Copper-Mediated Radical–Polar Crossover Enables Photocatalytic Oxidative Functionalization of Sterically Bulky Alkenes

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Supporting Information

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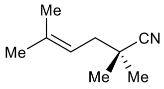
I. General Information

All reactions were performed under an N_2 atmosphere unless otherwise stated. All glassware was dried in an oven at 120 °C for at least 2 h prior to use and allowed to cool in a desiccator cabinet. Reactions carried out below 0 °C employed an acetone/dry ice bath or a cryocool equipped with an acetone bath. MeCN, THF, Et_2O, DMF, toluene, and CH_2Cl_2 were purified by elution through alumina as described by Grubbs.[1] 1,2-dichloroethane was distilled from CaH_2. All other chemicals were purchased from commercial suppliers and used as received.

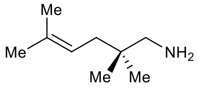
Flash column chromatography was performed with normal phase SiO_2 (Sigma-Aldrich or Macherey-Nagel, 60 Å pore size, 230-400 mesh, 40-63 μm particle size) according to the method of Still.[2] Reactions were monitored by thin-layer chromatography (Silicycle, 250 μm thickness), and visualization was accomplished with a 254 nm UV light or by staining with $KMnO_4$ solution (3.0 g of $KMnO_4$ and 20.0 g of K_2CO_3 in 5 mL of 5% aq. NaOH and 300 mL H_2O).

^1H and $^{13}C\{^1H\}$ NMR data for all previously uncharacterized compounds were obtained using a Bruker AVANCE-400 or Bruker AVANCE-500 spectrometer with DCH, Prodigy, or BBFO+ probes. ^1H spectra were internally referenced to tetramethyl silane (0.00 ppm) or the residual protio-solvent peak in DMSO-d_6. $^{13}C\{^1H\}$ spectra were internally referenced to $CDCl_3$ (77.16 ppm) or DMSO-d_6 (39.52 ppm). ^1H NMR spectra were tabulated as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, br = broad), coupling constant(s), and number of protons. ^{13}C NMR spectra were tabulated by observed peak. The spectrometers used for this work are supported by the NIH (S10 OD012245) and a generous gift from Paul J. and Margaret M. Bender. Mass spectrometry was performed with a Thermo Q Exactive^{TM} Plus. This instrument is supported by the NIH (S10 OD020022) and the University of Wisconsin. IR spectra were obtained using a Bruker Alpha Platinum FTIR spectrometer equipped with an attenuated total reflectance (ATR) sampling head. Melting points were obtained using a Stanford Research Systems DigiMelt apparatus.

II. Synthesis of Alkene Substrates

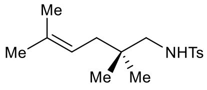


2,2,5-Trimethylhex-4-enenitrile (SI, **S1**). A solution of *i*-Pr_2NH (4.52 mL, 32.0 mmol) in THF (64 mL) at 0 °C was treated dropwise via addition funnel with *n*-BuLi (13.0 mL, 32.0 mmol) in hexanes (2.46 M) over 10 minutes and the resulting solution was stirred at 0 °C for 15 min. Isobutyronitrile (2.90 mL, 32.0 mmol) was added dropwise and the resulting solution was stirred at 0 °C for 15 min. Prenyl bromide (3.70 mL, 32.0 mmol) was added dropwise and the resulting solution was stirred at rt for 17 h. The reaction mixture was quenched with sat. aq. NH_4Cl (200 mL) and extracted with Et_2O (3 x 75 mL). The combined organic extracts were washed with H_2O (3x) and brine (3x), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give crude **S1** (4.10 g) as an orange oil which was used without further purification.



2,2,5-Trimethylhex-4-en-1-amine (SI, **S2**). To a suspension of $LiAlH_4$ (2.27 g, 59.8 mmol) in Et_2O (80 mL) at 0 ºC was added a solution of **S1** (4.10 g) in Et_2O (20 mL) dropwise via addition funnel over 10 minutes and the resulting mixture was stirred at rt for 1.5 h. The reaction mixture was cooled to 0 °C and quenched by dropwise addition of 3 M aq. NaOH (20 mL). The resulting mixture was stirred for 15 min, dried over Na2SO4, filtered, and concentrated under reduced pressure to give **S2** (4.04 g, 28.6 mmol, 89% over 2 steps) as a light yellow oil.

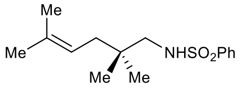
IR (ATR): ν 2958.2, 2920.5, 2864.6, 1569.1, 1463.6, 1371.8, 1312.0 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.20–5.14 (m, 1 H), 2.44 (s, 2 H), 1.89 (d, *J* = 7.6 Hz, 2 H), 1.72 (s, 3 H), 1.61 (s, 3 H), 0.84 (s, 6 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 133.1, 120.9, 52.9, 37.8, 35.9, 26.2, 24.8, 18.0; **HRMS** (ESI^+): $[M+H]^+$ calculated for $[C_9H_{20}N]^+$ required 142.1590 *m/z*, found 142.1594 *m/z*.



4-Methyl-*N*-(2,2,5-trimethylhex-4-en-1-yl)benzenesulfonamide (Table 1, **1**). To a solution of **S2** (1.00 g, 7.08 mmol) and Et_3N (1.48 mL, 10.6 mmol) in CH_2Cl_2 (24 mL) at 0 °C was added TsCl (1.48 g, 7.76 mmol) in a single portion and the resulting solution was stirred at rt for 2 h. The reaction mixture was concentrated under reduced pressure, taken up in Et_2O, eluted through a thin pad of SiO_2, and concentrated under reduced pressure to give crude **1** (2.10 g) as a white solid. The crude solid was purified by chromatography on SiO_2 (2-10% EtOAc in hexanes) to give **1** (1.77 g, 5.98 mmol, 84%) as a clear, colorless oil that solidified upon standing.

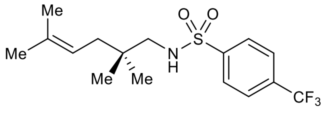
Mp 59–60 °C; **IR** (ATR): ν 3291.3, 3261.4, 2965.6, 2918.4, 2873.6, 1597.4, 1310.2, 1150.2 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76–7.69 (m, 2 H), 7.34–7.28 (m, 2 H), 5.04 (tp, *J* = 7.7, 1.4 Hz, 1 H), 4.43 (t, *J* = 6.8 Hz, 1 H), 2.68 (d, *J* = 6.8 Hz, 2 H), 2.43 (s, 3 H), 1.86 (d, *J* = 7.7 Hz, 2 H), 1.67 (d, *J* = 1.3 Hz, 3 H), 1.55 (s, 3 H), 0.84 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.4, 137.1, 134.2, 129.8, 127.2, 119.8, 53.2, 38.0, 35.0, 26.2, 25.0, 21.7, 18.0; **HRMS** (ESI^+): $[M+H]^+$ calculated for $[C_{16}H_{26}NO_2S]^+$ required 296.1679 *m/z*, found 296.1675 *m/z*.

***N*-(2,2,5-Trimethylhex-4-en-1-yl)benzenesulfonamide** (SI, **S3**). To a solution of **S2** (0.500 g, 3.54 mmol) and Et_3N (0.740 mL, 5.31 mmol) in CH_2Cl_2 (12 mL) at 0 °C was added $PhSO_2Cl$ (0.500 mL, 3.89 mmol) via syringe and the resulting solution was stirred at rt for 3.5 h. The reaction mixture was concentrated under reduced pressure, taken up in Et_2O, eluted through a thin pad of SiO_2, and concentrated under reduced pressure to give crude **S3** (1.02 g) as a light yellow oil. The crude residue was purified by chromatography on SiO_2 (10-15% EtOAc in hexanes) to give **S3** (0.877 g, 3.11 mmol, 88%) as a clear, colorless oil.



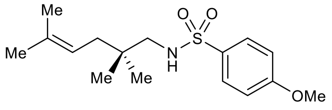
IR (ATR): ν 3270.6, 2963.8, 2867.1, 1448.4, 1319.0, 1156.3 cm^{-1}; ^{1}**H NMR** (500 MHz, $CDCl_3$): δ 7.90–7.84 (m, 2 H), 7.61–7.48 (m, 3 H), 5.04 (tp, *J* = 7.6, 1.4 Hz, 1 H), 4.64 (t, *J* = 6.6 Hz, 1 H), 2.70 (d, *J* = 6.8 Hz, 2 H), 1.87 (d, *J* = 7.7 Hz, 2 H), 1.67 (s, 3 H), 1.55 (s, 3 H), 0.84 (s, 6 H); ^{13}**C NMR** (125 MHz, $CDCl_3$): δ 140.1, 134.2, 132.6, 129.2, 127.1, 119.8, 53.2, 37.9, 35.0, 26.1, 24.9, 18.0; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{15}H_{24}NO_2S]^+$ required 282.1522 *m/z*, found 282.1517 *m/z*.

4-(Trifluoromethyl)-*N*-(2,2,5-trimethylhex-4-en-1-yl)benzenesulfonamide (SI, **S4**). To a solution of **S2** (0.422 g, 2.99 mmol) and Et_3N (0.615 mL, 4.48 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added 4-(trifluoromethyl)benzenesulfonyl chloride (0.810 g, 3.31 mmol) in a single portion and the resulting solution was stirred at rt for 2 h. The reaction mixture was concentrated under reduced pressure, taken up in Et_2O, eluted through a thin pad of SiO_2, and concentrated under reduced pressure to give crude **S4** (1.04 g) as a light yellow solid. The crude solid was purified by chromatography on SiO_2 (15% EtOAc in hexanes) to give **S4** (0.826 g, 2.36 mmol, 79%) as an off-white solid.



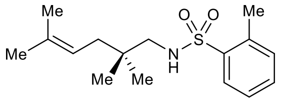
Mp 78–79 °C; **IR** (ATR): ν 3270.5, 2970.8, 2933.1, 1608.7, 1319.4 cm^{-1}; ^{1}**H NMR** (500 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.2 Hz, 2 H), 7.79 (d, *J* = 8.2 Hz, 2 H), 5.04 (ddt, *J* = 7.7, 6.3, 1.5 Hz, 1 H), 4.67 (t, *J* = 6.7 Hz, 1 H), 2.74 (d, *J* = 6.2 Hz, 2 H), 1.87 (d, *J* = 7.6 Hz, 2 H), 1.68 (s, 3 H), 1.55 (s, 3 H), 0.85 (s, 6 H); ^{13}**C NMR** (125 MHz, $CDCl_3$): δ 143.8 (q, *J* = 1.4 Hz), 134.5, 134.4 (q, *J* = 33.0 Hz, 127.7, 126.4 (q, *J* = 3.7 Hz), 123.4 (q, *J* = 272.9), 119.6, 55.3, 37.9, 35.1, 26.1, 25.0, 18.0; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{16}H_{23}F_3NO_2S]^+$ required 350.1396 *m/z*, found 350.1388 *m/z*.

4-Methoxy-*N*-(2,2,5-trimethylhex-4-en-1-yl)benzenesulfonamide (SI, **S5**). To a solution of **S2** (1.01 g, 7.15 mmol) and Et_3N (1.48 mL, 10.6 mmol) in CH_2Cl_2 (24 mL) at 0 °C was added 4-(methoxy)benzenesulfonyl chloride (1.62 g, 7.84 mmol) in a single portion and the resulting solution was stirred at rt for 2.5 h. The reaction mixture was concentrated under reduced pressure, taken up in Et_2O, eluted through a thin pad of SiO_2, and concentrated under reduced pressure to give crude **S5** (2.253 g) as a clear, light yellow oil. The crude residue was purified by chromatography on SiO_2 (15% EtOAc in hexanes) to give **S5** (2.01 g, 6.45 mmol, 90%) as a clear, colorless oil.



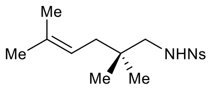
IR (ATR): ν 3283.0, 2961.8, 2919.4, 1594.2, 1151.0 cm^{-1}; ^{1}**H NMR** (500 MHz, $CDCl_3$): δ 7.85–7.73 (m, 2 H), 7.01–6.95 (m, 2 H), 5.04 (tt, *J* = 7.7, 1.4 Hz, 1 H); 4.51 (t, *J* = 6.8 Hz, 1 H), 3.87 (s, 3 H), 2.67 (d, *J* = 6.8 Hz, 2 H), 1.86 (d, *J* = 7.6 Hz, 2 H), 1.67 (d, *J* = 1.2 Hz, 3 H), 1.55 (s, 3 H), 0.83 (s, 6 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.9, 134.2, 131.7, 129.3, 119.9, 114.3, 55.7, 53.1, 38.0, 35.0, 26.2, 25.0, 18.0; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{16}H_{26}NO_3S]^+$ required 312.1628 *m/z*, found 312.1623 *m/z*.

2-Methyl-*N*-(2,2,5-trimethylhex-4-en-1-yl)benzenesulfonamide (SI, **S6**). To a solution of **S2** (0.498 g, 3.53 mmol) and Et_3N (0.740 mL, 5.31 mmol) in CH_2Cl_2 (18 mL) at 0 °C was added *o*-toluenesulfonyl chloride (0.560 g, 3.89 mmol) in a single portion and the resulting solution was stirred at rt for 17 h. The reaction mixture was concentrated under reduced pressure, taken up in Et_2O, eluted through a thin pad of SiO_2, and concentrated under reduced pressure to give crude **S6** (1.09 g) as a yellow oil. The crude residue was purified by chromatography on SiO_2 (10–20% Et_2O in hexanes) to give **S6** (0.900 g, 3.05 mmol, 86%) as a clear, colorless oil.



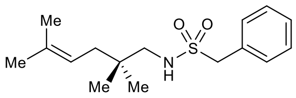
IR (ATR): ν 3304.5, 2964.7, 2925.1, 2875.7, 1462.1, 1321.0, 1159.4 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.99–7.92 (m, 1 H), 7.49–7.42 (m, 1 H), 7.35–7.28 (m, 2 H), 5.02 (tp, *J* = 7.7, 1.5 Hz, 1 H), 4.42 (t, *J* = 6.9 Hz, 1 H), 2.68 (d, *J* = 6.8 Hz, 2 H), 2.65 (s, 3 H), 1.85 (d, *J* = 7.6 Hz, 2 H), 1.67 (d, *J* = 1.4 Hz, 3 H), 1.56 (s, 3 H), 0.82 (s, 6 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 137.9, 137.0, 134.3, 132.8, 132.6, 129.8, 126.3, 119.8, 53.0, 38.0, 35.0, 26.2, 25.1, 20.4, 18.0; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{16}H_{26}NO_2S]^+$ required 296.1679 *m/z*, found 296.1675 *m/z*.

4-Nitro-*N*-(2,2,5-trimethylhex-4-en-1-yl)benzenesulfonamide (SI, **S7**). To a solution of **S2** (0.505 g, 4.46 mmol) and Et_3N (0.924 mL, 4.86 mmol) in CH_2Cl_2 (15 mL) at 0 °C was added 2-NsCl (1.10 g, 4.96 mmol) in a single portion and the resulting solution was stirred at rt for 1 h. The reaction mixture was concentrated under reduced pressure, taken up in Et_2O, eluted through a thin pad of SiO_2, and concentrated under reduced pressure to give crude **S7** (1.42 g) as a yellow oil. The crude residue was purified by chromatography on SiO_2 (20% EtOAc in hexanes) to give **S7** (1.04 g, 3.20 mmol, 72%) as a milky yellow oil.



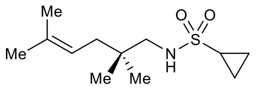
IR (ATR): ν 3359.7, 2962.5, 1590.5, 1539.2, 1351.2, 1166.9 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.15–8.09 (m, 1 H), 7.89–7.83 (m, 1 H), 7.77–7.71 (m, 2 H), 5.30 (t, *J* = 6.6 Hz, 1 H), 5.13–5.06 (m, 1 H), 2.84 (d, *J* = 6.5 Hz, 2 H), 1.92 (d, *J* = 7.7 Hz, 2 H), 1.70 (s, 3 H), 1.59 (s, 3 H), 0.89 (s, 6 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 148.2, 134.6, 133.8, 133.6, 132.9, 131.2, 125.5, 119.6, 53.6, 38.0, 35.2, 26.2, 25.1, 18.0; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{15}H_{23}N_2O_4S]^+$ required 327.1373 *m/z*, found 327.1369 *m/z*.

1-Phenyl-*N*-(2,2,5-trimethylhex-4-en-1-yl)methanesulfonamide (SI, **S8**). To a solution of **S2** (0.502 g, 3.56 mmol) and Et_3N (0.740 mL, 5.31 mmol) in CH_2Cl_2 (12 mL) at 0 °C was added phenylmethanesulfonyl chloride (0.746 g, 3.91 mmol) in a single portion and the resulting solution was stirred at rt for 1 h. The reaction mixture was concentrated under reduced pressure, taken up in Et_2O, eluted through a thin pad of SiO_2, and concentrated under reduced pressure to give crude **S8** as a white powder. The crude residue was purified by chromatography on SiO_2 (30% Et_2O in hexanes) to give **S8** (0.876 g, 2.97 mmol, 83%) as a white solid.



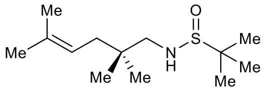
Mp 95–96 °C; **IR** (ATR): ν 3276.2, 2959.9, 2920.2, 1446.7, 1317.7, 1132.7 cm^{-1}; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.48–7.32 (m, 5 H), 5.08 (ddt, *J* = 7.7, 6.3, 1.5 Hz, 1 H), 4.25 (s, 2 H), 4.02 (t, *J* = 6.6 Hz, 1 H), 2.79 (d, *J* = 6.7 Hz, 2 H), 1.86 (d, *J* = 7.7 Hz, 2 H), 1.70 (d, *J* = 1.3 Hz, 3 H), 1.55 (s, 3, H), 0.86 (s, 6 H); ^{13}**C NMR** (125 MHz, $CDCl_3$): δ 134.3, 130.7, 129.6, 129.0, 128.9, 119.8, 58.6, 53.6, 38.0, 35.2, 26.2, 24.9, 18.0; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{16}H_{26}NO_2S]^+$ required 296.1679 *m/z*, found 296.1676 *m/z*.

***N*-(2,2,5-Trimethylhex-4-en-1-yl)cyclopropanesulfonamide** (SI, **S9**). To a solution of **S2** (0.502 g, 3.55 mmol) and Et_3N (0.740 mL, 5.31 mmol) in CH_2Cl_2 (18 mL) at 0 °C was added cyclopropylsulfonyl chloride (0.400 g, 3.89 mmol) in a single portion and the resulting solution was stirred at rt for 15 h. The reaction mixture was concentrated under reduced pressure, taken up in Et_2O, eluted through a thin pad of SiO_2, and concentrated under reduced pressure to give crude **S9** (1.00 g) as a clear, yellow oil. The crude residue was purified by chromatography on SiO_2 (40% Et_2O in hexanes) to give **S9** (0.768 g, 3.13 mmol, 89%) as a clear, colorless oil.



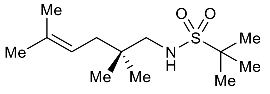
IR (ATR): ν 3287.9, 2963.4, 2920.9, 2872.0, 1425.0, 1323.3, 1145.2 cm^{-1}; ^{1}**H NMR** (400 MHz, DMSO-d_6): δ 6.91 (t, *J* = 6.7 Hz, 1 H), 5.17 (t, *J* = 7.8 Hz, 1 H), 2.76 (d, *J* = 6.7 Hz, 2 H), 1.87 (d, *J* = 7.7 Hz, 2 H), 1.69 (s, 3 H), 1.57 (s, 3 H), 0.92–0.88 (m, 4 H), 0.81 (s, 6 H); ^{13}**C NMR** (125 MHz, DMSO-d_6): δ 132.6, 120.5, 52.6, 37.3, 35.0, 29.1, 25.9, 24.5, 17.7, 4.4; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{12}H_{24}NO_2S]^+$ required 246.1522 *m/z*, found 246.1524 *m/z*.

2-Methyl-*N*-(2,2,5-trimethylhex-4-en-1-yl)propane-2-sulfinamide (SI, **S10**). To a solution of **S2** (0.550 g, 3.89 mmol) and Et_3N (0.810 mL, 5.84 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added *tert*-butyl sulfinyl chloride (0.450 mL, 4.28 mmol) in a single portion and the resulting solution was stirred at rt for 20 h. The reaction mixture was concentrated under reduced pressure, taken up in Et_2O, eluted through a thin pad of Celite, and concentrated under reduced pressure to give **S10** (0.953 g, 3.88 mmol, 100%) as a yellow oil.



IR (ATR): ν 3214.0, 2956.3, 2921.6, 2859.3, 1462.2, 1058.1 cm^{-1}; ^{1}**H NMR** (500 MHz, $CDCl_3$): δ 5.16 (tp, *J* = 7.6, 1.5 Hz, 1 H), 3.21 (dd, *J* = 9.4, 5.2 Hz, 1 H), 3.03 (dd, *J* = 12.8, 5.2 Hz, 1 H), 2.80 (dd, *J* = 12.8, 9.4 Hz, 1 H), 1.92 (d, *J* = 7.7 Hz, 2 H), 1.72 (s, 3 H), 1.61 (s, 3 H), 1.23 (s, 9 H), 0.88 (s, 6 H); ^{13}**C NMR** (125 MHz, $CDCl_3$): δ 133.8, 120.4, 56.0, 55.9, 38.2, 36.0, 26.2, 25.3, 25.1, 22.9, 18.1; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{13}H_{28}NOS]^+$ required 246.1886 *m/z*, found 246.1885 *m/z*.

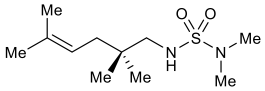
2-Methyl-*N*-(2,2,5-trimethylhex-4-en-1-yl)propane-2-sulfonamide (SI, **S11**). To a solution of **S10** (0.693 g, 2.82 mmol) in CH_2Cl_2 (10 mL) at -78 °C was added a solution of peroxyacetic acid (0.825 g, 4.23 mmol, 39% in acetic acid) in CH_2Cl_2 (4 mL) and the resulting solution was stirred at -78 °C for 2 h, warmed to -40 °C and stirred for 2 h, and warmed to 0 °C and stirred for 1 h. The reaction mixture was quenched by addition of sat. aq. $NaHCO_3$ (30 mL) and H_2O (50 mL) and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (2 x 50 mL) and the combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give crude **S11** (0.863 g)



as a yellow oil. The crude residue was purified by chromatography on SiO_2 (10% EtOAc in hexanes) to give **S11** (0.105 g, 0.402 mmol, 14%) as a white, crystalline solid.

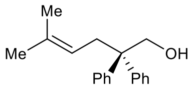
Mp 71–73 °C; **IR** (ATR): ν 3300.0, 2967.4, 2919.5, 1456.9, 1307.9, 1128.2 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.21–5.13 (m, 1 H), 3.86 (t, *J* = 6.3 Hz, 1 H), 2.98 (d, *J* = 6.3 Hz, 2 H), 1.94 (d, *J* = 7.7 Hz, 2 H), 1.73 (s, 3 H), 1.62 (s, 3 H), 1.40 (s, 9 H), 0.92 (s, 6 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 134.4, 120.0, 60.2, 55.1, 38.2, 35.5, 26.2, 25.0, 24.7, 18.1; **HRMS** (ESI^+): $[M+Na]^+$ calculated for $[C_{13}H_{27}NO_2SNa]^+$ required 294.1655 *m/z*, found 294.1653 *m/z*.

***N*-(2,2,5-trimethylhex-4-en-1-yl)-*N’*,*N’*-dimethyl sulfuric diamide** (SI, **S12**). To a solution of **S2** (0.340 g, 2.65 mmol) and Et_3N (0.500 mL, 3.61 mmol) in CH_2Cl_2 (12 mL) at 0 °C was added *N*,*N*-dimethylsulfamoyl chloride (0.275 mL, 2.65 mmol) via syringe and the resulting solution was stirred at rt for 16 h. The reaction mixture was concentrated under reduced pressure, taken up in Et_2O, eluted through a thin pad of SiO_2, and concentrated under reduced pressure to give crude **S12** (0.588 g) as a clear, colorless oil. The crude residue was purified by chromatography on SiO_2 (30-100% EtOAc in hexanes) to give **S12** (0.387 g, 1.56 mmol, 65%) as a clear, colorless oil.

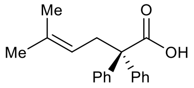


IR (ATR): ν 3296.9, 2920.6, 2877.4, 1458.5, 1324.6 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.18 (tp, *J* = 7.6, 1.4 Hz, 1 H), 4.09 (br. s, 1 H), 2.86 (d, *J* = 6.7 Hz, 2 H), 2.84 (s, 6 H), 1.95 (d, *J* = 7.7 Hz, 2 H), 1.75 (s, 3 H), 1.64 (s, 3 H), 0.94 (s, 6 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 134.3, 119.9, 53.7, 38.2, 38.2, 35.0, 26.2, 25.1, 18.1; **HRMS** (ESI^+): $[M+H]^+$ calculated for $[C_{11}H_{25}N_2O_2S]^+$ required 249.1631 *m/z*, found 249.1628 *m/z*.

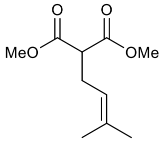
5-Methyl-2,2-diphenylhex-4-en-1-ol (SI, **S13**). Synthesized according to the method of Melchiorre and coworkers. All spectral data were in agreement with previously reported values.[3]



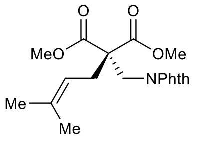
5-Methyl-2,2-diphenylhex-4-enoic acid (SI, **S14**). Synthesized according to the method of Melchiorre and coworkers. All spectral data were in agreement with previously reported values.[3]



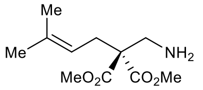
Dimethyl 2-(3-methylbut-2-en-1-yl)malonate (SI, **S15**). Synthesized according to the method of Sher and Mook, Jr. All spectral data were in agreement with previously reported values.[4]



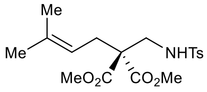
Dimethyl 2-((1,3-dioxoisoindolin-2-yl)methyl)-2-(3-methylbut-2-en-1-yl)malonate (SI, **S16**). To a suspension of NaH (1.59 g, 42.3 mmol, 60% dispersion in mineral oil) in THF (42 mL) at 0 °C was added a solution of **S15** (5.80 g, 29.0 mmol) in THF (11 mL) dropwise via syringe and the resulting solution was stirred at 0 °C for 30 min. *N*-(Chloromethyl)phthalimide (5.15 g, 26.3 mmol) was added in a single portion and the resulting solution was stirred at rt for 16 h. The reaction mixture



was quenched by dropwise addition of sat. aq. NH_4Cl (100 mL) at 0 °C and extracted with Et_2O (3 x 50 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give crude **S16** (7.68 g) as a white solid which was used without further purification.

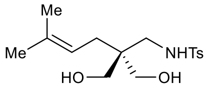


Dimethyl 2-(aminomethyl)-2-(3-methylbut-2-en-1-yl)malonate (SI, **S17**). A solution of **S16** (6.00 g) and $N_2H_4{\cdot}H_2O$ (0.890 mL, 18.4 mmol) in MeOH (42 mL) was stirred at reflux for 4 h. The mixture was quenched with 10% aq. NaOH (100 mL) and extracted with Et_2O (3 x 50 mL). The combined organic extracts were washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give crude **S17** (3.62 g) as a clear, colorless oil.



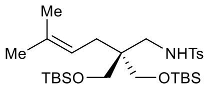
Dimethyl 2-(3-methylbut-2-en-1-yl)-2-(((4-methylphenyl)sulfonamido)methyl)malonate (SI, **S18**). To a solution of **S17** (3.62 g) and Et_3N (3.30 mL, 23.7 mmol) in CH_2Cl_2 (80 mL) at 0 °C was added TsCl (3.32 g, 17.4 mmol) in a single portion and the resulting solution was stirred at rt for 15 h. The reaction mixture was concentrated under reduced pressure, taken up in Et_2O, eluted through a thin pad of SiO_2, and concentrated under reduced pressure to give crude **S18** (5.53 g) as a white solid. The crude solid was purified by chromatography on SiO_2 (20-40% EtOAc in hexanes) to give **S18** (3.45 g, 9.00 mmol, 21% over 3 steps) as a white solid.

Mp 116–118 °C; **IR** (ATR): ν 3252.6, 3056.8, 2956.8, 1731.0, 1596.3 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.3 Hz, 2 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 5.07 (t, *J* = 7.0 Hz, 1 H), 4.88 (m, 1 H), 3.70 (s, 6 H), 3.31 (d, *J* = 7.0 Hz, 2 H), 2.64 (d, *J* = 7.5 Hz, 2 H), 2.43 (s, 3 H), 1.65 (s, 3 H), 1.60 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.7, 143.6, 137.1, 129.9, 127.2, 116.7, 58.5, 52.9, 45.9, 31.4, 26.1, 21.7, 18.1; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{18}H_{26}NO_6S]^+$ required 383.1475 *m/z*, found 383.1468 *m/z*.



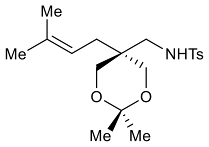
***N*-(2,2-bis(Hydroxymethyl)-5-methylhex-4-en-1-yl)-4-methylbenzenesulfonamide** (SI, **S19**). To a solution of **S18** (0.505 g, 1.32 mmol) in CH_2Cl_2 (6.5 mL) at -78 °C was added a solution of DIBAL–H (1.40 mL, 7.80 mmol) in toluene (4 mL) dropwise via syringe and the resulting solution was warmed to rt and stirred for 2 h. Sat. aq. Rochelle's salt (30 mL) was added and the resulting solution was stirred at rt for 30 min. 6 M aq. HCl was added until pH 2 and the mixture was extracted with CH_2Cl_2 (3x). The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give crude **S19** (0.449 g) as a clear, yellow oil. The crude residue was purified by chromatography on SiO_2 (60% EtOAc in hexanes) to give **S19** (0.264 g, 0.806 mmol, 61%) as a clear, colorless oil.

IR (ATR): ν 3484.7, 3282.6, 2922.9, 1598.3, 1323.1, 1156.8 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.78–7.68 (m, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 5.04–4.99 (m, 2 H), 3.64 (dd, *J* = 11.4, 5.0 Hz, 2 H), 3.59 (dd, *J* = 11.4, 6.3 Hz, 2 H), 3.02 (d, *J* = 6.9 Hz, 2 H), 2.60 (t, *J* = 6.0 Hz, 2 H), 2.44 (s, 3 H), 1.88 (d, *J* = 7.8 Hz, 2 H), 1.69 (s, 3 H), 1.59 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.8, 136.8, 135.6, 130.0, 127.1, 118.0, 66.6, 45.4, 43.8, 29.7, 26.2, 21.7, 18.0; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{16}H_{26}NO_4S]^+$ required 328.1577 *m/z*, found 328.1573 *m/z*.



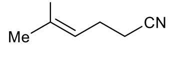
***N*-(2,2-bis(((*tert*-Butyldimethylsilyl)oxy)methyl)-5-methylhex-4-en-1-yl)-4-methylbenzenesulfonamide** (SI, **S20**). To a solution of **S19** (0.327 g, 1.00 mmol) and imidazole (0.205 g, 3.01 mmol) in CH_2Cl_2 (4.5 mL) at rt was added a solution of TBSCl (0.376 g, 2.49 mmol) in CH_2Cl_2 (1.5 mL) dropwise via syringe and the resulting solution was stirred at rt for 16 h. The mixture was diluted with CH_2Cl_2 (20 mL) and washed with aq. $NaHCO_3$ (20 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give crude **S20** (0.583 g) as a clear, colorless oil. The crude residue was purified by chromatography on SiO_2 (10% EtOAc in hexanes) to give **S20** (0.439 g, 0.790 mmol, 79%) as a clear, colorless oil.

IR (ATR): ν 3286.2, 2953.6, 2929.6, 2858.5, 1465.7 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.73–7.67 (m, 2 H), 7.31–7.26 (m, 2 H), 5.49 (t, *J* = 5.8 Hz, 1 H), 5.05–4.96 (m, 1 H), 3.40 (ABq, *J* = 9.9 Hz, 2 H), 3.38 (ABq, *J* = 9.9 Hz, 2 H), 2.85 (d, *J* = 5.9 Hz, 2 H), 2.42 (s, 3 H), 1.94 (d, *J* = 7.7 Hz, 2 H), 1.68 (d, *J* = 1.4 Hz, 3 H), 1.56 (s, 3 H), 0.86 (s, 18 H), 0.01 (s, 12 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.1, 136.9, 134.8, 129.7, 127.3, 118.8, 65.4, 48.0, 43.4, 29.2, 26.2, 26.0, 21.6, 18.2, 18.1, -5.5, -5.6; **HRMS** (ESI^+): $[M+H]^+$ calculated for $[C_{28}H_{54}NO_4SSi_2]^+$ required 556.3307 *m/z*, found 556.3306 *m/z*.

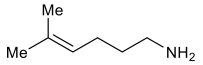


***N*-((2,2-Dimethyl-5-(3-methylbut-2-en-1-yl)-1,3-dioxan-5-yl)methyl)-4-methylbenzenesulfonamide** (SI, **S21**). A solution of **S19** (0.340 g, 1.04 mmol), 2-methoxypropene (0.300 mL, 3.12 mmol), and *p*-toluenesulfonic acid monohydrate (0.020 g, 0.11 mmol) in CH_2Cl_2 (2.10 mL) was stirred at rt for 1 h. The reaction mixture was diluted with H_2O (20 mL) and extracted with Et_2O (3 x 30 mL). The combined organic extracts were washed with brine (50 mL) and concentrated under reduced pressure to give crude **S21** (0.735 g) as a yellow oil. The crude residue was purified by chromatography on SiO_2 (30% EtOAc in hexanes) to give **S21** (0.254 g, 0.691 mmol, 66%) as a white, crystalline solid.

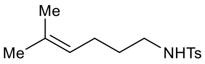
Mp 104–106 °C; **IR** (ATR): ν 3281.2, 2988.1, 2926.2, 2868.4, 1598.2, 1156.2 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.78–7.72 (m, 2 H), 7.34–7.29 (m, 2 H), 5.03–4.94 (m, 1 H), 4.67 (t, *J* = 6.8 Hz, 1 H), 3.62 (d, *J* = 12.3 Hz, 2 H), 3.51 (d, *J* = 12.3 Hz, 2 H), 3.00 (d, *J* = 6.8 Hz, 2 H), 2.43 (s, 3 H), 1.96 (d, *J* = 7.7 Hz, 2 H), 1.69 (d, *J* = 1.4 Hz, 3 H), 1.59 (s, 3 H), 1.38 (s, 3 H), 1.32 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.5, 136.8, 136.0, 129.8, 127.3, 117.3, 98.5, 65.8, 46.1, 36.9, 30.5, 26.4, 26.1, 21.7, 21.2, 18.0; **HRMS** (ESI^+): $[M+H]^+$ calculated for $[C_{19}H_{30}NO_4S]^+$ required 368.1890 *m/z*, found 368.1885 *m/z*.



5-Methylhex-4-enenitrile (SI, **S22**). To a solution of MeCN (0.370 mL, 7.04 mmol) in THF (18 mL) at -78 °C was added a solution of *n*-BuLi (2.90 mL, 7.25 mmol) in hexanes (2.5 M) and the resulting solution was stirred at -78 °C for 15 min. A solution of prenyl bromide (1.00 mL, 8.66 mmol) in THF (9 mL) was added dropwise via syringe and the resulting solution was warmed to rt and stirred for 2 h. The reaction mixture was quenched with sat. aq. NH_4Cl (50 mL) and extracted with Et_2O (3 x 50 mL). The combined organic extracts were washed with H_2O and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give crude **S22** (1.05 g) as a yellow oil which was used without further purification.

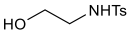


5-Methylhex-4-en-1-amine (SI, **S23**). To a suspension of $LiAlH_4$ (0.657 g, 17.3 mmol) in Et_2O (34 mL) at 0 °C was added a solution of crude **S22** (1.05 g) in Et_2O (9 mL) and the resulting solution was stirred at rt for 2 h. The reaction mixture was cooled to 0 °C and quenched by dropwise addition of 3 M aq. NaOH (10 mL). The resulting mixture was stirred for 15 min, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give crude **S23** (0.371 g) as a green oil which was used without further purification.

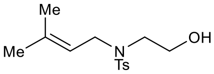


4-Methyl-*N*-(5-methylhex-4-en-1-yl)benzenesulfonamide (SI, **S24**). To a solution of crude **S23** (0.371 g) and Et_3N (0.685 g, 4.92 mmol) in CH_2Cl_2 (11 mL) at 0 °C was added TsCl (0.687 g, 3.60 mmol) in a single portion and the resulting solution was stirred at rt for 1 h. The reaction mixture was concentrated under reduced pressure, taken up in Et_2O, eluted through a thin pad of SiO_2, and concentrated under reduced pressure to give crude **S24** (0.917 g) as a yellow oil. The crude residue was purified by chromatography on SiO_2 (15% EtOAc in hexanes) to give **S24** (0.520 g, 1.94 mmol, 22% over 3 steps) as a clear, light yellow oil.

IR (ATR): ν 3281.3, 2925.5, 2867.1, 1598.2, 1321.6, 1153.0 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.77–7.72 (m, 2 H), 7.34–7.29 (m, 2 H), 4.99 (t, *J* = 6.7 Hz, 1 H), 4.45–4.27 (m, 1 H), 2.97–2.90 (m, 2 H), 2.43 (s, 3 H), 1.95 (q, *J* = 7.3 Hz, 2 H), 1.65 (s, 3 H), 1.54 (s, 3 H), 1.49 (p, *J* = 7.2 Hz, 2 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.5, 137.1, 133.0, 129.8, 127.2, 123.0, 43.1, 29.7, 25.8, 25.2, 21.7, 17.8; **HRMS** (ESI^+): $[M+H]^+$ calculated for $[C_{14}H_{22}NO_2S]^+$ required 268.1366 *m/z*, found 268.1364 *m/z*.

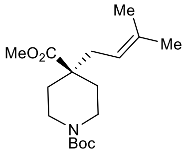


***N*-(2-Hydroxyethyl)-4-methylbenzenesulfonamide** (SI, **S25**). Synthesized according to the method of Aubineau and Cossy. All spectral data were in agreement with previously reported values.[5]

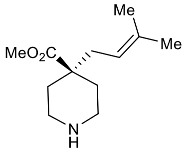


4-Methyl-*N*-(2-((3-methylbut-2-en-1-yl)oxy)ethyl)benzenesulfonamide (SI, **S26**). To a solution of **S25** (1.00 g, 4.64 mmol) in THF (9 mL) at rt was added NaH (0.186 g, 4.64 mmol, 60% dispersion in mineral oil) in a single portion and the resulting solution was stirred at rt for 1 h. Prenyl bromide (0.540 mL, 4.64 mmol) was added dropwise via syringe and the resulting solution was stirred at rt for 15 h. The reaction mixture was quenched with 6 M aq. NaOH (50 mL) and extracted with CH_2Cl_2 (3x). The combined organic extracts were washed with brine (2x), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give **S26** (0.712 g) as a yellow oil. The crude residue was purified by chromatography on SiO_2 (25-30% EtOAc in hexanes) to give **S26** (0.303 g, 1.07 mmol, 23%) as a clear, colorless oil.

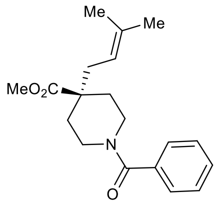
IR (ATR): ν 3520.1, 2924.9, 1598.1, 1376.3, 1154.5 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.75–7.67 (m, 2 H), 7.35–7.28 (m, 2 H), 5.03 (tp, *J* = 7.1, 1.5 Hz, 1 H), 3.84 (d, *J* = 7.1 Hz, 2 H), 3.72 (q, *J* = 5.0 Hz, 2 H), 3.20 (t, *J* = 5.3 Hz, 2 H), 2.44 (s, 3 H), 2.27 (t, *J* = 5.6 Hz, 1 H), 1.70–1.66 (m, 3 H), 1.63 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.6, 137.7, 136.5, 129.8, 127.5, 119.0, 61.4, 49.9, 47.2, 25.9, 21.7, 18.0; **HRMS** (ESI^+): $[M+H]^+$ calculated for $[C_{14}H_{22}NO_3S]^+$ required 284.1315 *m/z*, found 284.1307 *m/z*.



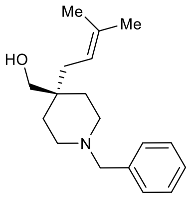
1-(*tert*-Butyl) 4-methyl 4-(3-methylbut-2-en-1-yl)piperidine-1,4-dicarboxylate (SI, **S27**). To a solution of *i*-Pr$_2$NH (3.50 mL, 24.7 mmol) in THF (40 mL) at -78 °C was added a solution of *n*-BuLi (9.90 mL, 24.8 mmol) in hexanes (2.5 M) dropwise via addition funnel and the resulting solution was stirred at -78 °C for 1 h. A solution of 1-*N*-Boc-4-piperidinecarboxylic acid methyl ester (5.02 g, 20.6 mmol) in THF (10 mL) was added dropwise via addition funnel and the resulting solution was stirred at -78 °C for 1 h. Prenyl bromide (2.85 mL, 24.7 mmol) was added dropwise and the resulting solution was stirred at rt for 1 h. The reaction mixture was quenched with sat. aq. NH$_4$Cl (100 mL) and extracted with Et$_2$O (3 x 100 mL). The combined organic extracts were washed with H$_2$O (2x) and brine (2x), dried over MgSO$_4$, filtered, and concentrated under reduced pressure to give crude **S27** (6.22 g) as a yellow oil which was used without further purification.



Methyl 4-(3-methylbut-2-en-1-yl)piperidine-4-carboxylate (SI, **S28**). A solution of crude **S27** (6.07 g, 19.5 mmol) and trifluoroacetic acid (7.50 mL, 97.5 mmol) in CH$_2$Cl$_2$ (20 mL) was stirred at rt for 1 h. The reaction mixture was diluted with H$_2$O (100 mL) and 1 M aq. NaOH was added to pH 12. The layers were separated and the aqueous phase was extracted with Et$_2$O (3 x 100 mL) and the combined organic extracts were dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure to give crude **S28** (4.60 g) as a yellow oil which was used without further purification.



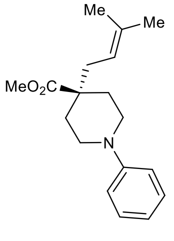
Methyl 1-benzoyl-4-(3-methylbut-2-en-1-yl)piperidine-4-carboxylate (SI, **S29**). To a solution of **S28** (0.401 g, 1.90 mmol) and Et$_3$N (0.400 mL, 2.84 mmol) in CH$_2$Cl$_2$ (9.60 mL) was added benzoyl chloride (0.240 mL, 2.08 mmol) dropwise via syringe and the resulting solution was stirred at rt for 20 h. The reaction mixture was diluted with CH$_2$Cl$_2$ (100 mL) and washed with 1 M aq. HCl (2x). The organic phase was dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure to give crude **S29** (0.625 g) as a yellow oil. The crude oil was purified by chromatography on SiO$_2$ (70% Et$_2$O in hexanes) to give **S29** (0.423 g, 1.34 mmol, 71%) as a clear, colorless oil.



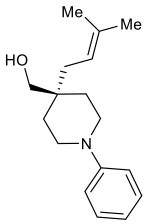
(1-Benzyl-4-(3-methylbut-2-en-1-yl)piperidin-4-yl)methanol (SI, **S30**). To a suspension of LiAlH$_4$ (0.254 g, 6.69 mmol) in Et$_2$O (3 mL) at 0 °C was added a solution of **S29** (0.522 g, 1.66 mmol) in Et$_2$O (2.50 mL) dropwise via syringe and the resulting solution was stirred at rt for 1 h. The reaction mixture was cooled to 0 °C, quenched with 1 M aq. NaOH (5 mL), and stirred for 15 min. The mixture was diluted with Et$_2$O (20 mL), dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure to give crude **S30** (0.422 g). Further drying *in vacuo* gave **S30** (0.380 g, 1.39 mmol, 84%) as a light yellow solid.

Mp 66–67 °C; **IR** (ATR): ν 3355.5, 2913.3, 2808.6, 2766.6, 1446.6, 1048.3 cm^{-1}; **^{1}H NMR** (500 MHz, CDCl$_3$): δ 7.35–7.28 (m, 4 H), 7.27–7.21 (m, 1 H), 5.20 (ddq, *J* = 7.7, 6.3, 1.4 Hz, 1 H), 3.51 (s, 2 H), 3.44 (s, 2 H), 2.41 (t, *J* = 5.7 Hz, 4 H), 2.07 (d, *J* = 7.7 Hz, 2 H), 1.72 (s, 3 H), 1.65 (s, 3 H), 1.50 (m, 4 H), 1.42 (br. s, 1 H); **^{13}C NMR** (125 MHz, CDCl$_3$): δ 138.6, 134.0, 129.3, 128.3, 127.1, 120.1, 68.3, 63.7, 49.5, 36.8, 33.9, 32.1, 26.3, 18.1; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for [C$_{18}$H$_{28}$NO]$^+$ required 274.2165 *m/z*, found 274.2160 *m/z*.

Methyl 4-(3-methylbut-2-en-1-yl)-1-phenylpiperidine-4-carboxylate (SI, **S31**). A solution of **S28** (0.501 g, 2.37 mmol), chlorobenzene (0.200 mL, 2.00 mmol), NaO*t*-Bu (0.231 g, 2.40 mmol), RuPhos (0.0047 g, 0.010 mmol), and RuPhos Pd G1 methyl *tert*-butyl ether adduct (0.0081 g, 0.010 mmol) in THF (4 mL) was stirred at 85 °C for 20 h. The reaction mixture was cooled to rt, diluted with CH_2Cl_2 (50 mL), washed with H_2O (2x), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give a brown oil (0.557 g). The oil was taken up in Et_2O, eluted through a thin pad of SiO_2, and concentrated under reduced pressure to give crude **S31** (0.367 g) as a yellow oil which was used without further purification.

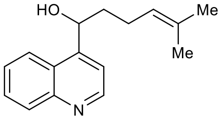


(4-(3-Methylbut-2-en-1-yl)-1-phenylpiperidin-4-yl)methanol (SI, **S32**). To a suspension of $LiAlH_4$ (0.135 g, 3.56 mmol) in Et_2O (6 mL) at 0 °C was added a solution of **S31** (0.516 g, 1.80 mmol) in Et_2O (3 mL) dropwise via syringe and the resulting solution was stirred at rt for 1 h. The reaction mixture was cooled to 0 °C, quenched by dropwise addition of 3 M aq. NaOH (5 mL), and stirred for 15 min. The mixture was diluted with Et_2O (20 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give crude **S32** (0.399 g) as a clear yellow oil. The crude oil was purified by chromatography on SiO_2 (20% EtOAc in hexanes) to give **S32** (0.314 g, 1.21 mmol, 61% over 2 steps) as a clear, colorless oil.

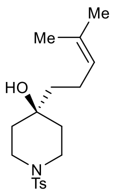


Mp 66–67 °C; **IR** (ATR): ν 3371.9, 2915.9, 2850.6, 1597.3, 1497.4 cm^{-1}; ^{1}**H NMR** (500 MHz, $CDCl_3$): δ 7.28–7.22 (m, 2 H), 6.97–6.91 (m, 2 H), 6.82 (td, *J* = 7.3, 1.1 Hz, 1 H), 5.24 (ddt, *J* = 7.7, 6.3, 1.5 Hz, 1 H), 3.51 (d, *J* = 5.9 Hz, 2 H), 3.26–3.10 (m, 4 H), 2.14 (d, *J* = 7.7 Hz, 2 H), 1.74 (s, 3 H), 1.71–1.58 (m, 4 H), 1.67 (s, 3 H), 1.38 (t, *J* = 6.0 Hz, 1 H); ^{13}**C NMR** (125 MHz, $CDCl_3$): δ 151.9, 134.4, 129.2, 119.8, 119.4, 116.3, 68.2, 45.5, 36.7, 33.4, 31.9, 26.3, 18.1; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{17}H_{26}NO]^+$ required 260.2009 *m/z*, found 260.2006 *m/z*.

5-Methyl-1-(quinolin-4-yl)hex-4-en-1-ol (SI, **S33**). To a solution of 4-quinolinecarboxyaldehyde (0.512 g, 3.26 mmol) in THF (8.3 mL) at 0 °C was added a solution of homoprenyl magnesium bromide (7.60 mL, 3.82 mmol) in THF (1.0 M) dropwise via syringe and the resulting solution was stirred at rt for 5 h. The reaction was quenched with sat. aq. NH_4Cl (50 mL) and extracted with Et_2O (3x). The combined organic extracts were washed with H_2O and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give crude **S33** (0.608 g) as a yellow oil. The crude residue was purified by chromatography on SiO_2 (50% EtOAc in hexanes) to give **S33** (0.170 g, 0.704 mmol, 22%) as a clear, pale yellow oil.

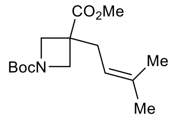


IR (ATR): ν 3204.7, 2963.7, 2917.8, 2855.7, 1586.3, 759.8 cm^{-1}; ^{1}**H NMR** (500 MHz, $CDCl_3$): δ 8.90 (d, *J* = 4.5 Hz, 1 H), 8.14 (d, *J* = 8.4 Hz, 1 H), 8.00 (d, *J* = 8.2 Hz, 1 H), 7.71 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1 H), 7.58 (d, *J* = 4.5 Hz, 1 H), 7.56 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1 H), 5.49 (dd, *J* = 8.6, 3.7 Hz, 1 H), 5.24–5.19 (m, 1 H), 2.34–2.17 (m, 2 H), 2.02–1.82 (m, 3 H), 1.73 (d, *J* = 0.7 Hz, 3 H), 1.64 (s, 3 H); ^{13}**C NMR** (125 MHz, $CDCl_3$): δ 150.5, 150.5, 148.4, 133.4, 130.5, 129.2, 126.6, 125.6, 123.4, 123.1, 117.4, 70.0, 38.5, 25.9, 24.8, 18.0; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{16}H_{20}NO]^+$ required 242.1539 *m/z,* found 242.1534 *m/z*.

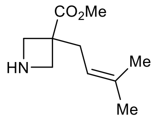


4-(4-Methylpent-3-en-1-yl)-1-tosylpiperidin-4-ol (SI, **S34**). To a roundbottom flask with a reflux condenser was added Mg^0 turnings (0.259 g, 10.7 mmol) and the flask was flame dried under vacuum and cooled to rt under N_2. THF (5 mL) was added followed by dibromoethane (0.090 mL, 0.49 mmol) and a solution of homoprenyl bromide (1.31 mL, 9.8 mmol) in THF (15 mL) dropwise via syringe. The mixture was stirred at reflux for 1 h. 1-*p*-Toluenesulfonyl-4-piperidone (1.24 g, 4.9 mmol) in THF (8 mL) was added dropwise via syringe and the resulting solution was stirred at rt for 30 min. The reaction mixture was quenched with sat. aq. NH_4Cl (50 mL) and extracted with Et_2O (3 x 50 mL). The combined organic extracts were washed with H_2O (2x) and brine (2x), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give crude **S34** (1.66 g) as a yellow oil. The crude residue was purified by chromatography on SiO_2 (30% EtOAc in hexanes) to give **S34** (0.197 g, 0.58 mmol, 12%) as a white, crystalline solid.

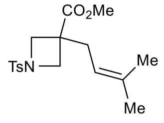
Mp 116–118 °C; **IR** (ATR): ν 3509.0, 2919.7, 2864.1, 1596.1, 1159.8 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.67–7.61 (m, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.10 (tt, *J* = 7.1, 1.5 Hz, 1 H), 3.55 (dt, *J* = 11.2, 2.5 Hz, 2 H), 2.63 (td, *J* = 11.9, 2.9 Hz, 2 H), 2.43 (s, 3 H), 2.05 (q, *J* = 7.6 Hz, 2 H), 1.76–1.63 (m, 5 H), 1.52–1.45 (m, 2 H), 1.10 (s, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.5, 133.4, 132.8, 129.8, 127.8, 124.0, 69.2, 42.8, 42.3, 36.4, 25.8, 21.8, 21.7, 17.9; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for $[C_{18}H_{28}NO_3S]^+$ required 338.1784 *m/z*, found 338.1779 *m/z*.



1-(*tert*-Butyl)-3-methyl-3-(3-methylbut-2-en-1-yl)azetidine-1,3-dicarboxylate (SI, **S35**). A solution of *i*-Pr_2NH (3.40 mL, 24.00 mmol) in THF (40 mL) at 0 °C was treated dropwise via syringe with a solution of *n*-BuLi (9.75 mL, 24.0 mmol) in hexanes (2.46 M) and the resulting solution was stirred at 0 °C for 30 min. Methyl 1-boc-azetidine-3-carboxylate (4.00 mL, 20.00 mmol) was added dropwise via syringe and the resulting solution was stirred at 0 °C for 30 min. Prenyl bromide (2.77 mL, 24.0 mmol) was added dropwise via syringe and the resulting solution was stirred at rt for 18 h. The reaction mixture was quenched with sat. aq. NH_4Cl (100 mL) and extracted with Et_2O (3 x 50 mL). The combined organic extracts were washed with H_2O (2x) and brine (2x), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give crude **S35** (5.32 g) as an orange oil. The crude residue was purified by chromatography on SiO_2 (20% Et_2O in hexanes) to give **S35** (1.50 g) as a yellow oil which was used without further purification.

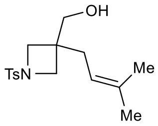


Methyl-3-(3-methylbut-2-en-1-yl)azetidine-3-carboxylate (SI, **S36**). A solution of **S35** (1.50 g) and trifluoroacetic acid (6.15 mL, 80.3 mmol) in CH_2Cl_2 (12 mL) was stirred at rt for 2 h. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and 6 M aq. NaOH was added to pH 11. The layers were separated and the organic phase was washed with 6 M aq. NaOH (2x) and H_2O (2x), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give crude **S36** (1.09 g) as a yellow oil which was used without further purification.



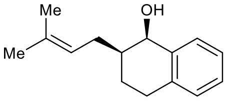
Methyl 3-(3-methylbut-2-en-1-yl)-1-tosylazetidine-3-carboxylate (SI, **S37**). To a solution of **S36** (1.09 g) and Et_3N (1.25 mL, 8.92 mmol) in CH_2Cl_2 (25 mL) at 0 °C was added TsCl (1.26 g, 6.61 mmol) in a single portion and the resulting solution was stirred at rt for 18 h. The reaction mixture was concentrated under reduced pressure, taken up in Et_2O, eluted through a thin pad of SiO_2, and concentrated under reduced pressure to give **S37** (0.965 g) as a yellow oil. The crude residue was purified by chromatography on SiO_2 (10-30% Et_2O in hexanes) to give **S37** (0.897 g) as a yellow oil which was used without further purification.

(3-(3-Methylbut-2-en-1-yl)-1-tosylazetidin-3-yl)methanol (SI, **S38**). To a suspension of $LiAlH_4$ (0.207 g, 5.45 mmol) in Et_2O (5 mL) at 0 °C was added a solution of **S37** (0.897 g) in Et_2O (4 mL) dropwise via syringe and the resulting solution was stirred at rt for 1.5 h. The mixture was cooled to 0 °C, quenched with 3 M aq. NaOH (5 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give crude **S38** (0.638 g) as a yellow oil. The crude oil was purified by chromatography on SiO_2 (30% EtOAc in hexanes) to give **S38** (0.577 g, 1.86 mmol, 9% over 4 steps) as a white solid.

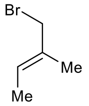


Mp 82–84 °C; **IR** (ATR): ν 3521.8, 2922.1, 2876.6, 1597.3, 1337.2, 1156.1 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.76–7.71 (m, 2 H), 7.41–7.34 (m, 2 H), 4.90–4.86 (m, 1 H), 3.56 (d, *J* = 8.0 Hz, 2 H), 3.51–3.45 (m, 4 H), 2.46 (s, 3 H), 2.12 (d, *J* = 7.5 Hz, 2 H), 1.62 (s, 3 H), 1.53 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.1, 135.7, 131.9, 129.8, 128.5, 118.0, 66.3, 66.3, 56.6, 38.5, 32.5, 26.0, 21.7, 18.1; **HRMS** (ESI^+): $[M+H]^+$ calculated for $[C_{16}H_{23}NO_3SNa]^+$ required 332.1291 *m/z*, found 332.1289 *m/z*.

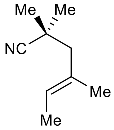
2-(3-Methylbut-2-en-1-yl)-1,2,3,4-tetrahydronaphthalen-1-ol (SI, **S39**). Synthesized according to the method of Park and coworkers.[6] All spectral data were in agreement with previously reported values.



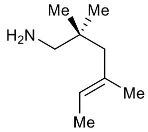
(*E*)-1-Bromo-2-methylbut-2-ene (SI, **S40**). Synthesized according to the method of Alexanian and coworkers.[7] All spectral data were in agreement with previously reported values.



(*E*)-2,2,4-Trimethylhex-4-enenitrile (SI, **S41**). A solution of *i*-Pr_2NH (0.495 mL, 3.51 mmol) in THF (5 mL) at 0 °C was added *n*-BuLi (1.40 mL, 3.51 mmol) in hexanes (2.51 M) dropwise via syringe and the resulting solution was stirred 0 °C for 10 min. Isobutyronitrile (0.315 mL, 3.51 mmol) was added dropwise via syringe and the resulting solution was stirred at 0 °C for 10 min. A solution of **S40** (0.523 g, 3.51 mmol) in THF (2 mL) was added dropwise via syringe and the resulting solution was stirred at rt for 2 h. The reaction mixture was quenched with sat. aq. NH_4Cl (20 mL) and extracted with Et_2O (3 x 20 mL). The combined organic extracts were washed with H_2O (2x) and brine (2x), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give crude **S41** (0.329 g) as an orange oil which was used without further purification.

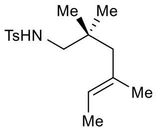


(*E*)-2,2,4-Trimethylhex-4-en-1-amine (SI, **S42**). To a suspension of $LiAlH_4$ (0.182 g, 4.80 mmol) in Et_2O (5 mL) at 0 °C was added a solution of crude **S41** (0.329 g) in Et_2O (3 mL) dropwise via syringe and the resulting solution was stirred at rt for 1 h. The reaction mixture was cooled to 0 °C and quenched by dropwise addition of 3 M aq. NaOH (5 mL). The reaction mixture was stirred at 0 °C for 10 min, diluted with Et_2O (50 mL),



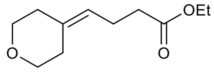
dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give crude **S42** (0.455 g) as a green-yellow oil.

(*E*)-4-Methyl-*N*-(2,2,4-trimethylhex-4-en-1-yl)benzenesulfonamide (SI, **S43**). To a solution of crude **S42** (0.455 g) and Et_3N (0.500 mL, 3.60 mmol) in CH_2Cl_2 (8 mL) at 0 °C was added TsCl (0.501 g, 2.63 mmol) in a single portion and the resulting solution was stirred at rt for 1 h. The reaction mixture was concentrated under reduced pressure, taken up in Et_2O, eluted through a thin pad of SiO_2, and concentrated under reduced pressure to give crude **S43** (0.676 g) as a yellow oil. The crude residue was purified by chromatography on SiO_2 (10% EtOAc in hexanes) to give **S43** (0.379 g, 1.28 mmol, 37% over 3 steps) as a yellow oil.

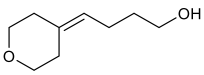


IR (ATR): ν 3284.9, 2963.4, 2918.7, 1324.2 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.3 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 5.12 (q, *J* = 6.6 Hz, 1 H), 4.57 (t, *J* = 6.7 Hz, 1 H), 2.67 (d, *J* = 6.8 Hz, 2 H), 2.43 (s, 3 H), 1.89 (s, 2 H), 1.59 (s, 3 H), 1.54 (d, *J* = 6.7 Hz, 3 H), 0.85 (s, 6 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.4, 137.1, 132.8, 129.8, 127.2, 123.5, 53.6, 49.5, 35.1, 25.7, 21.7, 18.7, 13.7; **HRMS** (ESI^+): $[M+H]^+$ calculated for $[C_{16}H_{26}NO_2S]^+$ required 296.1679 *m/z*, found 296.1689 *m/z*.

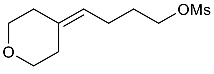
Ethyl-4-(tetrahydro-4*H*-pyran-4-ylidene)butanoate (SI, **S44**). Synthesized according to the method of Shenvi and coworkers.[8] All spectral data were in agreement with previously reported values.



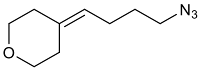
4-(Tetrahydro-4*H*-pyran-4-ylidene)butan-1-ol (SI, **S45**). To a suspension of $LiAlH_4$ (0.271 g, 7.14 mmol) in Et_2O (8 mL) at 0 °C was added a solution of **S44** (0.703 g, 3.55 mmol) in Et_2O (4 mL) dropwise via syringe and the resulting solution was stirred at rt for 1 h. The reaction mixture was cooled to 0 °C and quenched with 3 M aq. NaOH (7 mL). The mixture was stirred for 10 min, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give crude **S45** (0.830 g) as a clear, colorless oil which was used without further purification.



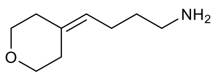
4-(Tetrahydro-4*H*-pyran-4-ylidene)butyl methanesulfonate (SI, **S46**). A solution of crude **S45** (0.830 g) and Et_3N (0.590 mL, 4.26 mmol) in CH_2Cl_2 (7.1 mL) at 0 °C was treated dropwise via syringe with MsCl (0.330 mL, 4.26 mmol) and the resulting solution was stirred at rt for 2 h. The reaction mixture was quenched by dropwise addition of sat. aq. $NaHCO_3$ (6 mL) and diluted with H_2O (50 mL). The mixture was extracted with CH_2Cl_2 (3x) and the combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give crude **S46** (0.738 g) as a clear, colorless oil which was used without further purification.



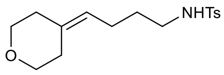
4-(4-Azidobutylidene)tetrahydro-2*H*-pyran (SI, **S47**). A solution of crude **S46** (0.738 g) and NaN_3 (0.625 g, 9.61 mmol) in DMF (11 mL) was stirred at 60 °C for 2 h. The reaction mixture was cooled to rt, diluted with H_2O (100 mL), and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were washed with H_2O (3x) and brine (1x), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a pale



yellow oil. The crude oil was eluted through a thin pad of SiO_2 with Et_2O and concentrated under reduced pressure to give crude **S47** (0.522 g) as a milky white oil which was used without further purification.

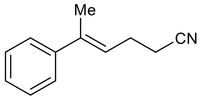


4-(Tetrahydro-4*H*-pyran-4-ylidene)butan-1-amine (SI, **S48**). To a suspension of $LiAlH_4$ (0.219 g, 5.76 mmol) in Et_2O (6.6 mL) at 0 °C was added a solution of crude **S47** (0.522 g) in Et_2O (3 mL) dropwise via syringe and the resulting solution was stirred at rt for 2 h. The reaction mixture was cooled to 0 °C, quenched by dropwise addition of 3 M aq. NaOH (6 mL), and stirred for 15 min. The mixture was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give crude **S48** (0.380 g) as a clear, colorless oil which was used without further purification.

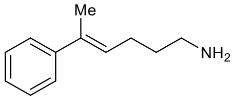


4-Methyl-*N*-(4-(tetrahydro-4*H*-pyran-4-ylidene)butyl)benzenesulfonamide (SI, **S49**). To a solution of crude **S48** (0.380 g) and Et_3N (0.510 g, 3.67 mmol) in CH_2Cl_2 (12 mL) was added TsCl (0.511 g, 2.68 mmol) in a single portion and the resulting solution was stirred at rt for 16 h. The reaction mixture was concentrated under reduced pressure, taken up in Et_2O, eluted through a thin pad of SiO_2, and concentrated under reduced pressure to give crude **S49** (0.735 g) as a clear, colorless oil. The crude residue was purified by chromatography on SiO_2 (20% EtOAc in hexanes) to give **S49** (0.577 g, 1.86 mmol, 53% over 5 steps) as a clear, colorless oil.

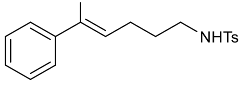
IR (ATR): ν 3276.1, 2954.5, 2848.6, 1598.2, 1158.4 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.78–7.71 (m, 2 H), 7.34–7.29 (m, 2 H), 5.12–5.03 (m, 1 H), 4.37 (t, *J* = 6.3 Hz, 1 H), 3.64 (t, *J* = 5.5 Hz, 2 H), 3.60 (t, *J* = 5.4 Hz, 2 H), 2.94 (q, *J* = 6.8 Hz, 2 H), 2.43 (s, 3 H), 2.21–2.18 (m, 2 H), 2.0 (q, *J* = 7.3 Hz, 2 H), 1.51 (p, *J* = 7.1 Hz, 2 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.6, 137.1, 135.8, 129.9, 127.2, 121.7, 69.7, 68.8, 43.0, 37.0, 30.0, 29.8, 24.1, 21.7; **HRMS** (ESI^+): $[M+H]^+$ calculated for $[C_{16}H_{23}NO_3SNa]^+$ required 332.1291 *m/z*, found 332.1286 *m/z*.



(*E*)-5-Phenylhex-4-enenitrile (SI, **S50**). Synthesized according to the method of Knowles and coworkers.[9] All spectral data were in agreement with previously reported values.



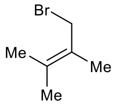
(*E*)-5-Phenylhex-4-en-1-amine (SI, **S51**). To a suspension of $LiAlH_4$ (0.662 g, 17.4 mmol) in Et_2O (35 mL) at 0 °C was added a solution of **S50** (1.489 g, 8.70 mmol) in Et_2O (9 mL) dropwise via syringe and the resulting solution was stirred at rt for 1 h. The reaction mixture was cooled to 0 °C, quenched by dropwise addition of 3 M aq. NaOH (10 mL), and stirred for 15 min. The resulting mixture was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give crude **S51** (1.45 g) as a yellow-green oil which was used without further purification.



