Synthesis and Stereochemical Assignment of Arenolide

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Supporting Information

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General Information

^{1}H NMR spectra were recorded on a Varian Gemini-500 (500 MHz), or a Varian Inova-500 (500 MHz), or a Varian Inova-600 (600 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm, THF-d_8: 3.58 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qi = quintet, sx = sextet, sp = septet, m = multiplet, br = broad), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian Gemini-500 (125 MHz), or a Varian Inova-500 (125 MHz), or a Varian Inova-600 (150 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm, THF-d_8: 67.57 ppm). Infrared (IR) spectra were recorded on a Bruker alpha-P Spectrometer. Frequencies are reported in wavenumbers (cm^{-1}) as follows: strong (s), broad (br), medium (m), and weak (w). High-resolution mass spectrometry (DART+) was performed at the Mass Spectrometry Facility, Boston College, Chestnut Hill, MA.

Liquid chromatography was performed using forced flow (flash chromatography) on silica gel (SiO_2, 230 – 400 Mesh) purchased from Silicycle. Thin layer chromatography (TLC) was performed on 25 μm silica gel glass backed plates from Silicycle. Visualization was performed using ultraviolet light (254 nm), phosphomolybdic acid (PMA) in ethanol and ceric ammonium molybdate (CAM) in ethanol.

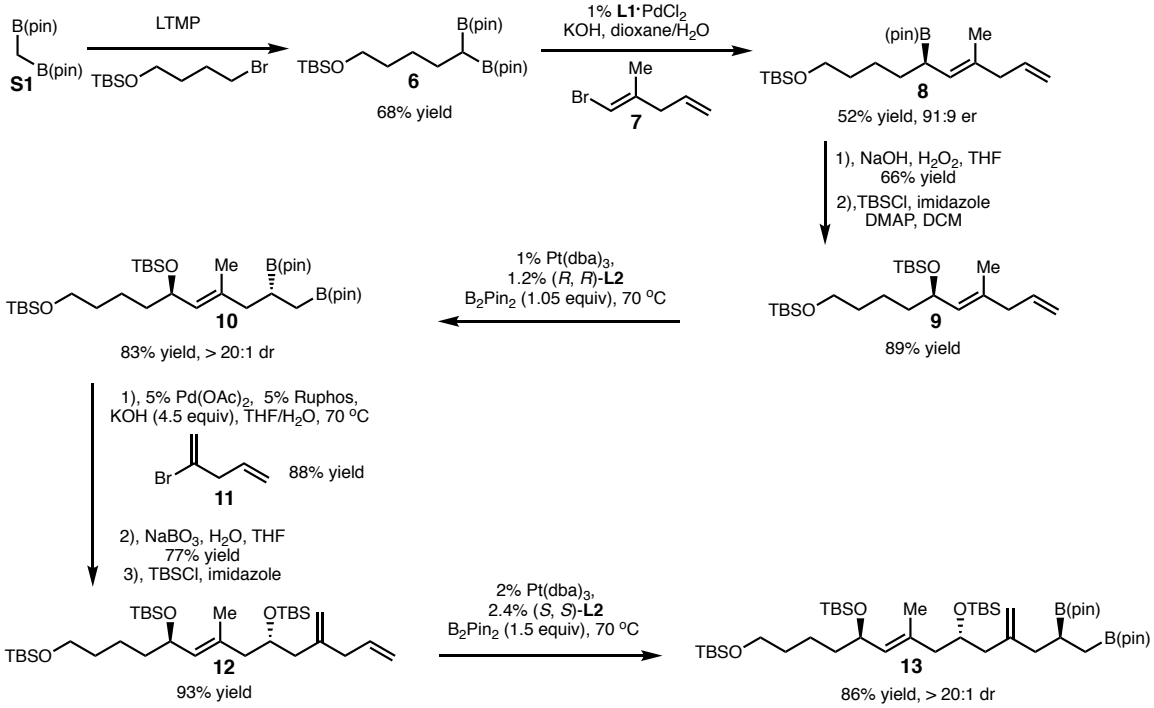
Analytical chiral supercritical fluid chromatography (SFC) was performed on a TharSFC Method Station II equipped with Waters 2998 Photodiode Array Detector.

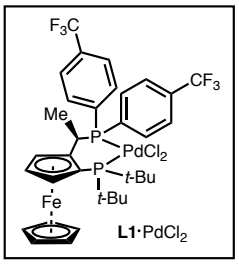
All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Tetrahydrofuran (THF), diethyl ether, dichloromethane and toluene were purified using Pure Solv MD-4 solvent purification system, from Innovative Technology, Inc., by passing the solvent through two activated alumina columns after being purged with argon.

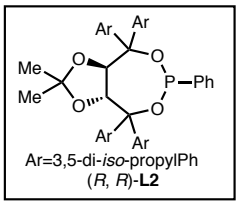
Bis(pinacolato)diboron was purchased from Frontier Scientific and used without further purification. Triethylamine was purchased from Alfa Aesar and distilled over calcium hydride prior to use. The following reagents were purchased and used without purification: copper(I) iodide (CuI) (Strem), lithium 2,2,6,6-tetramethylpiperidide (LTMP) (Aldrich), and *N*,*N*-dimethylformamide (DMF) (Acros). All other reagents were purchased from either Aldrich, Alfa Aesar or Acros and used without further purification.

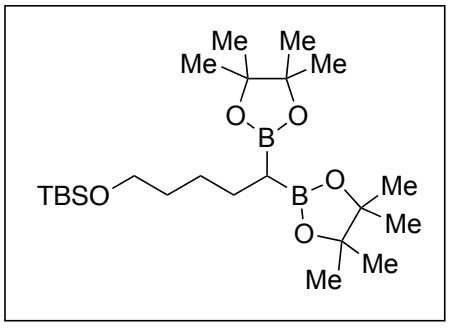
Experimental Procedures

I. Full Characterization of Compounds Leading to Isomer 1



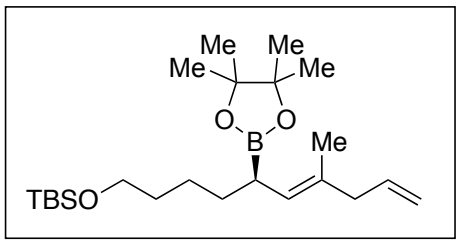




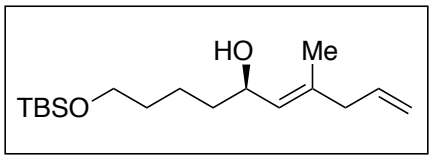


((5,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl) oxy)(*tert*-butyl)dimethylsilane (6). An oven dried 50 mL round bottom flask was added 2,2,6,6-tetramethylpiperidine (1.86 mL, 11 mmol) and THF (10 mL). The resulting solution was cooled down to -78 °C. *n*BuLi (4.4 mL, 2.5 M, 11 mmol) was added dropwise into the solution under N_2 protection, which was then warmed to room temperature gradually and stirred for 20 minutes give in orange clear LiTMP (lithium tetramethylpiperidide) solution. Another oven dried 100 mL round bottom flask was added bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane **S1** (2.68 g, 10 mmol) and THF (10 mL), The clear colorless solution was cooled to 0 °C. The LiTMP was cooled to 0 °C and added dropwise into the methyl diboronate ester solution, which lead to the formation of an orange cloudy slurry. The slurry was

stirred for 10 minutes at 0 °C, and then (4-bromobutoxy)(*tert*-butyl)dimethylsilane (3.47 g, 13 mmol) was added slowly. The mixture was stirred overnight, which resulted in orange cloudy solution. The reaction mixture was then quenched by diethyl ether, filtered through a short pad of silica gel. The filtrate was evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:2 hexanes/ethyl acetate, stain in CAM) to afford **6** as a clear colorless oil (3.1 g, 68%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.57 (t, *J* = 6.7 Hz, 2H), 1.57 – 1.53 (m, 2H), 1.50 (p, *J* = 6.9 Hz, 2H), 1.34 – 1.27 (m, 2H), 1.22 (s, 12H), 1.22 (s, 12H), 0.88 (d, *J* = 0.9 Hz, 9H), 0.72 (t, *J* = 7.9 Hz, 1H), 0.03 (d, *J* = 0.8 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 82.8, 63.4, 33.0, 28.8, 26.0, 25.6, 24.8, 24.5, 18.3, -5.3; ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.9; IR (neat): 2977.3 (w), 2929.6 (m), 2857.3 (w), 1462.9 (w), 1359.7 (m), 1310.6 (s), 1264.0 (m), 1215.1 (w), 1140.2 (s), 1099.6 (s), 1005.3 (w), 969.4 (m), 835.6 (s), 774.5 (m), 668.2 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{23}{}^{1}H_{48}{}^{11}B_2{}^{16}O_5{}^{28}Si_1{}^{23}Na_1$ $[M+Na]^+$: calculated: 477.3355, found: 477.3371.

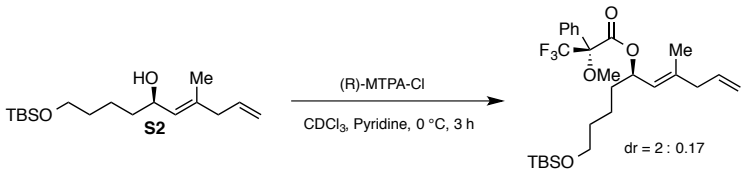


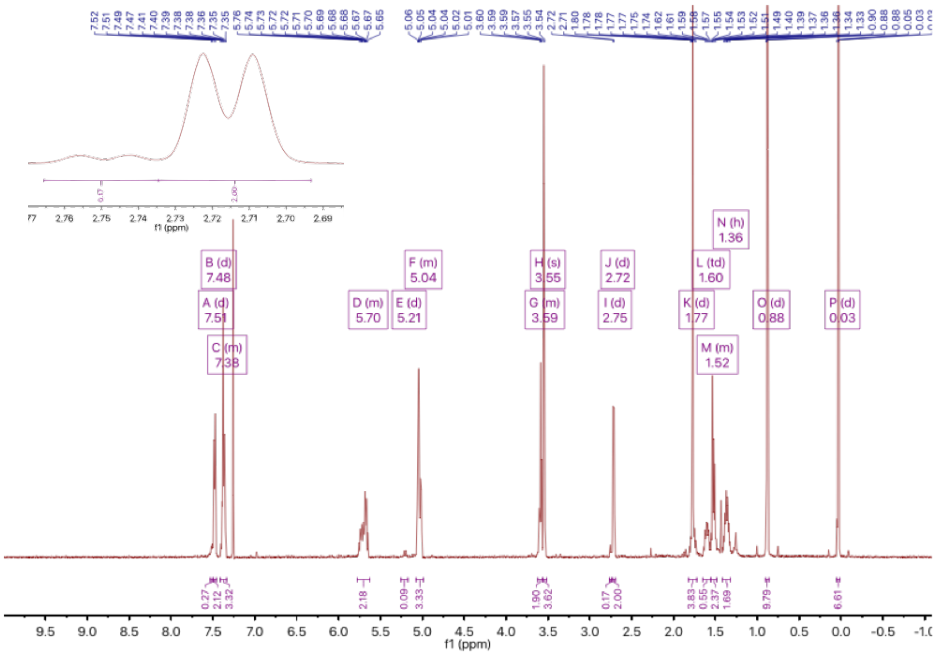
(*R*,*E*)-*tert*-butyldimethyl((7-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)deca-6,9-dien-1-yl)oxy)silane (8). This compound was prepared according to a literature procedure[1] with slightly modification. In the glove box, an oven dried two-dram vial was added (*R*)-1-[(*S*)-2-(di*tert*butylphosphanyl)ferrocenyl]ethyldi[4-(trifluoromethyl)phenyl]phosphine with $PdCl_2$ complex (1.8 mg, 0.002 mmol) and 1,4-dioxane (1 mL). The mixture was stirred for five minutes. Then 1,1-diborylalkane **6** (118.1 mg, 0.26 mmol) and (*E*)-1-bromo-2-methylpenta-1,4-diene (32.2 mg, 0.2 mmol) were added. The vial was sealed with a Teflon cap, taken outside of the glove box, and injected with degased 8M KOH (112 μL, 0.9 mmol). The orange clear solution was allowed to stir for 24 hours, resulting in a brown clear solution. This solution was extracted with diethyl ether, filtered through a short pad of silica gel pipet and concentrated *in vacuo*. The crude reaction mixture was then purified on silica gel (hexanes: ethyl acetate = 100:0.4 to 100:2) to afford **8** as a colorless oil (45.8 mg, 52%, 91:9 er). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.76 (ddt, *J* = 16.8, 10.0, 6.7 Hz, 1H), 5.08 (dd, *J* = 9.7, 1.3 Hz, 1H), 5.01 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.96 (ddt, *J* = 10.0, 2.3, 1.2 Hz, 1H), 3.58 (t, *J* = 6.6 Hz, 2H), 2.70 (d, *J* = 6.8, 1.5 Hz, 2H), 1.95 (dt, *J* = 9.6, 7.5 Hz, 1H), 1.58 (d, *J* = 1.3 Hz, 3H), 1.55 – 1.45 (m, 3H), 1.43 – 1.32 (m, 2H), 1.30 – 1.23 (m, 1H), 1.22 (s, 6H),1.21 (s, 6H), 0.88 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 137.5, 132.6, 126.6, 115.1, 82.9, 63.3, 44.3, 33.0, 31.3, 26.0, 25.6, 24.7, 24.5, 18.3, 16.3, -5.3; ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.0; IR (neat): 2977.1 (w), 2953.6 (w), 2928.7 (m), 2856.7 (m), 1471.6 (w), 1370.3 (m), 1317.5 (s), 1254.8 (m), 1214.9 (w), 1143.3 (s), 1099.8 (s), 1005.2 (w), 967.5 (w), 909.7 (w), 835.7 (s), 774.9 (m), 663.2 (w) cm^{-1}; $[\alpha]^{20}_{D}$ +2.2 (*c* 1.14, $CHCl_3$).

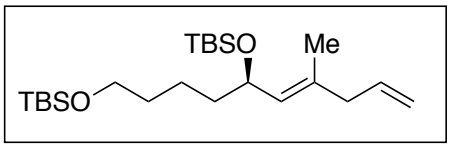


(*R*,*E*)-1-((*tert*-butyldimethylsilyl)oxy)-7-methyldeca-6,9-dien-5-ol (S2). THF (2 mL) and H_2O (1 mL) were added into a scintillation vial with (*R*,*E*)-*tert*-butyldimethyl((7-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)deca-6,9-dien-1-yl)oxy)silane **8** (45.8 mg, 0.11 mmol). The vial was cooled to 0 °C and charged with sodium perborate monohydrate (109.8 mg, 1.1 mmol). The cloudy white slurry was allowed to stir overnight. The crude reaction mixture was purified by column chromatography on silica gel (100:1 hexanes/ethyl acetate, stain in CAM) to afford **S2** as a colorless oil (21.7 mg, 66%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.77 (ddt, *J* = 17.0, 10.1, 6.9 Hz, 1H), 5.20 (ddt, *J* = 8.7, 2.5, 1.3 Hz, 1H), 5.09 – 5.00 (m, 2H), 4.36 (dt, *J* = 8.5, 6.5 Hz, 1H), 3.60 (t, *J* = 6.5 Hz, 2H), 2.73 (d, *J* = 6.9 Hz, 2H), 1.67 (s, 3H), 1.64 – 1.57 (m, 1H), 1.56 – 1.51 (m, 2H), 1.48 – 1.29 (m, 4H), 0.89 (d, *J* = 0.9 Hz, 9H), 0.04 (d, *J* = 0.9 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 136.9, 136.1, 128.8, 116.3, 68.6, 63.1, 43.9, 37.4, 32.7, 26.0, 21.7, 18.3, 16.6, -5.3; IR (neat): 3333.1 (br, w), 2928.7 (m), 2857.2 (m), 1637.3 (w), 1471.7 (w), 1462.1 (w), 1432.9 (w), 1385.9 (w), 1360.9 (w), 1253.4 (m), 1098.3 (s), 1004.4 (m), 912.3 (m), 833.3 (s), 733.4 (s), 712.6 (w), 661.4 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{17}{}^{1}H_{34}{}^{16}O_{2}{}^{28}Si_{1}{}^{23}Na_{1}$ $[M+Na]^+$: calculated: 321.2226, found: 321.2228; $[\alpha]^{20}_{D}$ +5.9 (*c* 1.09, $CHCl_3$).

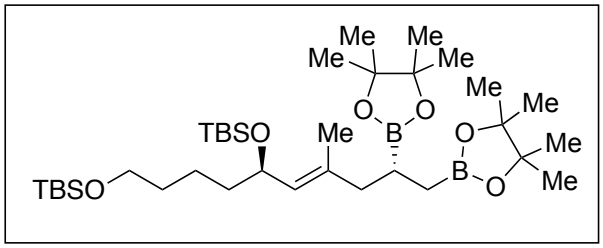
The enantioselectivity (92:8 er) was calculated by ^{1}H NMR analysis of the derived Mosher's ester derivative of alcohol S2, shown as below.





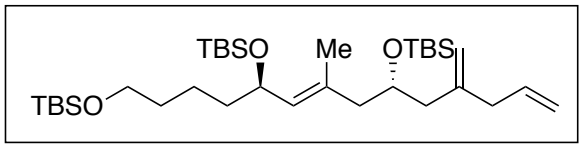


(*R*,*E*)-2,2,3,3,11,11,12,12-octamethyl-5-(2-methylpenta-1,4-dien-1-yl)-4,10-dioxa-3,11-disilatridecane (**9**). (*R*,*E*)-1-((*tert*-butyldimethylsilyl)oxy)-7-methyldeca-6,9-dien-5-ol **S2** (235 mg, 0.79 mmol), DCM (3 mL), and imidazole (133.9 mg, 1.97 mmol) were added into a 20 mL scintillation vial sequentially. The solution was stirred until all solids dissolved, and was then cooled to 0 °C. *tert*-Butyldimethylsilyl chloride (130 mg, 0.87 mmol) was subjected slowly into the above solution. A tip (about 2 mg) of 4-(dimethylamino)pyridine was then added. The white slurry was allowed to stir overnight, which was then quenched by water, extracted with DCM and filtered through a sodium sulfate padded pipet. The colorless solution was concentrated *in vacuo* to give a colorless oil. The crude reaction mixture was purified by column chromatography on silica gel (100:0.5 – 100:3 hexanes/ethyl acetate, stain in CAM) to afford **9** as a colorless oil (290 mg, 89%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.81 – 5.68 (m, 1H), 5.15 (dt, *J* = 8.7, 1.3 Hz, 1H), 5.08 – 4.94 (m, 2H), 4.31 (td, *J* = 7.7, 5.0 Hz, 1H), 3.59 (t, *J* = 6.5 Hz, 2H), 2.69 (d, *J* = 7.8 Hz, 2H), 1.60 (s, 3H), 1.53 – 1.46 (m, 2H), 1.39 – 1.33 (m, 2H), 1.32 – 1.24 (m, 2H), 0.89 (s, 9H), 0.87 (s, 9H), 0.04 (s, 6H), 0.02 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.4, 132.8, 130.5, 115.9, 69.8, 63.2, 44.0, 38.4, 32.9, 26.0, 25.9, 21.8, 18.6,18.5, 16.5, -4.2, -4.8, -5.3; IR (neat): 2928.6 (m), 2856.7 (m), 1252.24 (s), 1096.2 (s), 1004.5 (m), 938.3 (m), 912.9 (m), 832.0 (s), 771.8 (s), 664.0 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{23}{}^{1}H_{48}{}^{16}O_2{}^{28}Si_2{}^{23}Na_1$ $[M+Na]^+$: calculated: 435.3091, found: 435.3081; $[\alpha]^{20}_{D}$ +1.9 (*c* 1.26, $CHCl_3$).



(*R*)-2,2,3,3,11,11,12,12-octamethyl-5-((*R*,*E*)-2-methyl-4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-1-yl)-4,10-dioxa-3,11-disilatridecane (10). The reaction was performed according to a previous procedure[2] with slightly modification. To an oven dried 2-dram vial were added $Pt(dba)_3$ (8.1 mg, 0.009 mmol), (*R,R*)-3,5-di-iso-propylphenyl-TADDOLPPh (9.8 mg, 0.011 mmol), $B_2(pin)_2$ (240 mg, 0.945 mmol) and THF (0.9 mL) in the glove box. The vial was sealed with Teflon cap and heated at 70 °C for 20 minutes outside of the glovebox. The mixture was cooled to room temperature, and brought back into the glove box again. The solution was charged with (*R*,*E*)-2,2,3,3,11,11,12,12octamethyl-5-(2-methylpenta-1,4-dien-1-yl)-4,10-dioxa-3,11-disilatridecane **9** (357mg, 0.9 mmol). The vial was heated at 70 °C outside of the glove box for 12 hours. Upon completion, the yellow solution was extracted with diethyl ether, filtered through a silica gel pipet and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:1 – 100:3 hexanes/ethyl acetate, stain in CAM) to afford **10** as a light yellow clear oil (500 mg, 83%, >20:1 d.r. as determined by analysis of the ^{13}C and ^{1}H NMR data). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.12 (d, *J* = 8.7 Hz, 1H), 4.29 (td, *J* = 8.0, 5.2 Hz, 1H), 3.58 (t, *J* = 6.6 Hz, 2H), 2.20 (dd, *J* = 13.6, 7.0 Hz, 1H), 1.93 (dd, *J* = 13.6, 8.2 Hz, 1H), 1.57 (s, 3H), 1.53 – 1.44 (m, 3H), 1.39 – 1.32 (m, 1H), 1.32 – 1.24 (m, 3H), 1.22 (s, 24H), 0.89 (s, 9H), 0.86 (s, 9H), 0.77 (dd, *J* = 13.5, 7.5 Hz, 2H), 0.04 (s, 6H), 0.00 (d, *J* = 8.6 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.1, 130.4, 82.8, 82.7, 69.8, 63.3, 43.1, 38.5, 32.9, 25.99, 25.9, 24.91, 24.88, 24.83,

24.76, 21.9, 18.4, 18.2, 16.1, -4.2, -4.8, -5.3; ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.1; IR (neat): 2976.9 (w), 2954.6 (m), 2929.3 (s), 2856.9 (m), 1471.8 (w), 1370.4 (m), 1315.3 (m), 1253.8 (m), 1143.2 (m), 1095.8 (m), 968.9 (w), 834.9 (s), 774.1 (s) cm^{-1}; HRMS-(DART+) for $^{12}C_{35}{}^{1}H_{76}{}^{11}B_2{}^{16}O_6{}^{28}Si_2{}^{14}N_1$ $[M+NH_4]^+$: calculated: 684.5397, found: 684.5419; $[\alpha]^{20}_D$ +6.9 (*c* 1.35, $CHCl_3$).

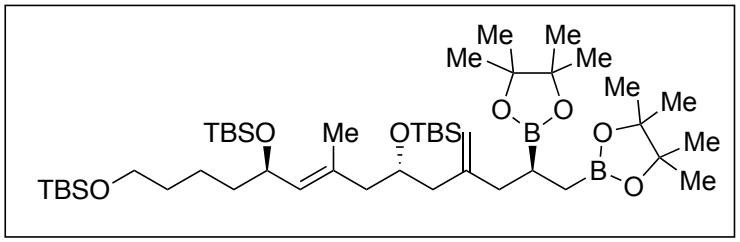


(5*R*,9*R*,*E*)-9-((*tert*-butyldimethylsilyl)oxy)-2,2,3,3,7,15,15,16,16-nonamethyl-5-(2-methylenepent-4-en-1-yl)-4,14-dioxa-3,15-disilaheptadec-7-ene (12). The reaction was performed according to a previous procedure[3] with slightly modification. In the glove box, an oven dried 20 mL vial was added $Pd(OAc)_2$ (7.52 mg, 0.0335 mmol), Ruphos (15.63 mg, 0.0335 mmol) and THF (6 mL). The mixture was allowed to stir for 5 minutes before adding **10** (445 mg, 0.67 mmol), and 2-bromopenta-1,4-diene (394 mg, 2.68 mmol) sequentially. The vial was sealed and brought outside of the glove box. Degassed 8M KOH (0.376 mL, 3.02 mmol) and degassed H_2O (0.6 mL) were added into the vial. The vial was heated at 70 °C overnight. The solution changed color from orange red to black. The reaction mixture was then extracted with diethyl ether, dried over Na_2SO_4 and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:1 – 100:3 hexanes/ethyl acetate, stain in CAM) to afford **(***R*)-2,2,3,3,11,11,12,12-octamethyl-5-((*R*,*E*)-2-methyl-6-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nona-1,8-dien-1-yl)-4,10-dioxa-3,11-disilatridecane **S3** as a yellow clear oil (358 mg, 88%).

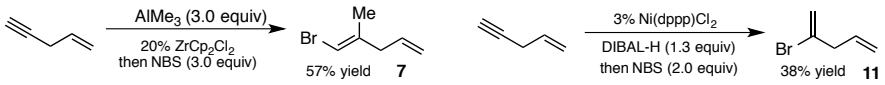
Compound **S3** was oxidized as follows: A 20 mL scintillation vial was added boronic ester **S3**, THF (8 mL) and H_2O (8 mL). The solution was cooled to 0 °C, and then subjected with sodium perborate monohydrate (439.9 mg, 4.4 mmol). The mixture was allowed to stir overnight. The solution was quenched by H_2O, extracted with diethyl ether, dried over Na_2SO_4 and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:1 – 100:3 hexanes/ethyl acetate, stain in CAM) to afford (6*R*,10*R*,*E*)-10,14-bis((*tert*-butyldimethylsilyl)oxy)-8-methyl-4-methylenetetradeca-1,8-dien-6-ol **S4** as a colorless oil (335 mg, 77%).

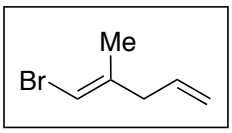
Alcohol **S4** was protected as shown: alcohol **S4** (277 mg, 0.56 mmol), DCM (2 mL) and imidazole (95 mg, 1.4 mmol) were added into a 20 mL scintillation vial sequentially. The mixture was stirred until all solids dissolved, and was then cooled to 0 °C. *tert*-Butyldimethylsilyl chloride (92.4 mg, 0.61 mmol) was added slowly into the above solution. A tip (about 2 mg) of 4-(dimethylamino)pyridine was then added. The white slurry was allowed to stir overnight, which was then quenched by water, extracted with DCM and dried over Na_2SO_4. The colorless solution was concentrated *in vacuo* to give a colorless oil. The crude reaction mixture was purified by column chromatography on silica gel (100:0 – 100:6 pentane/diethyl ether stain in CAM) to afford **12** as a colorless oil (316 mg, 93%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.85 – 5.74 (m, 1H), 5.16 (d, *J* = 8.7 Hz, 1H), 5.08 – 5.00 (m, 2H), 4.81 (d, *J* = 11.6 Hz, 2H), 4.31 (td, *J* = 7.7, 4.8 Hz, 1H), 3.99 – 3.86 (m, 1H), 3.59 (t, *J* = 6.5 Hz, 2H), 2.76 (d, *J* = 7.1 Hz, 2H), 2.21 – 2.14 (m, 2H), 2.09 (ddd, *J* = 16.6, 13.7, 7.0 Hz, 2H), 1.63 (s, 3H), 1.54 – 1.47 (m, 3H), 1.45 – 1.32 (m, 2H), 1.33 – 1.23 (m, 1H), 0.89 (d, *J* = 0.8 Hz, 9H), 0.87 (d, *J* = 0.7 Hz, 9H), 0.87 (d, *J* = 0.8 Hz,

9H), 0.05 – -0.00 (m, 18H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 145.2, 136.3, 132.5, 131.34, 116.2, 113.1, 69.8, 69.6, 63.2, 47.8, 43.6, 41.1, 38.3, 32.9, 26.0, 25.90, 25.88, 21.8, 18.4, 18.2, 18.1, 17.1, -4.2, -4.41, -4.45, -4.7, -5.3; IR (neat): 2928.6 (m), 2856.4 (m), 1471.9 (w), 1361.0 (w), 1252.1 (s), 1089.8 (s), 1004.7 (m), 938.5 (m), 912.5 (m), 831.3 (s), 771.4 (s), 735.4 (m), 663.2 (m) cm^{-1}. HRMS-(DART+) for $^{12}C_{34}{}^{1}H_{71}{}^{16}O_3{}^{28}Si_3$ $[M+H]^+$: calculated: 611.4711, found: 611.4717; $[\alpha]^{20}_D$ +7.6 (*c* 0.95, $CHCl_3$).

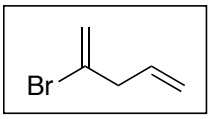


(5*R*,9*R*,*E*)-9-((*tert*-butyldimethylsilyl)oxy)-2,2,3,3,7,15,15,16,16-nonamethyl-5-((*S*)-2-methylene-4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)-4,14-dioxa-3,15-disilaheptadec-7-ene (13). An oven dried 2-dram vial was added $Pt(dba)_3$ (9.3 mg, 0.01 mmol), (*S,S*)-3,5-di-iso-propylphenyl-TADDOLPPh (11.4 mg, 0.013 mmol), $B_2(pin)_2$ (198 mg, 0.78 mmol) and THF (1 mL) in the glove box. The vial was sealed with Teflon cap, taken outside of the glove box and heated at 70 °C for twenty minutes. The vial was cooled to room temperature, and brought back into the glove box again to add **12** (316 mg, 0.52 mmol). The vial was then heated at 70 °C outside of the glove box for 12 hours. Upon completion, the yellow solution was extracted with diethyl ether, filtered through a silica gel pipet and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:1 – 100:4 hexanes/ethyl acetate, stain in CAM) to afford **13** as a light yellow clear oil (385 mg, 86%, >20:1 d.r. as determined by analysis of the ^{13}C and ^{1}H NMR data). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.15 (d, *J* = 8.5 Hz, 1H), 4.78 (d, *J* = 1.9 Hz, 1H), 4.73 (d, *J* = 1.9 Hz, 1H), 4.37 – 4.25 (m, 1H), 3.91 (p, *J* = 6.3 Hz, 1H), 3.59 (t, *J* = 6.6 Hz, 2H), 2.23 (dd, *J* = 14.5, 7.2 Hz, 1H), 2.19 – 2.04 (m, 4H), 1.98 (dd, *J* = 14.5, 8.4 Hz, 1H), 1.62 (s, 3H), 1.53 – 1.46 (m, 2H), 1.44 – 1.24 (m, 5H), 1.24 – 1.15 (m, 24H), 0.92 – 0.84 (m, 27H), 0.83 – 0.79 (m, 2H), 0.07 – -0.03 (m, 18H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.4, 132.3, 131.6, 112.5, 82.8, 70.2, 69.7, 63.3, 47.4, 43.8, 40.3, 38.3, 32.9, 31.6, 25.99, 25.96, 25.90, 24.9, 24.84, 24.80, 24.78, 22.7, 21.9, 18.4, 18.2, 18.1, 17.0, 14.09, -4.13, -4.31, -4.5, -4.8, -5.3; ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.8; IR (neat): 2980.1 (w), 2927.0 (w), 1731.8 (s), 1494.7 (w), 1453.7 (w), 1367.9 (m), 1149.3 (m), 1029.9 (m), 968.2 (w), 923.2 (w), 762.1 (w), 700.3 (s) cm-1; HRMS-(DART+) for $^{12}C_{46}{}^{1}H_{94}{}^{11}B_2{}^{16}O_7{}^{28}Si_3{}^{23}Na_1$ $[M+Na]^+$: calculated: 887.6391, found: 887.6410; $[\alpha]^{20}_D$ +6.7 (*c* 0.86, $CHCl_3$).



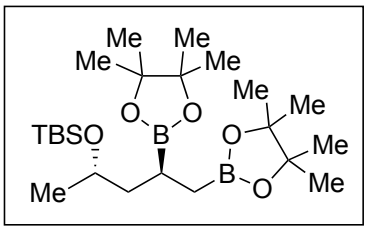


(*E*)-1-bromo-2-methylpenta-1,4-diene (7). The reaction was performed according to a previous procedure[4] with slightly modification. An oven dried 100 mL three necked round bottom flask was charged with bis(pentamethylcyclopentadienyl)zirconium dichloride (2.92g, 10 mmol) and DCM (15 mL). The mixture was then allowed to stir for 10 minutes. $AlMe_3$ (3.16 mL, 33 mmol) was added into the flask dropwise at room temperature under nitrogen protection. The mixture was stirred at room temperature for 30 minutes before being cooled to -78 °C. 1-Penten-4-yne (0.9 mL, 10 mmol) was added into the above mixture slowly at -78 °C. The solution was allowed to warm up to room temperature gradually and stirred overnight. The flask was cooled to -78 °C again, and NBS (5.3 g, 30 mmol) dissolved in diethyl ether (60 mL) was added as a slurry into the flask under nitrogen protection. The solution was allowed to warm up to room temperature and stirred for another three hours. Upon completion, the reaction mixture was poured into a beaker (containing 2 M HCl (30 mL) and ice chips), the layers were separated and the aqueous layer was extracted with pentane three times. The organic layers were combined, dried over Na_2SO_4 and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (pure pentane, stain in CAM) to afford **7** as a clear colorless oil (920 mg, 57%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.95 (s, 1H), 5.75 (ddt, *J* = 18.6, 9.5, 6.8 Hz, 1H), 5.13 – 4.94 (m, 2H), 2.83 (d, *J* = 6.8 Hz, 2H), 1.79 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 140.1, 134.7, 117.1, 102.3, 42.5, 19.2; IR (neat): 2978.9 (m), 2924.1 (s), 2869.2 (s), 2854.7 (s), 1457.1 (w), 1380.6 (w), 1142.2 (s), 419.5 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_6{}^1H_{10}{}^{79}Br$ $[M+H]^+$: calculated: 160.9966, found: 160.9966.

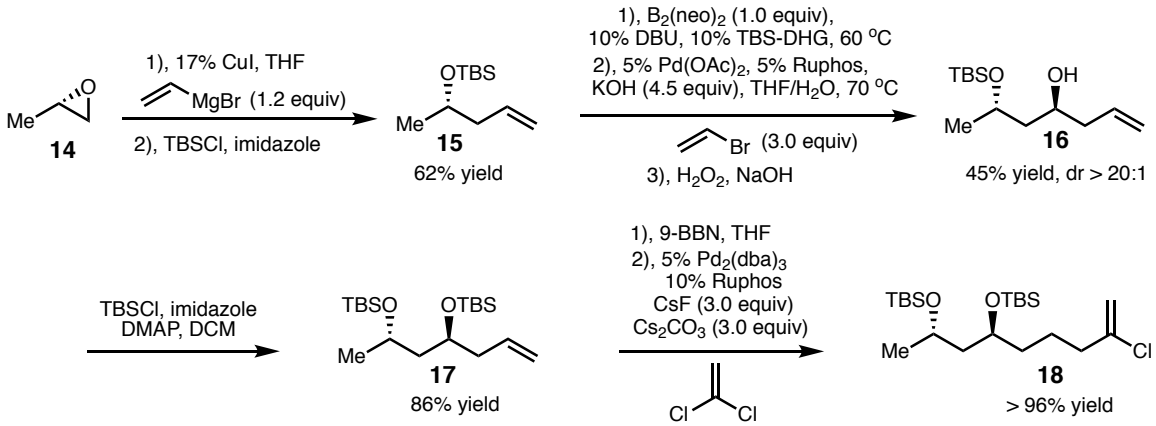


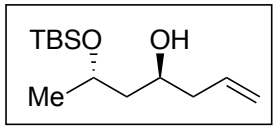
2-bromopenta-1,4-diene (11). The reaction was performed according to a previous procedure[5] with slightly modification. An oven dried 100 mL three necked round bottom flask was charged with nickel(II) chloride ($Ni(dppp)Cl_2$, 162.6 mg, 0.3 mmol) in the glove box. Outside of the glove box, THF (10 mL) and diisobutylaluminum hydride (neat, 2.32 mL, 13 mmol) were added sequentially into the flask under nitrogen protection. The mixture was stirred for ten minutes at room temperature before being cooled to 0 °C. Then 1-penten-4-yne (0.9 mL, 10 mmol) was added dropwise into the flask. The solution was allowed to warm up to room temperature gradually, and stirred for another two hours to resulting in a black slurry. The flask was cooled to 0 °C again, and subjected with *N*-bromosuccinimide (3.2 g, 18 mmol), which was dissolved in diethyl ether (30 mL). The solution was then warmed up to room temperature gradually, and stirred for another three hours. The reaction mixture was then poured into a separatory funnel containing Rochelle's salt (50 mL) and Et_2O (50 mL). The aqueous layer was then extracted with Et_2O (50 mL) twice. Organic layers were combined, dried over Na_2SO_4, and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (pure pentane, stain in $KMnO_4$) to afford **11** as a colorless oil (558 mg, 38%). ^{1}H NMR (600 MHz, $CDCl_3$): δ

5.88 – 5.79 (m, 1H), 5.62 (d, J = 1.5 Hz, 1H), 5.45 (d, J = 1.6 Hz, 1H), 5.22 – 5.15 (m, 2H), 3.18 (d, J = 6.7 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 133.8, 131.9, 118.0, 117.1, 45.7; IR (neat): 2955.9 (m), 2930.5 (m), 2870.1 (m), 1716.1 (w), 1630.7 (w), 1435.3 (w), 1379.2 (w), 1363.3 (w), 1251.1 (w) , 1141.8 (s), 1076.4 (m), 918.4 (w), 852.1 (w), 647.0 (w) cm^{-1}.



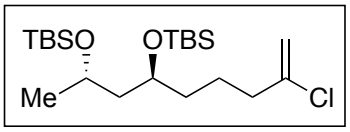
(((2*S*,4*S*)-4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-2-yl)oxy)(*tert*-butyl)dimethylsilane (**S5**). To an oven dried 2-dram vial was added $Pt(dba)_3$ (2.7 mg, 0.003 mmol), (*S*,*S*)-3,5-di-iso-propylphenyl-TADDOLPPh (2.9 mg, 0.0036 mmol), $B_2(pin)_2$ (80 mg, 0.315 mmol) and THF (0.3 mL) in the glove box. The vial was sealed with Teflon cap, taken outside of the glove box, and heated at 70 °C for twenty minutes. The mixture was cooled to room temperature, and returned to the glove box again to add (*S*)-*tert*-butyldimethyl(pent-4-en-2-yloxy)silane **15** (60 mg, 0.3 mmol). The vial was then heated at 70 °C outside of the glove box for 12 hours. Upon completion, the yellow solution was extracted with diethyl ether, filtered through a silica gel pipet and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:3 to 100:5 hexanes/ethyl acetate, stain in CAM) to afford **S5** as a colorless oil (130 mg, 95%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.85 (h, J = 6.2 Hz, 1H), 1.54 (dt, J = 13.9, 7.1 Hz, 1H), 1.42 (dt, J = 13.6, 7.0 Hz, 1H), 1.22 (s, 24H), 1.26 – 1.16 (m, overlap, 1H), 1.10 (d, J = 6.1 Hz, 3H), 0.88 (s, 9H), 0.83 (d, J = 7.5 Hz, 2H), 0.04 (d, J = 4.5 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 82.8, 82.7, 68.3, 43.3, 26.0, 24.9, 24.8, 24.7, 23.7, 18.2, -4.4, -4.6; ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.7; IR (neat): 2976.6 (m), 2928.6 (w), 2856.7 (w), 1437.9 (w), 1369.8 (s), 1313.2 (s), 1252.8 (m), 1213.8 (w), 1139.9 (s), 1068.8 (m), 1003.2 (m), 968.6 (m), 834.1 (s), 808.1 (m), 773.4 (s), 671.8 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{23}{}^{1}H_{48}{}^{11}B_2{}^{16}O_5{}^{28}Si_1{}^{23}Na_1$ $[M+Na]^+$: calculated: 477.3355, found: 477.3374; $[\alpha]^{20}_D$ +0.2 (*c* 1.12, $CHCl_3$).





(4*S*,6*S*)-6-((*tert*-butyldimethylsilyl)oxy)hept-1-en-4-ol (**16**). The reaction was performed according to a previous procedure[6] with slightly modification. In the glovebox, to an oven-dried 50 mL round bottom flask was added with

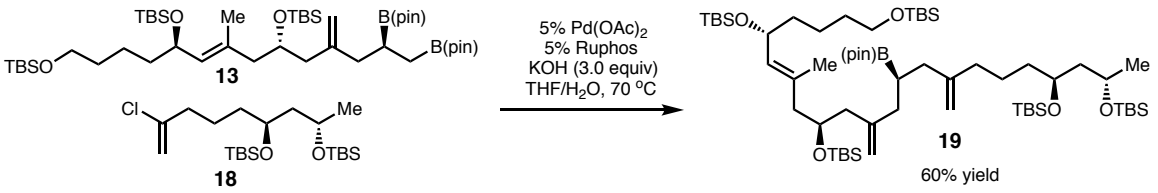
pseudoenantiomeric glycols 6-*tert*-butyldimethylsilyl-1,2-dihydroglucal (TBS-DHG) catalyst (79 mg, 0.3 mmol), bis(neopentylglycolato)diboron (677 mg, 3.0 mmol), (*S*)-*tert*-butyldimethyl(pent-4-en-2-yloxy)silane **15** (800 mg, 3.0 mmol, prepared according to literature[7]) and THF (3.0 mL). The mixture was allowed to stir for five minutes before adding DBU (0.045 mL, 0.3 mmol). The vial was then sealed with rubber septum, and removed from the glove box. The mixture was stirred at 60 °C for 24 hours. The flask was cooled to room temperature, returned to the glove box, and charged with $Pd(OAc)_2$ (7.52 mg, 0.0335 mmol) and RuPhos (15.63 mg, 0.0335 mmol). The vial was then taken outside of the glove box. THF (15 mL), 1M vinyl bromide in THF (9 mL, 9.0 mmol) and 8M KOH (1.69 mL, 13.5 mmol) were added sequentially into the flask. The reaction mixture was heated at 70 °C for 12 hours. Upon completion, the flask was cooled to room temperature, subjected with 3 M NaOH (4 mL), and 33% wt H_2O_2 dropwise at 0 °C. After three hours, the flask was cooled to 0 °C, $Na_2S_2O_3$ (aq, 4 mL) was added carefully to quench the reaction. The layers were separated, and the aqueous layer was extracted with diethyl ether twice. The combined organic layers were dried over Na_2SO_4 and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:1-100:10 pentane/diethyl ether, stain in $KMnO_4$) to afford **16** as a yellow clear oil (330 mg, 45%, > 20:1 dr as determined by analysis of the ^{13}C and ^{1}H NMR data). The spectra were in accordance with a previous report.[8] ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.84 (ddt, *J* = 17.3, 10.3, 7.1 Hz, 1H), 5.17 – 5.04 (m, 2H), 4.21 (pd, *J* = 6.1, 3.8 Hz, 1H), 4.05 – 3.96 (m, 1H), 3.30 (d, *J* = 2.3 Hz, 1H), 2.33 – 2.11 (m, 2H), 1.63 (ddd, *J* = 13.9, 9.9, 3.7 Hz, 1H), 1.53 (ddd, *J* = 14.3, 5.5, 2.3 Hz, 1H), 1.22 (d, *J* = 6.3 Hz, 3H), 0.90 (s, 9H), 0.09 (d, *J* = 4.3 Hz, 6H).

