Electronic Supplementary Information

for

Visible-light-induced dehydrogenative sulfonylation of tertiary amines under transition-metal- and photocatalyst-free conditions

Jinwen Tong, Heng Li, Yan Zhu, Ping Liu* and Peipei Sun*

School of Chemistry and Materials Science, Jiangsu Provincial Key Laboratory of Material Cycle Processes and Pollution Control, Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, Nanjing Normal University, Nanjing 210023, China

pingliu@njnu.edu.cn; sunpeipei@njnu.edu.cn

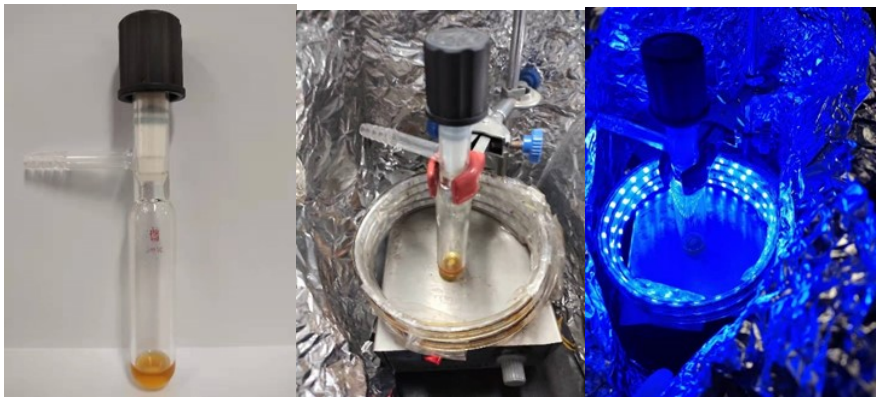
Contents

1 General information

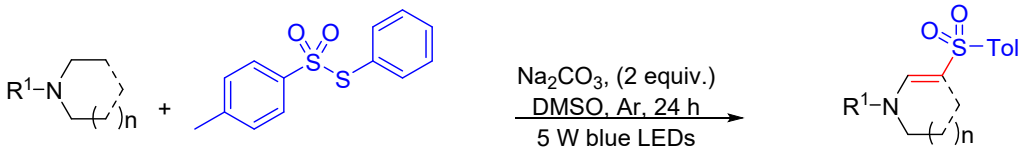
All reagents were obtained from commercial suppliers and used without further purification. Reactions were monitored by thin layer chromatography. Column chromatography was performed using silica gel (300−400 mesh). The NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C) in $CDCl_3$ or DMSO-d_6 using tetramethylsilane as the internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet, q = quartet. High-resolution mass spectra were obtained with an AB Triple 5600 mass spectrometer by ESI on a TOF mass analyzer. Melting points are uncorrected.

2 Experimental procedures

2.1 The photos of the photochemical reactor



2.2 General procedure for the preparation of 3

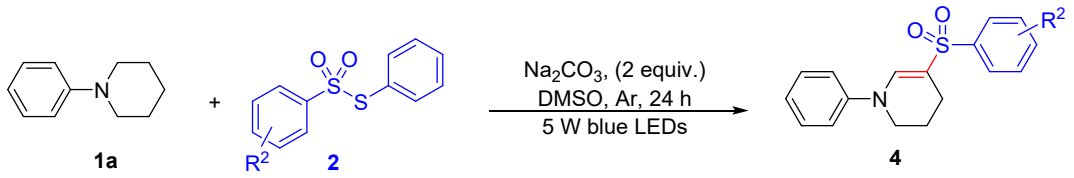


1 2a 3

An oven-dried Schlenk tube (25 mL) was equipped with a magnetic stir bar and charged with *S*-phenyl 4-methylbenzenesulfonothioate (158.4 mg, 0.6 mmol, 3.0 equiv.), Na_2CO_3 (42.4 mg, 0.4 mmol, 2.0 equiv.). The flask was evacuated and backfilled with argon for 3 times, and then DMSO (2 mL) and tertiary amines (0.2 mmol, 1.0 equiv.) were added. The reaction mixture was stirred under 5 W blue LED strip (425-465 nm) irradiation at room temperature for 24 h, then diluted with water (50 mL) and extracted with EtOAc (15 mL × 3). The combined organic phases were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo.

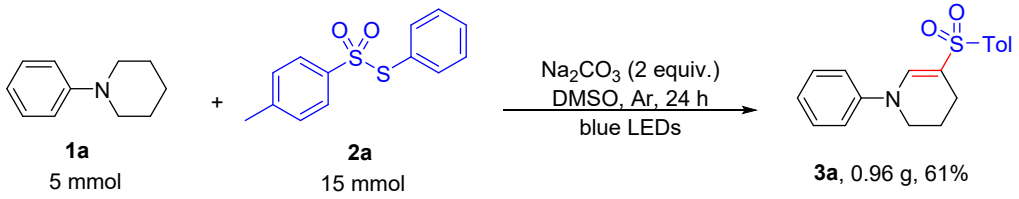
The resulting residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate as eluent to afford the desired products **3**.

2.2 General procedure for the preparation of 4



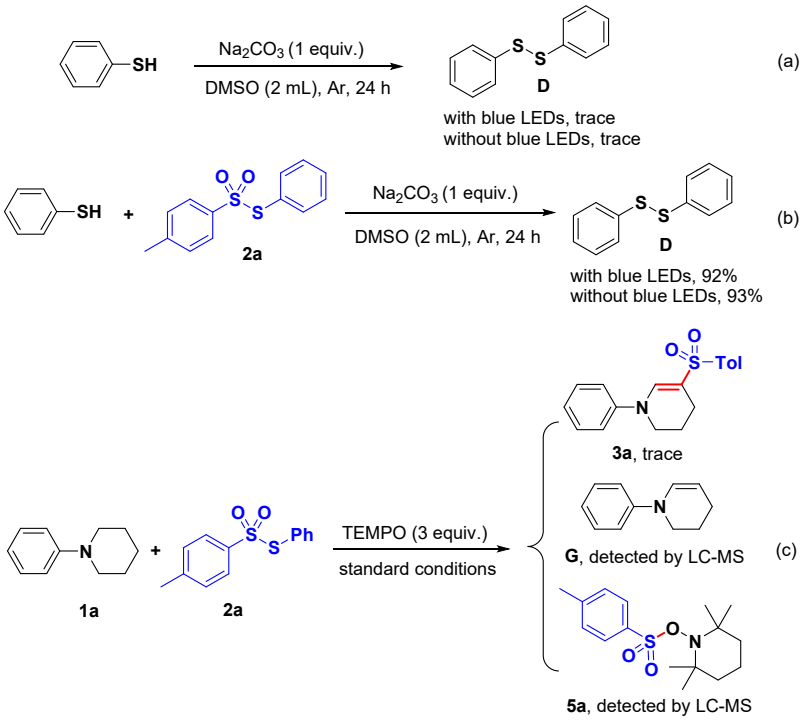
An oven-dried Schlenk tube (25 mL) was equipped with a magnetic stir bar and charged with *S*-phenyl benzenesulfonothioate (0.6 mmol, 3.0 equiv.), Na_2CO_3 (42.4 mg, 0.4 mmol, 2.0 equiv.). The flask was evacuated and backfilled with argon for 3 times, and then DMSO (2 mL) and 1-phenylpiperidine (32.2 mg, 32 μL, 0.2 mmol, 1.0 equiv.) were added. The reaction mixture was stirred under 5 W blue LED strip (425-465 nm) irradiation at room temperature for 24 h, then diluted with water (50 mL) and extracted with EtOAc (15 mL × 3). The combined organic phases were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate as eluent to afford the desired products **4**.

2.3 Gram-scale synthesis of 3a



An oven-dried Schlenk tube (100 mL) was equipped with a magnetic stir bar and charged with Na_2CO_3 (1.06 g, 10 mmol, 2.0 equiv.), *S*-phenyl-4-methylbenzenesulfonothioate (3.96 g, 15 mmol, 3.0 equiv.). The flask was evacuated and backfilled with argon for 3 times, and then DMSO (20 mL) and 1-phenylpiperidine (0.81 g, 0.81 mL, 5 mmol, 1.0 equiv.) were added. The reaction mixture was stirred under 5 W blue LED strip (425-465 nm) irradiation at room temperature for 24 h. Once completed, the mixture was diluted with water (100 mL) and extracted with EtOAc (30 mL × 3). The combined organic phases were washed with brine (50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel chromatography using petroleum ether/EtOAc (5:1, v/v) as eluent to afford the pure product **3a** in 61% yield.

3 Control experiments



(a) An oven-dried Schlenk tube (25 mL) was equipped with a magnetic stir bar and charged with benzenethiol (22.0 mg, 0.2 mmol, 1.0 equiv.) and Na_2CO_3 (21.2 mg, 0.2 mmol, 1.0 equiv.). The flask was evacuated and backfilled with argon for 3 times, and then DMSO (2 mL) were added. The reaction mixture was stirred under 5 W blue LED strip (425-465 nm) irradiation at room temperature for 24 h. After the reaction was stopped, trace amounts of the desired product **3a** were detected by TLC and LC-MS. When there was no blue LED strip irradiation in the reaction, similar results were obtained.

(b) An oven-dried Schlenk tube (25 mL) was equipped with a magnetic stir bar and charged with benzenethiol (22.0 mg, 0.2 mmol, 1.0 equiv.), *S*-phenyl 4-methylbenzenesulfonothioate (52.8 mg, 0.2 mmol, 1.0 equiv.) and Na_2CO_3 (21.2 mg, 0.2 mmol, 1.0 equiv.). The flask was evacuated and backfilled with argon for 3 times, and then DMSO (2 mL) were added. The reaction mixture was stirred under 5 W blue LED strip (425-465 nm) irradiation at room temperature for 24 h. After the reaction completed, the reaction mixture was diluted with H_2O (15 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel chromatography using petroleum ether/EtOAc (100:1, v/v) as eluent to afford the pure product **D** as a white solid in

92% yield. When there was no blue LED strip irradiation in the reaction, similar results were obtained.

(c) An oven-dried Schlenk tube (25 mL) was equipped with a magnetic stir bar and charged with *S*-phenyl 4-methylbenzenesulfonothioate (158.4 mg, 0.6 mmol, 3.0 equiv.), Na_2CO_3 (42.4 mg, 0.4 mmol, 2.0 equiv.) and TEMPO (93.8 mg, 0.6 mmol, 3.0 equiv.). The flask was evacuated and backfilled with argon for 3 times, and then DMSO (2 mL) and 1-phenylpiperidine (32.2 mg, 32 μL, 0.2 mmol, 1.0 equiv.) were added. The reaction mixture was stirred under 5 W blue LED strip (425-465 nm) irradiation at room temperature for 24 h. After the reaction was stopped, trace amounts of the desired product **3a** were detected by TLC and LC-MS, indicating that the reaction was inhibited. Meanwhile, a trapping product **5a** and 1-phenyl-1,2,3,4-tetrahydropyridine (**G**) was observed through the LC-MS analysis from the reaction.

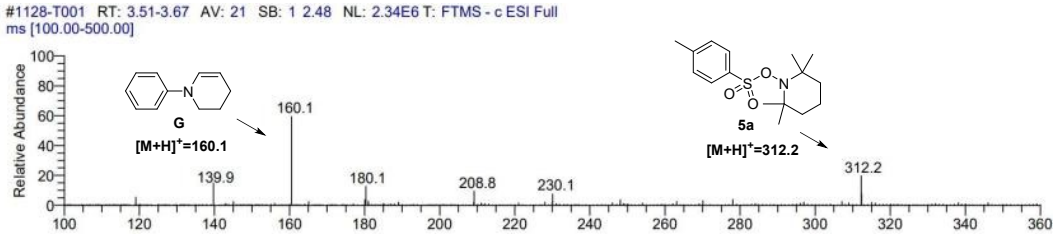
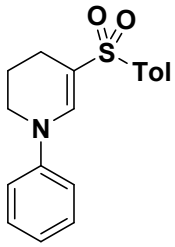
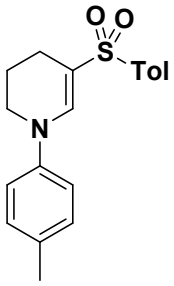


Figure S1 LC-MS analysis of the radical-trapping product **5a** and 1-phenyl-1,2,3,4-tetrahydropyridine (**G**).

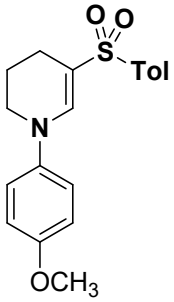
4 Experimental data for the products 3, 4 and D



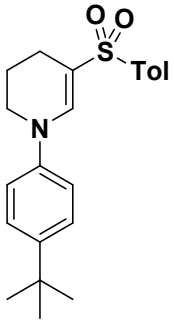
1-Phenyl-5-tosyl-1,2,3,4-tetrahydropyridine (3a).[1] Purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v) as eluent. White solid (139.0 mg, 74% yield). mp 134–136 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.87 (s, 1H), 7.77 (d, J = 7.9 Hz, 2H), 7.39–7.29 (m, 4H), 7.12–7.08 (m, 3H), 3.57 (t, J = 5.6 Hz, 2H), 2.43 (s, 3H), 2.29 (t, J = 6.3 Hz, 2H), 2.02–1.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 145.4, 142.9, 139.1, 138.9, 129.6, 129.5, 127.2, 123.4, 117.7, 108.0, 45.8, 21.6, 21.2, 20.0.



1-(*p*-Tolyl)-5-tosyl-1,2,3,4-tetrahydropyridine (3b).[1] Purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v) as eluent. White solid (143.3 mg, 73% yield). mp 91–93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.83 (s, 1H), 7.76 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 8.1 Hz, 2H), 3.53 (t, J = 5.5 Hz, 2H), 2.42 (s, 3H), 2.33 (s, 3H), 2.28 (t, J = 6.2 Hz, 2H), 1.99–1.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 143.1, 142.8, 139.4, 139.1, 133.1, 130.0, 129.6, 127.1, 117.9, 107.1, 46.0, 21.6, 21.1, 20.7, 20.0.

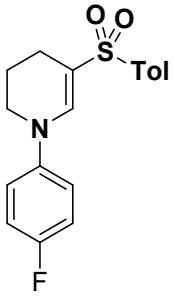


1-(4-Methoxyphenyl)-5-tosyl-1,2,3,4-tetrahydropyridine (3c).[1] Purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v) as eluent. white solid (142.1 mg, 69% yield). mp 176–178 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.77–7.75 (m, 3H), 7.30 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 9.0 Hz, 2H), 6.90 (d, J = 9.0 Hz, 2H), 3.82 (s, 3H), 3.55–3.52 (m, 2H), 2.43 (s, 3H), 2.28 (t, J = 6.2 Hz, 2H), 2.00–1.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 156.2, 142.7, 139.9, 139.3, 139.2, 129.5, 127.1, 119.9, 114.7, 106.3, 55.6, 46.6, 21.5, 21.2, 19.9.

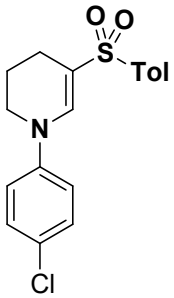


1-(4-(*tert*-Butyl)phenyl)-5-tosyl-1,2,3,4-tetrahydropyridine (3d).[1] Purified by silica gel column

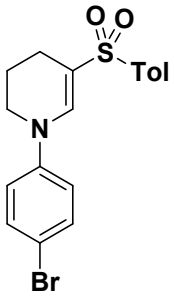
chromatography with petroleum ether/ethyl acetate (5:1, v/v) as eluent. Yellow viscous liquid (161.7 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86 (d, J = 1.1 Hz, 1H), 7.78–7.75 (m, 2H), 7.41–7.37 (m, 2H), 7.31–7.28 (m, 2H), 7.06–7.02 (m, 2H), 3.58–3.55 (m, 2H), 2.43 (s, 3H), 2.31–2.28 (m, 2H), 2.01–1.95 (m, 2H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.4, 143.0, 142.8, 139.3, 139.1, 129.6, 127.1, 126.3, 117.5, 107.3, 45.9, 34.3, 31.4, 21.6, 21.2, 20.0.



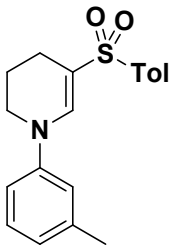
1-(4-Fluorophenyl)-5-tosyl-1,2,3,4-tetrahydropyridine (3e).[1] Purified by silica gel column chromatography with petroleum ether/ethyl acetate (4:1, v/v) as eluent. White solid (141.1 mg, 71% yield). mp 174–176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.77–7.75 (m, 3H), 7.31 (d, J = 7.9 Hz, 2H), 7.09–7.02 (m, 4H), 3.54 (t, J = 5.5 Hz, 2H), 2.44 (s, 3H), 2.29 (t, J = 6.2 Hz, 2H), 2.01–1.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.1 (d, J = 243.2 Hz), 142.9, 141.9 (d, J = 2.9 Hz), 139.3, 138.9, 129.6, 127.2, 119.6 (d, J = 8.0 Hz), 116.2 (d, J = 22.7 Hz), 108.0, 46.4, 21.6, 21.1, 19.9.



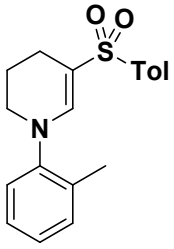
1-(4-Chlorophenyl)-5-tosyl-1,2,3,4-tetrahydropyridine (3f).[1] Purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v) as eluent. White solid (135.4 mg, 65% yield). mp 200–202 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.80–7.75 (m, 3H), 7.32 (dd, J = 8.4, 4.0 Hz, 4H), 7.01 (d, J = 8.9 Hz, 2H), 3.54 (t, J = 5.5 Hz, 2H), 2.44 (s, 3H), 2.29 (t, J = 6.2 Hz, 2H), 2.02–1.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 143.9, 143.1, 138.7, 138.4, 129.6, 129.5, 128.5, 127.2, 118.8, 109.1, 45.9, 21.6, 21.1, 19.9.