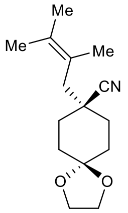
(*E*)-4-Methyl-*N*-(5-phenylhex-4-en-1-yl)benzenesulfonamide (SI, **S52**). To a solution of crude **S51** (1.45 g) and Et_3N (1.73 mL, 12.4 mmol) in CH_2Cl_2 (28 mL) at 0 °C was added TsCl (1.73 g, 9.07 mmol) in a single portion and the resulting solution was stirred at rt for 1 h. The reaction mixture was concentrated under reduced pressure, taken up in Et_2O, eluted through a thin pad of SiO_2 with Et_2O, and concentrated under reduced pressure to give crude **S52** (2.71 g) as a yellow oil. The crude oil was purified by chromatography on SiO_2 (10–30% EtOAc in hexanes) to give **S52** (2.09 g, 6.34 mmol, 73% over 2 steps) as a clear, colorless oil.

IR (ATR): ν 3279.8, 2930.3, 2865.9, 1597.5, 1154.1 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.2 Hz, 2 H), 7.53 (t, *J* = 5.8 Hz, 1 H), 7.38 (d, *J* = 8.4 Hz, 2 H), 7.35–7.26 (m, 4 H), 7.22–7.18 (m, 1 H), 5.67 (td, *J* = 7.3, 1.4 Hz, 1 H), 2.76 (q, *J* = 6.9 Hz, 2 H), 2.37 (s, 3 H), 2.12 (q, *J* = 7.4 Hz, 2 H), 1.92 (s, 3 H), 1.50 (p, *J* = 7.2 Hz, 2 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.4, 134.0, 138.1, 135.2, 130.1, 128.7, 127.4, 127.1, 127.0, 125.7, 42.6, 29.4, 25.8, 21.4, 15.9; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{19}H_{24}NO_2S]^+$ required 330.1522 *m/z*, found 330.1517 *m/z*.

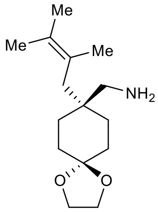
1-Bromo-2,3-dimethylbut-2-ene (SI, **S53**). Synthesized according to the method of Zhang and coworkers.[10] All spectral data were in agreement with previously reported values.



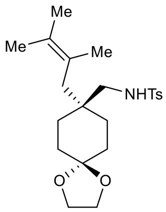
8-(2,3-Dimethylbut-2-en-1-yl)-1,4-dioxaspiro[4.5]decane-8-carbonitrile (SI, **S54**). A solution of *i*-Pr_2NH (1.00 mL, 7.36 mmol) in THF (10 mL) at 0 °C was treated dropwise via syringe with a solution of *n*-BuLi (3.00 mL, 7.36 mmol) in hexanes (2.46 M) and the resulting solution was stirred at 0 °C for 30 min. A solution of 1,4-dioxaspiro[4.5]decane-8-carbonitrile (1.24 g, 7.42 mmol) in THF (2 mL) was added dropwise via syringe and the resulting solution was stirred at 0 °C for 30 min. A solution of **S53** (1.00 g, 6.13 mmol) in THF (2 mL) was added dropwise via syringe and the solution was stirred at rt for 12 h. The reaction mixture was quenched with sat. aq. NH_4Cl (100 mL) and extracted with Et_2O (3 x 50 mL). The combined organic extracts were washed with H_2O (2x) and brine (2x), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give crude **S54** (1.45 g) as a yellow oil which was used without further purification.



(8-(2,3-Dimethylbut-2-en-1-yl)-1,4-dioxaspiro[4.5]decan-8-yl)methanamine (SI, **S55**). To a suspension of $LiAlH_4$ (0.439 g, 11.6 mmol) in Et_2O (13 mL) at 0 °C was added a solution of crude **S54** (1.45 g) in Et_2O (6.4 mL) dropwise via syringe and the resulting solution was stirred at rt for 1 h. The reaction mixture was cooled to 0 °C, quenched by dropwise addition of 3 M aq. NaOH (10 mL), and stirred at 0 °C for 15 min. The mixture was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give crude **S55** (1.42 g) as a clear, colorless oil which was used without further purification.

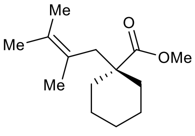


***N*-((8-(2,3-Dimethylbut-2-en-1-yl)-1,4-dioxaspiro[4.5]decan-8-yl)methyl)-4-methylbenzenesulfonamide** (SI, **S56**). To a solution of crude **S55** (1.42 g) and Et_3N (1.20 mL, 8.60 mmol) in CH_2Cl_2 (29 mL) at 0 °C was added TsCl (1.22 g, 6.40 mmol) in a single portion and the resulting solution was stirred at rt for 3 h. The reaction mixture was concentrated under reduced pressure, taken up in Et_2O, eluted through a thin pad of SiO_2 with Et_2O, and concentrated under reduced pressure to give crude **S56** (2.39 g) as a white, foaming solid. The crude foam was purified by chromatography on SiO_2 (10–20% EtOAc in hexanes) to give **S56** (1.00 g, 2.45 mmol, 40% over 3 steps) as a white powder.

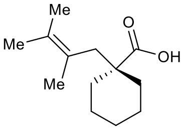


Mp 117–120 °C; **IR** (ATR): ν 3280.5, 2932.4, 2870.3, 1598.8, 1327.1, 1160.2 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.70 (d, J = 8.2 Hz, 2 H), 7.31 (d, J = 8.0 Hz, 2 H), 4.55 (t, J = 6.8 Hz, 1 H), 3.91 (s, 4 H), 2.84 (d, J = 6.8 Hz, 2 H), 2.43 (s, 3 H), 2.07 (s, 2 H), 1.66 (s, 3 H), 1.64 (s, 3 H), 1.61–1.51 (m, 11 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.4, 137.0, 129.8, 129.1, 127.2, 126.0, 108.6, 64.3, 64.3, 48.9, 43.2, 38.0, 31.8, 30.6, 21.7, 21.5, 21.5, 21.1; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{22}H_{34}NO_4S]^+$ required 408.2203 *m/z*, found 408.2201 *m/z*.

Methyl 1-(2,3-dimethylbut-2-en-1-yl)cyclohexane-1-carboxylate (SI, **S57**) To a solution of *i*-Pr_2NH (1.20 mL, 8.54 mmol) in THF (11 mL) at 0 ºC was treated dropwise via syringe with *n*-BuLi (3.40 mL, 8.54 mmol) in hexanes (2.5 M) and the resulting solution was stirred at 0 °C for 15 min. Methyl cyclohexanecarboxylate (1.00 mL, 7.11 mmol) was added dropwise and the resulting solution was stirred for 15 min. **S53** (1.39 g, 8.54 mmol) in THF (2 mL) was added and the resulting solution was stirred at rt for 16 h. The reaction mixture was quenched with sat. aq. NH_4Cl (50 mL) and extracted with Et_2O (3 x 50 mL). The combined organic extracts were washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give crude **S57** as an yellow oil. The crude oil was purified by chromatography on SiO_2 (10% EtOAc in hexanes) to give **S57** (1.68 g) as a yellow oil, which was used without further purification.

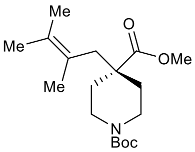


1-(2,3-Dimethylbut-2-en-1-yl)cyclohexane-1-carboxylic acid (SI, **S58**) To a solution of crude **S57** (1.68 g) and LiOH (2.28 g, 95.0 mmol) in EtOH (19 mL) and H_2O (19 mL) was stirred at reflux for 44 h. The reaction mixture was cooled to rt, diluted with H_2O and extracted with Et_2O (3x). The combined organic extracts were dried with Na_2SO_4, filtered through a thin pad of SiO_2, and concentrated under reduced pressure to give recovered **S57** (0.710 g) as a yellow oil. The aqueous washes were acidified to pH 2 with 6 M aq. HCl (75 mL) and extracted with $E_{t2}O$ (3x). The organic extracts were washed with H_2O (2x) and brine (1x), dried with Na2SO4, filtered through a thin pad of SiO_2, and concentrated under reduced pressure to give crude **S58** (0.649 g, 3.09 mmol, 43% over two steps) as a yellow solid.



Mp 55–57 °C; **IR** (ATR): ν 2924.8, 2857.3, 1685.4, 1451.3, 1246.8 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.83z (br s, 1 H), 2.37 (s, 2 H), 2.13 (d, J = 13.0 Hz, 2 H), 1.66 (s, 3 H), 1.65–1.57 (m, 9 H), 1.43–1.28 (m, 2 H), 1.28–1.12 (m, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 182.7, 128.9, 123.9, 48.7, 46.4, 34.8, 25.9, 23.8, 21.5, 21.1, 20.7; **HRMS** (ESI$^+$): $[M–H]^–$ calculated for $[C_{13}H_{21}O_2]^–$ required 209.1547 *m/z*, found 209.1548 *m/z*.

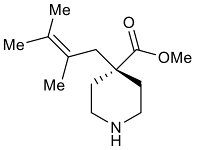
1-(*tert*-Butyl)-4-methyl-4-(2,3-dimethylbut-2-en-1-yl)piperidine-1,4-dicarboxylate (SI, **S59**) A solution of *i*-Pr_2NH (0.17 mL, 1.2 mmol) in THF (2.5 mL) at 0 °C was treated dropwise via syringe with *n*-BuLi (0.48 mL, 1.2 mmol) in hexanes (2.5 M) over 10 minutes and the resulting solution was stirred at 0 °C for 15 min. 1-(*tert*-butyl) 4-methyl piperidine-1,4-dicarboxylate (0.247 g, 1.0 mmol) was added dropwise and the resulting solution was stirred at 0 °C for 30 min. **S53** (0.13 mL, 1.2 mmol) was added dropwise and the resulting solution was allowed to warm to rt and stirred for 1 h. The reaction mixture was quenched with sat. aq. NH_4Cl (30 mL) and extracted with Et_2O (3 x 30 mL). The



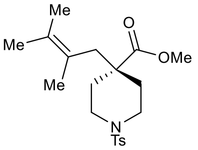
combined organic extracts were washed with H_2O (2x) and brine (2x), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give crude **S59** as an yellow oil. The crude oil was purified by chromatography on SiO_2 (10% EtOAc in hexanes) to give **S59** (0.18 g, 0.55 mmol, 55%) as a clear, colorless oil.

IR (ATR): ν 2971.0, 2922.4, 2865.3, 1691.2, 1418.8, 1166.3, 1143.4 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.95 (br s, 2 H), 3.68 (s, 3 H), 2.72 (br s, 2 H), 2.34 (s, 2 H), 2.12 (d, *J* = 13.3 Hz, 2 H), 1.63 (s, 2 H), 1.63 (s, 6 H), 1.57 (s, 3 H), 1.45 (s, 9 H), 1.42–1.33 (m, 2 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 176.3, 155.1, 129.3, 123.2, 79.5, 51.8, 47.4, 45.7, 34.0, 28.6, 21.4, 21.0, 20.5; **HRMS** (ESI^+): $[M+Na]^+$ calculated for $[C_{18}H_{31}NO_4Na]^+$ required 348.2145 *m/z*, found 348.2141 *m/z*.

Methyl-4-(2,3-dimethylbut-2-en-1-yl)piperidine-4-carboxylate (SI, **S60**). A solution of **S59** (2.50 g, 7.68 mmol) and trifluoroacetic acid (2.95 mL, 38.5 mmol) in CH_2Cl_2 (8 mL) was stirred at rt for 2 h. The reaction mixture was diluted with CH_2Cl_2 (15 mL) and 1 M aq. NaOH was added to pH 12. The layers were separated and the aqueous phase was extracted with Et_2O (3 x 30 mL) and the combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give crude **S60** (1.93 g) as a yellow oil which was used without further purification.

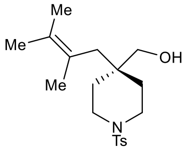


Methyl-4-(2,3-dimethylbut-2-en-1-yl)-1-tosylpiperidine-4-carboxylate (SI, **S61**). To a solution of **S60** (1.13 g, 5.00 mmol) and Et_3N (1.05 mL, 7.50 mmol) in CH_2Cl_2 (21 mL) at 0 °C was added TsCl (1.05 g, 5.50 mmol) in a single portion and the resulting solution was stirred at rt for 23 h. The reaction mixture was concentrated under reduced pressure, taken up in Et_2O, eluted through a thin pad of SiO_2, and concentrated under reduced pressure to give **S61** as a yellow oil. The crude residue was purified by chromatography on SiO_2 (15% EtOAc in hexanes) to give **S61** (1.07 g, 2.82 mmol, 37% over two steps) as a white solid.



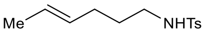
Mp 112–114 °C; **IR** (ATR): ν 2921.6, 2853.1, 1721.3, 1331.2, 1158.6 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.2 Hz, 2 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 3.69–3.63 (m, 2 H), 3.56 (s, 3 H), 2.42 (2, 3 H), 2.31 (s, 2 H), 2.29–2.22 (m, 2 H), 2.21–2.15 (m, 2 H), 1.64–1.55 (m, 8 H), 1.53 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 175.8, 143.5, 133.7, 129.8, 129.7, 127.7, 122.8, 51.9, 46.8, 45.4, 44.2, 33.4, 21.7, 21.4, 21.0, 20.5; **HRMS** (ESI^+): $[M+Na]^+$ calculated for $[C_{20}H_{29}NO_4SNa]^+$ required 402.1710 *m/z*, found 402.1706 *m/z*.

(4-(2,3-Dimethylbut-2-en-1-yl)-1-tosylpiperidin-4-yl)methanol (SI, **S62**). To a suspension of $LiAlH_4$ (0.102 g, 2.70 mmol) in Et_2O (4.5 mL) at 0 °C was added a solution of **S61** (0.342 g) in Et_2O (9.5 mL) dropwise via syringe and the resulting solution was stirred at rt for 1.5 h. The mixture was cooled to 0 °C, quenched with 3 M aq. NaOH (5 mL), and stirred for 15 min. The reaction mixture was diluted with $E_{t2}O$ (20 mL), dried over Na_2SO_4, filtered through a pad of celite, and concentrated under reduced pressure to give crude **S62** (0.247 g) as a clear oil. The crude oil was purified by chromatography on SiO_2 (40% EtOAc in hexanes) to give **S62** (0.184 g, 0.52 mmol, 58%) as a white solid.



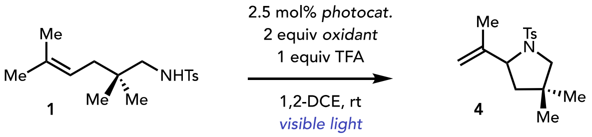
Mp 129–130 °C; **IR** (ATR): ν 3497.0, 2908.1, 2854.3, 1318.0, 1157.8 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.3 Hz, 2 H), 7.32 (d, *J* = 7.9 Hz, 2 H), 3.38 (d, *J* = 5.9 Hz, 2 H), 3.34–3.27 (m, 2 H), 2.75–2.65 (m, 2 H), 2.44 (s, 3 H), 2.08 (s, 2 H), 1.70–1.66 (m, 6 H), 1.64 (s, 3 H), 1.64–1.60 (m, 4 H), 1.49 (t, *J* = 6.0 Hz, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.6, 133.3, 129.8, 129.3, 127.9, 125.4, 66.4, 42.6, 42.3, 38.0, 32.0, 21.8, 21.7, 21.5, 21.1; **HRMS** (ESI^{+}): $[M+Na]^{+}$ calculated for $[C_{19}H_{29}NO_3SNa]^{+}$ required 374.1760 *m/z*, found 374.1759 *m/z*.

(*E*)-*N*-(Hex-4-en-1-yl)-4-methylbenzenesulfonamide (SI, **S63**). Synthesized according to the method of Marcotullio and coworkers.[11] All spectral data were in agreement with previously reported values.

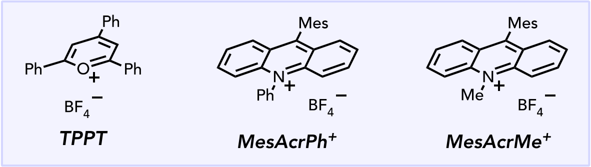


III. Optimization Studies for Oxidative Amination

Table S1. Optimization of Photocatalytic Oxidative Amination



entry[a]	photocat.	oxidant	% yield[b]
1	MesAcrPh^{+}	$CuBr_2$	0%
2	MesAcrPh^{+}	$Cu(OTf)_2$	3%
3	MesAcrPh^{+}	$Cu(OAc)_2$	48%
4	MesAcrPh^{+}	$Cu(TFA)_2$	57%
5	MesAcrPh^{+}	$Cu(OPiv)_2$	57%
6	**MesAcrPh^{+}**	**$Cu(EH)_2$**	**87%**
7	MesAcrMe^{+}	$Cu(EH)_2$	52%
8	TPPT	$Cu(EH)_2$	24%
9[c]	MesAcrPh^{+}	$Cu(EH)_2$	28%
10	none	$Cu(EH)_2$	0%
11	MesAcrPh^{+}	none	0%
12[d]	MesAcrPh^{+}	$Cu(EH)_2$	0%

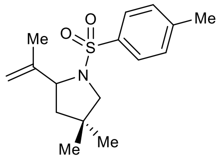


General Procedure for Optimization Studies: A solution of **1** (0.10 mmol), copper(II) salt (0.20 mmol), trifluoroacetic acid (0.007 mL, 0.1 mmol), and photocatalyst (0.0025 mmol, 2.5 mol%) in 1,2-DCE (4 mL) was degassed (freeze-pump-thaw, 3 cycles of 5 min each) and the resulting solution was stirred at rt under irradiation by two 450 nm blue LED flood lamps for 16 h. The reaction mixture was diluted with Et_2O, eluted through a thin pad of SiO_2, and concentrated under reduced pressure to give the crude reaction mixtures. Yields of **4** were determined by ^{1}H NMR analysis of the unpurified reaction mixtures using phenanthrene as an internal standard.

IV. Oxidative Heterofunctionalization Reactions

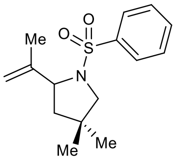
General Procedure for Oxidative Amination and Oxygenation: A solution of alkene (1 equiv), Cu(EH)$_2$ (2 equiv), trifluoroacetic acid or *p*-toluenesulfonic acid monohydrate (1-2 equiv), and MesAcrPh$^+$ (0.025 equiv, 2.5 mol%) in 1,2-DCE (0.025 M) was degassed (freeze-pump-thaw, 3 cycles of 5 min each) and the resulting solution was stirred for the indicated time at rt under irradiation by two 15 W blue LED flood lamps. The reaction mixtures were diluted with CH$_2$Cl$_2$, washed with 1 M aq. NaOH (3x), eluted through a thin pad of SiO$_2$ with Et$_2$O, and concentrated under reduced pressure. The residue was purified by chromatography on SiO$_2$ to afford pure product.

4,4-Dimethyl-2-(prop-1-en-2-yl)-1-tosylpyrrolidine (Table 2, **4**). Synthesized according to the general procedure using **1** (0.088 g, 0.30 mmol), Cu(EH)$_2$ (0.210 g, 0.600 mmol), TFA (0.023 mL, 0.30 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 18 h. After chromatography on SiO$_2$ (10% EtOAc in hexanes), **4** was isolated as a white solid (0.066 g, 0.22 mmol, 76%).



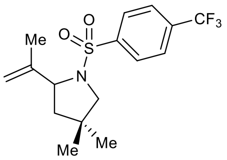
Mp 78–81 °C; **IR** (ATR): ν 2955.7, 2925.8, 1597.7, 1371.2, 1155.2 cm^{-1}; ^{1}**H NMR** (500 MHz, CDCl$_3$): δ 7.73–7.68 (m, 2 H), 7.33–7.27 (m, 2 H), 5.01–4.89 (m, 1 H), 4.83 (t, *J* = 1.5 Hz, 1 H), 4.11–3.98 (m, 1 H), 3.26 (dd, *J* = 10.6, 1.1 Hz, 1 H), 3.19 (d, *J* = 10.6 Hz, 1 H), 2.43 (s, 3 H), 1.72 (dd, *J* = 1.5, 0.8 Hz, 3 H), 1.68–1.61 (m, 2 H), 1.03 (s, 3 H), 0.58 (s, 3 H); ^{13}**C NMR** (125 MHz, CDCl$_3$): δ 145.4, 143.3, 135.4, 129.5, 127.6, 112.1, 65.7, 62.1, 46.4, 37.5, 26.4, 26.0, 21.7, 17.1; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for [C$_{16}$H$_{24}$NO$_2$S]$^+$ required 294.1522 *m/z*, found 294.1520 *m/z*.

4,4-Dimethyl-1-(phenylsulfonyl)-2-(prop-1-en-2-yl)pyrrolidine (Table 2, **5**). Synthesized according to the general procedure using **S3** (0.083 g, 0.30 mmol), Cu(EH)$_2$ (0.210 g, 0.600 mmol), TFA (0.023 mL, 0.30 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 24 h. After chromatography on SiO$_2$ (10% EtOAc in hexanes), **5** was isolated as a white solid (0.066 g, 0.24 mmol, 80%).



Mp 56–59 °C; **IR** (ATR): ν 2961.8, 2876.9, 1650.8, 1371.2, 1157.9 cm^{-1}; ^{1}**H NMR** (400 MHz, CDCl$_3$): δ 7.86–7.80 (m, 2 H), 7.61–7.47 (m, 3 H), 4.96 (dt, *J* = 1.8, 0.9 Hz, 1 H), 4.83 (t, *J* = 1.6 Hz, 1 H), 4.13–4.05 (m, 1 H), 3.29 (dd, *J* = 10.6, 1.1 Hz, 1 H), 3.20 (d, *J* = 10.7 Hz), 1.71 (d, *J* = 0.7 Hz, 3 H), 1.69–1.59 (m, 2 H), 1.03 (s, 3 H), 0.56 (s, 3 H); ^{13}**C NMR** (100 MHz, CDCl$_3$): δ 145.2, 138.4, 132.6, 128.9, 127.6, 112.2, 65.7, 62.0, 46.4, 37.6, 26.3, 25.9, 17.1; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for [C$_{15}$H$_{22}$NO$_2$S]$^+$ required 280.1366 *m/z*, found 280.1364 *m/z*.

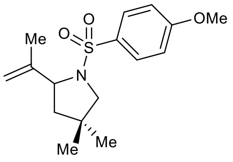
4,4-Dimethyl-2-(prop-1-en-2-yl)-1-((4-(trifluoromethyl)phenyl)sulfonyl)pyrrolidine (Table 2, **6**). Synthesized according to the general procedure using **S4** (0.104 g, 0.298 mmol), Cu(EH)$_2$ (0.211 g, 0.603 mmol), TFA (0.023 mL, 0.30 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 96 h. After chromatography on SiO$_2$ (10% EtOAc in hexanes), **6** was isolated as a yellow powder (0.067 g, 0.19 mmol, 65%).



Mp 78–81 °C; **IR** (ATR): ν 2966.6, 2862.2, 1453.3, 1319.2 cm^{-1}; ^{1}**H NMR** (500 MHz, CDCl$_3$): δ 7.95 (d, *J* = 8.1 Hz, 2 H), 7.78 (d, *J* = 8.2 Hz, 2 H), 4.96–4.94 (m, 1 H), 4.83 (app. p, *J* = 1.5 Hz, 1

H), 4.16 (dd, *J* = 9.6, 7.4 Hz, 1 H), 3.35 (dd, *J* = 10.6, 1.5 Hz, 1 H), 3.19 (d, *J* = 10.6 Hz, 1 H), 1.73 (ddd, *J* = 12.8, 7.4, 1.5 Hz, 1 H), 1.67–1.62 (m, 1 H), 1.64 (dd, *J* = 1.4, 0.8 Hz, 3 H), 1.06 (s, 3 H), 0.67 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.6, 142.4 (q, *J* = 1.5 Hz), 134.2 (q, *J* = 33.0 Hz), 127.9, 126.1 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 272.8 Hz), 112.9, 65.9, 62.0, 46.2, 37.8, 26.0, 25.9, 17.0; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{16}H_{21}F_3NO_2S]^+$ required 348.1240 *m/z*, found 348.1233 *m/z*.

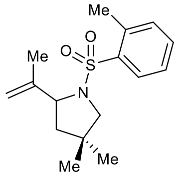
1-((4-Methoxyphenyl)sulfonyl)-4,4-dimethyl-2-(prop-1-en-2-yl)pyrrolidine (Table 2, **7**).



Synthesized according to the general procedure using **S5** (0.093 g, 0.30 mmol), $Cu(EH)_2$ (0.212 g, 0.606 mmol), TFA (0.023 mL, 0.30 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 8 h. After chromatography on SiO_2 (15% EtOAc in hexanes), **7** was isolated as a clear, colorless oil (0.067 g, 0.22 mmol, 72%).

IR (ATR): ν 2960.1, 1651.8, 1336.0, 1151.4 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81–7.68 (m, 2 H), 7.00–6.95 (m, 2 H), 4.98–4.92 (m, 1 H), 4.82 (app. p, *J* = 1.5 Hz, 1 H), 4.09–4.00 (m, 1 H), 3.87 (s, 3 H), 3.25 (dd, *J* = 10.6, 1.0 Hz, 1 H), 3.19 (d, *J* = 10.7 Hz, 1 H), 1.73 (dd, *J* = 1.5, 0.8 Hz, 3 H), 1.68–1.61 (m, 2 H), 1.04 (s, 3 H), 0.60 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.9, 145.5, 130.2, 129.7, 114.0, 112.0, 65.7, 62.1, 55.7, 46.4, 37.5, 26.4, 26.1, 17.1; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{16}H_{24}NO_3S]^+$ required 310.1471 *m/z*, found 310.1468 *m/z*.

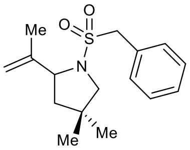
4,4-Dimethyl-2-(prop-1-en-2-yl)-1-(*o*-tolylsulfonyl)pyrrolidine (Table 2, **8**).



Synthesized according to the general procedure using **S6** (0.088 g, 0.30 mmol), $Cu(EH)_2$ (0.210 g, 0.600 mmol), TFA (0.023 mL, 0.30 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 24 h. After chromatography on SiO_2 (10% Et_2O in hexanes), **8** was isolated as a white solid (0.053 g, 0.18 mmol, 61%).

Mp 48–50 °C; **IR** (ATR): ν 3070.6, 2959.2, 2870.9, 1650.4, 1332.0, 1155.8 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 7.8, 1.4 Hz, 1 H), 7.39 (td, *J* = 7.5, 1.4 Hz, 1 H), 7.26–7.21 (m, 2 H), 4.81 (s, 1 H), 4.58 (p, *J* = 1.5 Hz, 1 H), 4.41 (dd, *J* = 9.8, 7.4 Hz, 1 H), 3.69 (dd, *J* = 10.5, 1.8 Hz, 1 H), 3.14 (d, *J* = 10.4 Hz, 1 H), 2.65 (s, 3 H), 1.80 (ddd, *J* = 12.6, 7.4, 1.7 Hz, 1 H), 1.64 (dd, *J* = 12.6, 9.8 Hz, 1 H), 1.38 (s, 3 H), 1.09 (s, 3 H), 1.00 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.0, 138.7, 137.5, 132.4, 132.3, 130.3, 125.8, 113.2, 65.5, 62.2, 46.6, 37.8, 25.9, 25.8, 20.9, 16.6; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{16}H_{24}NO_3S]^+$ required 294.1522 *m/z*, found 294.1519 *m/z*.

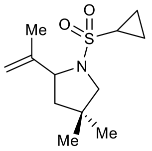
1-(Benzylsulfonyl)-4,4-dimethyl-2-(prop-1-en-2-yl)pyrrolidine (Table 2, **10**).



Synthesized according to the general procedure using **S8** (0.089 g, 0.30 mmol), $Cu(EH)_2$ (0.210 g, 0.600 mmol), TFA (0.023 mL, 0.30 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 42 h. After chromatography on SiO_2 (10% EtOAc in hexanes), **10** was isolated as a yellow oil (0.078 g, 0.27 mmol, 88%).

IR (ATR): ν 3069.2, 3034.3, 2958.7, 2871.6, 1650.4, 1329.7 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.44–7.32 (m, 5 H), 5.05 (d, *J* = 0.9 Hz, 1 H), 4.90–4.87 (m, 1 H), 4.50 (dd, *J* = 9.4, 7.6 Hz, 1 H), 4.25 (d, *J* = 13.6 Hz, 1 H), 4.14 (d, *J* = 13.7 Hz, 1 H), 3.31 (dd, *J* = 10.5, 1.6 Hz, 1 H), 2.78 (d, *J* = 10.5 Hz, 1 H), 1.83 (ddd, *J* = 12.6, 7.5, 1.7 Hz, 1 H), 1.72 (s, 3 H), 1.58 (dd, *J* = 12.6, 9.4 Hz, 1 H), 1.05 (s, 3 H), 1.03 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.9, 130.9, 129.4, 128.7, 128.6, 112.9, 61.9, 59.5, 46.0, 38.5, 25.8, 25.7, 17.8; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{16}H_{24}NO_2S]^+$ required 294.1522 *m/z*, found 294.1521 *m/z*.

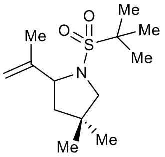
1-(Cyclopropylsulfonyl)-4,4-dimethyl-2-(prop-1-en-2-yl)pyrrolidine (Table 2, **11**).



Synthesized according to the general procedure using **S9** (0.073 g, 0.30 mmol), $Cu(EH)_2$ (0.212 g, 0.606 mmol), TFA (0.023 mL, 0.30 mmol), and $MesAcrMe^+$ (0.0036 g, 0.0075 mmol) and irradiating for 24 h. After chromatography on SiO_2 (10–30% Et_2O in hexanes), **11** was isolated as a yellow oil (0.065 g, 0.27 mmol, 90%).

IR (ATR): ν 2958.8, 2871.8, 1650.6, 1332.6, 1141.6 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.92 (s, 1 H), 4.74 (app. t, *J* = 1.8 Hz, 1 H), 4.36 (dd, *J* = 9.4, 7.4 Hz, 1 H), 3.35 (dd, *J* = 10.4, 1.5 Hz, 1 H), 3.05 (d, *J* = 10.4 Hz, 1 H), 2.62 (ddd, *J* = 12.2, 7.4, 5.3 Hz, 1 H), 1.83 (ddd, *J* = 12.6, 7.4, 1.5 Hz, 1 H), 1.70 (s, 3 H), 1.60 (dd, *J* = 12.5, 9.5 Hz, 1 H), 1.07 (s, 3 H), 1.06 (s, 3 H), 0.99–0.88 (m, 4 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 145.6, 111.1, 64.4, 61.2, 45.6, 37.5, 27.4, 25.7, 25.5, 17.0, 4.5, 4.2; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{12}H_{22}NO_2S]^+$ required 244.1366 *m/z*, found 244.1365 *m/z*.

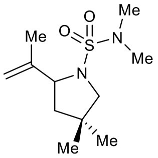
1-(*tert*-Butylsulfonyl)-4,4-dimethyl-2-(prop-1-en-2-yl)pyrrolidine (Table 2, **12**). Synthesized



according to the general procedure using **S11** (0.078 g, 0.30 mmol), $Cu(EH)_2$ (0.210 g, 0.600 mmol), TFA (0.023 mL, 0.30 mmol), and $MesAcrMe^+$ (0.0036 g, 0.0075 mmol) and irradiating for 48 h. After chromatography on SiO_2 (0–10% Et_2O in hexanes), **12** was isolated as a yellow oil (0.052 g, 0.20 mmol, 67%).

IR (ATR): ν 2958.3, 2868.4, 1649.1, 1458.4, 1308.0, 1120.3 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.00 (app. s, 1 H), 4.83 (t, *J* = 1.6 Hz, 1 H), 4.74 (dd, *J* = 9.3, 7.9 Hz, 1 H), 3.58 (dd, *J* = 10.8, 1.9 Hz, 1 H), 2.91 (d, *J* = 10.8 Hz, 1 H), 1.82 (ddd, *J* = 12.7, 7.9, 1.9 Hz, 1 H), 1.73 (s, 3 H), 1.61 (dd, *J* = 12.6, 9.3 Hz, 1 H), 1.32 (s, 9 H), 1.09 (app. s, 6 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.6, 114.4, 65.9, 63.7, 60.3, 45.2, 39.3, 25.7, 25.4, 24.4, 17.2; **HRMS** (ESI$^+$): $[M+Na]^+$ calculated for $[C_{13}H_{25}NO_2SNa]^+$ required 282.1497 *m/z*, found 282.1498 *m/z*.

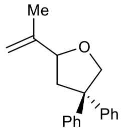
***N*,*N*,4,4-Tetramethyl-2-(prop-1-en-2-yl)pyrrolidine-1-sulfonamide** (Table 2, **13**). Synthesized



according to the general procedure using **S12** (0.074 g, 0.30 mmol), $Cu(EH)_2$ (0.212 g, 0.606 mmol), TFA (0.023 mL, 0.30 mmol), and $MesAcrMe^+$ (0.0036 g, 0.0075 mmol) and irradiating for 14 h. After chromatography on SiO_2 (15–20% EtOAc in hexanes), **13** was isolated as a clear yellow oil (0.045 g, 0.18 mmol, 62%).

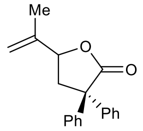
IR (ATR): ν 2957.2, 2871.5, 1650.6, 1333.9, 1142.1 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.99 (br. s, 1 H), 4.83 (p, *J* = 1.5 Hz, 1 H), 4.36 (dd, *J* = 9.4, 7.6 Hz, 1 H), 3.41 (dd, *J* = 10.5, 1.6 Hz, 1 H), 3.03 (d, *J* = 10.5 Hz, 1 H), 2.77 (s, 6 H), 1.84 (ddd, *J* = 12.6, 7.5, 1.6 Hz, 1 H), 1.75 (s, 3 H), 1.63 (dd, *J* = 12.6, 9.5 Hz, 1 H), 1.13 (s, 3 H), 1.09 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 145.3, 112.3, 66.0, 62.9, 46.2, 38.4, 38.0, 26.3, 26.2, 17.5; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{11}H_{23}N_2O_2S]^+$ required 247.1475 *m/z*, found 247.1471 *m/z*.

4,4-Diphenyl-2-(prop-1-en-2-yl)tetrahydrofuran (Table 2, **14**). Synthesized according to the general procedure using **S13** (0.079 g, 0.30 mmol), Cu(EH)$_2$ (0.210 g, 0.600 mmol), TFA (0.023 mL, 0.30 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 16 h. After chromatography on SiO$_2$ (2% EtOAc in hexanes), **14** was isolated as a yellow oil (0.063 g, 0.24 mmol, 80%).



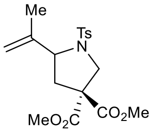
IR (ATR): ν 3058.1, 3026.7, 2970.9, 2862.1, 1652.4, 696.8 cm^{-1}; **^{1}H NMR** (500 MHz, CDCl$_3$): δ 7.37–7.26 (m, 6 H), 7.25–7.16 (m, 4 H), 5.04–4.99 (m, 1 H), 4.80 (app. s, 1 H), 4.76 (dd, *J* = 8.7, 1.3 Hz, 1 H), 4.41 (dd, *J* = 10.4, 5.9 Hz, 1 H), 4.11 (d, *J* = 8.7 Hz, 1 H), 2.60 (ddd, *J* = 12.0, 5.9, 1.3 Hz, 1 H), 2.48 (dd, *J* = 12.0, 10.3 Hz, 1 H), 1.73 (s, 3 H); **^{13}C NMR** (125 MHz, CDCl$_3$): δ 146.2, 145.6, 145.6, 128.6, 128.5, 127.3, 127.3, 126.7, 126.4, 110.5, 81.7, 77.5, 56.3, 44.0, 18.0; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for [$C_{19}H_{21}O$]$^+$ required 265.1587 *m/z*, found 265.1585 *m/z*.

3,3-Diphenyl-5-(prop-1-en-2-yl)dihydrofuran-2(3*H*)-one (Table 2, **15**). Synthesized according to the general procedure using **S14** (0.085 g, 0.30 mmol), Cu(EH)$_2$ (0.211 g, 0.603 mmol), TFA (0.023 mL, 0.30 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 18 h. After chromatography on SiO$_2$ (4% EtOAc in hexanes), **15** was isolated as a yellow oil that solidified upon standing (0.063 g, 0.19 mmol, 62%).



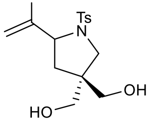
Mp 83–85 °C; **IR** (ATR): ν 3059.6, 3022.3, 2932.9, 2890.6, 1760.3, 1179.4 cm^{-1}; **^{1}H NMR** (500 MHz, CDCl$_3$): δ 7.42–7.36 (m, 4 H), 7.35–7.29 (m, 5 H), 7.28–7.23 (m, 1 H), 5.12 (s, 1 H), 4.99 (s, 1 H), 4.74 (dd, *J* = 11.0, 5.0 Hz, 1 H), 3.06 (dd, *J* = 12.9, 5.0 Hz, 1 H), 2.79 (dd, *J* = 12.9, 11.0 Hz, 1 H), 1.81 (s, 3 H); **^{13}C NMR** (125 MHz, CDCl$_3$): δ 177.0, 142.1, 141.5, 139.7, 129.1, 128.5, 127.9, 127.8, 127.5, 127.4, 113.5, 79.4, 58.4, 42.7, 17.6; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for [$C_{19}H_{19}O_2$]$^+$ required 296.1645 *m/z*, found 296.1642 *m/z*.

Dimethyl 5-(prop-1-en-2-yl)-1-tosylpyrrolidine-3,3-dicarboxylate (Table 2, **16**). Synthesized according to the general procedure using **S18** (0.114 g, 0.297 mmol), Cu(EH)$_2$ (0.209 g, 0.597 mmol), TFA (0.023 mL, 0.30 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 48 h. After chromatography on SiO$_2$ (10% EtOAc in hexanes), **16** was isolated as a red oil (0.082 g, 0.22 mmol, 72%).



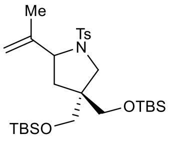
IR (ATR): ν 2962.8, 2922.1, 2866.4, 1717.6, 1655.5 cm^{-1}; **^{1}H NMR** (500 MHz, CDCl$_3$): δ 7.69 (d, *J* = 8.3 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 4.99 (s, 1 H), 4.89 (t, *J* = 1.6 Hz, 1 H), 4.14 (t, *J* = 7.8 Hz, 1 H), 4.05 (ABq, *J* = 11.6 Hz, 1 H), 3.96 (ABq, *J* = 11.5 Hz, 1 H), 3.71 (s, 3 H), 3.52 (s, 3 H), 2.51 (dd, *J* = 13.0, 7.8 Hz, 1 H), 2.44 (s, 3 H), 2.28 (dd, *J* = 13.2, 7.9 Hz, 1 H), 1.74 (s, 3 H); **^{13}C NMR** (125 MHz, CDCl$_3$): δ 169.7, 169.3, 143.7, 143.6, 134.6, 129.7, 127.9, 113.4, 65.1, 58.3, 54.6, 53.3, 38.5, 21.7, 17.3; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for [$C_{18}H_{24}NO_6S$]$^+$ required 382.1319 *m/z*, found 382.1314 *m/z*.

(5-(Prop-1-en-2-yl)-1-tosylpyrrolidine-3,3-diyl)dimethanol (Table 2, **17**). Synthesized according to the general procedure using **S19** (0.098 g, 0.30 mmol), Cu(EH)$_2$ (0.212 g, 0.606 mmol), TFA (0.023 mL, 0.30 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 36 h. After chromatography on SiO$_2$ (70% EtOAc in hexanes), **17** was isolated as a white powder (0.037 g, 0.11 mmol, 38%).



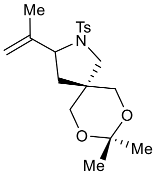
Mp 112–115 °C; **IR** (ATR): ν 3314.9, 2923.5, 2873.9, 1451.8, 1339.7, 1158.1 cm^{-1}; **^{1}H NMR** (500 MHz, CDCl$_3$): δ 7.71 (d, *J* = 8.2 Hz, 2 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 4.95 (s, 1 H), 4.84 (t, *J* = 1.5 Hz, 1 H), 4.04 (t, *J* = 8.3 Hz, 1 H), 3.69 (t, *J* = 5.4 Hz, 2 H), 3.46 (ABq, *J* = 11.3 Hz, 1 H), 3.32 (ABq, 11.5 Hz, 1 H), 3.32–3.29 (m, 1 H), 3.24 (dd, *J* = 10.9, 5.4 Hz, 1 H), 2.44 (s, 3 H), 2.18 (dt, *J* = 10.1, 5.1 Hz, 2 H), 1.81 (dd, *J* = 13.4, 8.1 Hz, 1 H), 1.73 (s, 3 H), 1.61 (dd, *J* = 13.4, 8.7 Hz, 1 H); **^{13}C NMR** (125 MHz, CDCl$_3$): δ 144.7, 143.7, 134.8, 129.7, 127.8, 112.6, 68.4, 66.4, 65.0, 54.0, 47.5, 36.9, 21.7, 17.2; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for [C$_{16}$H$_{24}$NO$_4$S]$^+$ required 326.1421 *m/z*, found 326.1416 *m/z*.

4,4-bis(((*tert*-Butyldimethylsilyl)oxy)methyl)-2-(prop-1-en-2-yl)-1-tosylpyrrolidine (Table 2, **18**). Synthesized according to the general procedure using **S20** (0.163 g, 0.293 mmol), Cu(EH)$_2$ (0.210 g, 0.600 mmol), TFA (0.023 mL, 0.30 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 15 h. After chromatography on SiO$_2$ (10% EtOAc in hexanes), **18** was isolated as a yellow oil (0.121 g, 0.218 mmol, 75%).



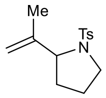
IR (ATR): ν 2950.2, 2931.1, 2856.7, 1601.2, 1341.0, 1079.0 cm^{-1}; **^{1}H NMR** (500 MHz, CDCl$_3$): δ 7.72–7.67 (m, 2 H), 7.34–7.29 (m, 2 H), 4.94 (dt, *J* = 1.8, 0.9 Hz, 1 H), 4.85 (t, *J* = 1.6 Hz, 1 H), 3.84 (t, *J* = 8.3 Hz, 1 H), 3.49 (d, *J* = 9.6 Hz, 1 H), 3.41 (d, *J* = 9.6 Hz, 1 H), 3.35 (d, *J* = 11.0 Hz, 1 H), 3.14 (d, *J* = 11.1 Hz, 1 H), 3.05 (d, *J* = 9.7 Hz, 1 H), 2.82 (d, *J* = 9.7 Hz, 1 H), 2.43 (s, 3 H), 1.78 (s, 3 H), 1.72 (dd, *J* = 13.2, 8.0 Hz, 1 H), 1.65 (dd, *J* = 13.2, 8.8 Hz, 1 H), 0.87 (s, 9 H), 0.79 (s, 9 H), 0.01 (d, *J* = 2.1 Hz, 6 H), -0.12 (d, *J* = 3.4 Hz, 6 H); **^{13}C NMR** (125 MHz, CDCl$_3$): δ 145.5, 143.4, 134.1, 129.7, 127.9, 112.1, 65.4, 64.5, 63.0, 54.2, 48.3, 35.6, 26.0, 25.9, 21.7, 18.4, 18.2, 17.0, -5.4, -5.5, -5.6, -5.6; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for [C$_{28}$H$_{51}$NO$_4$SSi$_2$]$^+$ required 554.3150 *m/z*, found 554.3157 *m/z*.

8,8-Dimethyl-3-(prop-1-en-2-yl)-2-tosyl-7,9-dioxa-2-azaspiro[4.5]decane (Table 2, **19**). Synthesized according to the general procedure using **S21** (0.085 g, 0.23 mmol), Cu(EH)$_2$ (0.164 g, 0.468 mmol), TFA (0.018 mL, 0.23 mmol), and MesAcrMe$^+$ (0.0027 g, 0.0059 mmol) and irradiating for 42 h. After chromatography on SiO$_2$ (30% EtOAc in hexanes), **19** was isolated as a clear, colorless oil (0.060 g, 0.16 mmol, 71%).



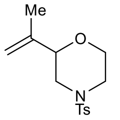
IR (ATR): ν 2989.7, 2927.4, 2865.4, 1343.8, 1158.3 cm^{-1}; **^{1}H NMR** (500 MHz, CDCl$_3$): δ 7.74–7.76 (m, 2 H), 7.35–7.29 (m, 2 H), 4.97 (dt, *J* = 1.7, 0.9 Hz, 1 H), 4.86 (p, *J* = 1.5 Hz, 1 H), 3.92 (t, *J* = 8.1 Hz, 1 H), 3.69 (dd, *J* = 11.5, 1.4 Hz, 1 H), 3.63 (d, *J* = 11.5 Hz, 1 H), 3.43 (ABq, *J* = 11.2 Hz, 1 H), 3.39 (ABq, *J* = 11.2 Hz, 1 H), 3.25 (d, *J* = 11.5 Hz, 1 H), 3.14 (dd, *J* = 11.5, 1.4 Hz, 1 H), 2.44 (s, 3 H), 1.81 (dd, *J* = 13.5, 8.1 Hz, 1 H), 1.75 (s, 3 H), 1.58 (dd, *J* = 13.4, 8.0 Hz, 1 H), 1.36 (s, 3 H), 1.35 (s, 3 H); **^{13}C NMR** (125 MHz, CDCl$_3$): δ 144.6, 143.7, 134.2, 129.7, 127.9, 112.7, 98.3, 67.3, 66.5, 64.7, 55.8, 40.7, 37.9, 24.9, 22.5, 21.7, 17.4; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for [C$_{19}$H$_{28}$NO$_4$S]$^+$ required 366.1734 *m/z*, found 366.1731 *m/z*.

2-(Prop-1-en-2-yl)-1-tosylpyrrolidine (Table 2, **20**). Synthesized according to the general procedure using **S24** (0.079 g, 0.30 mmol), Cu(EH)$_2$ (0.210 g, 0.600 mmol), TFA (0.023 mL, 0.30 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 30 h.



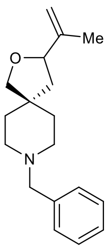
After chromatography on SiO$_2$ (20% EtOAc in hexanes), **20** was isolated as a clear, colorless oil that solidified upon standing to a yellow solid (0.065 g, 0.24 mmol, 83%).

Mp 69–72 °C; **IR** (ATR): ν 2979.9, 2951.6, 2865.8, 1655.7, 1490.1, 1333.2 cm^{-1}; ^{1}**H NMR** (500 MHz, CDCl$_3$): δ 7.72 (d, *J* = 8.2 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.03–4.98 (m, 1 H), 4.88–4.85 (m, 1 H), 4.04 (t, *J* = 6.3 Hz, 1 H), 3.46 (ddd, *J* = 10.2, 7.1, 5.1 Hz, 1 H), 3.29 (dt, *J* = 10.2, 7.3 Hz, 1 H), 2.43 (s, 3 H), 1.84–1.75 (m, 1 H), 1.74 (s, 3 H), 1.72–1.66 (m, 1 H), 1.59–1.51 (m, 1 H); ^{13}**C NMR** (125 MHz, CDCl$_3$): δ 145.2, 143.4, 135.1, 129.7, 127.7, 111.9, 65.1, 49.4, 31.5, 24.2, 21.7, 18.8; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for [$C_{14}H_{20}NO_2S$]$^+$ required 266.1209 *m/z*, found 266.1212 *m/z*.



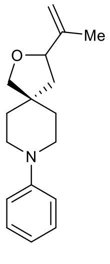
2-(Prop-1-en-2-yl)-4-tosylmorpholine (Table 2, **21**). Synthesized according to the general procedure using **S26** (0.074 g, 0.26 mmol), Cu(EH)$_2$ (0.184 g, 0.526 mmol), TFA (0.020 mL, 0.26 mmol), and MesAcrMe$^+$ (0.0030 g, 0.0065 mmol) and irradiating for 42 h. After chromatography on SiO$_2$ (10% EtOAc in hexanes), **21** was isolated as a white solid (0.037 g, 0.13 mmol, 51%).

Mp 102–104 °C; **IR** (ATR): ν 2976.2, 2913.2, 2854.5, 1653.4, 1339.3 cm^{-1}; ^{1}**H NMR** (500 MHz, CDCl$_3$): δ 7.64 (d, *J* = 8.2 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 4.99 (s, 1 H), 4.92 (t, *J* = 1.8 Hz, 1 H), 3.99–3.92 (m, 2 H), 3.72 (td, *J* = 11.6, 2.7 Hz, 1 H), 3.67 (dt, *J* = 11.4, 2.2 Hz, 1 H), 3.54 (dq, *J* = 11.5, 2.0 Hz, 1 H), 2.45 (s, 3 H), 2.41 (td, *J* = 11.6, 3.5 Hz, 1 H), 2.14 (dd, *J* = 11.3, 10.2 Hz, 1 H), 1.72 (s, 3 H); ^{13}**C NMR** (125 MHz, CDCl$_3$): δ 144.1, 142.2, 132.3, 129.9, 128.0, 112.8, 78.3, 66.0, 49.7, 45.6, 21.7, 19.3; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for [$C_{14}H_{20}NO_3S$]$^+$ required 282.1158 *m/z*, found 282.1159 *m/z*.



8-Benzyl-3-(prop-1-en-2-yl)-2-oxa-8-azaspiro[4.5]decane (Table 2, **22**). Synthesized according to the general procedure using **S30** (0.081 g, 0.30 mmol), Cu(EH)$_2$ (0.211 g, 0.603 mmol), TsOH·H$_2$O (0.116 g, 0.610 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 16 h. After chromatography on SiO$_2$ (40% EtOAc in hexanes with 1% Et$_3$N), **22** was isolated as a yellow oil (0.045 g, 0.17 mmol, 56%).

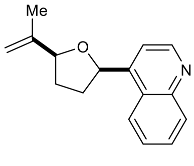
IR (ATR): ν 2918.4, 2846.0, 2805.2, 1701.8, 1649.4, 1445.9 cm^{-1}; ^{1}**H NMR** (500 MHz, CDCl$_3$): δ 7.33–7.29 (m, 4 H), 7.27–7.21 (m, 1 H), 4.98 (s, 1 H), 4.78 (t, *J* = 2.0 Hz, 1 H), 4.34 (dd, *J* = 9.6, 6.7 Hz, 1 H), 3.69–3.62 (m, 2 H), 3.48 (s, 3 H), 2.50–2.26 (m, 4 H), 1.93 (dd, *J* = 12.4, 6.9 Hz, 1 H), 1.71 (s, 3 H), 1.68–1.58 (m, 4 H), 1.48 (dd, *J* = 12.4, 9.4 Hz, 1 H); ^{13}**C NMR** (125 MHz, CDCl$_3$): δ 145.8, 138.7, 129.3, 128.3, 127.1, 109.9, 81.7, 78.2, 63.6, 51.8, 51.3, 43.2, 36.1, 35.1, 18.1; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for [$C_{18}H_{26}NO$]$^+$ required 272.2009 *m/z*, found 272.2006 *m/z*.



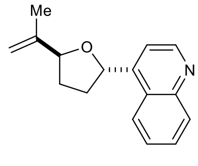
8-Phenyl-3-(prop-1-en-2-yl)-2-oxa-8-azaspiro[4.5]decane (Table 2, **23**). Synthesized according to the general procedure using **S32** (0.077 g, 0.30 mmol), Cu(EH)$_2$ (0.208 g, 0.594 mmol), TsOH·H$_2$O (0.116 g, 0.610 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 20 h. After chromatography on SiO$_2$ (20% EtOAc in hexanes), **23** was isolated as a yellow oil (0.042 g, 0.16 mmol, 55%).

IR (ATR): ν 2919.9, 2839.5, 1797.1, 1497.5, 1235.9 cm^{-1}; ^{1}**H NMR** (500 MHz, CDCl$_3$): δ 7.29–7.22 (m, 2 H), 6.98–6.91 (m, 2 H), 6.84 (td, *J* = 7.3, 1.1 Hz, 1 H), 5.04–4.99 (m, 1 H), 4.80 (s, 1 H), 4.43–4.35 (m, 1 H), 3.71–3.67 (m, 2 H), 3.20 (t, *J* = 5.8 Hz, 2 H), 3.14 (dd, *J* = 7.0, 4.5 Hz, 2 H), 2.00 (dd, *J* = 12.6, 6.9 Hz, 1 H), 1.83–1.73 (m, 4 H), 1.73 (s, 3 H), 1.56 (dd, *J* = 12.3, 9.4 Hz, 1 H); ^{13}**C NMR** (125 MHz, CDCl$_3$): δ 151.7, 145.7, 129.2, 119.7, 116.7, 110.1, 81.7, 78.0, 47.9, 47.5, 42.7, 42.3, 35.8, 34.8, 18.3; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for $[C_{17}H_{24}NO]^+$ required 258.1852 *m/z*, found 258.1847 *m/z*.

4-((2*R*,5*S*)-5-(Prop-1-en-2-yl)tetrahydrofuran-2-yl)quinoline (Table 2, **24**). Synthesized according to the general procedure using **S33** (0.067 g, 0.28 mmol), Cu(EH)$_2$ (0.211 g, 0.603 mmol), TsOH·H$_2$O (0.117 g, 0.613 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 18 h. After chromatography on SiO$_2$ (40% EtOAc in hexanes), **24** was isolated as a mixture of *cis* and *trans* isomers (0.035 g, 0.15 mmol, 53%, 1:1 d.r.). Analytically pure samples of each diastereomer were obtained by chromatography on SiO$_2$ (40% EtOAc in hexanes).



cis-**24**

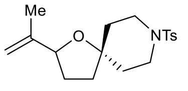


trans-**24**

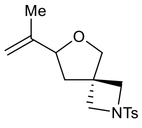
<u>*cis*-**24**</u>: Isolated as a 5.5:1 mixture of *cis*:*trans* diastereomers. Characteristic data:
IR (ATR): ν 3072.3, 3035.0, 2967.9, 2925.4, 2861.4, 1592.6, 1077.7 cm^{-1}; ^{1}**H NMR** (500 MHz, CDCl$_3$): δ 8.91 (d, *J* = 4.5 Hz, 1 H), 8.15 (d, *J* = 8.5 Hz, 1 H), 7.91 (d, *J* = 9.0 Hz, 1 H), 7.75–7.67 (m, 2 H), 7.56 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 1 H), 5.65 (t, *J* = 7.3 Hz, 1 H), 5.21 (app. s, 1 H), 4.96 (app. s, 1 H), 4.58–4.51 (m, 1 H), 2.74–2.61 (m, 1 H), 2.25–2.21 (m, 1 H), 1.96–1.77 (m, 2 H), 1.89 (s, 3 H); ^{13}**C NMR** (125 MHz, CDCl$_3$): δ 150.6, 149.2, 148.2, 144.8, 130.4, 129.1, 126.6, 125.7, 123.3, 117.0, 111.3, 83.1, 76.8, 34.0, 30.7, 18.9; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for $[C_{16}H_{18}NO]^+$ required 240.1383 *m/z*, found 240.1384 *m/z*.

<u>*trans*-**24**</u>:
IR (ATR): ν 3072.0, 3035.0, 2924.6, 2860.5, 1592.4, 1072.0 cm^{-1}; ^{1}**H NMR** (500 MHz, CDCl$_3$): δ 8.90 (d, *J* = 4.6 Hz, 1 H), 8.15 (d, *J* = 8.4 Hz, 1 H), 7.93 (d, *J* = 8.4 Hz, 1 H), 7.72 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1 H), 7.61 (d, *J* = 4.5 Hz, 1 H), 7.56 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1 H), 5.82 (t, *J* = 7.0 Hz, 1 H), 5.14 (app. s, 1 H), 4.92 (app. s, 1 H), 4.77 (t, *J* = 6.8 Hz, 1 H), 2.74–2.66 (m, 1 H), 2.24–2.15 (m, 1 H), 2.01–1.85 (m, 2 H), 1.83 (s, 3 H); ^{13}**C NMR** (125 MHz, CDCl$_3$): δ 150.7, 149.8, 148.2, 145.5, 130.4, 129.2, 126.5, 125.7, 123.3, 116.6, 110.6, 83.2, 34.4, 31.3, 18.4; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for $[C_{16}H_{18}NO]^+$ required 240.1383 *m/z*, found 240.1384 *m/z*.

2-(Prop-1-en-2-yl)-8-tosyl-1-oxa-8-azaspiro[4.5]decane (Table 2, **25**). Synthesized according to the general procedure using **S34** (0.100 g, 0.296 mmol), Cu(EH)$_2$ (0.209 g, 0.597 mmol), TFA (0.023 mL, 0.60 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 26 h. After chromatography on SiO$_2$ (20% EtOAc in hexanes), **25** was isolated as a clear, colorless oil that solidified upon standing to a yellow solid (0.057 g, 0.17 mmol, 57%).

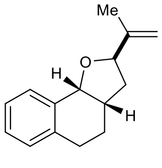


Mp 84–86 °C; **IR** (ATR): ν 2949.2, 2917.6, 2857.2, 1595.0, 1344.6 cm^{-1}; ^{1}**H NMR** (500 MHz, CDCl$_3$): δ 7.66–7.61 (m, 2 H), 7.32–7.27 (m, 2 H), 4.90 (dt, *J* = 2.1, 1.1 Hz, 1 H), 4.74 (m, 1 H), 4.33–4.25 (m, 1 H), 3.51–3.41 (m, 2 H), 2.85–2.74 (m, 2 H), 2.43 (s, 3 H), 2.09–1.97 (m, 1 H), 1.80–1.66 (m, 7 H), 1.64 (t, *J* = 1.1 Hz, 3 H); ^{13}**C NMR** (125 MHz, CDCl$_3$): δ 151.7, 145.7, 129.2, 119.7, 116.7, 110.1, 81.7, 78.0, 47.9, 47.5, 42.7, 42.3, 35.8, 34.8, 18.3; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for [$C_{17}H_{24}NO$]$^+$ required 258.1852 *m/z*, found 258.1847 *m/z*.

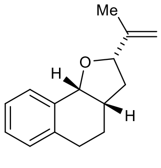


7-(Prop-1-en-2-yl)-2-tosyl-6-oxa-2-azaspiro[3.4]octane (Table 2, **26**). Synthesized according to the general procedure using **S38** (0.092 g, 0.30 mmol), Cu(EH)$_2$ (0.209 g, 0.597 mmol), TFA (0.023 mL, 0.30 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 96 h. After chromatography on SiO_2 (30% Et_2O in hexanes), **26** was isolated as yellow solid (0.049 g, 0.16 mmol, 54%).

Mp 95–97 °C; **IR** (ATR): ν 2924.2, 2867.7, 1449.0, 1342.8, 1160.0 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.76–7.30 (m, 2 H), 7.41–7.34 (m, 2 H), 4.93–4.89 (m, 1 H), 4.80–4.75 (m, 1 H), 4.23 (t, *J* = 7.4 Hz, 1 H), 3.82–3.63 (m, 6 H), 2.47 (s, 3 H), 2.08 (dd, *J* = 12.9, 7.1 Hz, 1 H), 1.78 (dd, *J* = 12.9, 7.7 Hz, 1 H), 1.64 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.5, 144.4, 131.7, 129.8, 128.5, 110.8, 81.7, 60.2, 60.1, 42.1, 40.5, 21.8, 18.2; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for [$C_{16}H_{22}NO_3S$]$^+$ required 308.1315 *m/z*, found 308.1312 *m/z*.

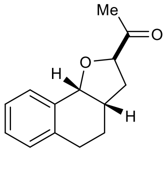


27-*Major*

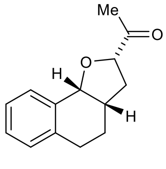


27-*Minor*

2-(Prop-1-en-2-yl)-2,3,3a,4,5,9b-hexahydronaphtho[1,2-*b*]furan (Table 2, **27**-*Major* and **27**-*Minor*). Synthesized according to the general procedure using **S39** (0.064 g, 0.30 mmol), Cu(EH)$_2$ (0.210 g, 0.600 mmol), TFA (0.023 mL, 0.30 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 20 h. After chromatography on SiO_2 (2% Et_2O in hexanes), **27** was isolated as a mixture of diastereomers (0.041 g, 0.19 mmol, 65%, 1:1 d.r.) which proved inseparable by column chromatography.



S63-*Major*



S63-*Minor*

1-(2,3,3a,4,5,9b-Hexahydronaphtho[1,2-*b*]furan-2-yl)ethan-1-one (SI, **S64**-*Major* and **S64**-*Minor*). To a solution of **27** (0.017 g, 0.079 mmol, 1.6:1 d.r.) in acetone/H_2O (1.7 mL, 10:1) was added 2,6-lutidine (0.020 mL, 0.16 mmol), *N*-methylmorpholine-*N*-oxide (0.014 g, 0.12 mmol), and a solution of OsO_4 (0.010 mL, 0.006 mmol, 4 wt% in H_2O) and the resulting solution was stirred at rt for 5 h. PhI(OAc)$_2$ (0.038 g, 0.012 mmol) was added in a single portion and the resulting solution was stirred at rt for 16 h. The reaction mixture was quenched with sat. aq. $Na_2S_2O_3$ (5 mL) and the solution was extracted with EtOAc (3 x 10 mL). The combined organic extracts were washed with sat. aq. $CuSO_4$ (2 x 5 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give crude **S64** (0.019 g) as a pale yellow oil. The crude residue was purified by chromatography on SiO_2 (20–30% Et_2O in hexanes) to give **S64** as a clear, colorless oil (0.012 g, 0.055 mmol, 70%, 1.7:1 d.r.). Analytically pure samples of each diastereomer were obtained by chromatography on SiO_2 (20–25% Et_2O in pentanes).

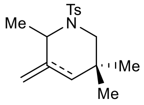
S64-*Major*:

IR (ATR): ν 2925.2, 2856.6, 1713.8, 1352.0, 1071.3 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.50–7.43 (m, 1 H), 7.27–7.19 (m, 2 H), 7.17–7.11 (m, 1 H), 4.92 (d, *J* = 5.5 Hz, 1 H), 4.47 (app. t, *J* = 8.0 Hz, 1 H), 2.81 (dt, *J* = 16.3, 4.3 Hz, 1 H), 2.69 (ddd, *J* = 16.3, 11.5, 4.6 Hz, 1 H), 2.50 (dddd, *J* = 12.5, 7.6, 5.0, 2.4 Hz, 1 H), 2.34–2.26 (m, 1 H), 2.31 (s, 3 H), 2.12 (m, 1 H), 1.85 (dq, *J* = 13.3, 4.5 Hz, 1 H), 1.61 (dtd, *J* = 13.1, 11.5, 4.5 Hz, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 211.3, 137.4, 134.2, 130.4, 128.7, 128.1, 126.5, 82.2, 78.6, 37.9, 35.7, 28.7, 26.0, 25.4; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for $[C_{14}H_{17}O_2]^+$ required 217.1223 *m/z*, found 217.1221 *m/z*.

<u>S64</u>-*<u>Minor</u>*:

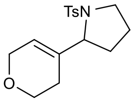
IR (ATR): ν 3022.6, 2925.8, 2856.7, 1715.6, 1353.5, 1072.6 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.50–7.42 (m, 1 H), 7.25–7.20 (m, 2 H), 7.17–7.10 (m, 1 H), 4.85 (d, *J* = 5.8 Hz, 1 H), 4.36 (dd, *J* = 8.5, 7.3 Hz, 1 H), 2.78 (dt, *J* = 16.3, 4.8 Hz, 1 H), 2.67 (ddd, *J* = 16.0, 10.6, 4.5 Hz, 1 H); 2.57–2.46 (m, 2 H), 2.13 (s, 3 H), 1.87–1.78 (m, 2 H), 1.54–1.45 (m, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 210.6, 137.7, 134.5, 130.6, 128.5, 127.9, 126.4, 83.3, 78.8, 37.2, 35.6, 28.5, 26.4, 26.1; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for $[C_{14}H_{17}O_2]^+$ required 217.1223 *m/z*, found 217.1220 *m/z*.

2,5,5-Trimethyl-3-methylene-1-tosylpiperidine (Table 2, **28**). Synthesized according to the general procedure using **S43** (0.088 g, 0.30 mmol), Cu(EH)$_2$ (0.210 g, 0.600 mmol), TFA (0.023 mL, 0.30 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 16 h. After chromatography on SiO_2 (10% EtOAc in hexanes), the products were isolated as an opaque yellow oil (0.081 g, 0.28 mmol, 93%, 4:1 r.r.). Analytically pure samples of the major regioisomer could be obtained via chromatography on SiO_2 (10% EtOAc in hexanes).



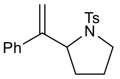
IR (ATR): ν 2957.7, 2928.4, 2867.7, 1779.0, 1335.9 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.71–7.65 (m, 2 H), 7.29–7.23 (m, 2 H), 4.87 (t, *J* = 1.8 Hz, 1 H), 4.65 (t, *J* = 1.9 Hz, 1 H), 4.62 (q, *J* = 6.9 Hz, 1 H), 3.27 (dd, *J* = 12.8, 1.6 Hz, 1 H), 2.83 (d, *J* = 12.8 Hz, 1 H), 2.41 (s, 3 H), 2.15 (dd, *J* = 13.6, 2.0 Hz, 1 H), 1.81 (dd, *J* = 13.6, 2.1 Hz, 1 H), 1.10 (d, *J* = 6.9 Hz, 3 H), 0.94 (s, 3 H), 0.74 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.3, 143.0, 138.5, 129.6, 127.2, 111.0, 55.3, 50.7, 42.3, 32.7, 28.1, 23.6, 21.6, 16.6; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for $[C_{16}H_{24}NO_2S]^+$ required 294.1522 *m/z*, found 294.1519 *m/z*.

2-(3,6-Dihydro-2*H*-pyran-4-yl)-1-tosylpyrrolidine (Table 2, **29**). Synthesized according to the general procedure using **S49** (0.092 g, 0.30 mmol), Cu(EH)$_2$ (0.210 g, 0.600 mmol), TFA (0.023 mL, 0.30 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 16 h. After chromatography on SiO_2 (50–60% Et_2O in hexanes), **29** was isolated as a white solid (0.051 g, 0.17 mmol, 56%).



