Supporting Information

Preparation of a 1,2-isoxazolidine synthon for the synthesis of zetekitoxin AB.

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General experimental considerations:

All reactions requiring anhydrous conditions were conducted in flame-dried glassware under a positive pressure of either nitrogen or argon. Commercially available reagents were used as received; otherwise, materials were purified according to *Purification of Laboratory Chemicals*.[1] Dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), diethyl ether (Et_2O) were degassed with nitrogen and passed through a solvent purification system (Innovative Technologies Pure Solv). Triethylamine (Et_3N) was distilled from CaH_2 immediately prior to use. Reactions were monitored by TLC and visualized by a dual short wave/long wave UV lamp and stained with aqueous solution of ceric ammonium molybdate. Flash chromatography was performed on Merck silica gel Kieselgel 60 (230-400 mesh) from EM Science with the indicated HPLC grade solvent.

Infrared spectra were obtained using Nicolet 380-FT IR spectrometer fitted with a Smart Orbit sample system. Optical rotations were obtained at ambient temperature on a Perkin Elmer Model 343 polarimeter (Na D line) using a microcell with a 1 decimeter path length. Mass spectra were determined on a Micromass Quattro II (ESI/APCI-TOF) for HRMS at the University of Utah Mass Spectrometry Facility. 1H NMR and 13C NMR spectra were recorded at 500 MHz, 400 MHz and 125 MHz, 100MHz respectively. Proton resonances were reported relative to the deuterated solvent peak: 7.26 ppm for $CDCl_3$ using the following format: chemical shift (δ) (multiplicity (s= singlet, brs= broad singlet, d= doublet, dd= double of doublet, ddd= doublet of doublet of doublet, t= triplet, m= multiplet), coupling constant(s)

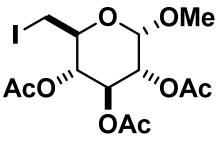
J in Hz, integration).[2] Carbon resonances were reported as chemical shifts (δ) in parts per million, relative to the center line signal of the respective solvent peak: 77.23 ppm for $CDCl_3$.

References:

1. *Purification of Laboratory Chemicals*. 2003, 5th Ed. Armarego, W. L. F.; Chai, C. L. L.
2. Hoye, T. R.; Hansen, P. R.; Vyvyan, J. R. *J. Org. Chem*. **1994**, *59*, 4096.

Experimental Procedures:

Methyl α-D-2,3,4-triacetoxy-6-deoxy-6-iodoglucopyranoside (4)

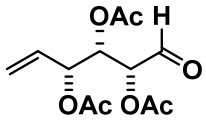


To a solution of methyl α-D-glucopyranoside **3** (15.00 g, 77.24 mmol) in toluene (1500 mL) was added triphenylphosphine (30.39 g, 115.9 mmol), imidazole (15.77 g, 231.7 mmol) and iodine (27.44 g, 108.1 mmol) at room temperature. After 5 min the reaction mixture was heated to 70 °C for 2 hrs. The reaction mixture was then cooled to room temperature and water (200 mL) was added and vigorously stirred for 15 min. The aqueous layer was separated and the organic layer was extracted with water (2 × 100 mL). The combined aqueous layers were concentrated under reduced pressure and allowed it to dry under high vacuum afford methyl α-D-6-deoxy-6-iodoglucopyranoside (28.00 g) as an off-white solid.

To a solution of methyl α-D-6-deoxy-6-iodoglucopyranoside (28.0 g, 92.1 mmol) in pyridine (150 mL), was added acetic anhydride (52.08 mL, 552.5 mmol) and DMAP (1.12 g, 9.20 mmol) at room temperature and allowed it to stir for 16 hrs. The solvent was evaporated under reduced pressure and the residue was dissolved in toluene (300 mL) and washed with water (200 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography (30 % EtOAc in hexanes) gave methyl α-D-2,3,4-triacetoxy-6-deoxy-6-iodoglucopyranoside **4** (23.26 g, 70% over 2 steps) as a colorless solid. R*f* = 0.48 (7.0:3.0 Hexanes: EtOAc); mp. 146-148°C. $[\alpha]^{20}_D$ = +127° (c = 0.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.45 (t, *J* = 10.0 Hz, 1H), 4.95 (d, *J* = 4.0 Hz, 1H), 4.88-4.83 (m, 2H), 3.80 (ddd, *J* = 18.5, 8.5, 3.0 Hz, 1H), 3.46 (s, 3H), 3.30 (dd, *J* = 10.5, 2.5 Hz, 1H), 3.14 (dd, *J* = 11.5, 8.5, Hz, 1H), 2.06 (s, 3H), 2.04 (s, 3H) 1.99 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.3,

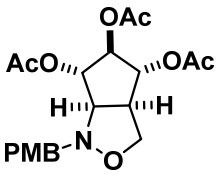
170.2, 169.8, 96.9, 72.7, 71.1, 69.9, 68.8, 55.9, 20.9, 20.8, 3.8 ppm; IR (Thin film) 1739, 1612, 1513, 1366, 1225, 1176, 1039 cm-1; HRMS (ESI) calcd for $C_{13}H_{19}IO_8Na$ (M+Na): 453.0023, found: 453.0023.

(2*R*,3*S*,4*R*)-1-oxohex-5-ene-2,3,4-triyl triacetate (5)



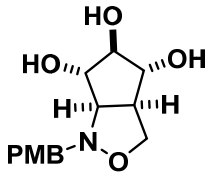
To a solution of methyl α-D-2,3,4-triacetoxy-6-deoxy-6-iodoglucopyranoside **4** (10.0 g, 23.2 mmol) in hot ethanol (250 mL) was added zinc dust (15.1 g, 232.5 mmol) and the mixture was heated at reflux for 1 hr. The contents of the flask were cooled down to room temperature and filtered through a pad of celite® and the pad was washed with an additional amount of ethanol (50 mL). The combined filtrates were concentrated and dried under reduced pressure to give the aldehyde **5** as a yellow oil (6.32 g, quantitative) which was used for the next step without further purification and characterization.

(3a*S*,4*S*,5*R*,6*R*,6a*S*)-1-(4-methoxybenzyl)hexahydro-1H-cyclopenta[c]isoxazole-4,5,6-triyl triacetate (6)



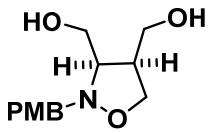
The crude aldehyde **5** (6.32 g, 23.2 mmol) obtained above was dissolved in ethanol (150 mL) and pyridine (30 mL). *p*-Methoxybenzylhydroxylamine (3.44 g, 27.9 mmol) was then added to the flask and the mixture heated at 65 °C for 3 hrs. The contents of the flask were cooled down to room temperature and the solvent was evaporated under reduced pressure. Purification by flash column chromatography (25% EtOAc in hexanes) gave tri-O-acetyl bicyclic isoxazolidine **6** (4.91 g, 52% over 2 steps) as a colorless solid. R*f* = 0.5 (5.0:5.0 Hexanes: EtOAc); mp. 94-96°C. $[\alpha]^{20}_D$ = -57° (c = 0.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.24 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 5.32 (t, *J* = 8.5 Hz, 1H), 5.18 (brs, 1H), 4.94 (t, *J* = 6.5 Hz, 1H), 4.13-4.08 (m, 2H), 3.94 (d, *J* = 13.0 Hz, 1H), 3.78 (s, 3H), 3.71 (d, *J* = 12.5 Hz, 1H), 3.56 (brs, 1H), 3.00-2.98 (m, 1H), 2.06 (s, 3H), 2.02 (s, 3H), 1.92 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.8, 170.7, 170.1, 159.3, 130.3, 128.6, 113.9, 78.8, 77.8, 70.8, 69.3, 58.9, 55.4, 49.5, 21.0, 21.0, 20.9, 1.2 ppm; IR (Thin film) 1752, 1369, 1244, 1221, 1044, 555 cm-1; HRMS (ESI) calcd for $C_{20}H_{25}NO_8Na$ (M+Na): 430.1478, found: 430.1479.