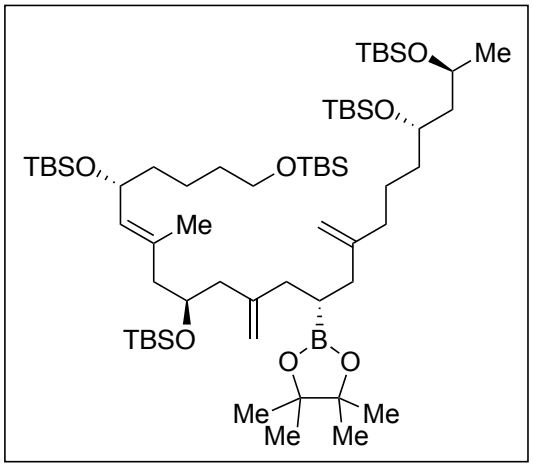


(5*S*,7*S*)-5-(4-chloropent-4-en-1-yl)-2,2,3,3,7,9,9,10,10-nonamethyl-4,8-dioxa-3,9-disilaundecane (**18**). (4*S*,6*S*)-6-((*tert*-Butyldimethylsilyl)oxy)hept-1-en-4-ol **(16)** (900 mg, 3.68 mmol), DCM (12 mL) and imidazole (626 mg, 9.2 mmol) were added into a 50 mL round bottom flask sequentially. The mixture was stirred until all solids dissolved, and was then cooled to 0 °C. *tert*-Butyldimethylsilyl chloride (610 mg, 4.05 mmol) was subjected slowly into the above solution. Lastly, a tip (about 2 mg) of 4-(dimethylamino)pyridine was added. The white slurry was allowed to stir overnight, which was then quenched by water, extracted with DCM, and dried over Na_2SO_4. The colorless solution was concentrated *in vacuo* to give a colorless oil. The crude reaction mixture was purified by column chromatography on silica gel (100:1-100:2 pentane/diethyl ether, stain in CAM) to afford (5*S*,7*S*)-5-allyl-2,2,3,3,7,9,9,10,10-nonamethyl-4,8-dioxa-3,9-disilaundecane **17** as a colorless oil (1.14 g, 86%).

This compound **(18)** was prepared according to a previous procedure with slightly modification.[9] In the glove box, to a four dram vial was added 9-BBN dimer (122.0 mg, 0.5 mmol), THF (2 mL) and (5*S*,7*S*)-5-allyl-2,2,3,3,7,9,9,10,10-nonamethyl-4,8-dioxa-3,9-disilaundecane **17** (358.7 mg, 1.0 mmol). The mixture was allowed to stir for 1.5 hours to result in yellow clear solution. $Pd_2(dba)_3$ (45.8 mg, 0.05 mmol), Ruphos (46.6 mg, 0.1 mmol), THF (6 mL), CsF (455.7 mg, 3.0 mmol), and Cs_2CO_3 (977.5 mg, 3.0 mmol) were then added sequentially into the vial. The vial was then sealed with a Teflon cap, and taken outside of the glove box. 1,1-Dichloroethylene (0.32 mL, 4.0 mmol) was added into the reaction solution. The vial was then heated at 70 °C for 12 hours. Upon completion, the reaction mixture was

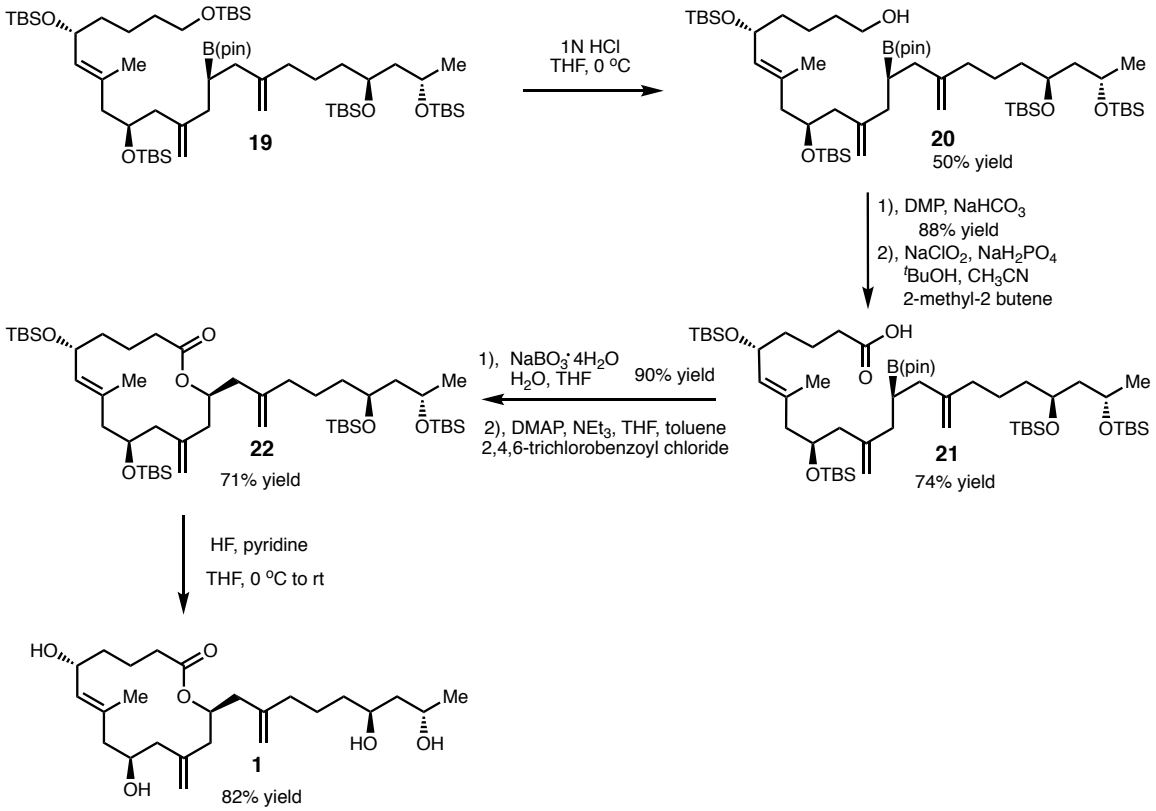
diluted with diethyl ether, filtered through a silica gel pipet, and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:0-100:3 pentane/diethyl ether, stain in CAM) to afford **18** as a yellow clear oil (421 mg, quantitative). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.14 (d, *J* = 1.0 Hz, 1H), 5.11 (dt, *J* = 1.0 Hz, 1H), 3.88 (h, *J* = 6.4 Hz, 1H), 3.76 (p, *J* = 5.8 Hz, 1H), 2.32 (t, *J* = 7.4 Hz, 2H), 1.65 – 1.57 (m, 3H), 1.54 – 1.39 (m, 3H), 1.14 (d, *J* = 6.2 Hz, 3H), 0.88 (s, 18H), 0.09 – 0.01 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 142.9, 111.9, 69.8, 66.3, 47.9, 39.2, 36.6, 25.9, 24.5, 22.6, 18.1, -3.9, -4.1, -4.2, -4.5; IR (neat): 2953.8 (m), 2928.8 (m), 2885.8 (w), 2856.6 (m), 1471.9 (w), 1374.9 (w), 1253.3 (m), 1118.7 (m), 1062.2 (m), 1004.8 (m), 938.9 (w), 872.2 (m), 832.6 (s), 805.6 (m), 771.1 (s), 704.8 (w), 663.9 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{21}{}^{1}H_{45}{}^{35}Cl_1{}^{16}O_2{}^{28}Si_2{}^{23}Na_1$ $[M+Na]^+$: calculated: 443.2544, found: 443.2545; $[\alpha]^{20}_{D}$ +6.9 (*c* 1.43, $CHCl_3$).

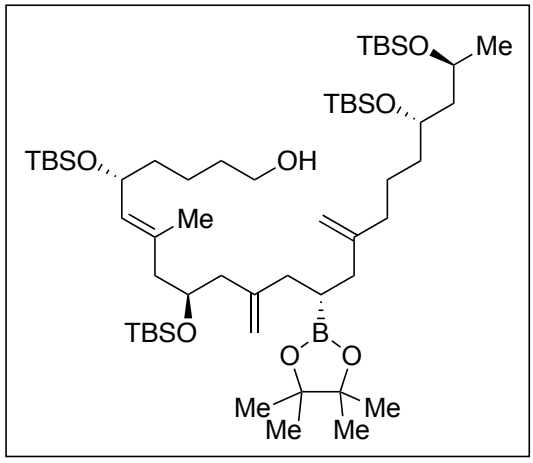




(9*R*,13*R*,17*S*,23*S*,25*S*,*E*)-9,13,23-tris((*tert*-butyldimethylsilyl)oxy)-2,2,3,3,11,25,27,27,28,28-decamethyl-15,19-dimethylene-17-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4,26-dioxa-3,27-disilanonacos-10-ene. **(19)** The reaction was performed according to a previous procedure[10] with slightly modification. In the glove box, an oven dried 20 mL vial was added $Pd(OAc)_2$ (7.52 mg, 0.0335 mmol), Ruphos (15.63 mg, 0.0335 mmol) and THF (3 mL). The mixture was allowed to stir for 5 minutes before adding (*E*)-2,2'-(1,8-diphenyloct-7-ene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **13** (290 mg, 0.335 mmol) and **18** (141.2 mg, 0.335 mmol) sequentially. The vial was sealed and brought outside of the glove box. Degased 8M KOH (0.19 mL, 1.5 mmol) and degassed H_2O (0.3 mL) were added into the vial. The vial was heated at 70 °C overnight. The solution changed color from orange red to black. The reaction mixture was extracted with diethyl ether, dried over Na_2SO_4 and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:0.5-100:1 hexanes/ethyl acetate, stain in CAM) to afford **19** as a colorless oil (199 mg, 60%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.16 (d, *J* = 8.5 Hz, 1H), 4.84 (d, *J* = 1.9 Hz, 1H), 4.75 (s, 1H), 4.74 (s, 1H), 4.69 (s, 1H), 4.30 (td, *J* = 8.1, 4.7 Hz, 1H), 3.96 – 3.84 (m, 2H), 3.77 – 3.71 (m, 1H), 3.59 (t, *J* = 6.6 Hz, 2H), 2.17 – 2.01 (m, 8H), 1.97 (d, *J* = 7.6 Hz, 2H), 1.67 – 1.56 (m, overlap, 1H), 1.61 (d, *J* = 1.3 Hz, 3H), 1.53 – 1.45 (m, 6H), 1.45 – 1.33 (m, 6H), 1.18 (s, 12H), 1.14 (d, *J* = 6.0 Hz, 3H), 0.91 – 0.82 (m, 45H), 0.08 – -0.04 (m, 30H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 149.1, 146.5, 132.5, 131.5, 112.1, 109.4, 82.9, 70.2, 70.0, 69.7, 66.3, 63.3, 48.0, 47.5, 44.0, 38.5, 38.3, 37.8, 37.6, 36.1, 32.9, 25.99, 25.95, 25.93, 25.90, 24.87, 24.81, 24.5, 23.1, 21.9, 19.9 (broad, C-B bond), 18.4, 18.20, 18.10, 18.06, 16.9, -3.9, -4.0, -4.1, -4.2, -4.4, -4.5, -4.7, -5.3; IR (neat): 2953.2 (m), 2928.5 (m),

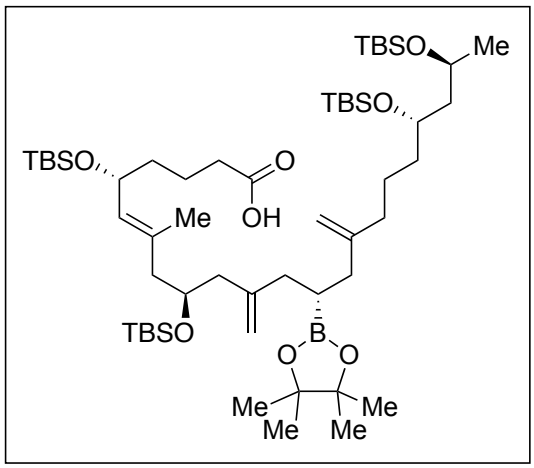
2886.1 (w), 2856.6 (m), 1471.9 (w), 1380.2 (w), 1253.1 (m), 1143.7 (m), 1091.4 (m), 1065.7 (m), 1005.2 (w), 833.7 (s), 807.4 (m), 772.9 (s), 664.7 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{61}{}^{1}H_{131}{}^{11}B_{1}{}^{16}O_{7}{}^{14}N_{1}{}^{28}Si_{5}$ $[M+NH_4]^+$: calculated: 1140.8865, found: 1140.8893; $[\alpha]^{20}_{D}$ +4.5 (*c* 0.33, $CHCl_3$).





(5*R*,9*R*,13*S*,19*S*,21*S*,*E*)-5,9,19,21-tetrakis((*tert*-butyl dimethylsilyl)oxy)-7-methyl-11,15-dimethylene-13-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)docos-6-en-1-ol (**20**). To a 20 mL scintillation vial was added **19** (80 mg, 0.08 mmol) and THF (8 mL). The solution was cooled to 0 °C and stirred for 15 minutes. HCl (0.08 mL, 1 M, 0.08 mmol) was added dropwise into the mixture, and the solution was stirred at 4 °C (cold room) overnight. The solution was cooled to 0 °C, $Na_2S_2O_3$ (0.5 mL) was added to quench the reaction. The mixture was extracted with diethyl ether, filtered through a pipet of $Na_2S_2O_4$, and evaporated *in vacuo*. The crude reaction mixture was then purified by column chromatography on silica gel (100:1-85:15

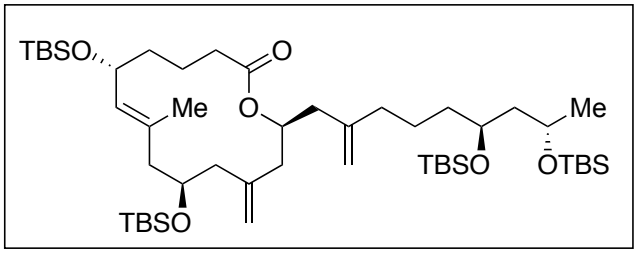
hexanes/ethyl acetate, stain in CAM) to afford **20** as a clear colorless oil (35 mg, 50%, the others are recovered starting material (19%) and multi-desilylated byproducts). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.16 (d, *J* = 8.4 Hz, 1H), 4.84 (d, *J* = 1.8 Hz, 1H), 4.75 (s, 1H), 4.74 (s, 1H), 4.70 (d, *J* = 1.8 Hz, 1H), 4.33 (td, *J* = 7.6, 4.4 Hz, 1H), 3.94 – 3.86 (m, 2H), 3.78 – 3.70 (m, 1H), 3.63 (t, *J* = 6.7 Hz, 2H), 2.16 – 2.01 (m, 8H), 2.01 – 1.94 (m, 2H), 1.62 (d, *J* = 1.3 Hz, 3H), 1.60 –1.22 (m, 13H), 1.19 (s, 12H), 1.14 (d, *J* = 6.1 Hz, 3H), 0.92 – 0.80 (m, 36H), 0.10 – -0.03 (m, 24H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 146.4, 132.2, 131.8, 112.2, 109.4, 82.9, 70.2, 70.0, 69.5, 66.3, 63.0, 48.0, 47.4, 43.9, 38.5, 38.2, 37.8, 37.6, 36.1, 32.8, 29.7, 26.0, 25.9, 24.9, 24.8, 24.5, 23.1, 21.6, 19.9 (broad, C-B bond), 18.2, 18.1, 17.1, -3.9, -4.0, -4.1, -4.2, -4.4, -4.5, -4.7; IR (neat): 2953.3 (m), 2928.7 (s), 2884.4 (m), 2856.7 (s), 1472.0 (w), 1462.1 (w), 1380.2 (m), 1253.5 (m), 1143.3 (s), 1086.8 (m), 1067.3 (m), 1005.2 (w), 891.3 (w), 834.7 (s), 807.1 (m), 773.5 (s) cm^{-1}; HRMS-(DART+) for $^{12}C_{55}{}^{1}H_{117}{}^{11}B_{1}{}^{16}O_{7}{}^{14}N_{1}{}^{28}Si_{4}$ $[M+NH_4]^+$: calculated: 1026.8000, found: 1026.7988; $[\alpha]^{20}_{D}$ +3.6 (*c* 0.23, $CHCl_3$).



(5*R*,9*R*,13*S*,19*S*,21*S*,*E*)-5,9,19,21-tetrakis((*tert*-butyl dimethylsilyl)oxy)-7-methyl-11,15-dimethylene-13-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)docos-6-enoic acid (**21**). To a 20 mL scintillation vial was added alcohol **20** (35 mg, 0.04 mmol) and DCM (1 mL). The mixture was cooled to 0°C, Dess-Martin periodinane[11] (20 mg, 0.048 mmol) and $NaHCO_3$ (16.6 mg, 0.198 mmol) were added. After 4 hours, the reaction mixture was concentrated *in vacuo*, then extracted by 1:1 hexane/Et_2O, filtered through silica gel padded sintered funnel, rinsed with 1:1 hexane/Et_2O and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:2-100:3 hexanes/ethyl acetate, stain in CAM) to afford (5*R*,9*R*,13*S*,19*S*,21*S*,*E*)-5,9,19,21-tetrakis((*tert*-butyldimethylsilyl)oxy)-7-methyl-11,15-dimethylene-13-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)docos-6-enal **S6** as a clear colorless oil (31 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.75 (t, *J* = 1.9 Hz, 1H), 5.16 (d, *J* = 8.4 Hz, 1H), 4.84 (s, 1H), 4.74 (s, 1H), 4.74 (s, 1H), 4.70 (s, 1H), 4.34 (td, *J* = 7.8, 5.0 Hz, 1H), 3.96 – 3.83 (m, 2H), 3.74 (p, *J* = 4.7 Hz, 1H), 2.41 (td, *J* = 7.5, 2.0 Hz, 2H), 2.17 – 1.95 (m, 10 H), 1.76 – 1.68 (m, 1H), 1.62 (s, 3H), 1.58– 1.23 (m, 10 H), 1.18 (s, 12H), 1.14 (d, *J* = 6.1 Hz, 3H), 0.91 – 0.83 (m, 36H), 0.10 – -0.03 (m, 24H).

(5*R*,9*R*,13*S*,19*S*,21*S*,*E*)-5,9,19,21-Tetrakis((*tert*-butyldimethylsilyl)oxy)-7-methyl-11,15-dimethylene-13-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)docos-6-enoic acid **21** was prepared according to a previous procedure[12] with slightly modification. A 20 mL scintillation vial was added aldehyde **S6** (4 mg, 0.0045 mmol), ^{t}BuOH (0.438 mL) and 2- methyl-2-butene (0.05 mL, 0.046 mmol) sequentially. The mixture was cooled to 0°C. A solution of $NaClO_2$ (4.92 mg, 0.055 mmol) and NaH_2PO_4 (5.99 mg, 0.046 mmol) in H_2O (0.14 mL) was added into the vial. THF (0.4 mL) was added last. The solution was then allowed to warm up to room temperature and stirred for another hour. The reaction mixture was quenched

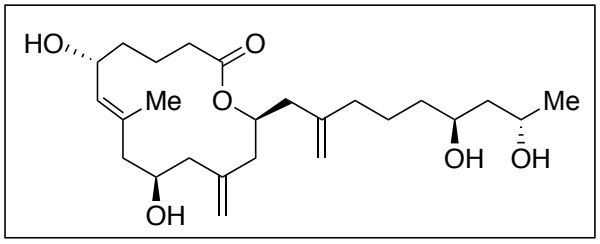
by H_2O, extracted with diethyl ether, filtered through a $Na_2S_2O_4$ pipet and evaporated *in vacuo*. The crude reaction mixture was then purified by column chromatography on silica gel (100:8-100:20 hexanes/ethyl acetate, stain in CAM) to afford **21** as a clear colorless oil (3 mg, 74%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.14 (d, *J* = 8.7 Hz, 1H), 4.84 (s, 1H), 4.75 (s, 1H), 4.74 (s, 1H), 4.70 (s, 1H), 4.41 – 4.32 (m, 1H), 4.00 – 3.84 (m, 2H), 3.78 – 3.71 (m, 1H), 2.38 – 2.31 (m, 2H), 2.25 – 1.94 (m, 10H), 1.65 (d, *J* = 1.4 Hz, 3H), 1.63 –1.24 (m, 11H), 1.20 (s, 12H), 1.14 (d, *J* = 6.2 Hz, 3H), 0.91 – 0.84 (m, 36H), 0.14 – -0.01 (m, 24H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 174.8, 149.1, 146.3, 132.3, 131.7, 112.4, 109.4, 83.2, 70.3, 70.1, 69.2, 66.4, 47.9, 43.5, 37.8, 37.7, 37.6, 36.1, 33.7, 33.5, 31.9, 29.7, 29.4, 25.9, 25.9, 24.8, 24.8, 24.5, 23.1, 22.7, 21.0, 18.2, 18.1, 18.0, 17.4, 14.1, -3.9, -4.0, -4.1, -4.2, -4.41, -4.44, -4.8.; IR (neat): 2954.6 (s), 2926.0 (s), 2855.3 (s), 1714.2 (w), 1557.1 (w), 1462.4 (m), 1380.3 (m), 1361.1 (m), 1254.1 (m), 1142.4 (s), 1086.5 (m), 835.6 (m), 807.1 (w), 774.4 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{55}{}^{1}H_{115}{}^{11}B_1{}^{16}O_8{}^{14}N_1{}^{28}Si_4$ $[M+NH_4]^+$: calculated: 1040.7793, found: 1040.7843. $[\alpha]^{20}_D$ -3.6 (*c* 0.4, $CHCl_3$).



(6*R*,10*R*,14*S*,*E*)-14-((6*S*,8*S*)-6,8-bis((*tert*-butyldimethylsilyl)oxy)-2-methylenenonyl)-6,10-bis((*tert*-butyldimethylsilyl)oxy)-8-methyl-12-methyleneoxacyclotetradec-7-en-2-one (**22**). To a 20 mL scintillation vial was added (**21**) (6 mg, 0.0067 mmol), THF (1 mL) and H_2O (1 mL). The solution was cooled to 0°C, and sodium perborate monohydrate (30 mg, 0.2 mmol) was added. The mixture was allowed to stir overnight. The solution was quenched by H_2O, extracted with diethyl ether, dried over Na_2SO_4 and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:0 – 100:20 hexanes/ethyl acetate, stain in CAM) to afford (5*R*,9*R*,13*S*,19*S*,21*S*,*E*)-5,9,19,21-tetrakis((*tert*-butyldimethylsilyl)oxy)-13-hydroxy-7-methyl-11,15-dimethylenedocos-6-enoic acid **S7** as a colorless oil (5.5 mg, 90 %).

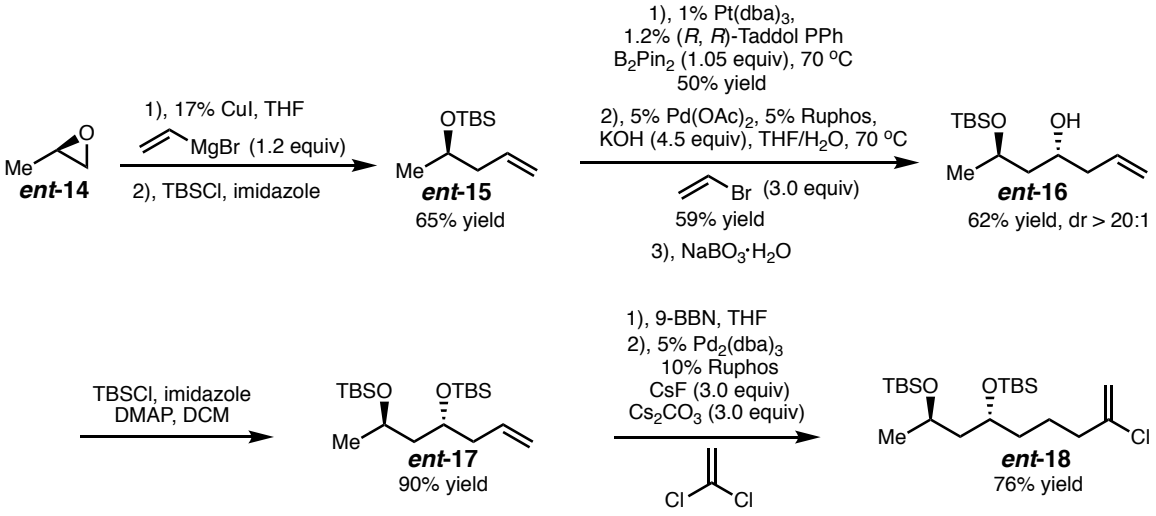
The Yamaguchi esterification was performed according to a previous procedure.[13] An oven dried 20 mL scintillation vial (charged with a stirring bar, cooled under vacumn) was charged with carboxylic acid **S7** (5.5 mg, 6 μmol), THF (1 mL), triethyl amine (6.1 mg, 8.36 μmol) and 2,4,6-trichlorobenzoylchloride (8.8 mg, 72 μmol). The solution was allowed to stir at room temperature for two hours before toluene (4 mL) was added. Then above mixture was then transferred into a syringe. The solution was added into an oven dried 50 mL round bottom flask (precharged with DMAP (8.8 mg, 72 μmol) and toluene (12 mL)) *via* syringe pump at 80 °C over three hours. The mixture was heated at 80 °C overnight, then cooled to room temperature and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:0-100:2 pentane/diethyl ether, stain in CAM) to afford **22** as a clear colorless oil (3.8 mg, 71%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.23 – 5.17 (m, 1H), 5.05 (d, *J* = 8.9 Hz, 1H), 4.98 (s, 1H), 4.83 (d, *J* = 2.1 Hz, 1H), 4.76 (d, *J* = 1.8 Hz, 1H), 4.72 (s, 1H), 4.29 (ddd, *J* = 10.3, 8.7, 3.2 Hz, 1H), 3.91 – 3.84 (m, 2H), 3.74 (p, *J* = 5.4 Hz, 1H), 2.45 (td, *J* = 14.2, 3.1 Hz, 2H), 2.40 – 2.28 (m, 2H), 2.22 (dd, *J* = 14.3, 6.0 Hz, 2H), 2.18 – 2.08 (m, 2H), 2.01 (td, *J* = 9.9, 3.8 Hz, 3H), 1.92

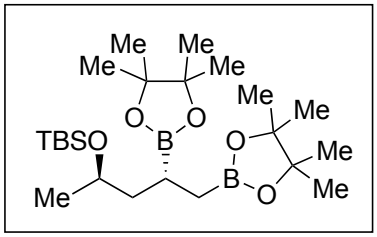
(dd, *J* = 14.0, 8.9 Hz, 1H), 1.72 (d, *J* = 1.3 Hz, 3H), 1.60 (ddd, *J* = 13.6, 7.1, 5.4 Hz, 2H), 1.54 – 1.46 (m, 1H), 1.46 – 1.39 (m, 5H), 1.33 – 1.24 (m, 2H), 1.13 (d, *J* = 6.2 Hz, 3H), 0.91 – 0.83 (m, 36H), 0.09 – -0.02 (m, 24H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 172.3, 145.7, 142.0, 133.0, 130.7, 128.0, 117.5, 112.0, 71.7, 71.3, 70.0, 69.2, 66.4, 48.0, 46.7, 43.5, 39.7, 39.1, 38.2, 37.4, 35.9, 34.8, 25.94, 25.93, 25.87, 24.5, 23.0, 21.3, 20.1, 18.2, 18.14, 18.10, -3.9, -4.1, -4.2, -4.36, -4.39, -4.5, -4.7, -4.8; IR (neat): 2954.0 (m), 2928.7 (s), 2856.4 (m), 1735.7 (m), 1472.1 (w), 1462.0 (w), 1374.2 (w), 1361.2 (w), 1253.6 (s), 1144.5 (w), 1117.0 (w), 1087.9 (m), 1050.5 (m), 1005.5 (w), 895.1 (w), 834.9 (s), 807.9 (w), 773.6 (s) cm^{-1}; HRMS-(DART+) for $^{12}C_{49}{}^{1}H_{102}{}^{16}O_6{}^{14}N_1{}^{28}Si_4$ $[M+NH_4]^+$: calculated: 912.6784, found: 912.6762; $[\alpha]^{20}_D$ +10.1 (*c* 1.03, $CHCl_3$).



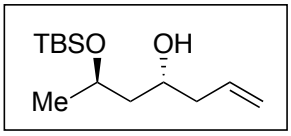
(6*R*,10*R*,14*S*,*E*)-14-((6*S*,8*S*)-6,8-dihydroxy-2-methylenenonyl)-6,10-dihydroxy-8-methyl-12-methyleneoxacyclotetradec-7-en-2-one (1). The global deprotection was performed according to a previous procedure. [14] To a Teflon vial was added (6*R*,10*R*,14*S*,*E*)-14-((6*S*,8*S*)-6,8-bis((*tert*-butyldimethylsilyl)oxy)-2-methylenenonyl)-6,10-bis((*tert*-butyldimethylsilyl)oxy)-8-methyl-12-methyleneoxacyclotetradec-7-en-2-one **22** (4.5 mg, 5 μmol) and THF (0.5 mL). The mixture was cooled to 0 °C, and HF•pyridine (20 μL) was added dropwise into it. Three more portions of HF•pyridine (20 μL) were added slowly into the vial in the following three days at room temperature. Upon completion, the reaction mixture was added carefully into a 20 mL scintillation vial containing saturated $NaHCO_3$ solution (3 mL) at 0 °C, which was then allowed to warm to room temperature and stirred for another twenty minutes. The aqueous layer was extracted with ethyl acetate (5×3 mL). The organic layers were combined, dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:10-10:90 hexanes/ethyl acetate, then, 100:10-100:20 hexane/MeOH stain in CAM) to afford **1** as a white solid (1.8 mg, 82%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.21 (tt, *J* = 7.5, 4.3 Hz, 1H), 5.09 (d, *J* = 9.3 Hz, 1H), 5.08 (s, 1H), 4.96 (d, *J* = 1.9 Hz, 1H), 4.78 (d, *J* = 1.7 Hz, 1H), 4.72 (s, 1H), 4.37 (ddd, *J* = 10.6, 9.0, 3.4 Hz, 1H), 4.15 (h, *J* = 6.0 Hz, 1H), 3.94 (p, *J* = 6.0 Hz, 1H), 3.84 (tdd, *J* = 10.2, 4.0, 1.8 Hz, 1H), 2.67 (d, *J* = 14.0 Hz, 1H), 2.64 (d, *J* = 14.8 Hz, 4.0 Hz, 1H), 2.42 (dd, *J* = 14.3, 3.5 Hz, 1H), 2.32 (dt, *J* = 14.2, 5.9 Hz, 1H), 2.27 – 2.22 (m, 2H), 2.18 – 2.12 (m, 2H), 2.04 (t, *J* = 7.9 Hz, 2H), 1.94 (dd, *J* = 14.1, 10.5 Hz, 1H), 1.89 (dd, *J* = 14.4, 10.0 Hz, 1H), 1.83 – 1.78 (m, 1H), 1.77 (d, *J* = 1.5 Hz, 3H), 1.75 – 1.22 (m, 9H), 1.22 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 172.47, 145.14, 142.49, 135.77, 129.34, 117.98, 112.63, 71.34, 69.13, 68.71, 68.11, 65.56, 44.59, 44.14, 43.60, 39.45, 38.40, 36.88, 36.53, 35.55, 34.29, 23.66, 23.63, 21.50, 20.13; IR (neat): 3375 (broad, O-H stretch, w), 2924.1 (s), 2869.7 (s), 2854.8 (s), 1731.6 (m), 1716.9 (m), 1556.2 (m), 1488.1 (m), 1456.8 (m), 1436.6 (m), 1380.7 (m), 1296.7 (w), 1243.9 (w), 1142.5 (s), 1075.5 (m), 908.2 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{25}{}^{1}H_{41}{}^{16}O_5$ $[M+H-H_2O]^+$: calculated: 421.2954, found: 421.2955; $[\alpha]^{20}_D$ +6.00 (*c* 0.0667, $CHCl_3$). The optical rotaion value reported for arenolide is $[\alpha]_D$ +13.0° (*c* 0.64, $CHCl_3$).[15]

II. Full Characterization of Compounds Leading to Isomer 2





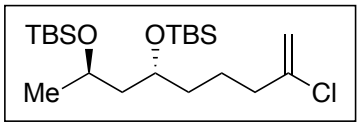
(((2*R*,4*R*)-4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-2-yl)oxy)(*tert*-butyl)dimethylsilane (*ent*-S5) To an oven dried 2-dram vial was added $Pt(dba)_3$ (2.7 mg, 0.003 mmol), (*R,R*)-3,5-di-iso-propylphenyl-TADDOLPPh (2.9 mg, 0.0036 mmol), $B_2(pin)_2$ (80 mg, 0.315 mmol) and THF (0.3 mL) in the glove box. The vial was sealed with Teflon cap, taken outside of the glove box, and heated at 70 °C for twenty minutes. The mixture was cooled to room temperature and returned to the glove box again. The solution was then charged with (*R*)-*tert*-butyldimethyl(pent-4-en-2-yloxy)silane *ent*-**14** (60 mg, 0.3 mmol). The vial was then heated at 70 °C outside of the glove box for 12 hours. Upon completion, the yellow solution was extracted with diethyl ether, filtered through a silica gel pipet and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:3 to 100:5 hexanes/ethyl acetate, stain in CAM) to afford ***ent*-S5** as a colorless oil (68 mg, 50%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.85 (h, *J* = 6.2 Hz, 1H), 1.54 (ddd, *J* = 13.2, 6.5, 5.3 Hz, 1H), 1.46 – 1.37 (m, 1H), 1.22 (s, 24H), 1.18 (t, *J* = 7.5 Hz, 1H), 1.10 (d, *J* = 6.0 Hz, 3H), 0.87 (s, 9H), 0.83 (d, *J* = 7.5 Hz, 2H), 0.04 (d, *J* = 3.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 82.8, 82.7, 68.3, 43.3, 26.0, 24.9, 24.84, 24.82, 24.76, 23.8, 18.2, -4.4, -4.6; ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.8; IR (neat): 2977.5 (m), 2929.3 (m), 2857.6 (m), 1370.9 (s), 1315.4 (s), 1254.2 (m), 1141.9 (s), 1070.6 (w), 835.7 (m), 774.2 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{23}{}^{1}H_{49}{}^{11}B_2{}^{16}O_5{}^{28}Si_1$ $[M+H]^+$: calculated: 455.3535, found: 455.3538; $[\alpha]^{20}_D$ -0.8 (*c* 1.05, $CHCl_3$).



(4*R*,6*R*)-6-((*tert*-butyldimethylsilyl)oxy)hept-1-en-4-ol (*ent*-16) [16] In the glovebox, to an oven dried two dram vial was added $Pd(OAc)_2$ (1.12 mg, 0.005 mmol), Ruphos (2.33 mg, 0.005 mmol), 1,2-bis(boronic) ester **(*ent*-S5)** (45.4 mg, 0.1 mmol) and THF (0.35 mL). The vial was taken outside of the glove box, 1M vinyl bromide (0.15 mL, 0.15 mmol) and 8M KOH (56 μL, 0.45 mmol) were added

sequentially. The reaction mixture was heated at 70 °C for 12 hours. Upon completion, the reaction mixture was cooled to room temperature, diluted with diethyl ether, filtered through a silica gel pipet and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:3-100:10 pentane/diethyl ether, stain in CAM) to afford *tert*-butyldimethyl-(((2*R*,4*R*)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-6-en-2-yl)oxy)silane **S7** as a colorless clear oil (21 mg, 59%, > 20:1 dr). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.79 (ddt, *J* = 17.0, 10.1, 6.9 Hz, 1H), 5.01 (ddt, *J* = 17.1, 2.2, 1.6 Hz, 1H), 4.94 (ddt, *J* = 10.2, 2.3, 1.2 Hz, 1H), 3.81 (ddt, *J* = 13.5, 11.8, 6.1 Hz, 1H), 2.22 – 2.09 (m, 2H), 1.51 – 1.41 (m, 2H), 1.27 – 1.19 (m, overlap, 1H), 1.23 (s, 12H), 1.12 (d, *J* = 6.0 Hz, 3H), 0.88 (d, *J* = 2.7 Hz, 9H), 0.05 (d, *J* = 4.2 Hz, 6H).

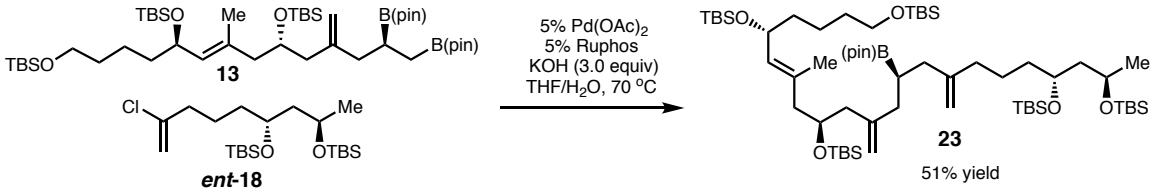
To a 20 mL scintillation vial was added boronic ester **S7** (260 mg, 0.73 mmol), THF (2 mL) and H_2O (2 mL). The solution was cooled to 0 °C, and then sodium perborate monohydrate (366 mg, 3.67 mmol) was added. The mixture was then allowed to stir overnight. The solution was quenched by H_2O, extracted with diethyl ether, dried over Na_2SO_4 and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:2 – 100:20 pentane/diethyl ether, stain in CAM) to afford ***ent*-16** as a colorless clear oil (110 mg, 62%). The spectra were in accordance with a previous report.[16] ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.84 (ddt, *J* = 17.3, 10.3, 7.1 Hz, 1H), 5.17 – 5.05 (m, 2H), 4.21 (pd, *J* = 6.1, 3.8 Hz, 1H), 4.02 (dddd, *J* = 9.6, 7.7, 5.2, 2.5 Hz, 1H), 3.30 (d, *J* = 2.3 Hz, 1H), 2.30 – 2.13 (m, 2H), 1.63 (ddd, *J* = 13.9, 9.9, 3.7 Hz, 1H), 1.53 (ddd, *J* = 14.2, 5.5, 2.2 Hz, 1H), 1.22 (d, *J* = 6.3 Hz, 3H), 0.89 (s, 9H), 0.09 (d, *J* = 4.3 Hz, 6H).

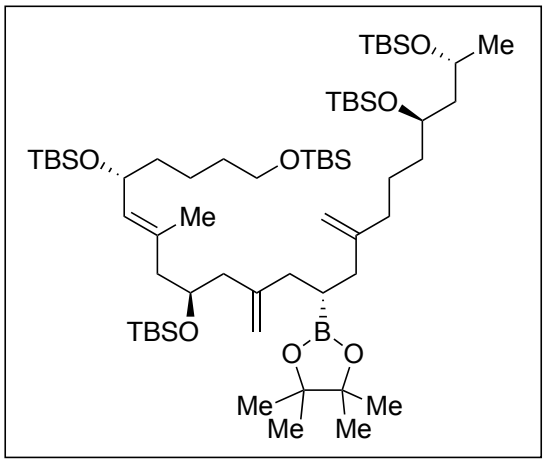


(5*R*,7*R*)-5-(4-chloropent-4-en-1-yl)-2,2,3,3,7,9,9,10,10-nonamethyl-4,8-dioxa-3,9-disilaundecane (***ent*-18**). Terminal alkene ***ent*-16** (110 mg, 0.45 mmol), DCM (2 mL), and imidazole (76.6 mg, 1.12 mmol) were added into a 20 mL scintillation vial sequentially. The mixture was stirred until all solids dissolved, and was then cooled to 0 °C. *tert*-Butyldimethylsilyl chloride (75 mg, 0.5 mmol) was added slowly into the above solution. Lastly, a spatula tip (ca. 2 mg) of 4-(dimethylamino)pyridine was added. The white slurry was allowed to stir overnight, which was then quenched by water, extracted with DCM and dried over Na_2SO_4. The colorless solution was concentrated *in vacuo* to give a colorless oil. The crude reaction mixture was purified by column chromatography on silica gel (100:0-100:2 pentane/diethyl ether, stain in CAM) to afford (5*R*,7*R*)-5-allyl-2,2,3,3,7,9,9,10,10-nonamethyl-4,8-dioxa-3,9-disilaundecane **(*ent*-17)** as a colorless oil (145 mg, 90%).

