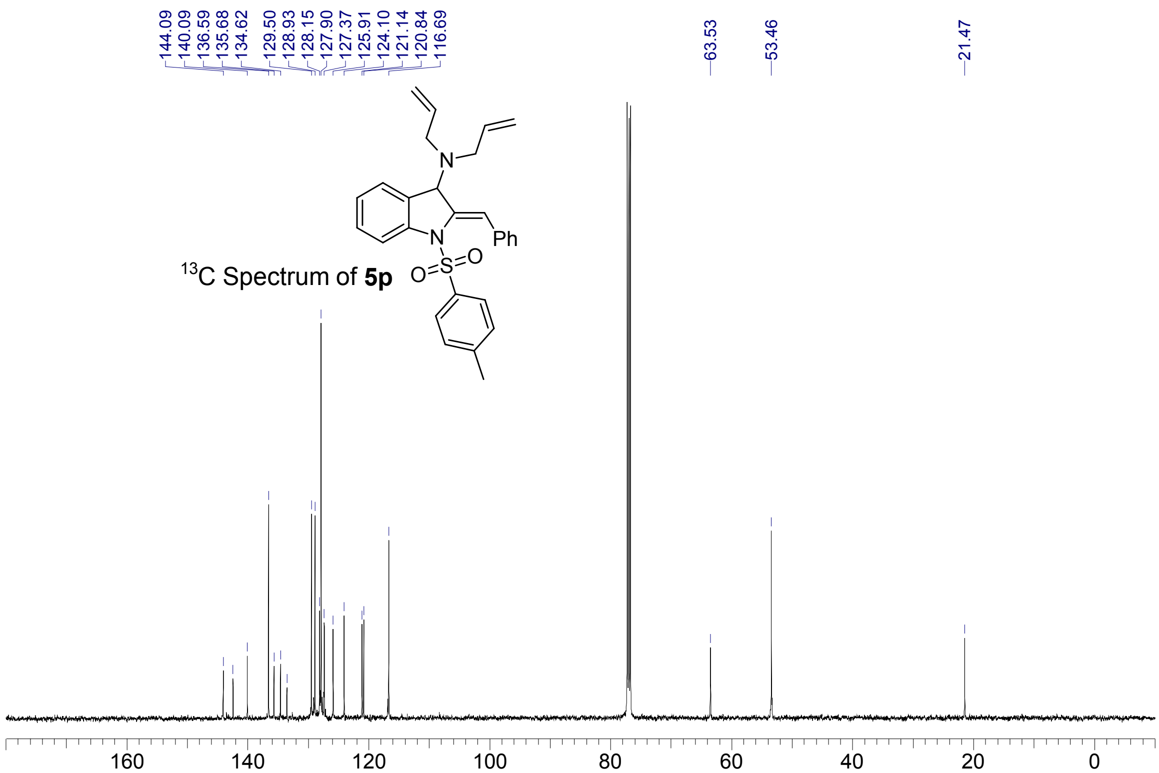
7.67 7.65 7.28 7.27 7.27 7.26 7.13 7.11 7.10 7.08 7.07 5.89 5.88 5.88 5.87 5.87 5.86 4.55 4.54 4.53 4.53 4.51 4.40 4.39 4.38 4.36 3.83 3.36 2.34 2.25 2.22 2.21 2.19 2.18 2.17 1.56 1.55 1.53 1.52 1.51 1.49 0.83 0.81 0.76 0.75
i-Bu
N
Bu-i
N
OMe
O=S=O
^{1}H Spectrum of **5o**
0.99 4.78 4.30 1.05 1.05 1.07 1.05 3.00 4.35 2.17 6.64
8 7 6 5 4 3 2 1 0



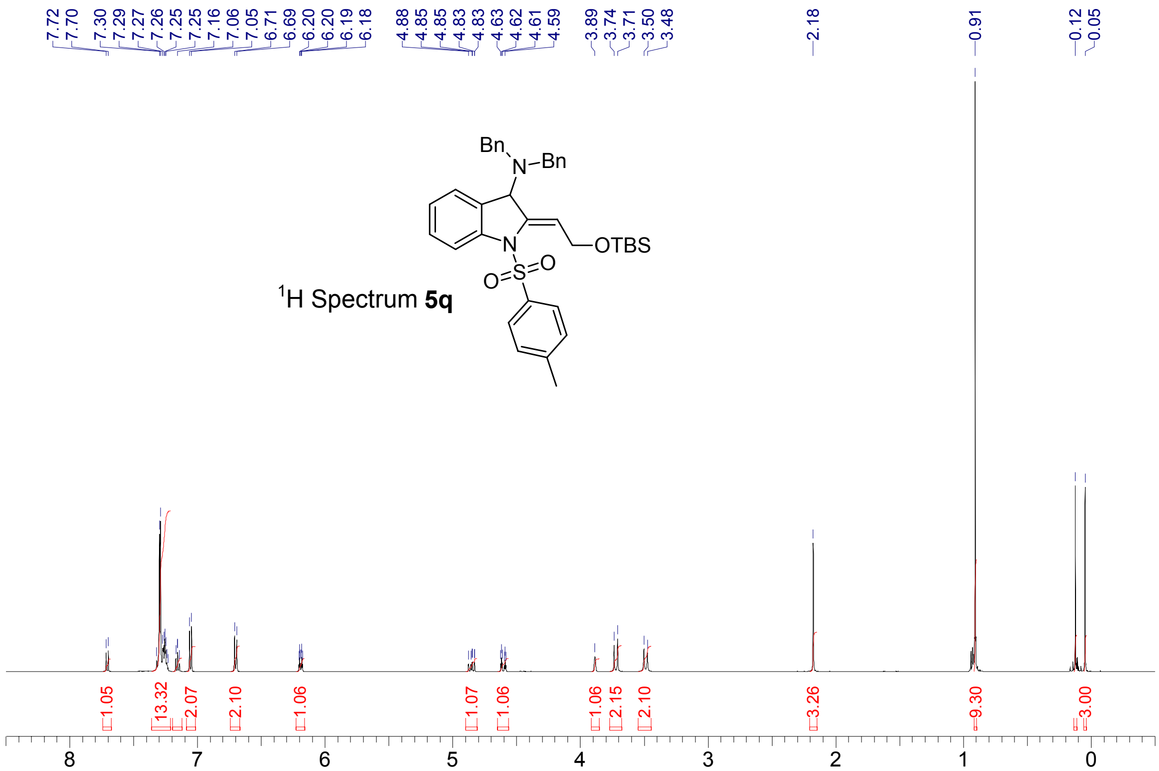
144.30 142.00 140.59 134.49 133.60 128.93 127.93 127.80 125.73 124.41 120.79 120.52 69.79 65.21 59.74 58.22 27.35 21.42 20.76 20.51
i-Bu
N
Bu-i
N
OMe
O=S=O
^{13}C Spectrum of **5o**
160 140 120 100 80 60 40 20 0



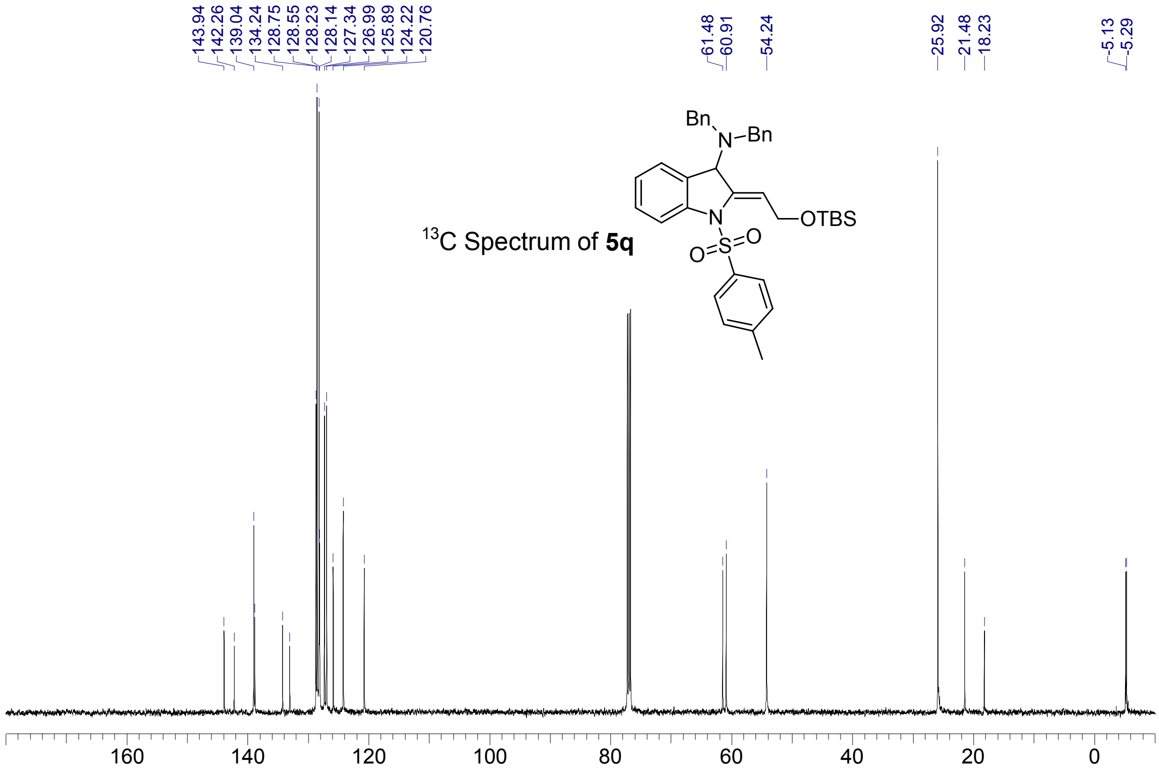
[1]H Spectrum of **5p**
N
N
O=S=O
Ph
7.84
7.83
7.79
7.40
7.39
7.37
7.30
7.28
7.26
7.16
7.13
7.06
7.04
6.64
6.64
5.70
5.70
5.69
5.68
5.67
5.08
5.07
5.04
5.04
5.02
5.02
4.19
4.19
3.24
3.23
3.21
3.21
3.07
3.06
3.04
3.03
2.33
0.96
3.01
2.02
1.02
2.05
4.28
1.01
2.23
2.12
3.00
8
7
6
5
4
3
2
1
0



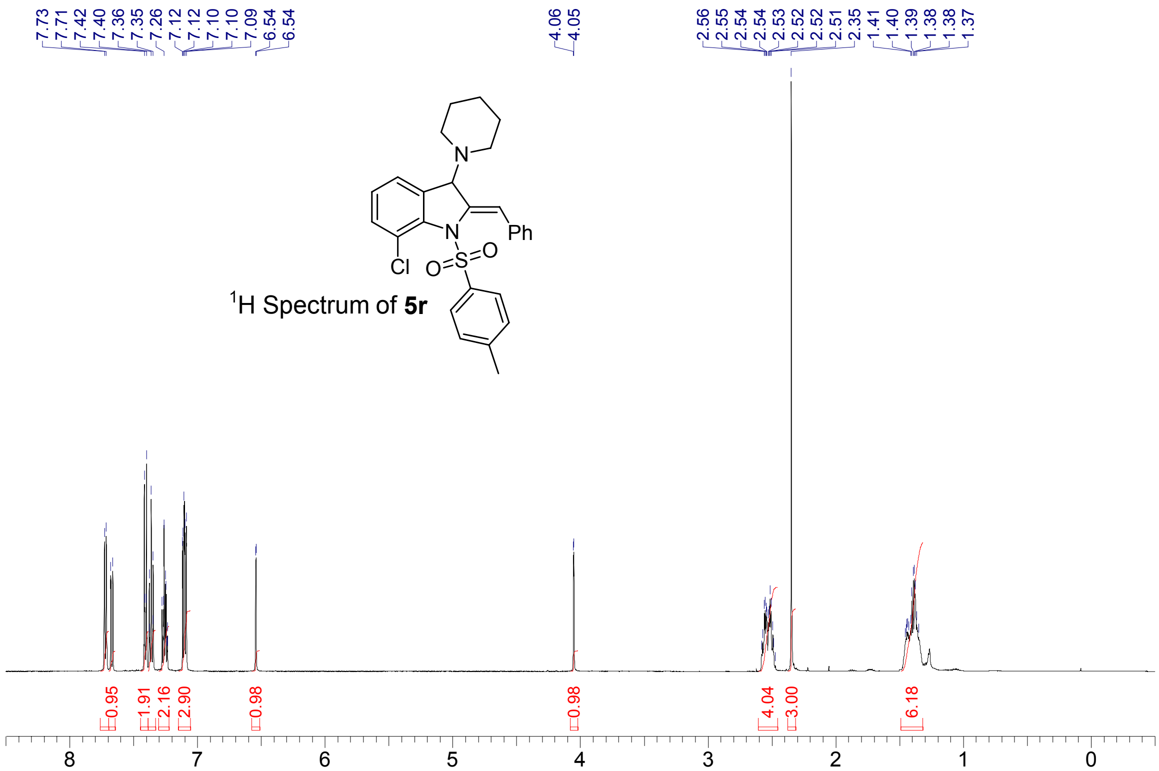
[13]C Spectrum of **5p**
N
N
O=S=O
Ph
144.09
140.09
136.59
135.68
134.62
129.50
128.93
128.15
127.90
127.37
125.91
124.10
121.14
120.84
116.69
63.53
53.46
21.47
160
140
120
100
80
60
40
20
0