(3a*S*,4*S*,5*R*,6*R*,6a*S*)-1-(4-methoxybenzyl)hexahydro-1H-cyclopenta[c]isoxazole-4,5,6-triol (7)



To a solution of tri-O-acetyl bicyclic isoxazolidine **6** (1.6 g, 3.93 mmol) in methanol (20 mL) was added sodium methoxide (0.63 g, 11.79 mmol) at 0 °C and the reaction mixture stirred at room temperature for 1 hr. Saturated ammonium chloride solution was added to adjust the pH ~ 7. The solvent was then evaporated under reduced pressure. Residue was dissolved in minimum amount of water and extracted several times with 20% *i*PrOH-$CHCl_3$ mixture. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography (5% MeOH in $CHCl_3$) gave triol **7** (0.88 g, 80%) as a colorless solid. R*f* = 0.4 (9.0:1.0 $CHCl_3$: MeOH); mp. 118-120°C. $[\alpha]^{20}_D$ = +52.5° (c = 0.4, MeOH); ^{1}H NMR (DMSO d_6, 500 MHz) δ 7.24 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 2H), 5.00 (d, *J* = 4.5 Hz, 1H), 4.97 (d, *J* = 5.5 Hz, 1H), 4.92 (d, *J* = 4.5 Hz, 1H), 3.96 (brs, 1H), 3.75 (s, 4H), 3.61 (d, *J* = 13.0 Hz, 1H), 3.54 (dd, *J* = 8.5, 1.5 Hz, 1H), 3.33 (brs, 3H), 3.16-3.15 (m, 1H), 2.69-2.68 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.2, 130.1, 128.6, 113.9, 80.3, 78.6, 71.9, 69.4, 59.0, 55.4, 49.7, 1.2 ppm; IR (Thin film) 3343, 2901, 2835, 1611, 1513, 1463, 1352, 1302, 1249, 1177, 1107, 1033, 824, 805, 762, 599, 580, 572, 561 cm-1; HRMS (ESI) calcd for $C_{14}H_{19}NO_5Na$ (M+Na): 304.1161, found: 304.1157.

((3*S*,4*R*)-2-(4-methoxybenzyl)isoxazolidine-3,4-diyl)dimethanol (9)

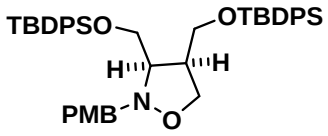


To a solution of the triol **7** (6.90 g, 24.5 mmol) in water (250 mL) was added $NaIO_4$ (18.4 g, 85.9 mmol, dissolved in 150 mL of water) and solid $NaHCO_3$ (to maintain the pH of the reaction ~ 8) at 0 °C. The mixture was allowed to stir at room temperature for 30 min. The mixture was filtered through a pad of celite® and the pad was washed with an additional EtOAc (50 mL). The organic layer was separated and the aqueous layer was extracted with EtOAC (3 × 50 mL).The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure to give **8**.

The crude compound **8** obtained above was dissolved in dry THF (250 mL) and cooled to 0 °C. $LiAlH_4$ (1.96 g, 51.7 mmol) was then added in portions and the reaction mixture stirred at room

temperature for 16 hrs. The mixture was again cooled to 0 °C and ethyl acetate (70 mL) was added carefully followed by water (30 mL) and then sodium sulfate. The mixture was then stirred until a clear solution persisten and the mixture filtered through a pad of celite® and the pad was washed with an additional portion of ethyl acetate(50 mL). Solvent was evaporated under reduced pressure and purification by flash column chromatography (3% MeOH in $CHCl_3$) gave diol **9** (4.34 g, 70% over 2 steps) as a colorless solid. R*f* = 0.45 (9.0:1.0 $CHCl_3$: MeOH); mp. 92-94°C. $[\alpha]^{20}_D$ = +73° (c = 0.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.27 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 4.20 (t, *J* = 8.5 Hz, 1H), 4.00 (d, *J* = 9.0 Hz, 1H), 3.84-3.81 (m, 2H), 3.79 (s, 3H), 3.75 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.68 (t, *J* = 7.0 Hz, 1H), 3.65-3.57 (m, 2H), 3.26 (ddd, *J* = 13.0, 8.0, 5.5 Hz, 1H), 3.06 (m, 1H), 2.96 (brs, 1H), 2.88 (brs, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.3, 130.5, 128.1, 114.1, 68.5, 66.9, 60.7, 60.7, 60.6, 55.4, 46.4 ppm; IR (Thin film) 3391, 2933, 2880, 1611, 1512, 1463, 1301, 1247, 1176, 1110, 1031, 824, 779, 757, 577 cm-1; HRMS (ESI) calcd for $C_{13}H_{19}NO_4Na$ (M+Na): 276.1212, found: 276.1211.

(3*S*,4*S*)-3,4-bis(((tert-butyldiphenylsilyl)oxy)methyl)-2-(4-methoxybenzyl)isoxazolidine (10)



To a solution of the diol **9** (2.79 g, 11.0 mmol) in dry dichloromethane (30 mL) was added imidazole (1.50 g, 22.0 mmol) and TBDPS-Cl (6.05 g, 22.0 mmol) at 0 °C and the mixture was stirred at room temperature for 1hr. Solvent was evaporated and the resulting oil was purified by flash column chromatography (4% EtOAc in hexanes) give the di-TBDPS protected isoxazolidine derivative **10** (7.79 g, 97%) as a colorless liquid. R*f* = 0.55 (9.0:1.0 hexanes: EtOAc); $[\alpha]^{20}_D$ = +45° (c = 0.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.58 (t, *J* = 8.5 Hz, 8H), 7.31-7.29 (m, 12H), 7.24 (d, *J* = 9.5 Hz, 2H), 6.82 (d, *J* = 9.5 Hz, 2H), 4.14 (t, *J* = 19.0 Hz, 1H), 4.00 (d, *J* = 16.5 Hz, 1H), 3.94-3.91 (m, 1H), 3.87 (d, *J* = 16.5 Hz, 1H), 3.78 (brs, 4H), 3.73-3.69 (m, 2H), 3.63-3.59 (m, 1H), 3.14-3.12 (m, 1H), 2.94-2.93 (m, 1H), 0.96 (s, 9H), 0.93 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.1, 135.7, 135.7, 135.7, 133.7, 133.6, 133.4, 133.3, 130.4, 130.0, 129.8, 129.8, 127.9, 127.9, 113.9, 69.4, 67.6, 63.2, 62.2, 61.9, 55.4, 47.4, 26.9, 26.9, 19.3, 19.2, 1.2 ppm;

IR (Thin film) 2929, 2855, 1512, 1471, 1427, 1247, 1173, 1111, 1084, 1037, 998, 822, 739, 701, 613 cm-1; HRMS (ESI) calcd for $C_{44}H_{55}NO_4Si_2Na$ (M+Na): 752.3568, found: 752.3569.

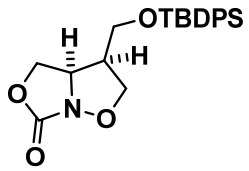
2,2,2-trichloroethyl(3*S*,4*S*)-3,4-bis(((tert-butyldiphenylsilyl)oxy)methyl)isoxazolidine-2-carboxylate (11). To a solution of the di-TBDPS protected 1,2-isoxazolidine **10** (9.2 g, 12.6 mmol) in 1,2-dichloroethane (100 mL) was added Troc-Cl (8.68 mL, 63.1 mmol) and LiI (1.77 g, 12.6 mmol) at room temperature. The reaction mixture was then heated at 70 °C for 4 hrs. Solvent was evaporated under reduced pressure and the residue was dissolved in EtOAc (200 mL) and washed with water (2 × 100 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure gave Troc protected 1,2-isoxazolidine derivative **11** as a colorless liquid, which was used for the next step without further purification. R*f* = 0.6 (9.0:1.0 hexanes: EtOAc); HRMS (ESI) calcd for $C_{40}H_{48}Cl_3NO_5Si_2Na$ (M+Na): 806.2035, found: 806.2034.

(3*R*,3a*S*)-3-(hydroxymethyl)tetrahydro-6H-oxazolo[3,4-b]isoxazol-6-one (12)

To a solution of the Troc carbamate **11** (9.87 g, 12.6 mmol) in dry THF (250 mL) was added tetra-*n*-butylammonium fluoride (1.0 M in THF) (9.89 g, 37.8 mmol) at 0 °C and stirred the reaction mixture at 60 °C for 12 hrs. The reaction mixture was cooled to room temperature and solvent evaporated under reduced pressure. The resulting oil was purified by flash column chromatography (70% EtOAc in hexanes) to afford the isoxazolidine cyclic carbamate **12** (1.76 g, 88 % over 2 steps) as a colorless liquid.

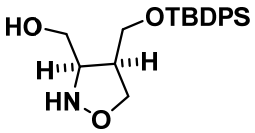
TLC R*f* = 0.45 (1.0:9.0 hexanes: EtOAc); $[\alpha]^{20}_D$ = -147.5° (c = 0.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.73 (dd, *J* = 9.5, 1.5 Hz, 1H), 4.59 (dd, *J* = 9.5, 7.0 Hz, 1H), 4.30 (t, *J* = 9.0 Hz, 1H), 4.13 (ddd, *J* = 17.5, 8.5, 1.5 Hz, 1H), 3.79-3.74 (m, 2H), 3.67 (t, *J* = 17.0 Hz, 1H), 2.99 (sextet, *J* = 9.0 Hz, 1H), 2.49 (brs, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.2, 73.0, 64.1, 59.6, 58.8, 45.1 ppm; IR (Thin film) 3481, 2920, 1766, 1468, 1384, 1191, 1112, 1043, 997, 929, 822, 790, 754 cm-1; HRMS (ESI) calcd for $C_6H_9NO_4Na$ (M+Na): 182.0430, found: 182.0428.

