Vicinal Diamination of Alkenes under Rh-Catalysis

Supplementary Material
(*30 pages*)

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General. All reagents were obtained commercially unless otherwise noted. Reactions were performed using glassware that was flame-dried under vacuum (~1 Torr). Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated under reduced pressure (~15 Torr) by rotary evaporation. Solvents were purified by passage under 12 psi N_2 through activated alumina columns. Chlorosulfonyl isocyanate was purchased from Acros Chemicals, transferred via cannula to a Schlenk flask, and stored at –20 ºC. Chromatography was performed on either Silicycle Silia-P Silica Gel (40-63 μm) or Fisher Davisil Grade 643 Type 150A silica gel (200-425 mesh). Compounds purified by chromatography were typically applied to the adsorbent bed using the indicated solvent conditions with a minimum amount of added chloroform as needed for solubility. Thin layer chromatography was performed on either Whatman Partisil K6F Silica Gel 60 Å plates (250 μm) or EMD Chemicals Silica Gel 60 F_{254} plates (250 μm). Visualization of the developed chromatogram was accomplished by fluorescence quenching or by staining with butanolic ninhydrin, aqueous potassium permanganate, or aqueous ceric ammonium molybdate (CAM).

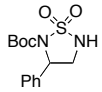
Nuclear magnetic resonance (NMR) spectra were acquired on either a Varian Inova-600 operating at 600 and 150 MHz, a Varian Inova-300 operating at 300 and 75 MHz, a Varian Mercury-400 operating at 400 and 100 MHz, or a Varian Inova-500 operating at 500 and 125 MHz for ^{1}H and ^{13}C, respectively, and are referenced internally according to residual solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; m, multiplet), integration, coupling constant (Hz). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Melting points were obtained on a Thomas-Hoover apparatus in open capillary tubes and are uncorrected. Infrared spectra were recorded on either a Thermo-Nicolet IR100 spectrometer or a Thermo-Nicolet IR300 spectrometer as thin films using NaCl salt plates or as KBr pellets and are reported in frequency of absorption. High-resolution mass spectra were obtained from the Vincent Coates Foundation Mass Spectrometry Laboratory at Stanford University.

General procedures and characterization data for all new compounds

General procedure for aziridination/rearrangement sequence. Solid $BocNHOSO_2NH_2$[1] (32 mg, 0.17 mmol, 1.1 equiv), MgO (14 mg, 0.35 mmol, 2.3 equiv), $Rh_2(esp)_2$ (2 mg, 3.0 μmol, 0.02 equiv), and $PhI(OAc)_2$ (53 mg, 0.17 mmol, 1.1 equiv) were added sequentially to a solution of olefin (0.15 mmol) in 0.5 mL of isopropyl acetate. The resulting green suspension was stirred at room temperature for 4-15 h until TLC indicated no further progress of the reaction. Following this time, NaI (25 mg, 0.17 mmol, 1.1 equiv) and 1.0 mL of DMF were added and the resulting mixture was stirred until the reaction was complete, as determined by TLC (3–24 h). Isolation of the product was performed using one of two possible work-up protocols (as indicated below):

Method A: The reaction mixture was transferred to a separatory funnel with 40 mL of H_2O. The aqueous layer was extracted with 4 x 10 mL of EtOAc. The combined organic fractions were washed with 1 x 10 mL of saturated aqueous NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The desired product was isolated following purification by chromatography on silica gel (conditions given below).

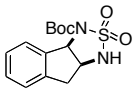
Method B: The reaction mixture was diluted with 1–2 mL of CH_2Cl_2 and filtered through a small pad of Celite. The flask and filter cake were rinsed with 5–10 mL of CH_2Cl_2 and the combined filtrates were concentrated under reduced pressure. The material was re-dissolved in 50 mL of toluene, and the solution concentrated a second time under reduced pressure with the rotary evaporator water bath temperature at 35 ºC. Residual DMF was removed by repeating this process two additional times. The desired product was isolated following purification by chromatography on silica gel (conditions given below).



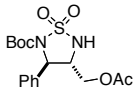
Work-up according to Method B. Purified by chromatography on silica gel (3:1 hexanes/EtOAc); white solid (73%): TLC R_f = 0.51 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44-7.38 (m, 2H), 7.37-7.32 (m, 3H), 5.25 (dd, 1H, J = 6.7, 3.5 Hz), 4.76 (br s, 1H), 3.92 (dd, 1H, J = 13.1, 6.7 Hz), 3.29 (dd, 1H, J = 13.1, 3.5 Hz), 1.42

(1) Kurokawa, T.; Kim, M.; Du Bois, J. *Angew. Chem. Int. Ed.* **2009**, *48*, 2777.

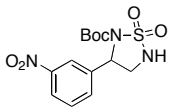
(s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.3, 138.5, 129.4, 128.7, 125.5, 84.7, 63.2, 47.8, 28.0 ppm; IR (thin film) ν 3255, 2980, 1709, 1371, 1325, 1179, 1148, 701 cm^{-1}; HRMS (ES$^+$) calcd for $C_{13}H_{18}N_2O_4SNa^+$ 321.0885 found 321.0897 (MNa^+).



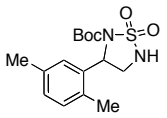
Work-up according to Method A. Purified by chromatography on silica gel (4:1 hexanes/EtOAc); white foam (84%): TLC R_f = 0.56 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60-7.56 (m, 1H), 7.36-7.25 (m, 3H), 5.59 (d, 1H, *J* = 5.5 Hz), 4.54-4.44 (m, 2H), 3.37 (dd, 1H, *J* = 17.7, 5.9 Hz), 3.04 (d, 1H, *J* = 17.7 Hz), 1.60 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.6, 138.9, 138.6, 129.7, 128.6, 126.9, 125.5, 84.9, 67.4, 55.3, 35.6, 28.2 ppm; IR (thin film) ν 3236, 2981, 2933, 1723, 1371, 1326, 1180, 1146 cm^{-1}; HRMS (ES$^+$) calcd for $C_{14}H_{18}N_2O_4SNa^+$ 333.0885 found 333.0878 (MNa^+).



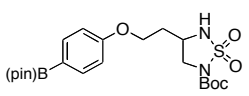
Work-up according to Method B. Purified by chromatography on silica gel (3:1 hexanes/EtOAc); The regiochemistry was assigned based on analogy to reactions of other styrenal olefins; white solid (77%): TLC R_f = 0.57 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.47-7.37 (m, 5H), 5.01 (d, 1H, *J* = 6.9 Hz), 4.40 (dd, 1H, *J* = 12.8, 4.7 Hz), 4.30 (dd, 1H, *J* = 12.8, 4.7 Hz), 3.81-3.75 (m, 1H), 2.22 (s, 3H), 1.40 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.6, 149.0, 137.6, 129.4, 129.0, 126.1, 84.8, 64.8, 60.8, 58.3, 27.9, 20.9 ppm; IR (thin film) ν 3233, 2981, 1731, 1370, 1321, 1232, 1181, 1150 cm^{-1}; HRMS (ES$^+$) calcd for $C_{16}H_{22}N_2O_6SNa^+$ 393.1096 found 393.1080 (MNa^+).



Work-up according to Method B. Purified by chromatography on silica gel (2:1 hexanes/EtOAc); white solid (75%): TLC R_f = 0.37 (1:1 hexanes/EtOAc); ^{1}H NMR (CD_3OD, 400 MHz) δ 8.28 (t, 1H, *J* = 2.2 Hz), 8.23 (ddd, 1H, *J* = 8.2, 2.2, 1.0 Hz), 7.81 (d, 1H, *J* = 8.2 Hz), 7.68 (t, 1H, *J* = 7.9 Hz), 5.38 (dd, 1H, *J* = 7.1, 3.8 Hz), 3.92 (dd, 1H, *J* = 13.1, 7.1 Hz), 3.28 (dd, 1H, *J* = 13.1, 3.8 Hz), 1.39 (s, 9H) ppm; ^{13}C NMR (CD_3OD, 100 MHz) δ 150.9, 149.9, 143.5, 133.2, 131.3, 124.0, 122.1, 85.2, 63.4, 47.9, 28.1 ppm; IR (thin film) ν 3201, 2976, 1688, 1536, 1350, 1329, 1180, 1149 cm^{-1}; HRMS (ES$^+$) calcd for $C_{13}H_{17}N_3O_6SNa^+$ 366.0736 found 366.0731 (MNa^+).

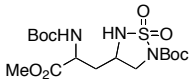


Work-up according to Method B. Purified by chromatography on silica gel (4:1 hexanes/EtOAc); white solid (90%): TLC R_f = 0.67 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.20 (s, 1H), 7.09 (d, 1H, *J* = 7.9 Hz), 7.05 (dd, 1H, *J* = 7.9, 1.2 Hz), 5.45 (dd, 1H, *J* = 6.7, 2.7 Hz), 4.64 (dd, 1H, *J* = 11.1, 7.5 Hz), 3.91 (ddd, 1H, *J* = 12.9, 11.1, 6.4 Hz), 3.20 (ddd, 1H, *J* = 13.2, 7.5, 2.7 Hz), 2.33 (s, 3H), 2.28 (s, 3H), 1.45 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.3, 136.7, 136.0, 131.2, 131.1, 129.1, 124.8, 84.6, 60.4, 46.5, 28.0, 21.3, 18.6 ppm; IR (thin film) ν 3255, 2979, 2930, 1709, 1370, 1324, 1181, 1149, 819 cm^{-1}; HRMS (ES$^+$) calcd for $C_{15}H_{22}N_2O_4SNa^+$ 349.1198 found 349.1192 (MNa^+).

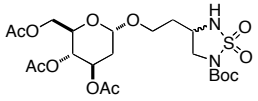


Work-up according to Method A. Purified by chromatography on silica gel (gradient elution: 3:1→7:3 hexanes/EtOAc); pale yellow oil (45%): TLC R_f = 0.42 (2:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.74 (d, 2H, *J* = 8.8 Hz), 6.86 (d, 2H, *J* = 8.8 Hz), 4.88 (br d, 1H, *J* = 8.8 Hz), 4.18-4.08 (m, 2H), 4.10-3.98 (m, 2H),

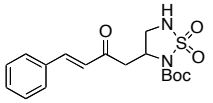
2.27-2.09 (m, 2H), 1.53 (s, 9H), 1.33 (s, 12H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.8, 149.6, 136.7, 113.8, 84.7, 83.8, 64.0, 52.6, 49.6, 32.0, 28.1, 25.0 ppm; IR (thin film) ν 3566, 3235, 2979, 2933, 1732, 1699, 1471, 1456, 1362, 1246, 1145, 1106 cm^{-1}; HRMS (ES$^+$) calcd for $C_{21}H_{33}BN_2O_7SNa^+$ 491.1994 found 491.1991 (MNa^+).



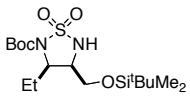
Work-up according to Method A. Performed on 2.10 mmol scale. Purification by chromatography on silica gel (gradient elution: 2:1→3:2 hexanes/EtOAc); white foam (496 mg, 56%). Characterized as a 1:1 mixture of diastereomers: TLC R_f = 0.2 (2:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.00 (br s, 0.5H), 5.36 (br t, 1H, *J* = 8 Hz), 5.10 (br s, 0.4H), 4.48-4.33 (m, 1H), 4.05-3.94 (m, 1H), 3.95-3.76 (m, 1H), 3.79 (s, 3H), 3.58-3.48 (m, 1H), 2.29-2.09 (m, 1.5H), 1.84-1.68 (m, 1H), 1.53 (s, 9H), 1.44 (s, 9H) ppm; ($CDCl_3$, 400 MHz) δ 172.0, 171.9, 149.5, 84.7, 84.6, 81.5, 80.9, 53.1, 52.4, 51.0, 50.8, 50.3, 48.6, 48.2, 37.5, 35.7, 28.4, 28.1 ppm; IR (thin film) ν 3378, 3225, 2980, 1724, 1517, 1478, 1438, 1334, 1259, 1154 cm^{-1}; HRMS (ES$^+$) calcd for $C_{16}H_{29}N_3O_8SNa^+$ 446.1568 found 446.1549 (MNa^+).



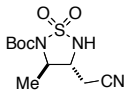
Work-up according to Method A. Purified by chromatography on silica gel (gradient elution: 2:1→3:2 hexanes/EtOAc); pale yellow oil (55%). Characterized as a 1:1 mixture of diastereomers: TLC R_f = 0.14 (3:2 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.25 (td, 1H, *J* = 10.6, 4.9 Hz), 5.04-4.94 (m, 2H), 4.84 (d, 0.4H, *J* = 8.8 Hz), 4.76 (d, 0.4H, *J* = 9.2 Hz), 4.32-4.24 (m, 1H), 4.14-4.00 (m, 2H), 3.98-3.88 (m, 2H), 3.90-3.76 (m, 1H), 3.61-3.55 (m, 1H), 3.55-3.47 (m, 1H), 2.24 (dd, 1H, *J* = 12.6, 5.4 Hz), 2.10 (s, 1.5H), 2.09 (s, 1.5H), 2.05 (s, 1.5H), 2.04 (s, 1.5H), 2.02 (s, 3H), 2.07-1.92 (m, 2H), 1.88-1.78 (m, 1H), 1.54 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.1, 170.4, 170.0, 149.6, 97.3, 97.0, 84.7, 69.8, 69.4, 68.9, 68.3, 68.1, 63.8, 63.6, 63.0, 62.6, 52.7, 52.6, 49.4, 49.1, 35.0, 34.9, 32.5, 32.3, 28.2, 21.1, 21.0, 20.9 ppm; IR (thin film) ν 3229, 2979, 1744, 1421, 1370, 1333, 1234, 1183, 1150, 1050 cm^{-1}; HRMS (ES$^+$) calcd for $C_{21}H_{34}N_2O_{12}SNa^+$ 561.1725 found 561.1721 (MNa^+).



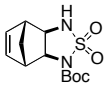
Work-up according to Method B. Purified by chromatography on silica gel (3:1 hexanes/EtOAc); clear oil (63%): TLC R_f = 0.30 (2:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.62 (d, 1H, *J* = 16.2 Hz), 7.58-7.53 (m, 2H), 7.44-7.39 (m, 1H), 6.72 (d, 1H, *J* = 16.2 Hz), 5.27 (dd, 1H, *J* = 10.6, 6.9 Hz), 4.60-4.55 (m, 1H), 3.80 (ddd, 1H, *J* = 6.9, 10.6, 17.6 Hz), 3.39 (ddd, 1H, *J* = 13.2, 6.9, 2.3 Hz), 3.32 (dd, 1H, *J* = 17.6, 7.8 Hz), 3.25 (dd, 1H, *J* = 17.6, 3.5 Hz), 1.54 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.8, 149.8, 144.9, 134.0, 131.3, 129.2, 128.7, 125.8, 84.9, 56.0, 44.0, 42.3, 28.1 ppm; IR (thin film) ν 3246, 2980, 2929, 1722, 1656, 1610, 1371, 1328, 1179, 1147 cm^{-1}; HRMS (ES$^+$) calcd for $C_{17}H_{22}N_2O_5SNa^+$ 389.1147 found 389.1139 (MNa^+).



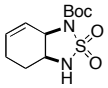
Work-up according to Method A. Purified by chromatography on silica gel (7:1 hexanes/EtOAc); off-white solid (39%): TLC R_f = 0.27 (7:1 hexanes/EtOAc); mp = 91–93 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.18 (br s, 1H), 3.91 (dd, 1H, *J* = 10.8, 5.2 Hz), 3.59 (dd, 1H, *J* = 11.2, 7.6 Hz), 3.10 (td, 1H, *J* = 7.4, 5.2 Hz), 2.93 (dd, 1H, *J* = 14.0, 7.2 Hz), 1.61 (quintd, 2H, *J* = 7.4, 2.6 Hz), 1.50, (s, 9H), 1.08 (t, 3H, *J* = 7.4 Hz), 0.89 (s, 9H), 0.07 (d, 6H, *J* = 4.8 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.1, 84.3, 59.8, 47.6, 46.5, 28.1, 25.9, 20.2, 18.4, 11.5, -5.2 ppm; IR (thin film) ν 3249, 2957, 2931, 2884, 2858, 2361, 1750, 1582, 1559, 1456, 1395, 1360, 1143, 1099 cm^{-1}; HRMS (ES$^+$) calcd for $C_{16}H_{34}N_2O_5SSiNa^+$ 417.1850 found 417.1841 (MNa^+).



Work-up according to Method A. Purified by chromatography on silica gel (2:1 hexanes/EtOAc); yellow oil (18%): TLC R_f = 0.17 (2:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.35 (br s, 1H), 4.21 (qd, 1H, *J* = 6.4, 1.6 Hz), 3.60 (td, 1H, *J* = 7.4, 1.6 Hz), 2.91 (ddd, 2H, *J* = 25.8, 17.0, 7.6 Hz), 1.55 (s, 9H), 1.51 (d, 3H, *J* = 6.4 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.0, 116.1, 85.5, 59.4, 54.3, 28.2, 22.6, 19.4 ppm; IR (thin film) ν 3242, 2982, 2924, 2850, 2257, 1723, 1458, 1371, 1325, 1261, 1179, 1151, 1105 cm^{-1}; HRMS (ES$^+$) calcd for $C_{10}H_{17}N_3O_4SNa^+$ 298.0832 found 298.0833 (MNa^+).

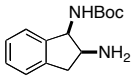


10 equiv of diene substrate was used relative to $BocNHSO_2NH_2$ (0.15 mmol); work-up according to Method B. Purified by chromatography on silica gel (3:1 hexanes/EtOAc); white solid (42%): TLC R_f = 0.40 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.19 (dd, 1H, *J* = 5.9, 3.0 Hz), 6.03 (dd, 1H, *J* = 5.9, 3.2 Hz), 4.91 (ddd, 1H, *J* = 6.4, 2.0, 0.9 Hz), 4.05 (dd, 1H, *J* = 6.5, 1.9 Hz), 3.16-3.13 (m, 1H), 2.91-2.89 (m, 1H), 2.16 (d, 1H, *J* = 10.2 Hz), 1.87 (dquint, 1H, *J* = 10.2, 1.8 Hz), 1.46 (s, 9H) ppm; IR (thin film) ν 2980, 2800, 2685, 1677, 1297, 1273, 973, 929, 914 cm^{-1}; HRMS (ES$^+$) calcd for $C_{12}H_{18}N_2O_4SNa^+$ 309.0885 found 309.0877 (MNa^+).