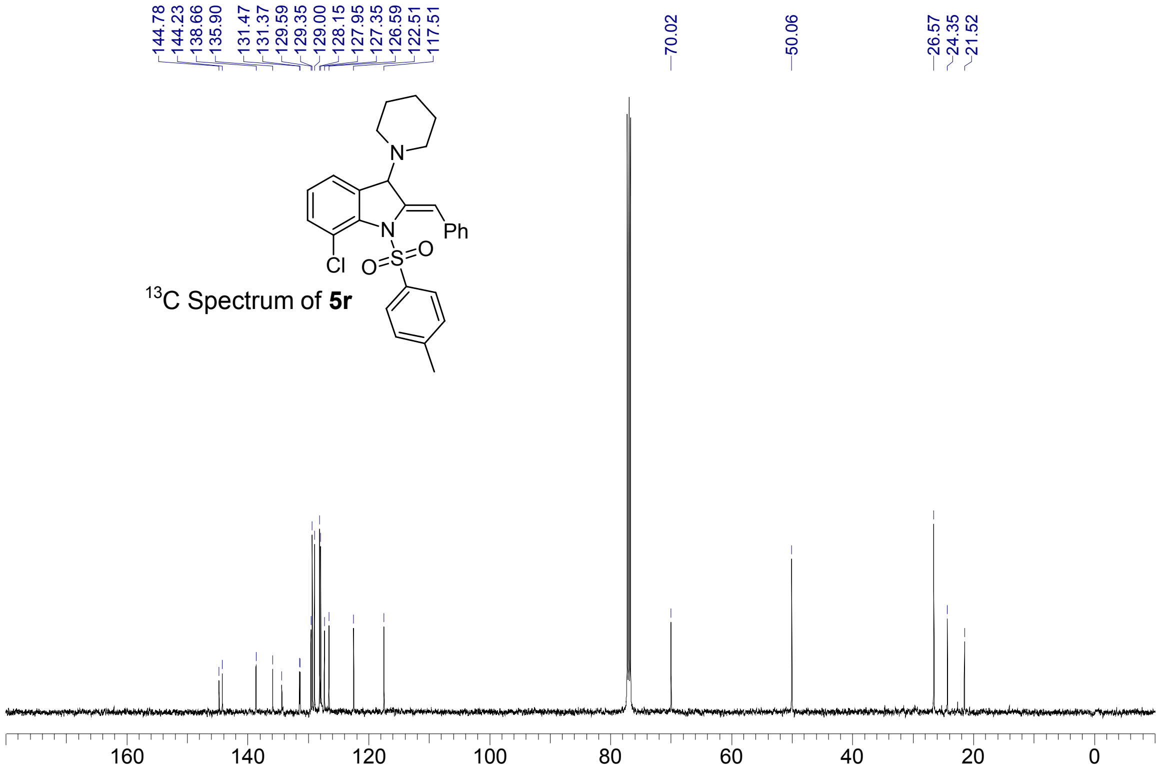


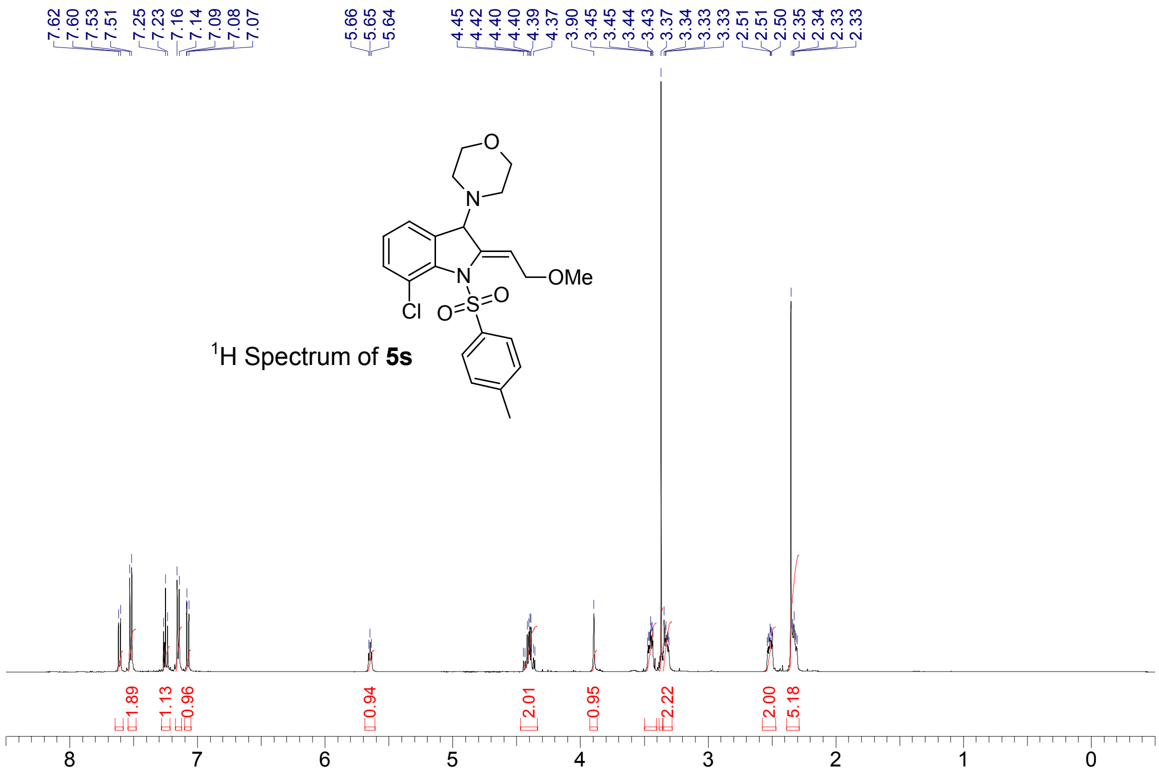
7.72
7.70
7.30
7.29
7.27
7.26
7.25
7.25
7.16
7.06
7.05
6.71
6.69
6.20
6.20
6.19
6.18
4.88
4.85
4.85
4.83
4.83
4.63
4.62
4.61
4.59
3.89
3.74
3.71
3.50
3.48
2.18
0.91
0.12
0.05
Bn
N
Bn
N
O
S
O
OTBS
1H Spectrum 5q
1.05
13.32
2.07
2.10
1.06
1.07
1.06
1.06
2.15
2.10
3.26
9.30
3.00
8
7
6
5
4
3
2
1
0

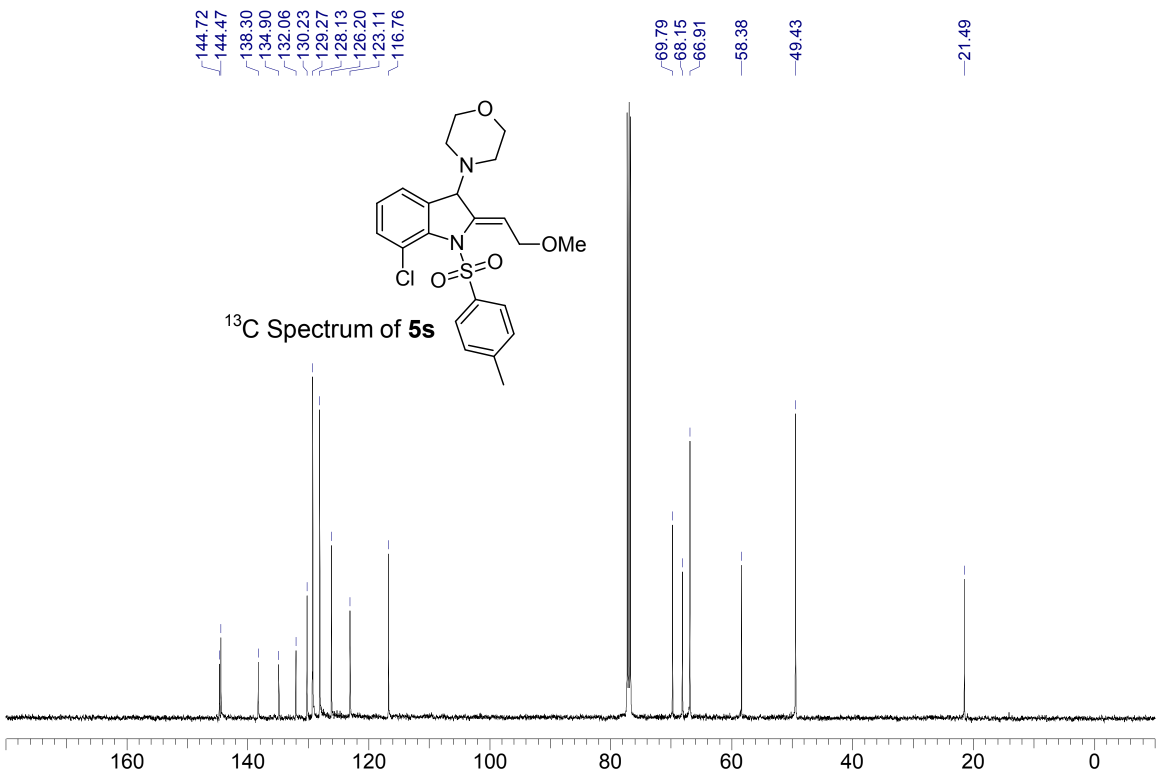


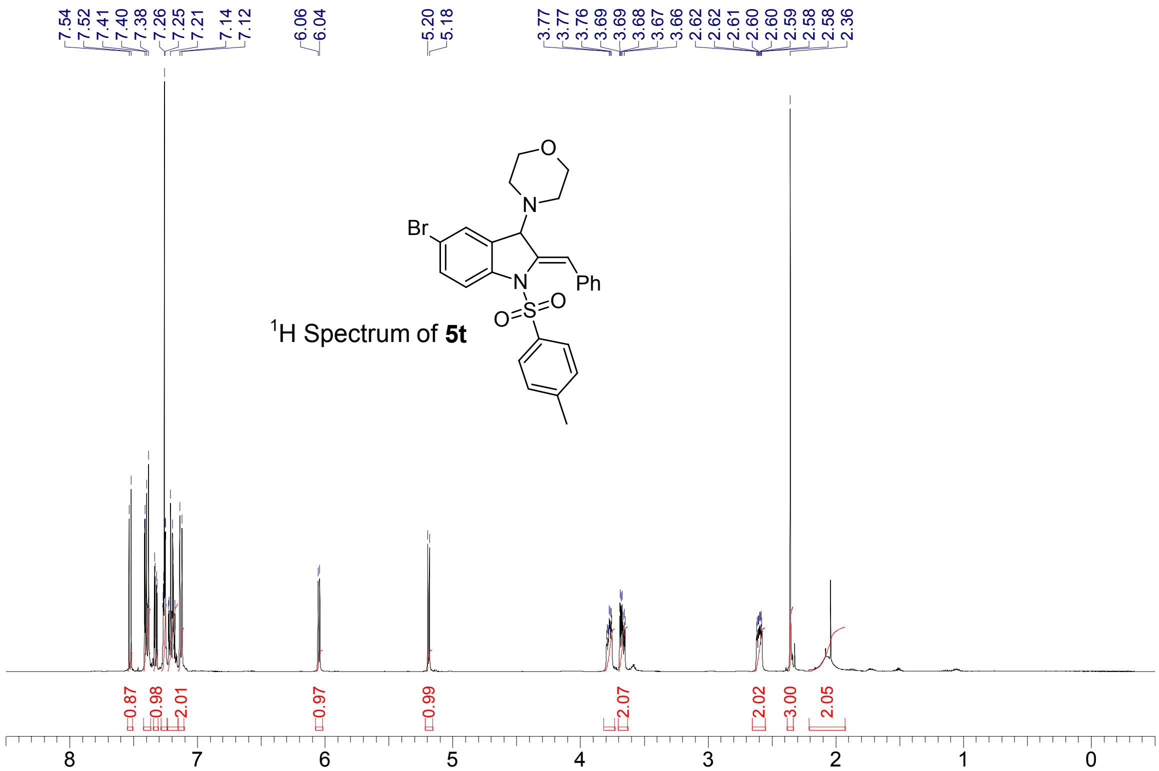
143.94
142.26
139.04
134.24
128.75
128.55
128.23
128.14
127.34
126.99
125.89
124.22
120.76
61.48
60.91
54.24
25.92
21.48
18.23
-5.13
-5.29
Bn
N
Bn
N
O
S
O
OTBS
13C Spectrum of 5q
160
140
120
100
80
60
40
20
0

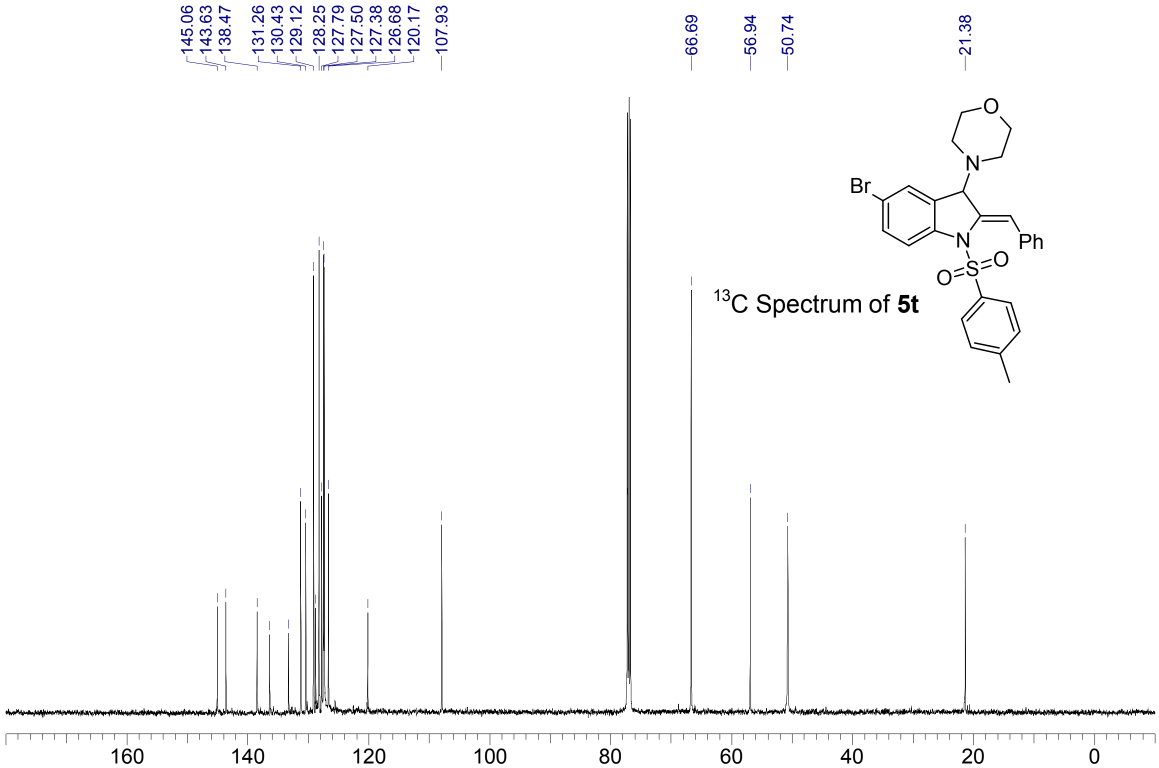

7.73
7.71
7.42
7.40
7.36
7.35
7.26
7.12
7.12
7.10
7.10
7.09
6.54
6.54
4.06
4.05
2.56
2.55
2.54
2.54
2.53
2.52
2.52
2.51
2.35
1.41
1.40
1.39
1.38
1.38
1.37
N
N
Ph
Cl
O=S=O
^{1}H Spectrum of **5r**
0.95
1.91
2.16
2.90
0.98
0.98
4.04
3.00
6.18
8
7
6
5
4
3
2
1
0

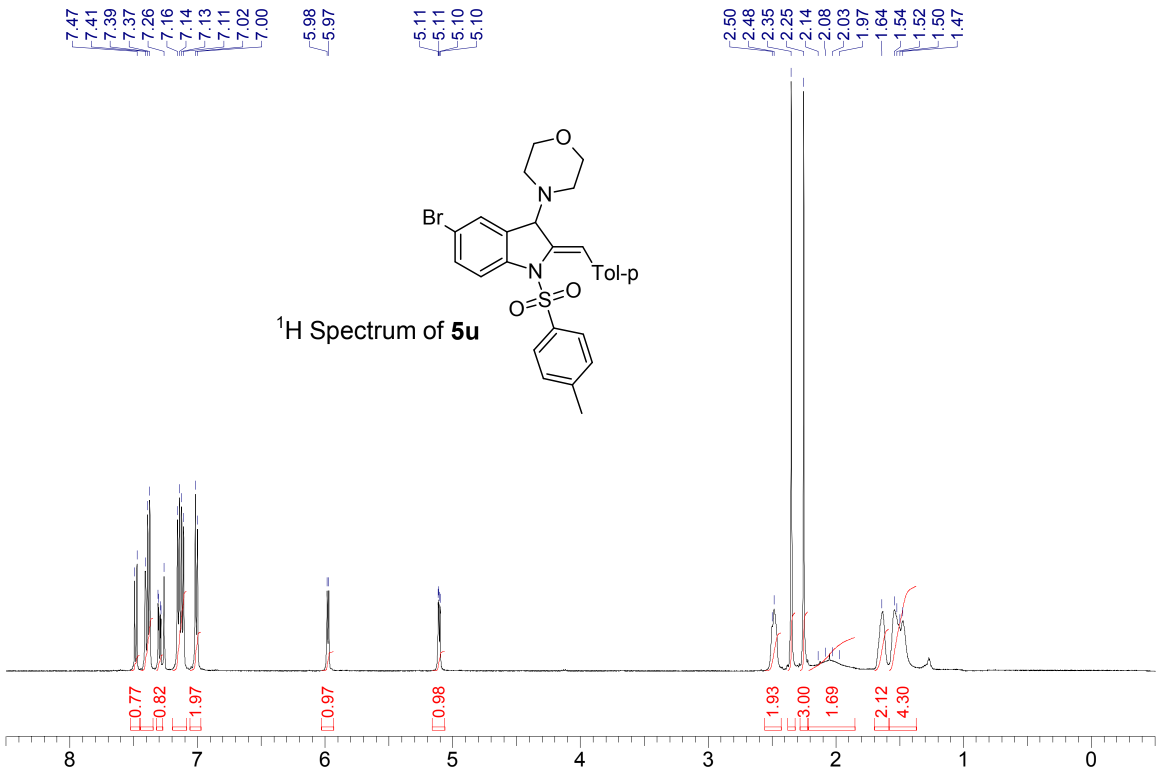

144.78
144.23
138.66
135.90
131.47
131.37
129.59
129.35
129.00
128.15
127.95
127.35
126.59
122.51
117.51
70.02
50.06
26.57
24.35
21.52
N
N
Ph
Cl
O=S=O
^{13}C Spectrum of **5r**
160
140
120
100
80
60
40
20
0

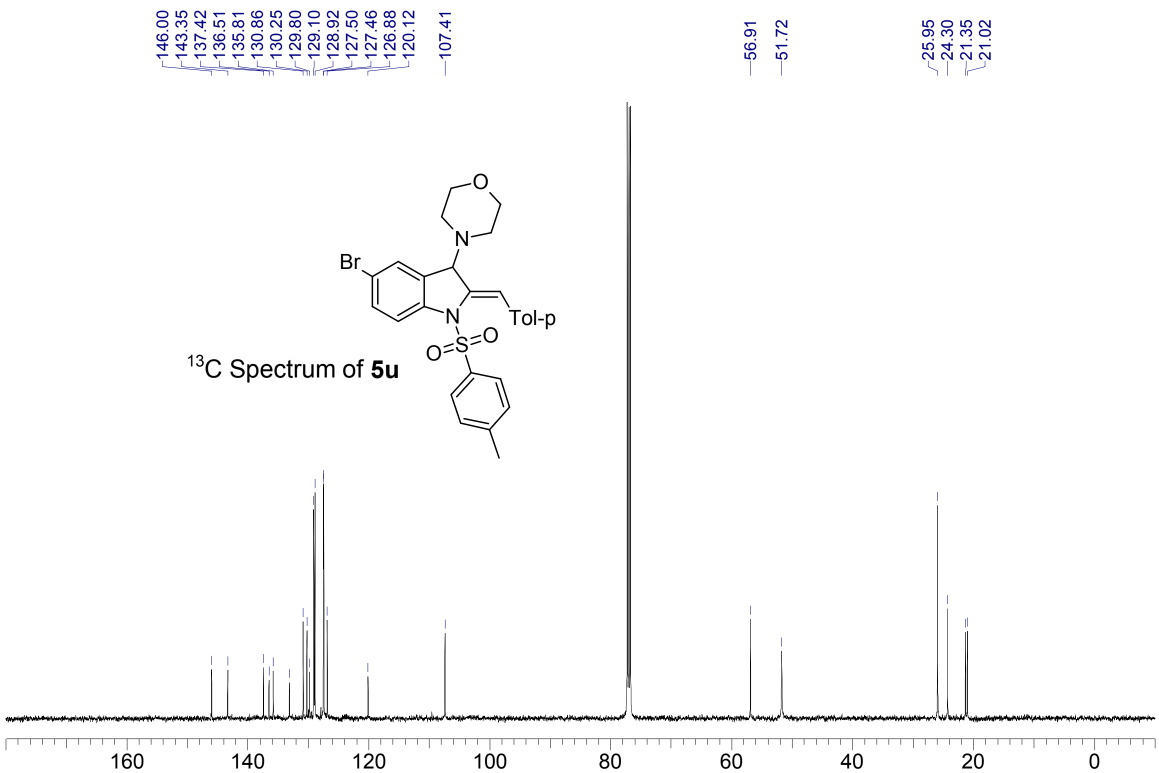

7.62
7.60
7.53
7.51
7.25
7.23
7.16
7.14
7.09
7.08
7.07
5.66
5.65
5.64
4.45
4.42
4.40
4.40
4.39
4.37
3.90
3.45
3.45
3.44
3.43
3.37
3.34
3.33
3.33
2.51
2.51
2.50
2.35
2.34
2.33
2.33
O
N
N
OMe
Cl
O=S=O
^{1}H Spectrum of **5s**
1.89
1.13
0.96
0.94
2.01
0.95
2.22
2.00
5.18
8
7
6
5
4
3
2
1
0

