Supporting Information for

Total Synthesis of the Reported Structure of Ceanothine D via a Novel Macrocyclization Strategy

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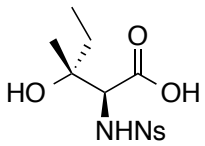
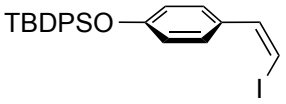
General Methods. All reactions were performed under an argon atmosphere except where otherwise noted. Solvents were purchased from Fisher Scientific and dried via an alumina column. Flash chromatography was carried out on Merck silica gel 60 (240-400 mesh) using the solvent conditions listed under individual experiments. Analytical thin-layer chromatography was performed on Merck silica gel (60F-254) plates (0.25 mm). Visualization of thin-layer chromatography plates was effected with ultraviolet light or phosphomolybdic acid (PMA) stain. Melting points (°C) are uncorrected. Proton magnetic resonance spectra (^{1}H NMR) and Carbon magnetic resonance spectra (^{13}C NMR) were performed on a Bruker NMR operating at 500 and 125 MHz respectively. Infrared spectra (IR) were obtained on a Bruker Alpha-P spectrometer. High resolution mass spectra (HRMS) were obtained on a Micromass Autospec or a Waters LCTOF-Xe premier. Optical rotations were measured on a Jasco P-1010 polarimeter. Single crystal X-ray structures were determined at the University of Pennsylvania. X-ray intensity data were collected on a Bruker APEXII [1] CCD area detector employing graphite monochromated Mo-Kα radiation (λ= 0.71073Å) at a temperature of 100K. Melting points were determined using a Thomas-Hoover capillary melting point apparatus and are uncorrected. All other starting materials and reagents were purchased from Sigma-Aldrich, TCI, Acros, or Strem and were used without further purification unless specified.

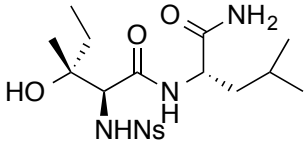


(2*S*,3*R*)-3-Hydroxy-3-methyl-2-((4-nitrophenyl)sulfonamido)pentanoic acid (5). To a solution of the known diol **6**[1] (1.95 g, 6.12 mmol) in MeCN (56 mL) and sodium phosphate buffer (0.25 M, pH 6.7, 24.5 mL), TEMPO (96 mg, 0.61 mmol), 80% $NaClO_2$ (1.52 g, 13.4 mmol), and NaOCl (0.11 mL of 8.25% bleach) were added. After stirring at 40 ^{o}C overnight, the reaction mixture was acidified to pH 3 with 10% aqueous citric acid solution. The resulting solution was extracted with EtOAc (3 x 100 mL), and the combined organic layers were concentrated *in vacuo*. The resulting residue was dissolved in saturated aqueous K_2CO_3 (35 mL) and water (35 mL) and washed with Et_2O (2 x 50 mL). The aqueous layer was acidified to pH 2 with conc. H_3PO_4, and extracted with EtOAc (5 x 70 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford the product **5** as a colorless oil (2.0 g, quant.), which was used without further purification. R_f = 0.2 (15% MeOH/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 6.9, 1.4 Hz, 1H), 7.94-7.92 (m, 1H), 7.80-7.75 (m, 2H), 6.44 (d, *J* = 9.6 Hz, 1H), 4.09 (d, *J* = 9.6 Hz, 1H), 2.19 (d, *J* = 0.8 Hz, 1H), 1.61 (dt, *J* = 18.0, 8.4 Hz, 2H), 1.28 (s, 3H), 0.91 (t, *J* = 7.22 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 147.5, 134.1, 133.5, 133.1, 130.5, 125.7, 74.7, 62.5, 30.9, 23.4, 7.7; IR (neat) 3306, 3103, 2922, 2853, 1723, 1541, 1443, 1355, 1303, 1170, 1125, 1058, 1004, 928, 855, 784, 743 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{12}H_{16}N_2O_7SNa$ $(M+Na)^+$: 355.0576, found: 355.0579; $[\alpha]_D^{22.5} = -129.1$ (*c* = 0.8 $CHCl_3$).

[1] Forbeck, E. M.; Evans, C. D.; Gilleran, J. A.; Li, P.; Joullié, M. M. *J. Am. Chem. Soc.* **2007**. *129*, 14463.



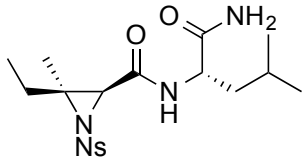
(*Z*)-*tert*-Butyl(4-(2-iodovinyl)phenoxy)diphenylsilane (4). To a suspension of methyltriphenylphosphonium iodide (5.19 g, 9.79 mmol) in anhydrous THF (54 mL) was added dropwise a solution of NaHMDS (1M in THF, 9.79 mL, 9.79 mmol) at room temperature. The resulting red-orange solution was left to stir at room temperature for 20 min. The resulting mixture was then cooled to −78 °C and to it was added HMPA (6.44 mL, 37.1 mmol) followed by a solution of 4-((2-methyl-2-propyl)diphenylsilyloxy)benzaldehyde[2] (2.67 g, 7.41 mmol) in anhydrous THF (37 mL) via cannula addition. The reaction mixture was left to stir at −78 °C for 2 h, and then quenched by addition of saturated aqueous $NaHCO_3$ (50 mL). The resulting mixture was warmed to room temperature, diluted with Et_2O (100 mL), and filtered through Celite. The biphasic layers were separated, and then organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash silica gel column chromatography (100% hexanes → 5% EtOAc/hexanes) afforded the desired product **4** as an yellow oil (2.87 g, 80%). R_f = 0.22 (100% hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.0, 1.0 Hz, 4H), 7.51-7.46 (m, 4H), 7.44-7.41 (m, 4H), 7.21 (d, *J* = 8.6 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 2H), 6.39 (dd, *J* = 8.6, 0.7 Hz, 1H), 1.17 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.9, 137.8, 135.5, 132.7, 130.0, 129.7, 129.4, 127.9, 119.4, 76.4, 26.5, 19.5; IR (neat) 3071, 3051, 3030, 2998, 2957, 2929, 2893, 2857, 1660, 1599, 1504, 1471, 1428, 1391, 1361, 1302, 1260, 1173, 1113, 1010, 998, 916, 843, 822, 741, 710, 701 cm^{-1}; HRMS (CI) *m/z* calculated for $C_{24}H_{25}OSiI$ $(M)^+$: 484.0708, found 484.0710.



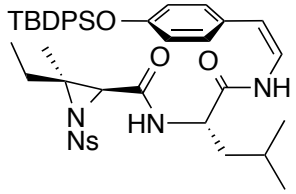
(2*S*,3*R*)-*N*-((*S*)-1-amino-4-methyl-1-oxopentan-2-yl)-3-hydroxy-3-methyl-2-((2-nitrophenyl)sulfonamido)pentanamide (7). To a solution of the acid **5** (406 mg, 1.24 mmol) in anhydrous DMF (12.4 mL) at 0 °C was added EDCI•HCl (473 mg, 2.47 mmol), HOBt (335 mg, 2.47 mmol), and NMM (0.4 mL, 3.71 mmol) sequentially. L-leucine amide (258 mg, 1.86 mmol) was then added in one portion and the resulting reaction mixture was allowed to warm to room temperature. After stirring at room temperature for 16 h, the reaction mixture was diluted with EtOAc (100 mL), washed with H_2O (2 x 40 mL), 10% aqueous $KHSO_4$ (30 mL), saturated aqueous $NaHCO_3$ (30 mL), and brine (30 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash silica gel chromatography (50% acetone/hexanes) afforded the product **7** (482 mg, 88%) as a white foam. R_f = 0.41 (50% acetone/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (dtdd, *J* = 5.3, 3.5, 2.4, 0.0 Hz, 1H), 7.92 (dt, *J* = 6.2, 3.3 Hz, 1H), 7.77 (dq, *J* = 6.2, 3.3 Hz, 2H), 7.14 (d, *J* = 8.7 Hz, 1H), 6.83 (d, *J* = 7.3 Hz, 1H), 6.62 (s, 1H), 6.15 (s, 1H), 4.37 (ddd, *J* = 12.1, 7.6, 4.3 Hz, 1H), 4.00 (s, 1H), 3.97 (d, *J* = 7.3 Hz, 1H), 1.55 (td, *J* = 9.1, 4.9 Hz, 3H), 1.46 (dd, *J* = 14.1, 7.3 Hz, 1H), 1.42-1.37 (m, 1H), 1.27 (s, 3H), 0.85 (d, *J* = 6.6 Hz, 3H), 0.80 (t, *J* = 7.4 Hz, 3H), 0.75 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 169.6, 147.6, 133.9, 133.11, 133.00, 131.0, 125.5, 74.6, 64.2, 51.6, 40.2, 29.9, 24.6, 23.3, 23.1, 21.3, 7.4; IR (neat) 3344, 3100, 2959, 2925, 2872, 2854, 1659, 1540, 1463, 1442, 1420, 1358, 1300, 1266, 1235, 1166, 1125, 1102, 1057, 1025, 926,

[2] Neubauer, T.; Kammerer-Pentier, C.; Bach, T. *Chem. Commun.* **2012**, *48*, 11629.

854, 784, 762, 735, 701 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{18}H_{28}N_4O_7SNa$ $(M+Na)^+$: 467.1576, found: 467.1573; $[a]_D^{22.1} = -36.9$ (c = 2.1 CH_2Cl_2).

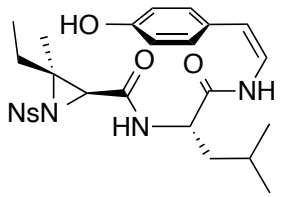


(2*S*,3*S*)-*N*-((*S*)-1-amino-4-methyl-1-oxopentan-2-yl)-3-ethyl-3-methyl-1-((2-nitrophenyl)sulfonyl)aziridine-2-carboxamide (3). To a solution of **7** (520 mg, 1.17 mmol) in anhydrous THF (12 mL) was added PPh_3 (461 mg, 1.75 mmol). The mixture was cooled to 0 °C and to it was added DIAD (350 mL, 1.75 mmol). The resulting reaction mixture was allowed to warm to room temperature and stirred until the complete consumption of the starting material was apparent via TLC. The reaction mixture was diluted with EtOAc (40 mL) and washed with 1M NaOH (10 mL) and brine (10 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Flash silica gel chromatography (20% acetone/methylene chloride) afforded the product **3** as a white solid (374 mg, 75%). R_f = 0.37 (30% acetone/dichloromethane); mp 144 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26-8.24 (m, 1H), 7.85-7.81 (m, 3H), 6.41-6.37 (m, 1H), 5.91-5.87 (m, 1H), 5.21-5.17 (m, 1H), 4.44-4.39 (m, 1H), 3.71 (s, 1H), 1.84 (s, 3H), 1.64-1.45 (m, 5H), 1.09 (t, *J* = 7.5 Hz, 3H), 0.90 (dd, *J* = 17.8, 6.3 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 165.5, 148.1, 134.9, 133.1, 132.6, 130.8, 124.8, 60.0, 53.9, 50.9, 40.9, 28.0, 24.8, 23.0, 21.6, 18.8, 9.7; IR (neat) 3453, 3248, 3194, 3080, 2957, 2871, 1677, 1532, 1368, 1341, 1244, 1162, 1125, 975, 923, 868, 858, 845, 777, 745cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{18}H_{27}N_4O_6S$ $(M+H)^+$: 427.1651, found: 427.1654; $[a]_D^{22.9} = +70.9$ (c = 0.5 $CHCl_3$).

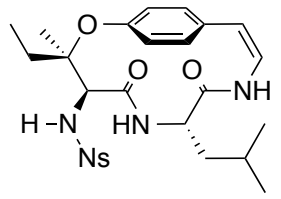


(2*S*,3*S*)-*N*-((*S*)-1-(((*Z*)-4-((*tert*-butyldiphenylsilyl)oxy)styryl)amino)-4-methyl-1-oxopentan-2-yl)-3-ethyl-3-methyl-1-((2-nitrophenyl)sulfonyl)aziridine-2-carboxamide (8). In a drybox, a 4 mL vial was charged with the aziridine **3** (50 mg, 0.117 mmol), CuI (4.0 mg, 0.019 mmol, 20 mol%), (1*S*,2*S*)-N,*N'*-dimethyl-1,2-diphenyl-1,2-ethylenediamine ((*S*,*S*)-DMPEDA, 10 mg, 0.039 mmol, 40 mol%), and Cs_2CO_3 (48 mg, 0.146 mmol). Vinyl iodide **4** (47 mg, 0.098 mmol) and anhydrous THF (1 mL) were then added, and the reaction vial was sealed with a Teflon-lined cap, removed from the drybox, and stirred at 70 °C for 16 h. The reaction was then cooled to room temperature and diluted with EtOAc (4 mL) and filtered through a Celite plug eluting with EtOAc (20 mL). The filtrate was then concentrated *in vacuo* and the residue was purified by flash silica gel chromatography (20% ethyl acetate/hexanes) to afford the desired product as a yellow oil (54 mg, 71%). R_f = 0.4 (30% ethyl acetate/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.91 (d, *J* = 11.1 Hz, 1H), 7.81-7.74 (m, 6H), 7.68 (td, *J* = 7.5, 1.3 Hz, 1H), 7.44 (dt, *J* = 5.2, 3.1 Hz, 2H), 7.39 (dddd, *J* = 7.0, 5.4, 3.6, 1.8 Hz, 4H), 7.01 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.61 (dd, *J* = 10.9, 9.7 Hz, 1H), 6.49 (d, *J* = 8.3 Hz, 1H), 5.64 (d, *J* = 9.6 Hz, 1H), 4.34 (td, *J* = 8.5, 5.6 Hz, 1H), 3.63 (s, 1H), 1.83 (s, 3H), 1.63-1.45 (m, 5H), 1.14 (s, 9H), 1.07 (s, 3H), 0.88 (dd, *J* = 20.9, 6.1 Hz, 6H); ^{13}C NMR

(125 MHz, $CDCl_3$) δ 168.3, 165.6, 154.7, 148.1, 135.5, 134.8, 132.70, 132.65, 132.4, 130.6, 130.0, 128.9, 127.90, 127.9, 127.83, 124.6, 120.3, 119.8, 111.3, 60.1, 53.6, 51.4, 40.2, 28.0, 26.5, 24.7, 22.9, 21.7, 19.5, 18.8, 9.8; IR (neat) 3303, 3073, 2959, 2932, 2859, 1656, 1604, 1546, 1518, 1489, 1429, 1390, 1366, 1343, 1256, 1203, 1168, 1114, 1059, 920, 850, 823, 742, 702 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{42}H_{50}N_4O_7SiS$ $(M+Na)^+$: 805.3067, found: 805.3063; $[a]_D^{21.8} = +38.9$ (*c* = 0.9 CH_2Cl_2).

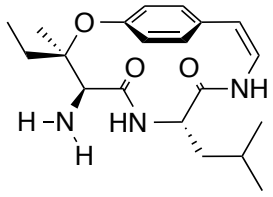


(2*S*,3*S*)-3-ethyl-*N*-((*S*)-1-(((*Z*)-4-hydroxystyryl)amino)-4-methyl-1-oxopentan-2-yl)-3-methyl-1-((2-nitrophenyl)sulfonyl)aziridine-2-carboxamide (2). To a solution of **8** (50 mg, 0.064 mmol) in anhydrous THF (1.3 mL) at 0 °C was added TBAF (1.0 M in THF, 70 mL, 0.070 mmol). The resulting mixture was stirred at 0 °C for 30 min until it was quenched with few drops of water. The mixture was then concentrated *in vacuo* and immediately purified via flash silica gel chromatography (40% ethyl acetate/hexanes) to afford the desired product as a colorless oil (32 mg, 91%). R_f = 0.5 (60% ethyl acetate/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 10.8 Hz, 1H), 8.14 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.81-7.71 (m, 3H), 7.12 (d, *J* = 8.5 Hz, 3H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.63 (td, *J* = 11.2, 9.4 Hz, 2H), 5.73 (d, *J* = 9.5 Hz, 1H), 4.47-4.42 (m, 1H), 3.68 (s, 1H), 1.81 (s, 3H), 1.63-1.56 (m, 3H), 1.55-1.47 (m, 2H), 1.06 (t, *J* = 7.5 Hz, 3H), 0.88 (dd, *J* = 27.8, 6.2 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.5, 166.4, 155.4, 148.0, 134.9, 132.67, 132.49, 130.6, 129.3, 127.0, 124.8, 119.7, 116.1, 112.1, 60.2, 53.5, 51.5, 40.0, 27.9, 24.7, 22.8, 21.7, 18.8, 9.7; IR (film) 3306, 2959, 2925, 1654, 1610, 1543, 1494, 1365, 1260, 1169, 1125, 853, 757 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{26}H_{31}N_4O_7S$ $(M-H)^+$: 543.1920, found: 543.1924; $[a]_D^{22.1} = +15.7$ (*c* = 0.5 $CHCl_3$).

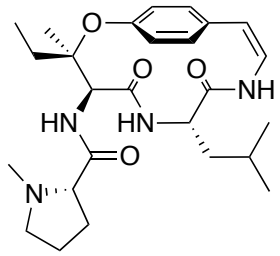


***N*-((3*R*,4*S*,7*S*,*Z*)-3-ethyl-7-isobutyl-3-methyl-5,8-dioxo-2-oxa-6,9-diaza-1(1,4)-benzenacycloundecaphan-10-en-4-yl)-2-nitrobenzenesulfonamide (9).** To a solution of **2** (45 mg, 0.083 mmol) in anhydrous MeCN (12 mL) was added 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 12 mg, 0.083 mmol). The reaction mixture was brought to 60 °C and was stirred until complete consumption of the starting material was apparent via TLC. Upon completion, the reaction mixture was concentrated *in vacuo* and the residue was purified via flash silica gel chromatography (60% ethyl acetate/hexanes) to afford the desired product as a white foam (14 mg, 40%). R_f = 0.2 (30% acetone/hexanes); ^{1}H NMR (500 MHz, acetone-d_6) δ 9.07 (d, *J* = 10.8 Hz, 1H), 8.12 (ddd, *J* = 16.2, 7.8, 1.2 Hz, 2H), 7.99 (td, *J* = 7.7, 1.4 Hz, 1H), 7.93 (td, *J* = 7.6, 1.2 Hz, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.03-7.01 (m, 1H), 6.99-6.97 (m, 2H), 6.70 (t, *J* = 10.2 Hz, 1H), 5.63 (d, *J* = 9.7 Hz, 1H), 4.49 (td, *J* = 8.8, 6.1 Hz, 1H), 4.43-4.42 (m, 1H), 2.14-2.08 (m, 1H), 1.88 (dq, *J* = 14.1, 7.2 Hz, 1H), 1.49 (ddd, *J* = 13.8, 8.2, 5.9 Hz, 1H), 1.41-1.33 (m, 1H), 1.29-1.23 (m, 1H), 1.22 (d, *J* = 6.9 Hz, 3H), 0.97 (t, *J* = 7.5 Hz, 3H), 0.82 (d, *J* = 6.6 Hz, 3H), 0.68 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, acetone-d_6) δ 169.7, 167.9,

153.4, 147.8, 134.19, 134.07, 133.3, 130.9, 130.1, 128.9, 125.7, 124.0, 121.2, 110.3, 84.0, 61.2, 51.1, 40.3, 31.6, 24.1, 22.4, 21.4, 20.3, 8.1; IR (film) 2959, 2924, 2854, 1650, 1542, 1490, 1465, 1363, 1171 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{52}H_{65}N_8O_{14}S_2$ $(2M+H)^+$: 1089.4062, found: 1089.4078; $[a]_D^{21.6} = +18.2$ (*c* = 0.3 $CHCl_3$).

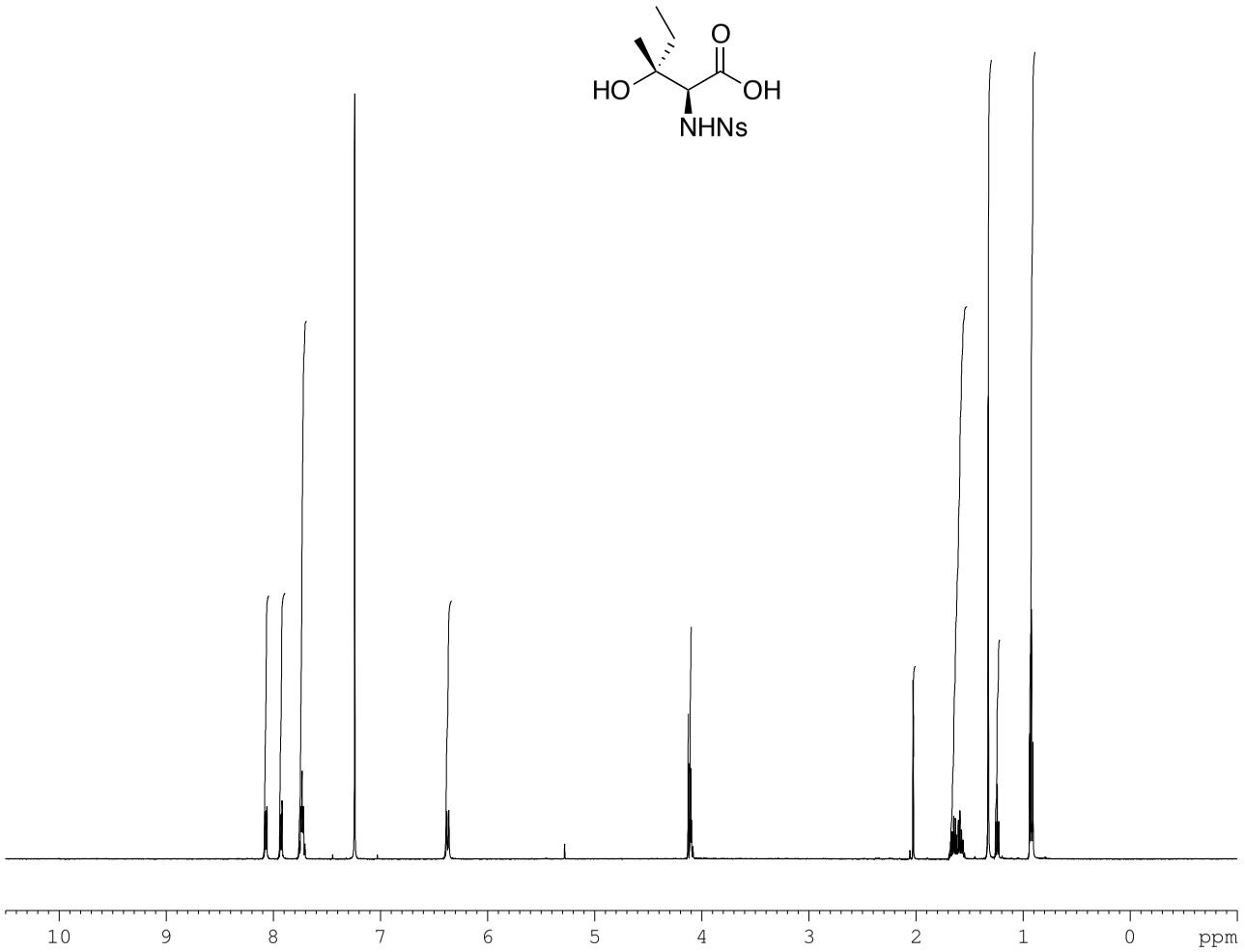


(3*R*,4*S*,7*S*,*Z*)-4-amino-3-ethyl-7-isobutyl-3-methyl-2-oxa-6,9-diaza-1(1,4)-benzenacycloundecaphan-10-ene-5,8-dione (10). To a solution of **9** (10 mg, 0.018 mmol) in anhydrous THF (0.18 mL) was added benzene thiol (6 mL, 0.055 mmol) and Cs_2CO_3 (8 mg, 0.024 mmol). The resulting mixture was allowed to stir at room temperature for 16 h. The reaction was then filtered through a Celite plug eluting with EtOAc (10 mL), and the resulting filtrate was concentrated *in vacuo*. Flash silica gel chromatography afforded the desired product as a colorless foam (5.3 mg, 82%). R_f = 0.45 (10% methanol/dichloromethane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.13 (d, *J* = 11.4 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.88 (dd, *J* = 11.2, 9.8 Hz, 1H), 5.67 (d, *J* = 9.7 Hz, 1H), 4.53-4.49 (m, 1H), 3.84 (s, 1H), 2.16-2.04 (m, 2H), 1.92-1.86 (m, 1H), 1.74-1.68 (m, 4H), 1.29 (s, 3H), 1.01 (d, *J* = 6.3 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.92 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.8, 169.5, 153.3, 130.3, 129.2, 121.3, 121.1, 109.7, 84.2, 60.5, 51.1, 38.2, 28.6, 24.6, 23.2, 21.4, 20.2, 7.8; IR (film) 3316, 2958, 2926, 2871, 2854, 1651, 1605, 1568, 1492, 1383, 1231, 1168, 1134, 895, 855, 755 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{20}H_{30}N_3O_3$ $(M+H)^+$: 360.2287, found: 360.2287; $[a]_D^{20.5} = +32.2$ (*c* = 0.3 $CHCl_3$).