1-(4-Bromophenyl)-5-tosyl-1,2,3,4-tetrahydropyridine (3g).[1] Purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v) as eluent. White solid (143.1 mg, 61% yield). mp 203–205 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.81–7.75 (m, 3H), 7.48–7.44 (m, 2H), 7.31 (d, J = 8.1 Hz, 2H), 6.98–6.94 (m, 2H), 3.55–3.52 (m, 2H), 2.44 (s, 3H), 2.29 (t, J = 6.1 Hz, 2H), 2.02–1.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.4, 143.1, 138.7, 138.3, 132.4, 129.6, 127.2, 119.1, 116.0, 109.4, 45.8, 21.6, 21.1, 19.9.

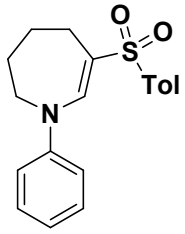


1-(*m*-Tolyl)-5-tosyl-1,2,3,4-tetrahydropyridine (3h). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (4:1, v/v) as eluent. White solid (127.58 mg, 65% yield). mp 110–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.87 (s, 1H), 7.77 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.24 (t, J = 8.1 Hz, 1H), 6.92–6.87 (m, 3H), 3.56–3.53 (m, 2H), 2.42 (s, 3H), 2.37 (s, 3H), 2.28 (t, J = 6.3 Hz, 2H), 2.00–1.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 145.4, 142.9, 139.5, 139.2, 139.0, 129.6, 129.3, 127.1, 124.2, 118.5, 114.8, 107.7, 45.9, 21.6, 21.5, 21.2, 20.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{22}NO_2S^+$ 328.1366; Found 328.1366.

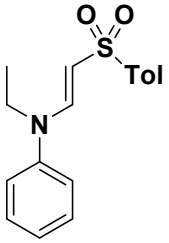


1-(*o*-Tolyl)-5-tosyl-1,2,3,4-tetrahydropyridine (3i). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (4:1, v/v) as eluent. White solid (133.5 mg, 68%

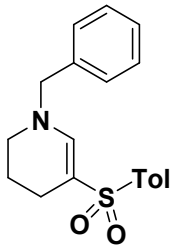
yield). mp 158–160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.75 (d, J = 8.2 Hz, 2H), 7.45 (s, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.25–7.17 (m, 3H), 7.06 (dd, J = 7.3, 1.8 Hz, 1H), 3.41–3.38 (m, 2H), 2.42 (s, 3H), 2.29 (d, J = 8.6 Hz, 5H), 1.99–1.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 145.4, 142.9, 142.6, 139.4, 133.4, 131.6, 129.6, 127.1, 127.0, 126.9, 125.6, 104.4, 48.3, 21.5, 21.4, 20.0, 18.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{22}NO_2S^+$ 328.1366; Found 328.1365.



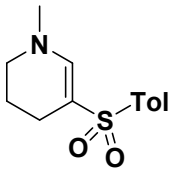
1-Phenyl-6-tosyl-2,3,4,5-tetrahydro-1H-azepine (3j).[1] Purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v) as eluent. Yellow viscous liquid (141.3 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.80–7.75 (m, 3H), 7.36–7.29 (m, 4H), 7.12–7.10 (m, 3H), 3.83–3.80 (m, 2H), 2.47–2.42 (m, 2H), 2.42 (s, 3H), 1.86 (t, J = 5.1 Hz, 2H), 1.79–1.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 147.3, 144.6, 142.9, 139.0, 129.6, 129.4, 127.3, 123.9, 119.7, 113.6, 51.7, 28.0, 26.0, 25.6, 21.6.



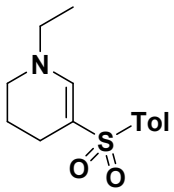
(*E*)-*N*-ethyl-*N*-(2-tosylvinyl)aniline (3k). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v) as eluent. Colorless viscous liquid (99.4 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.76–7.68 (m, 3H), 7.32 (t, J = 7.9 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.16–7.09 (m, 3H), 5.28 (d, J = 13.1 Hz, 1H), 3.59 (q, J = 7.2 Hz, 2H), 2.35 (s, 3H), 1.15 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.1, 144.5, 142.6, 141.6, 129.7, 129.6, 126.4, 125.5, 121.6, 98.0, 45.8, 21.5, 11.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{20}NO_2S^+$ 302.1209; Found 302.1208.



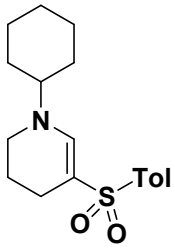
1-Benzyl-5-tosyl-1,2,3,4-tetrahydropyridine (3l).[2] Purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v) as eluent. White solid (123.7 mg, 63% yield). mp 155–157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.75 (d, J = 8.3 Hz, 2H), 7.52 (s, 1H), 7.40–7.31 (m, 5H), 7.22 (d, J = 6.5 Hz, 2H), 4.32 (s, 2H), 2.98–2.95 (m, 2H), 2.43 (s, 3H), 2.18 (t, J = 6.2 Hz, 2H), 1.81–1.75 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.2, 142.4, 139.7, 136.5, 129.5, 128.9, 128.0, 127.5, 126.9, 101.0, 59.7, 44.9, 21.5, 21.0, 19.6.



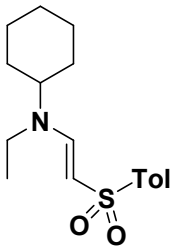
1-Methyl-5-tosyl-1,2,3,4-tetrahydropyridine (3m). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v) as eluent. White solid (93.4 mg, 62 % yield). mp 160–162 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.71 (d, J = 8.3 Hz, 2H), 7.28 (s, 1H), 7.26 (s, 2H), 3.03–3.00 (m, 2H), 2.96 (s, 3H), 2.41 (s, 3H), 2.15 (t, J = 6.2 Hz, 2H), 1.85–1.79 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.5, 142.2, 139.9, 129.4, 126.8, 100.1, 47.2, 42.7, 21.5, 21.0, 19.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{18}NO_2S^+$ 252.1053; Found 252.1051.



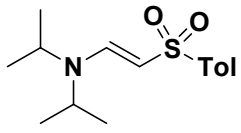
1-Ethyl-5-tosyl-1,2,3,4-tetrahydropyridine (3n).[2] Purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v) as eluent. White solid (114.5 mg, 72% yield). mp 120–122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.69 (d, J = 8.3 Hz, 2H), 7.30 (s, 1H), 7.25 (d, J = 8.0 Hz, 2H), 3.18 (q, J = 7.2 Hz, 2H), 3.05–3.02 (m, 2H), 2.39 (s, 3H), 2.14 (t, J = 6.2 Hz, 2H), 1.81–1.75 (m, 2H), 1.15 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 143.5, 142.2, 139.9, 129.4, 126.8, 99.6, 50.4, 44.8, 21.5, 21.1, 19.7, 13.8.



1-Cyclohexyl-5-tosyl-1,2,3,4-tetrahydropyridine (3o).[2] Purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v) as eluent. White solid (136.0 mg, 71% yield). mp 145–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.66 (d, J = 8.2 Hz, 2H), 7.35 (s, 1H), 7.22 (d, J = 7.9 Hz, 2H), 3.04–3.01 (m, 2H), 2.96–2.88 (m, 1H), 2.36 (s, 3H), 2.13 (t, J = 6.2 Hz, 2H), 1.81–1.70 (m, 6H), 1.63 (d, J = 13.1 Hz, 1H), 1.40–1.23 (m, 4H), 1.12–1.04 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 142.4, 142.0, 140.1, 129.3, 126.7, 99.0, 64.1, 43.0, 31.4, 25.6, 25.3, 21.4, 21.4, 20.3.

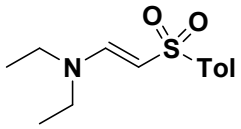


(*E*)-*N*-Ethyl-*N*-(2-tosylvinyl)cyclohexanamine (3p). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v) as eluent. White solid (129.0 mg, 70 % yield). mp 121–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.73 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 12.6 Hz, 1H), 7.25 (d, J = 7.9 Hz, 2H), 4.88 (d, J = 12.6 Hz, 1H), 3.12–3.00 (m, 3H), 2.39 (s, 3H), 1.84–1.80 (m, 4H), 1.68–1.64 (m, 1H), 1.45–1.37 (m, 2H), 1.32–1.23 (m, 2H), 1.15–1.06 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 147.2, 142.7, 141.9, 129.4, 126.1, 91.1, 64.9, 41.8, 32.5, 25.7, 25.2, 21.4, 12.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{26}NO_2S^+$ 308.1679; Found 308.1679.

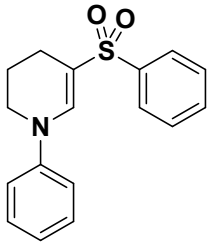


(*E*)-*N*-Isopropyl-*N*-(2-tosylvinyl)propan-2-amine (3q).[3] Purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v) as eluent. Colorless viscous liquid (121.5 mg, 72 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.74 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 12.8 Hz, 1H), 7.27 (d, J = 8.0 Hz, 2H), 4.97 (d, J = 12.8 Hz, 1H), 3.60 (s, 2H), 2.41 (s, 3H), 1.21

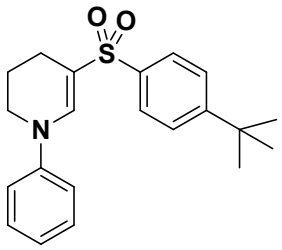
(s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.9, 142.7, 141.9, 129.4, 126.2, 91.7, 49.2, 47.5, 23.5, 21.5, 19.5.



(*E*)-*N*,*N*-Diethyl-2-tosylethen-1-amine (3r).[4] Purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v) as eluent. Colorless viscous liquid (110.9 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.73 (d, J = 7.9 Hz, 2H), 7.31–7.25 (m, 3H), 4.89 (d, J = 12.7 Hz, 1H), 3.22–3.11 (m, 4H), 2.40 (s, 3H), 1.15 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.8, 142.5, 142.0, 129.4, 126.1, 91.6, 50.0, 42.6, 21.5, 14.7, 11.1.

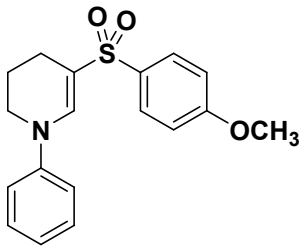


1-Phenyl-5-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (4a).[1] Purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v) as eluent. White solid (131.0 mg, 73% yield). mp 146–148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.89–7.87 (m, 3H), 7.57–7.48 (m, 3H), 7.36 (t, J = 8.0 Hz, 2H), 7.10 (t, J = 7.6 Hz, 3H), 3.57–3.55 (m, 2H), 2.29 (t, J = 6.2 Hz, 2H), 2.00–1.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 145.3, 141.9, 139.5, 132.2, 129.5, 129.0, 127.1, 123.5, 117.8, 107.6, 45.9, 21.1, 20.0.

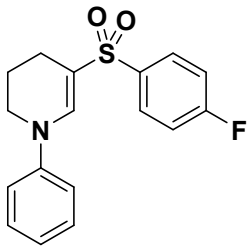


5-((4-(*tert*-Butyl)Phenyl)sulfonyl)-1-phenyl-1,2,3,4-tetrahydropyridine (4b).[1] Purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v) as eluent. Yellow viscous liquid (153.4 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.87 (s, 1H), 7.80 (d, J = 8.6 Hz, 2H), 7.51 (d, J = 8.6 Hz, 2H), 7.35–7.31 (m, 2H), 7.06 (dd, J = 7.9, 6.1 Hz, 3H), 3.56–3.53 (m, 2H), 2.30 (t, J = 6.3 Hz, 2H), 2.00–1.94 (m, 2H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 155.8, 145.4, 139.1, 138.9, 129.5, 126.9, 126.0, 123.3, 117.7, 108.0, 45.8, 35.1,

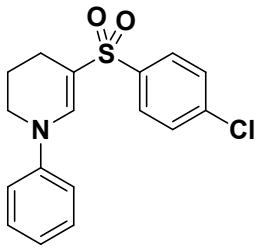
31.2, 21.2, 20.0.



5-((4-Methoxyphenyl)sulfonyl)-1-phenyl-1,2,3,4-tetrahydropyridine (4c).[1] Purified by silica gel column chromatography with petroleum ether/ethyl acetate (2:1, v/v) as eluent. Yellow viscous liquid (138.2 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.85 (s, 1H), 7.81 (t, J = 8.7 Hz, 2H), 7.34 (t, J = 7.8 Hz, 2H), 7.07 (d, J = 8.9 Hz, 3H), 6.97 (d, J = 8.6 Hz, 2H), 3.85 (s, 3H), 3.54 (t, J = 5.5 Hz, 2H), 2.27 (t, J = 6.2 Hz, 2H), 1.99–1.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 162.6, 145.4, 138.6, 133.5, 129.5, 129.2, 123.3, 117.6, 114.2, 108.4, 55.7, 45.8, 21.1, 20.0.

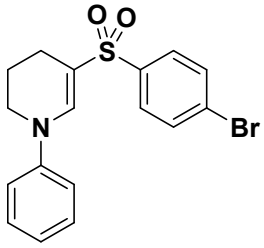


5-((4-Fluorophenyl)sulfonyl)-1-phenyl-1,2,3,4-tetrahydropyridine (4d).[1] Purified by silica gel column chromatography with petroleum ether/ethyl acetate (4:1, v/v) as eluent. White solid (138.9 mg, 73% yield). mp 153–155 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.91–7.87 (m, 3H), 7.38–7.34 (m, 2H), 7.17 (t, J = 8.6 Hz, 2H), 7.12–7.08 (m, 3H), 3.59–3.56 (m, 2H), 2.28 (t, J = 6.0 Hz, 2H), 2.02–1.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.9 (d, J = 253.7 Hz), 145.3, 139.6, 138.1 (d, J = 3.1 Hz), 129.8 (d, J = 9.2 Hz), 129.5, 123.6, 117.9, 116.1 (d, J = 22.4 Hz), 107.3, 45.9, 21.1, 20.0.

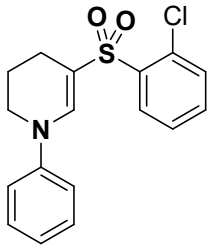


5-((4-Chlorophenyl)sulfonyl)-1-phenyl-1,2,3,4-tetrahydropyridine (4e).[1] Purified by silica gel column chromatography with petroleum ether/ethyl acetate (4:1, v/v) as eluent. White solid (143.9

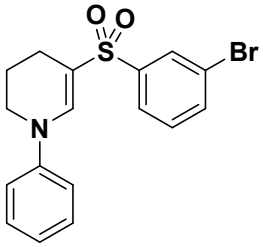
mg, 72% yield). mp 122–124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.87–7.81 (m, 3H), 7.47 (d, J = 8.4 Hz, 2H), 7.37 (t, J = 7.7 Hz, 2H), 7.10 (t, J = 6.1 Hz, 3H), 3.58 (t, J = 5.6 Hz, 2H), 2.29 (t, J = 6.2 Hz, 2H), 2.02–1.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 145.2, 140.6, 139.9, 138.6, 129.6, 129.2, 128.6, 123.7, 117.9, 107.0, 46.0, 21.1, 20.0.



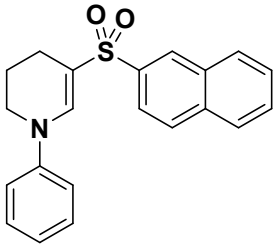
5-((4-Bromophenyl)sulfonyl)-1-phenyl-1,2,3,4-tetrahydropyridine (4f). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (4:1, v/v) as eluent. White solid (160.6 mg, 71% yield). mp 154–156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86 (s, 1H), 7.76–7.72 (m, 2H), 7.64–7.61 (m, 2H), 7.36 (dd, J = 8.6, 7.3 Hz, 2H), 7.12–7.07 (m, 3H), 3.58–3.55 (m, 2H), 2.28 (t, J = 6.2 Hz, 2H), 2.01–1.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 145.2, 141.1, 139.9, 132.2, 129.6, 128.7, 127.1, 123.7, 117.9, 106.9, 46.0, 21.1, 20.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}BrNO_2S^+$ 378.0158; Found 378.0157.



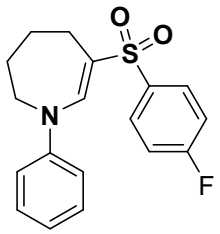
5-((2-Chlorophenyl)sulfonyl)-1-phenyl-1,2,3,4-tetrahydropyridine (4g). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v) as eluent. White solid (143.88 mg, 72% yield). mp 150–152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.89 (dd, J = 4.0, 2.8 Hz, 2H), 7.56–7.50 (m, 3H), 7.40–7.36 (m, 2H), 7.13–7.09 (m, 3H), 3.60–3.57 (m, 2H), 2.31 (t, J = 6.2 Hz, 2H), 2.03–1.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 145.3, 141.9, 139.5, 132.2, 129.5, 129.0, 127.1, 123.5, 118.1, 117.8, 107.6, 45.9, 21.1, 20.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}ClNO_2S^+$ 334.0663; Found 334.0662.



5-((3-Bromophenyl)sulfonyl)-1-phenyl-1,2,3,4-tetrahydropyridine (4h). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v) as eluent. White solid (156.1 mg, 69% yield). mp 154–156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.01 (s, 1H), 7.87–7.79 (m, 2H), 7.66 (d, J = 7.4 Hz, 1H), 7.40–7.35 (m, 3H), 7.10 (dd, J = 7.7, 4.3 Hz, 3H), 3.60–3.57 (m, 2H), 2.30 (t, J = 6.2 Hz, 2H), 2.03–1.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 145.2, 144.0, 140.2, 135.2, 130.6, 129.9, 129.6, 125.7, 123.8, 123.0, 118.0, 106.6, 46.0, 21.1, 20.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}BrNO_2S^+$ 378.0158; Found 378.0159.