(3*S*,3a*S*)-3-(((tert-butyldiphenylsilyl)oxy)methyl)tetrahydro-6H-oxazolo[3,4-b]isoxazol-6- one (13).



To a solution of the cyclic carbamate **12** (2.80 g, 17.6 mmol) in dry dichloromethane (20 mL) was added imidazole (1.20 g, 17.6 mmol) and TBDPSCl (4.61 mL, 17.6 mmol) at 0 °C and the contents were stirred at room temperature for 1 hr. Solvent was evaporated and the residue was purified by flash column chromatography (15% EtOAc in hexanes) gave TBDPS protected isoxazolidine cyclic carbamate derivative **13** (5.94 g, 85%) as a colorless solid. R*f* = 0.42 (8.0:2.0 hexanes: EtOAc); mp. 102-104°C. $[\alpha]^{20}_{D}$ = -81.5° (c = 0.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.63-7.60 (m, 4H), 7.47-7.39 (m, 6H), 4.72 (d, *J* = 9.5 Hz, 1H), 4.57 (dd, *J* = 10.0, 7.5 Hz, 1H), 4.19 (t, *J* = 8.5 Hz, 1H), 4.10 (dd, *J* = 9.0, 7.5 Hz, 1H), 3.78-3.71 (m, 2H), 3.61 (t, *J* = 9.0 Hz, 1H), 2.96 (sextet, *J* = 9.0 Hz, 1H), 1.06 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.4, 135.6, 135.6, 132.7, 132.5, 130.3, 128.1, 128.1, 72.5, 63.7, 61.2, 58.8, 46.0, 26.9, 19.3 ppm; IR (Thin film) 2929, 2857, 1786, 1427, 1391, 1379, 1216, 1187, 1132, 1111, 1040, 1012, 936, 822, 789, 741, 702, 649, 614, 590 cm-1; HRMS (ESI) calcd for $C_{22}H_{27}NO_4SiNa$ (M+Na): 420.1607, found: 420.1610.

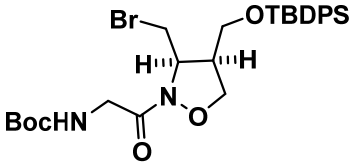
((3*S*,4*S*)-4-(((tert-butyldiphenylsilyl)oxy)methyl)isoxazolidin-3-yl)methanol



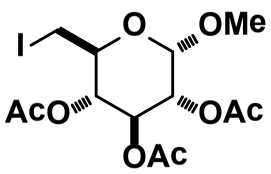
(14). To a solution of the TBDPS protected isoxazolidine cyclic carbamate derivative **13** (1.10 g, 2.76 mmol) in ethanol (10 mL) was added Cs_2CO_3 (0.99 g, 3.0 mmol) at 0 °C and the mixture stirred at room temperature for 2 hrs. Solvent was evaporated under reduced pressure (with cooling of the rotary evaporator bath) and the residue purified by flash column chromatography (65% EtOAc in hexanes) to furnish the 1,2-isoxazolidine amino alcohol **16** (0.74 g, 72%) as a colorless liquid. R*f* = 0.4 (100% EtOAc); $[\alpha]^{20}_{D}$ = -22° (c = 0.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 (d, *J* = 7.2 Hz, 4H), 7.47-7.38 (m, 6H), 3.93 (t, *J* = 16.8 Hz, 1H), 3.80-3.71 (m, 4H), 3.67 (t, *J* = 14.4 Hz, 1H), 3.59 (dd, *J* = 12.0, 6.4 Hz, 1H), 2.89 (sextet, *J* = 6.8 Hz, 1H), 1.06 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.7, 135.7, 133.0, 132.9, 130.2, 130.2, 128.1, 128.0, 128.0, 72.6, 63.3, 61.8, 59.6,

48.1, 27.0, 19.3, 1.2 ppm; IR (Thin film) 3214, 3070, 2929, 2856, 1588, 1471, 1427, 1390, 1361, 1111, 823, 741, 701, 613 cm-1; HRMS (ESI) calcd for $C_{21}H_{29}NO_3SiNa$ (M+Na): 394.1815, found: 394.1813.

tert-butyl-(2-((3*S*,4*S*)-3-(bromomethyl)-4-(((tert-butyldiphenylsilyl)oxy)methyl)isoxazolidin-2-yl)-2-oxoethyl)carbamate (16). To the solution of amino alcohol **14** (180 mg

