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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.

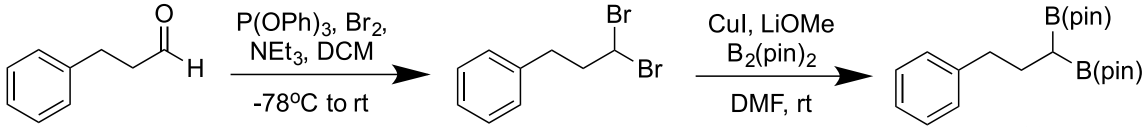
All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Tetrahydrofuran (THF), diethyl ether, dichloromethane and toluene were purified using Pure Solv MD-4 solvent purification system, from Innovative Technology, Inc., by passing the solvent through 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), potassium *tert*-butoxide (KO*t*-Bu) (Aldrich, sublimed grade), palmitic acid-1-^{13}C (Cambridge Isotope Laboratories), 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. Representative Procedures for Preparation of geminal-Diboronate Esters

Method A:

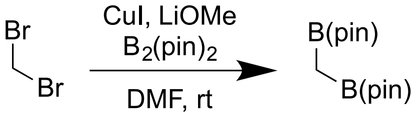


28

The 1,1-dibromide was prepared according to the literature procedure with modification.[1] To a stirred solution of triphenyl phosphite (8.53 g, 27.5 mmol) in anhydrous DCM (250 mL) at –78 °C under N_2 was added bromine (1.41 mL, 27.5 mmol) dropwise. Freshly distilled triethylamine (10.45 mL, 75.0 mmol) and hydrocinnamaldehyde (3.29 mL, 25.0 mmol) were added at –78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 hours. Upon completion, the solvent was evaporated *in vacuo* and the crude reaction mixture was purified on silica gel (100% hexanes) to afford the 1,1-dibromide.

In the glove box, an oven-dried 100 mL round-bottom flask with magnetic stir bar was charged with CuI (190 mg, 1.00 mmol), LiOMe (949 mg, 25.0 mmol) and $B_2(pin)_2$ (5.08 g, 20.0 mmol). The flask was sealed with a rubber septum, removed from the glove box, followed by the addition of DMF (20 mL) under N_2. After stirring at room temperature for 10 min, a solution of 1,1-dibromide (2.92 g, 10.5 mmol) in DMF (5 mL) was added *via* syringe at room temperature. The reaction mixture was allowed to stir at room temperature for 12 hours. Upon completion, 40 mL diethyl ether was added. The slurry was filtered through a silica gel plug, rinsed with diethyl ether, and concentrated *in vacuo*. The crude reaction mixture (DMF solution) was directly purified on silica gel (hexanes: diethyl ether = 10:1) to afford **28** as a white solid (3.09 g, 83%).

Method B:



S1

In the glove box, an oven-dried 500 mL round-bottom flask with magnetic stir bar was charged with CuI (1.428 g, 7.500 mmol), LiOMe (8.543 g, 225 mmol) and $B_2(pin)_2$ (38.09 g, 150.0 mmol). The flask was sealed with a rubber septum, removed from the glove box, followed by the addition of DMF (150 mL) under N_2. After stirring at room temperature for 10 min, dibromomethane (10.53 mL, 150.0 mmol) was added *via* syringe at room temperature. The reaction mixture was allowed to stir at room temperature for 12 hours. Upon completion, 200 mL diethyl ether was added. The slurry was filtered through a silica gel plug, rinsed with diethyl

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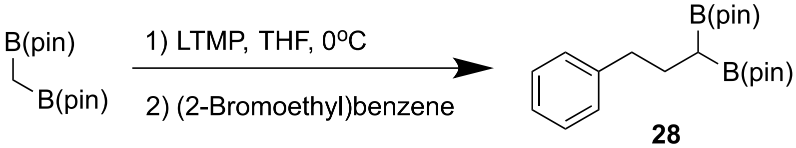
[1] Spaggiari, A.; Vaccari, D.; Davoli, P.; Torre, G.; Prati, F. *J. Org. Chem.* **2007**, *72*, 2216.

ether, and concentrated *in vacuo*. The crude reaction mixture in DMF was diluted with hexanes (300 mL), washed with H_2O (75 mL × 4), dried over Na_2SO_4, then concentrated *in vacuo* to afford **S1** as a white solid (15.72 g, 78%) and used without further purification.

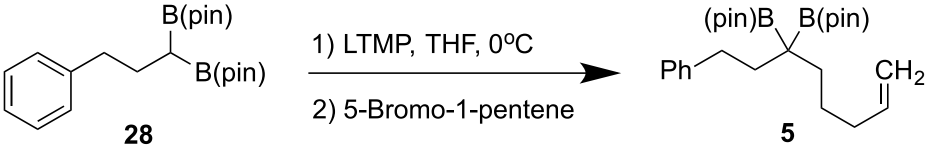
Method C:



28

In the glove box, an oven-dried 25 mL round-bottom flask with magnetic stir bar was charged with LTMP (773 mg, 5.25 mmol). The flask was sealed with a rubber septum, removed from the glove box, followed by the addition of THF (20 mL) under N_2. The reaction mixture was cooled to 0 °C, and a solution of 1,1-diborylmethane (1.34 g, 5.00 mmol) in THF (5 mL) was added *via* syringe and the mixture was allowed to stir at 0 °C for 10 minutes. (2-Bromoethyl)benzene (751 µL, 5.50 mmol) was added dropwise and the reaction was allowed to stir at 0 °C for 15 min. Upon completion, the reaction mixture was warmed to room temperature, filtered through a silica gel plug, rinsed with diethyl ether, and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (hexanes: diethyl ether = 9:1) to afford **28** as a white solid (1.54 g, 83%).

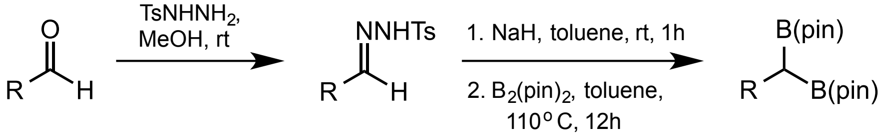
Method D:



28 **5**

In the glove box, an oven-dried 2 dram vial with magnetic stir bar was charged with LTMP (147 mg, 1.0 mmol). The flask was sealed with a rubber septum, removed from the glove box, followed by the addition of THF (2 mL) under N_2. The reaction mixture was cooled to 0 °C, and was transferred into a solution of 1,1-diboronate ester (372 mg, 1.00 mmol) in THF (2 mL) *via* syringe at 0 °C and the mixture was allowed to stir at 0 °C for 10 minutes. Then, 5-bromopent-1-ene (120 µL, 1.0 mmol) was added into the above mixture *via* syringe at 0 °C. The reaction mixture was allowed to stir at 0 °C for 15 min, then warmed to room temperature, filtered through a silica gel plug, rinsed with diethyl ether, and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (hexanes: diethyl ether = 20:1) to afford **5** as a white solid (360 mg, 84%).

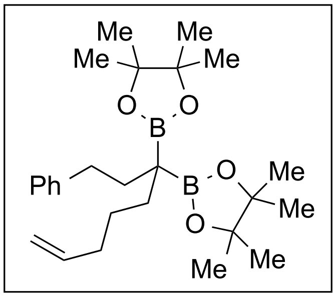
Method E:



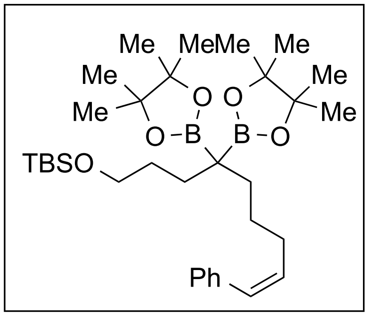
The 1,1-diboronates were prepared according to the literature procedure.[3] A 6-dram vial with magnetic stir bar was charged with aldehyde (1.00 equiv) and tosylhydrazine (1.00 equiv), and methanol (5 mL) was added. The mixture was stirred at room temperature. N-Tosylhydrazone precipitated after 15 minutes or longer and the reaction was monitored by TLC analysis (spot of the carbonyl compound). The precipitate was then collected, washed with pentane (5 mL × 3), and dried under vacuum.