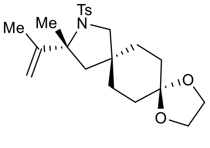
IR (ATR): ν 2920.8, 2855.1, 2805.3, 2756.0, 1337.7, 1157.0 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.3 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.70–5.66 (m, 1 H), 4.14 (qd, *J* = 2.6, 1.2 Hz, 2 H), 4.05 (dd, *J* = 7.9, 4.7 Hz, 1 H), 3.80 (dt, *J* = 10.7, 5.2 Hz, 1 H), 3.66 (ddd, *J* = 11.1, 6.7, 4.6 Hz, 1 H), 3.44 (ddd, *J* = 10.2, 7.2, 5.1 Hz, 1 H), 3.32 (dt, *J* = 10.2, 7.2 Hz, 1 H), 2.43 (s, 3 H), 2.14–1.97 (m, 2 H), 1.85–1.64 (m, 3 H), 1.64–1.57 (m, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.3, 135.4, 135.4, 129.7, 127.7, 122.0, 65.5, 64.6, 64.1, 49.3, 31.2, 25.1, 24.2, 21.7; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for $[C_{16}H_{22}NO_3S]^+$ required 308.1315 *m/z*, found 308.1310 *m/z*.

2-(1-Phenylvinyl)-1-tosylpyrrolidine (Table 2, **30**). Synthesized according to the general procedure using **S52** (0.98 g, 0.30 mmol), Cu(EH)$_2$ (0.212 g, 0.606 mmol), TsOH·H_2O (0.057 mL, 0.30 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for



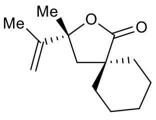
30 min. After chromatography on SiO_2 (10–20% EtOAc in hexanes), **30** was isolated as a yellow oil (0.066 g, 0.20 mmol, 68%).

IR (ATR): ν 3055.0, 2973.3, 2875.3, 1597.2, 1342.9, 1158.0 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.2 Hz, 2 H), 7.40–7.24 (m, 7 H), 5.38 (s, 1 H), 5.34 (s, 1 H), 4.75 (dd, *J* = 7.8, 3.1 Hz, 1 H), 3.53 (ddd, *J* = 10.2, 7.4, 2.9 Hz, 1 H), 3.29 (td, *J* = 9.5, 6.4 Hz, 1 H), 2.44 (s, 3 H), 1.87–1.73 (m, 1 H), 1.68–1.53 (m, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.0, 143.5, 140.0, 135.4, 129.8, 128.5, 127.8, 127.7, 127.1, 114.0, 63.1, 49.1, 32.0, 23.7, 21.7; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{19}H_{22}NO_2S]^+$ required 328.1366 *m/z*, found 328.1364 *m/z*.



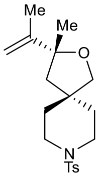
11-Methyl-11-(prop-1-en-2-yl)-10-tosyl-1,4-dioxa-10-azadispiro[4.2.4^8.2^5]tetradecane (Table 2, **31**). Synthesized according to the general procedure using **S56** (0.121 g, 0.297 mmol), $Cu(EH)_2$ (0.210 g, 0.600 mmol), TFA (0.023 mL, 0.30 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 42 h. After chromatography on SiO_2 (35–40% Et_2O in hexanes), **31** was isolated as a white solid (0.072 g, 0.18 mmol, 60%).

Mp 130–132 °C; **IR** (ATR): ν 2941.5, 2866.6, 1447.1, 1373.5, 1155.0 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.76–7.71 (m, 2 H), 7.29–7.24 (m, 2 H), 5.08 (s, 1 H), 4.88 (t, *J* = 1.4 Hz, 1 H), 3.90 (app. s, 4 H), 3.35 (ABq, *J* = 10.1 Hz, 1 H), 3.27 (ABq, *J* = 10.1 Hz, 1 H), 2.41 (s, 3 H), 1.99 (ABq, *J* = 13.4 Hz, 1 H), 1.81 (s, 3 H), 1.66 (ABq, *J* = 13.4 Hz, 1 H), 1.63 (s, 3 H), 1.63–1.40 (m, 8 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.6, 142.9, 138.4, 129.5, 127.4, 111.0, 108.3, 70.5, 64.4, 64.4, 59.1, 52.0, 39.5, 34.1, 33.9, 32.3, 32.1, 25.8, 21.6, 19.8; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{22}H_{32}NO_4S]^+$ required 406.2047 *m/z*, found 406.2045 *m/z*.

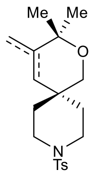


3-Methyl-3-(prop-1-en-2-yl)-2-oxaspiro[4.5]decan-1-one (Table 2, **32**) Synthesized according to the general procedure using **S58** (0.063 g, 0.300 mmol), $Cu(EH)_2$ (0.210 g, 0.600 mmol), TFA (0.023 mL, 0.30 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 18 h. After chromatography on SiO_2 (5–10% Et_2O in pentanes), **32** was isolated as a pale yellow oil (0.063 g, 0.30 mmol, 100%).

IR (ATR): ν 2932.3, 2858.2, 1762.9, 1447.8, 1226.8 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.06 (m, 1 H), 4.85–4.82 (m, 1 H), 2.37 (d, *J* = 13.3 Hz, 1 H), 1.93 (d, *J* = 13.2 Hz, 1 H), 1.84–1.73 (m, 5 H), 1.73–1.67 (m, 1 H), 1.66–1.53 (m, 4 H), 1.52 (s, 3 H), 1.32–1.24 (m, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 181.5, 147.9, 110.3, 84.6, 45.6, 43.4, 35.5, 34.0, 28.4, 25.2, 22.3, 22.2, 19.0; **HRMS** (ESI$^+$): $[M+H]^+$ calculated for $[C_{13}H_{21}O_2]^+$ required 209.1536 *m/z*, found 209.1536 *m/z*.



33-*Major*

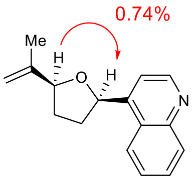


33-*Minor*

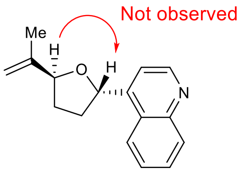
3-Methyl-3-(prop-1-en-2-yl)-8-tosyl-2-oxa-8-azaspiro[4.5]decane (Table 2, **33**). Synthesized according to the general procedure using **S62** (0.115 g, 0.33 mmol), $Cu(EH)_2$ (0.209 g, 0.60 mmol), $TsOH{\cdot}H_2O$ (0.115 g, 0.60 mmol), and MesAcrMe$^+$ (0.0036 g, 0.0075 mmol) and irradiating for 16 h. After chromatography on SiO_2 (15% EtOAc in hexanes), **33** was isolated as a white solid as a mixture of isomers (0.095 g, 0.27 mmol, 83%, 4:1 r.r.). Analytically pure samples of the major regioisomer could be obtained via chromatography on SiO_2 (15% EtOAc in hexanes).

Mp 120–124 °C; **IR** (ATR): ν 2973.3, 2920.5, 2845.7, 1441.9, 1335.0, 1159.1 cm^{-1}; ^{1}**H NMR** (500 MHz, CDCl$_3$): δ 7.63 (d, *J* = 8.2 Hz, 2 H), 7.33 (d, *J* = 7.9 Hz, 2 H), 4.97–4.92 (m, 1 H), 4.71 (app. P, *J* = 1.5 Hz, 1 H), 3.58 (d, *J* = 8.9 Hz, 1 H), 3.48 (d, *J* = 8.9 Hz, 1 H), 3.05–2.83 (m, 4 H), 2.44 (s, 3 H), 1.87 (d, *J* = 12.9 Hz, 1 H), 1.74–1.68 (m, 5 H), 1.64 (t, *J* = 5.7 Hz, 2 H), 1.49 (d, *J* = 12.9 Hz, 1 H), 1.29 (s, 3 H); ^{3}**C NMR** (125 MHz, CDCl$_3$): δ 149.5, 143.6, 133.4, 129.8, 127.8, 108.8, 85.3, 75.9, 47.9, 44.2, 44.2, 42.4, 35.9, 35.0, 27.8, 21.7, 19.3; **HRMS** (ESI$^+$): [M+H]$^+$ calculated for [C$_{19}$H$_{28}$NO$_3$S]$^+$ required 350.1784 *m/z*, found 350.1781 *m/z*.

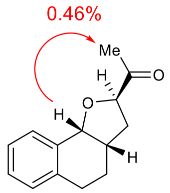
V. Assignment of Relative Stereochemistry by selective 1D NOESY



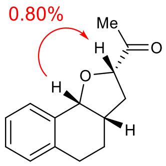
cis-**XX**



trans-**XX**



XX-*Major*



XX-*Minor*

VI. Cyclic Voltammetry Studies

Cyclic voltammetry experiments were performed in 1,2-DCE with analyte (1 mM) and $[(n\text{-Bu})_4N]^+[PF_6]^-$ (100 mM) using a glassy carbon working electrode, platinum wire electrode, a $Ag/AgNO_3$ MeCN reference electrode, and a scan rate of 50 mV/s. Ferrocene was added as a reference.

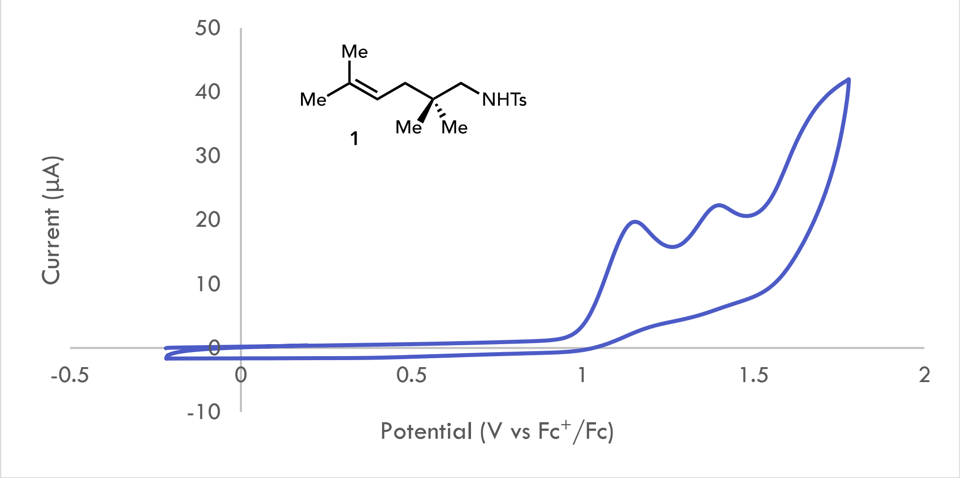


Figure S1. Cyclic voltammogram of alkene **1**

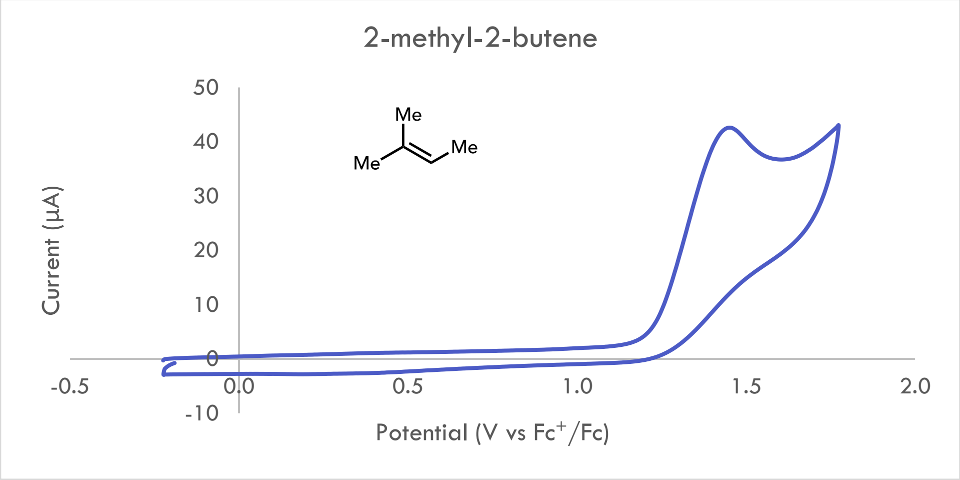


Figure S2. Cyclic voltammogram of 2-methyl-2-butene

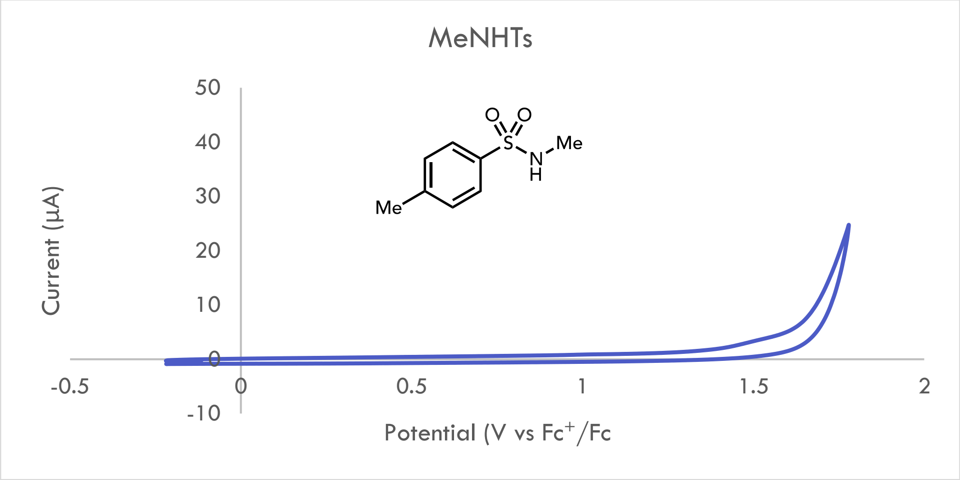


Figure S3. Cyclic voltammogram of MeNHTs

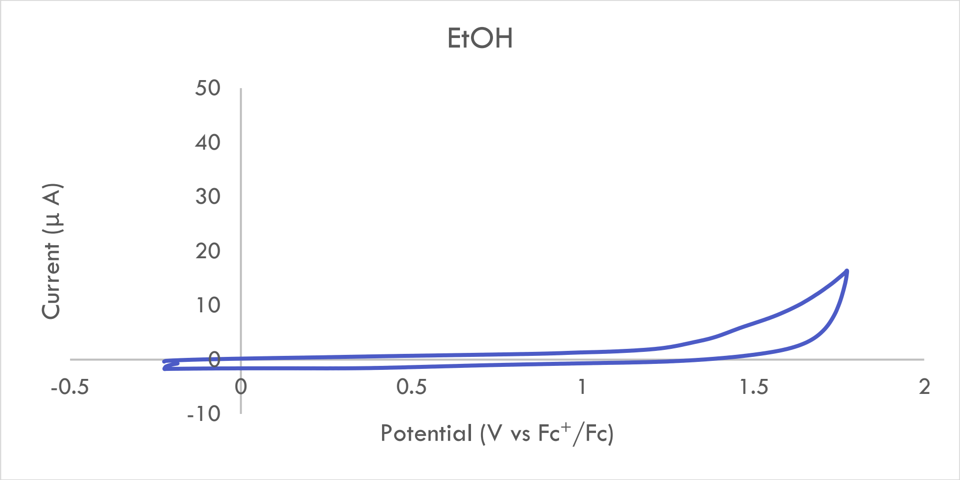


Figure S4. Cyclic voltammogram of EtOH

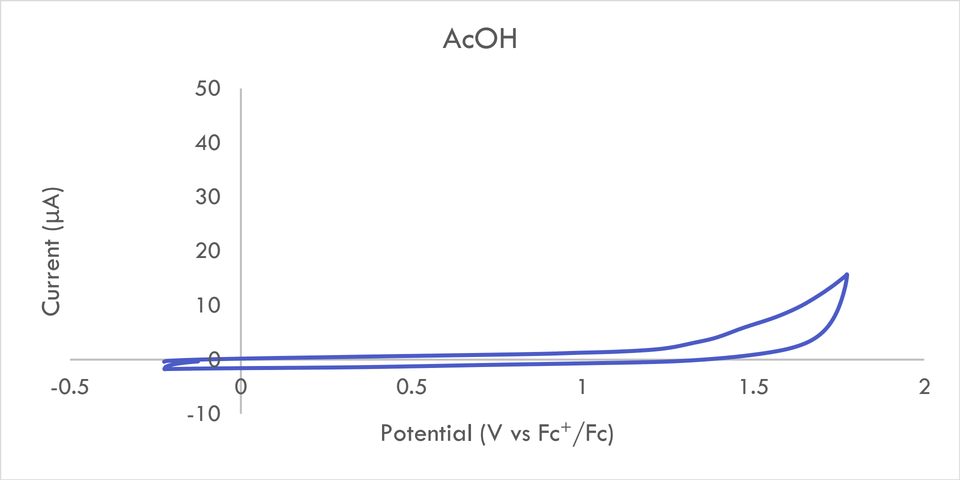
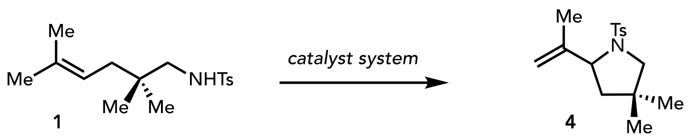


Figure S5. Cyclic voltammogram of AcOH

VII. Comparison to Pd(II)-Catalyzed Methods

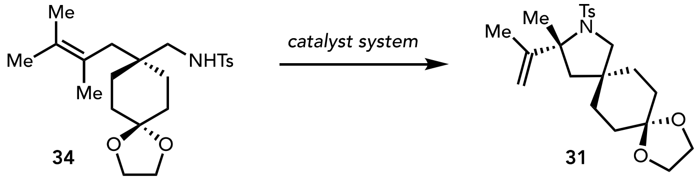
Table S2. Oxidative Amination of Highly Substituted Alkenes

A Oxidative Amination of Trisubstituted Alkene **1**



entry	catalyst system	% yield	% RSM
1	MesAcrPh$^+$/hν, Cu(EH)$_2$	87	0
2	Pd(OAc)$_2$/DMSO, O$_2$	trace	70
3	Pd(OAc)$_2$/pyridine, O$_2$	13	59
4	Pd(TFA)$_2$/(–)-sparteine, O$_2$	trace	69

B Oxidative Amination of Tetrasubstituted Alkene **34**



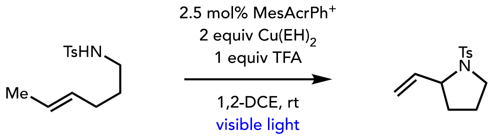
entry	catalyst system	% yield	% RSM
1	MesAcrPh$^+$/hν, Cu(EH)$_2$	56	31
2	Pd(OAc)$_2$/DMSO, O$_2$	4	66
3	Pd(OAc)$_2$/pyridine, O$_2$	22	60
4	Pd(TFA)$_2$/(–)-sparteine, O$_2$	7	78

Conditions for Entry 1: A solution of substrate (0.10 mmol), Cu(EH)$_2$ (0.070 g, 0.20 mmol), TFA (0.007 mL, 0.1 mmol), and MesAcrPh$^+$ (0.0025 mmol, 2.5 mol%) in 1,2-DCE (4 mL) was degassed (freeze-pump-thaw, 3 cycles of 5 min each) and the resulting solution was stirred at rt under irradiation by two 450 nm blue LED flood lamps for 16 h. The reaction mixture was diluted with Et$_2$O, eluted through a thin pad of SiO$_2$, and concentrated under reduced pressure to give the crude reaction mixtures. Yields were determined by ^{1}H NMR analysis of the unpurified reaction mixtures using phenanthrene as an internal standard.

Conditions for Entry 2: Adapted from the procedure of Larlock and coworkers.[12] To a 25 mL round bottom flask was added the substrate (0.25 mmol, 1 equiv), Pd(OAc)$_2$ (0.0028 g, 0.013 mmol), NaOAc (0.041 g, 0.50 mmol), DMSO (5 mL), and a stirbar. The headspace of the flask was purged with O$_2$, equipped with an O$_2$ balloon, and stirred at rt for 72 h. After 72 h, the reaction mixture was diluted with Et$_2$O and THF and transferred to a separatory funnel. The mixture was washed with brine and the aqueous layer was extracted twice with Et$_2$O (20 mL). The combined organic extracts were washed twice with 10% aqueous NaCl solution (20 mL), dried with MgSO$_4$, filtered, and concentrated under reduced pressure. The crude reaction mixture was analyzed by ^{1}H NMR using phenanthrene as an internal standard.

Conditions for Entry 3: Adapted from the procedure of Stahl and coworkers.[13,14] To a 5 mL round bottom flask was added the substrate (0.10 mmol, 1 equiv), pyridine (0.010 mL, 0.010 mmol), toluene (0.5 mL), and a stirbar. The headspace of the flask was purged with O_2 and equipped with an O_2 balloon. $Pd(OAc)_2$ (0.0011 g, 0.0050 mmol) in toluene (0.5 mL) was added via syringe and the reaction mixture was stirred for 24 h at 80 ºC. After 24 h, the reaction was cooled to rt and the solvent was evaporated under reduced pressure. The mixture was taken up in toluene, filtered through a thin pad of silica and concentrated under reduced pressure. The crude reaction mixture was analyzed by ^{1}H NMR using phenanthrene as an internal standard.

Conditions for Entry 4: Adapted from the procedure of Yang and coworkers.[15] To a 10 mL round bottom flask was added $Pd(TFA)_2$ (0.0067 g, 0.020 mmol), (–)-sparteine (0.019 g, 0.081 mmol), activated 3Å molecular sieves (0.50 g), toluene (1.5 mL) and a stirbar. After the reaction mixture was stirred for 30 min at rt, the substrate (0.20 mmol) was added followed by diisopropylethylamine (0.070 mL, 0.40 mmol). The reaction flask was fitted with a reflux condenser, the headspace purged with O_2, equipped with an O_2 balloon, and heated to 80 ºC. After 26 h, the reaction mixture was cooled to rt, filtered through a small pad of silica with EtOAc, and concentrated under reduced pressure. The crude reaction mixture was analyzed by ^{1}H NMR using phenanthrene as an internal standard.



S63

S65 0%
100% RSM

Reaction of Disubstituted Alkene: A solution of **S63** (0.025 g, 0.10 mmol), $Cu(EH)_2$ (0.071 g, 0.20 mmol), trifluoroacetic acid (0.007 mL, 0.1 mmol), and MesAcrPh$^+$ (0.0012 g, 0.0025 mmol, 2.5 mol%) in 1,2-DCE (4 mL) was degassed (freeze-pump-thaw, 3 cycles of 5 min each) and the resulting solution was stirred at rt under irradiation by a 450 nm blue LED flood lamp for 16 h. The reaction mixture was diluted with Et_2O, eluted through a thin pad of SiO_2, and concentrated under reduced pressure. ^{1}H NMR analysis of the unpurified reaction mixture using phenanthrene as an internal standard showed 0% yield of **S65** and 100% remaining **S63**.

VIII. References

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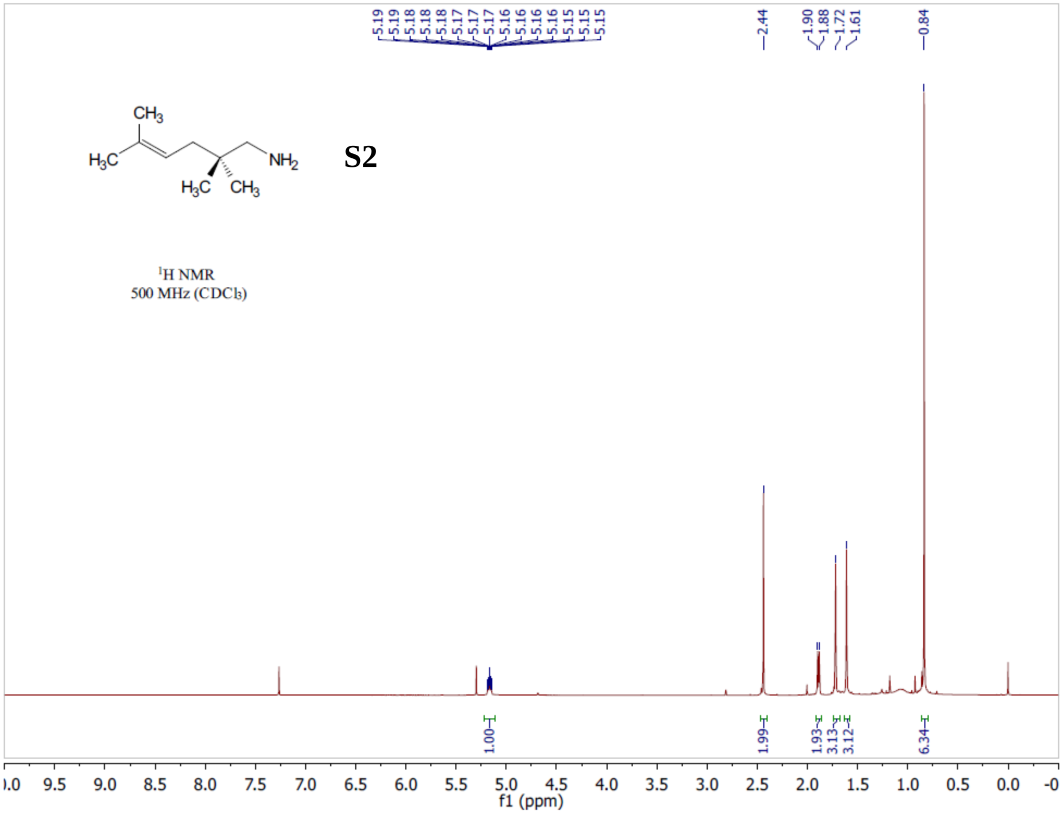
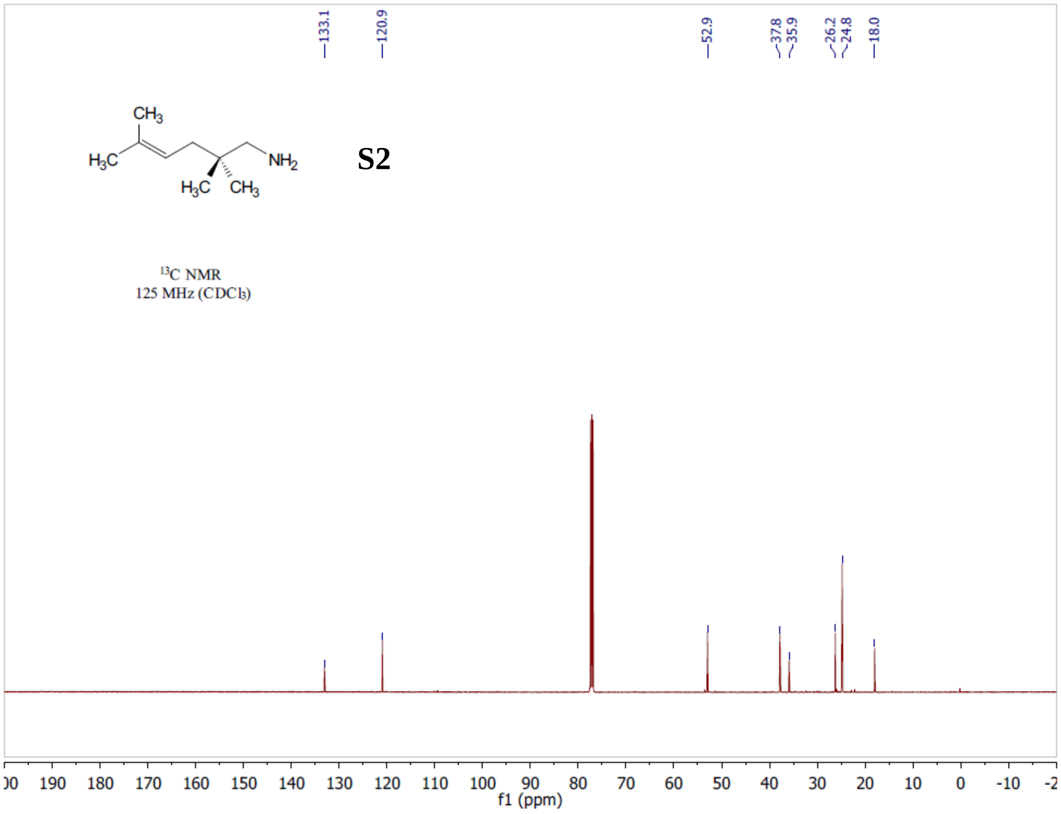
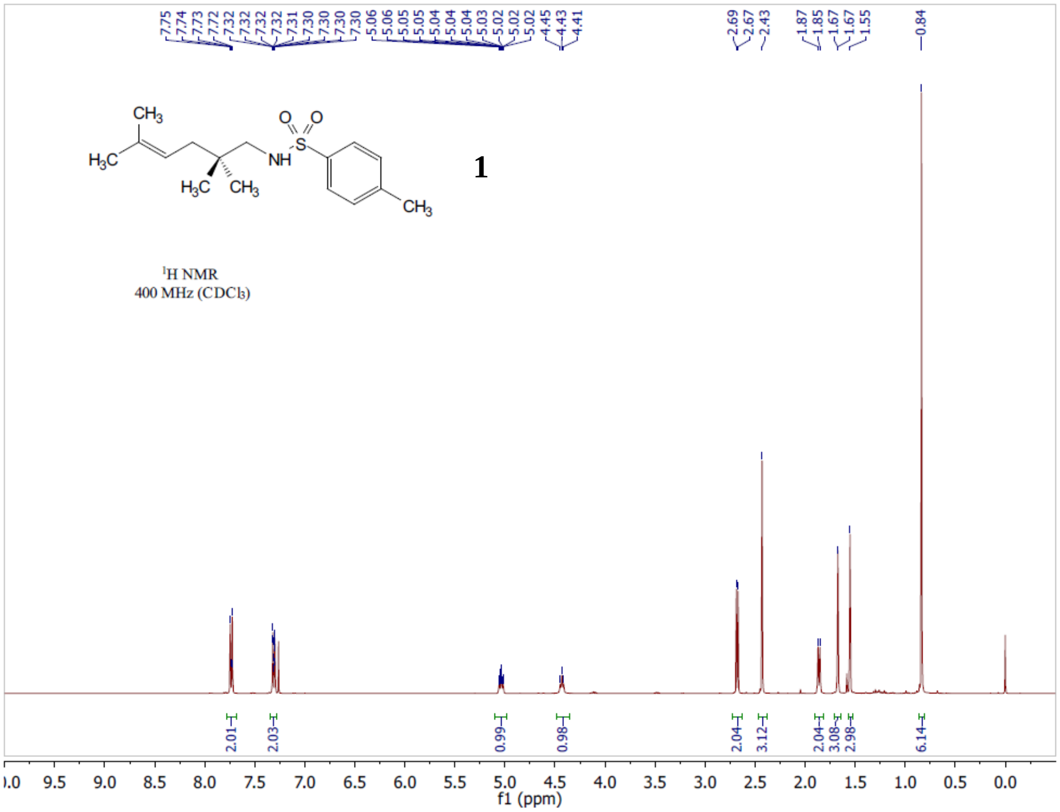
IX. Spectral Data



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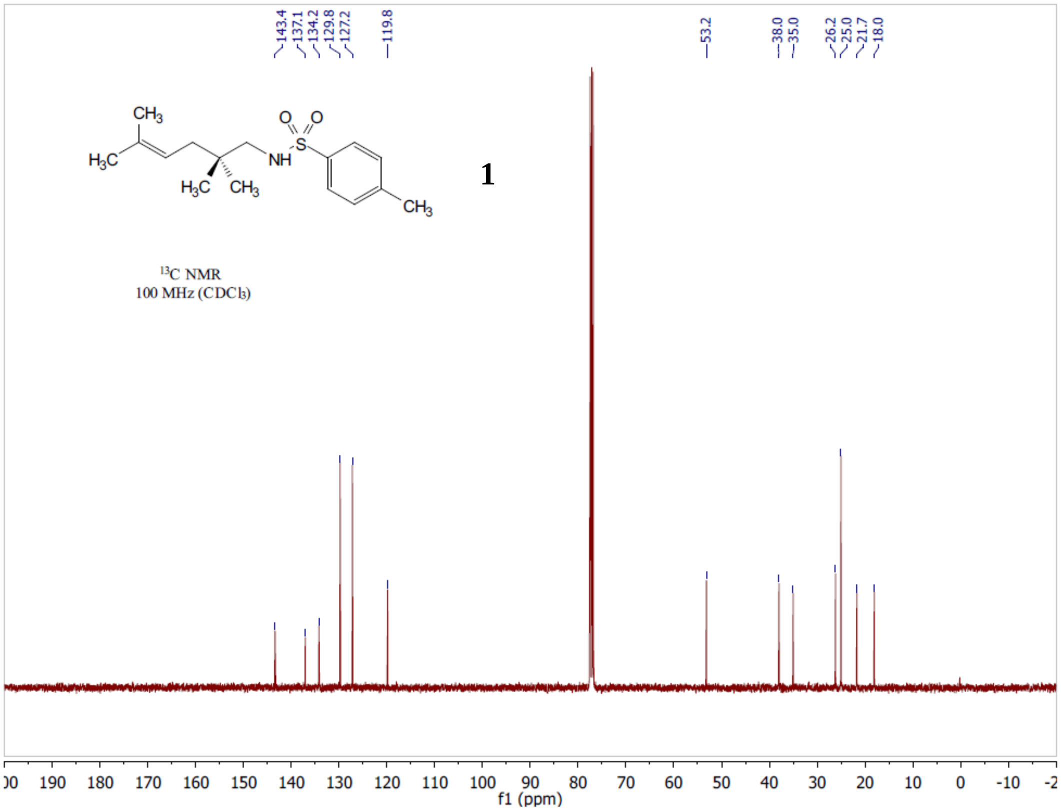
2.69 2.67 2.43 1.87 1.85 1.67 1.67 1.55 0.84
1
^{1}H NMR
400 MHz (CDCl$_3$)
2.01 2.03 0.99 0.98 2.04 3.12 2.04 3.08 2.98 6.14
f1 (ppm)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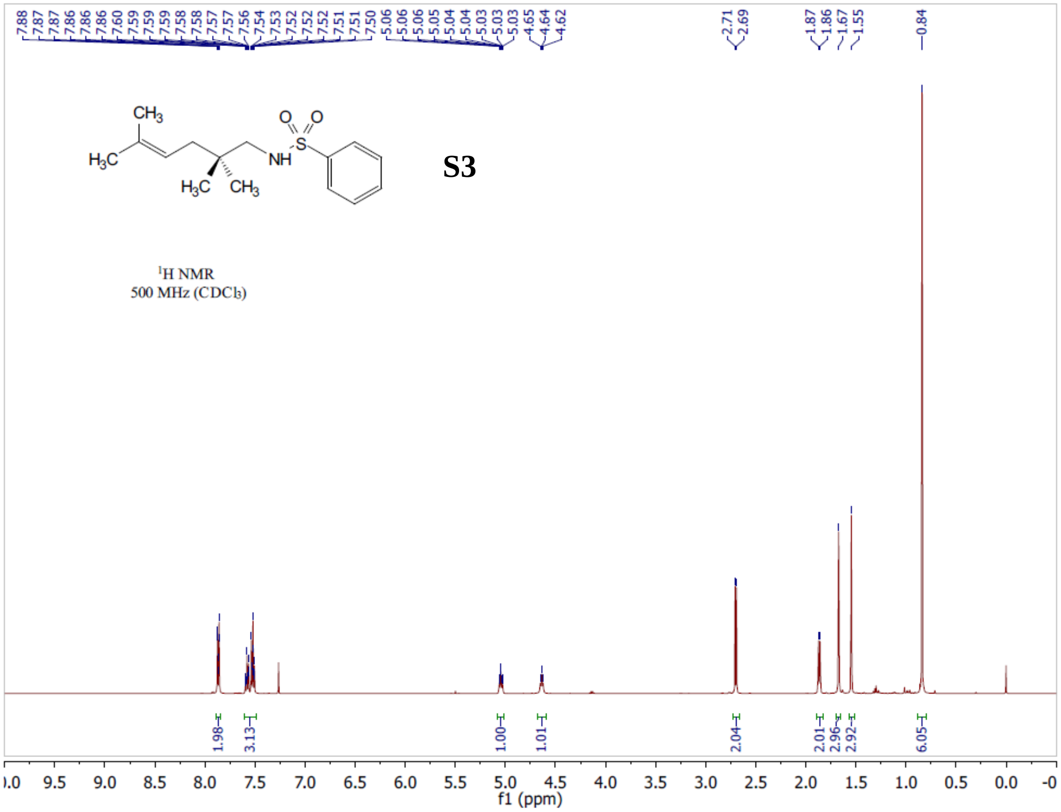
1
^{13}C NMR
100 MHz (CDCl$_3$)
f1 (ppm)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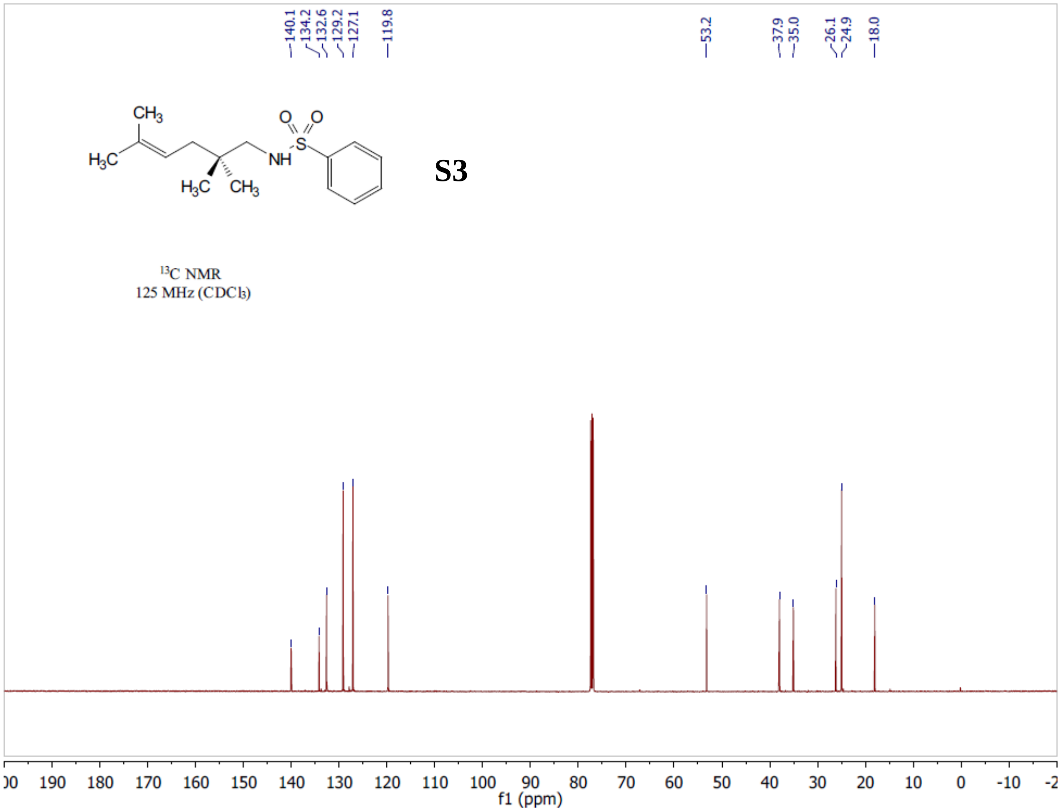
7.87
7.87
7.86
7.86
7.86
7.60
7.59
7.59
7.59
7.58
7.58
7.57
7.57
7.56
7.54
7.53
7.52
7.52
7.52
7.51
7.51
7.50
5.06
5.06
5.06
5.05
5.04
5.04
5.03
5.03
5.03
4.65
4.64
4.62
2.71
2.69
1.87
1.86
1.67
1.55
0.84
CH3
H3C
O
O
S
NH
H3C
CH3
S3
1H NMR
500 MHz (CDCl3)
1.98
3.13
1.00
1.01
2.04
2.01
2.96
2.92
6.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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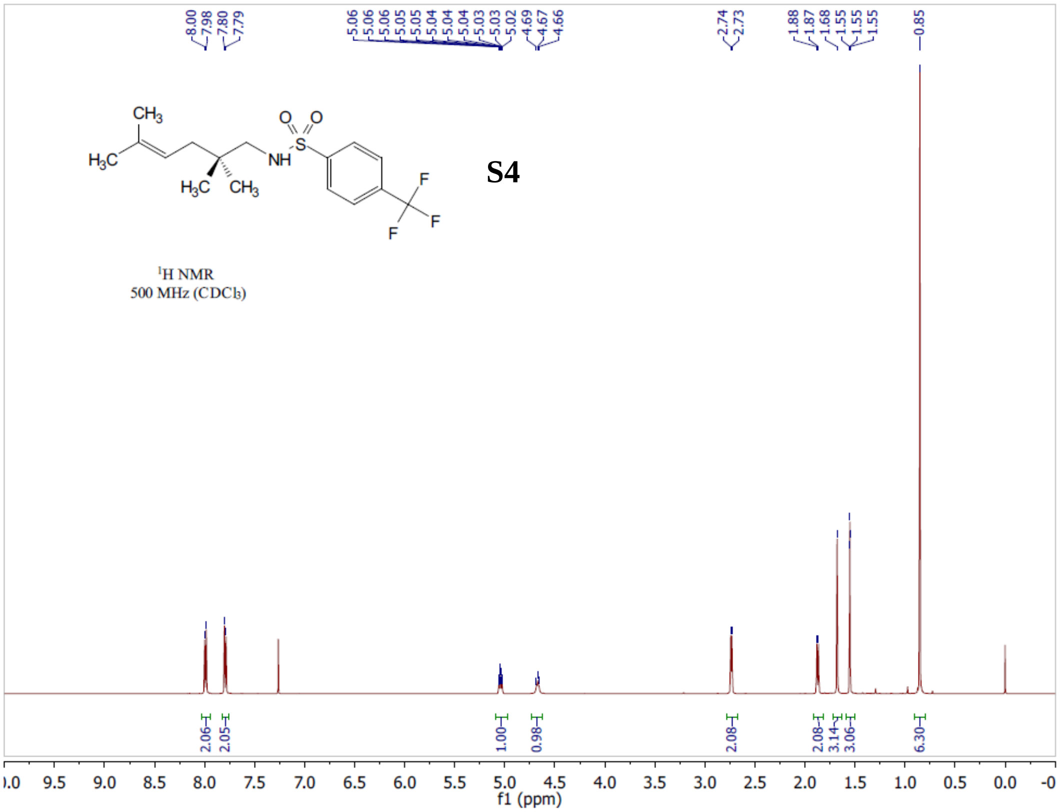
134.2
132.6
129.2
127.1
119.8
53.2
37.9
35.0
26.1
24.9
18.0
CH3
H3C
O
O
S
NH
H3C
CH3
S3
13C NMR
125 MHz (CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)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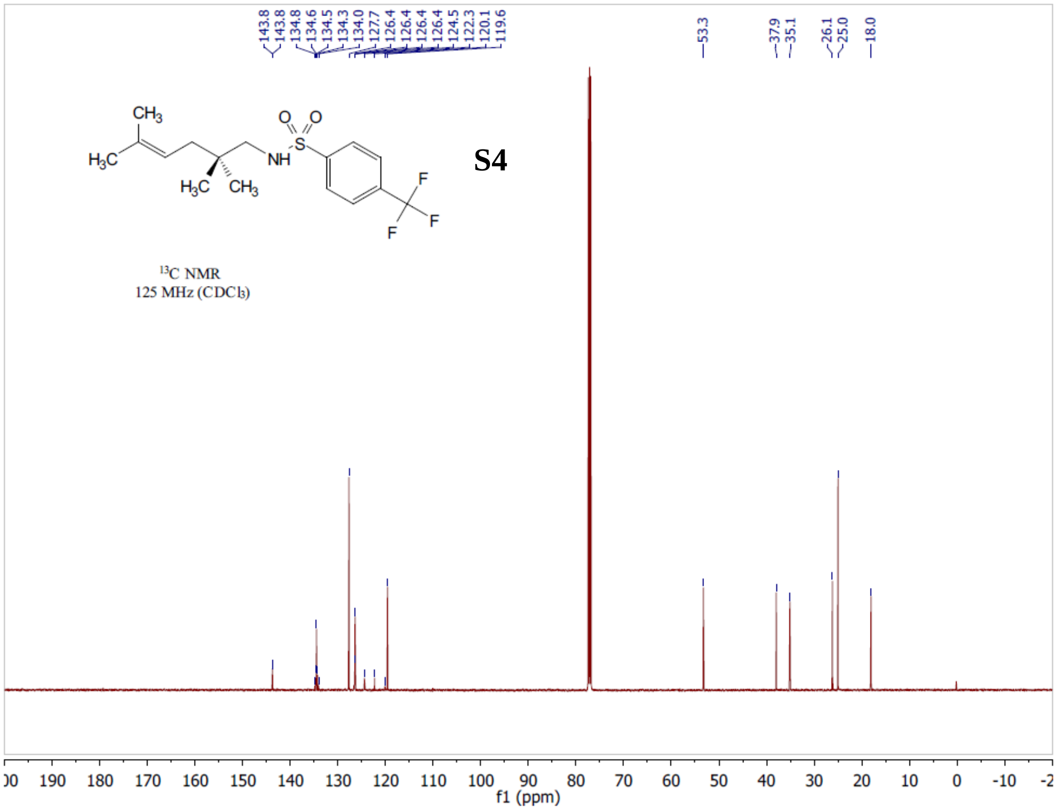
7.98
7.80
7.79
5.06
5.06
5.06
5.05
5.05
5.04
5.04
5.04
5.03
5.03
5.02
4.69
4.67
4.66
2.74
2.73
1.88
1.87
1.68
1.55
1.55
1.55
0.85
S4
^{1}H NMR
500 MHz (CDCl3)
2.06
2.05
1.00
0.98
2.08
2.08
3.14
3.06
6.30
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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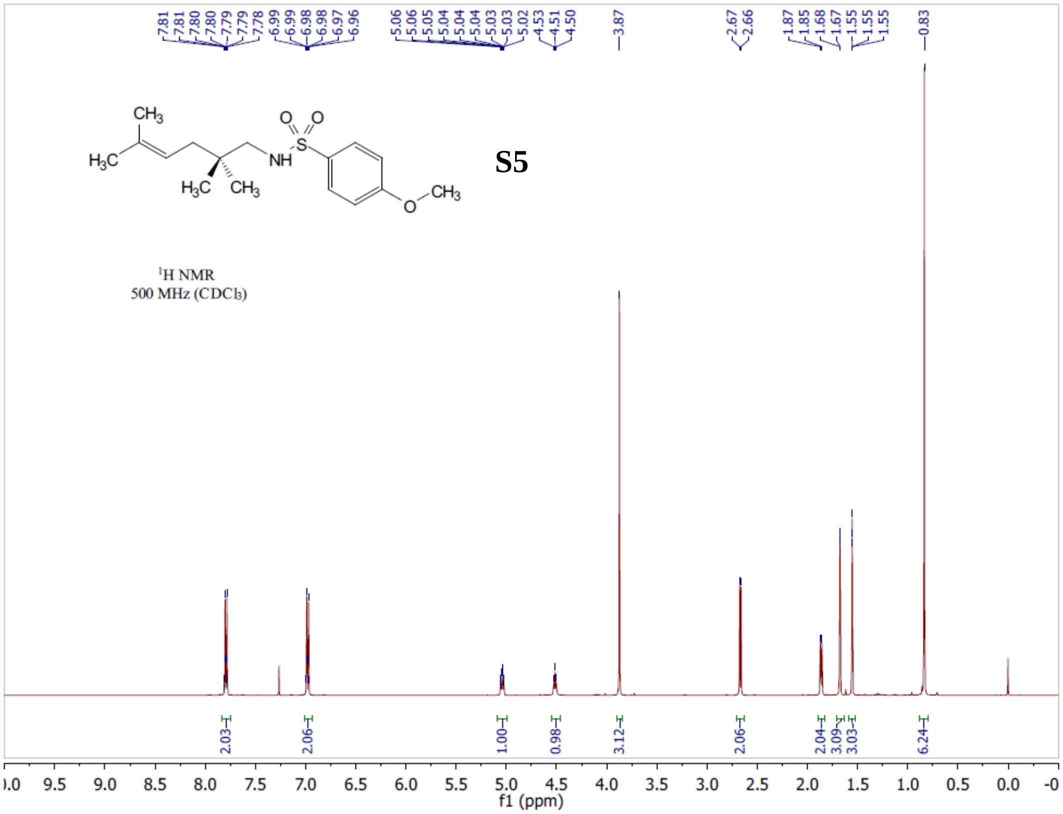
143.8
134.8
134.6
134.5
134.3
134.0
127.7
126.4
126.4
126.4
126.4
124.5
122.3
120.1
119.6
53.3
37.9
35.1
26.1
25.0
18.0
S4
^{13}C NMR
125 MHz (CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.81
7.80
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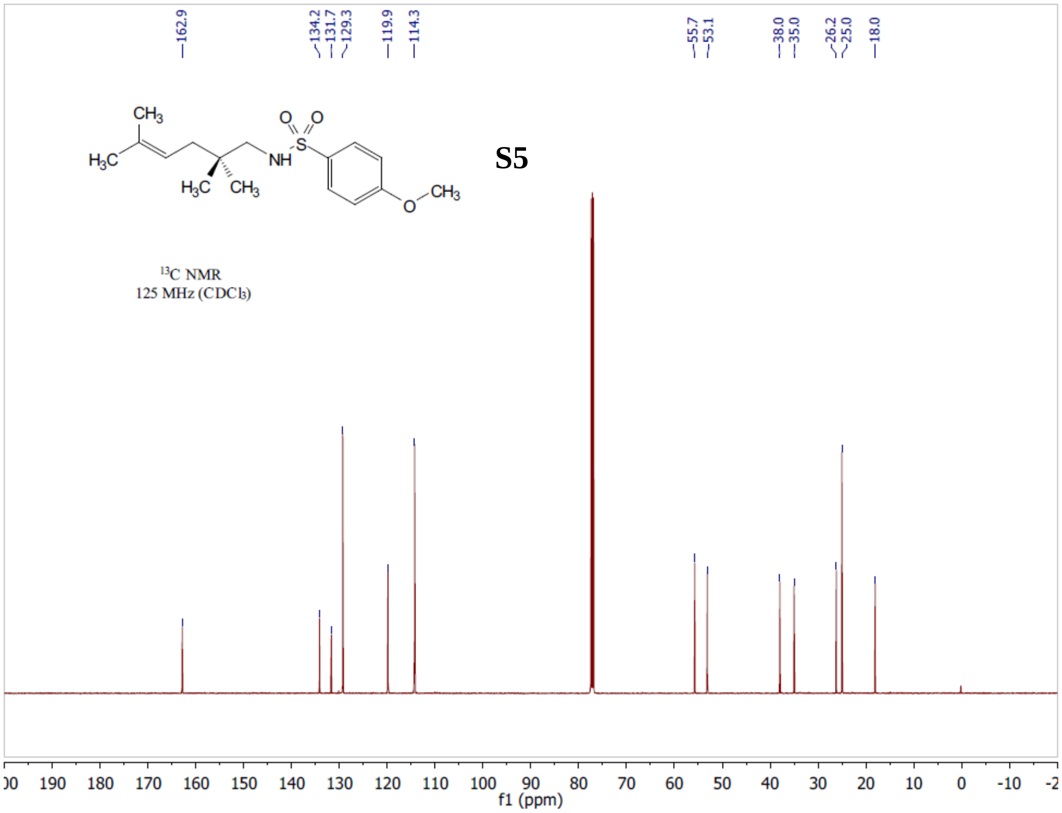
7.79
7.79
7.78
6.99
6.99
6.98
6.98
6.97
6.96
5.06
5.06
5.05
5.04
5.04
5.04
5.03
5.03
5.02
4.53
4.51
4.50
3.87
2.67
2.66
1.87
1.85
1.68
1.67
1.55
1.55
1.55
0.83
CH3
H3C
O
O
S
NH
H3C
CH3
O
CH3
S5
1H NMR
500 MHz (CDCl3)
2.03
2.06
1.00
0.98
3.12
2.06
2.04
3.09
3.03
6.24
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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129.3
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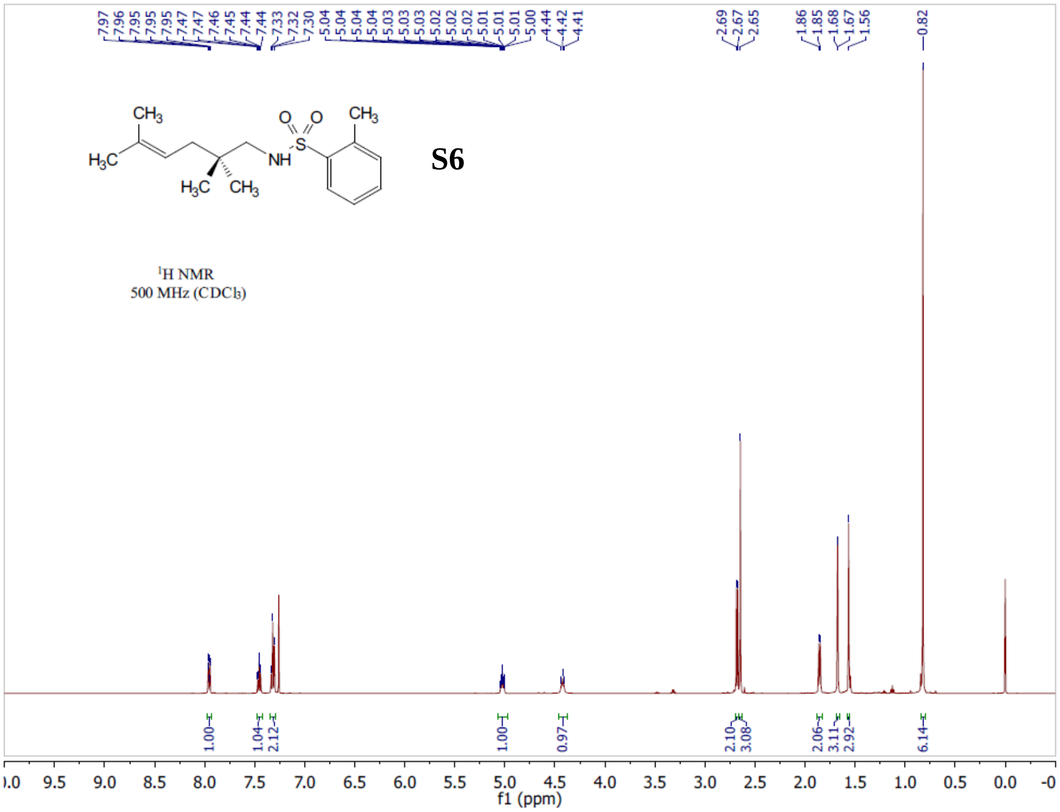
26.2
25.0
18.0
CH3
H3C
O
O
S
NH
H3C
CH3
O
CH3
S5
13C NMR
125 MHz (CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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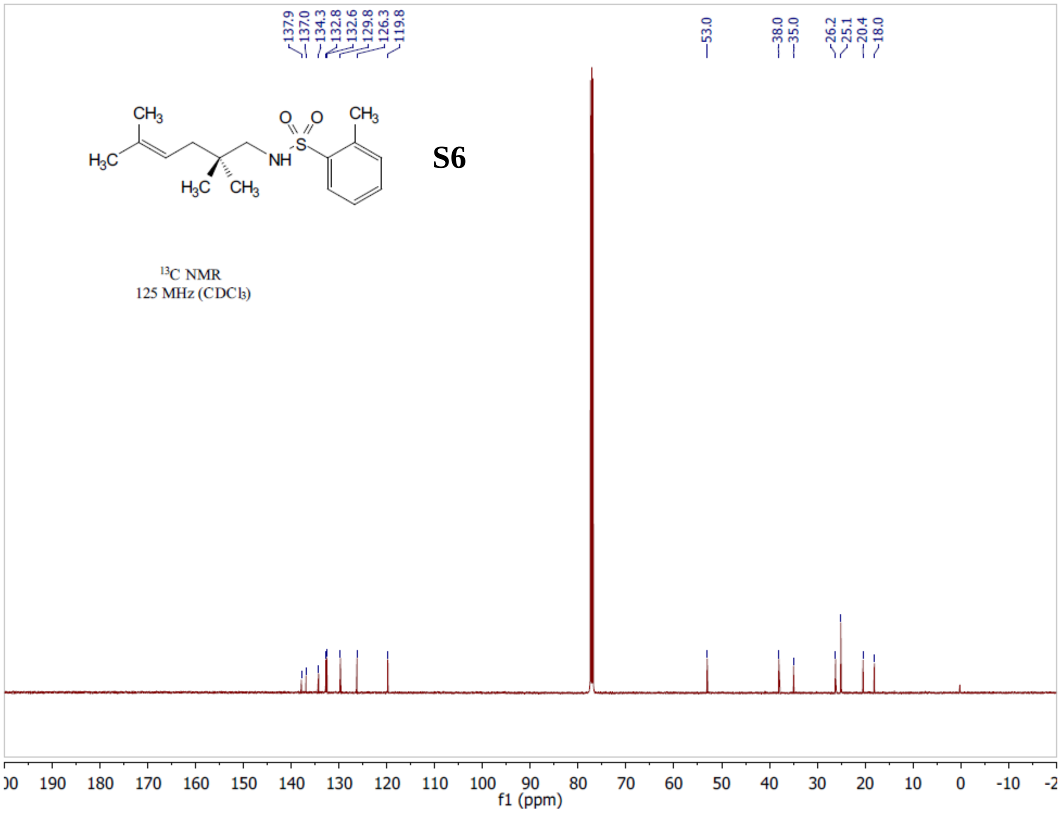
7.32
7.30
5.04
5.04
5.04
5.04
5.03
5.03
5.03
5.02
5.02
5.01
5.01
5.01
5.00
4.44
4.42
4.41
2.69
2.67
2.65
1.86
1.85
1.68
1.67
1.56
0.82
CH3
O
O
CH3
S
H3C
NH
H3C
CH3
S6
1H NMR
500 MHz (CDCl3)
1.00
1.04
2.12
1.00
0.97
2.10
3.08
2.06
3.11
2.92
6.14
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)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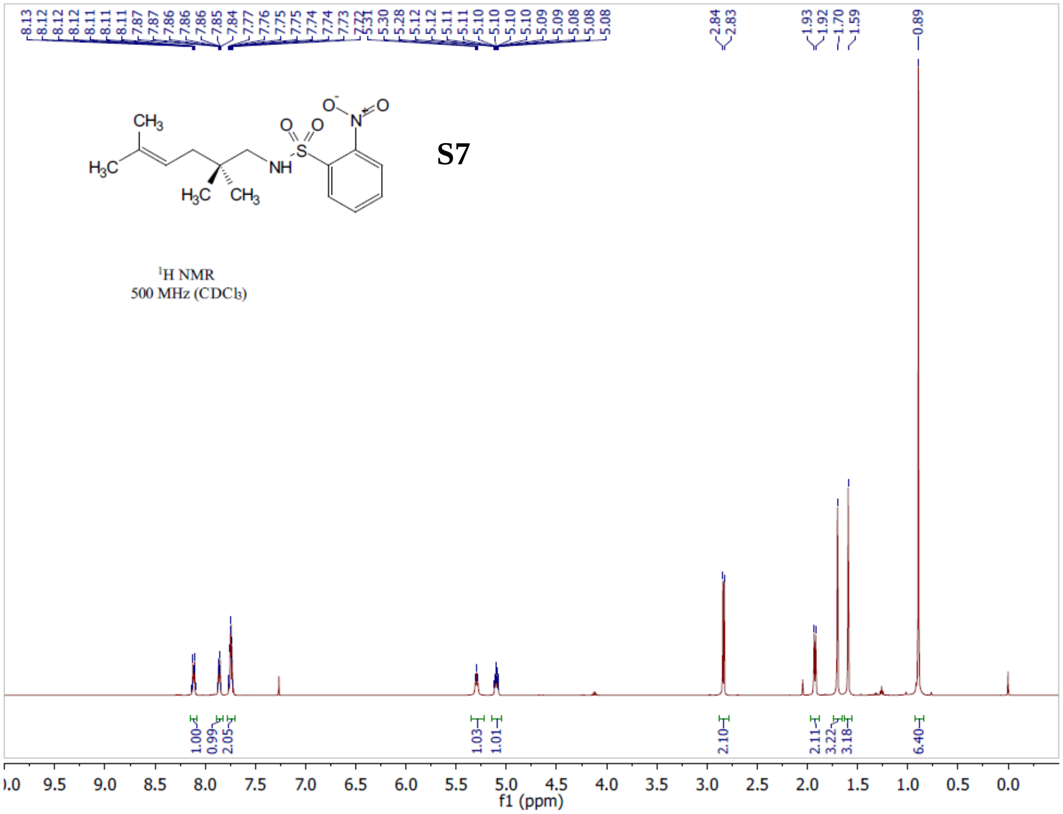
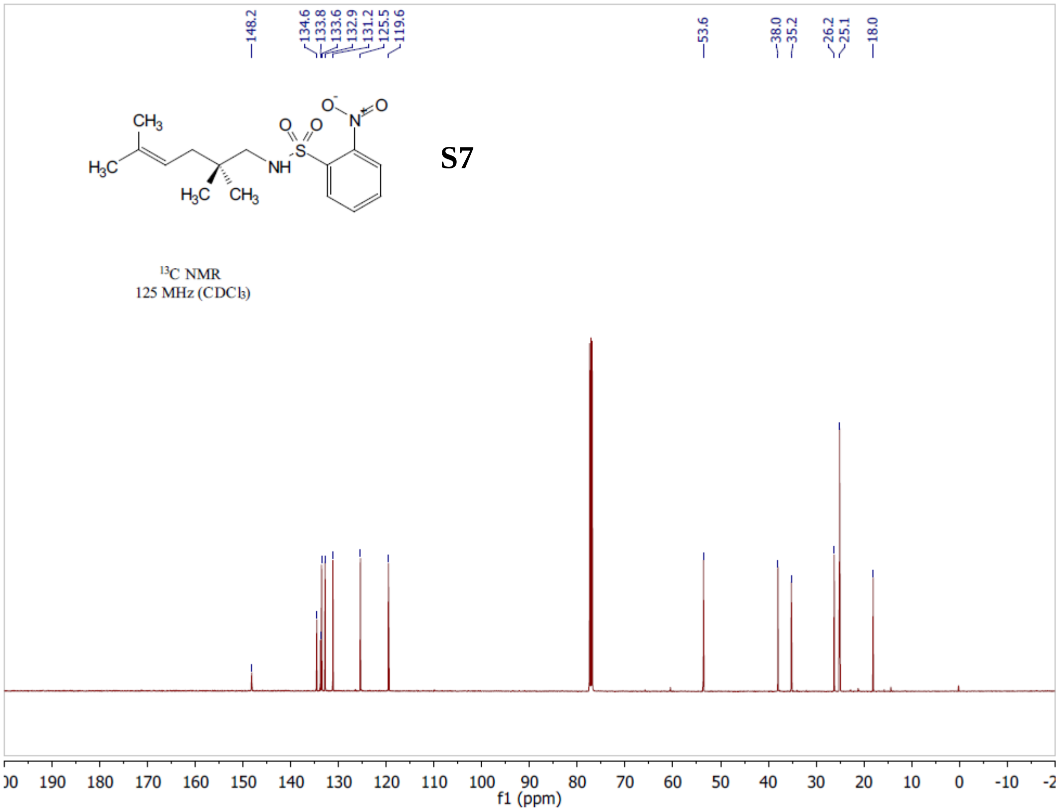
132.6
129.8
126.3
119.8
53.0
38.0
35.0
26.2
25.1
20.4
18.0
CH3
O
O
CH3
S
H3C
NH
H3C
CH3
S6
13C NMR
125 MHz (CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)