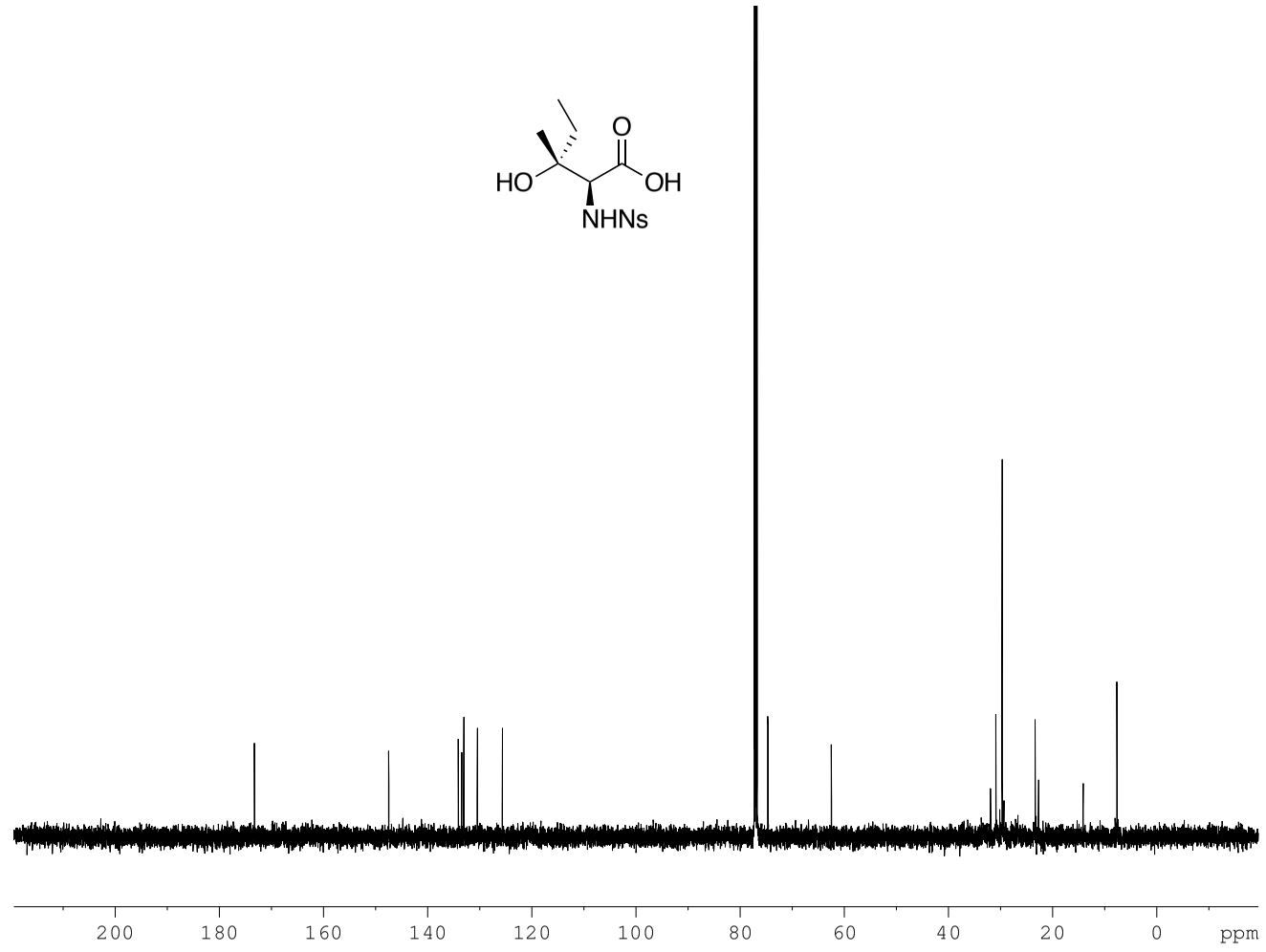


Ceanothine D: (*S*)-*N*-((3*R*,4*S*,7*S*,*Z*)-3-ethyl-7-isobutyl-3-methyl-5,8-dioxo 2-oxa-6,9-diaza-1(1,4)-benzenacycloundecaphan-10-en-4-yl)-1-methylpyrrolidine-2-carboxamide (1). To a solution of **10** (4 mg, 0.011 mmol) in anhydrous DMF at 0 °C was added *N*-methyl-L-proline (1.5 mg, 0.011 mmol), BOP (6 mg, 0.013 mmol), and Hünig's base (4 mL, 0.022 mmol). The resulting reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was diluted with EtOAc (5 mL) and washed with 10% aqueous $KHSO_4$ (1 mL), saturated aqueous $NaHCO_3$ (1 mL), and brine (1 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification via flash silica gel chromatography (5% methanol/methylene chloride) afforded the desired final product as a white foam (3.1 mg, 60%). R_f = 0.3 (5% methanol/chloroform); ^{1}H NMR (500 MHz, acetone-d_6) δ 9.04 (d, *J* = 11.3 Hz, 1H), 8.22 (d, *J* = 9.2 Hz, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 6.85 (t, *J* = 10.5 Hz, 1H), 5.70 (d, *J* = 9.8 Hz, 1H), 4.63-4.57 (m, 2H), 3.20-3.17 (m, 1H), 2.81 (dd, *J* = 9.9, 4.9 Hz, 1H), 2.41 (s, 3H), 2.38 (dd, *J* = 8.8, 7.1 Hz, 1H), 2.24-2.19 (m, 1H), 1.83-1.79 (m, 2H), 1.77-1.72 (m, 1H), 1.67 (ddd, *J* = 19.7, 10.0, 5.8 Hz, 1H), 1.57 (dtd, *J* = 22.0, 14.6, 7.3 Hz, 2H), 1.38 (s, 2H), 1.31 (s, 3H), 0.91 (d, *J* = 6.3 Hz, 3H), 0.86 (d, *J* = 6.3 Hz, 3H), 0.83 (t,

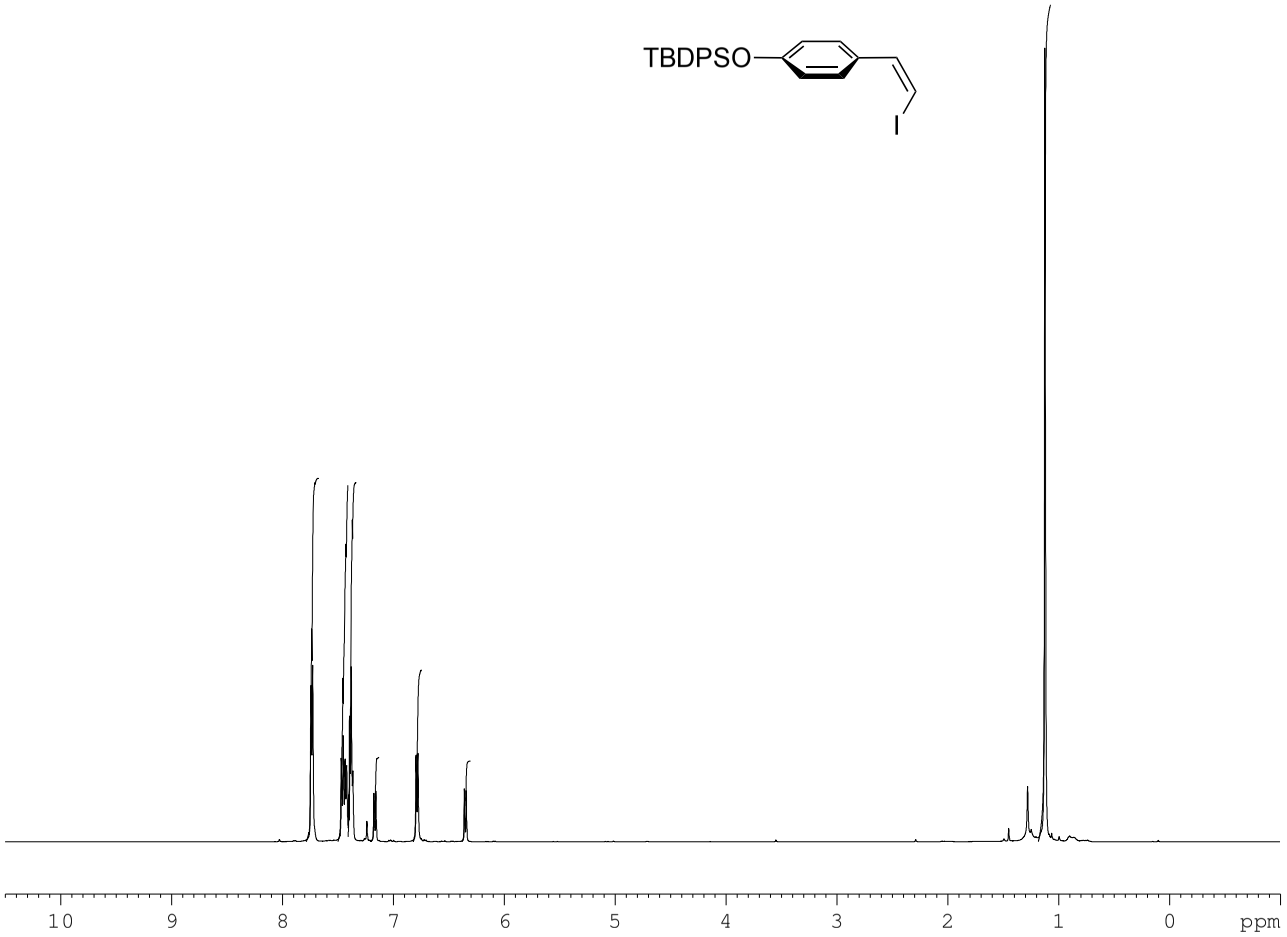
J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, acetone-d_6) δ 173.2, 170.5, 169.5, 153.1, 131.1, 128.9, 124.5, 120.8, 109.2, 83.5, 69.0, 56.3, 51.4, 40.8, 38.8, 30.7, 29.8, 29.2, 24.2, 24.0, 22.5, 20.8, 20.7, 8.0; IR (film) 3103, 3091, 3072, 3056, 2938, 2859, 1648, 1587, 1560, 1541, 1478, 1449, 1395, 1328, 1279, 1161, 1087, 1031, 1014, 974, 909, 877, 857, 829, 793 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{26}H_{39}N_4O_4$ $(M+H)^+$: 471.2971, found: 471.2962; $[a]_D^{22} = +128.6$ (c = 0.1 CH_3OH); $[a]_D^{22} = +14.1$ (c = 1.5 $CHCl_3$).