In the glove box, an oven-dried 6-dram vial with a magnetic stir bar was charged with *N*-tosylhydrazone (1.00 mmol, 1.00 equiv), NaH (1.20 mmol, 1.20 equiv), and toluene (8 mL). The mixture was stirred at room temperature for 1 hour. Next, $B_2(pin)_2$ (1.20 mmol, 1.20 equiv) in toluene was added, and the vial was sealed, removed from the glove box and heated at 110 °C for 12 hours. Upon completion, the reaction mixture was allowed to cooled to room temperature, and Et_2O (10 mL) and H_2O (10 mL) were added. The mixture was stirred vigorously for 10 minutes. After separation of the organic layer, the aqueous layer was extracted with Et_2O (2x5 mL). The combined organic layers were washed with saturated brine (10 mL) and dried over anhydrous Na_2SO_4. After the solvent was evaporated, the crude product was purified by silica gel chromatography.

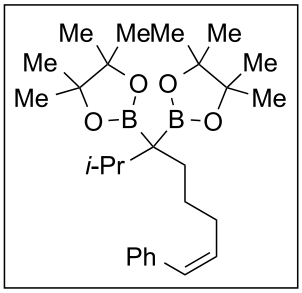
II. Full Characterization of geminal-Diboronate Esters



2,2'-(1-phenyloct-7-ene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5). The reaction was performed according to *Representative Procedure (Method D)* with diboronate ester (372 mg, 1.0 mmol), LTMP (147 mg, 1.0 mmol), 5-bromo-1-pentene (120 μL, 1.0 mmol) and THF (4 mL). The crude reaction mixture was purified by column chromatography on silica gel (20:1 hexanes/diethyl ether, stain in CAM) to afford a white solid (360 mg, 84%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.26-7.23 (m, 2H), 7.20-7.19 (m, 2H), 7.15-7.12 (m, 1H), 5.86 (ddt, *J* = 17.1, 10.3, 6.9 Hz, 1H), 5.01 (ddt, *J* = 17.1, 2.0, 1.5 Hz, 1H), 4.93 (ddt, *J* = 10.3, 2.4, 1.0 Hz , 1H), 2.52-2.49 (m, 2H), 2.10-2.06 (m, 2H), 1.91-1.88 (m, 2H), 1.74-1.71 (m, 2H), 1.41-1.35 (m, 2H), 1.23 (s, 24H); The ^{1}H NMR spectrum was in accord with previously reported data.[2]



(*Z*)-*tert*-butyldimethyl((9-phenyl-4,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)non-8-en-1-yl)oxy)silane) (S2). Prepared according to *Representative Procedure (Method D)* with LTMP (177 mg, 1.0 mmol), diboronate ester **S5** (412 mg, 1.0 mmol), (3-bromopropoxy)-*tert*-butyldimethylsilane (253 mg, 1.0 mmol), and THF (5 mL). The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 50:1) to afford the desired product as a white solid (455 mg, 77%). ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.33 – 7.22 (m, 4H), 7.21 – 7.16 (m,1H), δ 6.36 (d, *J* = 11.7 Hz, 1H), 5.68 (dt, *J* = 11.6, 7.3 Hz, 1H), 3.58 (t, *J* = 7.2 Hz, 2H), 2.31 (dt, *J* = 8.4, 6.5 Hz, 2H), 1.70 – 1.62 (m, 2H), 1.60 – 1.55 (m, 2H), 1.51 – 1.44 (m, 2H), 1.39 – 1.34 (m, 2H), 1.21 (s, 24H), 0.88 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 137.84, 133.44, 128.73, 128.38, 128.02, 126.27, 82.92, 64.32, 30.63, 29.56, 28.95, 27.60, 26.01, 24.74, 24.70, 18.40, -5.18; IR (neat): 2977.1 (m), 2929.4 (m), 2857.6 (w), 1461.6 (w), 1378.1.5 (m), 1371.8 (m), 1355.5 (m), 1307.2 (m), 1139.6 (s), 973.4 (w), 853.3 (m), 853.8 (m), 774.4 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{33}{}^{1}H_{59}{}^{11}B_{2}{}^{16}O_{5}{}^{28}Si_{1}$ [M+H]$^{+}$: calculated: 585.4318, found: 585.4309.



(*Z*)-2,2'-(2-methyl-8-phenyloct-7-ene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (S3). The reaction was performed according to *Representative Procedure (Method D)* with 2,2'-(2-methylpropane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (509 mg, 1.6 mmol, made according to previous procedure [3]), LTMP (236 mg, 1.60 mmol),

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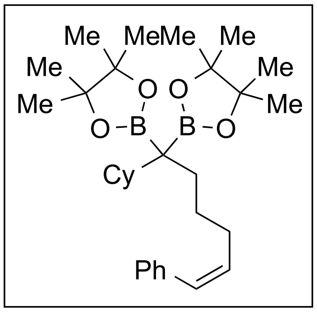
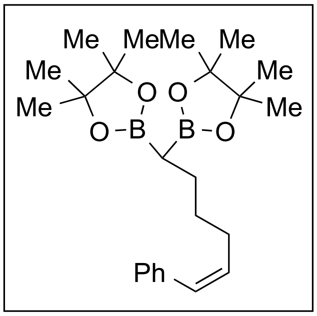
[2] K. Hong, X. Liu, and J. P. Morken *J. Am. Chem. Soc.* **2014**, *136,* 10581.

[3] Li, H.; Shangguan, X.; Zhang, Z.; Huang, S.; Zhang, Y.; Wang, J. *Org. Lett.* **2014**, *16*, 448.

(*Z*)-(5-bromopent-1-en-1-yl)benzene (361 mg, 1.60 mmol) and THF (8 mL). The crude reaction mixture was purified by column chromatography on silica gel (100:1 – 50:1 hexanes/ethyl acetate, stain in CAM) to afford a white solid (530 mg, 83%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.37 – 7.25 (m, 4H), 7.19 (m, 1H), 6.36 (d, *J* = 11.7, 1H), 5.71 (dt, *J* = 11.6, 7.2 Hz, 1H), 2.31 (qd, *J* = 7.4, 1.8 Hz, 2H), 2.04 (p, *J* = 6.8 Hz, 1H), 1.68 – 1.59 (m, 2H), 1.59 – 1.45 (m, 2H), 1.21 (s, 24H), 0.98 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 137.94, 133.70, 128.76, 128.24, 128.01, 126.24, 82.56, 30.04, 29.75, 29.21, 28.42, 24.81, 24.77, 21.29; IR (neat): 2976.8 (m), 2929.6 (m), 1728.5 (w), 1459.8 (w), 1378.0 (m), 1370.6 (m), 1296.1 (s), 1264.8 (m), 1215.1 (w), 1140.7 (s), 972.8 (w), 854.0 (w), 757.8 (s), 699.5 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{27}{}^{1}H_{45}{}^{11}B_2{}^{16}O_4$ [M+H]$^+$: calculated: 455.3504, found: 455.3504.