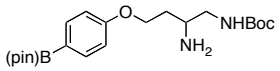


10 equiv of diene substrate was used relative to $BocNHSO_2NH_2$ (0.15 mmol); work-up according to Method B. Purified by chromatography on silica gel (4:1 hexanes/EtOAc); clear oil (77%): TLC R_f = 0.57 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.99-5.94 (m, 1H), 5.83-5.78 (m, 1H), 4.69-4.62 (m, 1H), 4.47 (br s, 1H), 4.08-4.02 (m, 1H), 2.24-2.02 (m, 3H), 1.99-1.89 (m, 1H), 1.55 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.6, 129.3, 123.3, 84.6, 57.7, 49.5, 28.2, 22.3, 18.7 ppm; IR (thin film) ν 3247, 2979, 2930, 1722, 1323, 1180, 1148, 652 cm^{-1}; HRMS (ES$^+$) calcd for $C_{11}H_{18}N_2O_4SNa^+$ 297.0885 found 297.0886 (MNa^+).

Experimental procedures for ring-opening reactions of cyclic sulfamides

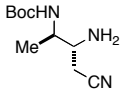


To a solution of cyclic sulfamide (80 mg, 0.26 mmol) in 1.0 mL of pyridine was added 0.1 mL of H_2O. The reaction mixture was stirred at 80 °C for 1 h. After cooling the solution to room temperature, the contents were transferred to a separatory funnel with 10 mL H_2O. The aqueous layer was extracted with 3 x 10 mL of $CHCl_3$. The combined organic extracts were washed with 2 x 5 mL of saturated aqueous NaCl, dried over $MgSO_4$, filtered, and concentrated to an off-white solid (71%). This material was deemed pure by ^{1}H NMR analysis: TLC R_f = 0.13 (100% EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz, 50°C) δ 7.32 (m, 1H), 7.22 (m, 3H), 5.12 (br s, 1H), 5.04 (br s, 1H), 3.87-3.82 (m, 1H), 3.15 (dd, 1H, *J* = 15.9, 6.2 Hz), 2.71 (dd, 1H, *J* = 15.9, 3.6 Hz), 1.51 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.2, 141.9, 140.8, 128.2, 127.2, 125.4, 125.0, 59.0, 55.0, 40.2, 29.8, 28.6 ppm; IR (thin film) ν 3358, 2976, 2929, 1709, 1519, 1458, 1391, 1366, 1248, 1169, 1048 cm^{-1}; HRMS (ES$^+$) calcd for $C_{14}H_{20}N_2O_2Na^+$ 271.1422 found 271.1422 (MNa^+).

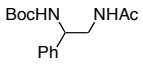


To a solution of cyclic sulfamide (24 mg, 51 μmol) in 0.26 mL of pyridine was added 26 μL of H_2O. The reaction mixture was stirred at 80 °C for 1.5 h. After cooling the solution to room temperature, all of the volatiles were removed under reduced pressure. The oily residue was redissolved in 2 mL of MeOH and the solution was concentrated under reduced pressure to afford a transparent yellow oil. Purification by chromatography on silica gel (94:5:1 CH_2Cl_2/MeOH/Et_3N) afforded the desired product as a pale yellow oil (86%): TLC R_f = 0.17 (94:5:1 CH_2Cl_2 /MeOH/ Et_3N); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.74 (d, 2H, *J* = 8.8 Hz), 6.88 (d, 2H, *J* = 8.8 Hz), 5.03 (br s,

1H), 4.11 (t, 2H, J = 6.0 Hz), 3.30-3.21 (m, 1H), 3.25-3.10 (m, 1H), 3.10-2.92 (m, 1H), 2.45-1.80 (br s, 2H), 1.99-1.89 (m, 1H), 1.79-1.68 (m, 1H), 1.44 (s, 9H), 1.32 (s, 12H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.3, 156.4, 136.6, 113.9, 83.6, 79.4, 65.1, 49.3, 47.0, 45.9, 34.6, 28.5, 24.9 ppm; IR (thin film) ν 3359, 2978, 2932, 1699, 1605, 1516, 1472, 1398, 1362, 1318, 1275, 1247, 1174, 1144, 1106 cm^{-1}; HRMS (ES$^+$) calcd for $C_{21}H_{35}BN_2O_5H^+$ 407.2712 found 407.2709 (MH^+).

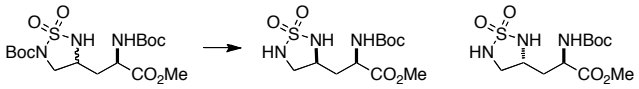


To a solution of cyclic sulfamide (19 mg, 69 μmol) in 0.35 mL of pyridine was added 35 μL of H_2O. The reaction mixture was stirred at 80 °C for 1.5 h. After cooling the solution to room temperature, all of the volatiles were removed under reduced pressure. The oily residue was redissolved in 2 mL of MeOH and the solution was concentrated under reduced pressure to afford a transparent yellow oil. Purification by chromatography on silica gel (gradient elution: 96:3:1 CH_2Cl_2/MeOH/Et_3N→94:5:1 CH_2Cl_2/MeOH/Et_3N) furnished the desired product as a pale orange oil (85%): TLC R_f = 0.25 (97:3 CH_2Cl_2/MeOH); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.75 (br d, 1H, J = 6.0 Hz), 3.79-3.68 (m, 1H), 3.22-3.12 (m, 1H), 2.58 (dd, 1H, J = 16.8, 4.4 Hz), 2.42 (dd, 1H, J = 16.6, 8.6 Hz), 1.98 (br s, 2H), 1.44 (s, 9H), 1.20 (d, 3H, J = 6.8 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.8, 118.4, 80.0, 52.5, 49.7, 28.5, 24.1, 18.6 ppm; IR (thin film) ν 3360, 2977, 2932, 2249, 1699, 1520, 1456, 1393, 1367, 1250, 1168, 1107 cm^{-1}; HRMS (ES$^+$) calcd for $C_{10}H_{19}N_3O_2H^+$ 214.1550 found 214.1554 (MH^+).



To a solution of cyclic sulfamide (80 mg, 0.27 mmol) in 1.0 mL of pyridine was added 0.1 mL of H_2O. The reaction mixture was stirred at 80 °C for 1.5 h and then cooled to room temperature. Acetic anhydride (0.127 mL, 5 equiv) was added to the mixture and the contents were stirred for 30 min. Following this time, all volatiles were removed under reduced pressure to give an oily residue. The desired product was isolated following purification by chromatography on silica gel (3:1 EtOAc/hexanes) as a white solid (80%): TLC R_f = 0.19 (2:1 EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37-7.32 (m, 2H), 7.30-7.27 (m, 3H), 6.11(br s, 1H), 5.48-5.40 (br m, 1H), 4.81-4.73 (br m, 1H), 3.68-3.58 (br m, 1H), 3.54-3.45 (br m, 1H), 1.97 (s, 3H), 1.42 (s, 9H) ppm; IR (thin film) ν 3302, 3064, 2978, 2932, 1693, 1656, 1527, 1366, 1170 cm^{-1}; HRMS (ES$^+$) calcd for $C_{15}H_{22}N_2O_3Na^+$ 301.1528 found 301.1525 (MNa^+).

Experimental procedures for the syntheses of (±)-enduracididine and (±)-allo-enduracididine

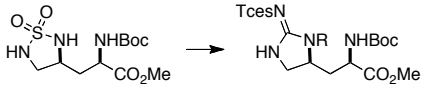


To a suspension of $MgBr_2$•OEt_2 (218 mg, 0.84 mmol, 1.5 equiv) in 5.4 mL of MeCN was added a solution of **3** (238 mg, 0.56 mmol) in 2.0 mL of MeCN. Transfer of **3** was made quantitative with 2 x 1 mL portions of MeCN. The reaction mixture was stirred at 60 °C for 12 h, following which time the solution was cooled to room temperature and all volatiles were removed under reduced pressure. This oily residue was dissolved in 15 mL of EtOAc, the solution transferred to a separatory funnel, and washed with 10 mL of a 1:1 mixture of saturated aqueous NaCl and aqueous $KHSO_4$ (pH = 1). The aqueous fractions were collected and extracted with 3 x 10 mL of EtOAc. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to an oily residue. Purification by chromatography on silica gel (gradient elution: 2:1→2:3 hexanes/EtOAc) afforded **4** and **5** as pale yellow viscous oils (110 mg, 61%). Chromatographic separation of the two diastereomers is possible at this stage.

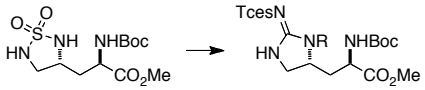
More polar diastereomer (relative stereochemistry unassigned): TLC R_f = 0.33 (2:3 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.59 (br d, 1H, J = 5.6 Hz), 5.33 (br d, 1H, J = 7.6 Hz), 4.55 (br t, 1H, J = 6.4 Hz), 4.45 (br t, 1H, J = 7.8 Hz), 3.95-3.85 (m, 1H), 3.78 (s, 3H), 3.67 (dt, 1H, J = 11.2, 6.4 Hz), 3.21 (dt, 1H, J = 11.2, 7.4 Hz), 2.17 (ddd, 1H, J = 13.9, 10.7, 3.2 Hz) 1.69 (t, 1H, J = 12.6 Hz), 1.44 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.4,

157.3, 81.1, 54.4, 53.0, 51.3, 48.3, 39.0, 28.4 ppm; IR (thin film) ν 3261, 2978, 2928, 1734, 1700, 1521, 1457, 1437, 1394, 1368, 1292, 1163, 1114 cm^{-1}; HRMS (ES^+) calcd for $C_{11}H_{21}N_3O_6SNa^+$ 346.1043 found 346.1048 (MNa^+).

Less polar diastereomer (relative stereochemistry unassigned): TLC R_f = 0.38 (2:3 hexanes/EtOAc); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.41 (br d, 1H, *J* = 6.8 Hz), 4.84 (br d, 1H, *J* = 6.8 Hz), 4.82-4.72 (m, 1H), 4.38 (br 2, 1H, *J* = 5.2 Hz), 4.01-3.91 (m, 1H), 3.78 (s, 3H), 3.72 (dt, 1H, *J* = 11.6, 6.8 Hz), 3.22 (dt, 1H, *J* = 11.6, 6.8 Hz), 2.23-2.04 (m, 2H), 1.44 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.5, 155.6, 80.8, 55.0, 53.1, 51.3, 49.7, 37.0, 28.4 ppm; IR (thin film) ν 3264, 2979, 1695, 1521, 1437, 1368, 1300, 1163, 1113 cm^{-1}; HRMS (ES^+) calcd for $C_{11}H_{21}N_3O_6SNa^+$ 346.1043 found 346.1045 (MNa^+).



4 **6** R = Tces

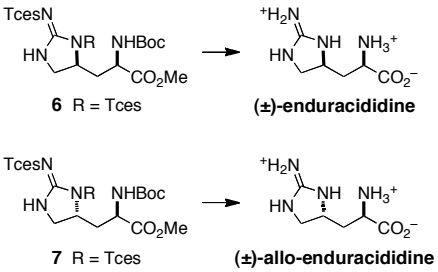


5 **7** R = Tces

To a solution of either **4** or **5** (46 mg, 0.14 mmol) in 1.8 mL of MeCN at –25 °C (4:1 ethylene glycol/EtOH and CO_2(s) bath) was added solid TcesN=C(SMe)Cl (50 mg, 0.16 mmol, 1.1 equiv) followed by $^iPr_2NEt$ (50 μL, 0.28 mmol, 2.0 equiv) and DMAP (26 mg, 0.21 mmol, 1.5 equiv). The transparent red-orange solution was stirred for 40 min before 0.45 mL of Cl_3CCH_2OH was added dropwise. The mixture was warmed to room temperature over 10 min. The reaction flask was then fitted with a reflux condenser and the contents were stirred at 50 °C for 18 h. Following this time, the mixture was cooled to room temperature and concentrated under reduced pressure. The isolated material was diluted with 5 mL of EtOAc. The contents were transferred to a separatory funnel and washed with 4 mL of a 1:1 mixture of saturated aqueous NaCl and aqueous $KHSO_4$ (pH = 1). The aqueous fraction was collected and extracted with 2 x 8 mL of EtOAc. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to an orange oil. Purification of this material by chromatography on silica gel (gradient elution: 3:1→2:1 hexanes/EtOAc) furnished **6** or **7** as light yellow foams (42 mg, 42%).

More polar diastereomer (relative stereochemistry unassigned): TLC R_f = 0.24 (2:1 hexanes/EtOAc); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.35 (br s, 1H), 5.33 (br d, 1H, *J* = 7.2 Hz), 5.09 (d, 1H, *J* = 11.6 Hz), 5.03 (d, 1H, *J* = 11.6 Hz), 4.82-4.75 (m, 1H), 4.67 (s, 2H), 4.27 (dd, 1H, *J* = 14.0, 6.8 Hz), 3.97 (t, 1H, *J* = 9.6 Hz), 3.88-3.80 (m, 1H), 3.80 (s, 3H), 2.55-2.43 (m, 1H), 2.16 (ddd, 1H, *J* = 14.0, 9.8, 6.6 Hz), 1.44 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.4, 155.3, 154.7, 93.5, 93.1, 82.7, 81.0, 78.7, 58.1, 53.2, 50.6, 46.7, 37.1, 28.4 ppm; IR (thin film) ν 3385, 2979, 1701, 1636, 1507, 1437, 1368, 1293, 1181 cm^{-1}; HRMS (ES^+) calcd for $C_{16}H_{24}Cl_6N_4O_{10}S_2Na^+$ 728.8957 found 728.8964 (MNa^+).

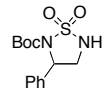
Less polar diastereomer (relative stereochemistry unassigned): TLC R_f = 0.27 (2:1 hexanes/EtOAc); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.30 (br s, 1H), 5.26 (br d, 1H, *J* = 8.0 Hz), 5.09 (d, 1H, *J* = 11.6 Hz), 5.03 (d, 1H, *J* = 11.6 Hz), 4.68 (s, 2H), 4.59-4.52 (m, 1H), 4.36-4.28 (m, 1H), 4.01 (dd, 1H, *J* = 10.4, 8.8 Hz), 3.80 (s, 3H), 3.72 (br d, 1H, *J* = 10.8 Hz), 2.33-2.24 (m, 1H), 1.44 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.3, 156.0, 154.8, 93.5, 93.1, 82.7, 81.1, 78.8, 57.8, 53.3, 50.0, 46.6, 37.1, 28.4 ppm; IR (thin film) ν 3384, 2978, 1743, 1707, 1637, 1508, 1438, 1368, 1291, 1180, 1131 cm^{-1}; HRMS (ES^+) calcd for $C_{16}H_{24}Cl_6N_4O_{10}S_2H^+$ 706.9138 found 706.9130 (MH^+).



To an ice cold solution of **6** or **7** (10 mg, 14 μmol) in 0.14 mL of THF and 0.11 mL of H_2O was added dropwise via syringe 1.0 M aqueous LiOH (30 μL, 28 μmol, 2.0 equiv). The reaction mixture was warmed to room temperature and stirred for 30 min following which time 0.14 mL of H_2O and 0.14 mL of CF_3CO_2H were added. The contents were stirred for 20 min and then Pd/C (30 mg of 10 wt%, 28 μmol, 2.0 equiv) was added. The solution was sparged with a balloon of hydrogen for 1 min and stirred under a balloon of H_2 for 18 h. The reaction vessel was flushed with N_2 and the black suspension filtered through a Fisher 0.2 μm PTFE syringe filter. The flask and filter were washed sequentially with 0.5 mL of H_2O and 1 mL of MeCN, and the combined filtrates were concentrated under reduced pressure to a pale yellow solid. Purification of this material was performed by reversed-phase HPLC (Silicycle AQ C18, 5 μm, 10 x 250 mm column, eluting with gradient flow over 40 min of 0:100→30:70 MeCN/10 mM aqueous $C_3F_7CO_2H$, 214 nm UV detection).

More polar diastereomer: (relative stereochemistry unassigned): At a flow rate of 4 mL/min, the desired guanidium amino acid had a retention time between 9−15 min and was isolated as a white solid (2.4 mg, 44%). ^{1}H NMR (D_2O, 600 MHz) δ 4.32-4.27 (m, 1H), 3.92 (t, 1H, J = 6.4 Hz), 3.78 (t, 1H, J = 4.6 Hz), 3.45 (dd, 1H, J = 6.4, 4.4 Hz), 2.24 (dt, 1H, J = 9.6, 4.9 Hz), 2.11 (dt, 1H, J = 9.6, 4.2 Hz) ppm; HRMS (ES^+) calcd for $C_6H_{13}N_4O_2^+$ 173.1033 found 173.1029.

Less polar diastereomer: (relative stereochemistry unassigned): At a flow rate of 4 mL/min, the desired guanidium amino acid had a retention time between 10−15 min and was isolated as a white solid (2.1 mg, 36%). ^{1}H NMR (D_2O, 600 MHz) δ 4.29-4.36 (m, 1H), 3.93-3.88 (m, 2H), 3.45 (dd, 1H, J = 6.2, 3.8 Hz), 2.26-2.14 (m, 2H) ppm; HRMS (ES^+) calcd for $C_6H_{13}N_4O_2^+$ 173.1033 found 173.1032.