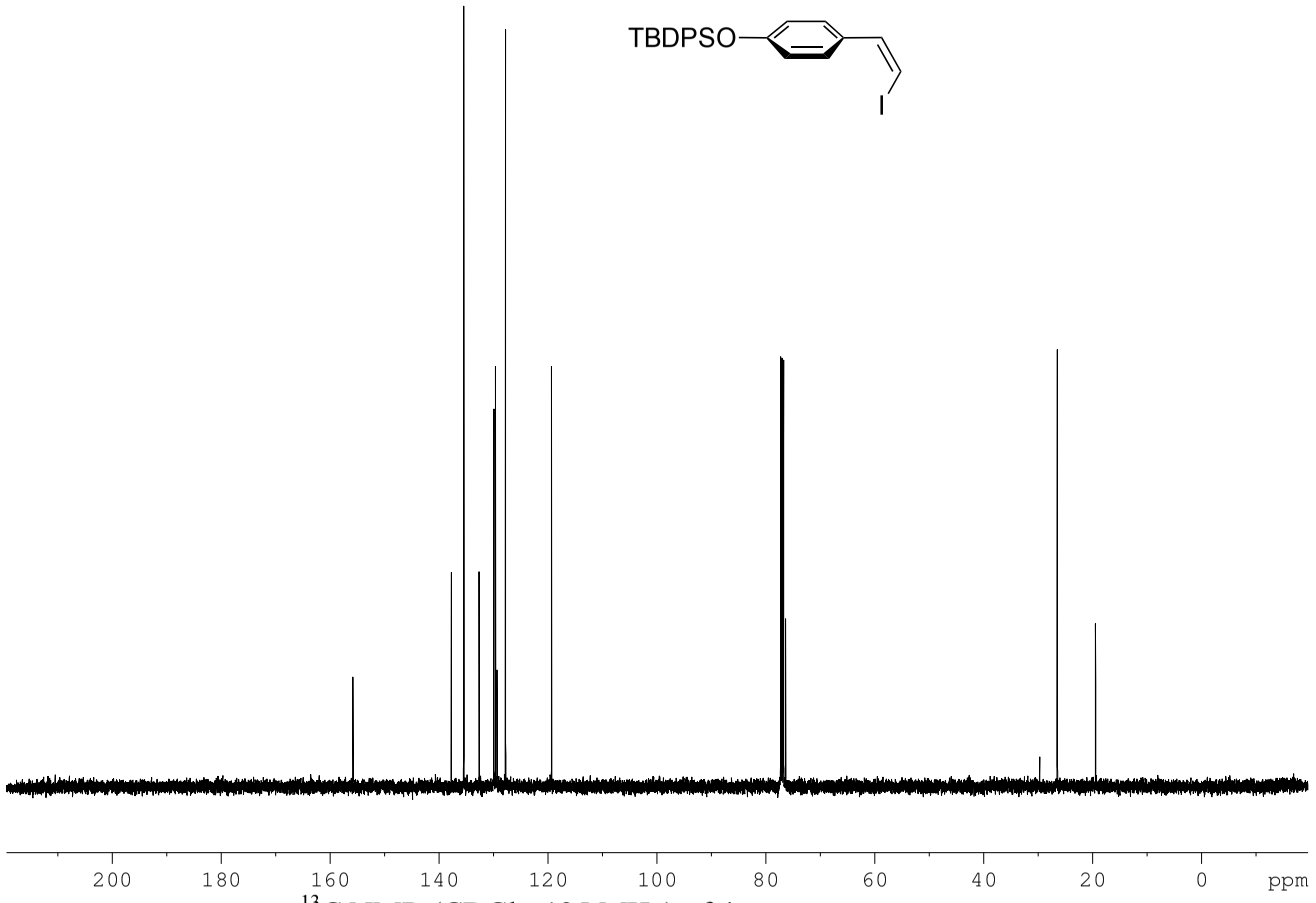
^{1}H NMR ($CDCl_3$, 500 MHz) of **5**



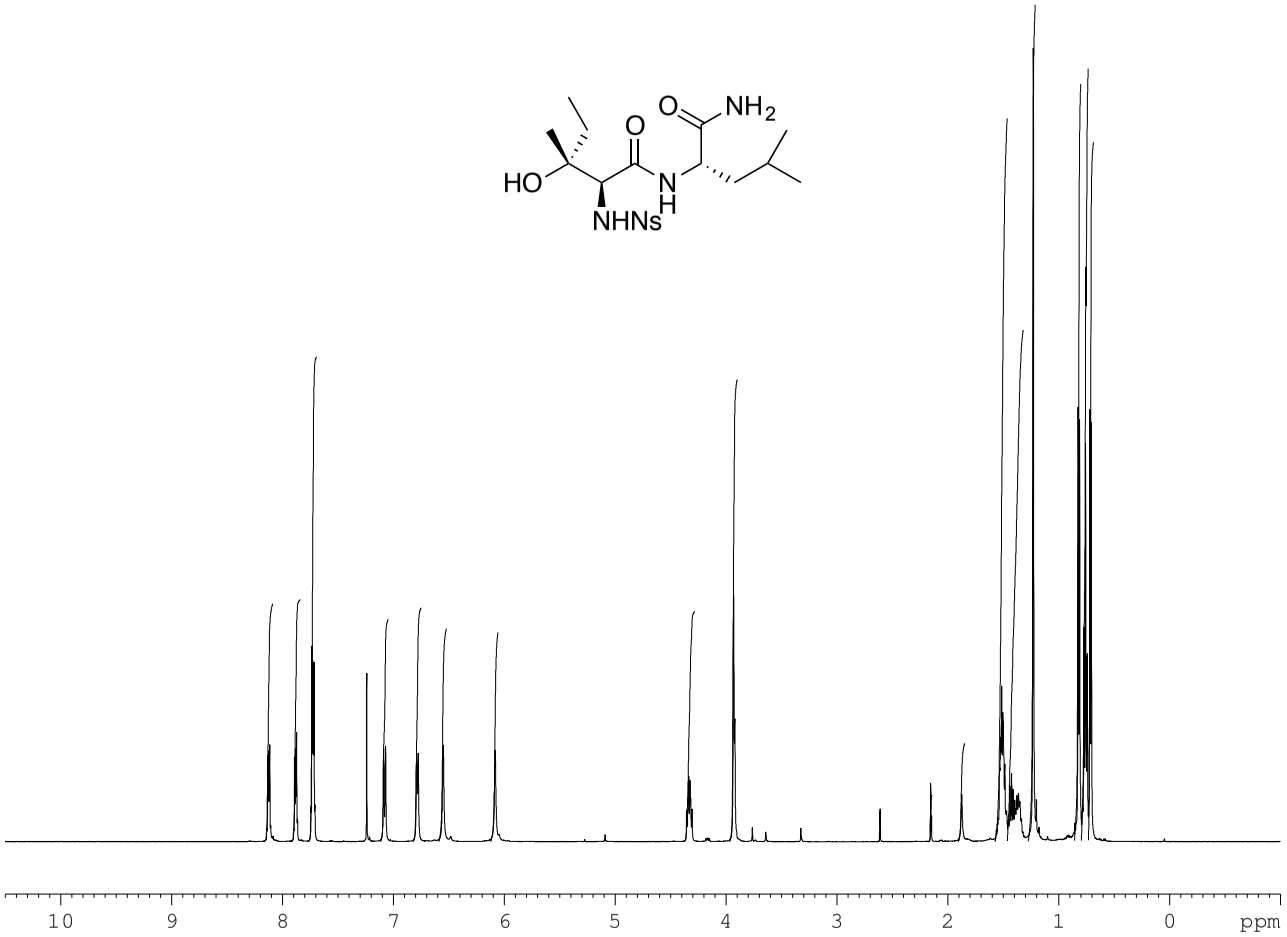
^{13}C NMR ($CDCl_3$, 125 MHz) of **5**



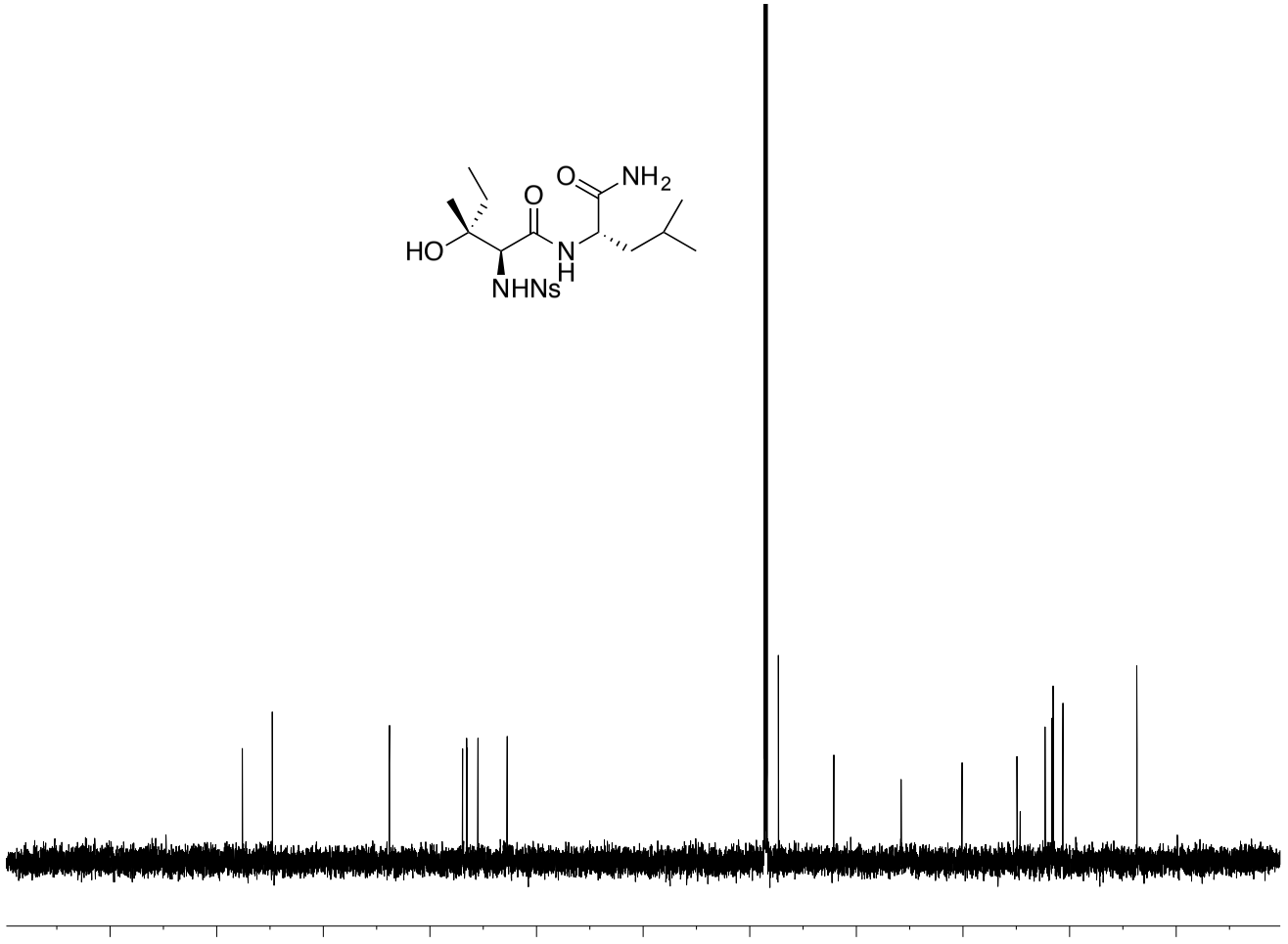
^{1}H NMR ($CDCl_3$, 500 MHz) of **4**



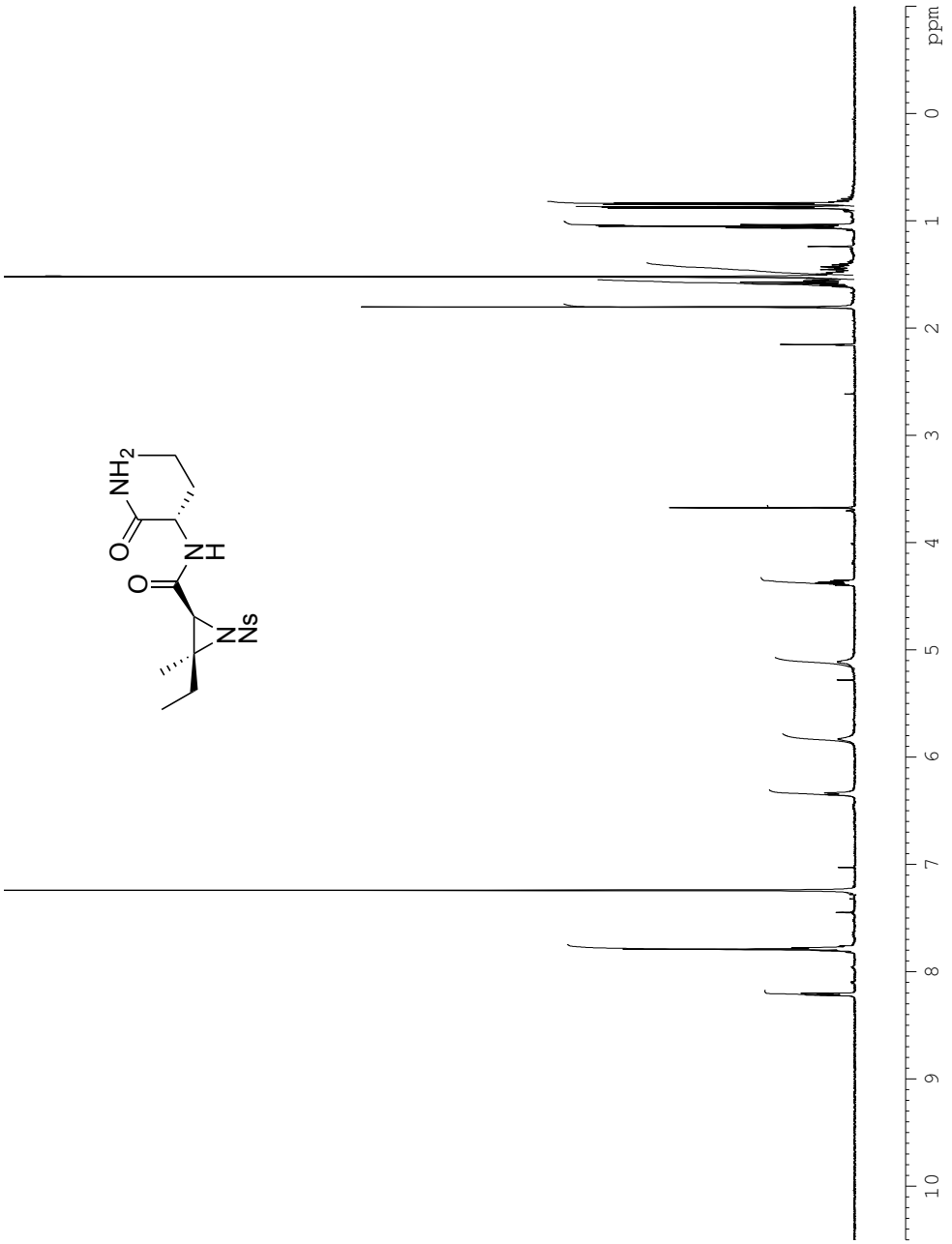
^{13}C NMR ($CDCl_3$, 125 MHz) of **4**



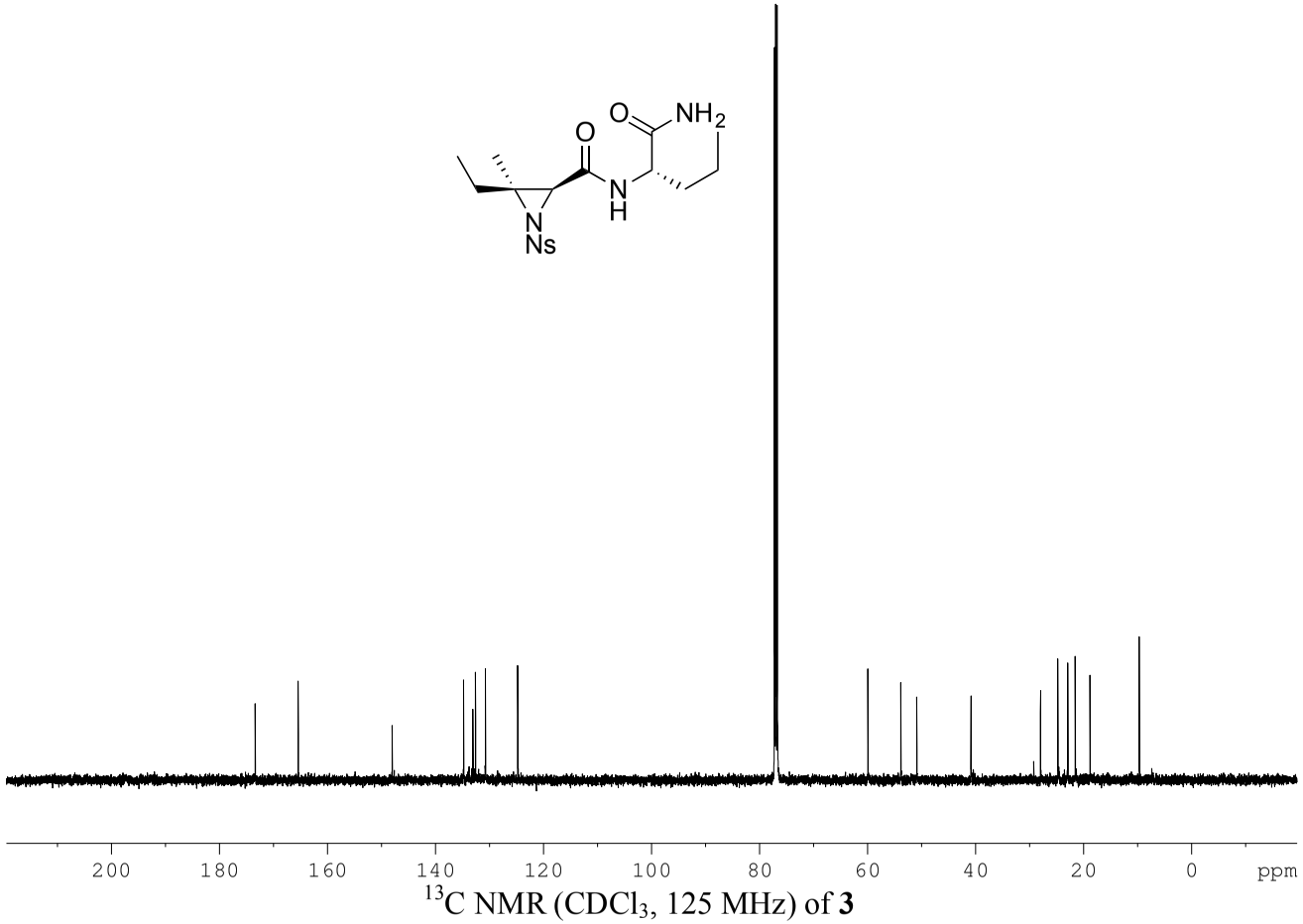
^{1}H NMR ($CDCl_3$, 500 MHz) of **7**



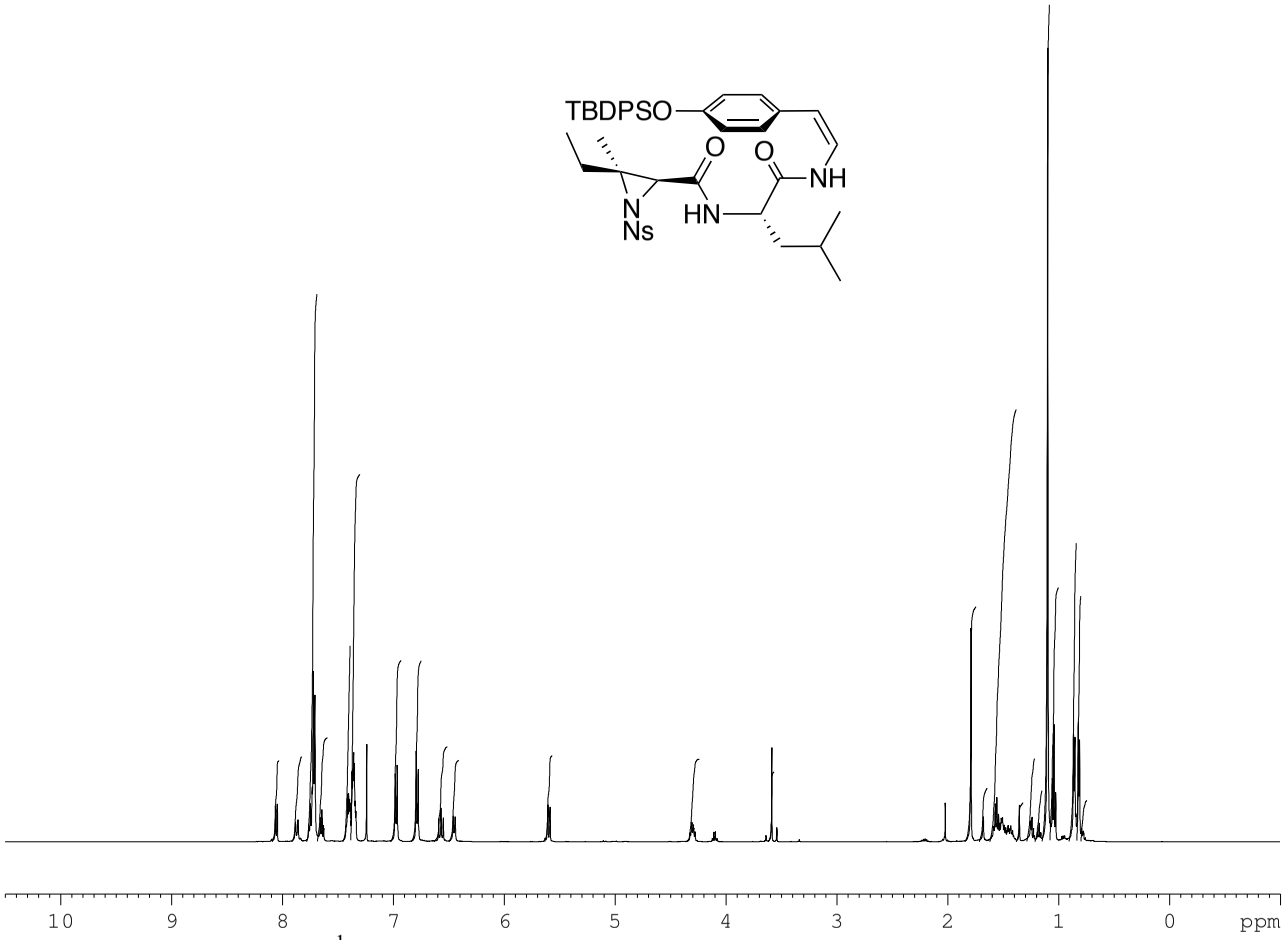
^{13}C NMR ($CDCl_3$, 125 MHz) of **7**



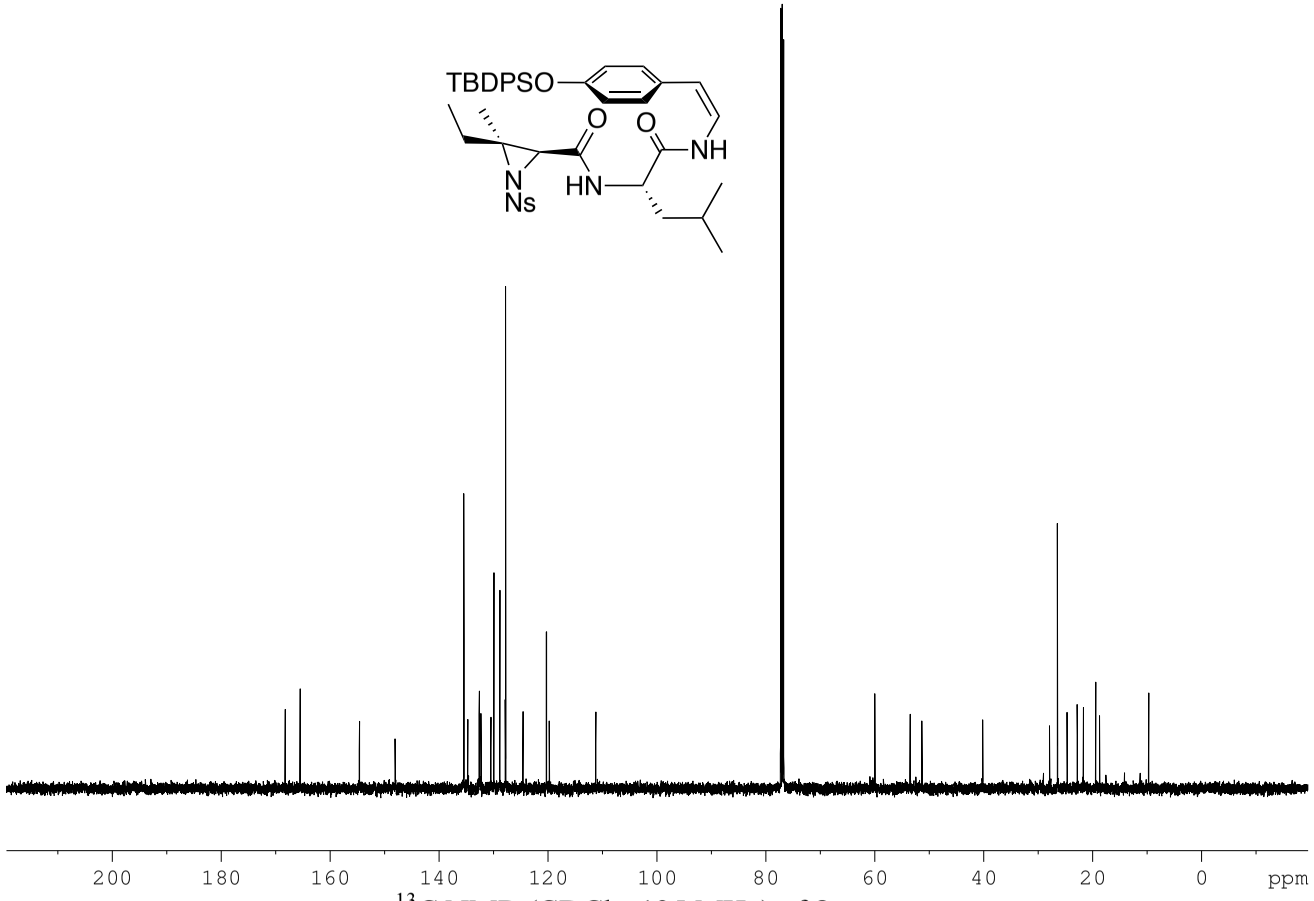
^{1}H NMR ($CDCl_3$, 500 MHz) of **3**



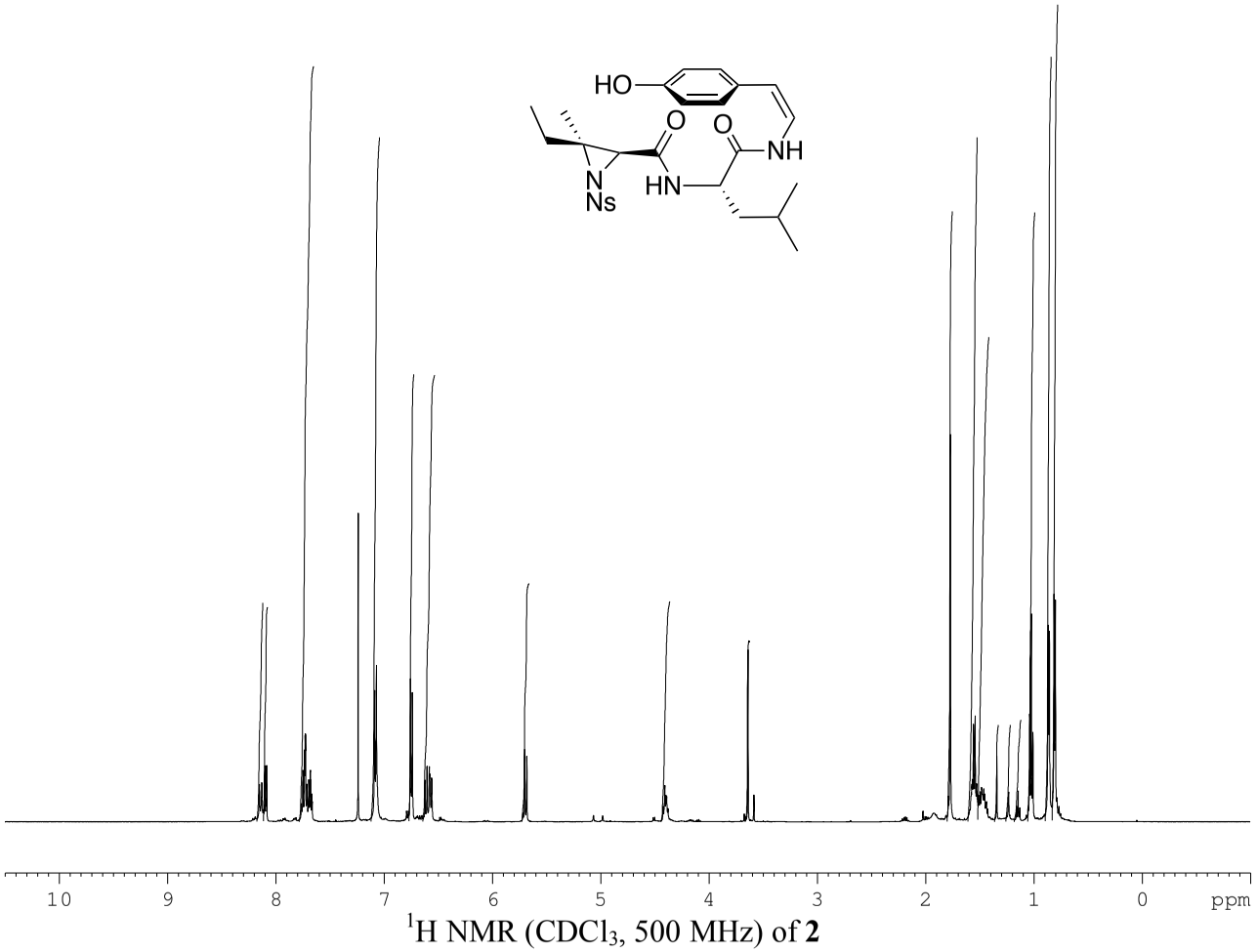
^{13}C NMR ($CDCl_3$, 125 MHz) of **3**



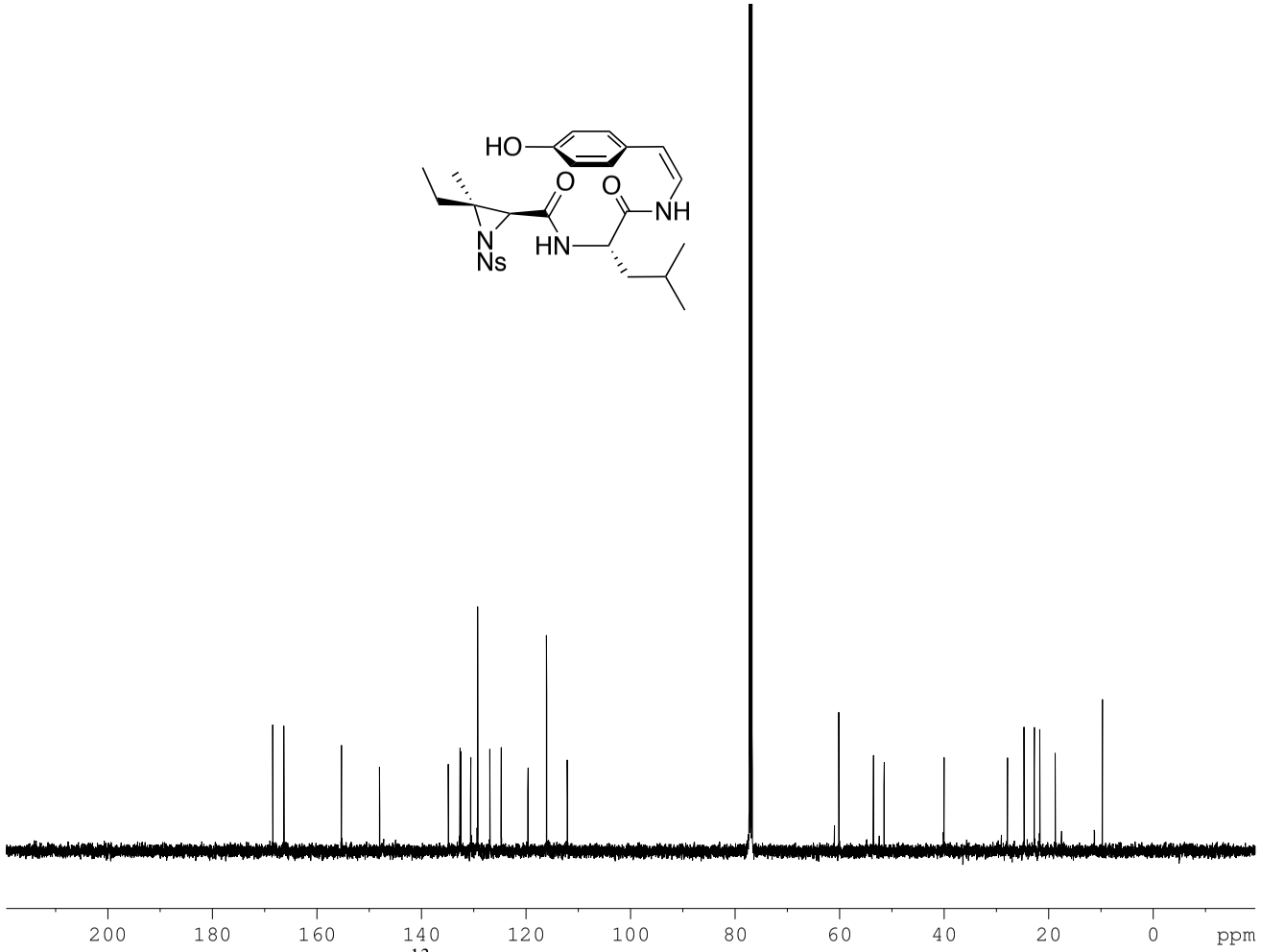
^{1}H NMR ($CDCl_3$, 500 MHz) of **8**