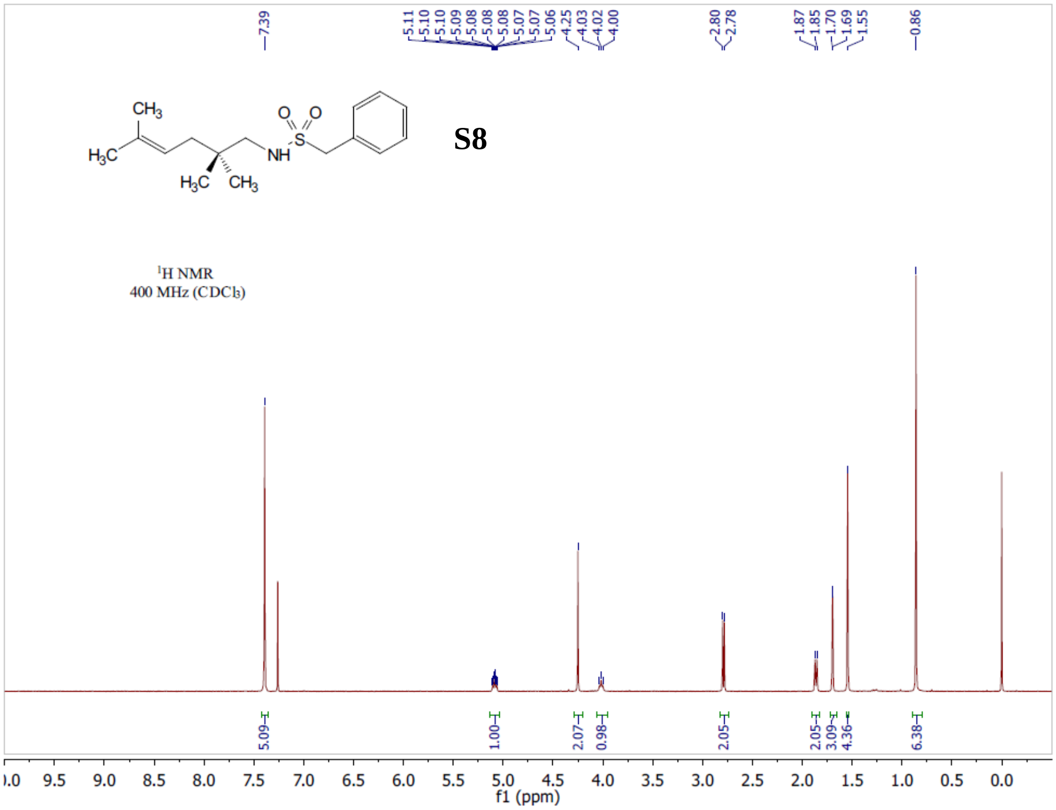
S7

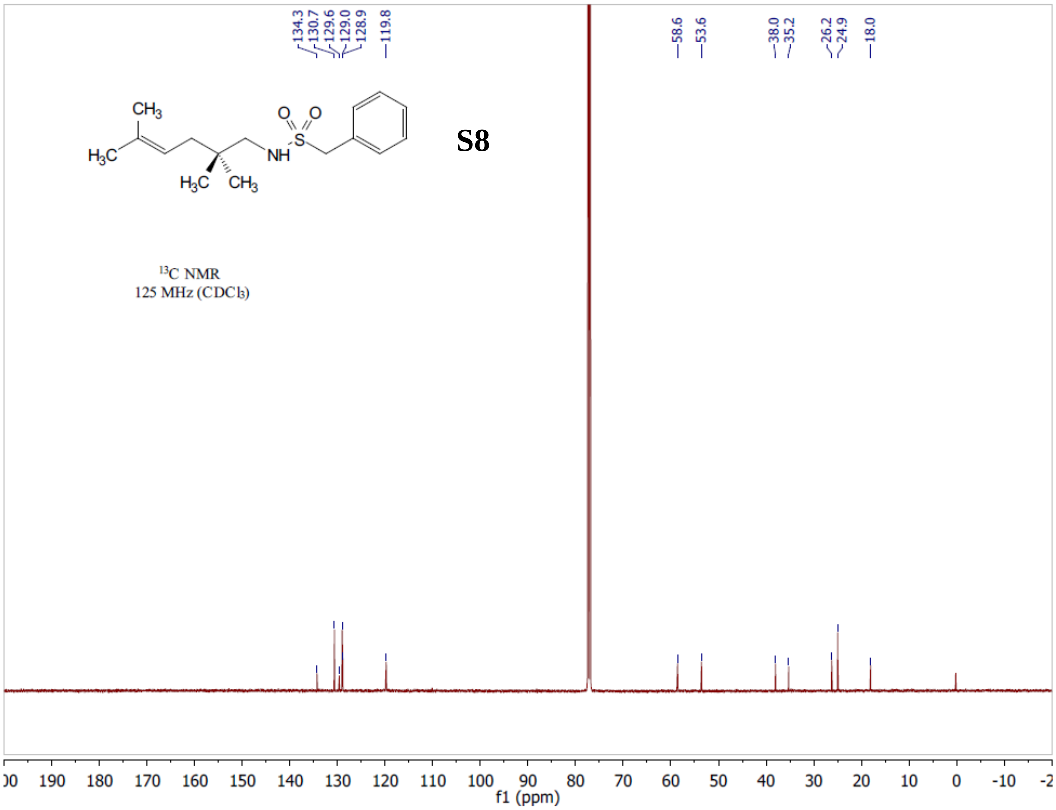
^1H NMR
500 MHz ($CDCl_3$)

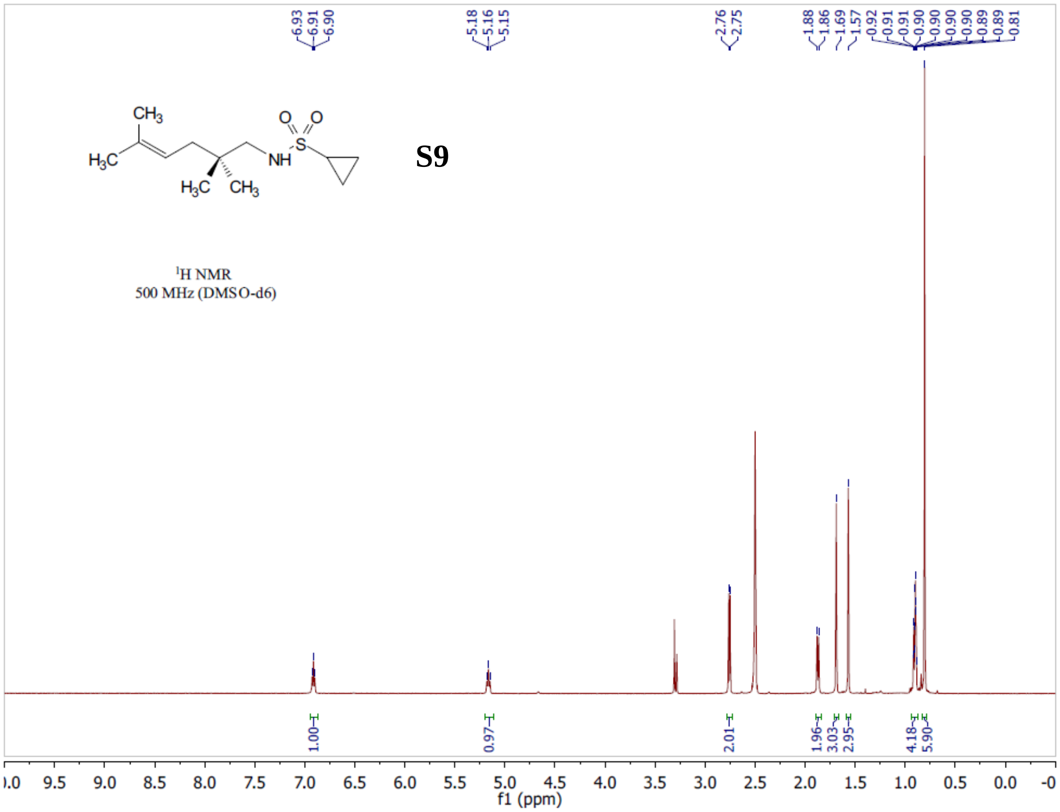


S7

^{13}C NMR
125 MHz ($CDCl_3$)

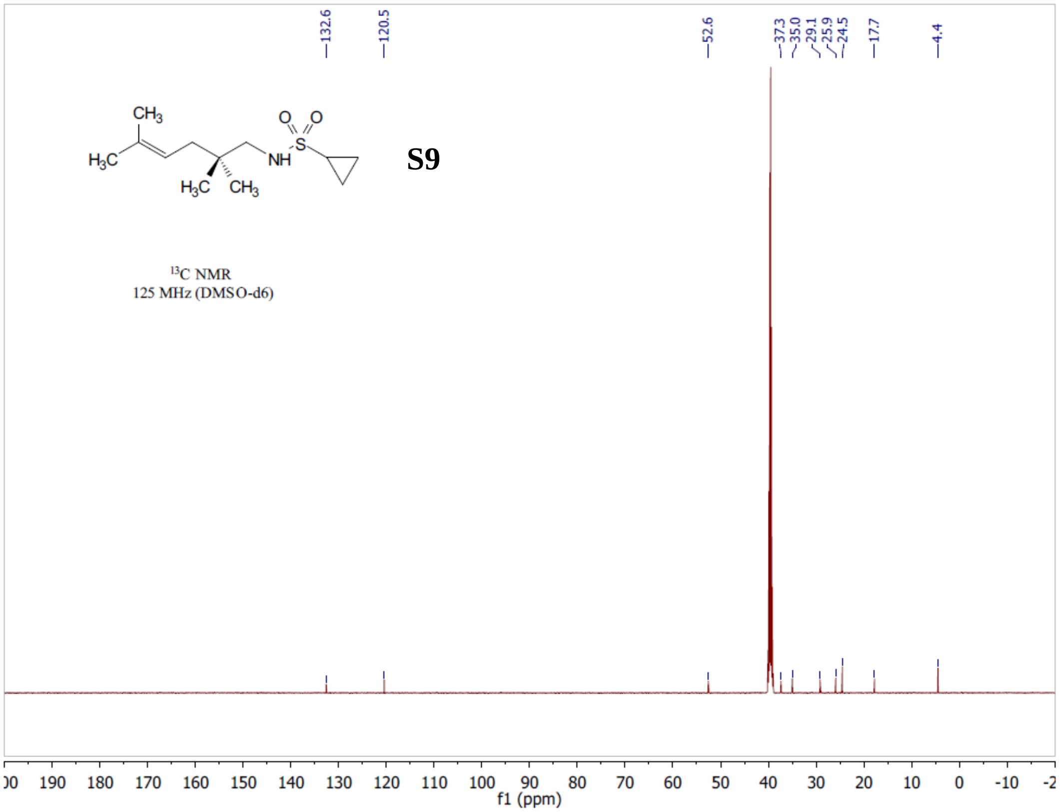

S8
^{1}H NMR
400 MHz (CDCl$_3$)
7.39
5.11
5.10
5.10
5.09
5.08
5.08
5.08
5.07
5.07
5.06
4.25
4.03
4.02
4.00
2.80
2.78
1.87
1.85
1.70
1.69
1.55
0.86
5.09
1.00
2.07
0.98
2.05
3.09
4.36
6.38
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


S8
^{13}C NMR
125 MHz (CDCl$_3$)
134.3
130.7
129.6
129.0
128.9
119.8
58.6
53.6
38.0
35.2
26.2
24.9
18.0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



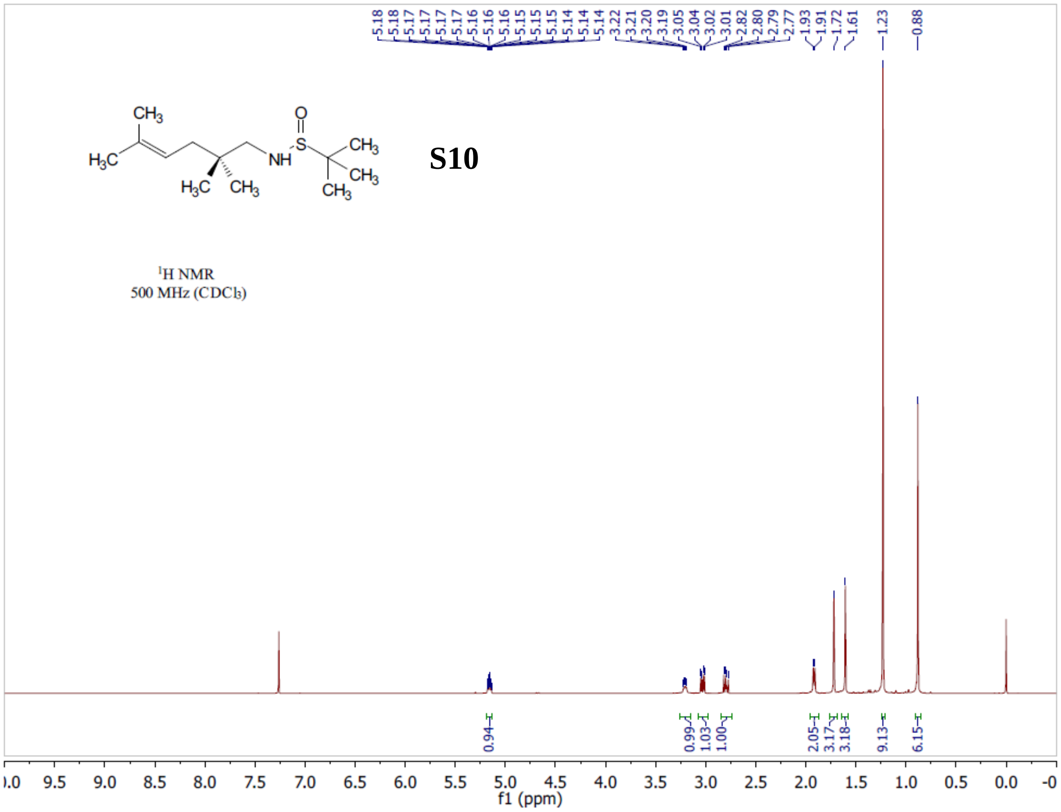
S9

^{1}H NMR
500 MHz (DMSO-d6)



S9

^{13}C NMR
125 MHz (DMSO-d6)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5.17
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5.16
5.16
5.16
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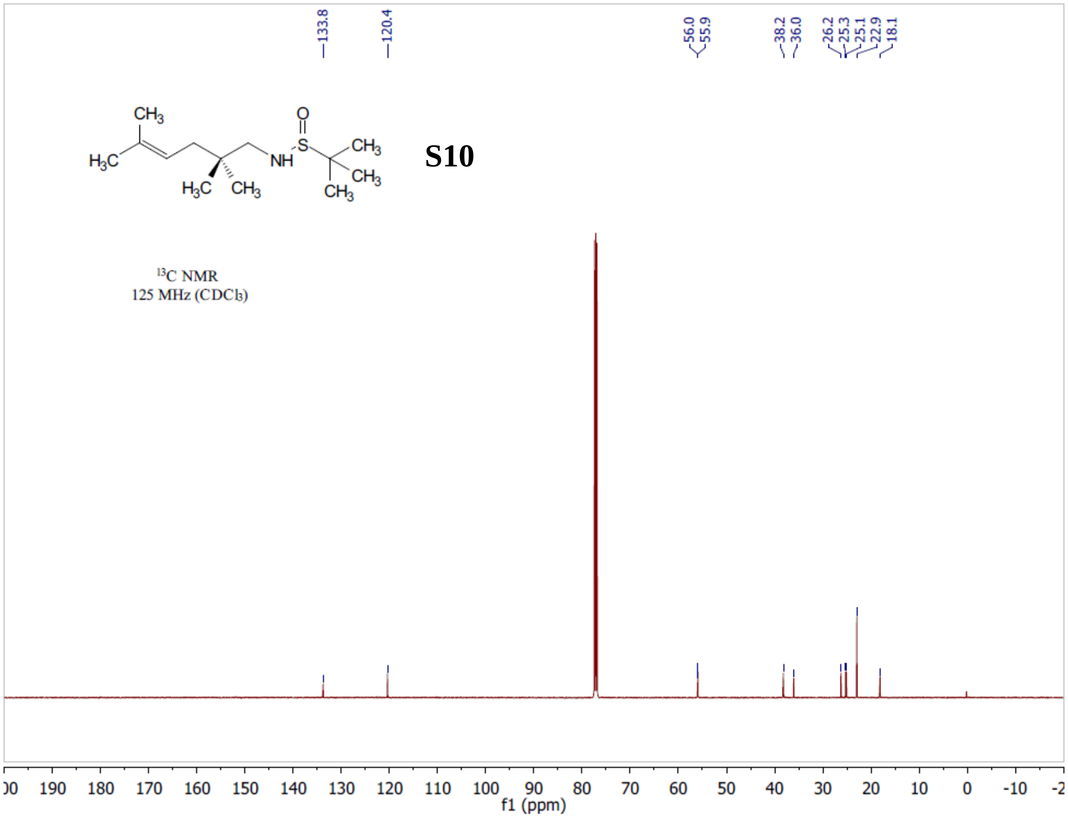
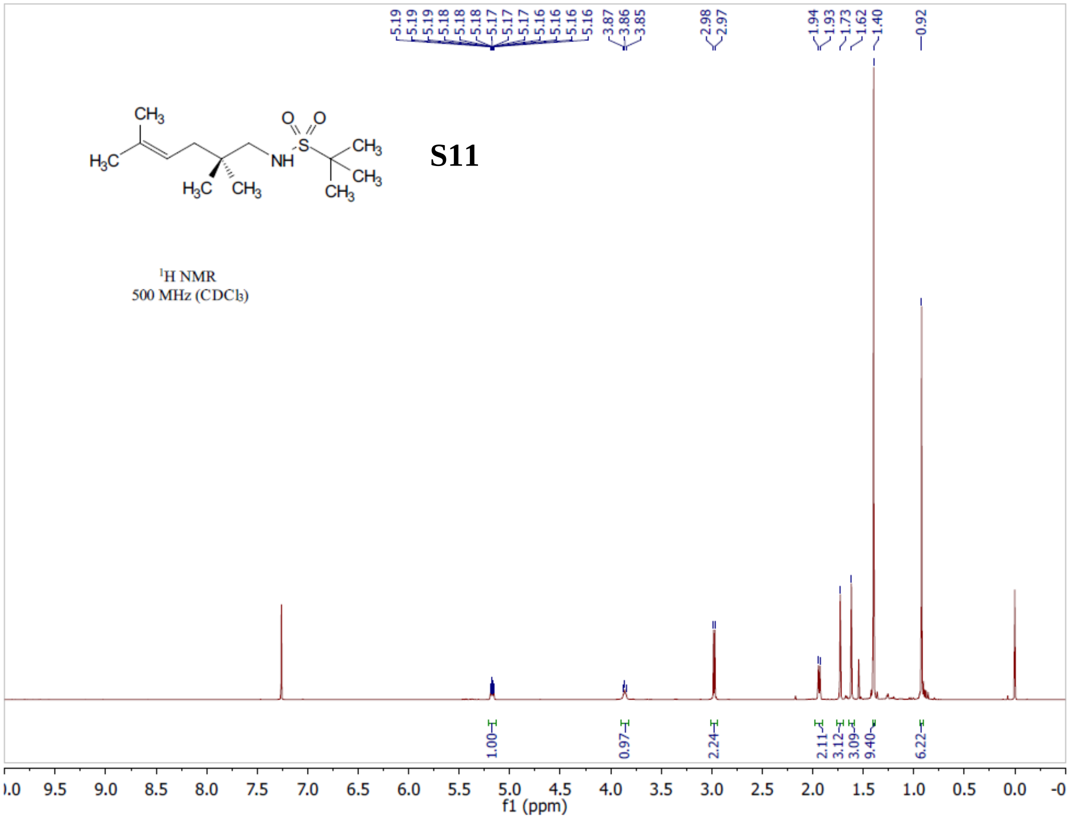
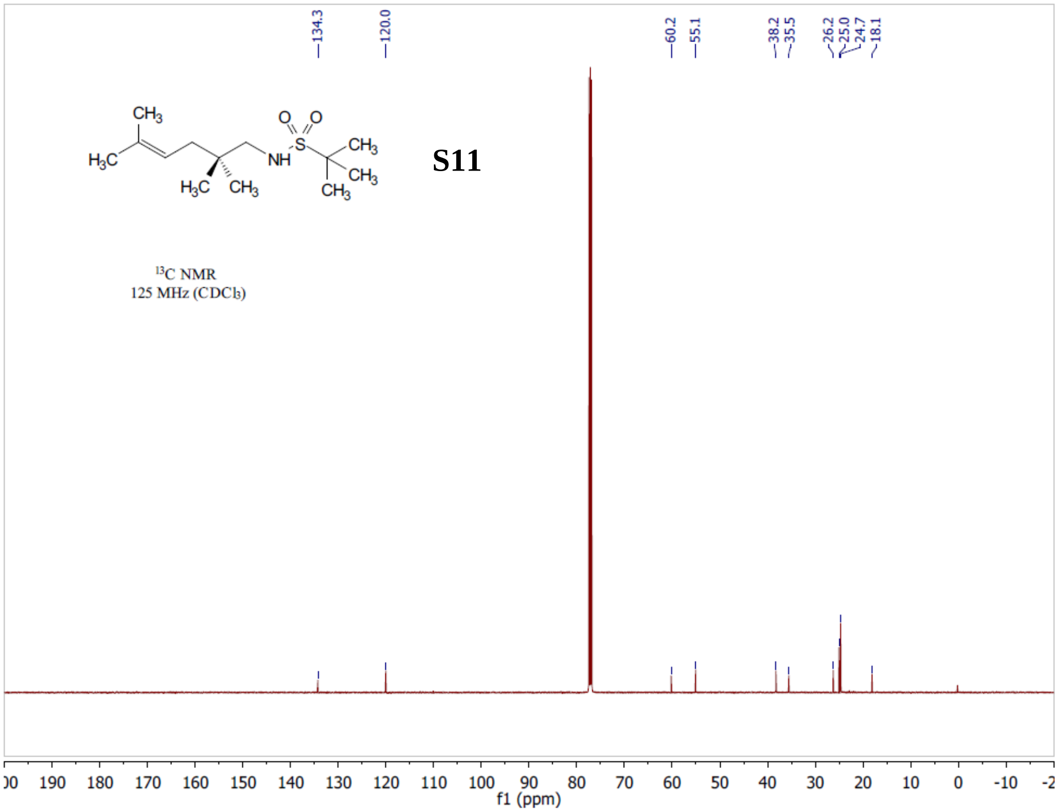
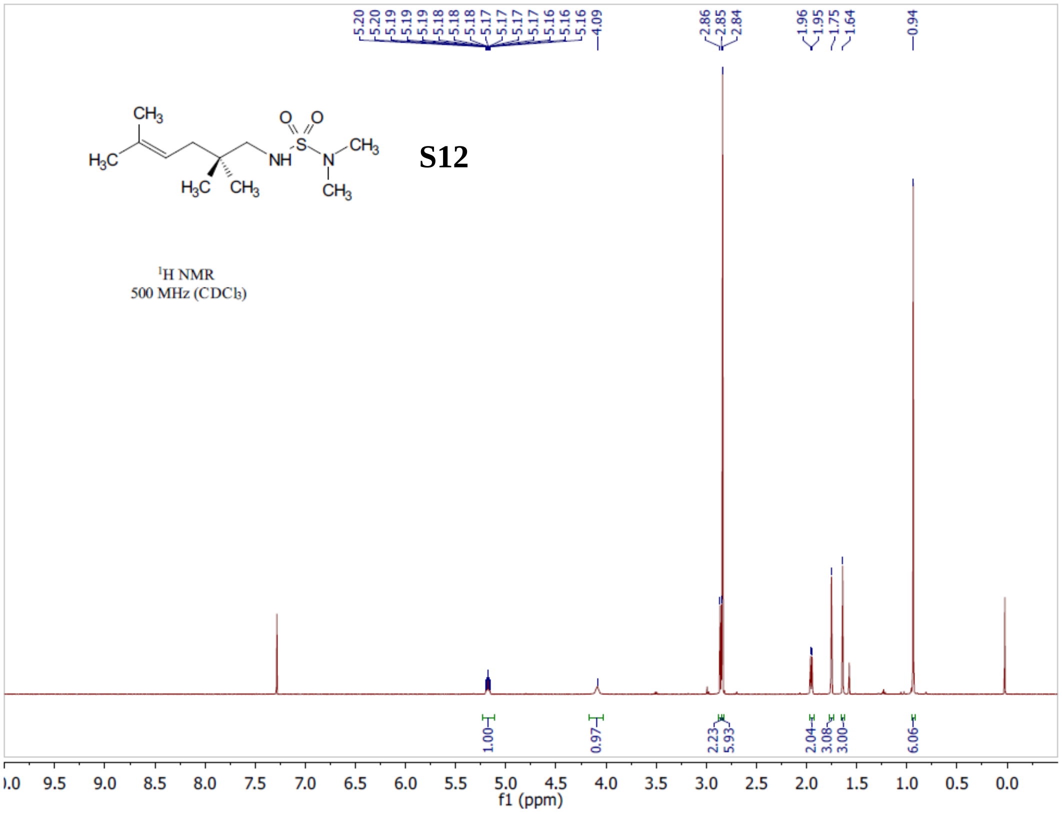
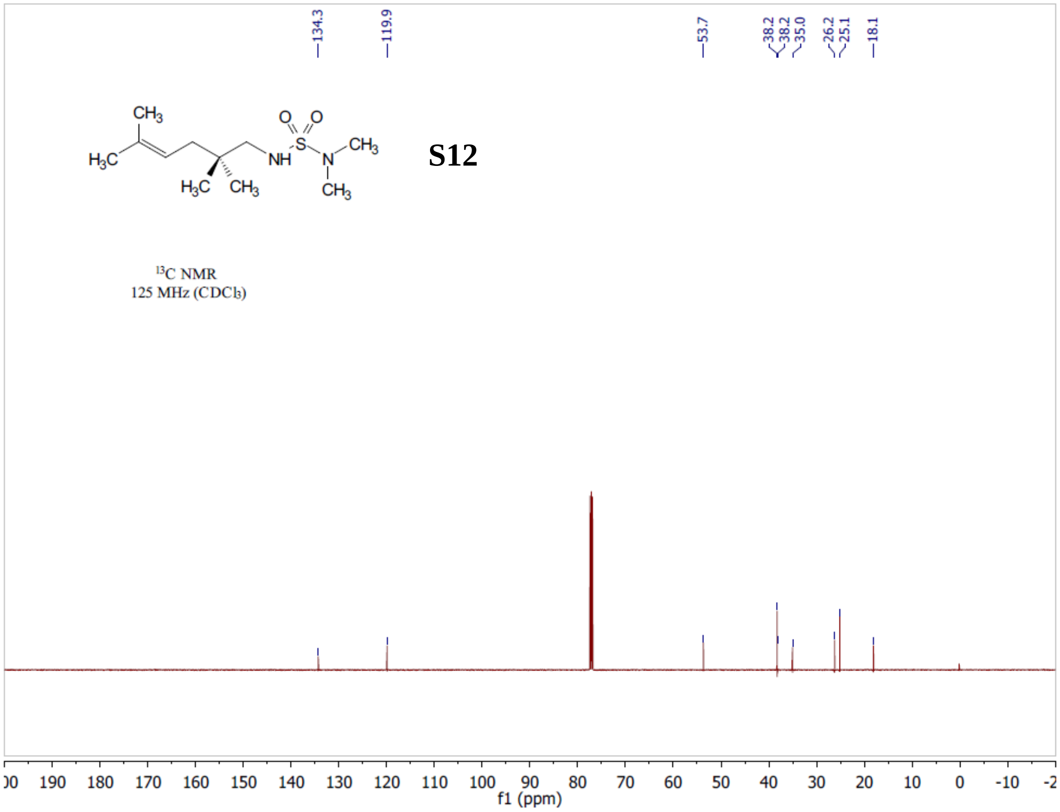
5.15
5.15
5.14
5.14
5.14
3.22
3.21
3.20
3.19
3.05
3.04
3.02
3.01
2.82
2.80
2.79
2.77
1.93
1.91
1.72
1.61
1.23
0.88
CH3
H3C
H3C
CH3
NH
O
S
CH3
CH3
CH3
S10
1H NMR
500 MHz (CDCl3)
0.94
0.99
1.03
1.00
2.05
3.17
3.18
9.13
6.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

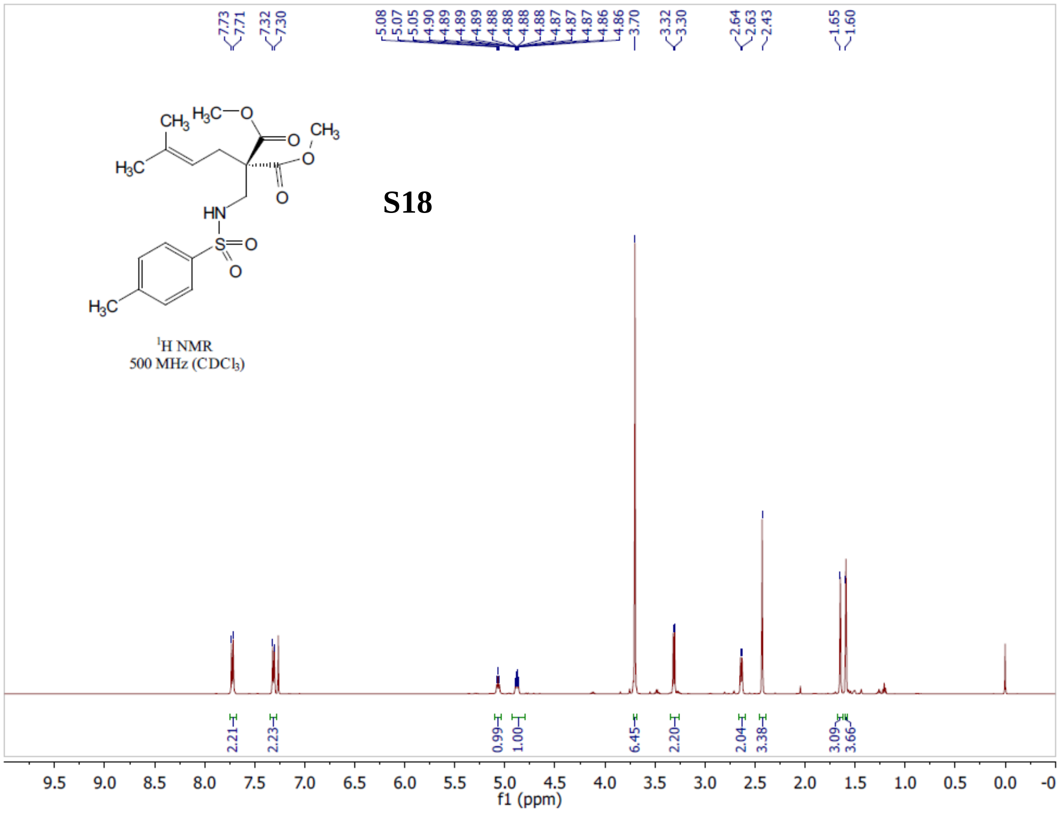

133.8
120.4
56.0
55.9
38.2
36.0
26.2
25.3
25.1
22.9
18.1
CH3
H3C
H3C
CH3
NH
O
S
CH3
CH3
CH3
S10
13C NMR
125 MHz (CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

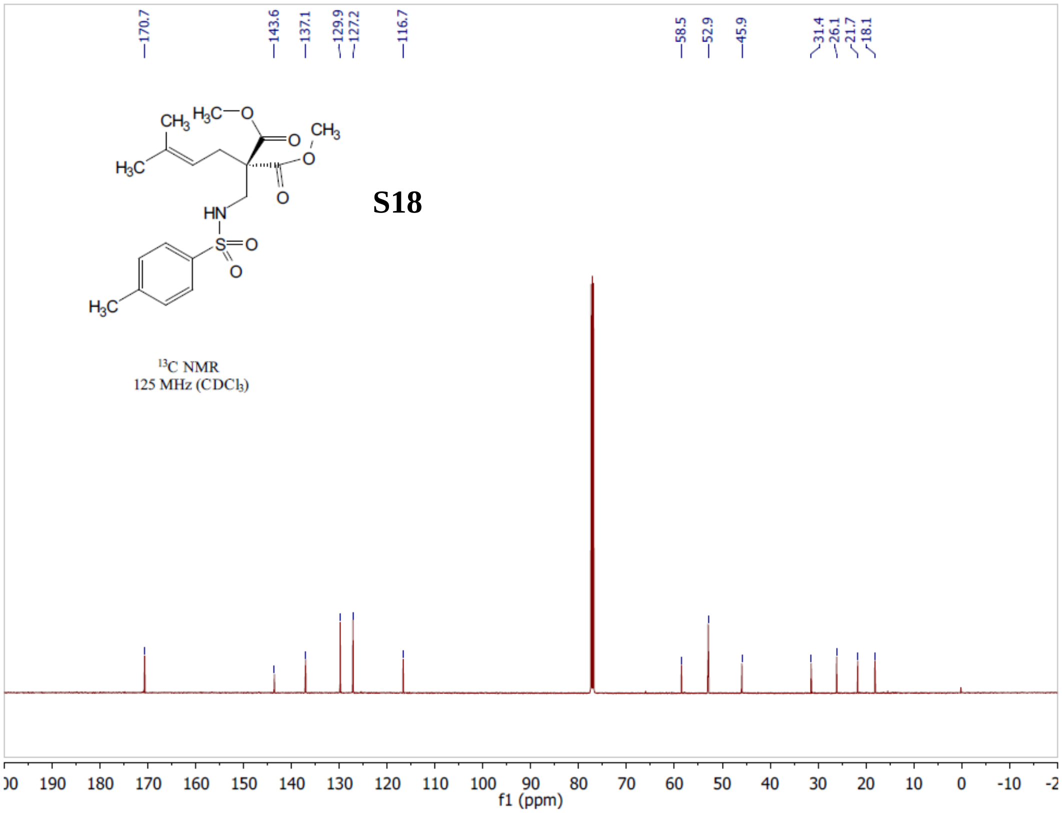

5.19
5.19
5.19
5.18
5.18
5.17
5.17
5.17
5.16
5.16
5.16
3.87
3.86
3.85
2.98
2.97
1.94
1.93
1.73
1.62
1.40
0.92
S11
¹H NMR
500 MHz (CDCl₃)
1.00
0.97
2.24
2.11
3.12
3.09
9.40
6.22
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

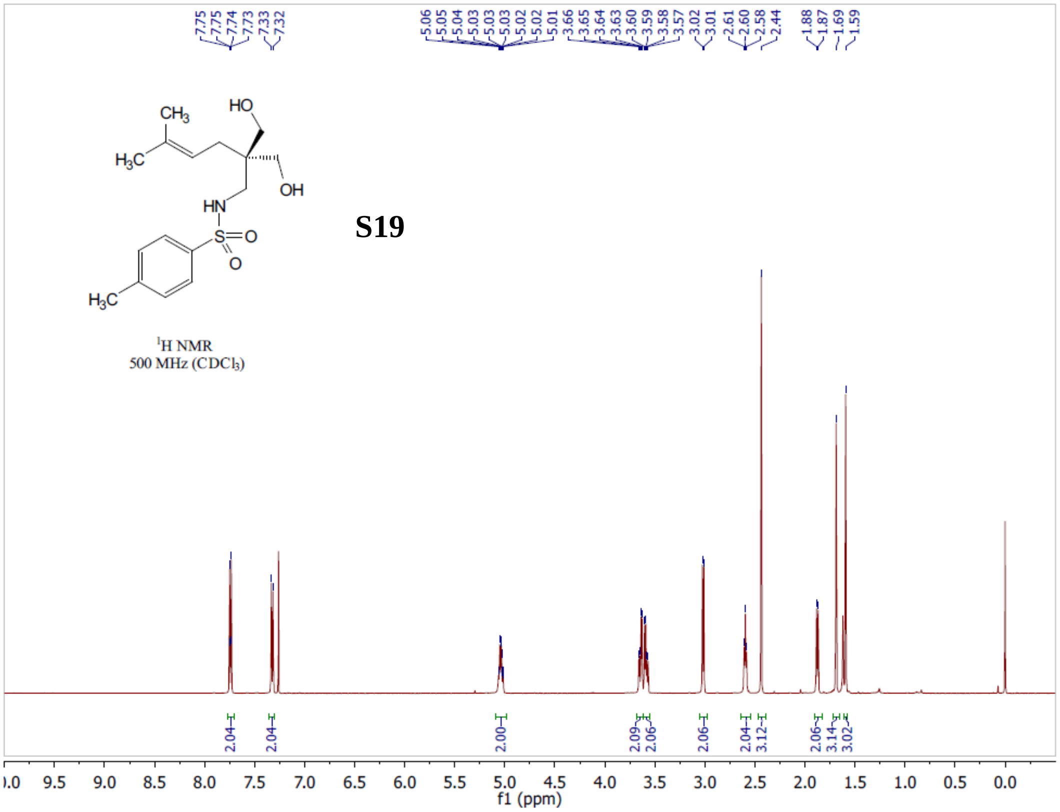

134.3
120.0
60.2
55.1
38.2
35.5
26.2
25.0
24.7
18.1
S11
¹³C NMR
125 MHz (CDCl₃)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

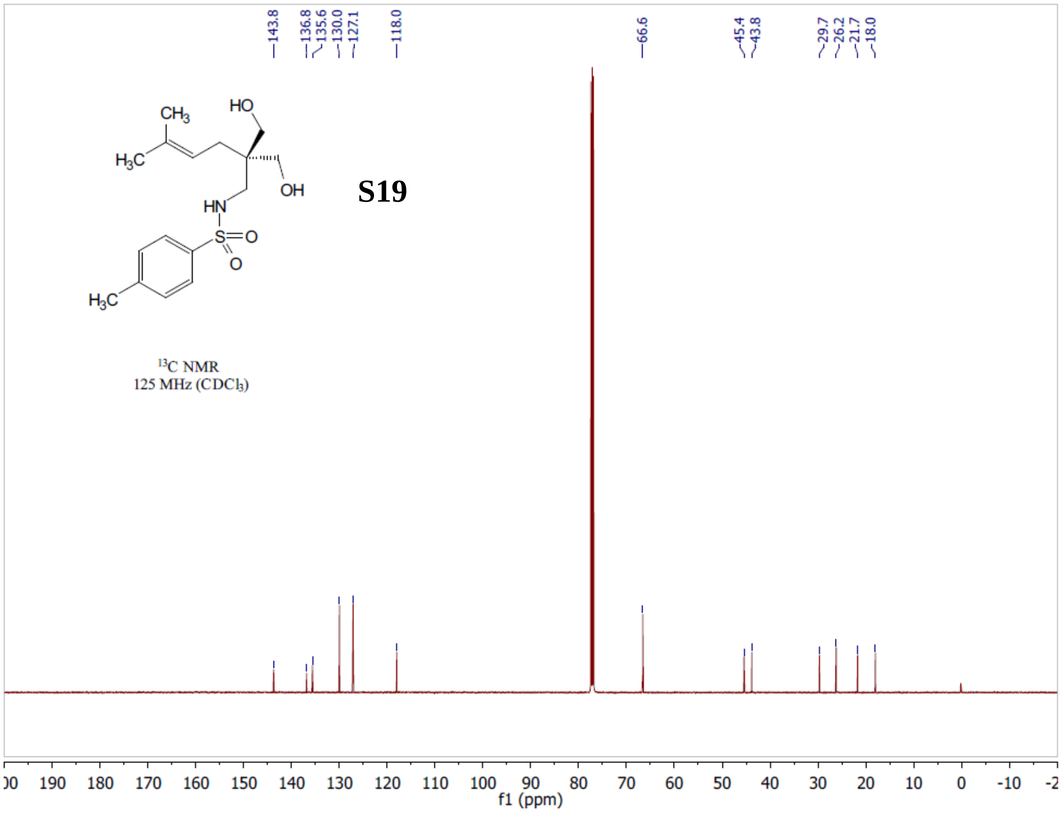

5.20
5.20
5.19
5.19
5.19
5.19
5.18
5.18
5.18
5.17
5.17
5.17
5.17
5.16
5.16
4.09
2.86
2.85
2.84
1.96
1.95
1.75
1.64
0.94
S12
^{1}H NMR
500 MHz (CDCl$_3$)
1.00
0.97
2.23
5.93
2.04
3.08
3.00
6.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

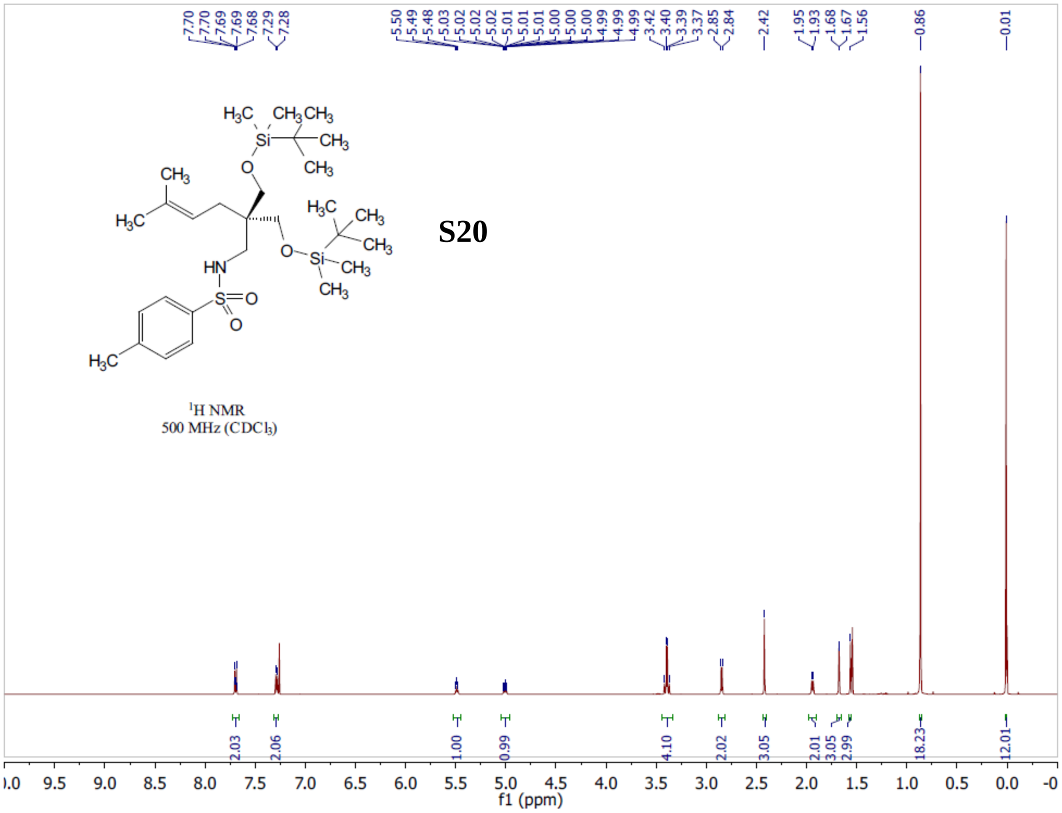

134.3
119.9
53.7
38.2
38.2
35.0
26.2
25.1
18.1
S12
^{13}C NMR
125 MHz (CDCl$_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.73
7.71
7.32
7.30
5.08
5.07
5.05
4.90
4.89
4.89
4.89
4.88
4.88
4.88
4.88
4.87
4.87
4.87
4.86
3.70
3.32
3.30
2.64
2.63
2.43
1.65
1.60
S18
1H NMR
500 MHz (CDCl3)
2.21
2.23
0.99
1.00
6.45
2.20
2.04
3.38
3.09
3.66
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


170.7
143.6
137.1
129.9
127.2
116.7
58.5
52.9
45.9
31.4
26.1
21.7
18.1
S18
13C NMR
125 MHz (CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)

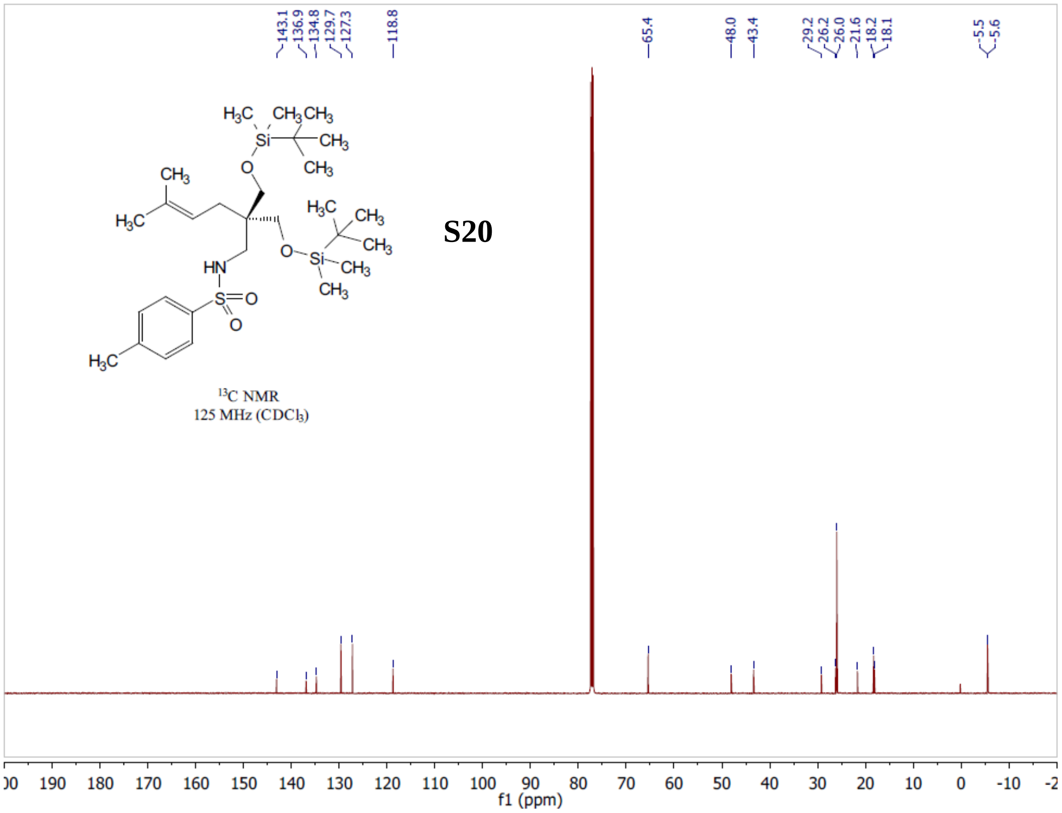

7.75
7.75
7.74
7.73
7.33
7.32
5.06
5.05
5.04
5.03
5.03
5.03
5.02
5.02
5.01
3.66
3.65
3.64
3.63
3.60
3.59
3.58
3.57
3.02
3.01
2.61
2.60
2.58
2.44
1.88
1.87
1.69
1.59
CH3
HO
H3C
OH
HN
S=O
O
H3C
S19
1H NMR
500 MHz (CDCl3)
2.04
2.04
2.00
2.09
2.06
2.06
2.04
3.12
2.06
3.14
3.02
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.8
136.8
135.6
130.0
127.1
118.0
66.6
45.4
43.8
29.7
26.2
21.7
18.0
CH3
HO
H3C
OH
HN
S=O
O
H3C
S19
13C NMR
125 MHz (CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)



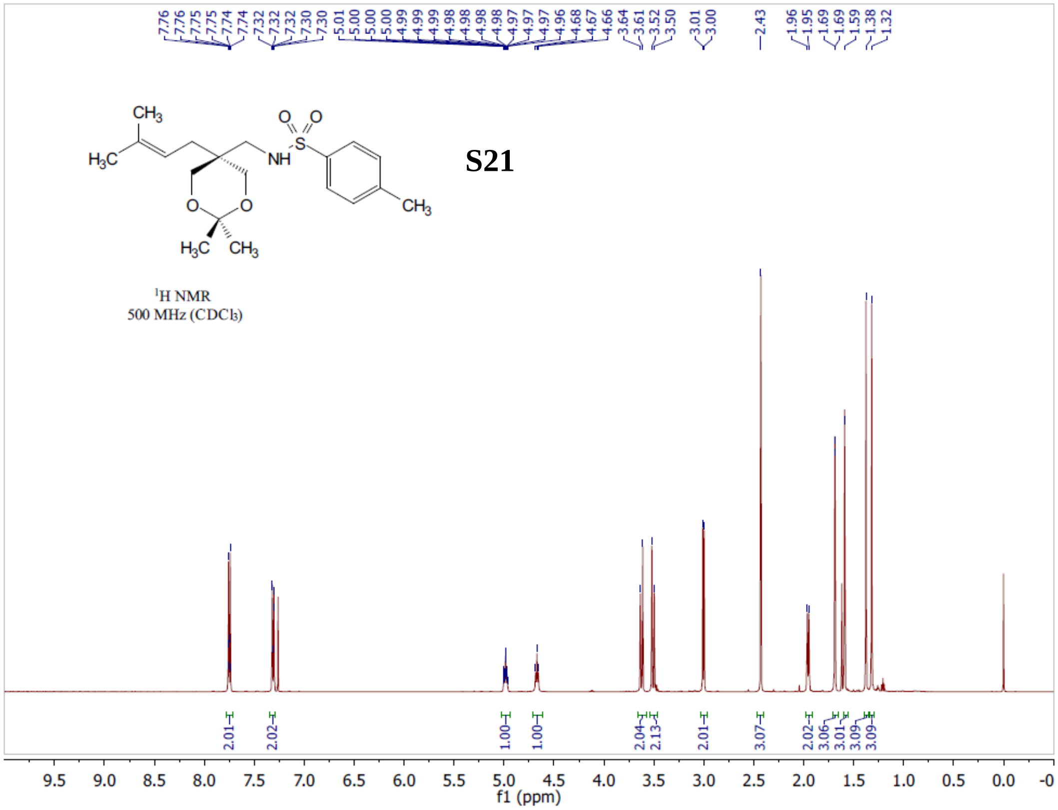
S20

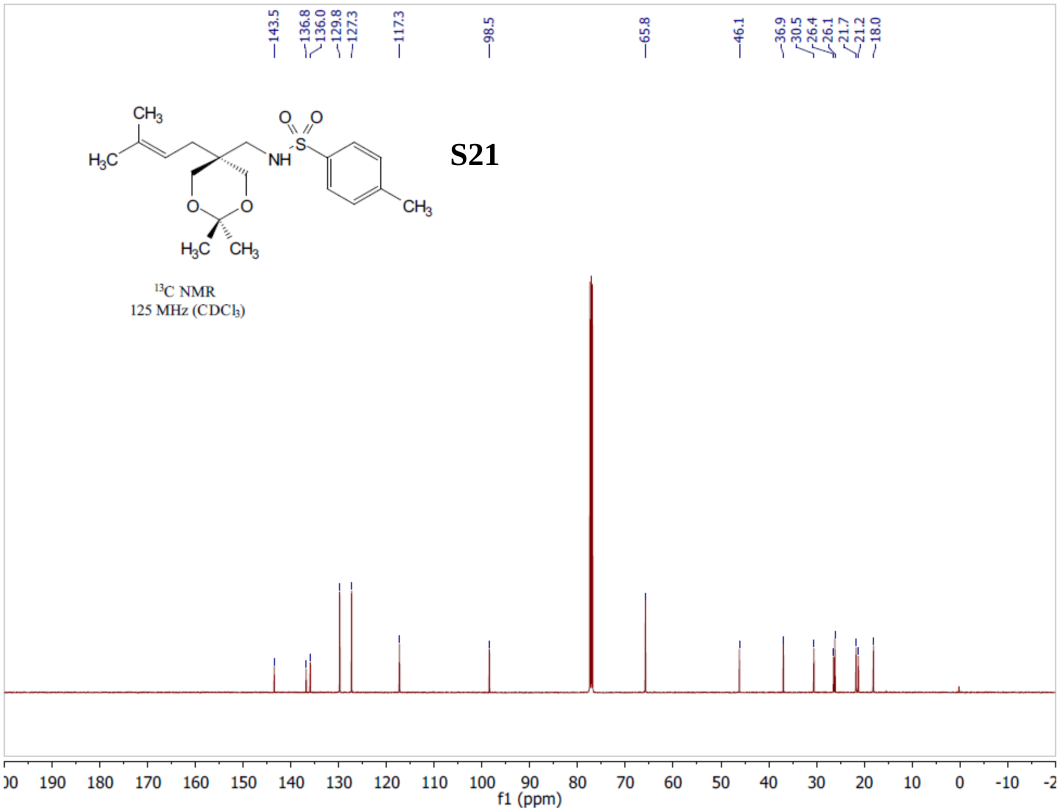
^{1}H NMR
500 MHz (CDCl$_3$)

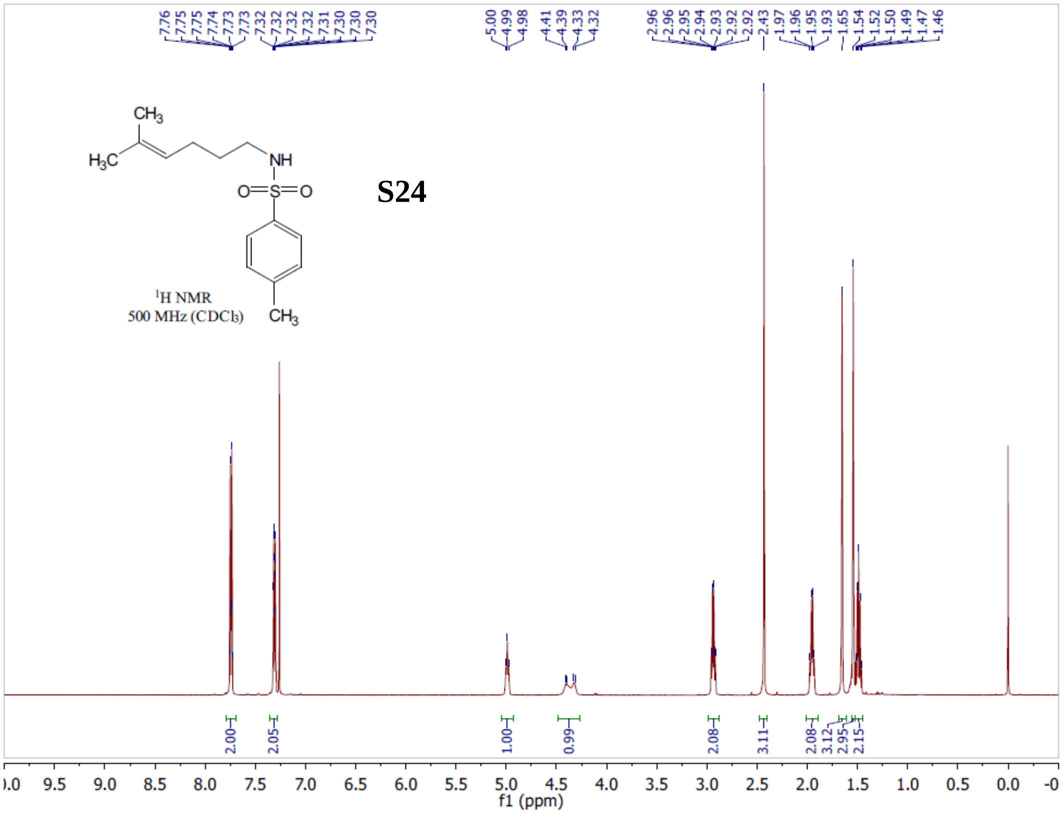


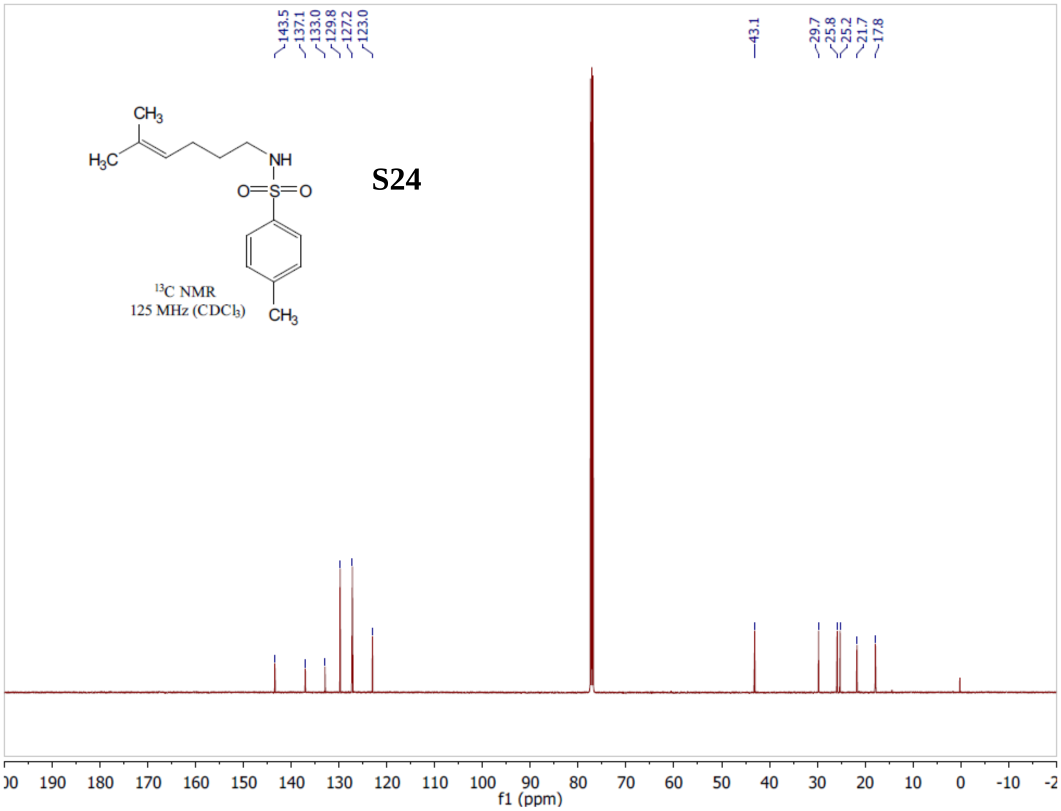
S20

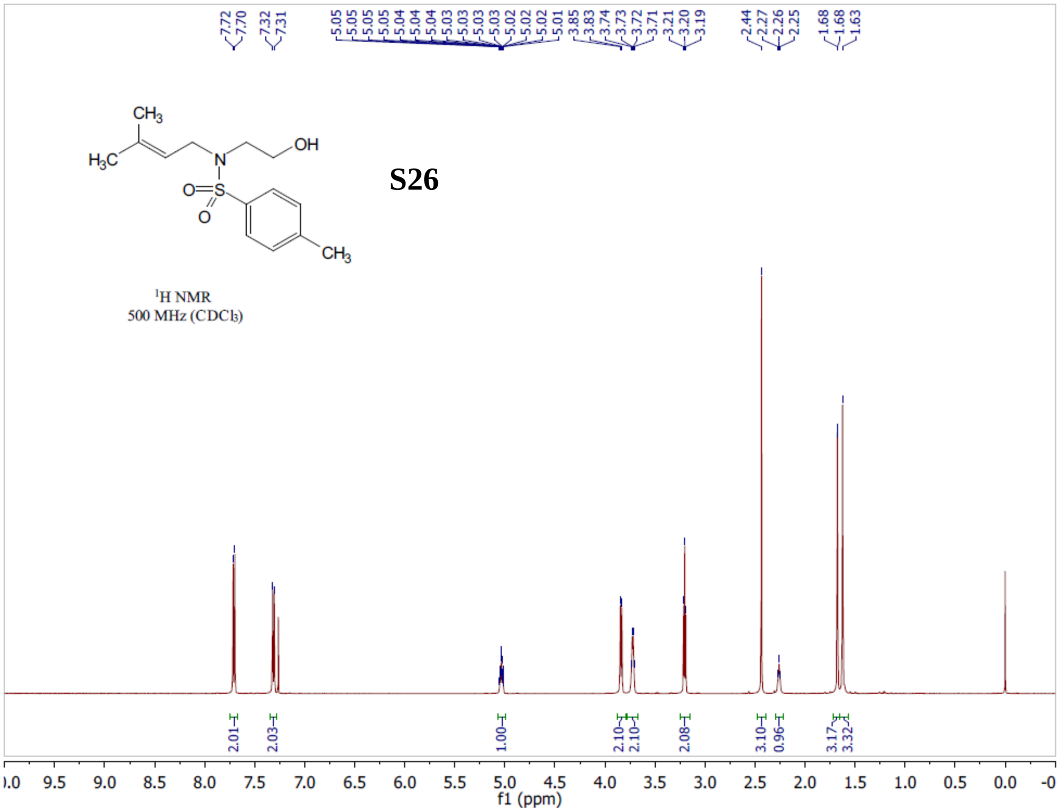
^{13}C NMR
125 MHz (CDCl$_3$)

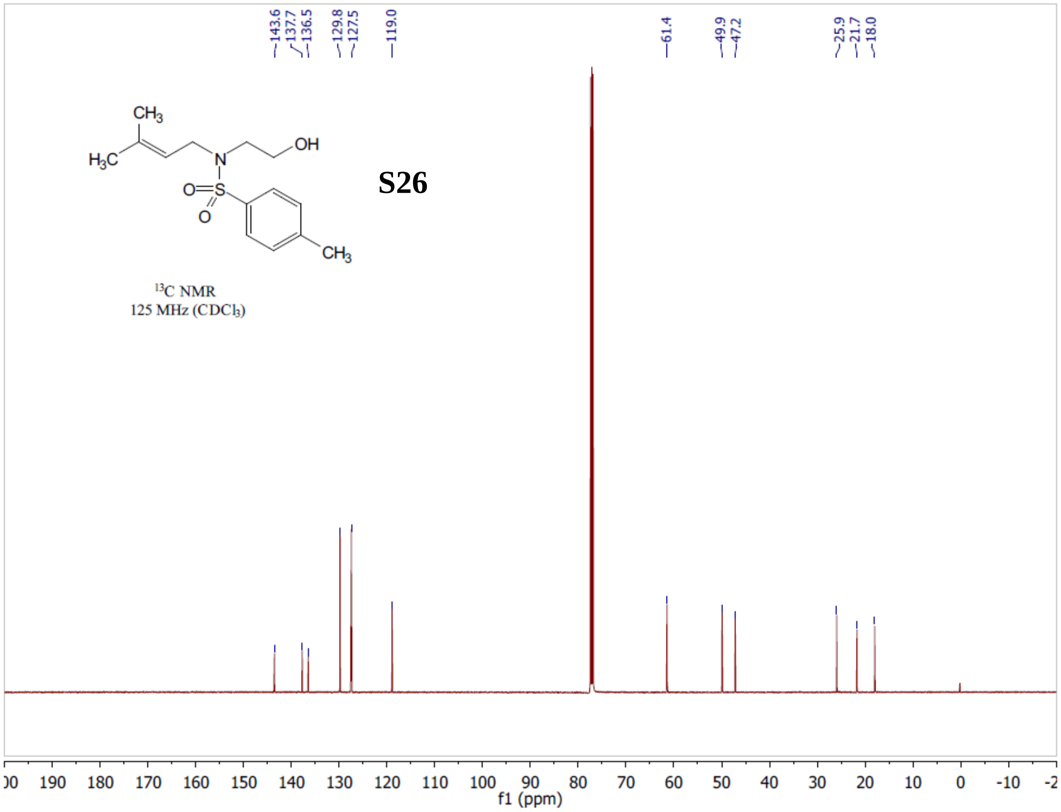

7.76 7.76 7.75 7.75 7.74 7.74 7.32 7.32 7.32 7.30 7.30 5.01 5.00 5.00 4.99 4.99 4.99 4.98 4.98 4.98 4.98 4.97 4.97 4.96 4.68 4.67 4.66 3.64 3.61 3.52 3.50 3.01 3.00 2.43 1.96 1.95 1.69 1.69 1.59 1.38 1.32
S21
CH3
H3C
O O
S
NH
CH3
O O
H3C CH3
1H NMR
500 MHz (CDCl3)
2.01 2.02 1.00 1.00 2.04 2.13 2.01 3.07 2.02 3.06 3.01 3.09 3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

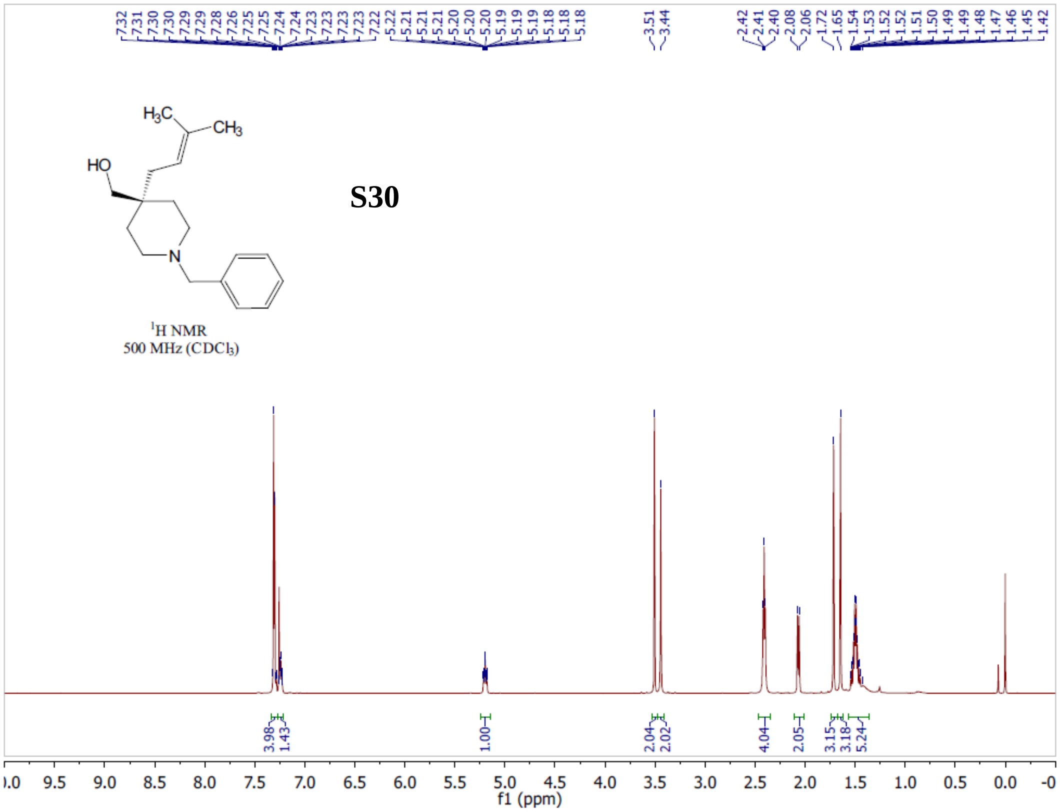

143.5 136.8 136.0 129.8 127.3 117.3 98.5 65.8 46.1 36.9 30.5 26.4 26.1 21.7 21.2 18.0
S21
CH3
H3C
O O
S
NH
CH3
O O
H3C CH3
13C NMR
125 MHz (CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