***Ent*-18** was prepared according to a previous literature with slightly modification.[17] In the glove box, to an oven dried four-dram vial were added 9-BBN dimer (48.8 mg, 0.2 mmol), THF (1 mL) and ***ent*-17** (145 mg, 0.4 mmol). The mixture was allowed to stir for 1.5 hours to resulting in yellow clear solution. $Pd_2(dba)_3$ (18.3 mg, 0.02 mmol), Ruphos (18.7 mg, 0.04 mmol), THF (3 mL), CsF (182.3 mg, 1.2 mmol) and Cs_2CO_3 (391 mg, 1.2 mmol) were added sequentially into the solution. The vial was sealed with a Teflon cap and taken outside of the glove box. 1,1-Dichloroethylene (0.128 mL, 1.6 mmol) was added

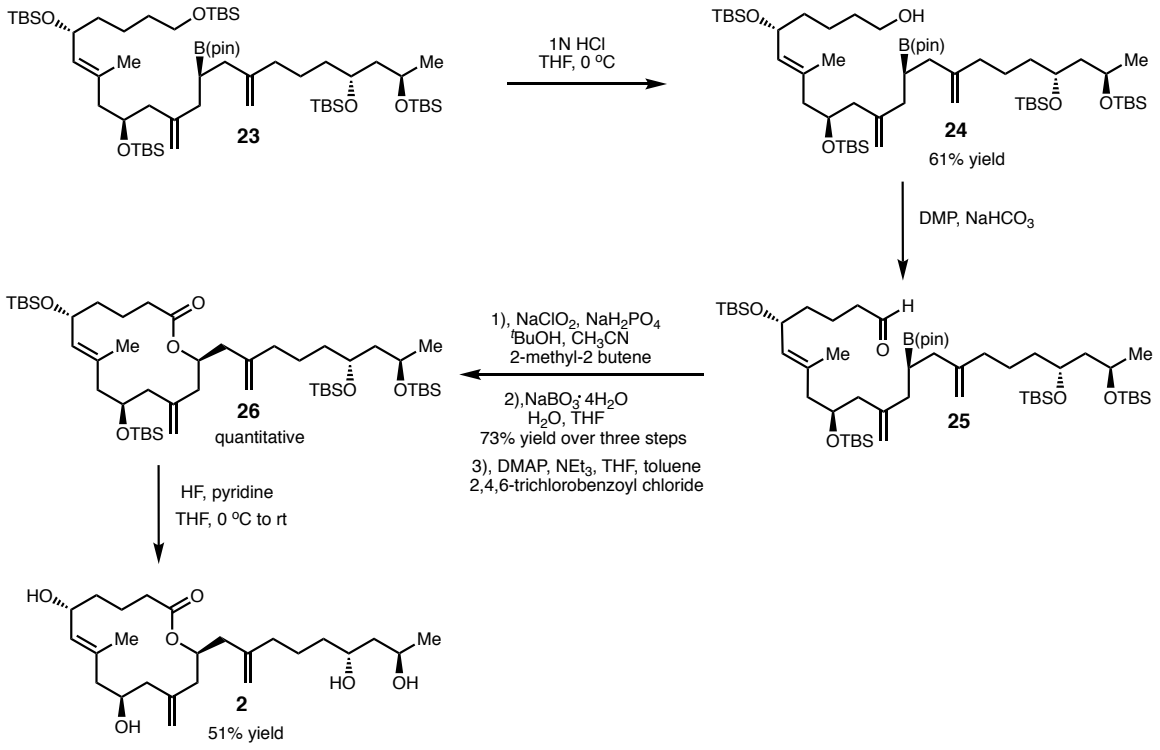
into the reaction solution. The solution was then heated at 70 °C for 12 hours. Upon completion, the reaction mixture was diluted with diethyl ether, filtered through a silica gel pipet and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:2-100:3 pentane/diethyl ether, stain in CAM) to afford ***ent*-18** as a colorless clear oil (128 mg, 76 %). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.14 (d, *J* = 1.2 Hz, 1H), 5.11 (t, *J* = 1.2 Hz, 1H), 3.88 (h, *J* = 6.3 Hz, 1H), 3.76 (p, *J* = 6.7 Hz, 1H), 2.32 (t, *J* = 7.4 Hz, 2H), 1.67 – 1.56 (m, 3H), 1.53 – 1.38 (m, 3H), 1.14 (dd, *J* = 6.1, 1.2 Hz, 3H), 0.88 (s, 18H), 0.09 – 0.02 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.9, 111.9, 69.8, 66.3, 47.9, 39.2, 36.6, 25.9, 24.5, 22.6, 18.1, -3.9, -4.1, -4.2, -4.5; IR (neat): 2954.0 (m), 2928.9 (m), 2886.8 (w), 2856.6 (m), 1472.1 (w), 1374.7 (w), 1253.2 (m), 1118.0 (m), 1061.8 (m), 1004.8 (m), 938.9 (w), 878.0 (m), 832.4 (s), 805.5 (s), 770.9 (s), 703.6 (w), 663.4 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{21}{}^{1}H_{46}{}^{35}Cl_1{}^{16}O_2{}^{28}Si_2$ $[M+H]^+$: calculated: 421.2725, found: 421.2745; $[\alpha]^{20}_D$ -7.0 (*c* 1.16, $CHCl_3$).

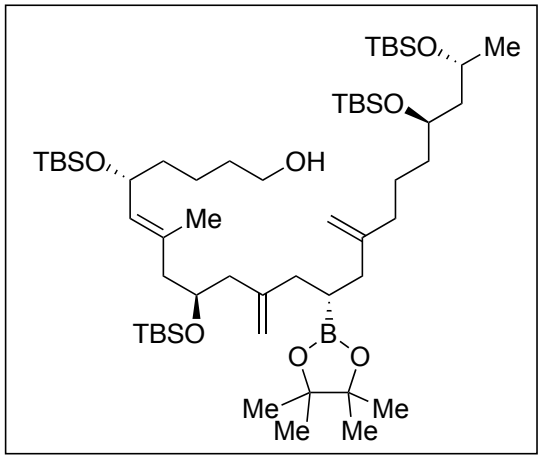




(9*R*,13*R*,17*S*,23*R*,25*R*,*E*)-9,13,23-tris((*tert*-butyldimethylsilyl)oxy)-2,2,3,3,11,25,27,27,28,28-decamethyl-15,19-dimethylene-17-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4,26-dioxa-3,27-disilanonacos-10-ene. (23) The reaction was performed according to a previous procedure[18] with slightly modification. In the glove box, an oven dried 20 mL vial was added $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), Ruphos (14 mg, 0.03 mmol) and THF (3 mL). The mixture was allowed to stir for 5 minutes before adding **13** (260 mg, 0.3 mmol) and ***ent*-18** (128 mg, 0.3 mmol) sequentially. The vial was sealed and taken outside of the glove box. Degassed 8M KOH (0.17 mL, 1.35 mmol) and degassed H_2O (0.3 mL) were added into the vial. The mixture was then heated at 70 °C overnight. The solution changed color from orange red to black. The reaction mixture was extracted by diethyl ether, dried over Na_2SO_4 and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:0.5-100:5 hexanes/ethyl acetate, stain in CAM) to afford **23** as a colorless oil (152 mg, 51%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.16 (d, *J* = 8.5 Hz, 1H), 4.84 (s, 1H), 4.75 (s, 1H), 4.74 (s, 1H), 4.69 (s, 1H), 4.31 (td, *J* = 7.9, 4.6 Hz, 1H), 3.94 – 3.85 (m, 2H), 3.74 (p, *J* = 5.4 Hz, 1H), 3.59 (t, *J* = 6.6 Hz, 2H), 2.19 – 2.00 (m, 8H), 2.01 – 1.95 (m, 2H), 1.61 (s, 3H), 1.66 – 1.58 (m, overlap, 1H), 1.54 – 1.23 (m, 12H), 1.18 (s, 12H), 1.14 (dd, *J* = 6.0, 1.2 Hz, 3H), 0.91 – 0.83 (m, 45H), 0.08 – -0.03 (m, 30H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 149.1, 146.5, 132.5, 131.5, 112.2, 109.4, 82.9, 70.2, 70.0, 69.7, 66.4, 63.3, 48.0, 47.5, 44.0, 38.5, 38.3, 37.8, 37.6, 36.1, 32.9, 26.0, 25.95, 25.93, 25.90, 24.87, 24.81, 24.5, 23.2, 21.9, 19.9, 18.4, 18.2, 18.10, 18.06, 16.9, -3.9, -4.0, -4.1, -4.2,

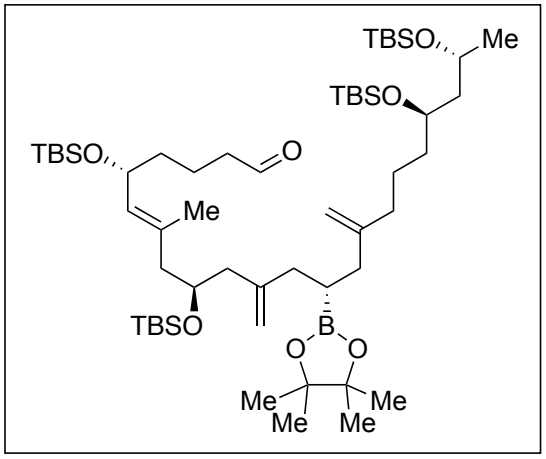
-4.4, -4.5, -4.7, -5.3; IR (neat): 2953.6 (m), 2928.5 (m), 2856.4 (m), 1471.9 (w), 1462.1 (w), 1380.0 (w), 1361.2 (w), 1252.8 (m), 1144.1 (m), 1090.8 (m), 1064.9 (m), 1005.1 (w), 938.6 (w), 890.9 (w), 832.9 (s), 807.0 (m), 772.1 (s), 665.1 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{61}{}^{1}H_{131}{}^{11}B_{1}{}^{16}O_{7}{}^{14}N_{1}{}^{28}Si_{5}$ $[M+NH_4]^+$: calculated: 1140.8865, found: 1140.8897; $[\alpha]^{20}_{D}$ +1.1 (*c* 1.63, $CHCl_3$).



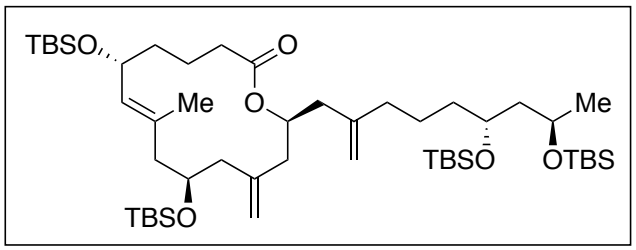


(5*R*,9*R*,13*S*,19*R*,21*R*,*E*)-5,9,19,21-tetrakis((*tert*-butyldimethylsilyl)oxy)-7-methyl-11,15-dimethylene-13-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)docos-6-en-1-ol (24). **A** 20 mL scintillation vial was charged with **23** (60 mg, 0.06 mmol) and THF (6 mL). The solution was cooled to 0 °C, and allowed to stir at 0 °C for 15 minutes. HCl (0.06 mL, 1 M, 0.06 mmol) was added dropwise into the mixture, and the mixture was allowed to stir at 4 °C (cold room) overnight. The vial was cooled to 0 °C again, and then quenched by adding one pipet of saturated $Na_2S_2O_3$ (0.5 mL). The reaction mixture was extracted with diethyl ether, filtered through a $Na_2S_2O_4$ pipet and evaporated *in vacuo*. The crude reaction mixture was then purified by column chromatography on silica gel (100:2-80:20 hexanes/ethyl acetate, stain in CAM) to afford **24** as a clear colorless oil (32.3 mg, 61%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.16 (d, *J* = 8.5 Hz, 1H), 4.84 (s, 1H), 4.75 (s, 1H), 4.74 (s, 1H), 4.70 (s, 1H), 4.33 (td, *J* = 7.9, 4.5 Hz, 1H), 3.92 (p, *J* = 5.9 Hz, 1H), 3.88

(h, *J* = 6.0 Hz, 1H), 3.75 (p, *J* = 5.5 Hz, 1H), 3.63 (q, *J* = 6.1 Hz, 2H), 2.18 – 2.01 (m, 8H), 1.97 (q, *J* = 7.3 Hz, 2H), 1.62 (s, 3H), 1.59 – 1.23 (m, 13H), 1.18 (s, 12H), 1.14 (d, *J* = 6.1 Hz, 3H), 0.92 – 0.82 (m, 36H), 0.12 – -0.04 (m, 24H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 149.1, 146.5, 132.2, 131.8, 112.2, 109.4, 82.9, 70.2, 70.1, 69.5, 66.4, 63.0, 48.0, 47.5, 43.9, 38.5, 38.2, 37.8, 37.6, 36.1, 32.8, 29.7, 26.0, 25.9, 24.9, 24.8, 24.5, 23.1, 21.6, 19.9, 18.2, 18.11, 18.08, 17.1, -3.9, -4.00, -4.1, -4.2, -4.37, -4.44, -4.7; IR (neat): 2952.7 (m), 2928.4 (s), 2856.4 (m), 1472.1 (w), 1462.1 (w), 1380.1 (m), 1361.5 (w), 1253.4 (m), 1144.2 (m), 1086.9 (m), 1064.2 (m), 1005.2 (w), 938.7 (w), 891.5 (w), 834.3 (s), 806.8 (m), 773.2 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{55}{}^{1}H_{117}{}^{11}B_{1}{}^{16}O_{7}{}^{14}N_{1}{}^{28}Si_{4}$ $[M+NH_4]^+$: calculated: 1026.8000, found: 1026.8042; $[\alpha]^{20}_{D}$ +1.4 (*c* 1.33, $CHCl_3$).



(5*R*,9*R*,13*S*,19*R*,21*R*,*E*)-5,9,19,21-tetrakis((*tert*-butyldimethylsilyl)oxy)-7-methyl-11,15-dimethylene-13-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)docos-6-enal (25) To a 20 mL scintillation vial was added **(24)** (10 mg, 9.9 μmol) and DCM (1 mL). The mixture was cooled to 0 °C, Dess-Martin periodinane (5 mg, 11.9 μmol) and $NaHCO_3$ (4.2 mg, 49.6 μmol) were added. After 4 hours, the reaction mixture was concentrated *in vacuo*, then extracted with 1:1 hexane/Et_2O, filtered through a silica gel padded sintered funnel, and then rinsed with 1:1 hexane/Et_2O, and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:2-100:3 hexanes/ethyl acetate, stain in CAM) to afford **25** as a clear colorless oil (8 mg, 80%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.75 (td, *J* = 1.0, 1.0 Hz, 1H), 5.16 (d, *J* = 8.1 Hz, 1H), 4.84 (s, 1H), 4.75 (s, 1H), 4.74 (s, 1H), 4.70 (s, 1H), 4.34 (td, *J* = 7.9, 4.8 Hz, 1H), 3.92 (p, *J* = 5.8 Hz, 1H), 3.88 (h, *J* = 5.9 Hz, 1H), 3.74 (p, *J* = 5.5 Hz, 1H), 2.41 (tt, *J* = 7.3, 1.4 Hz, 2H), 2.20 – 2.00 (m, 8H), 1.97 (q, *J* = 7.8 Hz, 2H), 1.73 (tdd, *J* = 12.8, 10.3, 6.1 Hz, 1H), 1.68 – 1.57 (m, 1H), 1.62 (s, 3H), 1.52 – 1.44 (m, 1H), 1.45 – 1.23 (m, 7H), 1.21 (td, *J* = 6.5, 5.9, 1.3 Hz, 1H), 1.18 (s, 12H), 1.14 (d, *J* = 6.1 Hz, 3H), 0.91 – 0.83 (m, 36H), 0.10 – -0.03 (m, 24H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 202.6, 149.1, 146.4, 132.2, 131.8, 112.2, 109.4, 82.9, 70.13, 70.06, 69.3, 66.4, 48.0, 47.4, 44.0, 43.8, 38.4, 37.82, 37.78, 37.6, 36.1, 29.7, 26.0, 25.94, 25.87, 24.9, 24.8, 24.5, 23.2, 19.9, 18.3, 18.2, 18.1, 18.0, 17.0, -3.9, -4.0, -4.1, -4.2, -4.3, -4.45, -4.46, -4.8; IR (neat): 2953.4 (m), 2928.5 (s), 2856.4 (m), 1731.6 (w), 1472.3 (w), 1462.1 (w), 1380.0 (m), 1361.8 (m), 1253.5 (m), 1144.3 (m), 1088.1 (m), 1065.32 (m), 1005.4 (w), 971.1 (w), 938.7 (w), 890.7 (w), 834.5 (s), 807.7 (m), 773.5 (s) cm^{-1}; HRMS-(DART+) for $^{12}C_{55}{}^{1}H_{115}{}^{11}B_{1}{}^{16}O_{7}{}^{14}N_{1}{}^{28}Si_{4}$ $[M+NH_4]^+$: calculated: 1024.7844, found: 1024.7869. $[\alpha]^{20}_{D}$ +2.1 (*c* 0.14, $CHCl_3$).

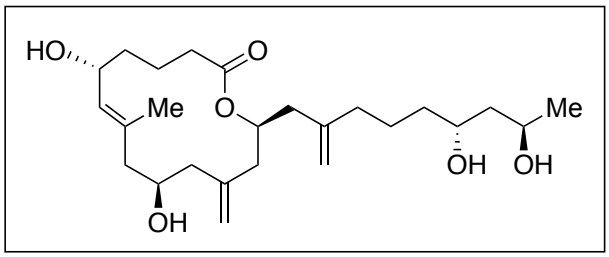


(6*R*,10*R*,14*S*,*E*)-14-((6*R*,8*R*)-6,8-bis((*tert*-butyldimethylsilyl)oxy)-2-methylenenonyl)-6,10-bis((*tert*-butyldimethylsilyl)oxy)-8-methyl-12-methyleneoxacyclotetradec-7-en-2-one (26). (5*R*,9*R*,13*S*,19*R*,21*R*,*E*)-5,9,19,21-tetrakis((*tert*-butyldimethylsilyl)oxy)-7-methyl-11,15-dimethylene-13-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)docos-6-enoic acid **S8** was prepared according to a previous procedure[19] with slightly modification. A 20 mL scintillation vial was charged with aldehyde **25** (32 mg, 31.8 μmol), ^{t}BuOH (1 mL), CH_3CN (1 mL) and 2-methyl-2-butene (0.75 mL, 2.2 mmol), sequentially. The vial was then cooled to 0 °C. A solution of $NaClO_2$ (28.8 mg, 0.32 mmol) and NaH_2PO_4 (43.6 mg, 0.32 mmol) in H_2O (1 mL) was added into the vial. The solution was then allowed to warm up to room temperature and stir for four hours. The reaction mixture was quenched by H_2O, extracted with diethyl ether, then filtered through a $Na_2S_2O_4$ pipet and evaporated *in vacuo*. The crude reaction mixture was then purified by column chromatography on silica gel (100:6-60:40 hexanes/ethyl acetate, stain in CAM) to afford **S8** as a clear colorless oil (48 mg, quantitative, with slight impurity) which was used directly in the next step.

To a 20 mL scintillation vial were added carboxylic acid **S8** (48 mg, 47.7 μmol), THF (2 mL) and H_2O (2 mL). The solution was cooled to 0 °C, and treated with sodium perborate tetrahydrate (220 mg, 1.43 mmol). The mixture was then allowed to stir overnight. The solution was quenched by H_2O, extracted with diethyl ether, dried over Na_2SO_4, evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:0 – 100:20 hexanes/ethyl acetate, stain in CAM) to afford (5*R*,9*R*,13*S*,19*R*,21*R*,*E*)-5,9,19,21-tetrakis((*tert*-butyldimethylsilyl)oxy)-13-hydroxy-7-methyl-11,15-dimethylenedocos-6-enoic acid **S9** as a colorless oil (21.5 mg, 73 % over three steps).

The Yamaguchi esterification was performed according to a previous procedure.[20] To an oven dried 20 mL scintillation vial (charged with stirring bar, cooled under vacumn) was added (5*R*,9*R*,13*S*,19*S*,21*S*,*E*)-5,9,19,21-tetrakis((*tert*-butyldimethylsilyl)oxy)-13-hydroxy-7-methyl-11,15-dimethylenedocos-6-enoic acid **S9** (21.5 mg, 23.5 μmol), THF (3 mL), triethyl amine (23.8 mg, 235 μmol) and 2,4,6-trichlorobenzoylchloride (34.4 mg, 141 μmol). The solution was allowed to stir at room temperature for two hours before toluene (20 mL) was added. The solution was transferred into a syringe. The above solution was added into an oven dried 100 mL round bottom flask (precharged with DMAP (34.5 mg, 282 μmol) and toluene (24 mL)) *via* syringe pump at 80°C over nine hours. The solution was heated at 80°C overnight, which was then cooled to room temperature and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:0-100:2 hexanes/ethyl acetate, stain in CAM) to afford **26** as a clear colorless oil (23 mg, quantitative). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.23 – 5.17 (m, 1H), 5.05 (d, *J* = 8.7 Hz, 1H), 4.98 (s, 1H), 4.83 (d, *J* = 2.1 Hz, 1H), 4.76 (d, *J* = 1.6 Hz, 1H), 4.72 (s, 1H), 4.29 (ddd, *J* = 10.2, 8.7, 3.2 Hz, 1H), 3.94 – 3.82 (m, 2H), 3.77 – 3.69 (m, 1H), 2.45 (t, *J* = 14.2 Hz, 2H), 2.36 – 2.29 (m, 2H), 2.23 (dd, *J* = 14.1, 6.0 Hz, 2H), 2.18 – 2.12 (m, 2H), 2.02 (tt, *J* = 9.0, 4.6 Hz, 3H), 1.92 (dd, *J* = 14.0, 9.0 Hz, 1H), 1.72 (d, *J* = 1.3 Hz, 3H), 1.64 – 1.57 (m,

2H), 1.53 –1.37 (m, 5H), 1.33 – 1.19 (m, 3H), 1.14 (d, *J* = 6.1 Hz, 3H), 0.92 – 0.83 (m, 36H), 0.10 – -0.04 (m, 24H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.3, 145.7, 141.9, 133.0, 130.7, 128.0, 117.5, 111.9, 71.7, 71.2, 70.0, 69.2, 66.4, 48.0, 46.7, 43.5, 39.7, 39.1, 38.2, 37.4, 35.9, 34.8, 25.93, 25.86, 24.5, 23.1, 21.3, 20.1, 18.2, 18.14, 18.10, -3.9, -4.1, -4.2, -4.36, -4.39, -4.5, -4.7, -4.8; IR (neat): 2954.5 (s), 2928.2 (s), 2856.3 (s), 1734.0 (m), 1472.4 (m), 1458.4 (m), 1253.7 (s), 1087.0 (m), 1050.5 (m), 835.2 (s), 806.7 (m), 807.9 (w), 774.0 (s) cm^{-1}; HRMS-(DART+) for $^{12}C_{49}{}^{1}H_{98}{}^{16}O_6{}^{28}Si_4{}^{23}Na_1$ $[M+Na]^+$: calculated: 917.6338, found: 917.6335; $[\alpha]^{20}_D$ +2.4 (*c* 0.72, $CHCl_3$).

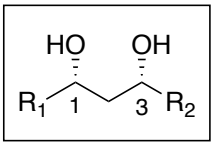


(6*R*,10*R*,14*S*,*E*)-14-((6*R*,8*R*)-6,8-dihydroxy-2-methylenenonyl)-6,10-dihydroxy-8-methyl-12-methyleneoxacyclotetradec-7-en-2-one (2) The global deprotection was performed according to a previous procedure.[21] To a Teflon vial was added **26** (4 mg, 4.5 μmol) and THF (0.5 mL). The solution was cooled to 0 °C and HF•pyridine (18 μL) was added dropwise into it. Three more portions of HF•pyridine (13 μL) were added slowly in the following three days at room temperature. Upon completion, the reaction mixture was added carefully into a 20 mL scintillation vial containing 2.2 mL saturated $NaHCO_3$ solution at 0 °C, after which the solution was then allowed to warm to room temperature and stirred for another twenty minutes. The aqueous layer was extracted with ethyl acetate (5×3 mL). The organic layers were combined, dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:10-10:90 hexanes/ethyl acetate, then, 100:10-100:20 DCM/MeOH stain in CAM) to afford **2** as a white solid (1 mg, 51%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.20 (tt, *J* = 7.7, 3.8 Hz, 1H), 5.10 (d, *J* = 12.1 Hz, 1H), 5.09 (s, 1H), 4.96 (s, 1H), 4.79 (s, 1H), 4.72 (s, 1H), 4.37 (td, *J* = 10.4, 3.3 Hz, 1H), 4.15 (h, *J* = 6.0 Hz, 1H), 3.96 (p, *J* = 5.8 Hz, 1H), 3.84 (t, *J* = 9.1 Hz, 1H), 2.68 (d, *J* = 14.2 Hz, 1H), 2.64 (dd, *J* = 13.5, 4.4 Hz, 1H), 2.43 (dd, *J* = 14.3, 3.5 Hz, 1H), 2.35 – 2.30 (m, 1H), 2.30 – 2.22 (m, 2H), 2.19 – 2.12 (m, 2H), 2.12 – 2.07 (m, 1H), 2.05 – 1.97 (m, 1H), 1.94 (dd, *J* = 14.0, 10.5 Hz, 1H), 1.89 (dd, *J* = 14.4, 10.0 Hz, 1H), 1.84 – 1.79 (m, 1H), 1.77 (d, *J* = 1.4 Hz, 3H), 1.72 – 1.36 (m, 9H), 1.22 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.53, 145.16, 142.51, 135.77, 129.33, 117.96, 112.72, 71.41, 68.80, 68.71, 68.11, 65.54, 44.61, 44.23, 43.60, 39.48, 38.39, 36.84, 36.58, 35.25, 34.35, 23.62, 23.58, 21.50, 20.13; IR (neat): 3385.4 (broad, O-H stretch, m), 2924.3 (s), 2853.3 (m), 1731.8 (s), 1716.0 (m), 1557.3 (s), 1488.6 (s), 1456.4 (s), 1435.5 (s), 1418.3 (s), 1386.8 (m), 1289.3 (m), 1243.9 (m), 1154.9 (m), 1077.0 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{25}{}^{1}H_{42}{}^{16}O_6{}^{23}Na_1$ $[M+Na]^+$: calculated: 461.2879, found: 461.2868; $[\alpha]_D$ -7.49° (*c* 0.0267, $CHCl_3$).

III. Analysis of ^{13}C NMR Chemical Shifts for anti-1,3 and syn-1,3-Diols

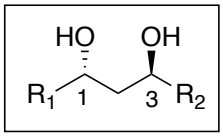
Hoffman and coworkers[22] found the ^{13}C chemical shifts of *anti*-1,3-diols normally occur upfield by about 4 ppm comparing to that of *syn*-1,3-diols. This is probably due to the axial substituent of *anti*-1,3-diols resulting from a hydrogen-bonded cyclic conformation, while the substituents on *syn*-1,3-diols usually adopts an equatorial position. They also noted that the sum of the two carbinol carbons of *anti*-1,3-diols is usually less than 140 ppm (Table 2) and the ^{13}C chemical resonance sum of *syn*-1,3-diols is usually more than 140 ppm. (Data shown in Table 1). This theory was later adopted by Brückner and coworkers[23] for assigning the configuration of their 1,3-diols .

Table 1. Carbon Chemical Shifts of *syn*-1,3-Diols



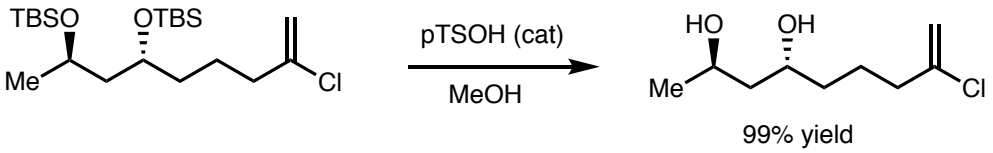
Entry	R_1	R_2	$\delta_{C\text{-}1}$ [ppm]	$\delta_{C\text{-}3}$ [ppm]	Sum [ppm]
1	CH_3	$-CH_2-CH=CH_2$	68.6	71.7	140.3
2	CH_3	$-(CH_2)_3-C(CH_3)=CH_2$	68.8	72.2	141.0
3	CH_3	$-C(CH_3)_2-CH=CH_2$	69.1	79.3	148.4
4	CH_3	$-CH_2CH_2CH_3$	68.5	72.1	140.6
5	CH_3	$-CH_2CH_2CH_2CH_3$	69.3	73.3	142.6
6	*c*Pr	CH_3	78.0	68.8	146.8
7	*i*Pr	CH_3	78.1	69.5	147.6

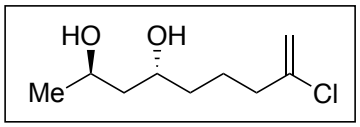
Table 2. Carbon Chemical Shifts of *anti*-1,3-Diols



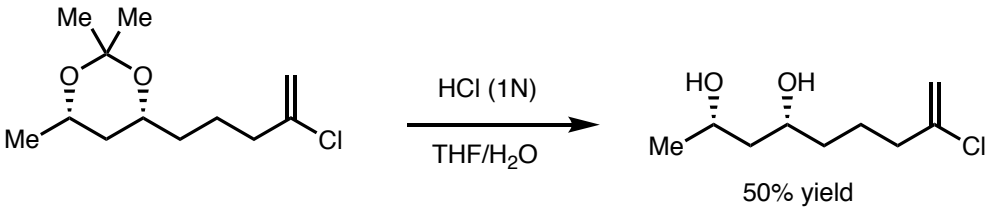
Entry	R_1	R_2	$\delta_{C\text{-}1}$ [ppm]	$\delta_{C\text{-}3}$ [ppm]	Sum [ppm]
1	CH_3	$-CH_2-CH=CH_2$	65.0	68.0	133.0
2	CH_3	$-(CH_2)_3-C(CH_3)=CH_2$	64.8	68.5	133.3
3	CH_3	$-C(CH_3)_2-CH=CH_2$	65.5	74.4	139.9
4	CH_3	$-CH_2CH_2CH_3$	64.9	68.5	133.4
5	CH_3	$-CH_2CH_2CH_2CH_3$	65.7	69.6	135.3
6	*c*Hex	CH_3	73.5	65.8	139.3
7	*i*Pr	CH_3	74.1	65.8	139.9

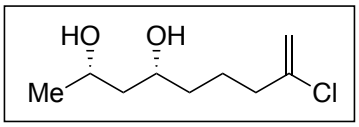
Our model studies of substrates **27** and **28** also supported this theory. The sum of ^{13}C chemical shifts of *anti*-1,3-diols is 134.61 ppm (Table 3, entry 1), while for *syn*-1,3-diols, the sum is 141.86 ppm (Table 3, entry 2).





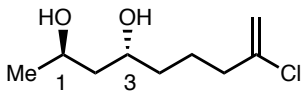
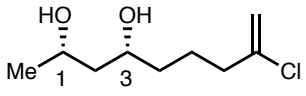
(2*R*,4*R*)-8-chloronon-8-ene-2,4-diol (**27**). To a 20 mL vial was added (5*R*,7*R*)-5-(4-chloropent-4-en-1-yl)-2,2,3,3,7,9,9,10,10-nonamethyl-4,8-dioxa-3,9-disilaundecane ***ent*-18** (21 mg, 0.05 mmol), a tip of *p*-toluenesulfonic acid and 1 mL MeOH. Upon completion, the reaction mixture was quenched with $NaHCO_3$, extracted with diethyl ether, filtered through a silica gel pipet and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (9:1-5:5 hexanse/ethyl acetate, stain in CAM) to afford **27** as a colorless clear oil (9.6 mg, 99%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.15 (dd, *J* = 10.3, 1.2 Hz, 2H), 4.23 – 4.14 (m, 1H), 4.01 – 3.93 (m, 1H), 2.38 (t, *J* = 7.2, 1.0 Hz, 2H), 2.31 (d, *J* = 4.5 Hz, 1H), 2.06 (d, *J* = 4.1 Hz, 1H), 1.79 – 1.68 (m, 1H), 1.66 – 1.59 (m, 3H), 1.57 – 1.44 (m, 2H), 1.26 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.6, 112.2, **69.0, 65.6**, 44.0, 39.0, 36.2, 23.6, 23.3; IR (neat): 3361.6 (m, broad), 2967.2 (m), 2931.9 (m), 2869.2 (m), 1634.6 (w), 1376.7 (w), 1142.6 (s), 880.0 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_9{}^{1}H_{18}{}^{35}Cl_1{}^{16}O_2$ $[M+H]^+$: calculated: 193.0995, found: 193.0999; $[\alpha]^{20}_D$ -4.37 (*c* 0.64, $CHCl_3$).



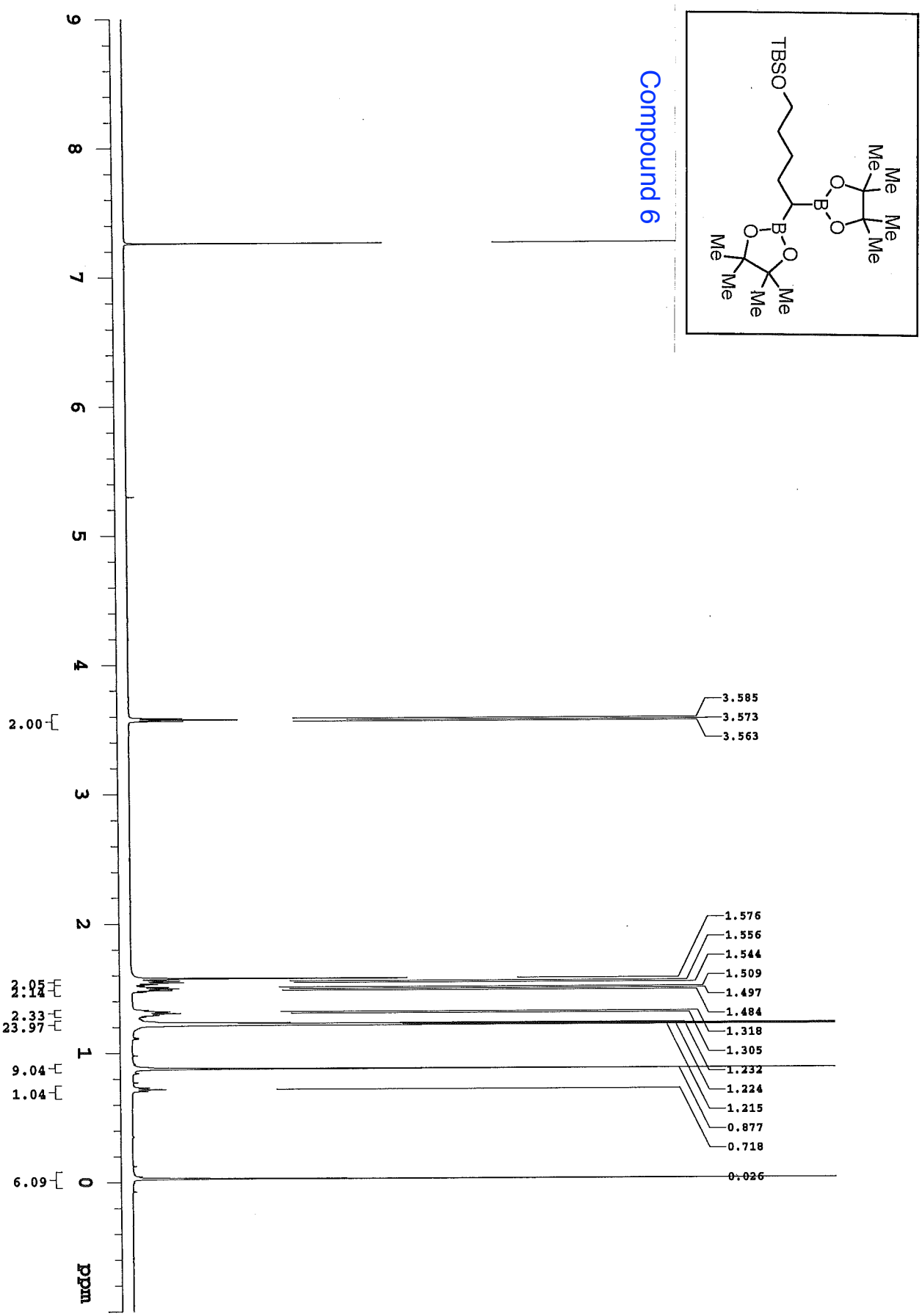


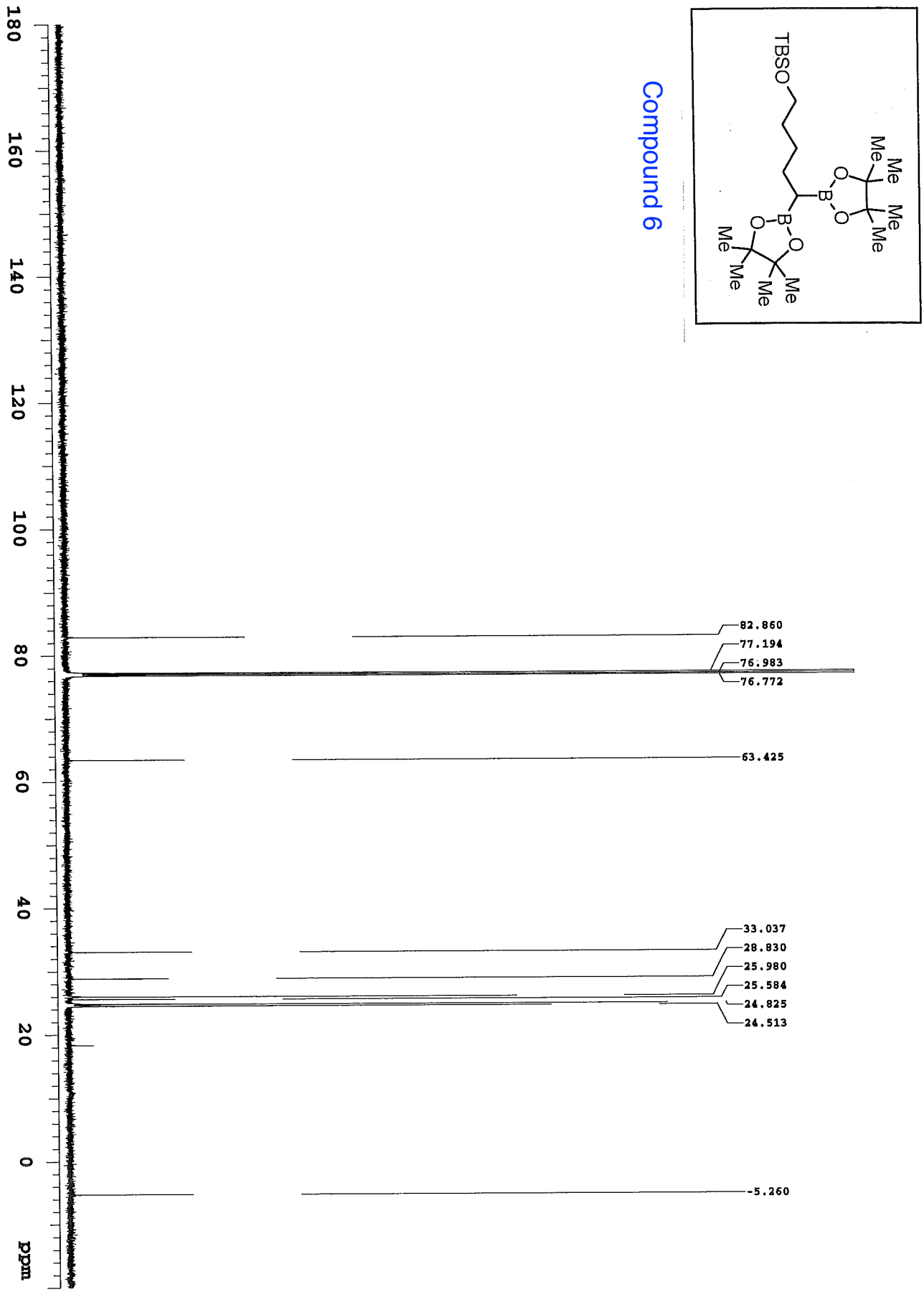
(2*S*,4*R*)-8-chloronon-8-ene-2,4-diol (**28**). To a 20 mL vial was added (4*R*,6*S*)-4-(4-chloropent-4-en-1-yl)-2,2,6-trimethyl-1,3-dioxane (11.6 mg, 0.05 mmol), HCl (1N, 2 mL) and THF (2 mL). Upon completion, the reaction mixture was quenched with $NaHCO_3$, extracted with diethyl ether, filtered through a silica gel pipet and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (9:1-5:5 hexanse/ethyl acetate, stain in CAM) to afford **28** as a colorless clear oil (4.8 mg, 50%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.15 (dd, *J* = 10.4, 1.2 Hz, 2H), 4.11 – 4.02 (m, 1H), 3.93 – 3.83 (m, 1H), 2.90 (s, 1H), 2.59 (s, 1H), 2.37 (t, *J* = 7.1 Hz, 2H), 1.71 (dddd, *J* = 13.0, 10.2, 8.6, 6.4 Hz, 1H), 1.66 – 1.56 (m, 2H), 1.56 – 1.41 (m, 3H), 1.22 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.6, 112.2, **72.6, 69.3**, 44.7, 39.0, 36.9, 24.4, 22.9; IR (neat): 3342.1 (s, broad), 2965.9 (s), 2933.6 (s), 2867.9 (s), 1634.5 (s), 1432.7 (m), 1374.8 (w), 1324.5 (w), 1131.9 (s), 1083.4 (m), 940.6 (w), 879.7 (s), 616.1 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_9{}^{1}H_{18}{}^{35}Cl_1{}^{16}O_2$ $[M+H]^+$: calculated: 193.0995, found: 193.0994; $[\alpha]^{20}_D$ +9.75 (*c* 0.27, $CHCl_3$).