^{13}C NMR ($CDCl_3$, 125 MHz) of **8**

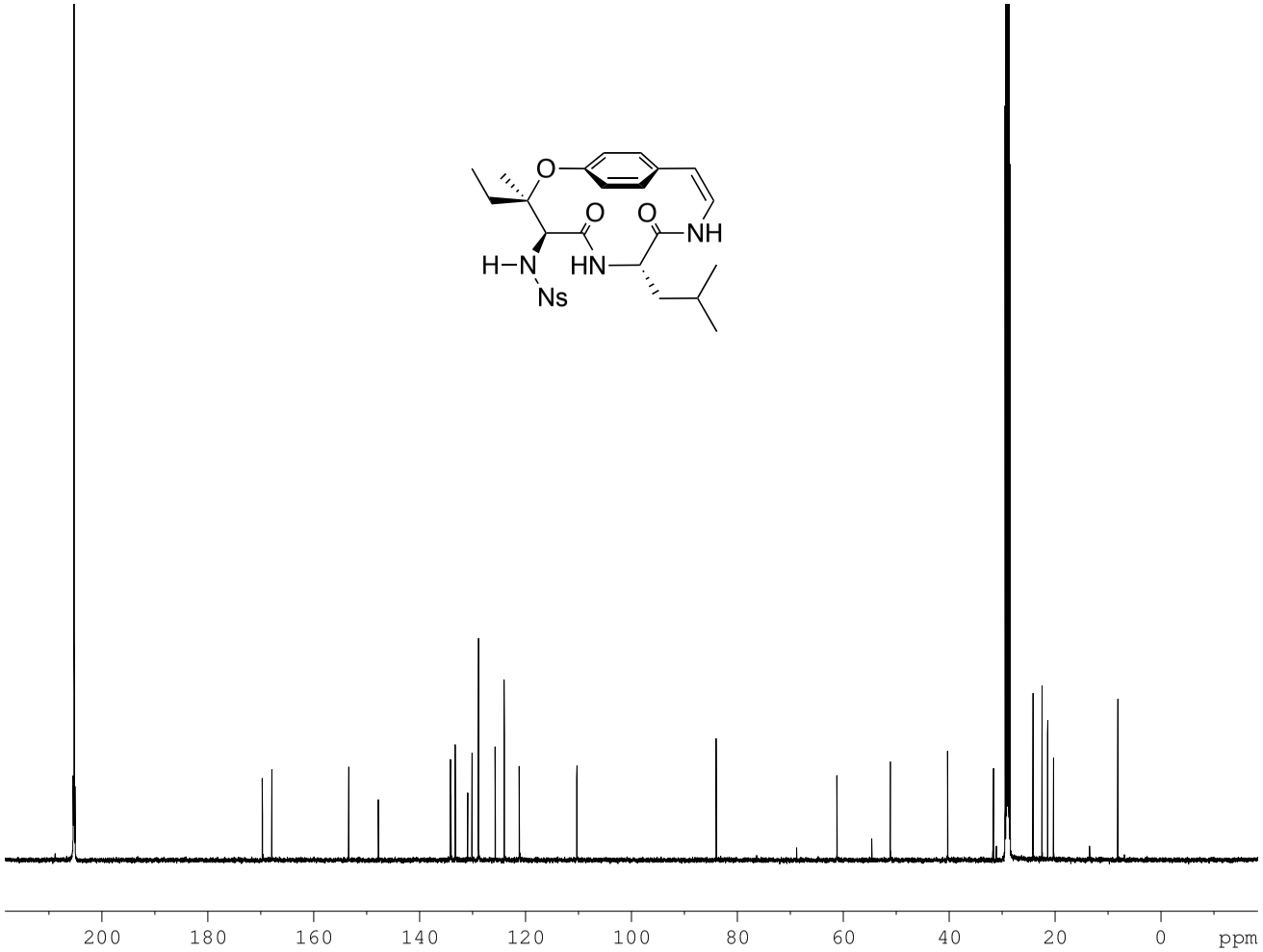


^{1}H NMR ($CDCl_3$, 500 MHz) of **2**

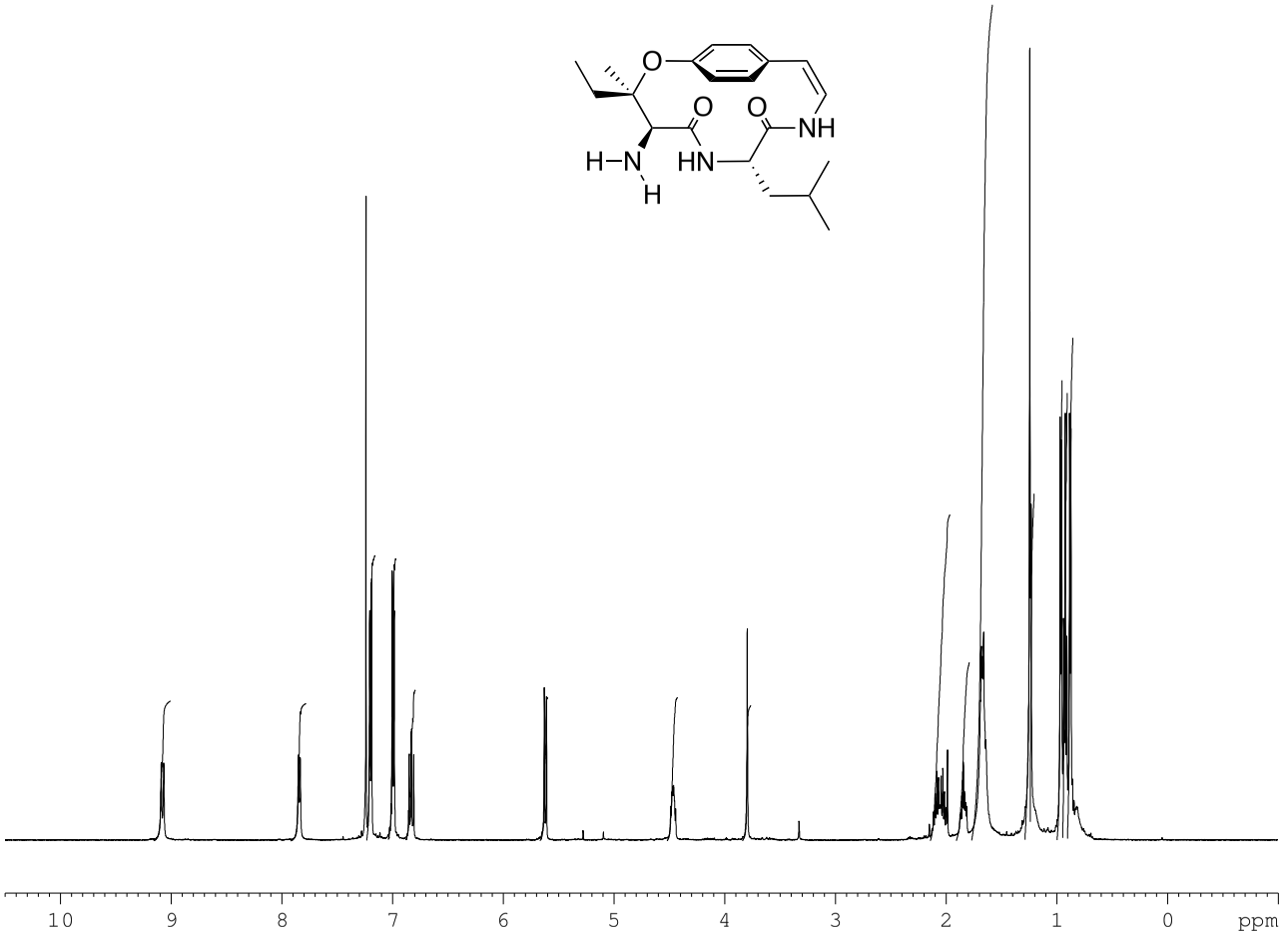


^{13}C NMR ($CDCl_3$, 125 MHz) of **2**

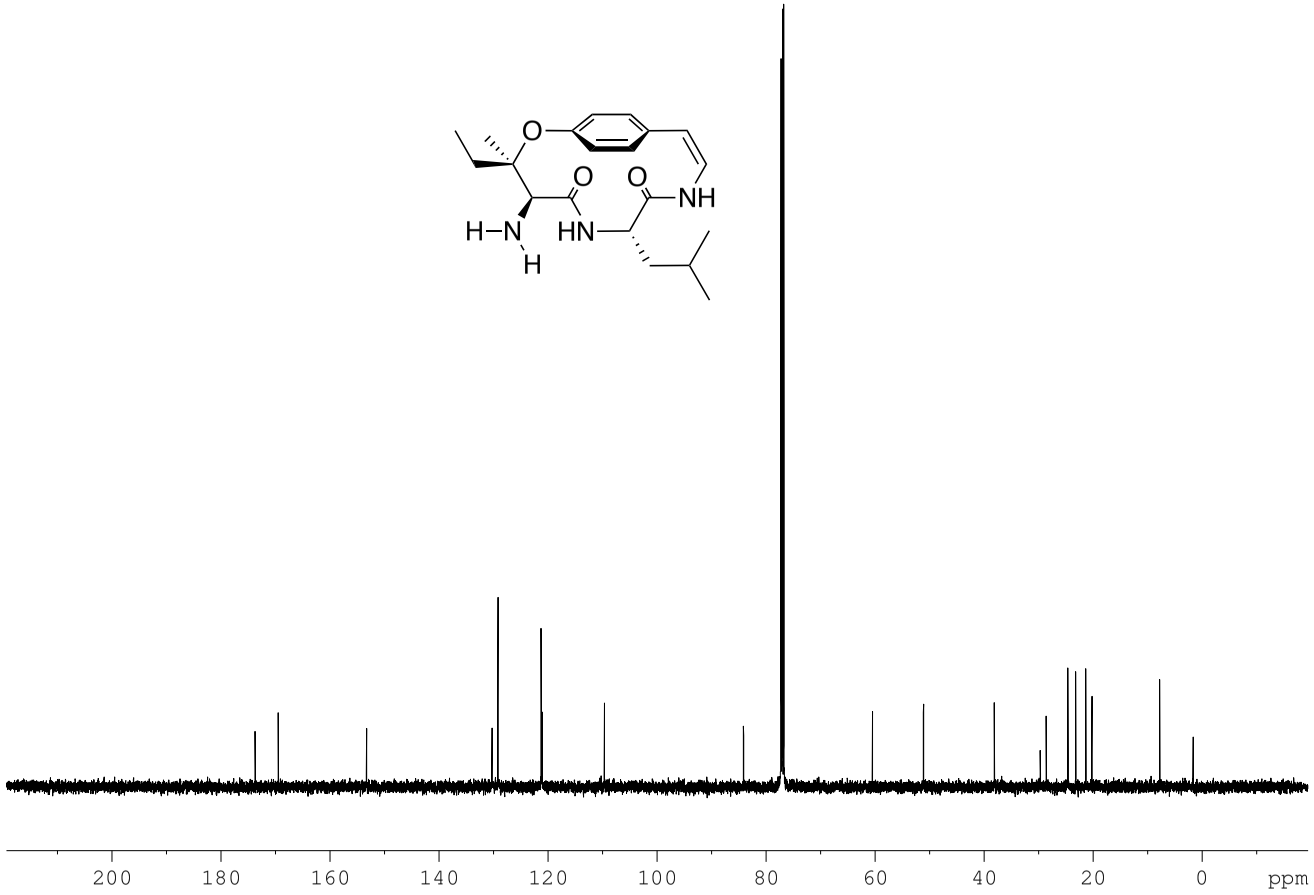
^{1}H NMR (acetone-d_6, 500 MHz) of **9**



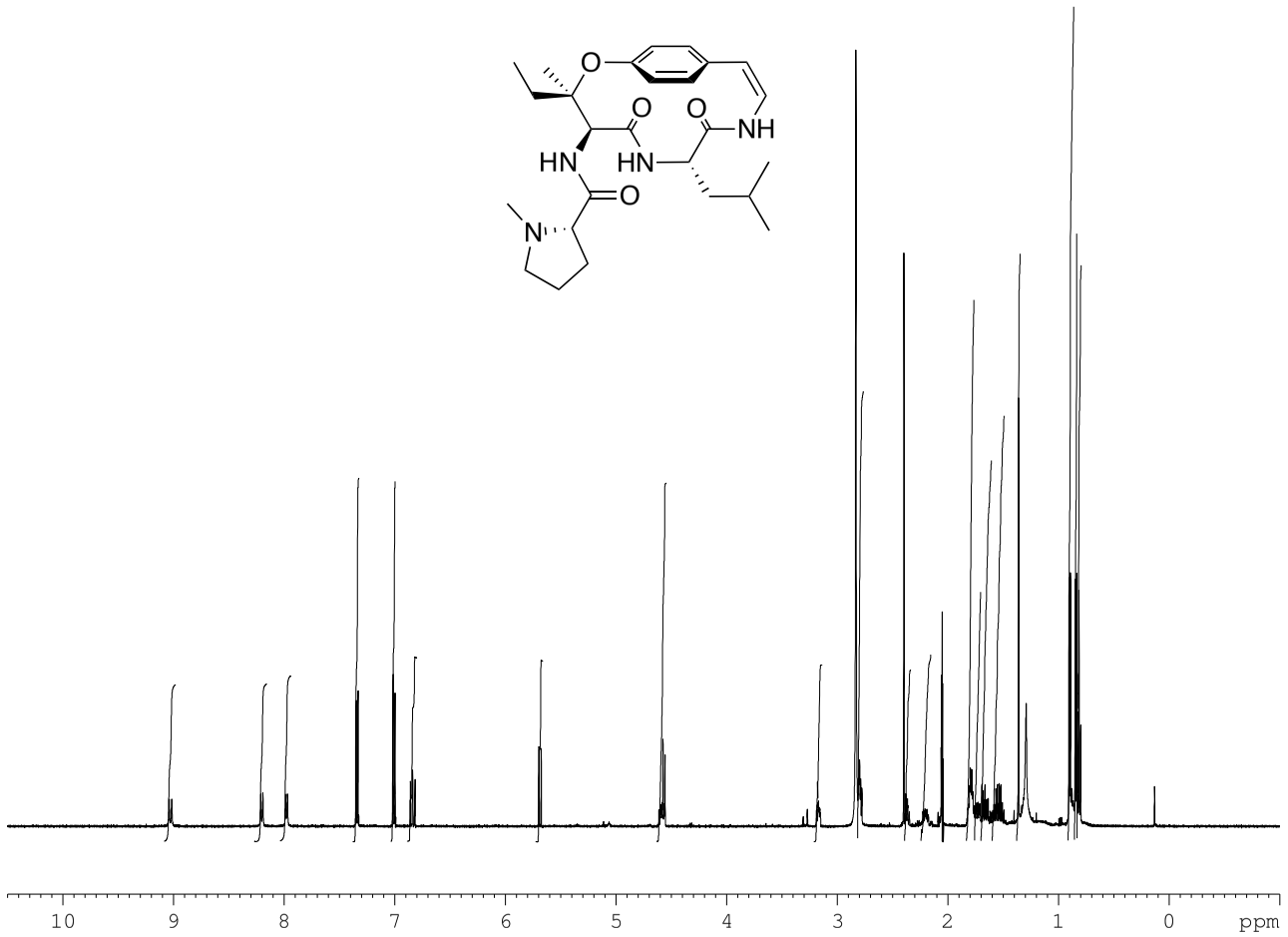
^{13}C NMR (acetone-d_6, 125 MHz) of **9**



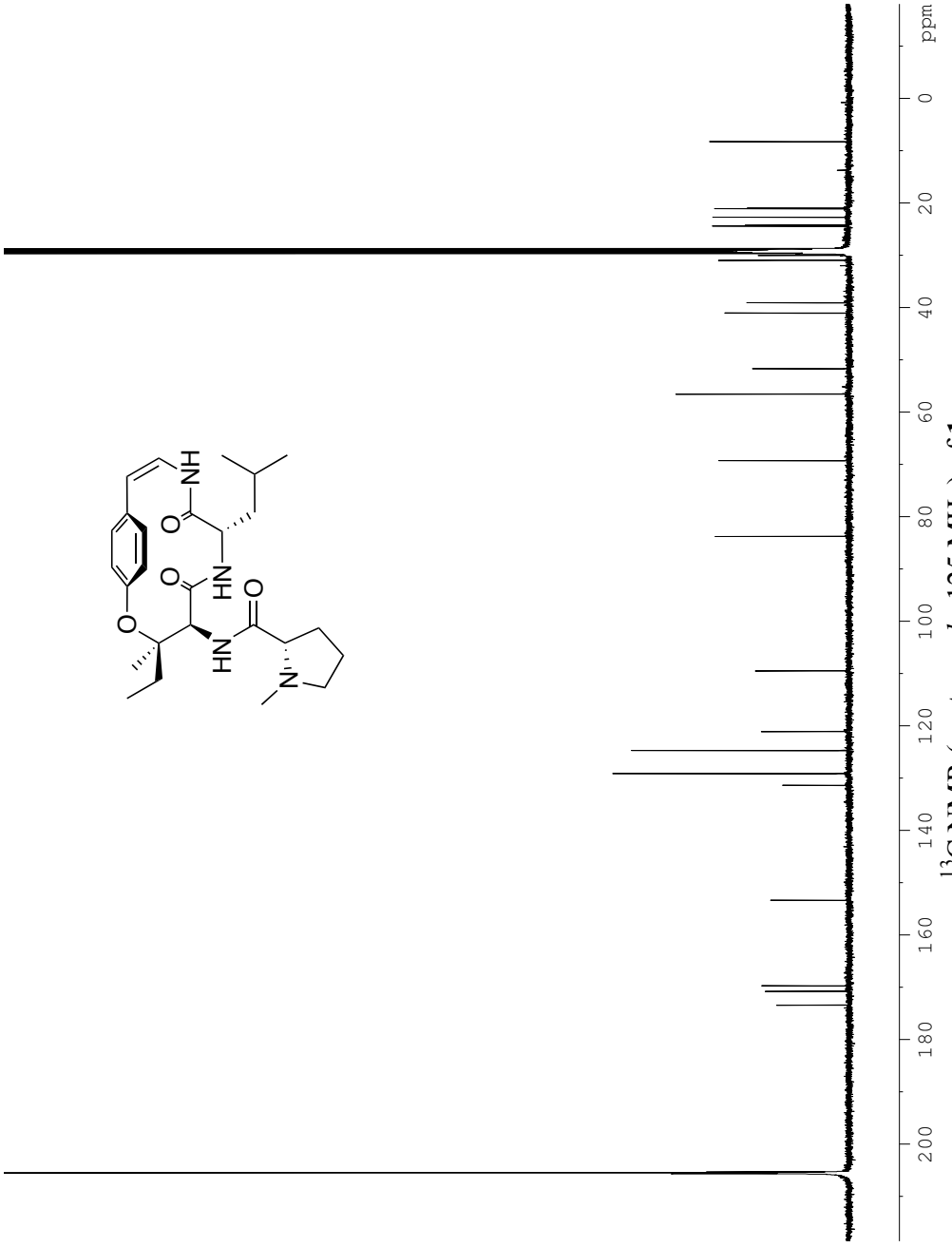
^{1}H NMR ($CDCl_3$, 500 MHz) of **10**



^{13}C NMR ($CDCl_3$, 125 MHz) of **10**

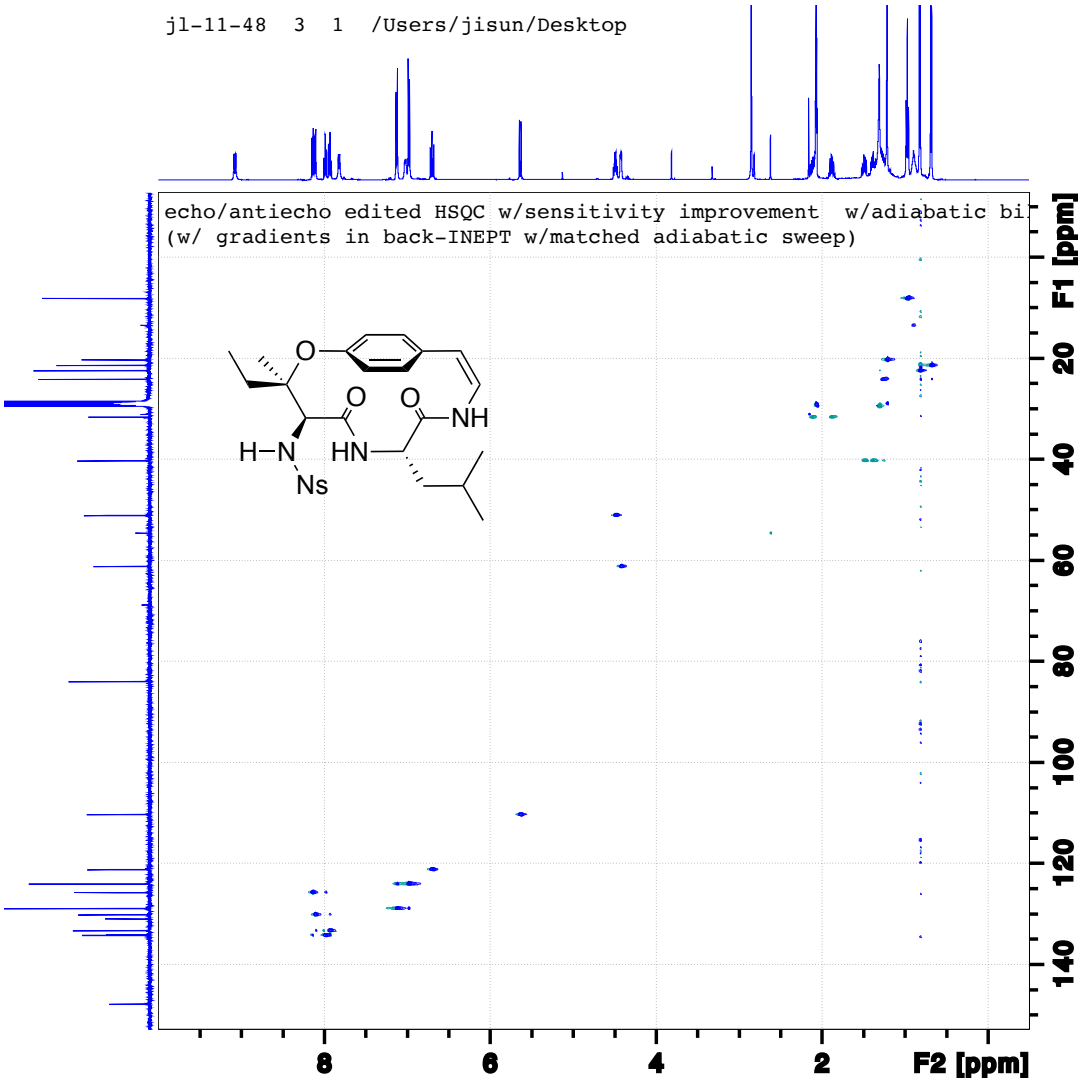


^{1}H NMR (acetone-d_6, 500 MHz) of **1**

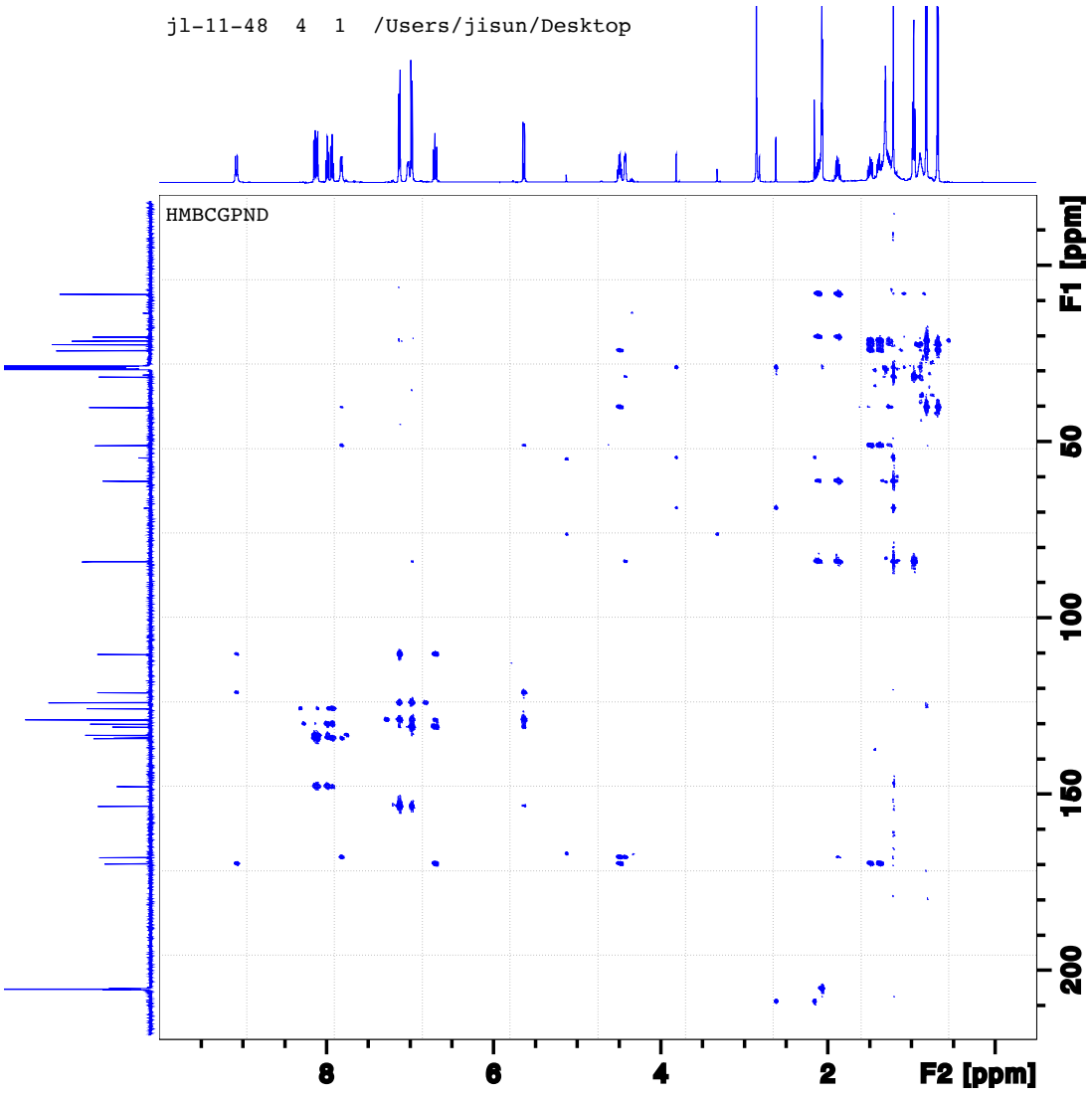


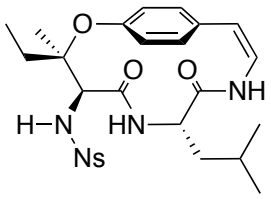
^{13}C NMR (acetone-d_6, 125 MHz) of **1**

2-D NMR Spectra:

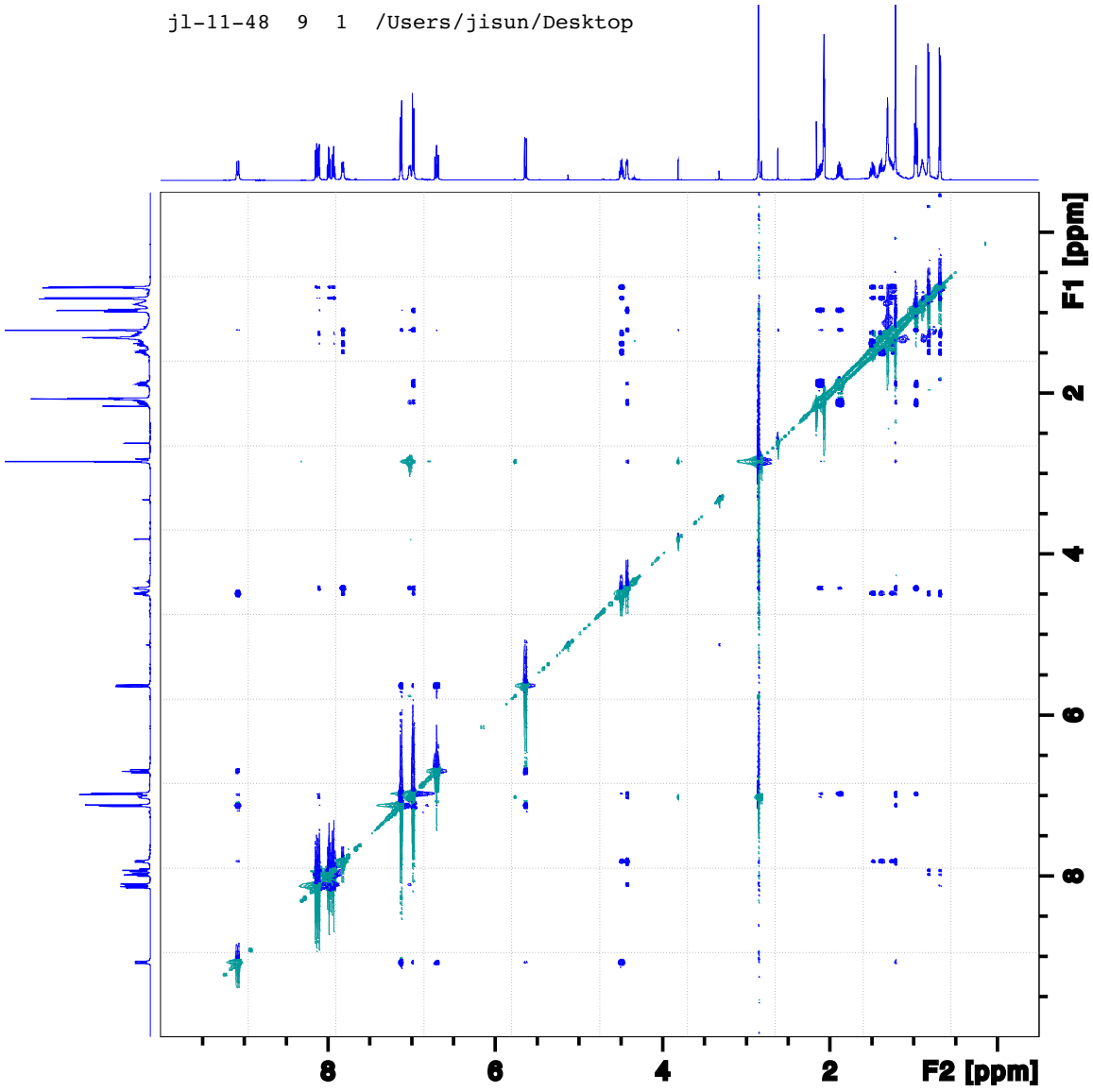


HSQC Spectrum (acetone-d_6, 500 MHz) of **9**

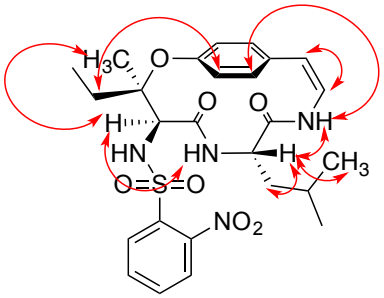




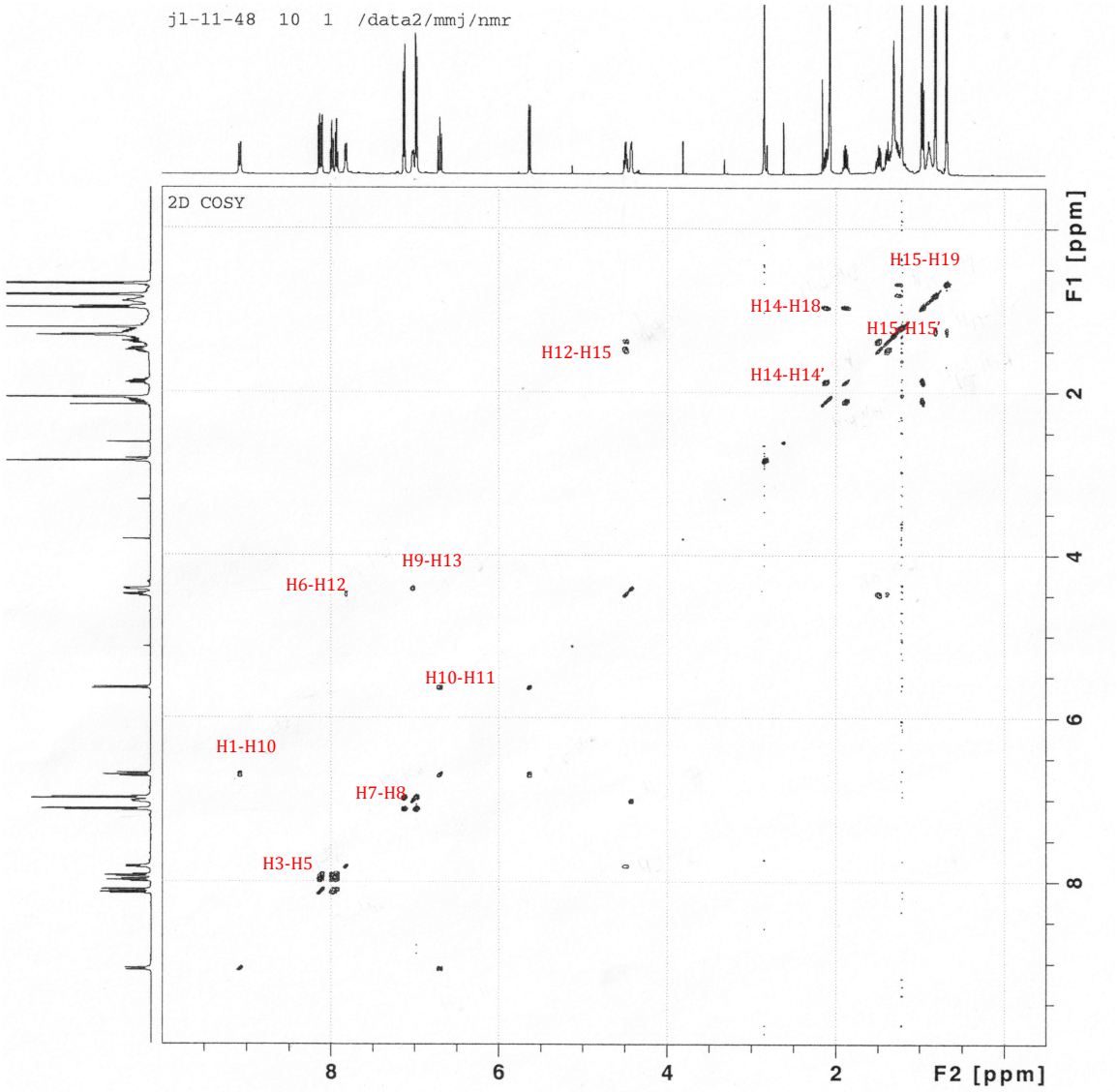
HMBC Spectrum (acetone-d_6, 500 MHz) of **9**

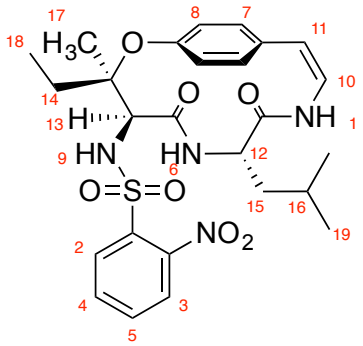


NOESY Spectrum (acetone-d_6, 500 MHz) of **9**



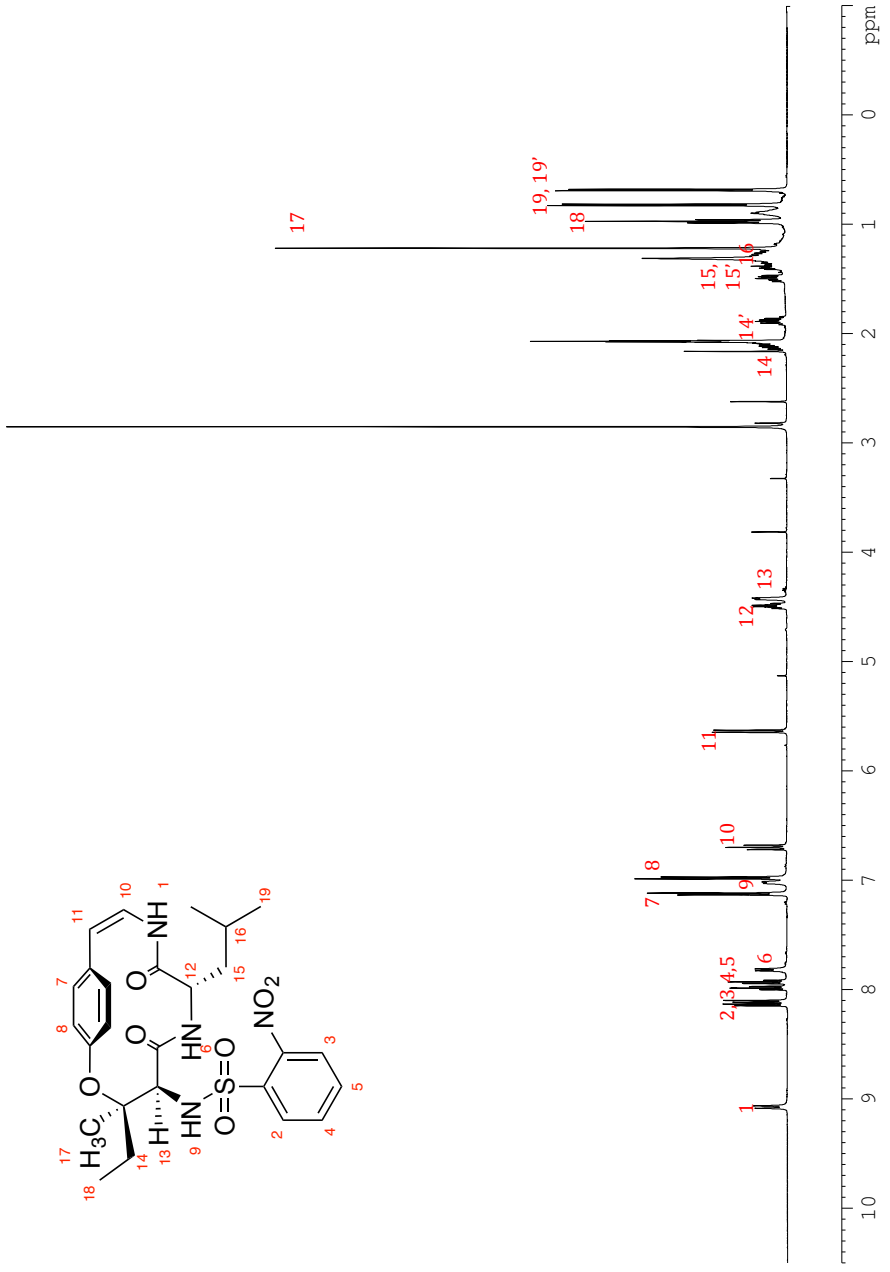
Strong ^{1}H-^{1}H NOESY correlations





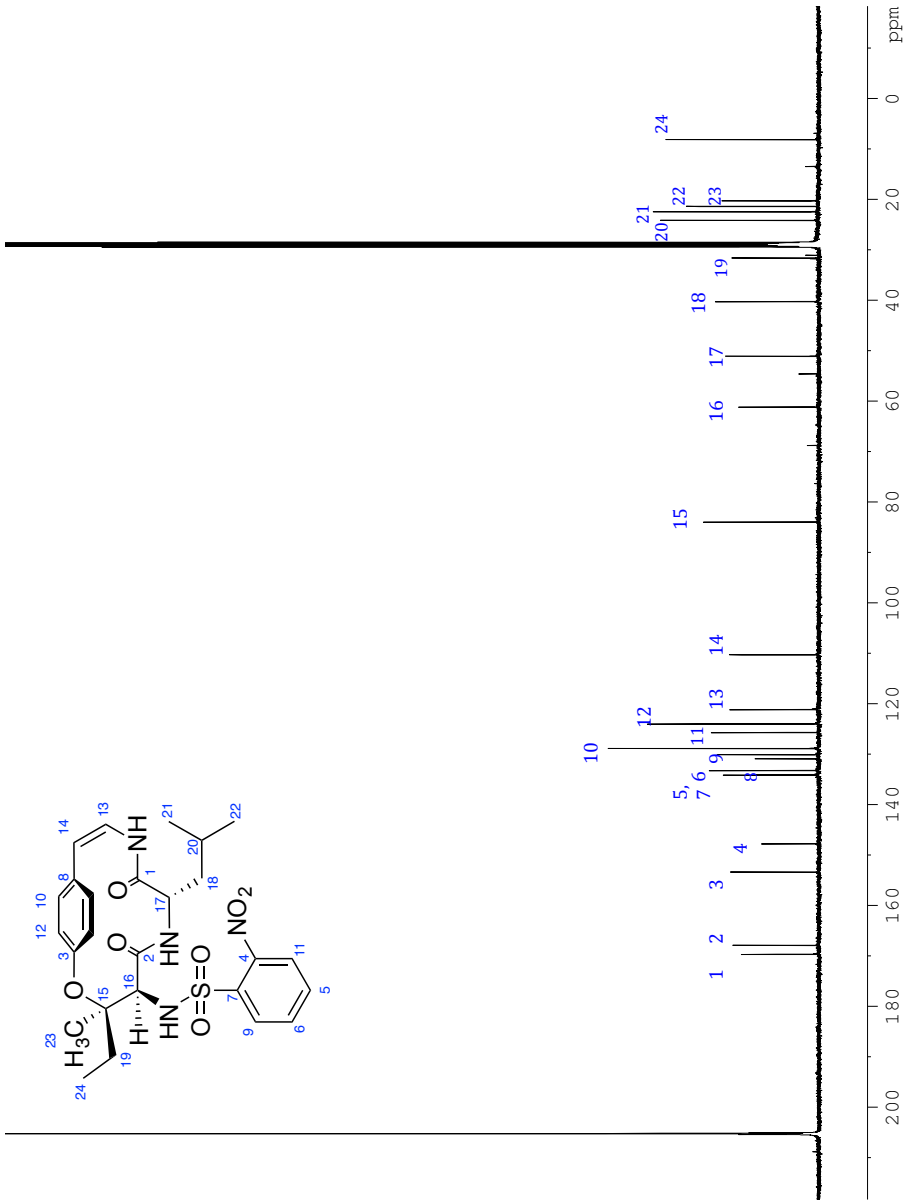
2D COSY Spectrum (acetone-d_6, 500 MHz) of **9**

^{1}H NMR Assignment for **9**:

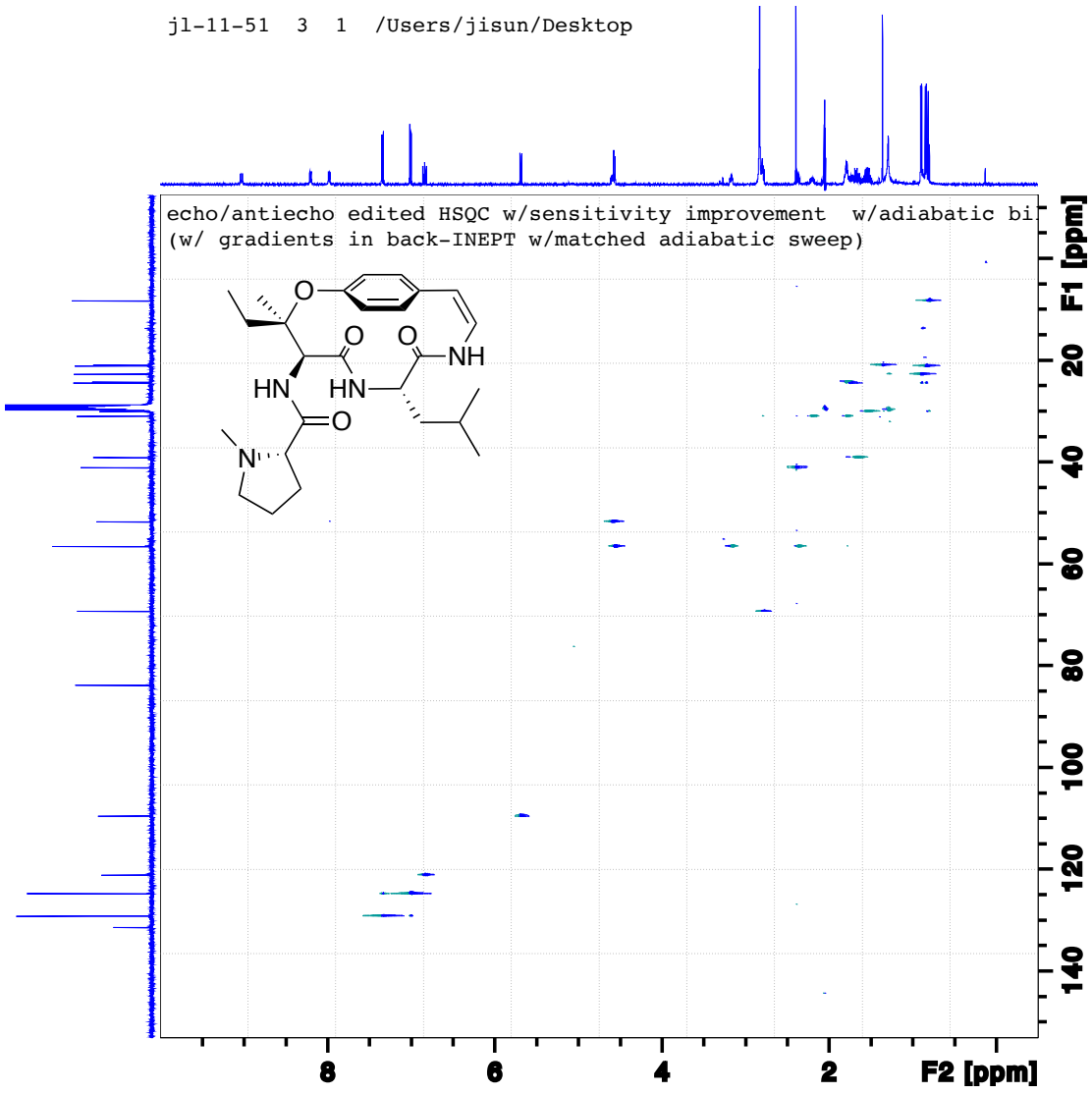


^{1}H NMR (acetone-d_6, 500 MHz) of **9**

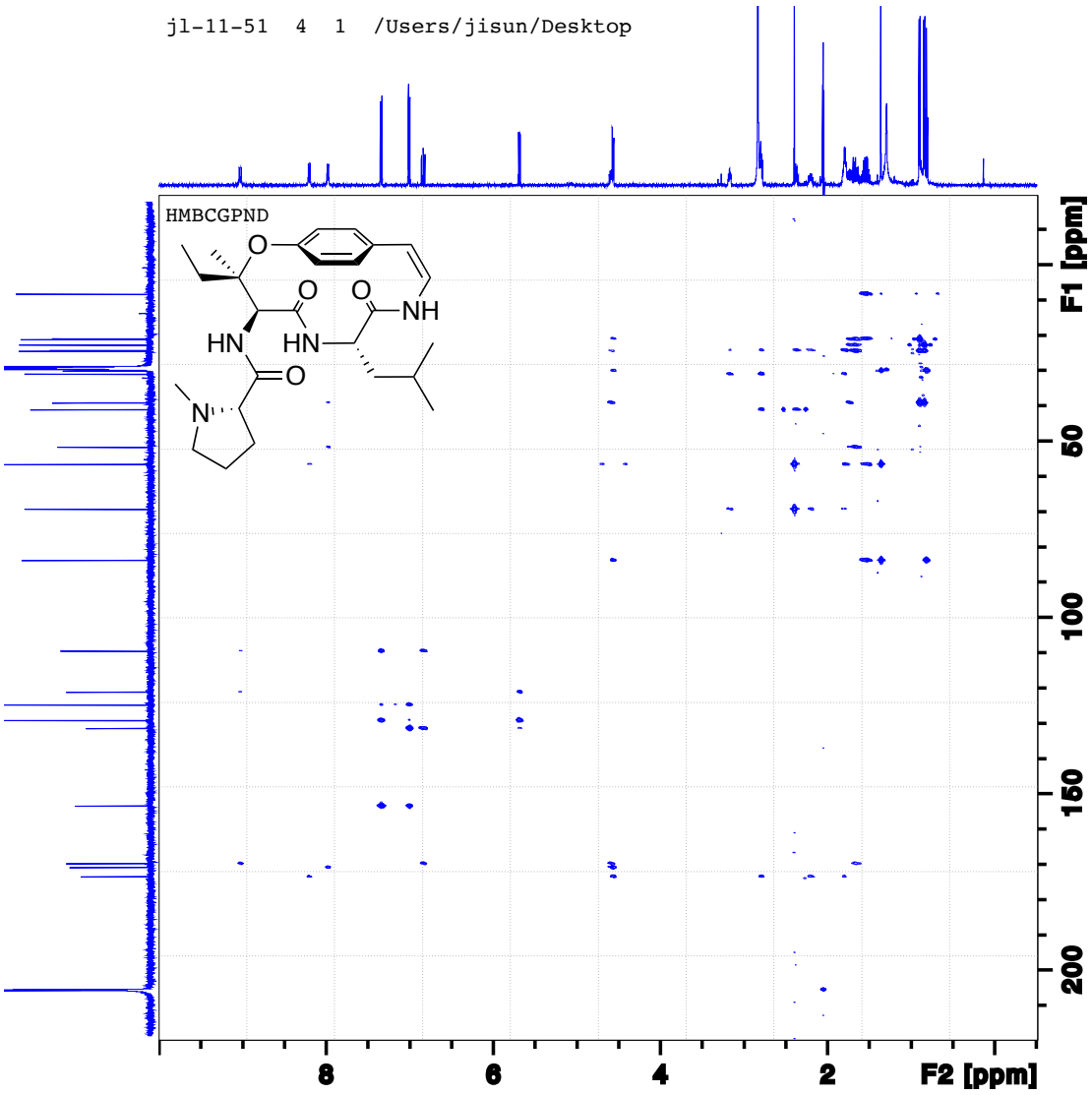
^{13}C NMR Assignment for **9**:



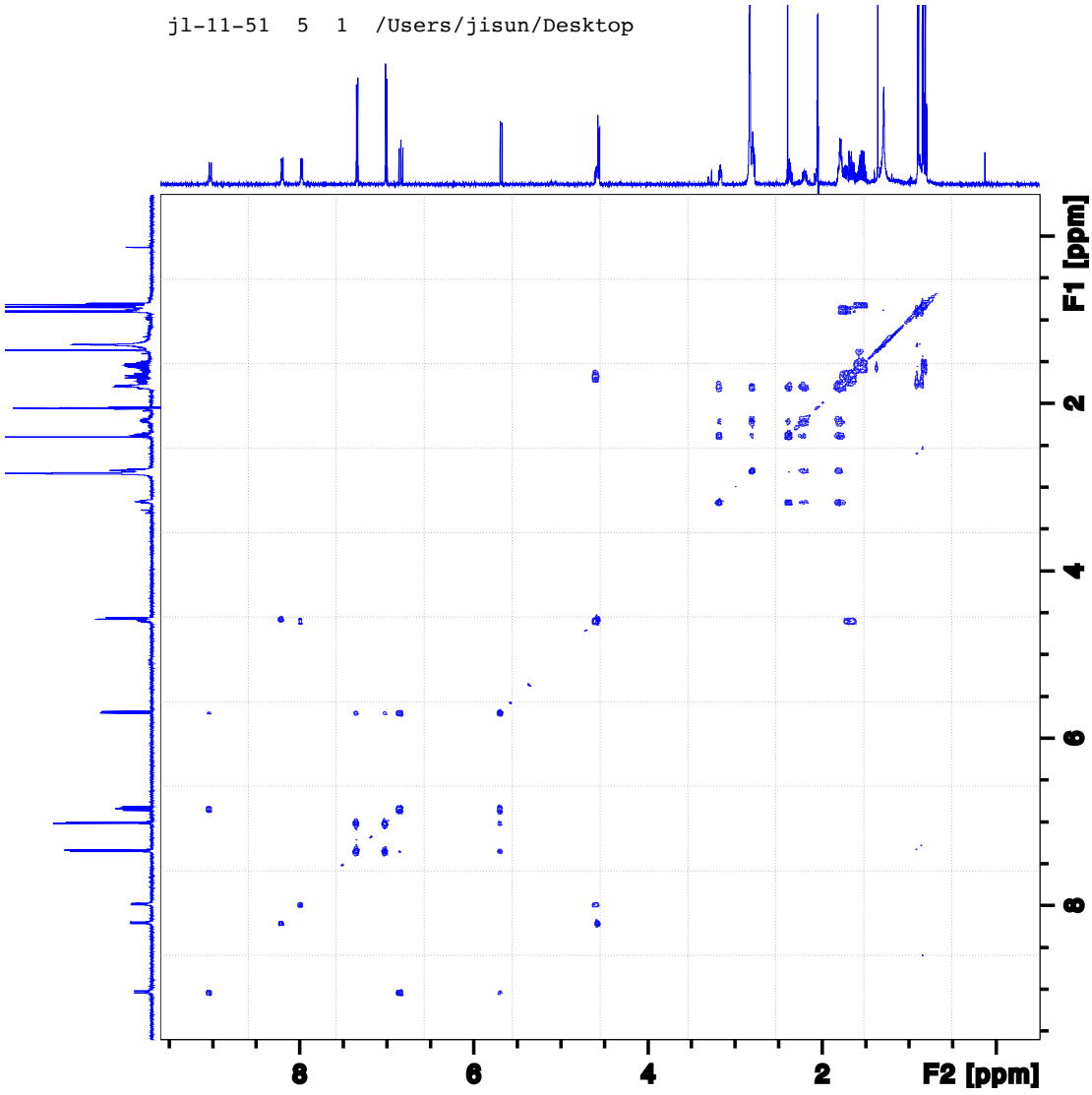
^{13}C NMR (acetone-d_6, 125 MHz) of **9**

