Supporting Information

Catalytic Asymmetric C–H Insertions of Rhodium(II) Azavinyl Carbenes

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Content

General Information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-600, a Bruker DRX-500, and a Bruker AMX-400 instruments. Infrared spectra were recorded on a Nicolet Avatar 370 and on a Perkin-Elmer Spectrum 100 Fourier transform infrared spectrometers. Melting points were determined using a Thomas-Hoover melting point apparatus and are uncorrected. HPLC was performed on an Agilent 1100 LC/MSD with an Agilent 1100 SL mass spectrometer (ES) eluting with 0.05% trifluoroacetic acid in H_2O and 0.05% trifluoroacetic acid in CH_3CN. Column chromatography was carried out employing EMD (Merck) Geduran Silica Gel 60 (40-63 μm). Precoated Merck F-254 silica gel plates were used for a thin layer analytical chromatography. Enantiomeric excess was determined by integration of HPLC traces, acquired using an Agilent Techologies 1200 series HPLC system with an integrated diod array detector. Optical rotations of chiral compounds were measured using a Rudolph Research Autopol III automatic polarimeter at 589 nm. The absolute configuration of chiral sulfonamide **5a** was determined by X-ray crystallographic analysis (CCDC 813723); configurations of all other chiral products were assigned by analogy. Anhydrous solvents and alkanes were purchased from Fischer, Sigma-Aldrich, Acros Organics or Alfa Aesar, dried over phosphorus pentoxide or sodium metal, and distilled. Subsequently, they were degassed by bubling nitrogen gas through for at least 60 minutes and then stored over molecular sieves under an inert atmosphere. Rh_2(*S*-PTAD)$_4$ was purchased from Strem Chemicals, and Rh_2(*S*-NTTL)$_4$ was prepared *via* literature procedure.[1] Sulfonyl azides were prepared using standard procedures.[2] All other reagents were purchased from Aldrich, Acros Organics, Strem Chemicals, Fisher, TCI or Alfa Aesar and used as received.

(1) (a) Müller, P.; Allenbach, Y. F.; Robert, E. *Tetrahedron: Asymmetry* **2003**, *14*, 779. (b) Müller, P.; Bernardinelli, G.; Allenbach, Y. F.; Ferry, M.; Flack, H. D. *Org. Lett*. **2004**, *6*, 1725.

(2) (a) Breslow, D. S.; Sloan, M. F.; Newburg, N. R.; Renfrow, W. B. *J. Am. Chem. Soc.* **1969**, *91*, 2273. (b) Danheiser, R. L.; Miller, R. F.; Brisbois, R. G.; Park, S. Z. *J. Org. Chem*. **1990**, *55*, 1959.

Starting Materials

N-Sulfonyl 1,2,3-triazoles **4** were prepared using the reported CuTC-catalyzed azide-alkyne cycloaddition (CuAAC) protocol.[3] However, due to potential danger of methanesulfonyl azide, we strongly recommend to avoid isolating this compound in large quantities. Generation of mesyl azide, followed by immediate use as described below, is highly preferred. 1-Sulfonyl 1,2,3-triazoles as previously reported[3b] may gradually hydrolyze if atmospheric moisture is not excluded. Therefore a glove box was used for a prolonged storage and manipulation of the triazoles. Compounds **3a**,[3b] **3b**,[3b] **3e**,[3b] **3g**,[3b] **3**i,[3a] and **3j**[3a] were previously reported.

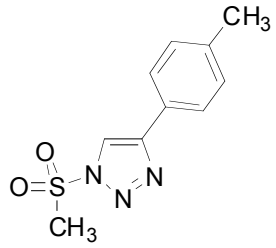
CAUTION! *Sulfonyl azides, especially methanesulfonyl azide, are potentially explosive materials and must be handled with caution!*

Preparation of 1-mesyl-substituted triazoles by CuTC-catalyzed azide-alkyne cycloaddition. Typical procedure. To a stirred solution of methansulfonyl chloride (5.73 g, 50 mmol) in 90 mL of acetone was added slowly a solution of sodium azide (4.88 g, 75 mmol) in 10 mL of water at 0 °C. The reaction mixture was stirred at this temperature for 1 h, and then for 2 hrs at rt. The solution was concentrated to about 25 mL, extracted with diethyl ether (2 x 50 mL), washed with 10 mL of water and then brine, and dried over anhydrous magnesium sulfate. After removal of the drying agent, the resulting solution of crude mesyl azide was concentrated to about 10 mL and used in the next step. To a stirred solution of phenylacetylene (5.1 g, 50 mmol) in toluene (100 mL) copper(I) thiophene-2-carboxylate (CuTC, 0.190 g, 1.0 mmol, 2 mol %) was added at room temperature. After stirring for 1–3 minutes, the solution of the crude methanesulfonyl azide in diethyl ether was added dropwise to the resulting suspension. The reaction mixture was stirred at room temperature for about 12 hrs until judged complete by LCMS or TLC analysis, then was concentrated under reduced pressure, and filtered through a short plug of silica to remove copper catalyst (40% EtOAc/hexanes used as eluent). After a removal of solvents in vacuum, an off-white solid was triturated with EtOAc (15 mL) and

(3) (a) Raushel, J.; Fokin, V. V. *Org. Lett.* **2010**, *12*, 4952. (b) Chuprakov, S.; Kwok, S. W.; Zhang, L.; Lercher, L.; Fokin, V. V. *J. Am. Chem. Soc*. **2009**, *131*, 18034.

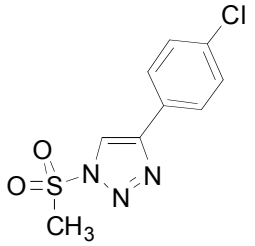
hexanes (70 mL) to afford 7.2 g (32.5 mmol, 65% over two steps) of 1-(methylsulfonyl)-4-phenyl-1*H*-1,2,3-triazole **3a**[3b] as a white crystalline solid.

1-(Methylsulfonyl)-4-(*p*-tolyl)-1*H*-1,2,3-triazole (3c)



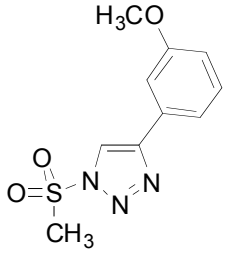
3c: (53%); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 8.26 (s, 1H), 7.76-7.75 (m, 2H), 7.28-7.27 (m, 2H), 3.56 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 147.7, 139.5, 129.9, 126.2, 125.9, 118.6, 42.8, 21.5; FT IR: 3147, 3030, 3017, 2932, 1495, 1371, 1349, 1335, 1235, 1194, 1178, 1102, 1031, 993, 950, 829, 797, 774 cm^{-1}; mp 120–122 °C (dec.); HRMS (ESI–TOF) *m*/*z* 238.0652 $[M + H]^+$, Calcd for 238.0645.

4-(4-Chlorophenyl)-1-(methylsulfonyl)-1*H*-1,2,3-triazole (3d)



3d: (51%); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 8.30 (s, 1H), 7.81-7.80 (m, 2H), 7.45-7.44 (m, 2H), 3.58 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 147.5, 135.3, 129.5, 127.5, 127.2, 119.1, 42.8; FT IR: 3142, 3021, 2934, 1606, 1482, 1411, 1370, 1360, 1327, 1235, 1199, 1175, 1102, 1028, 993, 999, 977, 970, 944, 839, 796, 777; mp 123–125 °C (dec.); HRMS (ESI–TOF) *m*/*z* 258.0111 $[M + H]^+$, Calcd for 258.0098.

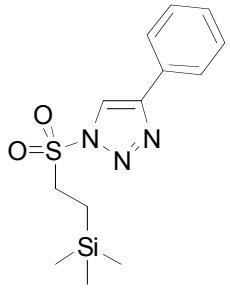
4-(3-Methoxyphenyl)-1-(methylsulfonyl)-1*H*-1,2,3-triazole (3f)



3f: (51%); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 8.30 (s, 1H), 7.45-7.43 (m, 1H), 7.40-7.36 (m, 2H), 6.96-6.95 (m, 1H), 3.88 (s, 3H), 3.57 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 160.3,

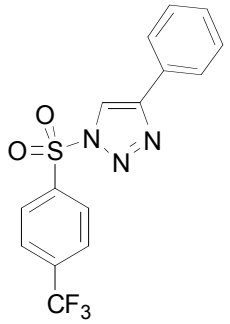
147.5, 130.3, 130.0, 119.2, 118.6, 115.4, 111.4, 55.5, 42.8; FT IR: 3145, 3012, 2929, 2839, 1608, 1586, 1557, 1480, 1376, 1327, 1285, 1254, 1223, 1180, 1044, 999, 952, 845, 834, 768, 689 cm^{-1}; mp 88–90 °C (dec.); HRMS (ESI–TOF) *m*/*z* 254.0586 $[M + H]^+$, Calcd for 254.0594.

4-Phenyl-1-((2-(trimethylsilyl)ethyl)sulfonyl)-1*H*-1,2,3-triazole (3h)



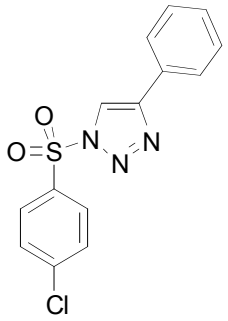
3h: (87%); ^1H NMR (500 MHz, $CDCl_3$) δ ppm 8.30 (s, 1H), 7.91-7.87 (m, 2H), 7.50-7.45 (m, 2H), 7.44-7.39 (m, 1H), 3.62-3.54 (m, 2H), 1.01-0.94 (m, 2H), 0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 147.2, 129.2, 129.1, 128.8, 126.1, 119.8, 52.6, 9.7, -2.1; FT IR: 3134, 2926, 1369, 1253, 1184, 1163, 991, 849, 883, 763, 742, 691, 553, 532 cm^{-1}; mp 122–123 °C (dec.); LRMS (ESI) *m/z* 641.3 $[2M + Na]^+$.

4-Phenyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)-1*H*-1,2,3-triazole (3k)



3k: (65%); ^1H NMR (500 MHz, $CDCl_3$) δ ppm 8.34 (s, 1H), 8.32-8.28 (m, 2H), 7.89-7.86 (m, 2H), 7.85-7.81 (m, 2H), 7.47-7.37 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 147.7, 139.7, 137.1 (q, J = 33.59 Hz), 129.4, 129.2, 129.1, 128.4, 127.0 (q, J = 3.64 Hz), 126.1, 122.7 (q, J = 273.53 Hz), 119.0; FT IR: 1395, 1321, 1195, 1131, 1062, 985, 844, 766, 717, 691 cm^{-1}; mp 142 °C (dec.); LRMS (ESI) *m/z* 354.2 $[M + H]^+$.

1-((4-Chlorophenyl)sulfonyl)-4-phenyl-1*H*-1,2,3-triazole (3l)

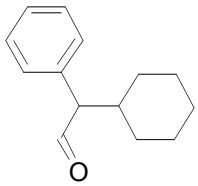


3l: (82%); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.32 (s, 1H), 8.11-8.06 (m, 2H), 7.84-7.81 (m, 2H), 7.60-7.55 (m, 2H), 7.46-7.41 (m, 2H), 7.40-7.36 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 147.5, 142.8, 134.5, 130.2, 130.0, 129.2, 129.0, 128.6, 126.1, 118.9; FT IR: 1391, 1187, 1175, 990, 825, 760, 692, 653, 629 cm^{-1}; mp 144 °C (dec.); LRMS (ESI) *m/z* 320.2 $[M + H]^+$.

Rh(II)-Catalyzed C–H Insertion

C–H insertion and imine hydrolysis. To an oven-dried 0.5-2 mL micro-wave vial equipped with a stirring bar 45 mg (0.2 mmol) of 1-(methanesulfonyl)-4-phenyl-1,2,3-triazole **3a** and 1.5 mg (0.001 mmol) of Rh_2(*S*-NTTL)$_4$ were added under inert atmosphere (glove box). The vial was sealed, and 0.5 mL of cyclohexane was added to the reaction mixture, followed by 0.5 mL of chloroform. The resulting green reaction mixture was then stirred at ambient temperature for about 1 hour until judged complete by LC and TLC analysis. An equal volume of methanol, few drops of water and 138 mg (1.0 mmol) of anhydrous potassium carbonate were added to the reaction mixture, and the obtained suspension was vigorously stirred for 0.5–1 h until hydrolysis of imine **4a** was complete. Solvents were removed in vacuum, and the residue purified by chromatography on silica gel to afford a pure sample of aldehyde **8a**.

(±)-2-Cyclohexyl-2-phenylacetaldehyde (8a) [4]



(4) Stratakis, M.; Kalaitzakis, D.; Stavroulakis, D.; Kosmas, G.; Tsangarakislis; C. *Org. Lett.* **2003**, *5*, 3471.

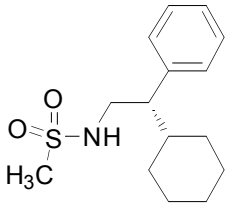
8a: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 9.72 (d, J = 3.5 Hz, 1H), 7.41-7.35 (m, 2H), 7.31 (d, J = 3.5 Hz, 1H), 7.22-7.19 (m, 2H), 3.27 (dd, J = 9.6, 3.5 Hz, 1H), 2.17-2.08 (m, 1H), 1.90-1.82 (m, 1H), 1.81-1.73 (m, 1H), 1.70-1.62 (m, 2H), 1.48-1.39 (m, 1H), 1.39-1.03 (m, 4H), 0.87-0.82 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 201.2, 135.2, 129.3, 128.9, 127.4, 65.8, 38.2, 31.8, 30.2, 26.2, 26.1, 26.0; 0% *ee* (Chiralcel OD-H, 0.5 mL/min, 2% *i*-PrOH/hexanes), t_R = 12.53 min and t_R = 14.97 min.

Rh(II)-Catalyzed C–H insertion/reduction.

Procedure A. To an oven-dried 2-5 mL micro-wave vial equipped with a stirring bar 1.0 mmol of triazole **3** and 0.0072 g (0.005 mmol) of Rh_2(*S*-NTTL)$_4$ **6** were added under inert atmosphere (glove box). The vial was sealed, and alkane (2.5 mL) was added to the vial *via* syringe, followed by 2.5 mL of chloroform. The resulting green reaction mixture was stirred at ambient temperature for 1-24 hrs until judged complete by LC and TLC analysis. The reaction mixture then was cooled in ice-water bath, and 0.5 mL of lithium aluminum hydride solution (2.4M in THF; 1.2 mmol) was added dropwise at 0 °C. The resulting mixture was stirred for 15 minutes at 0 °C, and then carefully quenched with 0.5 mL of methanol, followed by 10 mL of 1N HCl, extracted with ethyl acetate (2x50 mL), washed with water and brine, and dried over anhydrous sodium sulfate. After removal of solvent, the residue was purified by column chromatography on silica gel to afford sulfonamide **5** as a white solid.

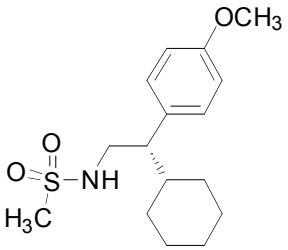
Procedure B. To an oven-dried 2-5 mL micro-wave vial equipped with a stirring bar 1.0 mmol of triazole **3** and 0.0078 g (0.005 mmol) of Rh_2(*S*-PTAD)$_4$ **7** were added under inert atmosphere (glove box). The vial was sealed, and alkane (2.5 mL) was added to the vial, followed by 2.5 mL of chloroform. The resulting green reaction mixture was stirred at 40 °C for 2-7 hrs until judged complete by LC and TLC analysis. The reaction mixture then was cooled in ice-water bath, and 0.5 mL of lithium aluminum hydride solution (2.4M in THF; 1.2 mmol) was added dropwise at 0 °C. The resulting mixture was stirred for 15 minutes at 0 °C, and then carefully quenched with 0.5 mL of methanol, followed by 10 mL of 1N HCl, extracted with ethyl acetate (2x50 mL), washed with water and brine, and dried over anhydrous sodium sulfate. After removal of solvent, the residue was purified by column chromatography on silica gel to afford sulfonamide **5** as white solid or colorless oil.

(*S*)-(−)-*N*-(2-Cyclohexyl-2-phenylethyl)methanesulfonamide (5a)



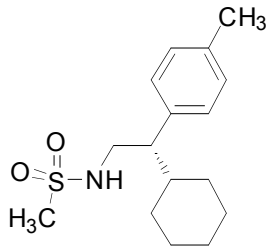
5a: (procedure **A**, 95% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.37-7.33 (m, 2H), 7.30-7.25 (m, 1H), 7.18-7.13 (m, 2H), 3.95-3.88 (m, 1H), 3.64 (ddd, J = 13.11, 8.72, 4.60 Hz, 1H), 3.29 (ddd, J = 12.46, 10.78, 3.68 Hz, 1H), 2.79 (s, 3H), 2.62-2.55 (m, 1H), 1.96-1.90 (m, 1H), 1.83-1.74 (m, 1H), 1.69-1.52 (m, 3H), 1.45-1.37 (m, 1H), 1.33-1.20 (m, 1H), 1.19-1.02 (m, 3H), 0.88-0.77 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 140.7, 128.8, 128.5, 127.1, 52.3, 40.1, 31.2, 31.0, 46.0, 40.9, 26.3, 26.2, 26.2; FT IR: 2946, 2917, 1313, 1151, 850, 778, 698 cm^{-1}; mp 108–109 °C; 96% *ee* (Chiralpak AD, 1.0 mL/min, 3% *i*-PrOH/hexanes), t_R = 17.00 min (minor), t_R = 18.39 min (major); $[\alpha]^{23}_D$ −21° (*c* 1.31, $CHCl_3$); LRMS (ESI) *m/z* 282.4 $[M + H]^+$; HRMS (ESI-TOF) *m/z* 282.1524 $[M + H]^+$, Calcd for $C_{15}H_{23}NO_2S$ 282.1522.

(*S*)-(−)-*N*-(2-Cyclohexyl-2-(4-methoxyphenyl)ethyl)methanesulfonamide (5b)



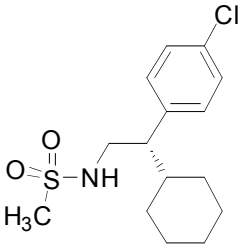
5b: (procedure **A**, 61% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.05-7.04 (m, 2H), 6.87-6.86 (m, 2H), 3.87-3.86 (m, 1H), 3.80 (s, 3H), 3.59 (ddd, J = 13.2, 9.0, 4.8 Hz, 1H), 3.21 (ddd, J = 12.0, 10.8, 3.0 Hz, 1H), 2.80 (s, 3H), 2.51 (ddd, J = 10.8, 9.0, 4.8 Hz, 1H), 1.89-1.70 (m, 1H), 1.76-1.74 (m, 1H), 1.62-1.61 (m, 1H), 1.53-1.47 (m, 1H), 1.40-1.38 (m, 1H), 1.25-1.20 (m, 2H), 1.12-1.08 (m, 2H), 1.03-0.97 (m, 1H), 0.82-0.75 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 159.5, 133.2, 130.2, 115.1, 56.1, 52.2, 50.0, 41.9, 41.0, 32.1, 31.8, 27.2, 27.1, 27.1; FT IR (film): 2984, 2933, 1737, 1612, 1513, 1447, 1373, 1302, 1239, 1179, 1154, 1097, 1044, 938, 846, 786 cm^{-1}; mp 97–99 °C ; 97% *ee* (Chiralcel OD-H, 0.3 mL/min, 10% *i*-PrOH / hexanes), t_R = 57.99 min (minor), t_R = 60.24 min (major); $[\alpha]^{23}_D$ −16º (*c* 1.00, $CHCl_3$); HRMS (ESI–TOF) *m/z* 312.1623 $[M + H]^+$, Calcd for $C_{16}H_{25}NO_3S$ 312.1628.

(*S*)-(−)-*N*-(2-Cyclohexyl-2-(*p*-tolyl)ethyl)methanesulfonamide (5c)



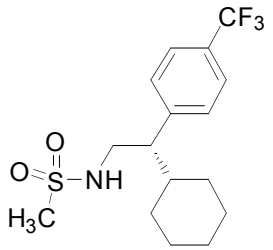
5c: (procedure **A**, 72% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.14-7.13 (m, 2H), 7.02-7.01 (m, 2H), 3.87-3.86 (m, 1H), 3.60 (ddd, *J* = 13.2, 9.0, 4.8 Hz, 1H), 3.23 (ddd, *J* = 12.0, 10.2, 3.6 Hz, 1H), 2.79 (s, 3H), 2.52 (10.8, 9.0, 4.8 Hz, 1H), 2.33 (s, 3H), 1.90-1.88 (m, 1H), 1.76-1.74 (m, 1H), 1.62-1.60 (m, 1H), 1.55-1.49 (m, 2H), 1.40-1.38 (m, 1H), 1.25-1.20 (m, 1H), 1.13-1.06 (m, 2H), 1.04-0.97 (m, 1H), 0.82-0.76 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 137.4, 136.7. 129.5, 128.3, 51.8, 46.0, 40.9, 40.0, 31.2, 31.0, 26.3, 26.2, 26.2, 21.0; FT IR (film): 3291, 2925, 2852, 1514, 1448, 1320, 1152, 1076, 969, 821, 757 cm^{-1}; mp 89–91 °C ; 94% *ee* (Chiralcel OG, 0.5 mL/min, 2% *i*-PrOH/hexanes), t_R = 109.54 min (minor), t_R = 118.85 min (major); $[\alpha]^{23}_D$ −19º (*c* 1.00, $CHCl_3$); HRMS (ESI–TOF) *m/z* 296.1683 $[M + H]^+$, Calcd for $C_{16}H_{25}NO_2S$ 296.1679.