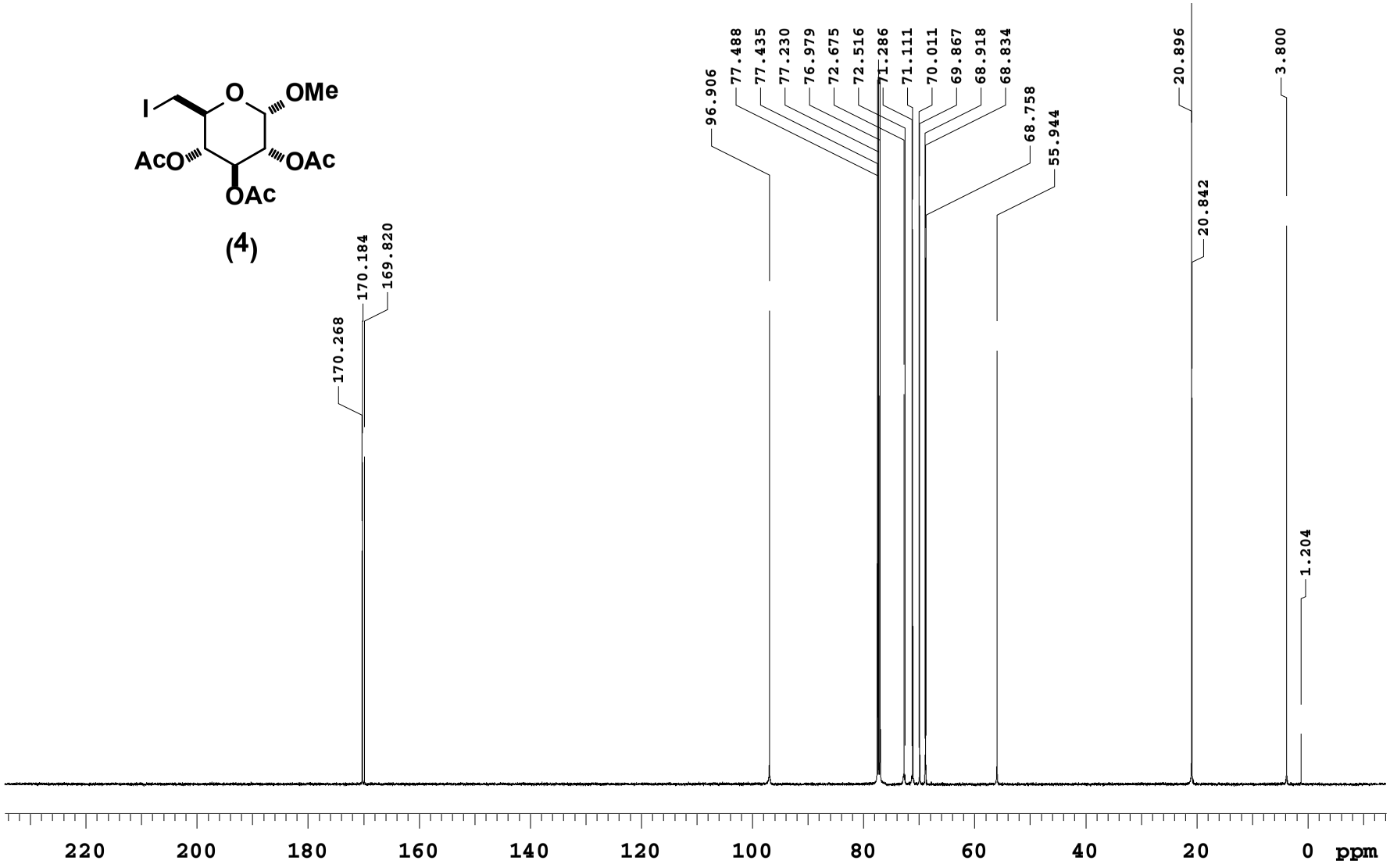


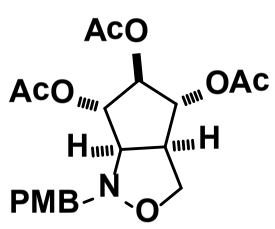
g, 0.48 mmol) in dry dichloromethane (10 mL) was added PPh_3 (0.15 g, 0.58 mmol) and CBr_4 (0.19 g, 0.58 mmol) at 0 °C and the reaction allowed to stir at room temperature for 2 hr. The mixture was cooled to 0 °C and *N*-Boc-Gly-OH (0.10 g, 0.58 mmol), EDCI (0.09 g, 0.58 mmol) and HOBt (0.09 g, 0.58 mmol) added simultaneously. The reaction mixture was stirred at room temperature for 16 hrs. The solvent was evaporated under reduced pressure and the residue purified by flash column chromatography (12 % EtOAc in Hexanes) give the bromomethyl isoxazoline amide **16** (114 mg, 40%) as a colorless liquid. R*f* = 0.48 (7:3 hexanes:EtOAc); $[\alpha]^{20}_D$ = +43.5° (c = 0.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.65-7.63 (m, 4H), 7.46-7.38 (m, 6H), 5.17 (brs, 1H), 4.64 (ddd, *J* = 14.0, 8.0, 6.0 Hz, 1H), 4.17-4.12 (m, 2H), 4.01-3.92 (m, 3H), 3.84 (dd, *J* = 10.0, 8.5 Hz, 1H), 3.64 (dd, *J* = 10.0, 5.0 Hz, 1H), 3.37 (dd, *J* = 10.5, 8.0 Hz, 1H), 3.01-2.94 (m, 1H), 1.45 (s, 9H), 1.06 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 171.0, 156.0, 135.7, 135.6, 135.6, 133.0, 132.9, 130.2, 130.1, 128.1, 79.9, 72.1, 60.1, 59.9, 59.5, 46.5, 46.3, 42.1, 41.0, 29.9, 28.7, 28.5, 27.1, 26.9, 19.3 ppm; IR (Thin film) 3428, 2930, 2857, 1711, 1589, 1502, 1427, 1391, 1365, 1244, 1165, 1105, 998, 941, 864, 822, 754, 700, 658, 612 cm-1; HRMS (ESI) calcd for $C_{28}H_{39}{}^{79}BrN_2O_5SiNa$ (M+Na): 613.1710, found: 613.1711.


O
OMe
I
AcO
OAc
OAc

(4)

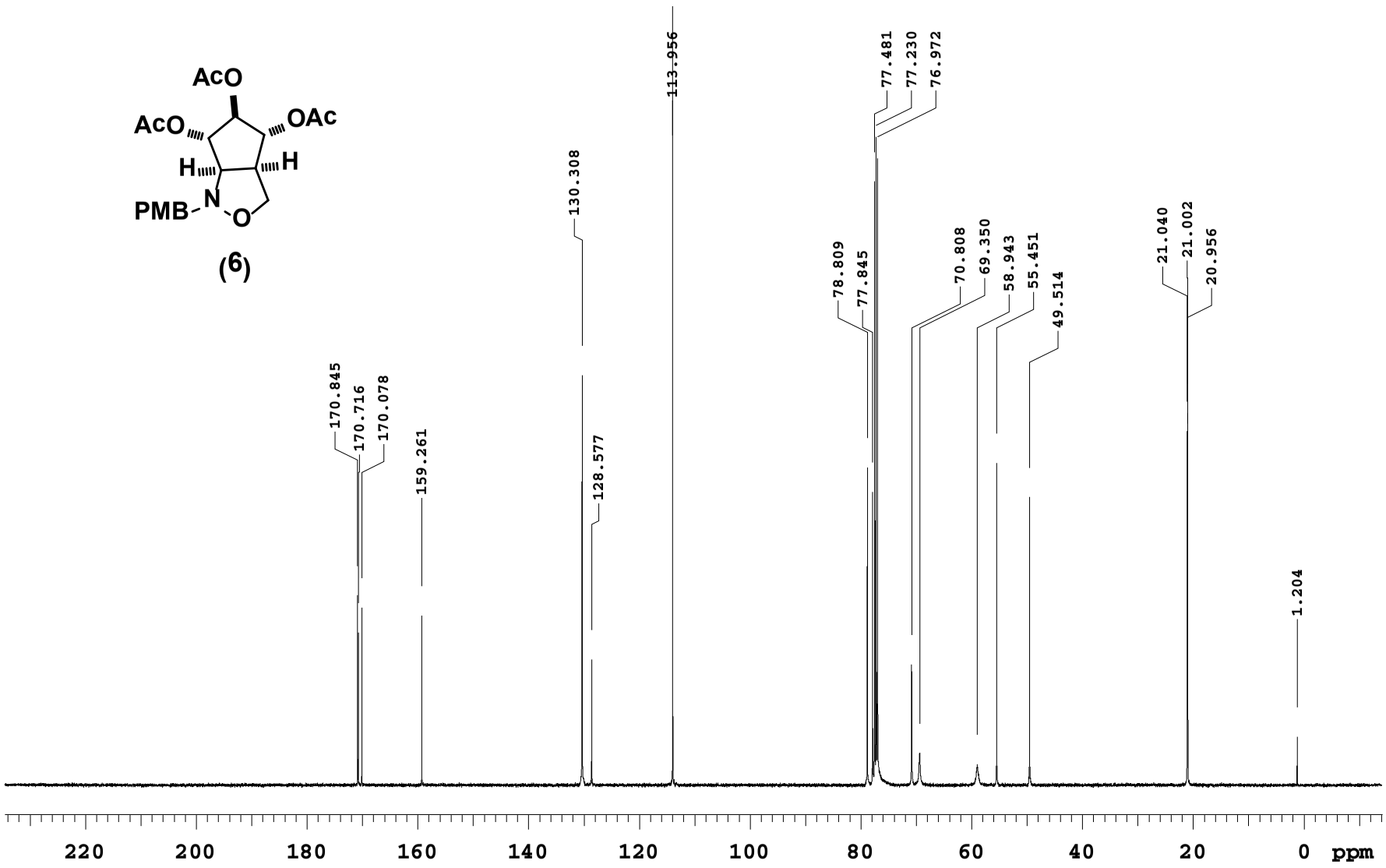
14
12
10
8
6
4
2
-0
ppm
0.88
1.85
0.93
2.87
1.00
0.95
1.01
2.71

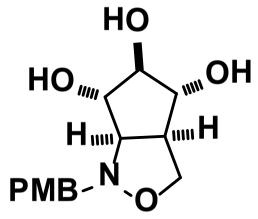

I
O
OMe
AcO
OAc
OAc
(4)
170.268
170.184
169.820
96.906
77.488
77.435
77.230
76.979
72.675
72.516
71.286
71.111
70.011
69.867
68.918
68.834
68.758
55.944
20.896
20.842
3.800
1.204
220
200
180
160
140
120
100
80
60
40
20
0
ppm


AcO
AcO
OAc
H
H
PMB
N
O

(6)

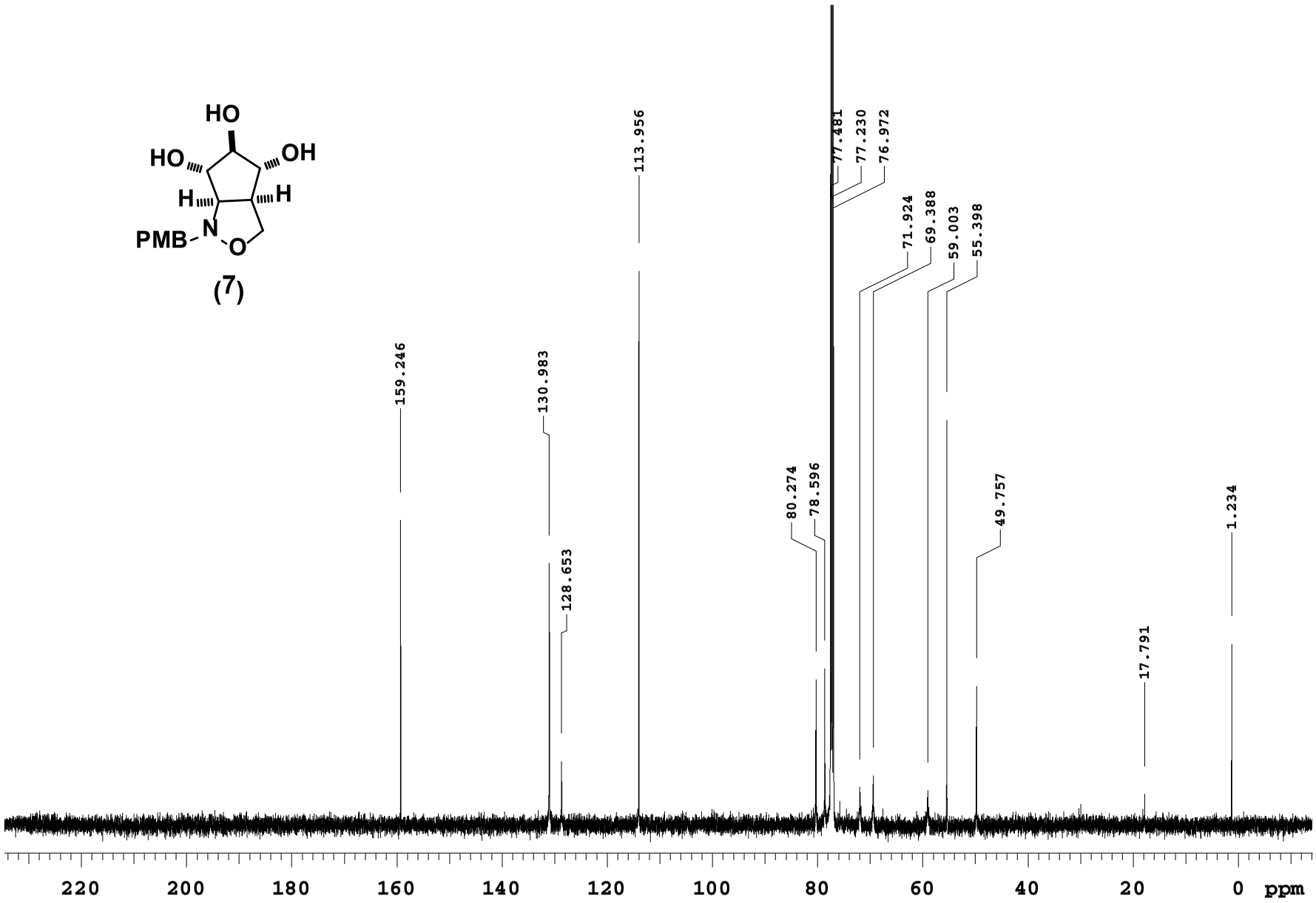
14
12
10
8
6
4
2
-0
ppm
1.78
1.81
0.91
0.94
0.84
1.00
2.92
5.59