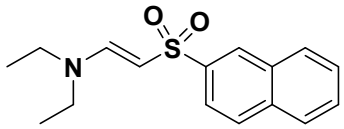


5-(Naphthalen-2-ylsulfonyl)-1-phenyl-1,2,3,4-tetrahydropyridine (4i).[1] Purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v) as eluent. White solid (134.1 mg, 64% yield). mp 140–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.49 (d, J = 1.8 Hz, 1H), 8.00–7.84 (m, 5H), 7.66–7.59 (m, 2H), 7.40–7.36 (m, 2H), 7.14–7.10 (m, 3H), 3.58–3.55 (m, 2H), 2.35–2.32 (m, 2H), 2.00–1.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 145.3, 139.6, 138.7, 134.7, 132.3, 129.6, 129.3, 129.3, 128.6, 128.3, 127.9, 127.4, 123.5, 122.7, 117.8, 107.6, 45.9, 21.2, 20.1.

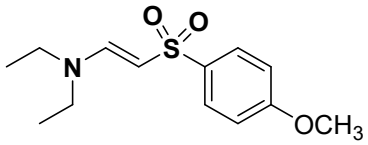


6-((4-Fluorophenyl)sulfonyl)-1-phenyl-2,3,4,5-tetrahydro-1H-azepine (4j). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v) as eluent. Light yellow solid (130.7 mg, 70% yield). mp 142–144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.91–7.88 (m,

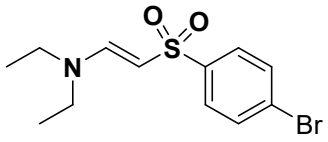
2H), 7.81 (d, J = 5.5 Hz, 1H), 7.36 (t, J = 7.7 Hz, 2H), 7.21–7.12 (m, 5H), 3.85–3.82 (m, 2H), 2.48–2.45 (m, 2H), 1.92–1.86 (m, 2H), 1.82–1.76 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.9 (d, J = 253.8 Hz), 147.4, 145.1, 138.1 (d, J = 3.2 Hz), 129.9 (d, J = 9.3 Hz), 129.5, 124.2, 119.9, 116.1 (d, J = 22.6 Hz), 112.7, 51.9, 28.0, 26.0, 25.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}FNO_2S^+$ 332.1115; Found 332.1115.



(*E*)-*N*,*N*-Diethyl-2-(naphthalen-2-ylsulfonyl)ethen-1-amine (4k).[4] Purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v) as eluent. White solid (123.2 mg, 64% yield). mp 124–125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.41 (s, 1H), 7.89–7.80 (m, 4H), 7.55–7.48 (m, 2H), 7.35 (dd, J = 12.7, 2.2 Hz, 1H), 4.94 (dd, J = 12.7, 1.8 Hz, 1H), 3.17–3.03 (m, 4H), 1.10–1.06 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 149.2, 142.3, 134.3, 132.3, 129.1, 129.1, 128.2, 127.8, 127.2, 126.4, 122.4, 91.1, 50.1, 42.7,14.7, 11.1.

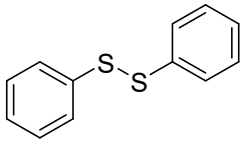


(*E*)-*N*,*N*-Diethyl-2-((4-methoxyphenyl)sulfonyl)ethen-1-amine (4l).[4] Purified by silica gel column chromatography with petroleum ether/ethyl acetate (2:1, v/v) as eluent. Colorless viscous liquid (113.0 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.81–7.77 (m, 2H), 7.32 (s, 1H), 6.97–6.92 (m, 2H), 4.90 (d, J = 12.7 Hz, 1H), 3.85 (s, 3H), 3.18 (s, 4H), 1.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 162.0, 148.5, 137.3, 128.2, 113.9, 92.1, 55.5. 50.1, 42.7, 14.7, 11.2.



(*E*)-2-((4-Bromophenyl)sulfonyl)-*N*,*N*-diethylethen-1-amine (4m).[4] Purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v) as eluent. White solid (135.0 mg, 71% yield). mp 75–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.73–7.70 (m, 2H), 7.60–7.57 (m, 2H), 7.30 (d, J = 12.5 Hz, 1H), 4.87 (d, J = 12.7 Hz, 1H), 3.25–3.11 (m, 4H), 1.18–1.13 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 149.3, 144.5, 132.0, 127.8, 126.1, 90.8, 50.2, 42.8,

14.8, 11.1.



1,2-Diphenyldisulfane (D).[5] Purified by silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v) as eluent. Light yellow solid (20.1 mg, 92% yield). mp 58–60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.75–7.72 (m, 4H), 7.49–7.45 (m, 4H), 7.41–7.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 137.3, 129.4, 127.7, 127.4.

5 References

(1) X. Rong, J. Guo, Z. Hu, L. Huang, Y. Gu, Y. Cai, G. Liang and Q. Xia, *Eur. J. Org. Chem.*, 2021, 701–708.

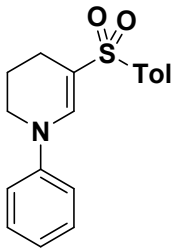
(2) R. J. Griffiths, W. C. Kong, S. A. Richards, G. A. Burley, M. C. Willis and E. P. A. Talbot, *Chem. Sci.*, 2018, **9**, 2295–2300.

(3) H.-S. Kim and S. Lee, *Eur. J. Org. Chem.*, 2019, 6951–6955.

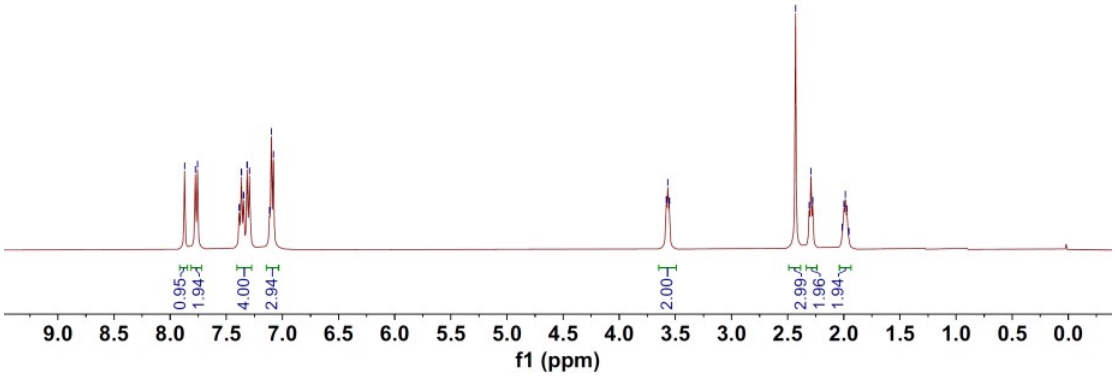
(4) H. Jiang, X. Tang, Z. Xu, H. Wang, K. Han, X. Yang, Y. Zhou, Y.-L. Feng, X.-Y. Yu and Q. Gui, *Org. Biomol. Chem.*, 2019, **17**, 2715–2720.

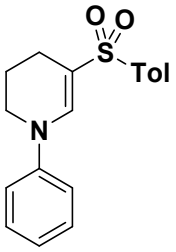
(5) H. Li, C. Tao, Y. Xie, A. Wang, Y. Chang, H. Yu, S. Yu and Y. Wei, *Green Chem.*, 2021, **23**, 6059–6064.

6 ^{1}H and ^{13}C NMR spectra of the products

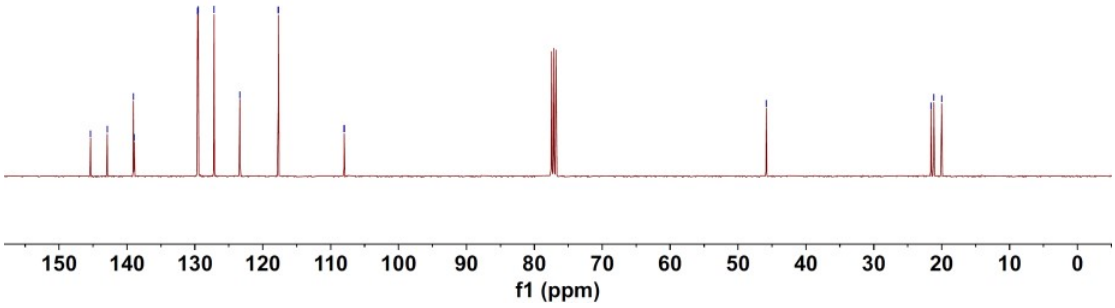


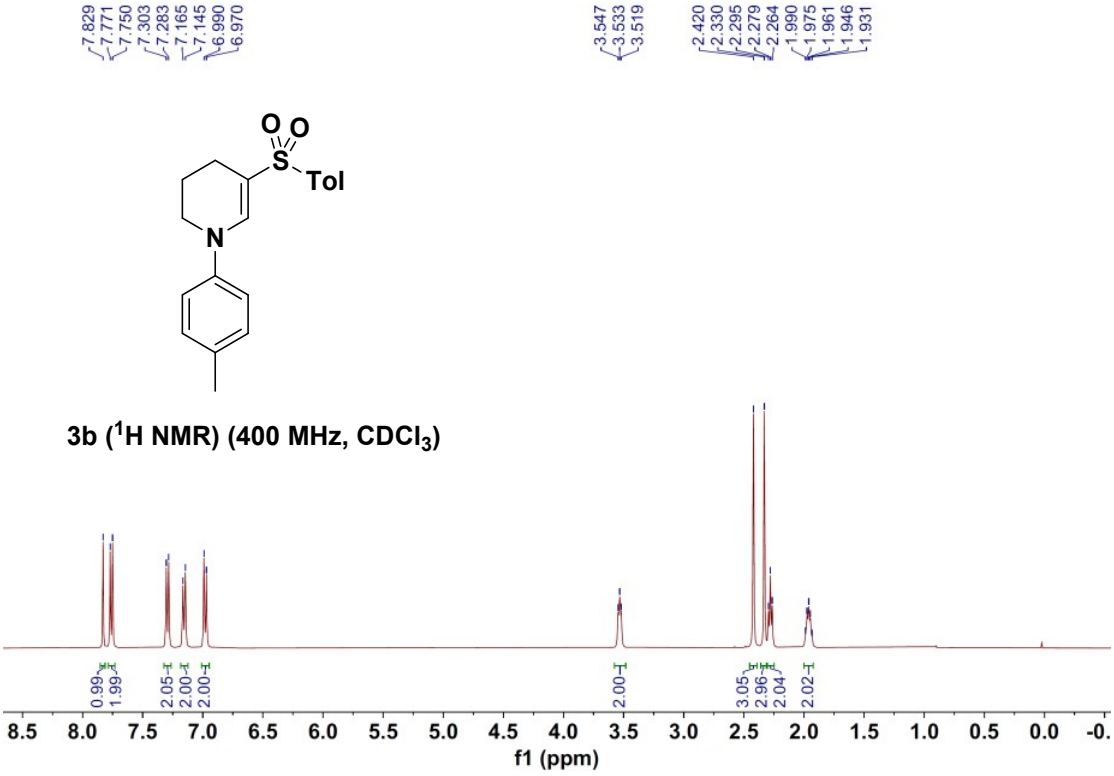
3a (^{1}H NMR) (400 MHz, $CDCl_3$)



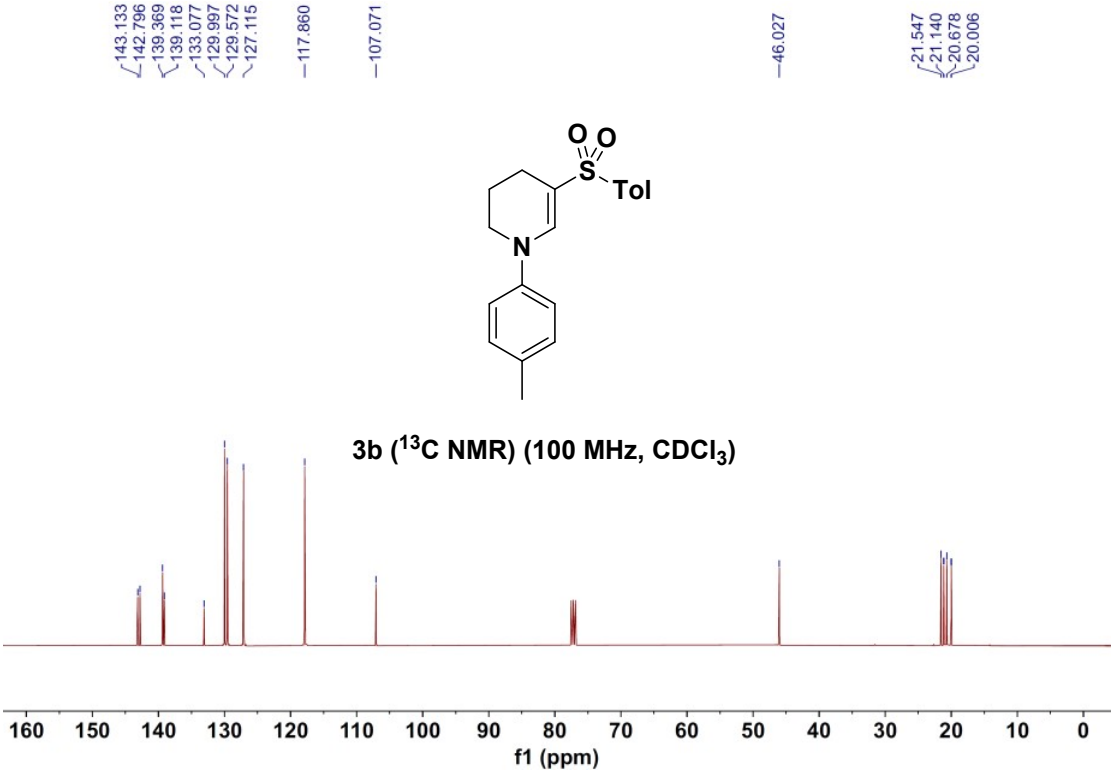


3a (^{13}C NMR) (100 MHz, $CDCl_3$)

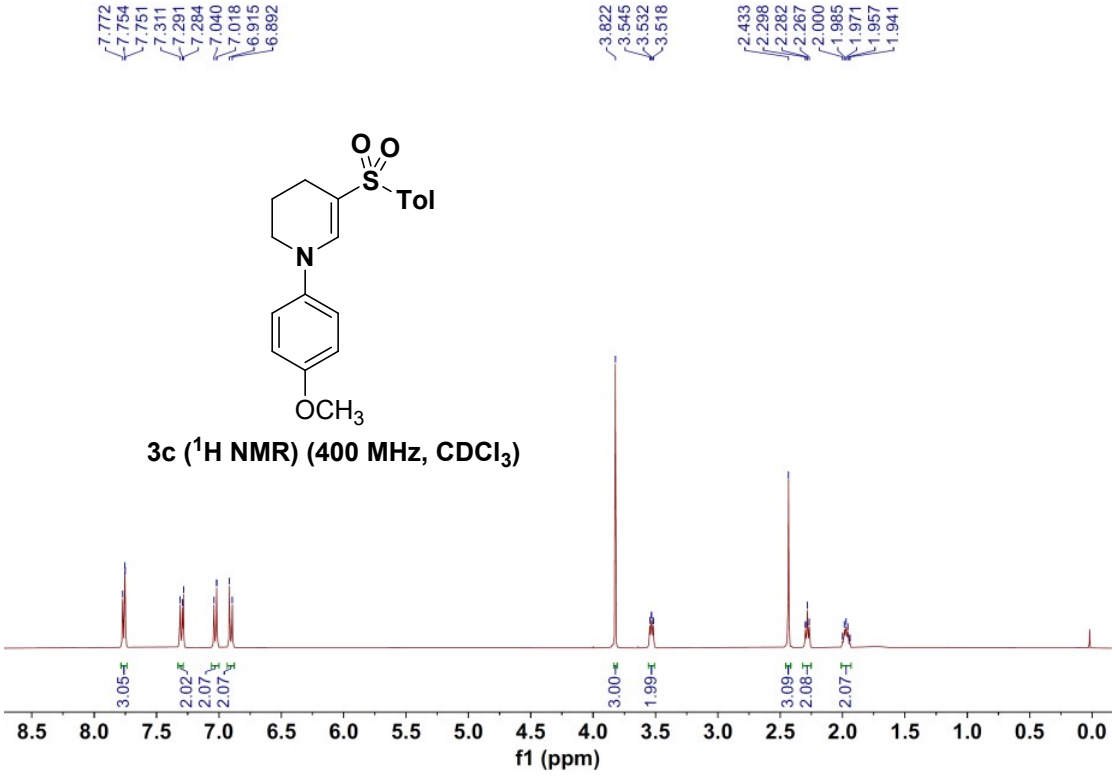




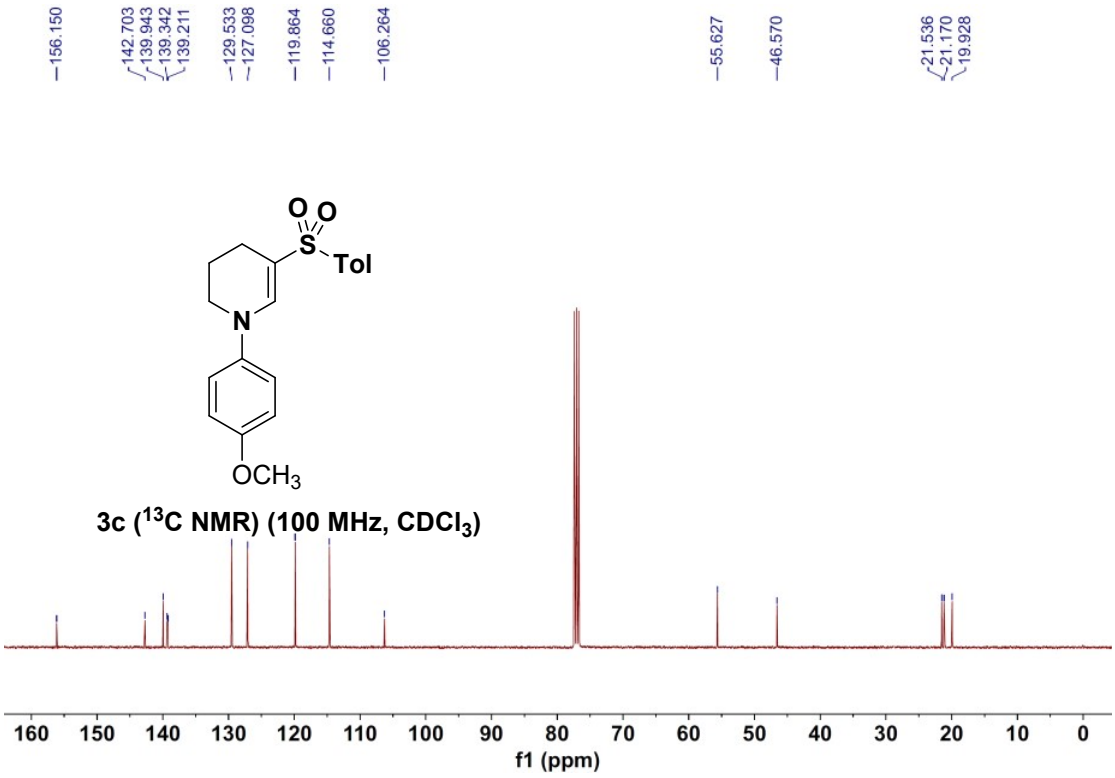
3b (^{1}H NMR) (400 MHz, $CDCl_3$)