(*S*)-(−)-*N*-(2-(4-Chlorophenyl)-2-cyclohexylethyl)methanesulfonamide (5d)



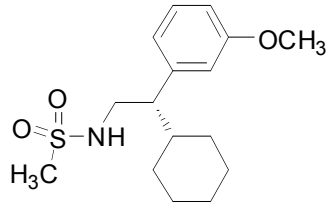
5d: (procedure **A**, 75% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.31-7.30 (m, 2H), 7.09-7.07 (m, 2H), 3.93 (d, *J* = 4.8 Hz, 1H), 3.59 (ddd, *J* = 12.6, 8.4, 4.8 Hz, 1H), 3.23 (ddd, *J* = 12.6, 10.2, 4.2 Hz, 1H), 2.79 (s, 3H), 2.56 (ddd, *J* = 10.2, 9.0, 4.2 Hz, 1H), 1.88-1.86 (m, 1H), 1.76-1.74 (m, 1H), 1.63-1.61 (m, 2H), 1.54-1.48 (m, 1H), 1.38-1.36 (m, 1H), 1.26-1.20 (m, 1H), 1.12-1.07 (m, 2H), 1.03-0.96 (m, 1H), 0.81-0.75 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 139.3, 132.0, 130.0, 129.1, 52.0, 46.0, 40.9, 40.4, 31.2, 30.9, 26.4, 26.3, 26.3; FTIR (film) 3292, 2925, 2852, 1492, 1449, 1320, 1152, 1093, 1014, 969, 830 cm^{-1}; mp 96–98 °C, 95% *ee* (Chiralpak AD, 1.0 mL/min, 3% *i*-PrOH/hexanes), t_R = 18.57 min (minor), t_R = 22.46 min (major); $[\alpha]^{23}_D$ −17º (*c* 1.00, $CHCl_3$); HRMS (ESI–TOF) *m/z* 316.1140 $[M + H]^+$, Calcd for $C_{15}H_{22}ClNO_2S$ 316.1132.

(*S*)-(−)-*N*-(2-Cyclohexyl-2-(4-(trifluoromethyl)phenyl)ethyl)methanesulfonamide (5e)



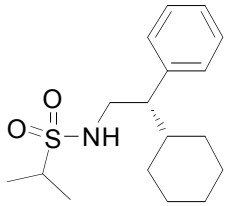
5e: (procedure **A**, 92% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.60-7.58 (m, 2H), 7.28-7.26 (m, 2H), 3.99-3.97 (m, 1H), 3.63 (ddd, J = 12.6, 8.4, 4.2 Hz, 1H), 3.30 (ddd, J = 13.2, 10.8, 4.8 Hz, 1H), 2.79 (s, 3H), 2.67 (ddd, J = 10.2, 9.0, 4.2 Hz, 1H), 1.90-1.89 (m, 1H), 1.77-1.75 (m, 1H), 1.62-1.60 (m, 1H), 1.60-1.54 (m, 2H), 1.37-1.35 (m, 1H), 1.25-1.21 (m, 2H), 1.14-1.08 (m, 2H), 1.05-0.98 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 145.2, 129.6 (q, J = 32.5 Hz), 129.1, 125.8 (q, J = 3.6 Hz), 124.2 (q, J = 272.1 Hz), 52.5, 45.9, 40.9, 40.4, 31.2, 30.9, 26.3, 26.2, 26.2; FTIR (film) 3284, 2929, 2854, 1619, 1449, 1421, 1325, 1157, 1123, 1068, 1018, 908, 841, 733 cm^{-1}; mp 88–90 °C; 97% *ee* (Chiralpak AD, 1.0 mL/min, 3% *i*–PrOH/hexanes), t_R = 17.08 min (minor), t_R = 14.34 min (major); $[\alpha]^{23}_D$ −18º (*c* 1.00, $CHCl_3$); HRMS (ESI–TOF) *m*/*z* 350.1401 $[M + H]^+$, Calcd for $C_{16}H_{22}F_3NO_2S$ 350.1396.

(*S*)-(−)-*N*-(2-Cyclohexyl-2-(3-methoxyphenyl)ethyl)methanesulfonamide (5f)



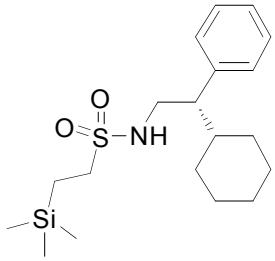
5f: (procedure **A**, 98% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.26-7.24 (m, 1H), 6.79-6.78 (m, 1H), 6.73-6.72 (m, 1H), 6.67 (s, 1H), 3.89 (d, J = 6.6 Hz, 1H), 3.81 (s, 3H), 3.61 (ddd, J = 13.2, 9.0, 4.8 Hz, 1H), 3.23 (ddd, J = 12.6, 9.6, 3.0 Hz, 1H), 2.80 (s, 3H), 2.53 (ddd, J = 13.2, 10.8, 4.8 Hz, 1H), 1.91-1.89 (m, 1H), 1.77-1.75 (m, 1H), 1.62-1.61 (m, 2H), 1.57-1.50 (m, 1H), 1.41-1.39 (m, 1H), 1.25-1.21 (m, 1H), 1.12-1.09 (m, 2H), 1.05-0.98 (m, 1H), 0.84-0.79 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ ppm 160.1, 142.5, 130.0, 120.8, 114.8, 112.0, 55.3, 52.5, 46.1, 41.0, 40.2, 31.3, 31.2, 26.4, 26.3, 26.3; FTIR (film) 3293, 2926, 2851, 1599, 1495, 1450, 1320, 1258, 1152, 1047, 972, 871, 782, 705 cm^{-1}; mp 93–96 °C ; 95% *ee* (Chiralcel OG, 0.5 mL/min, 10% *i*-PrOH/hexanes), t_R = 45.76 min (minor), t_R = 61.78 min (major); $[\alpha]^{23}_D$ −17º (*c* 1.00, $CHCl_3$); HRMS (ESI–TOF) *m*/z 312.1619 $[M + H]^+$, Calcd for $C_{16}H_{25}NO_3S$ 312.1628.

(*S*)-(−)-*N*-(2-Cyclohexyl-2-phenylethyl)propane-2-sulfonamide (5g)



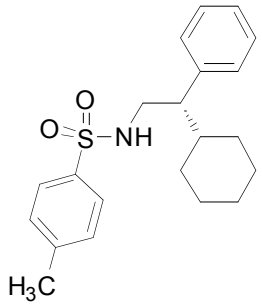
5g: (procedure **A**, 82% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.37-7.33 (m, 2H), 7.30-7.25 (m, 1H), 7.19-7.14 (m, 2H), 3.72-3.60 (m, 2H), 3.31-3.24 (m, 1H), 3.05 (sept., J = 6.9 Hz, 1H), 2.61-2.54 (m, 1H), 1.96-1.87 (m, 1H), 1.82-1.72 (m, 1H), 1.68-1.49 (m, 3H), 1.44-1.34 (m, 1H), 1.30 (d, J = 6.8 Hz, 3H), 1.29-1.23 (m,1H), 1.22 (d, J = 6.8 Hz, 3H), 1.18-0.98 (m, 3H), 0.82 (ddd, J = 14.4, 12.7, 2.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 140.8, 128.8, 128.5, 127.1, 53.0, 52.8, 46.4, 41.0, 30.9, 26.3, 26.2, 26.2, 31.2, 16.6, 16.4.; FT IR: 3282, 2924, 2852, 1450, 1315, 1267, 1138, 1102, 842, 768, 696 cm^{-1}; mp 63–64 °C; 94% *ee* (Chiralpak AD, 0.5 mL/min, 10% *i*-PrOH/hexanes), t_R = 13.09 min (minor), t_R = 18.88 min (major); $[\alpha]^{23}_D$ −26° (*c* 1.12, $CHCl_3$); LRMS (ESI) *m/z* 310.4 $[M + H]^+$; HRMS (ESI-TOF) *m/z* 310.1835 $[M + H]^+$, Calcd for $C_{17}H_{27}NO_2S$ 310.1835.

(*S*)-(−)-*N*-(2-Cyclohexyl-2-phenylethyl)-2-(trimethylsilyl)ethanesulfonamide (5h)



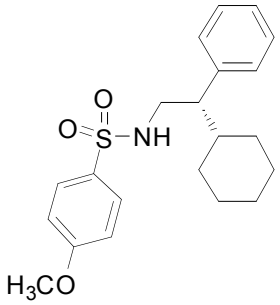
5h: (procedure **A**, 93% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.38-7.32 (m, 2H), 7.30-7.25 (m, 1H), 7.18-7.14 (m, 2H), 3.78 (dd, J = 8.5, 3.4 Hz, 1H), 3.62 (ddd, J = 12.9, 8.7, 4.5 Hz, 1H), 3.24 (ddd, J = 12.4, 10.7, 3.6 Hz, 1H), 2.84-2.75 (m, 2H), 2.57 (ddd, J = 10.5, 8.7, 4.5 Hz, 1H), 1.96-1.89 (m, 1H), 1.78 (ddd, J = 10.5, 8.7, 4.5 Hz, 1H), 1.68-1.61 (m, 2H), 1.61-1.51 (m, 1H), 1.44-1.37 (m, 1H), 1.31-1.22 (m, 1H), 1.18-1.09 (m, 2H), 1.09-0.99 (m, 1H), 0.92-0.71 (m, 3H), 0.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 140.8, 128.8, 128.5, 127.1, 52.5, 48.4, 46.1, 40.9, 31.2, 31.0, 26.3, 26.2, 26.2, 10.4, -2.0; FT IR: 3282, 2923, 2853, 1449, 1318, 1250, 1141, 1079, 840, 758, 701 cm^{-1}; 86% *ee* (Chiralpak AD, 0.2 mL/min, 2% *i*-PrOH/hexanes), t_R = 71.30 min (minor), t_R = 77.45 min (major); $[\alpha]^{23}_D$ −14° (*c* 0.94, $CHCl_3$); LRMS (ESI) *m/z* 368.3 $[M + H]^+$; HRMS (ESI-TOF) *m/z* 368.2072 $[M + H]^+$, Calcd for $C_{19}H_{33}NO_2SSi$ 368.2074.

(*S*)-(−)-*N*-(2-Cyclohexyl-2-phenylethyl)-4-methylbenzenesulfonamide (5i)



5i: (procedure **B**, 71% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.70-7.60 (m, 2H), 7.37-7.21 (m, 5H), 7.00-6.93 (m, 2H), 4.06-3.95 (m, 1H), 3.51 (ddd, J = 13.6, 9.2, 4.7 Hz, 1H), 3.02 (dt, J = 12.2, 2.9 Hz, 1H), 2.49-2.40 (m, 1H), 2.47 (s, 3H), 1.86-1.77 (m, 1H), 1.73 (d, J = 11.7 Hz, 1H), 1.59 (m, 2H), 1.49-1.40 (m, 1H), 1.34-1.26 (m, 1H), 1.26-1.15 (m, 1H), 1.14-1.01 (m, 2H), 0.99-0.88 (m, 1H), 0.79-0.67 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 143.3, 140.4, 136.8, 129.6, 128.7, 128.4, 127.1, 127.0, 51.5, 45.6, 40.9, 30.9, 31.1, 26.3, 26.2, 26.1, 21.5; FT IR: 3307, 2915, 2849, 1318, 1149, 1093, 851, 821, 701, 677 cm^{-1}; mp 141–142 °C; 90% *ee* (Chiralpak AD, 0.5 mL/min, 10% *i*-PrOH/hexanes), t_R = 18.89 min (minor), t_R = 21.15 min (major); $[\alpha]^{23}_{D}$ −4.8° (*c* 1.40, $CHCl_3$); LRMS (ESI) *m/z* 358.4 $[M + H]^+$; HRMS (ESI-TOF) *m/z* 358.1827 $[M + H]^+$, Calcd for $C_{21}H_{27}NO_2S$ 358.1835

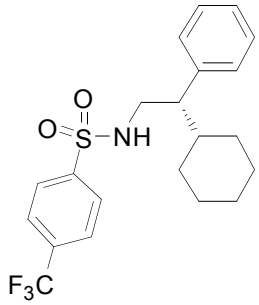
(*S*)-(−)-*N*-(2-Cyclohexyl-2-phenylethyl)-4-methoxybenzenesulfonamide (5j)



5j: (procedure **B**, 72% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.73-7.66 (m, 2H), 7.31-7.22 (m, 3H), 7.01-6.94 (m, 4H), 4.00-3.94 (m, 1H), 3.91 (s, 3H), 3.49 (ddd, J = 13.5, 9.2, 4.6 Hz, 1H), 3.01 (dt, J = 12.5, 12.1, 2.7 Hz, 1H), 2.47-2.40 (m, 1H), 1.85-1.78 (m, 1H), 1.76-1.69 (m, 1H), 1.59 (m, 2H), 1.49-1.39 (m, 1H), 1.35-1.26 (m, 1H), 1.25-1.15 (m, 1H), 1.13-1.02 (m, 2H), 0.99-0.88 (m, 1H), 0.79-0.68 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 162.8, 140.4, 131.4, 129.2, 128.7, 128.4, 127.0, 114.2, 55.6, 51.5, 45.6, 41.0, 31.1, 30.9, 26.3, 26.2, 26.2; FT IR: 3281, 1301, 1251, 1147, 1096, 1025, 864, 708 cm^{-1}; mp 103–104 °C; 88% *ee* (Chiralcel OD-H,

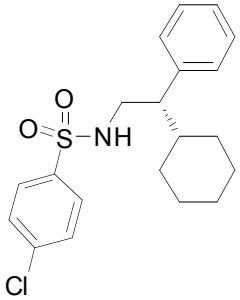
0.5 mL/min, 10% *i*-PrOH/hexanes), t_R = 22.79 min (minor), t_R = 27.03 min (major); $[\alpha]^{23}_D$ −0.7° (*c* 1.16, $CHCl_3$); LRMS (ESI) *m/z* 374.4 $[M + H]^+$; HRMS (ESI-TOF) *m/z* 374.1790 $[M + H]^+$, Calcd for $C_{21}H_{27}NO_3S$ 374.1784.

(*S*)-(−)-*N*-(2-Cyclohexyl-2-phenylethyl)-4-(trifluoromethyl)benzenesulfonamide (5k)



5k: (procedure **B** at rt, 86% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.89-7.82 (m, 2H), 7.80-7.74 (m, 2H), 7.30-7.22 (m, 3H), 6.97-6.93 (m, 2H), 4.20-4.14 (m, 1H), 3.56 (ddd, *J* = 12.9, 8.6, 4.6 Hz, 1H), 3.07 (ddd, *J* = 12.3, 10.7, 3.3 Hz, 1H), 2.45 (ddd, *J* = 10.7, 8.6, 4.6 Hz, 1H), 1.86-1.78 (m, 1H), 1.78-1.70 (m, 1H), 1.65-1.53 (m, 2H), 1.50-1.41 (m, 1H), 1.35-1.26 (m, 1H), 1.26-1.16 (m, 1H), 1.14-1.01 (m, 2H), 0.99-0.88 (m, 1H), 0.79-0.70 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 143.5, 140.2, 134.3 (q, *J* = 32.9 Hz), 128.9, 128.3, 127.5, 127.2, 126.2 (q, *J* = 3.6 Hz), 123.3 (q, *J* = 272.7 Hz), 51.7, 45.8, 40.9, 31.1, 30.9, 26.3, 26.2, 26.1; FT IR: 3282, 2921, 2852, 1320, 1159, 1128, 1061, 843, 705 cm^{-1}; mp 106–108 °C; 93% *ee* (Chiralcel OD-H, 0.5 mL/min, 10% *i*-PrOH/hexanes), t_R = 16.69 min (minor), t_R = 22.40 min (major); $[\alpha]^{23}_D$ −10° (*c* 1.04, $CHCl_3$); LRMS (ESI) *m/z* 412.3 $[M + H]^+$; HRMS (ESI-TOF) *m/z* 412.1548 $[M + H]^+$, Calcd for $C_{21}H_{24}F_3NO_2S$ 412.1553.

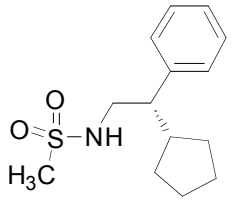
(*S*)-(−)-4-Chloro-*N*-(2-cyclohexyl-2-phenylethyl)benzenesulfonamide (5l)



5l: (procedure **B** at rt, 85% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.70-7.64 (m, 2H), 7.50-7.47 (m, 2H), 7.31-7.23 (m, 3H), 6.98-6.94 (m, 2H), 4.07 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.52 (ddd, *J* = 13.2, 8.9, 4.7 Hz, 1H), 3.07-3.00 (m, 1H), 2.44 (ddd, *J* = 10.7, 8.7, 4.6 Hz, 1H), 1.86-1.79 (m, 1H), 1.77-1.71 (m, 1H), 1.65-1.55 (m, 2H), 1.49-1.41 (m, 1H), 1.34-1.26 (m, 1H), 1.26-1.15 (m,

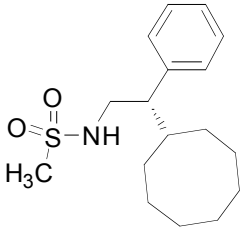
1H), 1.14-1.02 (m, 2H), 0.99-0.89 (m, 1H), 0.79-0.70 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 140.2, 139.0, 138.3, 129.3, 128.8, 128.5, 128.3, 127.1, 51.6, 45.7, 40.9, 31.1, 30.9, 26.2, 26.2, 26.1; FT IR: 3310, 2916, 2848, 1322, 1153, 1092, 851, 831, 749, 700 cm^{-1}; mp 144–145 °C; 91% *ee* (Chiralcel OD-H, 0.5 mL/min, 10% *i*-PrOH/hexanes), t_R = 17.36 min (minor), t_R = 24.44 min (major); $[\alpha]^{23}_D$ −4° (*c* 1.31, $CHCl_3$); LRMS (ESI) *m/z* 378.3 $[M + H]^+$; HRMS (ESI-TOF) *m/z* 378.1289 $[M + H]^+$, Calcd for $C_{20}H_{24}ClNO_2S$ 378.1289.

(*S*)-(−)-*N*-(2-Cyclopentyl-2-phenylethyl)methanesulfonamide (5m)



5m: (procedure **A**, 75% yield); ^{1}H NMR ($CDCl_3$, 500MHz) δ ppm 7.36-7.30 (m, 2H), 7.28-7.22 (m, 1H), 7.20-7.15 (m, 2H), 3.94-3.87 (m, 1H), 3.56 (ddd, *J* = 13.0, 8.5, 4.5 Hz, 1H), 3.24 (ddd, *J* = 13.0, 10.5, 4.0 Hz, 1H), 2.75 (s, 3H), 2.55 (dt, *J* = 10.5, 4.0 Hz, 1H), 2.09-1.99 (m, 1H), 1.99-1.91 (m, 1H), 1.74-1.63 (m, 1H), 1.63-1.48 (m, 2H), 1.48-1.35 (m, 2H), 1.32-1.22 (m, 1H), 1.06-0.95 (m, 1H); ^{13}C NMR ($CDCl_3$, 125MHz) δ ppm 141.7, 128.9, 128.1, 127.2, 52.5, 47.9, 43.6, 40.2, 31.6, 31.3, 25.3, 24.6; FT IR: 3277, 2964, 1310, 1150, 1139, 1085, 1066, 978, 849, 782, 759, 696 cm^{-1}; mp 110–111 ^{o}C; 93% *ee* (Chiralpak AD, 0.5 mL/min, 10% *i*-PrOH/hexanes), t_R = 15.22 min (minor), t_R = 16.96 min (major); $[\alpha]^{23}_D$ −19° (*c* 1.00, $CHCl_3$); LRMS (ESI) *m/z* 290.3 $[M + Na]^+$.

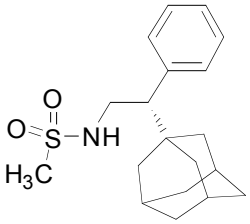
(*S*)-(−)-*N*-(2-cyclooctyl-2-phenylethyl)methanesulfonamide (5n)



5n: (procedure **A**, 86% yield); ^{1}H NMR (500MHz, $CDCl_3$) δ ppm 7.46-7.39 (m, 2H), 7.36-7.31 (m, 1H), 7.27-7.22 (m, 2H), 3.94 (dd, *J* = 7.8, 2.4 Hz, 1H), 3.70 (ddd, *J* = 12.7, 8.8, 4.2 Hz, 1H), 3.32 (ddd, *J* = 12.7,10.9, 3.6 Hz, 1H), 2.65 (s, 3H), 2.70 (dt, *J* = 10.2, 4.2 Hz, 1H), 1.96-1.75 (m, 3H), 1.74-1.43 (m, 10H), 1.37-1.25 (m, 1H), 1.25-1.15 (m, 1H); ^{13}C NMR ($CDCl_3$, 125MHz) δ ppm 141.2, 128.9, 128.5, 127.1, 52.5, 46.6, 40.2, 40.0, 30.0, 29.9, 27.2, 27.0, 26.4, 25.6, 25.1; FT

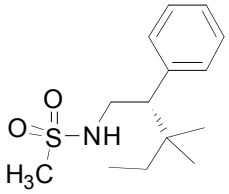
IR: 3275, 2918, 2855, 1314, 1150, 750, 699 cm^{-1}; mp 74–75 °C; 93% *ee* (Chiralpak AD, 0.5 mL/min, 10% *i*-PrOH/hexanes), t_R = 15.22 min (minor), t_R = 16.96 min (major); $[\alpha]^{23}_D$ −29° (*c* 1.00, $CHCl_3$); LRMS (ESI) *m/z* 310.4 $[M + H]^+$.