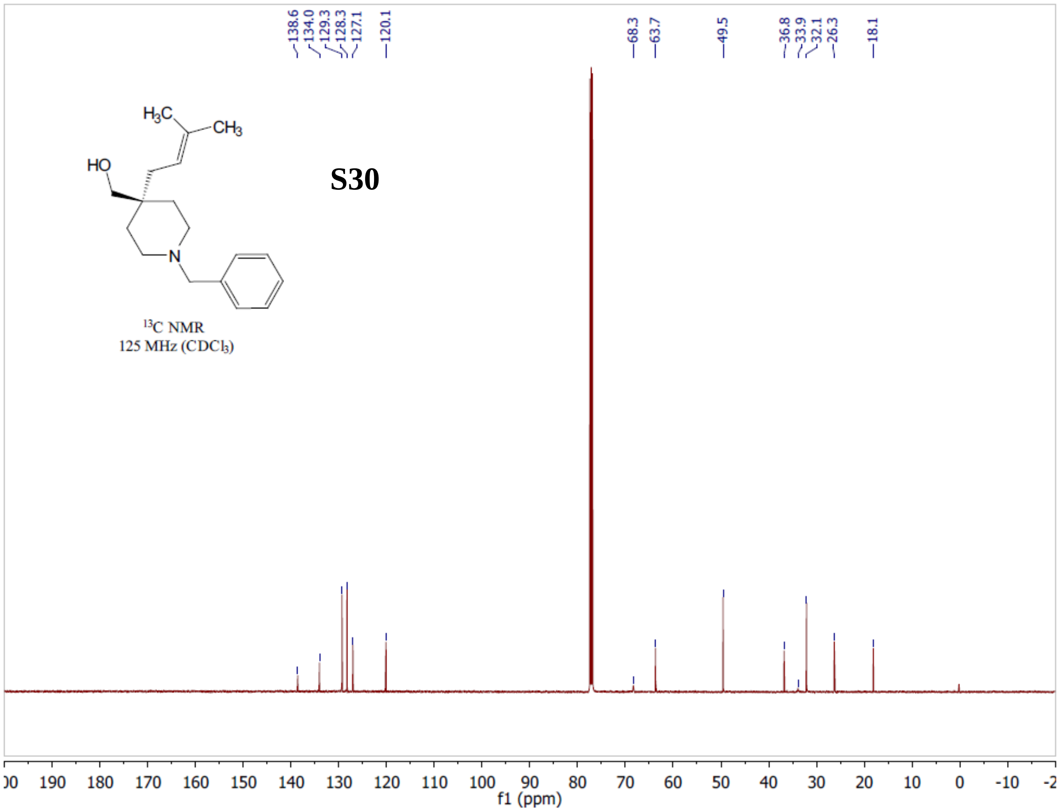

7.76
7.75
7.75
7.74
7.73
7.73
7.32
7.32
7.32
7.32
7.31
7.30
7.30
7.30
5.00
4.99
4.98
4.41
4.39
4.33
4.32
2.96
2.96
2.95
2.94
2.93
2.93
2.92
2.92
2.43
1.97
1.96
1.95
1.93
1.65
1.54
1.52
1.50
1.49
1.47
1.46
CH3
H3C
NH
O=S=O
CH3
S24
1H NMR
500 MHz (CDCl3)
2.00
2.05
1.00
0.99
2.08
3.11
2.08
3.12
2.95
2.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

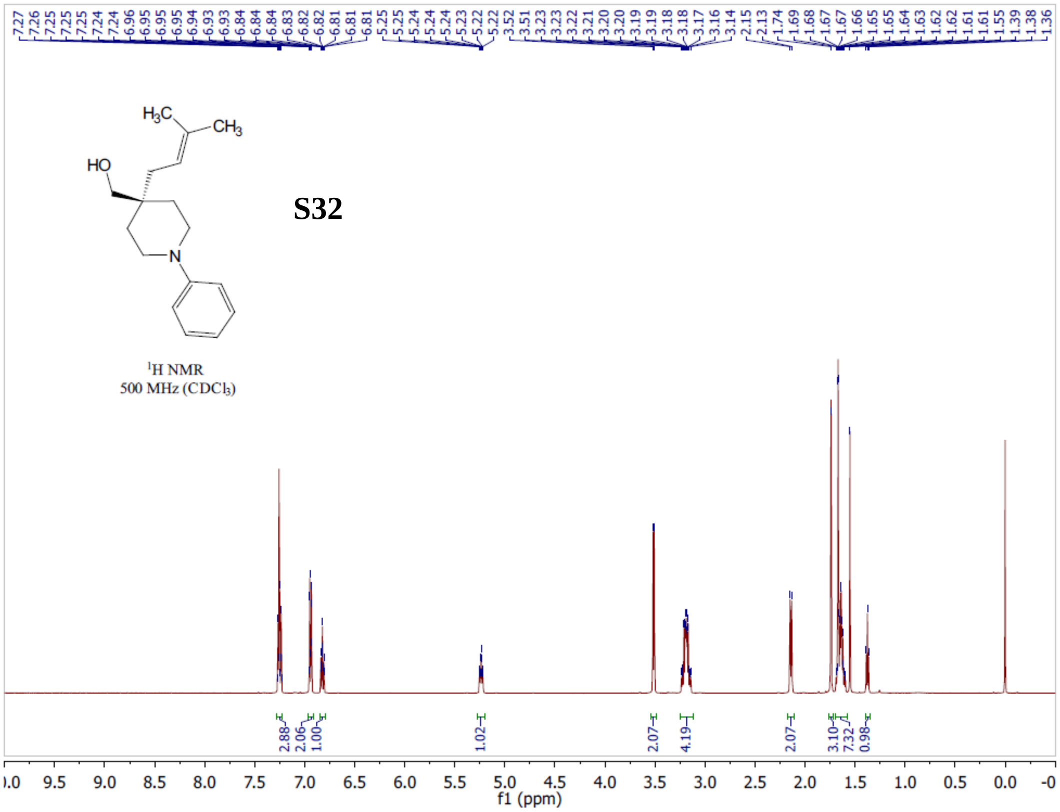

143.5
137.1
133.0
129.8
127.2
123.0
43.1
29.7
25.8
25.2
21.7
17.8
CH3
H3C
NH
O=S=O
CH3
S24
13C NMR
125 MHz (CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

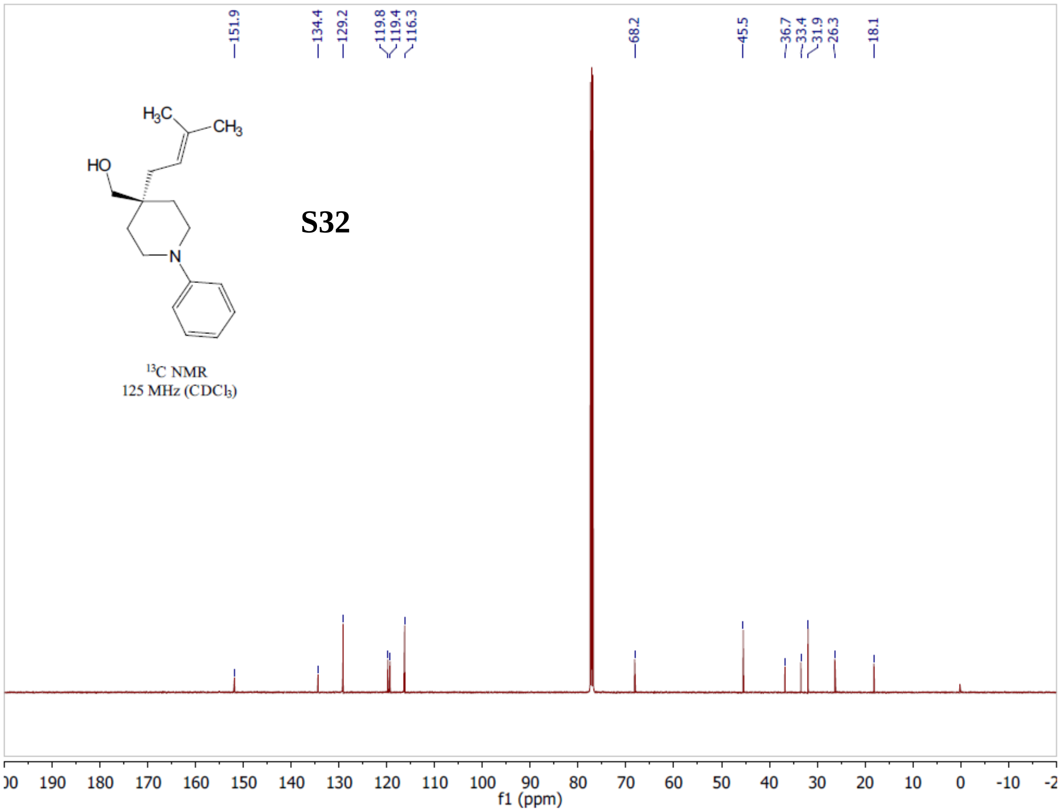

7.72
7.70
7.32
7.31
5.05
5.05
5.05
5.05
5.04
5.04
5.04
5.03
5.03
5.03
5.03
5.02
5.02
5.02
5.01
3.85
3.83
3.74
3.73
3.72
3.71
3.21
3.20
3.19
2.44
2.27
2.26
2.25
1.68
1.68
1.63
CH3
H3C
N
OH
O=S
O
CH3
S26
1H NMR
500 MHz (CDCl3)
2.01
2.03
1.00
2.10
2.10
2.08
3.10
0.96
3.17
3.32
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

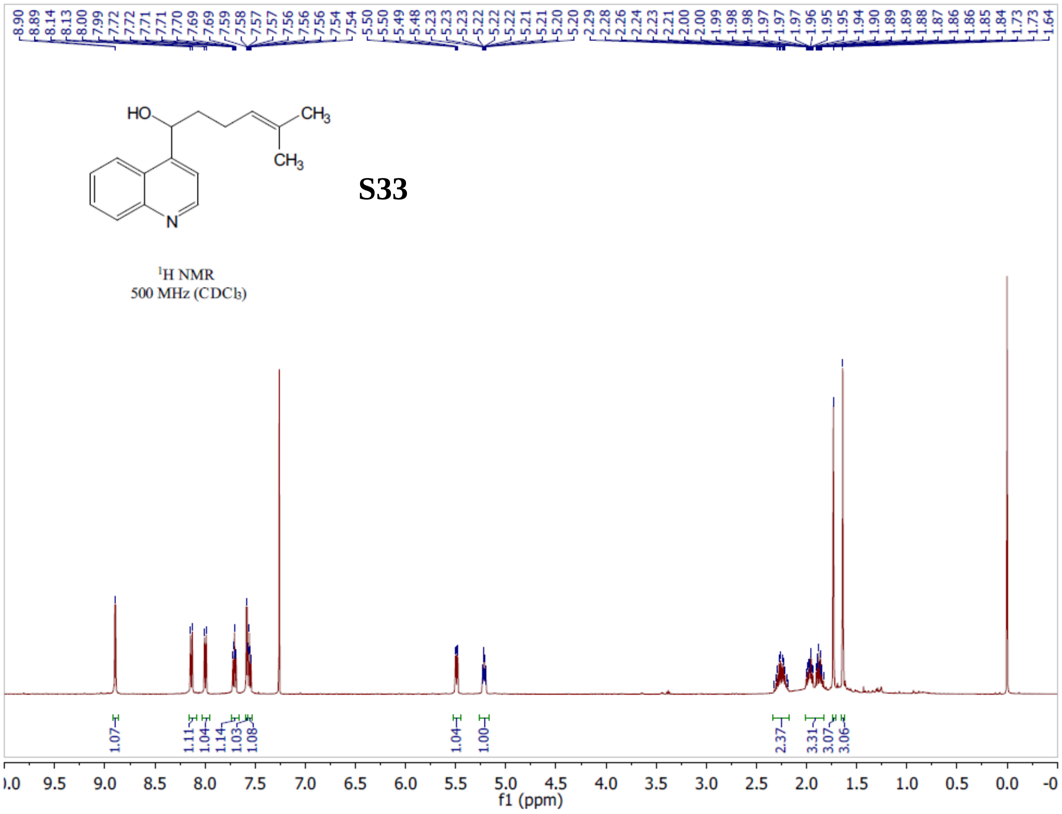

143.6
137.7
136.5
129.8
127.5
119.0
61.4
49.9
47.2
25.9
21.7
18.0
CH3
H3C
N
OH
O=S
O
CH3
S26
13C NMR
125 MHz (CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)

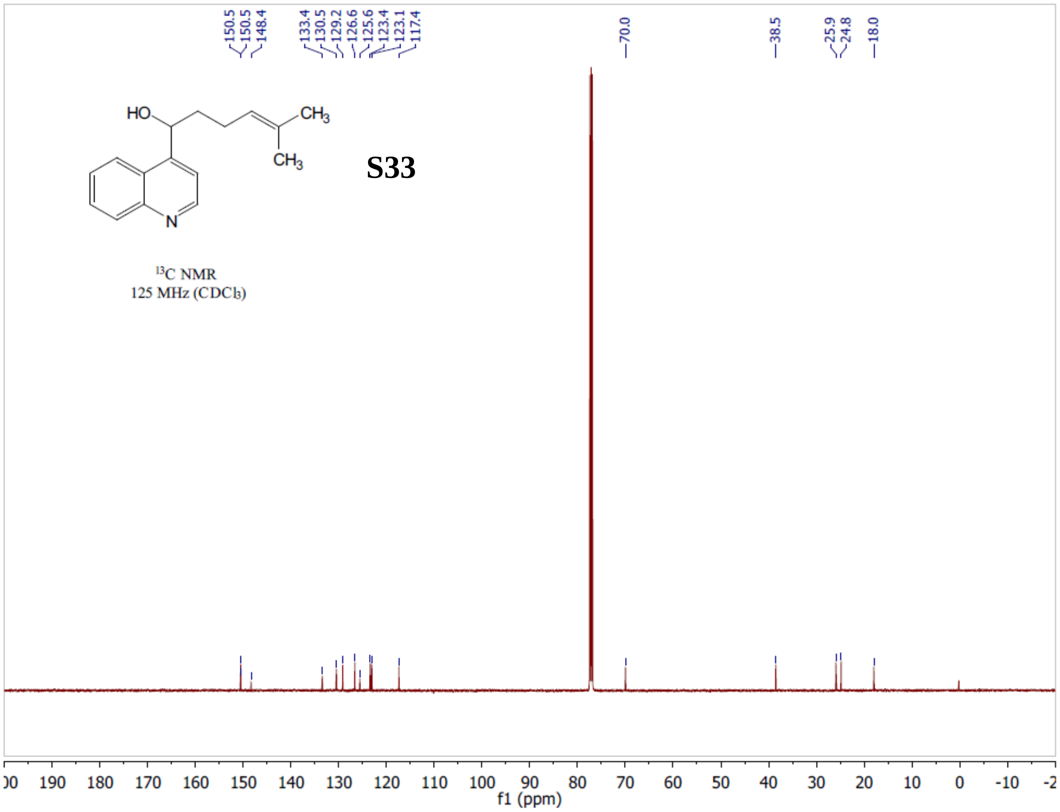

7.32
7.31
7.30
7.30
7.29
7.29
7.28
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.23
7.23
7.22
5.22
5.21
5.21
5.21
5.20
5.20
5.20
5.19
5.19
5.18
5.18
5.18
3.51
3.44
2.42
2.41
2.40
2.08
2.06
1.72
1.65
1.54
1.53
1.52
1.52
1.51
1.50
1.49
1.49
1.48
1.47
1.46
1.45
1.42
H3C
CH3
HO
N
S30
1H NMR
500 MHz (CDCl3)
3.98
1.43
1.00
2.04
2.02
4.04
2.05
3.15
3.18
5.24
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


138.6
134.0
129.3
128.3
127.1
120.1
68.3
63.7
49.5
36.8
33.9
32.1
26.3
18.1
H3C
CH3
HO
N
S30
13C NMR
125 MHz (CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)


7.27
7.26
7.25
7.25
7.25
7.24
7.24
6.96
6.95
6.95
6.95
6.94
6.93
6.93
6.84
6.84
6.84
6.83
6.82
6.82
6.81
6.81
6.81
5.25
5.25
5.24
5.24
5.24
5.23
5.22
5.22
3.52
3.51
3.23
3.23
3.22
3.21
3.20
3.20
3.19
3.19
3.18
3.18
3.17
3.16
3.14
2.15
2.13
1.74
1.69
1.68
1.67
1.67
1.66
1.65
1.65
1.64
1.63
1.62
1.62
1.61
1.61
1.55
1.39
1.38
1.36
H3C
CH3
HO
N
S32
1H NMR
500 MHz (CDCl3)
2.88
2.06
1.00
1.02
2.07
4.19
2.07
3.10
7.32
0.98
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


151.9
134.4
129.2
119.8
119.4
116.3
68.2
45.5
36.7
33.4
31.9
26.3
18.1
H3C
CH3
HO
N
S32
13C NMR
125 MHz (CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)


8.90
8.89
8.14
8.13
8.00
7.99
7.72
7.72
7.71
7.71
7.70
7.69
7.69
7.59
7.58
7.57
7.57
7.56
7.56
7.54
5.50
5.50
5.49
5.48
5.23
5.23
5.23
5.22
5.22
5.22
5.21
5.21
5.20
2.29
2.28
2.26
2.24
2.23
2.21
2.00
2.00
1.99
1.98
1.98
1.97
1.97
1.97
1.96
1.95
1.94
1.90
1.89
1.89
1.88
1.87
1.86
1.85
1.84
1.73
1.73
1.64
HO
CH3
CH3
N
S33
1H NMR
500 MHz (CDCl3)
1.07
1.11
1.04
1.14
1.03
1.08
1.04
1.00
2.37
3.31
3.07
3.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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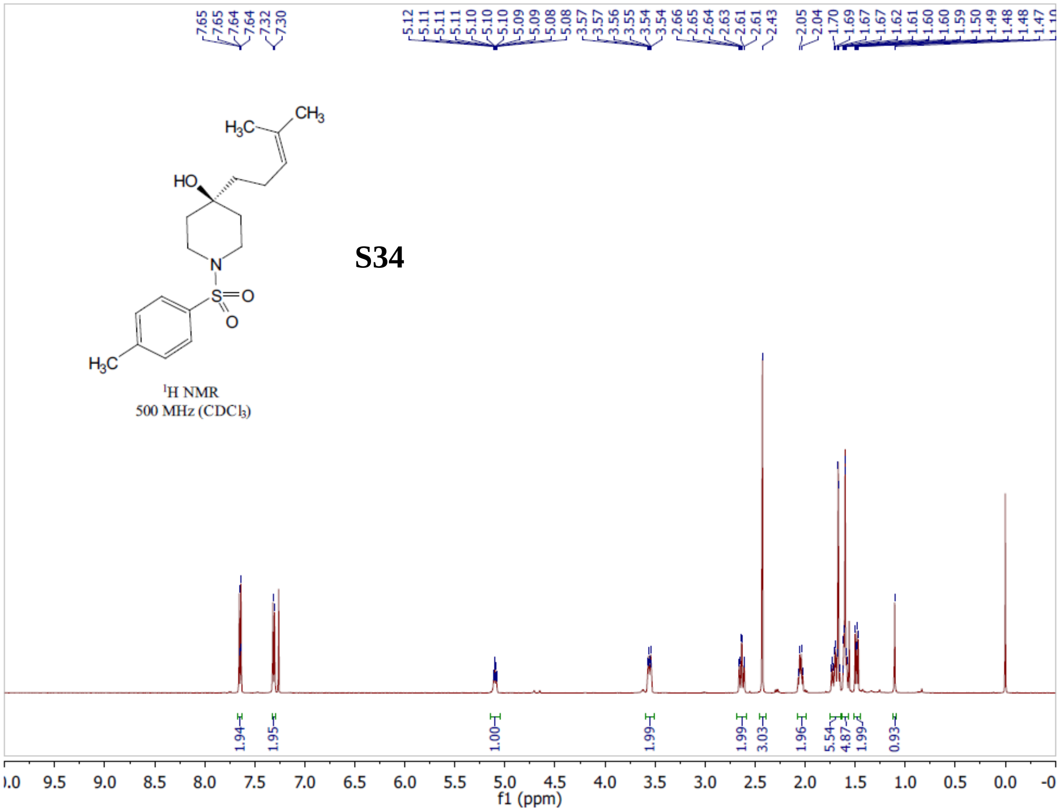
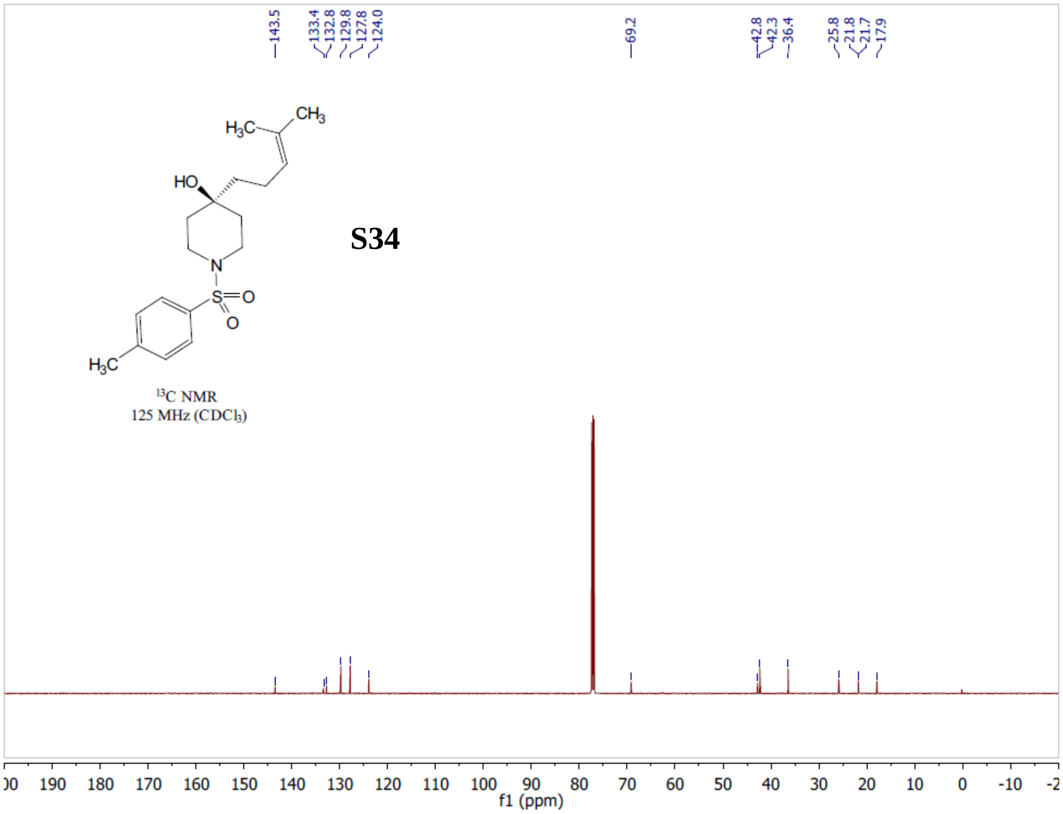
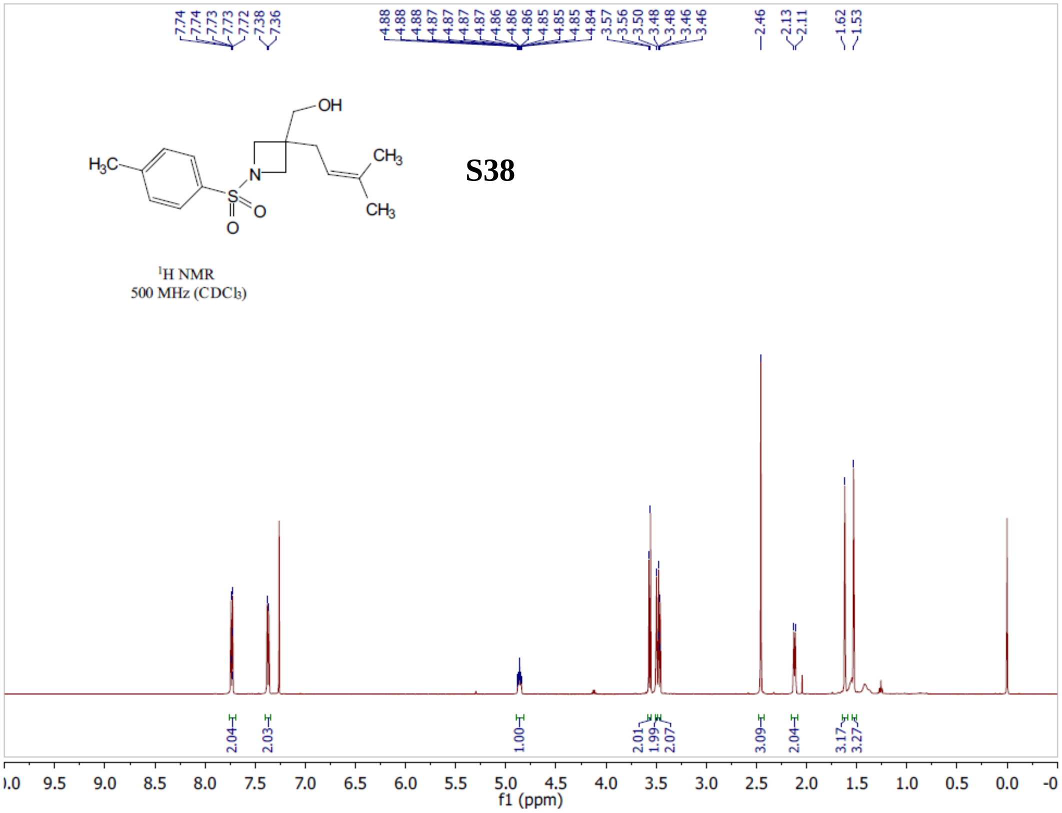
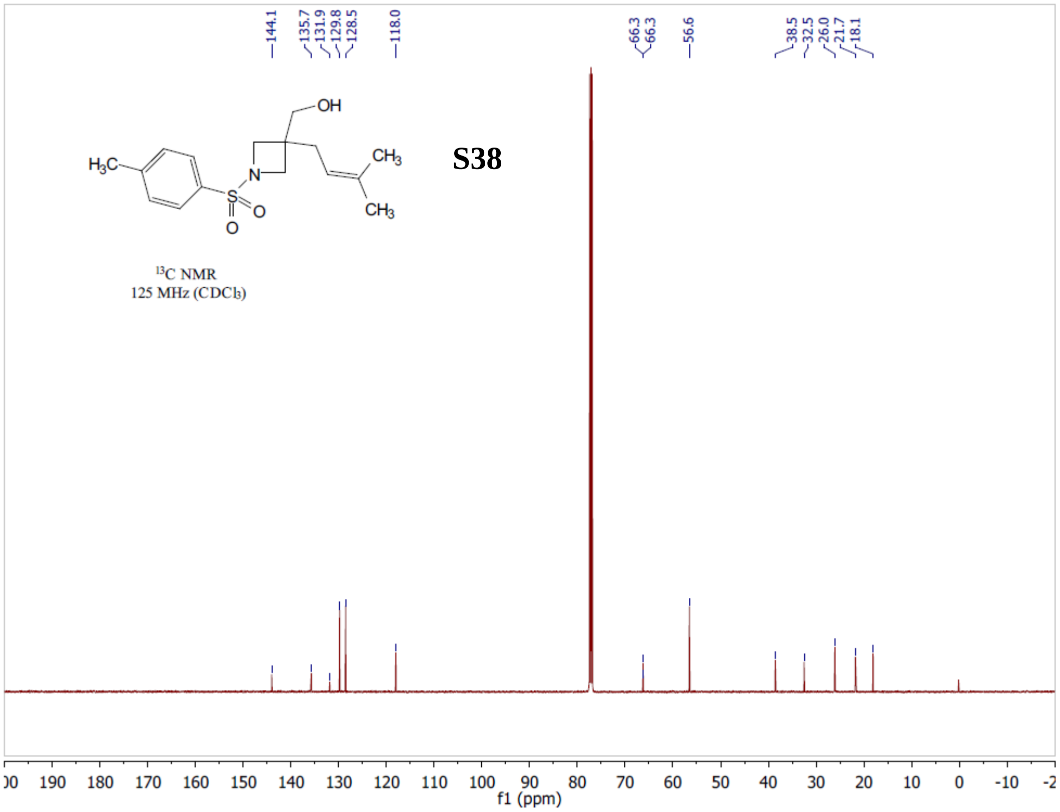
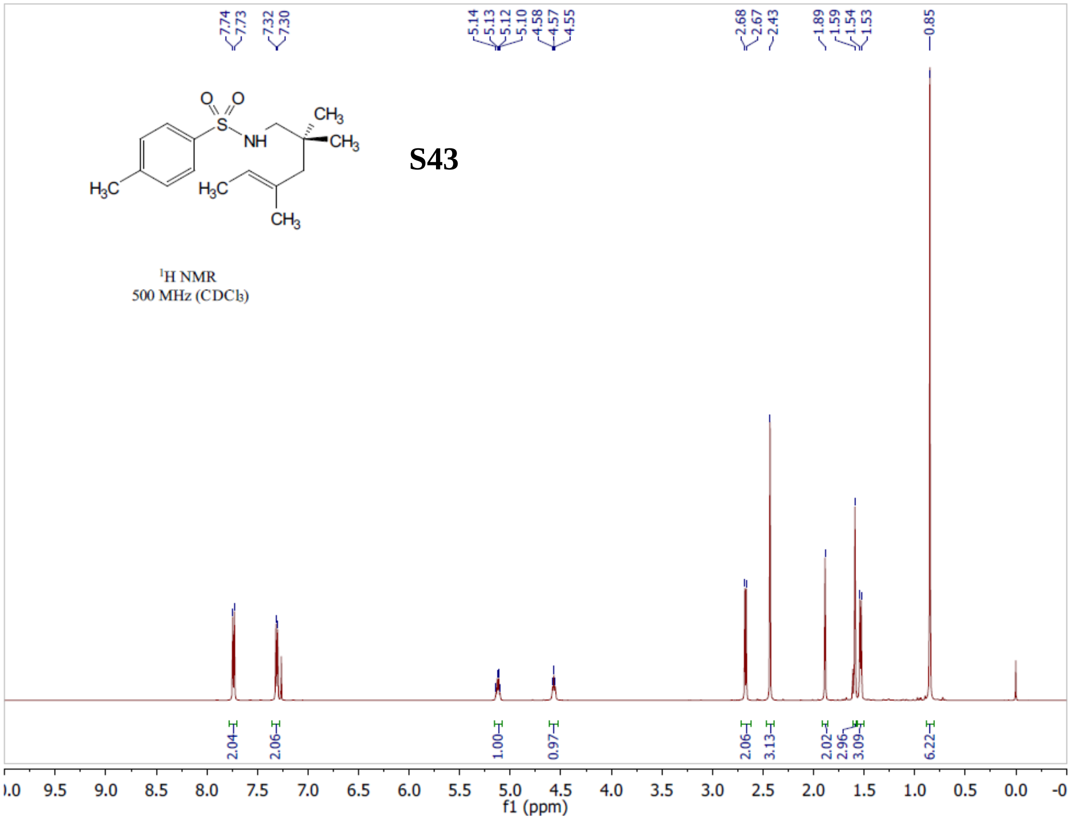
150.5
148.4
133.4
130.5
129.2
126.6
125.6
123.4
123.1
117.4
70.0
38.5
25.9
24.8
18.0
HO
CH3
CH3
N
S33
13C NMR
125 MHz (CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

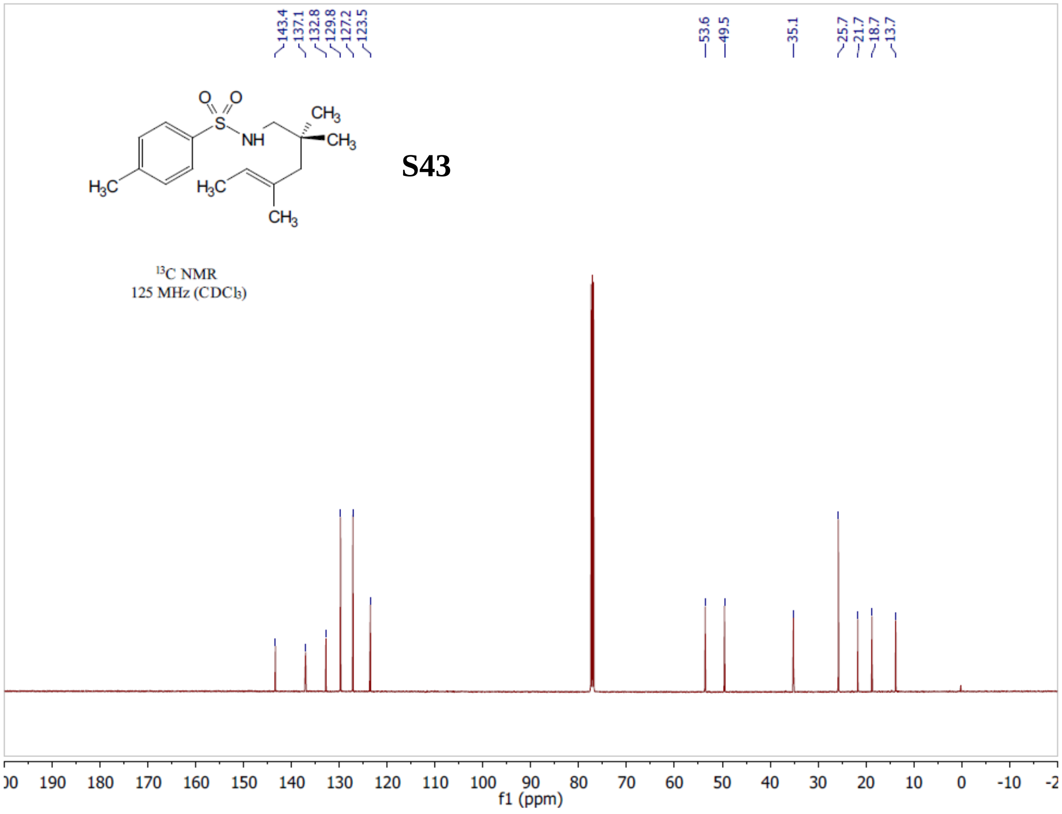

7.65
7.65
7.64
7.64
7.32
7.30
5.12
5.11
5.11
5.11
5.10
5.10
5.10
5.09
5.09
5.08
3.57
3.56
3.55
3.54
3.54
2.66
2.65
2.64
2.63
2.61
2.61
2.43
2.05
2.04
1.70
1.69
1.67
1.67
1.62
1.61
1.60
1.59
1.50
1.49
1.48
1.47
1.1
CH3
H3C
HO
N
S
O
O
H3C
S34
1H NMR
500 MHz (CDCl3)
1.94
1.95
1.00
1.99
1.99
3.03
1.96
5.54
4.87
1.99
0.93
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

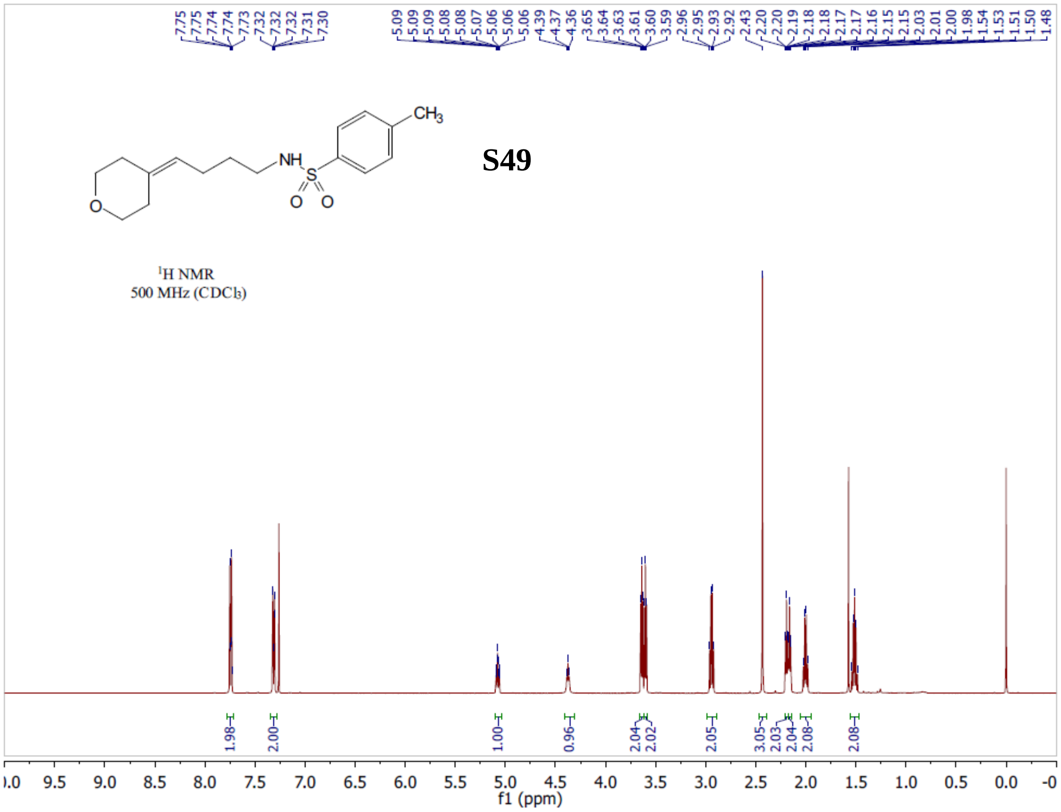

143.5
133.4
132.8
129.8
127.8
124.0
69.2
42.8
42.3
36.4
25.8
21.8
21.7
17.9
CH3
H3C
HO
N
S
O
O
H3C
S34
13C NMR
125 MHz (CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)

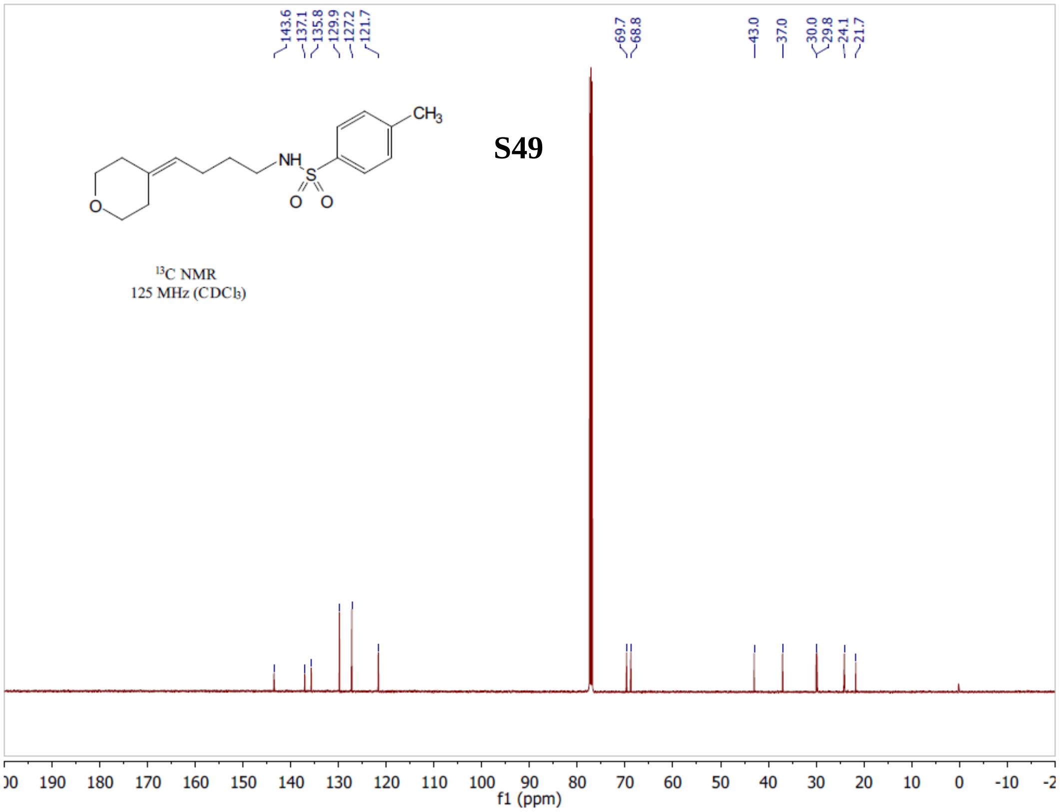

7.74
7.74
7.73
7.73
7.72
7.38
7.36
4.88
4.88
4.88
4.87
4.87
4.87
4.87
4.86
4.86
4.86
4.85
4.85
4.85
4.84
3.57
3.56
3.50
3.48
3.48
3.46
3.46
2.46
2.13
2.11
1.62
1.53
OH
H3C
N
S
O
O
CH3
CH3
S38
1H NMR
500 MHz (CDCl3)
2.04
2.03
1.00
2.01
1.99
2.07
3.09
2.04
3.17
3.27
f1 (ppm)

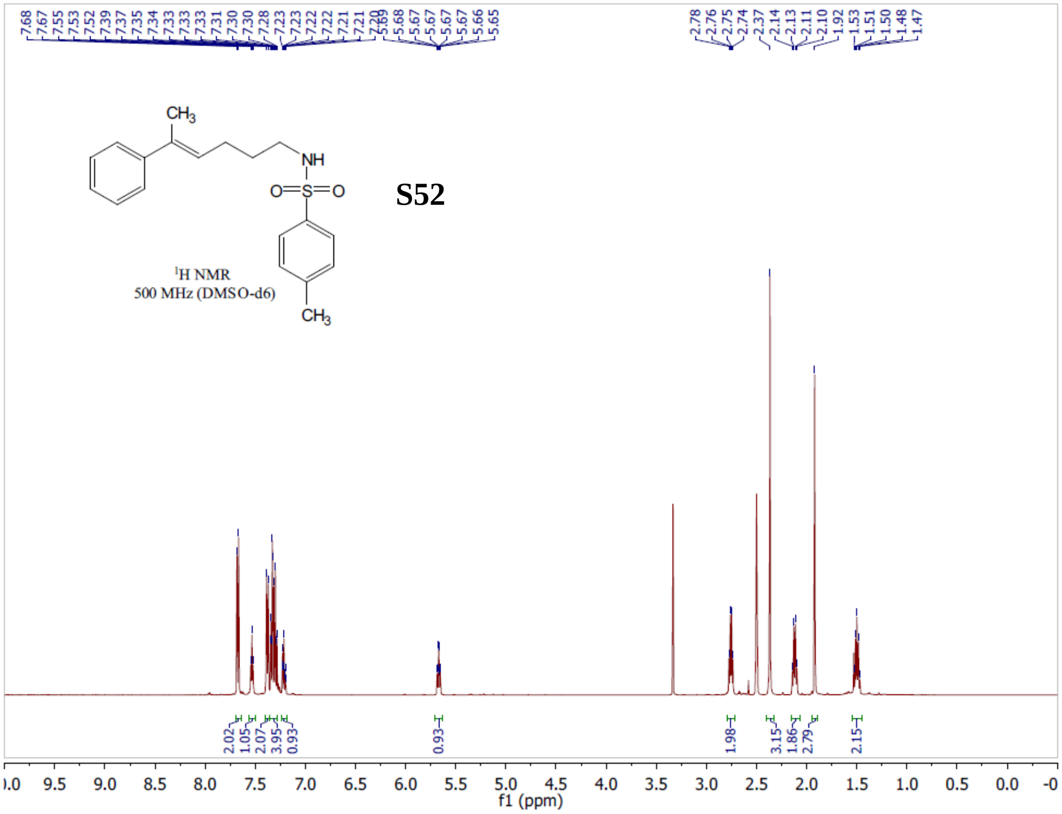

144.1
135.7
131.9
129.8
128.5
118.0
66.3
66.3
56.6
38.5
32.5
26.0
21.7
18.1
OH
H3C
N
S
O
O
CH3
CH3
S38
13C NMR
125 MHz (CDCl3)
f1 (ppm)

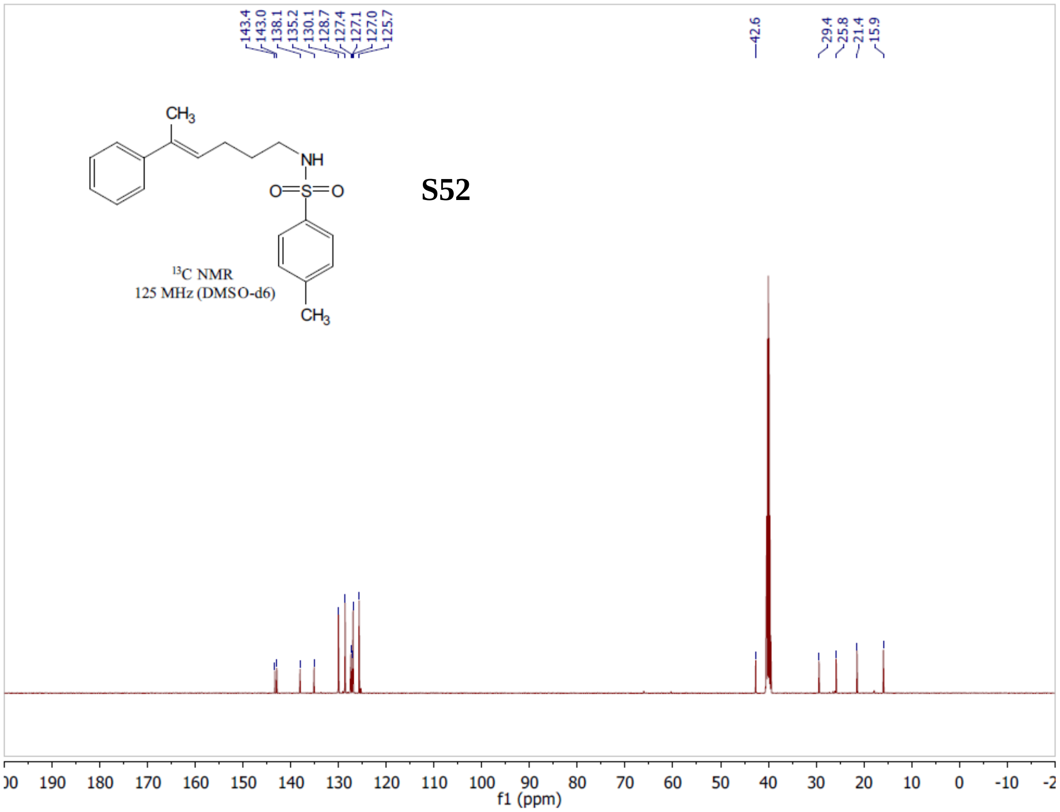

7.74
7.73
7.32
7.30
5.14
5.13
5.12
5.10
4.58
4.57
4.55
2.68
2.67
2.43
1.89
1.59
1.54
1.53
0.85
S43
O
O
S
NH
CH3
CH3
H3C
H3C
CH3
1H NMR
500 MHz (CDCl3)
2.04
2.06
1.00
0.97
2.06
3.13
2.02
2.96
3.09
6.22
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

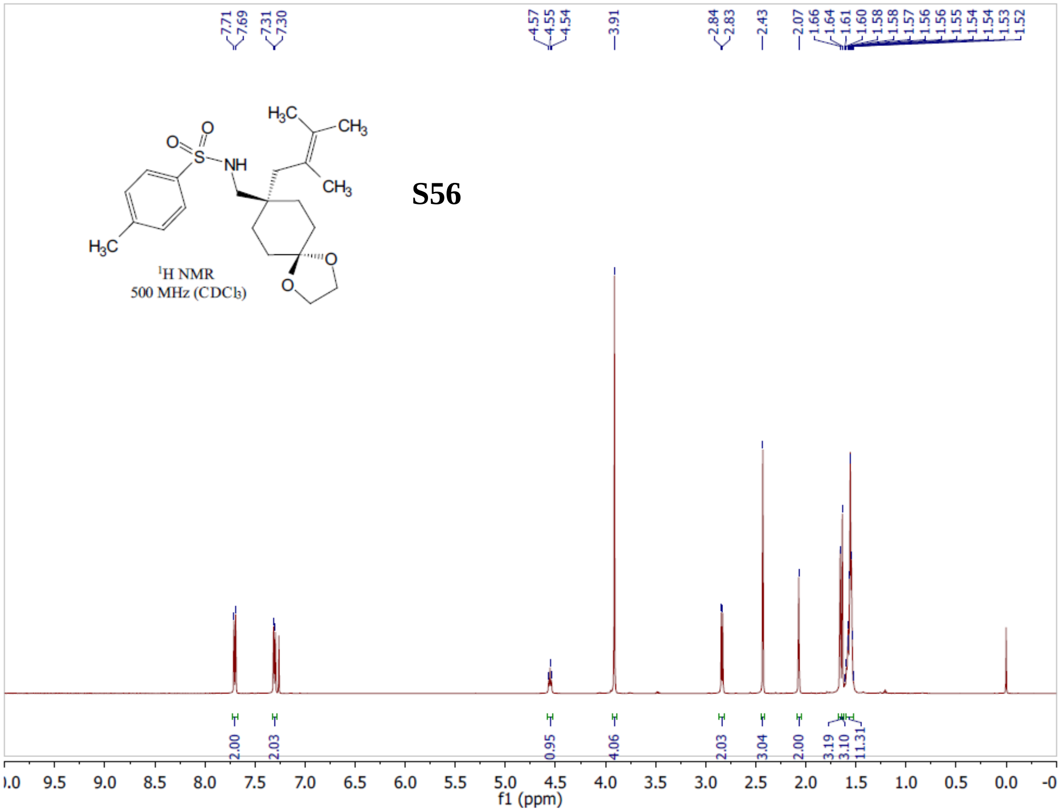

143.4
137.1
132.8
129.8
127.2
123.5
53.6
49.5
35.1
25.7
21.7
18.7
13.7
S43
O
O
S
NH
CH3
CH3
H3C
H3C
CH3
13C NMR
125 MHz (CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

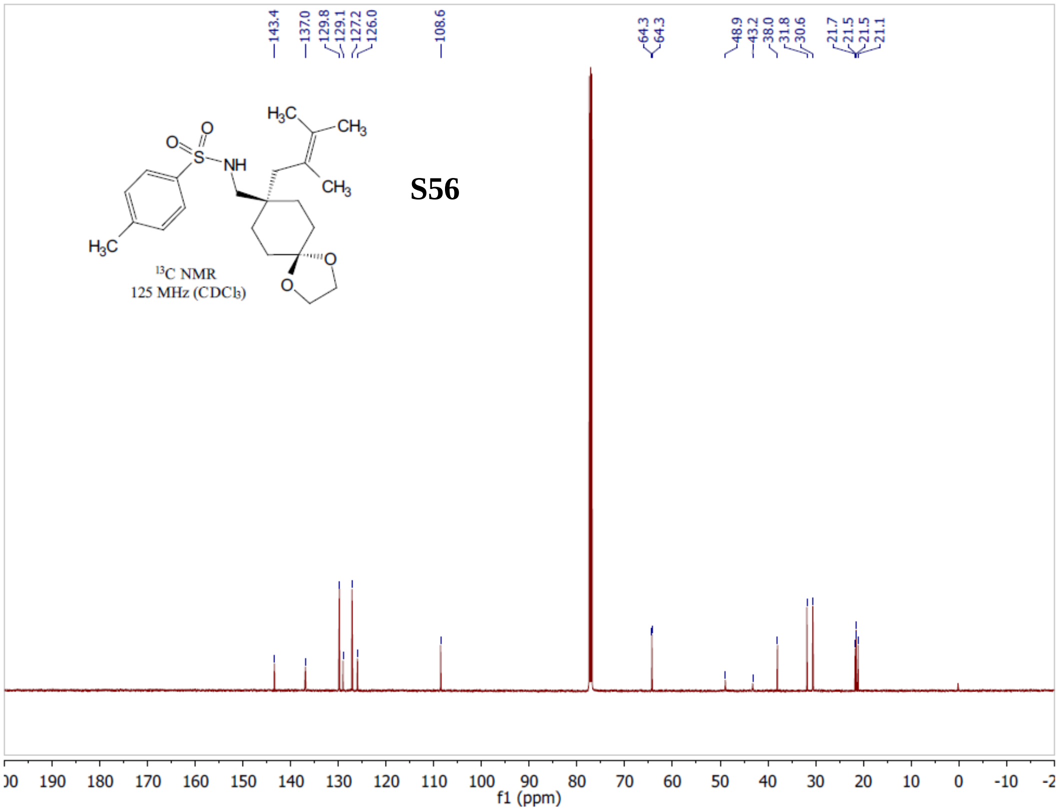

7.75
7.75
7.74
7.74
7.73
7.32
7.32
7.32
7.31
7.30
5.09
5.09
5.09
5.08
5.08
5.07
5.06
5.06
5.06
4.39
4.37
4.36
3.65
3.64
3.63
3.61
3.60
3.59
2.96
2.95
2.93
2.92
2.43
2.20
2.20
2.19
2.18
2.18
2.17
2.17
2.16
2.15
2.15
2.03
2.01
2.00
1.98
1.54
1.53
1.51
1.50
1.48
CH3
NH
S
O
O
O
S49
1H NMR
500 MHz (CDCl3)
1.98
2.00
1.00
0.96
2.04
2.02
2.05
3.05
2.03
2.04
2.08
2.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

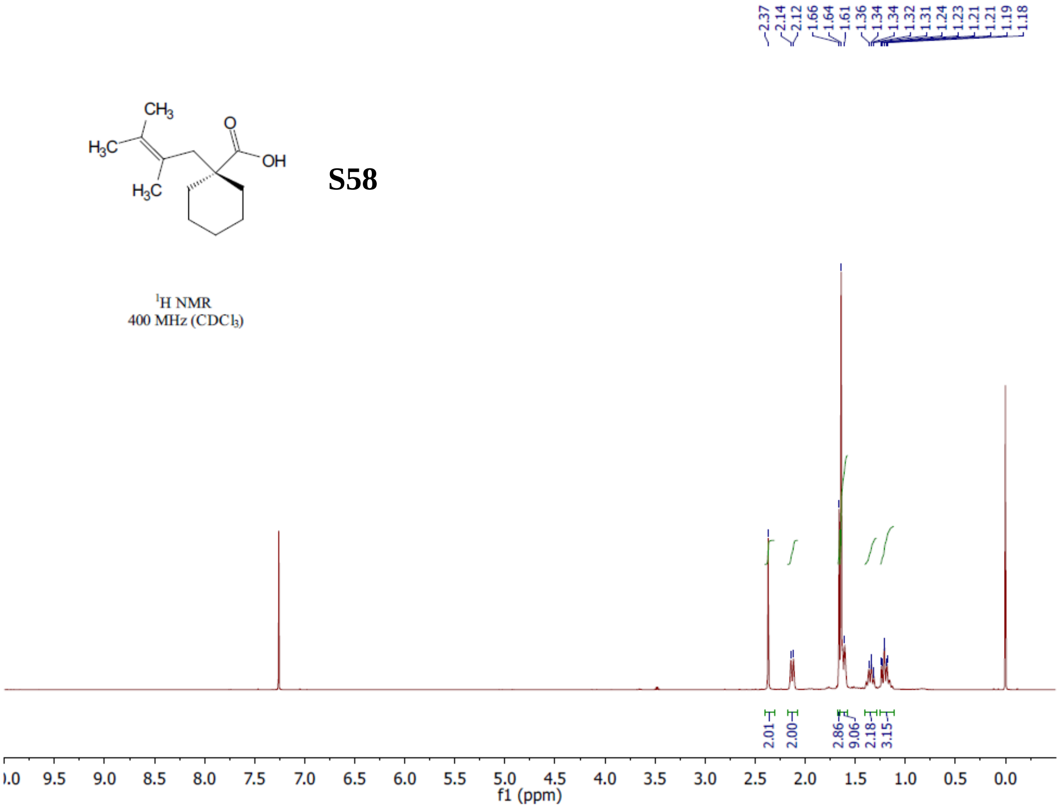

143.6
137.1
135.8
129.9
127.2
121.7
69.7
68.8
43.0
37.0
30.0
29.8
24.1
21.7
CH3
NH
S
O
O
O
S49
13C NMR
125 MHz (CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.68
7.67
7.55
7.53
7.52
7.39
7.37
7.35
7.34
7.33
7.33
7.33
7.31
7.30
7.30
7.28
7.23
7.23
7.22
7.22
7.21
7.21
7.20
5.69
5.68
5.67
5.67
5.67
5.66
5.65
2.78
2.76
2.75
2.74
2.37
2.14
2.13
2.11
2.10
1.92
1.53
1.51
1.50
1.48
1.47
CH3
NH
O=S=O
CH3
S52
1H NMR
500 MHz (DMSO-d6)
2.02
1.05
2.07
3.95
0.93
0.93
1.98
3.15
1.86
2.79
2.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


143.4
143.0
138.1
135.2
130.1
128.7
127.4
127.1
127.0
125.7
42.6
29.4
25.8
21.4
15.9
CH3
NH
O=S=O
CH3
S52
13C NMR
125 MHz (DMSO-d6)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)

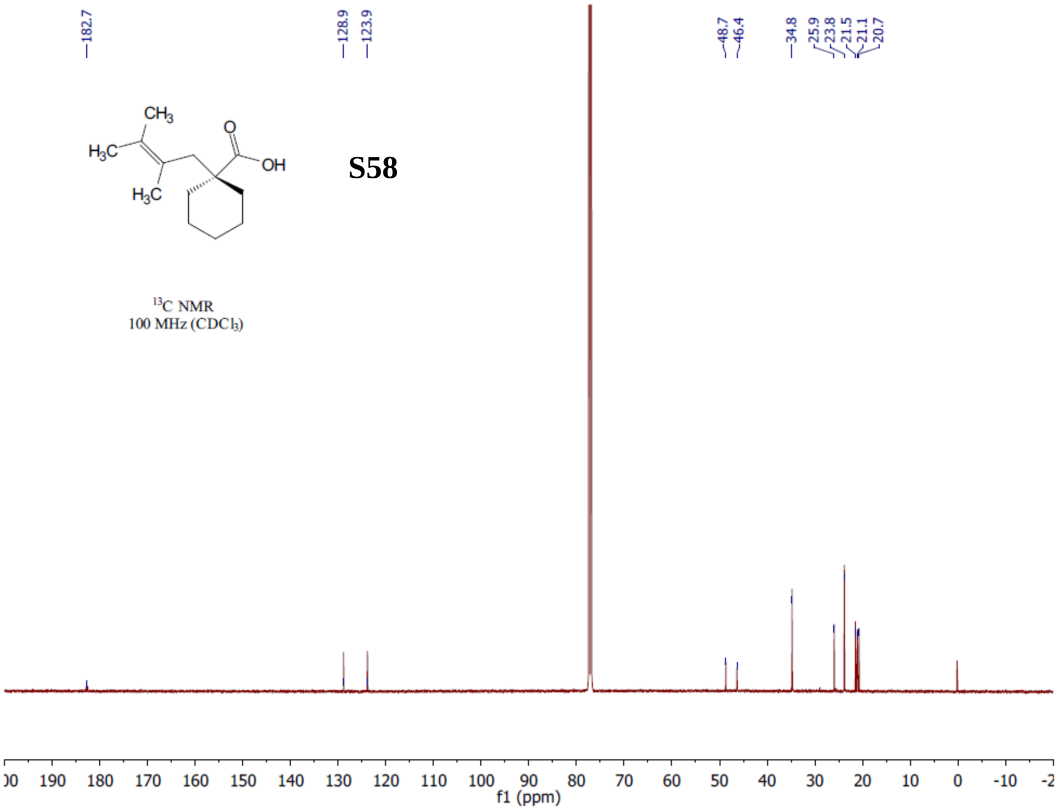

7.71
7.69
7.31
7.30
4.57
4.55
4.54
3.91
2.84
2.83
2.43
2.07
1.66
1.64
1.61
1.60
1.58
1.58
1.57
1.56
1.56
1.55
1.54
1.54
1.53
1.52
S56
^{1}H NMR
500 MHz (CDCl$_3$)
2.00
2.03
0.95
4.06
2.03
3.04
2.00
3.19
3.10
11.31
f1 (ppm)


143.4
137.0
129.8
129.1
127.2
126.0
108.6
64.3
64.3
48.9
43.2
38.0
31.8
30.6
21.7
21.5
21.5
21.1
S56
^{13}C NMR
125 MHz (CDCl$_3$)
f1 (ppm)



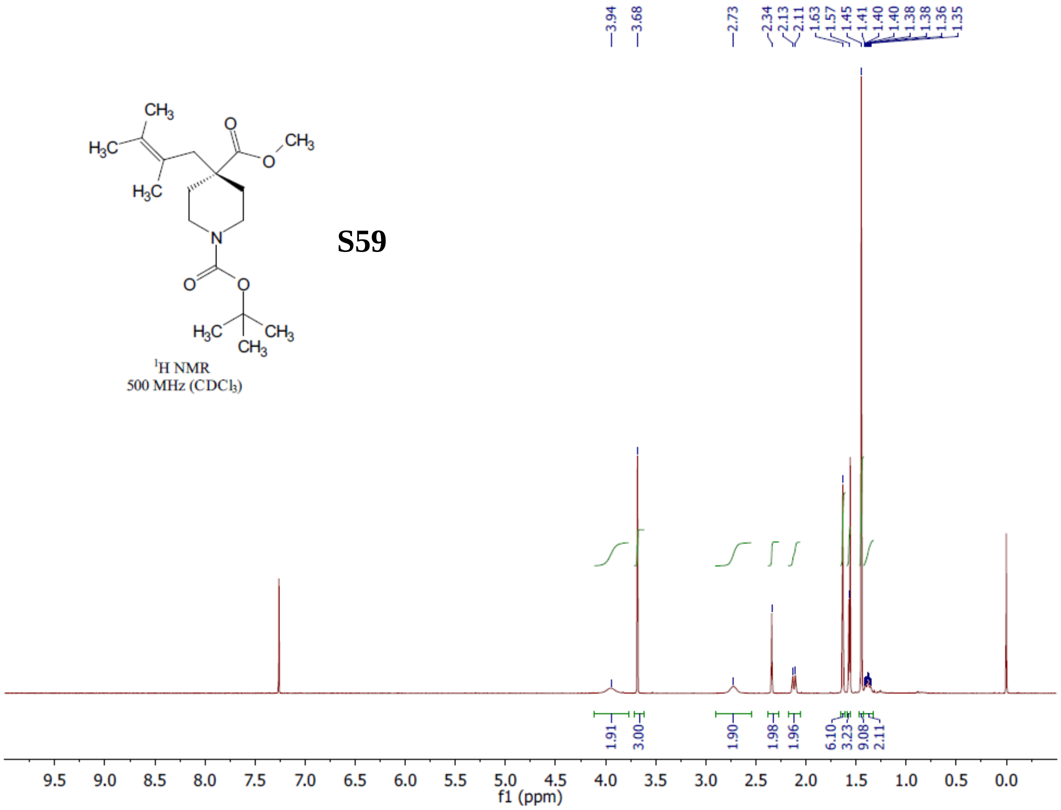
S58

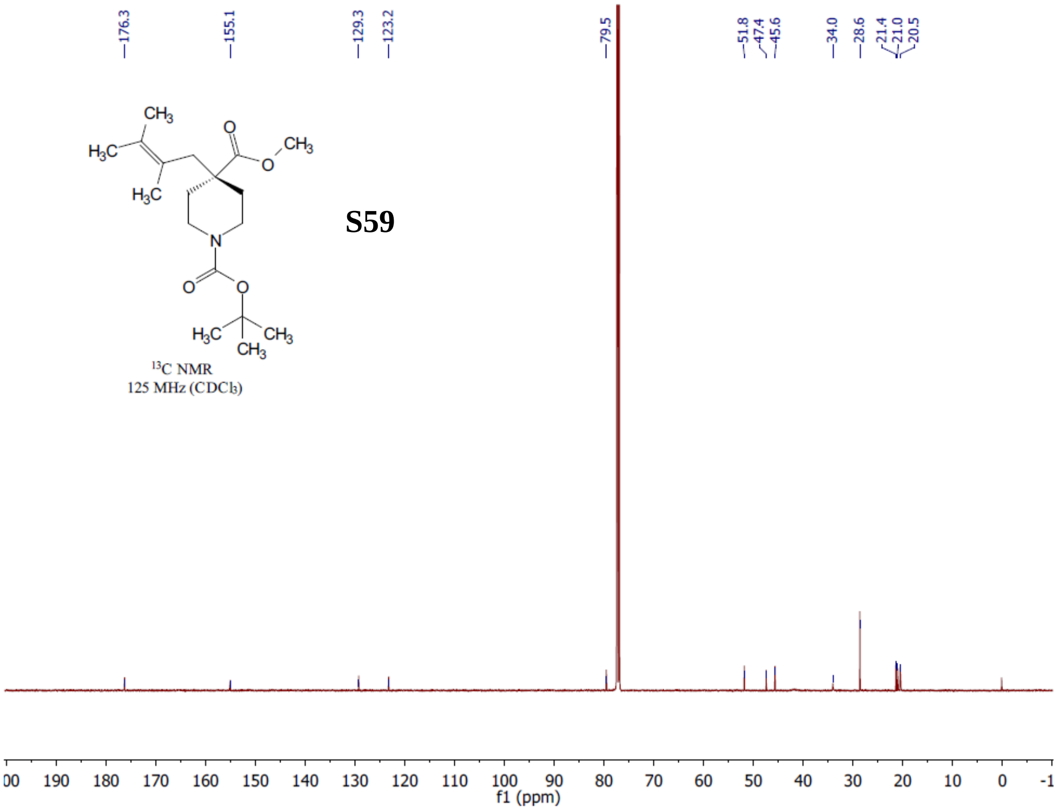
^{1}H NMR
400 MHz ($CDCl_3$)