STANDARD 1H OBSERVE

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Sample directory:

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Solvent: CDCl3

Relax. delay 0.500 sec
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Width 4997.5 Hz
16 repetitions
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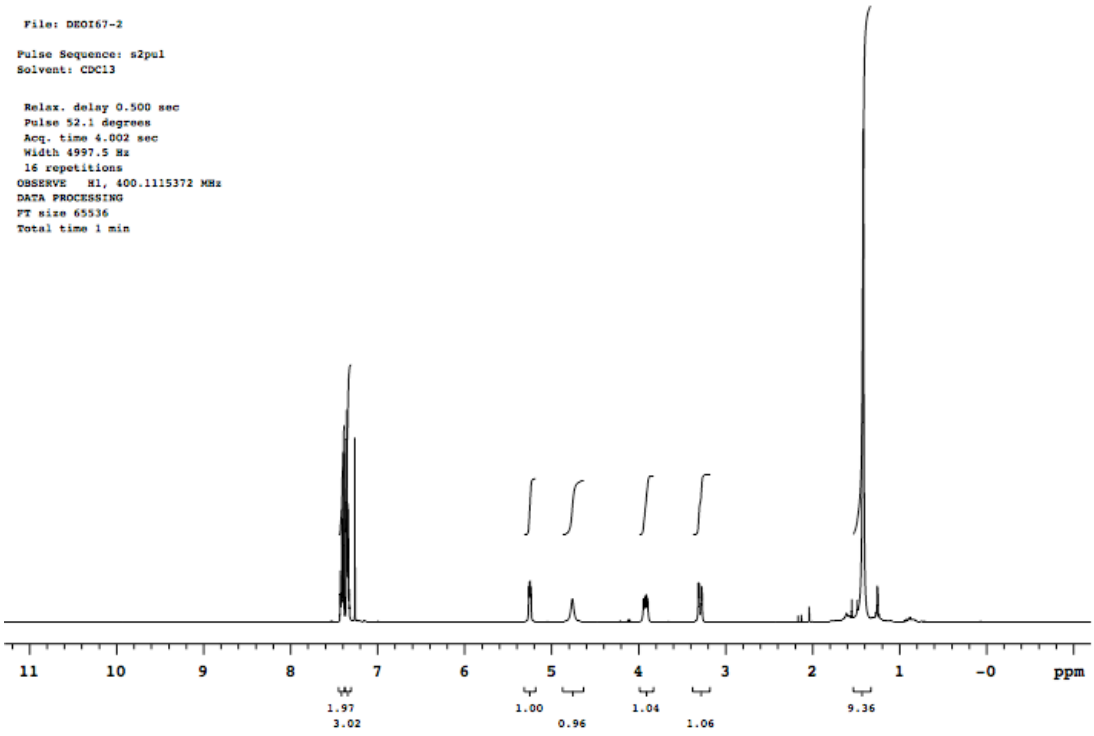
DATA PROCESSING
FT size 65536
Total time 1 min



13C OBSERVE

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Sample directory:

File: DEOI67-3

Pulse Sequence: s2pul
Solvent: CDCl3

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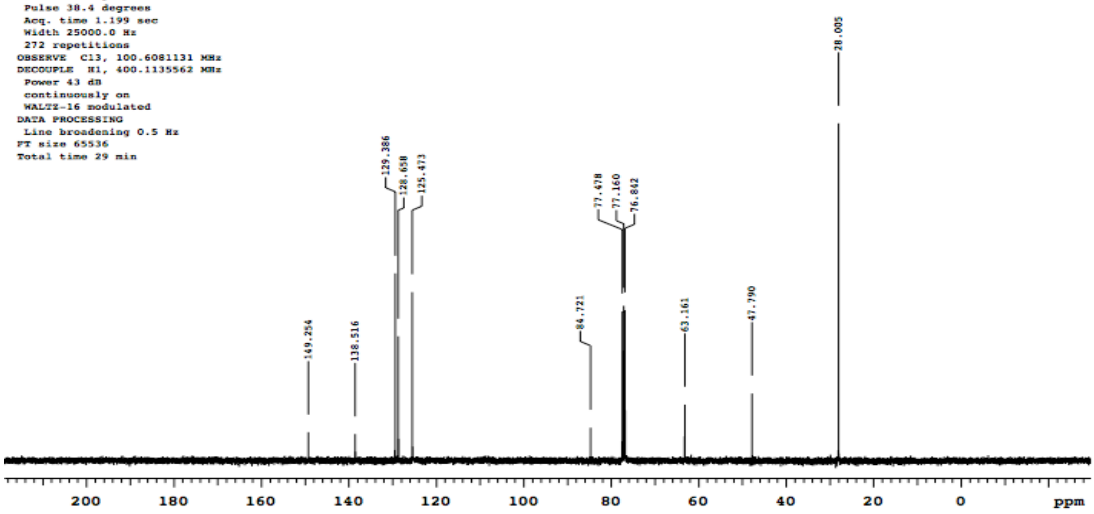
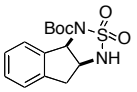
Pulse 38.4 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
272 repetitions
OBSERVE C13, 100.6081131 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 29 min





STANDARD 1H OBSERVE

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Sample directory:

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Pulse Sequence: s2pul
Solvent: CDCl3

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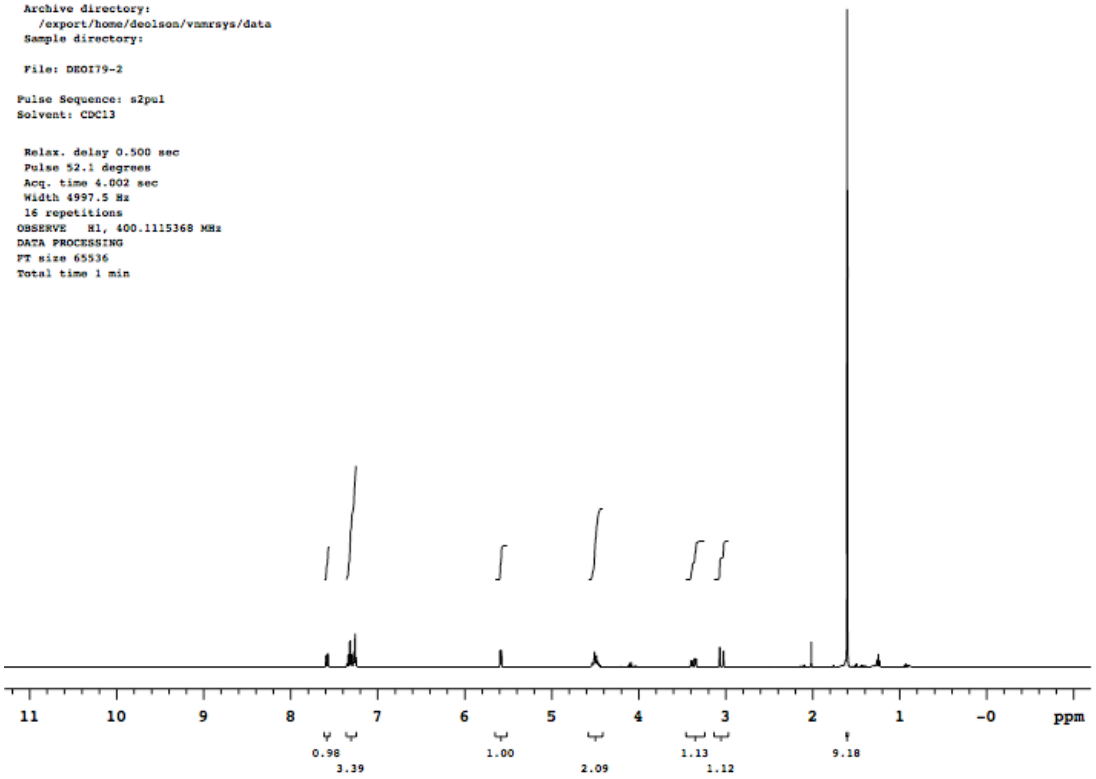
Width 4997.5 Hz
16 repetitions
OBSERVE H1, 400.1115368 MHz
DATA PROCESSING
FT size 65536
Total time 1 min



13C OBSERVE

Archive directory:
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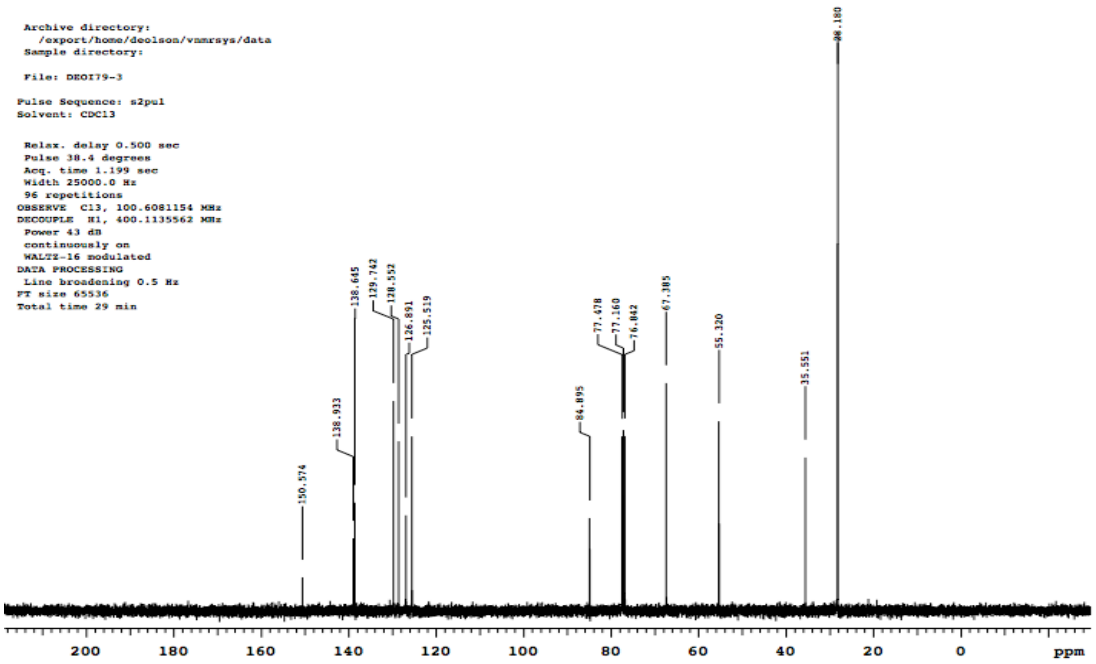
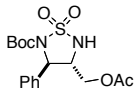
Sample directory:

File: DEOI79-3

Pulse Sequence: s2pul
Solvent: CDCl3

Relax. delay 0.500 sec
Pulse 38.4 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
96 repetitions
OBSERVE C13, 100.6081154 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 29 min





STANDARD 1H OBSERVE

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Sample directory:

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Solvent: CDCl3

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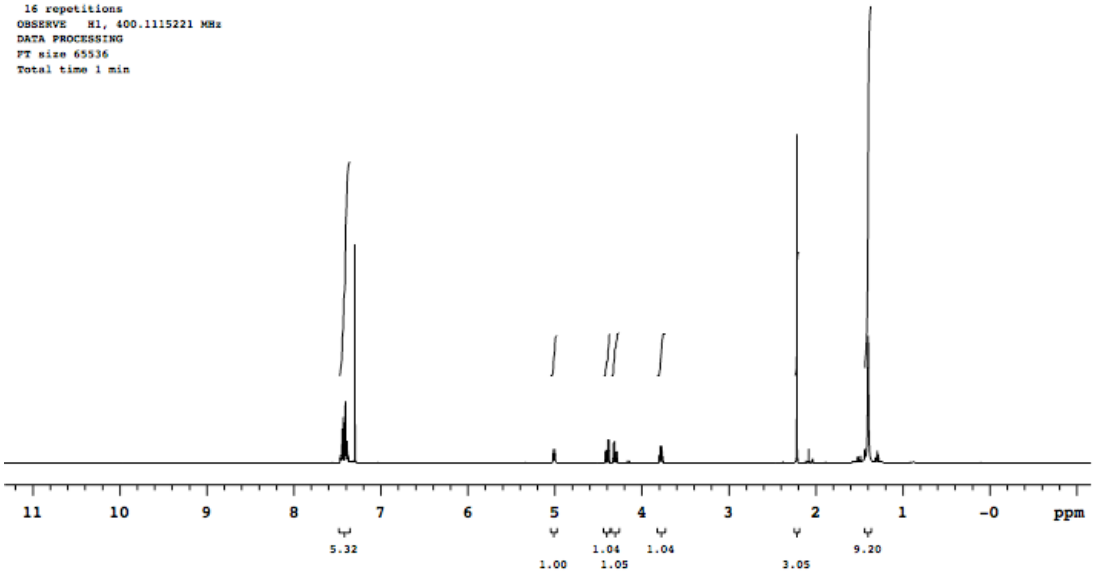
Width 4997.5 Hz
16 repetitions
OBSERVE H1, 400.1115221 MHz
DATA PROCESSING
FT size 65536
Total time 1 min



13C OBSERVE

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Solvent: CDCl3

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Pulse 38.4 degrees
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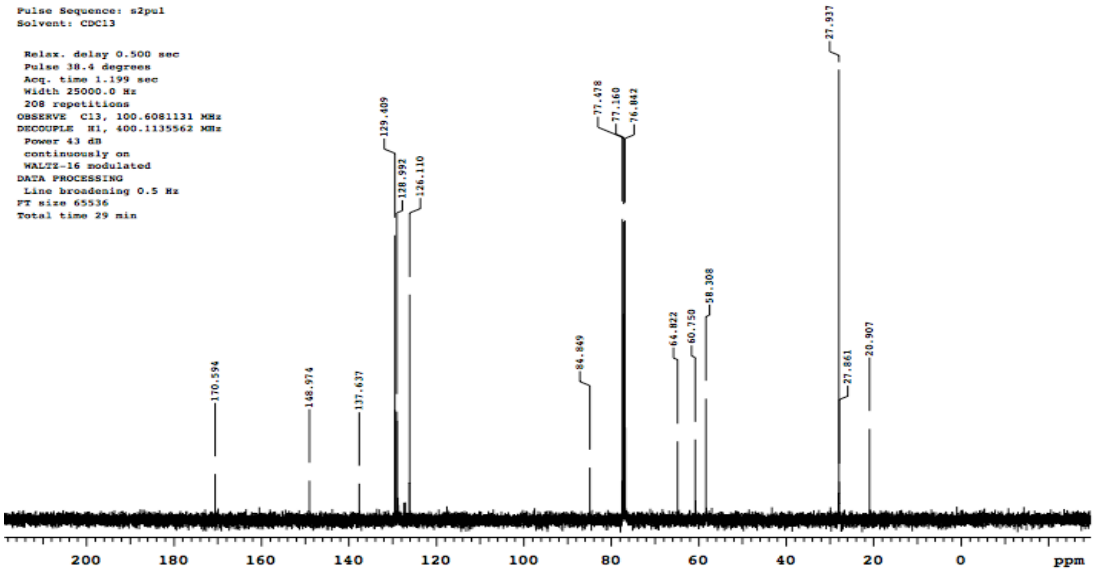
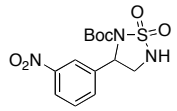
Width 25000.0 Hz
208 repetitions
OBSERVE C13, 100.6081131 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 29 min





STANDARD 1H OBSERVE

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File: DEOI93-5

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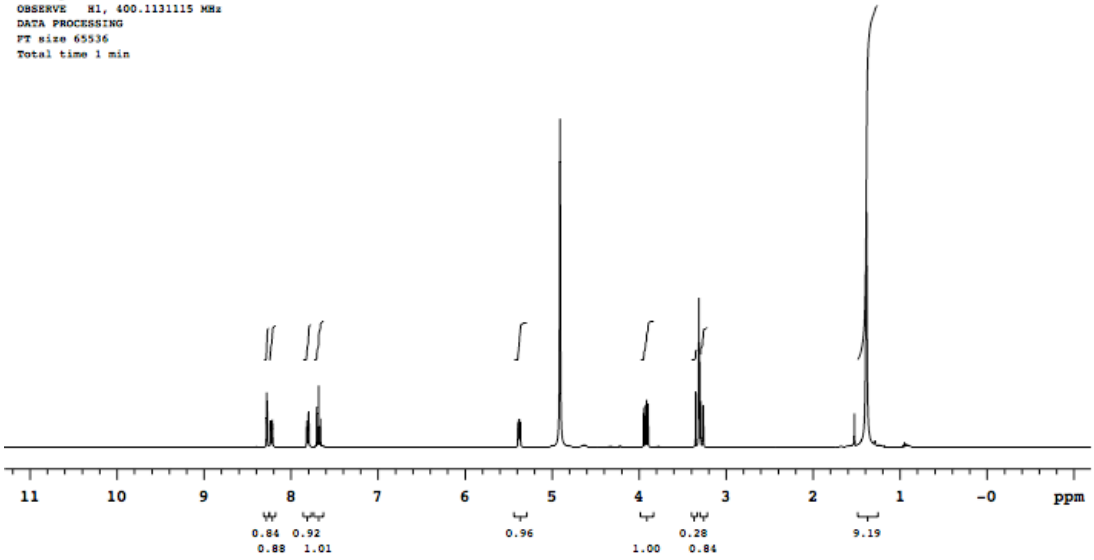
Solvent: CD3OD

Relax. delay 0.500 sec
Pulse 52.1 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
16 repetitions
OBSERVE H1, 400.1131115 MHz
DATA PROCESSING
FT size 65536
Total time 1 min



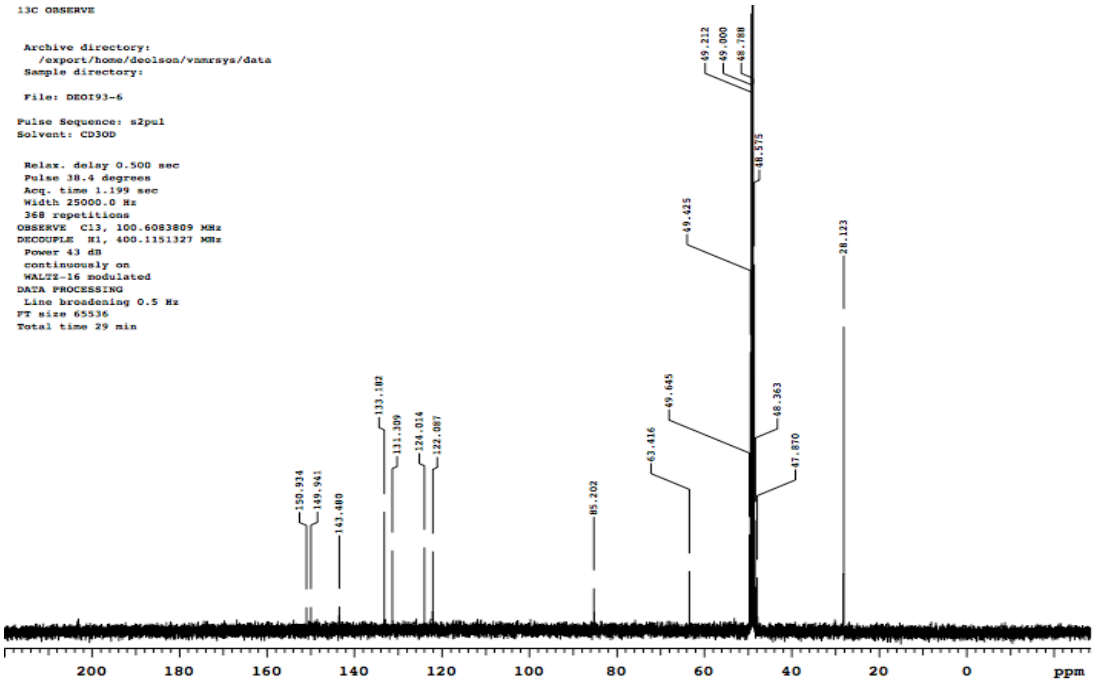
13C OBSERVE

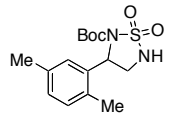
Archive directory:
/export/home/deolson/vnmrsys/data
Sample directory:

File: DEOI93-6

Pulse Sequence: s2pul
Solvent: CD3OD

Relax. delay 0.500 sec
Pulse 38.4 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
368 repetitions
OBSERVE C13, 100.6083809 MHz
DECOUPLE H1, 400.1151327 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 29 min