_N_-(_S_)-(−)-2-(-Adamantan-1-yl)-2-phenylethyl)methanesulfonamide (5o)



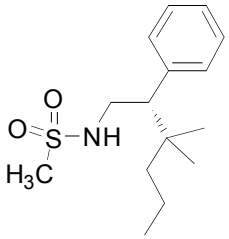
5o: (procedure **A**, 95% yield); ^1H NMR (500MHz, $CDCl_3$) δ ppm 7.35-7.30 (m, 2H), 7.29-7.25 (m, 1H), 7.15-7.11 (m, 2H), 3.80-3.74 (m, 1H), 3.68 (m, 1H), 3.45 (dt, *J* = 12.0, 2.5 Hz, 1H), 2.80 (t, 3H), 2.46 (dd, *J* = 12.0, 5.0 Hz, 1H), 1.97-1.91 (m, 3H), 1.69-1.52 (m, 9H), 1.38-14 (m, 3H); ^{13}C NMR ($CDCl_3$, 125MHz) δ ppm 128.2, 128.4, 127.3, 57.8, 42.4, 40.4, 40.2, 36.8, 35.2, 28.5; FT IR: 3280, 2906, 2846, 1708, 1327, 1316, 1140, 1069, 965, 771, 751, 699 cm^{-1}; mp 84 °C; 94% *ee* (Chiralpak AD, 0.5 mL/min, 10% *i*-PrOH/hexanes), t_R = 15.28 min (minor), t_R = 16.53 min (major); $[\alpha]^{23}_D$ −18° (*c* 1.00, $CHCl_3$); LRMS (ESI) *m/z* 334.4 $[M + H]^+$.

(_S_)-(−)-_N_-(3,3-Dimethyl-2-phenylpentyl)methanesulfonamide (5p)



5p: (procedure **A**, 87% yield); ^1H NMR (500 MHz, $CDCl_3$) δ ppm 7.37-7.32 (m, 2H), 7.31-7.27 (m, 1H), 7.22-7.18 (m, 2H), 3.83 (d, *J* = 7.1 Hz, 1H), 3.64 (ddd, *J* = 12.6, 8.9, 3.9 Hz, 1H), 3.47 (dt, *J* = 12.2, 3.1 Hz, 1H), 2.81 (s, 3H), 2.74 (dd, *J* = 12.0, 3.9 Hz, 1H), 1.30 (ddd, *J* = 14.6, 7.4, 1.9 Hz, 2H), 0.93 (s, 3H), 0.89 (t, *J* = 7.5 Hz, 3H), 0.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 138.9, 128.4, 127.2, 54.6, 43.3, 40.3, 35.9, 33.0, 24.7, 24.4, 8.1; FT IR: 3283, 2965, 1317, 1147, 1074, 967, 849, 782, 702 cm^{-1}; 92% *ee* (Chiralcel OD-H, 0.5 mL/min, 10% *i*-PrOH/hexanes), t_R = 20.10 min (minor), t_R = 30.06 min (major); $[\alpha]^{23}_D$ −18° (*c* 0.89, $CHCl_3$); LRMS (ESI) *m/z* 270.3 $[M + H]^+$; HRMS (ESI-TOF) *m/z* 270.1518 $[M + H]^+$, Calcd for $C_{14}H_{23}NO_2S$ 270.1522.

(_S_)-(−)-_N_-(3,3-Dimethyl-2-phenylhexyl)methanesulfonamide (5q)



5q: (procedure **A**, 63% yield)[5]; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.37-7.32 (m, 2H), 7.31-7.27 (m, 1H), 7.21-7.18 (m, 2H), 3.82 (d, J = 6.8 Hz, 1H), 3.64 (ddd, J = 12.6, 8.9, 4.0 Hz, 1H), 3.48 (dt, J = 12.2, 3.1 Hz, 1H), 2.81 (s, 3H), 2.73 (dd, J = 12.0, 3.9 Hz, 1H), 1.37-1.18 (m, 3H), 0.93 (s, 3H), 0.90 (t, J = 7.2 Hz, 3H), 0.83 (s, 3H), 0.78 (dd, J = 32.7, 6.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 138.9, 128.4, 127.2, 55.0, 43.3, 43.2, 40.3, 36.0, 25.4, 24.9, 16.9, 14.9; 91% *ee* (Chiralcel OD-H, 0.5 mL/min, 10% *i*-PrOH/hexanes), t_R = 17.79 min (minor), t_R = 28.48 min (major); LRMS (ESI) *m/z* 284.3 $[M + H]^+$; HRMS (ESI-TOF) *m/z* 284.1674 $[M + H]^+$, Calcd for $C_{15}H_{25}NO_2S$ 284.1679.

Deuterium Kinetic Isotope Effect Studies

Experimental Procedure. To an oven-dried 0.5-2 mL micro-wave vial equipped with a stirring bar 0.045g (0.2 mmol) of 1-(methansulfonyl)-4-phenyl-1*H*-1,2,3-triazole **3a** was added under

(5) Isolated as a non-separable mixture with 12% of isomeric products of insertion into C-4 methylene C–H bond.

inert atmosphere (glove box). The vial was sealed, and cyclohexane (0.100 mL) and cyclohexane-d_{12} (0.100 mL) were added to the vial *via* syringe, followed by a solution of 0.0029 g (0.002 mmol) of Rh_2(*S*-NTTL)$_4$ **6** in 1.0 mL of chloroform. The resulting green reaction mixture was stirred at ambient temperature for 5 minutes when a 0.100 mL aliquot was taken from the vial, placed in a scintillation vial, and immediately treated with 0.1 mL (2.4M solution in THF) of lithium aluminum hydride. The resulting mixture was stirred for 5 minutes, quenched with methanol, and analyzed by LC/MS with a pre-calibrated diode array detector. The results are summarized in the table below. Another aliquot (0.050 mL) was taken to determine conversion by ^{1}H NMR with dibromomethane as the internal standard (typically 20-30% conversion was observed).

	area of **5a**[a]	area of **5a**-d_{12}[a]	k_H/k_D[b]	average k_H/k_D
trial 1	6869000	3519000	1.80	
trial 2	11175000	5348000	1.92	**1.9±0.1**
trial 3	11880000	5944500	1.84	

[a] Integration of the LC trace at 254 nm. [b] Adjusted value according to instrument calibration.

X-Ray Crystallographic Analysis of the Compound 5a

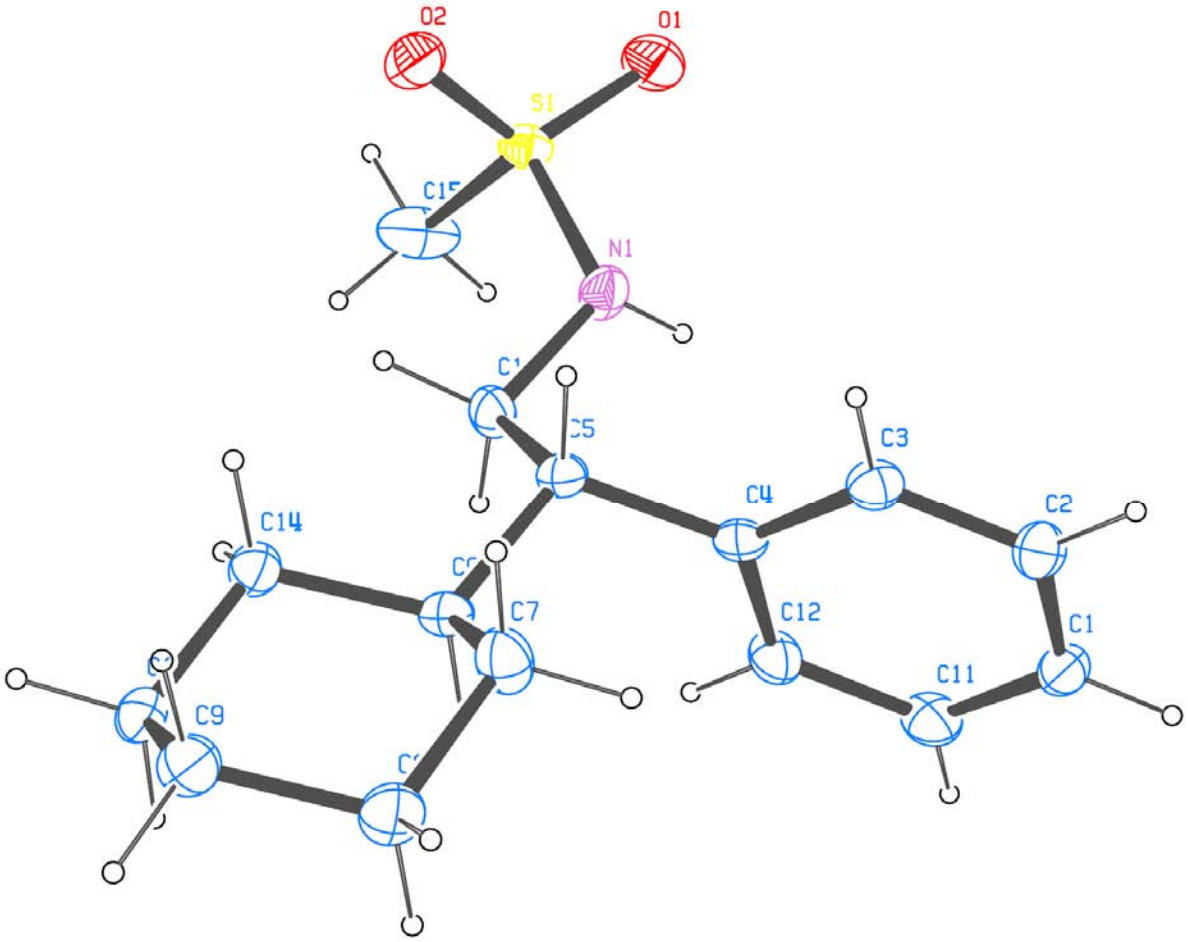
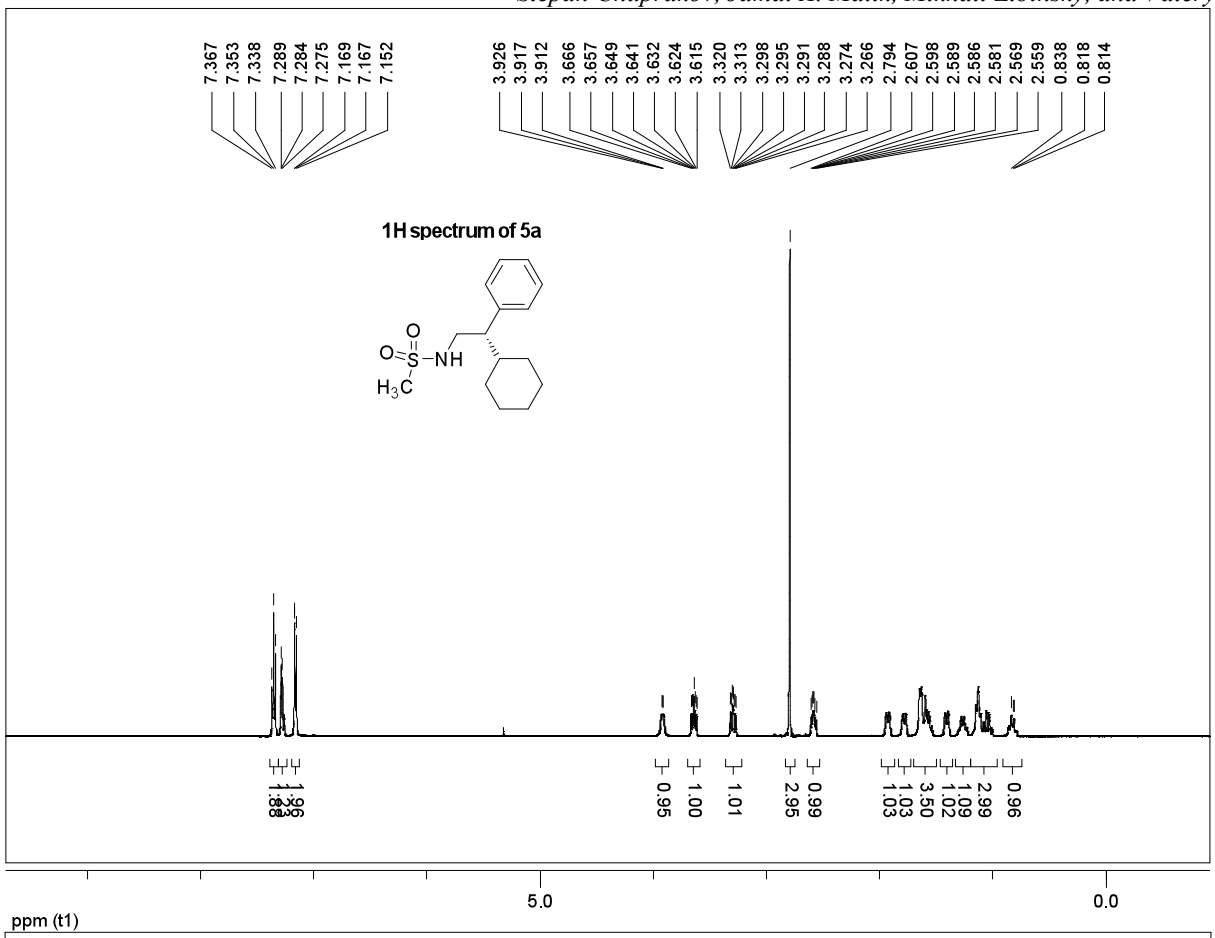