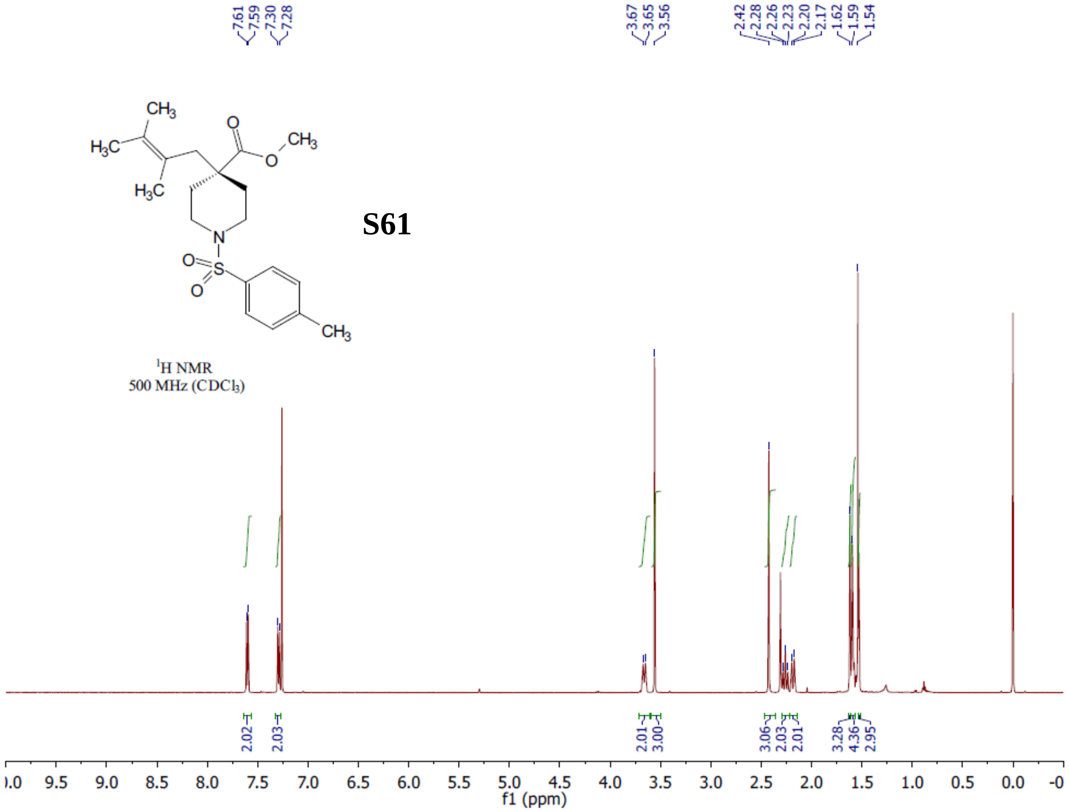


S58

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

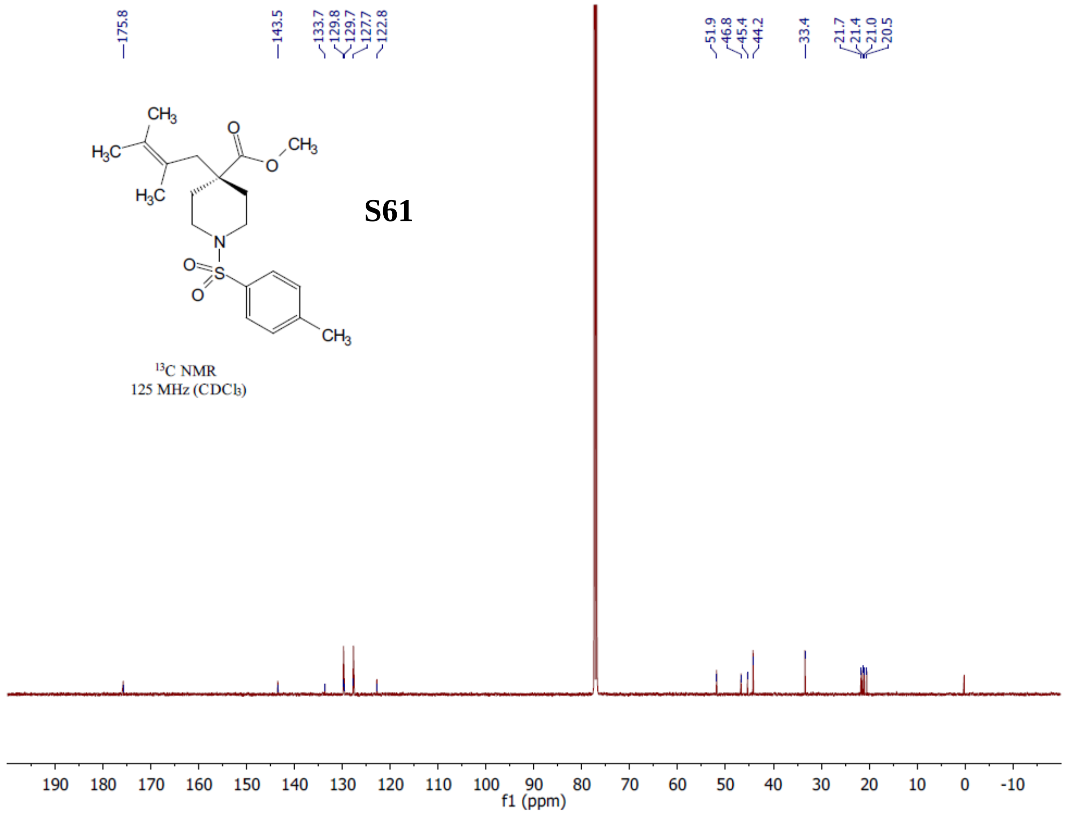

3.94
3.68
2.73
2.34
2.13
2.11
1.63
1.57
1.45
1.41
1.40
1.40
1.38
1.38
1.36
1.35
S59
CH3
H3C
H3C
O
O
CH3
N
O
O
H3C
CH3
CH3
¹H NMR
500 MHz (CDCl3)
1.91
3.00
1.90
1.98
1.96
6.10
3.23
9.08
2.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


176.3
155.1
129.3
123.2
79.5
51.8
47.4
45.6
34.0
28.6
21.4
21.0
20.5
S59
CH3
H3C
H3C
O
O
CH3
N
O
O
H3C
CH3
CH3
¹³C NMR
125 MHz (CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)



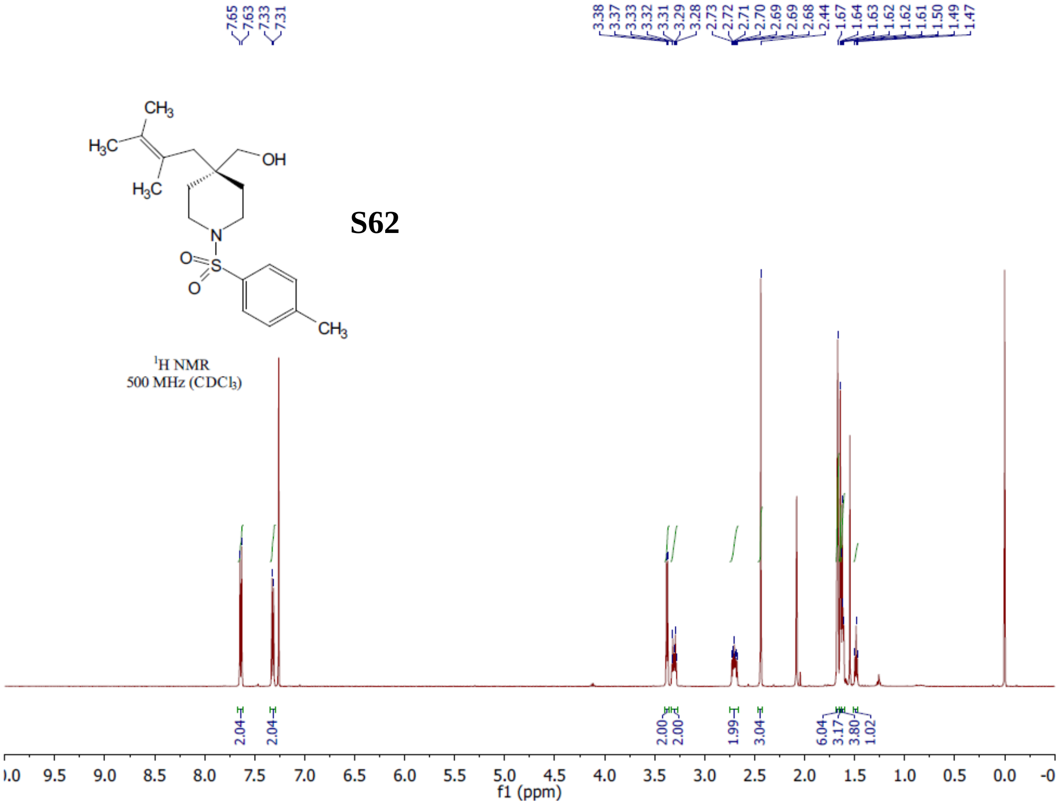
S61

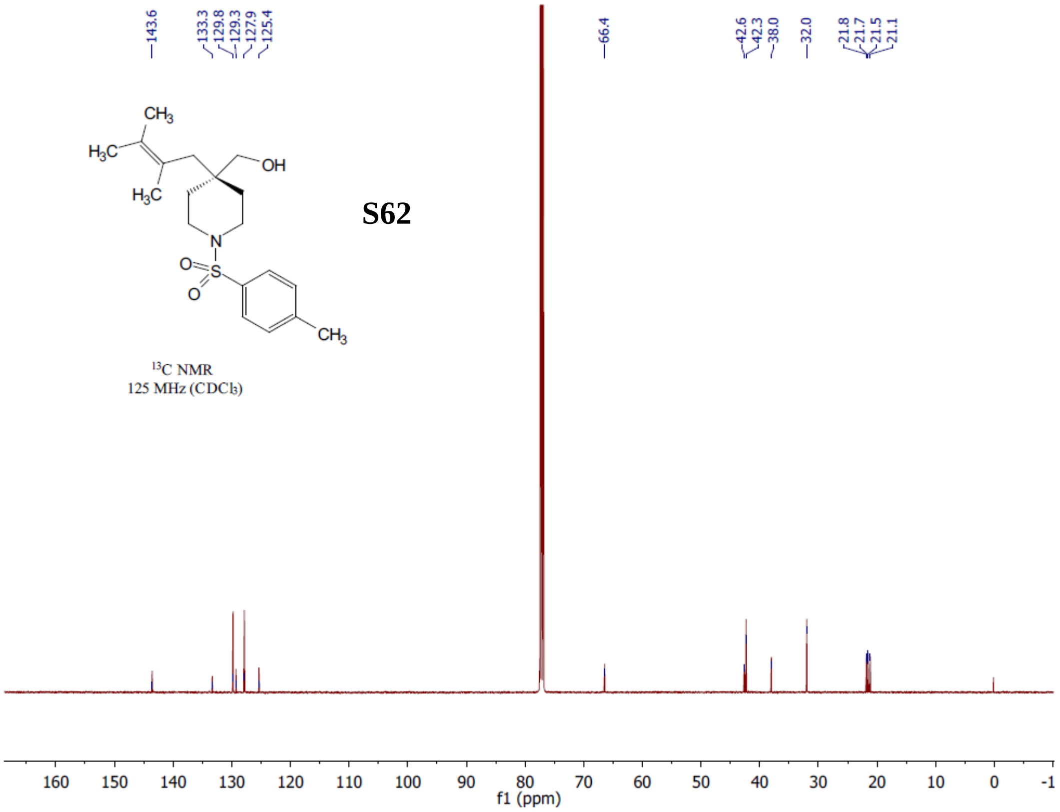
7.61
7.59
7.30
7.28
3.67
3.65
3.56
2.42
2.28
2.26
2.23
2.20
2.17
1.62
1.59
1.54
^{1}H NMR
500 MHz (CDCl$_3$)
2.02
2.03
2.01
3.00
3.06
2.03
2.01
3.28
4.36
2.95
f1 (ppm)

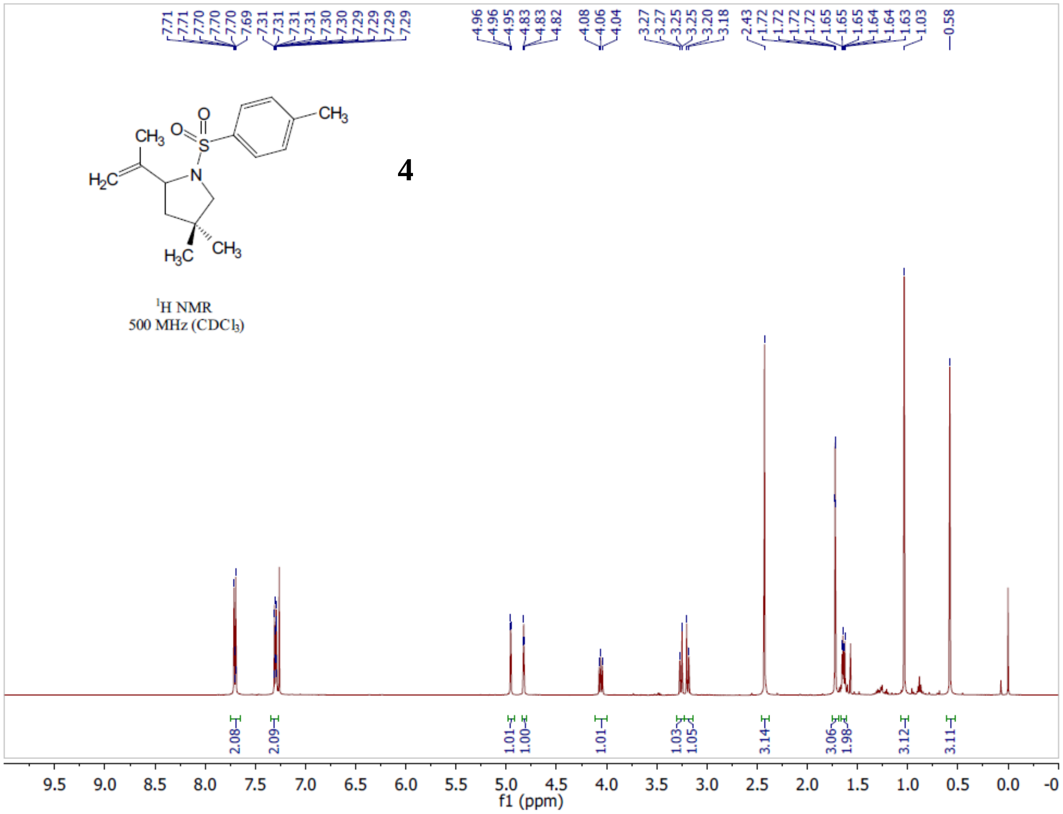


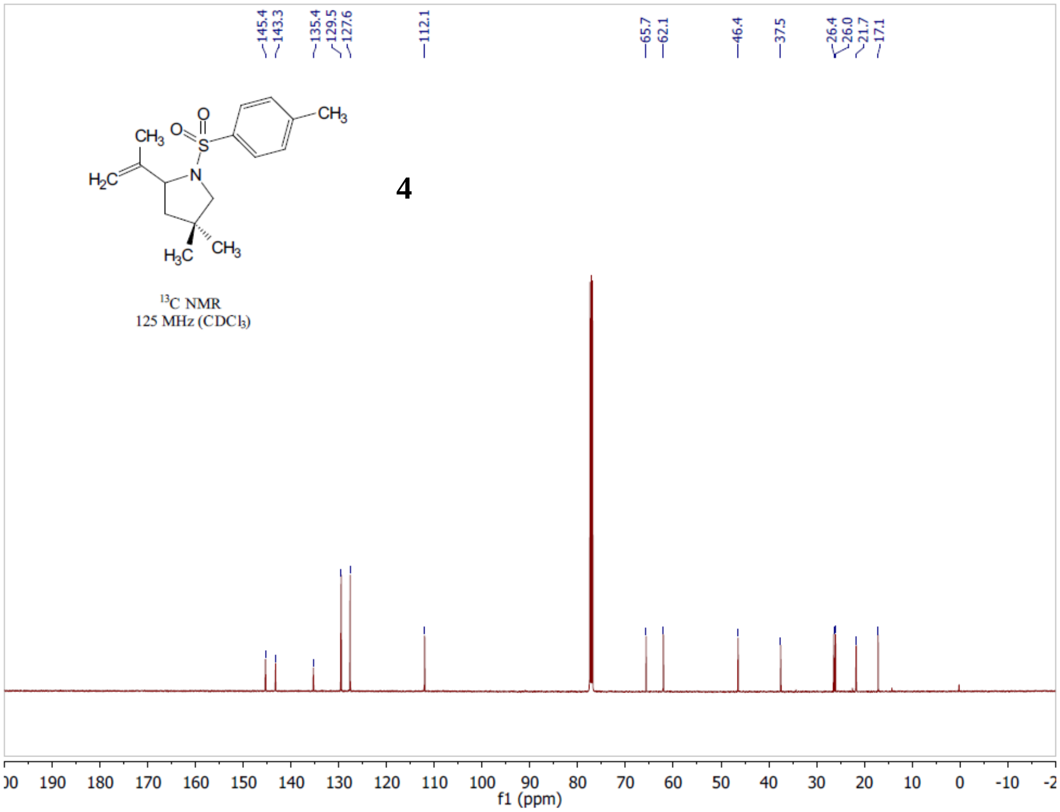
S61

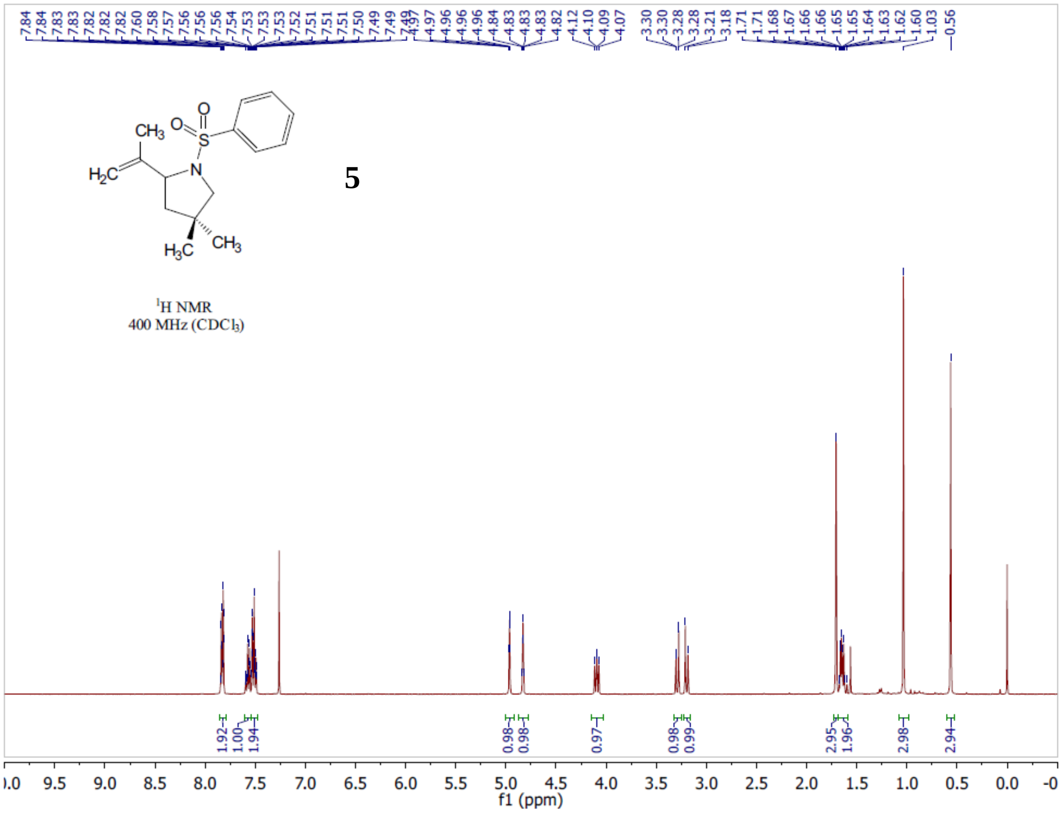
175.8
143.5
133.7
129.8
129.7
127.7
122.8
51.9
46.8
45.4
44.2
33.4
21.7
21.4
21.0
20.5
^{13}C NMR
125 MHz (CDCl$_3$)
f1 (ppm)


7.65
7.63
7.33
7.31
3.38
3.37
3.33
3.32
3.31
3.29
3.28
2.73
2.72
2.71
2.70
2.69
2.69
2.68
2.44
1.67
1.64
1.63
1.62
1.62
1.61
1.50
1.49
1.47
CH3
H3C
OH
H3C
N
O
S
O
CH3
S62
1H NMR
500 MHz (CDCl3)
2.04
2.04
2.00
2.00
1.99
3.04
6.04
3.17
3.80
1.02
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

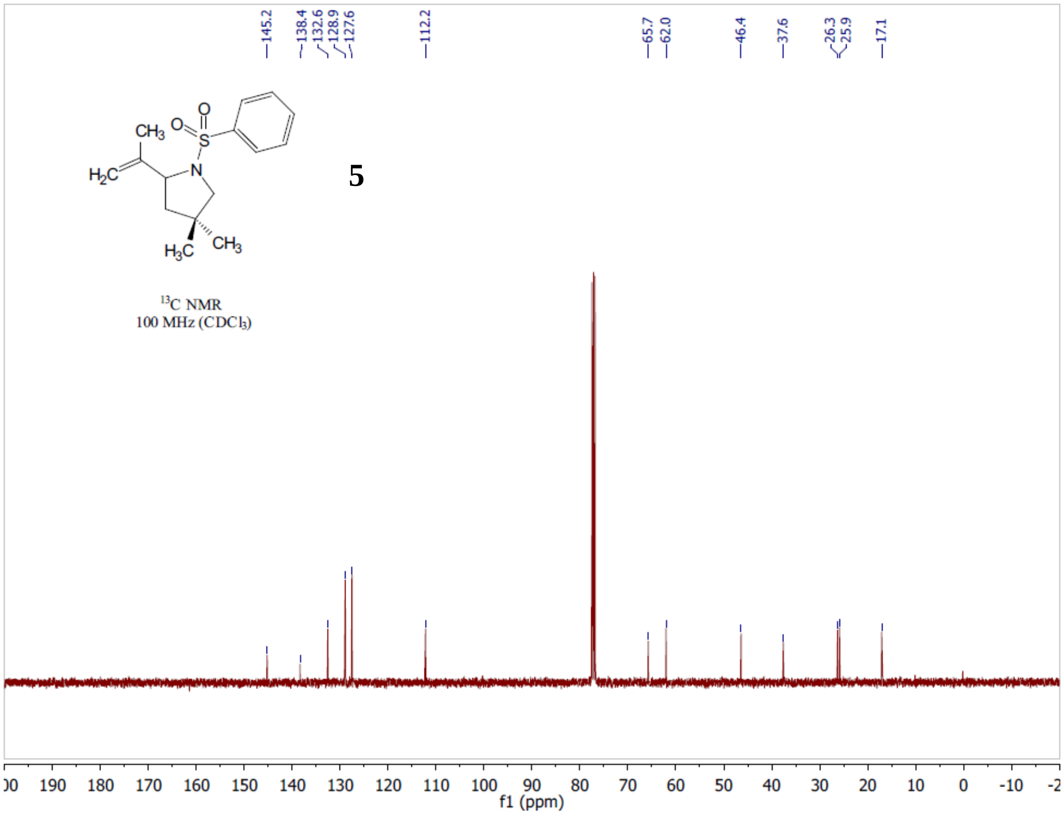

143.6
133.3
129.8
129.3
127.9
125.4
66.4
42.6
42.3
38.0
32.0
21.8
21.7
21.5
21.1
CH3
H3C
OH
H3C
N
O
S
O
CH3
S62
13C NMR
125 MHz (CDCl3)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


7.71 7.71 7.70 7.70 7.70 7.69 7.31 7.31 7.31 7.31 7.30 7.30 7.29 7.29 7.29 7.29
4.96 4.96 4.95 4.83 4.83 4.82 4.08 4.06 4.04 3.27 3.27 3.25 3.25 3.20 3.18 2.43 1.72 1.72 1.72 1.72 1.65 1.65 1.65 1.64 1.64 1.63 1.03 0.58
CH3
O
O
S
CH3
H2C
N
H3C
CH3
4
^{1}H NMR
500 MHz (CDCl$_3$)
2.08 2.09 1.01 1.00 1.01 1.03 1.05 3.14 3.06 1.98 3.12 3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

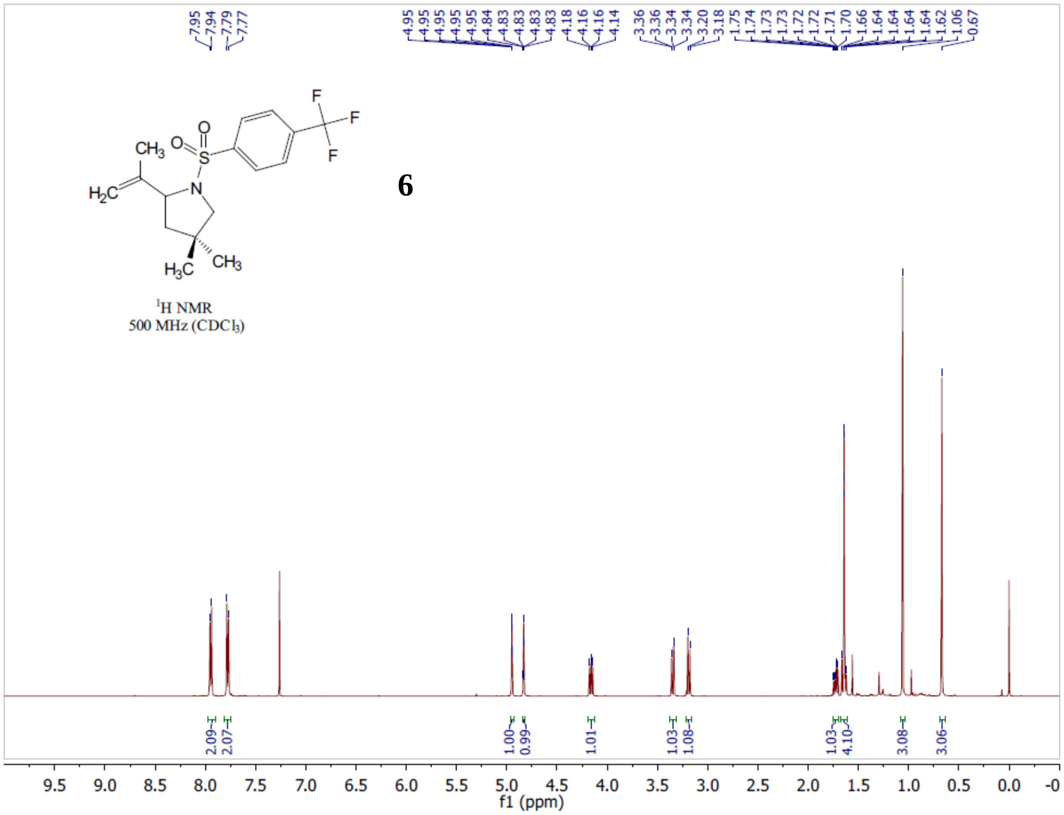

145.4 143.3 135.4 129.5 127.6 112.1 65.7 62.1 46.4 37.5 26.4 26.0 21.7 17.1
CH3
O
O
S
CH3
H2C
N
H3C
CH3
4
^{13}C NMR
125 MHz (CDCl$_3$)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

7.84
7.84
7.83
7.83
7.82
7.82
7.82
7.60
7.58
7.57
7.56
7.56
7.56
7.54
7.53
7.53
7.53
7.52
7.51
7.51
7.51
7.50
7.49
7.49
4.97
4.97
4.96
4.96
4.96
4.84
4.83
4.83
4.83
4.82
4.12
4.10
4.09
4.07
3.30
3.30
3.28
3.28
3.21
3.18
1.71
1.71
1.68
1.67
1.66
1.66
1.65
1.65
1.64
1.63
1.62
1.60
1.03
0.56
CH3
O
O
S
H2C
N
H3C
CH3
1H NMR
400 MHz (CDCl3)
1.92
1.00
1.94
0.98
0.98
0.97
0.98
0.99
2.95
1.96
2.98
2.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

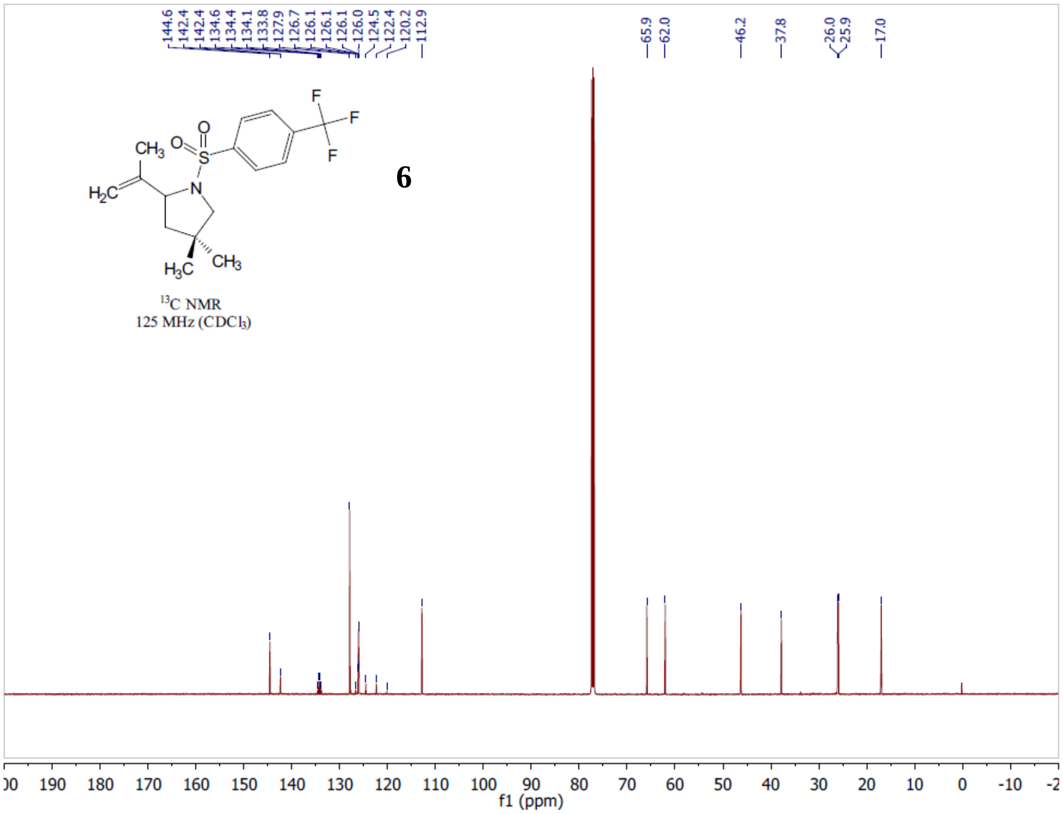
5

145.2
138.4
132.6
128.9
127.6
112.2
65.7
62.0
46.4
37.6
26.3
25.9
17.1
CH3
O
O
S
H2C
N
H3C
CH3
13C NMR
100 MHz (CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

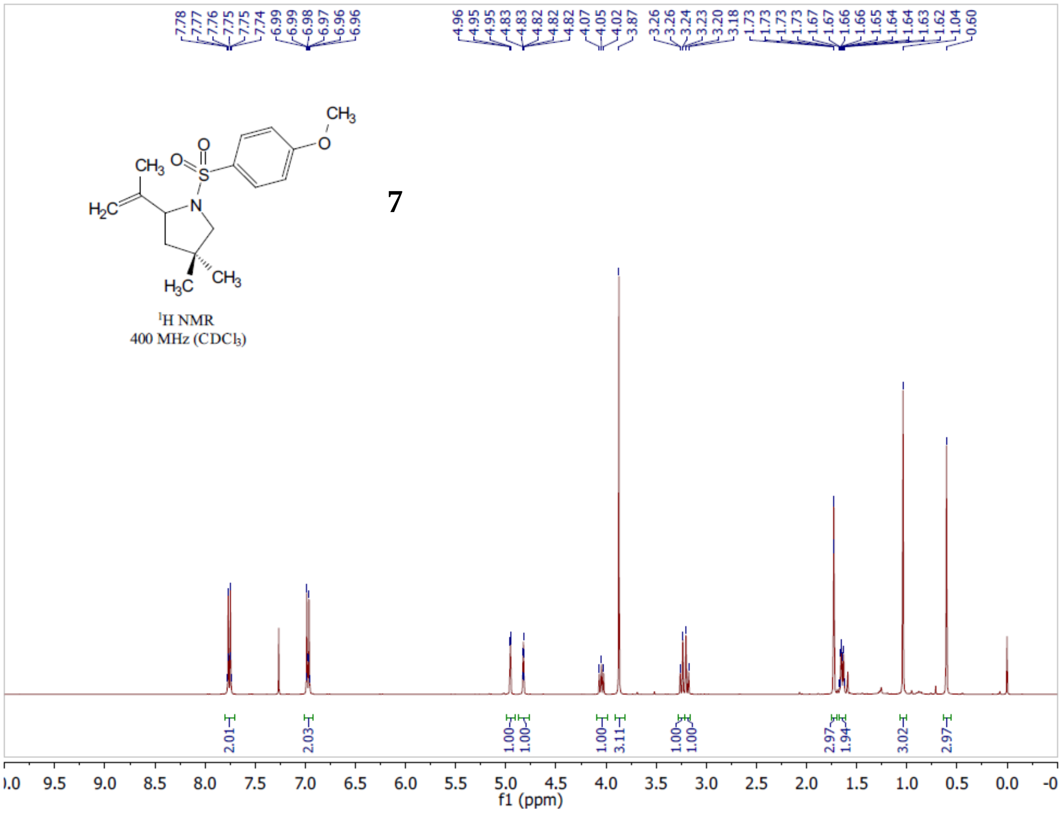
5



7.95
7.94
7.79
7.77
4.95
4.95
4.95
4.95
4.95
4.84
4.83
4.83
4.83
4.83
4.18
4.16
4.16
4.14
3.36
3.36
3.34
3.34
3.20
3.18
1.75
1.74
1.73
1.73
1.72
1.72
1.71
1.70
1.66
1.64
1.64
1.64
1.64
1.62
1.06
0.67
CH3
O
O
S
F
F
F
N
H2C
H3C
CH3
6
1H NMR
500 MHz (CDCl3)
2.09
2.07
1.00
0.99
1.01
1.03
1.08
1.03
4.10
3.08
3.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

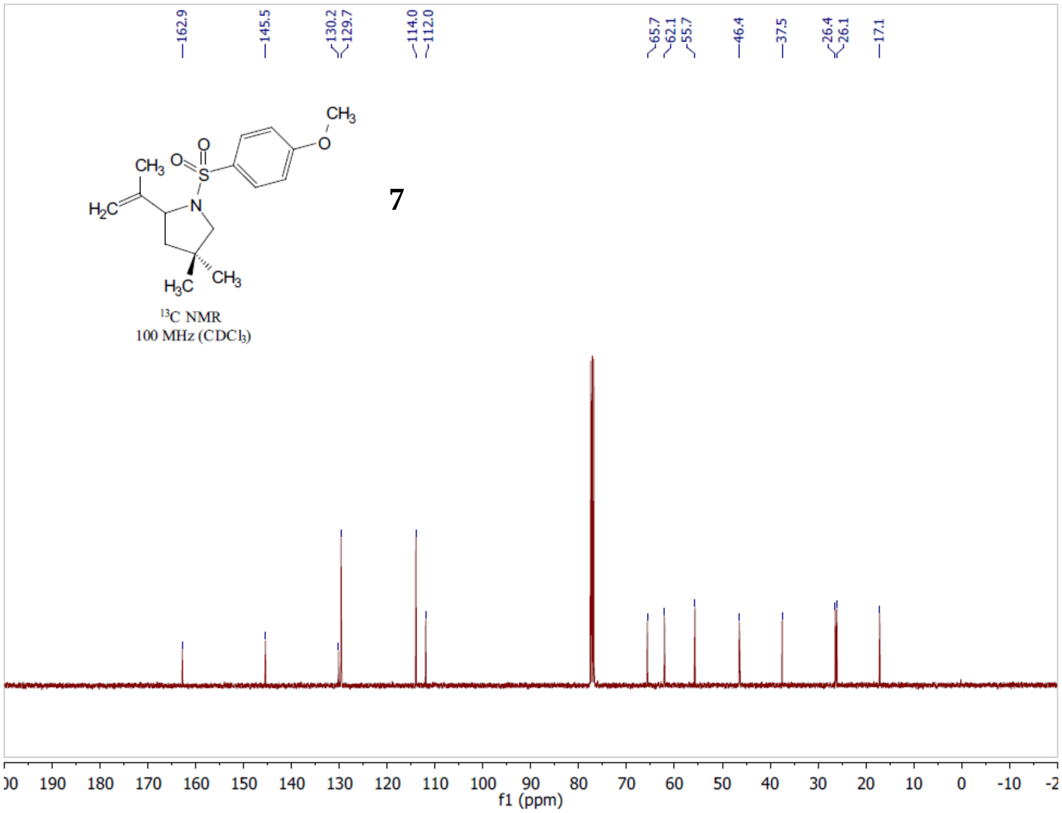


144.6
142.4
142.4
134.6
134.4
134.1
133.8
127.9
126.7
126.1
126.1
126.1
126.0
124.5
122.4
120.2
112.9
65.9
62.0
46.2
37.8
26.0
25.9
17.0
CH3
O
O
S
F
F
F
N
H2C
H3C
CH3
6
13C NMR
125 MHz (CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)



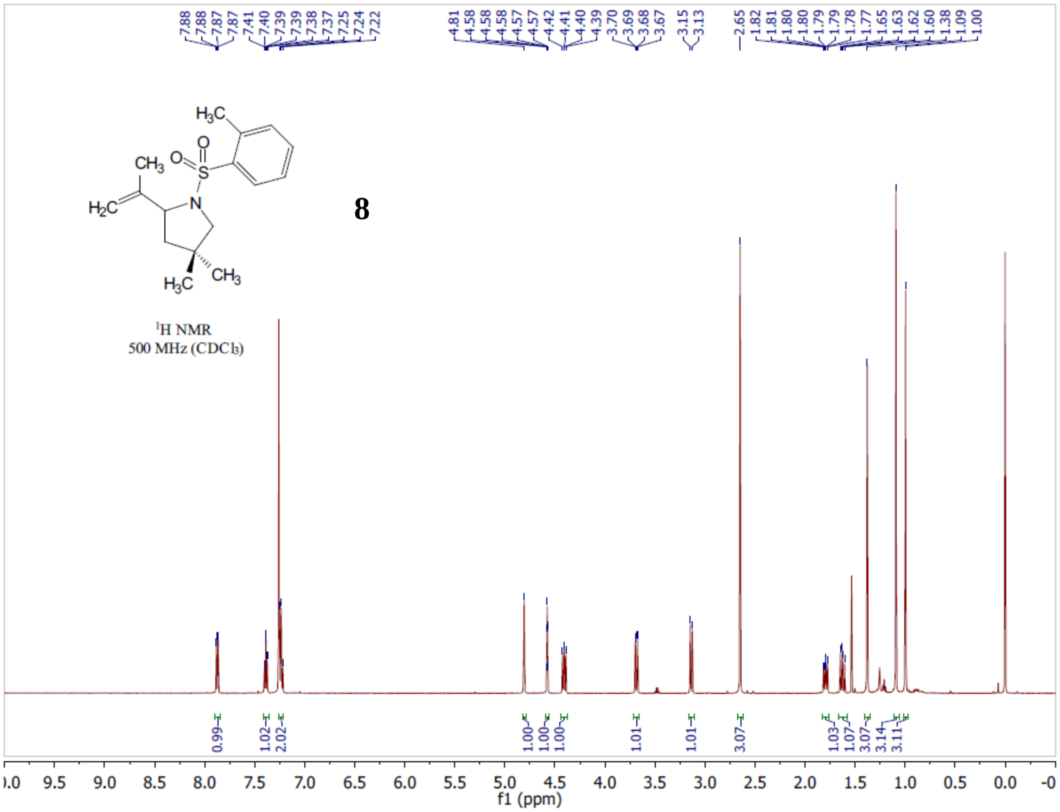
7

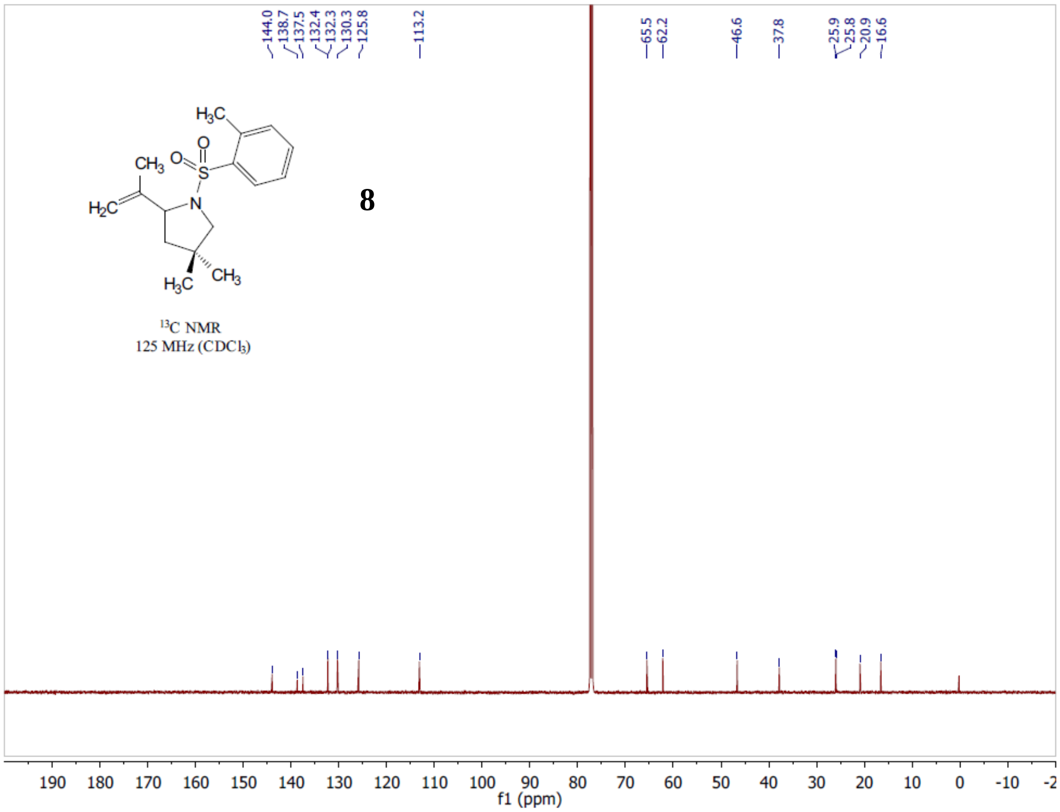
^{1}H NMR
400 MHz (CDCl$_3$)

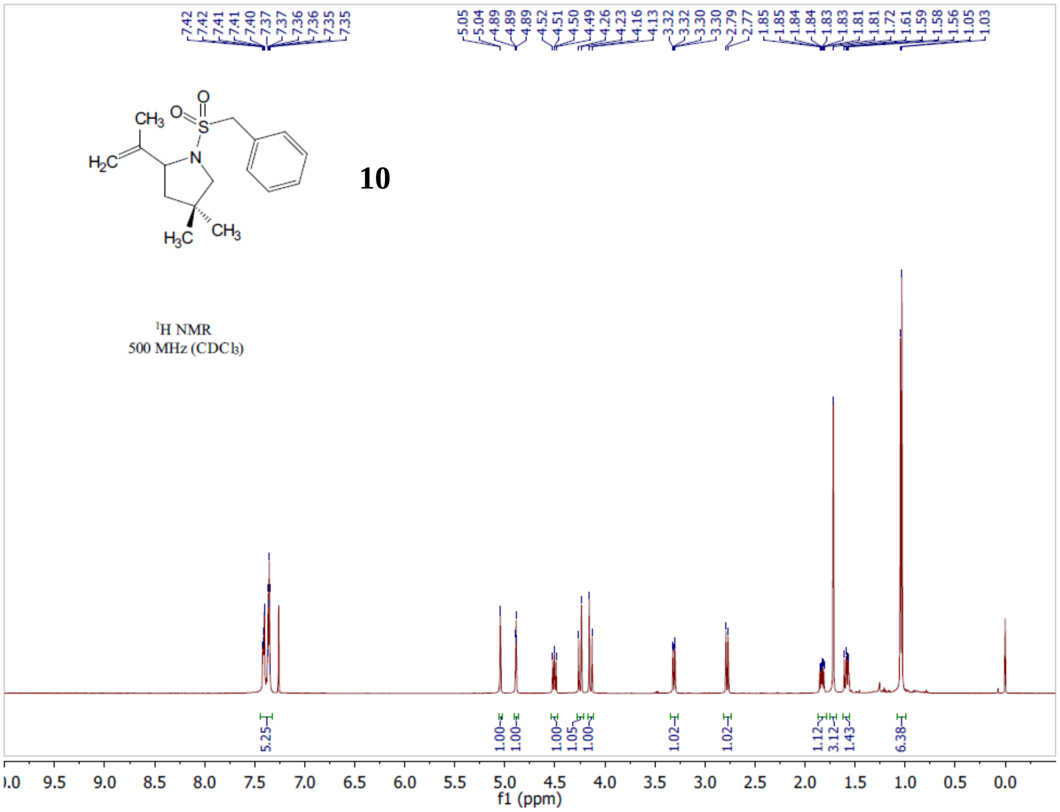


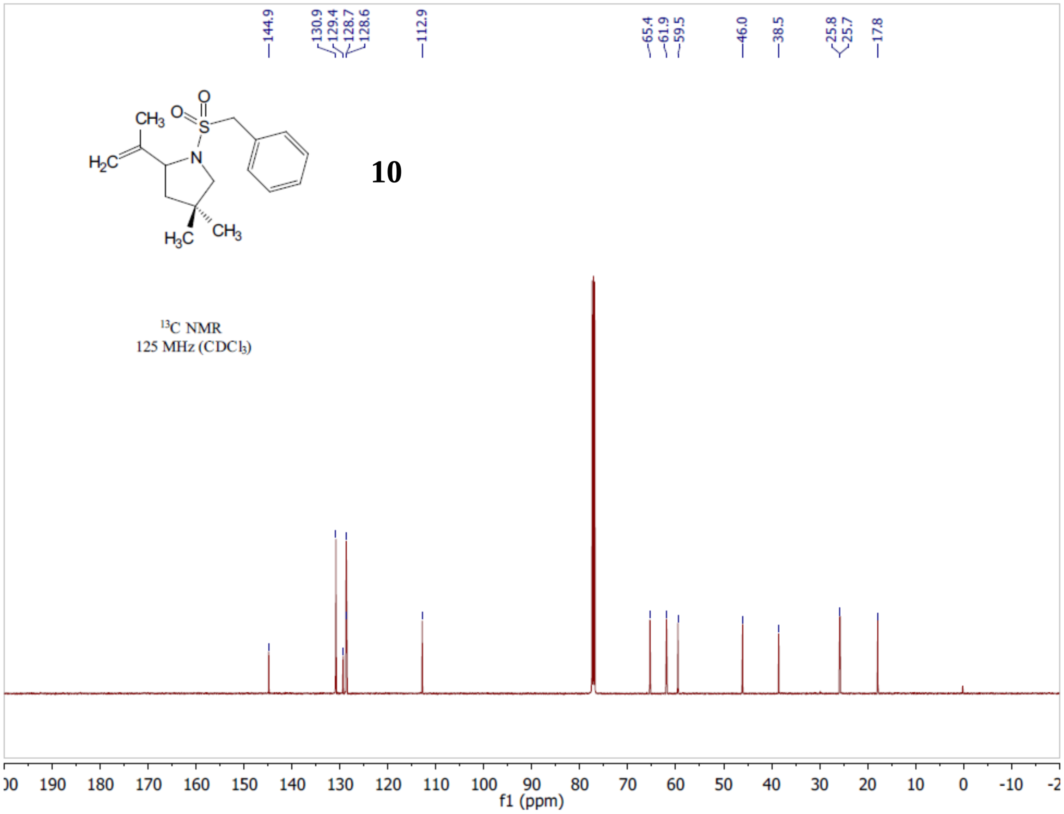
7

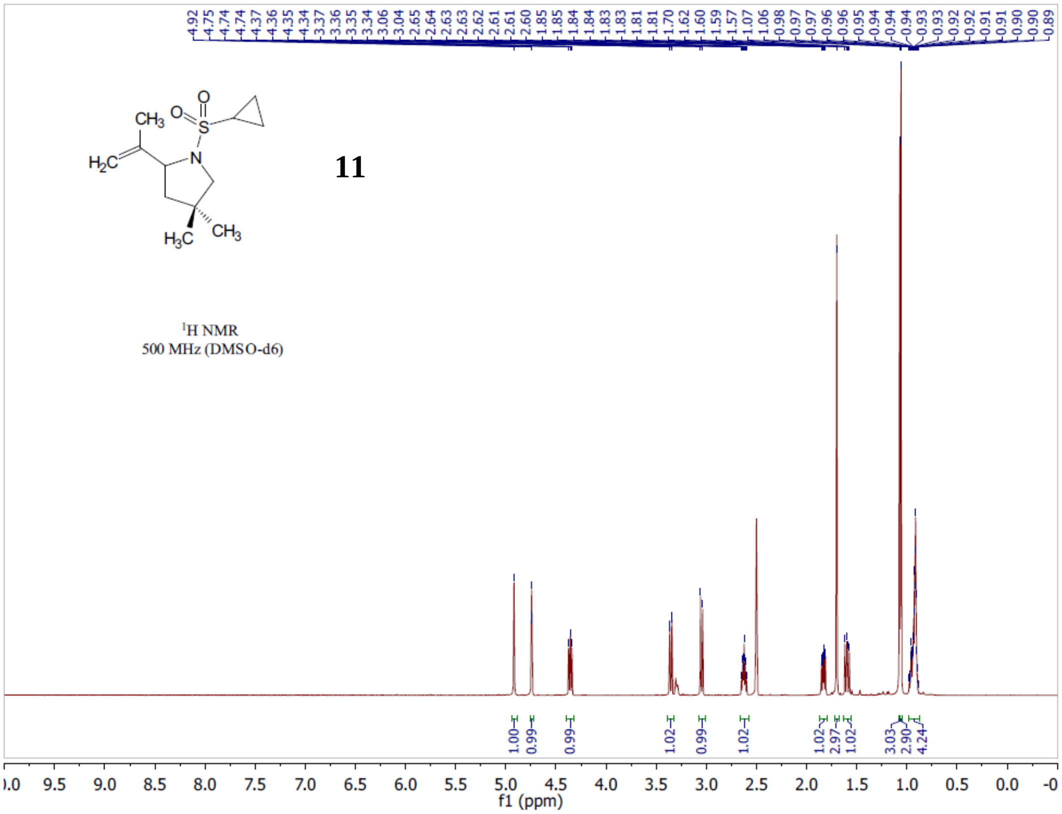
^{13}C NMR
100 MHz (CDCl$_3$)

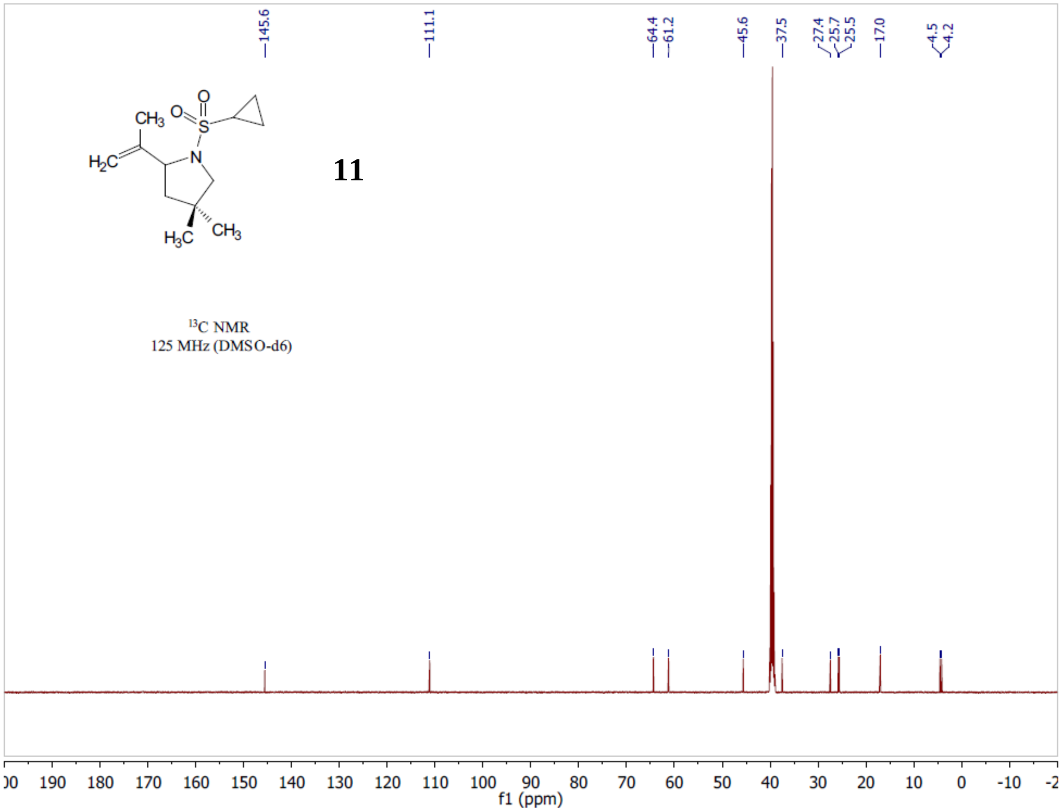

7.88
7.88
7.87
7.87
7.41
7.40
7.39
7.39
7.38
7.37
7.25
7.24
7.22
4.81
4.58
4.58
4.58
4.57
4.57
4.42
4.41
4.40
4.39
3.70
3.69
3.68
3.67
3.15
3.13
2.65
1.82
1.81
1.80
1.80
1.79
1.79
1.78
1.77
1.65
1.63
1.62
1.60
1.38
1.09
1.00
H_3C
CH_3
H_2C
O
S
N
CH_3
H_3C
8
^{1}H NMR
500 MHz (CDCl$_3$)
0.99
1.02
2.02
1.00
1.00
1.00
1.01
1.01
3.07
1.03
1.07
3.07
3.14
3.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

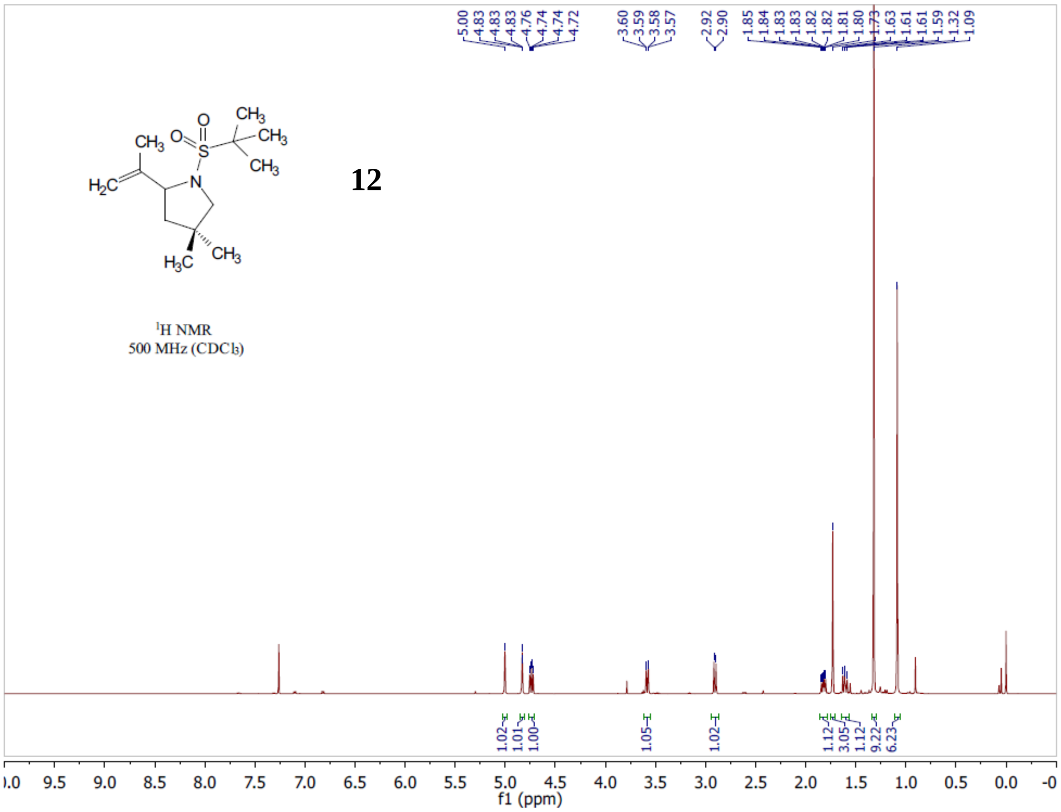

144.0
138.7
137.5
132.4
132.3
130.3
125.8
113.2
65.5
62.2
46.6
37.8
25.9
25.8
20.9
16.6
H_3C
CH_3
H_2C
O
S
N
CH_3
H_3C
8
^{13}C NMR
125 MHz (CDCl$_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

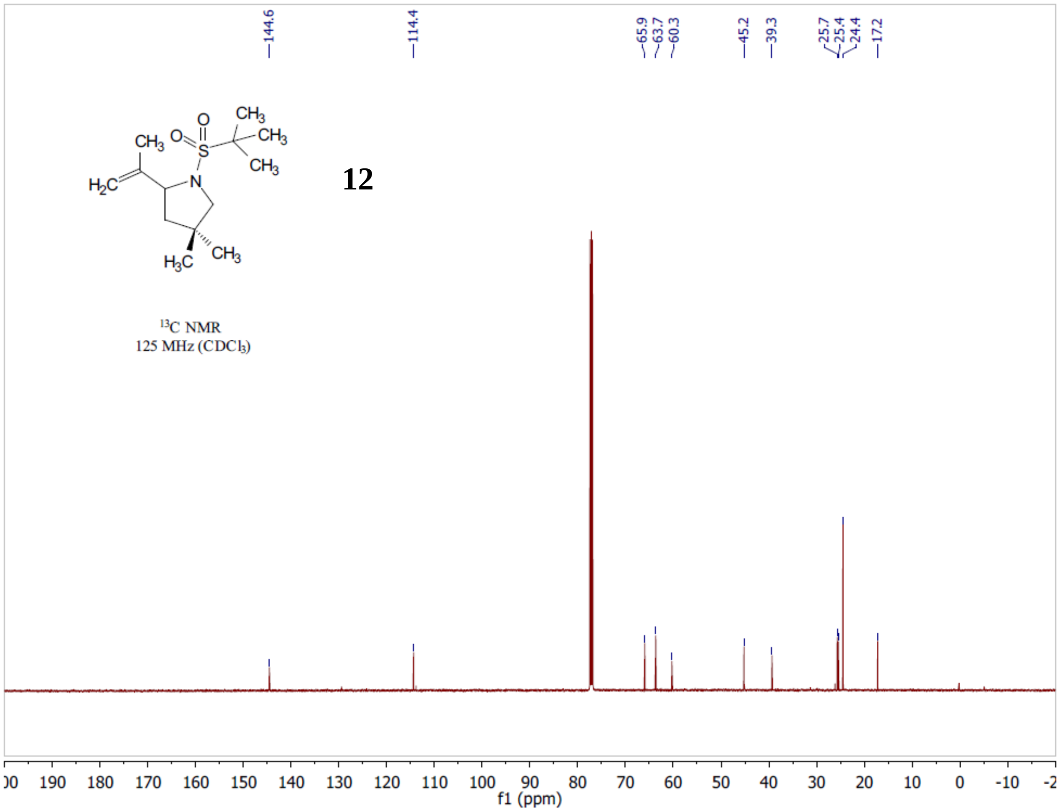

7.42
7.42
7.41
7.41
7.40
7.37
7.37
7.36
7.36
7.35
7.35
5.05
5.04
4.89
4.89
4.89
4.52
4.51
4.50
4.49
4.26
4.23
4.16
4.13
3.32
3.32
3.30
3.30
2.79
2.77
1.85
1.85
1.84
1.84
1.83
1.83
1.81
1.81
1.72
1.61
1.59
1.58
1.56
1.05
1.03
10
^{1}H NMR
500 MHz (CDCl$_3$)
5.25
1.00
1.00
1.00
1.05
1.00
1.02
1.02
1.12
3.12
1.43
6.38
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

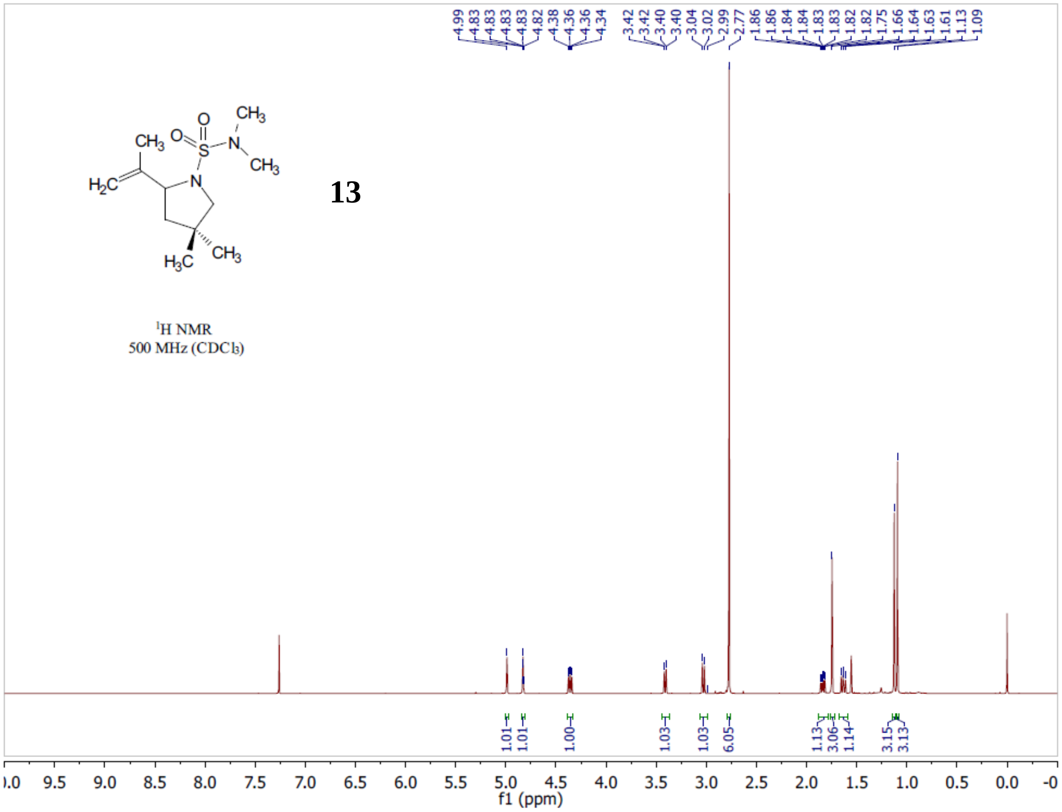

144.9
130.9
129.4
128.7
128.6
112.9
65.4
61.9
59.5
46.0
38.5
25.8
25.7
17.8
10
^{13}C NMR
125 MHz (CDCl$_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


4.92
4.75
4.74
4.74
4.37
4.36
4.35
4.34
3.37
3.36
3.35
3.34
3.06
3.04
2.65
2.64
2.63
2.63
2.62
2.61
2.61
2.60
1.85
1.85
1.84
1.84
1.83
1.83
1.81
1.81
1.70
1.62
1.60
1.59
1.57
1.07
1.06
0.98
0.97
0.97
0.96
0.96
0.95
0.94
0.94
0.94
0.93
0.93
0.92
0.92
0.91
0.91
0.90
0.90
0.89
CH3
O
O
S
N
H2C
H3C
CH3
11
1H NMR
500 MHz (DMSO-d6)
1.00
0.99
0.99
1.02
0.99
1.02
1.02
2.97
1.02
3.03
2.90
4.24
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


145.6
111.1
64.4
61.2
45.6
37.5
27.4
25.7
25.5
17.0
4.5
4.2
CH3
O
O
S
N
H2C
H3C
CH3
11
13C NMR
125 MHz (DMSO-d6)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

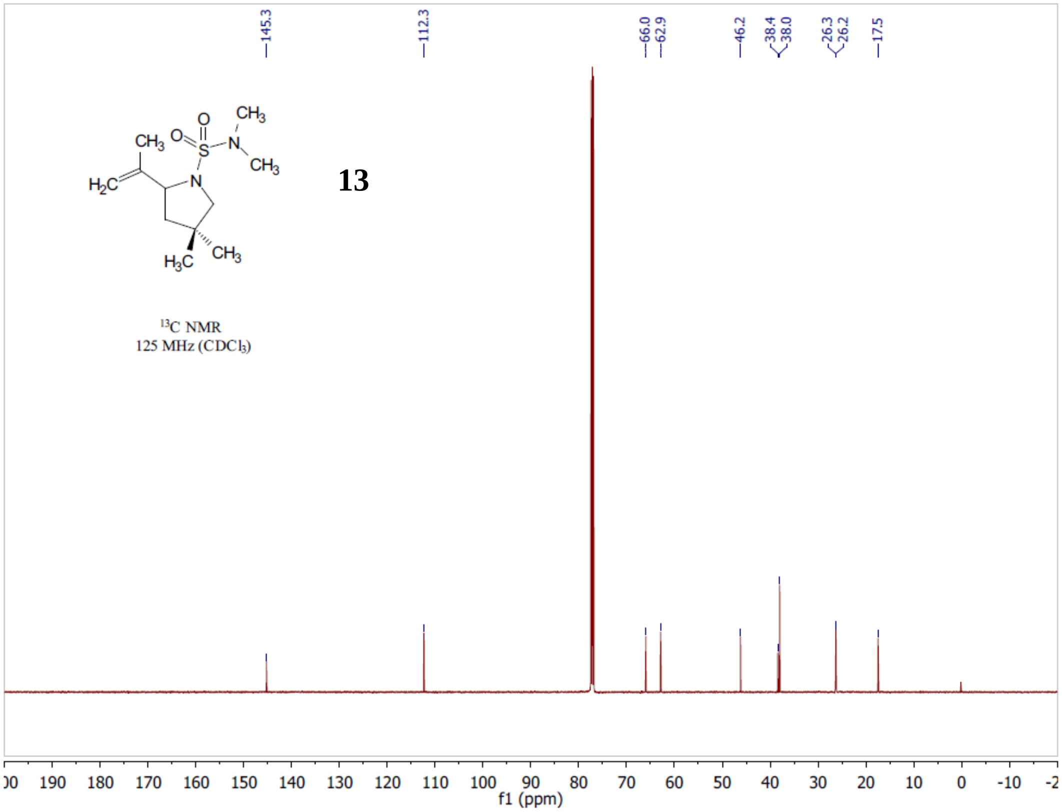

12
¹H NMR
500 MHz (CDCl₃)
5.00
4.83
4.83
4.83
4.76
4.74
4.74
4.72
3.60
3.59
3.58
3.57
2.92
2.90
1.85
1.84
1.83
1.83
1.82
1.82
1.81
1.80
1.73
1.63
1.61
1.61
1.59
1.32
1.09
1.02
1.01
1.00
1.05
1.02
1.12
3.05
1.12
9.22
6.23
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


12
¹³C NMR
125 MHz (CDCl₃)
144.6
114.4
65.9
63.7
60.3
45.2
39.3
25.7
25.4
24.4
17.2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