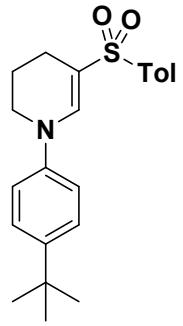
3b (^{13}C NMR) (100 MHz, $CDCl_3$)



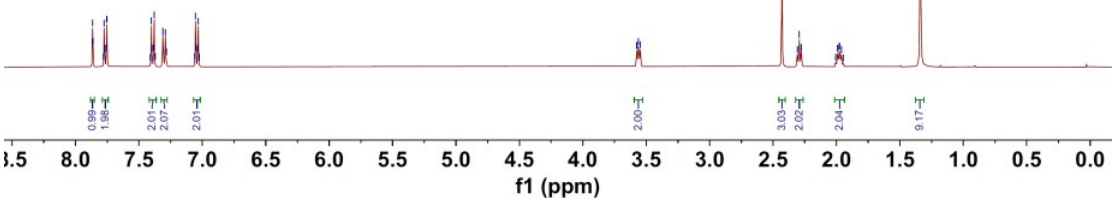
3c (^{1}H NMR) (400 MHz, $CDCl_3$)

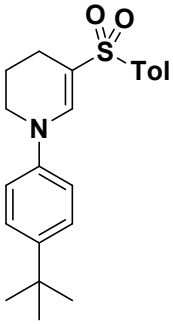


3c (^{13}C NMR) (100 MHz, $CDCl_3$)

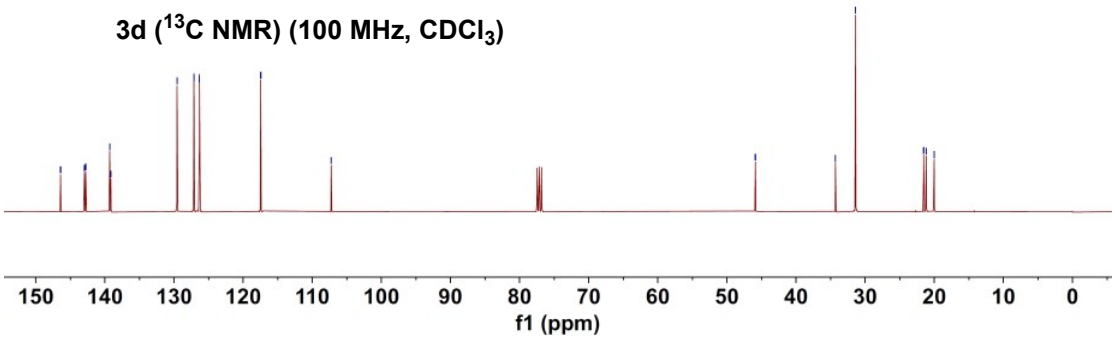


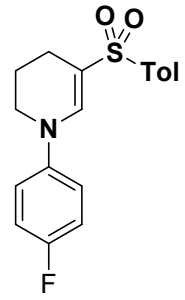
3d (^{1}H NMR) (400 MHz, $CDCl_3$)



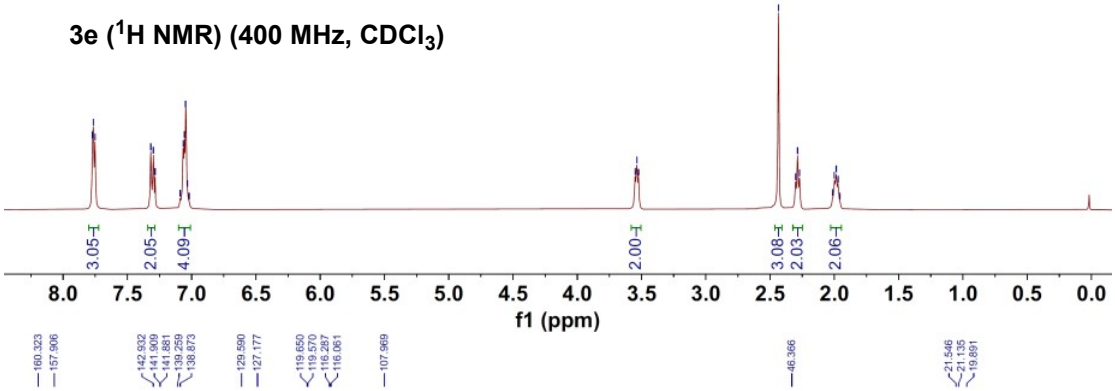


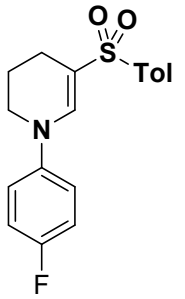
3d (^{13}C NMR) (100 MHz, $CDCl_3$)



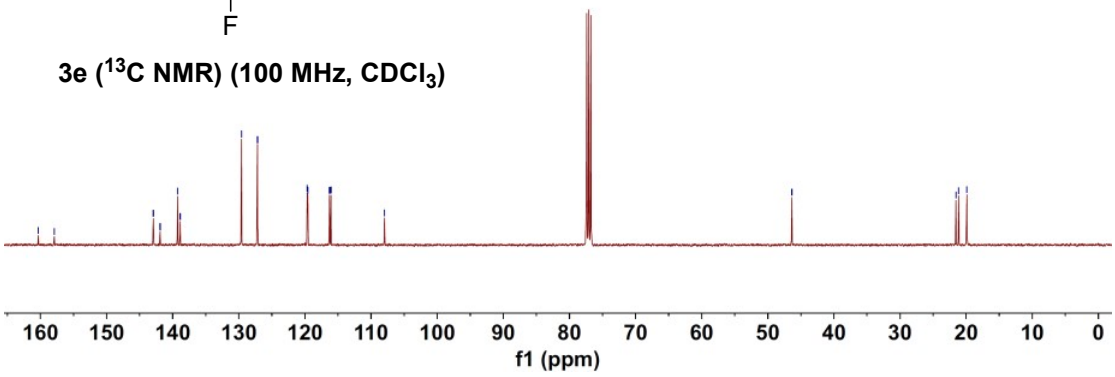


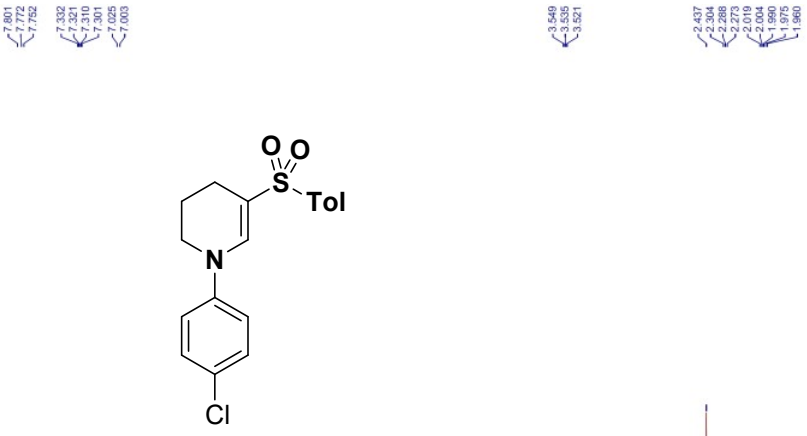
3e (^{1}H NMR) (400 MHz, $CDCl_3$)



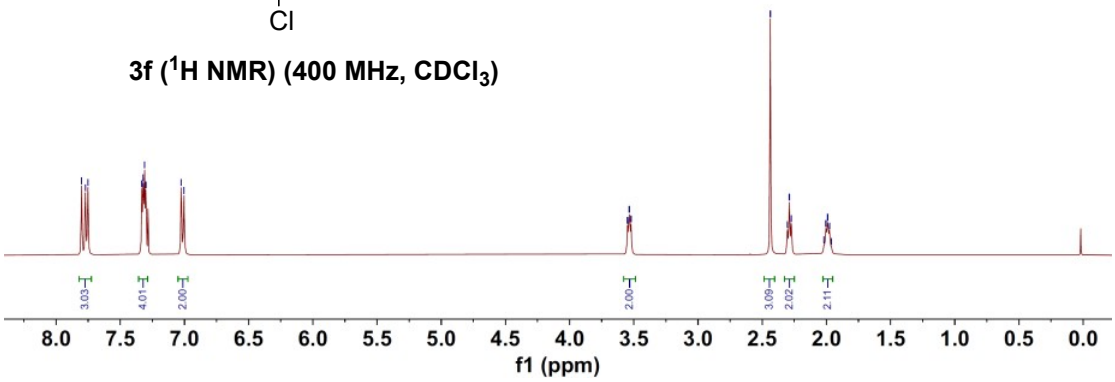


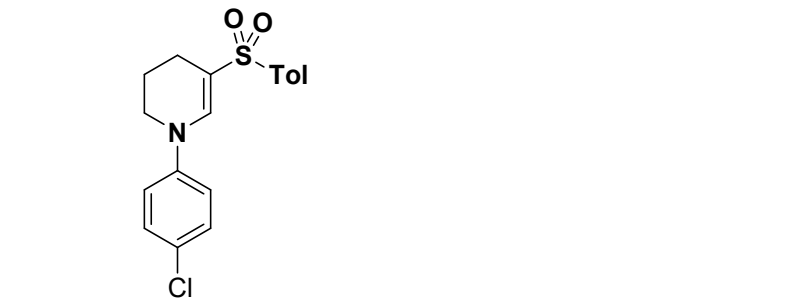
3e (^{13}C NMR) (100 MHz, $CDCl_3$)



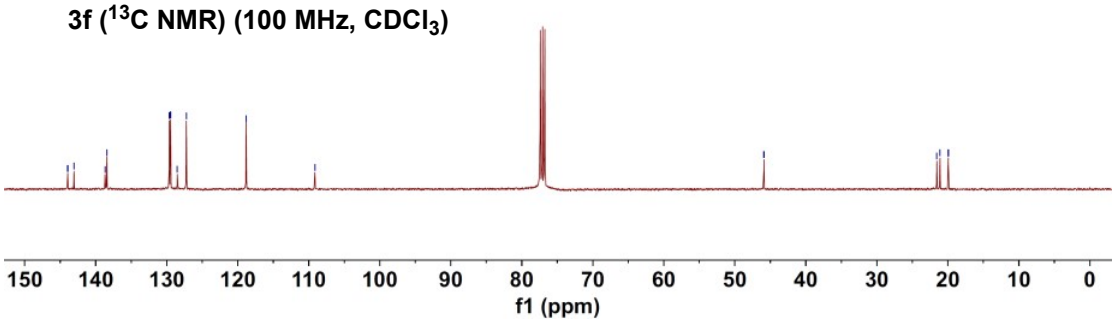


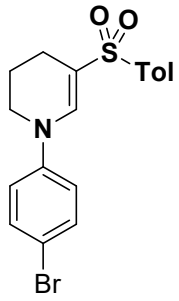
3f (^{1}H NMR) (400 MHz, $CDCl_3$)



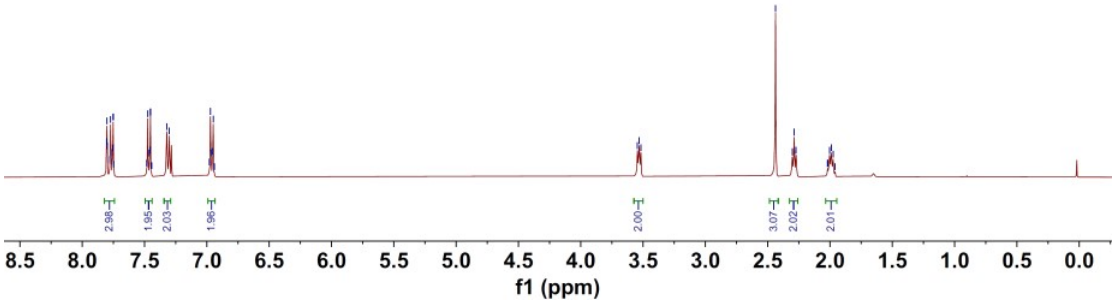


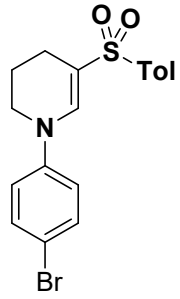
3f (^{13}C NMR) (100 MHz, $CDCl_3$)



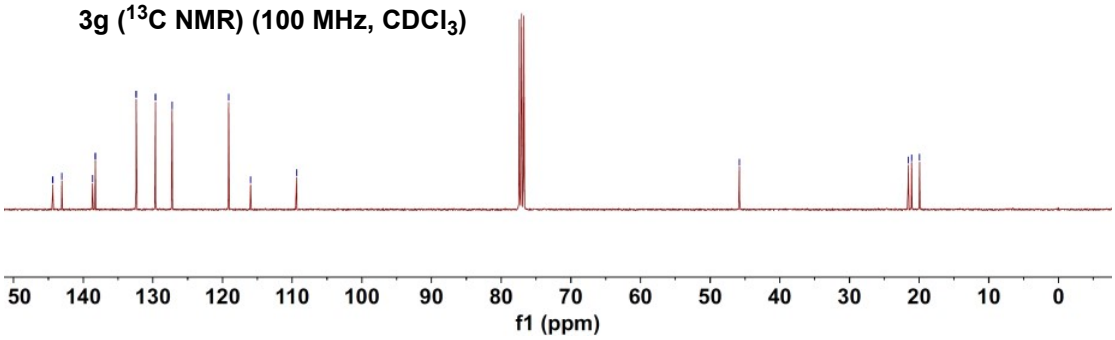


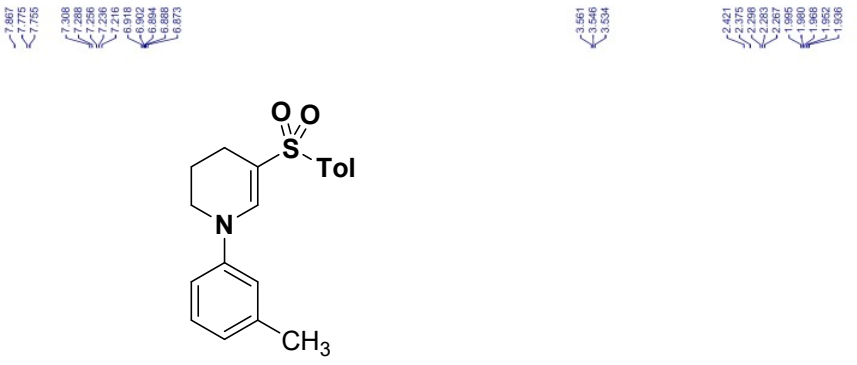
3g (^{1}H NMR) (400 MHz, $CDCl_3$)



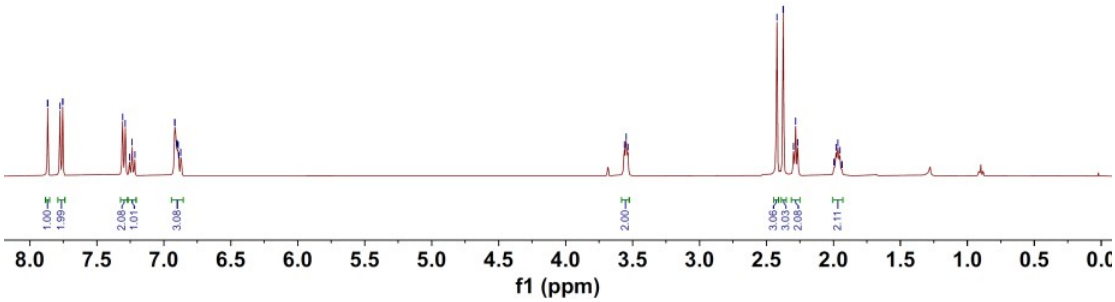


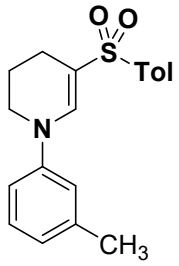
3g (^{13}C NMR) (100 MHz, $CDCl_3$)



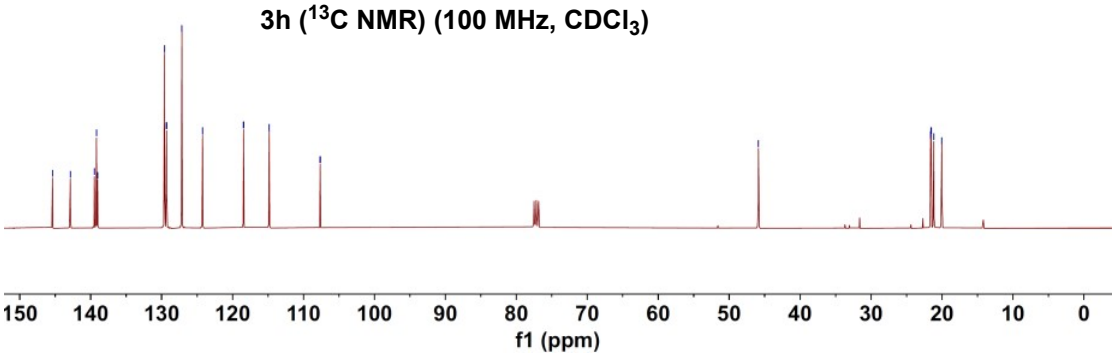


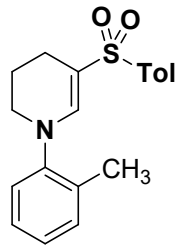
3h (^{1}H NMR) (400 MHz, $CDCl_3$)