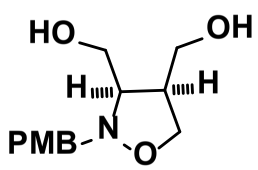

AcO
AcO
OAc
H
H
PMB
N
O
(6)
170.845
170.716
170.078
159.261
130.308
128.577
113.956
77.481
77.230
76.972
78.809
77.845
70.808
69.350
58.943
55.451
49.514
21.040
21.002
20.956
1.204
220
200
180
160
140
120
100
80
60
40
20
0
ppm


HO
HO
OH
H
H
PMB
N
O

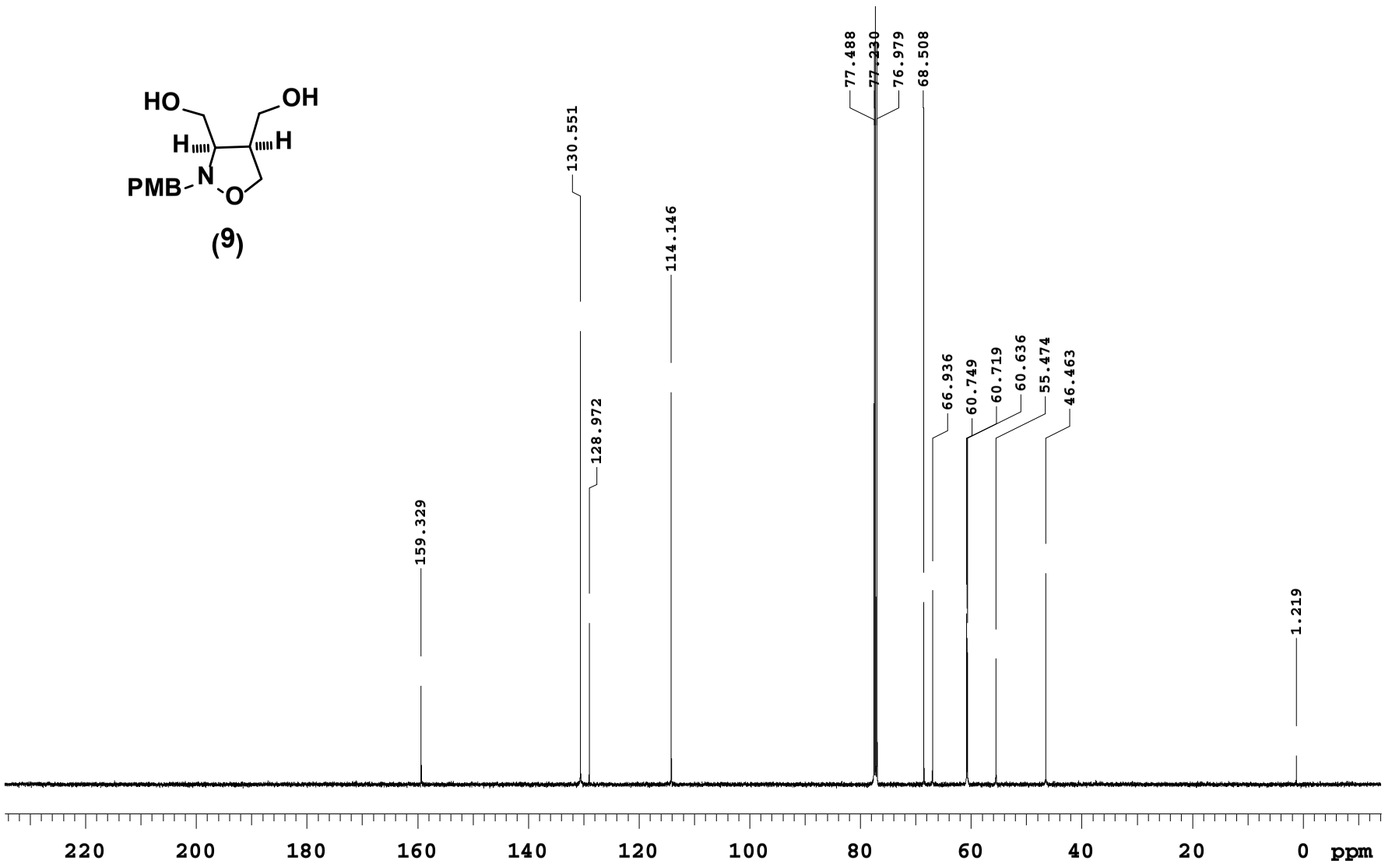
(7)

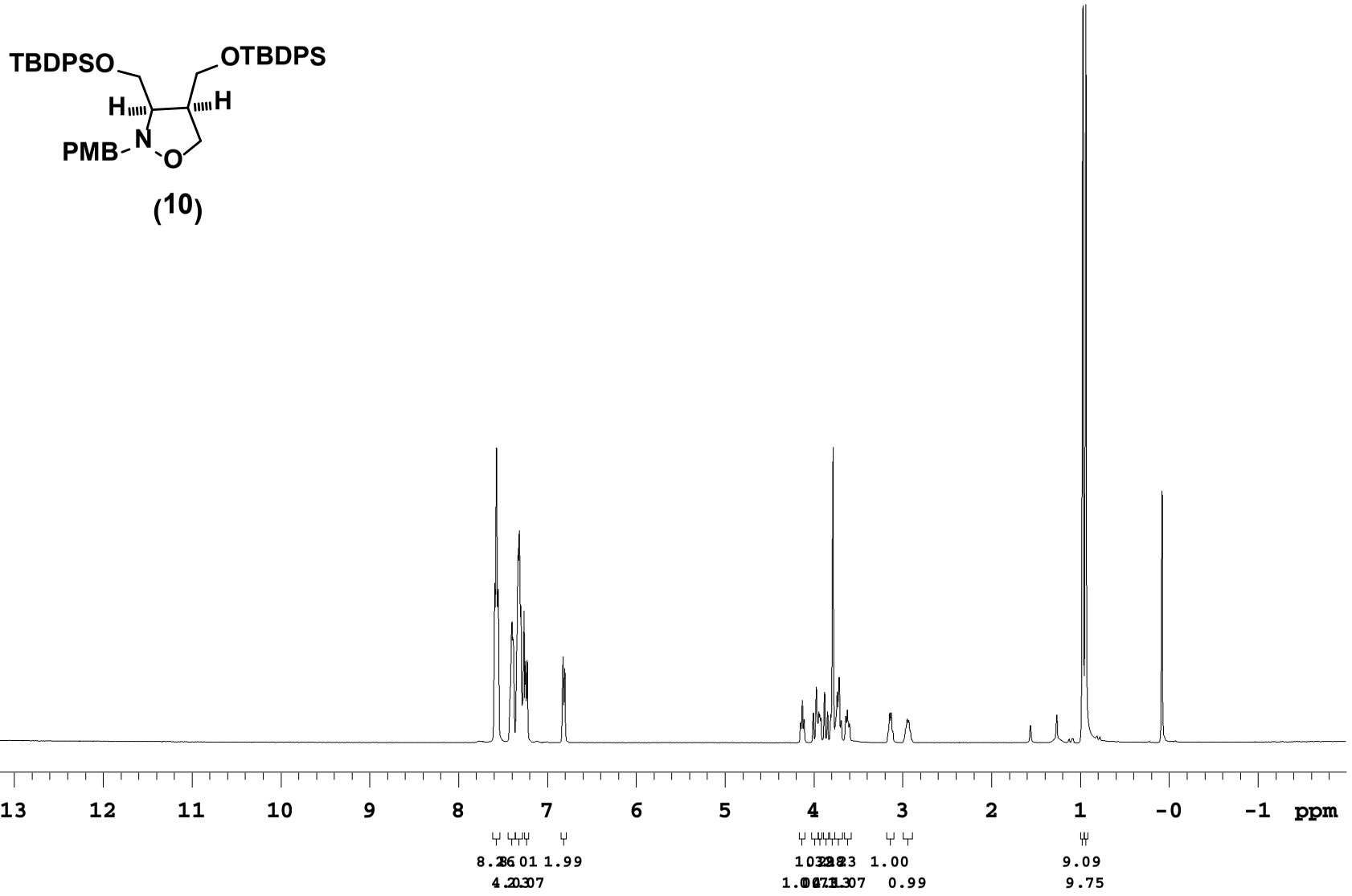
14
12
10
8
6
4
2
-0
ppm
1.99
1.92
10.09
0.96
4
3.82
0.91
1.06
3.99
1.12
1.00