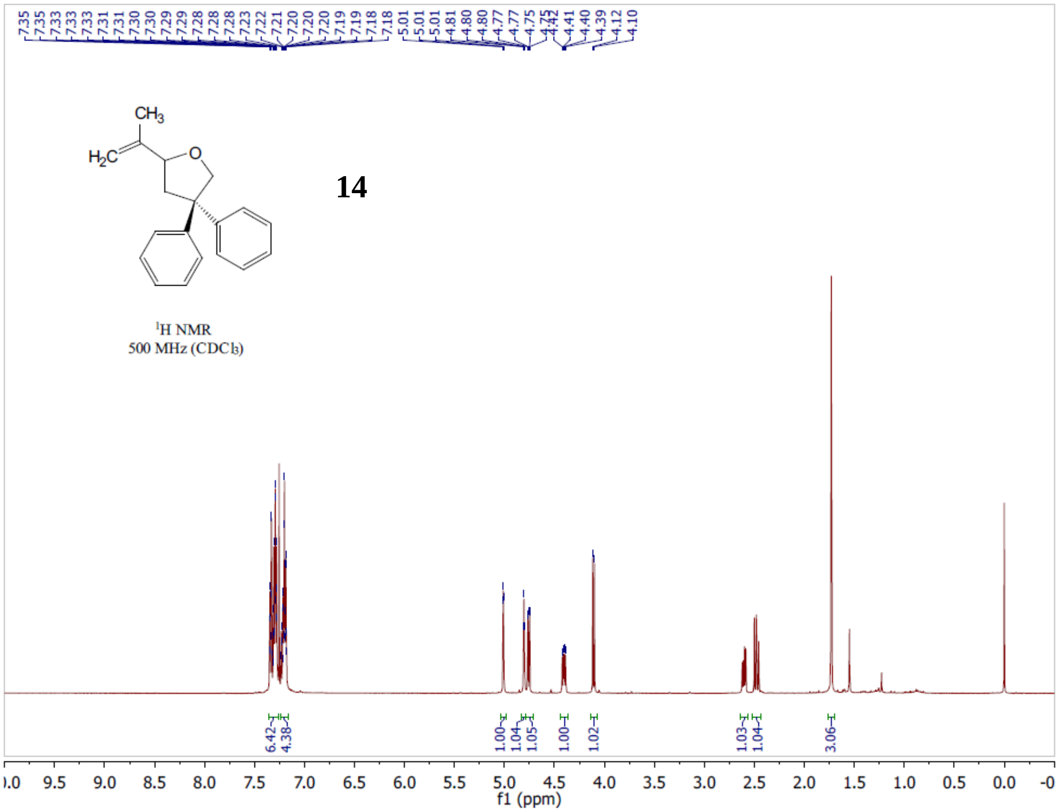
13

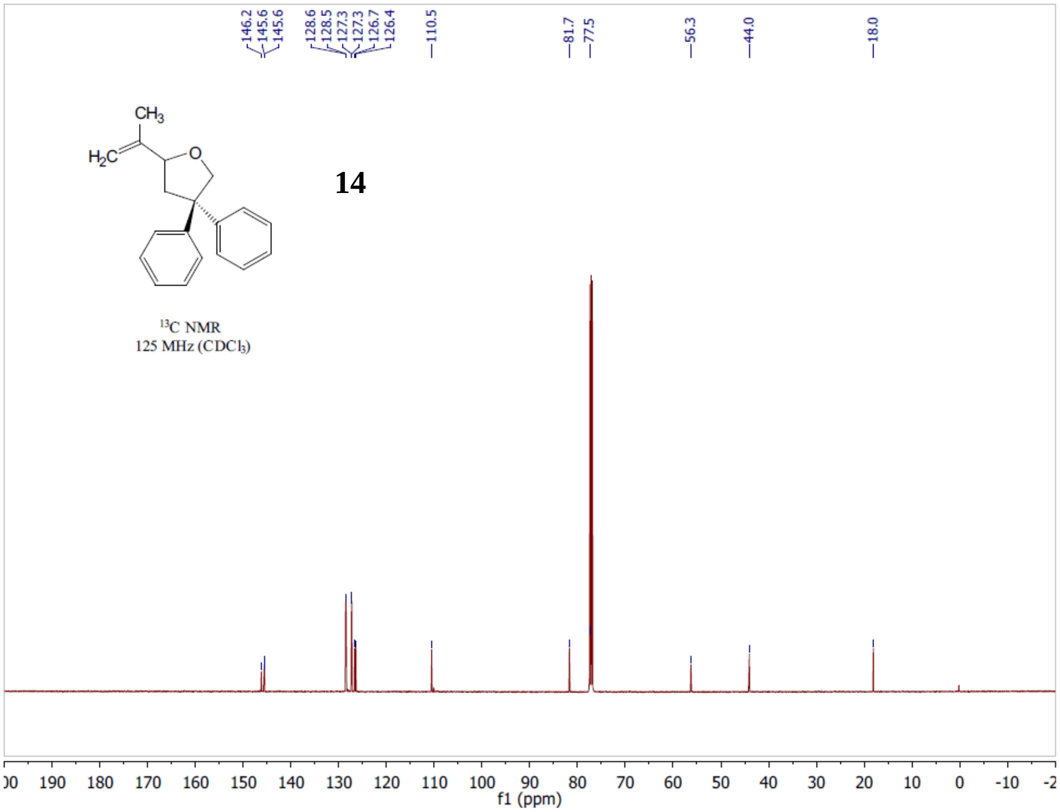
^{1}H NMR
500 MHz (CDCl$_3$)
4.99
4.83
4.83
4.83
4.83
4.82
4.38
4.36
4.36
4.34
3.42
3.42
3.40
3.40
3.04
3.02
2.99
2.77
1.86
1.86
1.84
1.84
1.83
1.83
1.82
1.82
1.75
1.66
1.64
1.63
1.61
1.13
1.09
1.01
1.01
1.00
1.03
1.03
6.05
1.13
3.06
1.14
3.15
3.13
f1 (ppm)

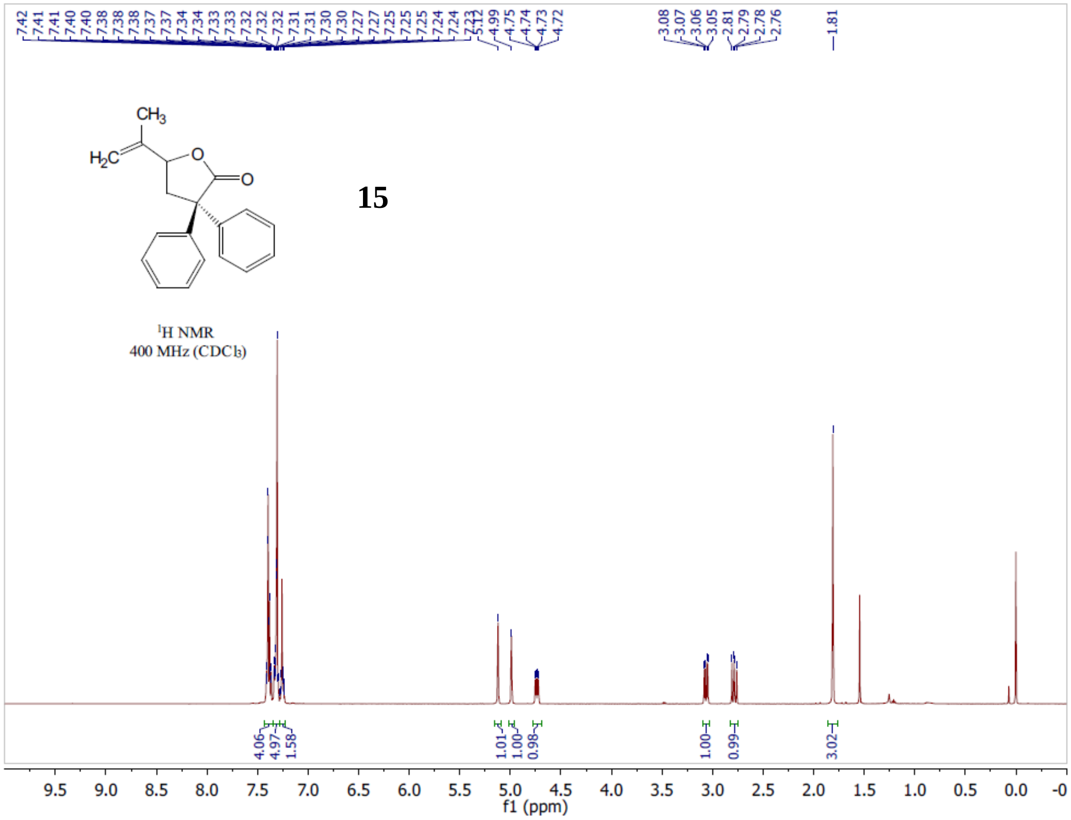


13

^{13}C NMR
125 MHz (CDCl$_3$)
145.3
112.3
66.0
62.9
46.2
38.4
38.0
26.3
26.2
17.5
f1 (ppm)

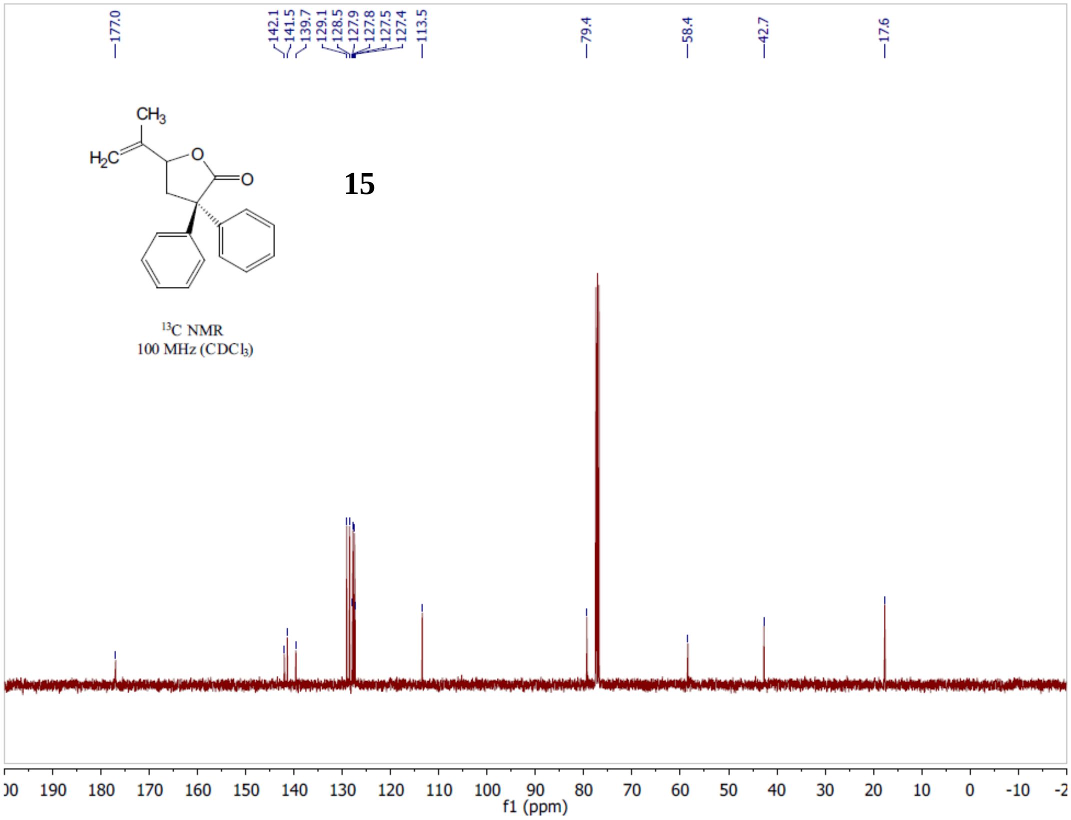

7.35
7.35
7.33
7.33
7.33
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.28
7.23
7.22
7.21
7.20
7.20
7.20
7.19
7.19
7.18
7.18
5.01
5.01
5.01
4.81
4.80
4.80
4.77
4.77
4.75
4.75
4.42
4.41
4.40
4.39
4.12
4.10
CH3
H2C
O
14
1H NMR
500 MHz (CDCl3)
6.42
4.38
1.00
1.04
1.05
1.00
1.02
1.03
1.04
3.06
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


146.2
145.6
145.6
128.6
128.5
127.3
127.3
126.7
126.4
110.5
81.7
77.5
56.3
44.0
18.0
CH3
H2C
O
14
13C NMR
125 MHz (CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)



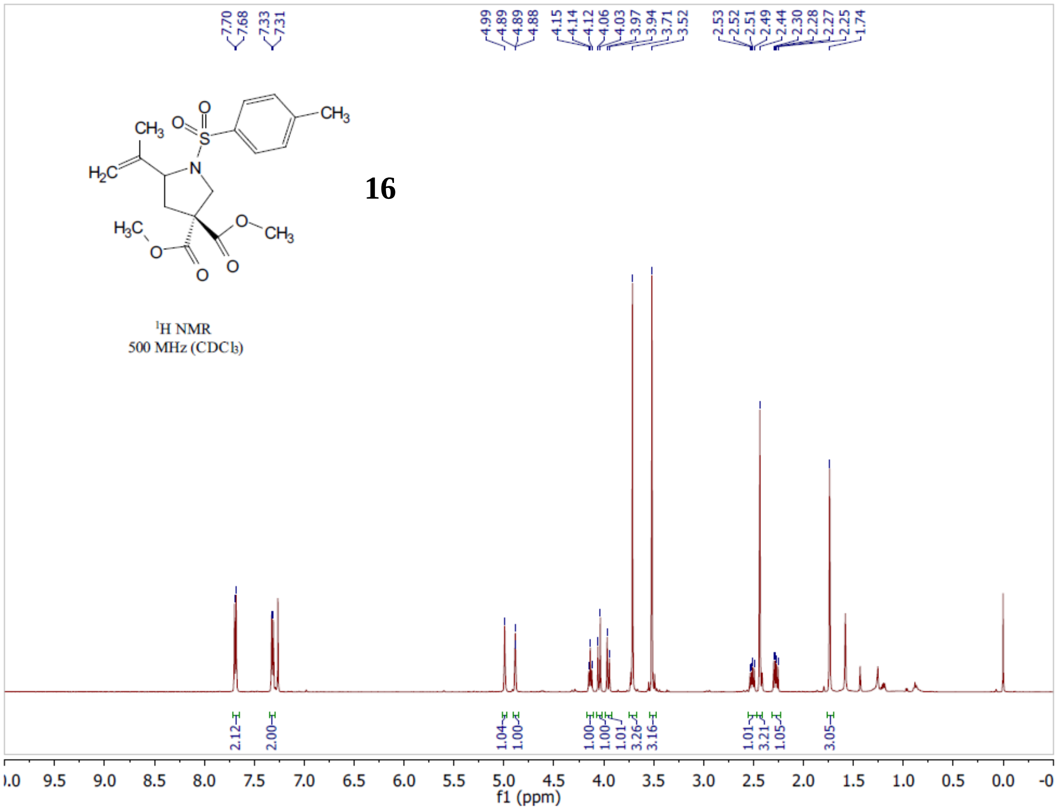
15

^{1}H NMR
400 MHz (CDCl$_3$)

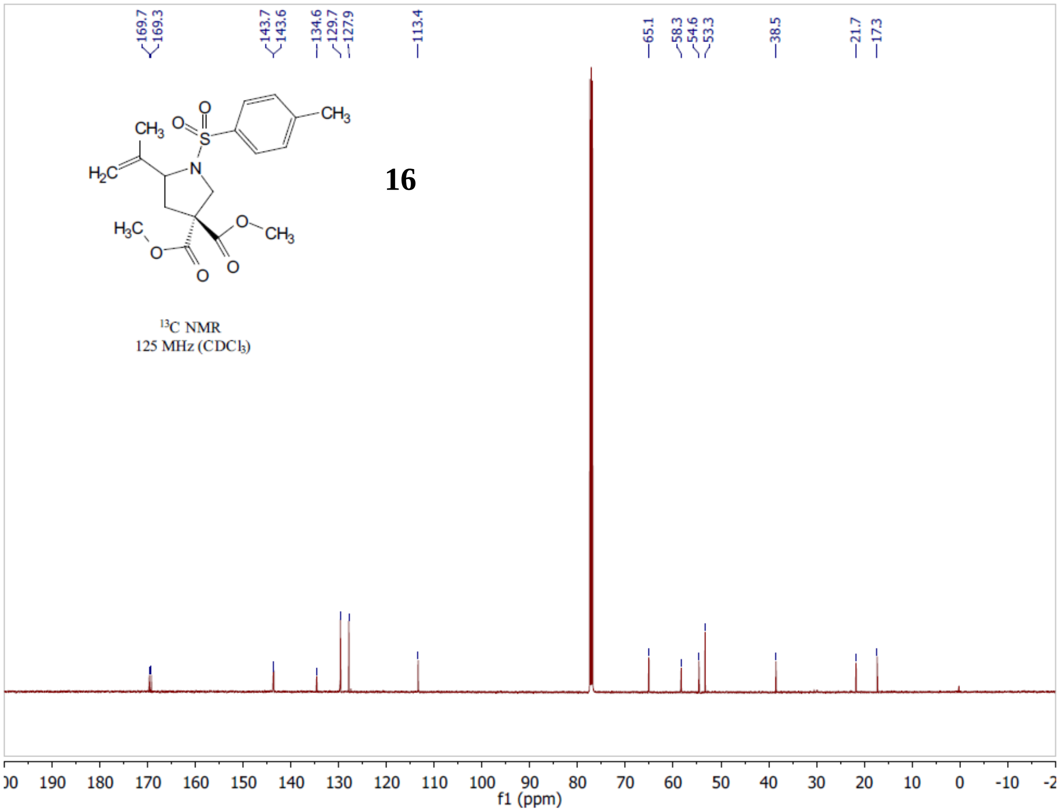


15

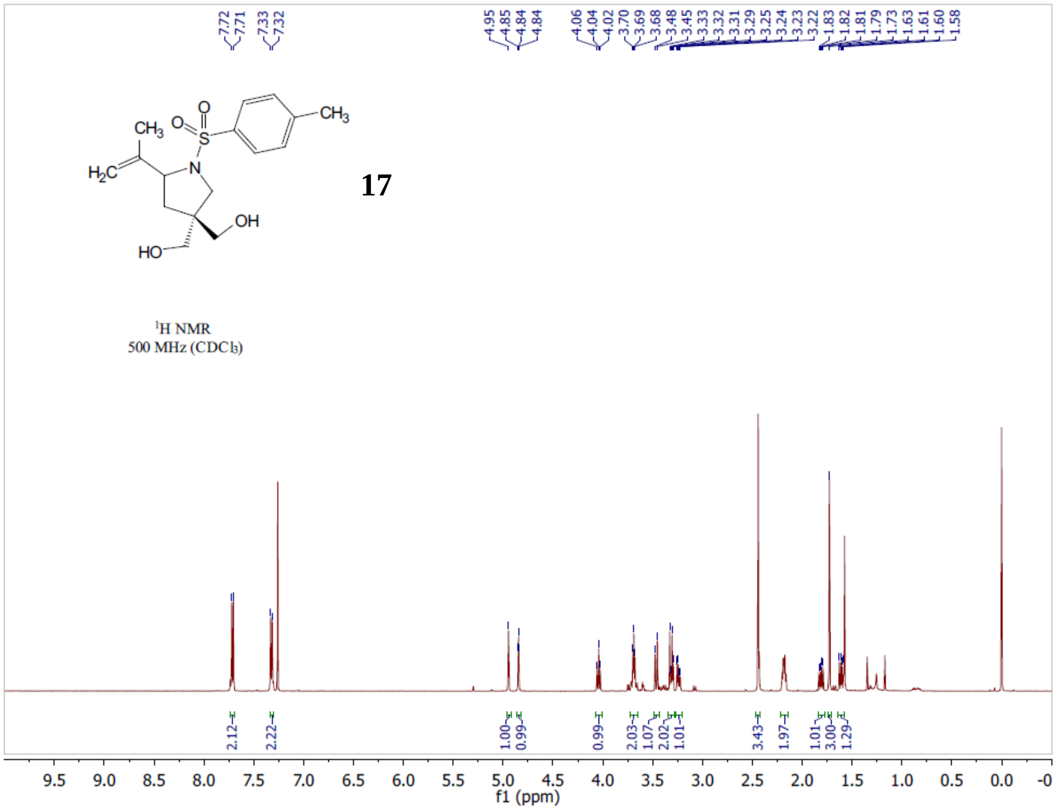
^{13}C NMR
100 MHz (CDCl$_3$)

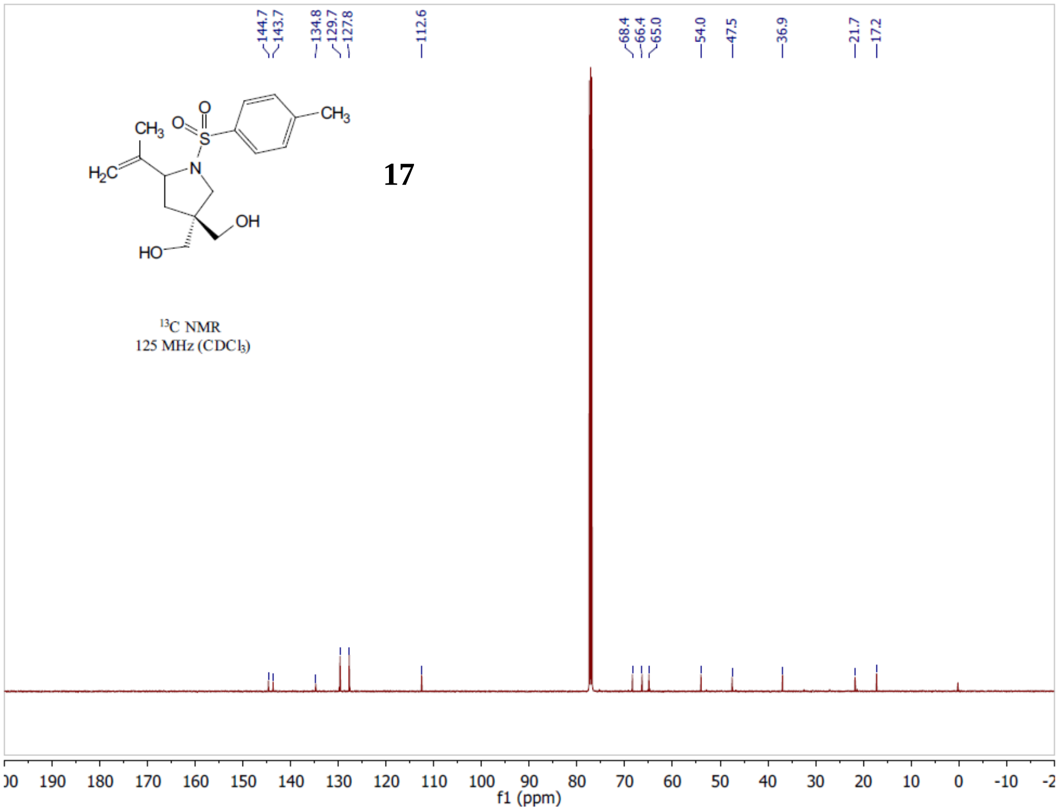


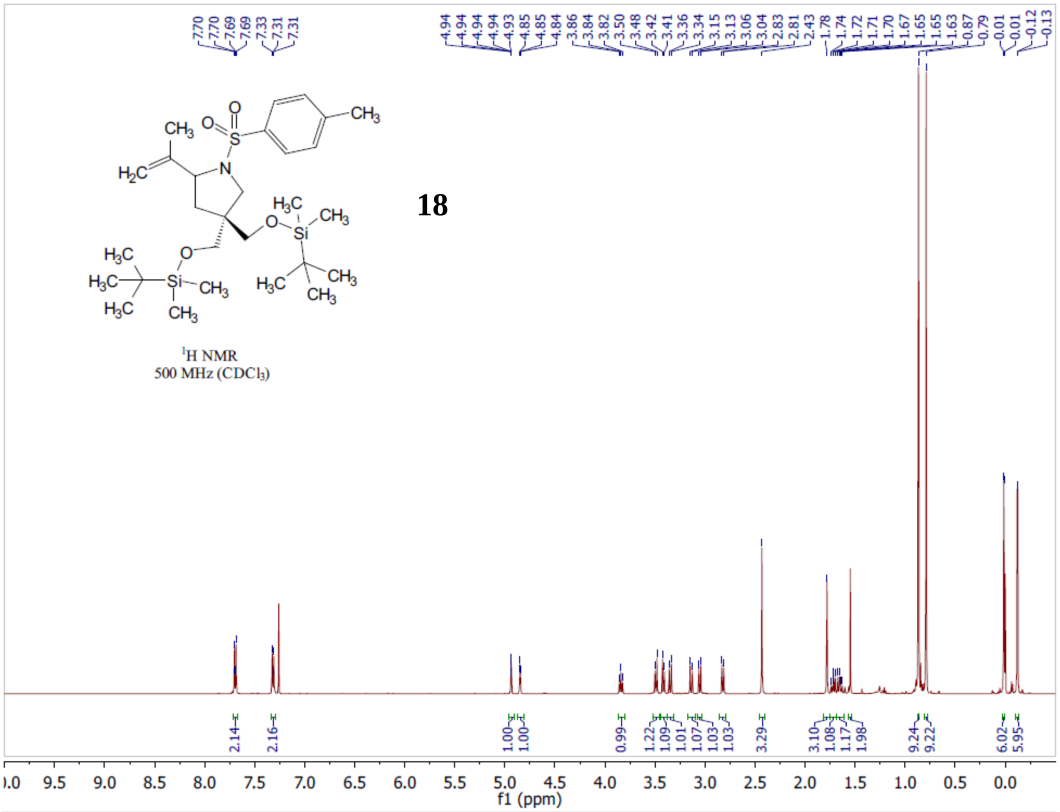
7.70
7.68
7.33
7.31
4.99
4.89
4.89
4.88
4.15
4.14
4.12
4.06
4.03
3.97
3.94
3.71
3.52
2.53
2.52
2.51
2.49
2.44
2.30
2.28
2.27
2.25
1.74
CH3
O
O
S
CH3
H2C
N
H3C
O
CH3
O
O
O
16
1H NMR
500 MHz (CDCl3)
2.12
2.00
1.04
1.00
1.00
1.00
1.01
3.26
3.16
1.01
3.21
1.05
3.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



169.7
169.3
143.7
143.6
134.6
129.7
127.9
113.4
65.1
58.3
54.6
53.3
38.5
21.7
17.3
CH3
O
O
S
CH3
H2C
N
H3C
O
CH3
O
O
O
16
13C NMR
125 MHz (CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

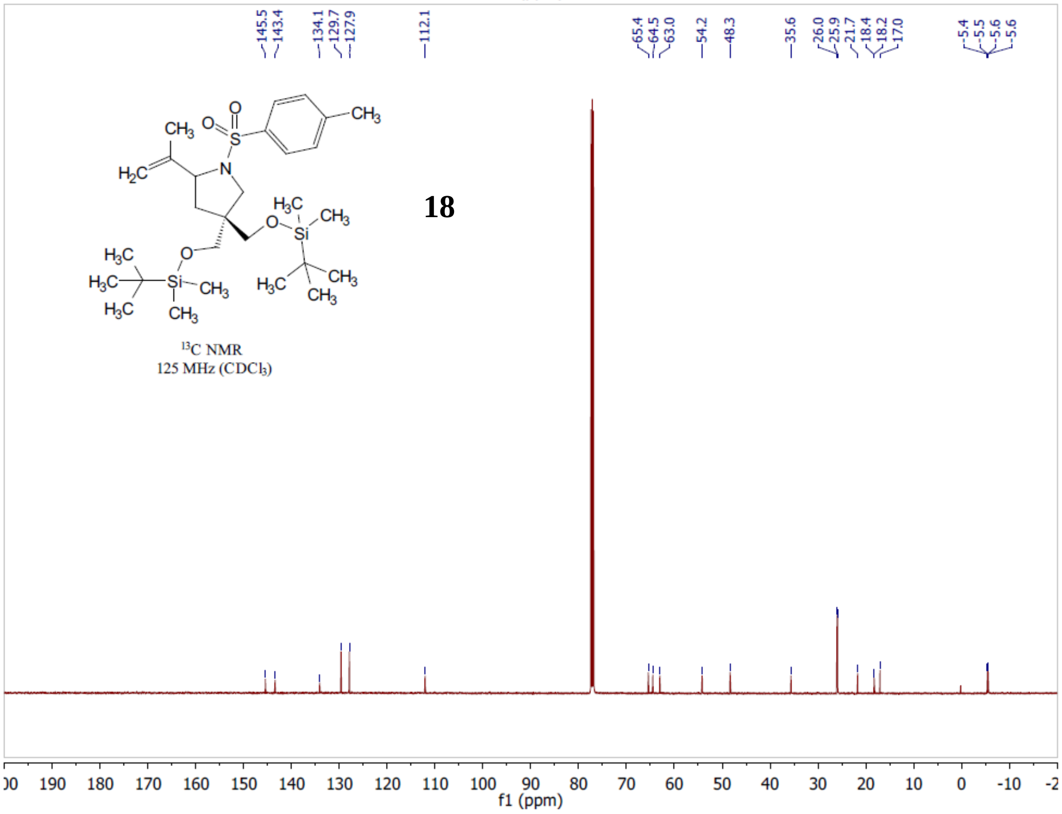

7.72
7.71
7.33
7.32
4.95
4.85
4.84
4.84
4.06
4.04
4.02
3.70
3.69
3.68
3.48
3.45
3.33
3.32
3.31
3.29
3.25
3.24
3.23
3.22
1.83
1.82
1.81
1.79
1.73
1.63
1.61
1.60
1.58
CH3
O
O
S
CH3
H2C
N
OH
HO
17
1H NMR
500 MHz (CDCl3)
2.12
2.22
1.00
0.99
0.99
2.03
1.07
2.02
1.01
3.43
1.97
1.01
3.00
1.29
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


144.7
143.7
134.8
129.7
127.8
112.6
68.4
66.4
65.0
54.0
47.5
36.9
21.7
17.2
CH3
O
O
S
CH3
H2C
N
OH
HO
17
13C NMR
125 MHz (CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)



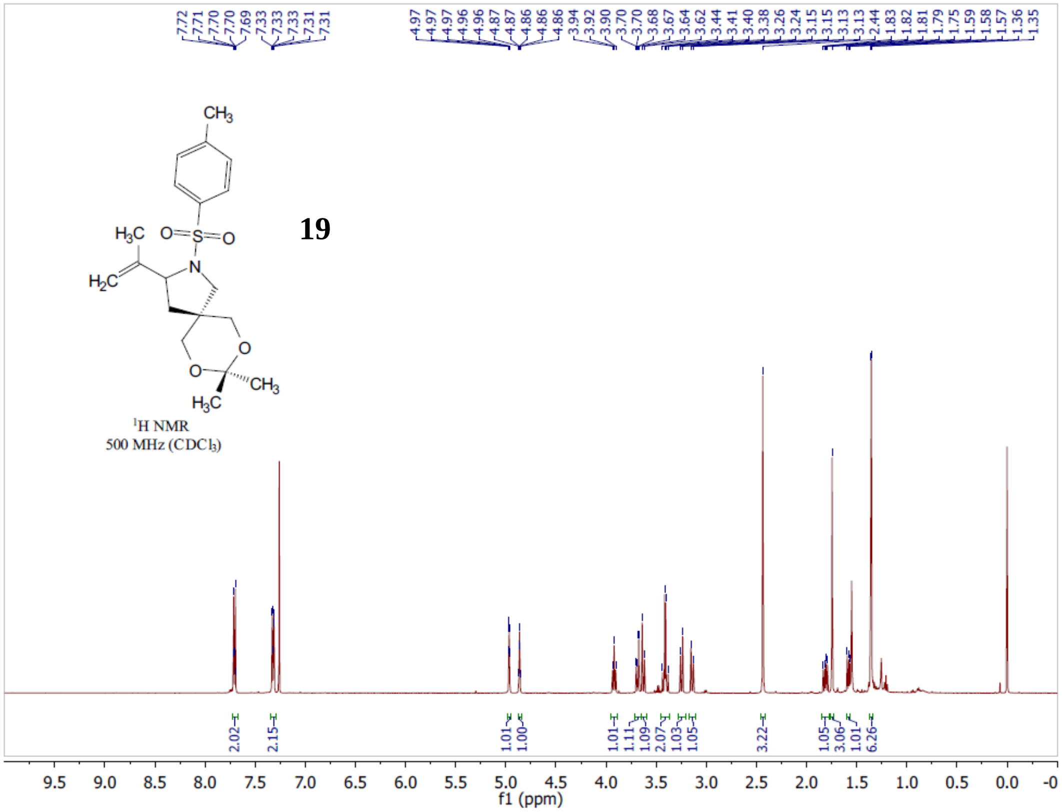
18

^{1}H NMR
500 MHz (CDCl$_3$)

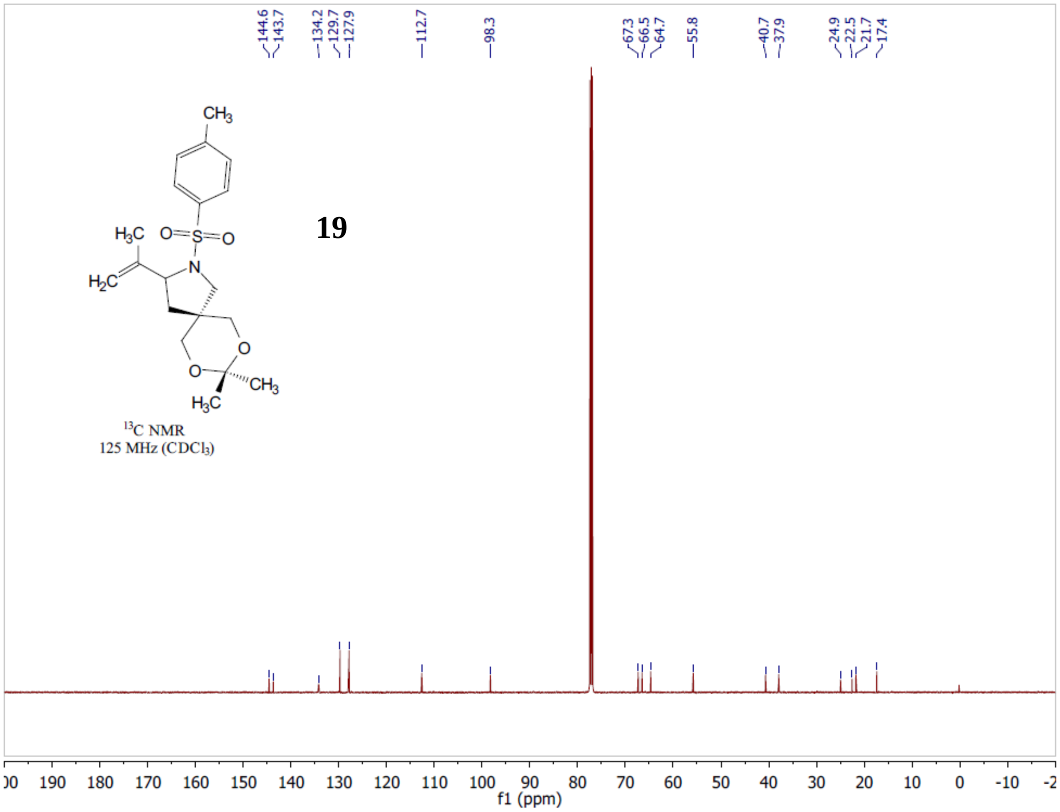


18

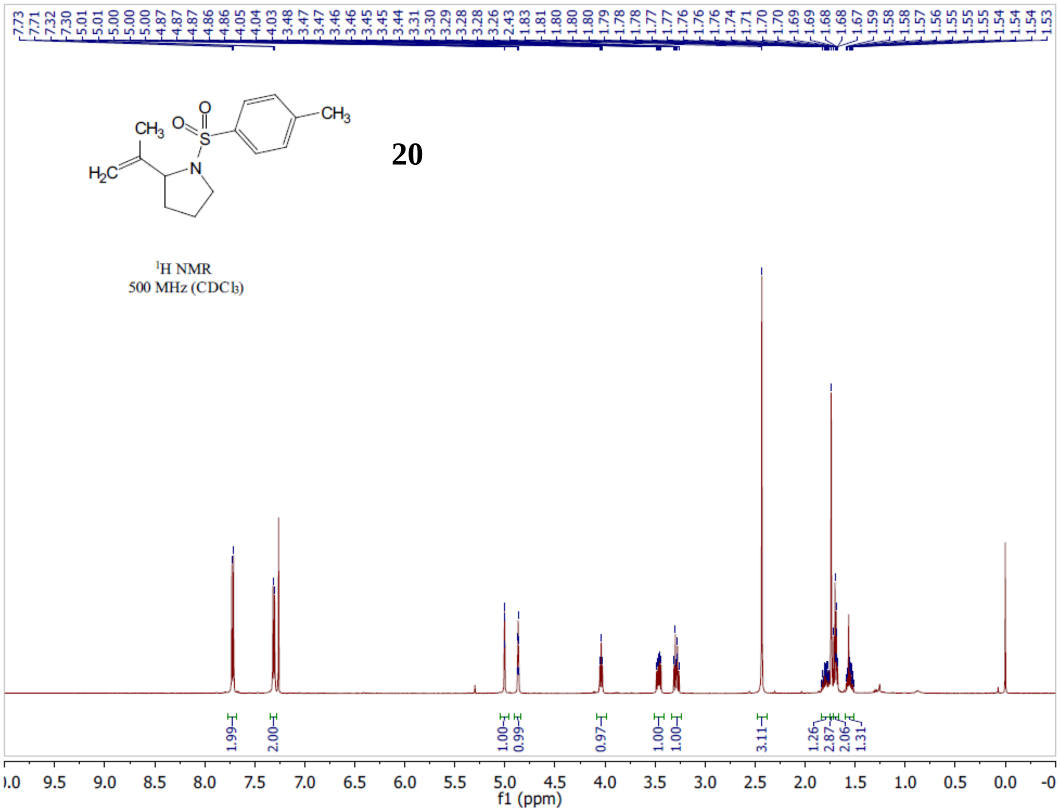
^{13}C NMR
125 MHz (CDCl$_3$)

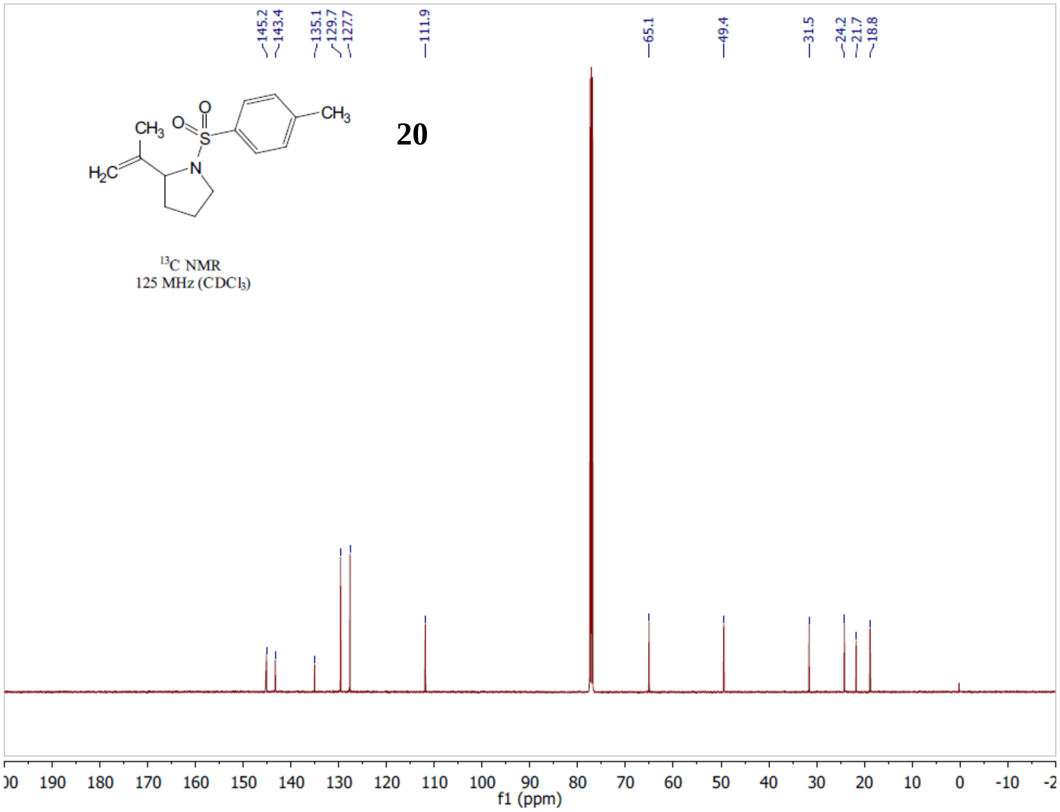

19

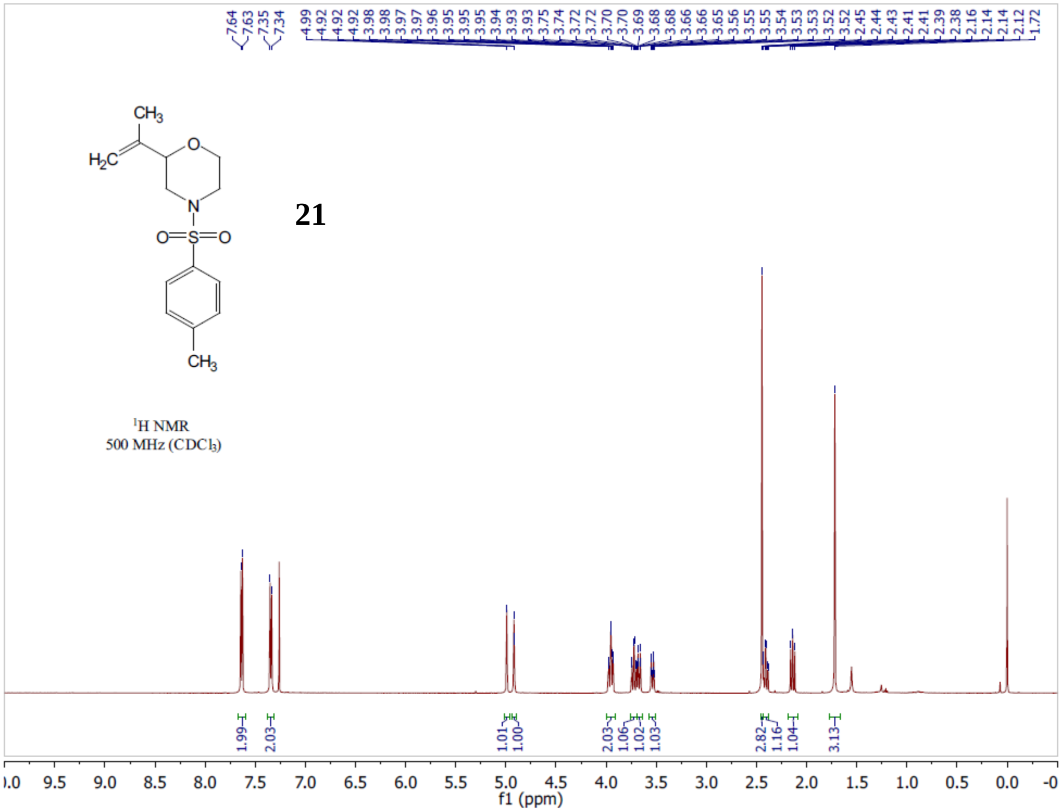
^{1}H NMR
500 MHz (CDCl$_3$)


19

^{13}C NMR
125 MHz (CDCl$_3$)

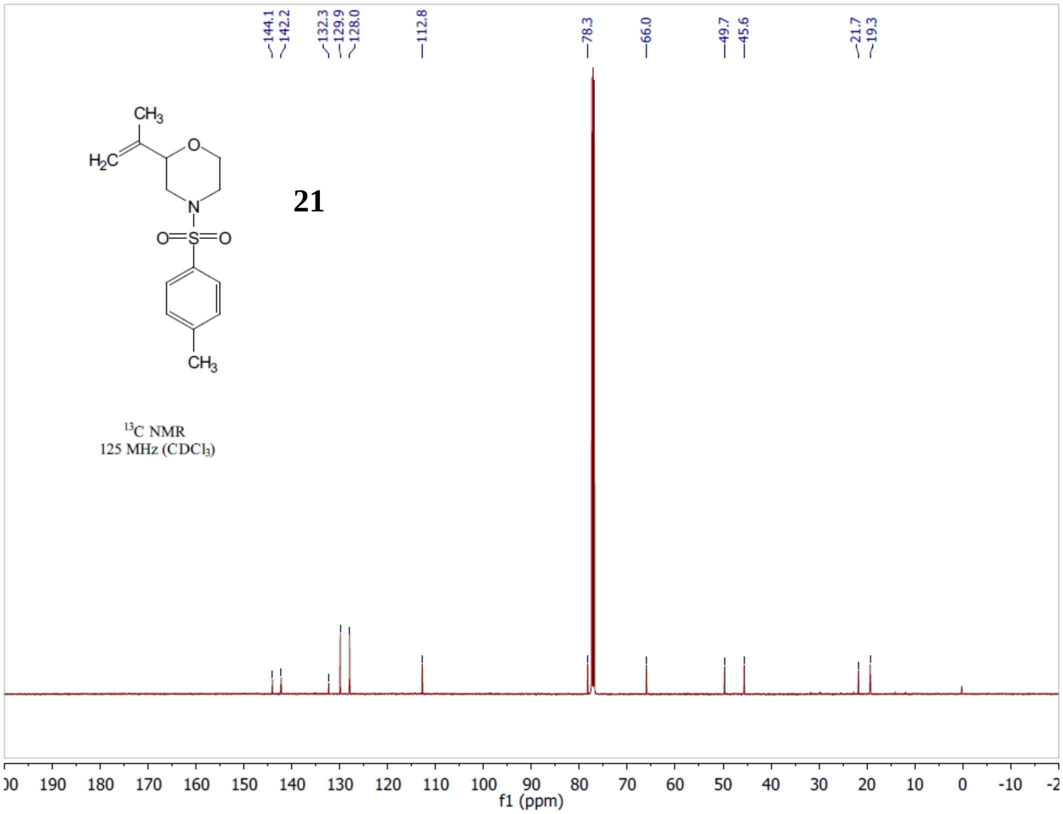

7.73 7.71 7.32 7.30 5.01 5.01 5.00 5.00 5.00 4.87 4.87 4.87 4.86 4.86 4.05 4.04 4.03 3.48 3.47 3.47 3.46 3.46 3.45 3.45 3.44 3.31 3.30 3.29 3.28 3.28 3.26 2.43 1.83 1.81 1.80 1.80 1.80 1.79 1.78 1.78 1.77 1.77 1.76 1.76 1.76 1.74 1.71 1.70 1.70 1.69 1.69 1.68 1.68 1.67 1.59 1.58 1.58 1.57 1.56 1.55 1.55 1.55 1.54 1.54 1.54 1.53
CH3
O
O
S
CH3
H2C
N
20
1H NMR
500 MHz (CDCl3)
1.99
2.00
1.00
0.99
0.97
1.00
1.00
3.11
1.26
2.87
2.06
1.31
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


145.2
143.4
135.1
129.7
127.7
111.9
65.1
49.4
31.5
24.2
21.7
18.8
CH3
O
O
S
CH3
H2C
N
20
13C NMR
125 MHz (CDCl3)
)0 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)



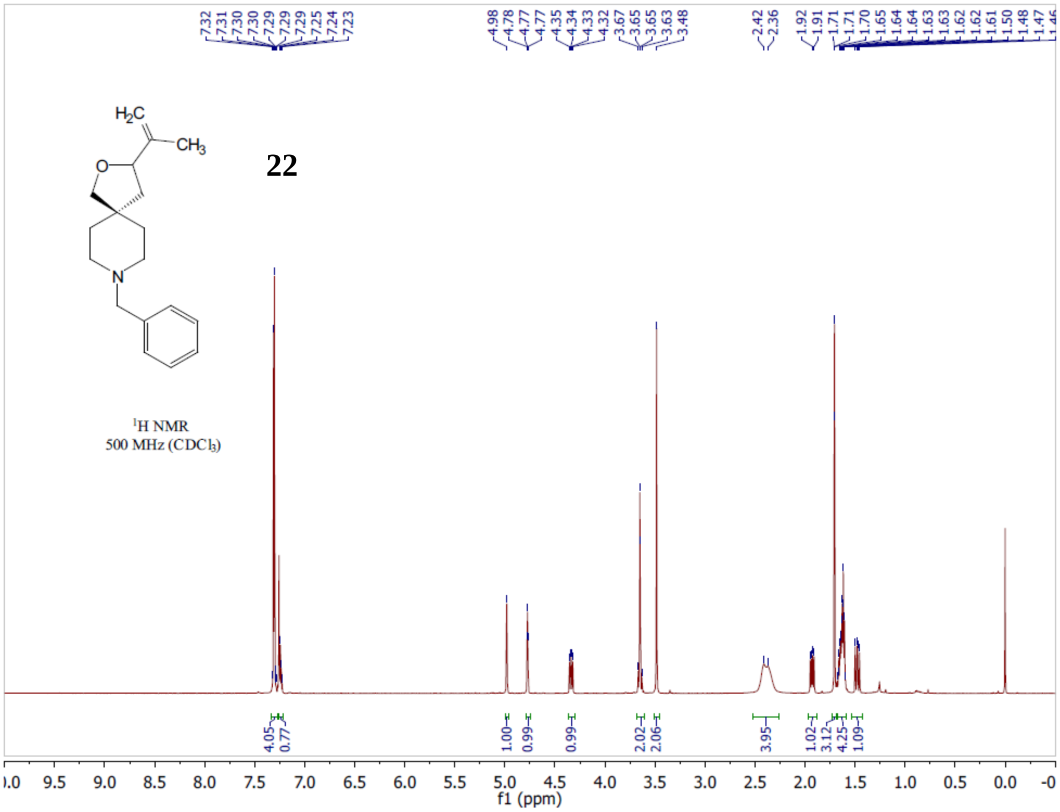
21

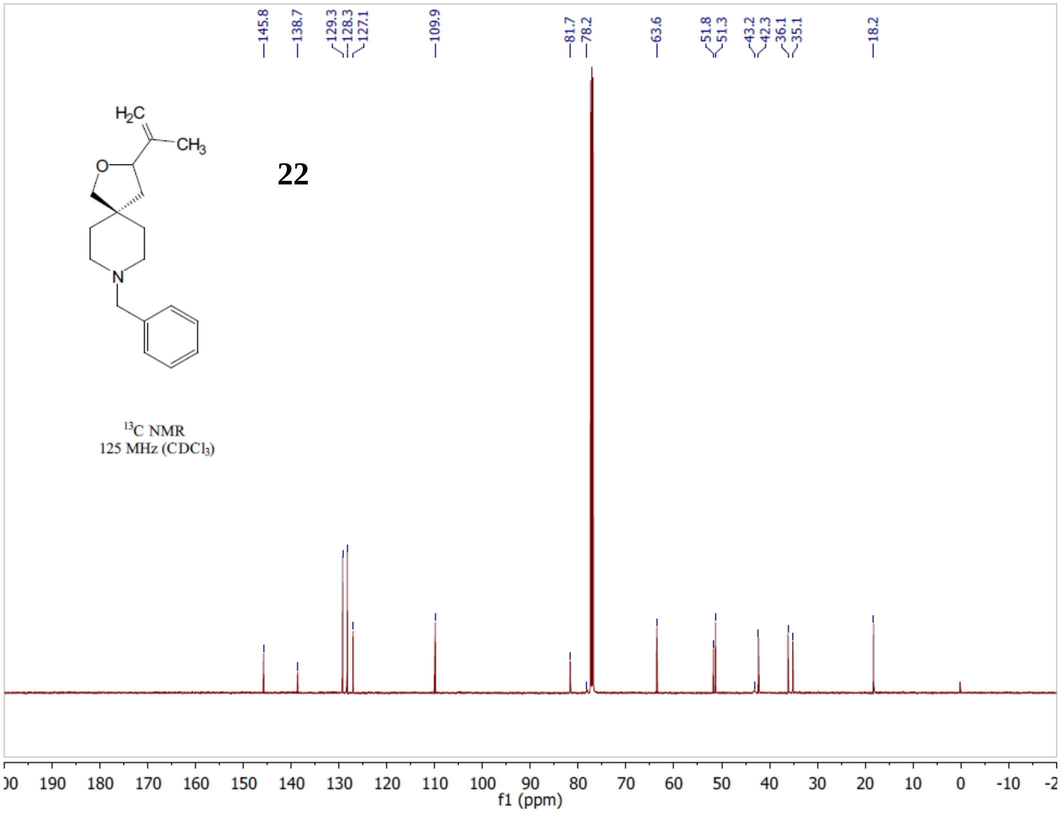
^{1}H NMR
500 MHz (CDCl$_3$)

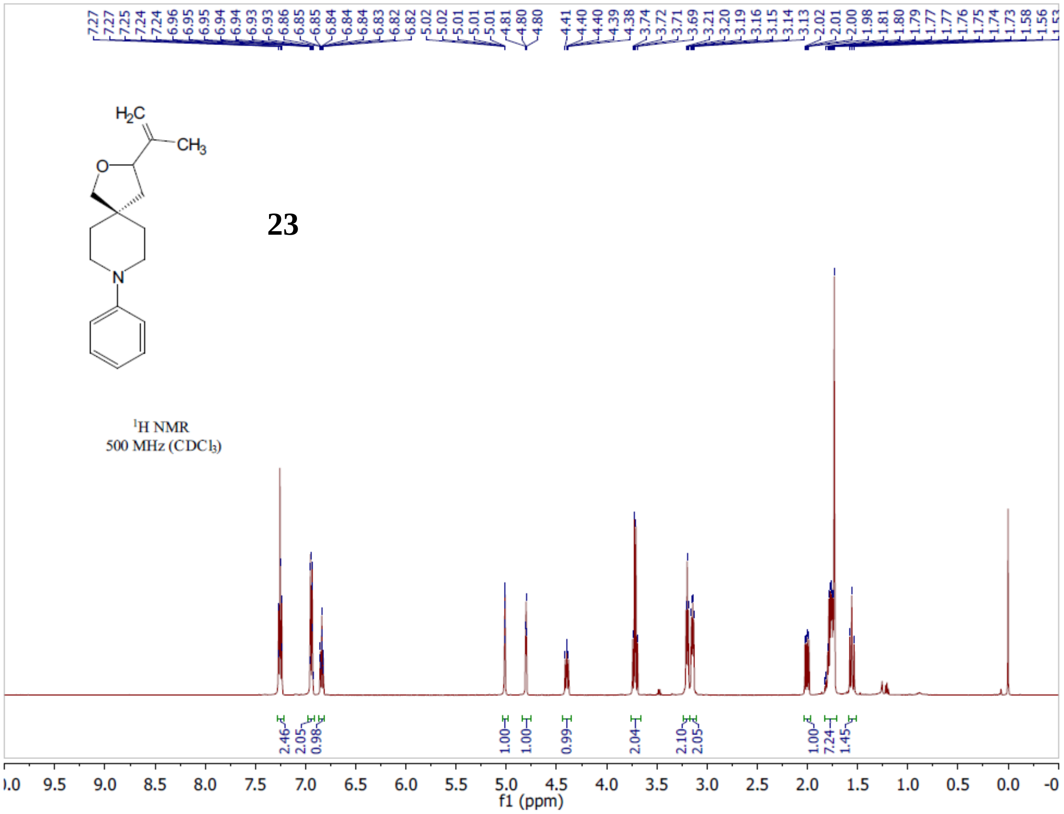


21

^{13}C NMR
125 MHz (CDCl$_3$)

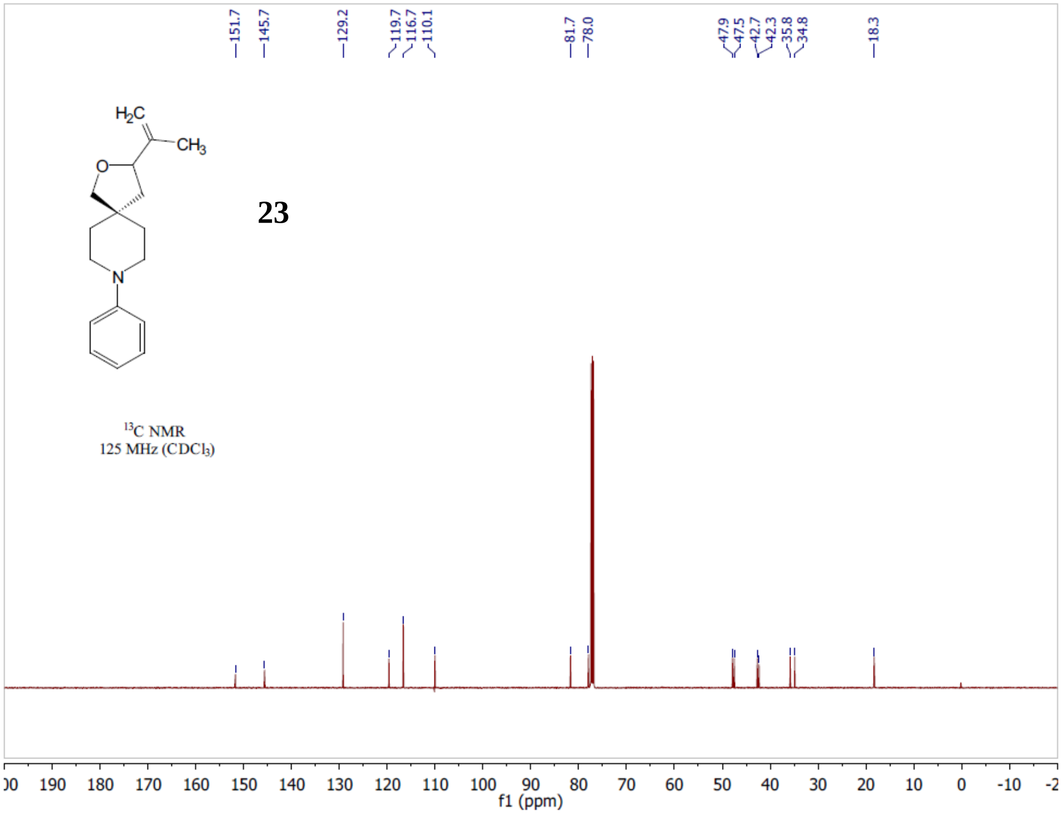

7.32
7.31
7.30
7.29
7.29
7.29
7.25
7.24
7.23
4.98
4.78
4.77
4.77
4.35
4.34
4.33
4.32
3.67
3.65
3.65
3.63
3.48
2.42
2.36
1.92
1.91
1.71
1.71
1.70
1.65
1.64
1.64
1.63
1.63
1.62
1.62
1.61
1.50
1.48
1.47
1.46
H_2C
CH_3
O
N
22
^{1}H NMR
500 MHz (CDCl$_3$)
4.05
0.77
1.00
0.99
0.99
2.02
2.06
3.95
1.02
3.12
4.25
1.09
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


145.8
138.7
129.3
128.3
127.1
109.9
81.7
78.2
63.6
51.8
51.3
43.2
42.3
36.1
35.1
18.2
H_2C
CH_3
O
N
22
^{13}C NMR
125 MHz (CDCl$_3$)
)0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)



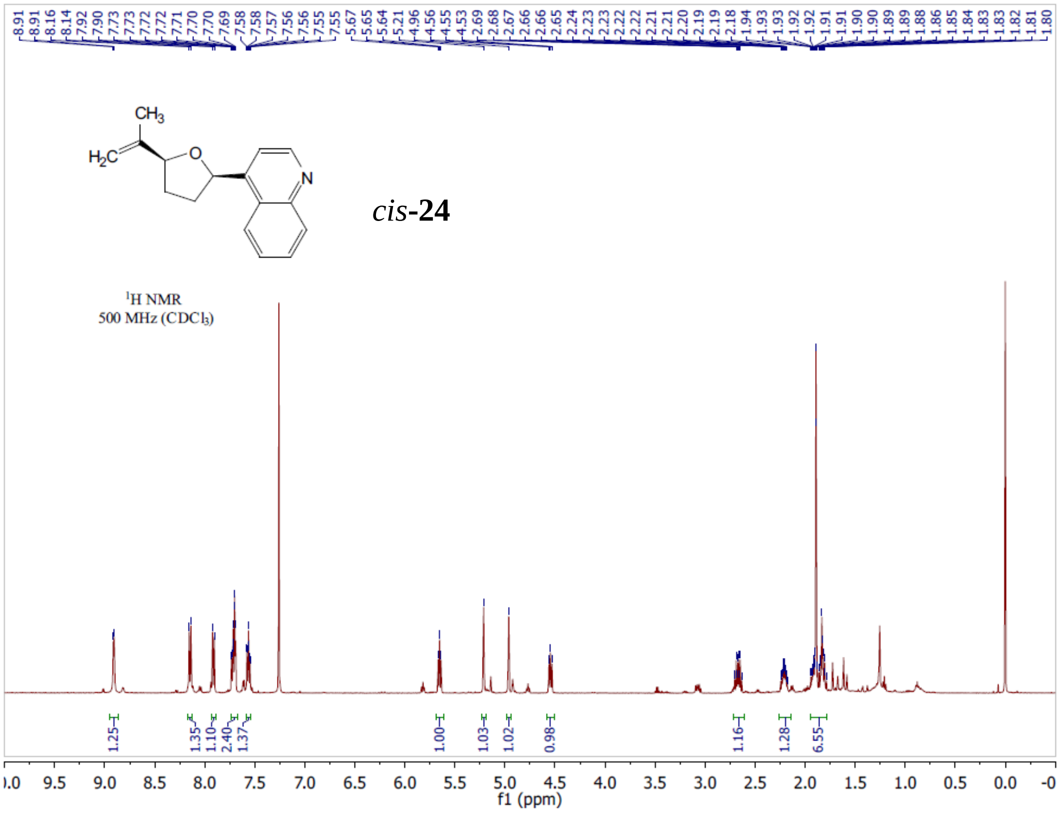
23

^{1}H NMR
500 MHz (CDCl$_3$)



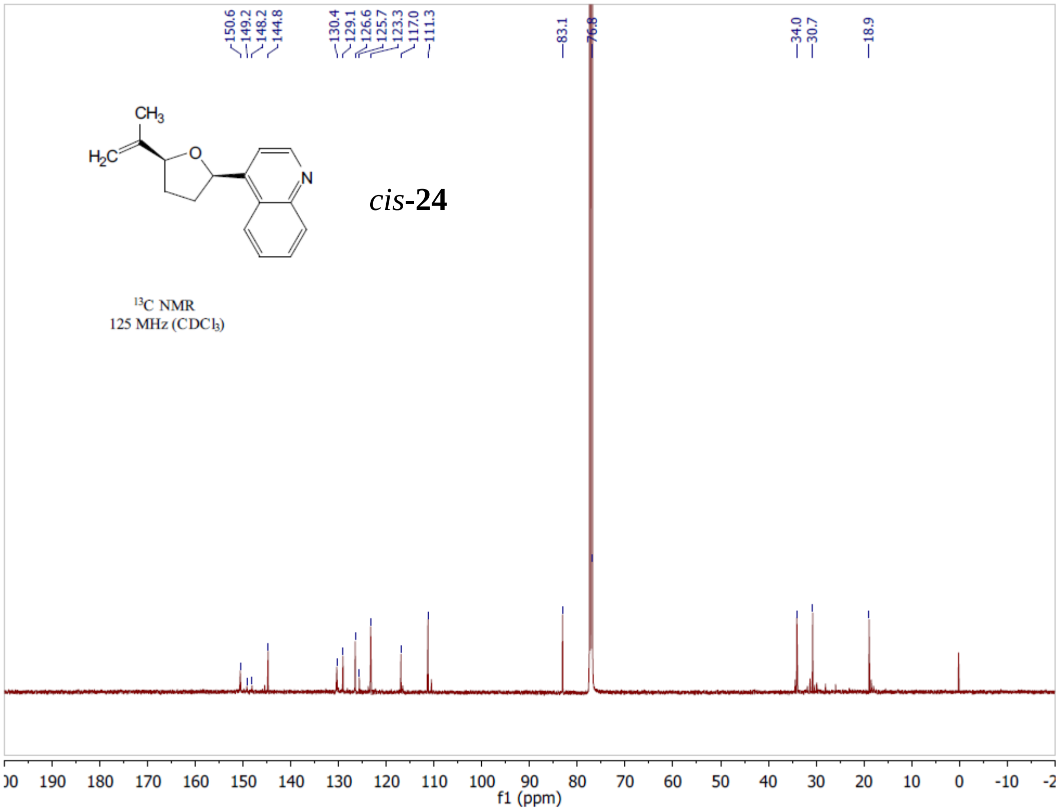
23

^{13}C NMR
125 MHz (CDCl$_3$)