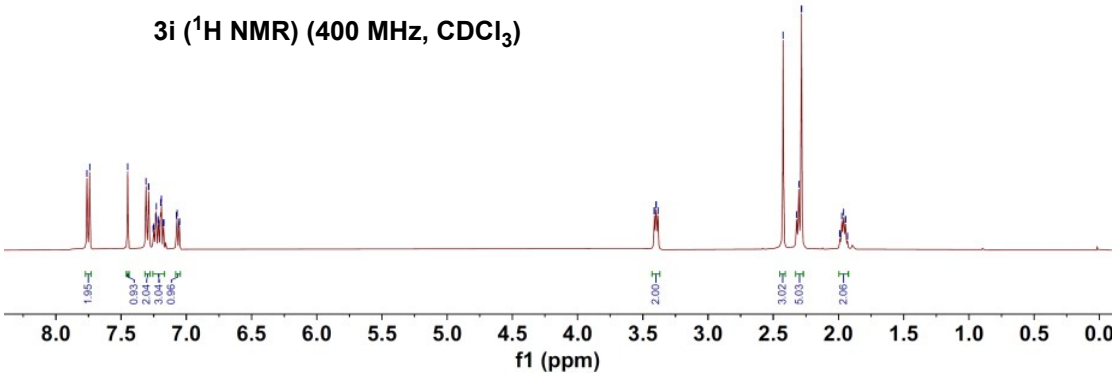


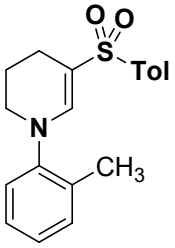
3h (^{13}C NMR) (100 MHz, $CDCl_3$)



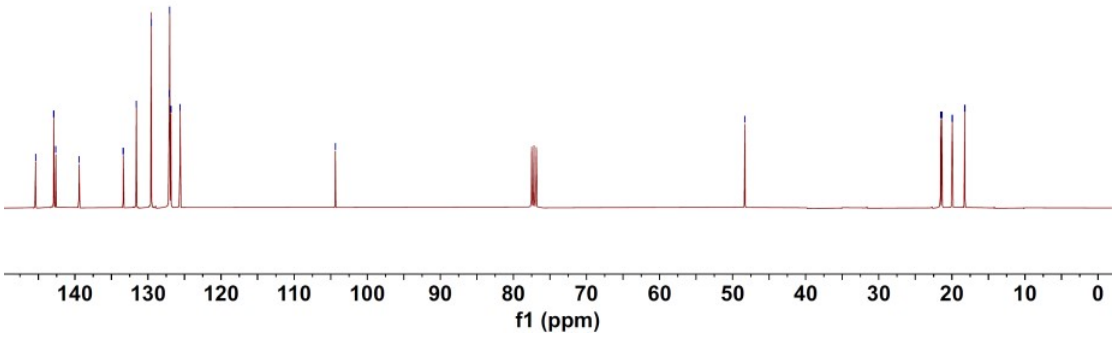


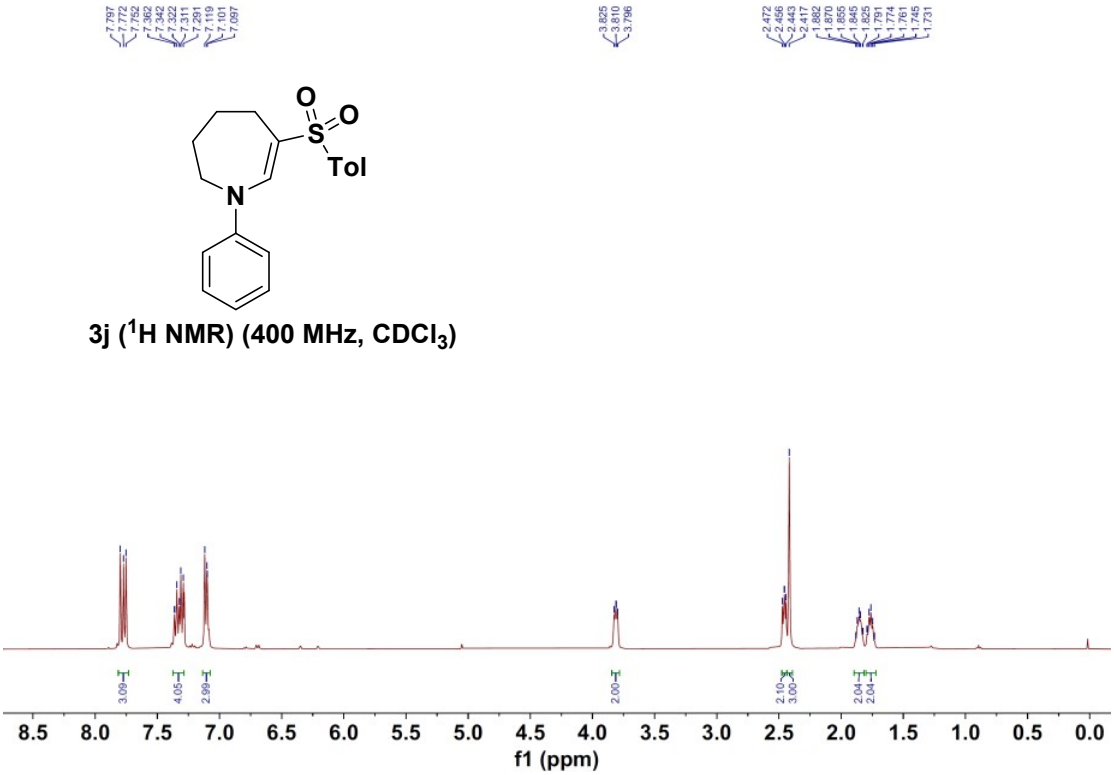
3i (^{1}H NMR) (400 MHz, $CDCl_3$)



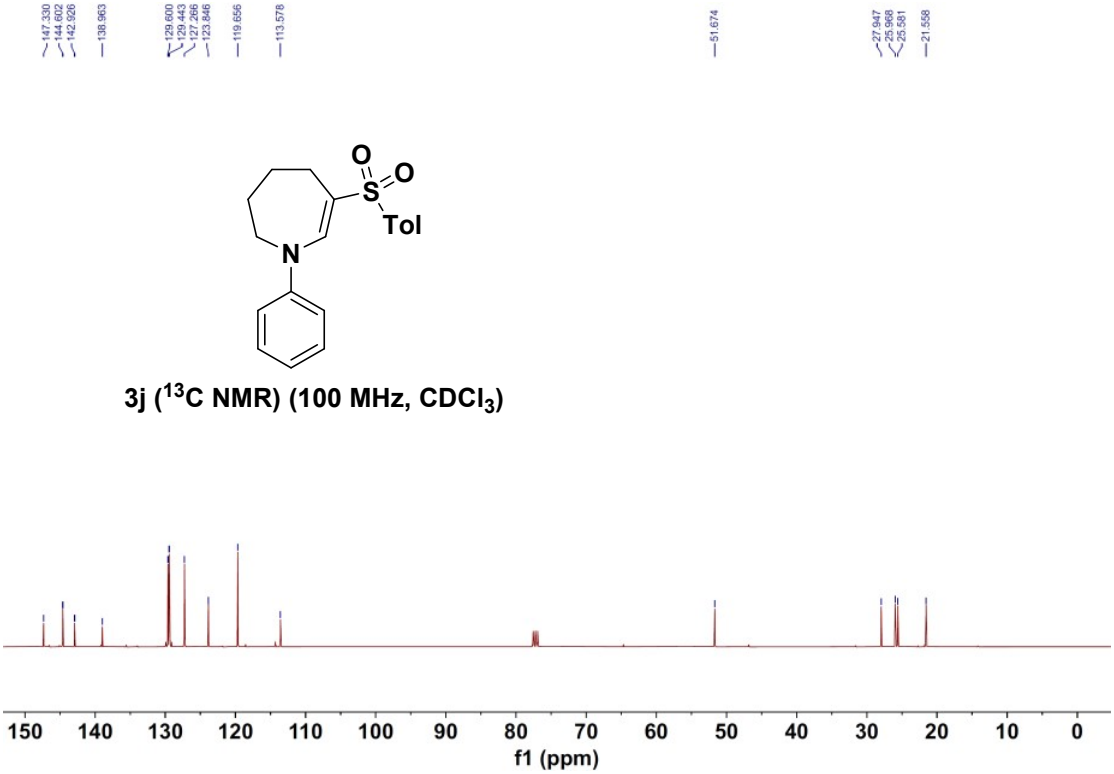


3i (^{13}C NMR) (100 MHz, $CDCl_3$)

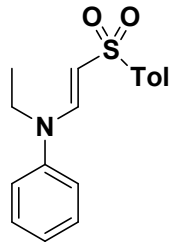




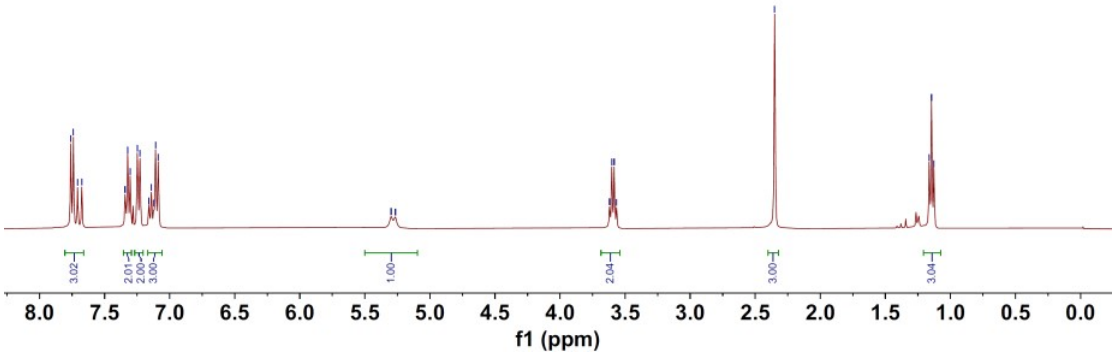
3j (^{1}H NMR) (400 MHz, $CDCl_3$)

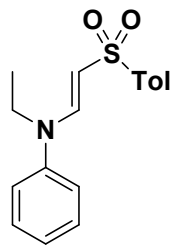


3j (^{13}C NMR) (100 MHz, $CDCl_3$)

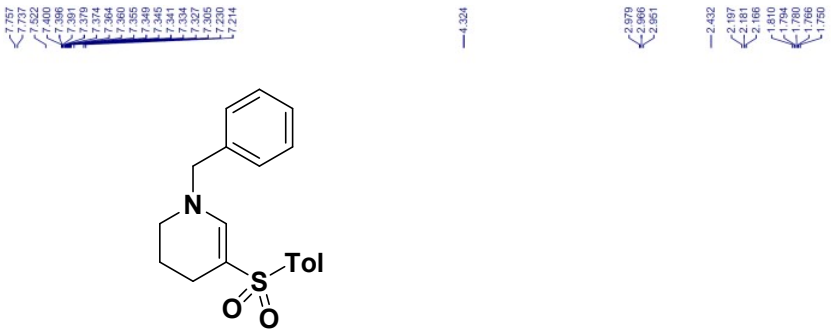


3k (^{1}H NMR) (400 MHz, $CDCl_3$)

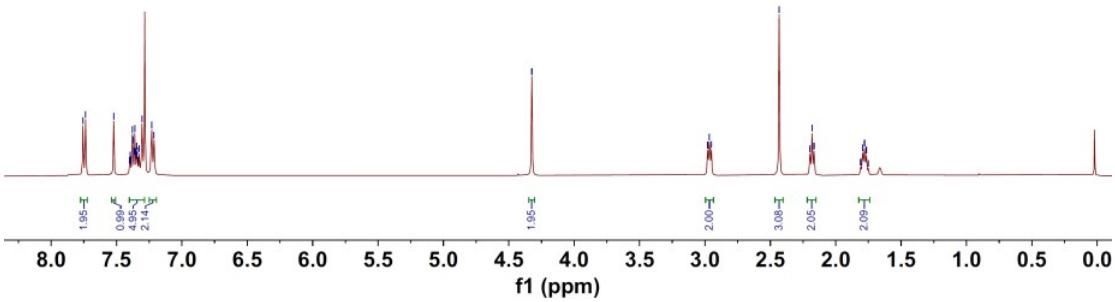


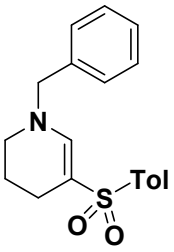


3k (^{13}C NMR) (100 MHz, $CDCl_3$)

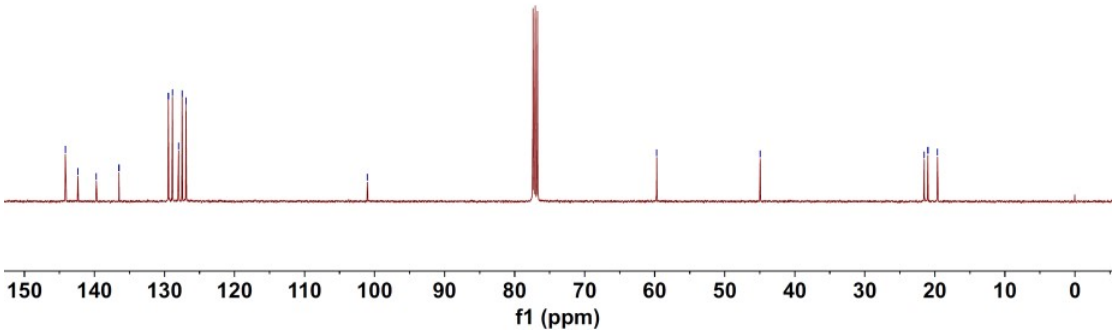


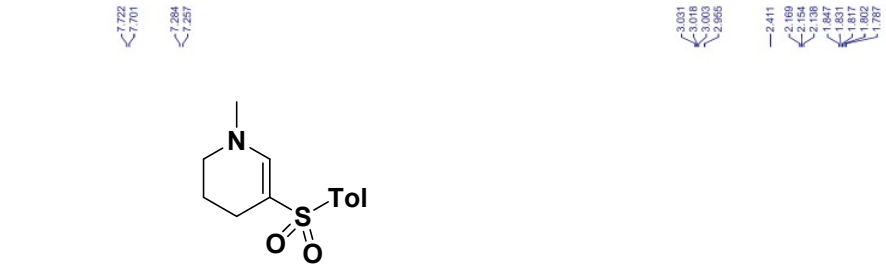
3l (^{1}H NMR) (400 MHz, $CDCl_3$)



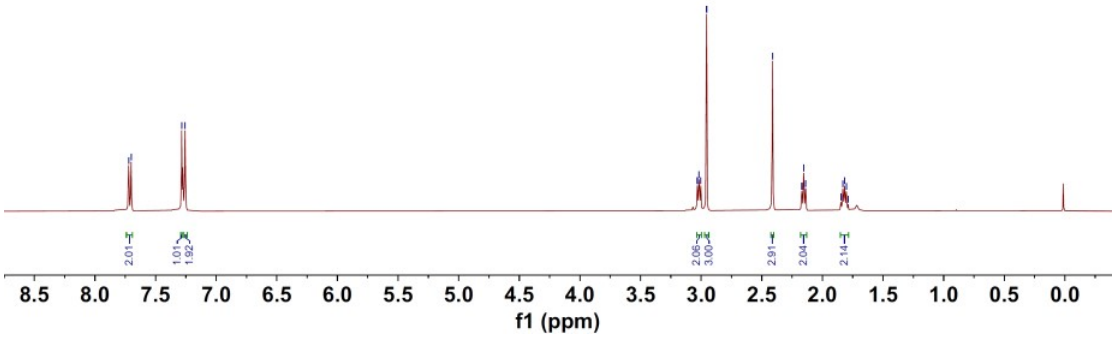


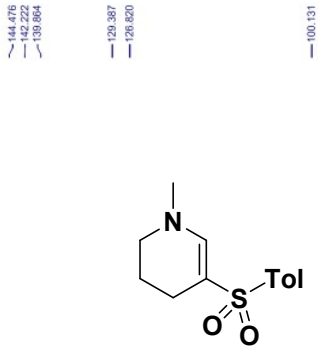
3l (^{13}C NMR) (100 MHz, $CDCl_3$)



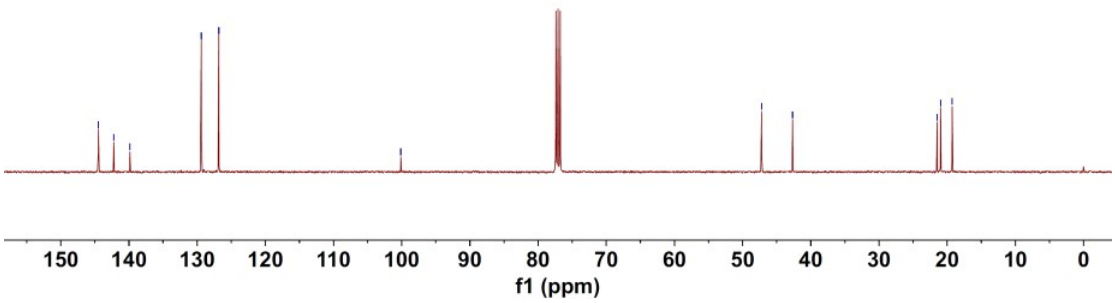


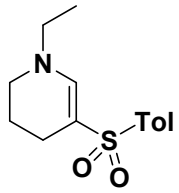
3m (^{1}H NMR) (400 MHz, $CDCl_3$)