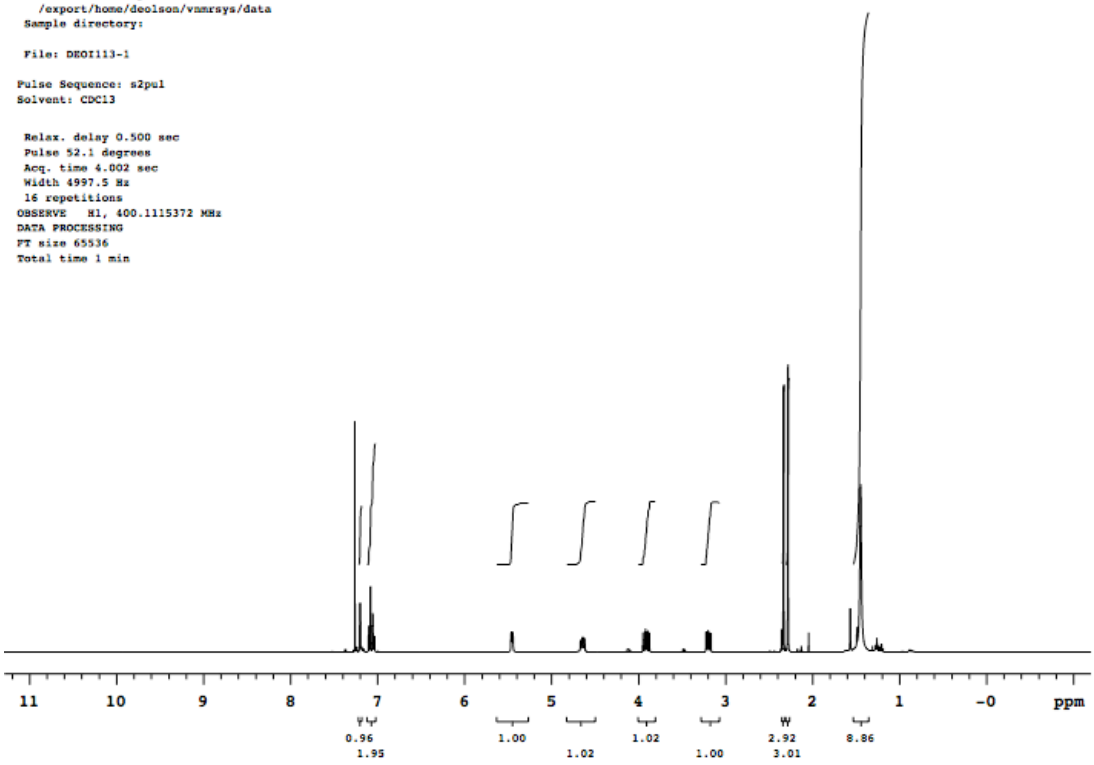
STANDARD 1H OBSERVE

Archive directory:
/export/home/deolson/vnmrsys/data
Sample directory:

File: DEOI113-1

Pulse Sequence: s2pul
Solvent: CDCl3

Relax. delay 0.500 sec
Pulse 52.1 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
16 repetitions
OBSERVE H1, 400.1115372 MHz
DATA PROCESSING
FT size 65536
Total time 1 min



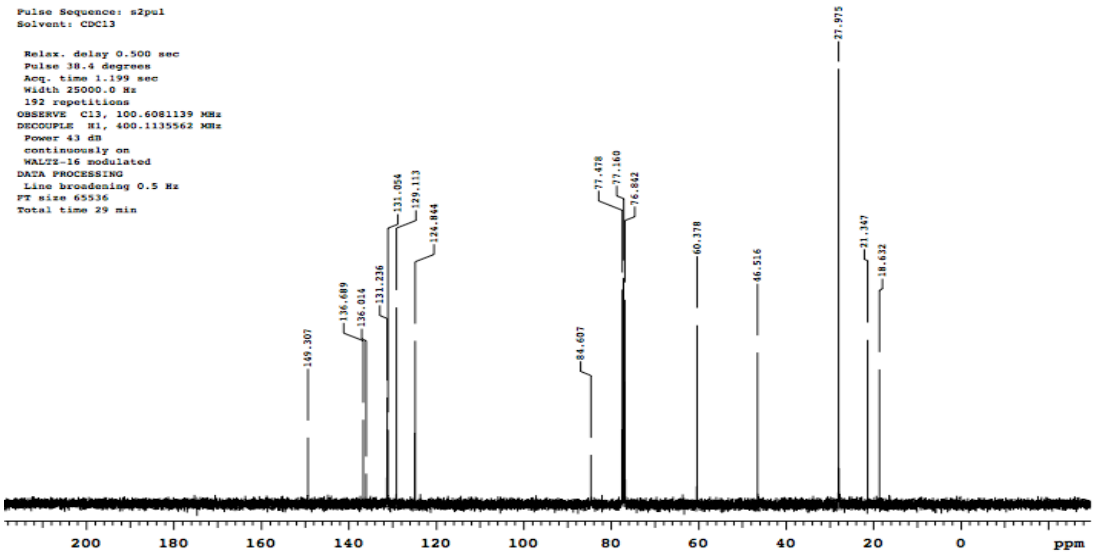
13C OBSERVE

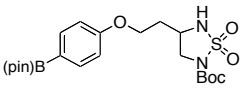
Archive directory:
/export/home/deolson/vnmrsys/data
Sample directory:

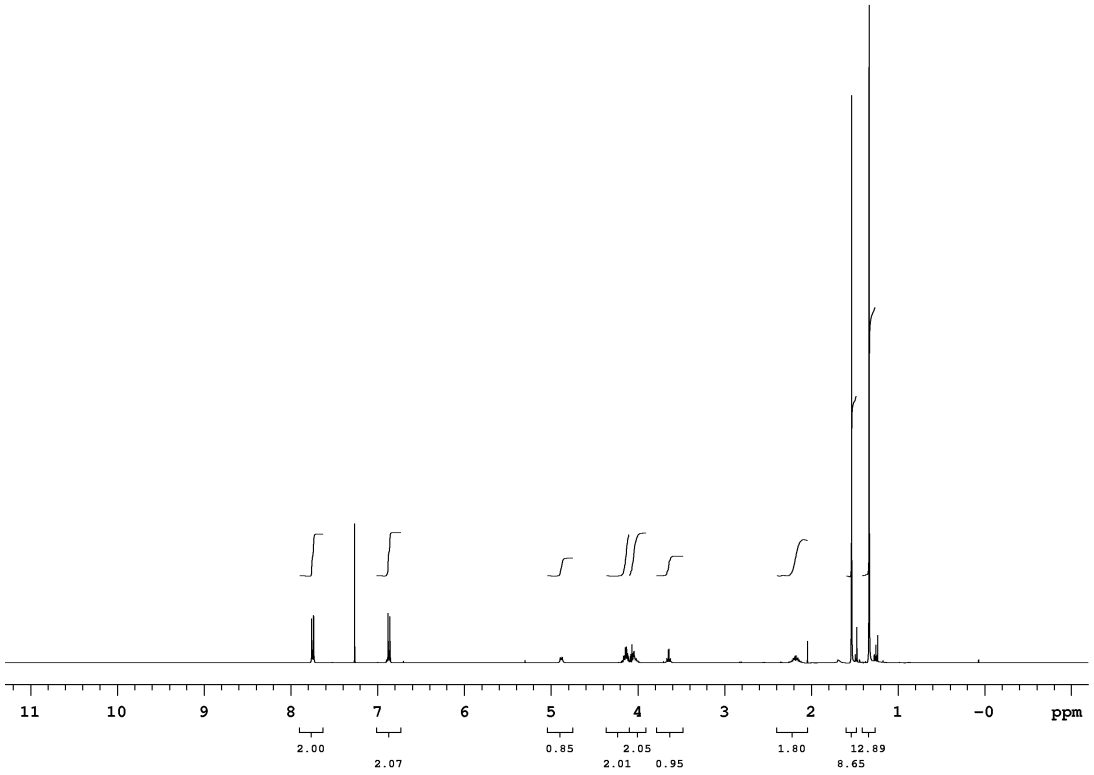
File: DEOI107-3

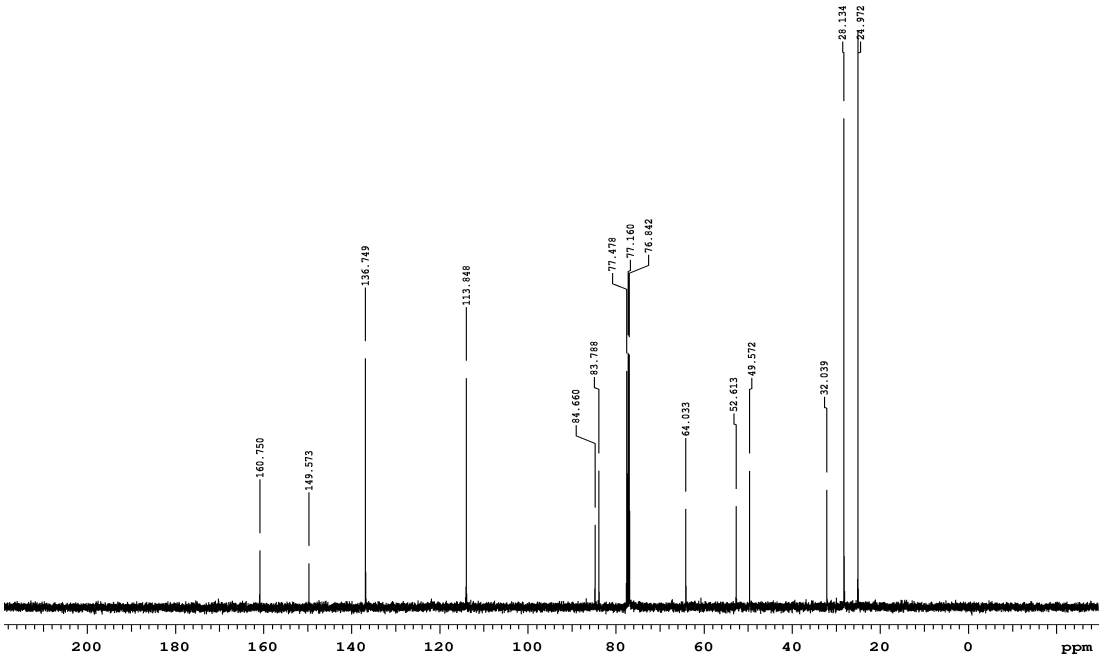
Pulse Sequence: s2pul
Solvent: CDCl3

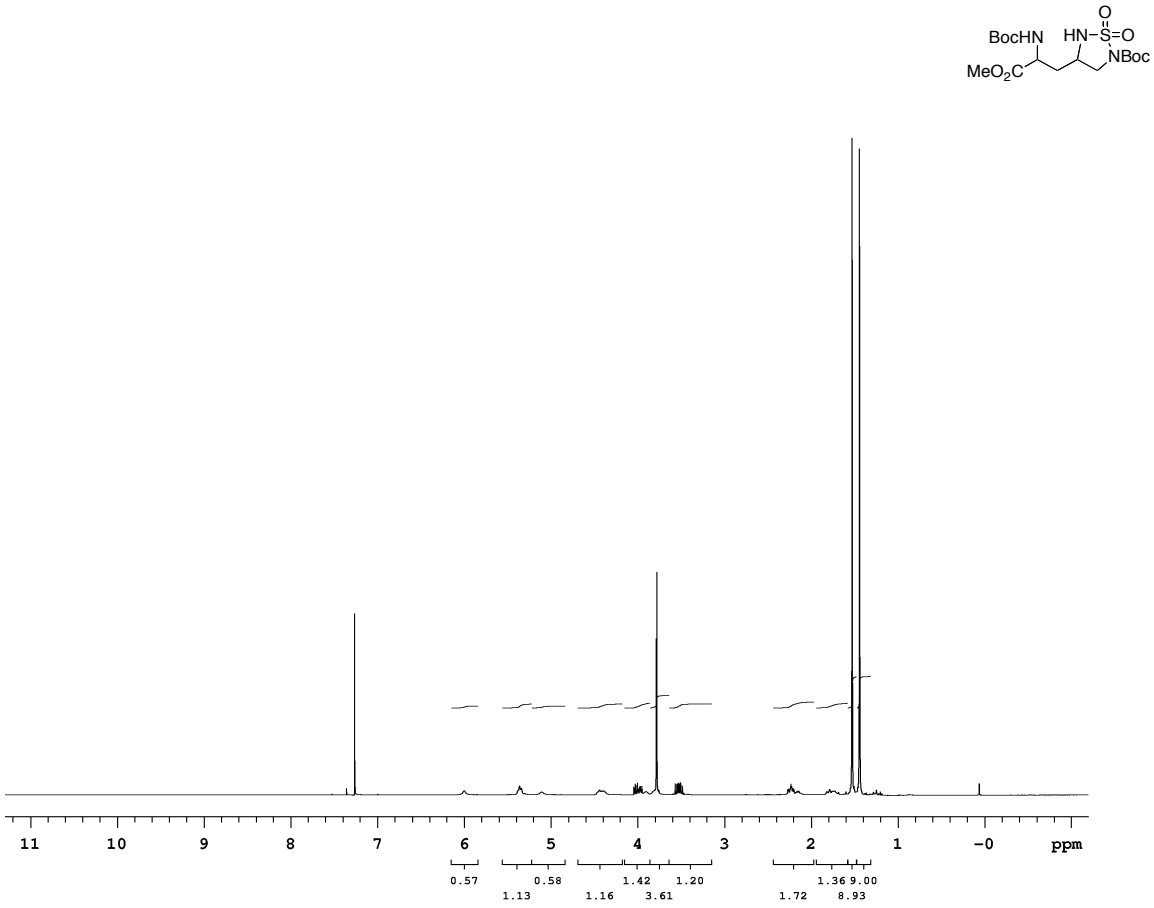
Relax. delay 0.500 sec
Pulse 38.4 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
192 repetitions
OBSERVE C13, 100.6081139 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 29 min