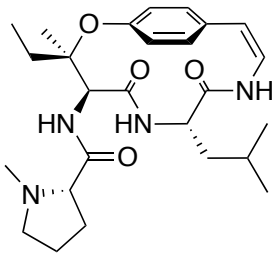


HSQC Spectrum (acetone-d_6, 500 MHz) of **1**

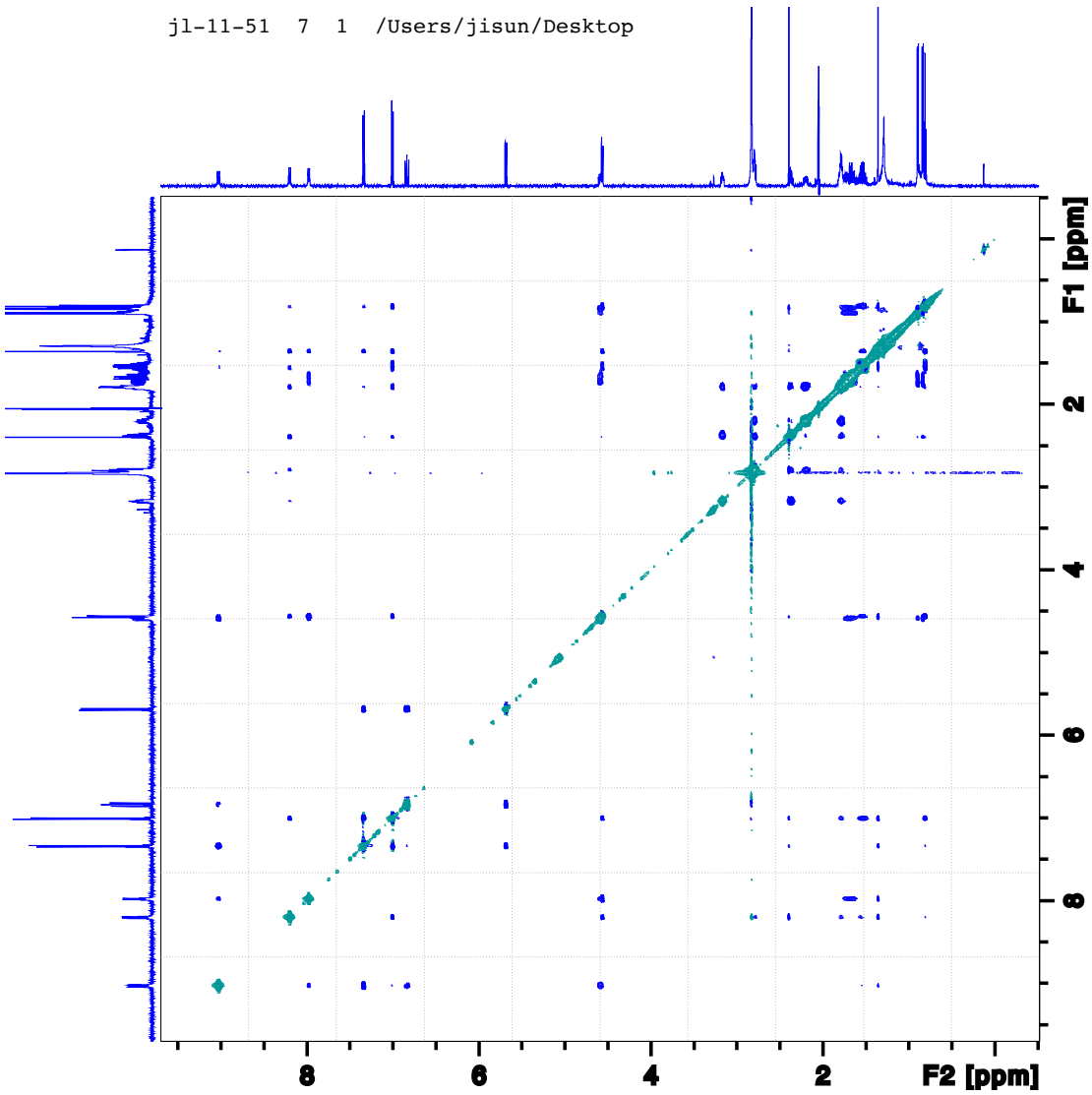


HMBC Spectrum (acetone-d_6, 500 MHz) of **1**

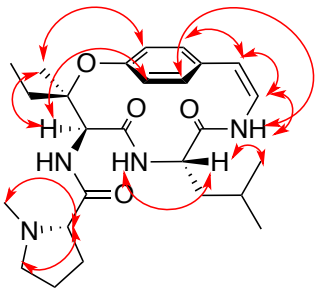




2D COSY Spectrum (acetone-d_6, 500 MHz) of **1**

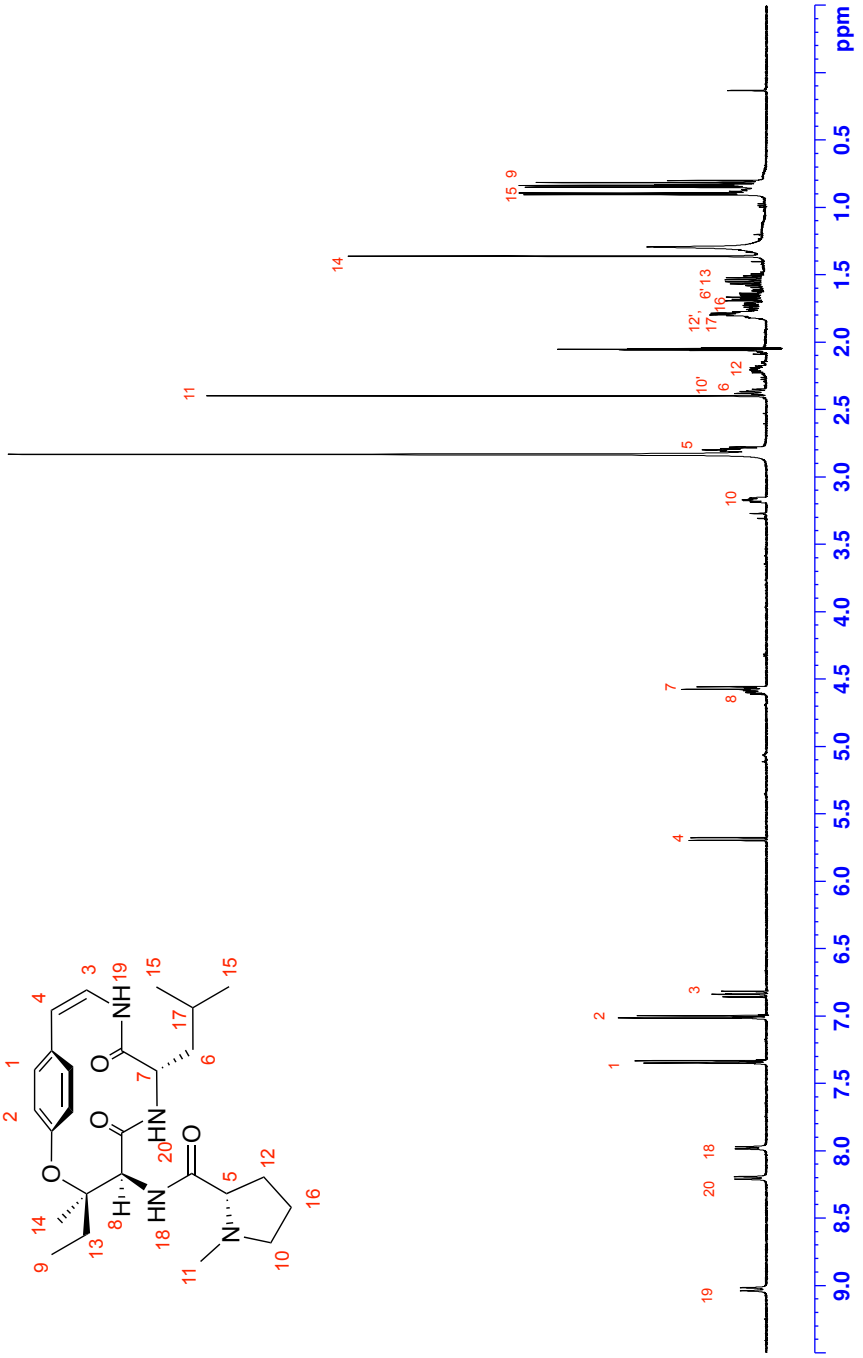


NOESY Spectrum (acetone-d_6, 500 MHz) of **1**



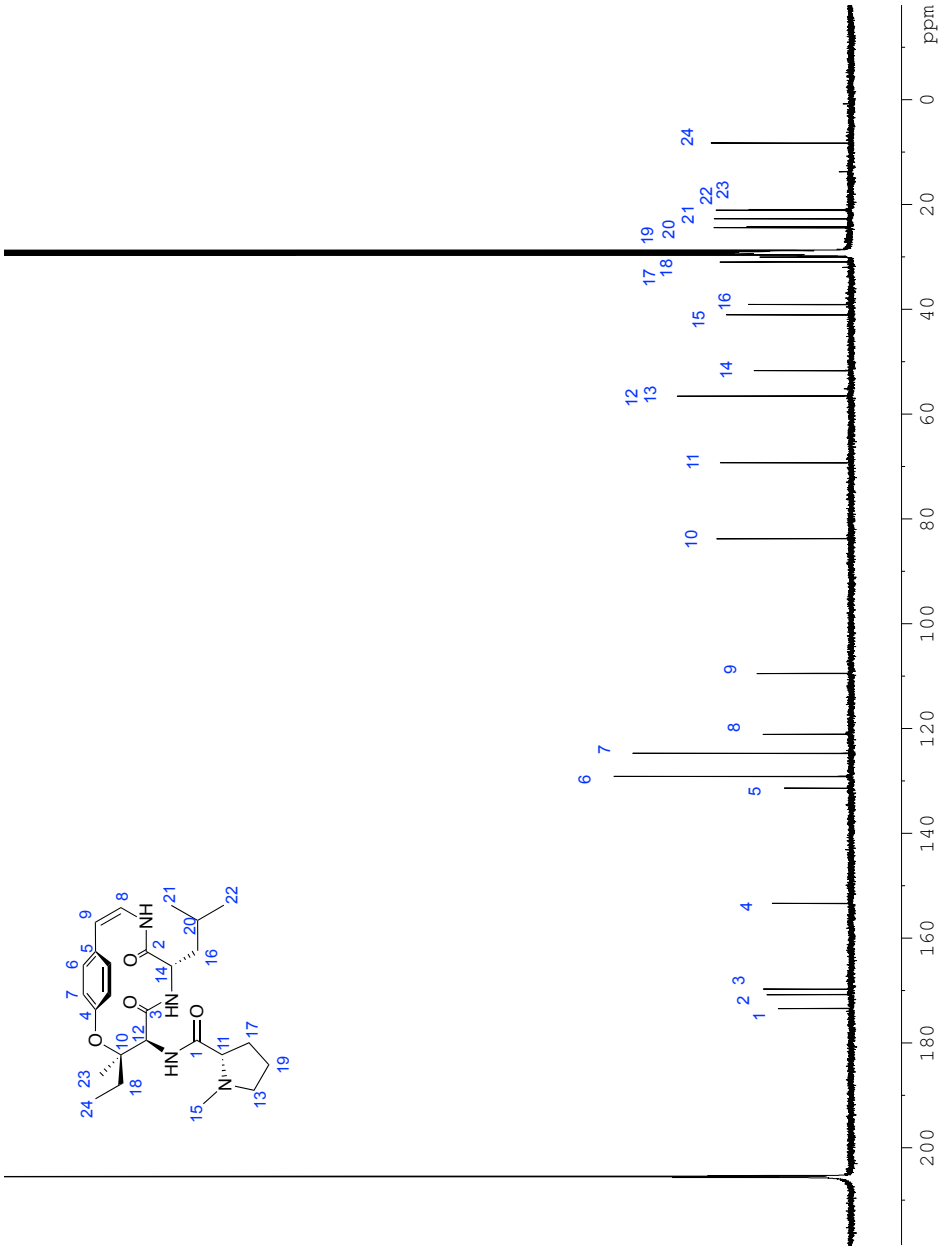
Strong ^{1}H-^{1}H NOESY correlations

^{1}H NMR Assignment of **1**:



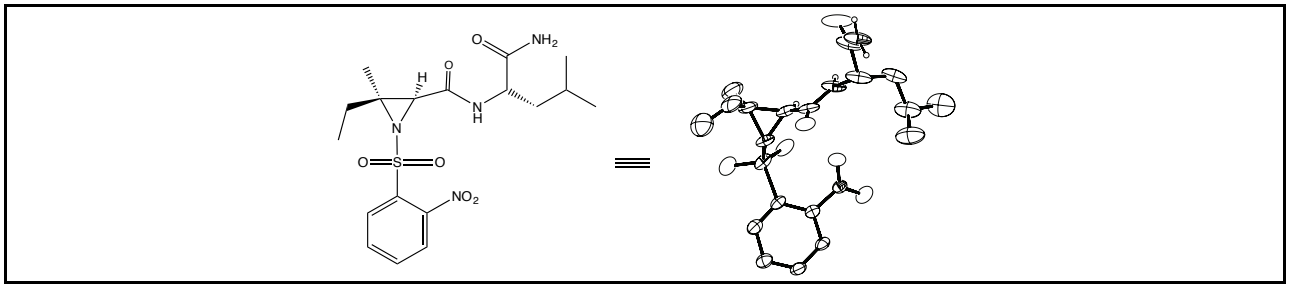
^{1}H NMR (acetone-d_6, 500 MHz) of **1**

^{13}C NMR Assignment of **1**:



^{13}C NMR (acetone-d_6, 125 MHz) of **1**

X-ray Structure Determination of Compound 3



Compound **3**, $C_{18}H_{26}N_4O_6S$, crystallizes in the triclinic space group P1 with a=7.4225(5)Å, b=16.5812(10)Å, c=21.1102(14)Å, α=82.789(3)°, β=85.375(3)°, γ=84.403(3)°, V=2559.1(3)Å^3, Z=4, and d_{calc}=1.107 g/cm$_3$. X-ray intensity data were collected on a Bruker APEXII [1] CCD area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073Å) at a temperature of 100K. Preliminary indexing was performed from a series of thirty-six 0.5° rotation frames with exposures of 10 seconds. A total of 2718 frames were collected with a crystal to detector distance of 37.6 mm, rotation widths of 0.5° and exposures of 30 seconds:

scan type	2θ	ω	ϕ	χ	Frames
Phi	19.50	59.55	352.89	-26.26	725
Omega	-18.00	243.20	310.97	36.30	208
Omega	-3.00	322.28	307.71	72.15	75
Phi	-23.00	328.34	120.37	79.39	334
Phi	-23.00	334.21	38.95	73.66	473
Phi	-15.50	258.48	12.33	19.46	495
Phi	-23.00	315.83	12.48	28.88	408

Rotation frames were integrated using SAINT [2], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values. A total of 55465 reflections were measured over the ranges $2.486 \le 2\theta \le 50.982°$, $-8 \le h \le 8$, $-20 \le k \le 20$, $-25 \le l \le 22$ yielding 15564 unique reflections (R_{int} = 0.0388). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS [3] (minimum and maximum transmission 0.5768, 0.7452). The structure was solved by direct methods - SHELXS [4]. The asymmetric unit consists of four molecules of the title compound. There was a region of disordered solvent for which a reliable disorder model could not be devised; the X-ray data were corrected for the presence of disordered solvent using SQUEEZE [5]. Refinement was by full-matrix least squares based on F^2 using SHELXL-2014 [6]. All reflections were used during refinement. The weighting scheme used was

$w=1/[\sigma^2(F_o^2)+ (0.0833P)^2 + 3.6118P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0659 and wR2=0.1670 for 14407 observed reflections for which $F > 4\sigma(F)$ and R1=0.0702 and wR2=0.1696 and GOF =1.073 for all 15564 unique, non-zero reflections and 1061 variables. The maximum Δ/σ in the final cycle of least squares was 0.016 and the two most prominent peaks in the final difference Fourier were +0.72 and -0.42 e/Å^3. The Flack absolute structure parameter was calculated by the Parsons method as 0.12(2) using 5153 quotients; thus corroborating the assignment of the absolute stereochemistry.

Table 1. lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Tables 2. and 3. Anisotropic thermal parameters are in Table 4. Tables 5. and 6. list bond distances and bond angles. Figure 1. is an ORTEP representation of the molecule with 50% probability thermal ellipsoids displayed.

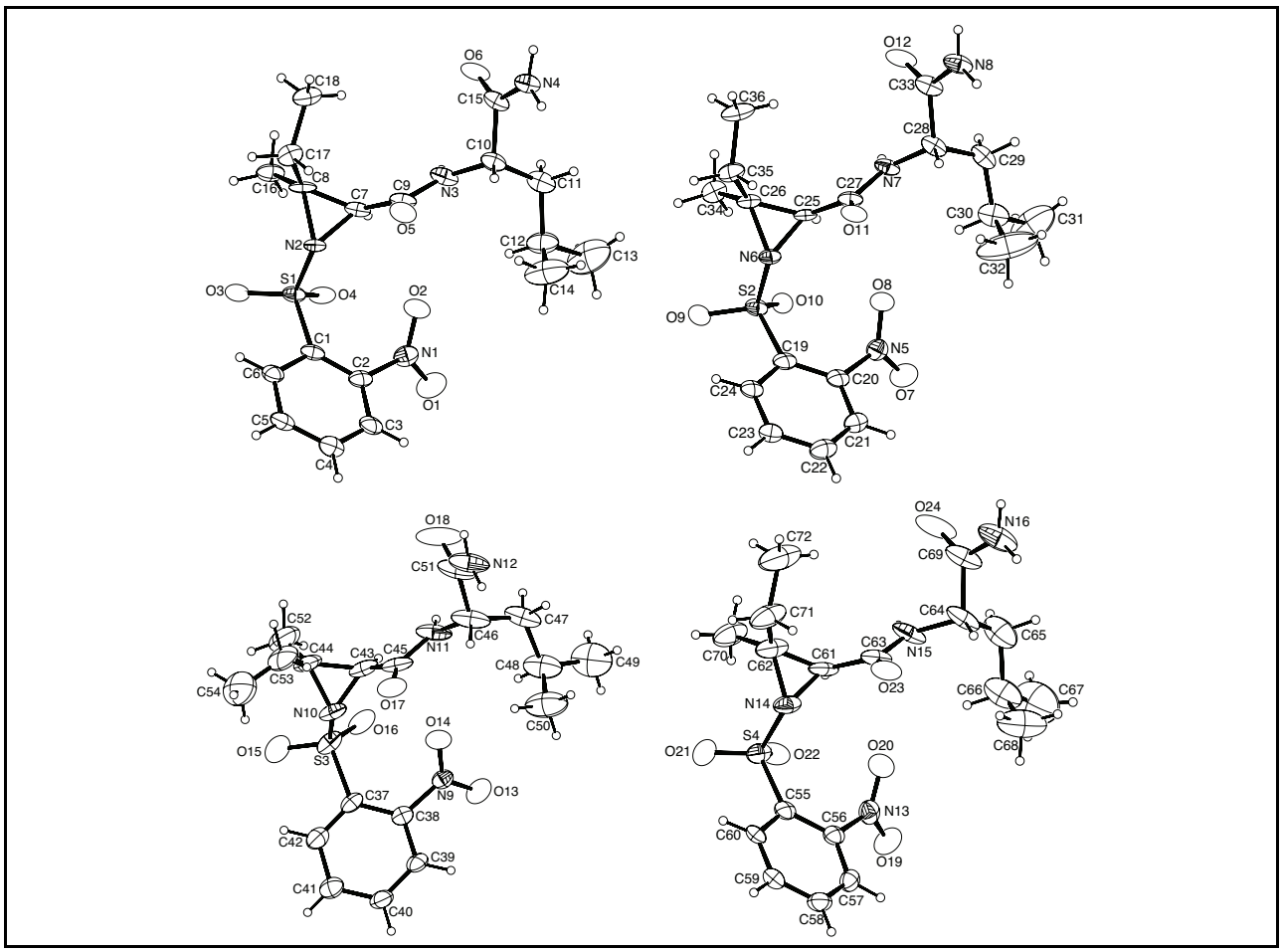


Figure 1. ORTEP drawing of the four molecules in the asymmetric unit with 50% thermal ellipsoids.

Table 1. Summary of Structure Determination of Compound 3

Empirical formula	$C_{18}H_{26}N_4O_6S$
Formula weight	426.49
Temperature/K	100
Crystal system	triclinic
Space group	P1
a	7.4225(5)Å
b	16.5812(10)Å
c	21.1102(14)Å
α	82.789(3)°
β	85.375(3)°
γ	84.403(3)°
Volume	2559.1(3)$Å^3$
Z	4
d_{calc}	1.107 g/cm^3
μ	0.161 mm^{-1}
F(000)	904.0
Crystal size, mm	0.45 × 0.32 × 0.03
2θ range for data collection	2.486 - 50.982°
Index ranges	$-8 \le h \le 8$, $-20 \le k \le 20$, $-25 \le l \le 22$
Reflections collected	55465
Independent reflections	15564[R(int) = 0.0388]
Data/restraints/parameters	15564/879/1061
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0659, wR_2 = 0.1670
Final R indexes [all data]	R_1 = 0.0702, wR_2 = 0.1696
Largest diff. peak/hole	0.72/-0.42 $eÅ^{-3}$
Flack parameter	0.12(2)

Table 2 . Refined Positional Parameters for Compound 3

Atom	*x*	*y*	*z*	U(eq)
S1	0.55130(17)	-0.06183(9)	0.82653(8)	0.0248(3)
O1	0.6170(7)	-0.0147(3)	1.0133(3)	0.0432(12)
O2	0.3874(6)	0.0013(3)	0.9547(2)	0.0372(11)
O3	0.6253(5)	-0.1011(3)	0.7726(2)	0.0308(10)
O4	0.6258(5)	0.0098(3)	0.8406(2)	0.0278(9)
O5	-0.0075(6)	-0.0250(2)	0.8965(2)	0.0317(10)
O6	-0.2503(6)	0.2223(3)	0.8453(3)	0.0347(10)
N1	0.5226(7)	-0.0392(3)	0.9760(3)	0.0315(12)
N2	0.3280(6)	-0.0475(3)	0.8214(2)	0.0213(10)
N3	0.0186(7)	0.1110(3)	0.8914(3)	0.0335(13)
N4	-0.4576(7)	0.1727(3)	0.9211(3)	0.0321(12)
C1	0.5687(7)	-0.1371(3)	0.8949(3)	0.0240(12)
C2	0.5676(7)	-0.1218(4)	0.9576(3)	0.0268(12)
C3	0.5933(8)	-0.1826(4)	1.0076(3)	0.0301(14)
C4	0.6210(8)	-0.2636(4)	0.9944(4)	0.0344(14)
C5	0.6221(8)	-0.2819(4)	0.9316(4)	0.0329(14)
C6	0.5999(8)	-0.2167(4)	0.8811(3)	0.0283(13)
C7	0.2353(8)	0.0338(4)	0.8305(3)	0.0279(13)
C8	0.2448(8)	0.0059(3)	0.7656(3)	0.0279(13)
C9	0.0711(8)	0.0351(3)	0.8761(3)	0.0279(13)
C10	-0.1397(8)	0.1305(4)	0.9334(3)	0.0297(13)
C11	-0.0895(9)	0.1813(4)	0.9839(4)	0.0402(16)
C12	0.0605(10)	0.1409(5)	1.0264(4)	0.0450(18)
C13	0.1132(17)	0.2013(7)	1.0697(6)	0.089(4)
C14	0.0057(15)	0.0654(6)	1.0643(6)	0.073(3)
C15	-0.2887(8)	0.1783(3)	0.8946(3)	0.0282(13)
C16	0.3669(8)	0.0468(4)	0.7124(3)	0.0315(14)
C17	0.0812(9)	-0.0292(4)	0.7439(4)	0.0336(15)
C18	-0.0537(9)	0.0402(4)	0.7162(4)	0.0359(15)
S2	0.92687(17)	0.52075(8)	0.85057(8)	0.0248(3)
O7	1.0978(6)	0.4690(3)	0.6673(3)	0.0400(12)
O8	0.8432(6)	0.4534(3)	0.7237(2)	0.0362(11)
O9	0.9627(6)	0.5616(3)	0.9035(2)	0.0309(10)
O10	1.0391(5)	0.4492(3)	0.8376(2)	0.0270(9)
O11	0.4150(5)	0.4850(2)	0.7831(2)	0.0284(10)
O12	0.2488(6)	0.2363(3)	0.8417(3)	0.0381(11)
N5	0.9691(7)	0.4934(3)	0.7026(3)	0.0302(12)
N6	0.7077(6)	0.5068(3)	0.8574(2)	0.0223(10)
N7	0.4888(7)	0.3472(3)	0.7925(3)	0.0270(11)