Figure 1. Crystal structure of the compound **5a** (the probability level used for the ellipsoids is 50%).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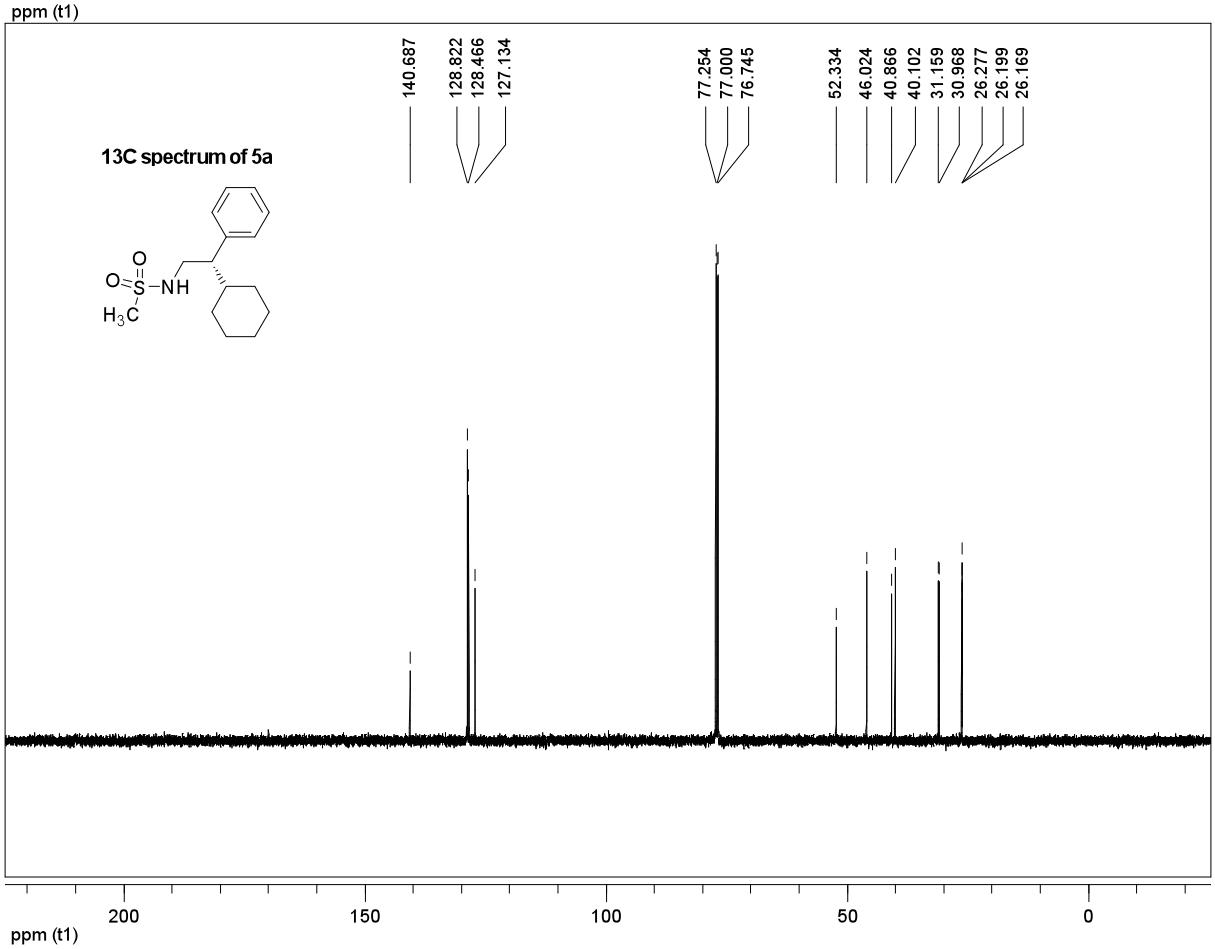
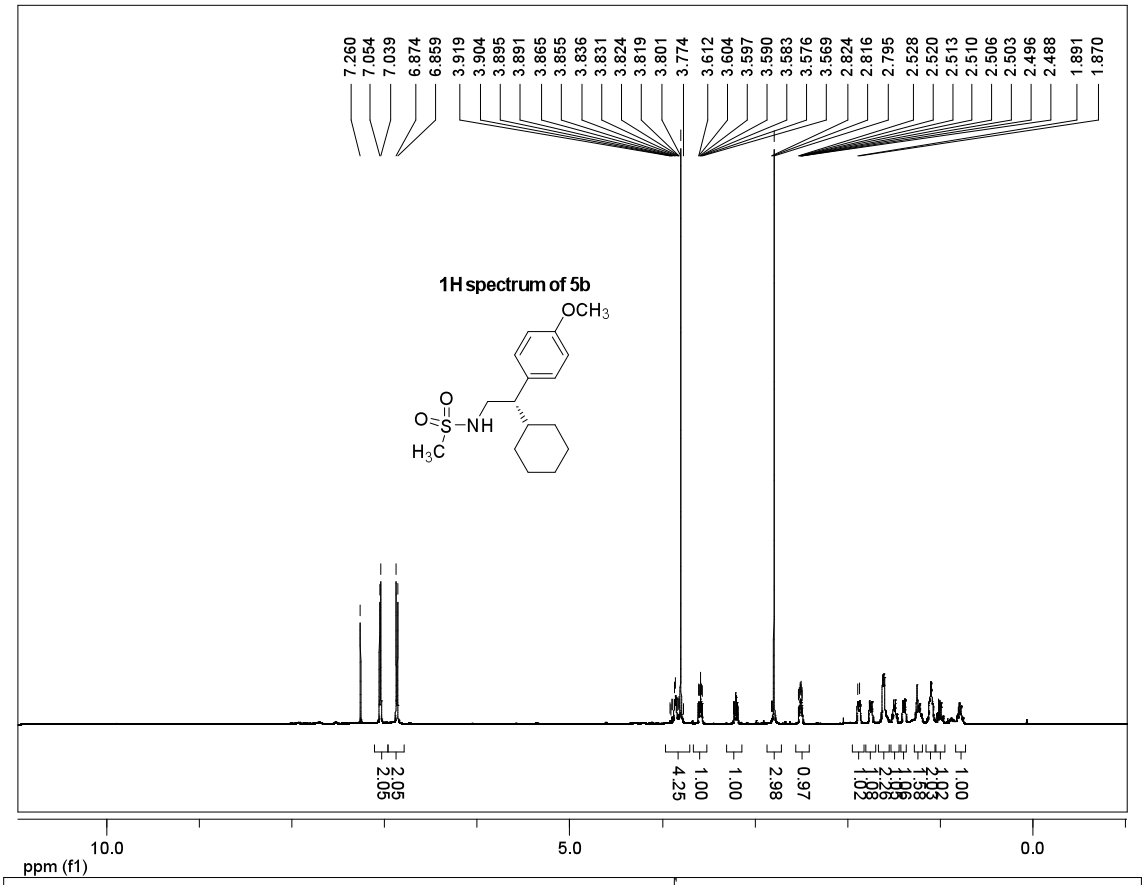
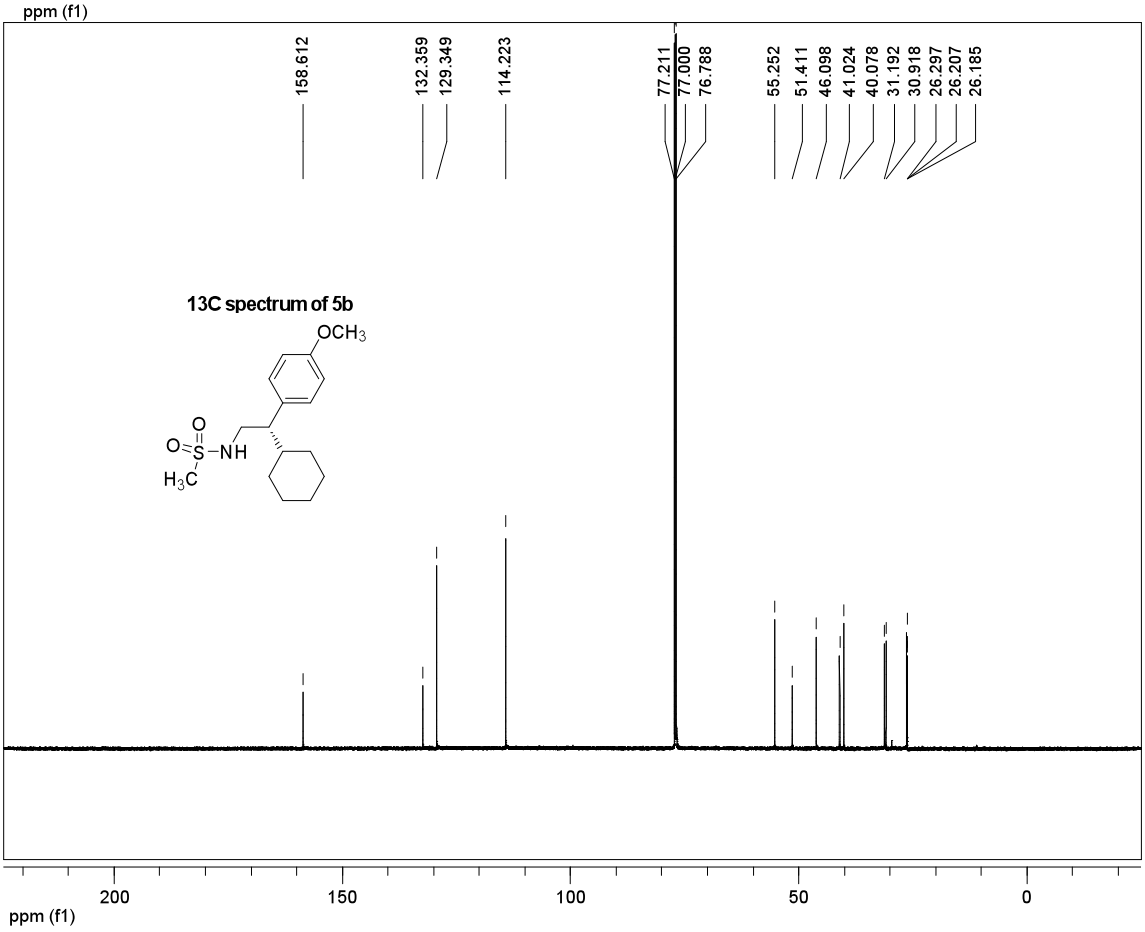
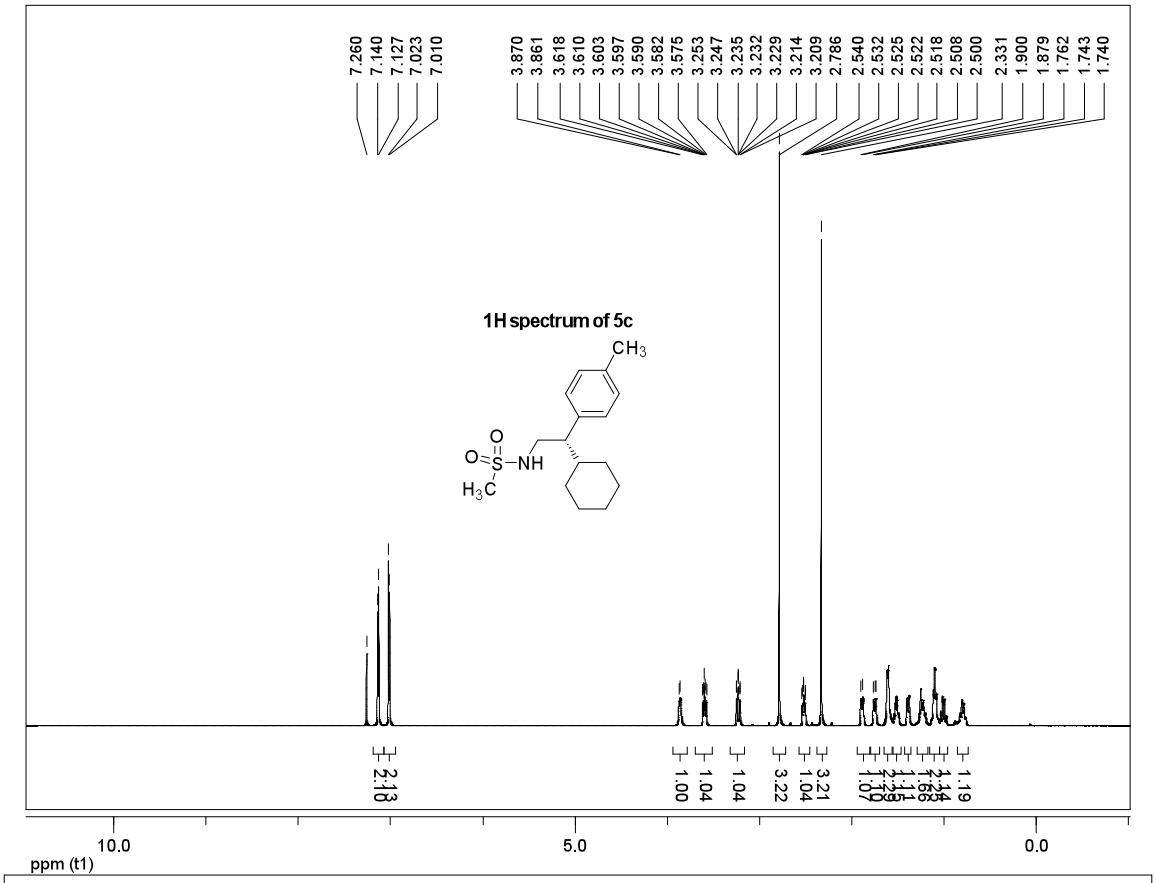
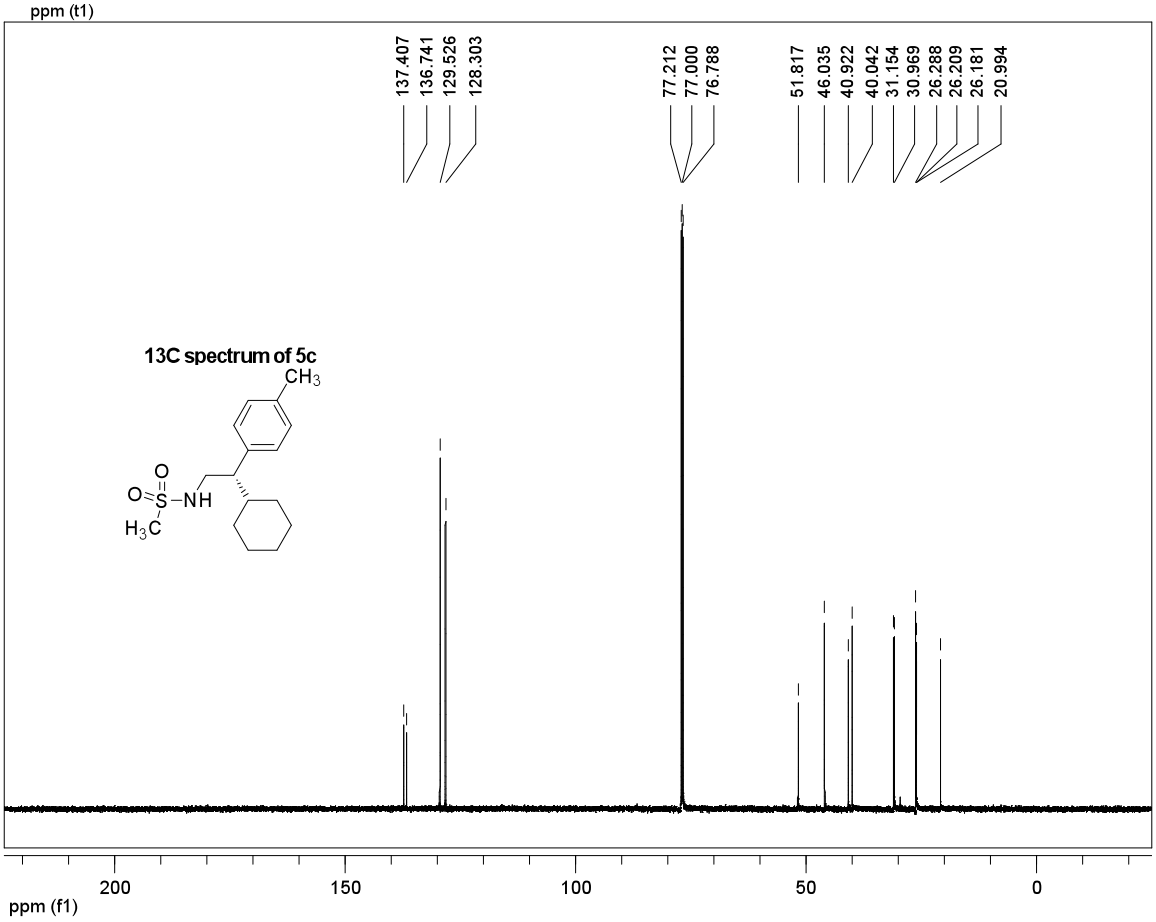
7.353
7.338
7.289
7.284
7.275
7.169
7.167
7.152
3.926
3.917
3.912
3.666
3.657
3.649
3.641
3.632
3.624
3.615
3.320
3.313
3.298
3.295
3.291
3.288
3.274
3.266
2.794
2.607
2.598
2.589
2.586
2.581
2.569
2.559
0.838
0.818
0.814
1H spectrum of 5a
O
O
S
NH
H3C
1.88
1.33
1.96
0.95
1.00
1.01
2.95
0.99
1.03
1.03
3.50
1.02
1.09
2.99
0.96
5.0
0.0
ppm (t1)

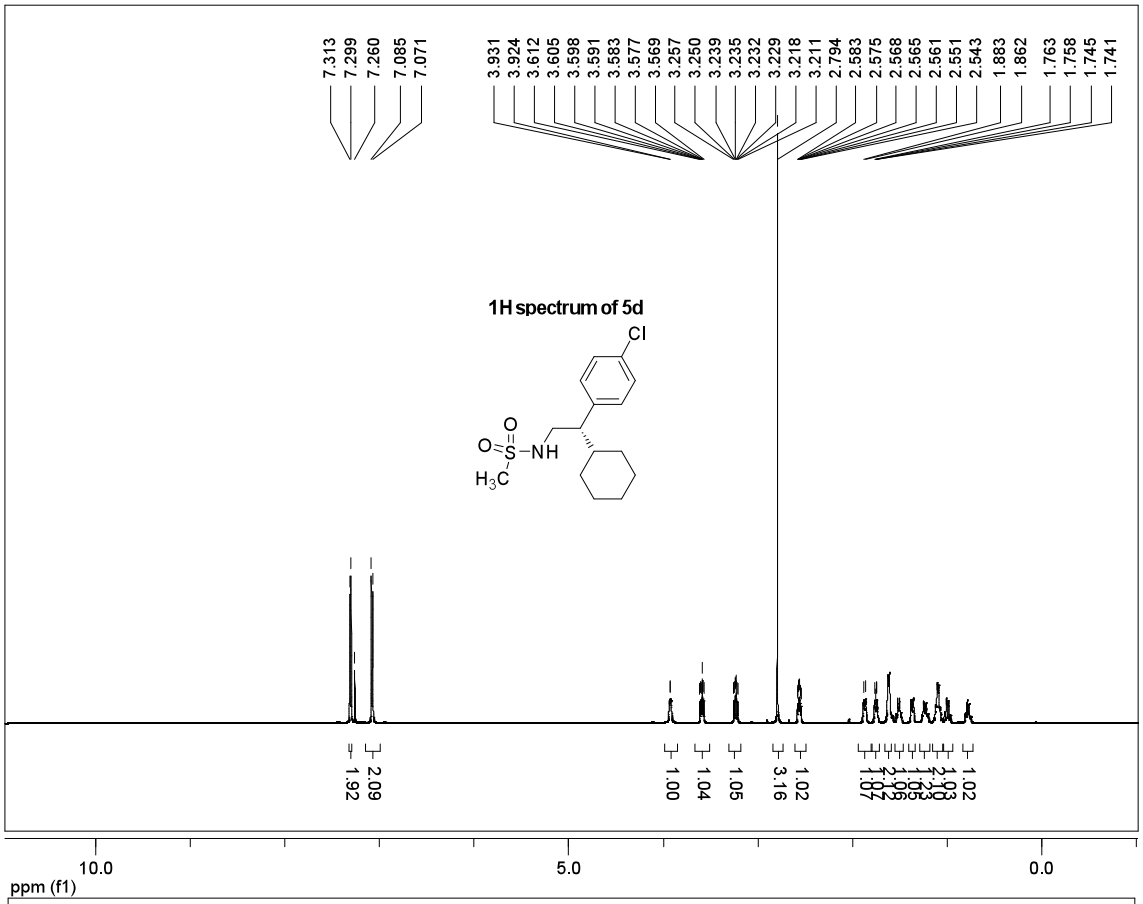

140.687
128.822
128.466
127.134
77.254
77.000
76.745
52.334
46.024
40.866
40.102
31.159
30.968
26.277
26.199
26.169
13C spectrum of 5a
O
O
S
NH
H3C
200
150
100
50
0
ppm (t1)

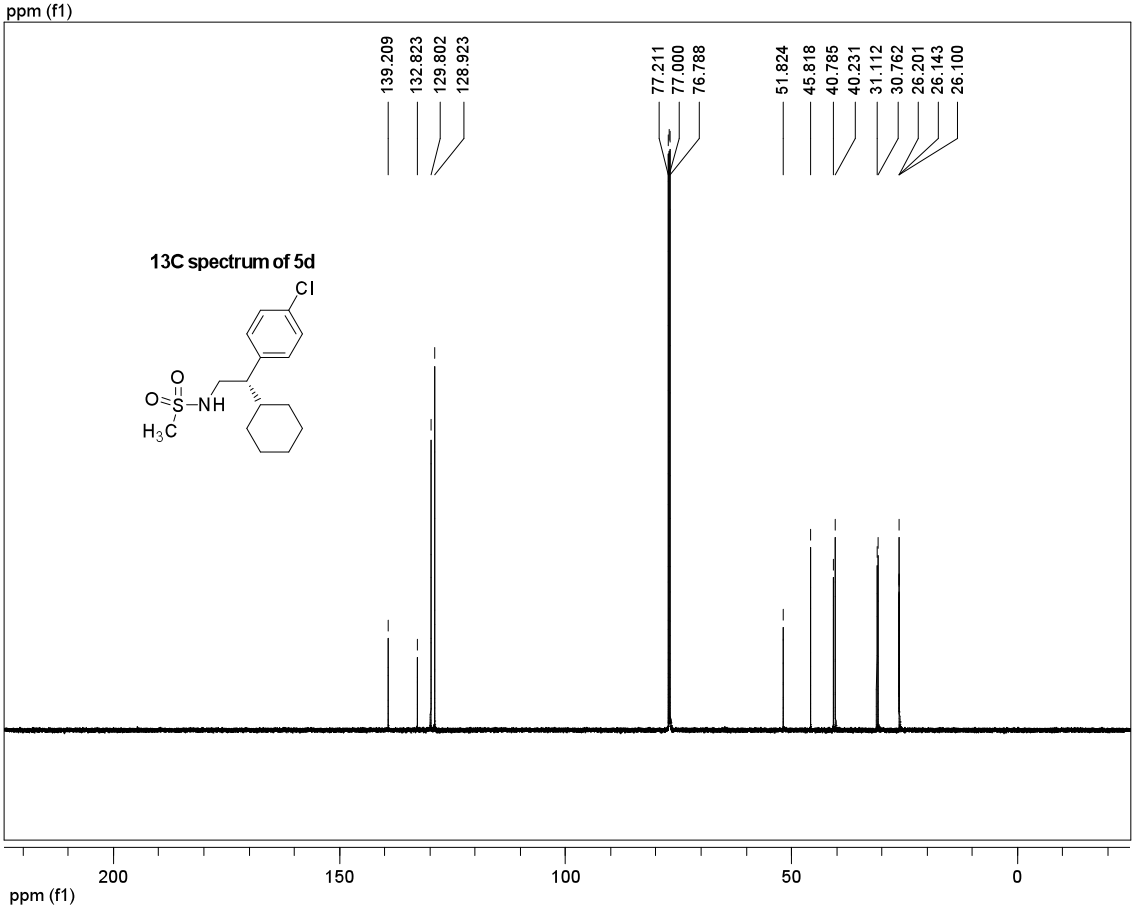

7.260
7.054
7.039
6.874
6.859
3.919
3.904
3.895
3.891
3.865
3.855
3.836
3.831
3.824
3.819
3.801
3.774
3.612
3.604
3.597
3.590
3.583
3.576
3.569
2.824
2.816
2.795
2.528
2.520
2.513
2.510
2.506
2.503
2.496
2.488
1.891
1.870
1H spectrum of 5b
OCH3
O
O=S–NH
H3C
2.05
2.05
4.25
1.00
1.00
2.98
0.97
1.00
10.0
5.0
0.0
ppm (f1)

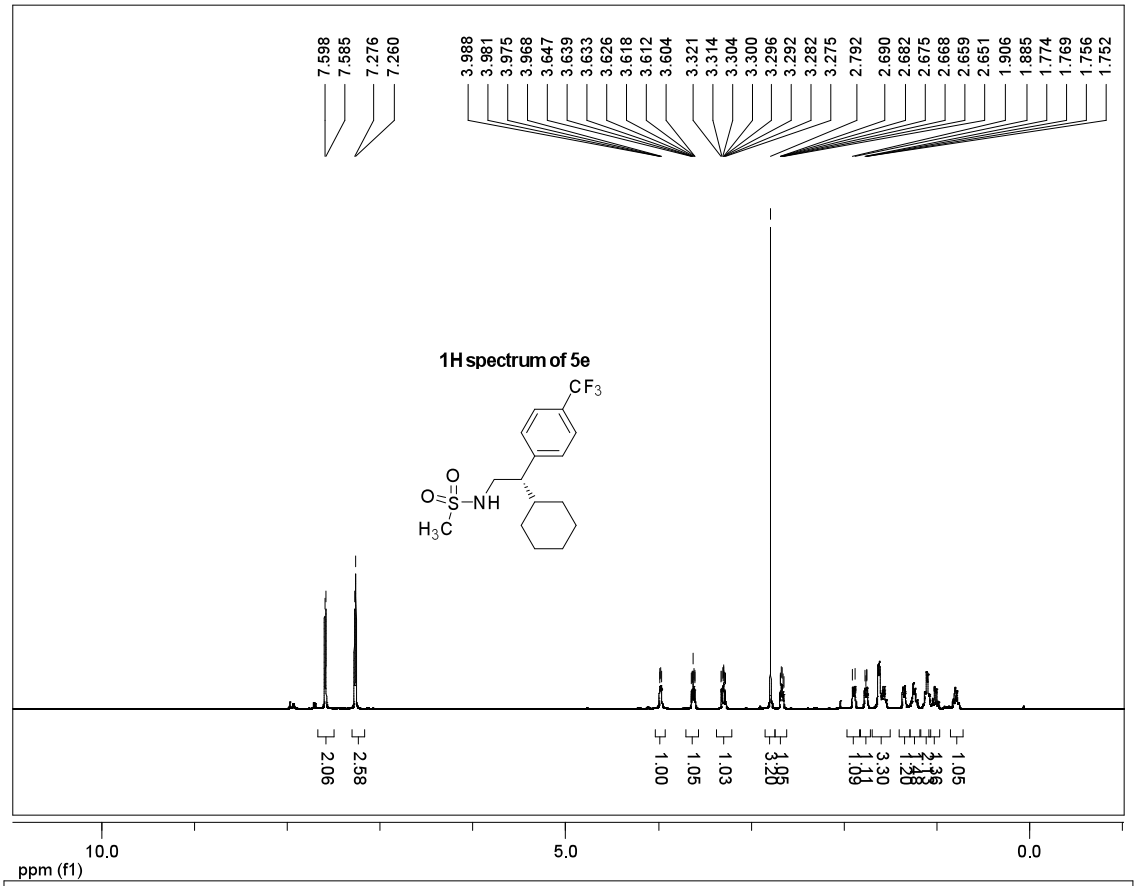

158.612
132.359
129.349
114.223
77.211
77.000
76.788
55.252
51.411
46.098
41.024
40.078
31.192
30.918
26.297
26.207
26.185
13C spectrum of 5b
OCH3
O
O=S–NH
H3C
200
150
100
50
0
ppm (f1)