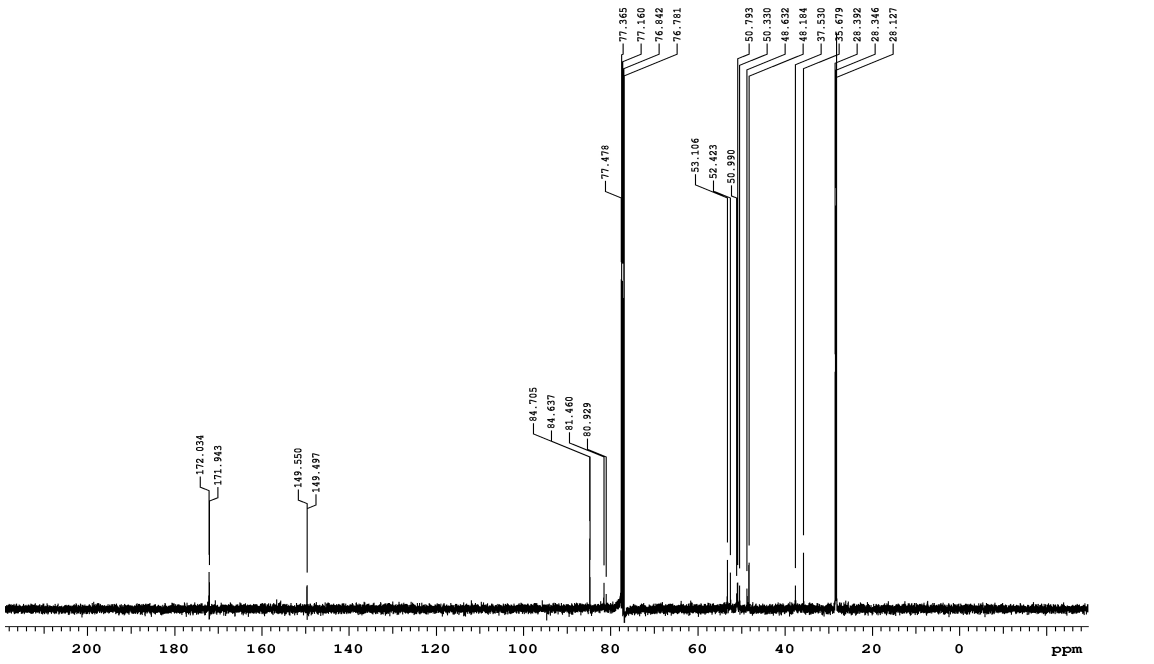



H
N
O
S
O
O
N
Boc
(pin)B

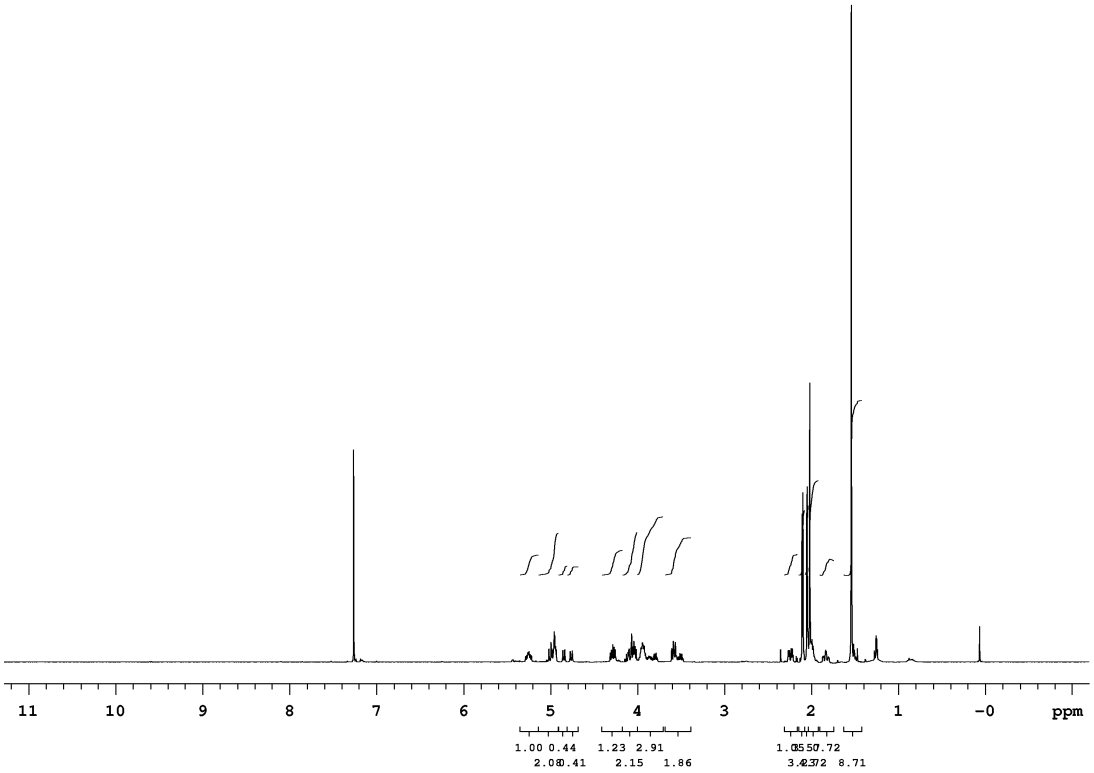

11
10
9
8
7
6
5
4
3
2
1
−0
ppm
2.00
2.07
0.85
2.01
2.05
0.95
1.80
8.65
12.89

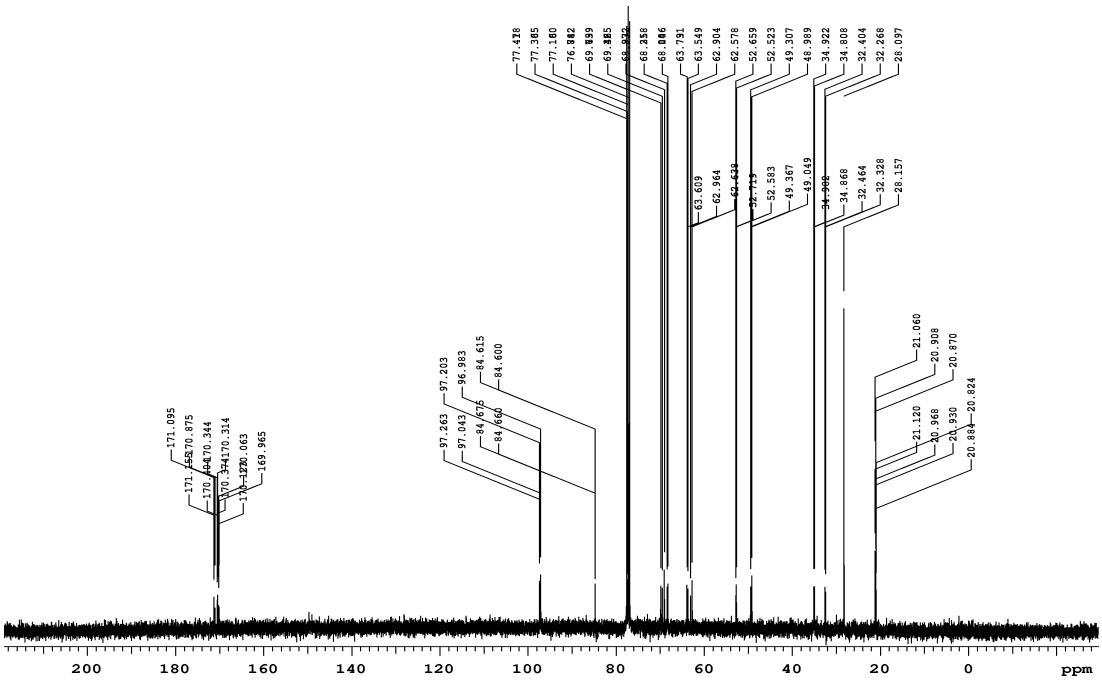

160.750
149.573
136.749
113.848
84.660
83.788
77.478
77.160
76.842
64.033
52.613
49.572
32.039
28.134
24.972
200
180
160
140
120
100
80
60
40
20
0
ppm

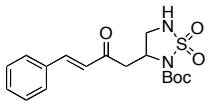

BocHN
HN
S
O
NBoc
MeO2C
11
10
9
8
7
6
5
4
3
2
1
−0
ppm
0.57
0.58
1.42
1.20
1.36
9.00
1.13
1.16
3.61
1.72
8.93

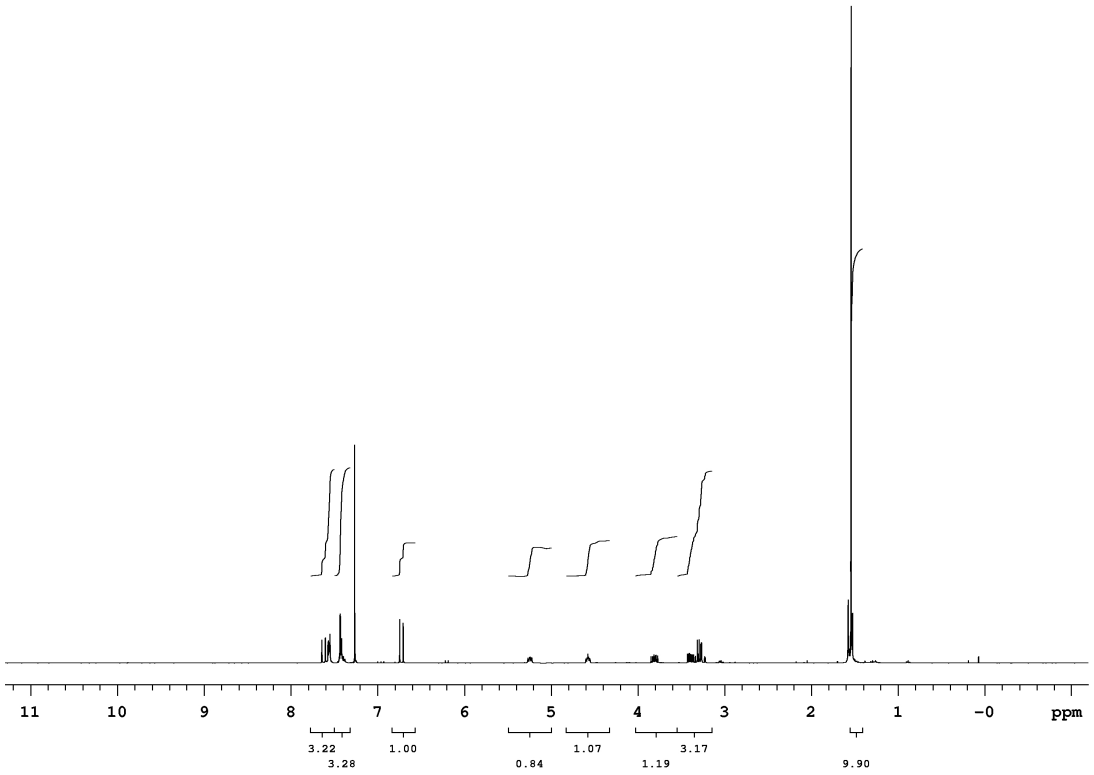

77.365
77.160
76.842
76.781
77.478
84.705
84.637
81.460
80.929
172.034
171.943
149.550
149.497
53.106
52.423
50.990
50.793
50.330
48.632
48.184
37.530
35.679
28.392
28.346
28.127
200
180
160
140
120
100
80
60
40
20
0
ppm

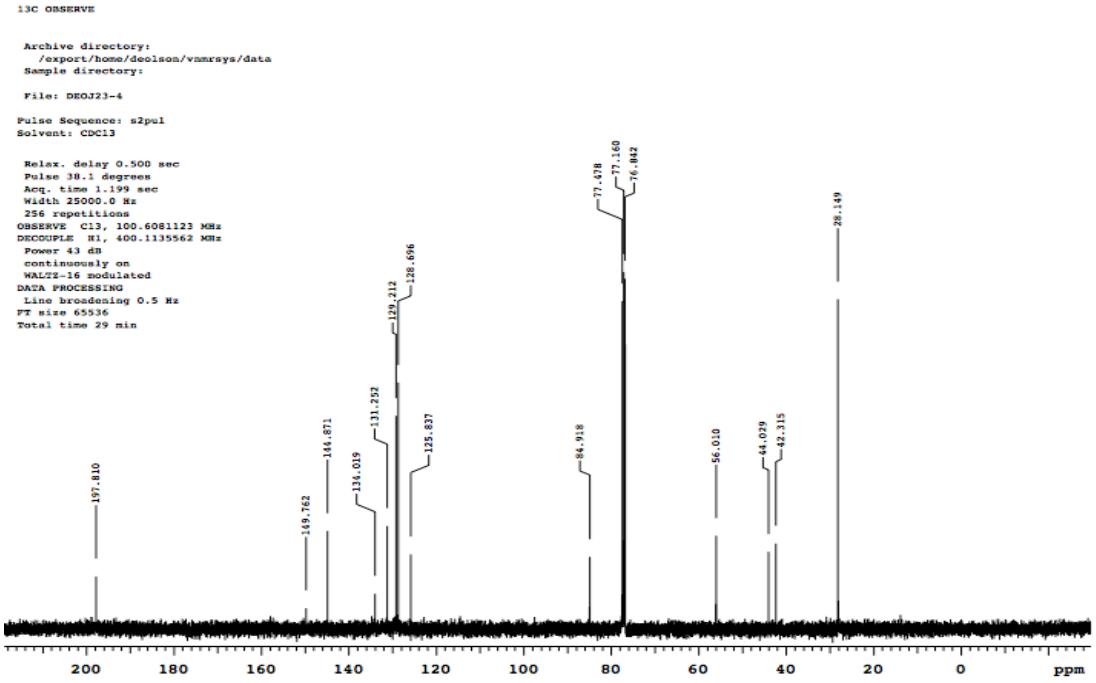

AcO
AcO
OAc
O
O
H
N
S
O
O
N
Boc

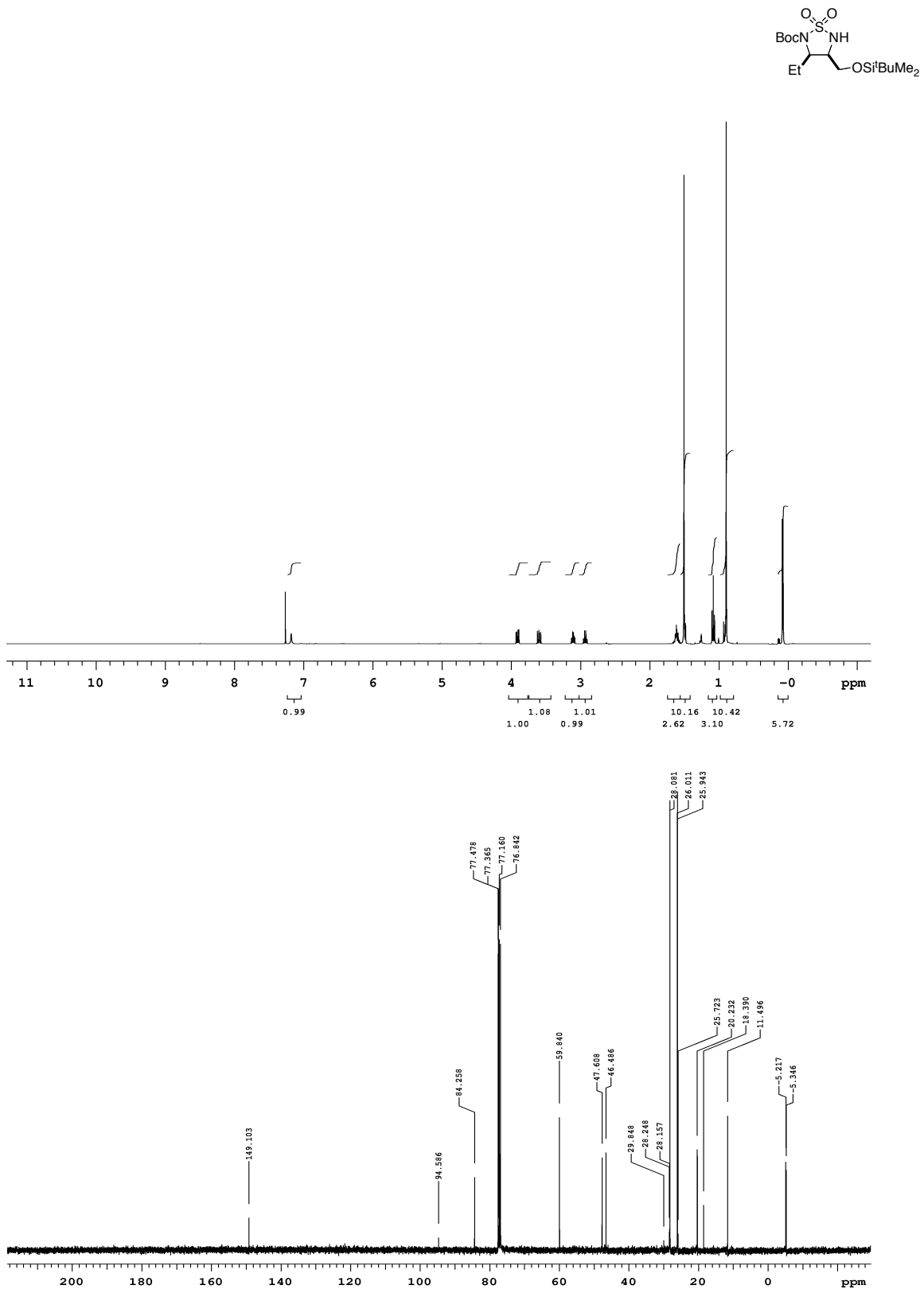

11
10
9
8
7
6
5
4
3
2
1
−0
ppm
1.00 0.44
1.23 2.91
2.15 1.86
8.71

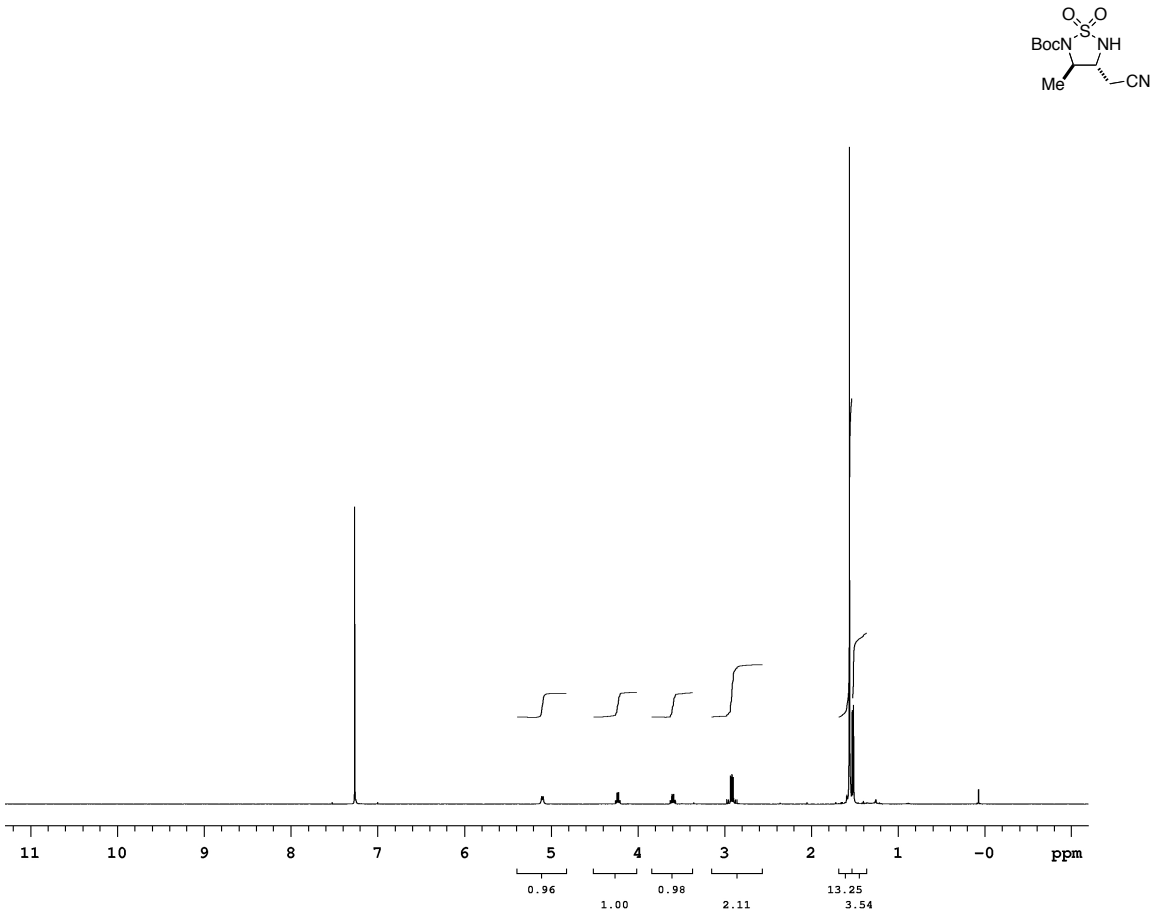

77.478
77.365
77.180
63.791
63.549
62.904
62.578
52.659
52.523
49.307
48.989
34.922
34.808
32.404
32.268
28.097
63.609
62.964
52.583
49.367
49.049
34.868
32.464
32.328
28.157
97.203
96.983
84.615
84.600
97.263
97.043
84.675
84.660
171.095
170.875
170.344
170.314
169.965
21.060
20.908
20.870
21.120
20.968
20.930
20.824
20.884
200
180
160
140
120
100
80
60
40
20
0
ppm

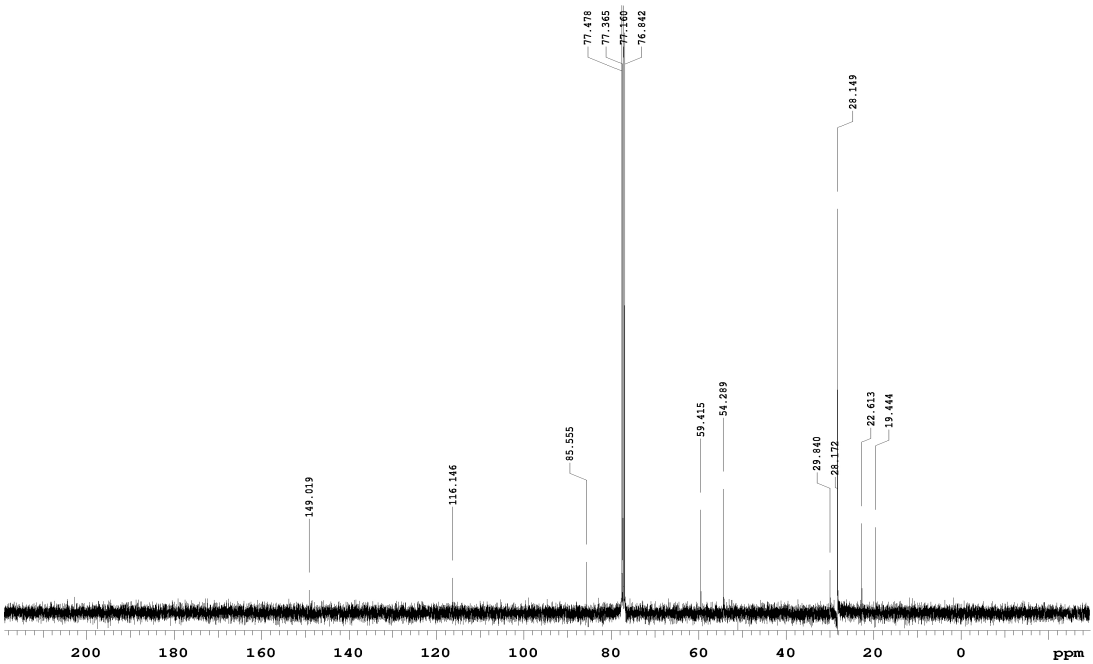

H
N
O
S
O
O
N
Boc

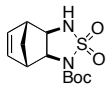

11
10
9
8
7
6
5
4
3
2
1
-0
ppm
3.22
3.28
1.00
0.84
1.07
1.19
3.17
9.90


13C OBSERVE
Archive directory:
/export/home/deolson/vnmrsys/data
Sample directory:
File: DEOJ23-4
Pulse Sequence: s2pul
Solvent: CDCl3
Relax. delay 0.500 sec
Pulse 38.1 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
256 repetitions
OBSERVE C13, 100.6081123 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 29 min
197.810
149.762
144.871
134.019
131.252
129.212
128.696
125.837
84.918
77.478
77.160
76.842
56.010
44.029
42.315
28.149
200
180
160
140
120
100
80
60
40
20
0
ppm