Table 3. Carbon Chemical Shifts of Model 1,3-Diols

1,3-Diol Substrates	$\delta_{C\text{-}1}$ [ppm]	$\delta_{C\text{-}3}$ [ppm]	Sum [ppm]
	65.61	69.00	134.61
	69.29	72.57	141.86

The reported ^{13}C chemical shifts of arenolide at C19 and C21 are 69.1 and 65.5 ppm respectively. The sum of these two number is 134.6 ppm. These data indicated that the 1,3-diols of C19 and C21 in arenolide are in a *anti* relationship.


Compound 6
TBSO
Me
Me
Me
Me
Me
Me
Me
Me
3.585
3.573
3.563
1.576
1.556
1.544
1.509
1.497
1.484
1.318
1.305
1.232
1.224
1.215
0.877
0.718
0.026
2.00
2.05
2.14
2.33
23.97
9.04
1.04
6.09
ppm


Compound 6
TBSO
Me
Me
Me
Me
Me
Me
Me
Me
82.860
77.194
76.983
76.772
63.425
33.037
28.830
25.980
25.584
24.825
24.513
-5.260
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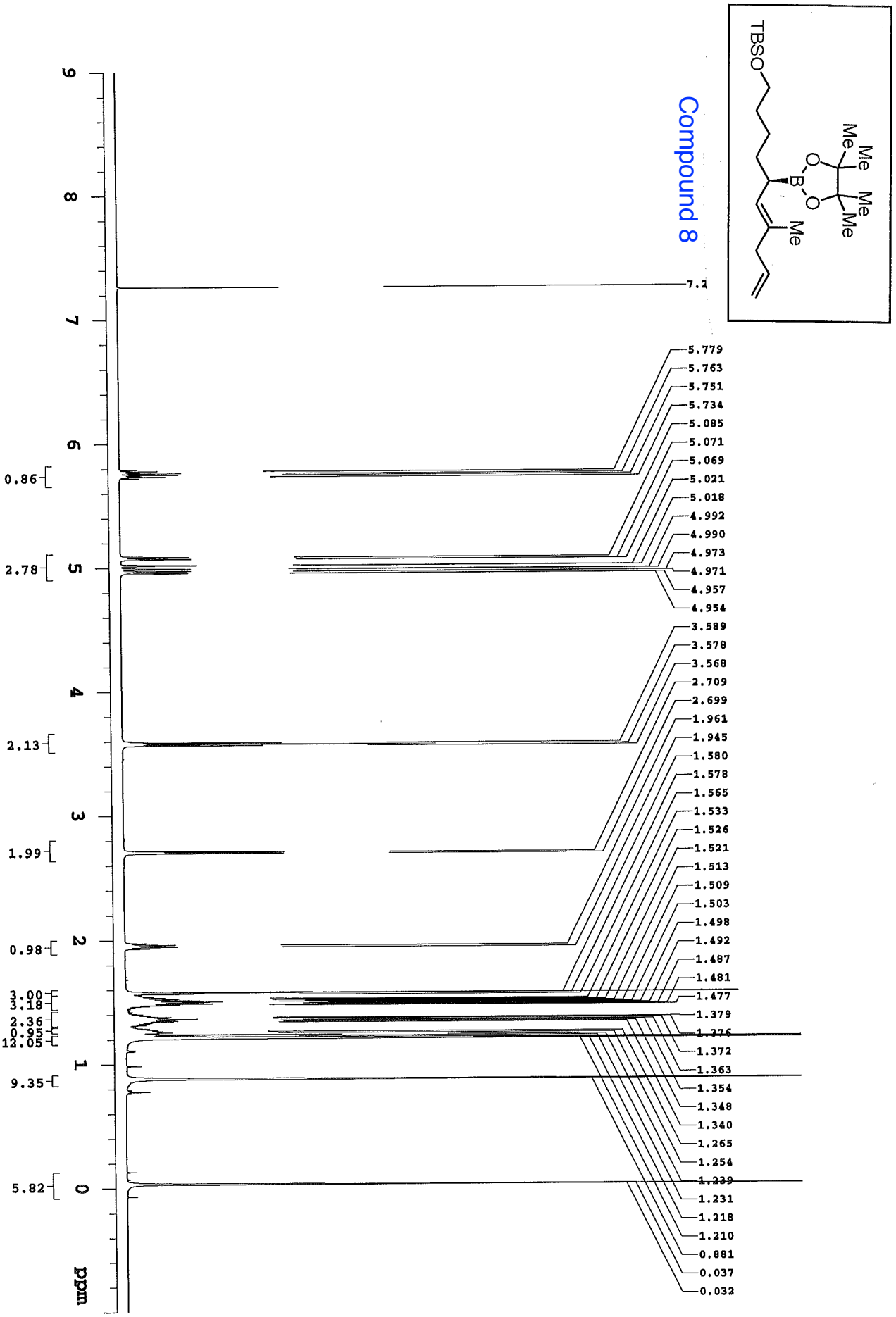
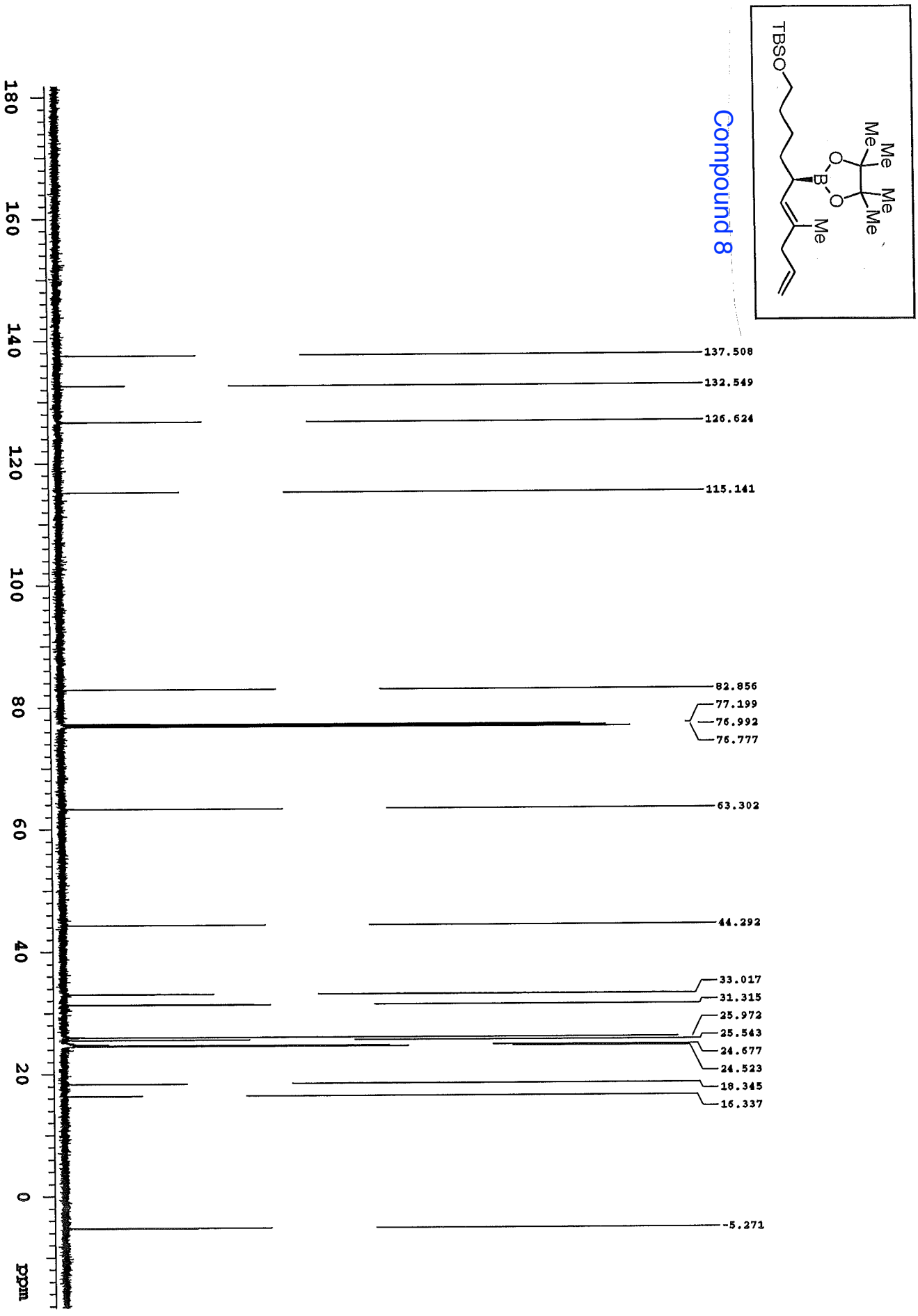
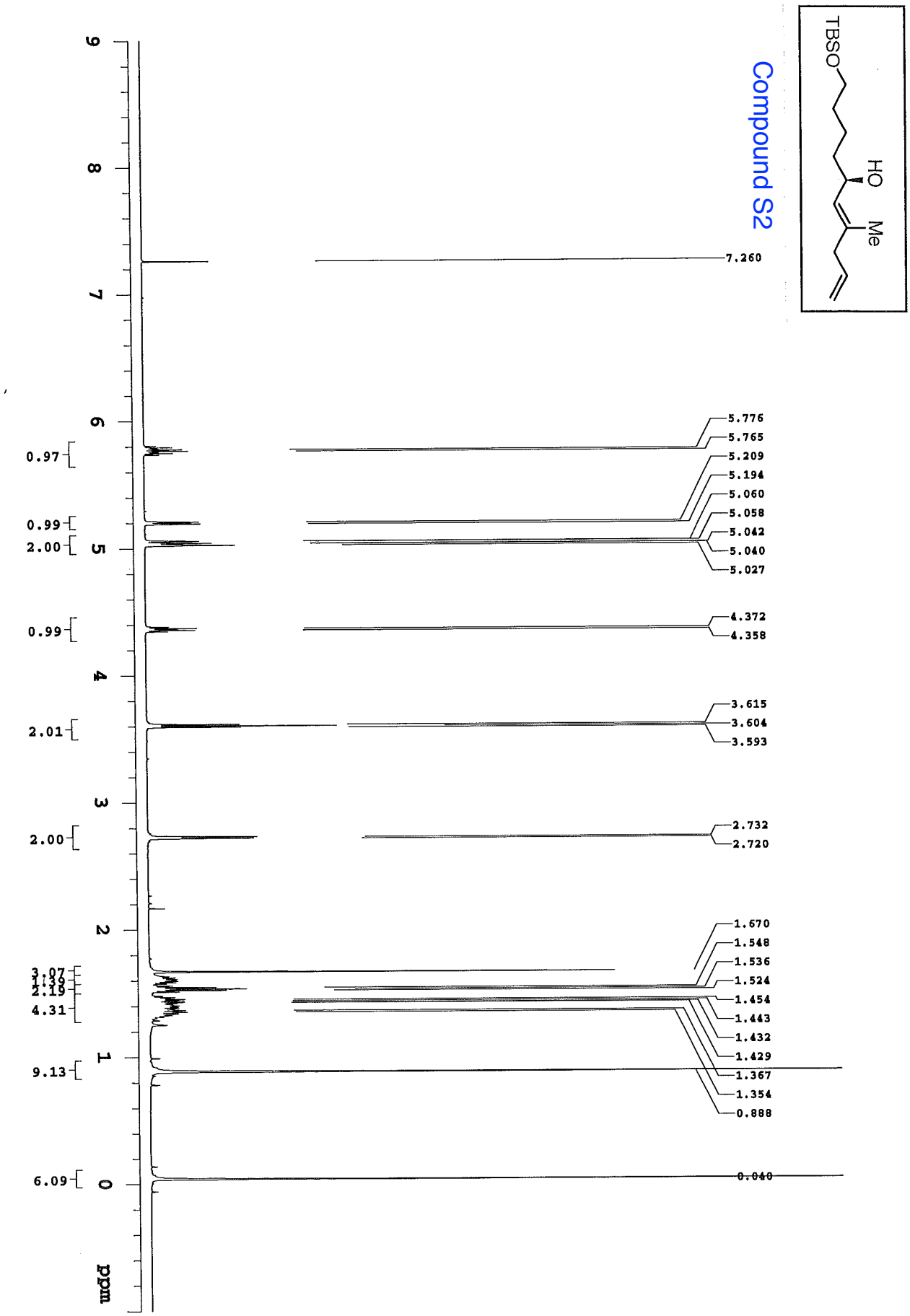
160
140
120
100
80
60
40
20
0
ppm


Compound 8
TBSO
Me
Me
Me
Me
Me
B
O
O
7.2
5.779
5.763
5.751
5.734
5.085
5.071
5.069
5.021
5.018
4.992
4.990
4.973
4.971
4.957
4.954
3.589
3.578
3.568
2.709
2.699
1.961
1.945
1.580
1.578
1.565
1.533
1.526
1.521
1.513
1.509
1.503
1.498
1.492
1.487
1.481
1.477
1.379
1.376
1.372
1.363
1.354
1.348
1.340
1.265
1.254
1.239
1.231
1.218
1.210
0.881
0.037
0.032
0.86
2.78
2.13
1.99
0.98
3.00
3.18
2.36
0.95
12.05
9.35
5.82
9
8
7
6
5
4
3
2
1
0
ppm


Compound 8
TBSO
Me
Me
Me
Me
Me
137.508
132.549
126.624
115.141
82.856
77.199
76.992
76.777
63.302
44.292
33.017
31.315
25.972
25.543
24.677
24.523
18.345
16.337
-5.271
180
160
140
120
100
80
60
40
20
0
ppm


Compound S2
TBSO
HO
Me
7.260
5.776
5.765
5.209
5.194
5.060
5.058
5.042
5.040
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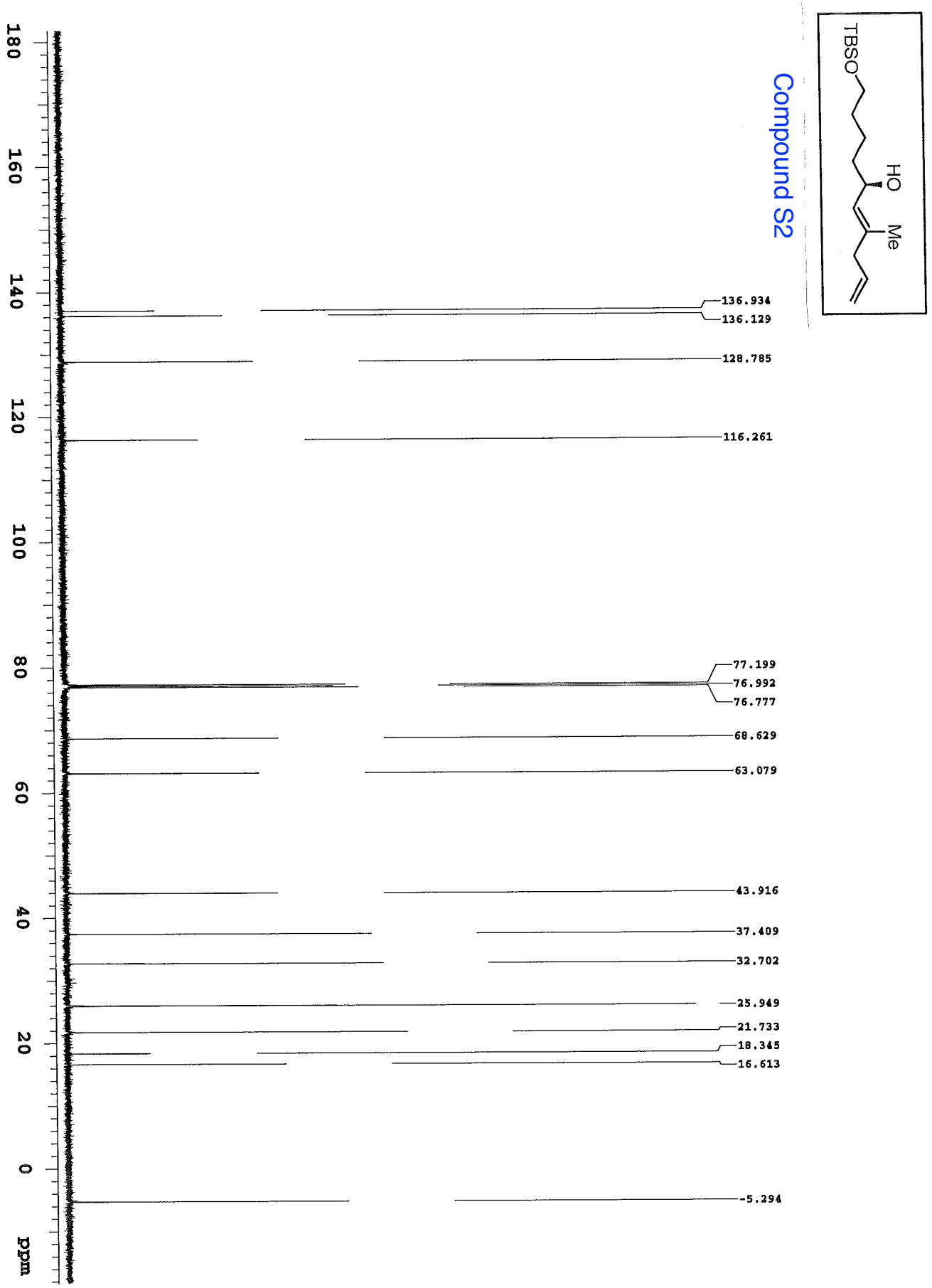
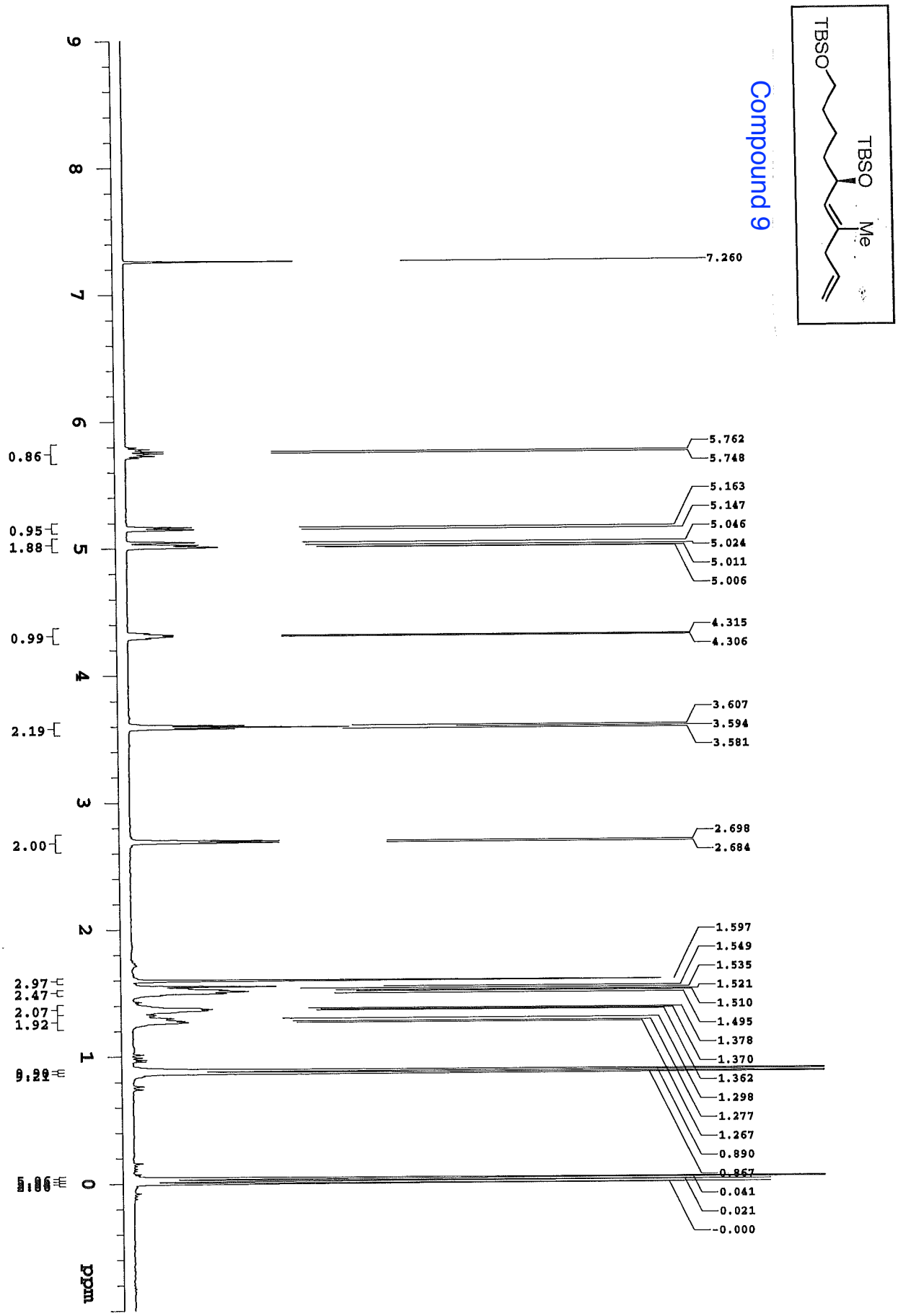
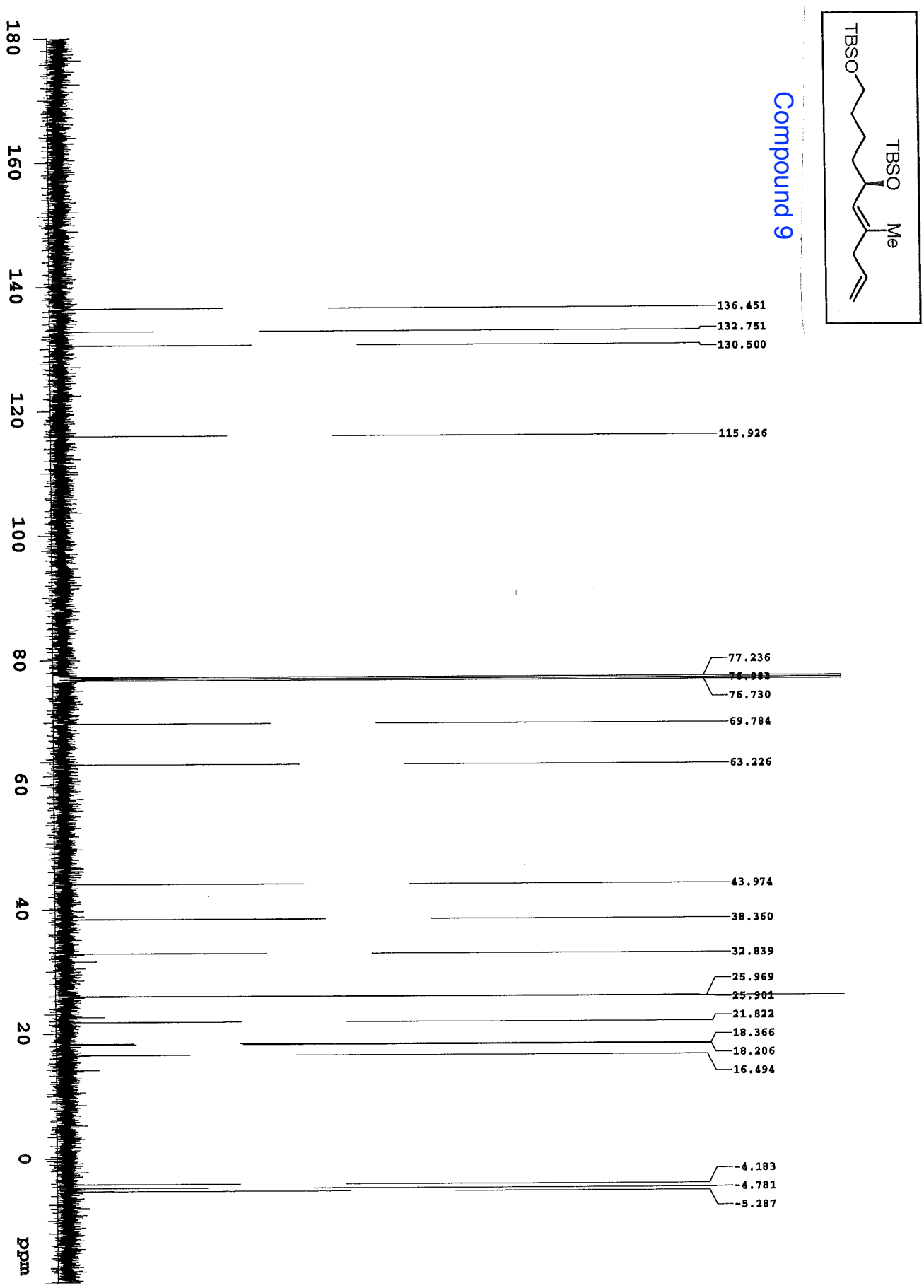
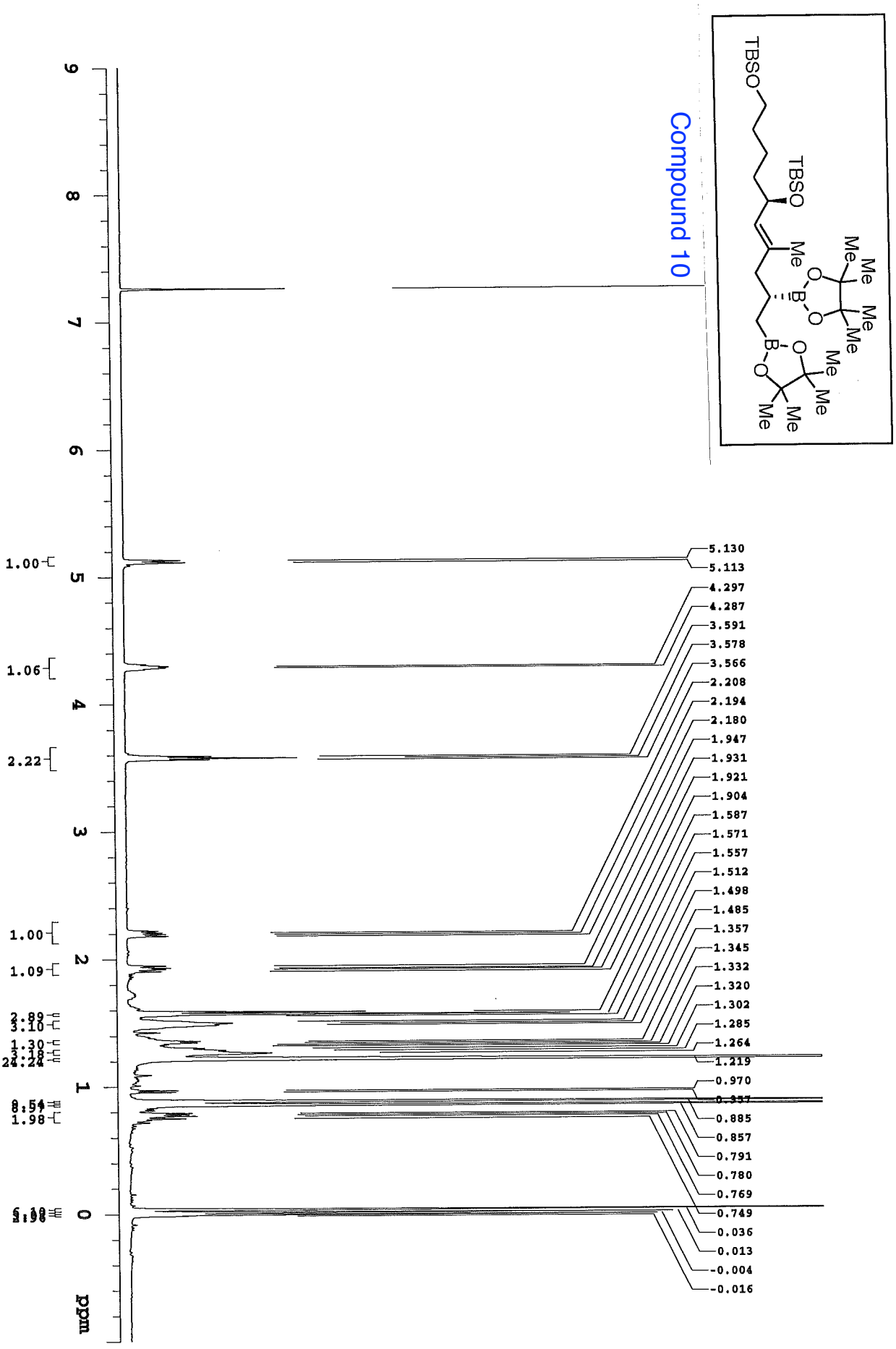
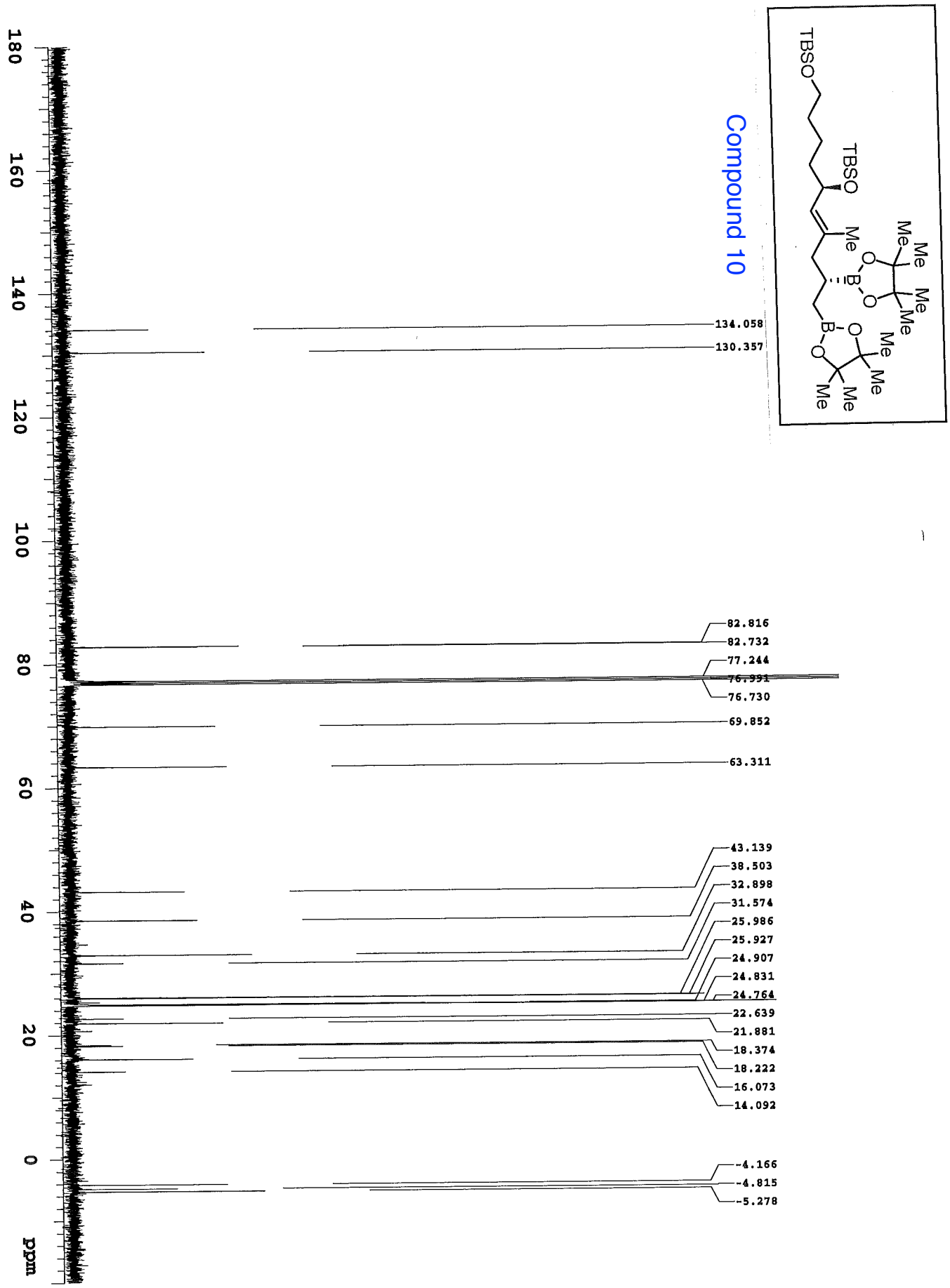
4.372
4.358
3.615
3.604
3.593
2.732
2.720
1.670
1.548
1.536
1.524
1.454
1.443
1.432
1.429
1.367
1.354
0.888
0.040
0.97
0.99
2.00
0.99
2.01
2.00
3.07
1.39
2.19
4.31
9.13
6.09
ppm

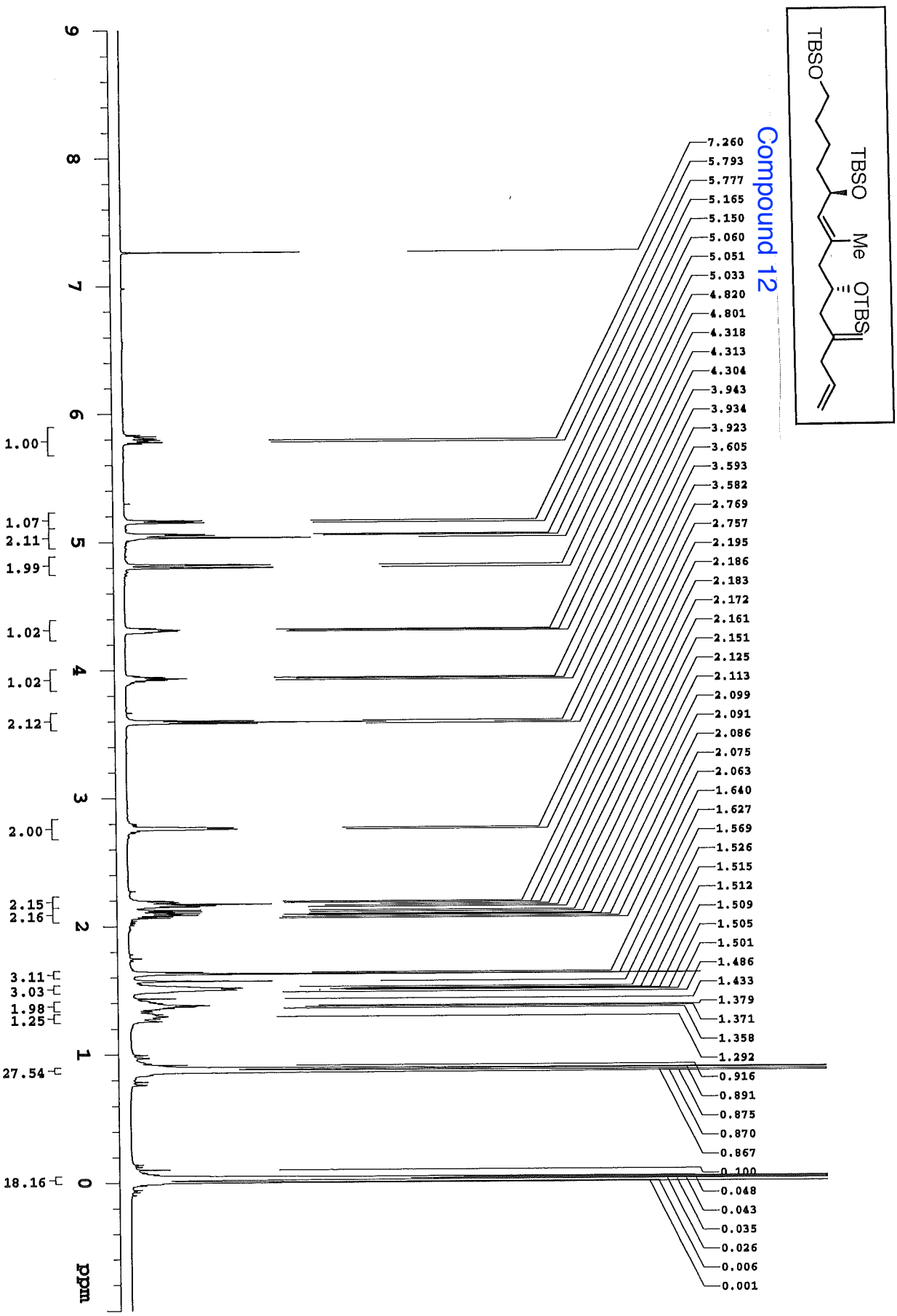

Compound S2
TBSO
HO
Me
180
160
140
120
100
80
60
40
20
0
ppm
136.934
136.129
128.785
116.261
77.199
76.992
76.777
68.629
63.079
43.916
37.409
32.702
25.949
21.733
18.345
16.613
-5.294

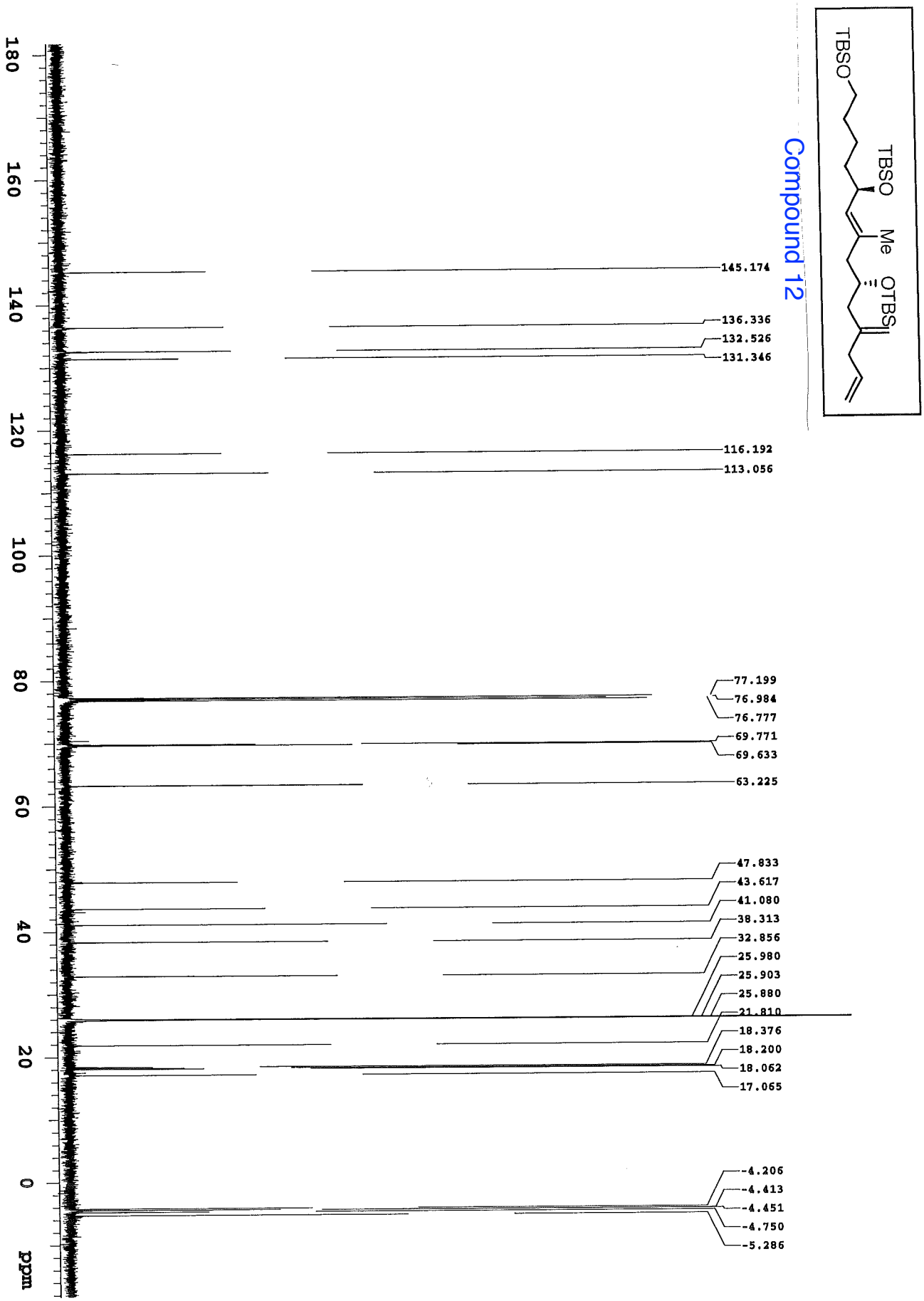

Compound 9
TBSO
TBSO
Me
7.260
5.762
5.748
5.163
5.147
5.046
5.024
5.011
5.006
4.315
4.306
3.607
3.594
3.581
2.698
2.684
1.597
1.549
1.535
1.521
1.510
1.495
1.378
1.370
1.362
1.298
1.277
1.267
0.890
0.867
0.041
0.021
-0.000
0.86
0.95
1.88
0.99
2.19
2.00
2.97
2.47
2.07
1.92
ppm