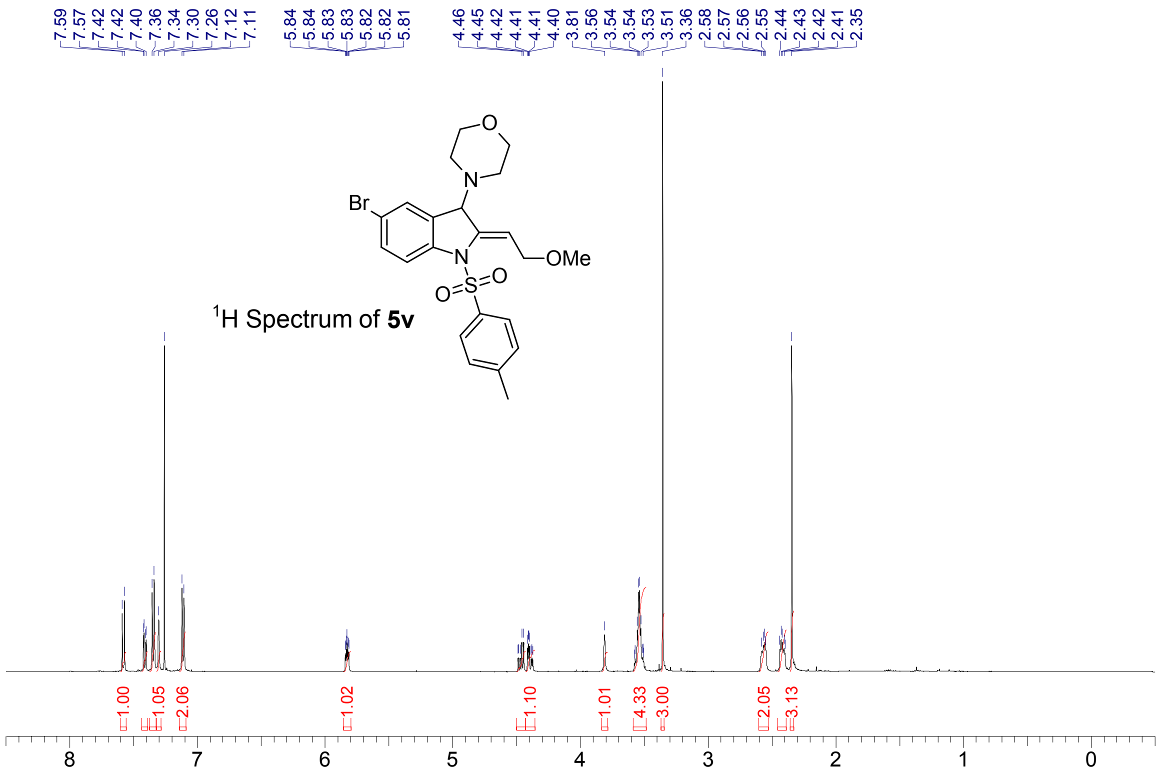

144.72
144.47
138.30
134.90
132.06
130.23
129.27
128.13
126.20
123.11
116.76
69.79
68.15
66.91
58.38
49.43
21.49
O
N
N
OMe
Cl
O=S=O
^{13}C Spectrum of **5s**
160
140
120
100
80
60
40
20
0

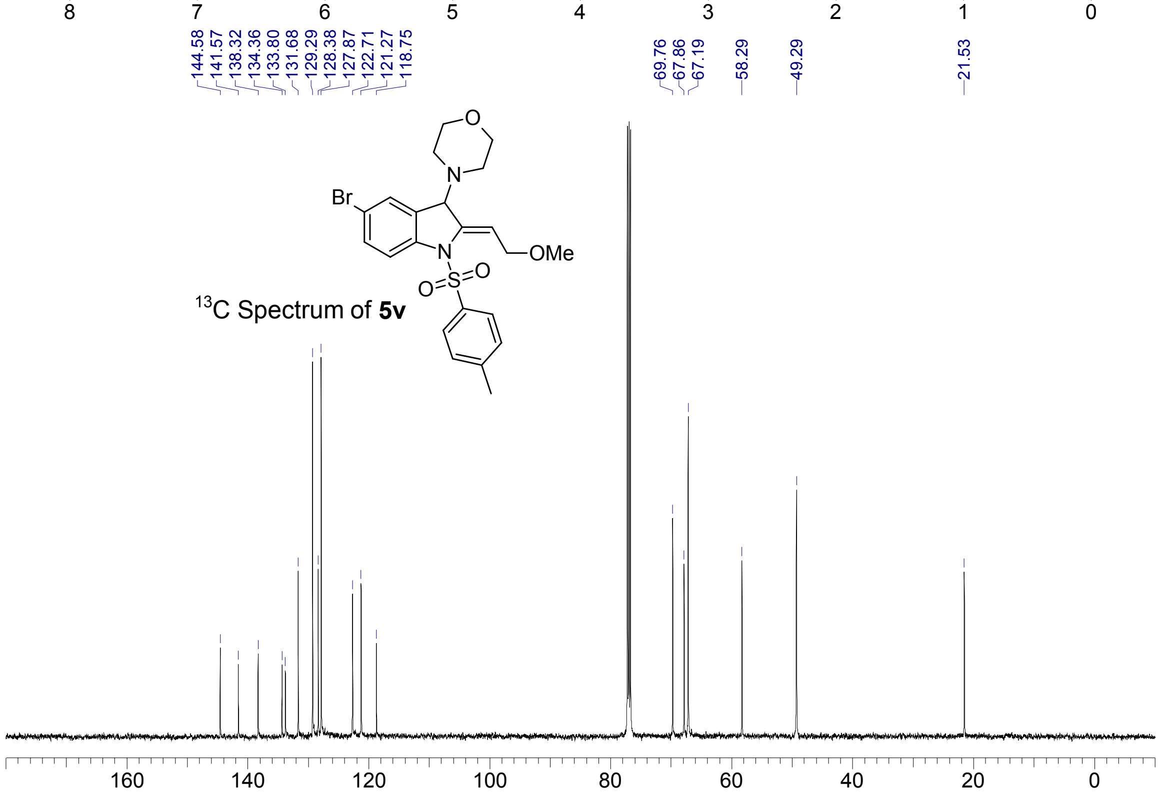

7.54
7.52
7.41
7.40
7.38
7.26
7.25
7.21
7.14
7.12
6.06
6.04
5.20
5.18
3.77
3.77
3.76
3.69
3.69
3.68
3.67
3.66
2.62
2.62
2.61
2.60
2.60
2.59
2.58
2.58
2.36
Br
O
N
N
Ph
O=S=O
[1]H Spectrum of 5t
0.87
0.98
2.01
0.97
0.99
2.07
2.02
3.00
2.05
8
7
6
5
4
3
2
1
0

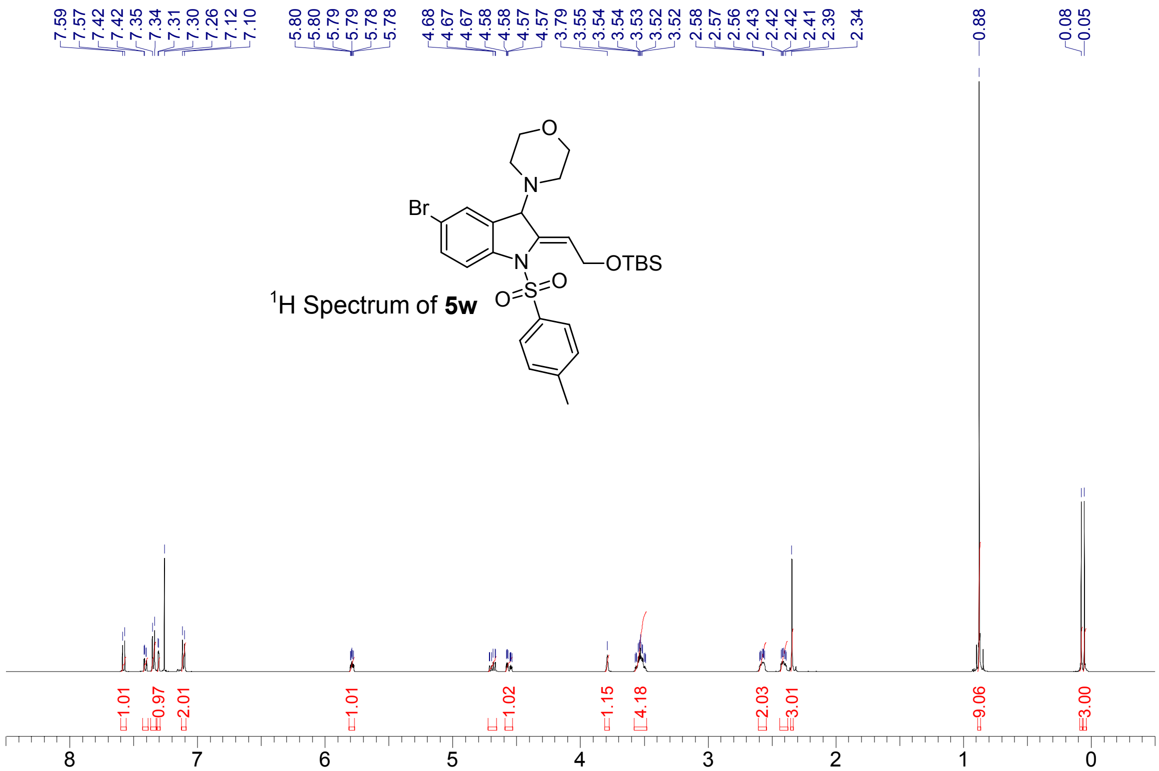

145.06
143.63
138.47
131.26
130.43
129.12
128.25
127.79
127.50
127.38
126.68
120.17
107.93
66.69
56.94
50.74
21.38
Br
O
N
N
Ph
O=S=O
[13]C Spectrum of 5t
160
140
120
100
80
60
40
20
0


7.47 7.41 7.39 7.37 7.26 7.16 7.14 7.13 7.11 7.02 7.00
5.98 5.97
5.11 5.11 5.10 5.10
2.50 2.48 2.35 2.25 2.14 2.08 2.03 1.97 1.64 1.54 1.52 1.50 1.47
Br
N
O
N
S
O
O
Tol-p
[1]H Spectrum of 5u
0.77 0.82 1.97 0.97 0.98 1.93 3.00 1.69 2.12 4.30
8 7 6 5 4 3 2 1 0

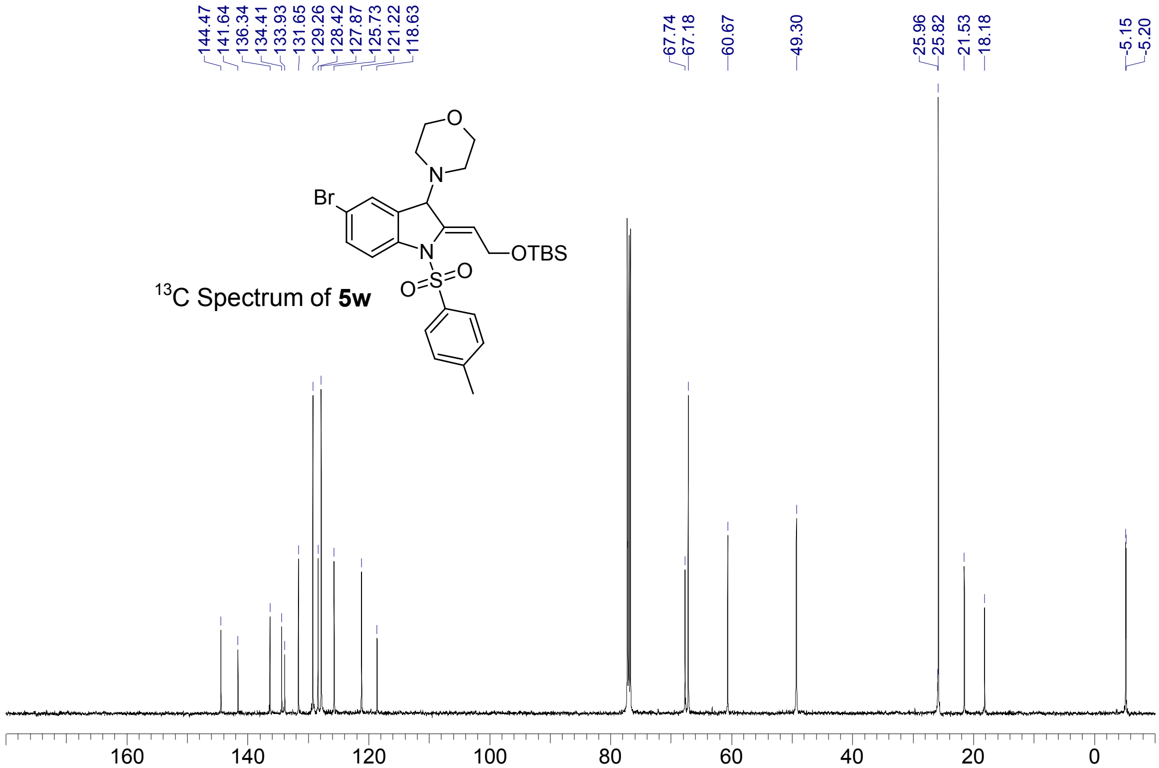

146.00 143.35 137.42 136.51 135.81 130.86 130.25 129.80 129.10 128.92 127.50 127.46 126.88 120.12
107.41
56.91 51.72
25.95 24.30 21.35 21.02
Br
N
O
N
S
O
O
Tol-p
[13]C Spectrum of 5u
160 140 120 100 80 60 40 20 0


7.59
7.57
7.42
7.42
7.40
7.36
7.34
7.30
7.26
7.12
7.11
5.84
5.84
5.83
5.83
5.82
5.82
5.81
4.46
4.45
4.42
4.41
4.41
4.40
3.81
3.56
3.54
3.54
3.53
3.51
3.36
2.58
2.57
2.56
2.55
2.44
2.43
2.42
2.41
2.35
Br
N
O
N
OMe
O=S=O
^{1}H Spectrum of **5v**
1.00
1.05
2.06
1.02
1.10
1.01
4.33
3.00
2.05
3.13
8
7
6
5
4
3
2
1
0