(*Z*)-2,2'-(1-cyclohexyl-6-phenylhex-5-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**S4**). The reaction was performed according to *Representative Procedure (Method D)* with 2,2'-(cyclohexylmethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (350 mg, 1.0 mmol; made according to previously reported procedure [4]), LTMP (147 mg, 1.0 mmol), (*Z*)-(5-bromopent-1-en-1-yl)benzene (225 mg, 1.60 mmol) and THF (5 mL). The crude reaction mixture was purified by column chromatography on silica gel (100:1 – 50:1 hexanes/ethyl acetate, stain in CAM) to afford a colorless oil (378 mg, 76%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.37 – 7.28 (m, 4H), 7.31 – 7.15 (m, 1H), 6.37 (d, *J* = 11.6, 1H), 5.72 (dt, *J* = 11.6, 7.2 Hz, 1H), 2.30 (qd, *J* = 7.4, 1.8 Hz, 2H), 1.80 – 1.73 (m, 2H), 1.73 – 1.58 (m, 6H), 1.57 – 1.46 (m, 2H), 1.21 (s, 24H), 1.31 – 1.02 (m, 4H), 0.91 – 0.82 (m, 1H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 137.97, 133.80, 128.77, 128.20, 128.02, 126.24, 82.57, 40.24, 31.53, 30.13, 29.41, 28.66, 27.42, 26.96, 24.82, 24.80; IR (neat): 2977.4 (m), 2925.9 (m), 2851.9 (w), 1447.1 (w), 1377.5 (m), 1370.6 (m), 1344.1 (m), 1293.8 (m), 1137.7 (s), 974.0 (w), 850.9 (w), 699.5 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{30}{}^{1}H_{49}{}^{11}B_2{}^{16}O_4$ [M+H]$^+$: calculated: 495.3817, found: 495.3819.



(*Z*)-2,2'-(6-phenylhex-5-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)) (S5). The reaction was performed according to *Representative Procedure (Method D)* with methyl diboronate ester (429 mg, 1.60 mmol), LTMP (236 mg, 1.60 mmol), (*Z*)-(5-bromopent-1-en-1-yl)benzene (361 mg, 1.60 mmol) and THF (8 mL). The crude reaction mixture was purified by column chromatography on silica gel (50:1 – 20:1 hexanes/ethyl acetate, stain in CAM) to afford a white solid (500 mg, 76%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.36 – 7.22 (m, 4H), 7.22 – 7.17 (m, 1H), 6.37 (d, *J* = 11.7 Hz, 1H), 5.67 (dt, *J* = 11.6, 7.3 Hz, 1H), 2.31 (qd, *J* = 7.5, 1.9 Hz, 2H), 1.60 (q, *J* = 7.8 Hz, 2H), 1.50 – 1.40 (m,

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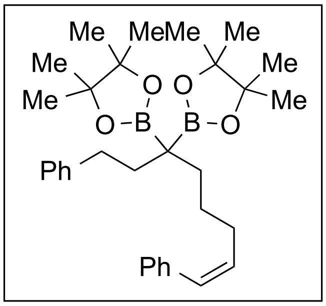
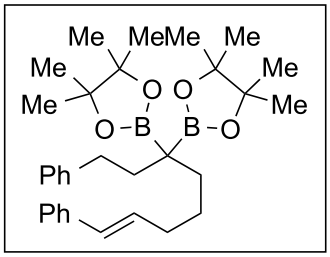
[4] K. Hong, X. Liu, and J. P. Morken *J. Am. Chem. Soc.* **2014**, *136,* 10581.

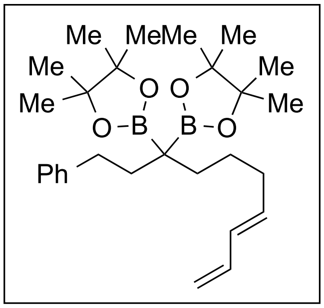
2H), 1.22 (s, 12H), 1.21 (s, 12H), 0.74 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 137.80, 133.28, 128.70, 128.43, 128.02, 126.27, 82.90, 32.88, 28.86, 25.57, 24.83, 24.48; IR (neat): 2976.8 (m), 2927.3 (w), 1368.7 (m), 1311.6 (s), 1267.5 (m), 1214.5 (w), 1139.3 (s), 969.4 (m), 849.7 (m), 699.8 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{24}{}^{1}H_{39}{}^{11}B_2{}^{16}O_4$ [M+H]$^+$: calculated: 413.3034, found: 413.3052.



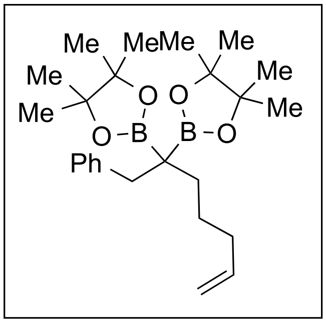
(*Z*)-2,2'-(1,8-diphenyloct-7-ene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)) (37). The reaction was performed according to *Representative Procedure (Method D)* with diboronate ester **30** (441 mg, 1.18 mmol), LTMP (174.5 mg, 1.18 mmol), (*Z*)-(5-bromopent-1-en-1-yl)benzene (267 mg, 1.186 mmol) and THF (6 mL). The crude reaction mixture was purified by column chromatography on silica gel (20:1 hexanes/ethyl acetate, stain in CAM) to afford a white solid (543 mg, 89%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.37 – 7.10 (m, 10H), 6.40 (d, *J* = 11.7 Hz, 1H), 5.73 (dt, *J* = 11.6, 7.3 Hz, 1H), 2.56 – 2.48 (m, 2H), 2.37 (qd, *J* = 7.4, 1.8 Hz, 2H), 1.96 – 1.88 (m, 2H), 1.82 – 1.73 (m, 2H), 1.52 – 1.41 (m, 2H), 1.24 (two sets of singlet, 24H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 143.72, 137.83, 133.38, 128.73, 128.53, 128.46, 128.08, 128.04, 126.32, 125.34, 82.98, 33.83, 31.92, 29.56, 28.95, 27.68, 24.78, 24.71; IR (neat): 2977.2 (m), 2928.4 (w), 1454.5 (w), 1370.5 (m), 1352.4 (m), 1308.8 (s), 1254.6 (m), 1214.1 (w), 1138.1 (s), 968.9 (w), 854.6 (w), 699.2 (m) cm^{-1}. HRMS-(DART+) for $^{12}C_{32}{}^{1}H_{47}{}^{11}B_2{}^{16}O_4$ [M+H]$^+$: calculated: 517.3660, found: 517.3639.



(*E*)-2,2'-(1,8-diphenyloct-7-ene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (21). The reaction was performed according to *Representative Procedure (Method D)* with diboronate ester **30** (1.0 g, 2.69 mmol), LTMP (417 mg, 2.83 mmol), (*E*)-(5-bromopent-1-en-1-yl)benzene (636 mg, 2.83 mmol) and THF (10.8 mL). The crude reaction mixture was purified by column chromatography on silica gel (20:1 hexanes/ethyl acetate, stain in CAM) to afford a white solid (543 mg, 39%). ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.36 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.32 – 7.22 (m, 4H), 7.23 – 7.17 (m, 3H), 7.20 – 7.11 (m, 1H), 6.40 (d, *J* = 15.7 Hz, 1H), 6.28 (dt, *J* = 15.9, 6.7 Hz, 1H), 2.56 – 2.49 (m, 2H), 2.25 (q, *J* = 6.9 Hz, 2H), 1.95 – 1.89 (m, 2H), 1.81 – 1.75 (m, 2H), 1.52 – 1.43 (m, 2H), 1.24 (s, 24H); ^{13}C NMR (150 MHz, CDCl$_3$): δ 143.73, 138.07, 131.42, 129.48, 128.48, 128.40, 128.09, 126.62, 125.91, 125.35, 83.00, 33.86, 33.83, 31.91, 28.77, 27.10, 24.81, 24.71; IR (neat): 2977.5 (w), 2929.4 (w), 1453.7 (w), 1378.5 (m), 1307.6 (m), 1253.4 (m), 1138.4 (s), 967.5 (w), 851.2 (w), 751.4 (m), 698.1 (w) cm^{-1}HRMS-(DART+) for $^{12}C_{32}{}^{1}H_{47}{}^{11}B_2{}^{16}O_4$ [M+H]$^+$: calculated: 517.3660, found: 517.3664.