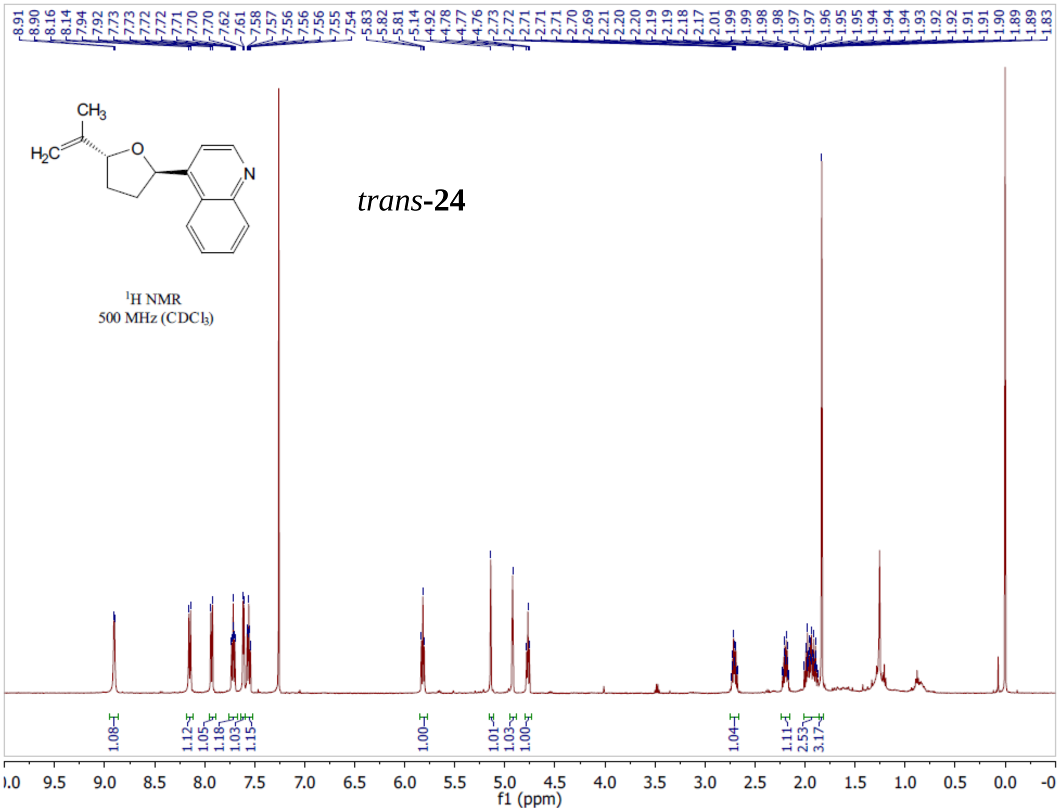
cis-**24**

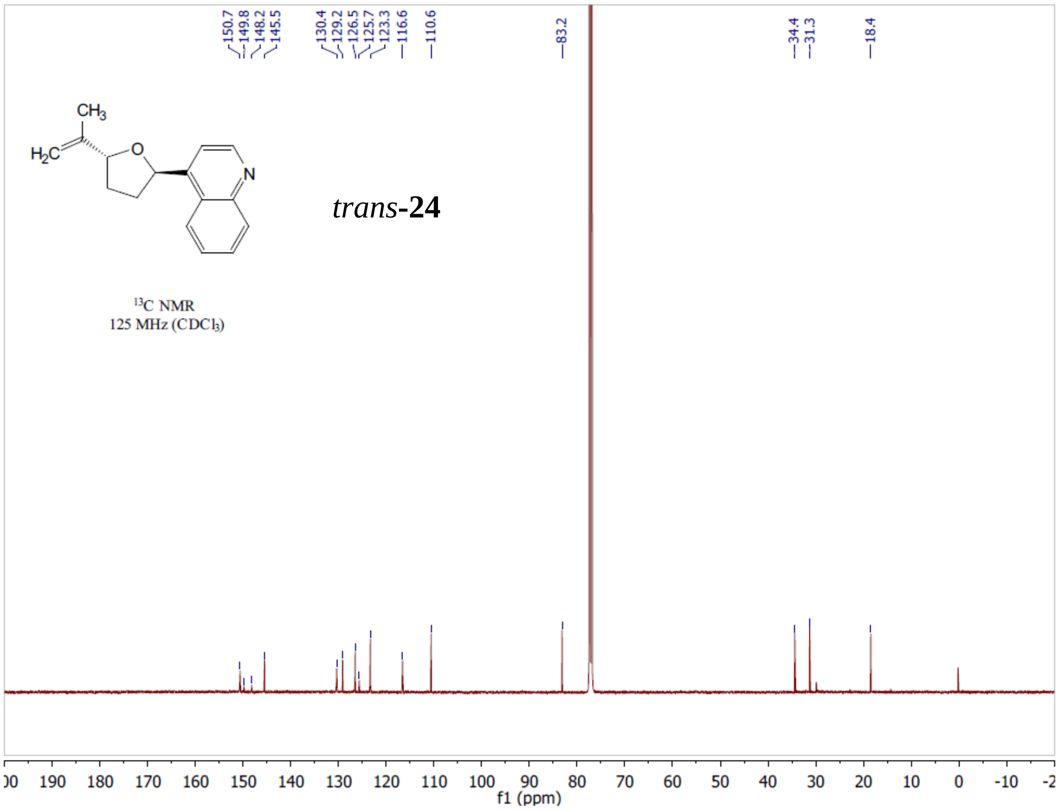
^{1}H NMR
500 MHz ($CDCl_3$)

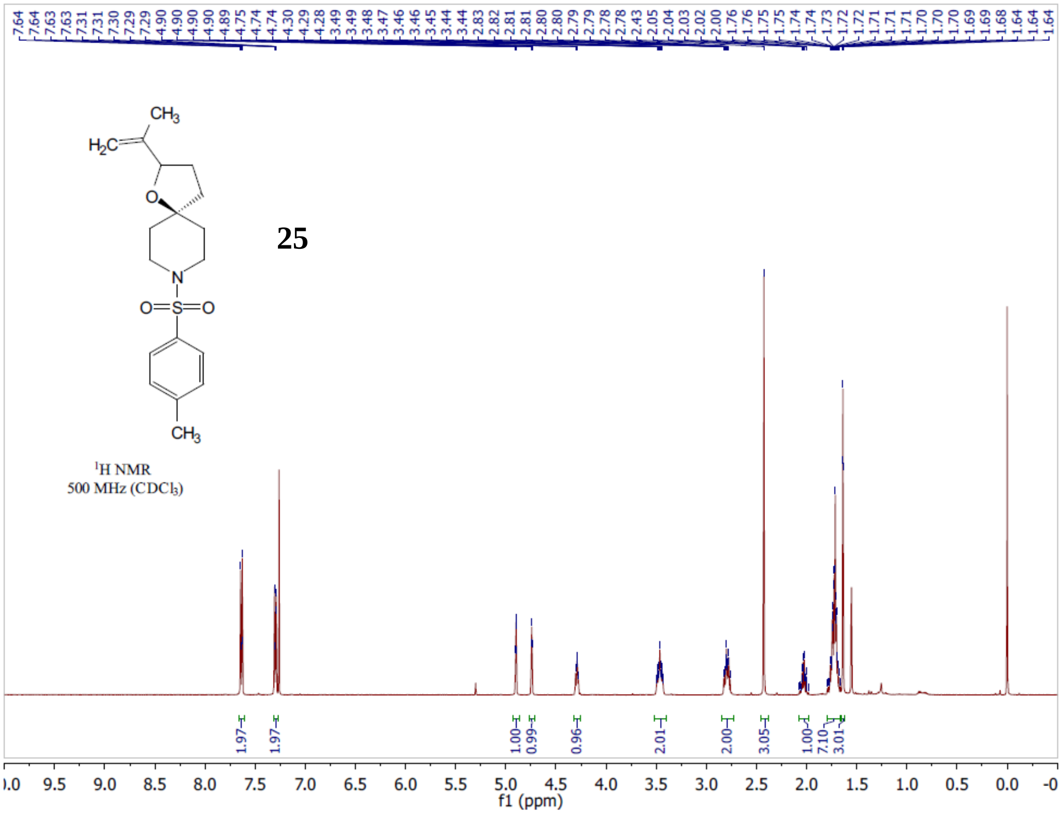


cis-**24**

^{13}C NMR
125 MHz ($CDCl_3$)

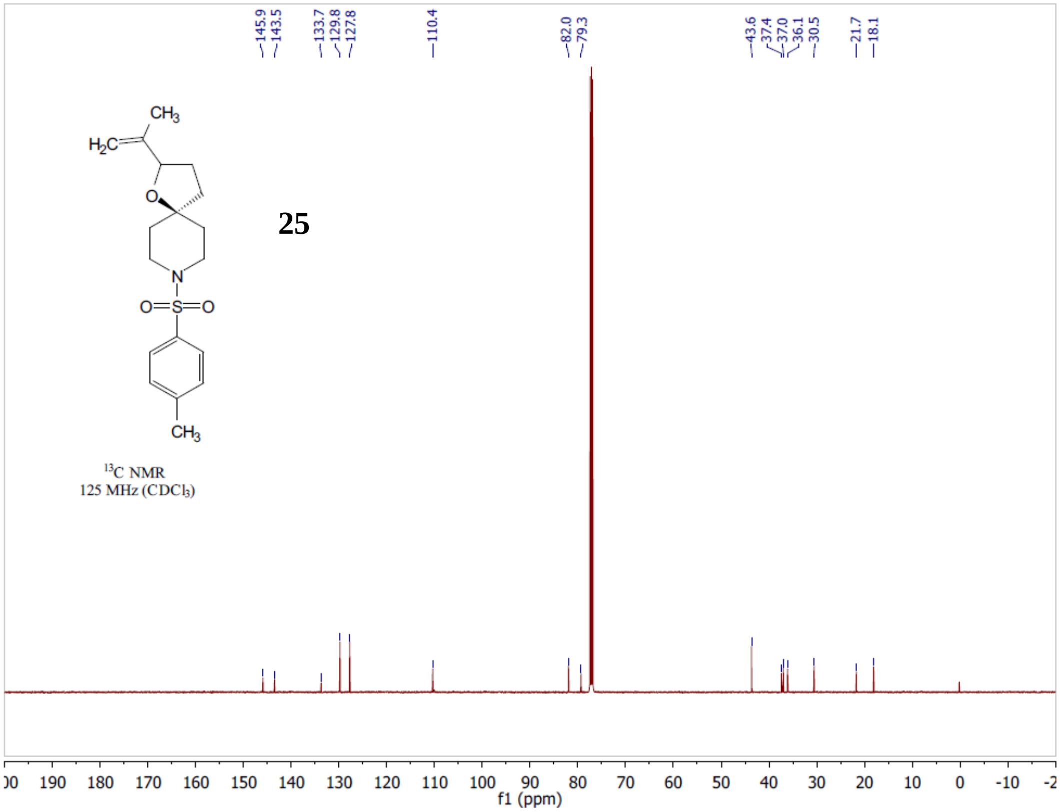

8.91
8.90
8.16
8.14
7.94
7.92
7.73
7.73
7.72
7.72
7.71
7.70
7.70
7.62
7.61
7.58
7.57
7.56
7.56
7.55
7.54
5.83
5.82
5.81
5.14
4.92
4.78
4.77
4.76
2.73
2.72
2.71
2.71
2.71
2.70
2.69
2.21
2.20
2.20
2.19
2.19
2.18
2.17
2.01
1.99
1.99
1.98
1.98
1.97
1.97
1.96
1.95
1.95
1.94
1.94
1.94
1.93
1.92
1.92
1.91
1.91
1.90
1.89
1.89
1.83
CH3
H2C
O
N
trans-24
1H NMR
500 MHz (CDCl3)
1.08
1.12
1.05
1.18
1.03
1.15
1.00
1.01
1.03
1.00
1.04
1.11
2.53
3.17
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


150.7
149.8
148.2
145.5
130.4
129.2
126.5
125.7
123.3
116.6
110.6
83.2
34.4
31.3
18.4
CH3
H2C
O
N
trans-24
13C NMR
125 MHz (CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)



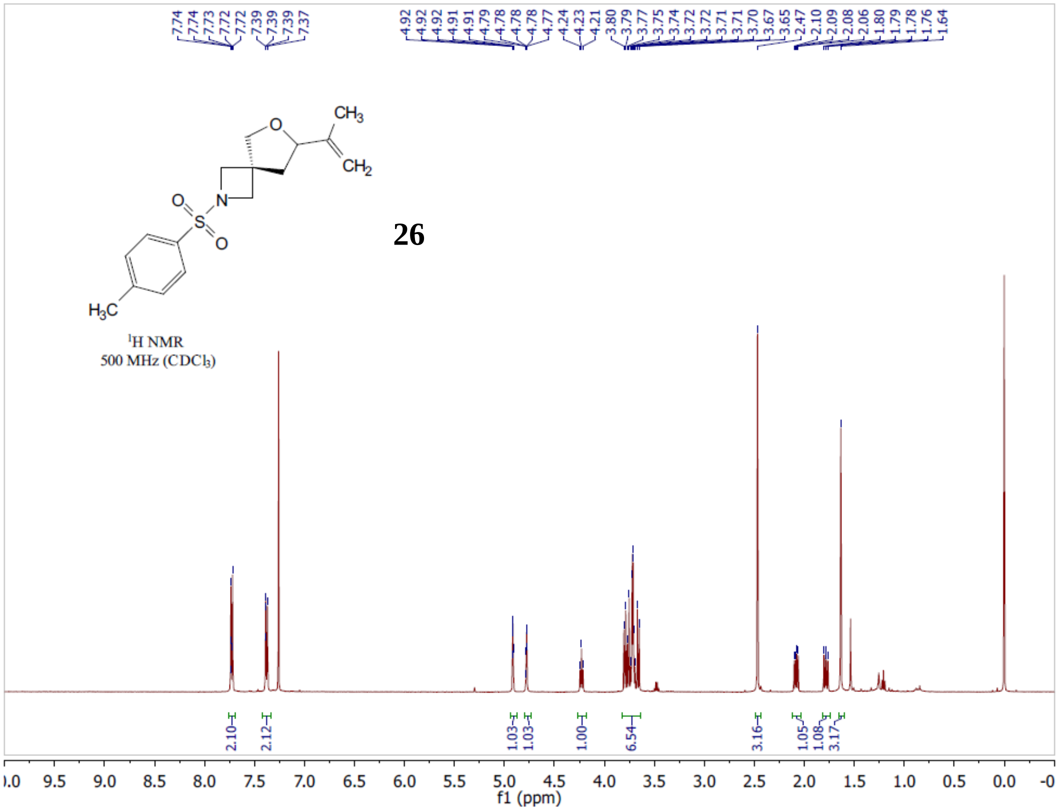
25

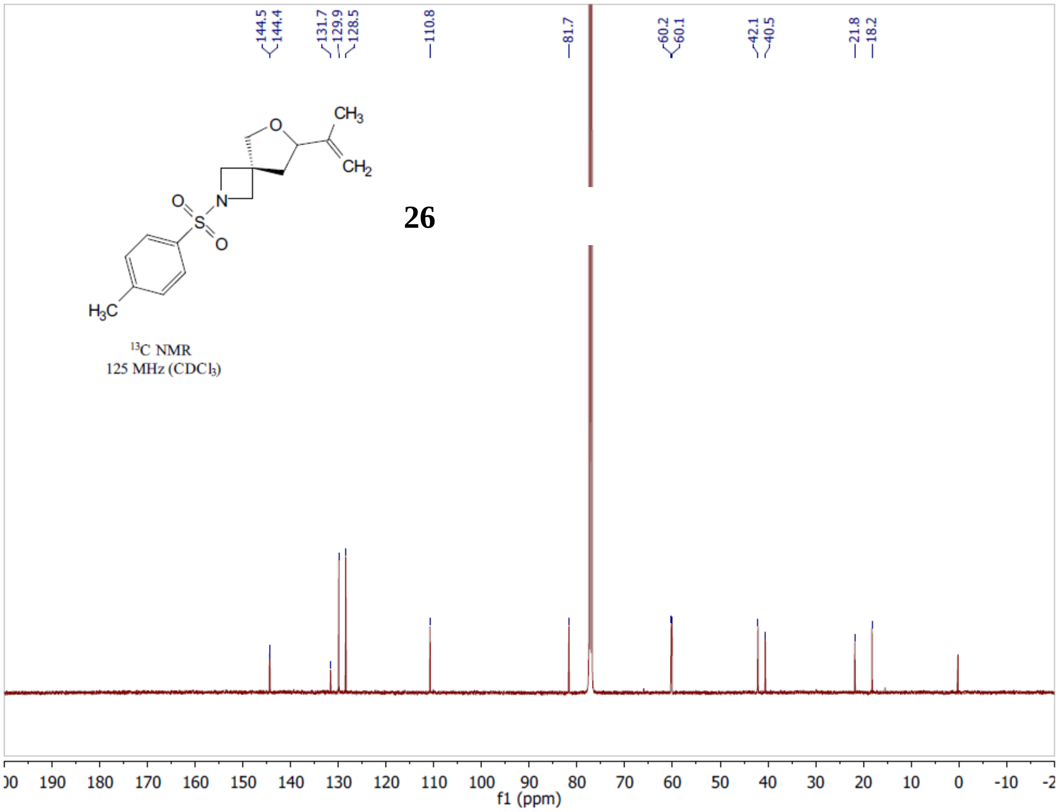
^{1}H NMR
500 MHz (CDCl$_3$)

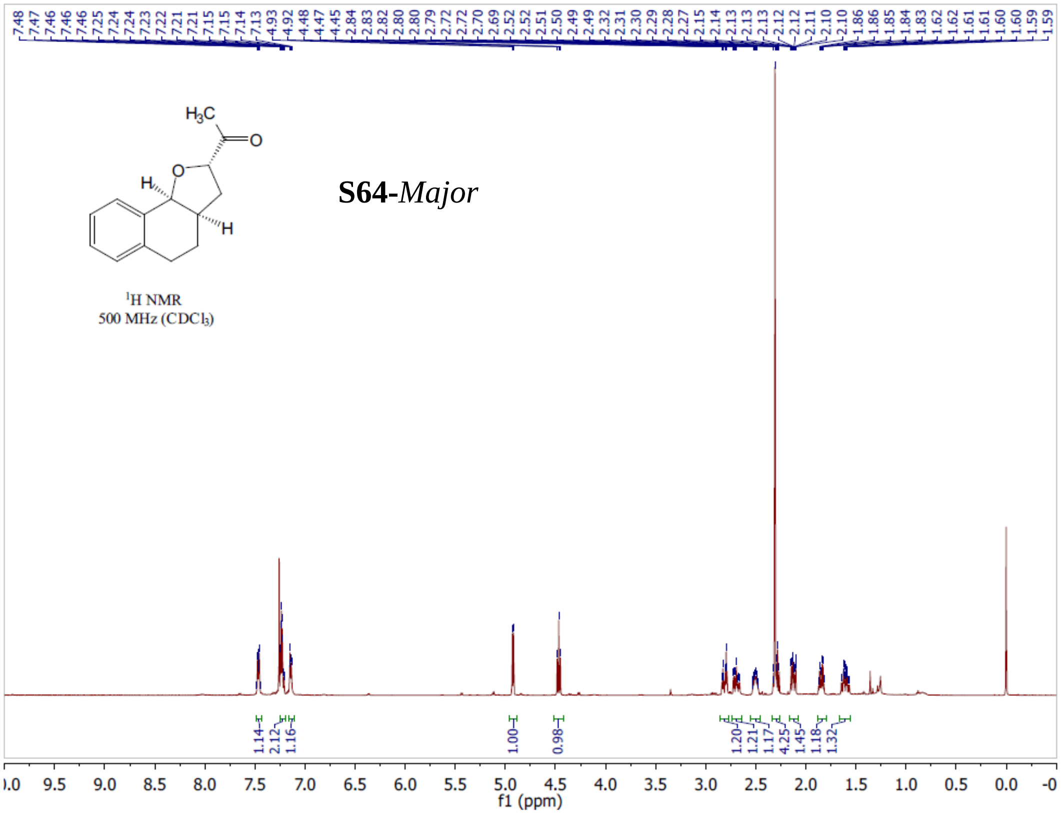


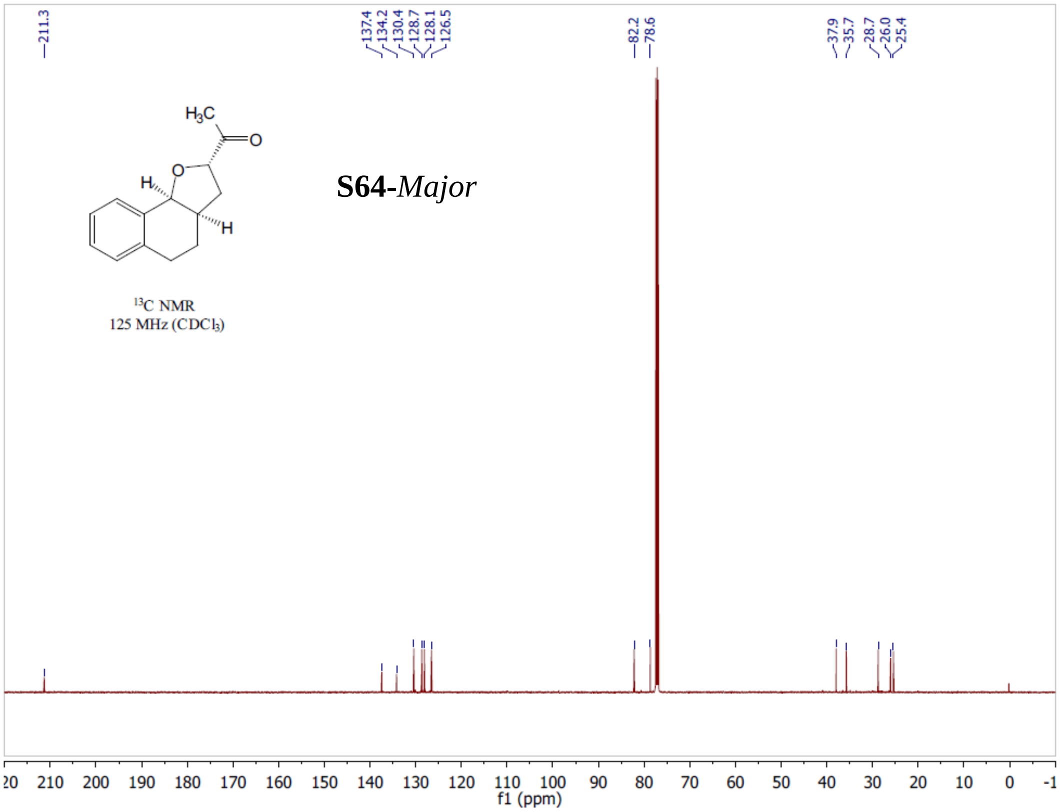
25

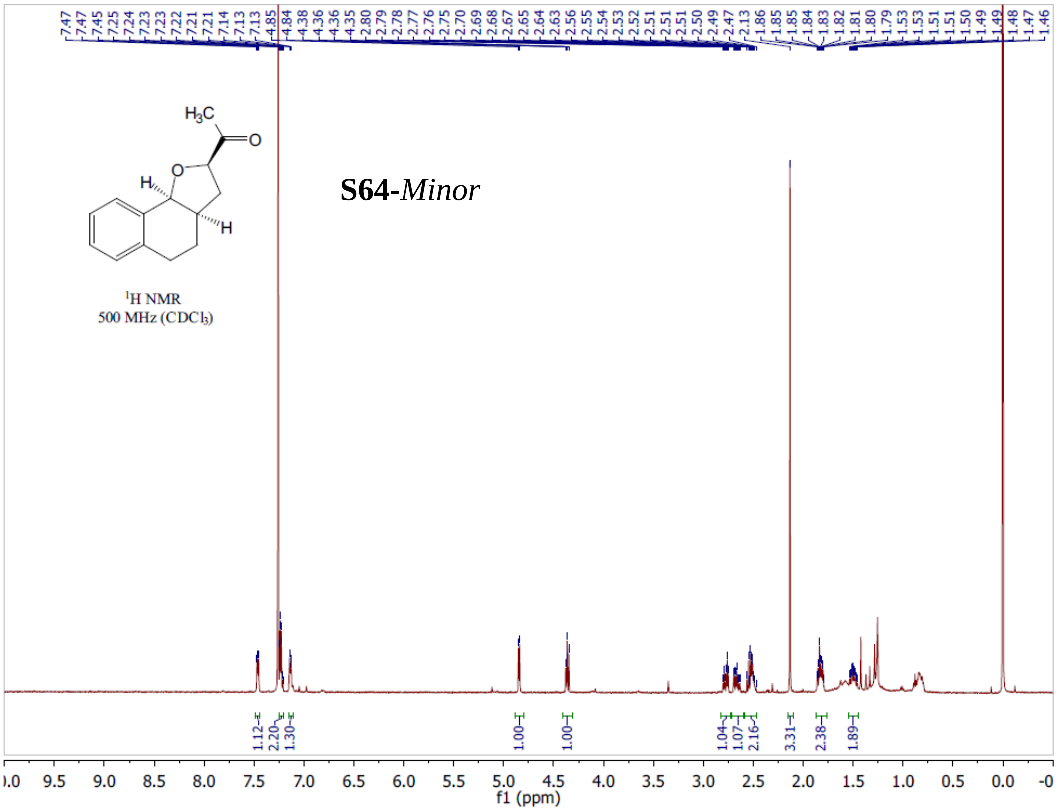
^{13}C NMR
125 MHz (CDCl$_3$)


7.74
7.74
7.73
7.72
7.72
7.39
7.39
7.39
7.37
4.92
4.92
4.92
4.91
4.91
4.79
4.78
4.78
4.78
4.77
4.24
4.23
4.21
3.80
3.79
3.77
3.75
3.74
3.72
3.72
3.71
3.70
3.67
3.65
2.47
2.10
2.09
2.08
2.06
1.80
1.79
1.78
1.76
1.64
CH3
O
CH2
N
O
S
O
H3C
26
1H NMR
500 MHz (CDCl3)
2.10
2.12
1.03
1.03
1.00
6.54
3.16
1.05
1.08
3.17
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

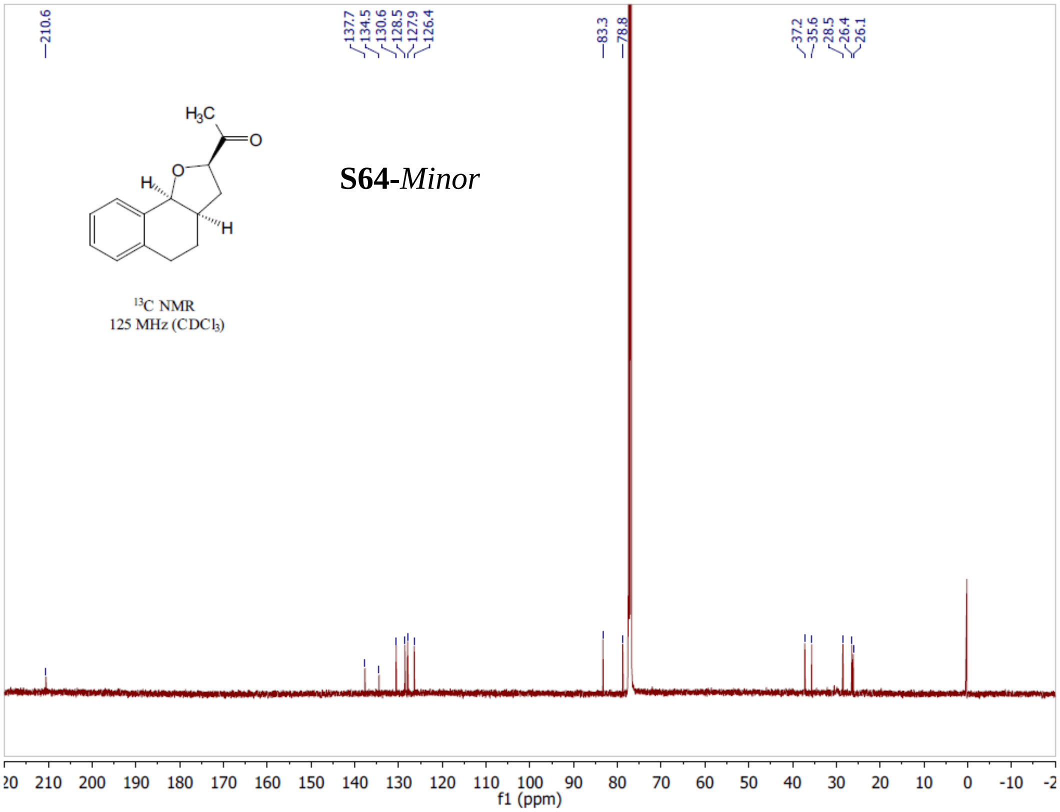

144.5
144.4
131.7
129.9
128.5
110.8
81.7
60.2
60.1
42.1
40.5
21.8
18.2
CH3
O
CH2
N
O
S
O
H3C
26
13C NMR
125 MHz (CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)


7.48
7.47
7.46
7.46
7.25
7.24
7.23
7.22
7.21
7.15
7.15
7.14
7.13
4.93
4.92
4.48
4.47
4.45
2.84
2.83
2.82
2.80
2.80
2.79
2.72
2.72
2.70
2.69
2.52
2.52
2.51
2.50
2.49
2.49
2.32
2.31
2.30
2.29
2.28
2.27
2.15
2.14
2.13
2.13
2.13
2.12
2.12
2.11
2.10
1.86
1.86
1.85
1.84
1.83
1.62
1.61
1.61
1.60
1.60
1.59
1.59
H3C
O
O
H
H
S64-Major
1H NMR
500 MHz (CDCl3)
1.14
2.12
1.16
1.00
0.98
1.20
1.21
1.17
4.25
1.45
1.18
1.32
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

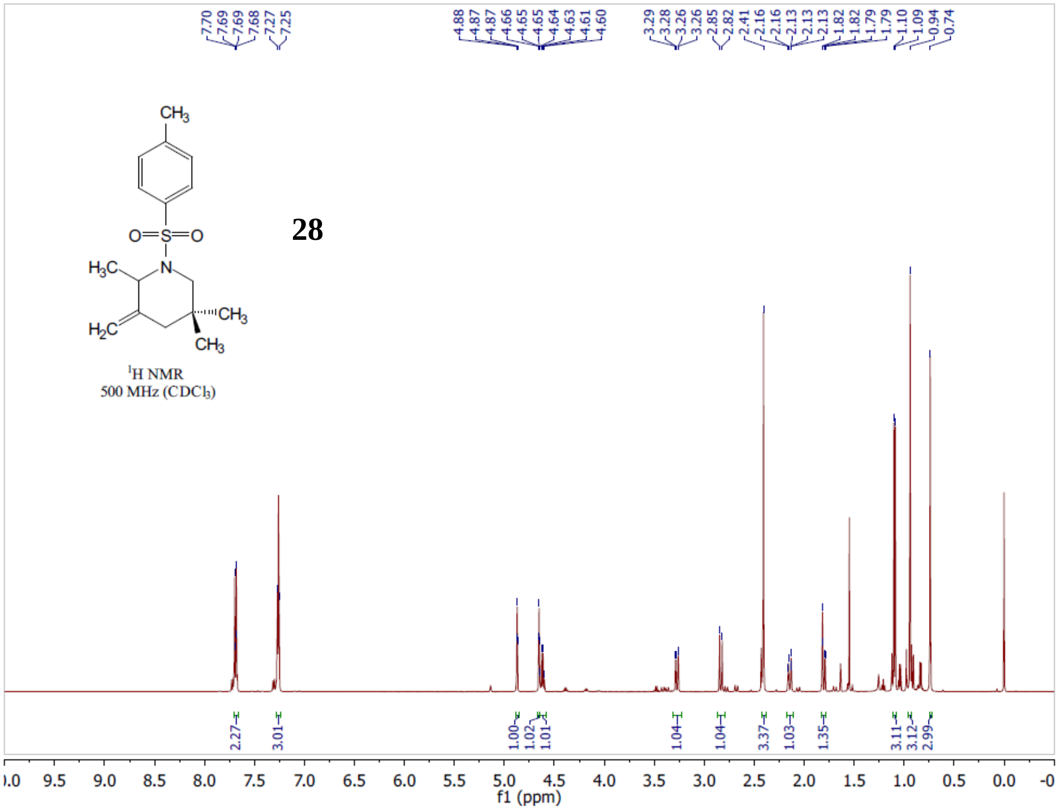

211.3
137.4
134.2
130.4
128.7
128.1
126.5
82.2
78.6
37.9
35.7
28.7
26.0
25.4
H3C
O
O
H
H
S64-Major
13C NMR
125 MHz (CDCl3)
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

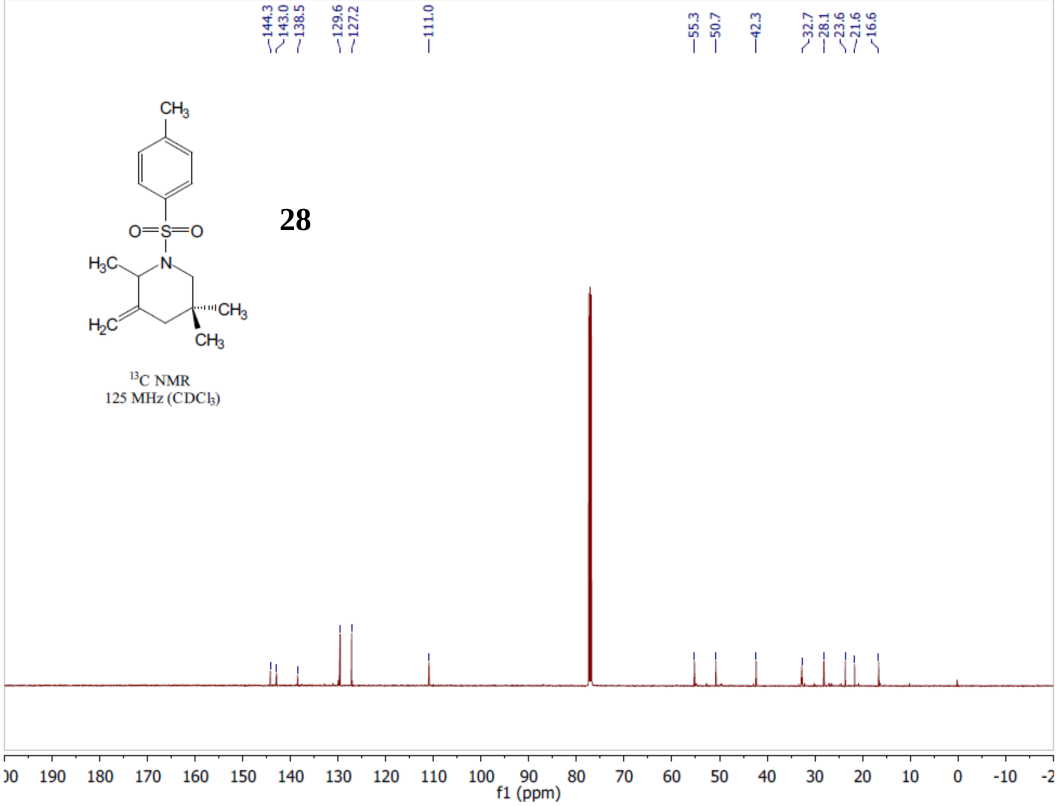


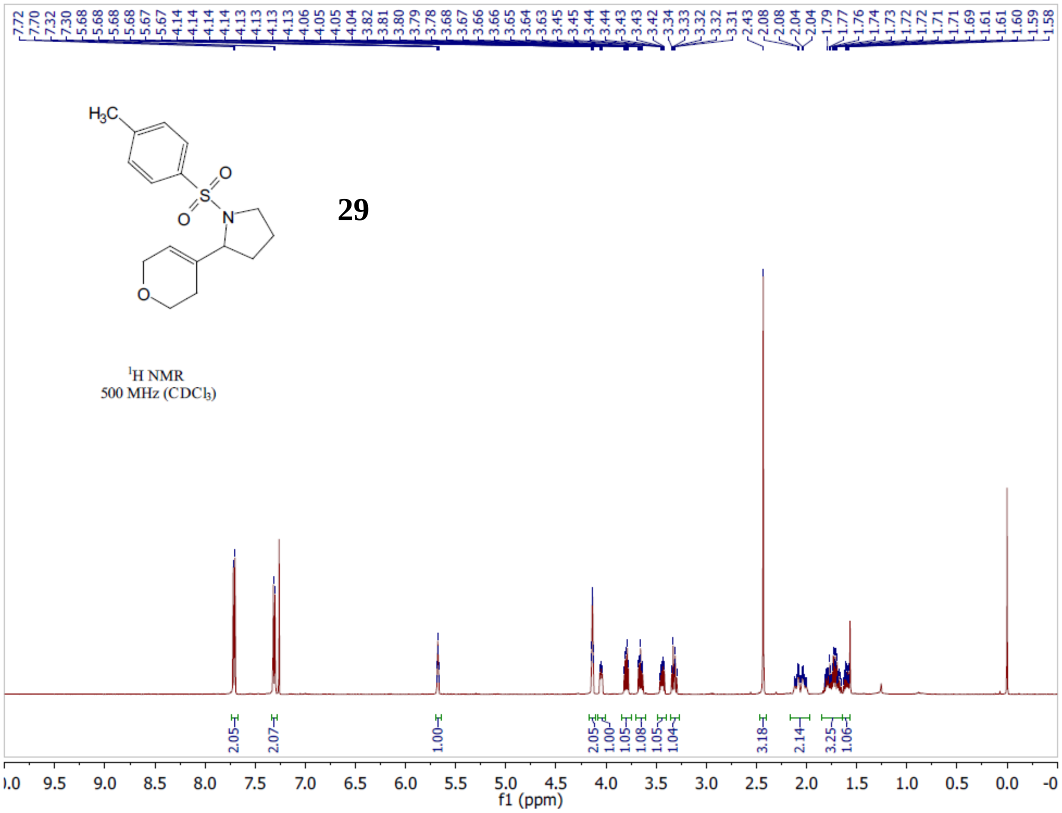
S64-*Minor*

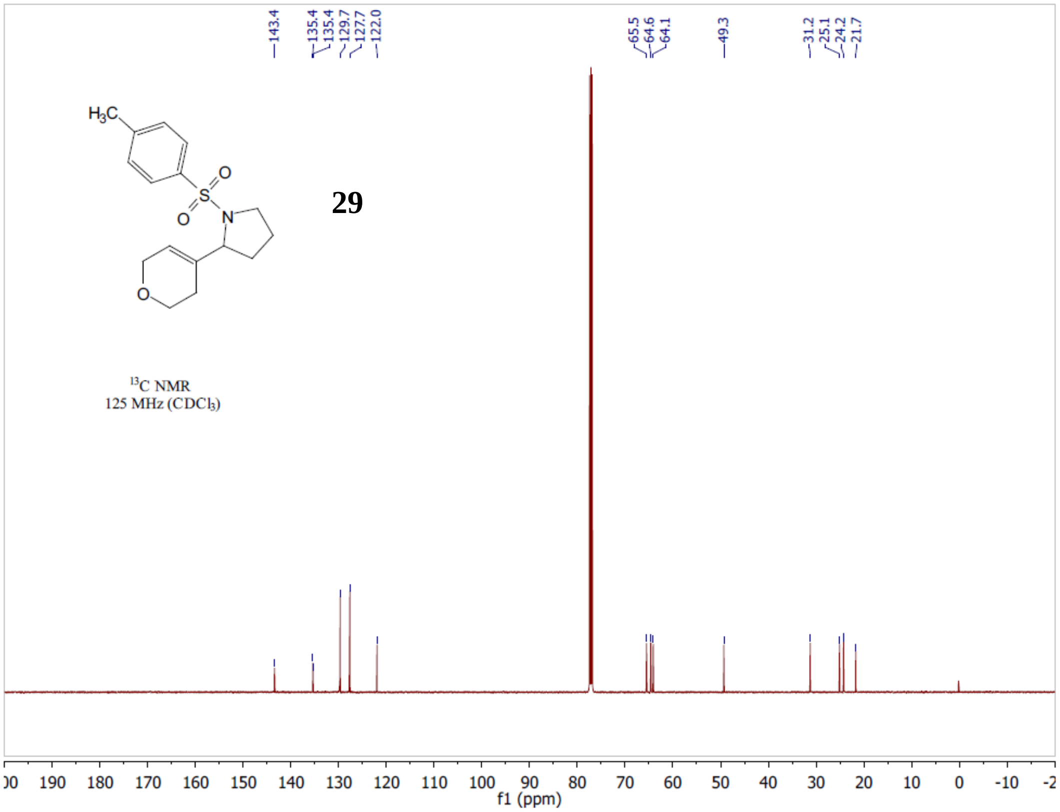


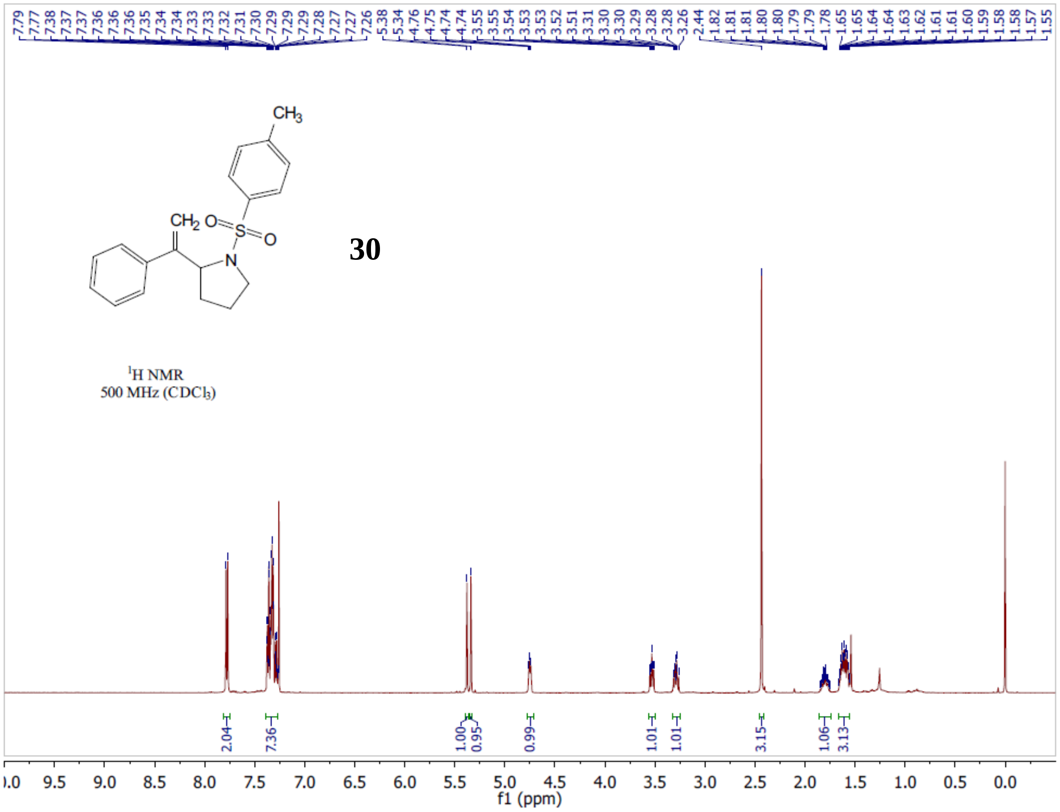
S64-*Minor*

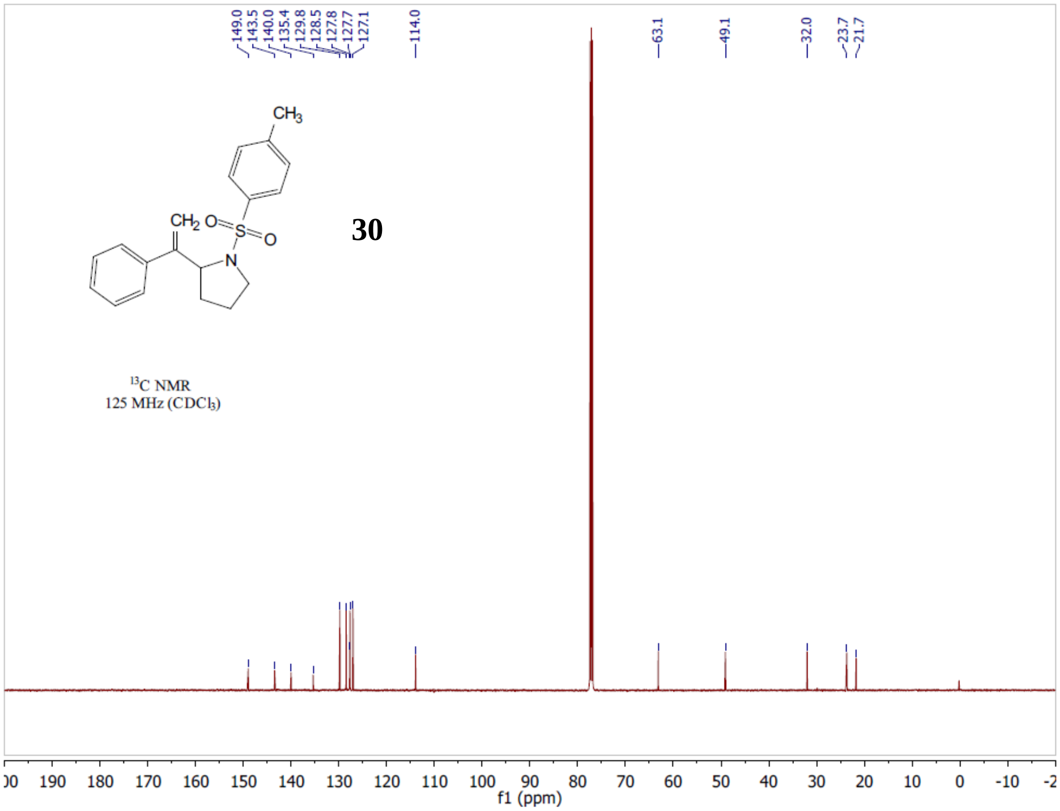

7.70
7.69
7.69
7.68
7.27
7.25
4.88
4.87
4.87
4.66
4.65
4.65
4.64
4.63
4.61
4.60
3.29
3.28
3.26
3.26
2.85
2.82
2.41
2.16
2.16
2.13
2.13
2.13
1.82
1.82
1.79
1.10
1.09
0.94
0.74
CH3
O=S=O
H3C
N
CH3
H2C
CH3
28
1H NMR
500 MHz (CDCl3)
2.27
3.01
1.00
1.02
1.01
1.04
1.04
3.37
1.03
1.35
3.11
3.12
2.99
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

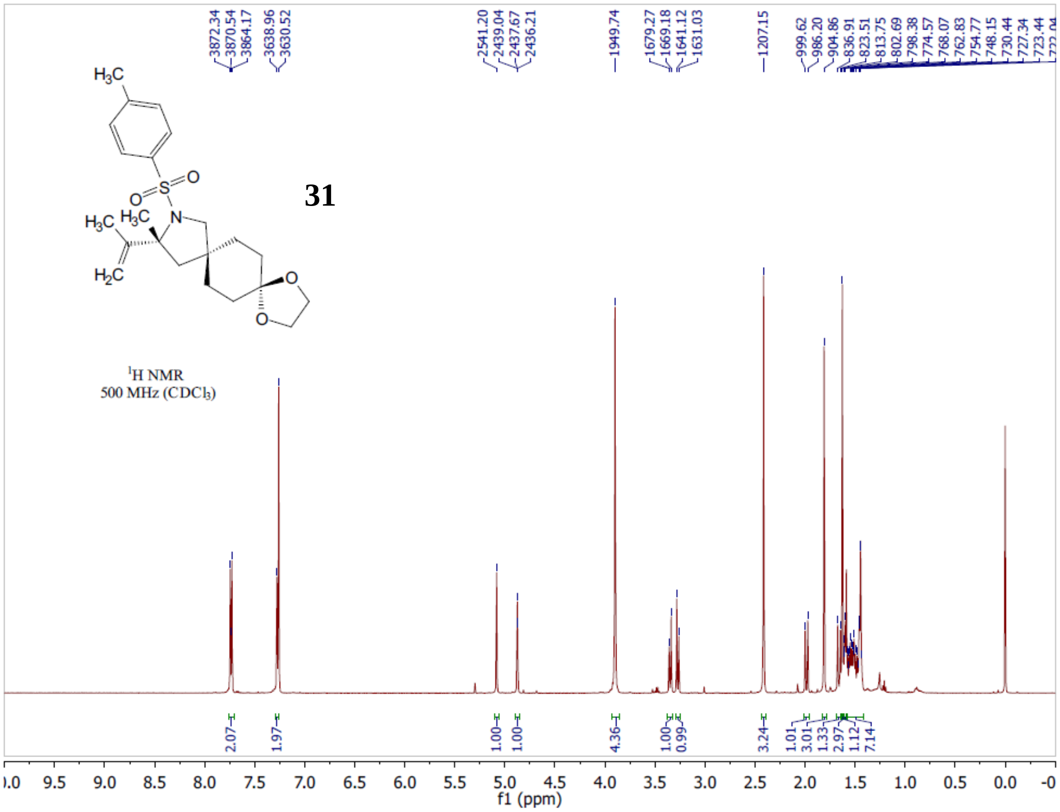

144.3
143.0
138.5
129.6
127.2
111.0
55.3
50.7
42.3
32.7
28.1
23.6
21.6
16.6
CH3
O=S=O
H3C
N
CH3
H2C
CH3
28
13C NMR
125 MHz (CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

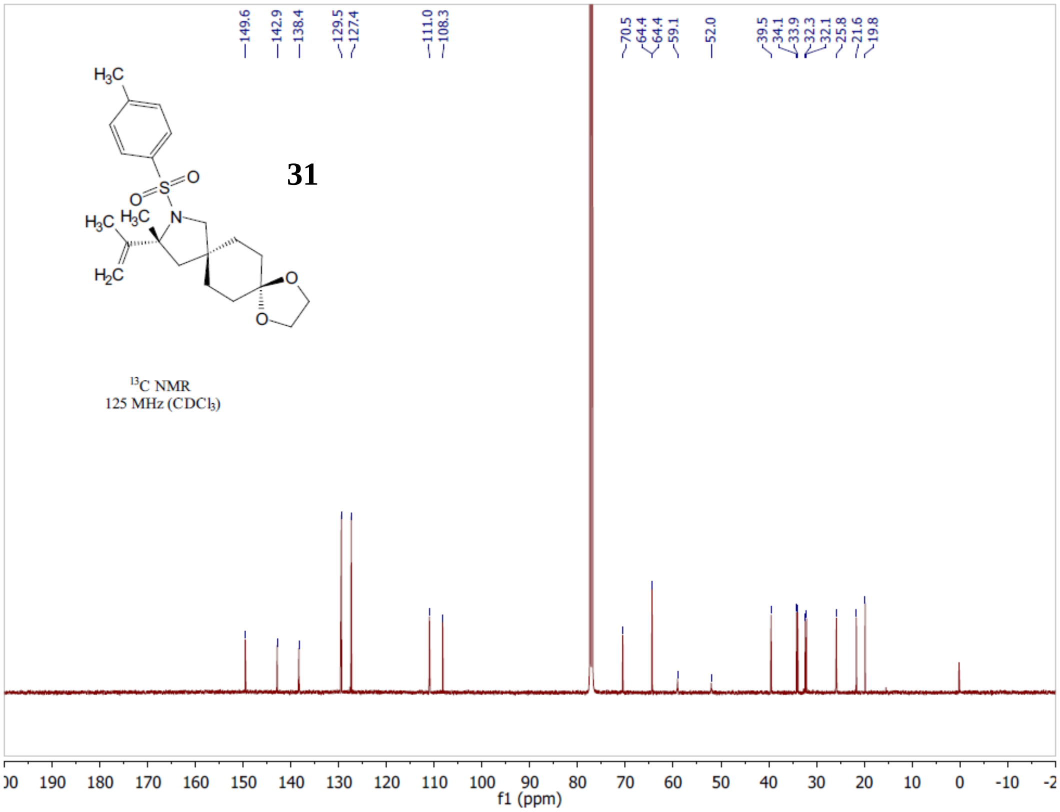

7.72, 7.70, 7.32, 7.30, 5.68, 5.68, 5.68, 5.68, 5.67, 4.14, 4.14, 4.14, 4.14, 4.13, 4.13, 4.13, 4.13, 4.06, 4.05, 4.05, 4.04, 3.82, 3.81, 3.80, 3.79, 3.78, 3.68, 3.67, 3.66, 3.66, 3.65, 3.64, 3.63, 3.45, 3.45, 3.44, 3.44, 3.43, 3.43, 3.42, 3.34, 3.33, 3.32, 3.32, 3.31, 2.43, 2.08, 2.08, 2.04, 2.04, 1.79, 1.77, 1.76, 1.74, 1.73, 1.72, 1.72, 1.71, 1.71, 1.69, 1.61, 1.61, 1.60, 1.59, 1.58
H_3C
S
O
O
N
O
29
^{1}H NMR
500 MHz (CDCl$_3$)
2.05, 2.07, 1.00, 2.05, 1.00, 1.05, 1.08, 1.05, 1.04, 3.18, 2.14, 3.25, 1.06
10.0, 9.5, 9.0, 8.5, 8.0, 7.5, 7.0, 6.5, 6.0, 5.5, 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5, 0.0, -0
f1 (ppm)

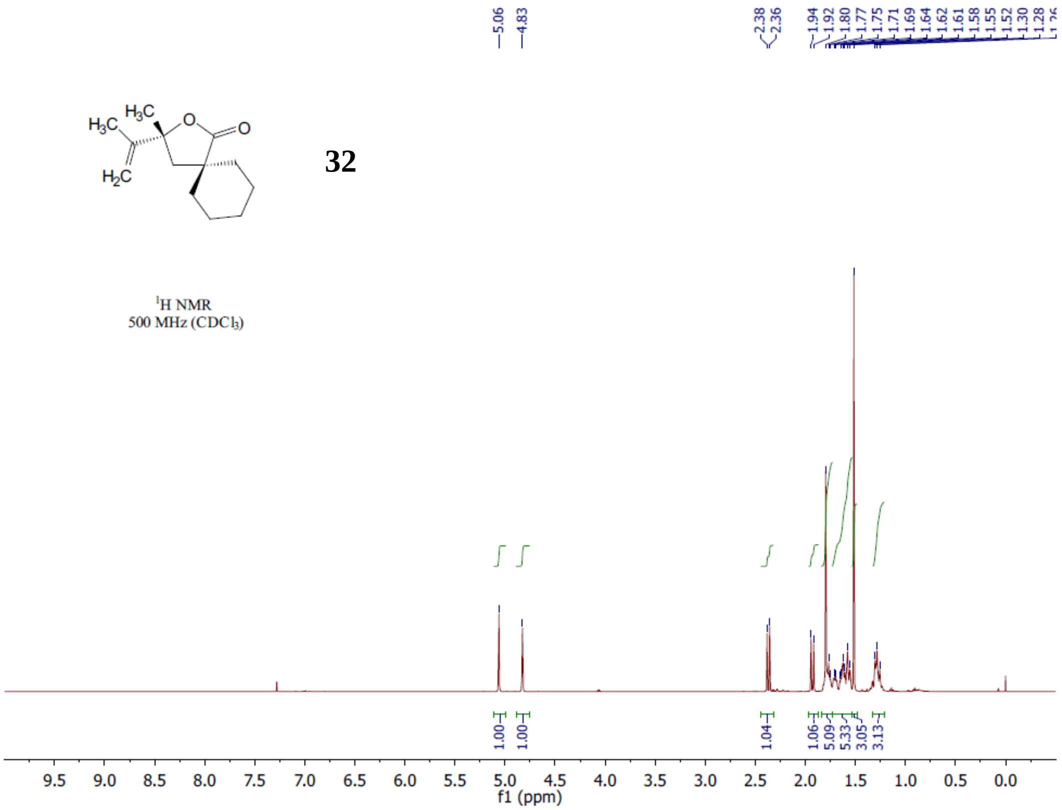

143.4, 135.4, 135.4, 129.7, 127.7, 122.0, 65.5, 64.6, 64.1, 49.3, 31.2, 25.1, 24.2, 21.7
H_3C
S
O
O
N
O
29
^{13}C NMR
125 MHz (CDCl$_3$)
200, 190, 180, 170, 160, 150, 140, 130, 120, 110, 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 0, -10, -2
f1 (ppm)


7.79
7.77
7.38
7.37
7.37
7.36
7.36
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.31
7.30
7.29
7.29
7.29
7.28
7.27
7.27
7.26
5.38
5.34
4.76
4.75
4.74
4.74
3.55
3.55
3.54
3.53
3.53
3.52
3.51
3.31
3.30
3.30
3.29
3.28
3.28
3.26
2.44
1.82
1.81
1.81
1.80
1.80
1.79
1.79
1.78
1.65
1.65
1.64
1.64
1.63
1.62
1.61
1.61
1.60
1.59
1.58
1.58
1.57
1.55
CH3
CH2
O
S
O
N
30
^{1}H NMR
500 MHz (CDCl$_3$)
2.04
7.36
1.00
0.95
0.99
1.01
1.01
3.15
1.06
3.13
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


149.0
143.5
140.0
135.4
129.8
128.5
127.8
127.7
127.1
114.0
63.1
49.1
32.0
23.7
21.7
CH3
CH2
O
S
O
N
30
^{13}C NMR
125 MHz (CDCl$_3$)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)

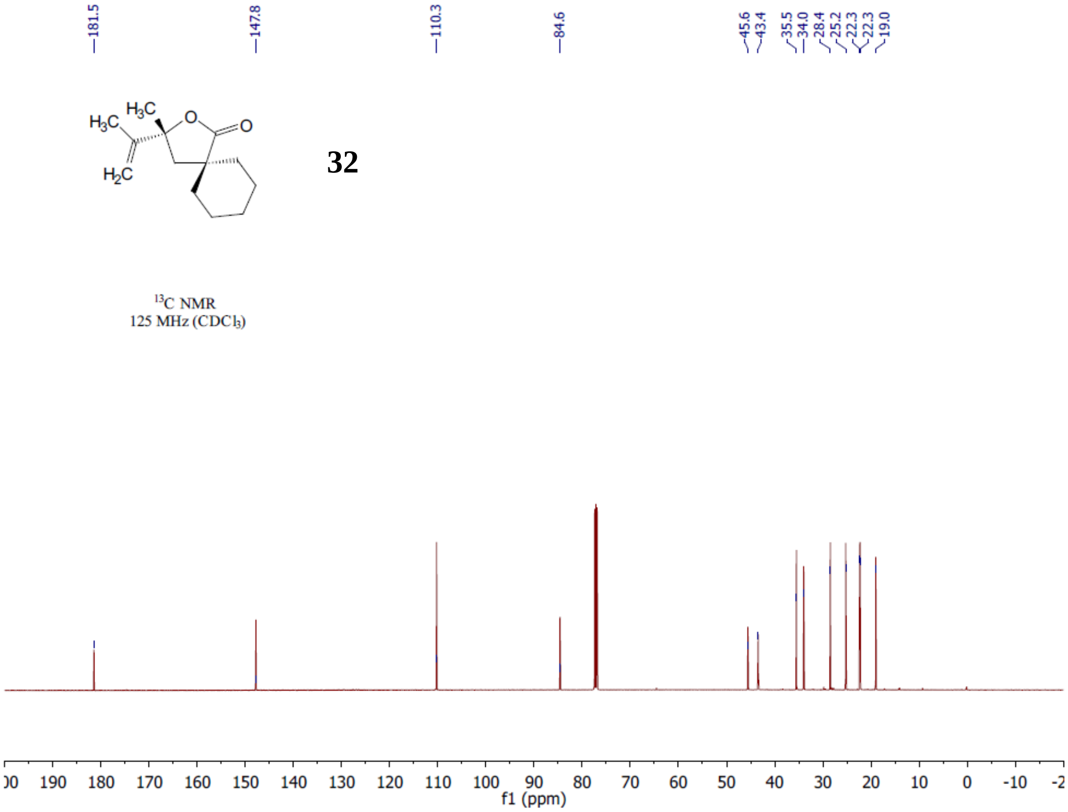

3872.34
3870.54
3864.17
3638.96
3630.52
2541.20
2439.04
2437.67
2436.21
1949.74
1679.27
1669.18
1641.12
1631.03
1207.15
999.62
986.20
904.86
836.91
823.51
813.75
802.69
798.38
774.57
768.07
762.83
754.77
748.15
730.44
727.34
723.44
H_3C
O
S
O
H_3C
H_3C
N
H_2C
O
O
31
^{1}H NMR
500 MHz ($CDCl_3$)
2.07
1.97
1.00
1.00
4.36
1.00
0.99
3.24
1.01
3.01
1.33
2.97
1.12
7.14
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


149.6
142.9
138.4
129.5
127.4
111.0
108.3
70.5
64.4
64.4
59.1
52.0
39.5
34.1
33.9
32.3
32.1
25.8
21.6
19.8
H_3C
O
S
O
H_3C
H_3C
N
H_2C
O
O
31
^{13}C NMR
125 MHz ($CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



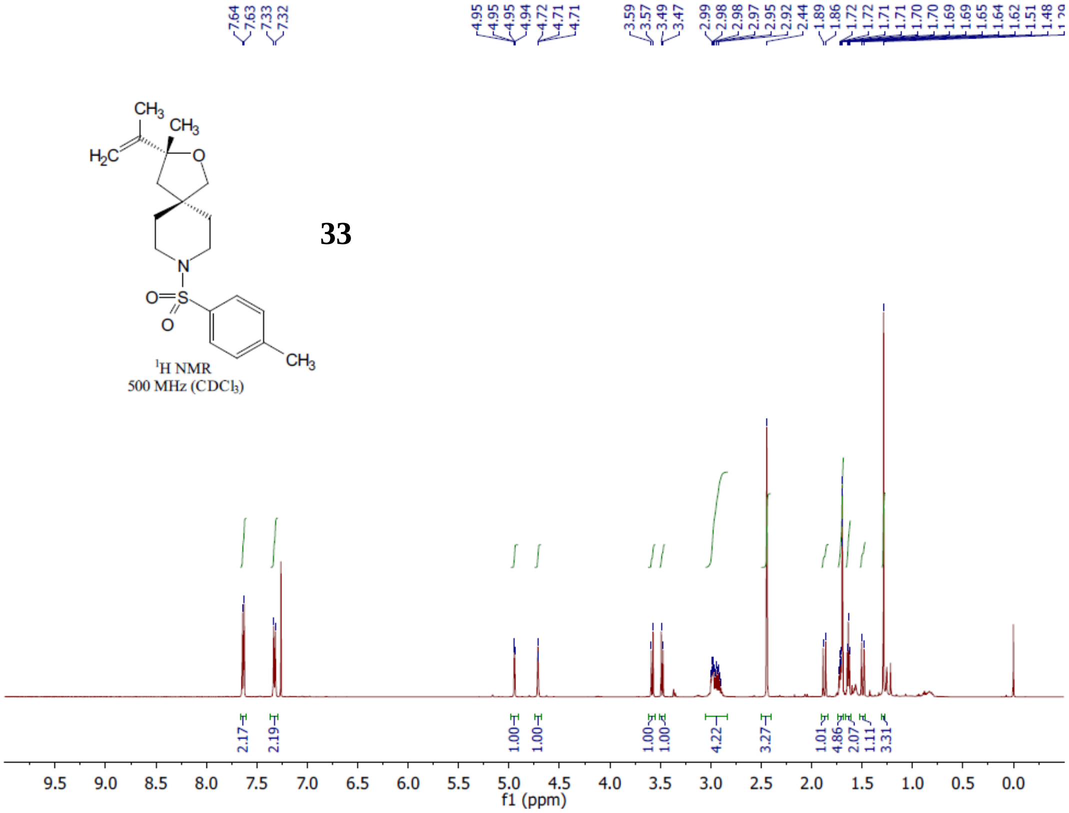
32

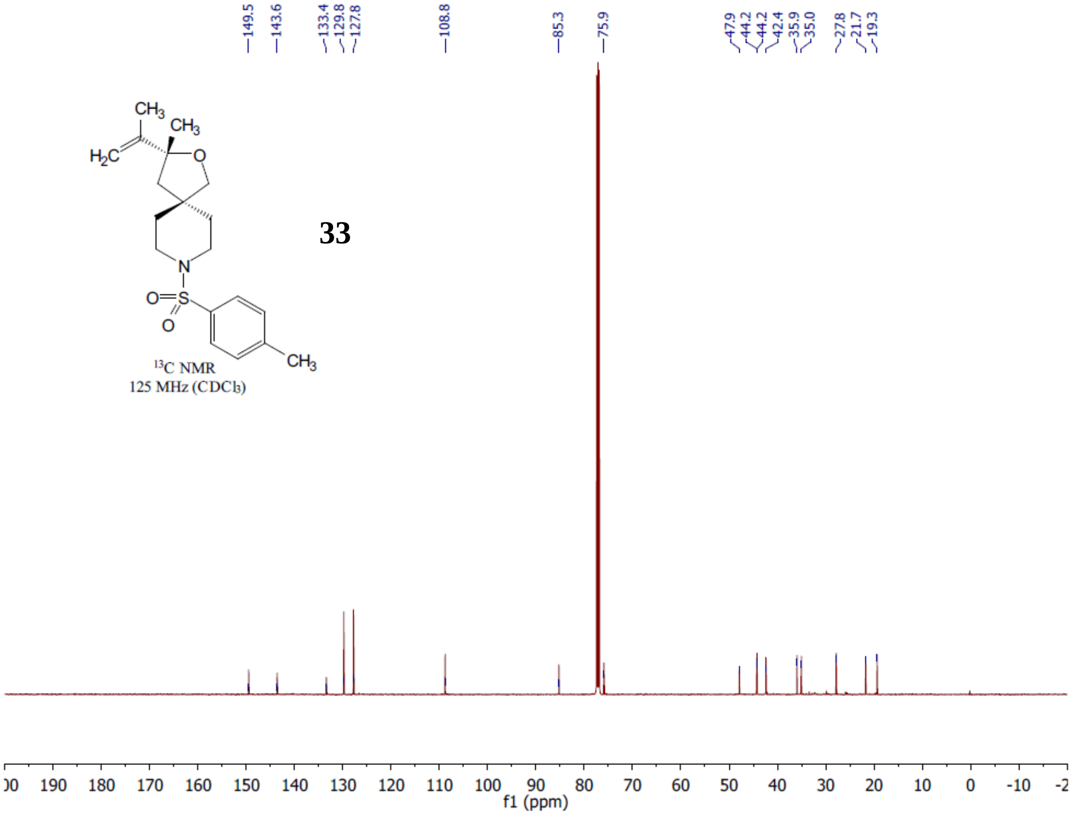
^{1}H NMR
500 MHz ($CDCl_3$)



32

^{13}C NMR
125 MHz ($CDCl_3$)


7.64
7.63
7.33
7.32
4.95
4.95
4.95
4.94
4.72
4.71
4.71
3.59
3.57
3.49
3.47
2.99
2.98
2.98
2.97
2.95
2.92
2.44
1.89
1.86
1.72
1.72
1.71
1.71
1.70
1.69
1.69
1.65
1.64
1.62
1.51
1.48
CH3
CH3
H2C
O
N
O=S
O
CH3
33
¹H NMR
500 MHz (CDCl3)
2.17
2.19
1.00
1.00
1.00
1.00
4.22
3.27
1.01
4.86
2.07
1.11
3.31
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


149.5
143.6
133.4
129.8
127.8
108.8
85.3
75.9
47.9
44.2
44.2
42.4
35.9
35.0
27.8
21.7
19.3
CH3
CH3
H2C
O
N
O=S
O
CH3
33
¹³C NMR
125 MHz (CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)