BocN
NH
Et
OSi^{t}BuMe$_2$
11 10 9 8 7 6 5 4 3 2 1 −0 ppm
0.99
1.00
1.08
0.99
1.01
2.62
10.16
3.10
10.42
5.72
149.103
94.586
84.258
77.478
77.365
77.160
76.842
59.840
47.608
46.486
29.848
28.248
28.157
28.081
26.011
25.943
25.723
20.232
18.390
11.496
-5.217
-5.346
200 180 160 140 120 100 80 60 40 20 0 ppm


BocN
NH
Me
CN
11
10
9
8
7
6
5
4
3
2
1
−0
ppm
0.96
1.00
0.98
2.11
13.25
3.54


77.478
77.365
77.160
76.842
149.019
116.146
85.555
59.415
54.289
29.840
28.172
28.149
22.613
19.444
200
180
160
140
120
100
80
60
40
20
0
ppm



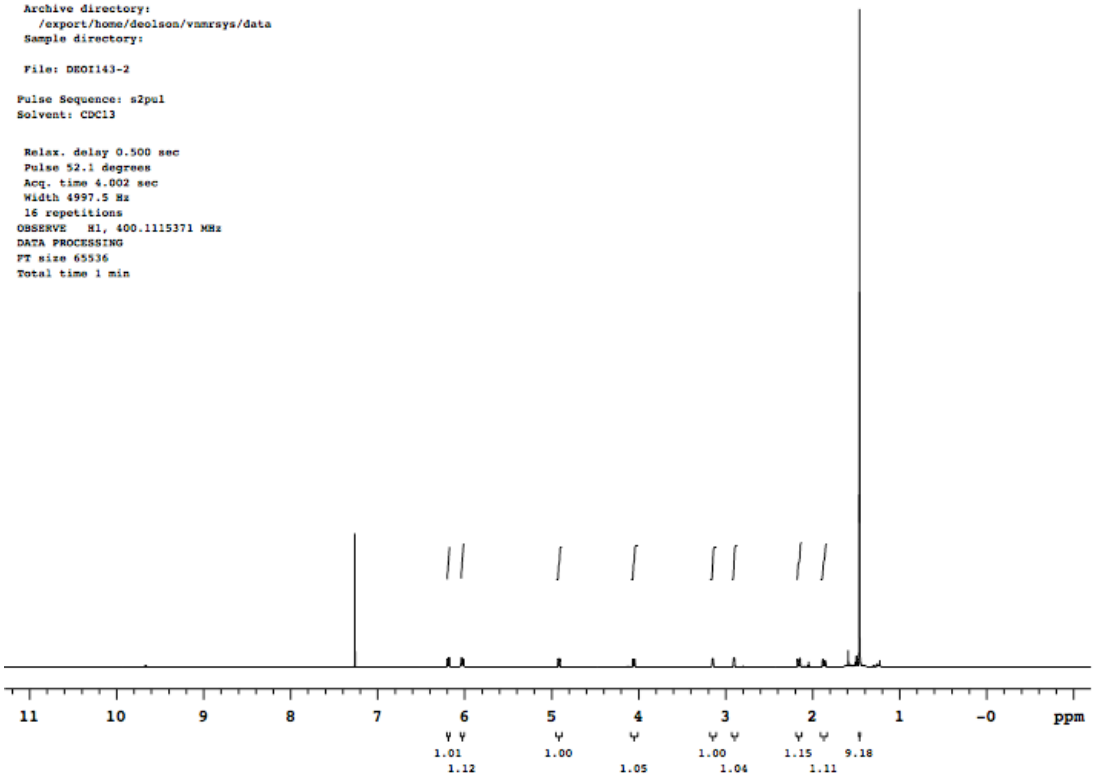
STANDARD 1H OBSERVE

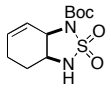
Archive directory:
/export/home/deolson/vnmrsys/data
Sample directory:

File: DEOI143-2

Pulse Sequence: s2pul
Solvent: CDCl3

Relax. delay 0.500 sec
Pulse 52.1 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
16 repetitions
OBSERVE H1, 400.1115371 MHz
DATA PROCESSING
FT size 65536
Total time 1 min





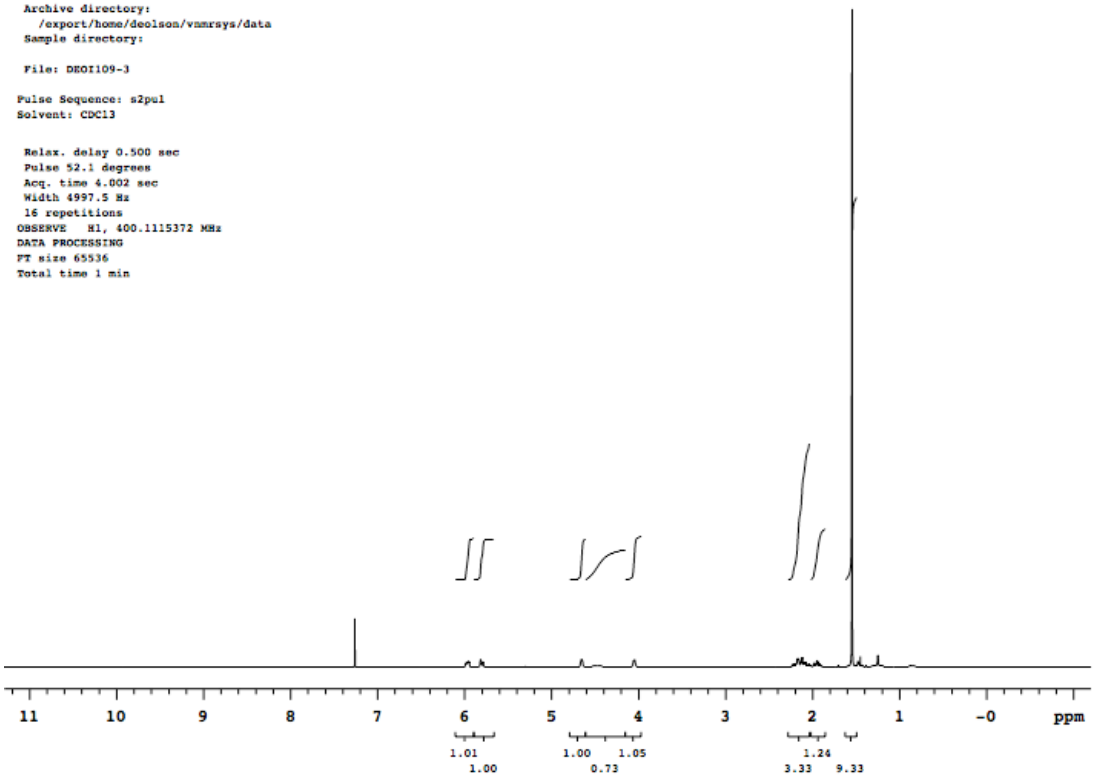
STANDARD 1H OBSERVE

Archive directory:
/export/home/deolson/vnmrsys/data
Sample directory:

File: DEOI109-3

Pulse Sequence: s2pul
Solvent: CDCl3

Relax. delay 0.500 sec
Pulse 52.1 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
16 repetitions
OBSERVE H1, 400.1115372 MHz
DATA PROCESSING
FT size 65536
Total time 1 min



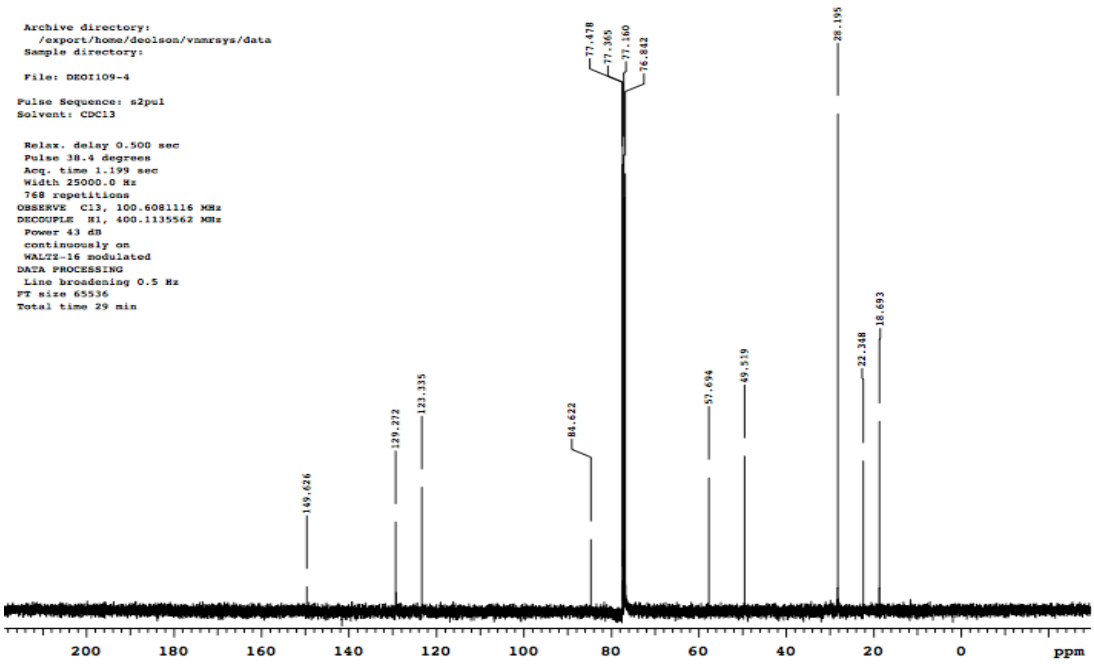
13C OBSERVE

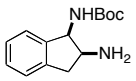
Archive directory:
/export/home/deolson/vnmrsys/data
Sample directory:

File: DEOI109-4

Pulse Sequence: s2pul
Solvent: CDCl3

Relax. delay 0.500 sec
Pulse 38.4 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
768 repetitions
OBSERVE C13, 100.6081116 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 29 min





STANDARD PROTON PARAMETERS

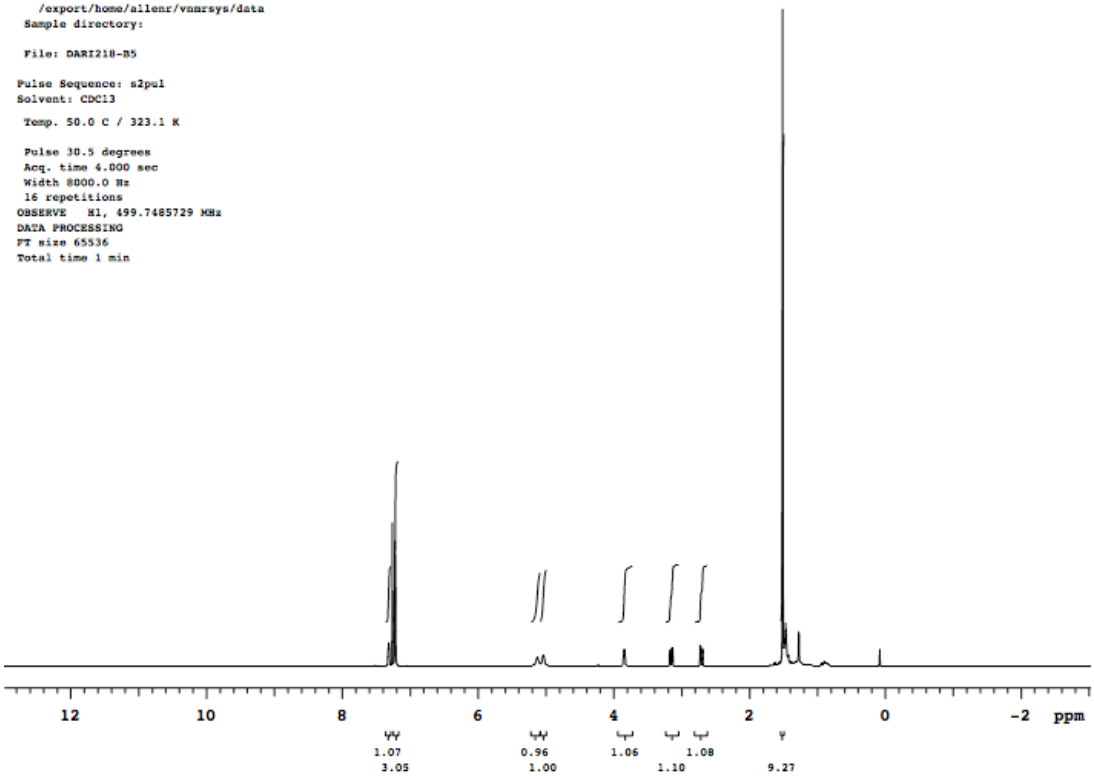
Archive directory:
/export/home/allenr/vnmrsys/data
Sample directory:

File: DARI218-B5

Pulse Sequence: s2pul
Solvent: CDCl3

Temp. 50.0 C / 323.1 K

Pulse 30.5 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.7485729 MHz
DATA PROCESSING
FT size 65536
Total time 1 min



13C OBSERVE

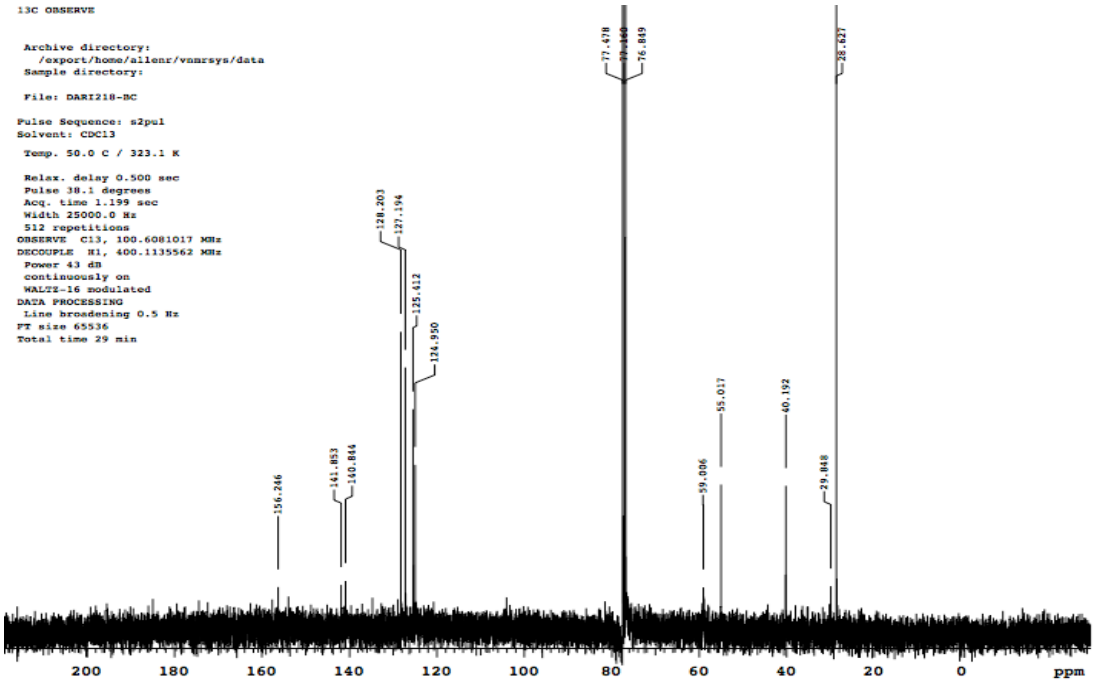
Archive directory:
/export/home/allenr/vnmrsys/data
Sample directory:

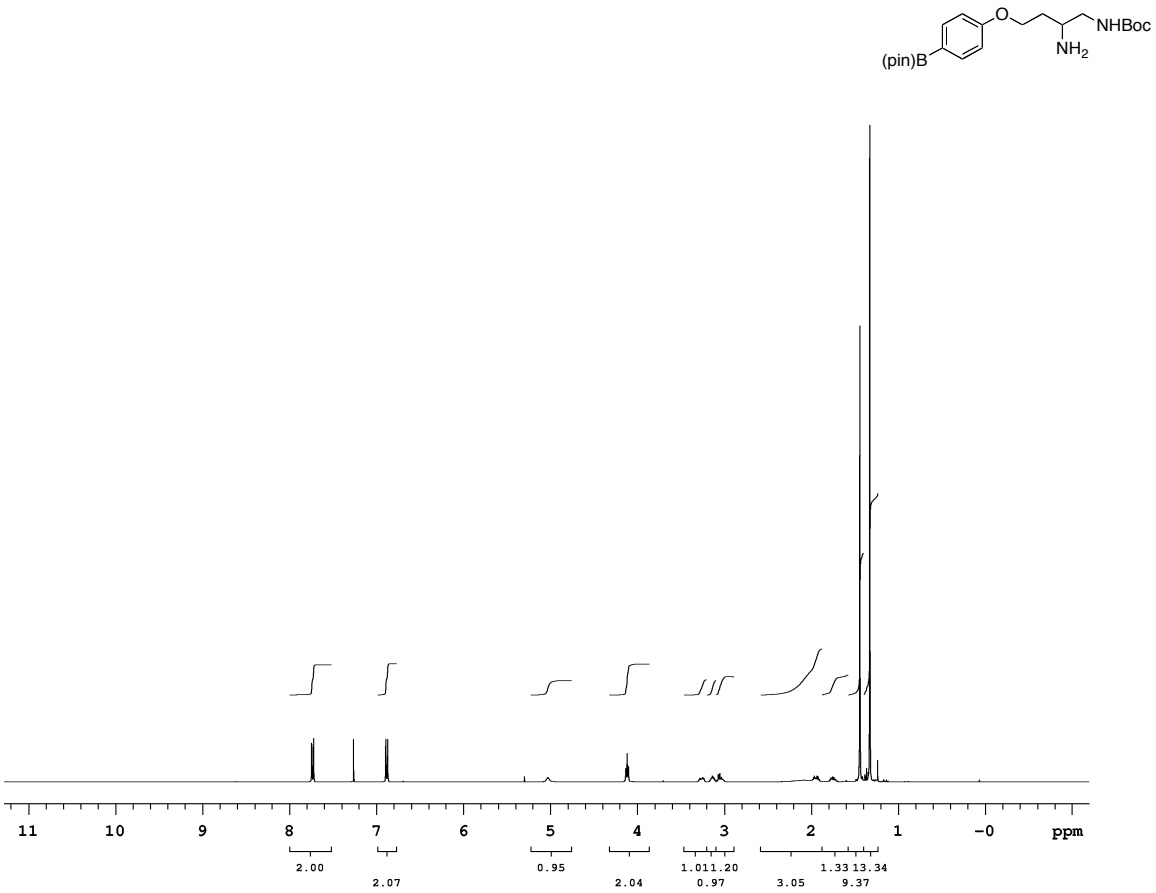
File: DARI218-BC

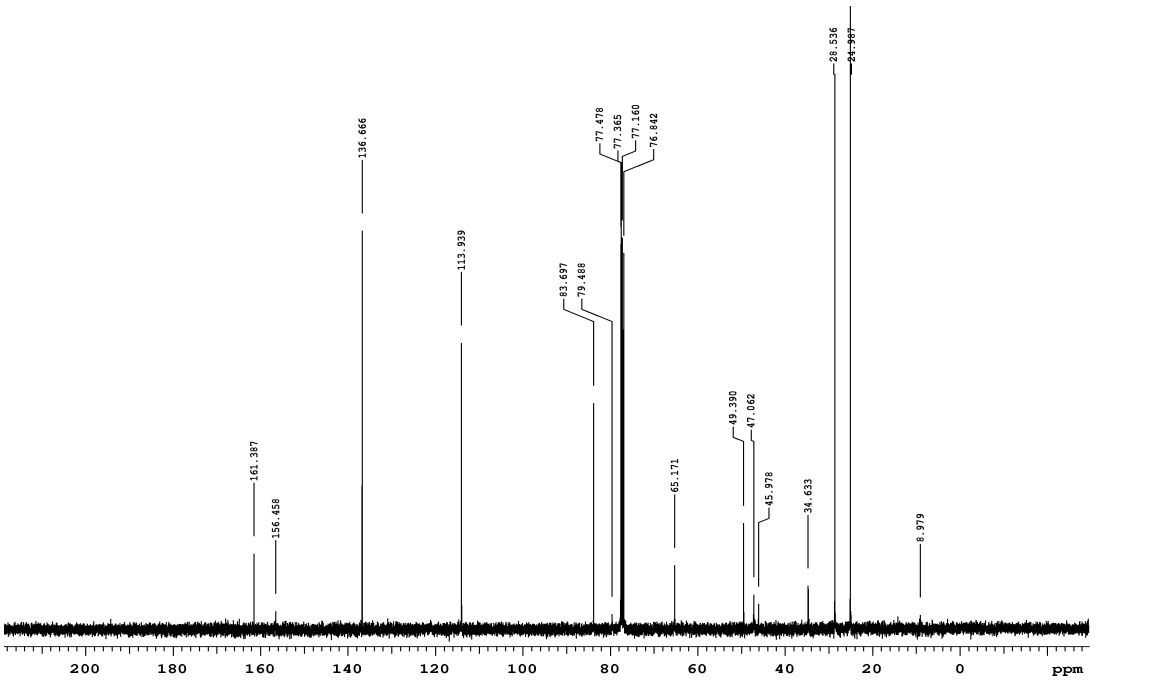
Pulse Sequence: s2pul
Solvent: CDCl3

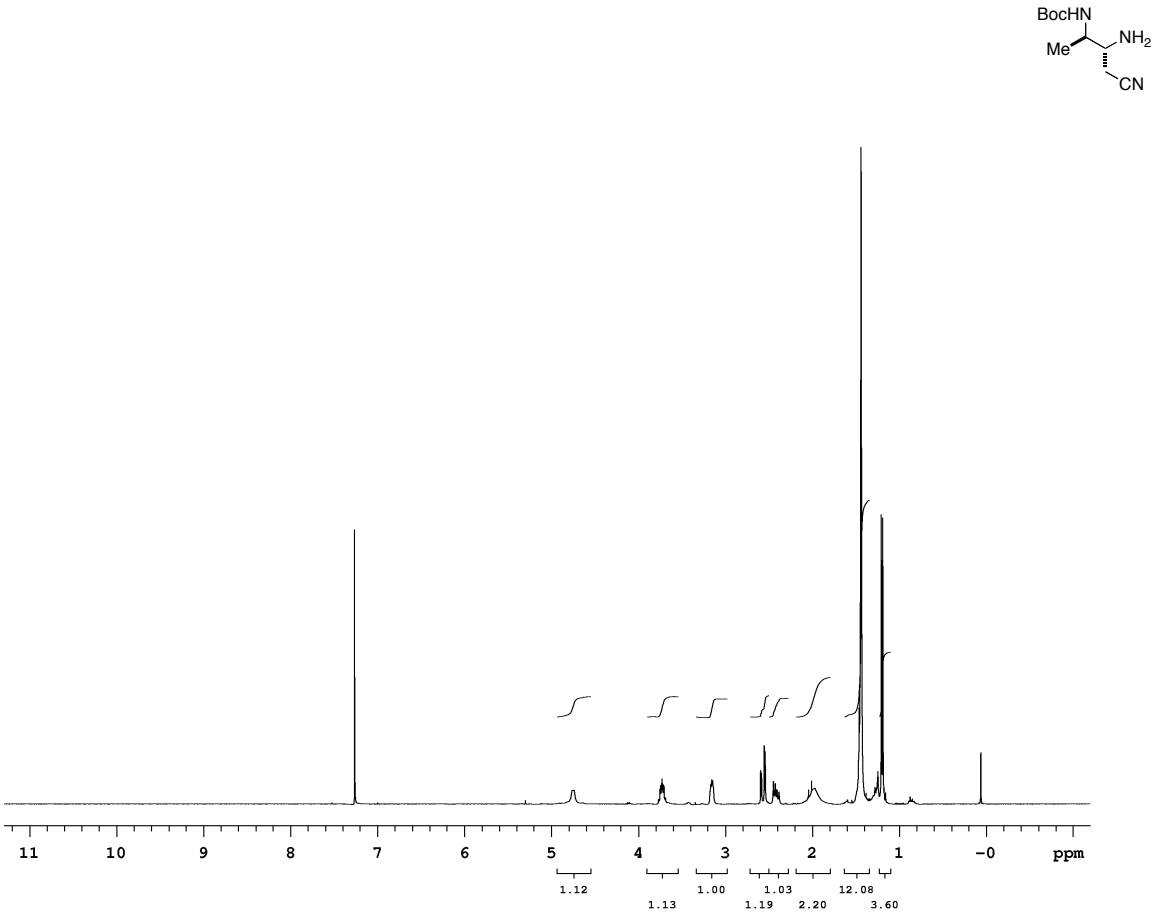
Temp. 50.0 C / 323.1 K

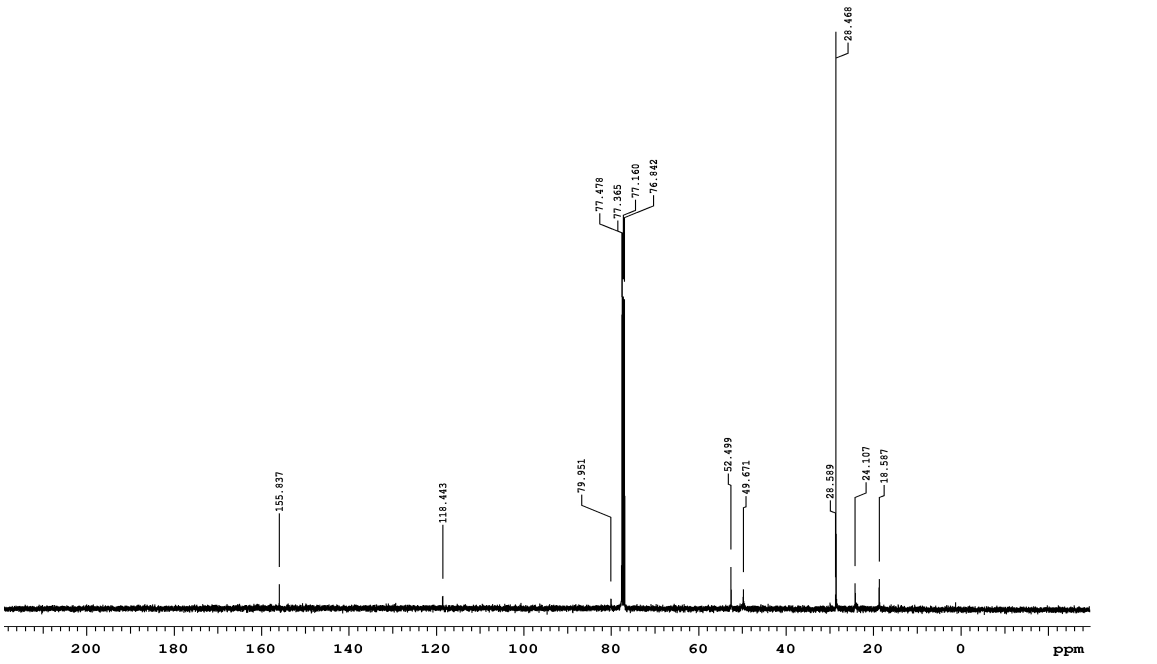
Relax. delay 0.500 sec
Pulse 38.1 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
512 repetitions
OBSERVE C13, 100.6081017 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 29 min

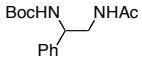


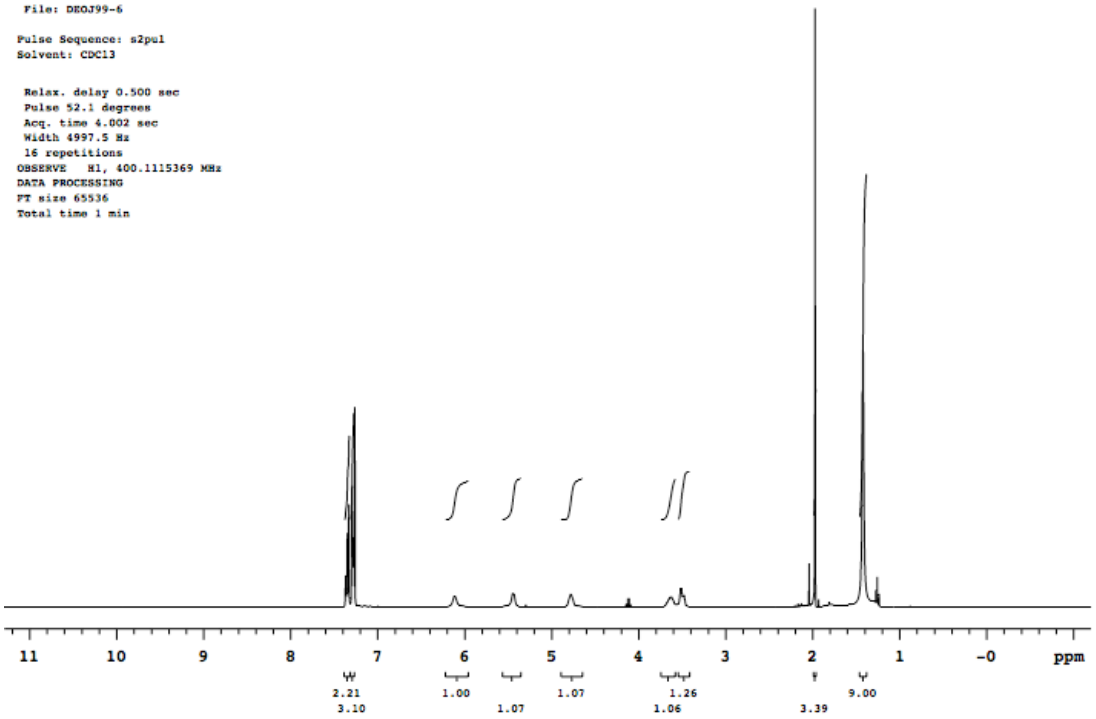

(pin)B
O
NHBoc
NH2
11
10
9
8
7
6
5
4
3
2
1
−0
ppm
2.00
2.07
0.95
2.04
1.01
1.20
0.97
3.05
1.33
13.34
9.37

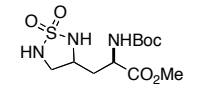

161.387
156.458
136.666
113.939
83.697
79.488
77.478
77.365
77.160
76.842
65.171
49.390
47.062
45.978
34.633
28.536
24.387
8.979
200
180
160
140
120
100
80
60
40
20
0
ppm


BocHN
Me
NH2
CN
11
10
9
8
7
6
5
4
3
2
1
−0
ppm
1.12
1.13
1.00
1.03
1.19
2.20
12.08
3.60

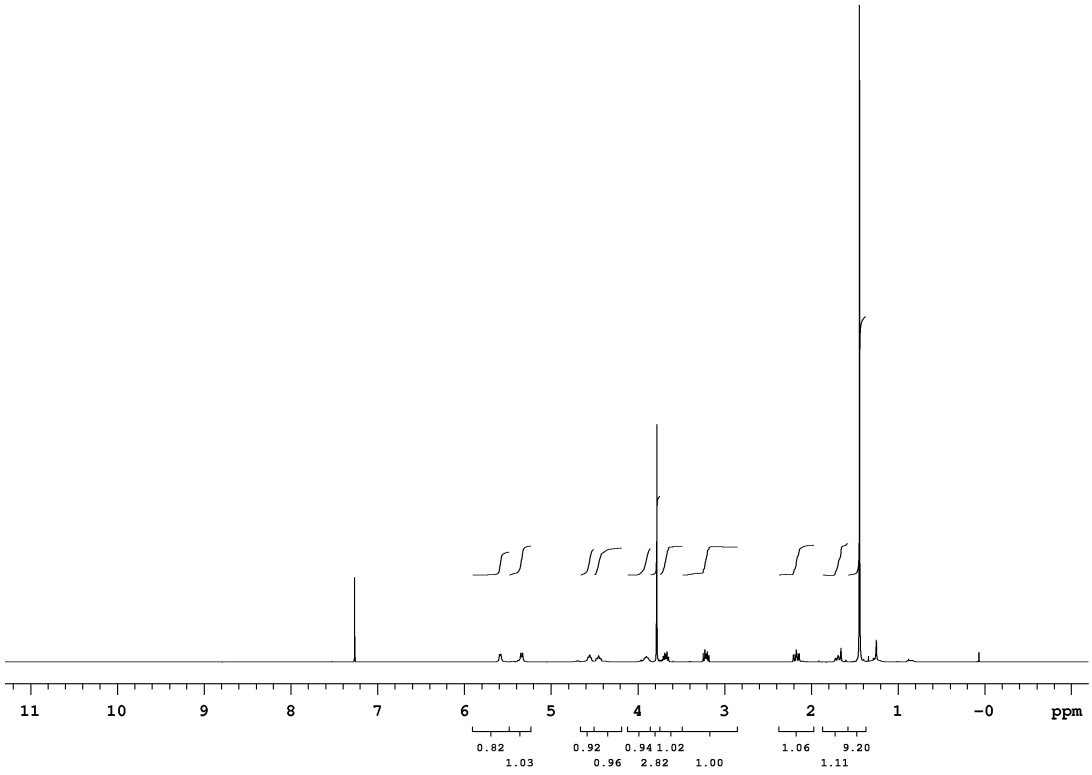

155.837
118.443
79.951
77.478
77.365
77.160
76.842
52.499
49.671
28.589
28.468
24.107
18.587
200
180
160
140
120
100
80
60
40
20
0
ppm

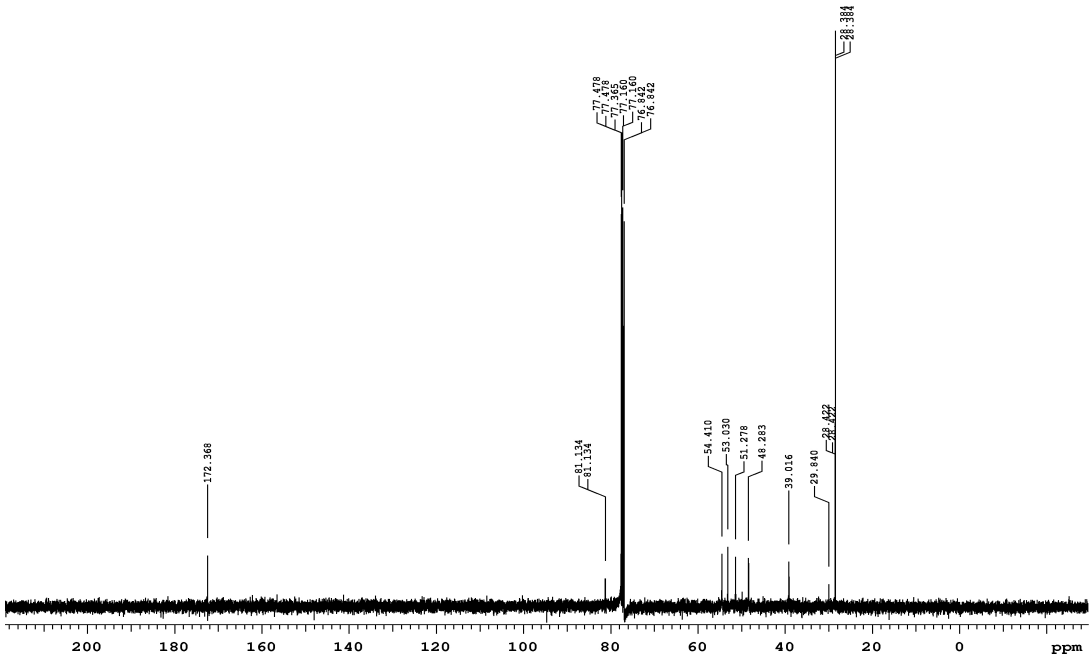

BocHN
NHAc
Ph

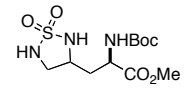

STANDARD 1H OBSERVE
Archive directory:
/export/home/deolson/vnmrsys/data
Sample directory:
File: DEOJ99-6
Pulse Sequence: s2pul
Solvent: CDCl3
Relax. delay 0.500 sec
Pulse 52.1 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
16 repetitions
OBSERVE H1, 400.1115369 MHz
DATA PROCESSING
FT size 65536
Total time 1 min
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
2.21
3.10
1.00
1.07
1.07
1.26
1.06
3.39
9.00