(*E*)-2,2'-(1-phenyldeca-7,9-diene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (22). The reaction was performed according to *Representative Procedure (Method D)* with diboronate ester **30** (633 mg, 1.7 mmol), LTMP (250 mg, 1.7 mmol), (*E*)-7-bromohepta-1,3-diene (296 mg, 1.7 mmol) and THF (7 mL). The crude reaction mixture was purified by column chromatography on silica gel (50:1 hexanes/ethyl acetate, stain in CAM) to afford a white solid (713 mg, 90%). ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.28 – 7.10 (m, 5H), 6.32 (dt, *J* = 17.0, 10.3 Hz, 1H), 6.06 (dd, *J* = 15.3, 10.3 Hz, 1H), 5.75 (dt, *J* = 14.5, 6.8 Hz, 1H), 5.08 (dd, *J* = 17.0, 1.7 Hz, 1H), 4.94 (dd, *J* = 10.1, 1.7 Hz, 1H), 2.53 – 2.47 (m, 2H), 2.11 (q, *J* = 7.2 Hz, 2H), 1.92 – 1.86 (m, 2H), 1.75 – 1.69 (m, 2H), 1.42 – 1.34 (m, 2H), 1.23 (s, 24H); ^{13}C NMR (150 MHz, CDCl$_3$): δ 143.74, 137.52, 135.85, 130.64, 128.48, 128.09, 125.35, 114.37, 82.99, 33.84, 33.34, 31.87, 28.76, 26.89, 24.80, 24.71; IR (neat): 2976.8 (w), 2929.1 (w), 1455.0 (w), 1378.0 (m), 1305.6 (m), 1252.2 (m), 1137.0 (s), 1003.9 (m), 852.2 (m), 699.2 (w) cm^{-1}; HRMS-(DART+) for ^{12}C$_{28}$^{1}H$_{45}$^{11}B$_2$^{16}O$_4$ [M+H]$^+$: calculated: 467.3504, found: 467.3519.



2,2'-(1-phenylhept-6-ene-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)) (S6). The reaction was performed according to *Representative Procedure (Method D)* with 2,2'-(2-phenylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (429.7mg, 1.2 mmol, made according to previous procedure[5]), LTMP (194.3 mg, 1.32 mmol), 5-bromo-1-pentene (197 mg, 1.32 mmol) and THF (6 mL). The crude reaction mixture was purified by column chromatography on silica gel (50:1 hexanes/ethyl acetate, stain in CAM) to afford a colorless oil (450 mg, 88%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.26 – 7.17 (m, 4H), 7.15 – 7.07 (m, 1H), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 4.97 (dq, *J* = 17.2, 1.8 Hz, 1H), 4.90 (ddt, *J* = 10.2, 2.4, 1.3 Hz, 1H), 2.97 (s, 2H), 2.00 (q, *J* = 7.1 Hz, 2H), 1.56 – 1.51 (m, 2H), 1.49 – 1.41 (m, 2H), 1.24 (s, 12H), 1.20 (s, 12H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 141.82, 139.32, 129.70, 127.65, 125.41, 113.82, 83.16, 34.58, 34.44, 28.45, 26.77, 25.00, 24.69; IR (neat): 2978.4 (m), 2931.7 (w), 2862.9 (m), 1378.4 (m), 1353.4 (m), 1261.8 (m), 1138.8 (s), 854.3 (w), 699.9 (w) cm^{-1}; HRMS-(DART+) for ^{12}C$_{25}$^{1}H$_{41}$^{11}B$_2$^{16}O$_4$ [M+H]$^+$: calculated: 427.3191, found: 427.3189.

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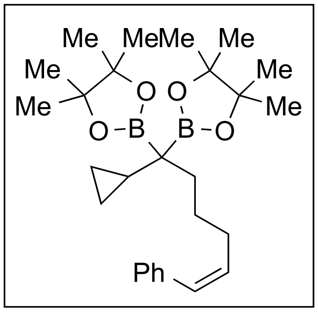
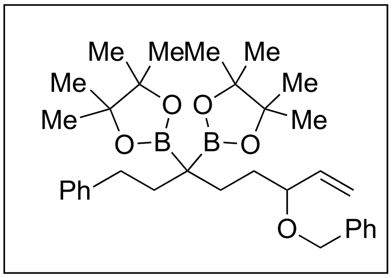


(*Z*)-2,2'-(1-cyclopropyl-6-phenylhex-5-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**31**). The reaction was performed according to *Representative Procedure (Method D)* with 2,2'-(cyclopropylmethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (154 mg, 0.5 mmol, made according to previous procedure [6]), LTMP (77.3 mg, 0.53 mmol), (*Z*)-(5-bromopent-1-en-1-yl)benzene (118.2 mg, 0.53mmol) and THF (2 mL). The crude reaction mixture was purified by column chromatography on silica gel (100:1 – 50:1 hexanes/ethyl acetate, stain in CAM) to afford a white solid (226 mg, 86%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.42 – 7.24 (m, 4H), 7.25 – 7.17 (m, 1H), 6.38 (d, *J* = 11.7 Hz, 1H), 5.73 (dt, *J* = 11.5, 7.7 Hz, 1H), 2.35 (q, *J* = 7.0 Hz, 2H), 1.82 – 1.53 (m, 4H), 1.22 (s, 24H), 0.86 (tt, *J* = 8.1, 5.6 Hz, 1H), 0.49 – 0.28 (m, 4H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 137.92, 133.70, 128.76, 128.28, 128.02, 126.26, 82.76, 33.04, 29.80, 28.64, 24.72, 24.71, 12.93, 3.62; IR (neat): 2977.3 (m), 2931.1 (w), 1378.7 (m), 1342.2 (m), 1305.2 (s), 1268.1 (m), 1214.4 (w), 1137.5 (s), 853.5 (w), 699.2 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{30}{}^{1}H_{49}{}^{11}B_2{}^{16}O_4$ [M+H]$^+$: calculated: 495.3817, found: 495.3819.



2,2'-(6-(benzyloxy)-1-phenyloct-7-ene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)) (**S7**). The reaction was performed according to *Representative Procedure (Method D)* with diboronate ester **28** (186 mg, 0.5 mmol), LTMP (73.6 mg, 0.5 mmol), 3-(benzyloxy)pent-4-en-1-yl 4-methylbenzenesulfonate (193 mg, 0.56 mmol) and THF (5 mL). The crude reaction mixture was purified by column chromatography on silica gel (100:2 – 100:4 hexanes/ethyl acetate, stain in CAM) to afford a colorless oil (220 mg, 81%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.37 – 7.30 (m, 4H), 7.26 – 7.21 (m, 3H), 7.20 – 7.16 (m, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 5.84 – 5.69 (m, 1H), 5.25 – 5.22 (m, 2H), 4.60 (d, *J* = 12.1 Hz, 1H), 4.40 (d, *J* = 12.1 Hz, 1H), 3.73 (q, *J* = 6.8 Hz, 1H), 2.50 (td, *J* = 7.3, 3.7 Hz, 2H), 1.88 (dd, *J* = 10.7, 6.9 Hz, 2H), 1.80 – 1.63 (m, 3H), 1.59 – 1.50 (m, 1H), 1.22 (s, 24H); ^{13}C NMR (150 MHz, CDCl$_3$): δ 143.76, 139.03, 128.51, 128.21, 128.07, 127.58, 127.20, 125.32, 117.22, 82.99, 81.33, 69.77, 33.79, 32.81, 31.96, 24.91, 24.78, 24.65; IR (neat): 2977.4 (m), 2932.1 (w), 1378.5 (w), 1370.5 (w), 1309.9 (s), 1138.56 (s), 851.8 (w), 698.5 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{33}{}^{1}H_{52}{}^{11}B_2{}^{16}O_5{}^{14}N_1$ [M+NH$_4$]$^+$: calculated: 564.4032, found: 564.4058.