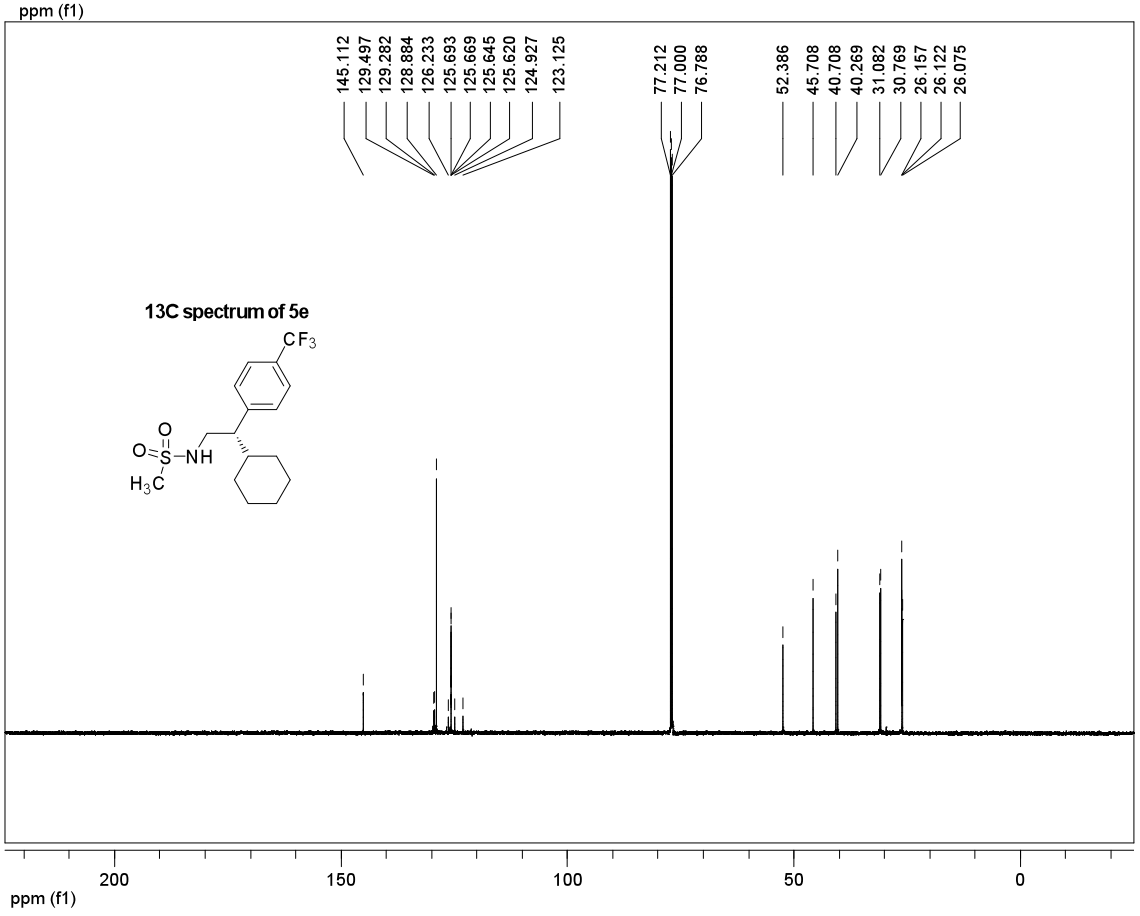

7.260
7.140
7.127
7.023
7.010
3.870
3.861
3.618
3.610
3.603
3.597
3.590
3.582
3.575
3.253
3.247
3.235
3.232
3.229
3.214
3.209
2.786
2.540
2.532
2.525
2.522
2.518
2.508
2.500
2.331
1.900
1.879
1.762
1.743
1.740
1H spectrum of 5c
CH3
O
O=S–NH
H3C
2.13
2.10
1.00
1.04
1.04
3.22
3.21
1.04
1.19
10.0
5.0
0.0
ppm (t1)

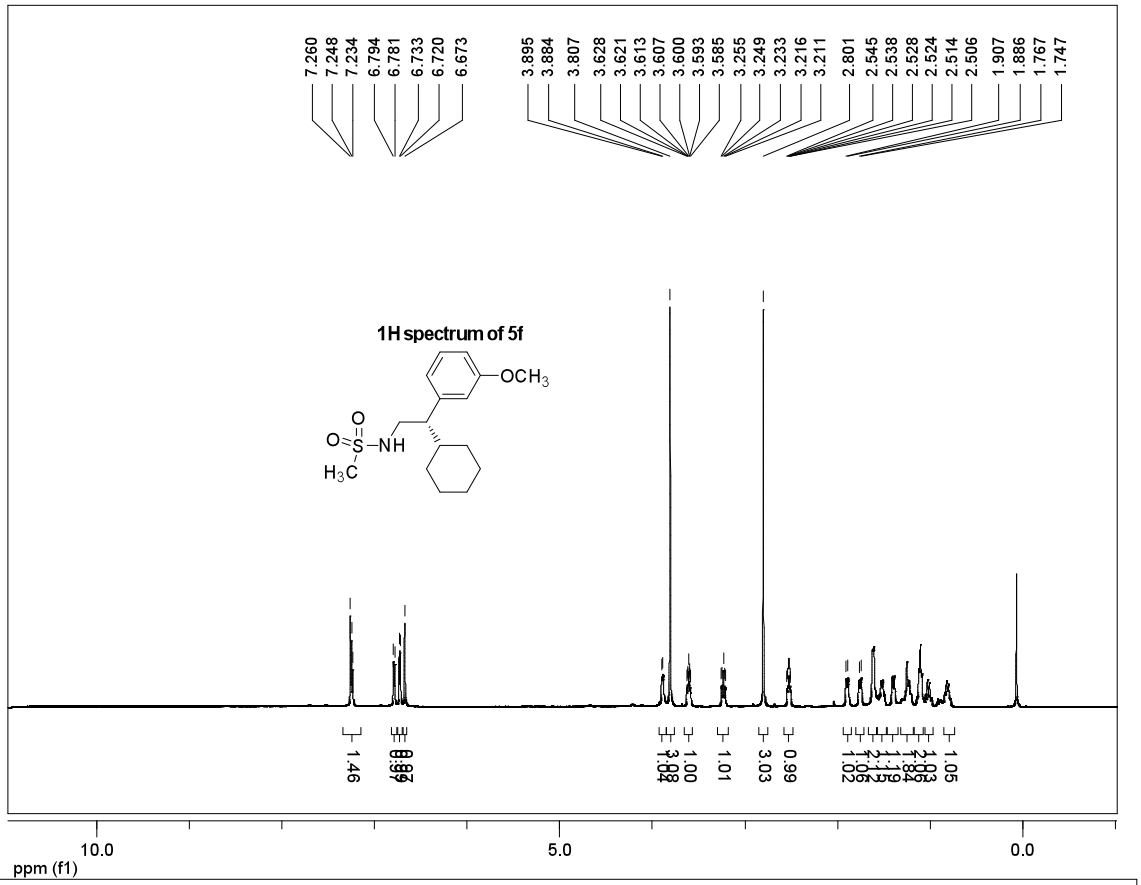

137.407
136.741
129.526
128.303
77.212
77.000
76.788
51.817
46.035
40.922
40.042
31.154
30.969
26.288
26.209
26.181
20.994
13C spectrum of 5c
CH3
O
O=S–NH
H3C
200
150
100
50
0
ppm (f1)

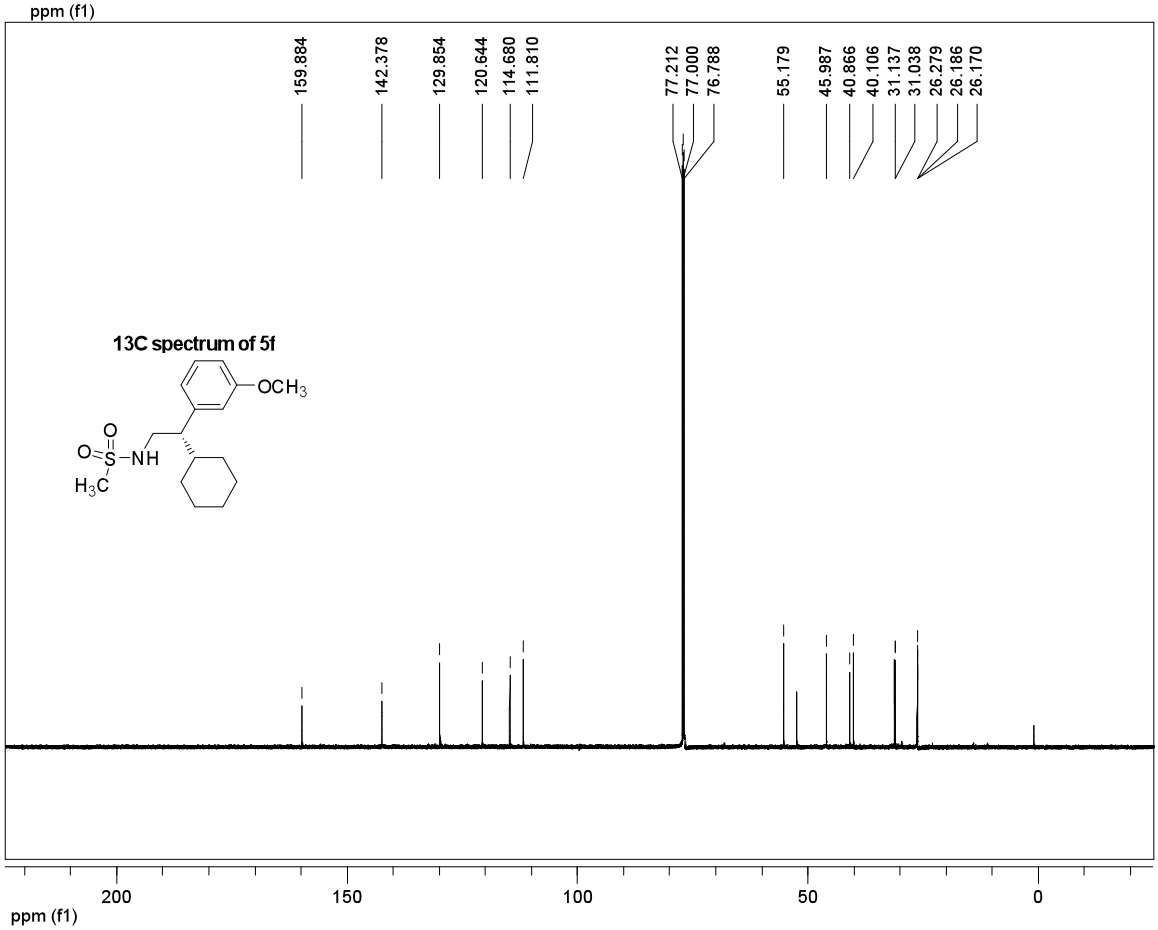

7.313
7.299
7.260
7.085
7.071
3.931
3.924
3.612
3.605
3.598
3.591
3.583
3.577
3.569
3.257
3.250
3.239
3.235
3.232
3.229
3.218
3.211
2.794
2.583
2.575
2.568
2.565
2.561
2.551
2.543
1.883
1.862
1.763
1.758
1.745
1.741
1H spectrum of 5d
Cl
O
O=S–NH
H3C
1.92
2.09
1.00
1.04
1.05
3.16
1.02
1.02
10.0
5.0
0.0
ppm (f1)

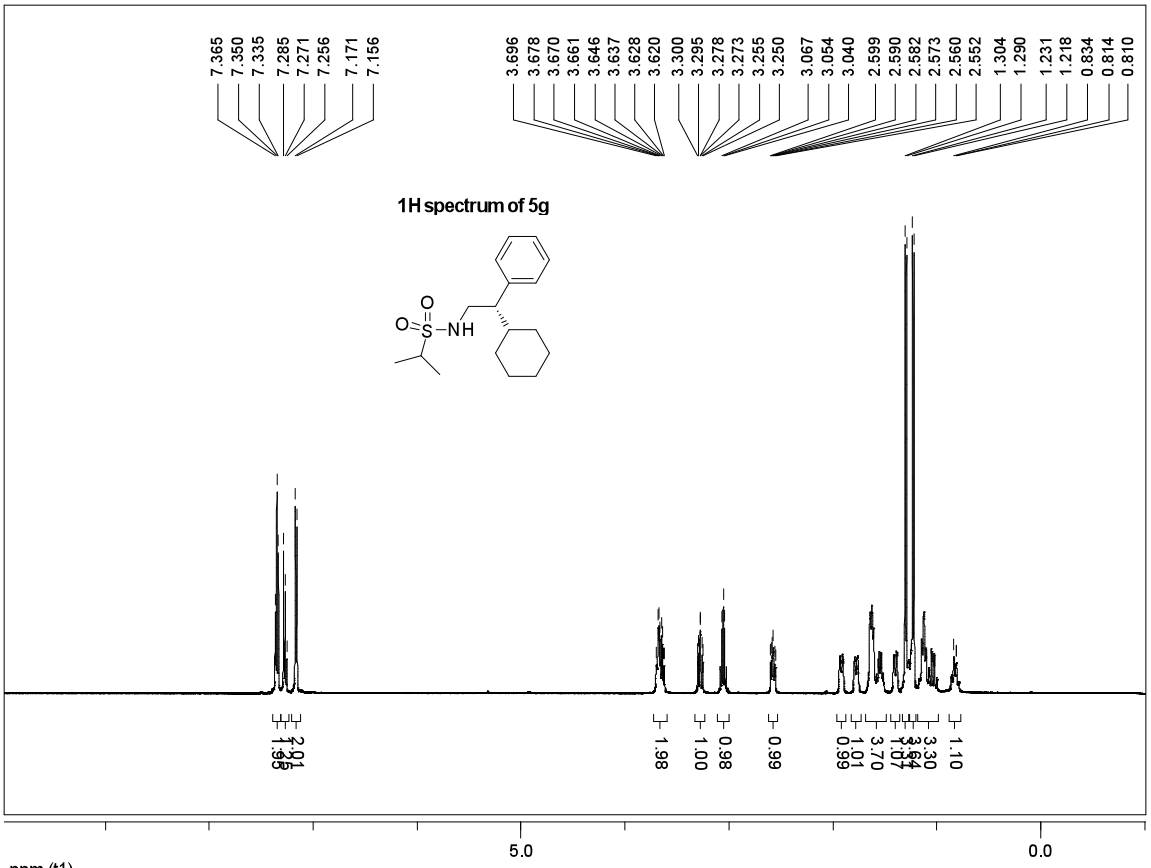

139.209
132.823
129.802
128.923
77.211
77.000
76.788
51.824
45.818
40.785
40.231
31.112
30.762
26.201
26.143
26.100
13C spectrum of 5d
Cl
O
O=S–NH
H3C
200
150
100
50
0
ppm (f1)

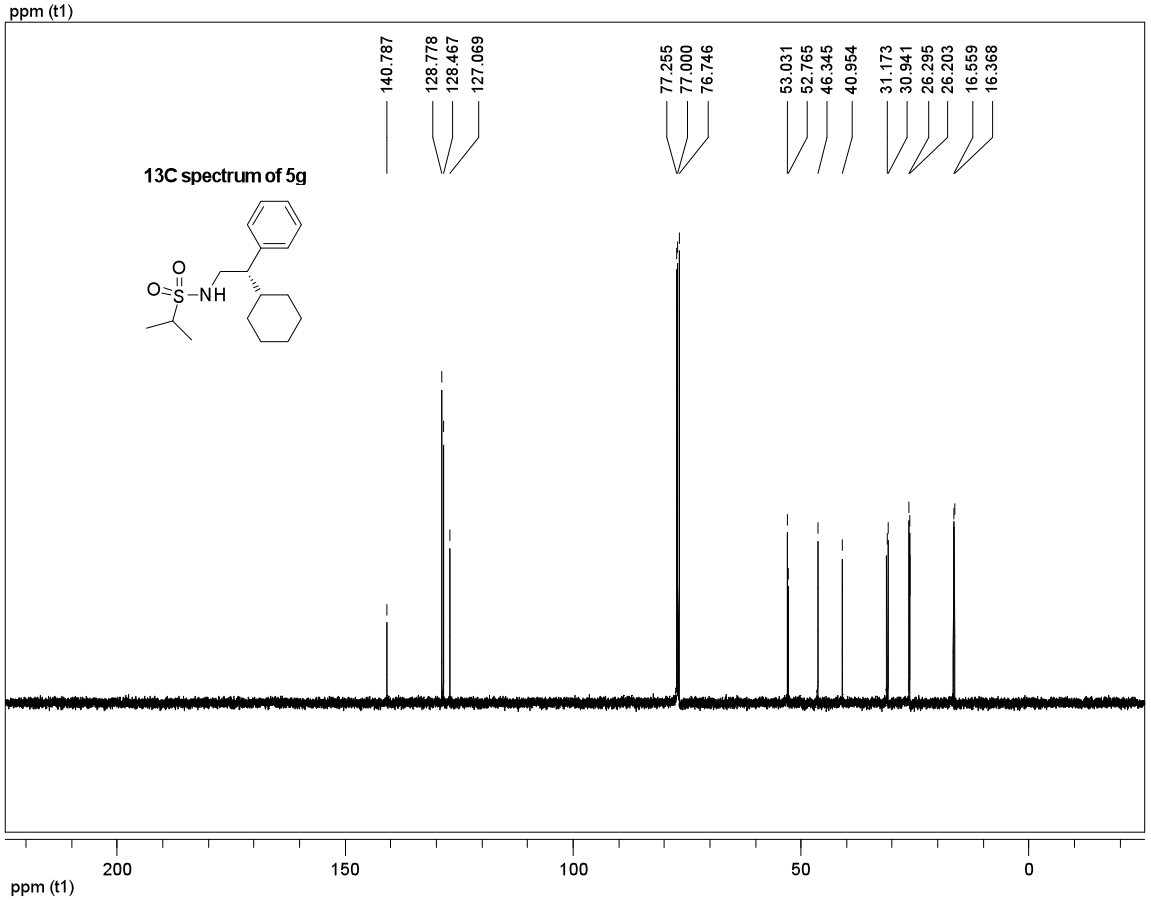

7.598
7.585
7.276
7.260
3.988
3.981
3.975
3.968
3.647
3.639
3.633
3.626
3.618
3.612
3.604
3.321
3.314
3.304
3.300
3.296
3.292
3.282
3.275
2.792
2.690
2.682
2.675
2.668
2.659
2.651
1.906
1.885
1.774
1.769
1.756
1.752
1H spectrum of 5e
CF3
O
O=S–NH
H3C
2.06
2.58
1.00
1.05
1.03
3.20
1.11
3.30
1.05
10.0
5.0
0.0
ppm (f1)

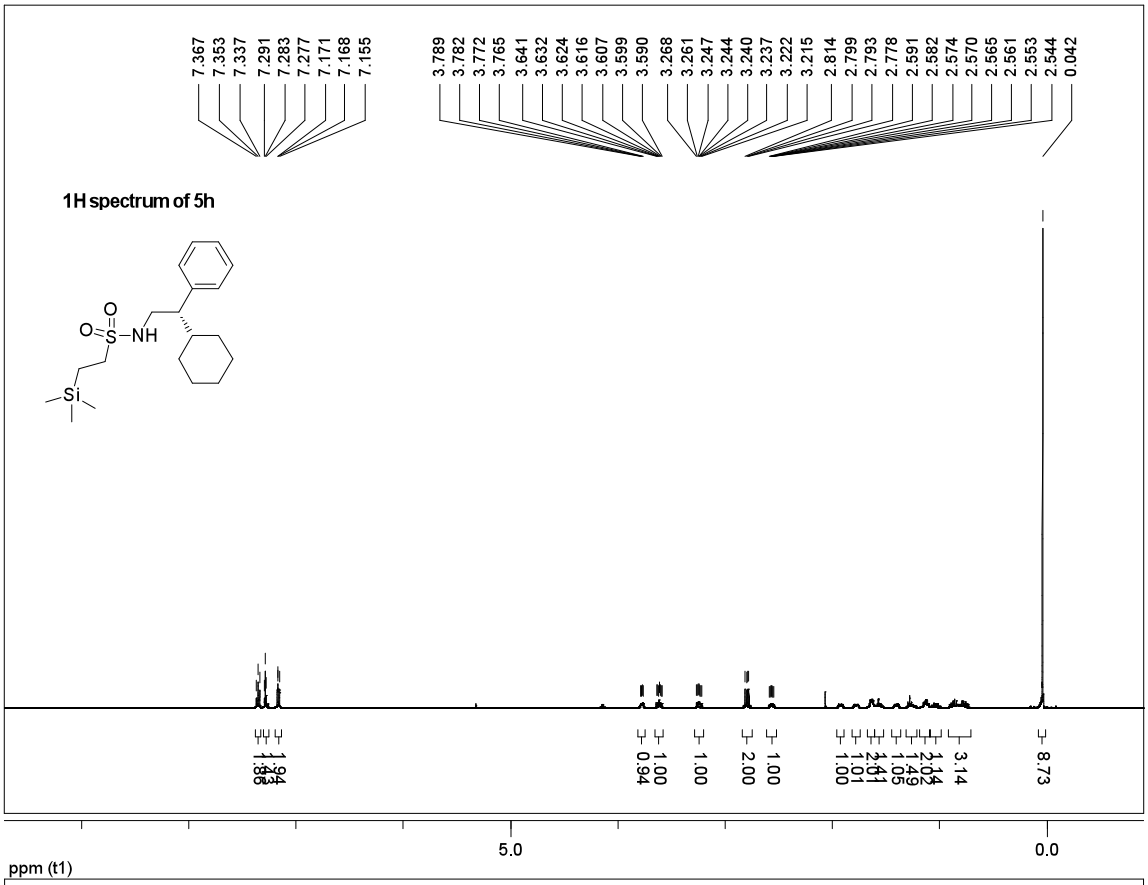

145.112
129.497
129.282
128.884
126.233
125.693
125.669
125.645
125.620
124.927
123.125
77.212
77.000
76.788
52.386
45.708
40.708
40.269
31.082
30.769
26.157
26.122
26.075
13C spectrum of 5e
CF3
O
O=S–NH
H3C
200
150
100
50
0
ppm (f1)