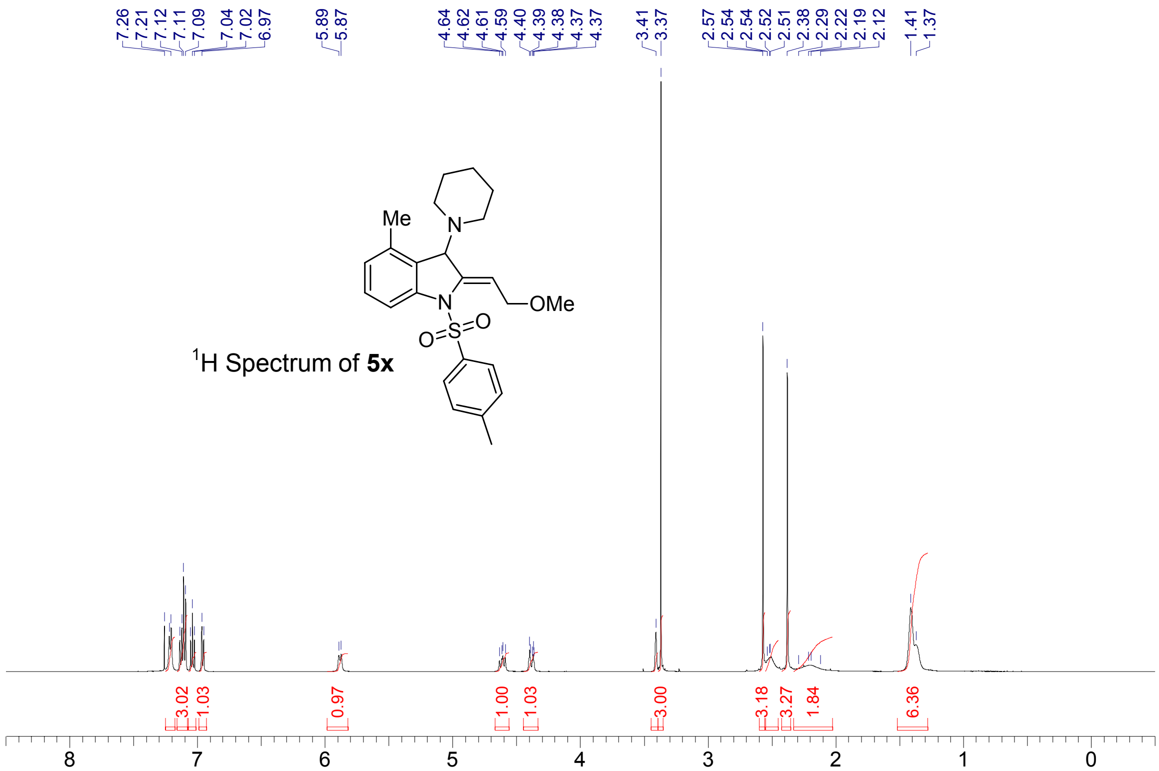

144.58
141.57
138.32
134.36
133.80
131.68
129.29
128.38
127.87
122.71
121.27
118.75
69.76
67.86
67.19
58.29
49.29
21.53
Br
N
O
N
OMe
O=S=O
^{13}C Spectrum of **5v**
160
140
120
100
80
60
40
20
0

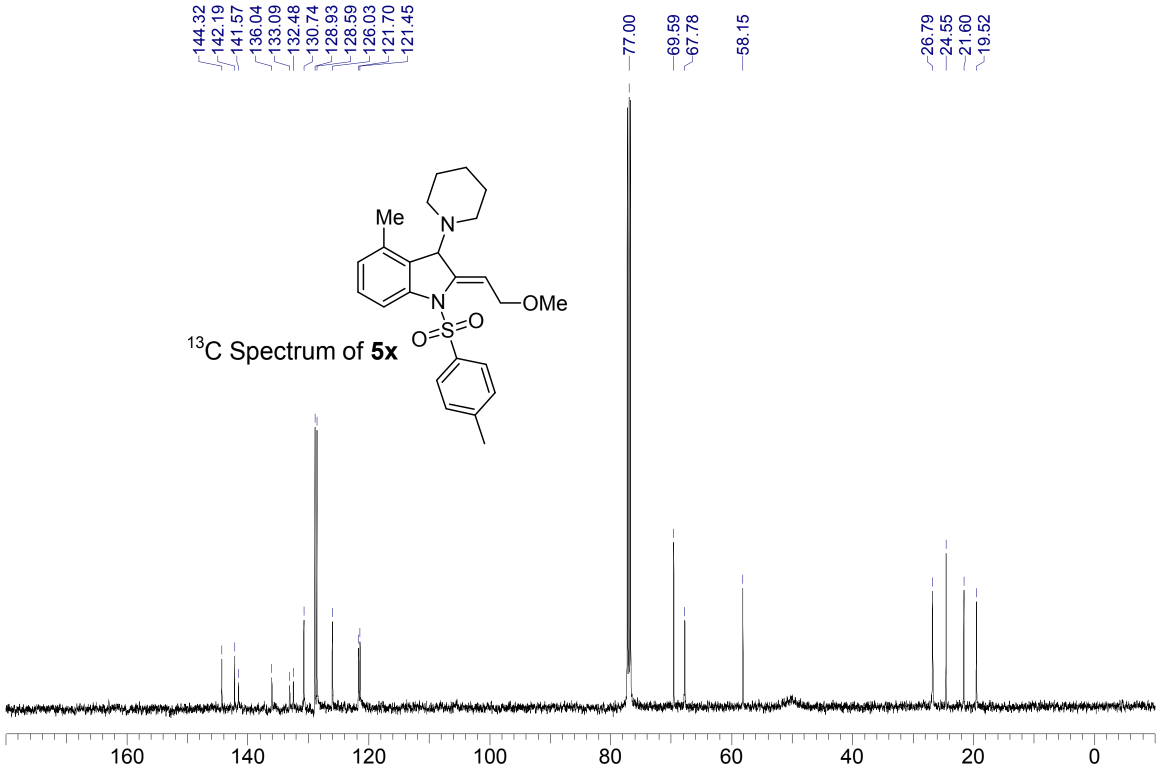


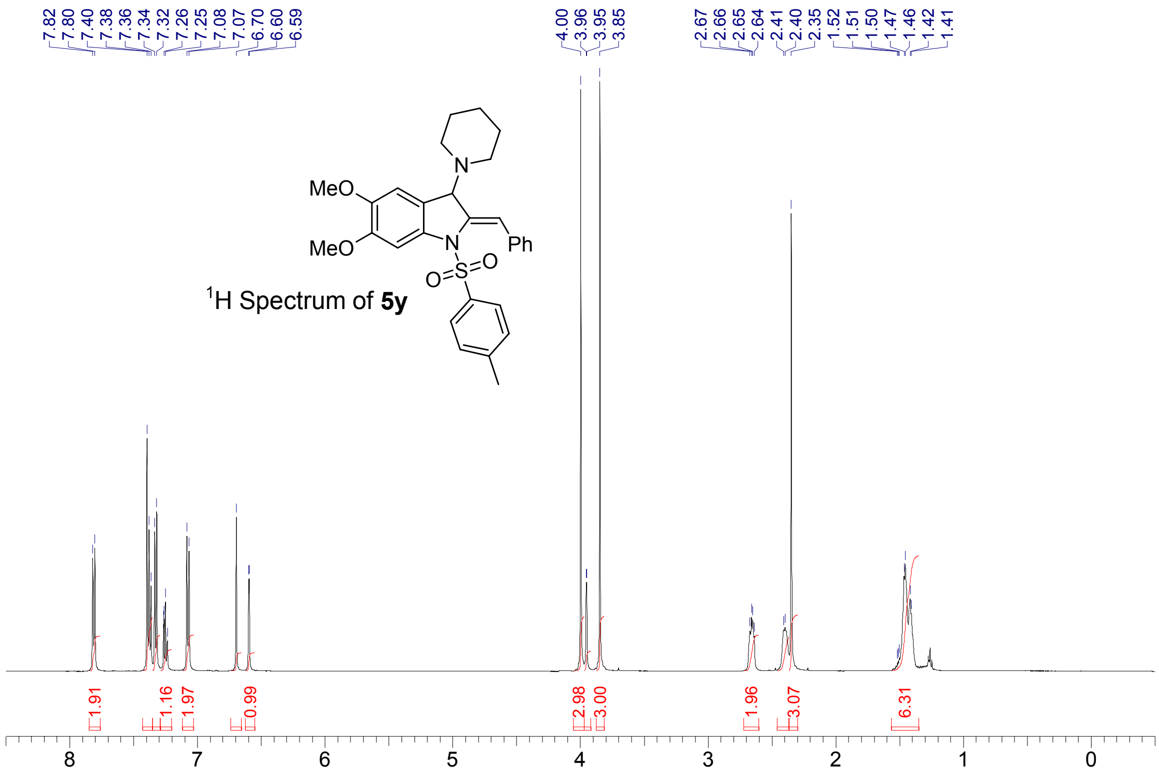
7.59
7.57
7.42
7.42
7.35
7.34
7.31
7.30
7.26
7.12
7.10
5.80
5.80
5.79
5.79
5.78
5.78
4.68
4.67
4.67
4.58
4.58
4.57
4.57
3.79
3.55
3.54
3.54
3.53
3.52
3.52
2.58
2.57
2.56
2.43
2.42
2.42
2.41
2.39
2.34
0.88
0.08
0.05
Br
O
N
OTBS
S
^{1}H Spectrum of **5w**
1.01
0.97
2.01
1.01
1.02
1.15
4.18
2.03
3.01
9.06
3.00
8
7
6
5
4
3
2
1
0

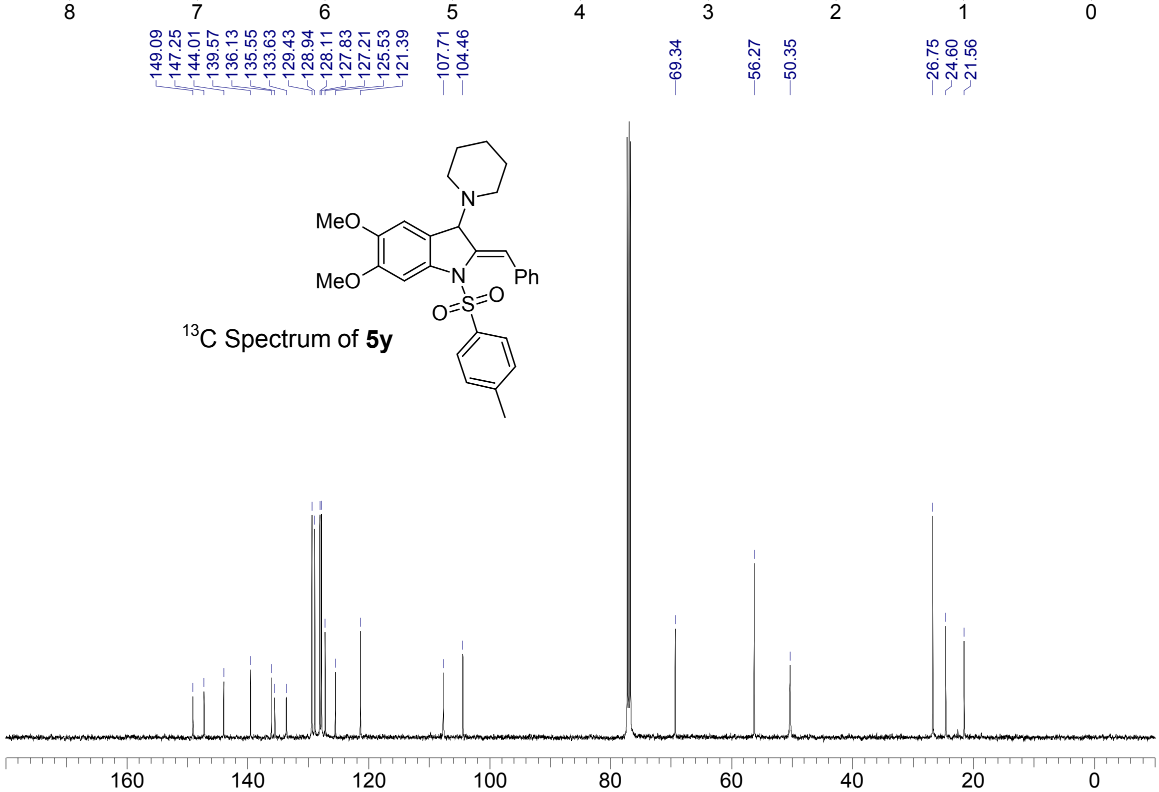


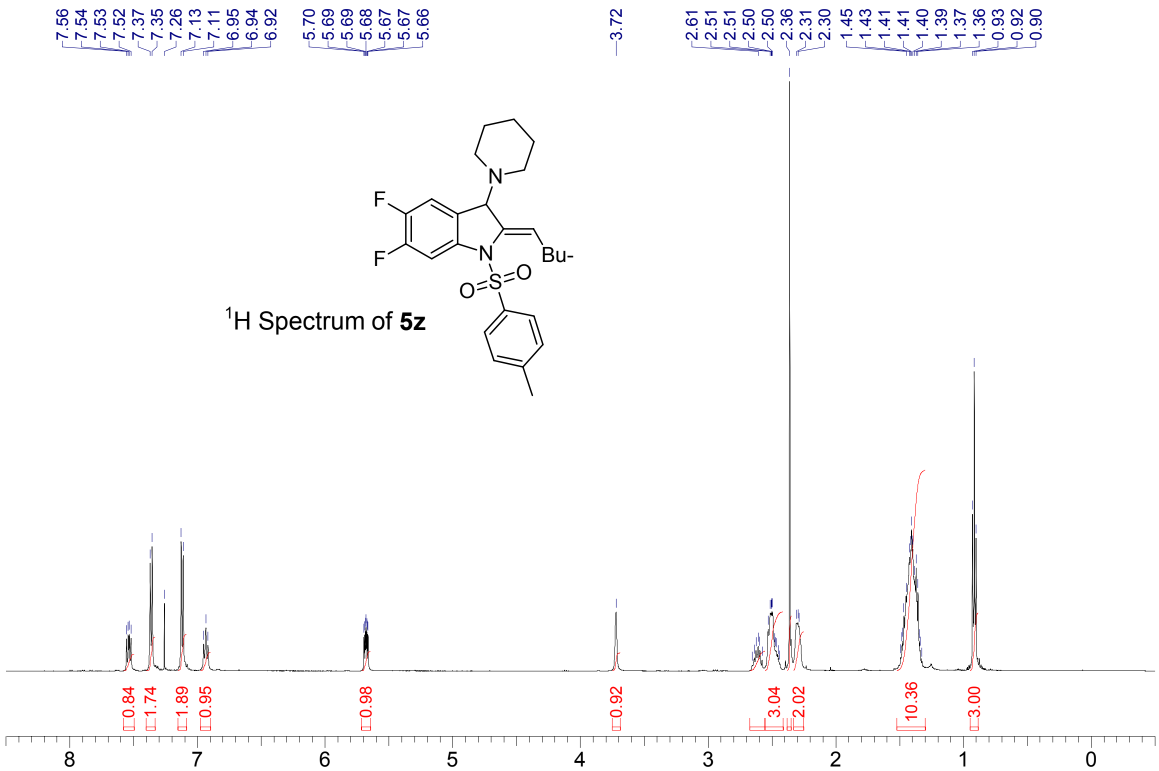
144.47
141.64
136.34
134.41
133.93
131.65
129.26
128.42
127.87
125.73
121.22
118.63
67.74
67.18
60.67
49.30
25.96
25.82
21.53
18.18
-5.15
-5.20
Br
O
N
OTBS
S
^{13}C Spectrum of **5w**
160
140
120
100
80
60
40
20
0


7.26
7.21
7.12
7.11
7.09
7.04
7.02
6.97
5.89
5.87
4.64
4.62
4.61
4.59
4.40
4.39
4.38
4.37
4.37
3.41
3.37
2.57
2.54
2.54
2.52
2.51
2.38
2.29
2.22
2.19
2.12
1.41
1.37
Me
N
N
OMe
O=S=O
[1]H Spectrum of 5x
3.02
1.03
0.97
1.00
1.03
3.00
3.18
3.27
1.84
6.36
8
7
6
5
4
3
2
1
0

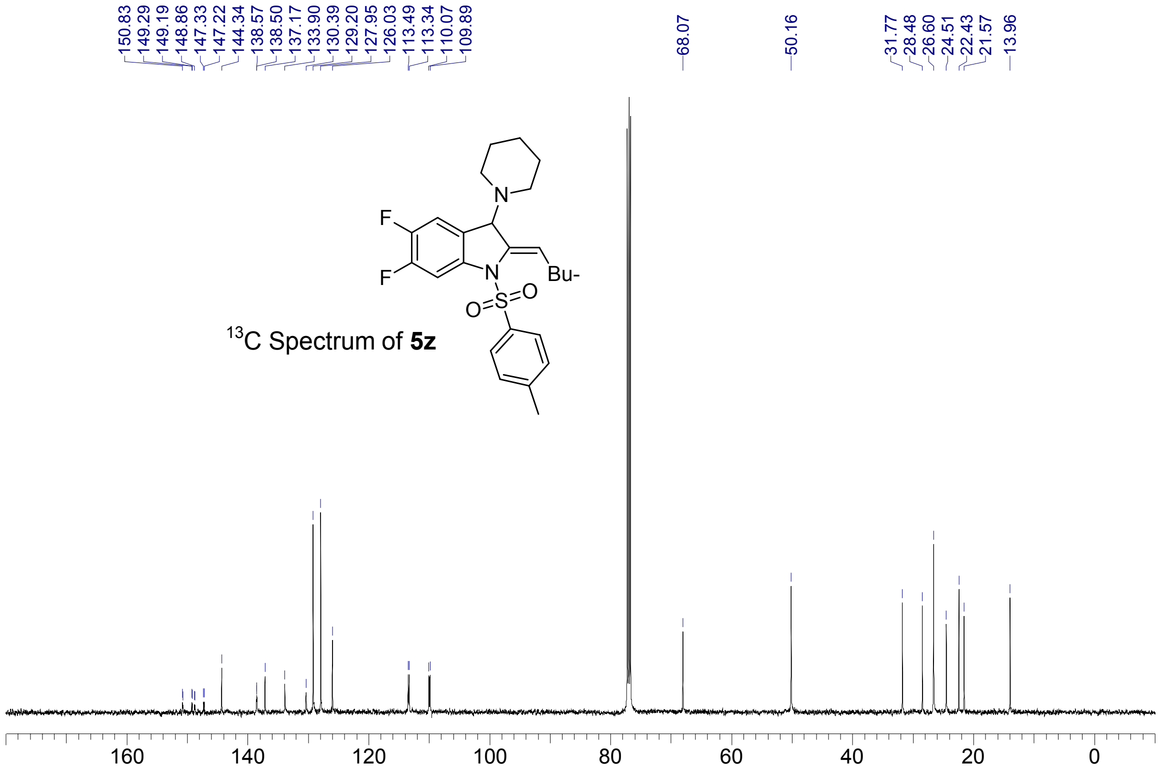

144.32
142.19
141.57
136.04
133.09
132.48
130.74
128.93
128.59
126.03
121.70
121.45
77.00
69.59
67.78
58.15
26.79
24.55
21.60
19.52
Me
N
N
OMe
O=S=O
[13]C Spectrum of 5x
160
140
120
100
80
60
40
20
0