The 3-(benzyloxy)pent-4-en-1-yl 4-methylbenzenesulfonate was prepared as shown in the scheme below:

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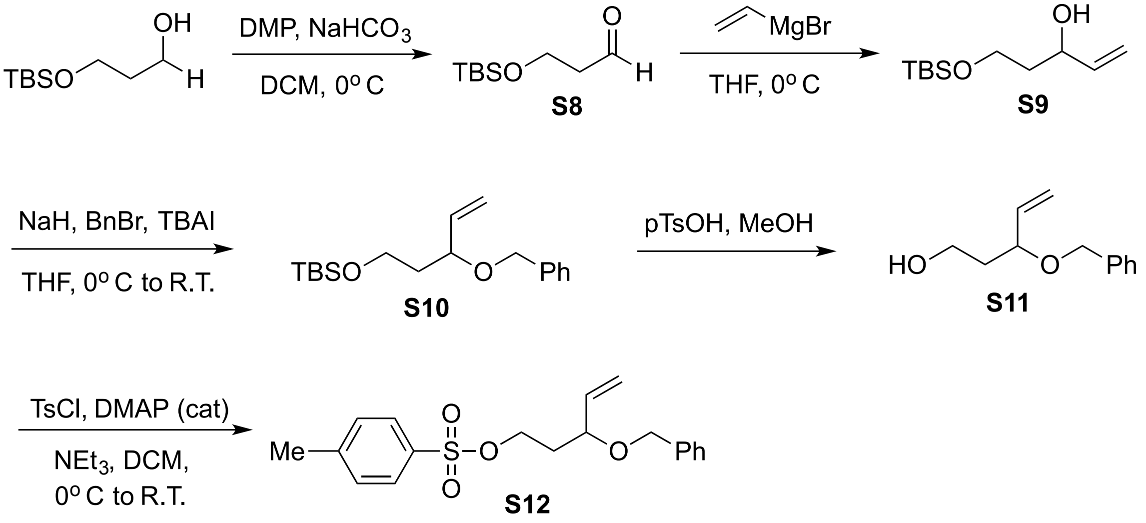
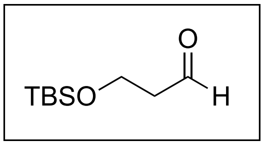
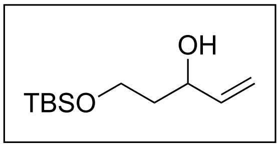
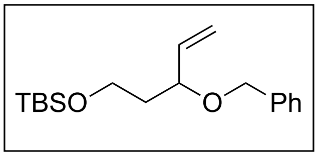




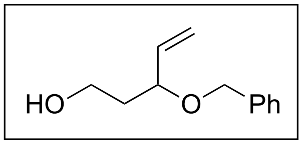
3-((*tert*-butyldimethylsilyl)oxy)propanal (S8). To an oven dried 20 mL vial, 3-((*tert*-butyldimethylsilyl)oxy)propan-1-ol (522 mg, 2.9 mmol) is added followed by anhydrous DCM (6 mL). The solution is brought to 0°C then Dess-Martin periodinane (1.48 g, 3.48 mmol) and $NaHCO_3$ (1.22 g, 14.5 mmol) added. The reaction is then allowed to stir for 4h, gradually reaching room temperature. At this point, the mixture is concentrated *in vacuo* then extracted with 1:1 hexane/Et_2O and the combined extracts filtered through a pad of silica gel, rinsing with 1:1 hexane/Et_2O. The filtrate is concentrated *in vacuo* and the resulting crude oil is purified by column chromatography on silica gel (80:20 pentane/diethyl ether, stain in PMA) to afford a clear colorless oil (380 mg, 69%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.80 (s, 1H), 3.98 (t, *J* = 6.0 Hz, 2H), 2.59 (td, *J* = 6.1, 2.0 Hz, 2H), 0.88 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.95, 57.38, 46.55, 25.78, 18.19, -5.47; IR (neat): 2868.7 (m), 1725.6 (w), 1256.2 (w), 1141.3 (s), 908.6 (s), 835.7 (s), 778.1 (m), 732.3 (s) cm^{-1}; HRMS-(DART+) for $^{12}C_9{}^1H_{21}{}^{28}Si^{16}O_2$ $[M+H]^+$: calculated: 189.1311, found: 189.1319.



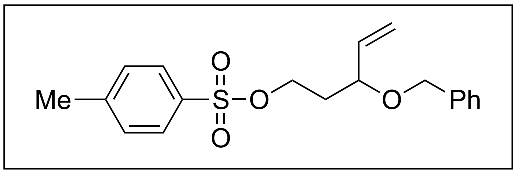
5-((*tert*-butyldimethylsilyl)oxy)pent-1-en-3-ol (S9). An oven-dried 125 mL round bottom flask fitted with magnetic stir bar is sealed and evacuated/refilled with N_2 3x then charged with 3-((*tert*-butyldimethylsilyl)oxy)propanal **(S8)** (3.18 g, 16.9 mmol) followed by anhydrous THF (32 mL). The vessel and contents are then cooled to 0°C and vinylmagnesium bromide solution (33.8 mL, 1 M in THF, 33.8 mmol) added across ca. 15 min. The resulting clear, yellow solution is allowed to stir overnight at room temperature, then quenched with a saturated aqueous solution of ammonium chloride. The reaction mixture is then poured into a separatory funnel where it is diluted with DI water and the organics are extracted with diethyl ether 5x. The combined organics are dried over Na_2SO_4 then concentrated *in vacuo*. The crude residue is then purified by column chromatography on silica gel (100:3 to 80:20 pentane/diethyl ether, stain in $KMnO_4$) to afford a orange clear oil. (1566 mg, 43%). <u>^{1}H NMR</u> (500 MHz, $CDCl_3$): δ 6.01 – 5.77 (m, 1H), 5.29 (dd, *J* = 17.2, 2.1 Hz, 1H), 5.11 (dd, *J* = 10.5, 2.1 Hz, 1H), 4.39 – 4.33 (m, 1H), 3.95 – 3.87 (m, 1H), 3.81 (ddt, *J* = 10.1, 7.3, 4.1 Hz, 1H), 3.31 (d, *J* = 3.6 Hz, 1H), 1.85 – 1.67 (m, 2H), 0.91 (s, 9H), 0.08 (s, 6H); <u>^{13}C NMR</u> (125 MHz, $CDCl_3$): δ 140.51, 113.98, 72.32, 61.79, 38.15, 25.72, 18.00, -5.65; <u>IR</u> (neat): 3462.4(broad), 2954.5 (w), 2857.9 (w), 1255.4 (w), 1082.1 (w), 906.4 (s), 834.6 (s), 777.4 (m), 729.4 (s), 648.5 (m) cm^{-1}; <u>HRMS</u>-(DART+) for $^{12}C_{11}{}^1H_{25}{}^{28}Si_1{}^{16}O_2$ [M+H]$^+$: calculated: 217.1624, found: 217.1632.