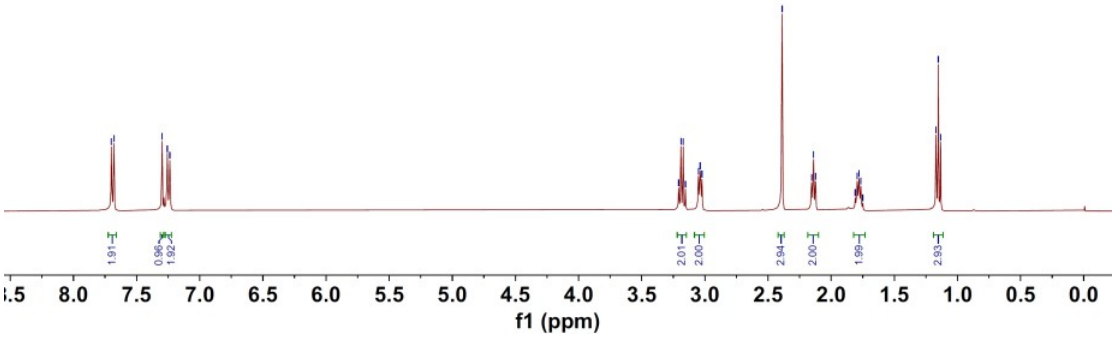


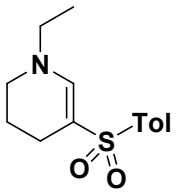
3m (^{13}C NMR) (100 MHz, $CDCl_3$)



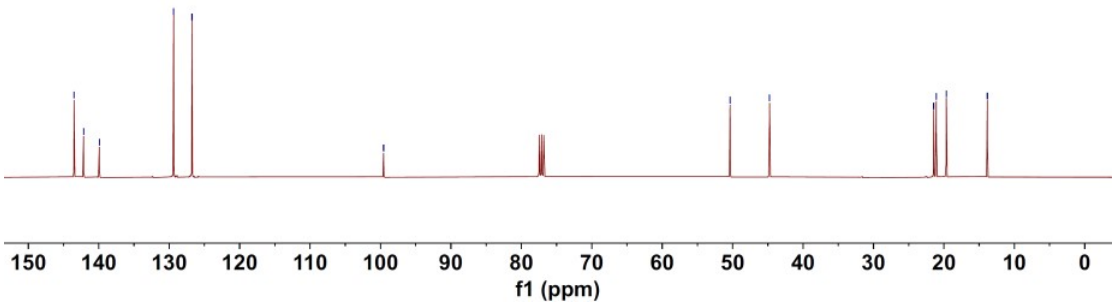


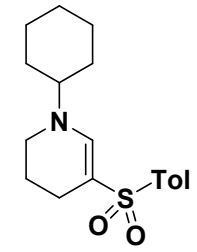
3n (^{1}H NMR) (400 MHz, $CDCl_3$)



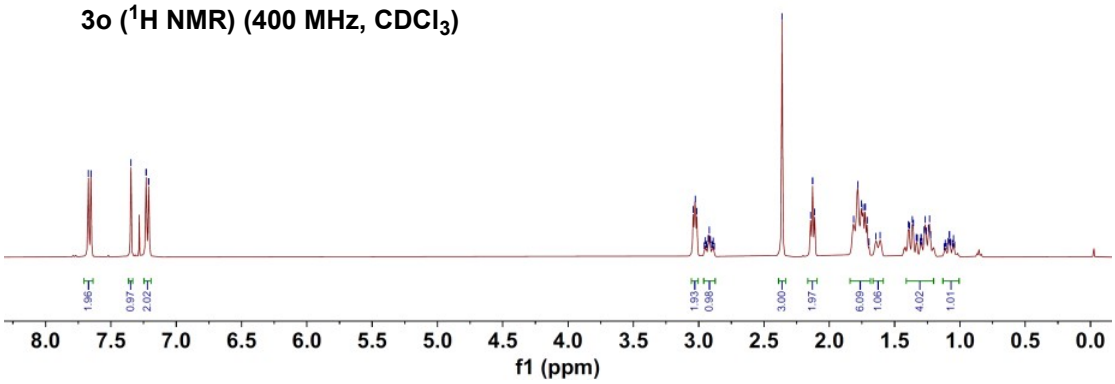


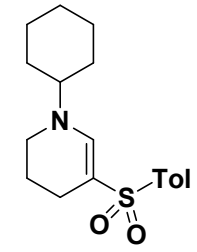
3n (^{13}C NMR) (100 MHz, $CDCl_3$)



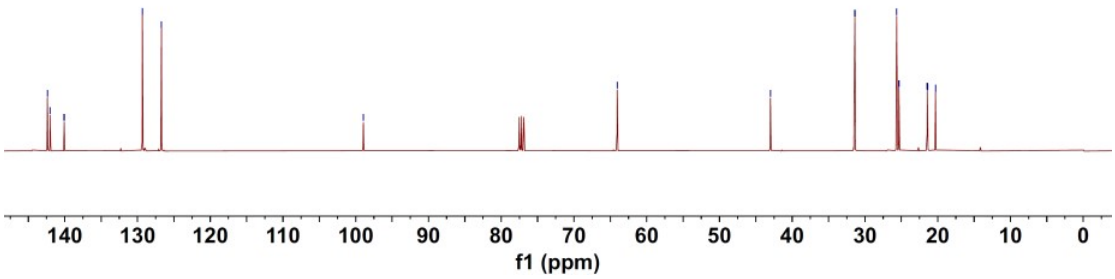


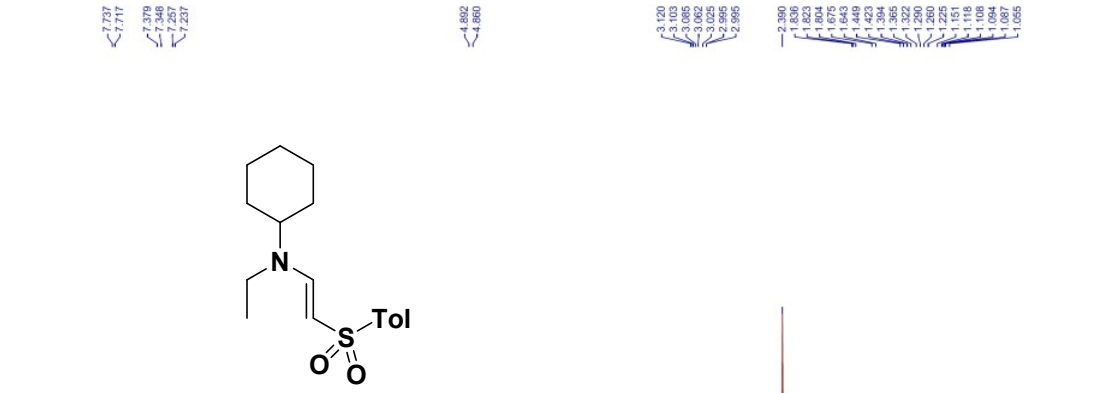
3o (^{1}H NMR) (400 MHz, $CDCl_3$)



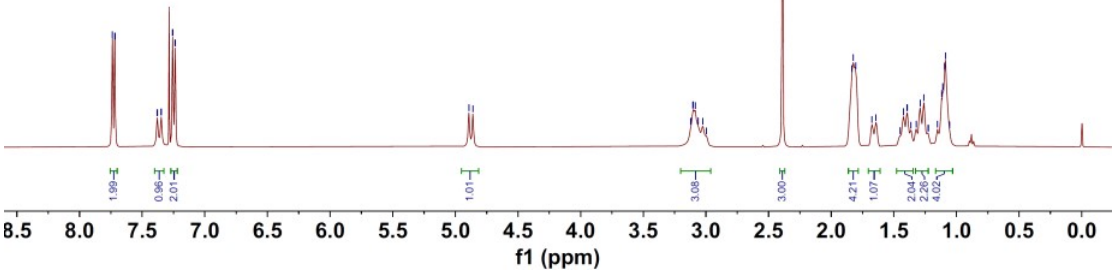


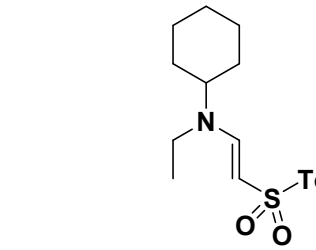
3o (^{13}C NMR) (100 MHz, $CDCl_3$)



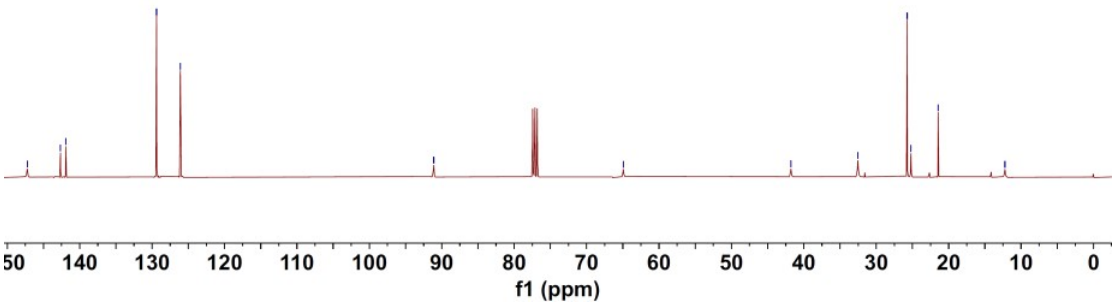


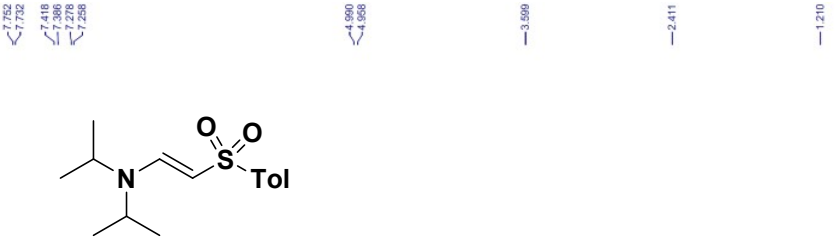
3p (^{1}H NMR) (400 MHz, $CDCl_3$)



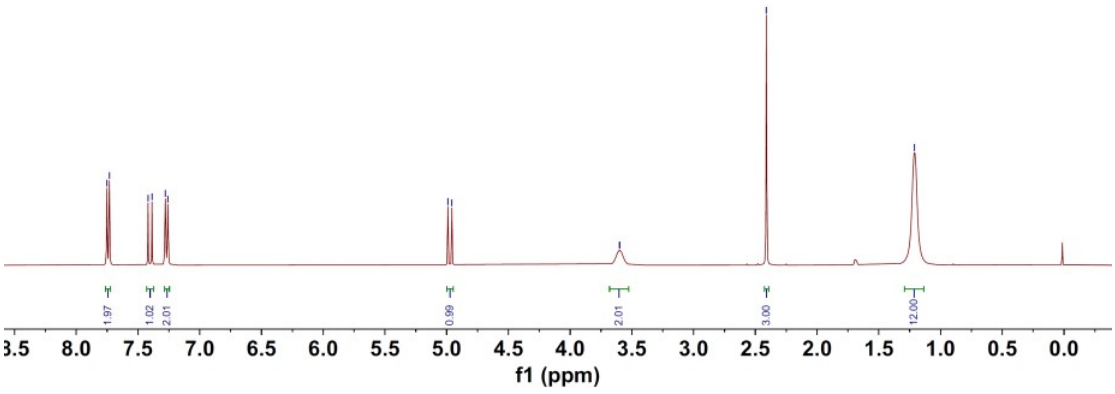


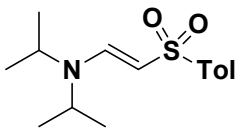
3p (^{13}C NMR) (100 MHz, $CDCl_3$)



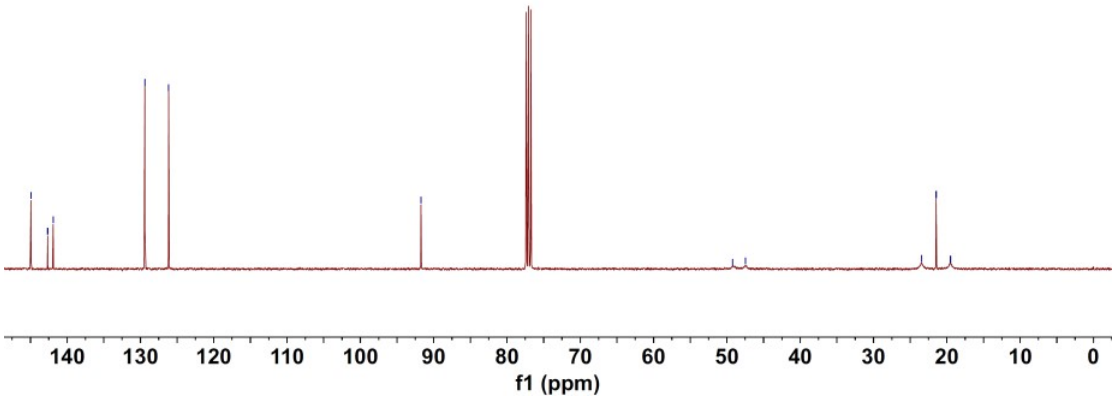


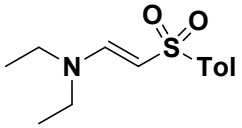
3q (^{1}H NMR) (400 MHz, $CDCl_3$)



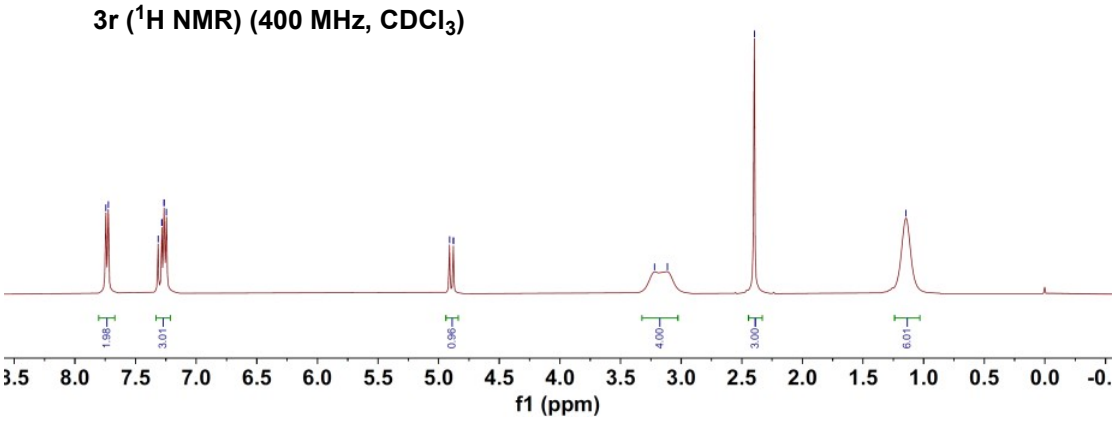


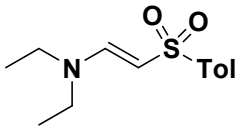
3q (^{13}C NMR) (100 MHz, $CDCl_3$)



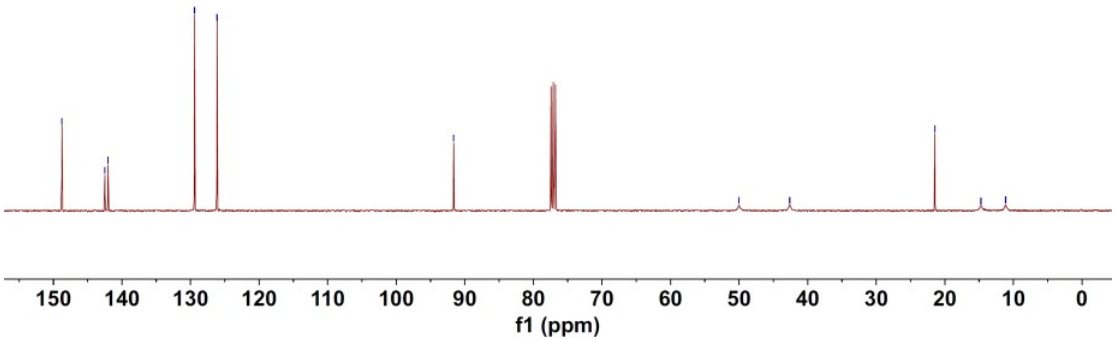


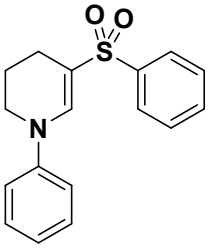
3r (^{1}H NMR) (400 MHz, $CDCl_3$)



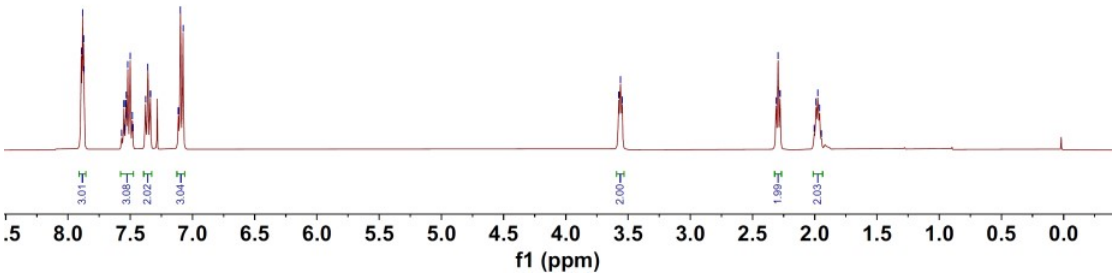


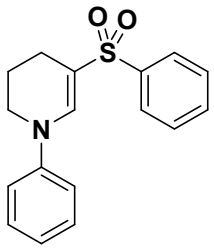
3r (^{13}C NMR) (100 MHz, $CDCl_3$)