N8	0.0527(7)	0.2837(3)	0.7650(3)	0.0352(13)
C19	0.9346(7)	0.5950(4)	0.7819(3)	0.0278(13)
C20	0.9624(7)	0.5767(4)	0.7188(3)	0.0263(12)
C21	0.9790(8)	0.6372(4)	0.6684(3)	0.0294(13)
C22	0.9568(9)	0.7178(4)	0.6785(4)	0.0378(15)
C23	0.9269(8)	0.7381(4)	0.7399(3)	0.0296(13)
C24	0.9178(7)	0.6758(4)	0.7918(3)	0.0266(13)
C25	0.6545(7)	0.4269(3)	0.8501(3)	0.0230(12)
C26	0.6267(7)	0.4540(3)	0.9140(3)	0.0248(12)
C27	0.5060(7)	0.4253(4)	0.8049(3)	0.0255(12)
C28	0.3584(7)	0.3275(3)	0.7513(3)	0.0276(13)
C29	0.4556(10)	0.2726(4)	0.7025(4)	0.0394(16)
C30	0.605(1)	0.3113(4)	0.6605(4)	0.0454(18)
C31	0.7252(18)	0.2514(7)	0.6250(6)	0.097(4)
C32	0.5324(16)	0.3863(8)	0.6165(8)	0.121(6)
C33	0.2133(8)	0.2798(4)	0.7902(4)	0.0324(14)
C34	0.7479(8)	0.4131(4)	0.9661(3)	0.0314(14)
C35	0.4414(9)	0.4882(4)	0.9380(4)	0.0344(15)
C36	0.3230(9)	0.4215(5)	0.9673(4)	0.0443(19)
S3	0.5417(2)	0.82645(10)	0.54393(9)	0.0383(4)
O13	0.4605(7)	0.5748(3)	0.5610(3)	0.0427(12)
O14	0.6880(6)	0.6466(3)	0.5340(2)	0.0410(12)
O15	0.4852(8)	0.9085(3)	0.5576(3)	0.0491(13)
O16	0.4653(7)	0.7947(3)	0.4930(3)	0.0438(12)
O17	1.0998(6)	0.7130(3)	0.5367(2)	0.0412(12)
O18	1.3224(7)	0.7040(5)	0.3429(3)	0.072(2)
N9	0.5544(7)	0.6297(3)	0.5681(3)	0.0299(11)
N10	0.7718(8)	0.8189(4)	0.5354(3)	0.0379(13)
N11	1.0497(8)	0.6825(5)	0.4390(3)	0.0505(16)
N12	1.5248(8)	0.6258(6)	0.4050(3)	0.063(2)
C37	0.5008(8)	0.7618(4)	0.6176(3)	0.0298(13)
C38	0.4986(8)	0.6767(4)	0.6222(3)	0.0269(12)
C39	0.4545(8)	0.6309(4)	0.6790(3)	0.0321(14)
C40	0.4124(9)	0.6701(4)	0.7339(4)	0.0378(16)
C41	0.4041(9)	0.7544(4)	0.7299(4)	0.0386(16)
C42	0.4535(9)	0.7997(4)	0.6701(4)	0.0382(15)
C43	0.8625(10)	0.7877(5)	0.4792(4)	0.0406(15)
C44	0.8662(12)	0.8768(5)	0.4873(4)	0.0512(19)
C45	1.0156(9)	0.7249(5)	0.4892(3)	0.0406(16)
C46	1.202(1)	0.6197(6)	0.4339(4)	0.057(2)
C47	1.1438(10)	0.5454(6)	0.4078(4)	0.056(2)
C48	0.9971(12)	0.4993(7)	0.4506(4)	0.065(2)
C49	0.9304(17)	0.4319(9)	0.4173(7)	0.097(4)
C50	1.0581(16)	0.4672(9)	0.5145(5)	0.086(3)

C51	1.3529(10)	0.6565(7)	0.3902(4)	0.058(2)
C52	0.7637(16)	0.9355(6)	0.4425(5)	0.070(3)
C53	1.0325(12)	0.9037(6)	0.5130(5)	0.060(2)
C54	0.9881(17)	0.9583(7)	0.5605(6)	0.089(4)
S4	0.1591(2)	0.62274(10)	0.12401(9)	0.0349(4)
O19	-0.0261(7)	0.8704(3)	0.1182(3)	0.0432(12)
O20	0.2251(7)	0.8026(3)	0.1434(3)	0.0455(12)
O21	0.1353(6)	0.5451(3)	0.1060(3)	0.0430(12)
O22	0.0412(6)	0.6545(3)	0.1740(3)	0.0431(12)
O23	0.6633(6)	0.7265(3)	0.1392(2)	0.0409(12)
O24	0.8209(7)	0.7116(5)	0.3358(3)	0.0642(17)
N13	0.1001(8)	0.8188(3)	0.1085(3)	0.0340(12)
N14	0.3776(7)	0.6219(4)	0.1371(3)	0.0377(13)
N15	0.5801(7)	0.7470(5)	0.2400(3)	0.0462(16)
N16	1.0175(8)	0.7924(6)	0.2791(3)	0.062(2)
C55	0.1433(8)	0.6920(4)	0.0525(3)	0.0303(13)
C56	0.1102(8)	0.7785(4)	0.0500(3)	0.0293(13)
C57	0.0869(8)	0.8274(4)	-0.0055(3)	0.0312(14)
C58	0.1123(9)	0.7929(4)	-0.0637(4)	0.0357(15)
C59	0.1451(9)	0.7113(4)	-0.0625(4)	0.0340(14)
C60	0.1554(8)	0.6613(4)	-0.0050(3)	0.0325(14)
C61	0.4268(9)	0.6523(5)	0.1946(3)	0.0393(15)
C62	0.4623(10)	0.5635(5)	0.1879(4)	0.0509(19)
C63	0.5697(9)	0.7127(5)	0.1877(3)	0.0387(15)
C64	0.7056(9)	0.8078(6)	0.2463(4)	0.0492(19)
C65	0.6105(12)	0.8759(7)	0.2785(5)	0.070(3)
C66	0.4559(14)	0.9229(8)	0.2387(6)	0.080(3)
C67	0.350(2)	0.9842(11)	0.2798(8)	0.124(5)
C68	0.5220(17)	0.9614(10)	0.1752(7)	0.105(4)
C69	0.8525(9)	0.7660(6)	0.2902(4)	0.0511(19)
C70	0.3453(11)	0.5042(6)	0.2308(5)	0.060(2)
C71	0.6523(10)	0.5268(6)	0.1677(5)	0.067(3)
C72	0.7673(14)	0.5046(8)	0.2255(7)	0.095(4)

Table 3 . Positional Parameters for Hydrogens in Compound 3

Atom	*x*	*y*	*z*	U(eq)
H3	0.0842	0.1509	0.8749	0.045
H4a	-0.5494	0.2017	0.903	0.043
H4b	-0.4768	0.1399	0.9566	0.043
H3a	0.5921	-0.1698	1.0502	0.04
H4	0.6393	-0.3063	1.0283	0.046
H5	0.6373	-0.337	0.9227	0.044
H6	0.6066	-0.2281	0.8379	0.038
H7	0.3189	0.0763	0.8346	0.037
H10	-0.1856	0.0786	0.9553	0.04
H11a	-0.1997	0.1941	1.0117	0.053
H11b	-0.0501	0.2336	0.9619	0.053
H12	0.1697	0.1261	0.9979	0.06
H13a	0.0032	0.2282	1.0895	0.133
H13b	0.1834	0.2425	1.0441	0.133
H13c	0.1868	0.1719	1.1033	0.133
H14a	0.111	0.036	1.0847	0.11
H14b	-0.0412	0.0309	1.0362	0.11
H14c	-0.089	0.0791	1.0973	0.11
H16a	0.2945	0.089	0.6863	0.047
H16b	0.4238	0.006	0.6855	0.047
H16c	0.4613	0.0718	0.7311	0.047
H17A	0.0208	-0.0617	0.7807	0.045
H17B	0.1216	-0.0658	0.7109	0.045
H18a	-0.0614	0.0855	0.7422	0.054
H18b	-0.1737	0.0201	0.7166	0.054
H18c	-0.012	0.0592	0.6721	0.054
H7a	0.5613	0.3073	0.8106	0.036
H8a	-0.0338	0.2551	0.7846	0.047
H8b	0.0334	0.3149	0.7289	0.047
H21	1.006	0.6231	0.6262	0.039
H22	0.9621	0.7594	0.6433	0.05
H23	0.9124	0.7937	0.7473	0.039
H24	0.8998	0.69	0.8342	0.035
H25	0.7583	0.3844	0.8452	0.031
H28	0.3008	0.3787	0.7282	0.037
H29a	0.5073	0.2213	0.7262	0.052
H29b	0.3647	0.2582	0.675	0.052
H30	0.6837	0.3321	0.69	0.06
H31a	0.8086	0.2195	0.6543	0.145

H31b	0.7949	0.281	0.5897	0.145
H31c	0.6506	0.2147	0.608	0.145
H32a	0.634	0.4167	0.5973	0.181
H32b	0.4487	0.4215	0.6415	0.181
H32c	0.4683	0.3686	0.5826	0.181
H34a	0.6889	0.3674	0.9905	0.047
H34b	0.7677	0.4529	0.9949	0.047
H34c	0.8648	0.3927	0.9464	0.047
H35a	0.3807	0.521	0.902	0.046
H35b	0.4553	0.5249	0.9705	0.046
H36a	0.3249	0.3801	0.9379	0.067
H36b	0.1982	0.4452	0.9751	0.067
H36c	0.3695	0.3961	1.0079	0.067
H11	0.9771	0.6927	0.4075	0.067
H12a	1.6191	0.6404	0.3796	0.084
H12b	1.5409	0.5914	0.4398	0.084
H39	0.4526	0.5735	0.6811	0.043
H40	0.3895	0.6388	0.7741	0.05
H41	0.3661	0.7816	0.7664	0.051
H42	0.4532	0.8574	0.6673	0.051
H43	0.7791	0.777	0.4468	0.054
H46	1.2473	0.6025	0.4773	0.075
H47a	1.2523	0.5068	0.4016	0.074
H47b	1.0967	0.5632	0.3653	0.074
H48	0.8906	0.5399	0.4573	0.087
H49a	1.0214	0.3848	0.419	0.145
H49b	0.9113	0.4524	0.3725	0.145
H49c	0.8158	0.4153	0.439	0.145
H50a	0.9631	0.437	0.539	0.129
H50b	1.0827	0.5127	0.5371	0.129
H50c	1.1691	0.4306	0.5097	0.129
H52a	0.6594	0.9105	0.4302	0.105
H52b	0.8424	0.9509	0.4042	0.105
H52c	0.7209	0.9842	0.4632	0.105
H53a	1.1062	0.8549	0.532	0.079
H53b	1.1072	0.9309	0.4772	0.079
H54a	0.97	1.0144	0.5394	0.133
H54b	1.0874	0.9542	0.5889	0.133
H54c	0.8764	0.9438	0.5855	0.133
H15	0.5068	0.7323	0.2734	0.061
H16d	1.1049	0.7718	0.3037	0.083
H16e	1.039	0.8306	0.2472	0.083
H57	0.0539	0.8841	-0.0054	0.042
H58	0.1062	0.8268	-0.1034	0.047

H59	0.1615	0.6879	-0.1016	0.045
H60	0.1713	0.6039	-0.0055	0.043
H61	0.321	0.6657	0.2251	0.052
H64	0.7618	0.8285	0.2034	0.065
H65a	0.6992	0.9144	0.2851	0.093
H65b	0.558	0.8541	0.321	0.093
H66	0.3709	0.8822	0.2314	0.106
H67a	0.4078	1.0355	0.2735	0.186
H67b	0.349	0.9618	0.325	0.186
H67c	0.2248	0.9945	0.267	0.186
H68a	0.4183	0.9856	0.1513	0.158
H68b	0.5914	0.92	0.1516	0.158
H68c	0.6	1.0041	0.1807	0.158
H70a	0.2189	0.5277	0.2333	0.09
H70b	0.3899	0.4949	0.2738	0.09
H70c	0.3525	0.4523	0.2128	0.09
H71a	0.7127	0.5666	0.1362	0.089
H71b	0.6424	0.4773	0.1469	0.089
H72a	0.7783	0.5538	0.2458	0.143
H72b	0.8882	0.4815	0.2114	0.143
H72c	0.7088	0.4644	0.2564	0.143

Table 4 . Refined Thermal Parameters (U's) for Compound 3

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	0.0143(6)	0.0271(7)	0.0313(9)	0.0047(6)	-0.0051(6)	-0.0018(5)
O1	0.044(3)	0.047(3)	0.042(3)	0.002(2)	-0.012(2)	-0.020(2)
O2	0.030(2)	0.034(2)	0.045(3)	0.001(2)	-0.009(2)	0.0063(18)
O3	0.020(2)	0.036(2)	0.032(3)	0.0093(19)	-0.0005(18)	0.0017(17)
O4	0.0158(19)	0.034(2)	0.033(3)	0.0074(19)	-0.0091(17)	-0.0080(16)
O5	0.024(2)	0.024(2)	0.046(3)	0.0042(19)	-0.0033(19)	-0.0066(16)
O6	0.021(2)	0.027(2)	0.051(3)	0.010(2)	-0.0070(19)	0.0020(16)
N1	0.031(3)	0.034(3)	0.029(3)	0.004(2)	-0.003(2)	-0.007(2)
N2	0.019(2)	0.019(2)	0.025(3)	0.0056(19)	-0.0097(18)	-0.0006(17)
N3	0.021(2)	0.026(2)	0.051(4)	0.008(2)	-0.006(2)	0.0016(19)
N4	0.023(2)	0.030(3)	0.041(3)	0.004(2)	-0.005(2)	0.000(2)
C1	0.013(2)	0.023(3)	0.034(3)	0.004(2)	-0.006(2)	-0.003(2)
C2	0.015(3)	0.035(3)	0.030(3)	0.003(2)	-0.005(2)	-0.003(2)
C3	0.016(3)	0.036(3)	0.035(4)	0.003(3)	0.000(2)	0.004(2)
C4	0.026(3)	0.033(3)	0.039(4)	0.009(3)	0.005(3)	0.001(2)
C5	0.022(3)	0.032(3)	0.041(4)	0.005(3)	0.000(3)	0.007(2)
C6	0.018(3)	0.035(3)	0.031(3)	-0.001(3)	-0.004(2)	0.003(2)
C7	0.021(3)	0.020(3)	0.042(4)	0.007(2)	-0.013(2)	-0.002(2)
C8	0.024(3)	0.021(3)	0.036(3)	0.016(2)	-0.014(2)	-0.003(2)
C9	0.018(3)	0.020(3)	0.045(4)	0.006(2)	-0.014(2)	-0.003(2)
C10	0.025(3)	0.020(3)	0.042(4)	0.004(3)	-0.005(2)	0.000(2)
C11	0.033(3)	0.029(3)	0.058(4)	0.000(3)	-0.012(3)	-0.002(3)
C12	0.038(4)	0.046(4)	0.053(5)	0.001(3)	-0.020(3)	-0.006(3)
C13	0.106(9)	0.083(7)	0.091(8)	-0.008(6)	-0.050(7)	-0.042(6)
C14	0.081(7)	0.061(5)	0.078(7)	0.018(5)	-0.038(5)	-0.017(5)
C15	0.022(3)	0.012(2)	0.051(4)	-0.001(2)	-0.006(2)	-0.004(2)
C16	0.027(3)	0.028(3)	0.036(4)	0.015(3)	-0.005(3)	-0.005(2)
C17	0.031(3)	0.035(3)	0.037(4)	-0.001(3)	-0.009(3)	-0.012(3)
C18	0.025(3)	0.048(4)	0.032(4)	0.012(3)	-0.007(3)	-0.008(3)
S2	0.0155(6)	0.0270(7)	0.0315(9)	0.0020(6)	-0.0044(6)	-0.0045(5)
O7	0.034(2)	0.039(3)	0.043(3)	0.002(2)	0.003(2)	0.003(2)
O8	0.035(2)	0.037(2)	0.037(3)	0.001(2)	-0.002(2)	-0.0136(19)
O9	0.028(2)	0.032(2)	0.034(3)	0.0017(19)	-0.0102(18)	-0.0078(18)
O10	0.0166(19)	0.038(2)	0.027(2)	-0.0001(19)	-0.0087(16)	-0.0037(16)
O11	0.0168(19)	0.024(2)	0.043(3)	0.0060(19)	-0.0064(18)	-0.0043(16)
O12	0.025(2)	0.033(2)	0.055(3)	0.013(2)	-0.012(2)	-0.0133(18)
N5	0.034(3)	0.029(3)	0.027(3)	0.004(2)	-0.007(2)	-0.005(2)
N6	0.014(2)	0.025(2)	0.026(3)	0.002(2)	0.0030(18)	-0.0044(17)
N7	0.023(2)	0.017(2)	0.039(3)	0.007(2)	-0.006(2)	-0.0064(18)

N8	0.021(2)	0.030(3)	0.053(4)	0.012(3)	-0.015(2)	-0.008(2)
C19	0.013(3)	0.036(3)	0.033(3)	0.002(2)	-0.001(2)	-0.005(2)
C20	0.012(2)	0.035(3)	0.031(3)	0.003(2)	-0.006(2)	-0.006(2)
C21	0.024(3)	0.033(3)	0.030(3)	0.004(2)	-0.004(2)	-0.002(2)
C22	0.033(3)	0.040(3)	0.037(4)	0.010(3)	-0.002(3)	-0.005(3)
C23	0.023(3)	0.030(3)	0.036(3)	0.000(3)	-0.002(2)	-0.005(2)
C24	0.016(3)	0.031(3)	0.033(3)	0.001(2)	-0.004(2)	-0.005(2)
C25	0.018(2)	0.021(3)	0.028(3)	0.005(2)	0.005(2)	-0.007(2)
C26	0.020(3)	0.023(3)	0.029(3)	0.009(2)	0.003(2)	-0.005(2)
C27	0.012(2)	0.026(3)	0.037(3)	0.002(2)	0.003(2)	-0.002(2)
C28	0.016(3)	0.018(3)	0.048(4)	0.001(2)	-0.012(2)	0.003(2)
C29	0.043(4)	0.027(3)	0.052(4)	-0.008(3)	-0.009(3)	-0.010(3)
C30	0.033(3)	0.034(4)	0.066(5)	0.004(3)	-0.001(3)	0.000(3)
C31	0.106(8)	0.081(7)	0.078(8)	0.019(6)	0.039(7)	0.046(6)
C32	0.066(7)	0.095(7)	0.159(12)	0.088(8)	0.041(7)	0.034(6)
C33	0.021(3)	0.024(3)	0.050(4)	0.004(3)	-0.007(2)	-0.001(2)
C34	0.025(3)	0.032(3)	0.034(4)	0.002(3)	-0.003(3)	0.006(2)
C35	0.028(3)	0.034(3)	0.037(4)	0.002(3)	0.012(3)	0.001(2)
C36	0.026(3)	0.048(4)	0.050(5)	0.019(4)	0.012(3)	-0.002(3)
S3	0.0329(8)	0.0371(9)	0.0439(11)	0.0122(8)	-0.0117(7)	-0.0123(7)
O13	0.044(3)	0.043(3)	0.044(3)	0.005(2)	-0.019(2)	-0.017(2)
O14	0.039(3)	0.051(3)	0.032(3)	-0.002(2)	0.006(2)	-0.011(2)
O15	0.057(3)	0.038(3)	0.049(3)	0.010(2)	-0.015(3)	0.001(2)
O16	0.039(3)	0.042(3)	0.049(3)	0.017(2)	-0.017(2)	-0.014(2)
O17	0.035(2)	0.063(3)	0.028(3)	0.005(2)	-0.009(2)	-0.021(2)
O18	0.023(3)	0.157(6)	0.030(3)	0.016(3)	0.000(2)	-0.018(3)
N9	0.029(3)	0.034(3)	0.027(3)	0.001(2)	-0.006(2)	-0.006(2)
N10	0.037(3)	0.050(3)	0.027(3)	0.010(2)	-0.005(2)	-0.024(2)
N11	0.030(3)	0.106(5)	0.017(3)	-0.003(3)	-0.003(2)	-0.015(3)
N12	0.024(3)	0.129(7)	0.033(4)	-0.003(4)	0.003(3)	-0.008(3)
C37	0.018(3)	0.033(3)	0.038(3)	0.006(2)	-0.001(2)	-0.012(2)
C38	0.018(3)	0.035(3)	0.028(3)	0.000(2)	-0.004(2)	-0.004(2)
C39	0.024(3)	0.032(3)	0.039(4)	0.003(3)	0.004(3)	-0.009(2)
C40	0.040(4)	0.038(3)	0.033(4)	0.006(3)	0.005(3)	-0.010(3)
C41	0.031(3)	0.044(3)	0.041(4)	0.000(3)	-0.002(3)	-0.013(3)
C42	0.032(3)	0.033(3)	0.046(4)	0.005(3)	0.003(3)	-0.002(3)
C43	0.036(3)	0.053(4)	0.030(4)	0.016(3)	-0.002(3)	-0.022(3)
C44	0.064(4)	0.057(4)	0.032(4)	0.008(3)	0.010(3)	-0.030(3)
C45	0.029(3)	0.074(4)	0.019(3)	0.012(3)	-0.002(2)	-0.025(3)
C46	0.026(3)	0.119(6)	0.023(4)	0.001(4)	-0.002(3)	-0.006(3)
C47	0.034(4)	0.104(6)	0.029(4)	-0.014(4)	0.001(3)	0.005(4)
C48	0.038(4)	0.119(7)	0.042(5)	-0.010(5)	-0.005(3)	-0.021(4)
C49	0.072(7)	0.14(1)	0.086(8)	-0.018(7)	-0.021(6)	-0.029(7)
C50	0.078(7)	0.134(10)	0.049(5)	0.009(6)	-0.011(5)	-0.038(7)

C51	0.030(3)	0.129(7)	0.020(4)	-0.015(4)	-0.006(3)	-0.014(4)
C52	0.095(7)	0.059(5)	0.050(5)	0.020(4)	-0.002(5)	-0.022(5)
C53	0.052(4)	0.063(5)	0.066(6)	0.006(4)	0.004(4)	-0.039(4)
C54	0.096(8)	0.087(7)	0.091(8)	-0.014(6)	-0.009(6)	-0.040(6)
S4	0.0235(8)	0.0402(9)	0.0376(10)	0.0116(7)	-0.0030(7)	-0.0062(6)
O19	0.042(3)	0.038(3)	0.044(3)	0.001(2)	0.011(2)	0.005(2)
O20	0.043(3)	0.049(3)	0.046(3)	-0.006(2)	-0.012(2)	-0.004(2)
O21	0.035(3)	0.032(2)	0.057(3)	0.011(2)	0.002(2)	-0.0096(19)
O22	0.023(2)	0.067(3)	0.037(3)	0.002(2)	-0.001(2)	-0.003(2)
O23	0.028(2)	0.065(3)	0.027(3)	0.012(2)	-0.0039(19)	-0.010(2)
O24	0.030(3)	0.133(5)	0.030(3)	0.003(3)	-0.007(2)	-0.022(3)
N13	0.037(3)	0.034(3)	0.032(3)	-0.001(2)	0.001(2)	-0.012(2)
N14	0.020(2)	0.047(3)	0.041(3)	0.013(3)	-0.005(2)	0.000(2)
N15	0.022(3)	0.094(5)	0.023(3)	0.004(3)	-0.007(2)	-0.021(3)
N16	0.022(3)	0.126(7)	0.040(4)	-0.013(4)	0.003(3)	-0.017(3)
C55	0.015(3)	0.037(3)	0.039(3)	0.005(2)	-0.008(2)	-0.010(2)
C56	0.020(3)	0.034(3)	0.033(3)	0.000(2)	-0.005(2)	-0.004(2)
C57	0.027(3)	0.027(3)	0.039(4)	0.000(3)	-0.001(3)	-0.005(2)
C58	0.038(4)	0.038(3)	0.030(4)	0.002(3)	-0.009(3)	-0.003(3)
C59	0.031(3)	0.036(3)	0.037(4)	-0.007(3)	-0.010(3)	-0.004(3)
C60	0.023(3)	0.037(3)	0.041(4)	-0.004(3)	-0.016(3)	-0.009(2)
C61	0.028(3)	0.060(4)	0.026(4)	0.015(3)	-0.012(3)	0.000(3)
C62	0.030(3)	0.067(4)	0.047(5)	0.026(3)	-0.007(3)	-0.002(3)
C63	0.022(3)	0.064(4)	0.025(3)	0.012(3)	-0.007(2)	0.000(3)
C64	0.024(3)	0.097(5)	0.030(4)	-0.010(4)	-0.005(3)	-0.017(3)
C65	0.045(4)	0.096(6)	0.075(6)	-0.025(5)	-0.012(4)	-0.010(4)
C66	0.055(5)	0.109(7)	0.080(7)	-0.018(5)	-0.020(5)	-0.004(5)
C67	0.100(9)	0.154(12)	0.124(12)	-0.057(10)	-0.009(8)	0.018(9)
C68	0.071(7)	0.156(12)	0.079(7)	0.015(7)	-0.021(6)	0.019(7)
C69	0.024(3)	0.104(6)	0.026(4)	-0.010(4)	-0.002(3)	-0.009(3)
C70	0.044(4)	0.067(5)	0.058(6)	0.030(4)	0.000(4)	-0.003(4)
C71	0.027(3)	0.068(5)	0.091(7)	0.039(5)	0.000(4)	0.001(3)
C72	0.052(5)	0.099(8)	0.117(9)	0.068(7)	-0.019(5)	-0.015(5)