7.82
7.80
7.40
7.38
7.36
7.34
7.32
7.26
7.25
7.08
7.07
6.70
6.60
6.59
4.00
3.96
3.95
3.85
2.67
2.66
2.65
2.64
2.41
2.40
2.35
1.52
1.51
1.50
1.47
1.46
1.42
1.41
MeO
MeO
N
N
Ph
O=S=O
1H Spectrum of 5y
1.91
1.16
1.97
0.99
2.98
3.00
1.96
3.07
6.31
8
7
6
5
4
3
2
1
0

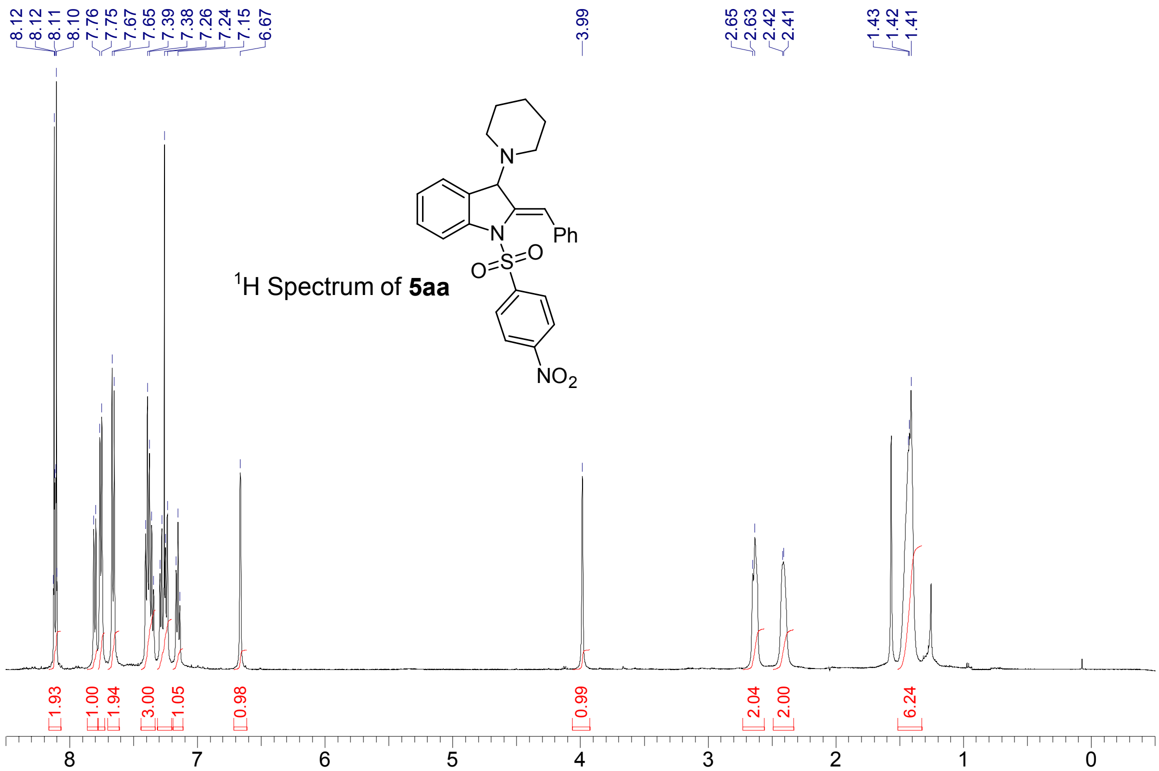

149.09
147.25
144.01
139.57
136.13
135.55
133.63
129.43
128.94
128.11
127.83
127.21
125.53
121.39
107.71
104.46
69.34
56.27
50.35
26.75
24.60
21.56
MeO
MeO
N
N
Ph
O=S=O
13C Spectrum of 5y
160
140
120
100
80
60
40
20
0

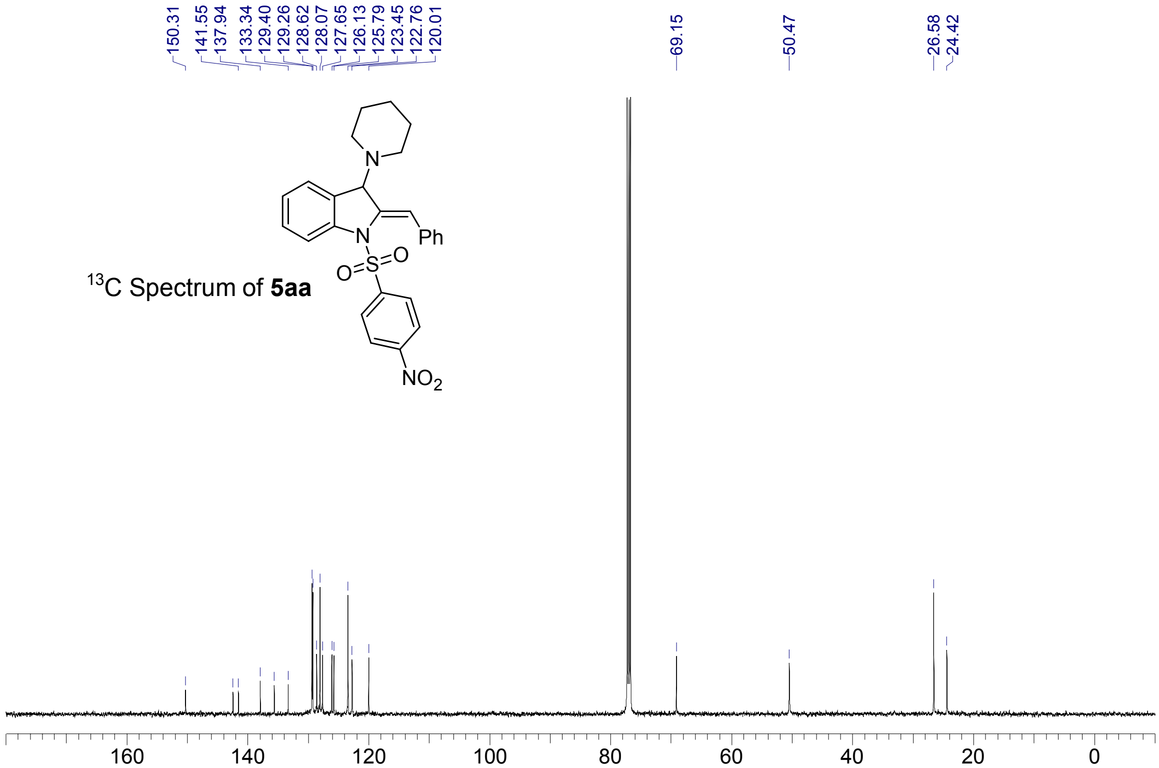


7.56 7.54 7.53 7.52 7.37 7.35 7.26 7.13 7.11 6.95 6.94 6.92 5.70 5.69 5.69 5.68 5.67 5.67 5.66 3.72 2.61 2.51 2.51 2.50 2.50 2.36 2.31 2.30 1.45 1.43 1.41 1.41 1.40 1.39 1.37 1.36 0.93 0.92 0.90
F
F
N
N
Bu-
O=S=O
^{1}H Spectrum of **5z**
0.84 1.74 1.89 0.95 0.98 0.92 3.04 2.02 10.36 3.00
8 7 6 5 4 3 2 1 0



150.83 149.29 149.19 148.86 147.33 147.22 144.34 138.57 138.50 137.17 133.90 130.39 129.20 127.95 126.03 113.49 113.34 110.07 109.89 68.07 50.16 31.77 28.48 26.60 24.51 22.43 21.57 13.96
F
F
N
N
Bu-
O=S=O
^{13}C Spectrum of **5z**
160 140 120 100 80 60 40 20 0


8.12
8.12
8.11
8.10
7.76
7.75
7.67
7.65
7.39
7.38
7.26
7.24
7.15
6.67
3.99
2.65
2.63
2.42
2.41
1.43
1.42
1.41
N
N
S
O
O
Ph
NO2
1H Spectrum of 5aa
1.93
1.00
1.94
3.00
1.05
0.98
0.99
2.04
2.00
6.24
8
7
6
5
4
3
2
1
0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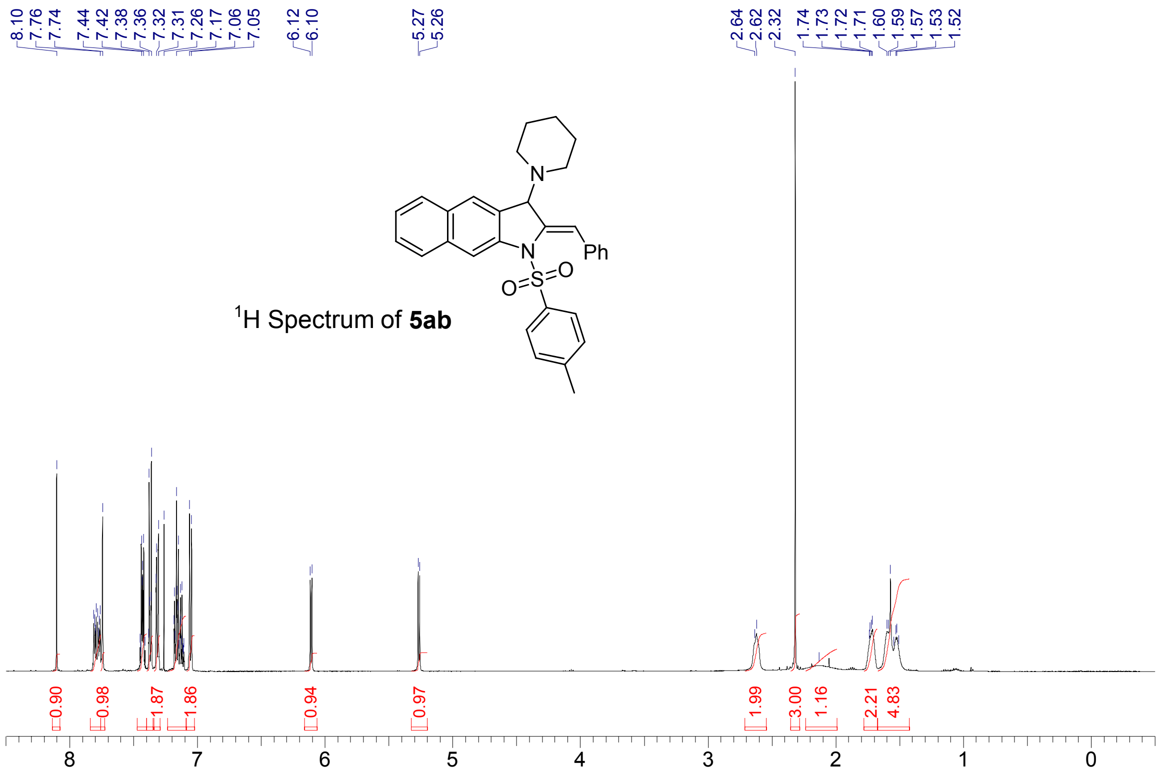
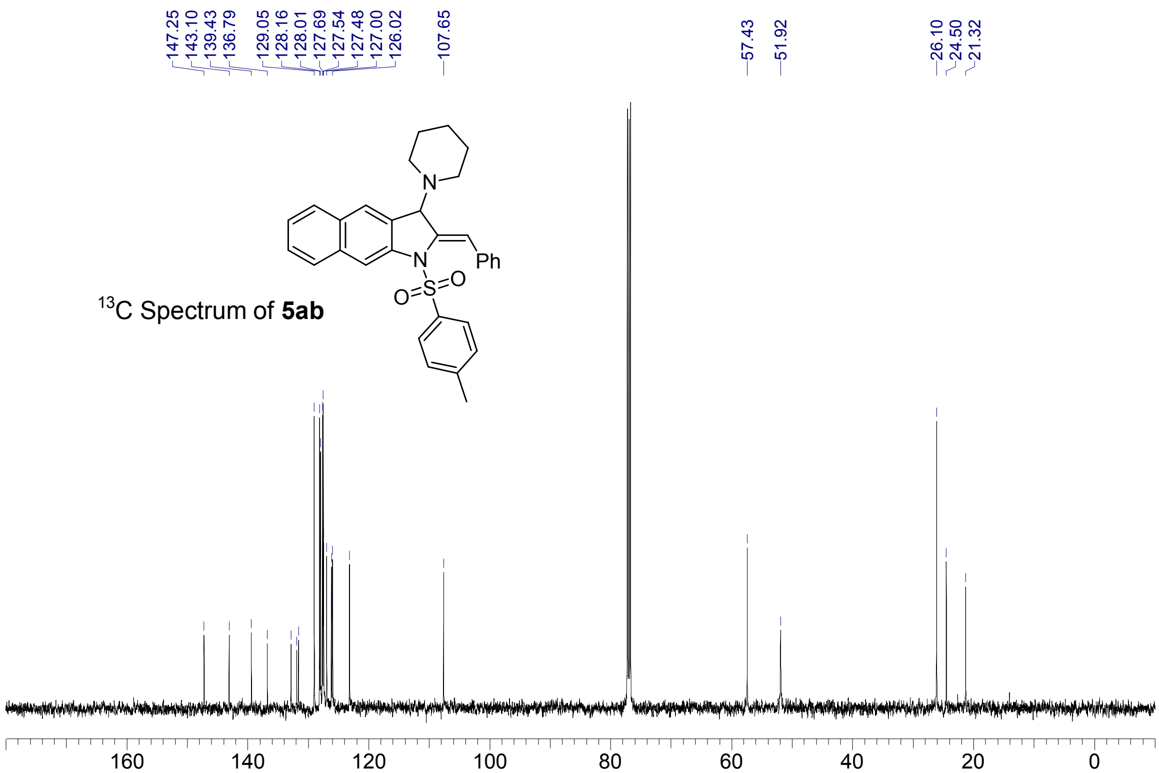
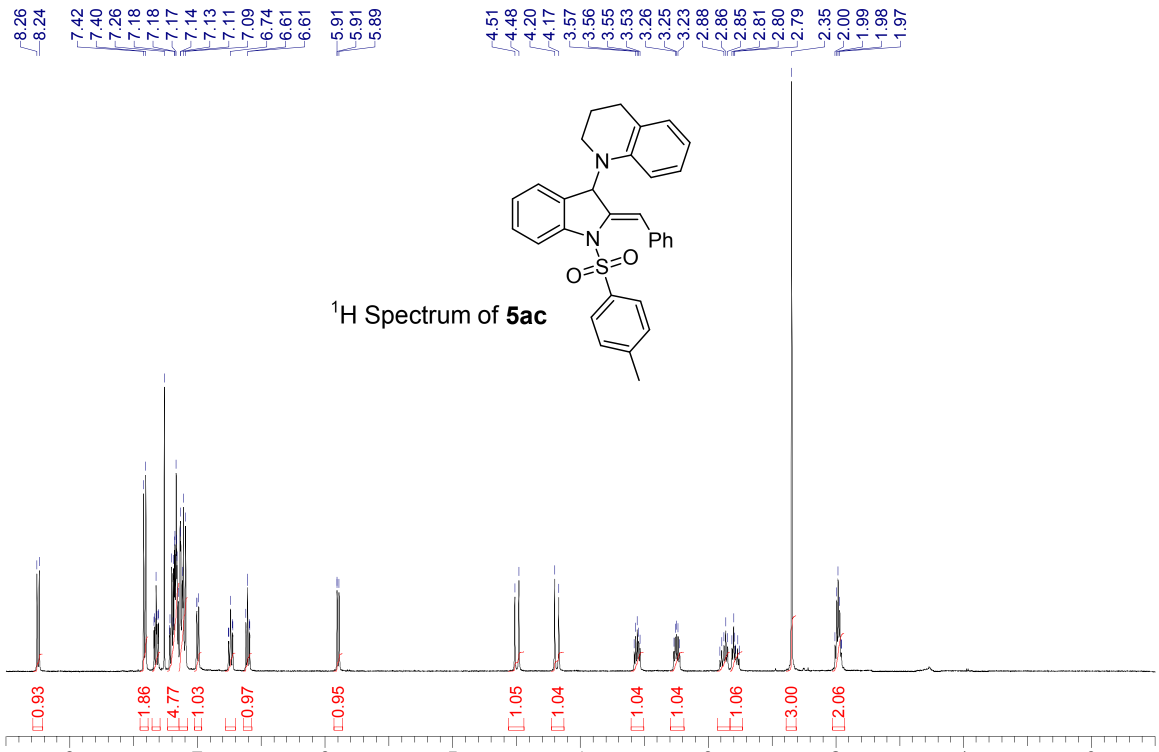
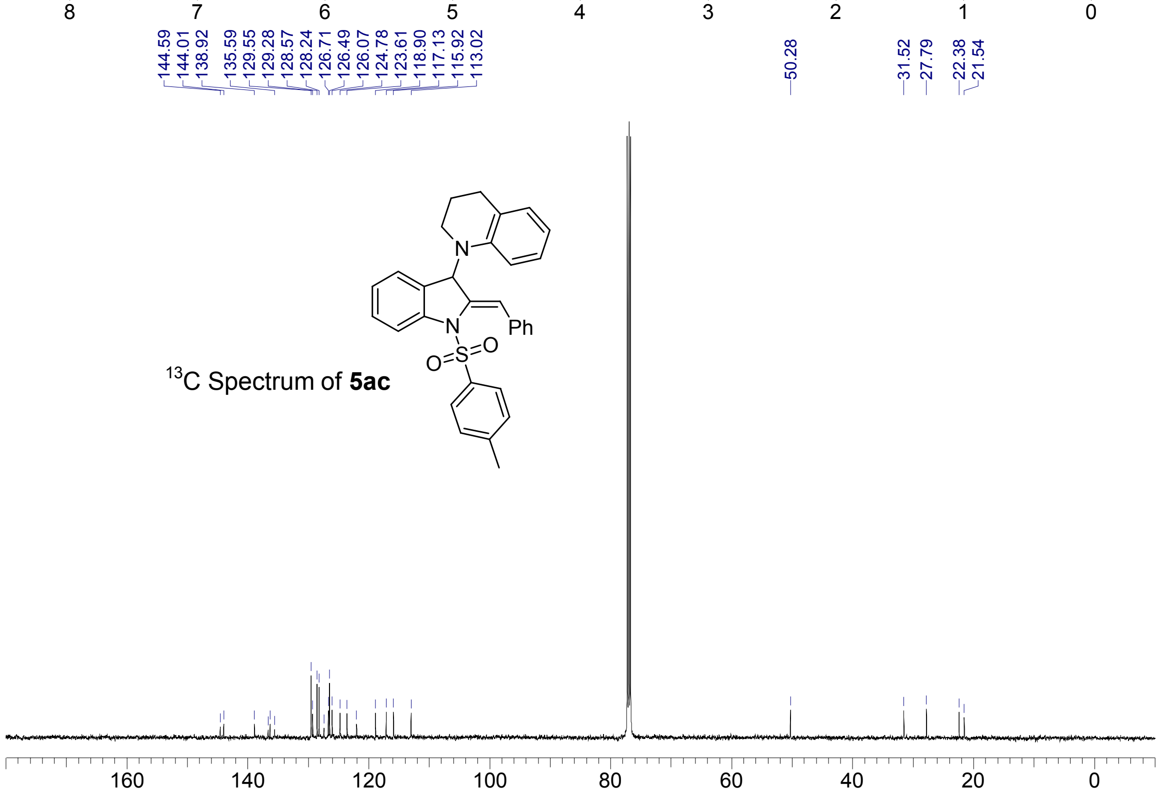
141.55
137.94
133.34
129.40
129.26
128.62
128.07
127.65
126.13
125.79
123.45
122.76
120.01
69.15
50.47
26.58
24.42
N
N
S
O
O
Ph
NO2
13C Spectrum of 5aa
160
140
120
100
80
60
40
20
0