((3-(benzyloxy)pent-4-en-1-yl)oxy)(*tert*-butyl)dimethylsilane) (S10). An oven-dried 20 mL vial is charged with sodium hydride (220 mg, 60 wt%, 5.5 mmol), and anhydrous THF (5 mL) then cooled to 0°C. A solution of 5-((*tert*-butyldimethylsilyl)oxy) pent-1-en-3-ol **(S9)** (237 mg, 1.1 mmol) in anhydrous THF (2 mL) is then gradually added to the reaction vessel and the resulting mixture allowed to stir for 30 minutes at 0°C. Benzyl bromide (0.17 mL, 1.43 mmol) is then added followed by tetrabutylammonium iodide (122 mg, 0.33 mmol). The resulting light yellow slurry is allowed to stir overnight, gradually warming to room temperature. Upon return, the mixture is brought back to 0°C where it is quenched by a saturated aqueous solution of ammonium chloride. Organics are then extracted with diethyl ether 3x and combined organics dried over Na_2SO_4, and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (100:2 to 100:5 pentane/diethyl ether, stain in $KMnO_4$) to afford a clear colorless oil (313 mg, 89%). <u>^{1}H NMR</u> (500 MHz, $CDCl_3$): δ 7.28 – 7.23 (m, 3H), 7.22 – 7.16 (m, 2H), 5.73 – 5.64 (m, 1H), 5.21 – 5.12 (m, 2H), 4.52 (d, *J* = 11.7 Hz, 1H), 4.28 (d, *J* = 11.6 Hz, 1H), 3.93 – 3.83 (m, 1H), 3.67 (ddd, *J* = 10.1, 7.2, 5.8 Hz, 1H), 3.63 – 3.58 (m, 1H), 1.80 (ddt, *J* = 13.7, 7.7, 5.9 Hz, 1H), 1.69 – 1.58 (m, 1H), 0.81 (s, 9H), -0.04 (s, 6H); <u>^{13}C NMR</u> (125 MHz, $CDCl_3$): δ 138.89, 128.27, 127.75, 127.68, 127.35, 116.98, 70.23, 59.31, 38.72, 25.91, 18.25, -5.35; <u>IR</u> (neat): 2953.7 (w), 2928.0 (w), 2856.4 (w), 1253.8 (m), 1090.6 (s), 925.3 (m), 834.8 (s), 775.2 (m), 733.2 (m), 696.7 (w) cm^{-1}; <u>HRMS</u>-(DART+) for $^{12}C_{18}{}^1H_{31}{}^{28}Si_1{}^{16}O_2$ [M+H]$^+$: calculated: 307.2093, found: 307.2089.

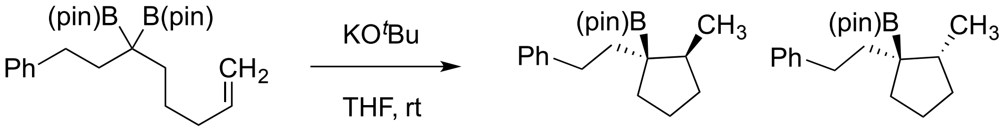


3-(benzyloxy)pent-4-en-1-ol (S11). A 125 mL round bottom flask is charged with ((3-(benzyloxy)pent-4-en-1-yl)oxy)(*tert*-butyl) dimethylsilane) **(S10)** (180 mg, 0.54 mmol), and THF (54 mL) then cooled to 0°C and HCl (0.54 mL, 1N, 0.54 mmol) slowly added. The resulting clear, colorless solution is then allowed to stir at 4°C overnight. Upon completion, the reaction is cooled to 0°C and slowly treated with saturated, aqueous $NaHCO_3$ solution (0.54 mL). The mixture is then concentrated *in vacuo* and the crude residue purified by column chromatography on silica gel (100:3 to 80:20 pentane/diethyl ether, stain in $KMnO_4$) to afford a clear colorless oil (101 mg, 86%). <u>^{1}H NMR</u> (500 MHz, $CDCl_3$): δ 7.36 – 7.15 (m, 5H), 5.73 (ddd, *J* = 17.6, 10.5, 7.8 Hz, 1H), 5.20 (d, *J* = 17.1 Hz, 1H), 5.19 (d, *J* = 10.5 Hz, 1H), 4.56 (d, *J* = 11.8 Hz, 1H), 4.29 (d, *J* = 11.7 Hz, 1H), 3.95 (td, *J* = 8.0, 4.4 Hz, 1H), 3.79 – 3.61 (m, 2H), 2.31 (dd, *J* = 6.5, 4.4 Hz, 1H), 1.81 (dtd, *J* = 15.3, 7.7, 4.2 Hz, 1H), 1.73 (ddt, *J* = 10.5, 6.7, 4.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.17, 138.10, 128.45, 127.79, 127.68, 117.51, 79.88, 70.29, 60.58, 37.79; IR (neat): 3383.2 (w, broad), 2865.8 (w), 1454.3(w), 1055.7 (s), 927.9 (m), 736.3 (m), 698.0 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{12}{}^{1}H_{17}{}^{16}O_2$ $[M+H]^+$: calculated: 193.1229, found: 193.1229.



3-(benzyloxy)pent-4-en-1-yl 4-methylbenzenesulfonate (S12). An oven dried 20 mL vial equipped with magnetic stir bar is charged with 4-toluenesulfonyl chloride (203.4 mg, 1.07 mmol), DMAP (11.8 mg, 0.097 mmol), DCM (2 mL), and reagent grade triethylamine (0.27 mL, 1.94 mmol) in succession. The vessel and contents are then cooled to 0°C and a solution of 3-(benzyloxy)pent-4-en-1-ol **(S11)** (187 mg, 0.97 mmol) in DCM (2 mL) is slowly added under nitrogen protection. The resulting clear-yellow solution is then allowed to stir overnight and upon return is quenched by DI H_2O. The organics are then extracted with DCM, and dried over Na_2SO_4 and the combined organics concentrated *in vacuo*. The crude residue is then purified by column chromatography on silica gel (50:1 to 100:5 hexanes/ethyl acetate, stain in $KMnO_4$) to afford a clear colorless oil (268 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 – 7.75 (m, 2H), 7.35 – 7.29 (m, 2H), 7.29 – 7.27 (m, 1H), 7.24 – 7.21 (m, 2H), 5.67 (ddd, *J* = 17.1, 10.4, 7.7 Hz, 1H), 5.25 – 5.19 (m, 2H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.27 – 4.17 (m, 2H), 4.10 (dt, *J* = 9.7, 5.6 Hz, 1H), 3.87 (td, *J* = 8.0, 4.9 Hz, 1H), 2.42 (s, 3H), 2.02 – 1.80 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.68, 138.18, 137.61, 133.09, 129.79, 128.32, 127.90, 127.66, 127.55, 118.15, 76.47, 70.36, 67.15, 34.86, 21.60; IR (neat): 2927.4 (w), 2865.8 (w), 1598.2 (w), 1496.2 (w), 1454.5 (w),1359.8 (m), 1176.5 (s), 916.0 (m), 836.7 (w), 739.9 (w), 664.0 (m), 554.5 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{19}{}^{1}H_{26}{}^{14}N_1{}^{32}S_1{}^{16}O_4$ $[M+NH_4]^+$: calculated: 364.1583, found: 364.158.

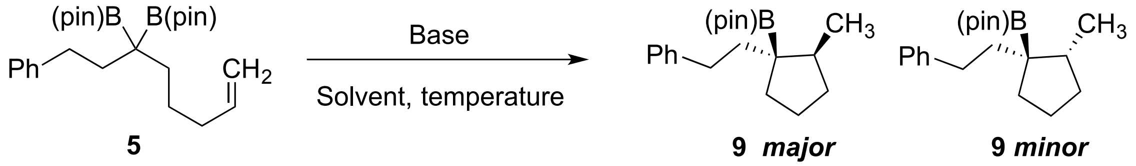
III. Representative Procedure for Deborylative Cyclization



5 **9** ***major*** **9** ***minor***

In the glove box, an oven-dried 2-dram vial equipped with magnetic stir bar is charged with 1,1-diboronate ester **5** (48.4 mg, 0.10 mmol), base (0.20 mmol) and THF (0.50 mL). The vial is sealed with a polypropylene cap, removed from the glove box, and allowed to stir at room temperature for overnight. Upon completion, the reaction mixture is diluted with wet diethyl ether (2 mL), filtered through a silica gel plug, rinsed with diethyl ether, and concentrated *in vacuo*. The crude reaction mixture is then purified on silica gel (hexanes: ethyl acetate = 100 : 0.8) to afford the desired product **9** ***major*** and **9** ***minor***.