7.260
7.248
7.234
6.794
6.781
6.733
6.720
6.673
3.895
3.884
3.807
3.628
3.621
3.613
3.607
3.600
3.593
3.585
3.255
3.249
3.233
3.216
3.211
2.801
2.545
2.538
2.528
2.524
2.514
2.506
1.907
1.886
1.767
1.747
1H spectrum of 5f
OCH3
O
S
NH
H3C
1.46
1.00
1.01
3.03
0.99
1.05
10.0
5.0
0.0
ppm (f1)


159.884
142.378
129.854
120.644
114.680
111.810
77.212
77.000
76.788
55.179
45.987
40.866
40.106
31.137
31.038
26.279
26.186
26.170
13C spectrum of 5f
OCH3
O
S
NH
H3C
200
150
100
50
0
ppm (f1)


7.365
7.350
7.335
7.285
7.271
7.256
7.171
7.156
3.696
3.678
3.670
3.661
3.646
3.637
3.628
3.620
3.300
3.295
3.278
3.273
3.255
3.250
3.067
3.054
3.040
2.599
2.590
2.582
2.573
2.560
2.552
1.304
1.290
1.231
1.218
0.834
0.814
0.810
1H spectrum of 5g
2.01
1.98
1.00
0.98
0.99
0.90
1.01
3.70
3.07
3.64
3.30
1.10
5.0
0.0
ppm (t1)


140.787
128.778
128.467
127.069
77.255
77.000
76.746
53.031
52.765
46.345
40.954
31.173
30.941
26.295
26.203
16.559
16.368
13C spectrum of 5g
200
150
100
50
0
ppm (t1)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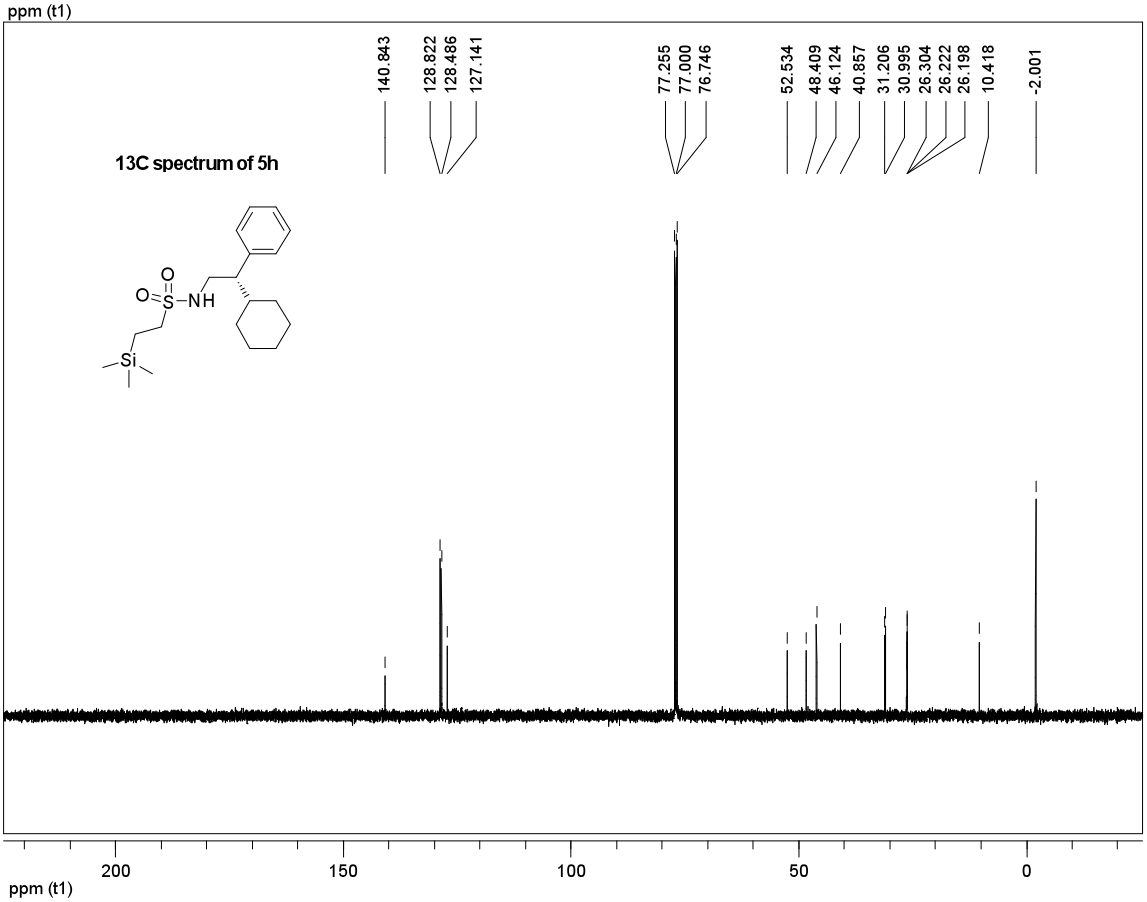
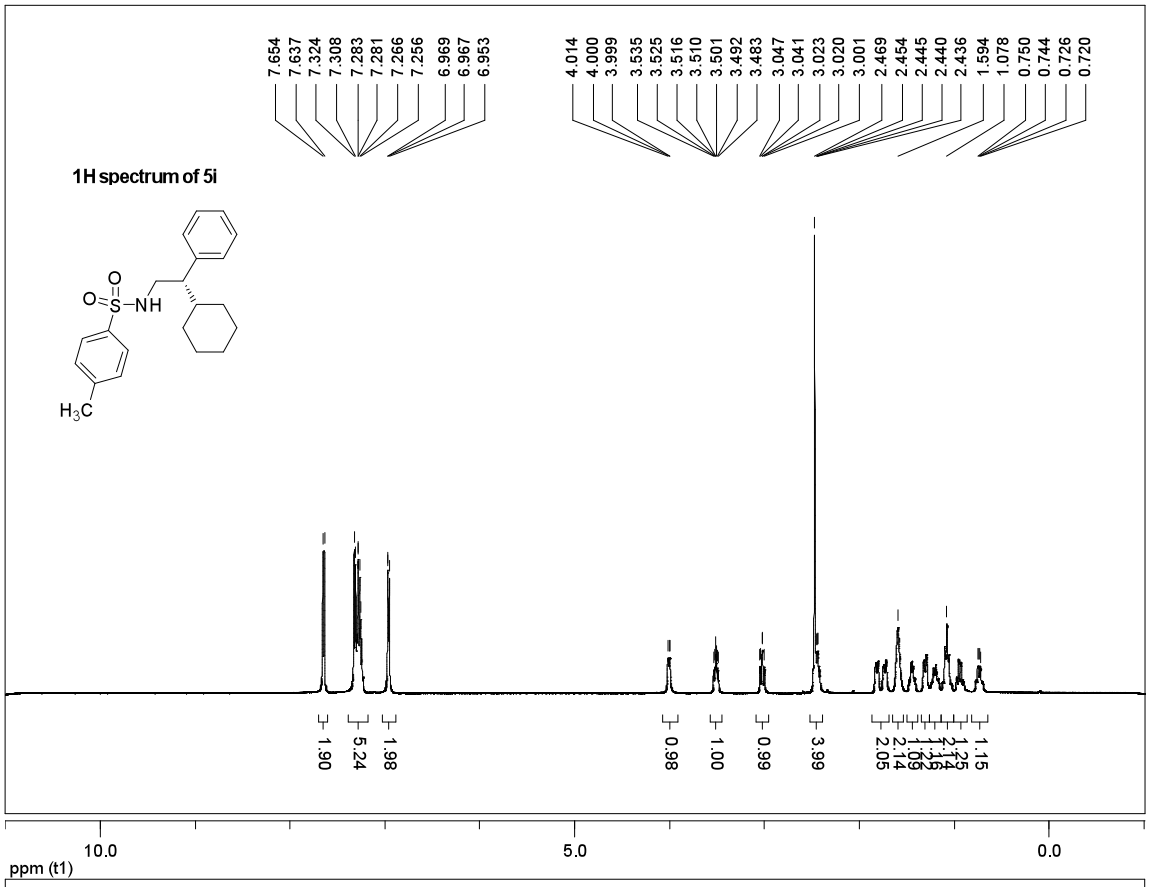
7.353
7.337
7.291
7.283
7.277
7.171
7.168
7.155
3.789
3.782
3.772
3.765
3.641
3.632
3.624
3.616
3.607
3.599
3.590
3.268
3.261
3.247
3.244
3.240
3.237
3.222
3.215
2.814
2.799
2.793
2.778
2.591
2.582
2.574
2.570
2.565
2.561
2.553
2.544
0.042
1H spectrum of 5h
O
O=S–NH
Si
1.88
1.94
0.94
1.00
1.00
2.00
1.00
1.00
1.01
1.41
1.49
1.05
1.14
1.02
3.14
8.73
5.0
0.0
ppm (t1)


140.843
128.822
128.486
127.141
77.255
77.000
76.746
52.534
48.409
46.124
40.857
31.206
30.995
26.304
26.222
26.198
10.418
-2.001
13C spectrum of 5h
O
O=S–NH
Si
200
150
100
50
0
ppm (t1)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7.637
7.324
7.308
7.283
7.281
7.266
7.256
6.969
6.967
6.953
4.014
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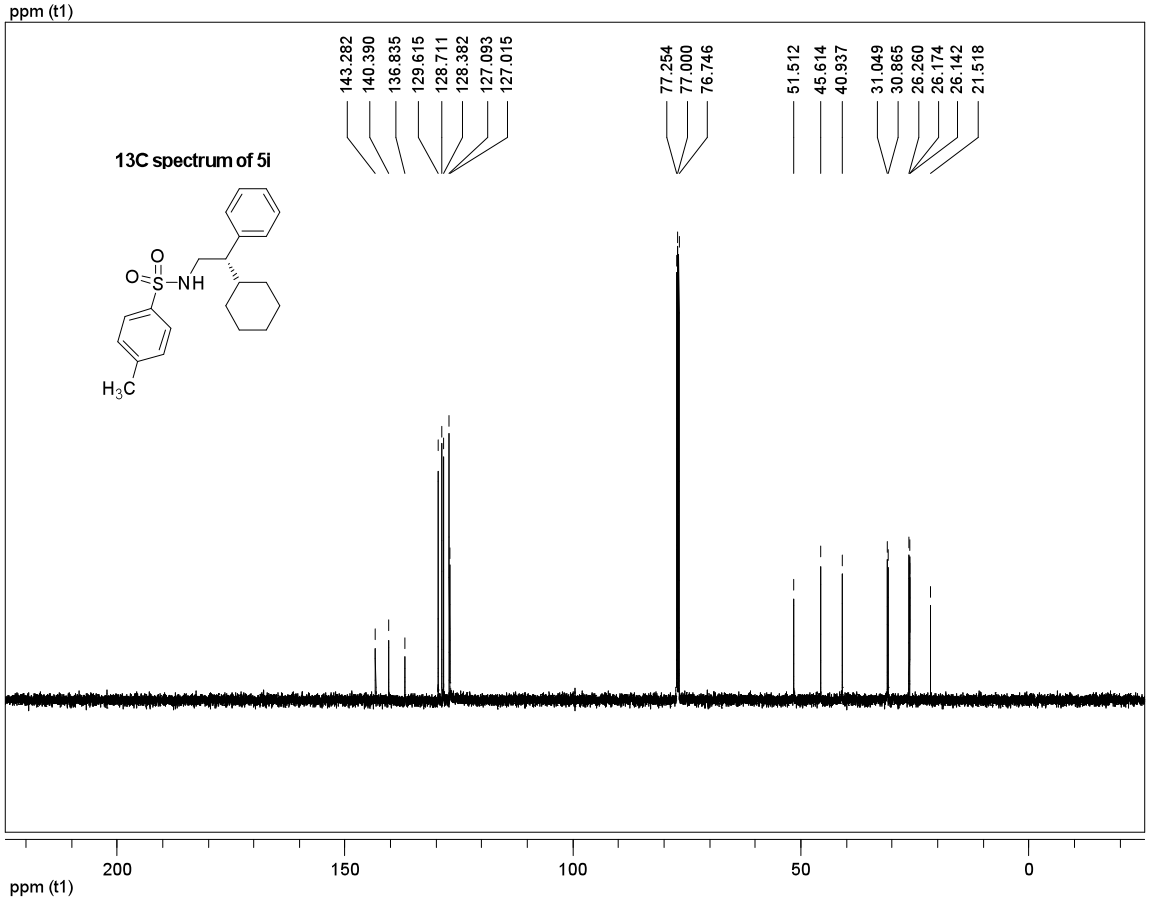
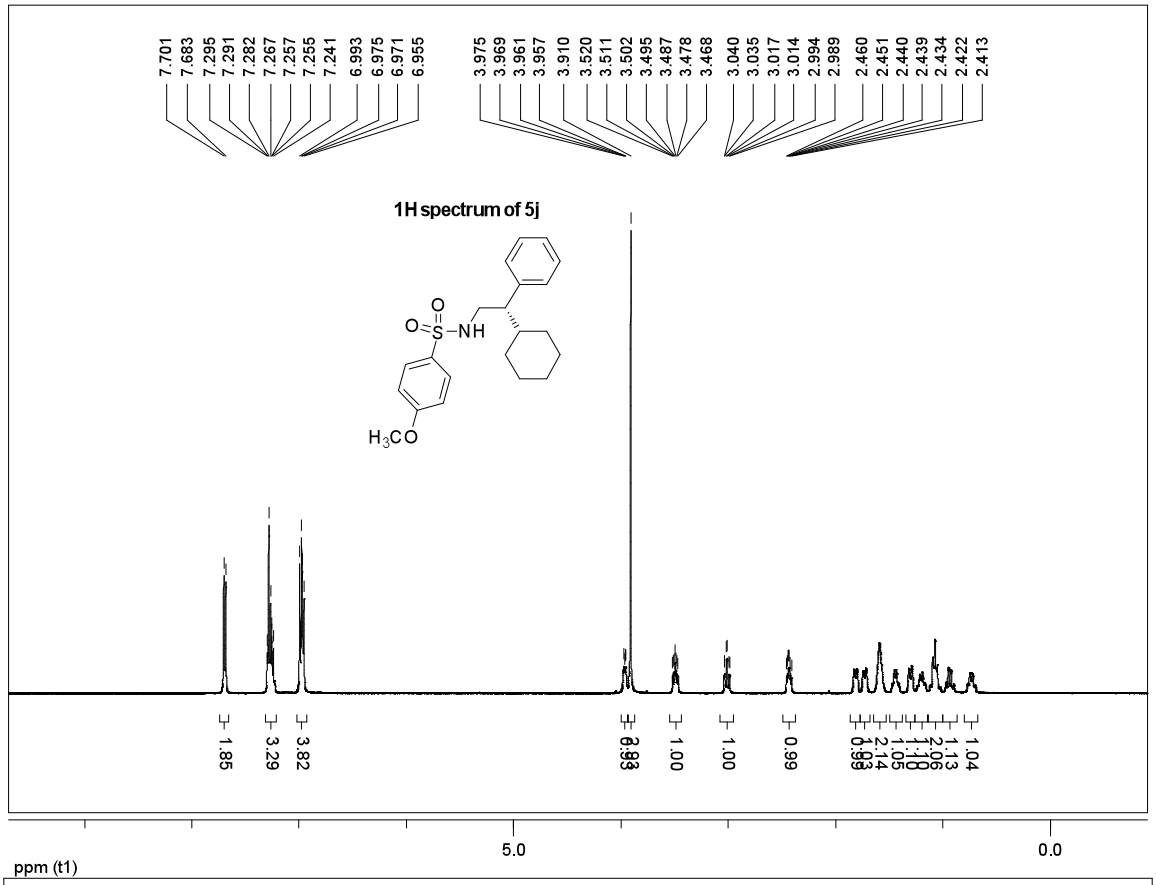
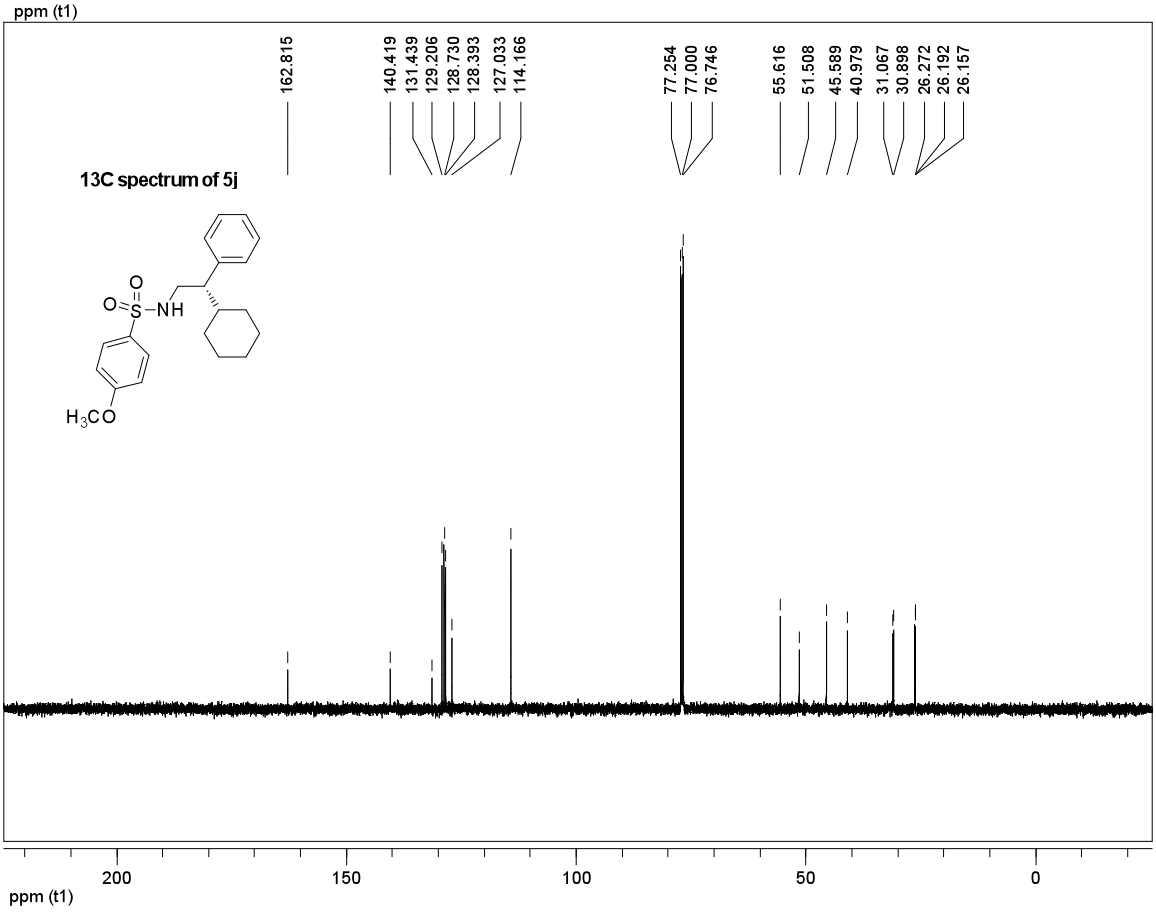
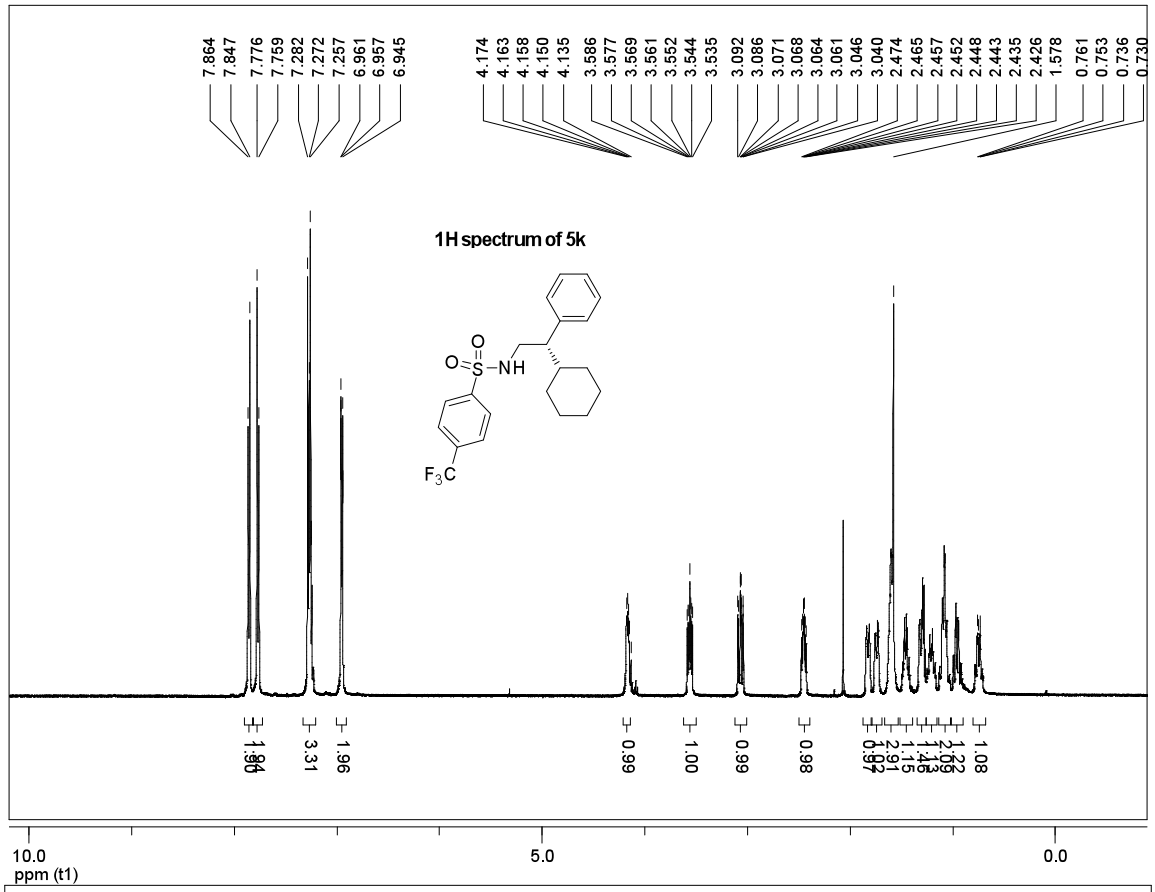
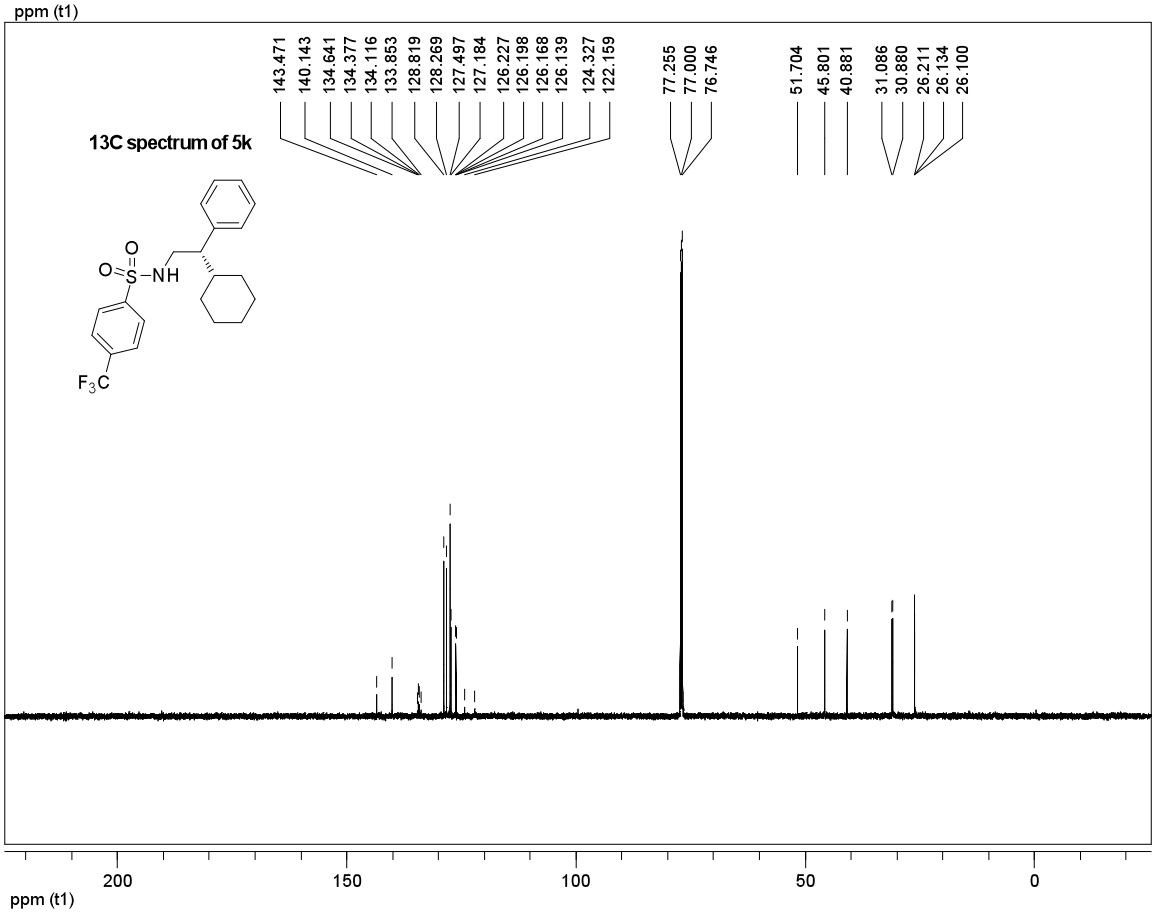
3.999
3.535
3.525
3.516
3.510
3.501
3.492
3.483
3.047
3.041
3.023
3.020
3.001
2.469
2.454
2.445
2.440
2.436
1.594
1.078
0.750
0.744
0.726
0.720
1H spectrum of 5i
1.90
5.24
1.98
0.98
1.00
0.99
3.00
2.05
2.14
1.15
10.0
5.0
0.0
ppm (t1)