8.10
7.76
7.74
7.44
7.42
7.38
7.36
7.32
7.31
7.26
7.17
7.06
7.05
6.12
6.10
5.27
5.26
2.64
2.62
2.32
1.74
1.73
1.72
1.71
1.60
1.59
1.57
1.53
1.52
N
N
Ph
O=S=O
^{1}H Spectrum of **5ab**
0.90
0.98
1.87
1.86
0.94
0.97
1.99
3.00
1.16
2.21
4.83

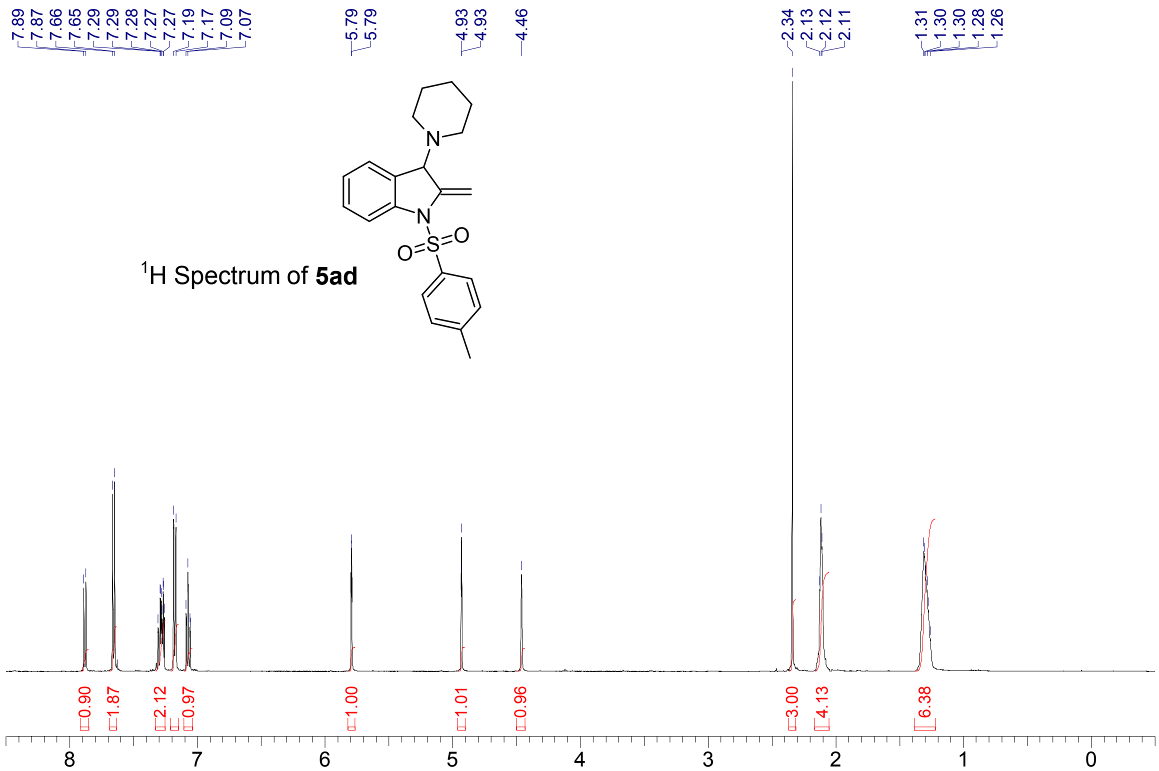

147.25
143.10
139.43
136.79
129.05
128.16
128.01
127.69
127.54
127.48
127.00
126.02
107.65
57.43
51.92
26.10
24.50
21.32
N
N
Ph
O=S=O
^{13}C Spectrum of **5ab**

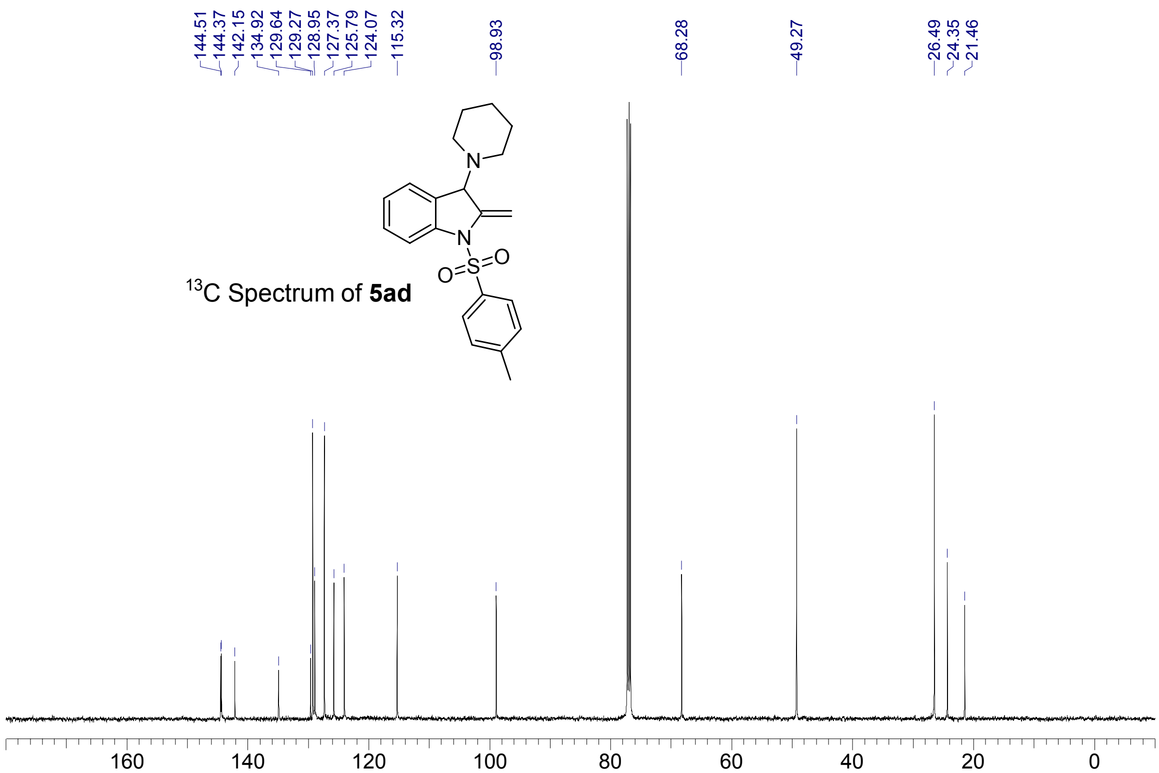


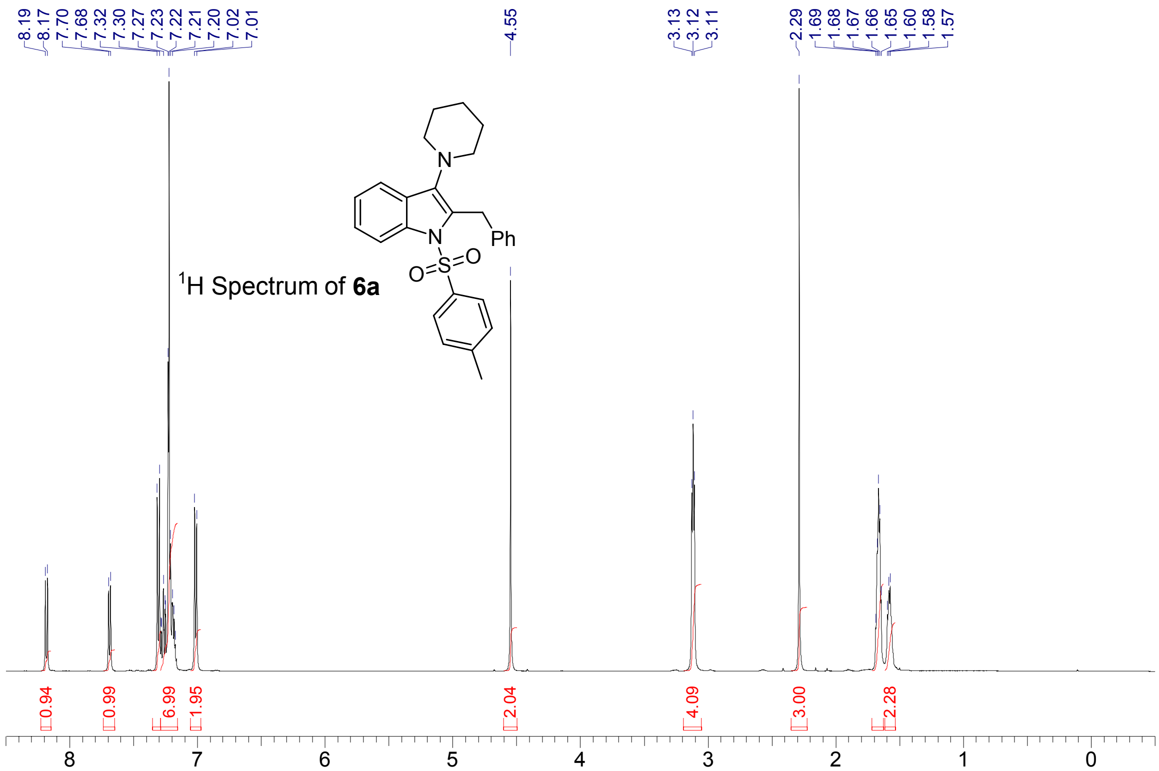
8.26
8.24
7.42
7.40
7.26
7.18
7.18
7.17
7.14
7.13
7.11
7.09
6.74
6.61
6.61
6.61
5.91
5.91
5.89
4.51
4.48
4.20
4.17
3.57
3.56
3.55
3.53
3.26
3.25
3.23
2.88
2.86
2.85
2.81
2.80
2.79
2.35
2.00
1.99
1.98
1.97
N
N
Ph
S
O
O
^{1}H Spectrum of **5ac**
0.93
1.86
4.77
1.03
0.97
0.95
1.05
1.04
1.04
1.04
1.06
3.00
2.06
8
7
6
5
4
3
2
1
0

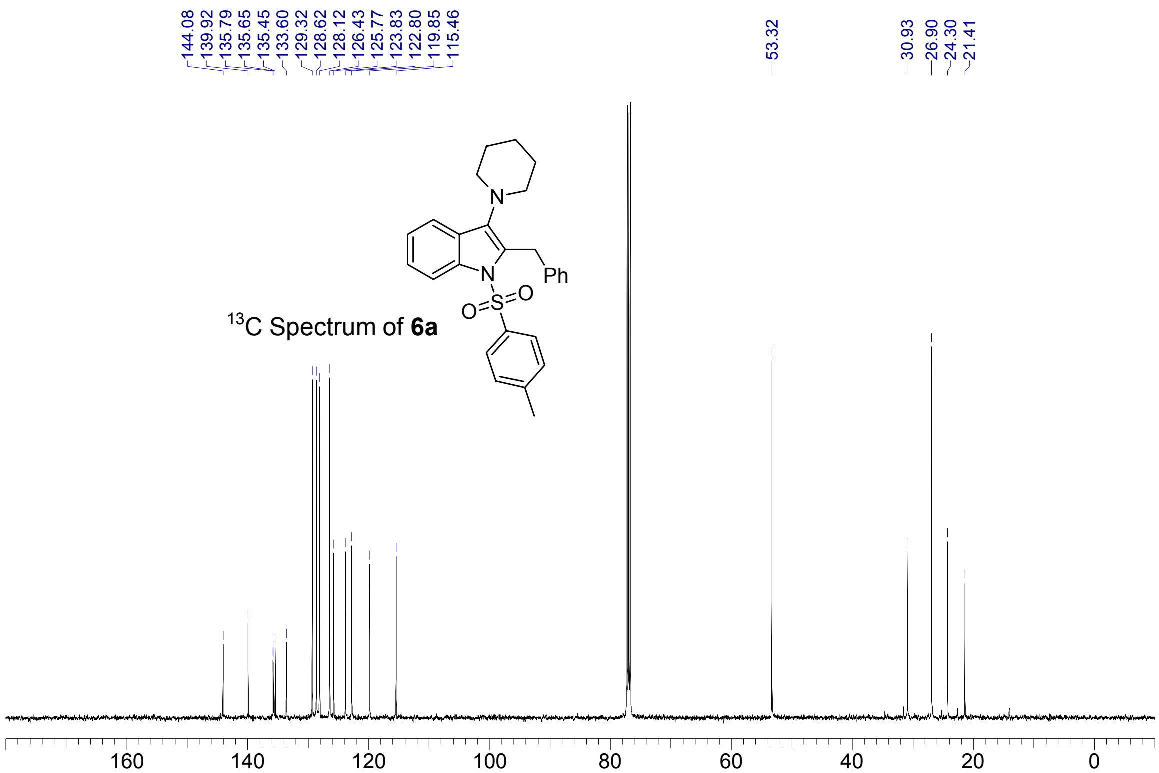


144.59
144.01
138.92
135.59
129.55
129.28
128.57
128.24
126.71
126.49
126.07
124.78
123.61
118.90
117.13
115.92
113.02
50.28
31.52
27.79
22.38
21.54
N
N
Ph
S
O
O
^{13}C Spectrum of **5ac**
160
140
120
100
80
60
40
20
0