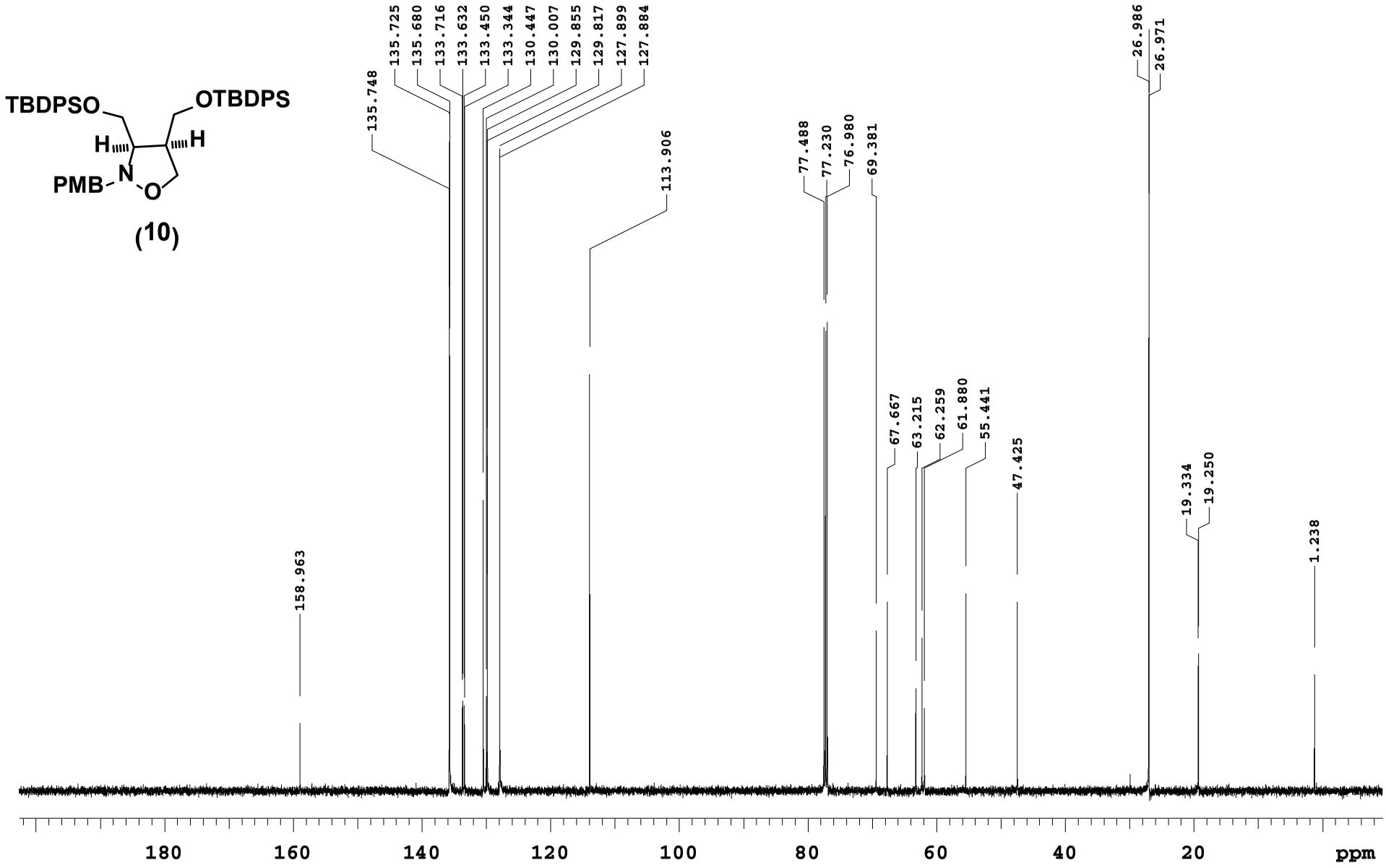

HO
HO
OH
H
H
PMB
N
O
(7)
159.246
130.983
128.653
113.956
80.274
78.596
77.481
77.230
76.972
71.924
69.388
59.003
55.398
49.757
17.791
1.234
220
200
180
160
140
120
100
80
60
40
20
0
ppm

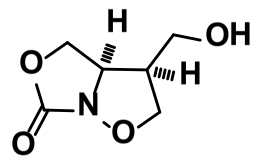


(9)

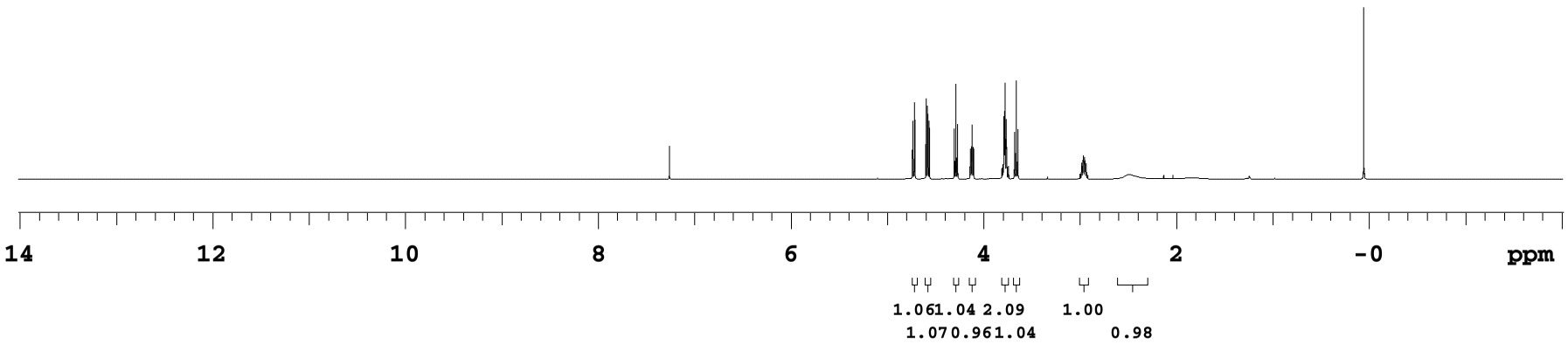

HO
OH
H
H
PMB
N
O
(9)
159.329
130.551
128.972
114.146
77.488
77.230
76.979
68.508
66.936
60.749
60.719
60.636
55.474
46.463
1.219
220
200
180
160
140
120
100
80
60
40
20
0
ppm

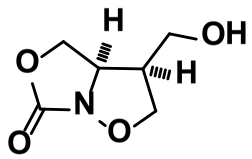

TBDPSO
OTBDPS
H
H
PMB
N
O
(10)
14
13
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm
8.26
6.01
1.99
4.20
3.07
1.00
0.99
9.09
9.75


TBDPSO
OTBDPS
H
H
PMB
N
O
(10)
135.748
135.725
135.680
133.716
133.632
133.450
133.344
130.447
130.007
129.855
129.817
127.899
127.884
113.906
77.488
77.230
76.980
69.381
67.667
63.215
62.259
61.880
55.441
47.425
26.986
26.971
19.334
19.250
1.238
158.963
180
160
140
120
100
80
60
40
20
ppm



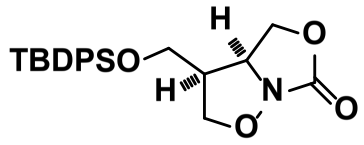
(12)