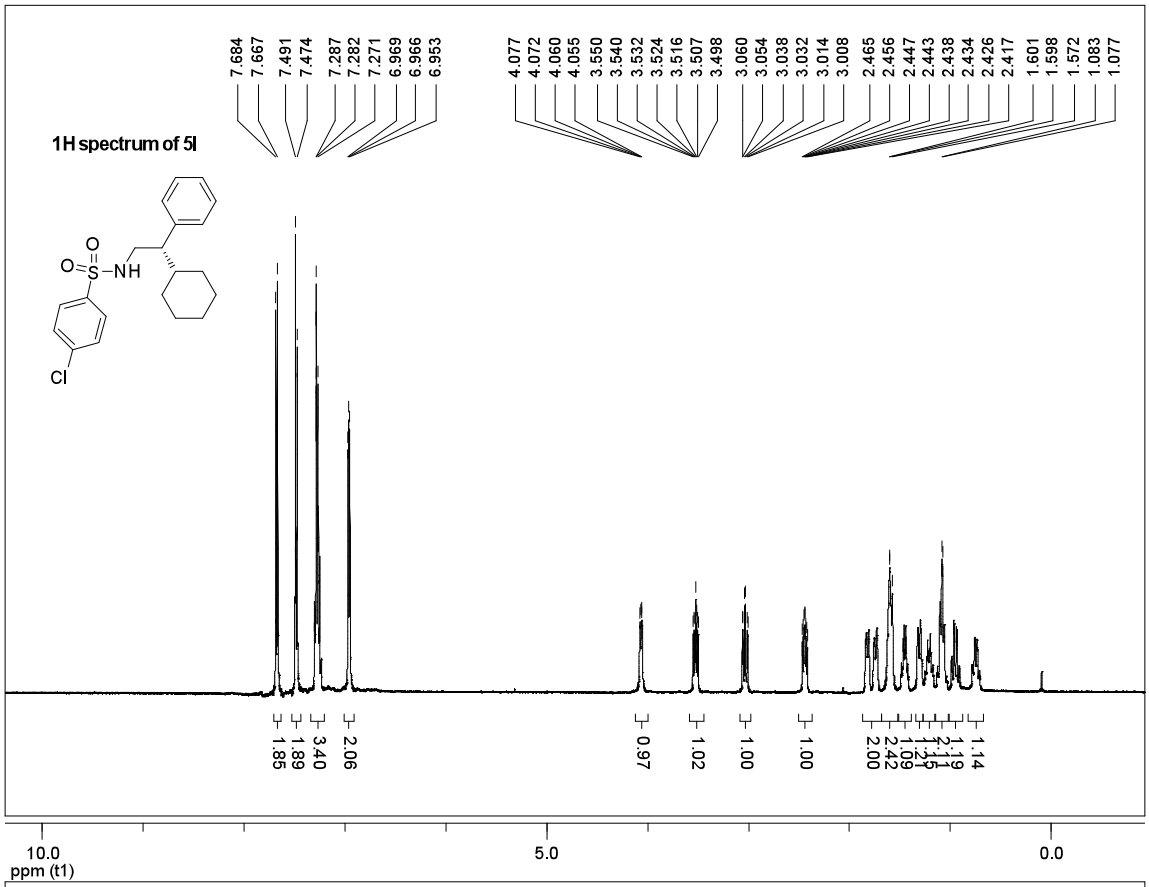

143.282
140.390
136.835
129.615
128.711
128.382
127.093
127.015
77.254
77.000
76.746
51.512
45.614
40.937
31.049
30.865
26.260
26.174
26.142
21.518
13C spectrum of 5i
200
150
100
50
0
ppm (t1)

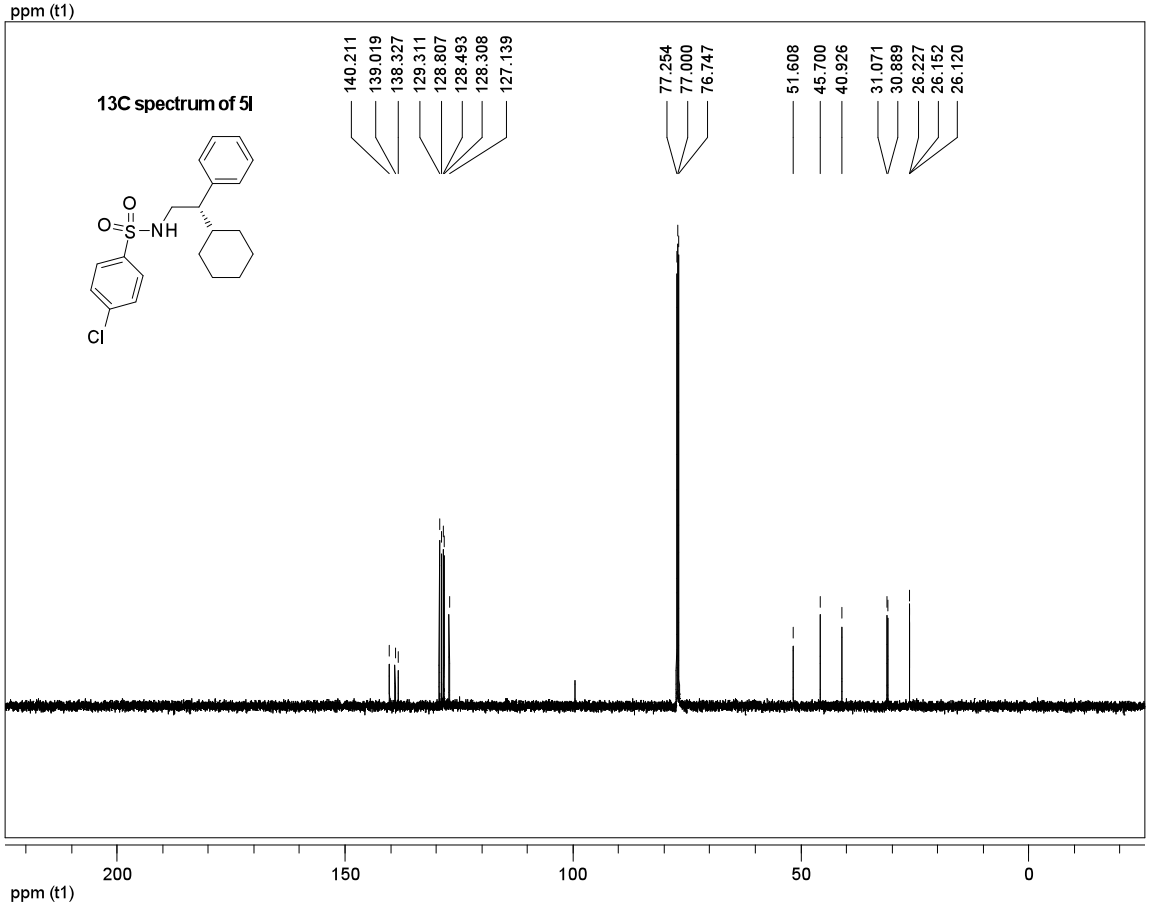

7.701
7.683
7.295
7.291
7.282
7.267
7.257
7.255
7.241
6.993
6.975
6.971
6.955
3.975
3.969
3.961
3.957
3.910
3.520
3.511
3.502
3.495
3.487
3.478
3.468
3.040
3.035
3.017
3.014
2.994
2.989
2.460
2.451
2.440
2.439
2.434
2.422
2.413
1H spectrum of 5j
O
O=S–NH
H3CO
1.85
3.29
3.82
1.00
1.00
0.99
1.04
5.0
0.0
ppm (t1)

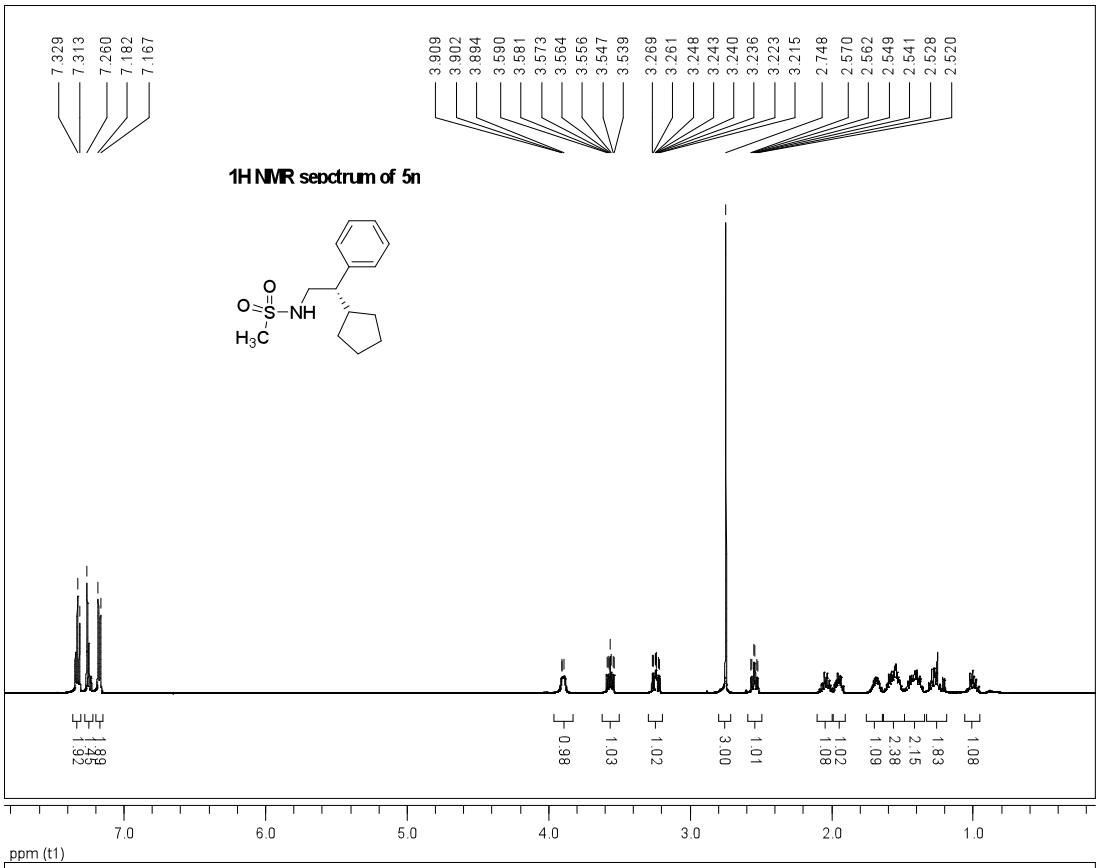

162.815
140.419
131.439
129.206
128.730
128.393
127.033
114.166
77.254
77.000
76.746
55.616
51.508
45.589
40.979
31.067
30.898
26.272
26.192
26.157
13C spectrum of 5j
O
O=S–NH
H3CO
200
150
100
50
0
ppm (t1)

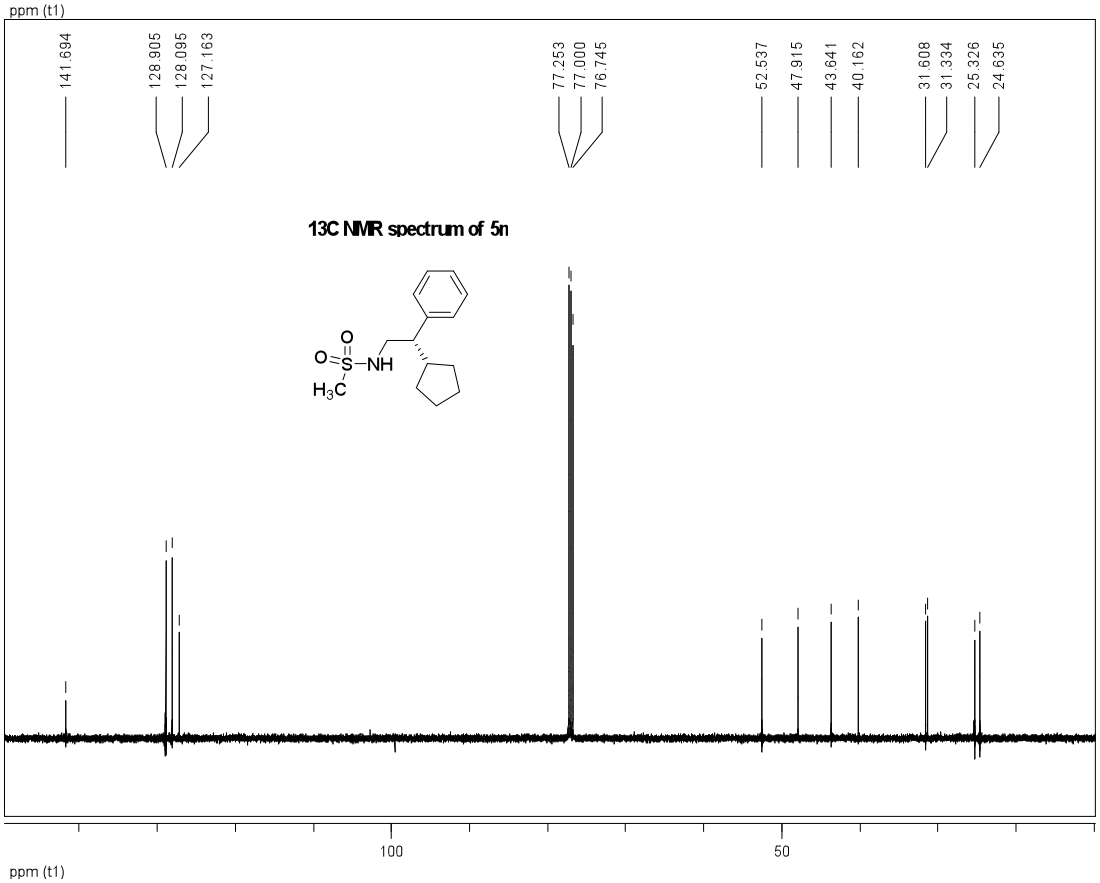

7.864
7.847
7.776
7.759
7.282
7.272
7.257
6.961
6.957
6.945
4.174
4.163
4.158
4.150
4.135
3.586
3.577
3.569
3.561
3.552
3.544
3.535
3.092
3.086
3.071
3.068
3.064
3.061
3.046
3.040
2.474
2.465
2.457
2.452
2.448
2.443
2.435
2.426
1.578
0.761
0.753
0.736
0.730
1H spectrum of 5k
O
O=S–NH
F3C
1.94
3.31
1.96
0.99
1.00
0.99
0.98
1.08
10.0
5.0
0.0
ppm (t1)