7.89
7.87
7.66
7.65
7.29
7.29
7.28
7.27
7.27
7.19
7.17
7.09
7.07
5.79
5.79
4.93
4.93
4.46
2.34
2.13
2.12
2.11
1.31
1.30
1.30
1.28
1.26
N
N
S
O
O
^{1}H Spectrum of **5ad**
0.90
1.87
2.12
0.97
1.00
1.01
0.96
3.00
4.13
6.38
8
7
6
5
4
3
2
1
0


144.51
144.37
142.15
134.92
129.64
129.27
128.95
127.37
125.79
124.07
115.32
98.93
68.28
49.27
26.49
24.35
21.46
N
N
S
O
O
^{13}C Spectrum of **5ad**
160
140
120
100
80
60
40
20
0


8.19
8.17
7.70
7.68
7.32
7.30
7.27
7.23
7.22
7.21
7.20
7.02
7.01
4.55
3.13
3.12
3.11
2.29
1.69
1.68
1.67
1.66
1.65
1.60
1.58
1.57
N
N
Ph
O=S=O
1H Spectrum of 6a
0.94
0.99
6.99
1.95
2.04
4.09
3.00
2.28
8
7
6
5
4
3
2
1
0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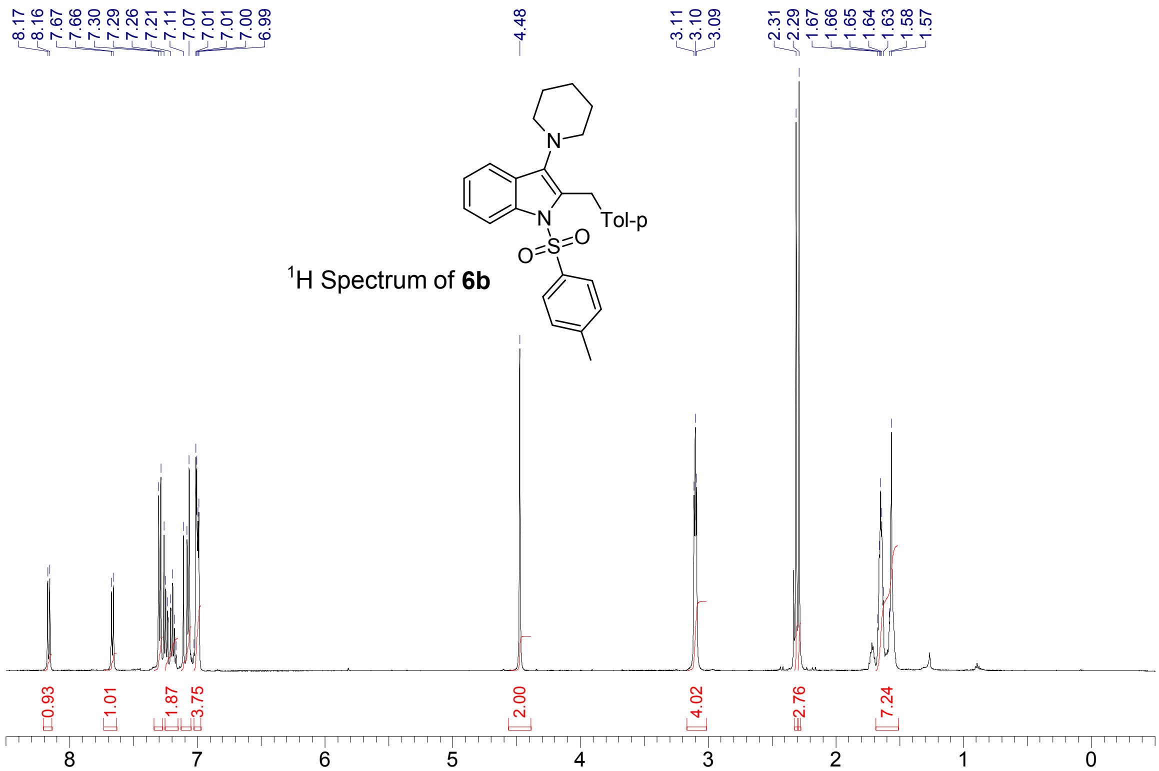
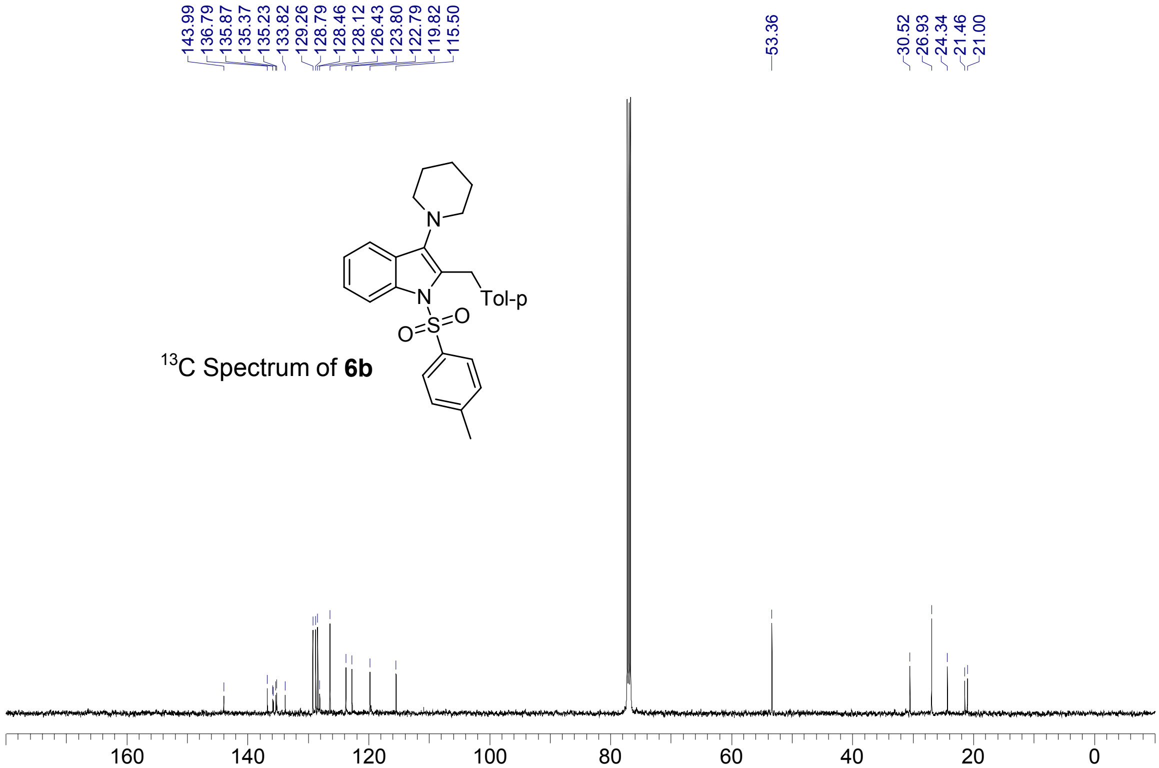
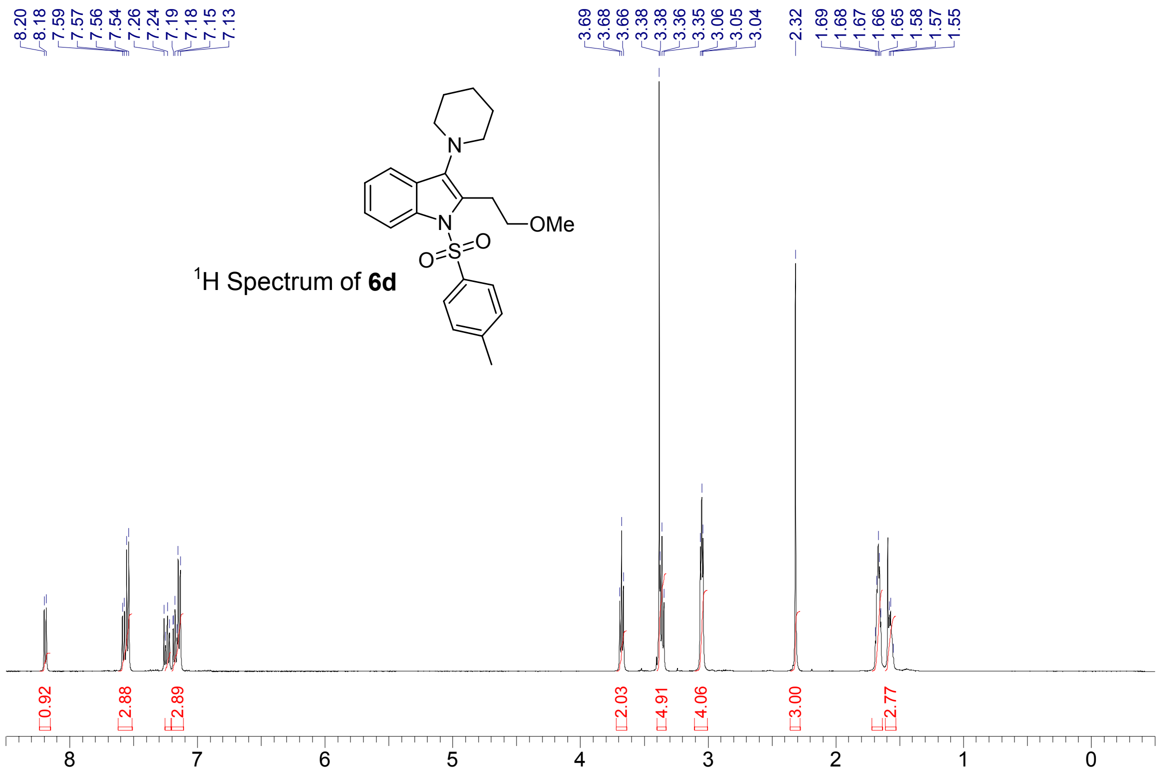
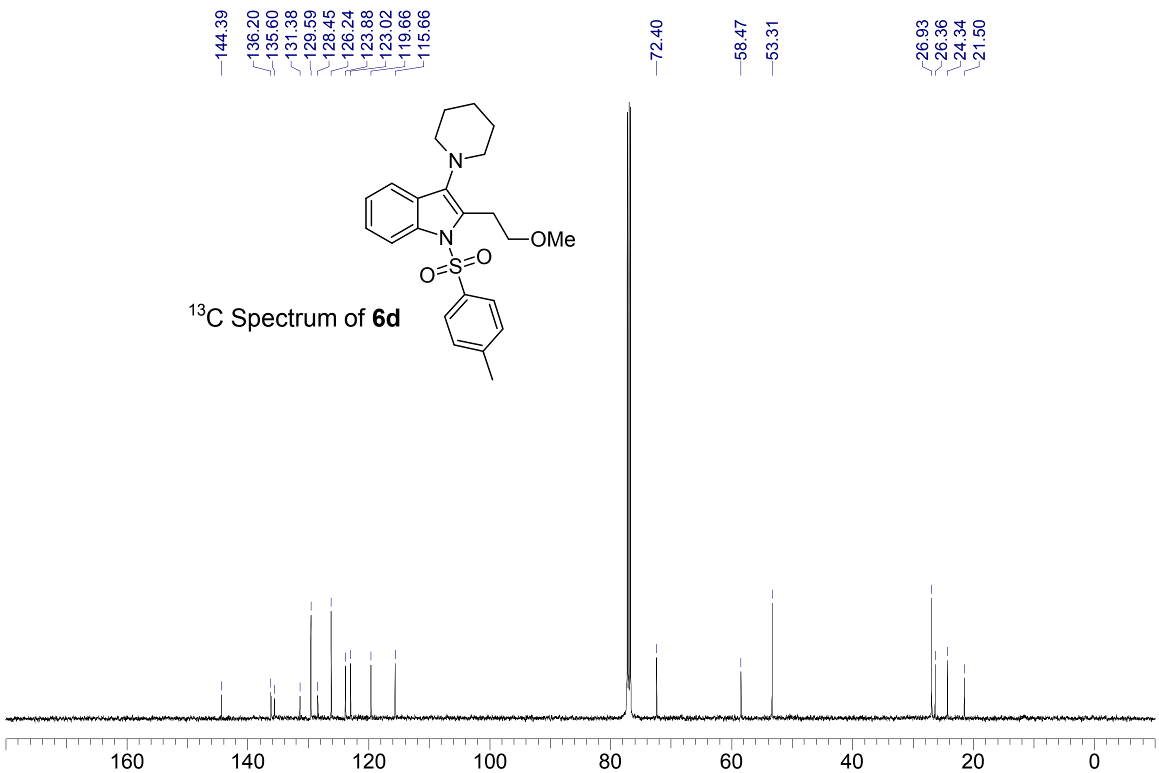
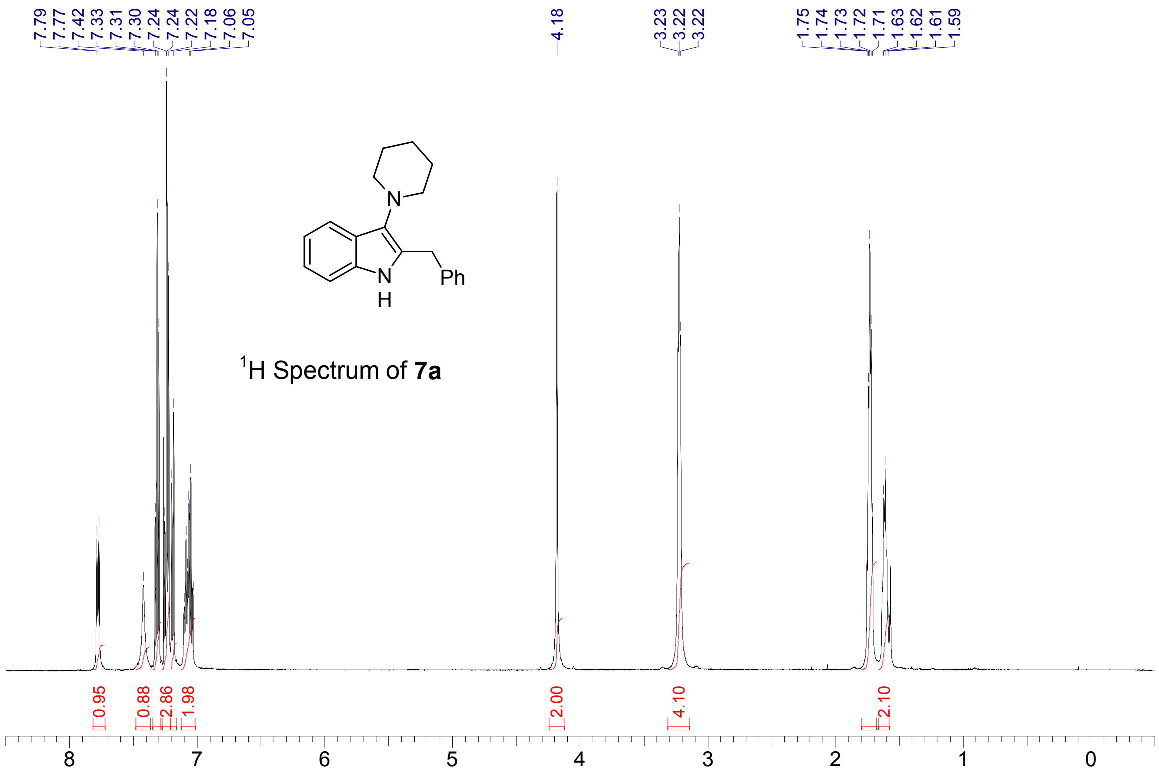
139.92
135.79
135.65
135.45
133.60
129.32
128.62
128.12
126.43
125.77
123.83
122.80
119.85
115.46
53.32
30.93
26.90
24.30
21.41
N
N
Ph
O=S=O
13C Spectrum of 6a
160
140
120
100
80
60
40
20
0