(more polar diastereomer)







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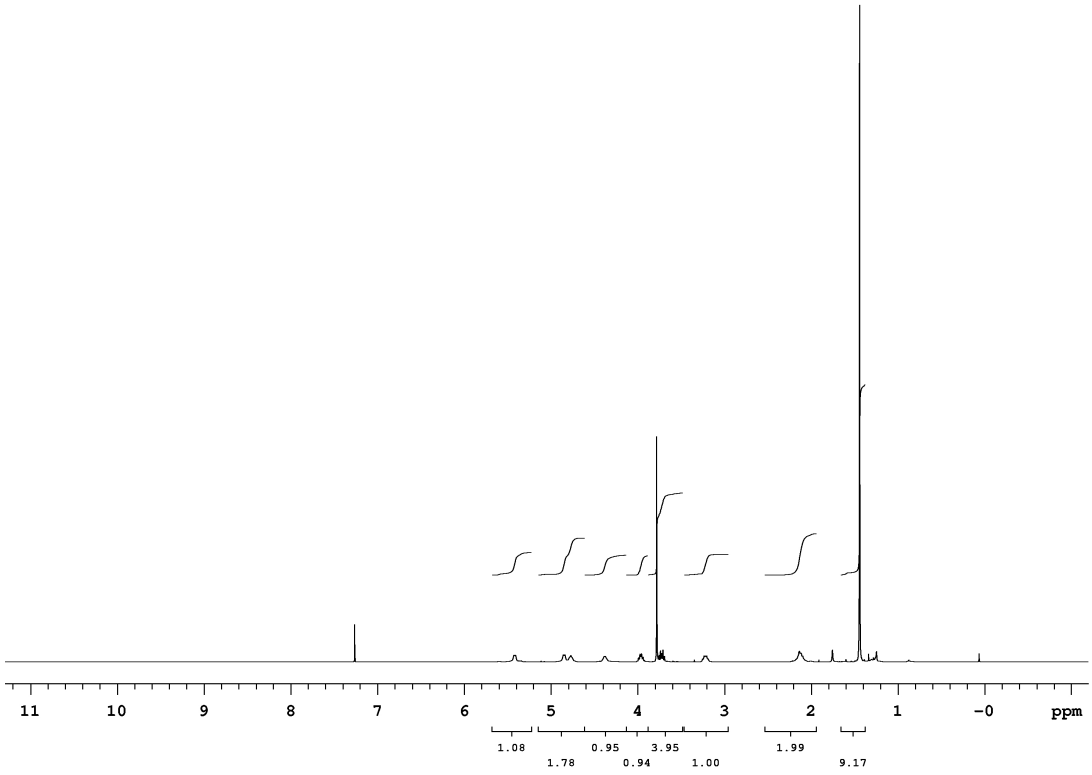

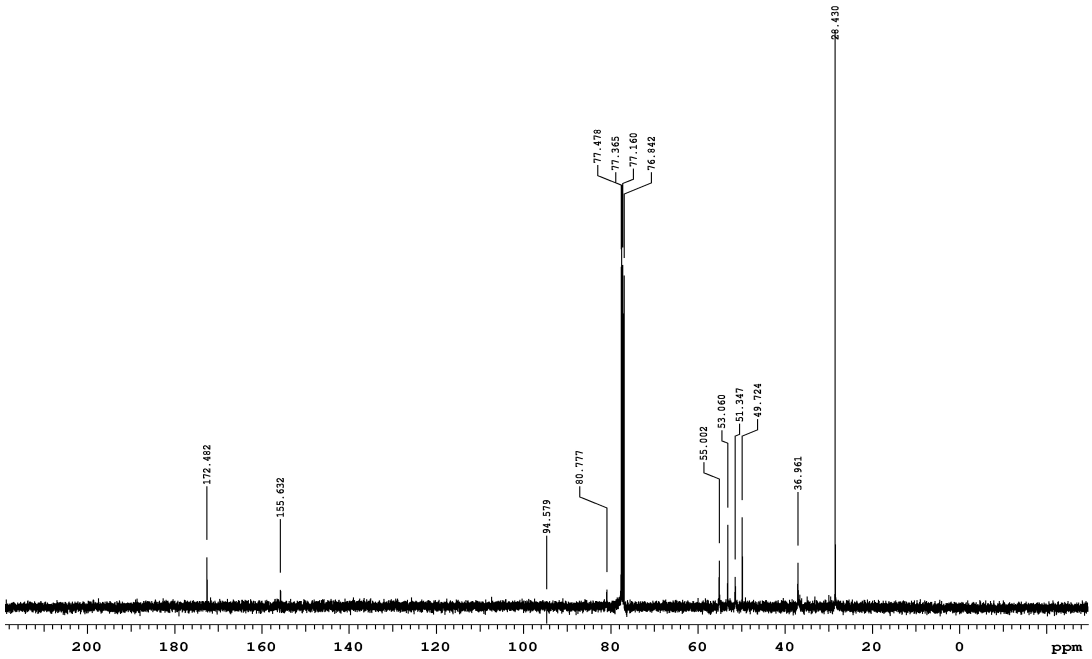

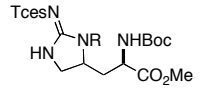

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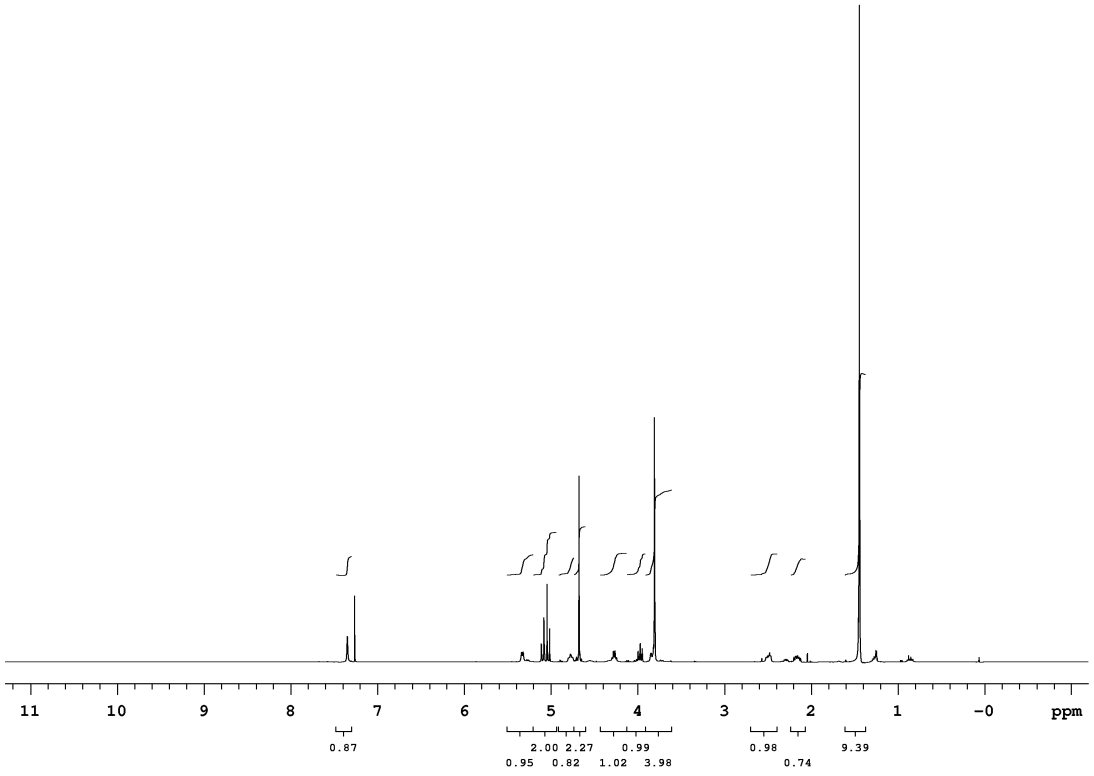
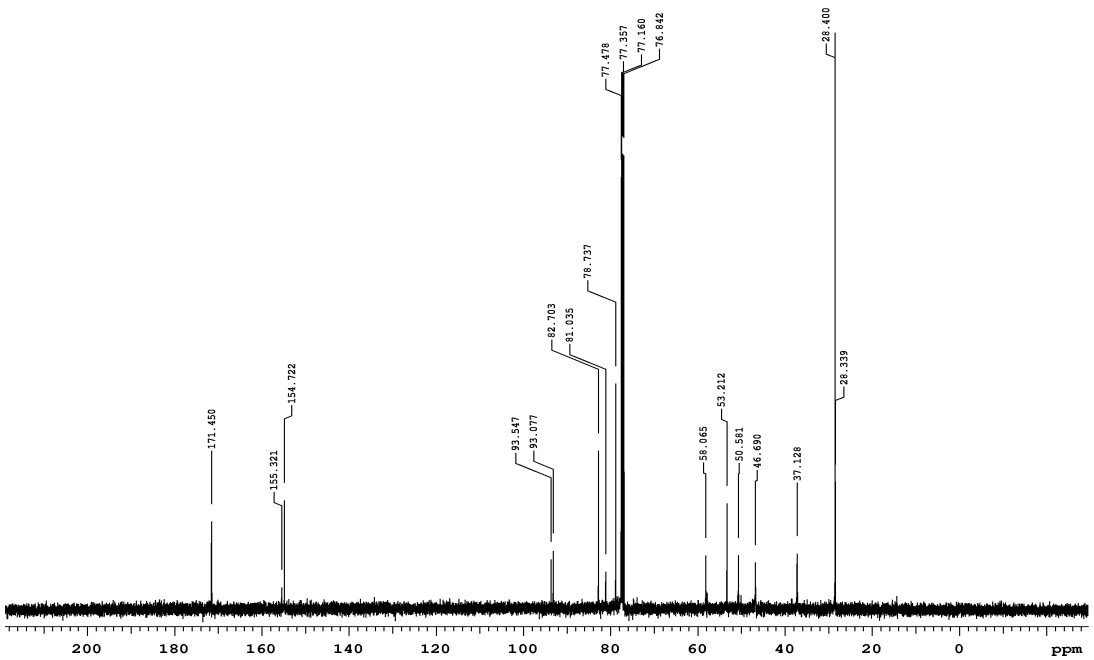
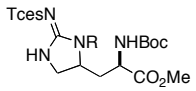
(more polar diastereomer)







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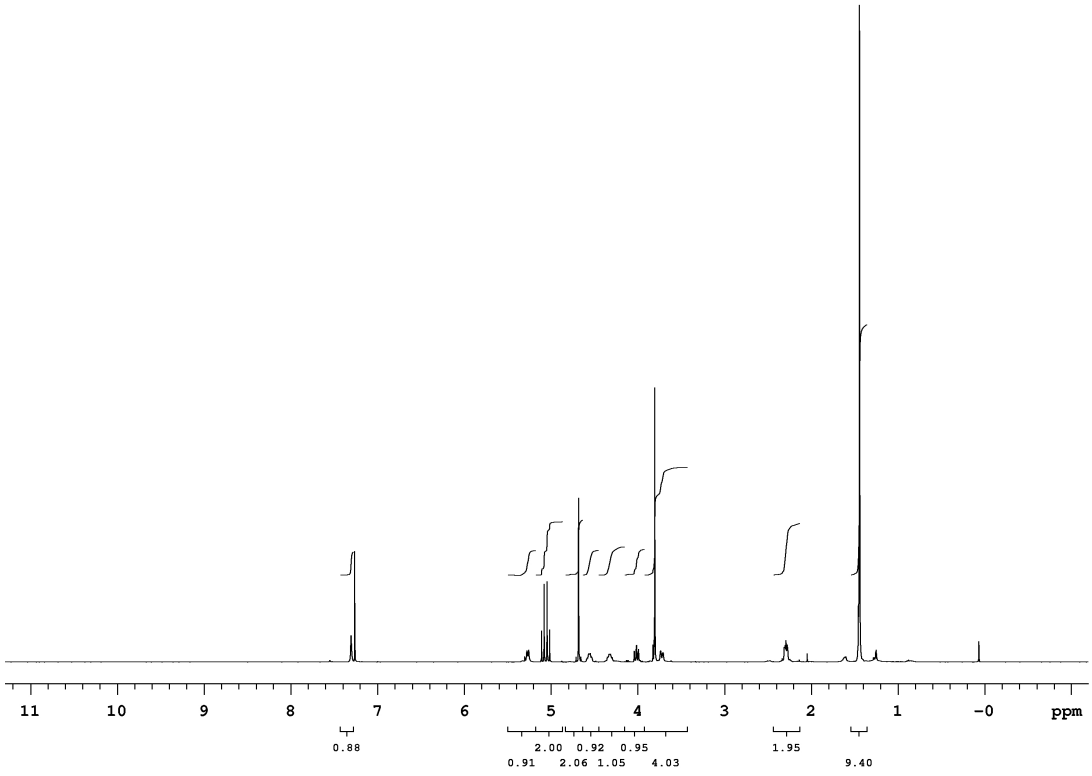

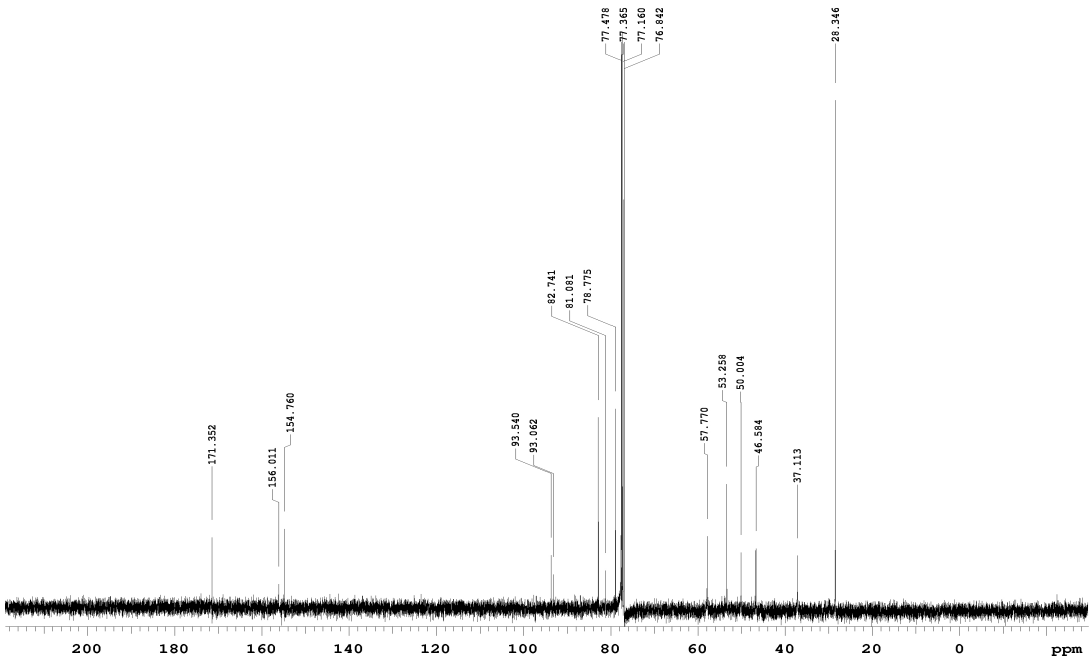

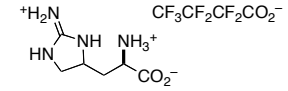

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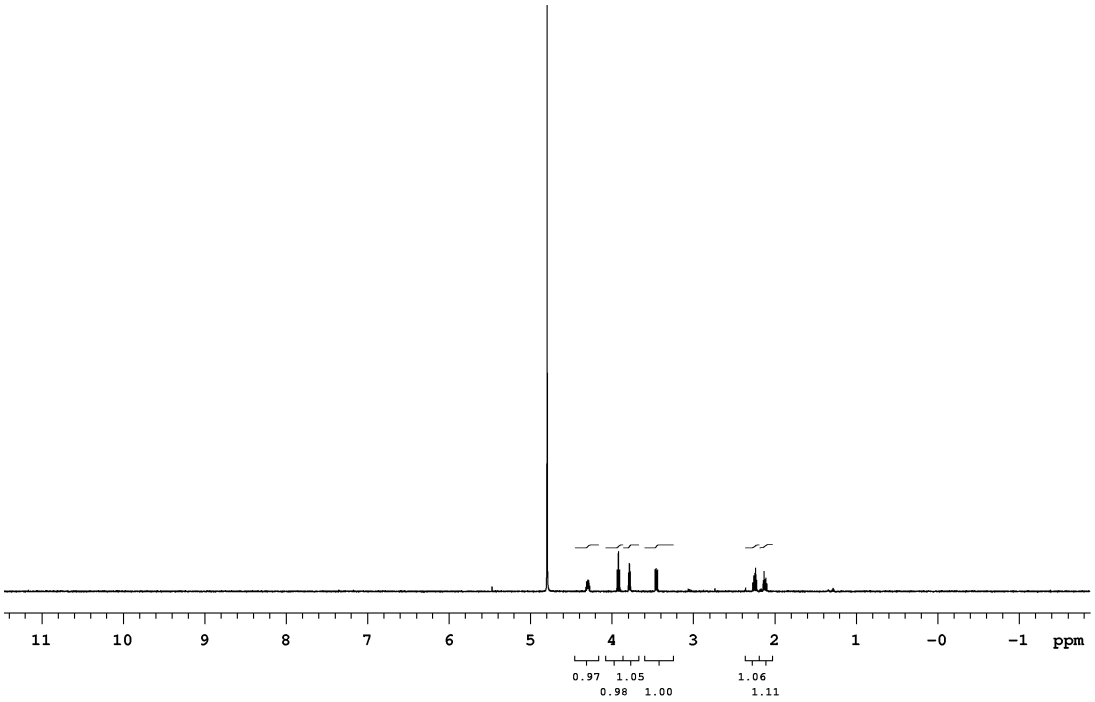

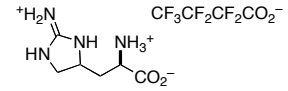

(less polar diastereomer)