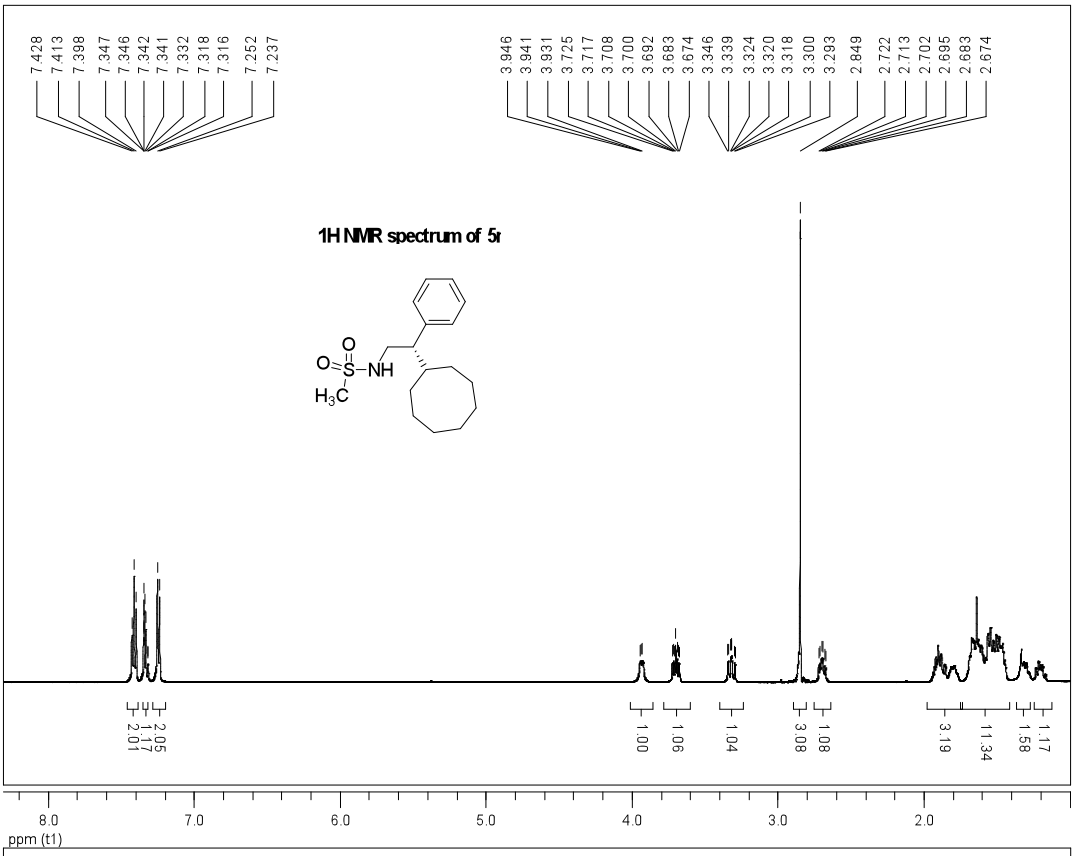

143.471
140.143
134.641
134.377
134.116
133.853
128.819
128.269
127.497
127.184
126.227
126.198
126.168
126.139
124.327
122.159
77.255
77.000
76.746
51.704
45.801
40.881
31.086
30.880
26.211
26.134
26.100
13C spectrum of 5k
O
O=S–NH
F3C
200
150
100
50
0
ppm (t1)

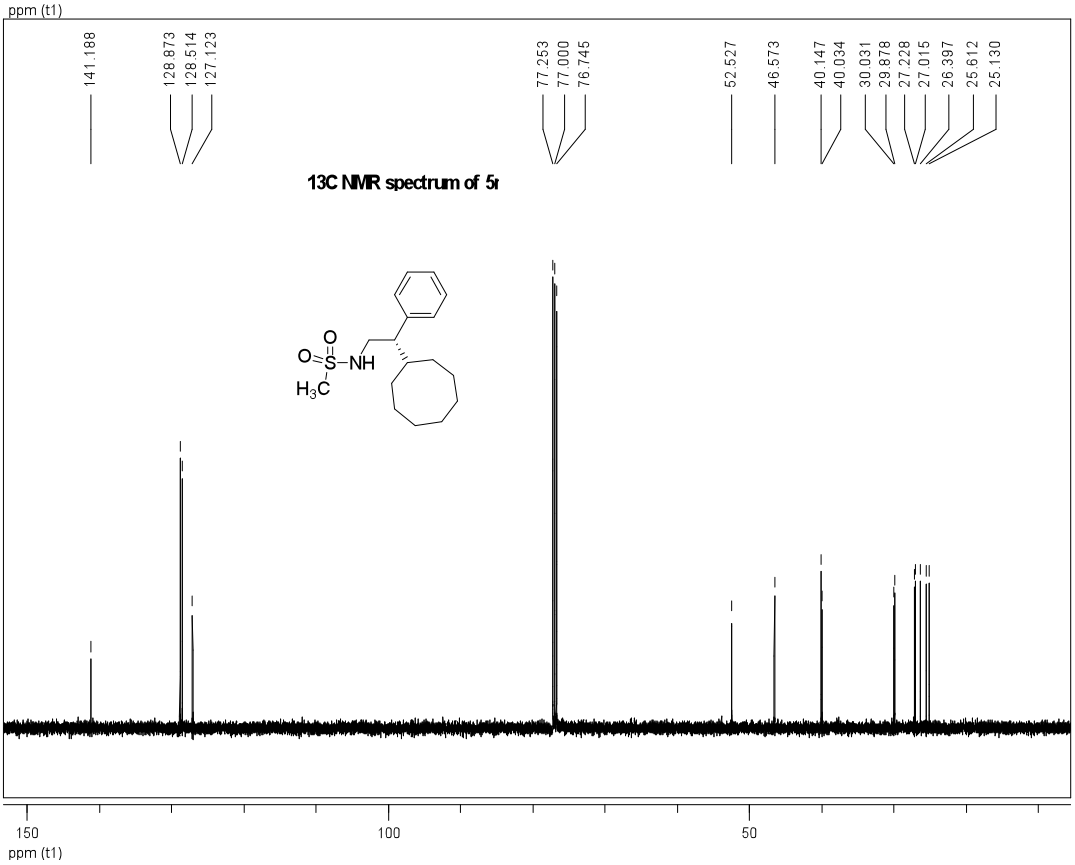

1H spectrum of 5l
7.684
7.667
7.491
7.474
7.287
7.282
7.271
6.969
6.966
6.953
4.077
4.072
4.060
4.055
3.550
3.540
3.532
3.524
3.516
3.507
3.498
3.060
3.054
3.038
3.032
3.014
3.008
2.465
2.456
2.447
2.443
2.438
2.434
2.426
2.417
1.601
1.598
1.572
1.083
1.077
1.85
1.89
3.40
2.06
0.97
1.02
1.00
1.00
2.00
2.42
1.14
10.0
5.0
0.0
ppm (t1)

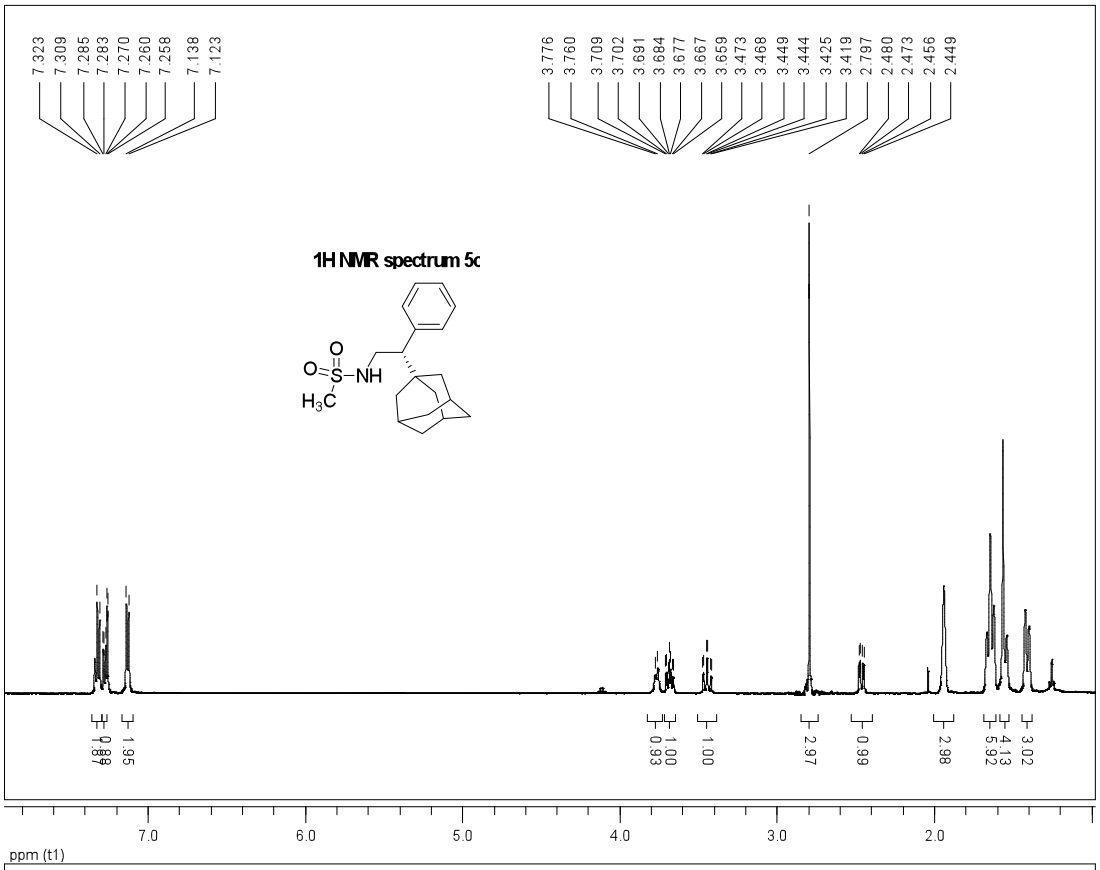

13C spectrum of 5l
140.211
139.019
138.327
129.311
128.807
128.493
128.308
127.139
77.254
77.000
76.747
51.608
45.700
40.926
31.071
30.889
26.227
26.152
26.120
200
150
100
50
0
ppm (t1)

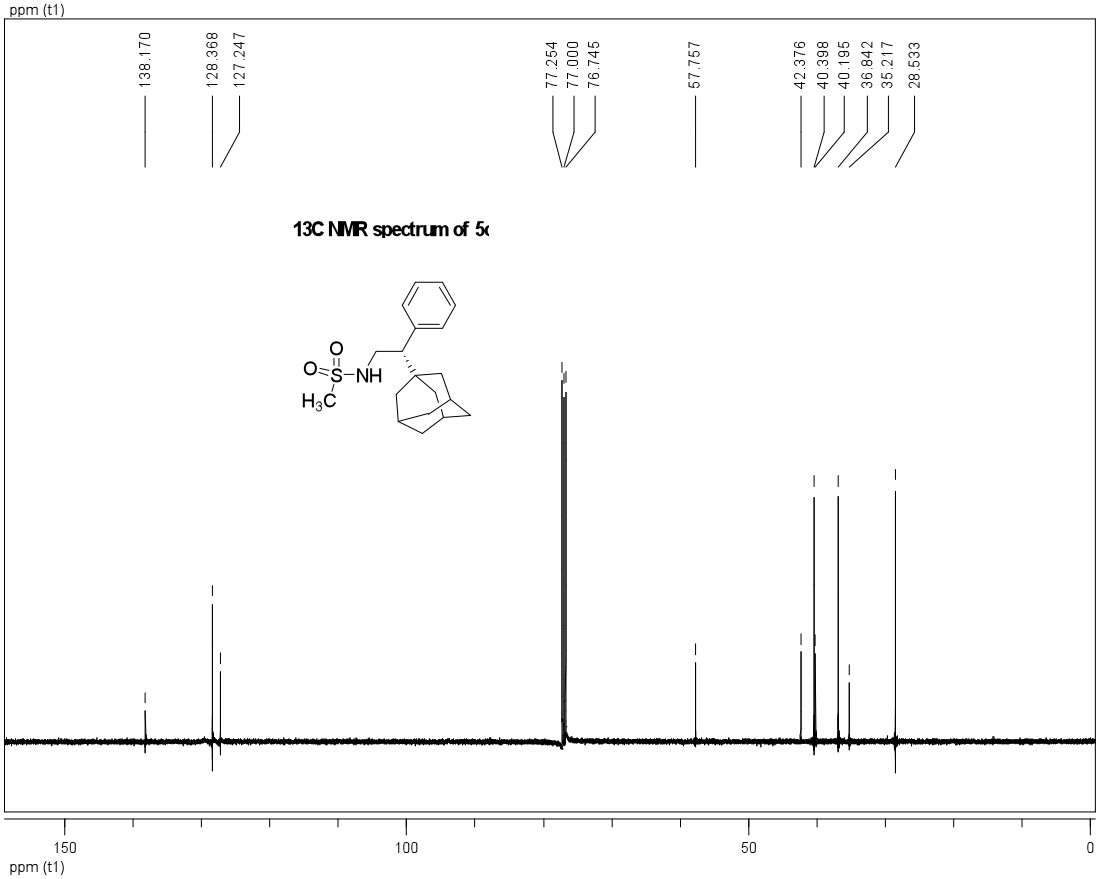

7.329
7.313
7.260
7.182
7.167
3.909
3.902
3.894
3.590
3.581
3.573
3.564
3.556
3.547
3.539
3.269
3.261
3.248
3.243
3.240
3.236
3.223
3.215
2.748
2.570
2.562
2.549
2.541
2.528
2.520
1H NMR spectrum of 5n
O
O
S
NH
H3C
1.92
1.45
1.89
0.98
1.03
1.02
3.00
1.01
1.08
1.02
1.09
2.38
2.15
1.83
1.08
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

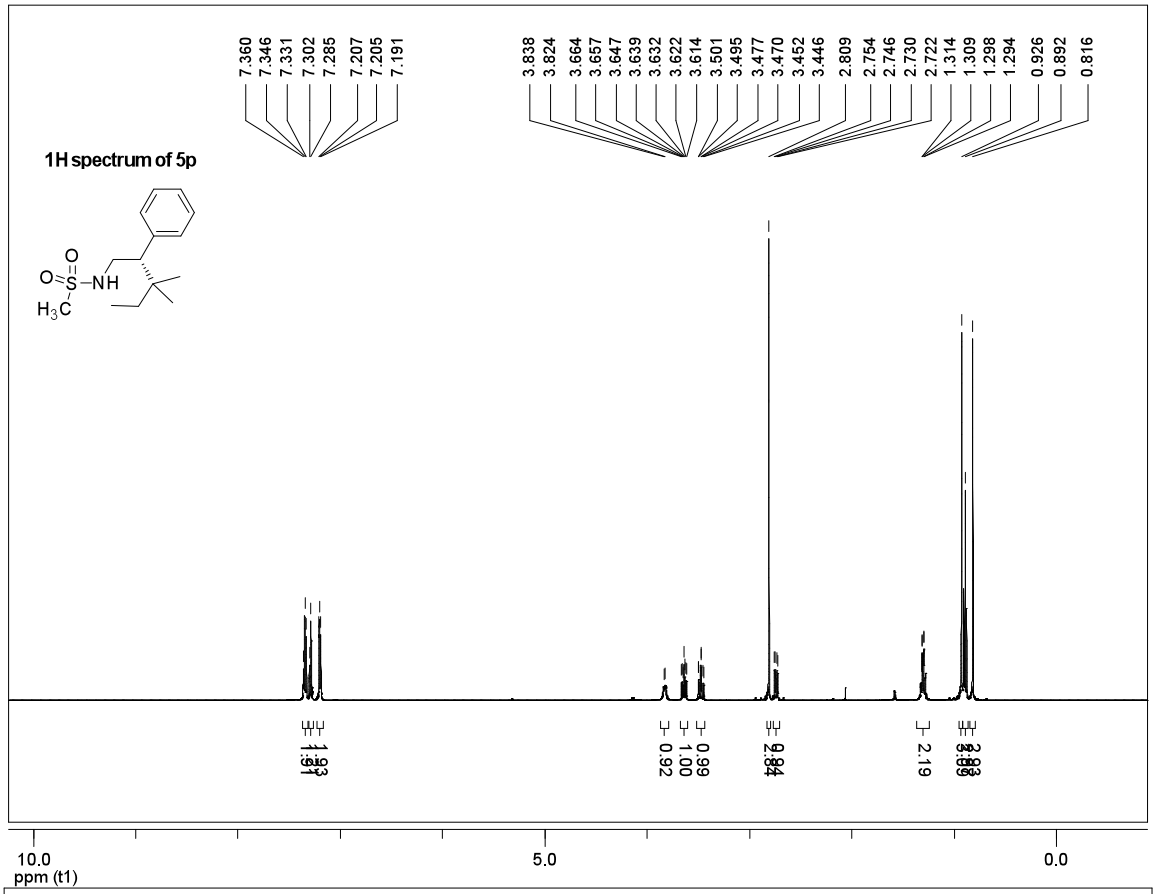

141.694
128.905
128.095
127.163
77.253
77.000
76.745
52.537
47.915
43.641
40.162
31.608
31.334
25.326
24.635
13C NMR spectrum of 5n
O
O
S
NH
H3C
100
50
ppm (t1)

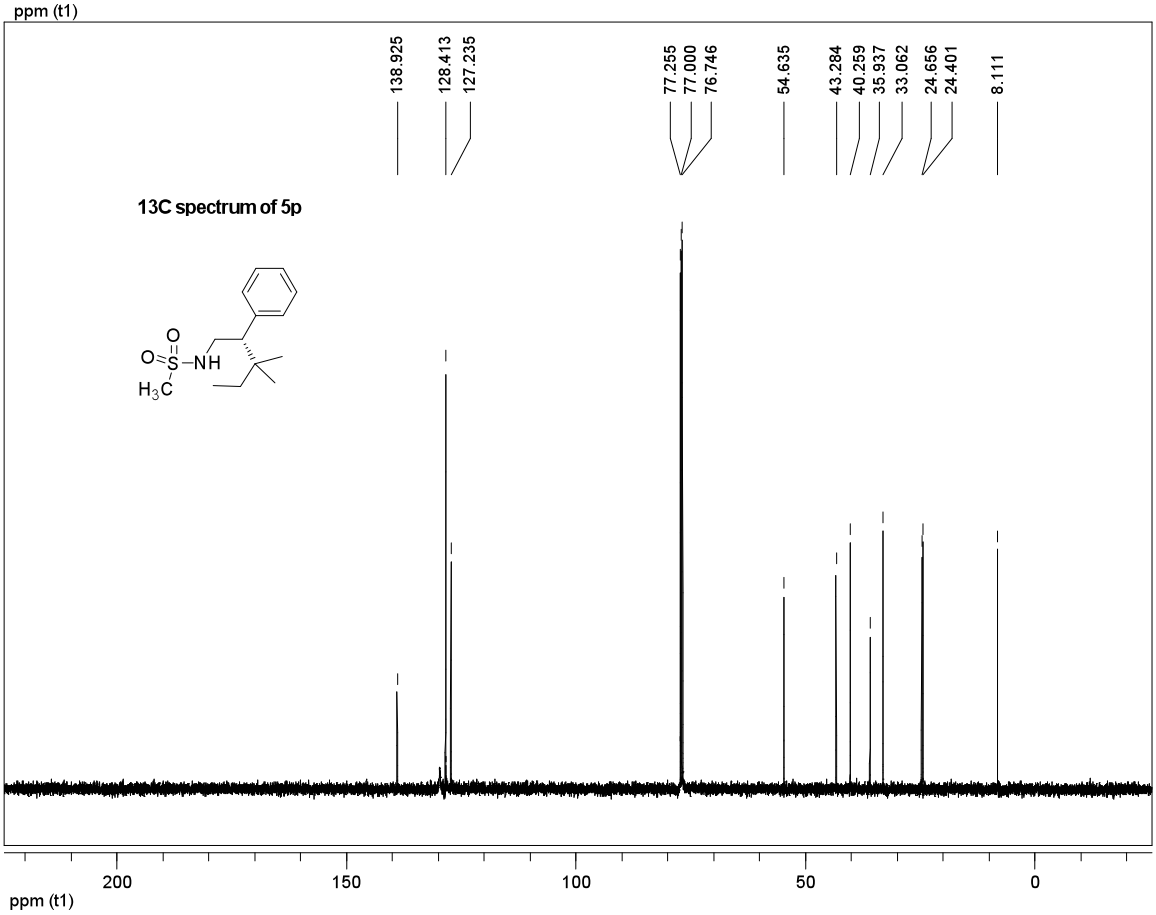

7.428
7.413
7.398
7.347
7.346
7.342
7.341
7.332
7.318
7.316
7.252
7.237
3.946
3.941
3.931
3.725
3.717
3.708
3.700
3.692
3.683
3.674
3.346
3.339
3.324
3.320
3.318
3.300
3.293
2.849
2.722
2.713
2.702
2.695
2.683
2.674
1H NMR spectrum of 5r
2.01
1.17
2.05
1.00
1.06
1.04
3.08
1.08
3.19
11.34
1.58
1.17
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


141.188
128.873
128.514
127.123
77.253
77.000
76.745
52.527
46.573
40.147
40.034
30.031
29.878
27.228
27.015
26.397
25.612
25.130
13C NMR spectrum of 5r
150
100
50
ppm (t1)


7.323
7.309
7.285
7.283
7.270
7.260
7.258
7.138
7.123
3.776
3.760
3.709
3.702
3.691
3.684
3.677
3.667
3.659
3.473
3.468
3.449
3.444
3.425
3.419
2.797
2.480
2.473
2.456
2.449
1H NMR spectrum 5c
O
O
S
NH
H3C
0.87
0.89
1.95
0.93
1.00
1.00
2.87
0.99
2.98
5.92
4.13
3.02
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


138.170
128.368
127.247
77.254
77.000
76.745
57.757
42.376
40.398
40.195
36.842
35.217
28.533
13C NMR spectrum of 5c
O
O
S
NH
H3C
150
100
50
0
ppm (t1)


1H spectrum of 5p
7.360
7.346
7.331
7.302
7.285
7.207
7.205
7.191
3.838
3.824
3.664
3.657
3.647
3.639
3.632
3.622
3.614
3.501
3.495
3.477
3.470
3.452
3.446
2.809
2.754
2.746
2.730
2.722
1.314
1.309
1.298
1.294
0.926
0.892
0.816
1.93
1.91
0.92
1.00
0.99
2.84
2.19
10.0
5.0
0.0
ppm (t1)


13C spectrum of 5p
138.925
128.413
127.235
77.255
77.000
76.746
54.635
43.284
40.259
35.937
33.062
24.656
24.401
8.111
200
150
100
50
0
ppm (t1)