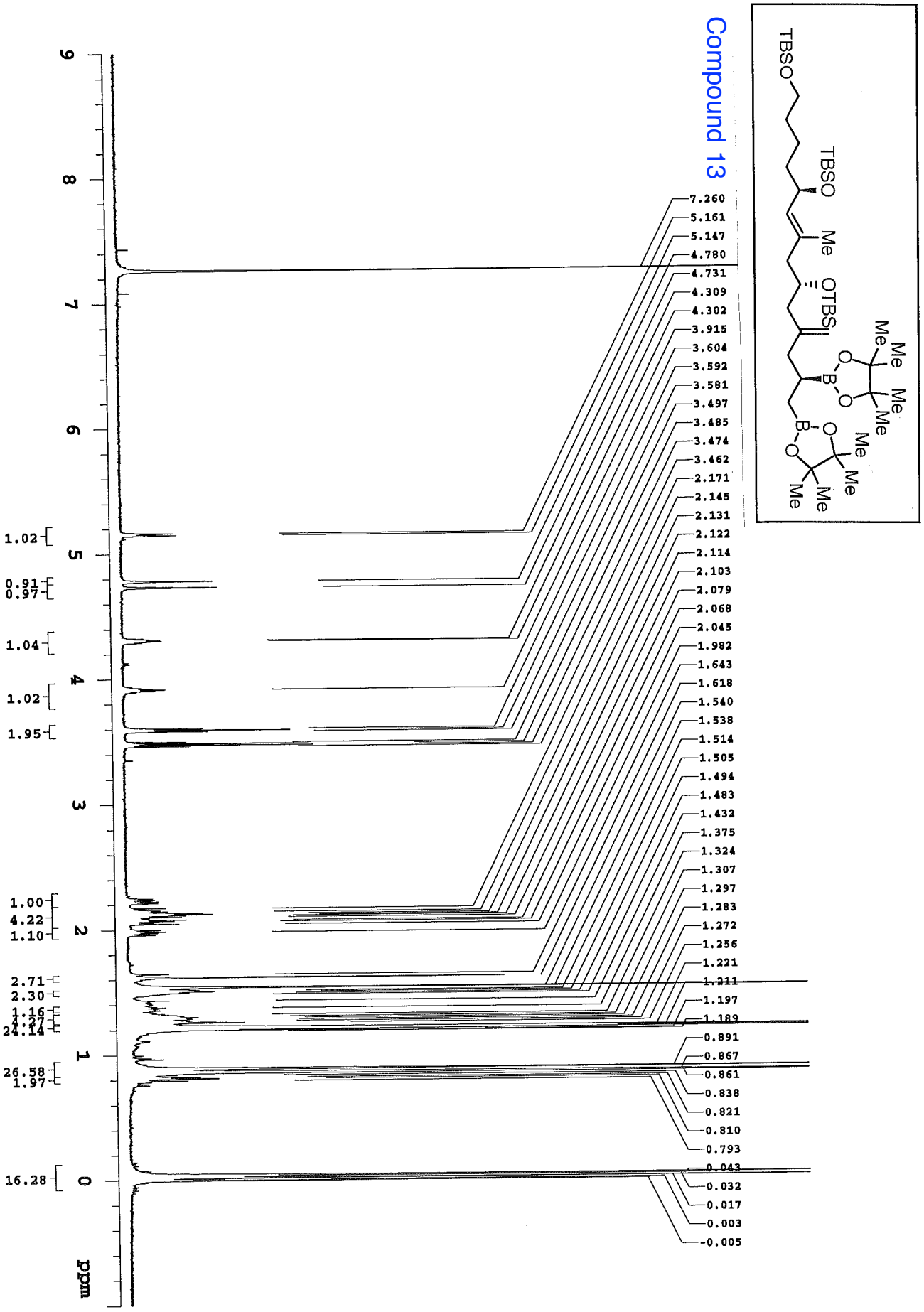

Compound 9
TBSO
TBSO
Me
180
160
140
120
100
80
60
40
20
0
ppm
136.451
132.751
130.500
115.926
77.236
76.983
76.730
69.784
63.226
43.974
38.360
32.839
25.969
25.901
21.822
18.366
18.206
16.494
-4.183
-4.781
-5.287

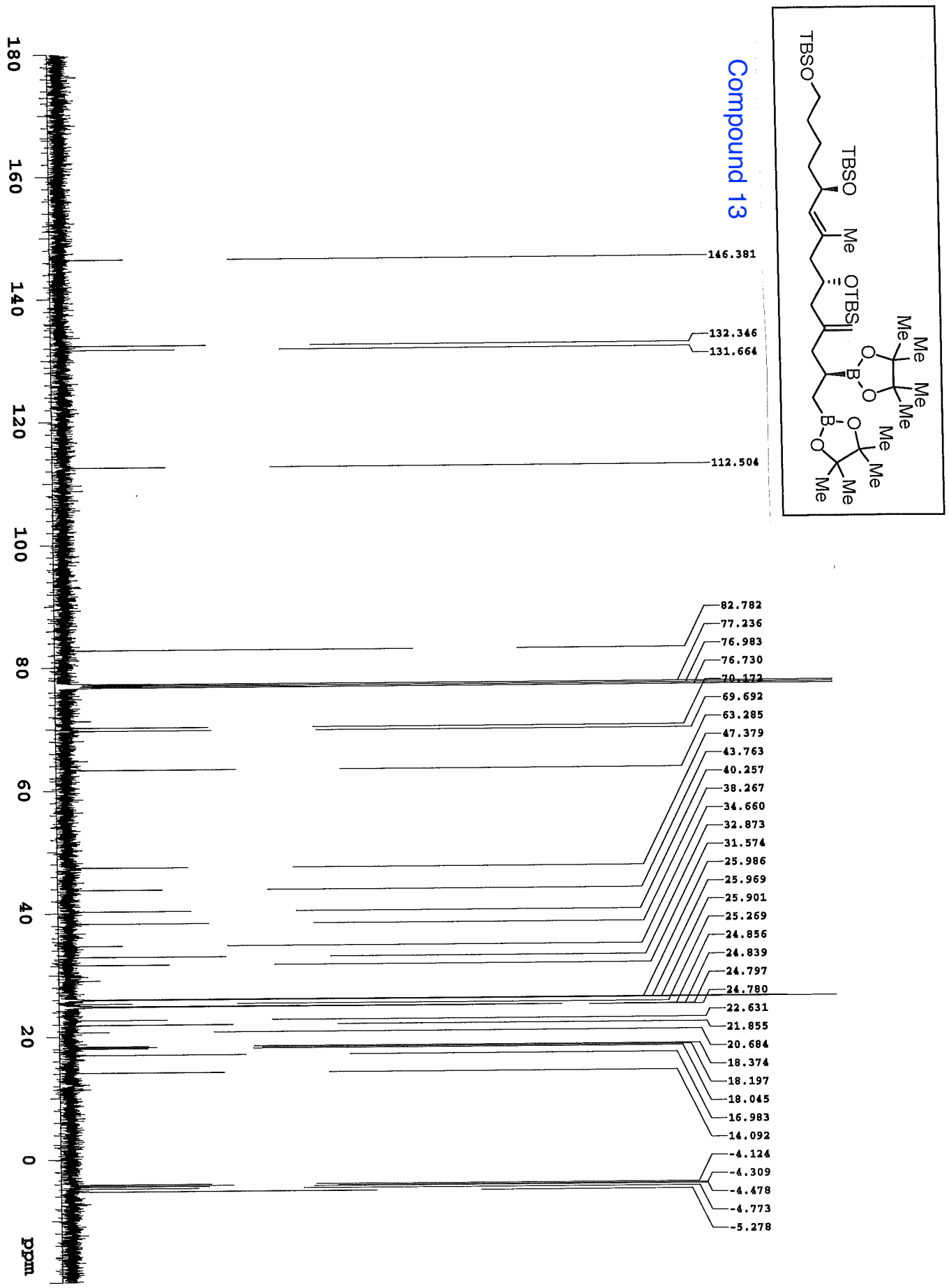

Compound 10
TBSO
TBSO
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me
1.00
1.06
2.22
1.00
1.09
2.89
3.10
1.30
1.98
5.130
5.113
4.297
4.287
3.591
3.578
3.566
2.208
2.194
2.180
1.947
1.931
1.921
1.904
1.587
1.571
1.557
1.512
1.498
1.485
1.357
1.345
1.332
1.320
1.302
1.285
1.264
1.219
0.970
0.885
0.857
0.791
0.780
0.769
0.749
0.036
0.013
-0.004
-0.016
9
8
7
6
5
4
3
2
1
0
ppm

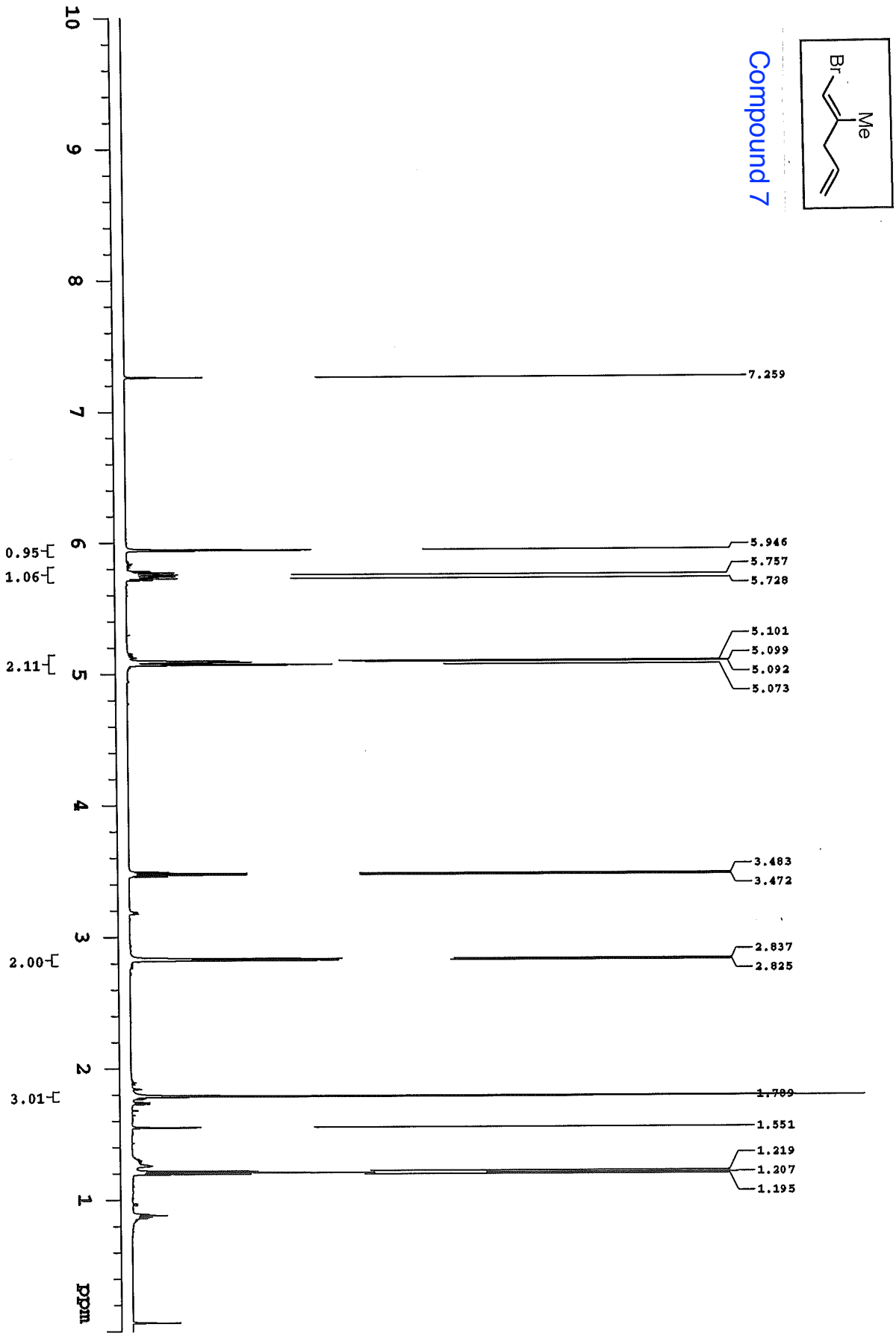

Compound 10
TBSO
TBSO
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me
134.058
130.357
82.816
82.732
77.244
76.991
76.730
69.852
63.311
43.139
38.503
32.898
31.574
25.986
25.927
24.907
24.831
24.764
22.639
21.881
18.374
18.222
16.073
14.092
-4.166
-4.815
-5.278
180
160
140
120
100
80
60
40
20
0
ppm

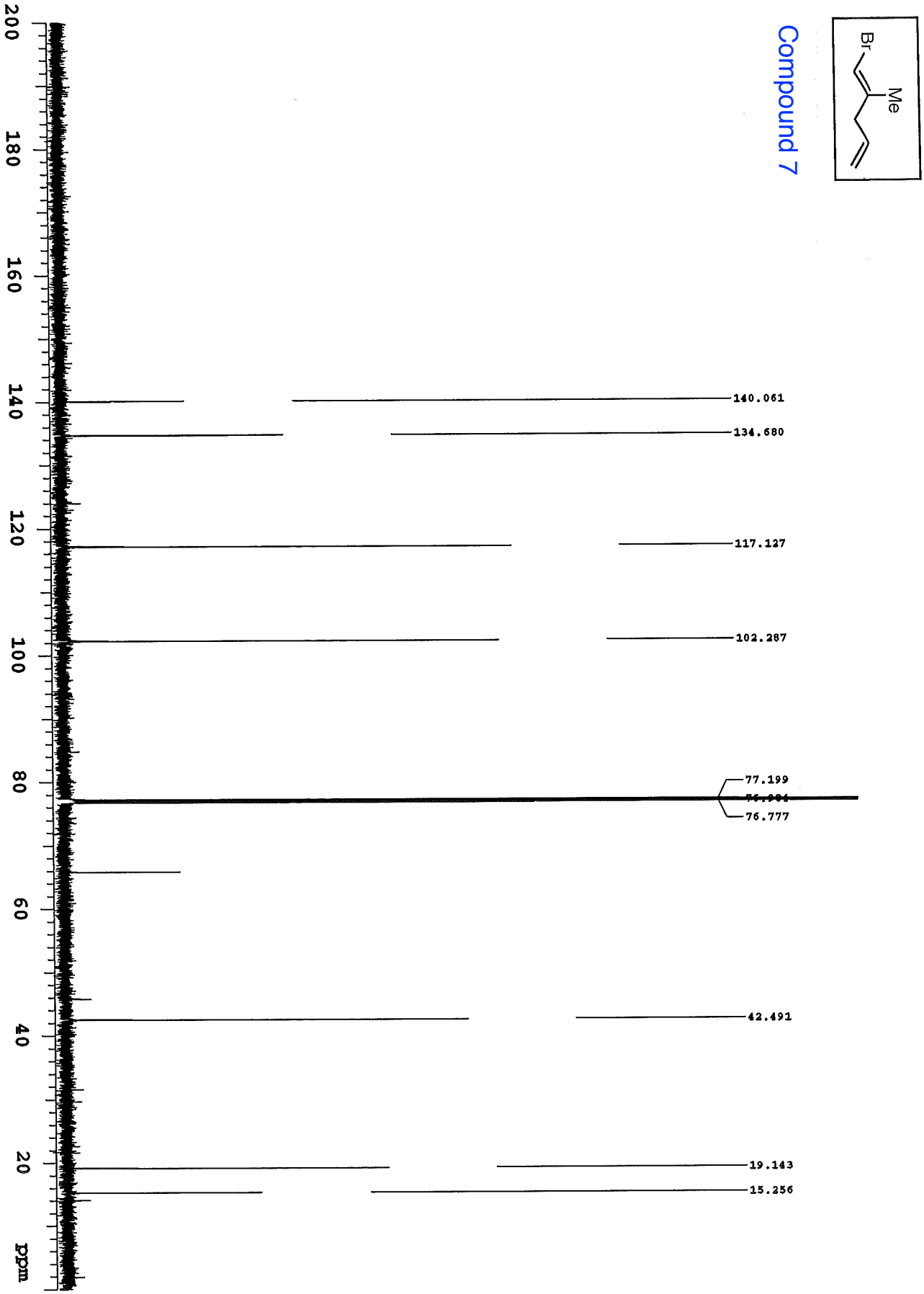

Compound 12
TBSO
TBSO
Me
OTBS
7.260
5.793
5.777
5.165
5.150
5.060
5.051
5.033
4.820
4.801
4.318
4.313
4.304
3.943
3.934
3.923
3.605
3.593
3.582
2.769
2.757
2.195
2.186
2.183
2.172
2.161
2.151
2.125
2.113
2.099
2.091
2.086
2.075
2.063
1.640
1.627
1.569
1.526
1.515
1.512
1.509
1.505
1.501
1.486
1.433
1.379
1.371
1.358
1.292
0.916
0.891
0.875
0.870
0.867
0.100
0.048
0.043
0.035
0.026
0.006
0.001
1.00
1.07
2.11
1.99
1.02
1.02
2.12
2.00
2.15
2.16
3.11
3.03
1.98
1.25
27.54
18.16
9
8
7
6
5
4
3
2
1
0
ppm

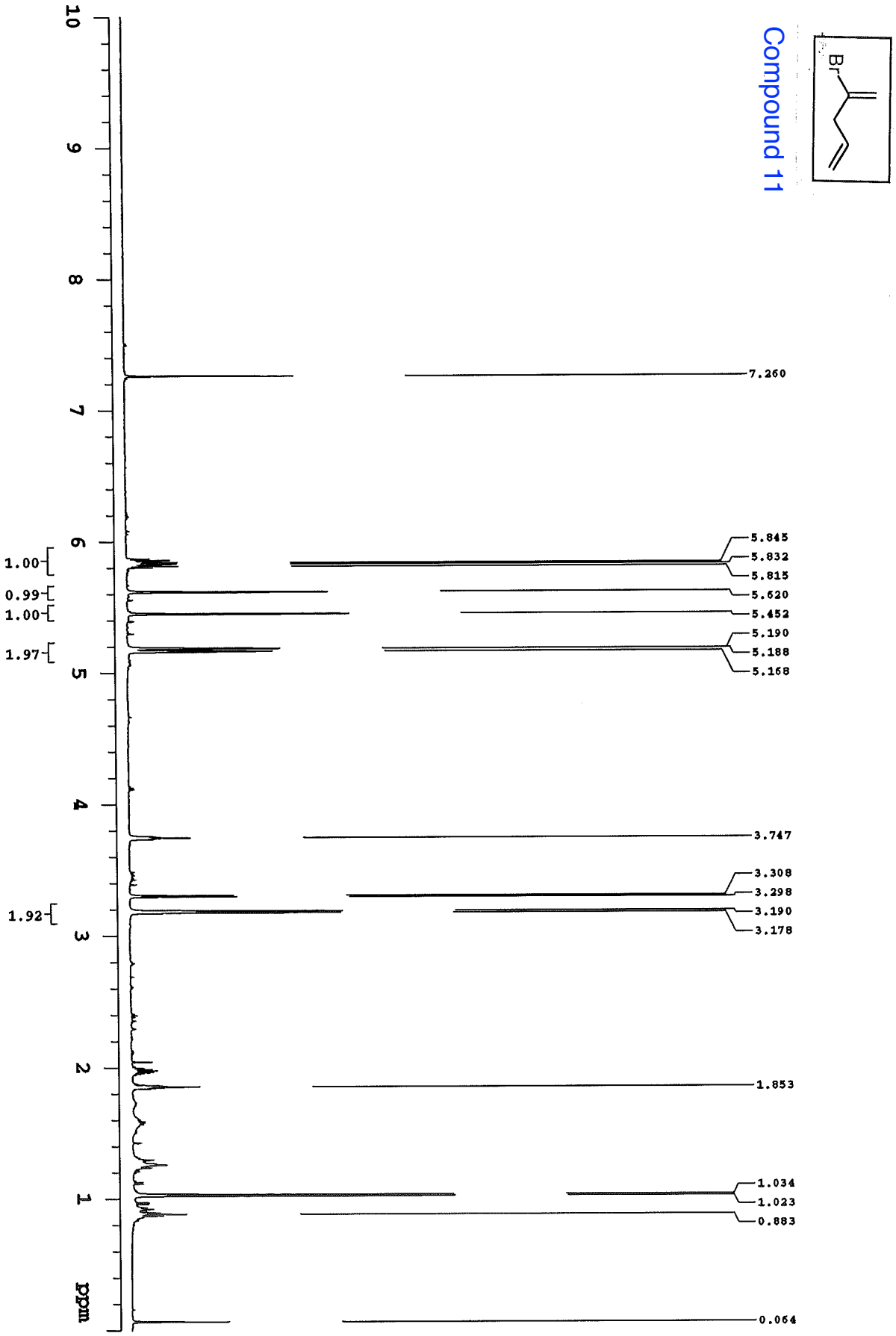

TBSO
TBSO
Me
OTBS
Compound 12
145.174
136.336
132.526
131.346
116.192
113.056
77.199
76.984
76.777
69.771
69.633
63.225
47.833
43.617
41.080
38.313
32.856
25.980
25.903
25.880
21.810
18.376
18.200
18.062
17.065
-4.206
-4.413
-4.451
-4.750
-5.286
180
160
140
120
100
80
60
40
20
0
ppm

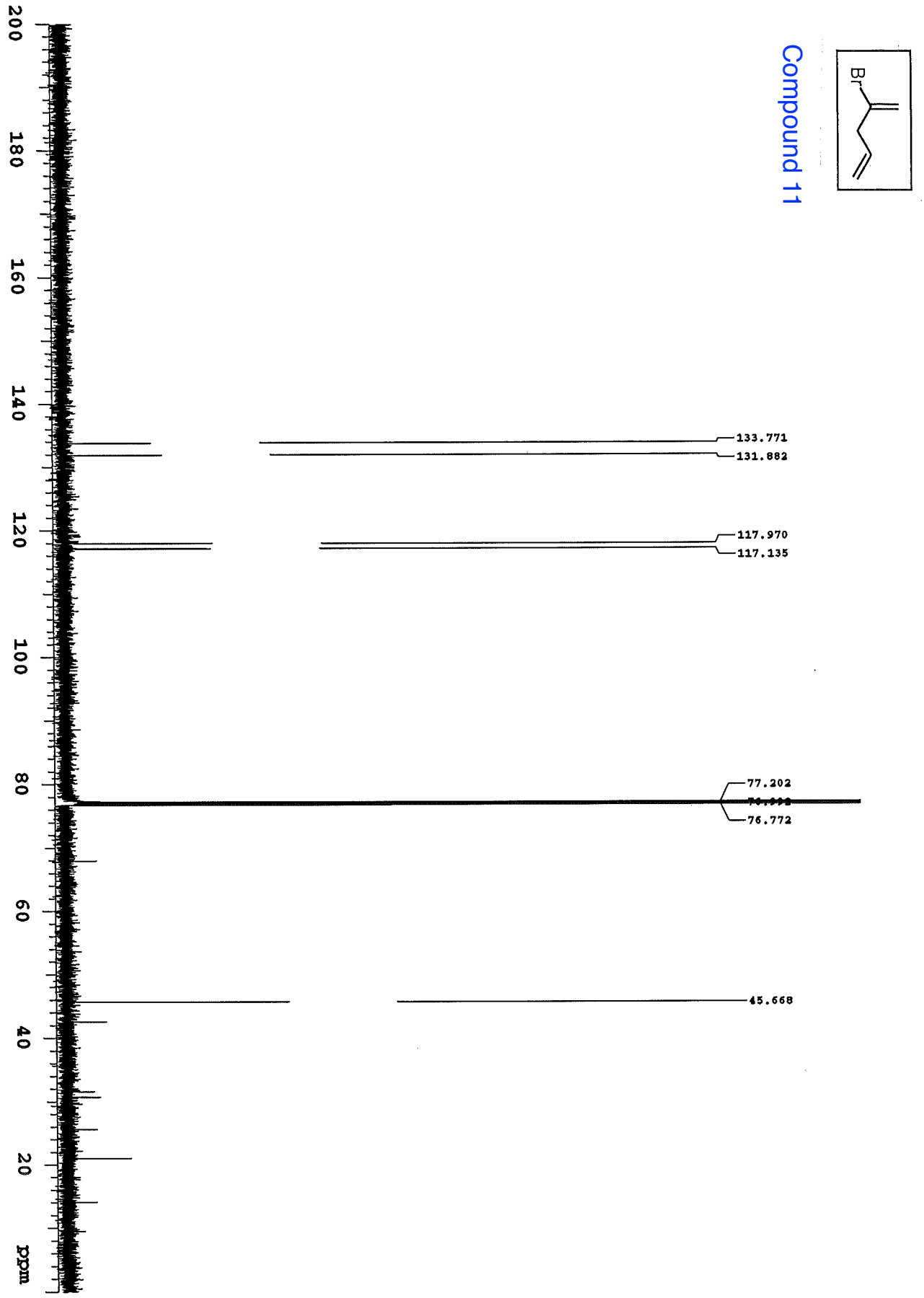

Compound 13
TBSO
TBSO
Me
OTBS
Me
Me
Me
Me
Me
Me
Me
Me
7.260
5.161
5.147
4.780
4.731
4.309
4.302
3.915
3.604
3.592
3.581
3.497
3.485
3.474
3.462
2.171
2.145
2.131
2.122
2.114
2.103
2.079
2.068
2.045
1.982
1.643
1.618
1.540
1.538
1.514
1.505
1.494
1.483
1.432
1.375
1.324
1.307
1.297
1.283
1.272
1.256
1.221
1.211
1.197
1.189
0.891
0.867
0.861
0.838
0.821
0.810
0.793
0.043
0.032
0.017
0.003
-0.005
1.02
0.91
0.97
1.04
1.02
1.95
1.00
4.22
1.10
2.71
2.30
1.16
4.27
24.14
26.58
1.97
16.28
9
8
7
6
5
4
3
2
1
0
ppm

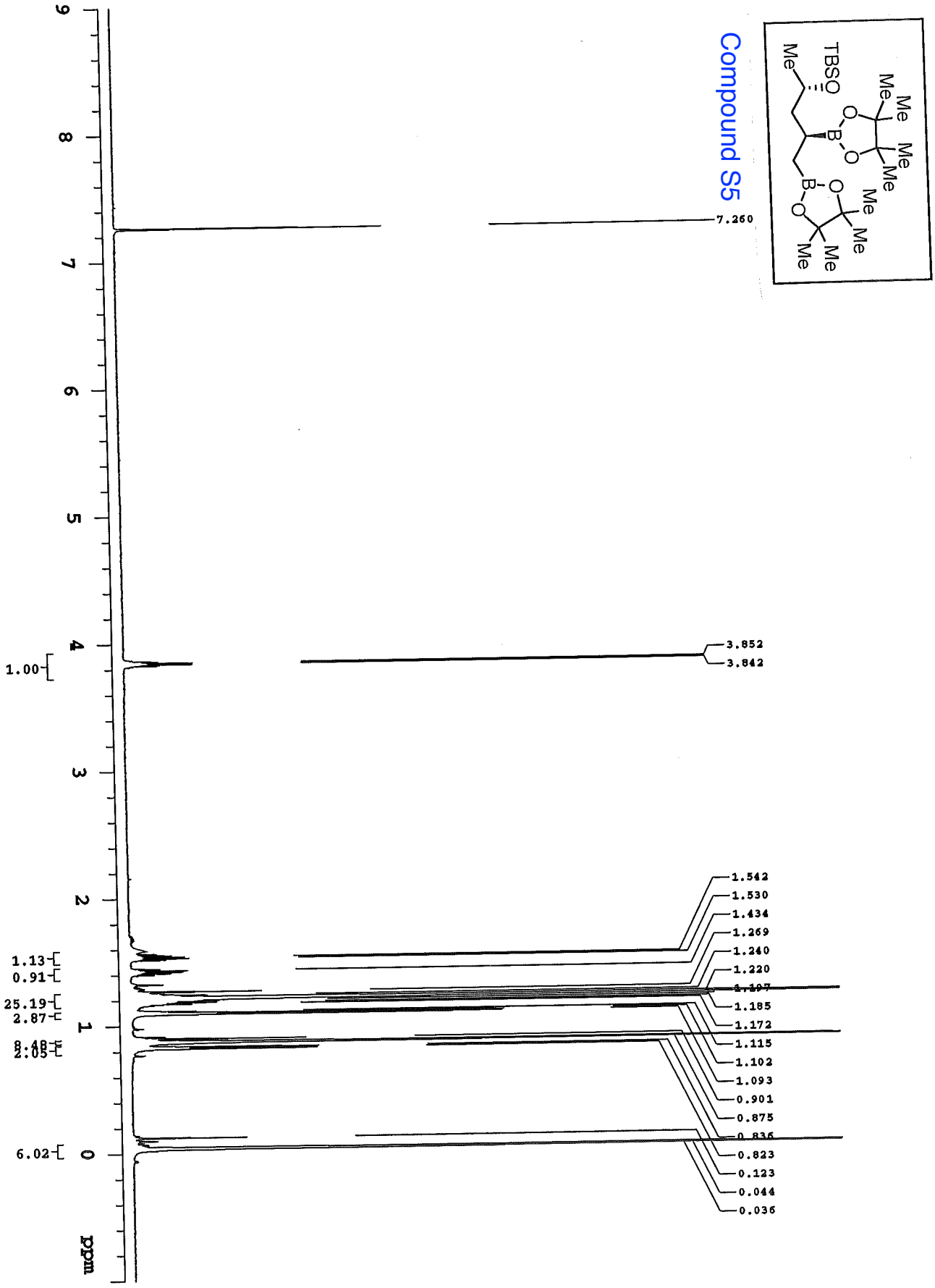

Compound 13
TBSO
TBSO
Me
OTBS
Me
Me
Me
Me
Me
Me
Me
Me
Me
146.381
132.346
131.664
112.504
82.782
77.236
76.983
76.730
70.172
69.692
63.285
47.379
43.763
40.257
38.267
34.660
32.873
31.574
25.986
25.969
25.901
25.269
24.856
24.839
24.797
24.780
22.631
21.855
20.684
18.374
18.197
18.045
16.983
14.092
-4.124
-4.309
-4.478
-4.773
-5.278
180
160
140
120
100
80
60
40
20
0
ppm

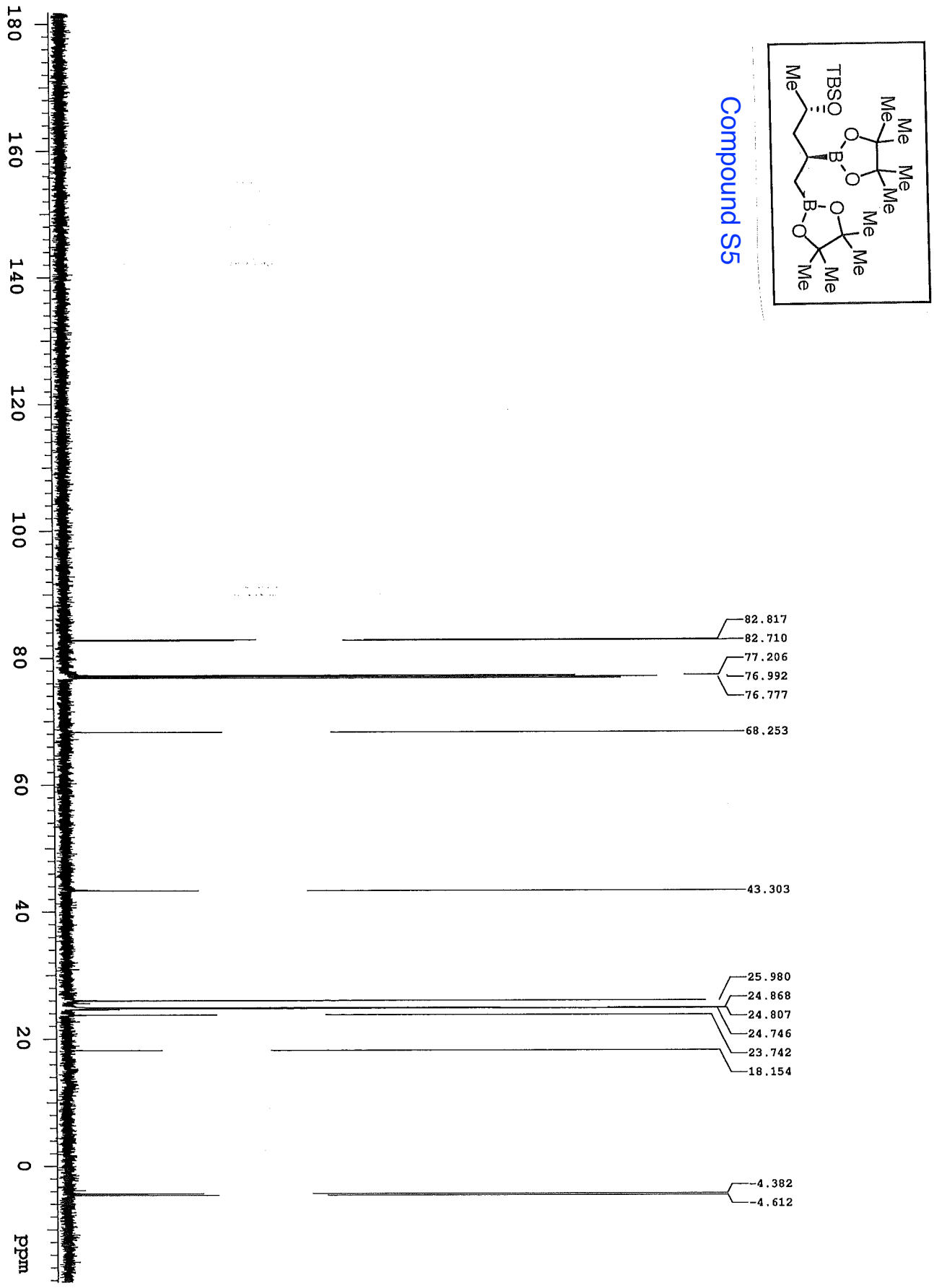

Compound 7
Br
Me
7.259
5.946
5.757
5.728
5.101
5.099
5.092
5.073
3.483
3.472
2.837
2.825
1.709
1.551
1.219
1.207
1.195
0.95
1.06
2.11
2.00
3.01
ppm

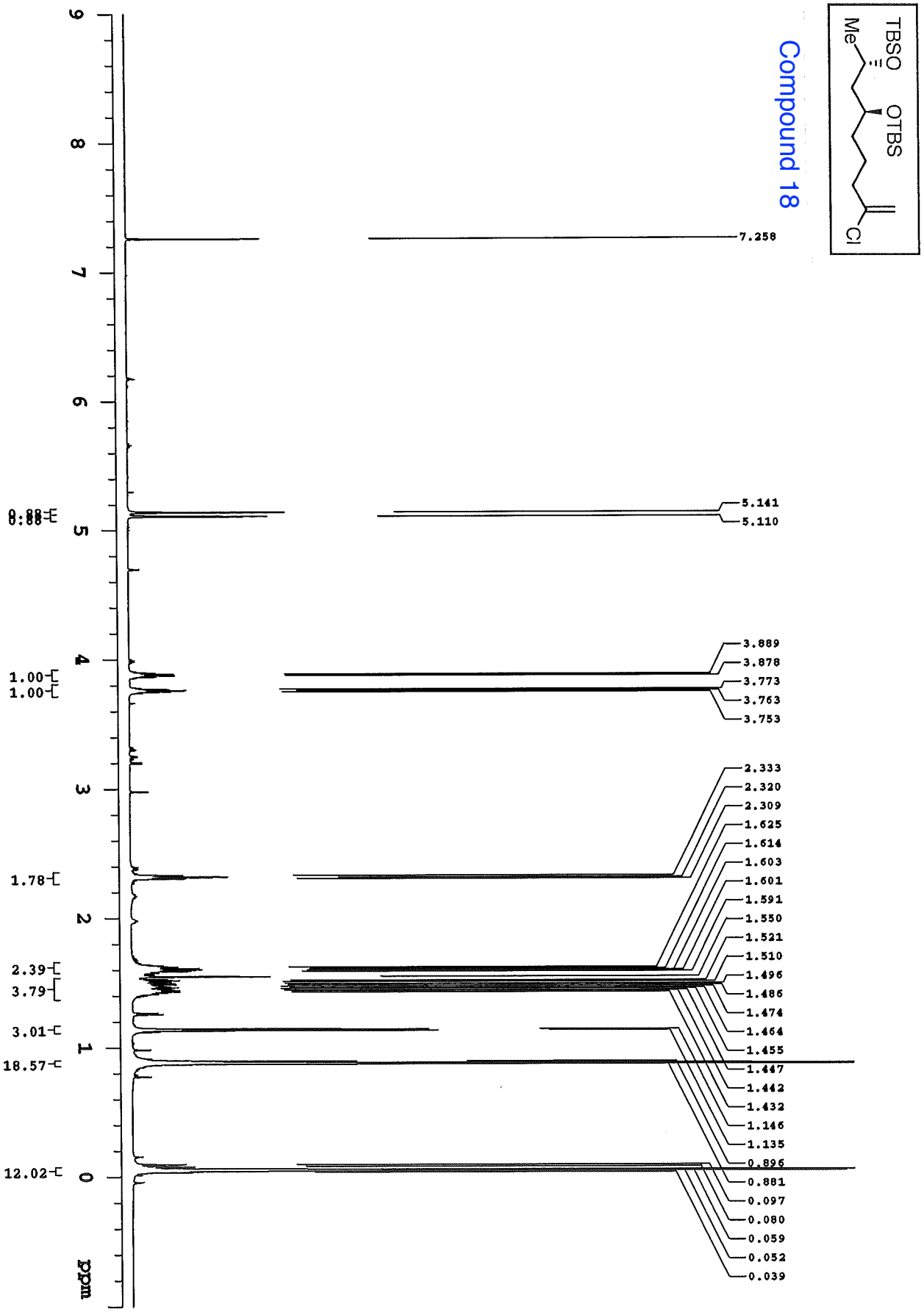

Compound 7
Br
Me
200
180
160
140
120
100
80
60
40
20
ppm
140.061
134.680
117.127
102.287
77.199
76.984
76.777
42.491
19.143
15.256

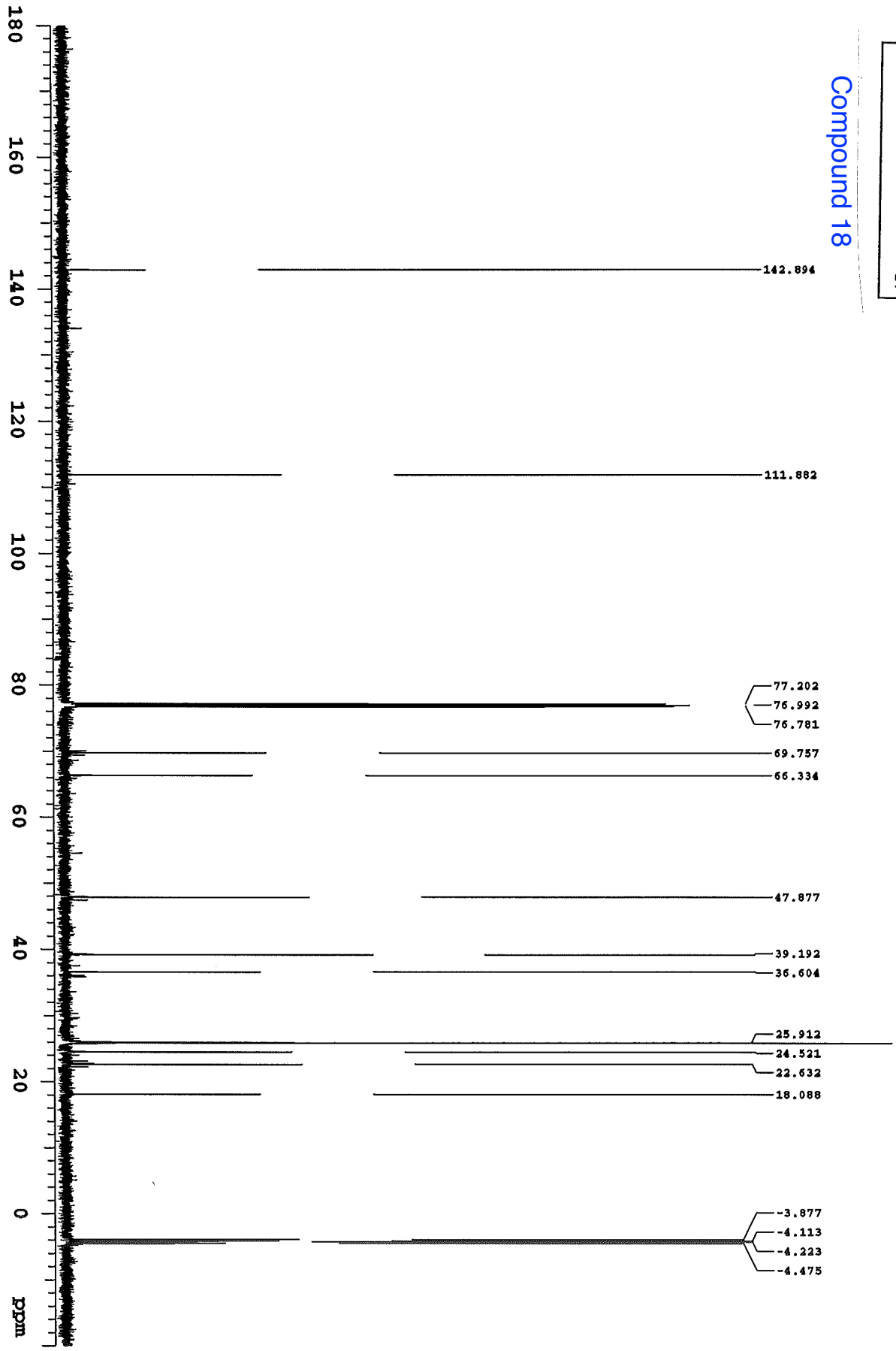

Compound 11
Br
7.260
5.845
5.832
5.815
5.620
5.452
5.190
5.188
5.168
3.747
3.308
3.298
3.190
3.178
1.853
1.034
1.023
0.883
0.064
1.00
0.99
1.00
1.97
1.92
10
9
8
7
6
5
4
3
2
1
ppm