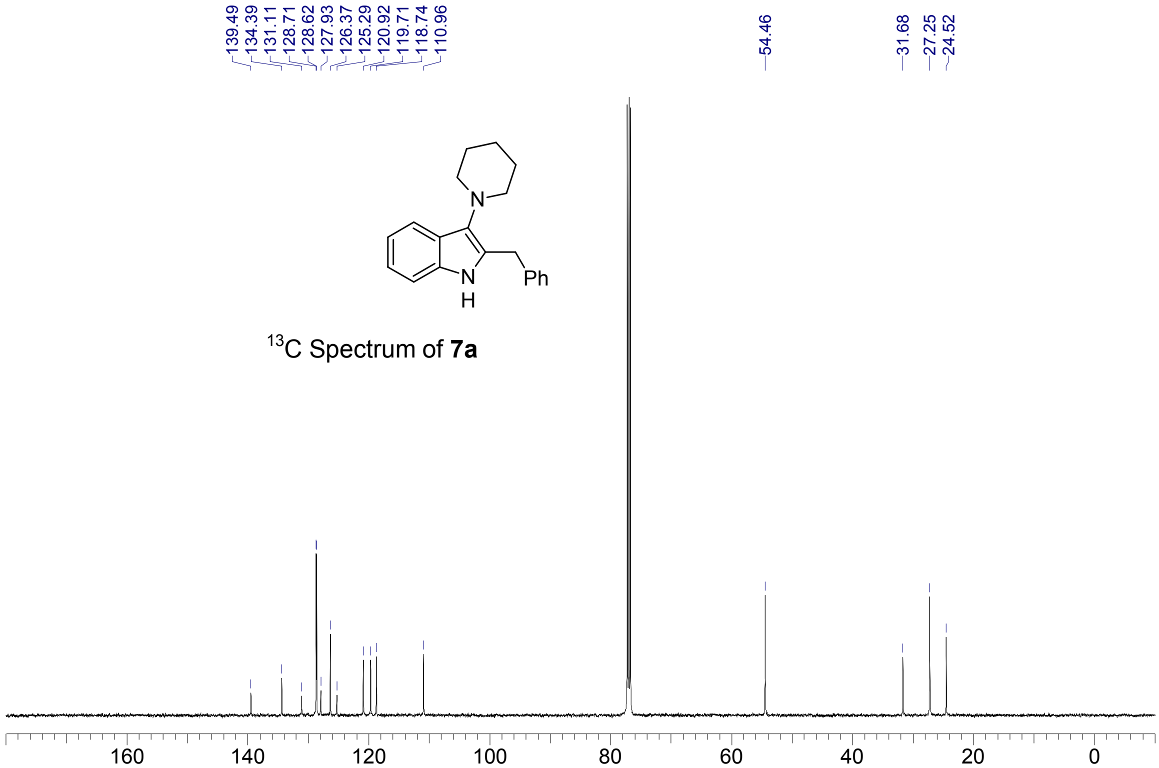

8.17
8.16
7.67
7.66
7.30
7.29
7.26
7.21
7.11
7.07
7.01
7.01
7.00
6.99
4.48
3.11
3.10
3.09
2.31
2.29
1.67
1.66
1.65
1.64
1.63
1.58
1.57
Tol-p
^{1}H Spectrum of **6b**
0.93
1.01
1.87
3.75
2.00
4.02
2.76
7.24


143.99
136.79
135.87
135.37
135.23
133.82
129.26
128.79
128.46
128.12
126.43
123.80
122.79
119.82
115.50
53.36
30.52
26.93
24.34
21.46
21.00
Tol-p
^{13}C Spectrum of **6b**


8.20
8.18
7.59
7.57
7.56
7.54
7.26
7.24
7.19
7.18
7.15
7.13
3.69
3.68
3.66
3.38
3.38
3.36
3.35
3.06
3.05
3.04
2.32
1.69
1.68
1.67
1.66
1.65
1.58
1.57
1.55
N
N
OMe
O=S=O
¹H Spectrum of 6d
0.92
2.88
2.89
2.03
4.91
4.06
3.00
2.77
8
7
6
5
4
3
2
1
0


144.39
136.20
135.60
131.38
129.59
128.45
126.24
123.88
123.02
119.66
115.66
72.40
58.47
53.31
26.93
26.36
24.34
21.50
N
N
OMe
O=S=O
¹³C Spectrum of 6d
160
140
120
100
80
60
40
20
0


7.79
7.77
7.42
7.33
7.31
7.30
7.24
7.24
7.22
7.18
7.06
7.05
4.18
3.23
3.22
3.22
1.75
1.74
1.73
1.72
1.71
1.63
1.62
1.61
1.59
N
Ph
N
H
1H Spectrum of 7a
0.95
0.88
2.86
1.98
2.00
4.10
2.10
8
7
6
5
4
3
2
1
0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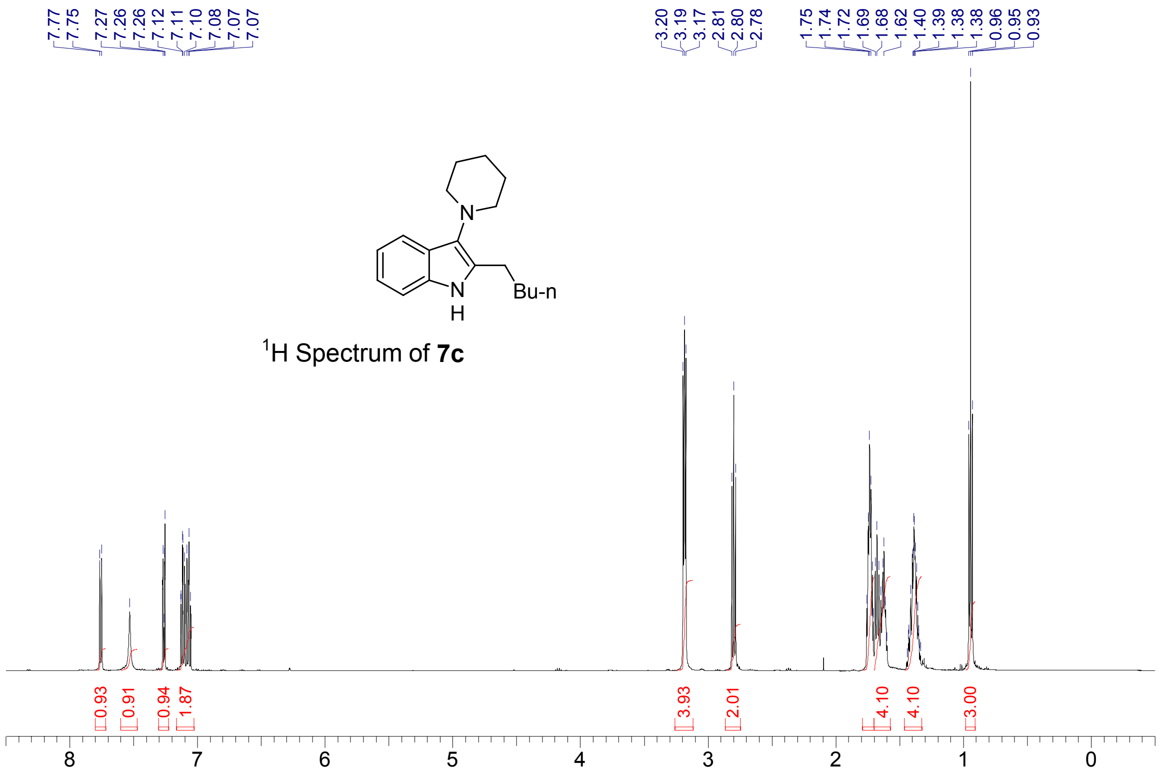
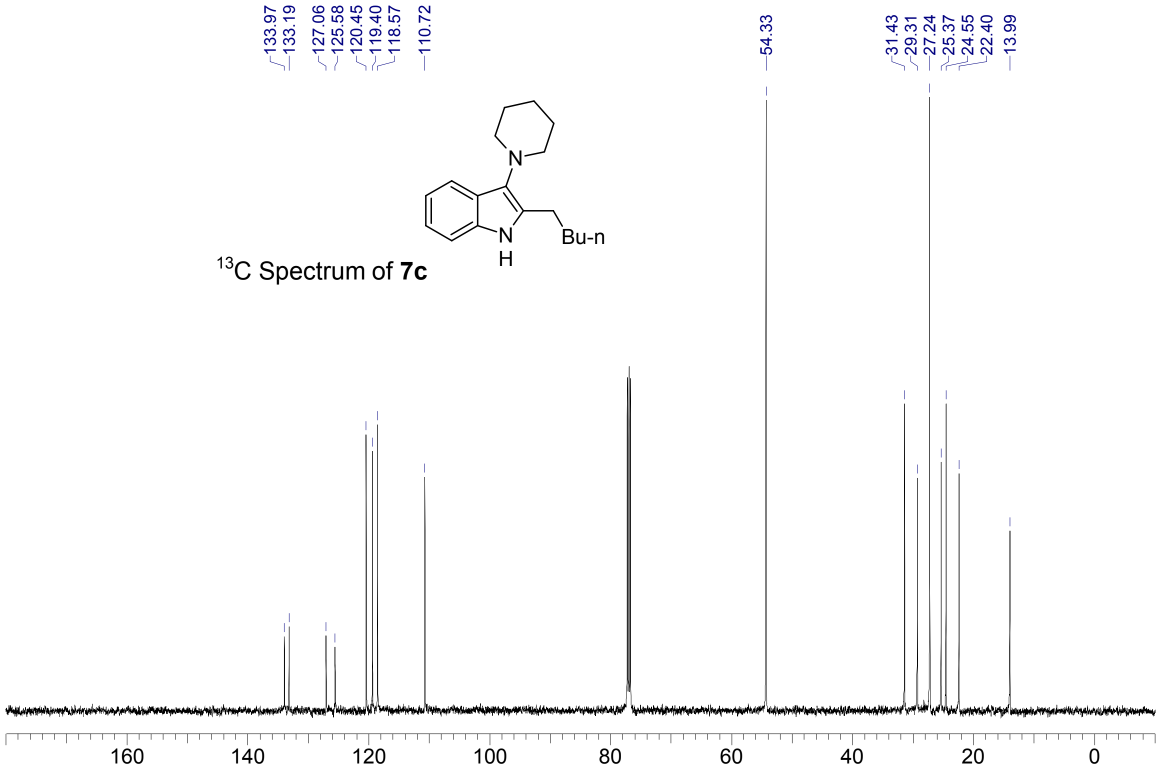
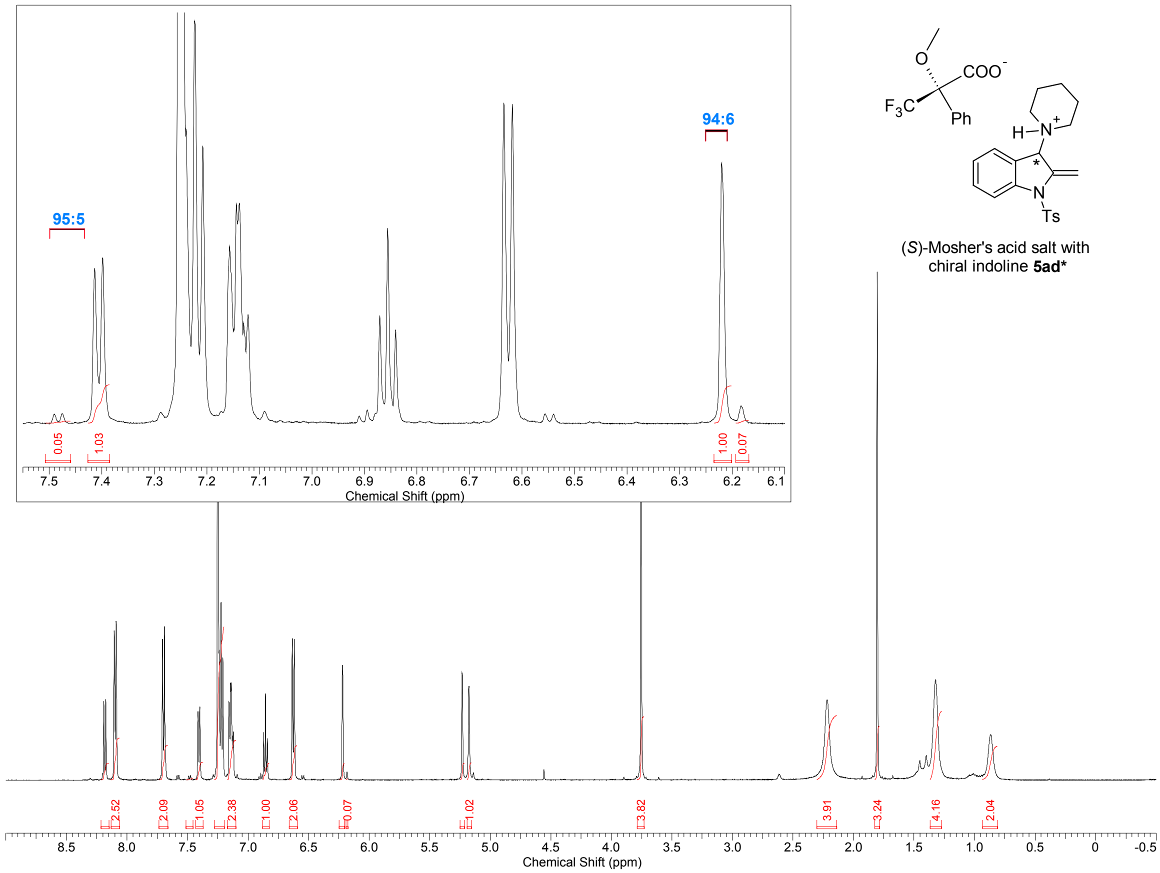
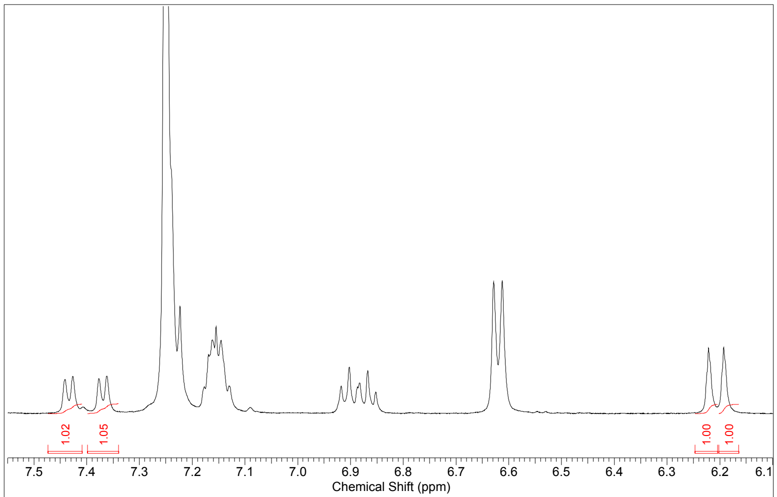
134.39
131.11
128.71
128.62
127.93
126.37
125.29
120.92
119.71
118.74
110.96
54.46
31.68
27.25
24.52
N
Ph
N
H
13C Spectrum of 7a
160
140
120
100
80
60
40
20
0

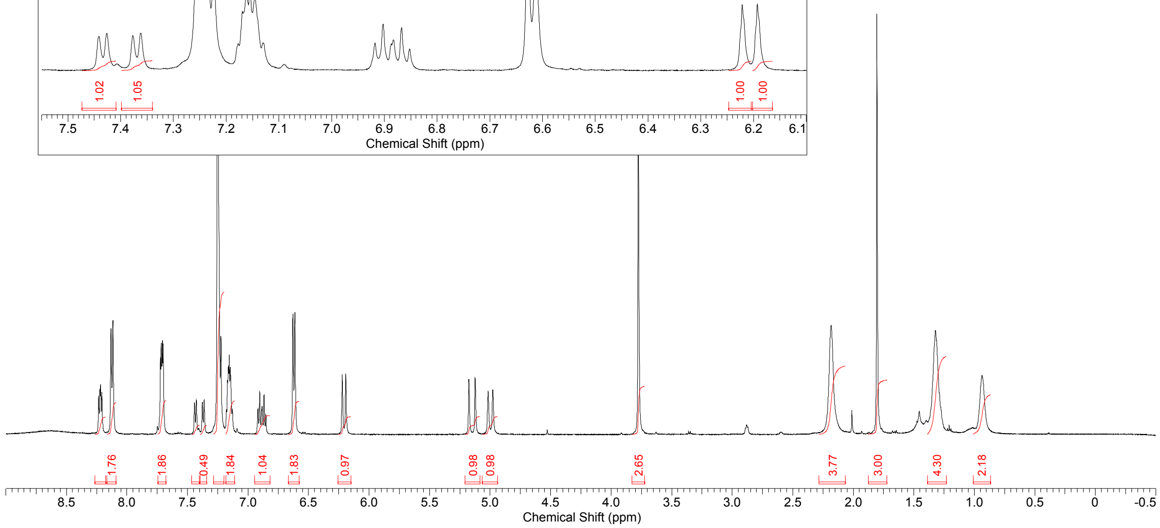

7.77
7.75
7.27
7.26
7.26
7.12
7.11
7.10
7.08
7.07
7.07
3.20
3.19
3.17
2.81
2.80
2.78
1.75
1.74
1.72
1.69
1.68
1.62
1.40
1.39
1.38
1.38
0.96
0.95
0.93
N
N
H
Bu-n
1H Spectrum of 7c
0.93
0.91
0.94
1.87
3.93
2.01
4.10
4.10
3.00
8
7
6
5
4
3
2
1
0

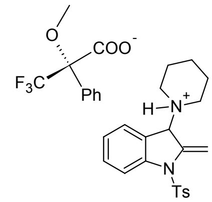

133.97
133.19
127.06
125.58
120.45
119.40
118.57
110.72
54.33
31.43
29.31
27.24
25.37
24.55
22.40
13.99
N
N
H
Bu-n
13C Spectrum of 7c
160
140
120
100
80
60
40
20
0



(*S*)-Mosher's acid salt with chiral indoline **5ad***







(*S*)-Mosher's acid salt with racemic indoline **5ad**