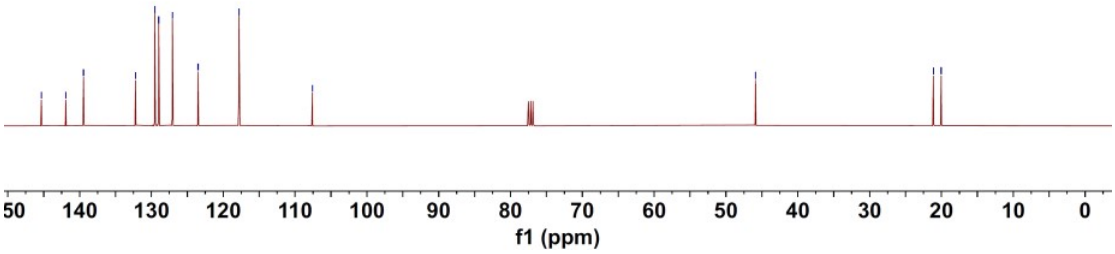


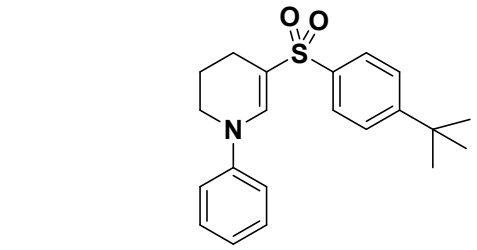
4a (^{1}H NMR) (400 MHz, $CDCl_3$)



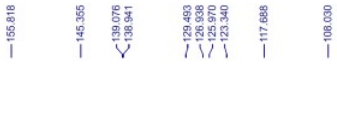


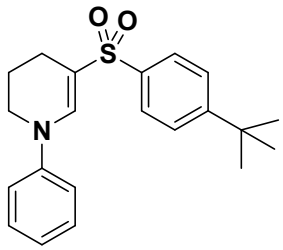
4a (^{13}C NMR) (100 MHz, $CDCl_3$)



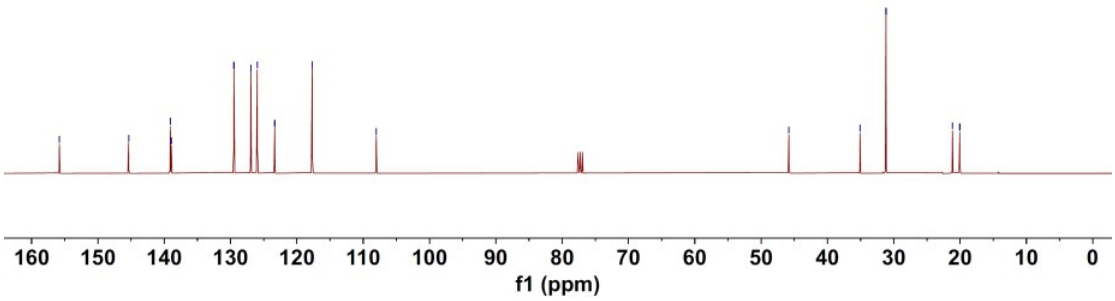


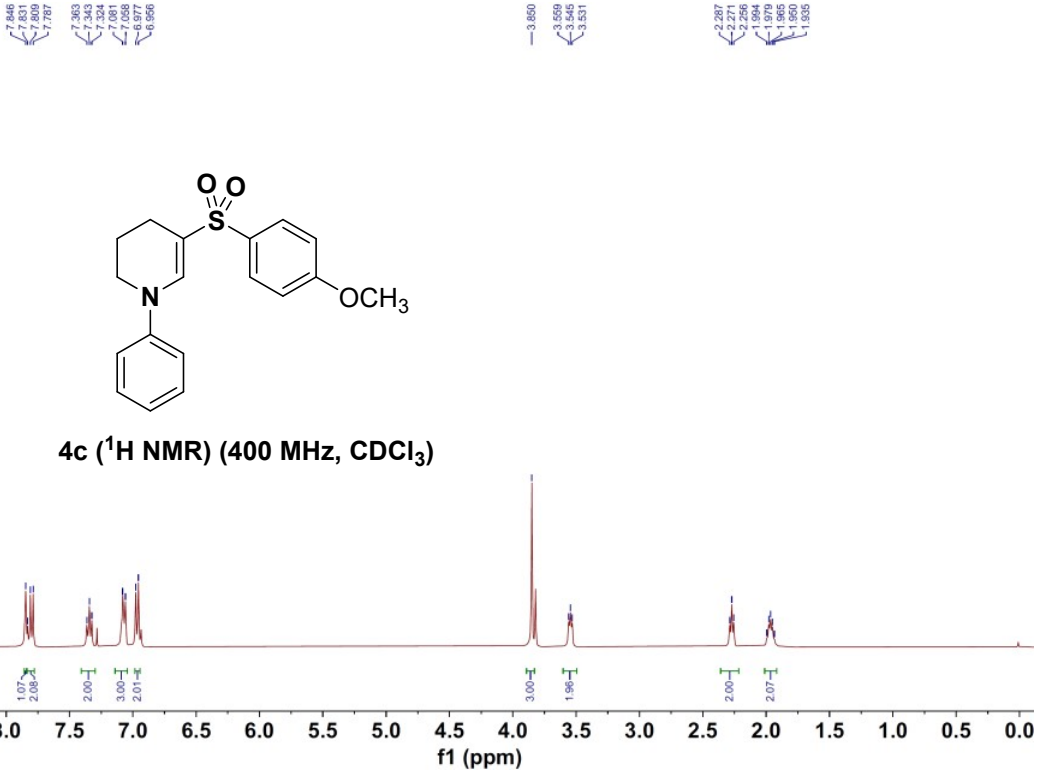
4b (^{1}H NMR) (400 MHz, $CDCl_3$)



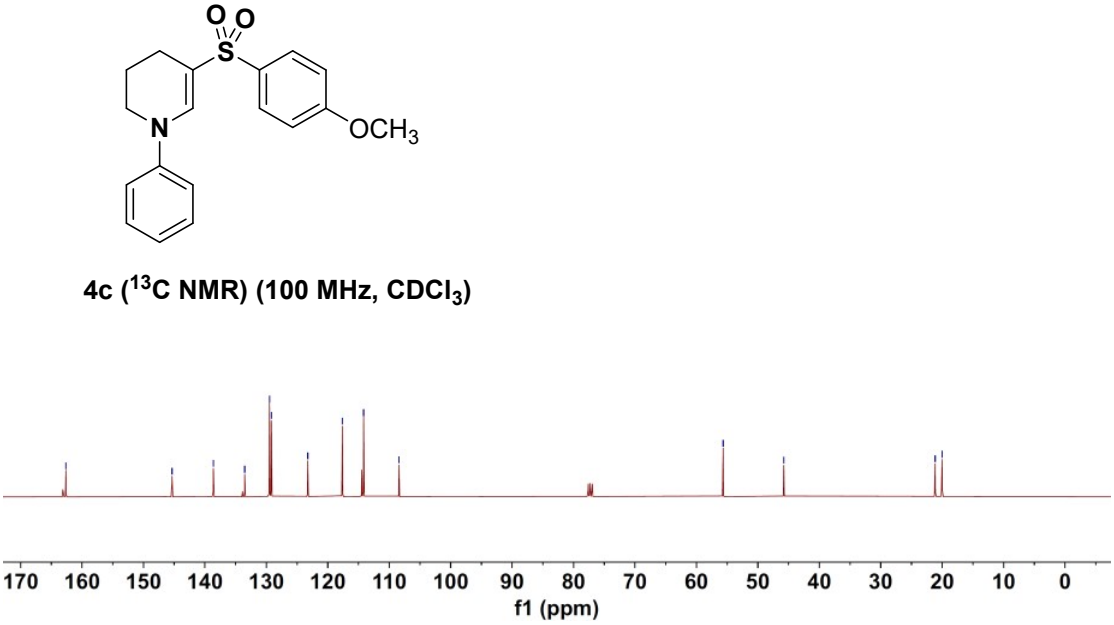


4b (^{13}C NMR) (100 MHz, $CDCl_3$)

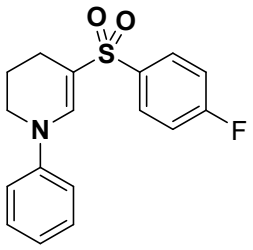




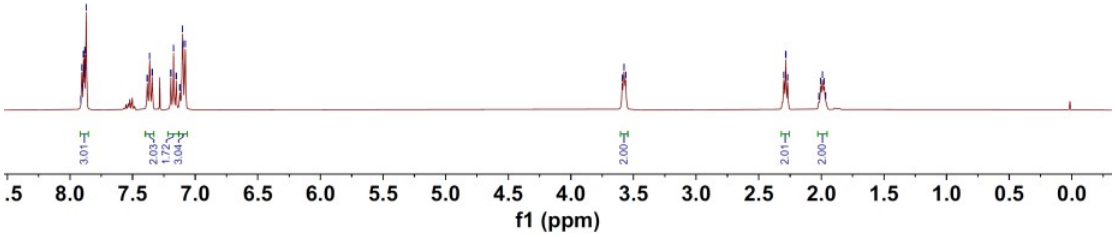
4c (^{1}H NMR) (400 MHz, $CDCl_3$)

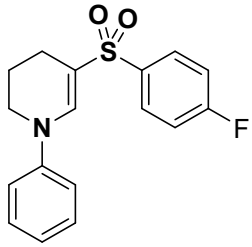


4c (^{13}C NMR) (100 MHz, $CDCl_3$)

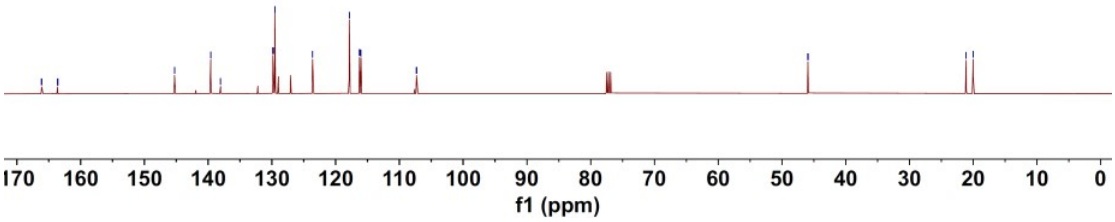


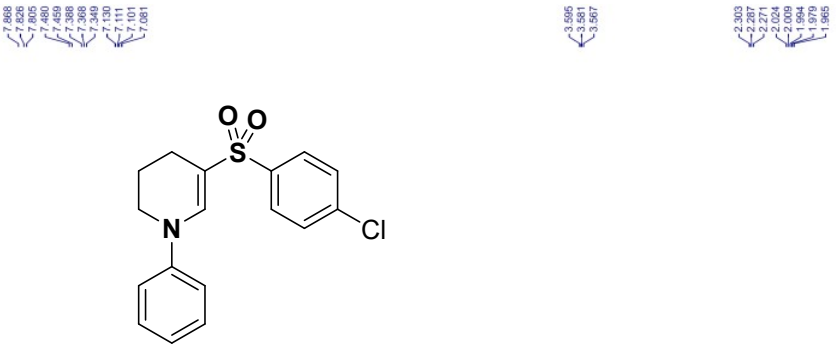
4d (^{1}H NMR) (400 MHz, $CDCl_3$)



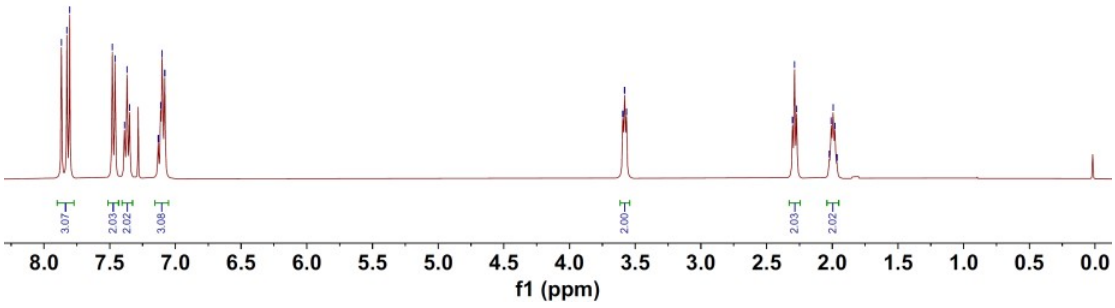


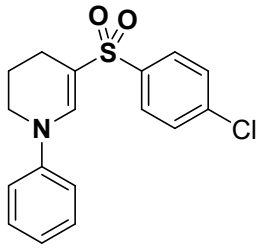
4d (^{13}C NMR) (100 MHz, $CDCl_3$)



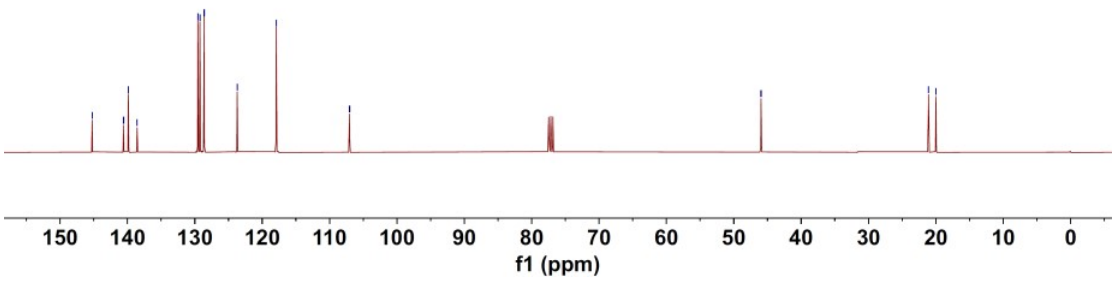


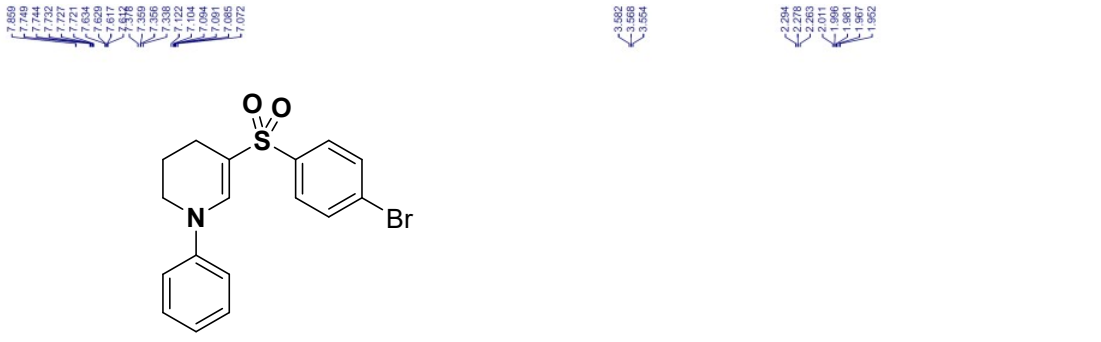
4e (^{1}H NMR) (400 MHz, $CDCl_3$)



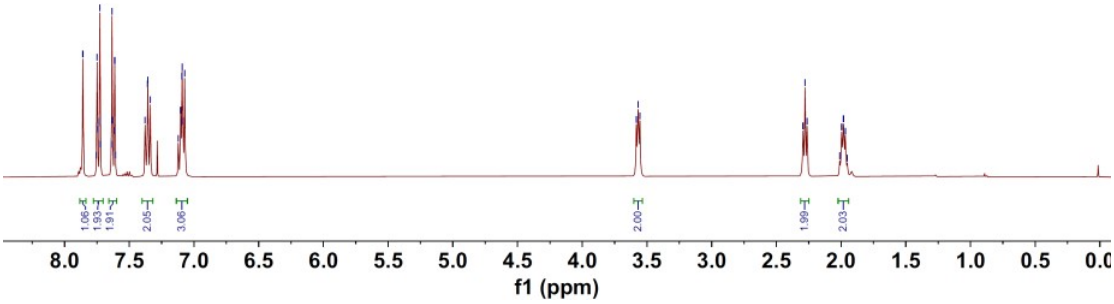


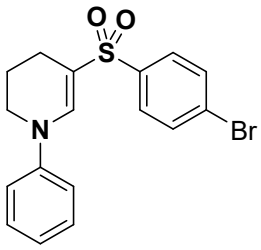
4e (^{13}C NMR) (100 MHz, $CDCl_3$)



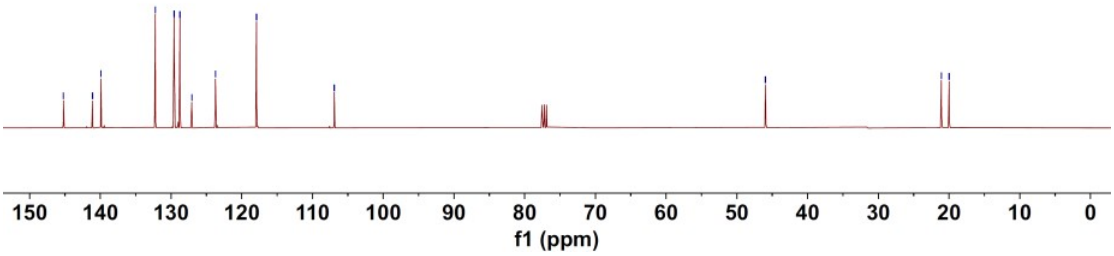


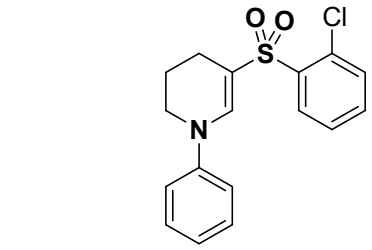
4f (^{1}H NMR) (400 MHz, $CDCl_3$)