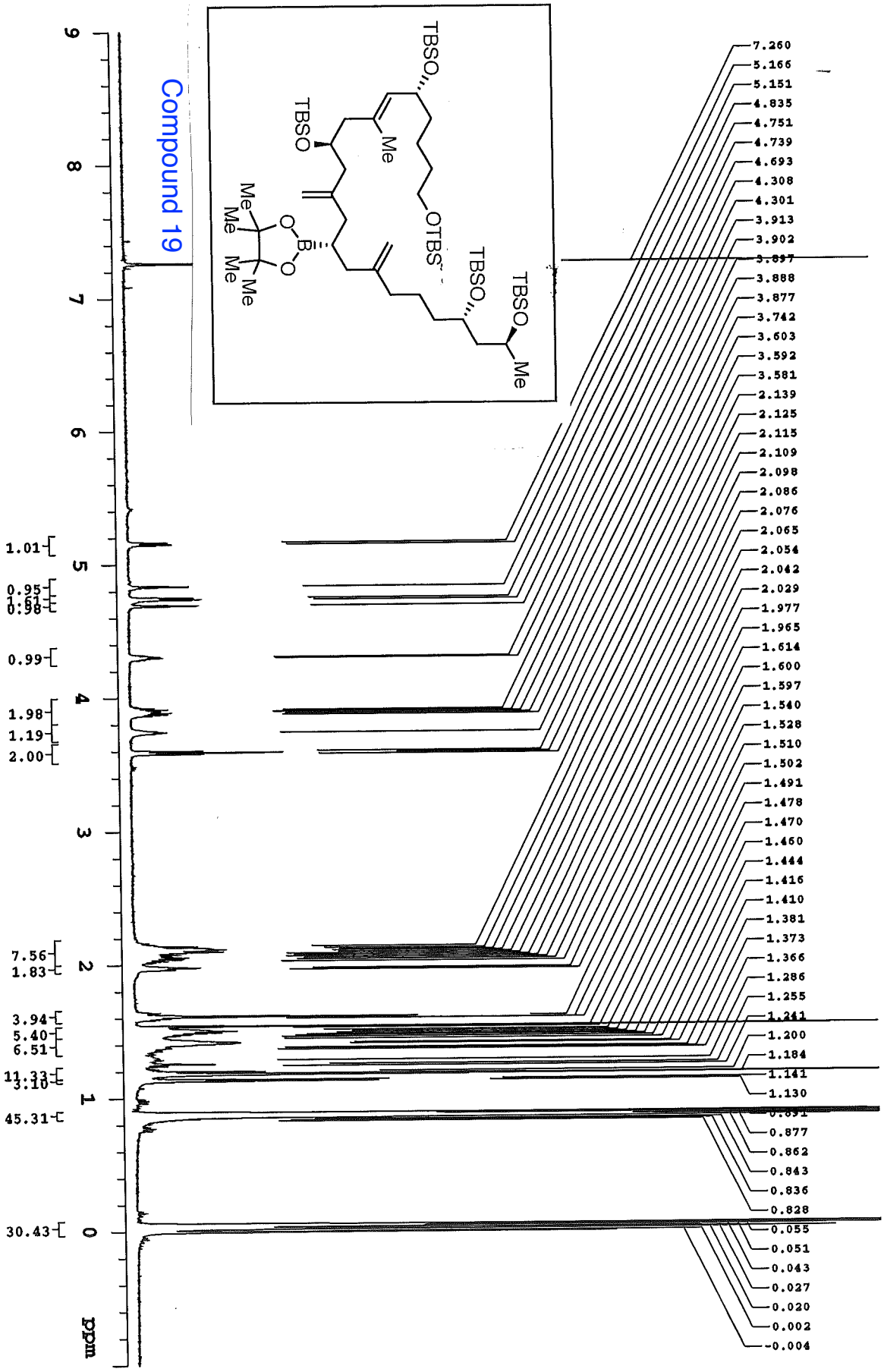

Compound 11
Br
200
180
160
140
120
100
80
60
40
20
ppm
133.771
131.882
117.970
117.135
77.202
76.772
45.668

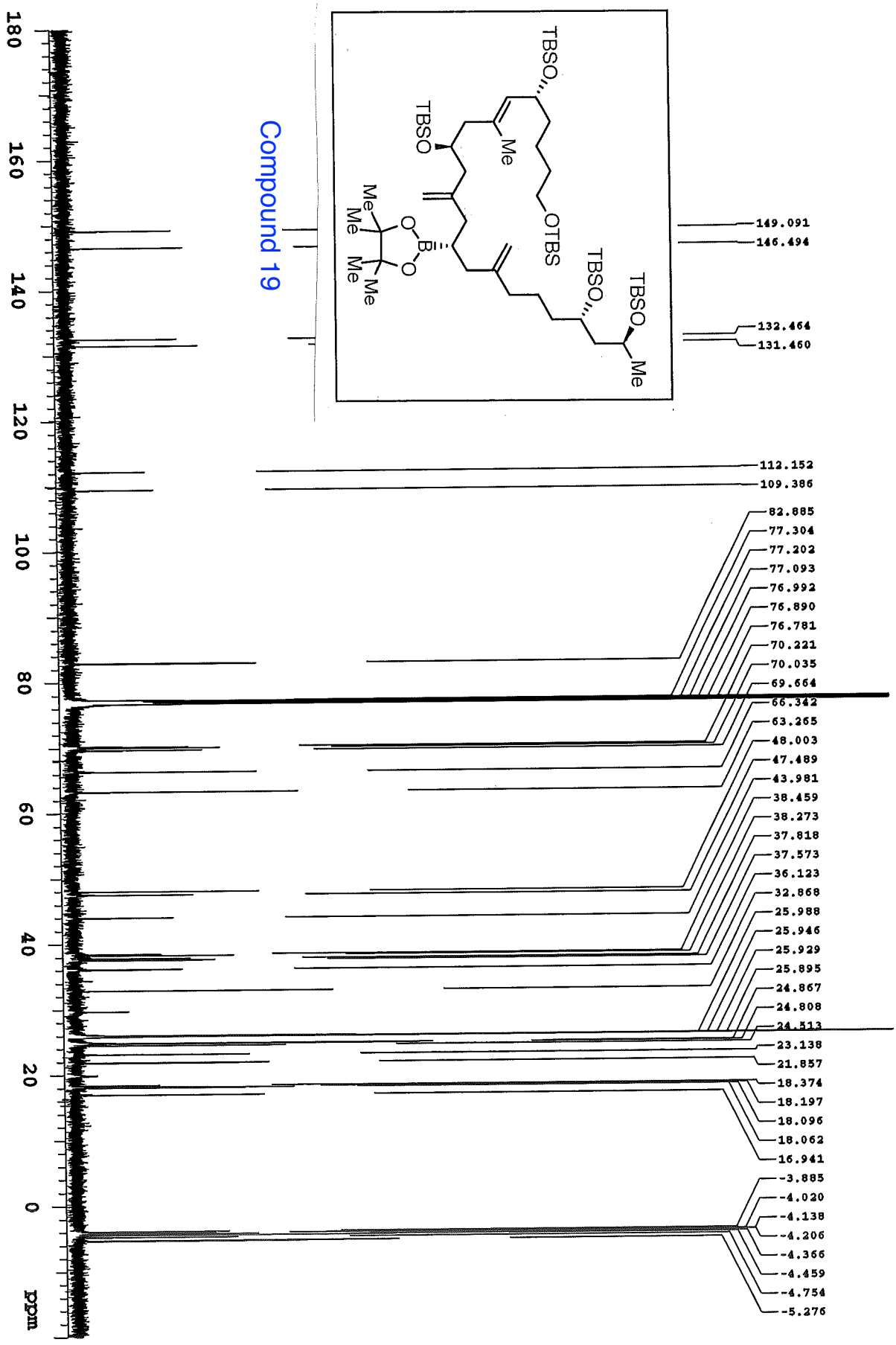

Compound S5
TBSO
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me
7.260
3.852
3.842
1.542
1.530
1.434
1.269
1.240
1.220
1.197
1.185
1.172
1.115
1.102
1.093
0.901
0.875
0.836
0.823
0.123
0.044
0.036
1.00
1.13
0.91
25.19
2.87
8.48
2.05
6.02
ppm

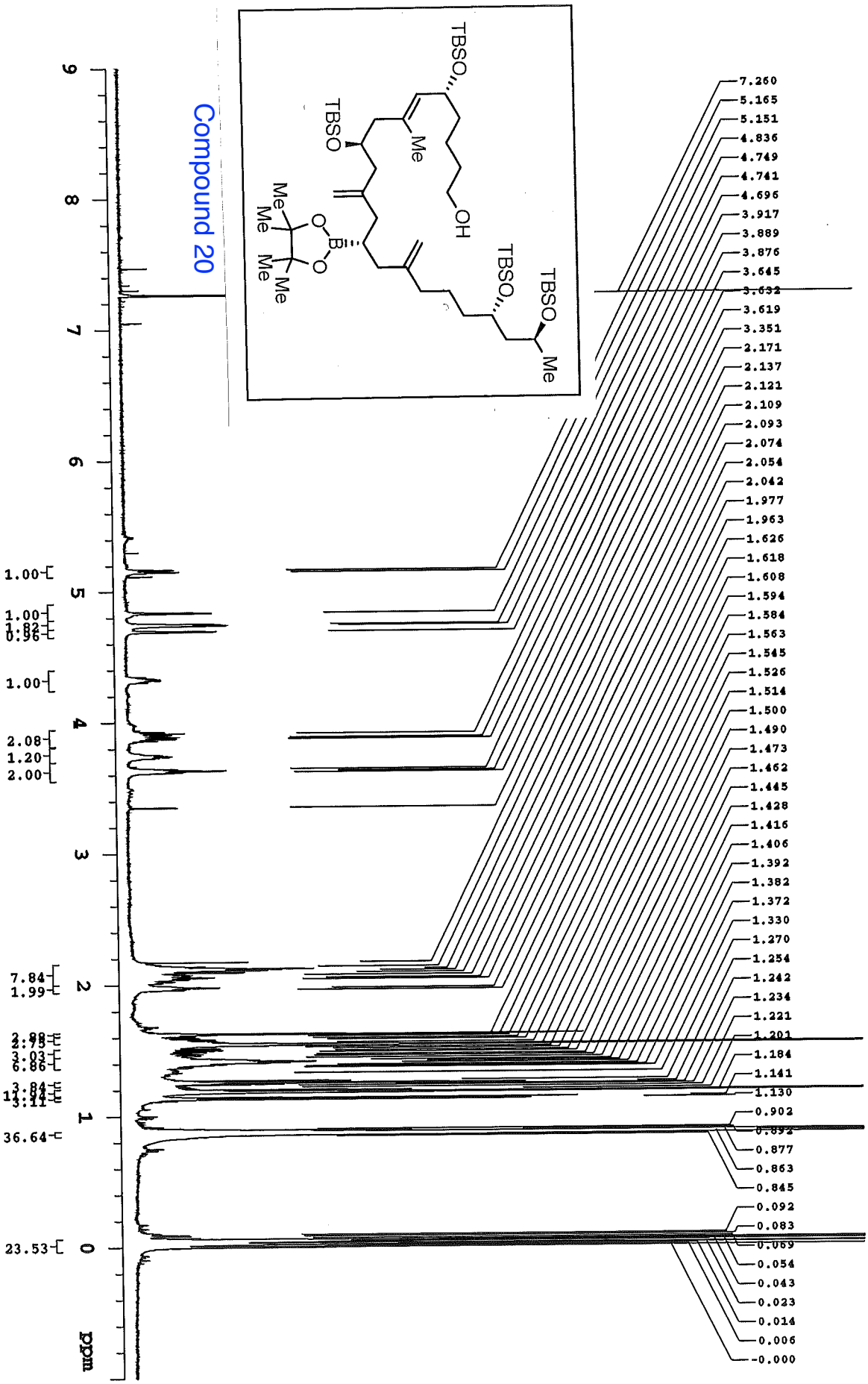

Compound S5
TBSO
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me
82.817
82.710
77.206
76.992
76.777
68.253
43.303
25.980
24.868
24.807
24.746
23.742
18.154
-4.382
-4.612
180
160
140
120
100
80
60
40
20
0
ppm

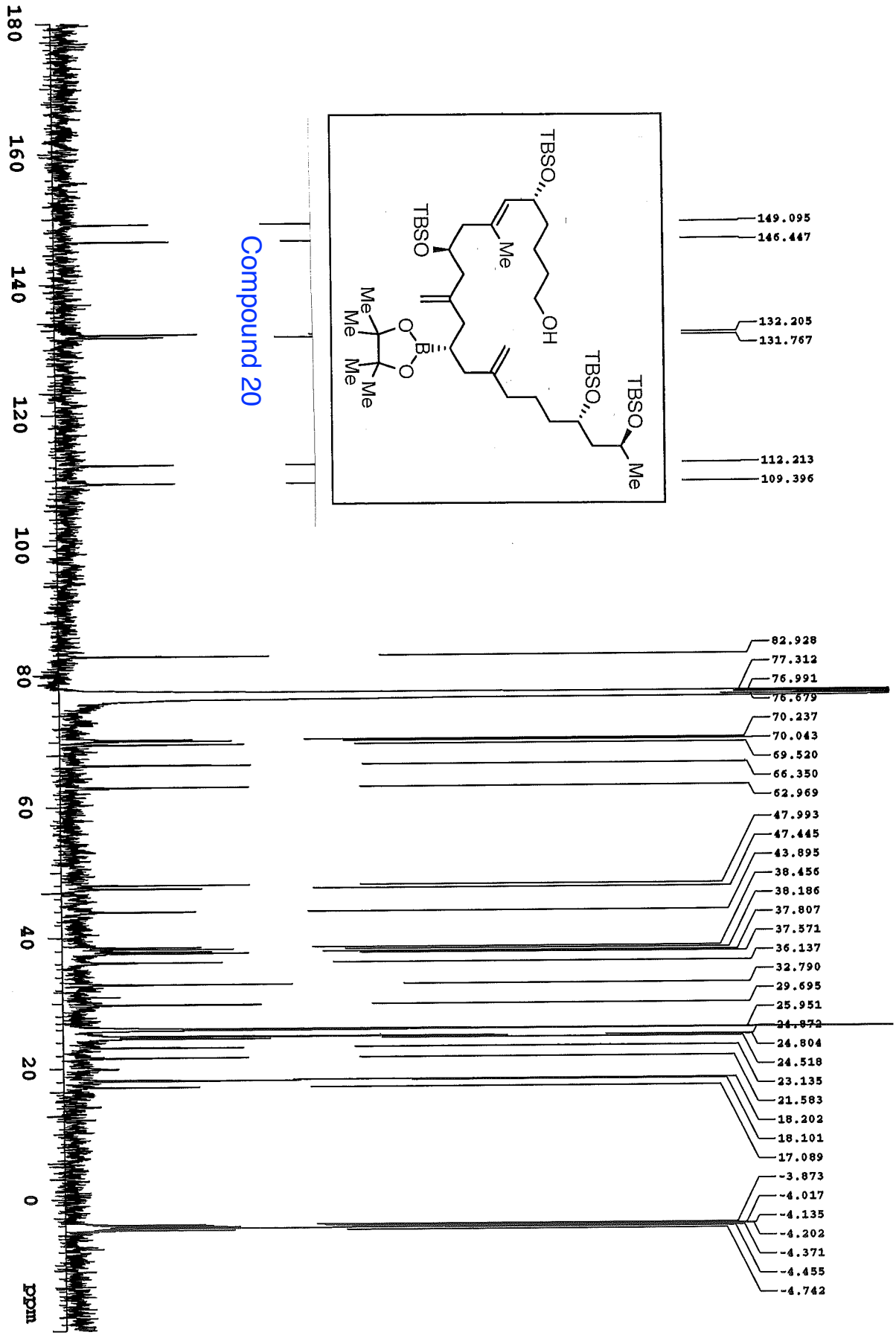

Compound 18
TBSO
OTBS
Me
Cl
7.258
5.141
5.110
3.889
3.878
3.773
3.763
3.753
2.333
2.320
2.309
1.625
1.614
1.603
1.601
1.591
1.550
1.521
1.510
1.496
1.486
1.474
1.464
1.455
1.447
1.442
1.432
1.146
1.135
0.896
0.881
0.097
0.080
0.059
0.052
0.039
1.00
1.00
1.78
2.39
3.79
3.01
18.57
12.02
ppm

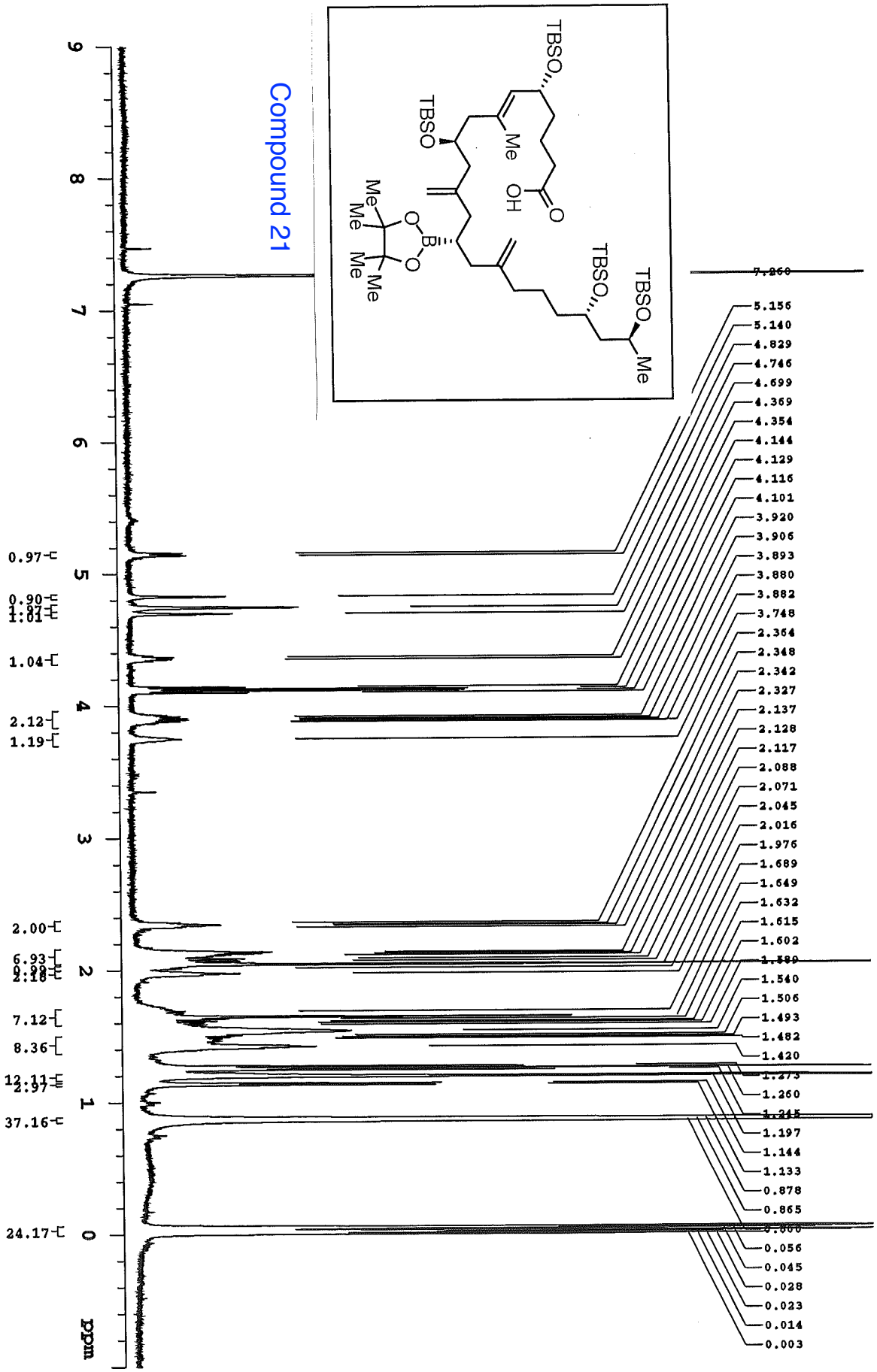

TBSO
OTBS
Me
Cl
Compound 18
142.894
111.882
77.202
76.992
76.781
69.757
66.334
47.877
39.192
36.604
25.912
24.521
22.632
18.088
-3.877
-4.113
-4.223
-4.475
180
160
140
120
100
80
60
40
20
0
ppm

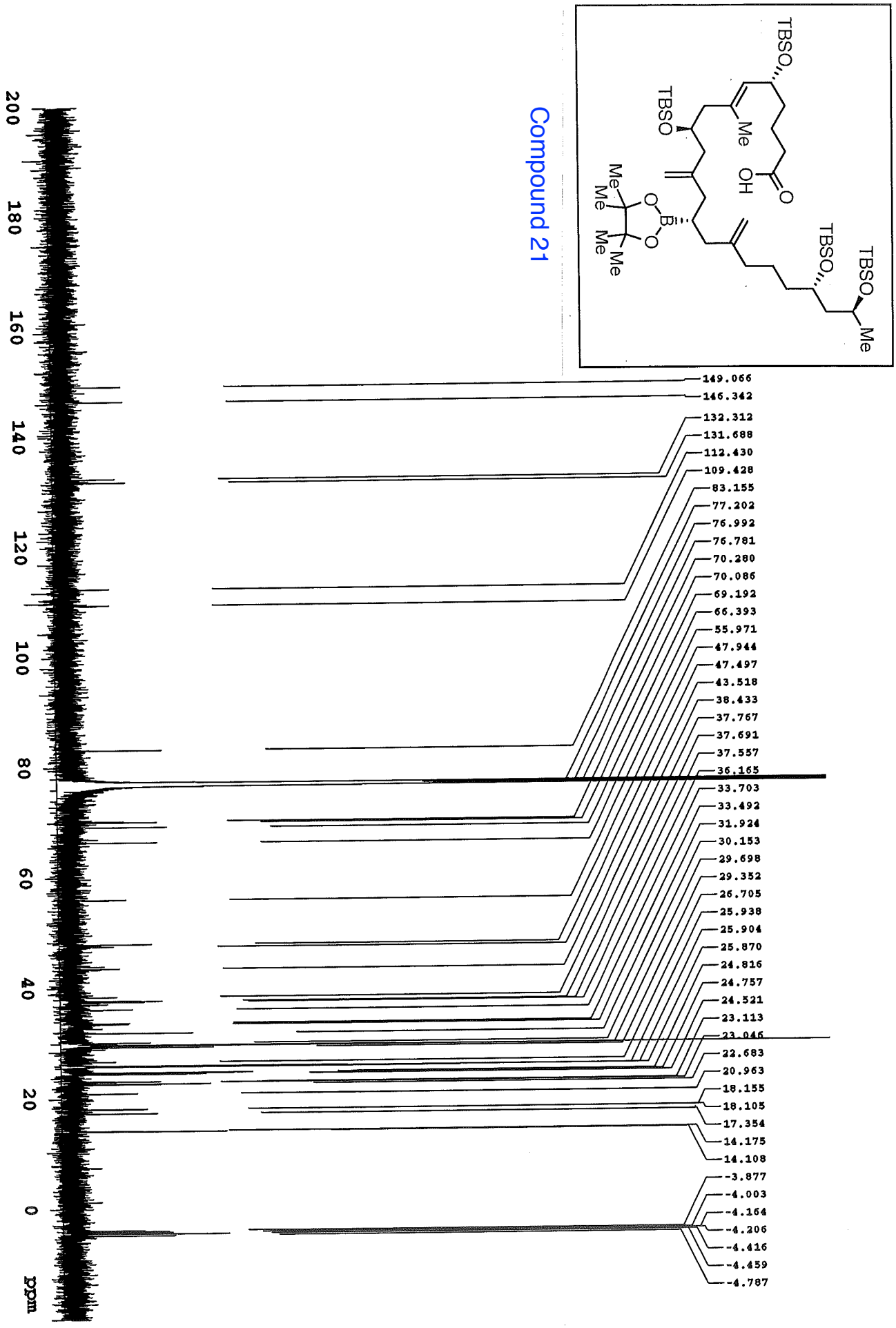

Compound 19
TBSO
TBSO
Me
OTBS
TBSO
TBSO
Me
Me
Me
Me
Me
O
O
B
7.260
5.166
5.151
4.835
4.751
4.739
4.693
4.308
4.301
3.913
3.902
3.897
3.888
3.877
3.742
3.603
3.592
3.581
2.139
2.125
2.115
2.109
2.098
2.086
2.076
2.065
2.054
2.042
2.029
1.977
1.965
1.614
1.600
1.597
1.540
1.528
1.510
1.502
1.491
1.478
1.470
1.460
1.444
1.416
1.410
1.381
1.373
1.366
1.286
1.255
1.241
1.200
1.184
1.141
1.130
0.877
0.862
0.843
0.836
0.828
0.055
0.051
0.043
0.027
0.020
0.002
-0.004
1.01
0.95
1.61
0.98
0.99
1.98
1.19
2.00
7.56
1.83
3.94
5.40
6.51
11.33
3.10
45.31
30.43
9
8
7
6
5
4
3
2
1
0
ppm

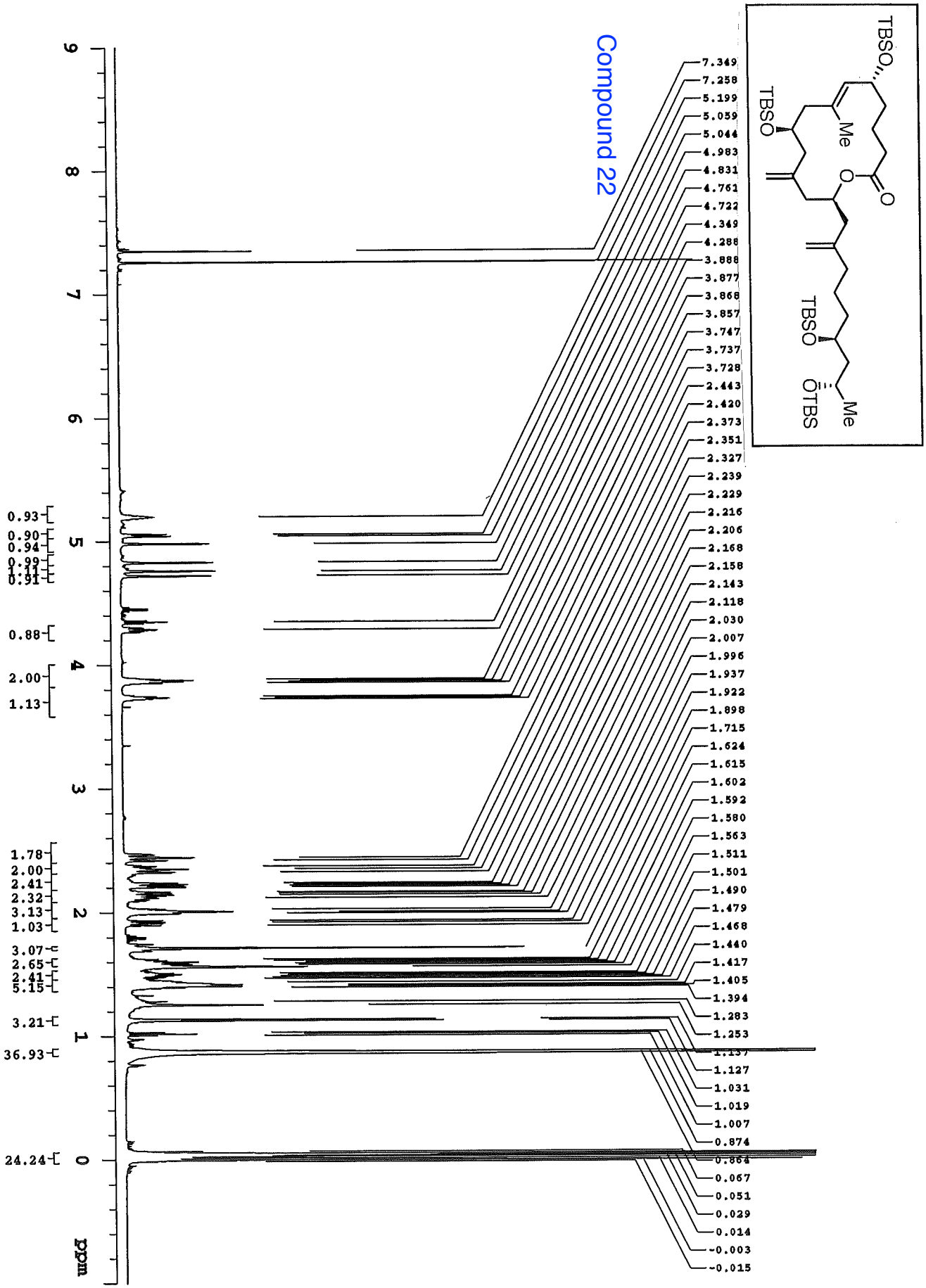

Compound 19
TBSO
TBSO
Me
OTBS
TBSO
TBSO
Me
Me
Me
Me
Me
B
O
O
149.091
146.494
132.464
131.460
112.152
109.386
82.885
77.304
77.202
77.093
76.992
76.890
76.781
70.221
70.035
69.664
66.342
63.265
48.003
47.489
43.981
38.459
38.273
37.818
37.573
36.123
32.868
25.988
25.946
25.929
25.895
24.867
24.808
24.513
23.138
21.857
18.374
18.197
18.096
18.062
16.941
-3.885
-4.020
-4.138
-4.206
-4.366
-4.459
-4.754
-5.276
180
160
140
120
100
80
60
40
20
0
ppm

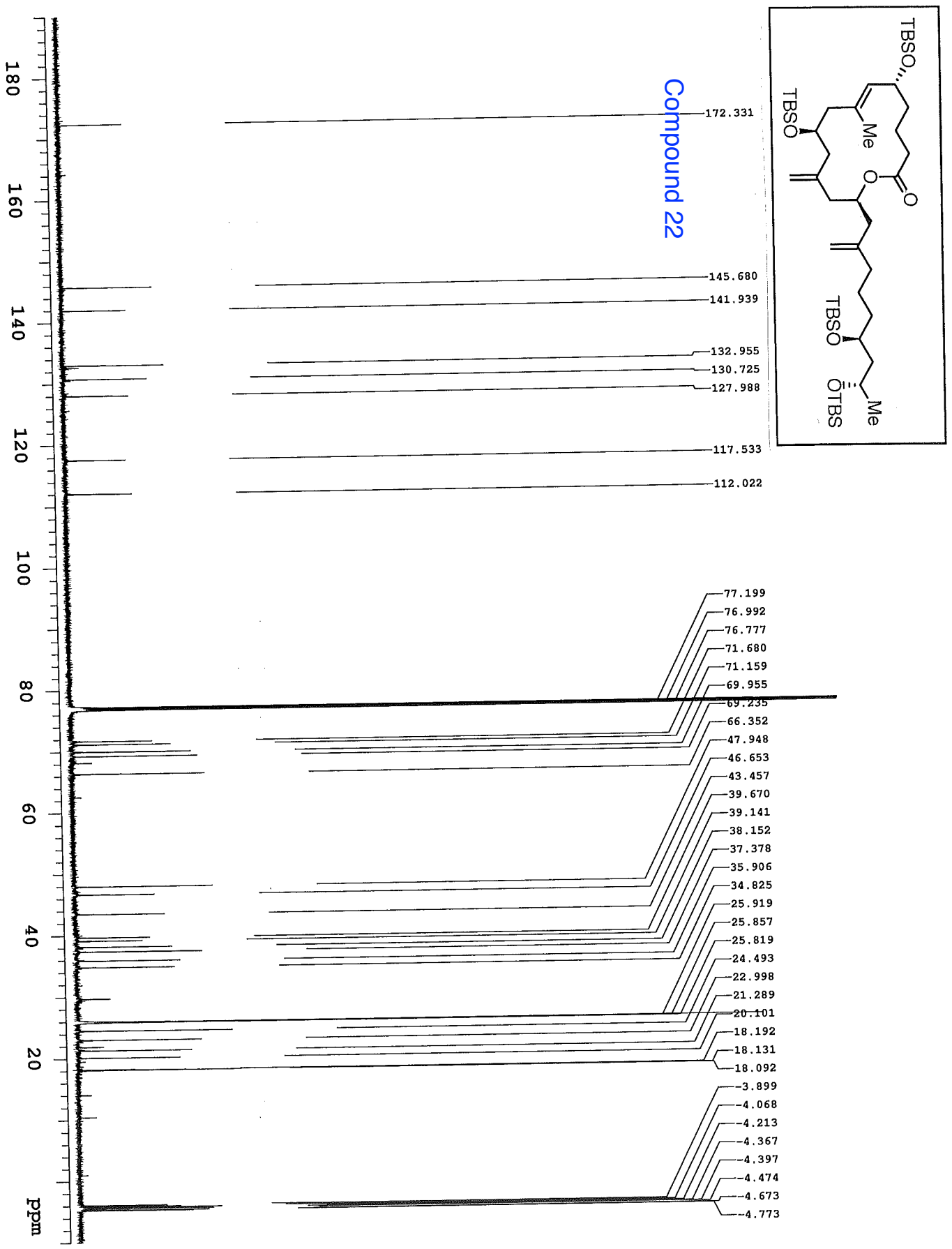

Compound 20
TBSO
TBSO
Me
OH
TBSO
TBSO
Me
Me
Me
Me
Me
B
O
O
7.260
5.165
5.151
4.836
4.749
4.741
4.696
3.917
3.889
3.876
3.645
3.632
3.619
3.351
2.171
2.137
2.121
2.109
2.093
2.074
2.054
2.042
1.977
1.963
1.626
1.618
1.608
1.594
1.584
1.563
1.545
1.526
1.514
1.500
1.490
1.473
1.462
1.445
1.428
1.416
1.406
1.392
1.382
1.372
1.330
1.270
1.254
1.242
1.234
1.221
1.201
1.184
1.141
1.130
0.902
0.892
0.877
0.863
0.845
0.092
0.083
0.069
0.054
0.043
0.023
0.014
0.006
-0.000
1.00
1.00
1.82
0.96
1.00
2.08
1.20
2.00
7.84
1.99
2.88
2.75
3.03
6.86
3.84
14.94
3.11
36.64
23.53
9
8
7
6
5
4
3
2
1
0
ppm

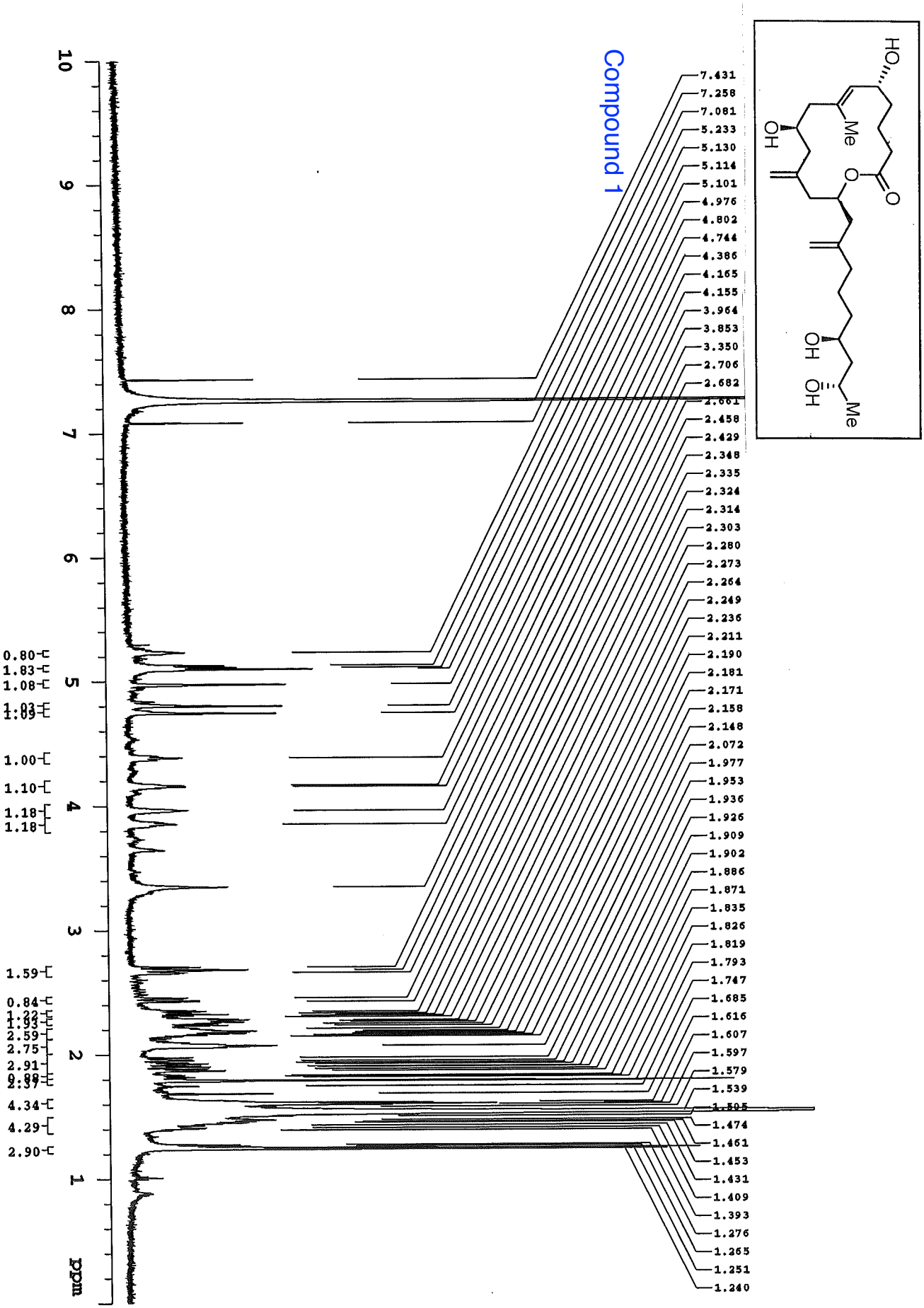

Compound 20
TBSO
TBSO
Me
OH
TBSO
TBSO
Me
Me
Me
Me
Me
B
O
O
149.095
146.447
132.205
131.767
112.213
109.396
82.928
77.312
76.991
76.679
70.237
70.043
69.520
66.350
62.969
47.993
47.445
43.895
38.456
38.186
37.807
37.571
36.137
32.790
29.695
25.951
24.804
24.518
23.135
21.583
18.202
18.101
17.089
-3.873
-4.017
-4.135
-4.202
-4.371
-4.455
-4.742
180
160
140
120
100
80
60
40
20
0
ppm

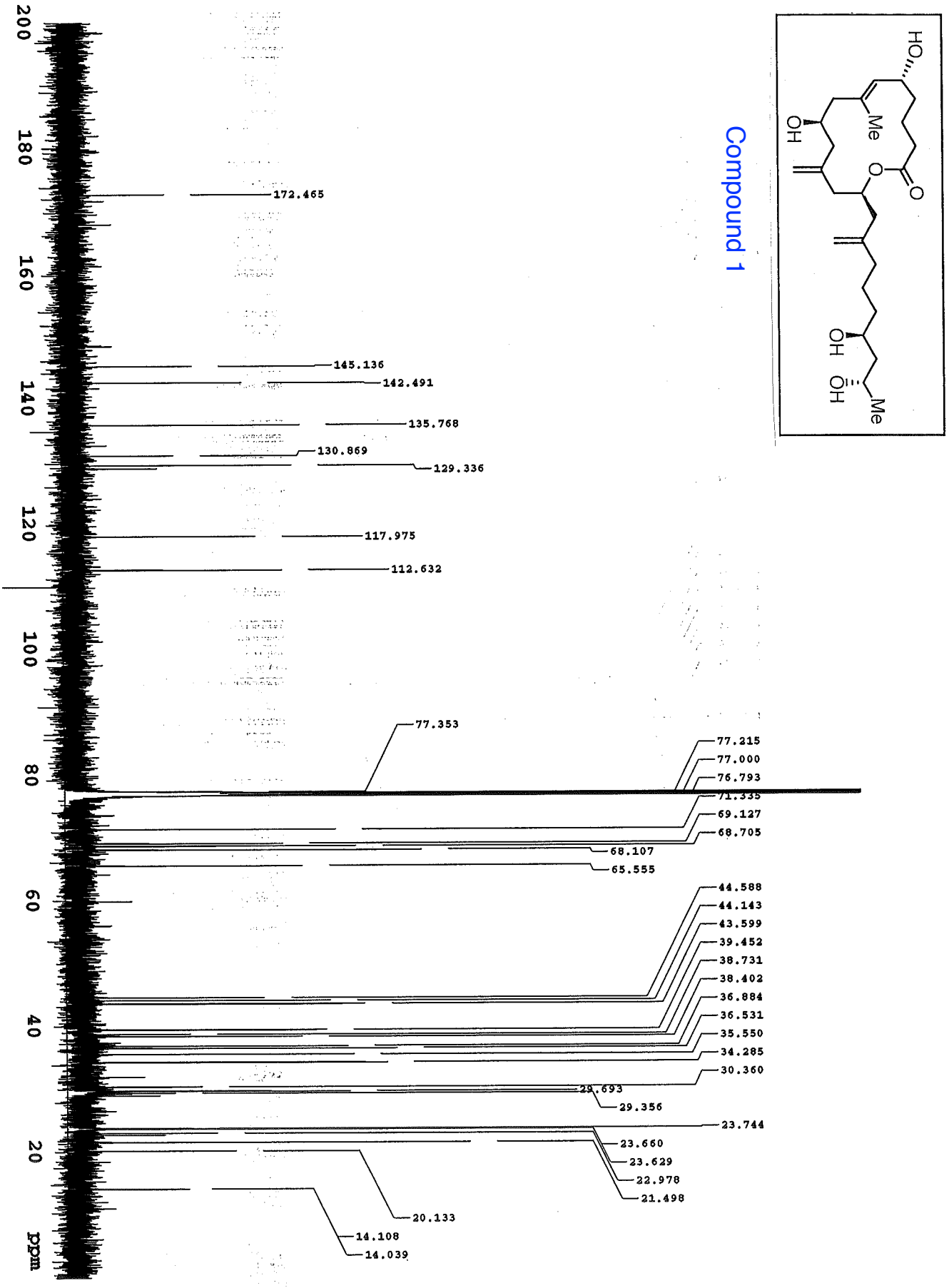

Compound 21
TBSO
TBSO
Me
OH
O
Me
Me
Me
Me
B
O
O
TBSO
TBSO
Me
7.260
5.156
5.140
4.829
4.746
4.699
4.369
4.354
4.144
4.129
4.116
4.101
3.920
3.906
3.893
3.880
3.882
3.748
2.364
2.348
2.342
2.327
2.137
2.128
2.117
2.088
2.071
2.045
2.016
1.976
1.689
1.649
1.632
1.615
1.602
1.589
1.540
1.506
1.493
1.482
1.420
1.260
1.197
1.144
1.133
0.878
0.865
0.056
0.045
0.028
0.023
0.014
0.003
0.97
0.90
1.01
1.04
2.12
1.19
2.00
6.93
2.18
7.12
8.36
12.11
2.97
37.16
24.17
9
8
7
6
5
4
3
2
1
0
ppm