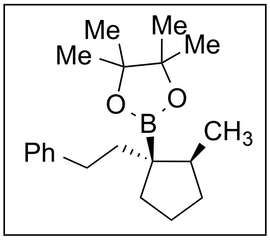
IV. Table S1. Full Optimization[a]



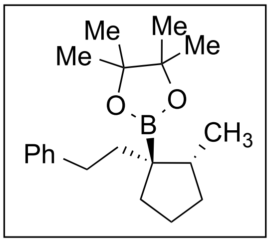
entry	base	solvent	yield (%)	d.r. (9 major : 9 minor)
1	NaO*t*-Bu	THF	12	13 : 1
2	NaO*t*-Bu	toluene	<5	N/A
3	KOMe	toluene	<5	N/A
4	KO*t*-Bu	DCE	<5	N/A
5	KO*t*-Bu	hexanes	39	2.2 : 1
6	KO*t*-Bu	THF	51	5 : 1 [b]
7	KO*t*-Bu	THF	52	4 : 1
8	KO*t*-Bu	toluene	52	2 : 1 [b]
9	KO*t*-Bu	toluene	61	1.2 : 1

[a] Reaction conditions: 1,1-diboronate ester (0.10 mmol, 0.2 M), and base (0.20 mmol). Yield refers to the isolated yield of purified material. Diastereoselectivity was determined based on NMR integration. [b] Reaction conducted at 50 °C.

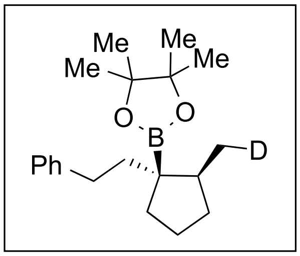
V. Full Characterization of Reaction Products and Proof of Stereochemistry



4,4,5,5-tetramethyl-2-(2-methyl-1-phenethylcyclopentyl)-1,3,2-dioxaborolane (9, *major diastereomer*). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **5** (88 mg, 0.2 mmol), KO*t*-Bu (44.8 mg, 0.4 mmol) and THF (1 mL). The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 100 : 0.8) to afford the desired product as a colorless oil (32.7 mg, 52%, 4:1 dr). <u>^{1}H NMR</u> (500 MHz, $CDCl_3$): δ 7.28-7.25(m, 2H), 7.20 (d, J = 7.3 Hz, 2H), 7.16 (t, J = 7.3 Hz, 1H), 2.59-2.53 (m, 2H), 2.05-1.95 (m, 2H), 1.84-1.78 (m, 1H), 1.77-1.70 (m, 1H), 1.64-1.56 (m, 2H), 1.40-1.22 (m,3H), 1.27 (12H, s, overlap), 1.00 (d, J = 6.9 Hz, 3H); The ^{1}H NMR spectrum was in accord with previously reported data.[7]



4,4,5,5-tetramethyl-2-(1-phenyltetradecan-2-yl)-1,3,2-dioxaborolane (9, *minor diastereomer*). <u>^{1}H NMR</u> (500 MHz, $CDCl_3$): δ 7.27 (t, J = 7.3 Hz, 2H), 7.21 (d, J = 7.3 Hz, 2H), 7.18-7.15 (m, 1H), 2.58-2.49 (m, 2H), 2.04 (sx, J = 7.3 Hz, 1H), 1.89-1.83 (m, 1H), 1.79-1.54 (m, 5H), 1.44-1.36 (m, 1H), 1.31-1.24 (m, 1H), 1.27 (s, overlap, 12H), 0.91 (dd, J = 7.3, 1.4 Hz, 3H); The ^{1}H NMR spectrum was in accord with previously reported data.[8]



4,4,5,5-tetramethyl-2-((1*R*,2*S*)-2-(methyl-*d*)-1-phenethylcyclopentyl)-1,3,2-dioxaborolane (10). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **5** (88 mg, 0.2 mmol), KO*t*-Bu (44.8 mg, 0.4 mmol) and THF (1 mL). Upon completion, the reaction mixture was quenched with D_2O (100 μL, 5.0 mmol), then diluted with diethyl ether (2 mL) and filtered through a silica gel plug, rinsing with diethyl ether, and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a colorless oil (28.1 mg, 45%, > 20:1 dr). <u>^{1}H NMR</u> (500 MHz, $CDCl_3$): δ 7.27 (t, J = 7.6 Hz, 2H), 7.23 – 7.14 (m, 3H), 2.63 – 2.50 (m, 2H), 2.07 – 1.92 (m, 2H), 1.86 – 1.68 (m, 2H), 1.63 – 1.55 (m, 2H), 1.39 – 1.20 (m, 3H), 1.27 (s, 12H), 0.99 (d, J = 7.0, 2H); <u>^{13}C NMR</u> (125 MHz, $CDCl_3$): δ 143.88, 128.30, 128.19, 125.40, 125.40, 82.89, 44.93, 41.24, 34.26, 34.19, 34.14, 25.28, 24.82, 22.70, 17.63, 17.50, 17.37; <u>IR</u> (neat): 2977.4 (m), 2931.9 (m), 2857.6 (w), 1730.2 (w), 1454.4 (w), 1387.8 (m), 1301.7 (m), 1195.1 (w), 1143.6 (s), 966.8 (w), 855.5 (w), 748.8 (w), 698.9 (w) cm^{-1}; <u>HRMS</u>-(DART+) for $^{12}C_{20}{}^1H_{31}{}^2D_1{}^{11}B_1{}^{16}O_2$ $[M+H]^+$: calculated: 316.2558, found: 316.2560.

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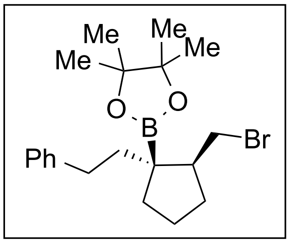
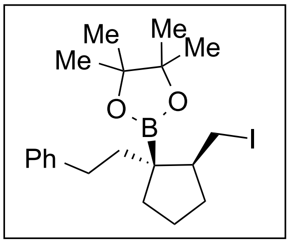
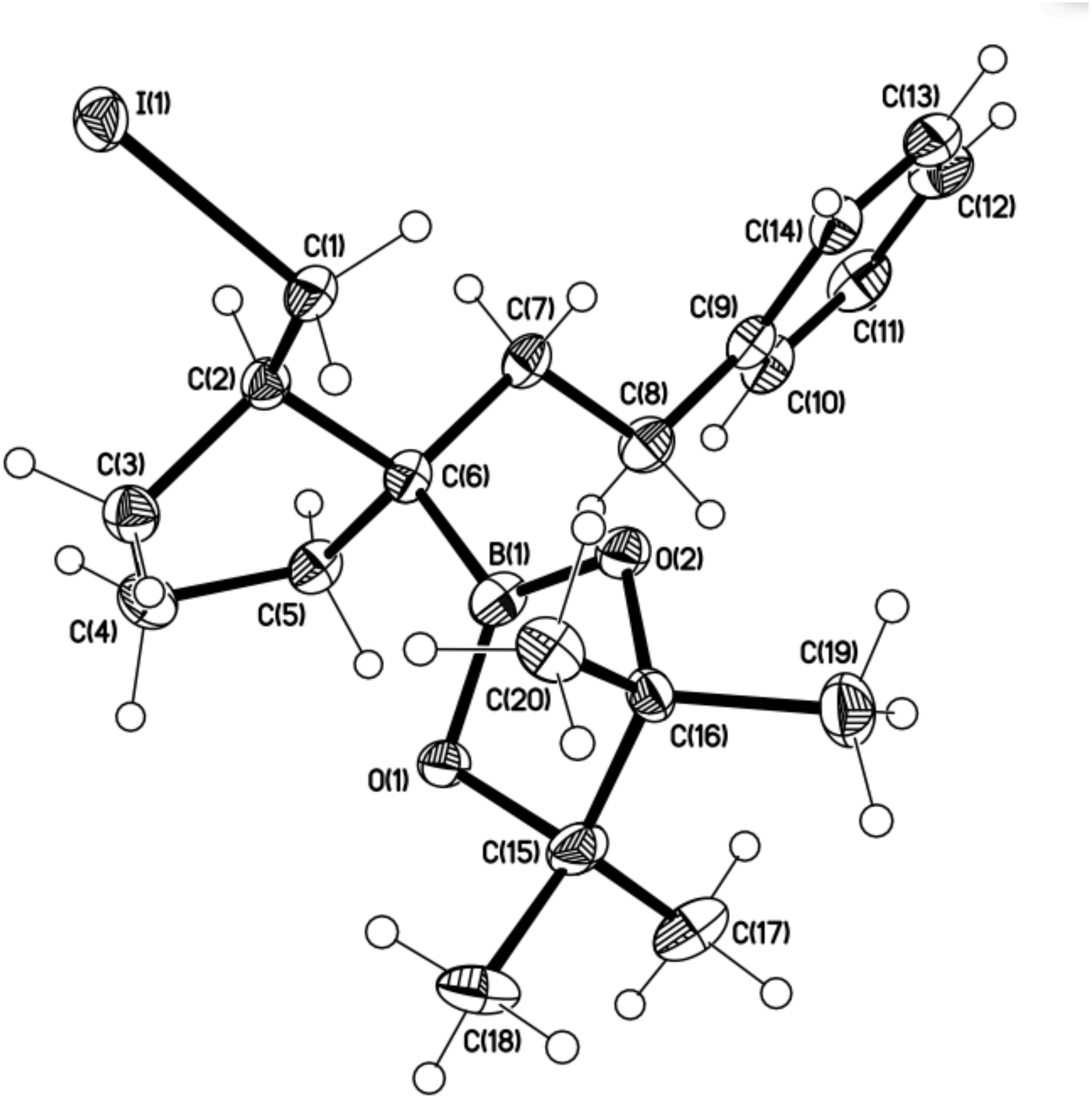
[7] K. Hong, X. Liu, and J. P. Morken *J. Am. Chem. Soc.* **2014**, *136,* 10581.