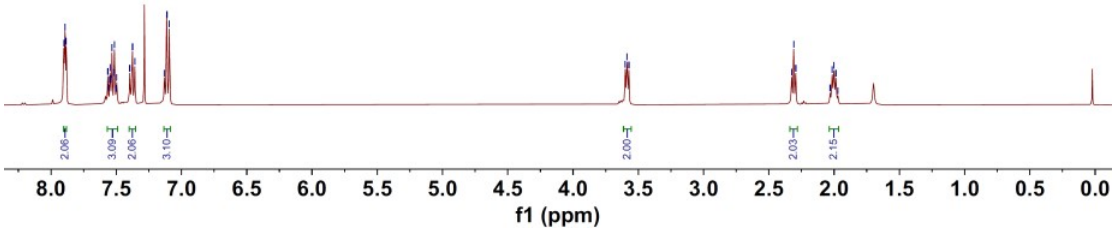


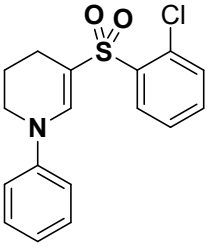
4f (^{13}C NMR) (100 MHz, $CDCl_3$)



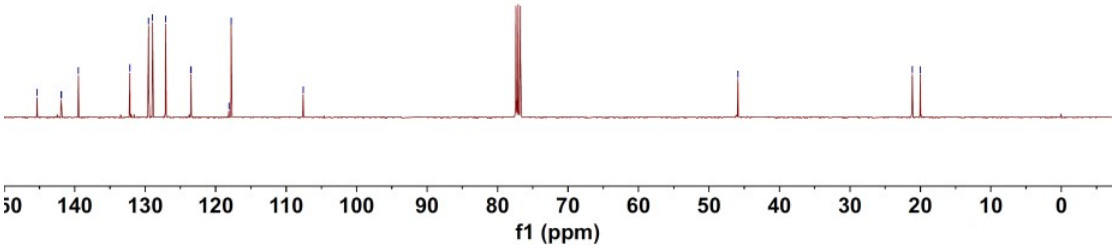


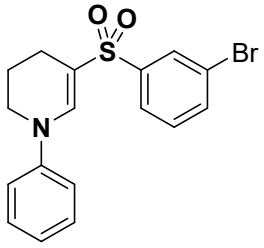
4g (^{1}H NMR) (400 MHz, $CDCl_3$)



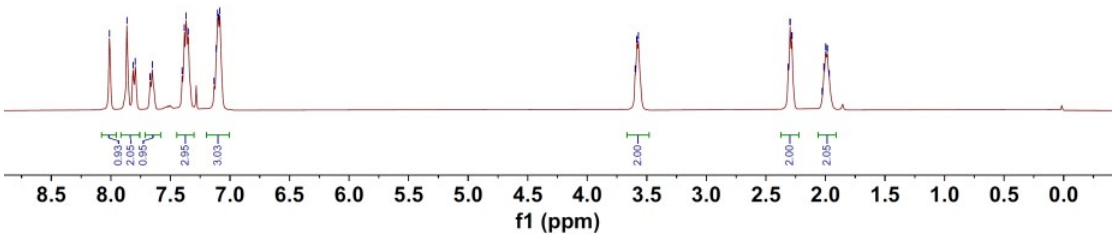


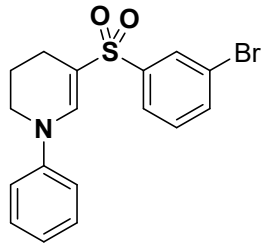
4g (^{13}C NMR) (100 MHz, $CDCl_3$)



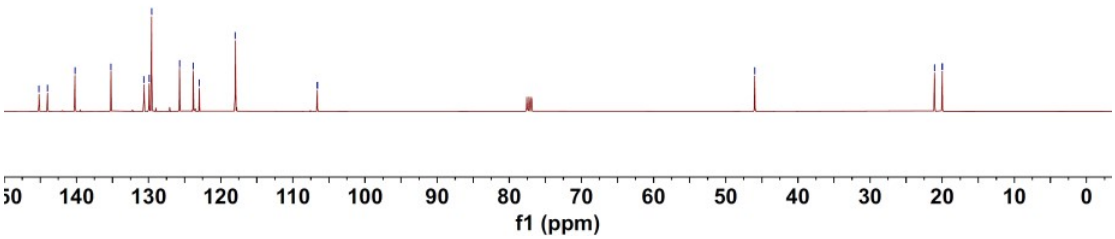


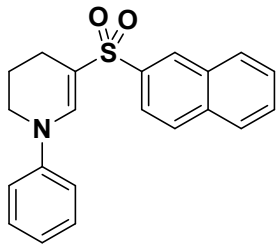
4h (^{1}H NMR) (400 MHz, $CDCl_3$)



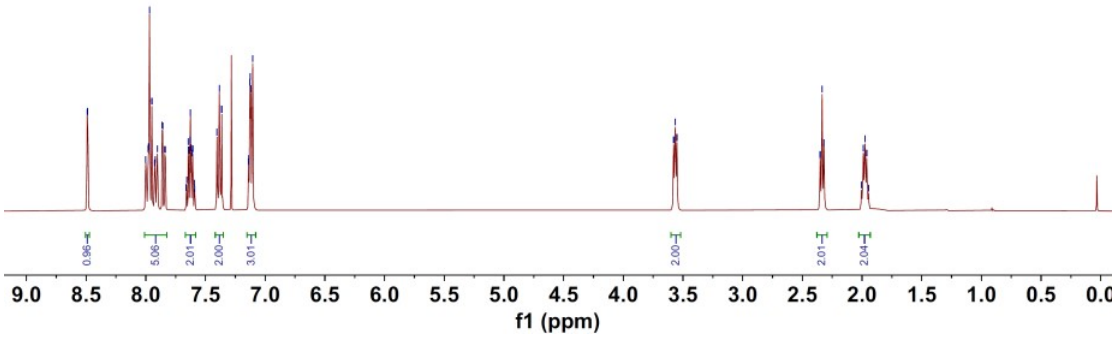


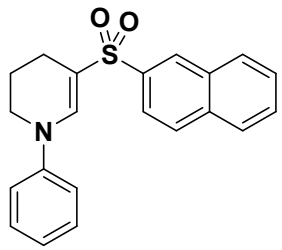
4h (^{13}C NMR) (100 MHz, $CDCl_3$)



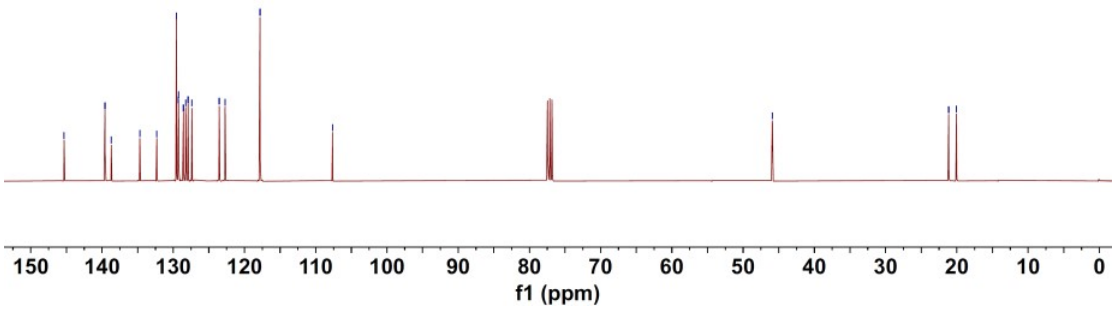


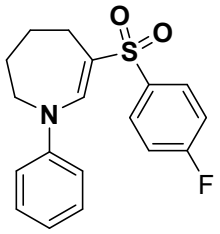
4i (^{1}H NMR) (400 MHz, $CDCl_3$)



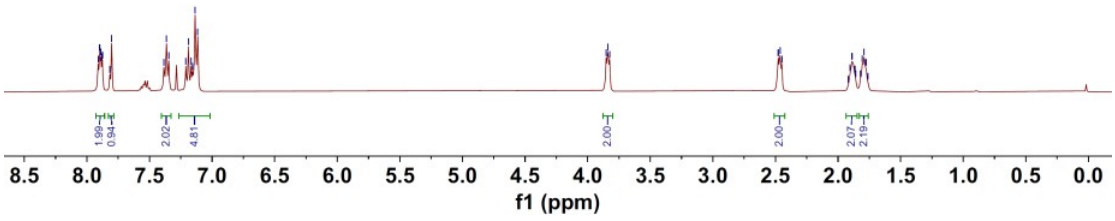


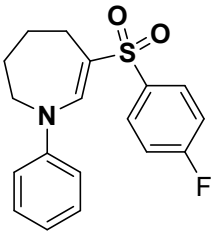
4i (^{13}C NMR) (100 MHz, $CDCl_3$)



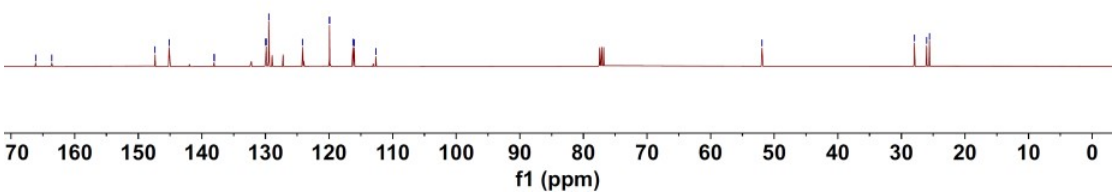


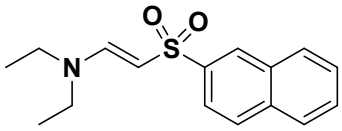
4j (^{1}H NMR) (400 MHz, $CDCl_3$)



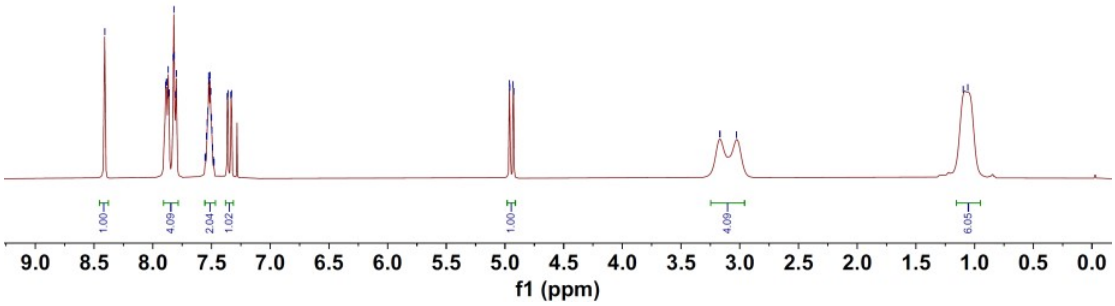


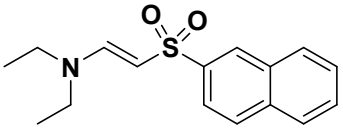
4j (^{13}C NMR) (100 MHz, $CDCl_3$)



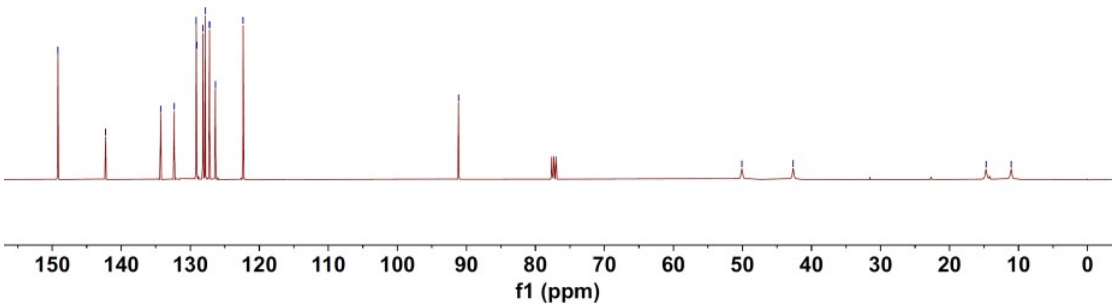


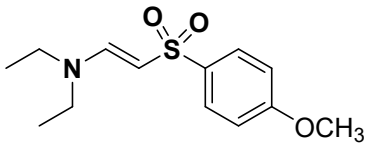
4k (^{1}H NMR) (400 MHz, $CDCl_3$)



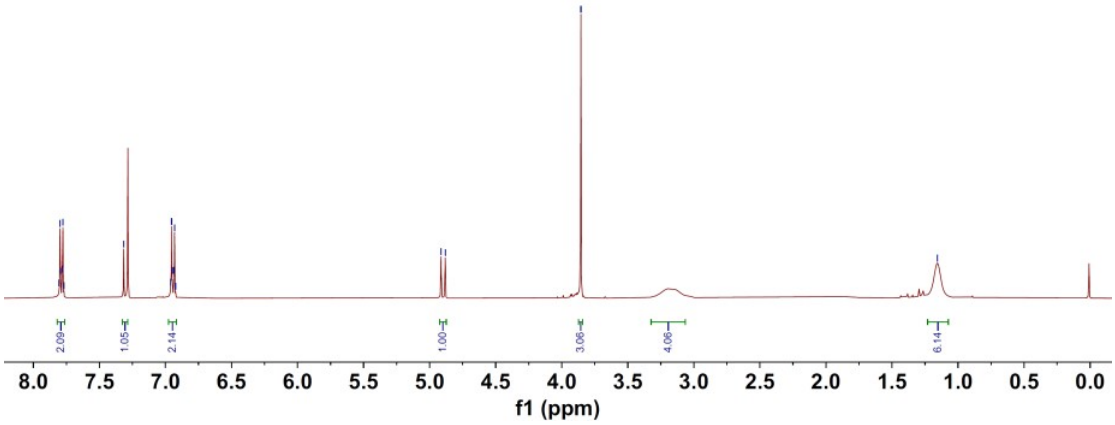


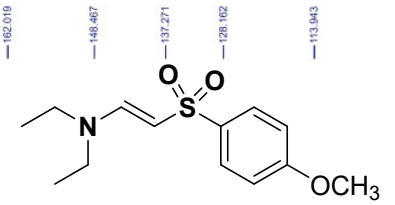
4k (^{13}C NMR) (100 MHz, $CDCl_3$)



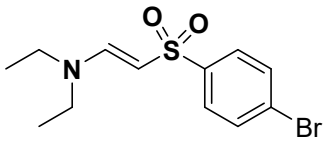


4l (^{1}H NMR) (400 MHz, $CDCl_3$)

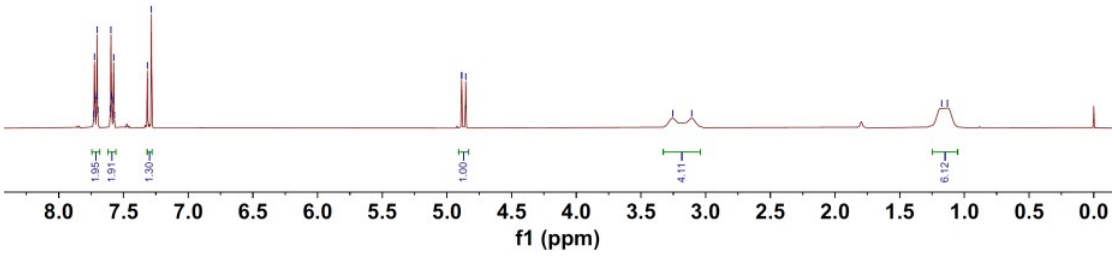


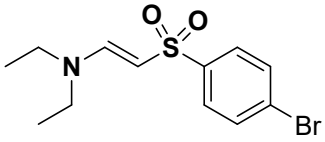


4l (^{13}C NMR) (100 MHz, $CDCl_3$)

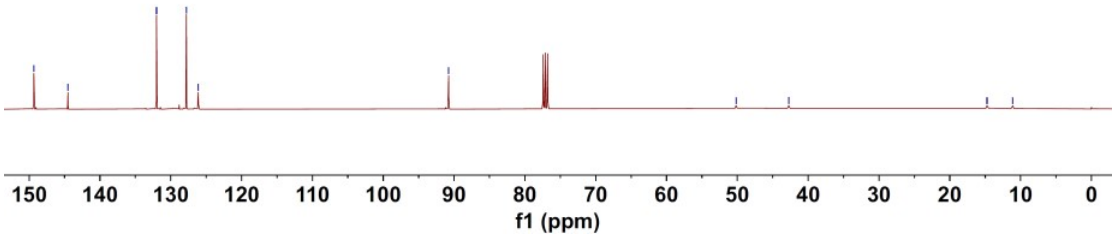


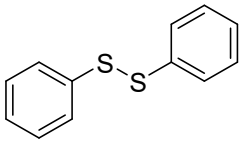
4m (^{1}H NMR) (400 MHz, $CDCl_3$)



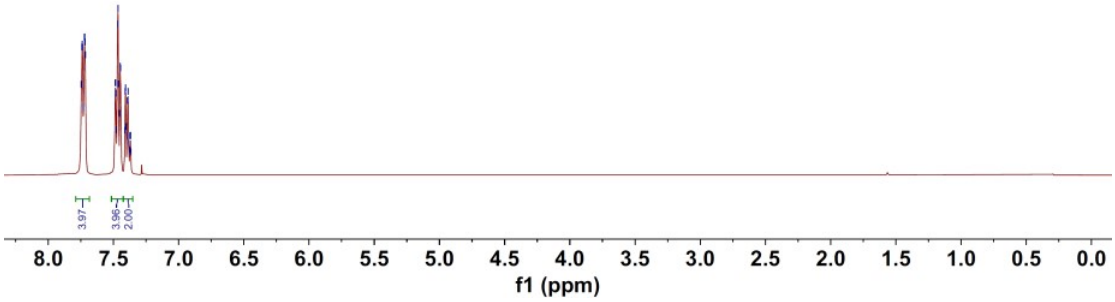


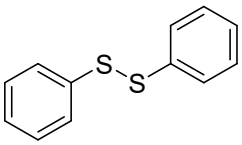
4m (^{13}C NMR) (100 MHz, $CDCl_3$)





D (^{1}H NMR) (400 MHz, $CDCl_3$)





D (^{13}C NMR) (100 MHz, $CDCl_3$)