H
OH
O
H
N
O
O

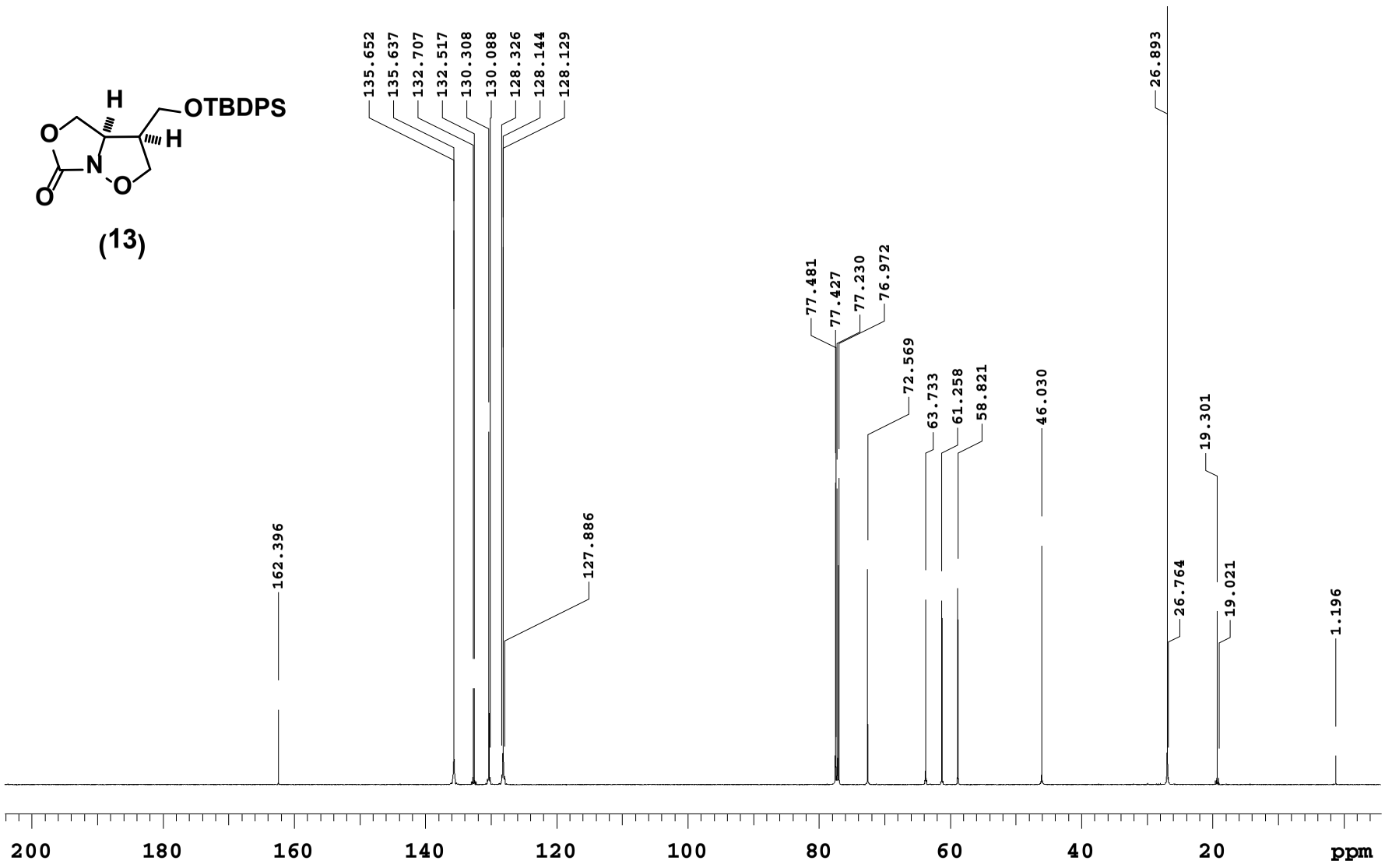
(12)

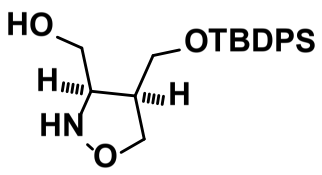
77.230
76.972
73.009
64.082
59.573
58.859
45.142
77.481
163.185
220
200
180
160
140
120
100
80
60
40
20
0
ppm


TBDPSO
H
H
O
N
O
O

(13)

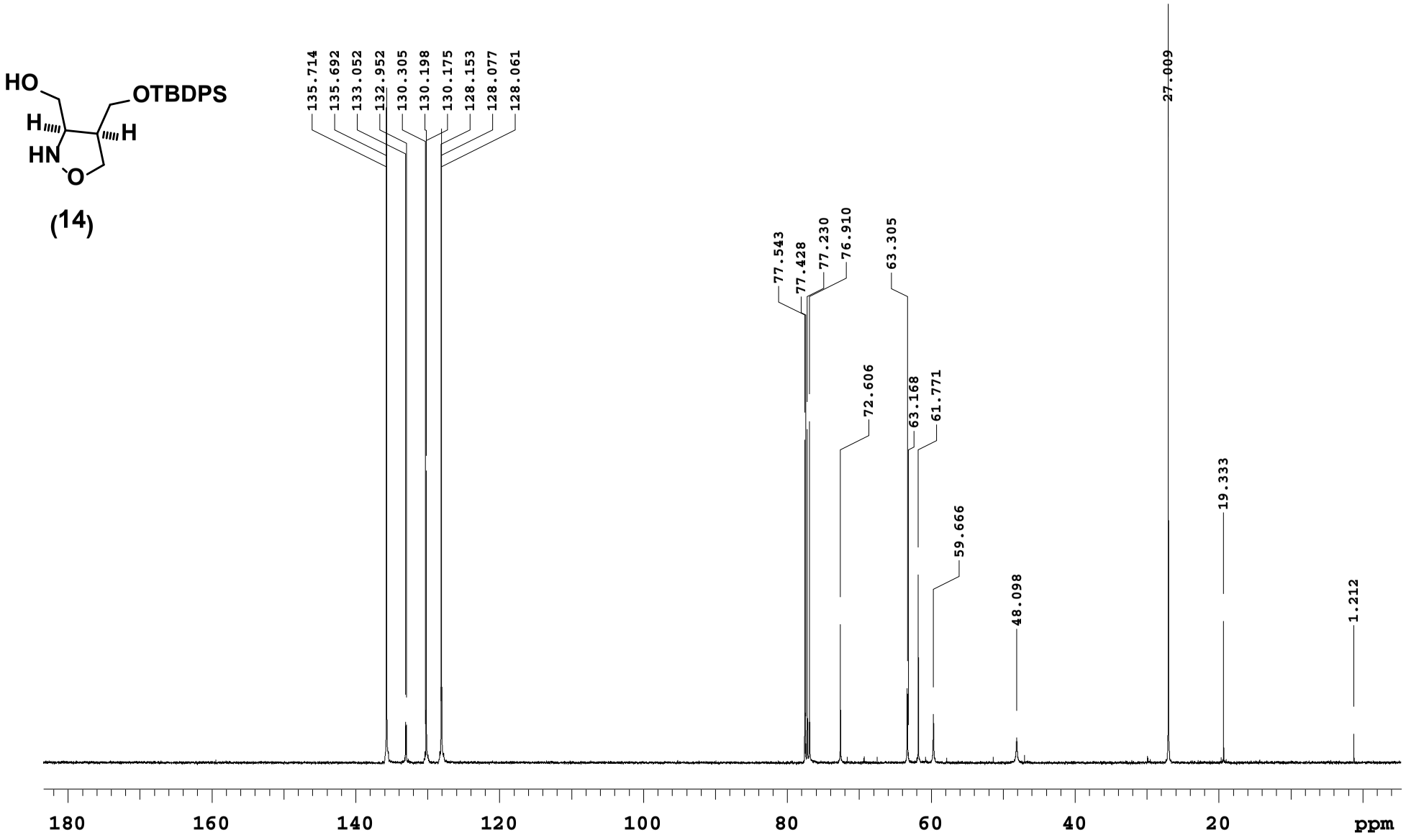
10
9
8
7
6
5
4
3
2
1
ppm
3.81
5.59
1.05
1.03
1.02
0.95
2.08
1.02
1.00
9.32