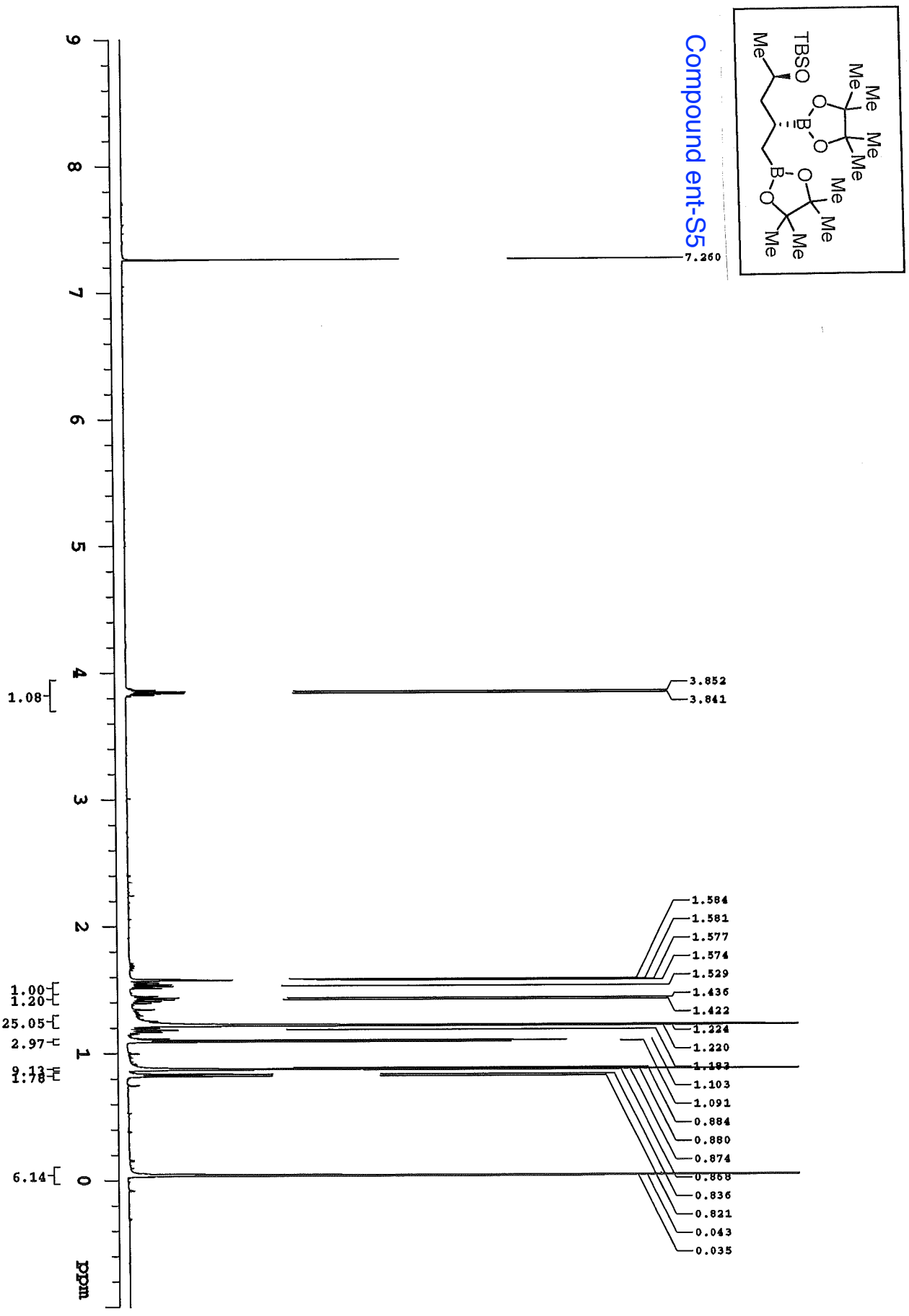

Compound 21
TBSO
TBSO
Me
OH
O
TBSO
TBSO
Me
Me
Me
Me
Me
B
O
O
149.066
146.342
132.312
131.688
112.430
109.428
83.155
77.202
76.992
76.781
70.280
70.086
69.192
66.393
55.971
47.944
47.497
43.518
38.433
37.767
37.691
37.557
36.165
33.703
33.492
31.924
30.153
29.698
29.352
26.705
25.938
25.904
25.870
24.816
24.757
24.521
23.113
23.046
22.683
20.963
18.155
18.105
17.354
14.175
14.108
-3.877
-4.003
-4.164
-4.206
-4.416
-4.459
-4.787
200
180
160
140
120
100
80
60
40
20
0
ppm

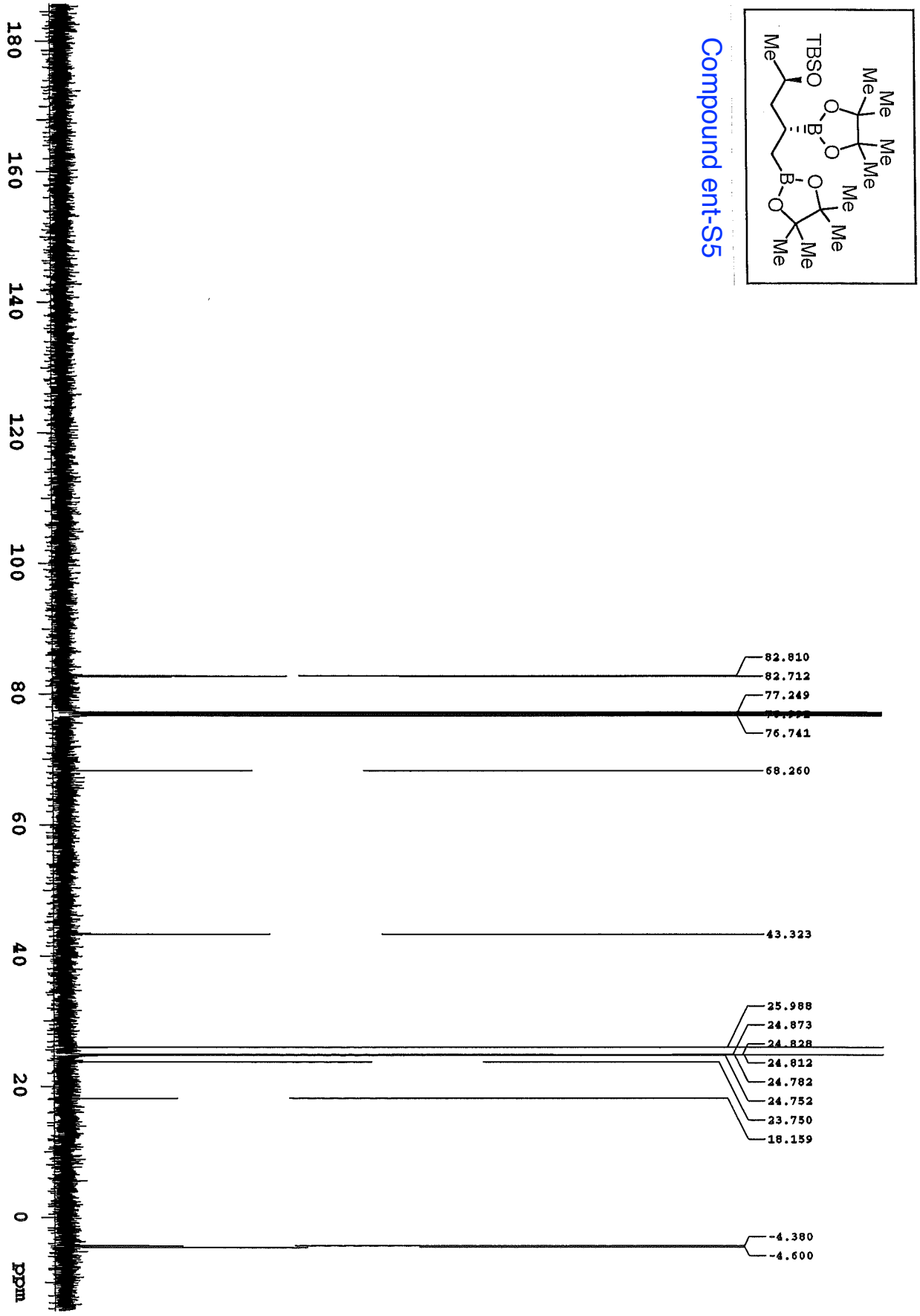

Compound 22
TBSO
Me
O
O
TBSO
OTBS
Me
7.349
7.258
5.199
5.059
5.044
4.983
4.831
4.761
4.722
4.349
4.288
3.888
3.877
3.868
3.857
3.747
3.737
3.728
2.443
2.420
2.373
2.351
2.327
2.239
2.229
2.216
2.206
2.168
2.158
2.143
2.118
2.030
2.007
1.996
1.937
1.922
1.898
1.715
1.624
1.615
1.602
1.592
1.580
1.563
1.511
1.501
1.490
1.479
1.468
1.440
1.417
1.405
1.394
1.283
1.253
1.127
1.031
1.019
1.007
0.874
0.067
0.051
0.029
0.014
-0.003
-0.015
0.93
0.90
0.94
0.91
0.88
2.00
1.13
1.78
2.00
2.41
2.32
3.13
1.03
3.07
2.65
2.41
5.15
3.21
36.93
24.24
9
8
7
6
5
4
3
2
1
0
ppm

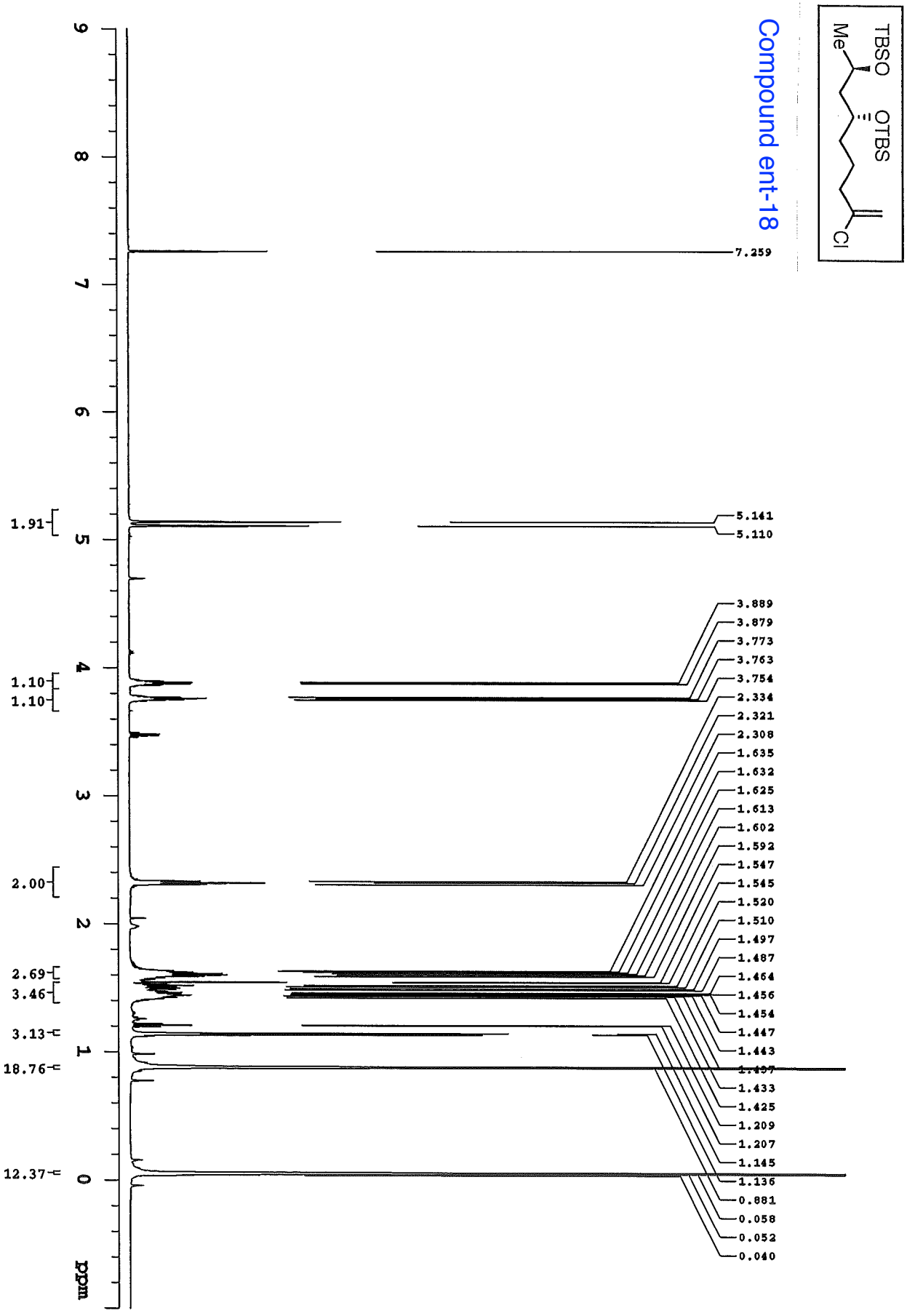

Compound 22
TBSO
TBSO
Me
O
O
TBSO
OTBS
Me
172.331
145.680
141.939
132.955
130.725
127.988
117.533
112.022
77.199
76.992
76.777
71.680
71.159
69.955
69.235
66.352
47.948
46.653
43.457
39.670
39.141
38.152
37.378
35.906
34.825
25.919
25.857
25.819
24.493
22.998
21.289
20.101
18.192
18.131
18.092
-3.899
-4.068
-4.213
-4.367
-4.397
-4.474
-4.673
-4.773
180
160
140
120
100
80
60
40
20
ppm

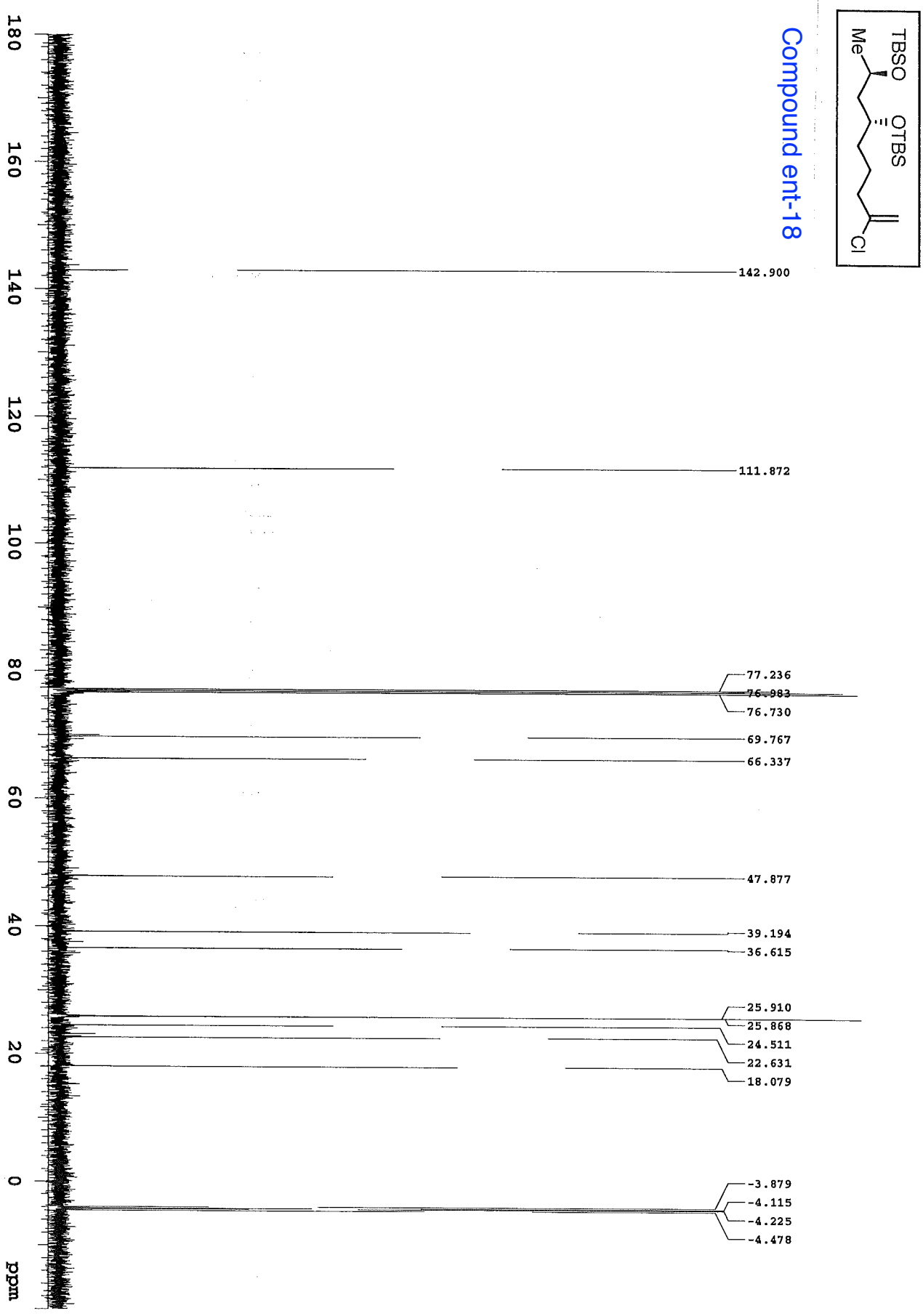

Compound 1
HO
Me
OH
O
O
OH
OH
Me
7.431
7.258
7.081
5.233
5.130
5.114
5.101
4.976
4.802
4.744
4.386
4.165
4.155
3.964
3.853
3.350
2.706
2.682
2.661
2.458
2.429
2.348
2.335
2.324
2.314
2.303
2.280
2.273
2.264
2.249
2.236
2.211
2.190
2.181
2.171
2.158
2.148
2.072
1.977
1.953
1.936
1.926
1.909
1.902
1.886
1.871
1.835
1.826
1.819
1.793
1.747
1.685
1.616
1.607
1.597
1.579
1.539
1.505
1.474
1.461
1.453
1.431
1.409
1.393
1.276
1.265
1.251
1.240
0.80
1.83
1.08
1.03
1.09
1.00
1.10
1.18
1.18
1.59
0.84
1.22
1.93
2.59
2.75
2.91
0.88
2.37
4.34
4.29
2.90
10
9
8
7
6
5
4
3
2
1
ppm

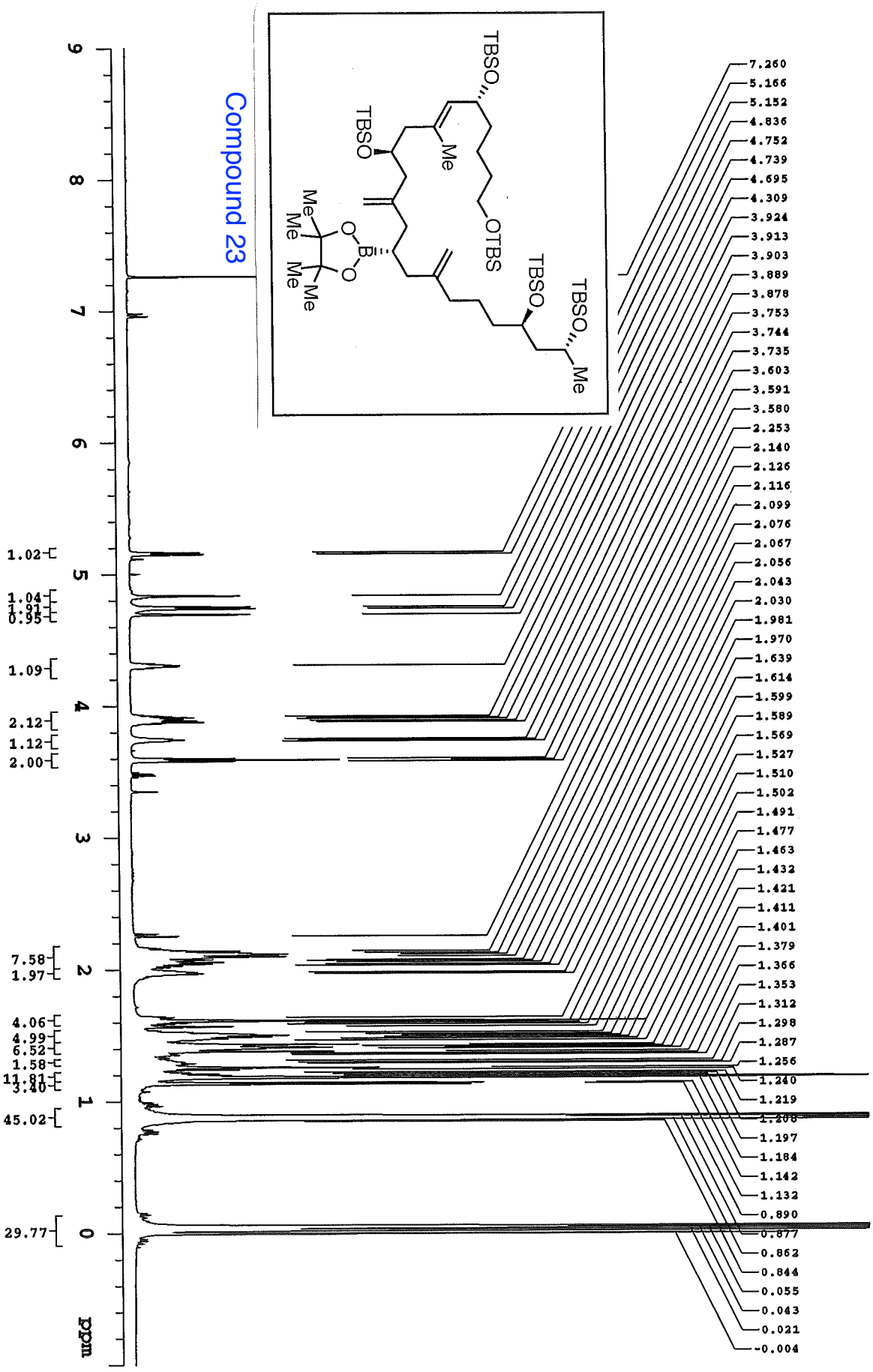

Compound 1
HO
Me
OH
O
O
OH
OH
Me
200
180
160
140
120
100
80
60
40
20
ppm
172.465
145.136
142.491
135.768
130.869
129.336
117.975
112.632
77.353
77.215
77.000
76.793
71.335
69.127
68.705
68.107
65.555
44.588
44.143
43.599
39.452
38.731
38.402
36.884
36.531
35.550
34.285
30.360
29.693
29.356
23.744
23.660
23.629
22.978
21.498
20.133
14.108
14.039

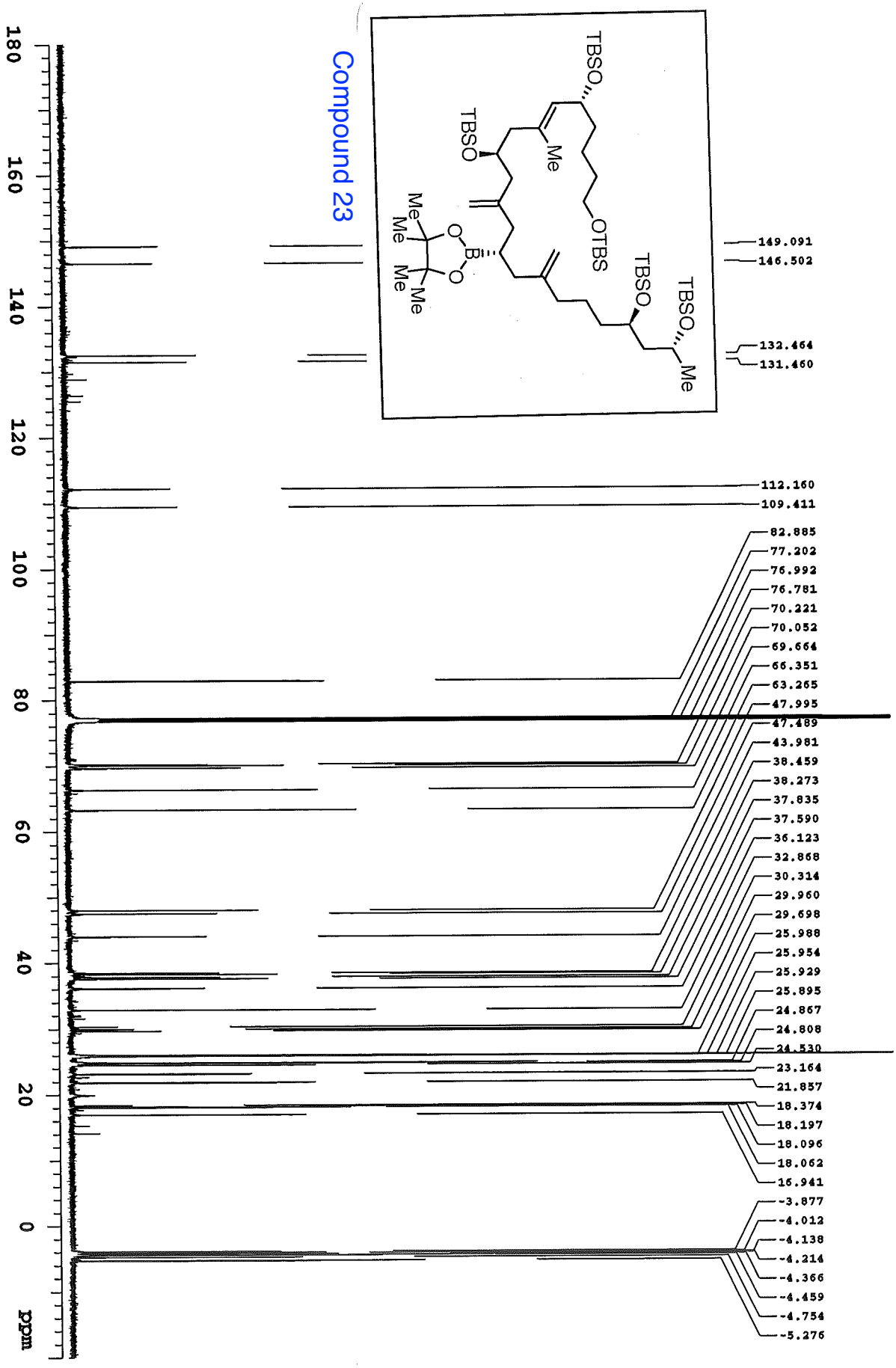

Compound ent-S5
TBSO
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me
7.260
3.852
3.841
1.584
1.581
1.577
1.574
1.529
1.436
1.422
1.224
1.220
1.183
1.103
1.091
0.884
0.880
0.874
0.868
0.836
0.821
0.043
0.035
1.08
1.00
1.20
25.05
2.97
9.13
1.78
6.14
ppm

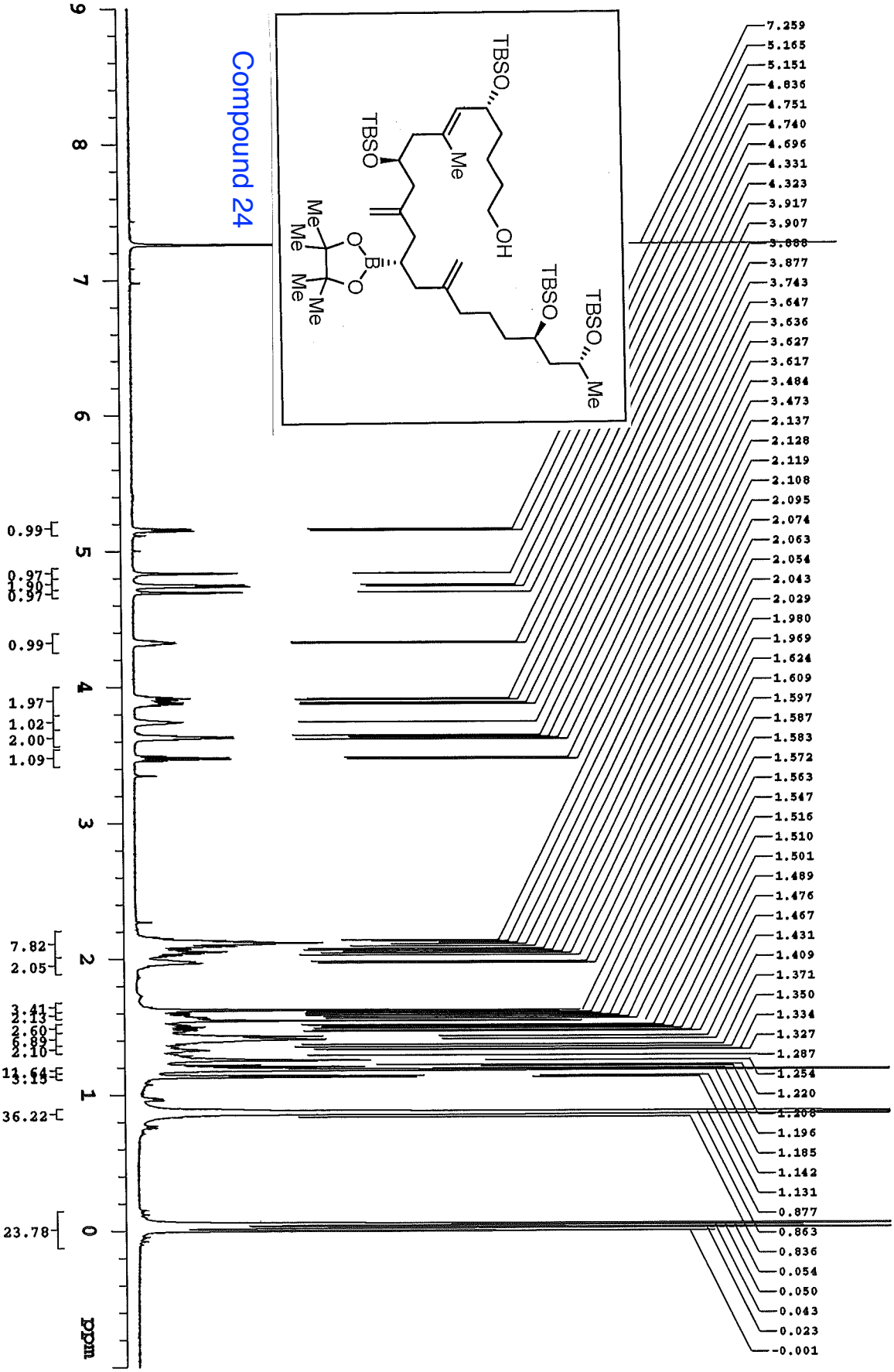

Compound ent-S5
TBSO
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me
82.810
82.712
77.249
76.741
68.260
43.323
25.988
24.873
24.828
24.812
24.782
24.752
23.750
18.159
-4.380
-4.600
180
160
140
120
100
80
60
40
20
0
ppm

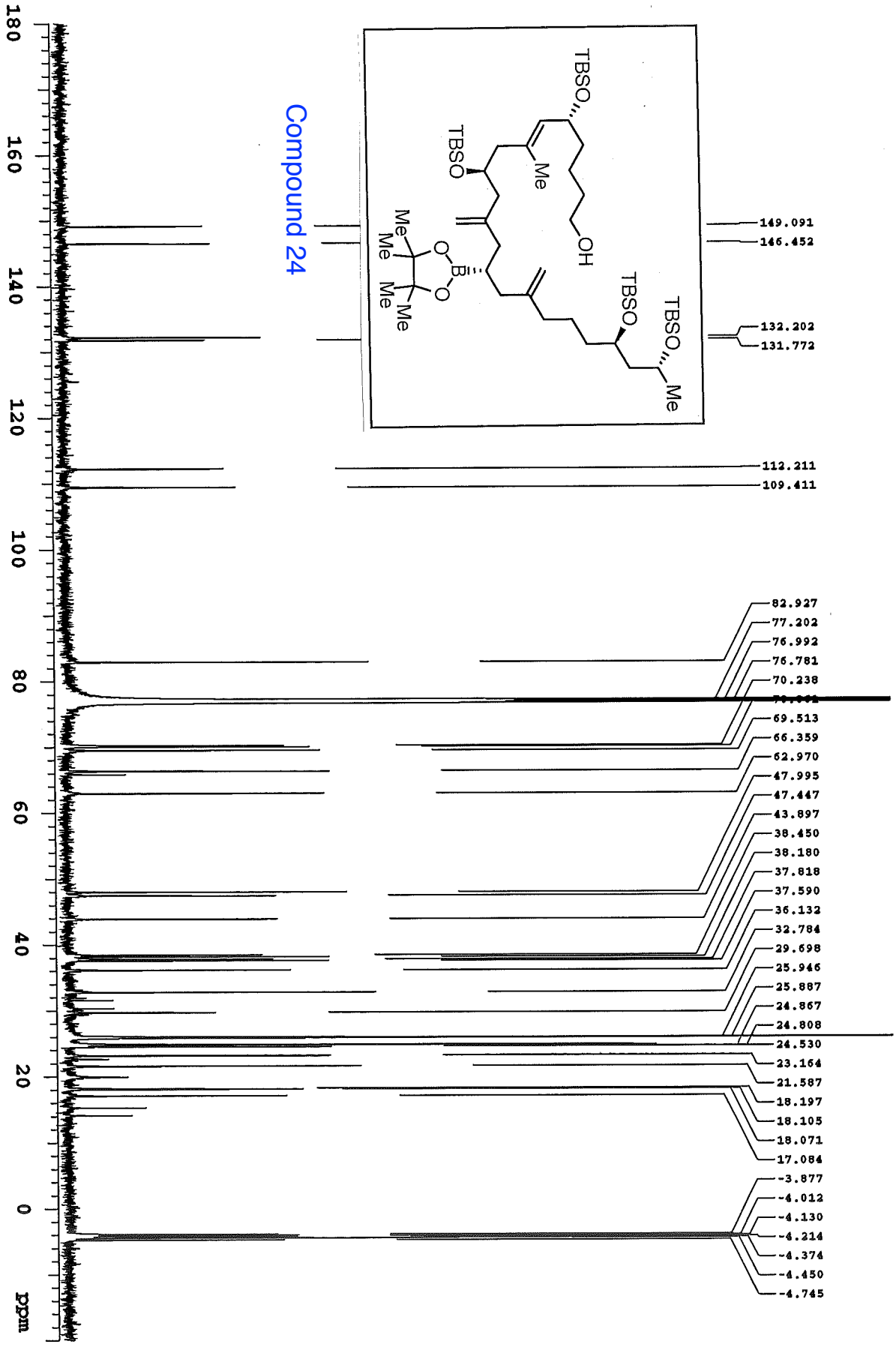

Compound ent-18
TBSO
OTBS
Me
Cl
7.259
5.141
5.110
3.889
3.879
3.773
3.763
3.754
2.334
2.321
2.308
1.635
1.632
1.625
1.613
1.602
1.592
1.547
1.545
1.520
1.510
1.497
1.487
1.464
1.456
1.454
1.447
1.443
1.433
1.425
1.209
1.207
1.145
1.136
0.881
0.058
0.052
0.040
1.91
1.10
1.10
2.00
2.69
3.46
3.13
18.76
12.37
ppm

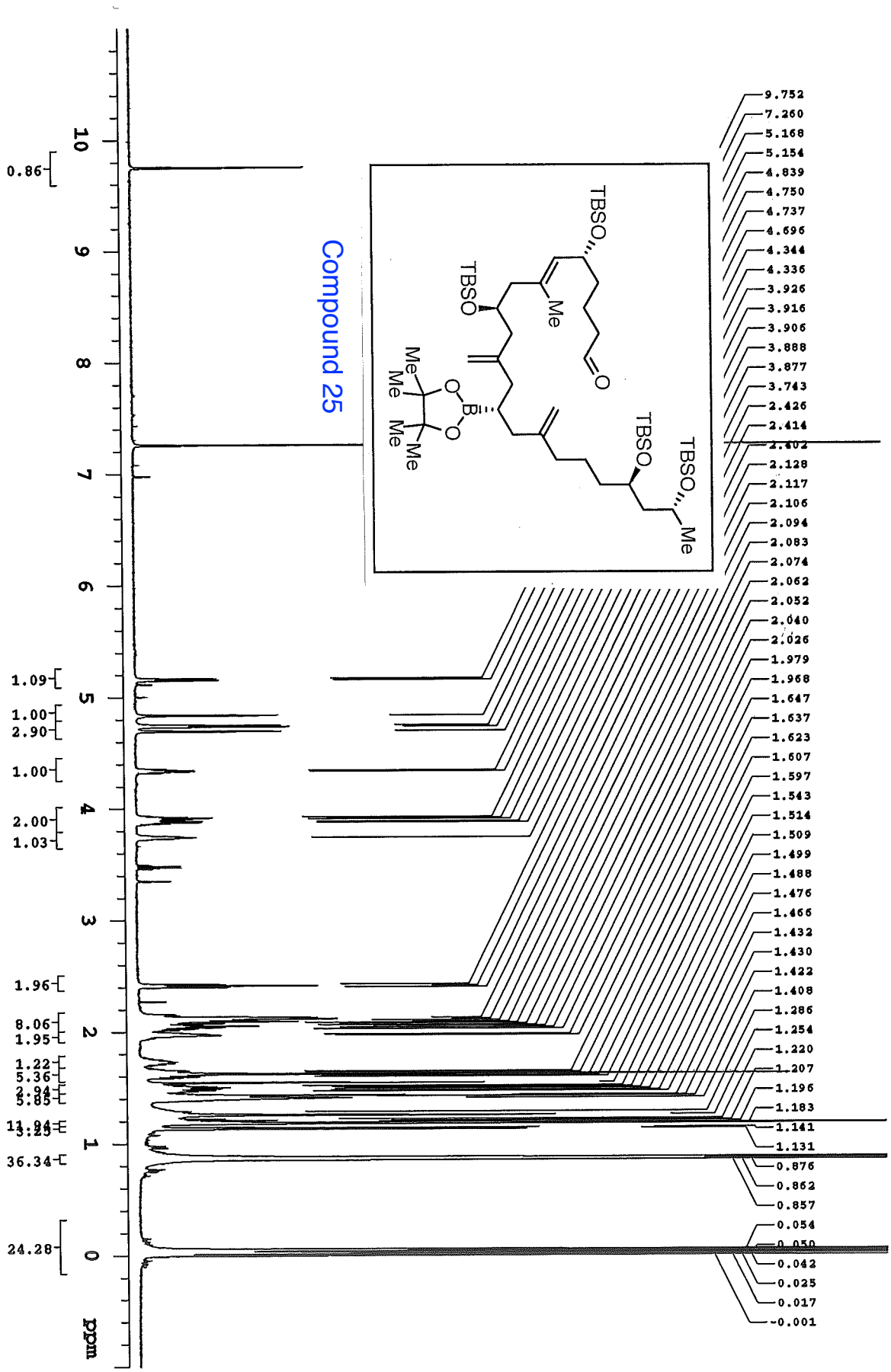

Compound ent-18
TBSO
OTBS
Me
Cl
142.900
111.872
77.236
76.983
76.730
69.767
66.337
47.877
39.194
36.615
25.910
25.868
24.511
22.631
18.079
-3.879
-4.115
-4.225
-4.478
180
160
140
120
100
80
60
40
20
0
ppm