Table 5 . Bond Distances in Compound 3, Å

S1-O3	1.426(5)	S1-O4	1.432(4)	S1-N2	1.662(5)
S1-C1	1.790(6)	O1-N1	1.224(7)	O2-N1	1.235(7)
O5-C9	1.219(7)	O6-C15	1.224(8)	N1-C2	1.469(8)
N2-C7	1.480(7)	N2-C8	1.518(8)	N3-C9	1.351(8)
N3-C10	1.449(8)	N4-C15	1.338(8)	C1-C2	1.377(9)
C1-C6	1.382(9)	C2-C3	1.376(9)	C3-C4	1.398(9)
C4-C5	1.395(10)	C5-C6	1.428(10)	C7-C8	1.494(10)
C7-C9	1.491(9)	C8-C16	1.520(9)	C8-C17	1.522(8)
C10-C11	1.528(10)	C10-C15	1.529(9)	C11-C12	1.537(10)
C12-C13	1.535(12)	C12-C14	1.472(13)	C17-C18	1.539(10)
S2-O9	1.432(5)	S2-O10	1.424(4)	S2-N6	1.658(5)
S2-C19	1.781(7)	O7-N5	1.232(7)	O8-N5	1.222(7)
O11-C27	1.206(7)	O12-C33	1.258(9)	N5-C20	1.459(8)
N6-C25	1.449(7)	N6-C26	1.510(7)	N7-C27	1.372(8)
N7-C28	1.438(8)	N8-C33	1.337(8)	C19-C20	1.399(9)
C19-C24	1.374(9)	C20-C21	1.374(9)	C21-C22	1.373(10)
C22-C23	1.375(10)	C23-C24	1.410(10)	C25-C26	1.467(9)
C25-C27	1.518(9)	C26-C34	1.528(9)	C26-C35	1.509(8)
C28-C29	1.549(9)	C28-C33	1.523(9)	C29-C30	1.505(10)
C30-C31	1.499(12)	C30-C32	1.537(13)	C35-C36	1.520(9)
S3-O15	1.442(6)	S3-O16	1.432(6)	S3-N10	1.697(6)
S3-C37	1.797(7)	O13-N9	1.230(7)	O14-N9	1.212(7)
O17-C45	1.209(9)	O18-C51	1.214(12)	N9-C38	1.473(8)
N10-C43	1.446(10)	N10-C44	1.489(9)	N11-C45	1.338(10)
N11-C46	1.467(11)	N12-C51	1.372(11)	C37-C38	1.404(9)
C37-C42	1.348(10)	C38-C39	1.370(9)	C39-C40	1.397(10)
C40-C41	1.386(10)	C41-C42	1.425(11)	C43-C44	1.512(11)
C43-C45	1.474(11)	C44-C52	1.470(14)	C44-C53	1.515(12)
C46-C47	1.523(13)	C46-C51	1.518(11)	C47-C48	1.555(12)
C48-C49	1.533(15)	C48-C50	1.475(15)	C53-C54	1.431(14)
S4-O21	1.419(5)	S4-O22	1.435(5)	S4-N14	1.665(6)
S4-C55	1.782(7)	O19-N13	1.228(7)	O20-N13	1.220(8)
O23-C63	1.202(8)	O24-C69	1.258(11)	N13-C56	1.469(9)
N14-C61	1.457(10)	N14-C62	1.487(10)	N15-C63	1.313(9)
N15-C64	1.462(10)	N16-C69	1.334(10)	C55-C56	1.427(9)
C55-C60	1.368(10)	C56-C57	1.351(10)	C57-C58	1.411(10)
C58-C59	1.347(10)	C59-C60	1.385(10)	C61-C62	1.494(12)
C61-C63	1.514(10)	C62-C70	1.536(11)	C62-C71	1.530(11)
C64-C65	1.482(12)	C64-C69	1.544(12)	C65-C66	1.564(15)
C66-C67	1.536(17)	C66-C68	1.478(18)	C71-C72	1.532(15)

Table 6 . Bond Angles in Compound 3, °

O3-S1-O4	119.7(3)	O3-S1-N2	107.2(3)	O3-S1-C1	106.5(3)
O4-S1-N2	112.2(2)	O4-S1-C1	108.1(3)	N2-S1-C1	101.5(3)
O1-N1-O2	122.9(6)	O1-N1-C2	118.7(6)	O2-N1-C2	118.4(5)
C7-N2-S1	118.5(4)	C7-N2-C8	59.8(4)	C8-N2-S1	121.5(4)
C9-N3-C10	123.8(5)	C2-C1-S1	126.0(5)	C2-C1-C6	119.0(6)
C6-C1-S1	114.8(5)	C1-C2-N1	121.5(6)	C3-C2-N1	115.4(6)
C3-C2-C1	122.9(6)	C2-C3-C4	118.7(6)	C5-C4-C3	120.3(7)
C4-C5-C6	119.1(6)	C1-C6-C5	120.0(6)	N2-C7-C8	61.4(4)
N2-C7-C9	116.5(5)	C9-C7-C8	125.0(5)	N2-C8-C16	119.8(5)
N2-C8-C17	112.3(5)	C7-C8-N2	58.9(4)	C7-C8-C16	118.8(5)
C7-C8-C17	119.5(6)	C16-C8-C17	115.4(6)	O5-C9-N3	124.1(6)
O5-C9-C7	123.9(5)	N3-C9-C7	112.0(5)	N3-C10-C11	110.0(5)
N3-C10-C15	109.9(6)	C11-C10-C15	109.5(5)	C10-C11-C12	115.3(6)
C13-C12-C11	110.2(7)	C14-C12-C11	111.5(7)	C14-C12-C13	111.2(9)
O6-C15-N4	124.1(6)	O6-C15-C10	120.7(5)	N4-C15-C10	115.0(6)
C8-C17-C18	110.1(5)	O9-S2-N6	107.3(3)	O9-S2-C19	106.2(3)
O10-S2-O9	118.8(3)	O10-S2-N6	112.9(2)	O10-S2-C19	109.5(3)
N6-S2-C19	100.3(3)	O7-N5-C20	118.1(5)	O8-N5-O7	124.5(5)
O8-N5-C20	117.4(5)	C25-N6-S2	118.4(4)	C25-N6-C26	59.4(4)
C26-N6-S2	121.0(4)	C27-N7-C28	123.3(5)	C20-C19-S2	124.5(5)
C24-C19-S2	117.7(5)	C24-C19-C20	117.7(6)	C19-C20-N5	122.2(6)
C21-C20-N5	116.5(6)	C21-C20-C19	121.3(6)	C22-C21-C20	120.6(6)
C21-C22-C23	119.6(7)	C22-C23-C24	119.7(6)	C19-C24-C23	121.0(6)
N6-C25-C26	62.4(4)	N6-C25-C27	116.0(5)	C26-C25-C27	125.1(5)
N6-C26-C34	119.7(5)	C25-C26-N6	58.2(4)	C25-C26-C34	118.6(5)
C25-C26-C35	120.3(6)	C35-C26-N6	113.1(5)	C35-C26-C34	114.9(5)
O11-C27-N7	124.6(6)	O11-C27-C25	124.2(5)	N7-C27-C25	111.2(5)
N7-C28-C29	109.1(5)	N7-C28-C33	110.3(6)	C33-C28-C29	107.7(5)
C30-C29-C28	114.1(5)	C29-C30-C32	112.0(7)	C31-C30-C29	113.1(7)
C31-C30-C32	112.9(9)	O12-C33-N8	122.9(6)	O12-C33-C28	120.6(5)
N8-C33-C28	116.5(6)	C26-C35-C36	112.2(5)	O15-S3-N10	106.5(3)
O15-S3-C37	105.9(3)	O16-S3-O15	119.7(3)	O16-S3-N10	111.8(3)
O16-S3-C37	109.6(3)	N10-S3-C37	101.7(3)	O13-N9-C38	116.7(5)
O14-N9-O13	124.3(6)	O14-N9-C38	119.0(5)	C43-N10-S3	119.0(5)
C43-N10-C44	62.0(5)	C44-N10-S3	119.8(6)	C45-N11-C46	123.4(7)
C38-C37-S3	124.2(5)	C42-C37-S3	116.4(5)	C42-C37-C38	119.1(6)
C37-C38-N9	122.9(6)	C39-C38-N9	115.2(5)	C39-C38-C37	121.8(6)
C38-C39-C40	119.0(6)	C41-C40-C39	120.2(7)	C40-C41-C42	118.9(7)
C37-C42-C41	120.8(6)	N10-C43-C44	60.4(5)	N10-C43-C45	117.1(7)
C45-C43-C44	124.9(7)	N10-C44-C43	57.6(5)	N10-C44-C53	111.4(7)

C43-C44-C53	118.5(8)	C52-C44-N10	121.0(8)	C52-C44-C43	116.2(8)
C52-C44-C53	118.1(8)	O17-C45-N11	124.1(8)	O17-C45-C43	124.5(7)
N11-C45-C43	111.4(7)	N11-C46-C47	111.1(6)	N11-C46-C51	108.4(8)
C51-C46-C47	110.4(7)	C46-C47-C48	115.2(7)	C49-C48-C47	111.7(8)
C50-C48-C47	112.5(8)	C50-C48-C49	111.3(11)	O18-C51-N12	123.0(7)
O18-C51-C46	122.2(7)	N12-C51-C46	114.6(9)	C54-C53-C44	112.8(8)
O21-S4-O22	119.7(3)	O21-S4-N14	106.6(3)	O21-S4-C55	105.5(3)
O22-S4-N14	112.6(3)	O22-S4-C55	109.2(3)	N14-S4-C55	101.6(3)
O19-N13-C56	119.3(6)	O20-N13-O19	122.9(6)	O20-N13-C56	117.7(5)
C61-N14-S4	119.1(5)	C61-N14-C62	61.0(5)	C62-N14-S4	121.5(5)
C63-N15-C64	124.4(6)	C56-C55-S4	125.2(5)	C60-C55-S4	118.9(5)
C60-C55-C56	115.9(6)	C55-C56-N13	120.9(6)	C57-C56-N13	116.8(6)
C57-C56-C55	122.3(6)	C56-C57-C58	119.1(6)	C59-C58-C57	119.3(7)
C58-C59-C60	120.8(7)	C55-C60-C59	122.1(6)	N14-C61-C62	60.5(5)
N14-C61-C63	118.4(6)	C62-C61-C63	125.3(6)	N14-C62-C61	58.5(5)
N14-C62-C70	119.6(6)	N14-C62-C71	113.8(7)	C61-C62-C70	117.8(7)
C61-C62-C71	120.9(7)	C71-C62-C70	114.7(7)	O23-C63-N15	124.4(7)
O23-C63-C61	122.5(7)	N15-C63-C61	113.1(6)	N15-C64-C65	110.4(6)
N15-C64-C69	107.3(7)	C65-C64-C69	107.2(7)	C64-C65-C66	112.1(8)
C67-C66-C65	108.1(10)	C68-C66-C65	113.4(9)	C68-C66-C67	112.8(13)
O24-C69-N16	120.3(8)	O24-C69-C64	123.1(6)	N16-C69-C64	116.6(8)
C62-C71-C72	111.1(9)				

This report has been created with Olex2 [7], compiled on 2017.08.10 svn.r3458 for OlexSys.

References

[1] APEX2 2014.11-0
[2] SAINT v8.34A
[3] SADABS v2014/5
[4] SHELXS-97
[5] PLATON (V-150216)
[6] SHELXL-2014/7
[7] Olex2 (Dolomanov et al., 2009)

Computational Methods: General Information

Calculations were performed using WebMO running *Gaussian 09*. Computed ^{13}C chemical shifts reported herein were determined using the GIAO method in *Gaussian09* at the *SCRF*-B3LYP/6-31G(d,p)//B3LYP/6-31G(d) level of theory, and are empirically scaled. *SCRF* refers to inclusion of solvent effects (acetone) using the PCM implicit solvent model. For the starting point geometry optimization, NOESY NMR data of **1** was taken into account to approximate the molecular structure. Subsequent conformational analysis was conducted based on starting point geometry optimization results (and corroboration with NOESY data) to afford seven additional conformers. Upon obtaining the geometry optimized conformers, subsequent NMR calculations were performed respectively. The computed ^{13}C chemical shifts for **1** matched the experimental values exceptionally well (R^2 values >0.998). Of the eight conformers, the best fitting data is represented in **Table 1**.

References for computational methods:

WebMO: Schmidt, J. R.; Polik, W. F. *WebMO Enterprise*, version 17.0; WebMO LLC: Holland, MI, USA, 2017; http://www.webmo.net (accessed October, 2017).

Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

GIAO: a) London, F. *J. Phys. Radium* **1937,** *8,* 397-409. (b) McWeeny, R. *Phys. Rev.* **1962**, *126*, 1028-1034. (c) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789-807. (e) Wolinski, K.; Hilton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251-8260. (f) Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys.* **1996,** *104,* 5497-5509.

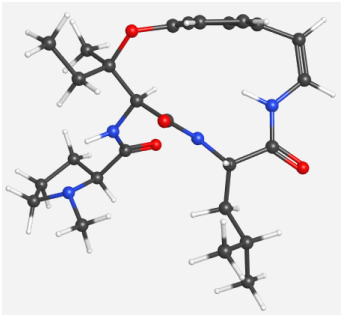
B3LYP: (a) Becke, A.D. *J. Chem. Phys.* **1993,** *98,* 1372-1377. (b) Becke, A.D. *J. Chem. Phys.* **1993,** *98,* 5648-5652. (c) Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev. B* **1988,** *37,* 785-789. (d) Stephens, P.J.; Devlin, F. J.; Chabalowski, C.F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623-11627. (e) Tirado-Rives, J.; Jorgensen, W. L. *J. Chem. Theory Comput.* **2008**, *4*, 297-306.

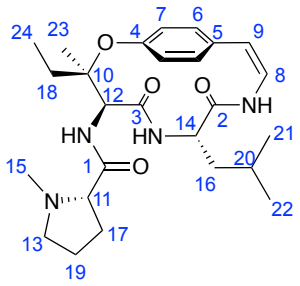
PCM: J. R. Cheeseman, G. W. Trucks, T. A. Keith, M. J. Frisch, *J. Chem. Phys.* **1996**, *104*, 5497.

Empirical Scaling of Computed Chemical Shifts: Computed chemical shifts are commonly scaled empirically in order to remove potential systematic errors. The scaling factors have been determined by comparison of computed NMR data with known experimental chemical shifts for large databases of molecules. These factors (slope and intercept from a best fit line) are specific for each level of theory. The scaling factor (for *SCRF*-B3LYP/6-31+G(d,p)//B3LYP/6-31G(d) level of theory, slope: -0.9600, intercept: 190.0155) used in this study was taken from a database made available by Tantillo and co-workers (http://cheshirenmr.info). Equation for empirical scaling: $\delta = \frac{b-\sigma}{-m}$, where δ=computed chemical shift relative to TMS, σ=computed isotropic shielding constant, m=slope, b=intercept.

Selected references: (a) Lodewyk, M. W.; Soldi, C.; Jones, P. B.; Olmstead, M. M.; Rita, J.; Shaw, J. T.; Tantillo, D. J. *J. Am. Chem. Soc.* **2012**, *134*, 18550. (b) Pierens, G. K. *J. Comput. Chem.* **2014**, *35*, 1388.

Table 1. Comparison of Experimental and Computed (conformer #1) ^{13}C NMR Chemical Shifts (ppm) of **1** in Acetone.





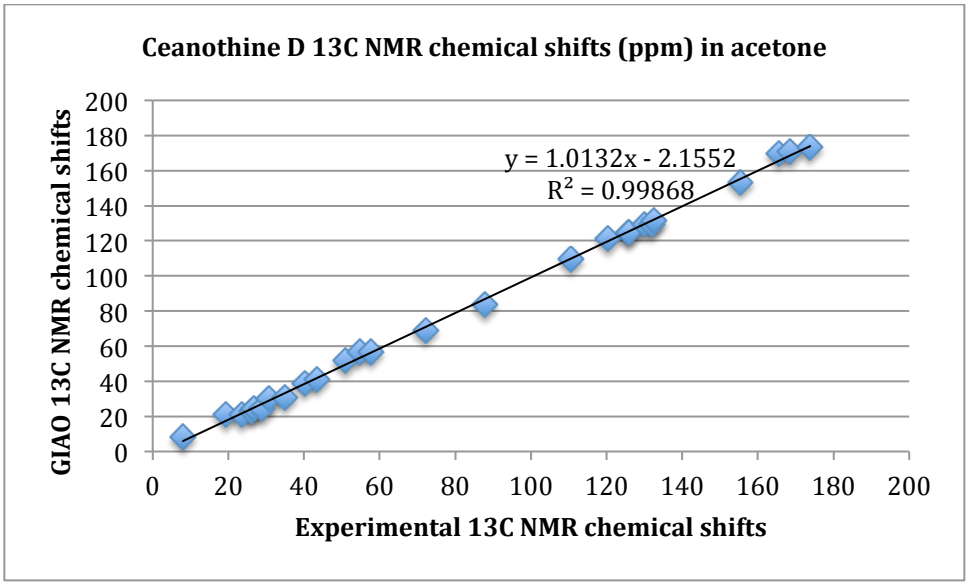
Position	Expt. ^{13}C [δ/ppm][a]	GIAO ^{13}C [δ/ppm][b]
1	173.4627	173.8161
2	170.8070	168.5154
3	169.7592	165.4530
4	153.3888	155.4218
5	131.3898	132.4295
6	129.1398	131.9751
6'	129.1398	130.0560
7	124.7338	125.9972
7'	124.7338	125.7415
8	121.1038	120.2624
9	109.4942	110.5354
10	83.7822	87.7921
11	69.2749	72.1510
12	56.5534	57.7358
13	56.5534	54.6006
14	51.6885	50.9869
15	41.0598	43.2829
16	39.0827	40.1792
17	30.9511	34.9083
18	30.0188	30.7639
19	24.4241	29.0362
20	24.2401	26.7955
21	22.7175	26.1651
22	21.0885	23.5370
23	20.9349	19.3511
24	8.2686	8.0183

Largest Outlier Δδ=4.61

[a]Experimental ^{13}C NMR chemical shift values (500 MHz) in acetone-*d6*.

[b] GIAO values calculated at the B3LYP/6-31G(d,p)//B3LYP/6-31G(d) level of theory (including acetone as the implicit solvent in the NMR single-point calculation, *SCRF*=PCM, Solvent=Acetone).

Figure S1. Correlation plot of Ceanothine D (**1**) calculated (conformer #1) *vs.* experimental ^{13}C NMR chemical shifts in acetone-*d6*.



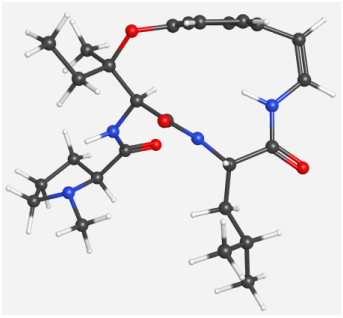
The corresponding R^2 value (0.99868) shown in Figure S1 was obtained by a linear regression carried with its points. The findings suggest a good agreement between the calculated NMR data (conformer #1) and experimental data of **1**. [1]

[1] Caro, M. S. B.; de Oliveira, L. H.; Ilha, V.; Burrow, R. A.; Dacol, I I.; Morel, A. F. *J. Nat. Prod.* **2012**, *75*, 1220.

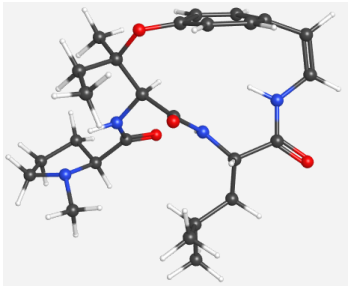
Conformers of Ceanothine D

Structures of all eight conformers at the B3LYP/6-31G(d) level of theory (gas-phase) are shown below. The difference between the lowest and highest RB3LYP energy conformers was 4.05 kcal/mol.

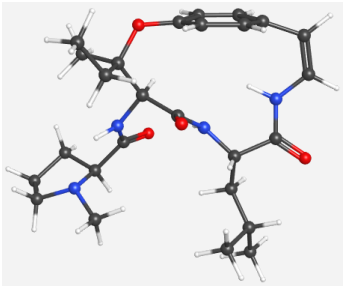
conformer #1



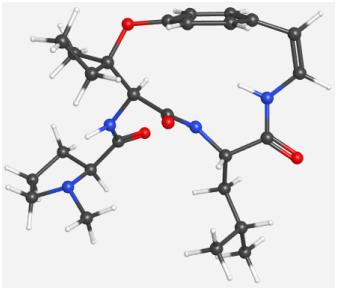
conformer #2



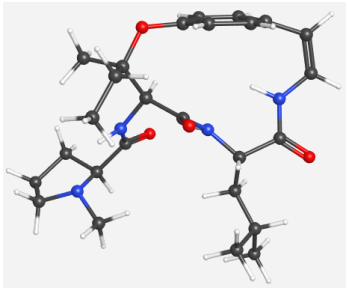
conformer #3



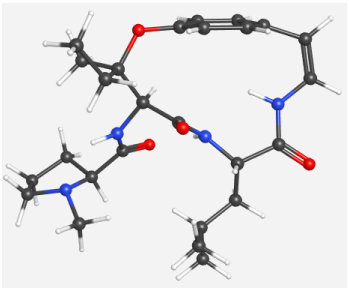
conformer #4



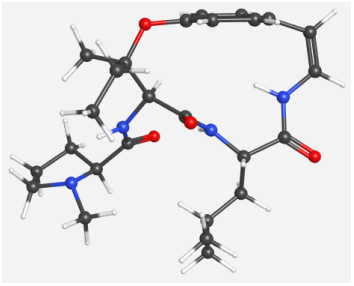
conformer #5



conformer #6



conformer #7



conformer #8

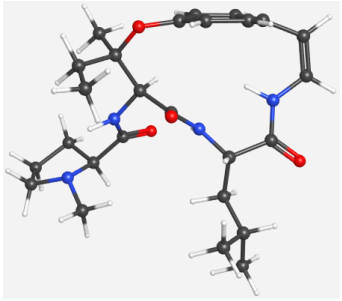
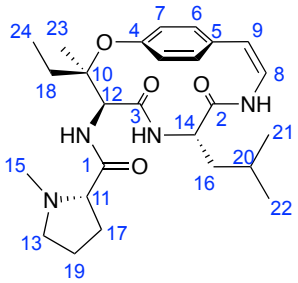


Table 2. Comparison of Experimental and Averaged Computed (conformers #1-8) ^{13}C NMR Chemical Shifts (ppm) of **1** in Acetone.



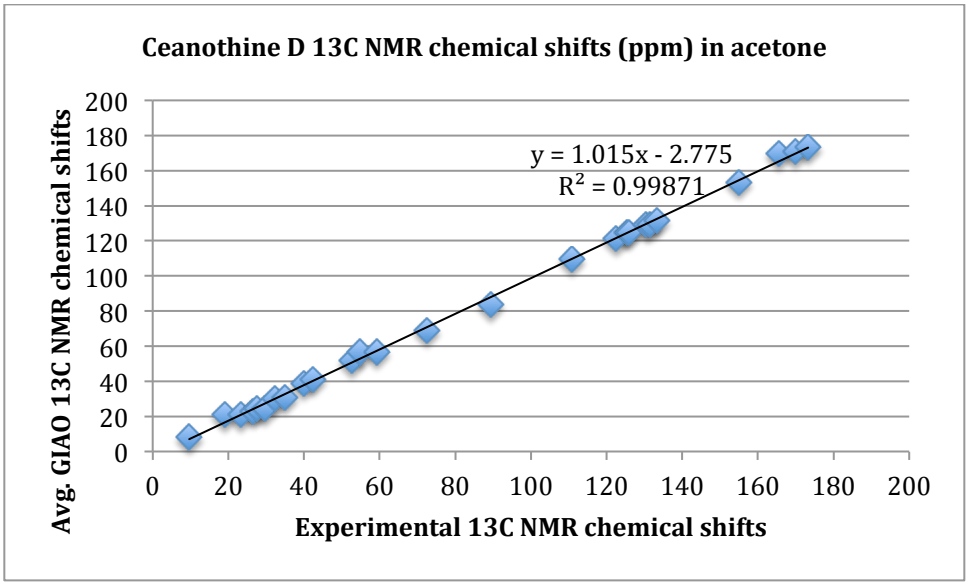
Position	Expt. ^{13}C [δ/ppm][a]	GIAO ^{13}C [δ/ppm][b]
1	173.4627	173.2876
2	170.8070	169.9657
3	169.7592	165.5261
4	153.3888	155.0293
5	131.3898	133.2513
6	129.1398	131.5042
6'	129.1398	130.5180
7	124.7338	125.9319
7'	124.7338	125.4075
8	121.1038	122.5488
9	109.4942	110.7706
10	83.7822	89.3241
11	69.2749	72.4154
12	56.5534	59.3100
13	56.5534	54.8168
14	51.6885	52.7176
15	41.0598	42.3681
16	39.0827	39.9269
17	30.9511	34.9424
18	30.0188	32.3198
19	24.4241	29.6748
20	24.2401	27.4628
21	22.7175	26.3443
22	21.0885	23.4298
23	20.9349	19.0841
24	8.2686	9.6556

Largest Outlier Δδ=5.54

[a]Experimental ^{13}C NMR chemical shift values (500 MHz) in acetone-*d6*.

[b] GIAO values calculated at the B3LYP/6-31G(d,p)//B3LYP/6-31G(d) level of theory (including acetone as the implicit solvent in the NMR single-point calculation, *SCRF*=PCM, Solvent=Acetone).

Figure S2. Correlation plot of Ceanothine D (**1**) calculated (average of conformers #1-8) *vs.* experimental ^{13}C NMR chemical shifts in acetone-*d6*.



The corresponding R^2 value (0.99871) shown in Figure S2 was obtained by a linear regression carried with its points. The findings suggest a good agreement between the calculated NMR data (average of conformers #1-8) and experimental data of **1**.