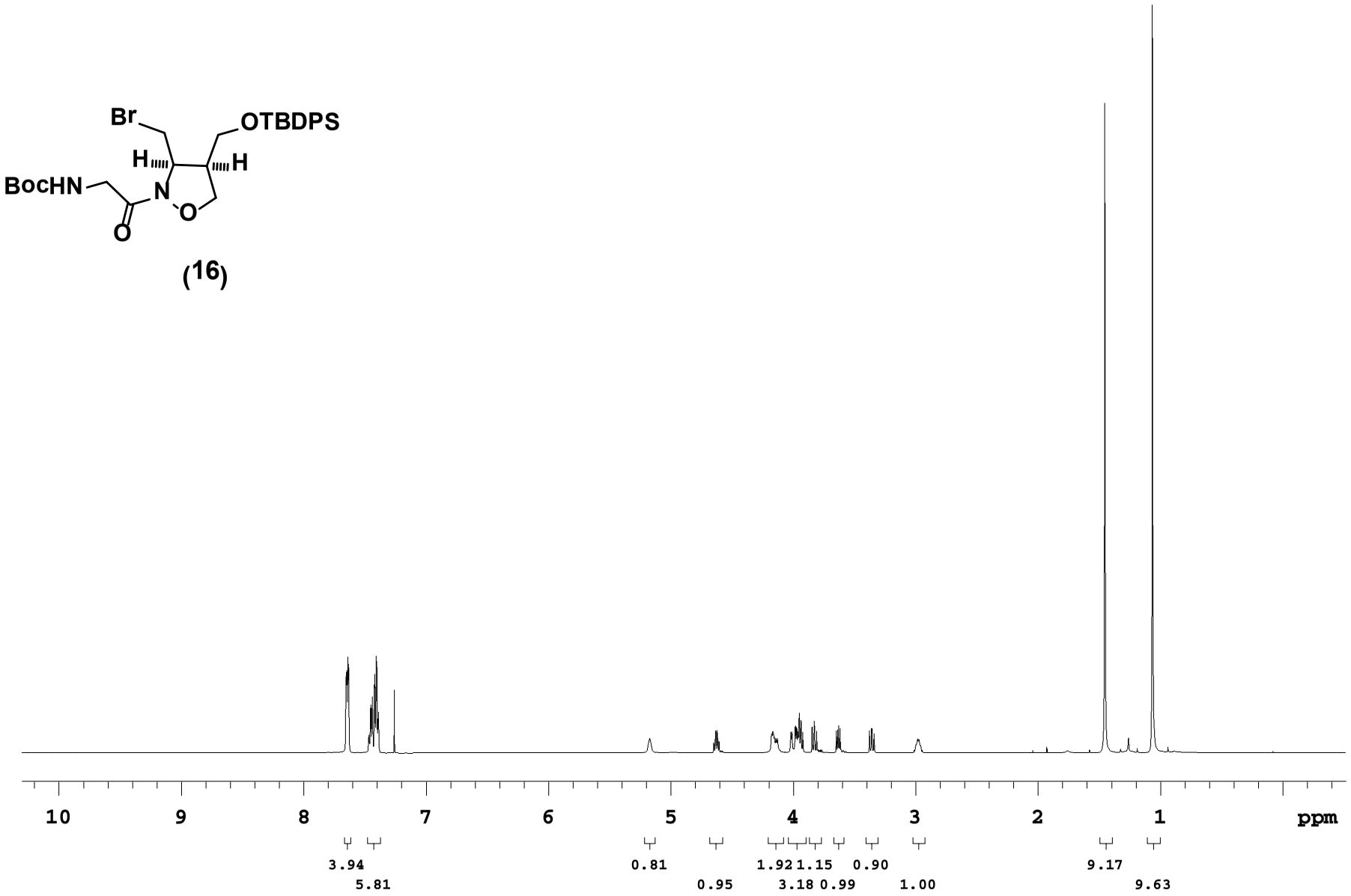

H
OTBDPS
O
H
N
O
O
(13)
135.652
135.637
132.707
132.517
130.308
130.088
128.326
128.144
128.129
26.893
77.481
77.427
77.230
76.972
72.569
63.733
61.258
58.821
46.030
19.301
162.396
127.886
26.764
19.021
1.196
200
180
160
140
120
100
80
60
40
20
ppm

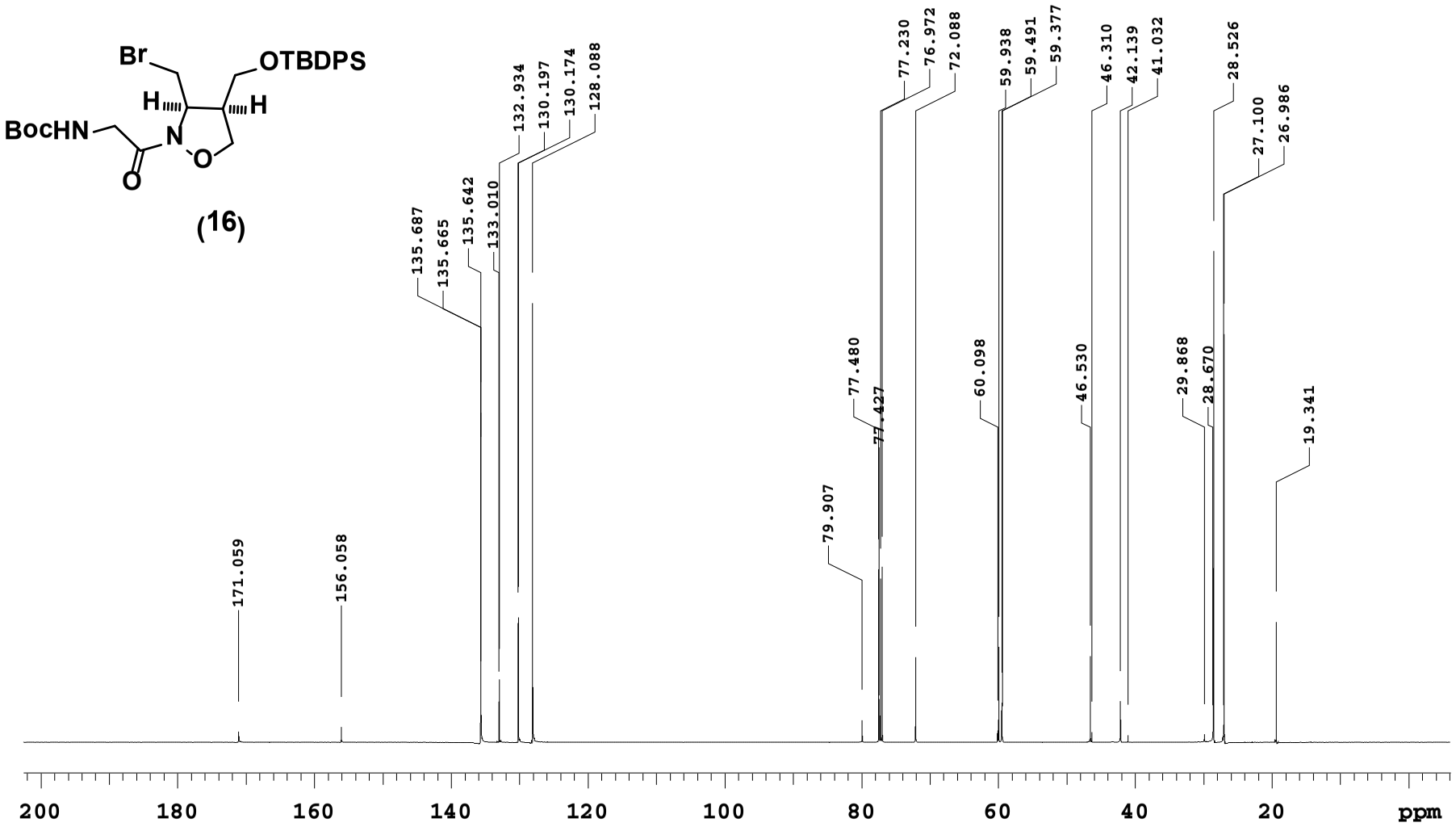

HO
OTBDPS
H
H
HN
O

(14)

10
9
8
7
6
5
4
3
2
1
ppm
4.12
6.05
1.08
1.28
3.85
5.10
1.00
9.75


HO
OTBDPS
H
H
HN
O
(14)
135.714
135.692
133.052
132.952
130.305
130.198
130.175
128.153
128.077
128.061
77.543
77.428
77.230
76.910
72.606
63.305
63.168
61.771
59.666
48.098
27.009
19.333
1.212
180
160
140
120
100
80
60
40
20
ppm


Br
OTBDPS
H
H
BocHN
N
O
O
(16)
10
9
8
7
6
5
4
3
2
1
ppm
3.94
5.81
0.81
0.95
1.92
1.15
3.18
0.99
0.90
1.00
9.17
9.63


Br
OTBDPS
H
H
BocHN
N
O
O
(16)
171.059
156.058
135.687
135.665
135.642
133.010
132.934
130.197
130.174
128.088
79.907
77.480
77.427
77.230
76.972
72.088
60.098
59.938
59.491
59.377
46.530
46.310
42.139
41.032
29.868
28.670
28.526
27.100
26.986
19.341
200
180
160
140
120
100
80
60
40
20
ppm