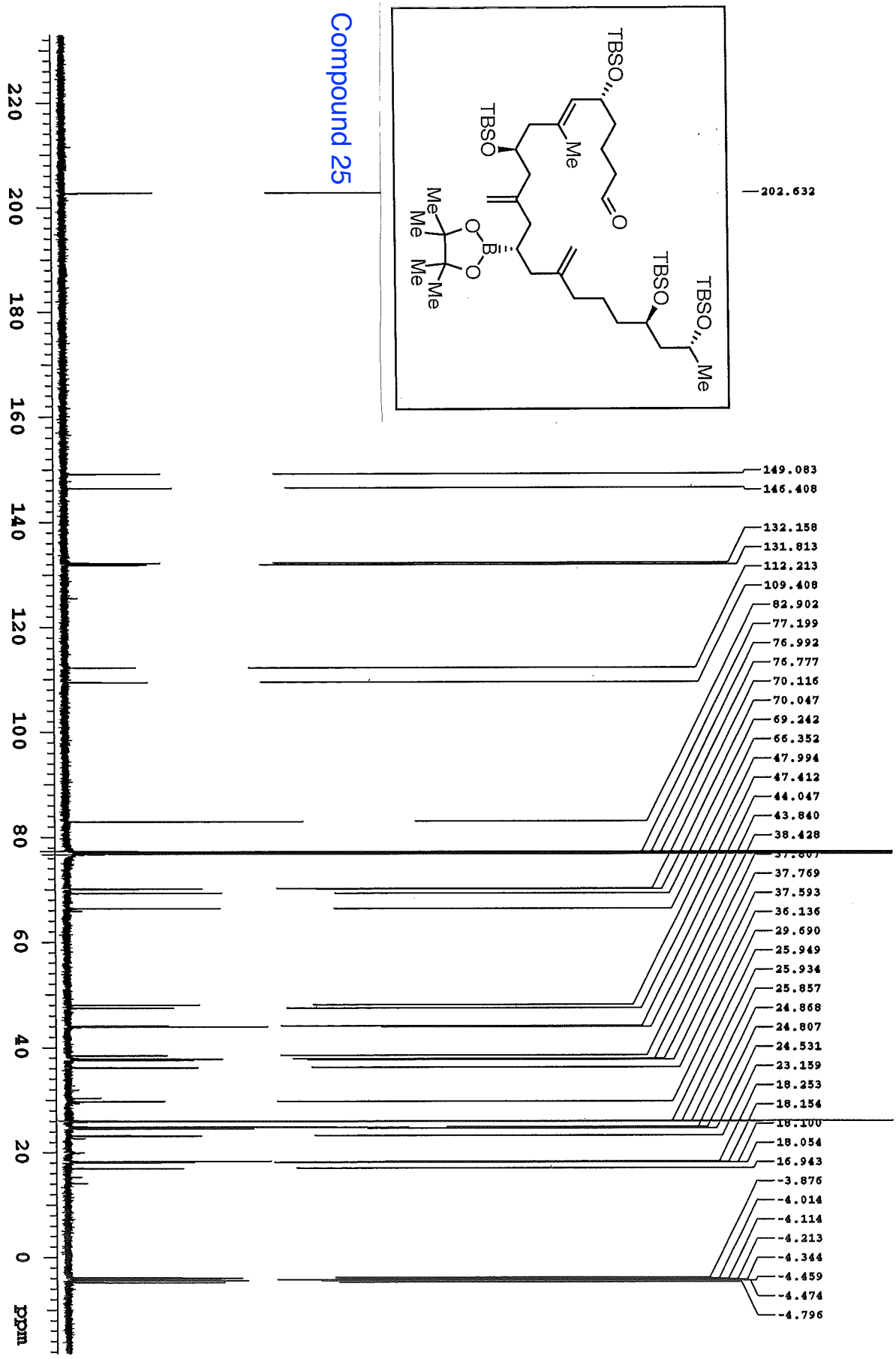

Compound 23
TBSO
TBSO
Me
OTBS
TBSO
TBSO
Me
Me
Me
Me
Me
O
B
O
7.260
5.166
5.152
4.836
4.752
4.739
4.695
4.309
3.924
3.913
3.903
3.889
3.878
3.753
3.744
3.735
3.603
3.591
3.580
2.253
2.140
2.126
2.116
2.099
2.076
2.067
2.056
2.043
2.030
1.981
1.970
1.639
1.614
1.599
1.589
1.569
1.527
1.510
1.502
1.491
1.477
1.463
1.432
1.421
1.411
1.401
1.379
1.366
1.353
1.312
1.298
1.287
1.256
1.240
1.219
1.208
1.197
1.184
1.142
1.132
0.890
0.877
0.862
0.844
0.055
0.043
0.021
-0.004
1.02
1.04
1.91
0.95
1.09
2.12
1.12
2.00
7.58
1.97
4.06
4.99
6.52
1.58
11.81
3.40
45.02
29.77
9
8
7
6
5
4
3
2
1
0
ppm

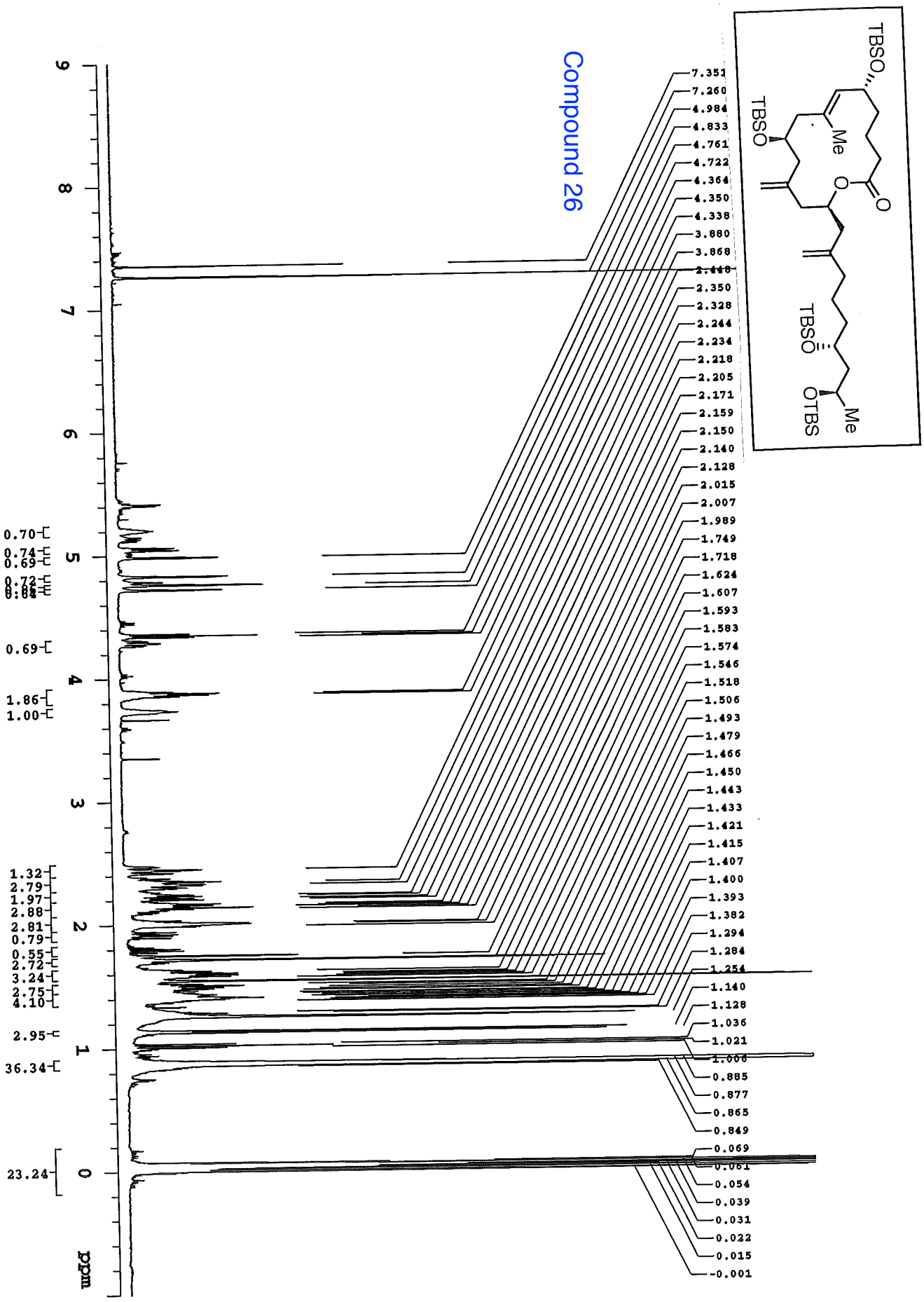

Compound 23
TBSO
TBSO
Me
OTBS
TBSO
TBSO
Me
Me
Me
Me
Me
O
B
O
149.091
146.502
132.464
131.460
112.160
109.411
82.885
77.202
76.992
76.781
70.221
70.052
69.664
66.351
63.265
47.995
47.489
43.981
38.459
38.273
37.835
37.590
36.123
32.868
30.314
29.960
29.698
25.988
25.954
25.929
25.895
24.867
24.808
24.530
23.164
21.857
18.374
18.197
18.096
18.062
16.941
-3.877
-4.012
-4.138
-4.214
-4.366
-4.459
-4.754
-5.276
180
160
140
120
100
80
60
40
20
0
ppm

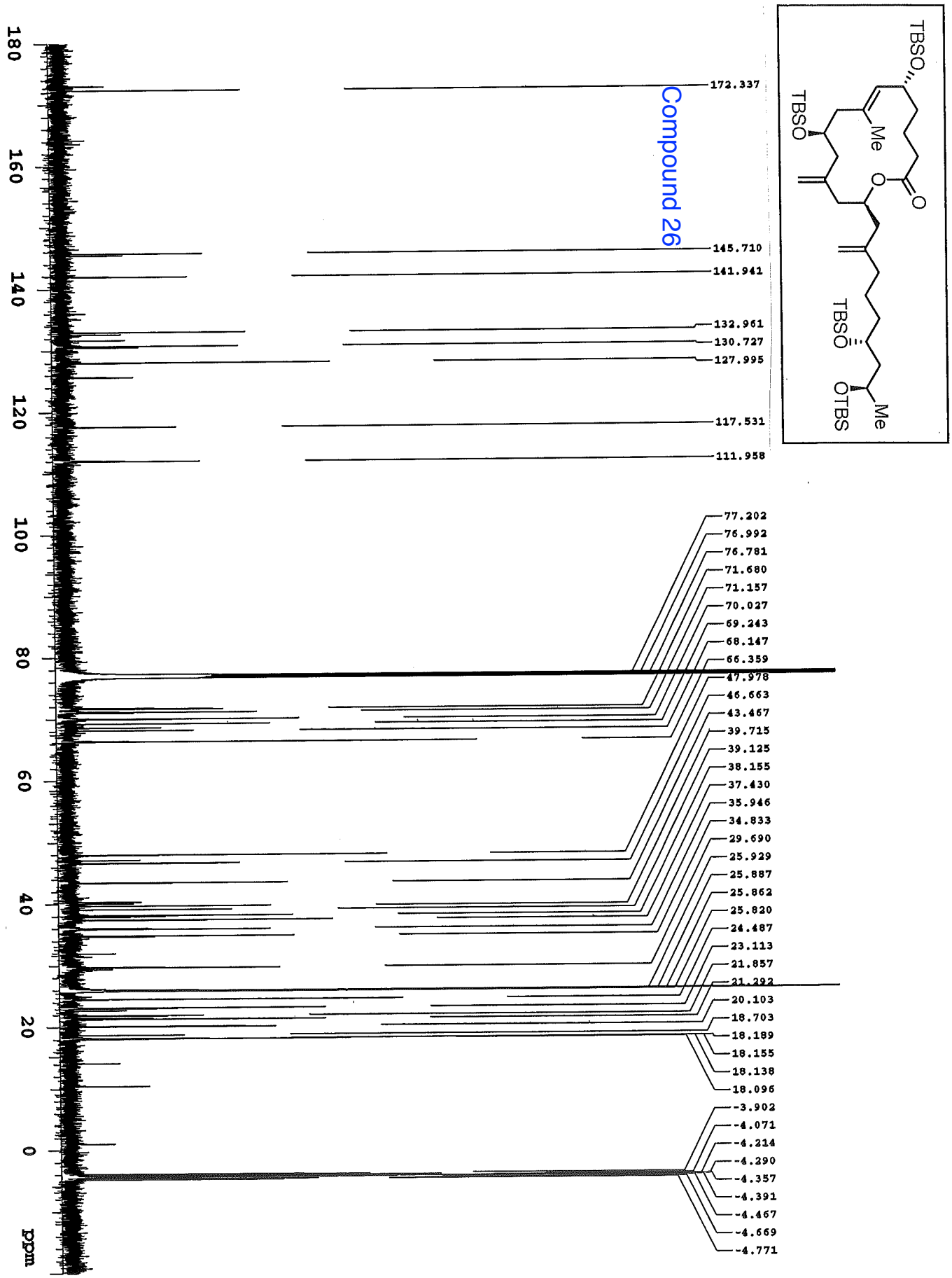

Compound 24
TBSO
TBSO
Me
OH
TBSO
TBSO
Me
Me
Me
Me
Me
B
O
O
7.259
5.165
5.151
4.836
4.751
4.740
4.696
4.331
4.323
3.917
3.907
3.888
3.877
3.743
3.647
3.636
3.627
3.617
3.484
3.473
2.137
2.128
2.119
2.108
2.095
2.074
2.063
2.054
2.043
2.029
1.980
1.969
1.624
1.609
1.597
1.587
1.583
1.572
1.563
1.547
1.516
1.510
1.501
1.489
1.476
1.467
1.431
1.409
1.371
1.350
1.334
1.327
1.287
1.254
1.220
1.206
1.196
1.185
1.142
1.131
0.877
0.863
0.836
0.054
0.050
0.043
0.023
-0.001
0.99
0.97
1.90
0.97
0.99
1.97
1.02
2.00
1.09
7.82
2.05
3.41
2.13
2.60
6.89
2.10
11.64
3.15
36.22
23.78
9
8
7
6
5
4
3
2
1
0
ppm

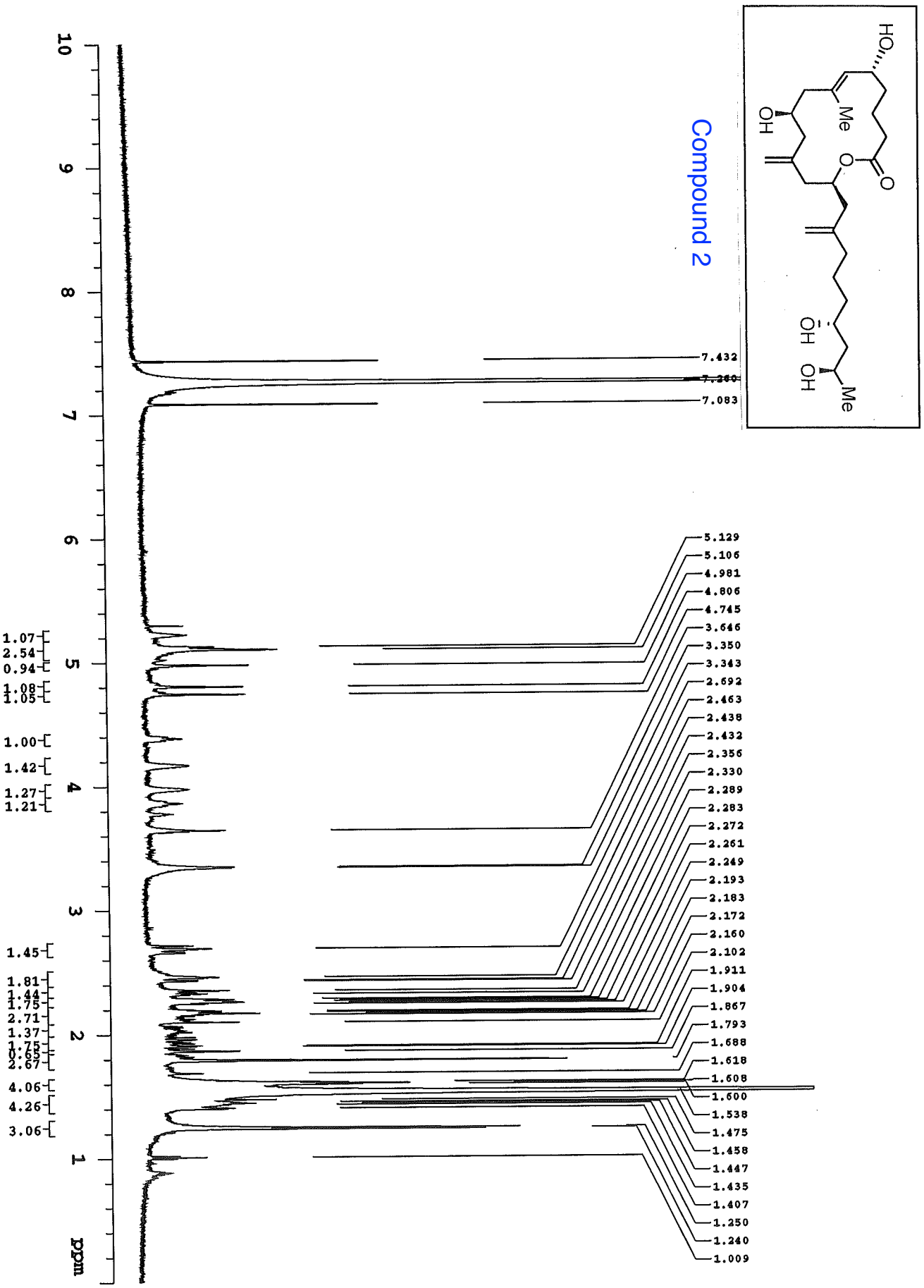

Compound 24
TBSO
TBSO
Me
OH
TBSO
TBSO
Me
Me
Me
Me
Me
B
O
O
149.091
146.452
132.202
131.772
112.211
109.411
82.927
77.202
76.992
76.781
70.238
69.513
66.359
62.970
47.995
47.447
43.897
38.450
38.180
37.818
37.590
36.132
32.784
29.698
25.946
25.887
24.867
24.808
24.530
23.164
21.587
18.197
18.105
18.071
17.084
-3.877
-4.012
-4.130
-4.214
-4.374
-4.450
-4.745
180
160
140
120
100
80
60
40
20
0
ppm

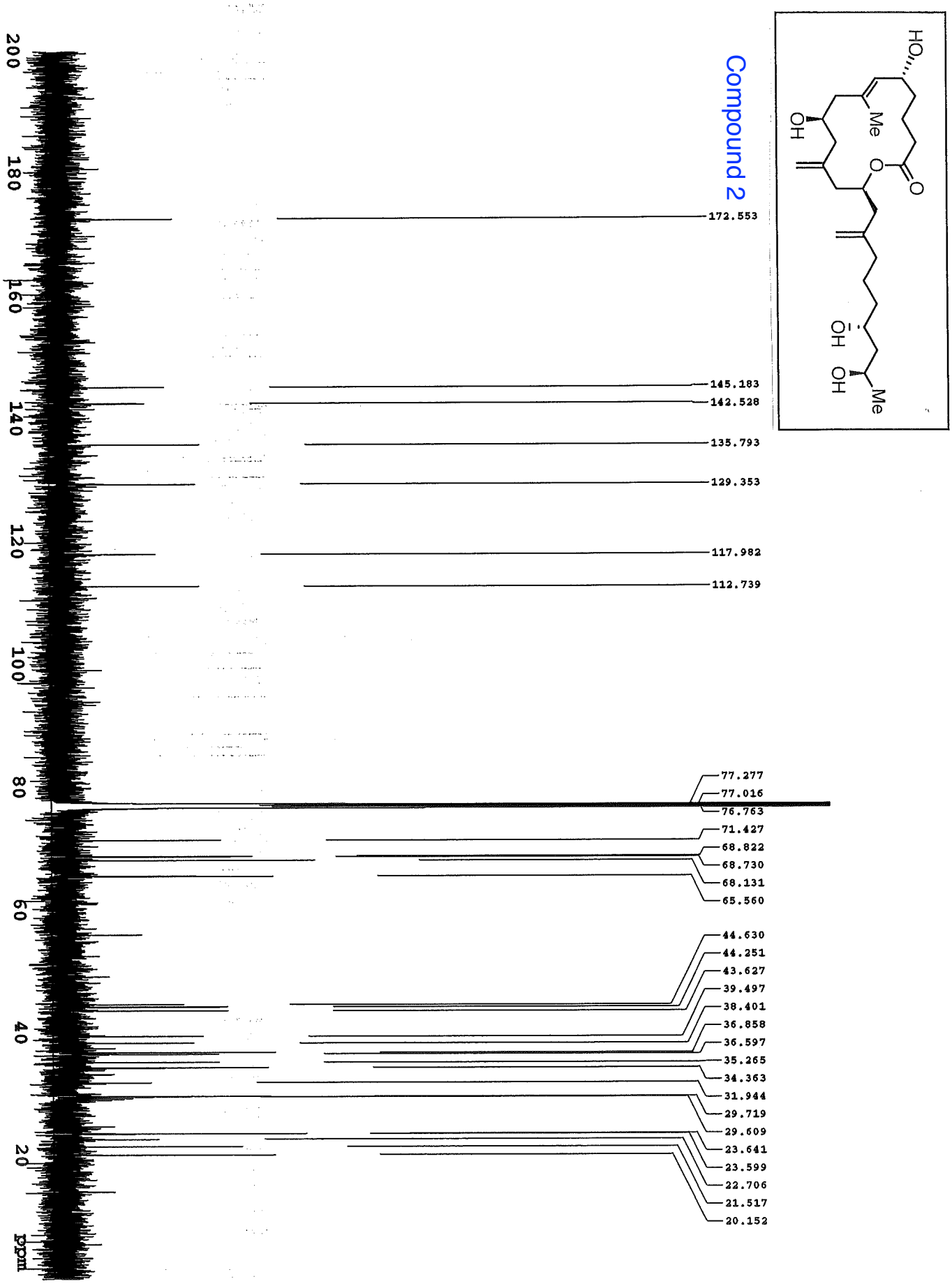

Compound 25
TBSO
TBSO
Me
O
TBSO
TBSO
Me
Me
Me
Me
Me
O
O
B
9.752
7.260
5.168
5.154
4.839
4.750
4.737
4.696
4.344
4.336
3.926
3.916
3.906
3.888
3.877
3.743
2.426
2.414
2.402
2.128
2.117
2.106
2.094
2.083
2.074
2.062
2.052
2.040
2.026
1.979
1.968
1.647
1.637
1.623
1.607
1.597
1.543
1.514
1.509
1.499
1.488
1.476
1.466
1.432
1.430
1.422
1.408
1.286
1.254
1.220
1.207
1.196
1.183
1.141
1.131
0.876
0.862
0.857
0.054
0.050
0.042
0.025
0.017
-0.001
0.86
1.09
1.00
2.90
1.00
2.00
1.03
1.96
8.06
1.95
1.22
5.36
2.94
5.85
11.94
3.25
36.34
24.28
10
9
8
7
6
5
4
3
2
1
0
ppm

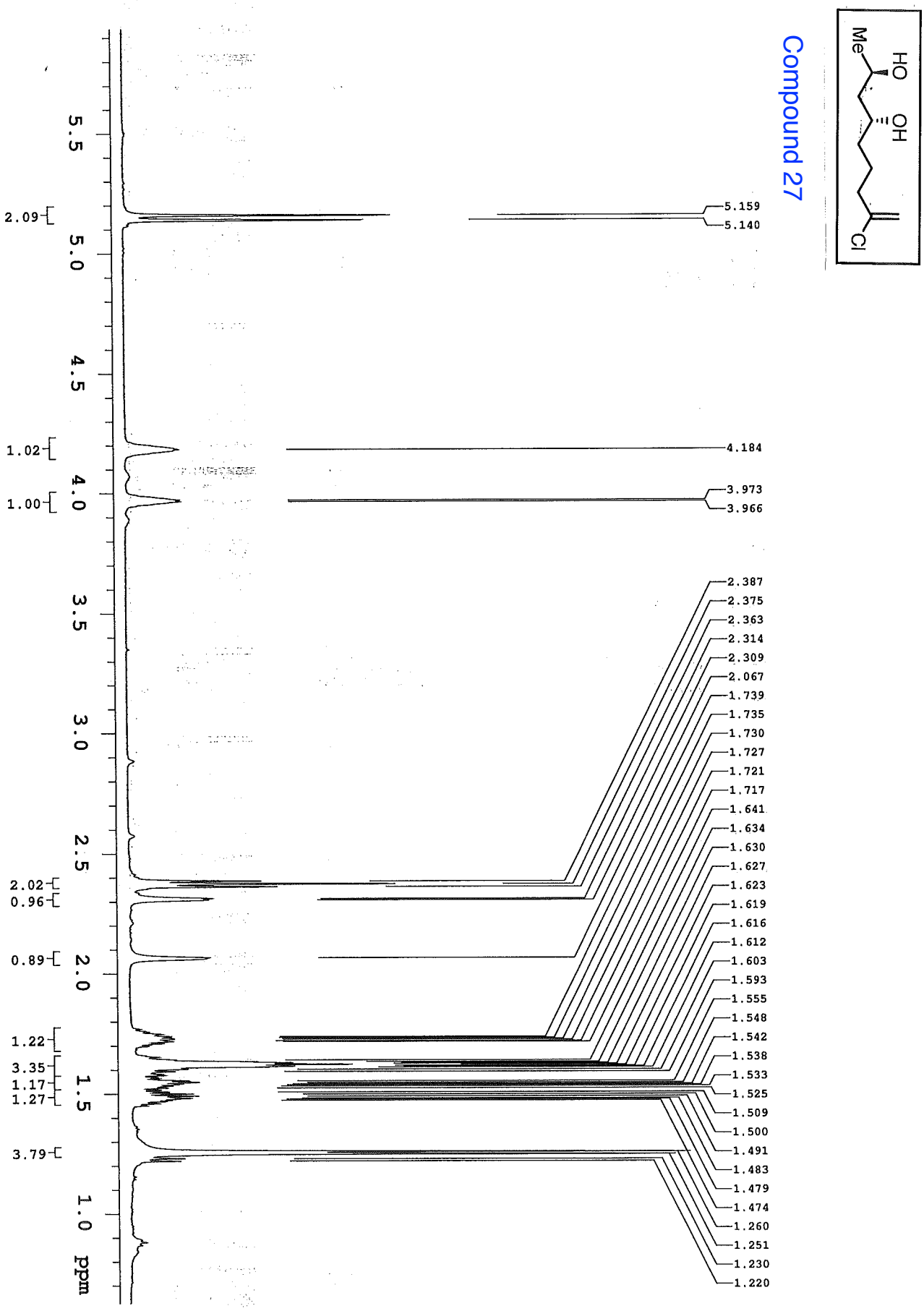

Compound 25
TBSO
TBSO
Me
O
TBSO
TBSO
Me
Me
Me
O
B
O
Me
Me
Me
202.632
149.083
146.408
132.158
131.813
112.213
109.408
82.902
77.199
76.992
76.777
70.116
70.047
69.242
66.352
47.994
47.412
44.047
43.840
38.428
37.769
37.593
36.136
29.690
25.949
25.934
25.857
24.868
24.807
24.531
23.159
18.253
18.154
18.100
18.054
16.943
-3.876
-4.014
-4.114
-4.213
-4.344
-4.459
-4.474
-4.796
220
200
180
160
140
120
100
80
60
40
20
0
ppm

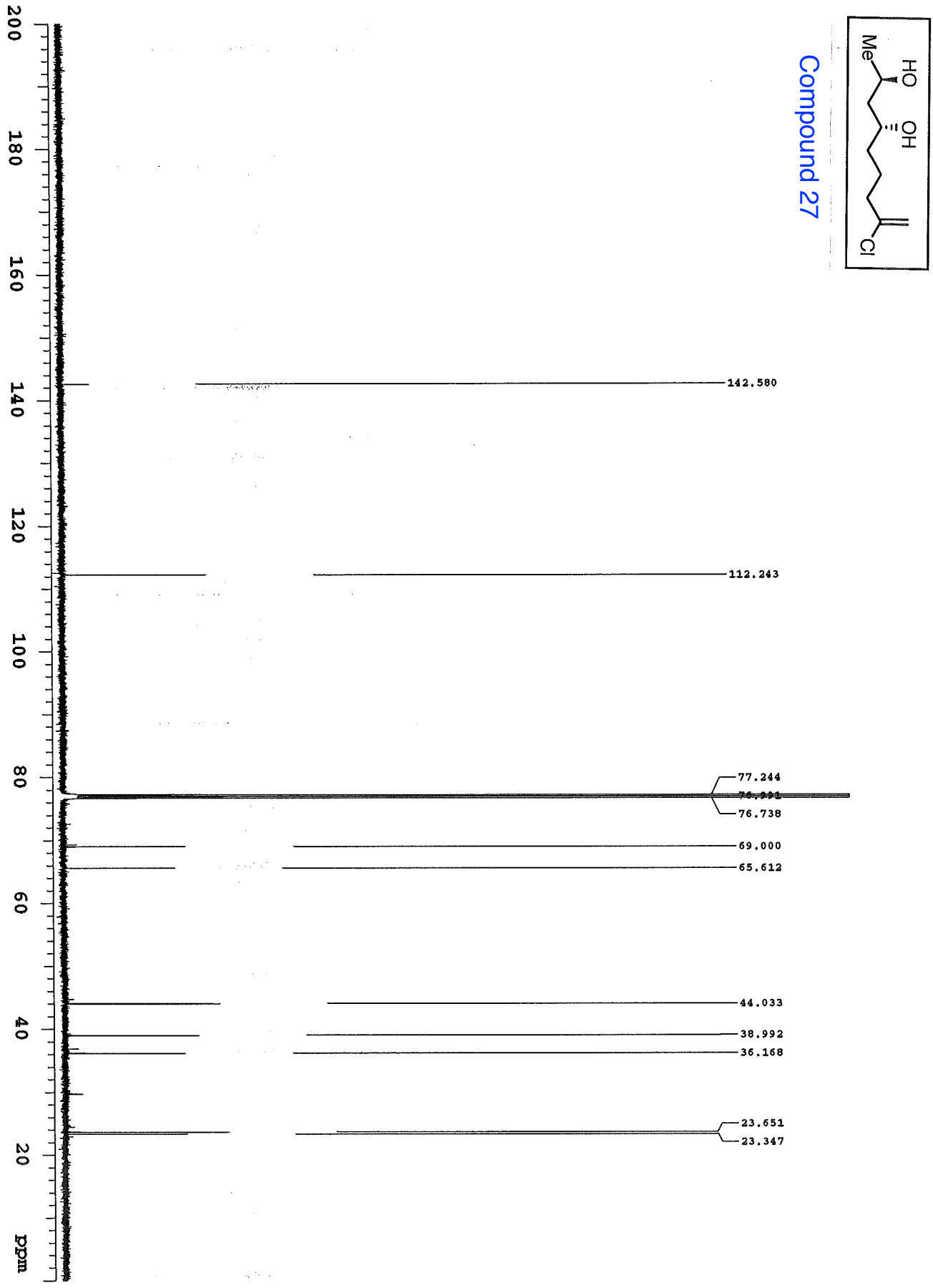

Compound 26
TBSO
TBSO
Me
O
O
TBSO
OTBS
Me
7.351
7.260
4.984
4.833
4.761
4.722
4.364
4.350
4.338
3.880
3.868
2.448
2.350
2.328
2.244
2.234
2.218
2.205
2.171
2.159
2.150
2.140
2.128
2.015
2.007
1.989
1.749
1.718
1.624
1.607
1.593
1.583
1.574
1.546
1.518
1.506
1.493
1.479
1.466
1.450
1.443
1.433
1.421
1.415
1.407
1.400
1.393
1.382
1.294
1.284
1.254
1.140
1.128
1.036
1.021
1.006
0.885
0.877
0.865
0.849
0.069
0.061
0.054
0.039
0.031
0.022
0.015
-0.001
0.70
0.74
0.69
0.72
0.69
1.86
1.00
1.32
2.79
1.97
2.88
2.81
0.79
0.55
2.72
3.24
2.75
4.10
2.95
36.34
23.24
9
8
7
6
5
4
3
2
1
0
ppm

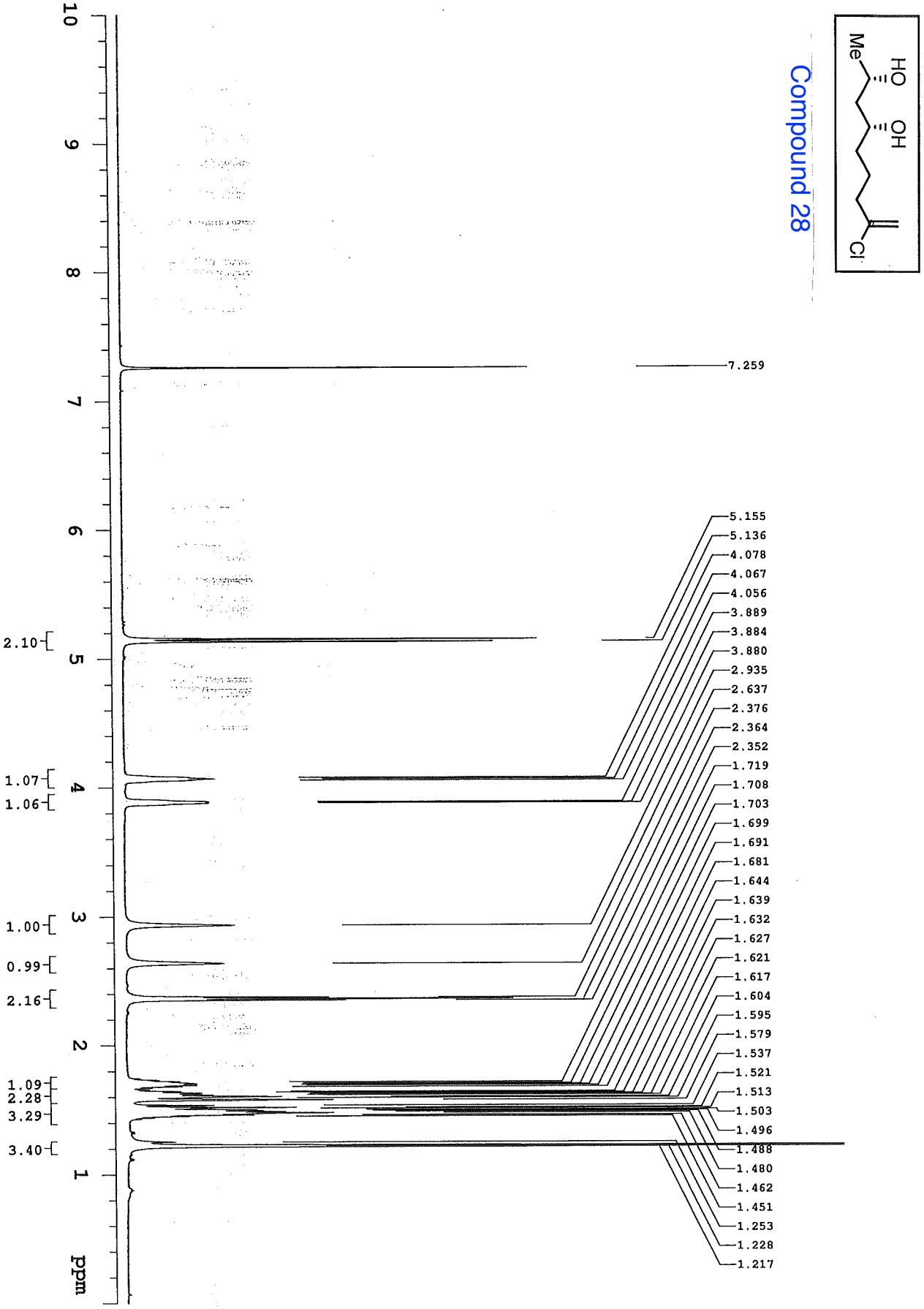

Compound 26
TBSO
TBSO
Me
O
O
TBSO
OTBS
Me
172.337
145.710
141.941
132.961
130.727
127.995
117.531
111.958
77.202
76.992
76.781
71.680
71.157
70.027
69.243
68.147
66.359
47.978
46.663
43.467
39.715
39.125
38.155
37.430
35.946
34.833
29.690
25.929
25.887
25.862
25.820
24.487
23.113
21.857
21.292
20.103
18.703
18.189
18.155
18.138
18.096
-3.902
-4.071
-4.214
-4.290
-4.357
-4.391
-4.467
-4.669
-4.771
180
160
140
120
100
80
60
40
20
0
ppm

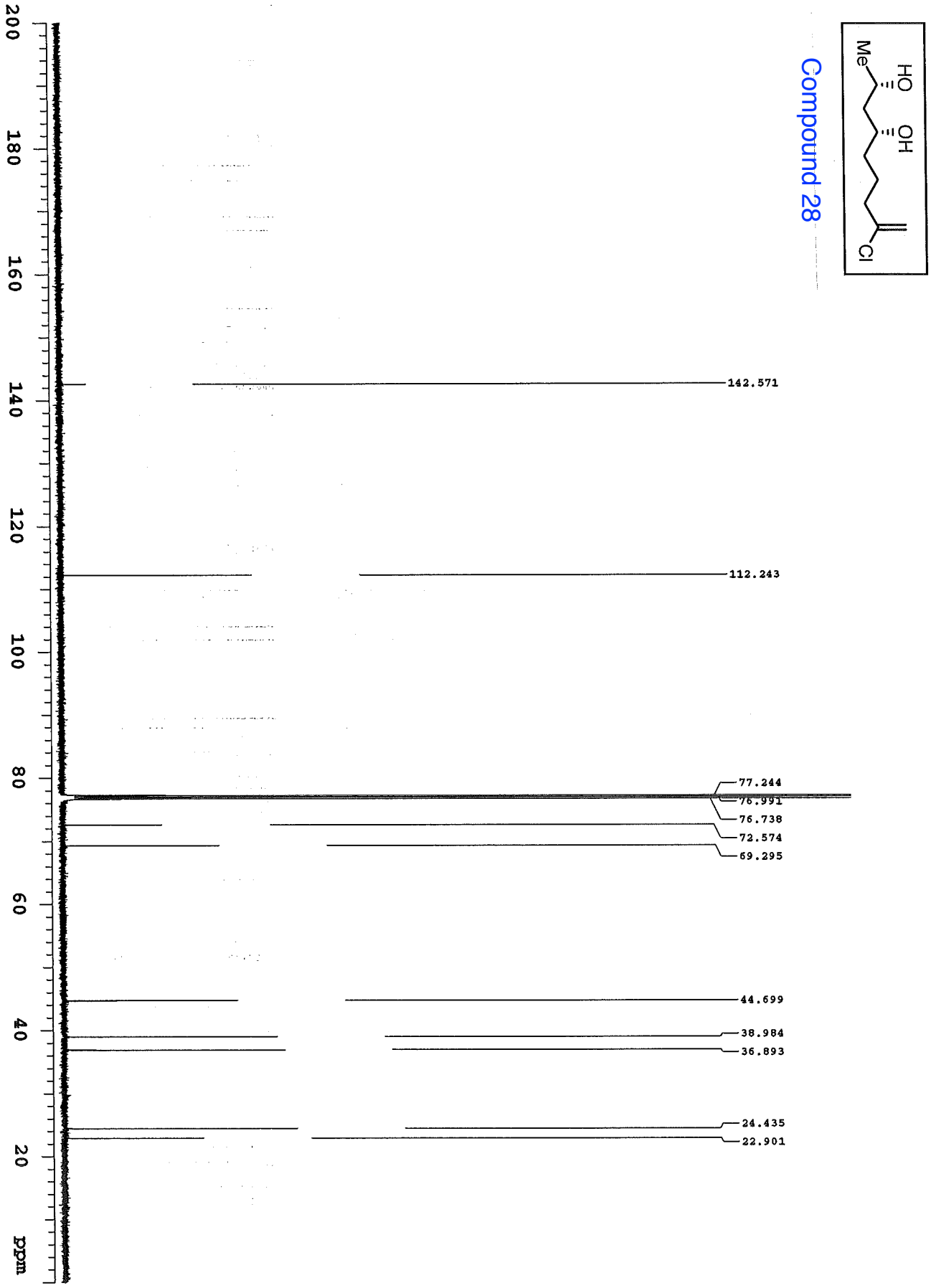

Compound 2
HO
Me
O
OH
O
OH
OH
Me
7.432
7.260
7.083
5.129
5.106
4.981
4.806
4.745
3.646
3.350
3.343
2.692
2.463
2.438
2.432
2.356
2.330
2.289
2.283
2.272
2.261
2.249
2.193
2.183
2.172
2.160
2.102
1.911
1.904
1.867
1.793
1.688
1.618
1.608
1.600
1.538
1.475
1.458
1.447
1.435
1.407
1.250
1.240
1.009
1.07
2.54
0.94
1.08
1.05
1.00
1.42
1.27
1.21
1.45
1.81
1.44
1.75
2.71
1.37
1.75
0.65
2.67
4.06
4.26
3.06
10
9
8
7
6
5
4
3
2
1
ppm


Compound 2
HO
Me
OH
O
O
OH
OH
Me
200
180
160
140
120
100
80
60
40
20
ppm
172.553
145.183
142.528
135.793
129.353
117.982
112.739
77.277
77.016
76.763
71.427
68.822
68.730
68.131
65.560
44.630
44.251
43.627
39.497
38.401
36.858
36.597
35.265
34.363
31.944
29.719
29.609
23.641
23.599
22.706
21.517
20.152


Compound 27
HO
OH
Me
Cl
5.159
5.140
4.184
3.973
3.966
2.387
2.375
2.363
2.314
2.309
2.067
1.739
1.735
1.730
1.727
1.721
1.717
1.641
1.634
1.630
1.627
1.623
1.619
1.616
1.612
1.603
1.593
1.555
1.548
1.542
1.538
1.533
1.525
1.509
1.500
1.491
1.483
1.479
1.474
1.260
1.251
1.230
1.220
2.09
1.02
1.00
2.02
0.96
0.89
1.22
3.35
1.17
1.27
3.79
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


Compound 27
HO
OH
Me
Cl
142.580
112.243
77.244
76.738
69.000
65.612
44.033
38.992
36.168
23.651
23.347
200
180
160
140
120
100
80
60
40
20
ppm


Compound 28
HO
OH
Me
Cl
7.259
5.155
5.136
4.078
4.067
4.056
3.889
3.884
3.880
2.935
2.637
2.376
2.364
2.352
1.719
1.708
1.703
1.699
1.691
1.681
1.644
1.639
1.632
1.627
1.621
1.617
1.604
1.595
1.579
1.537
1.521
1.513
1.503
1.496
1.488
1.480
1.462
1.451
1.253
1.228
1.217
2.10
1.07
1.06
1.00
0.99
2.16
1.09
2.28
3.29
3.40
10
9
8
7
6
5
4
3
2
1
ppm


Compound 28
HO
OH
Me
Cl
200
180
160
140
120
100
80
60
40
20
ppm
142.571
112.243
77.244
76.991
76.738
72.574
69.295
44.699
38.984
36.893
24.435
22.901

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