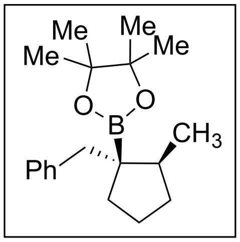


2-((1*R*,2*S*)-2-(bromomethyl)-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11). The reaction was performed according to *Representative Procedure for Deborylative Cyclization n* with 1,1-diboronate ester **5** (88 mg, 0.2 mmol), KO*t*-Bu (44.8 mg, 0.4 mmol) and THF (1 mL). Upon completion, the reaction mixture was quenched with NBS (71.2 mg, 0.4 mmol) in anhydrous THF (1 mL), then diluted with diethyl ether (2 mL) and filtered through a silica gel plug, rinsing with diethyl ether. Filtrate was then concentrated *in vacuo* and crude purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a white solid (40.3 mg, 51.2%, >20:1 dr). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.23 (m, 3H), 7.18 (dd, *J* = 7.7, 1.1 Hz, 2H), 3.72 (dd, *J* = 9.6, 3.7 Hz, 1H), 3.37 (dd, *J* = 11.4, 9.6 Hz, 1H), 2.62 – 2.50 (m, 2H), 2.18 – 2.04 (m, 2H), 2.06 – 1.91 (m, 2H), 1.79 – 1.56 (m, 2H), 1.51 – 1.37 (m, 3H), 1.26 (d, *J* = 1.6 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.13, 128.30, 128.23, 125.64, 83.31, 53.24, 41.18, 37.96, 35.71, 33.87, 32.22, 25.10, 24.82, 22.35; IR (neat): 2976.4 (m), 2956.2 (m), 2932.3 (m), 2868.7 (w), 1454.3 (w), 1381.0 (m), 1312.3 (m), 1210.3 (m), 1142.9 (s), 967.1 (w), 855.0 (w), 748.5 (w), 698.8 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{20}{}^{1}H_{31}{}^{11}B_{1}{}^{79}Br_{1}{}^{16}O_{2}$ $[M+H]^+$: calculated: 393.1601, found: 393.1608.

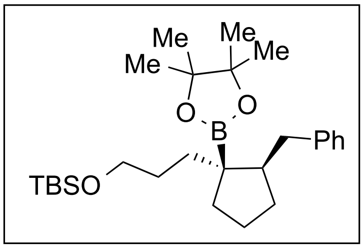


2-((1*R*,2*S*)-2-(iodomethyl)-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **5** (88 mg, 0.2 mmol), KO*t*-Bu (44.8 mg, 0.4 mmol) and THF (1 mL). Upon completion, the reaction mixture was quenched with I_2 (101.5 mg, 0.4 mmol) in anhydrous THF (1 mL), then diluted with diethyl ether (2 mL) and filtered through a silica gel plug, rinsing with diethyl ether. Filtrate was then concentrated *in vacuo* and the crude residue purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a white solid (43mg, 49%, >20:1 dr, crude NMR shows the same diastereoselectivity). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30 – 7.24 (m, 2H), 7.22 – 7.14 (m, 3H), 3.53 (dd, *J* = 9.4, 3.3 Hz, 1H), 3.14 (dd, *J* = 12.1, 9.4 Hz, 1H), 2.61 – 2.50 (m, 2H), 2.20 – 2.10 (m, 2H), 2.04 – 1.94 (m, 2H), 1.81 – 1.70 (m, 1H), 1.69 – 1.57 (m, 1H), 1.48 – 1.40 (m, 2H), 1.43 – 1.32 (m, 1H), 1.26 (s, 6H) , 1.26 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.13, 128.30, 128.22, 125.64, 83.30, 53.97, 41.19, 36.08, 33.90, 25.11, 24.82, 21.83, 11.61; IR (neat): 2976.5 (m), 2956.3 (m), 2932.3 (m), 2867.2 (w), 1454.1 (w), 1380.7 (m), 1345.3 (m), 1210.3 (w), 1142.4 (s), 966.8 (w), 854.2 (w), 755.1 (m), 698.4 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{20}{}^{1}H_{31}{}^{11}B_{1}{}^{127}I_{1}{}^{16}O_{2}$ $[M+H]^+$: calculated: 441.1462, found: 441.1478. The relative stereochemistry was assigned by X-ray crystallography.

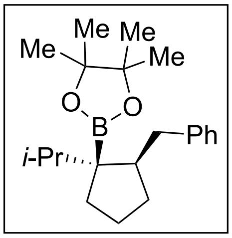




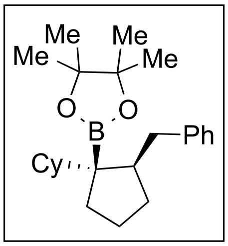
2-((1*R*,2*S*)-1-benzyl-2-methylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **S6** (85.2 mg, 0.2 mmol), KO*t*-Bu (44.8 mg, 0.4 mmol) and THF (1 mL). The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a colorless oil (39.2 mg, 65%, > 20:1 dr, crude NMR shows the same diastereoselectivity). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27 – 7.18 (m, 4H), 7.17 – 7.10 (m, 1H), 2.97 (d, *J* = 13.2 Hz, 1H), 2.43 (d, *J* = 13.3 Hz, 1H), 1.87 – 1.79 (m, 2H), 1.75 – 1.50 (m, 3H), 1.47 – 1.36 (m, 1H), 1.30 – 1.20 (m, 1H), 1.19 (s, 6H), 1.14 (s, 6H), 1.05 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.15, 130.14, 127.56, 125.49, 82.91, 44.35, 42.89, 33.97, 33.77, 25.14, 24.93, 22.24, 17.55; IR (neat): 2976.8 (m), 2953.6 (m), 2930.1 (m), 2869.0 (w), 1453.4 (w), 1387.9 (m), 1298.8 (m), 1211.8 (w), 1143.0 (s), 965.7 (w), 858.5 (w), 758.5 (w), 701.1 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{19}{}^{1}H_{29}{}^{11}B_{1}{}^{16}O_{2}$ [M+H]$^{+}$: calculated: 301.2339, found: 301.2336.



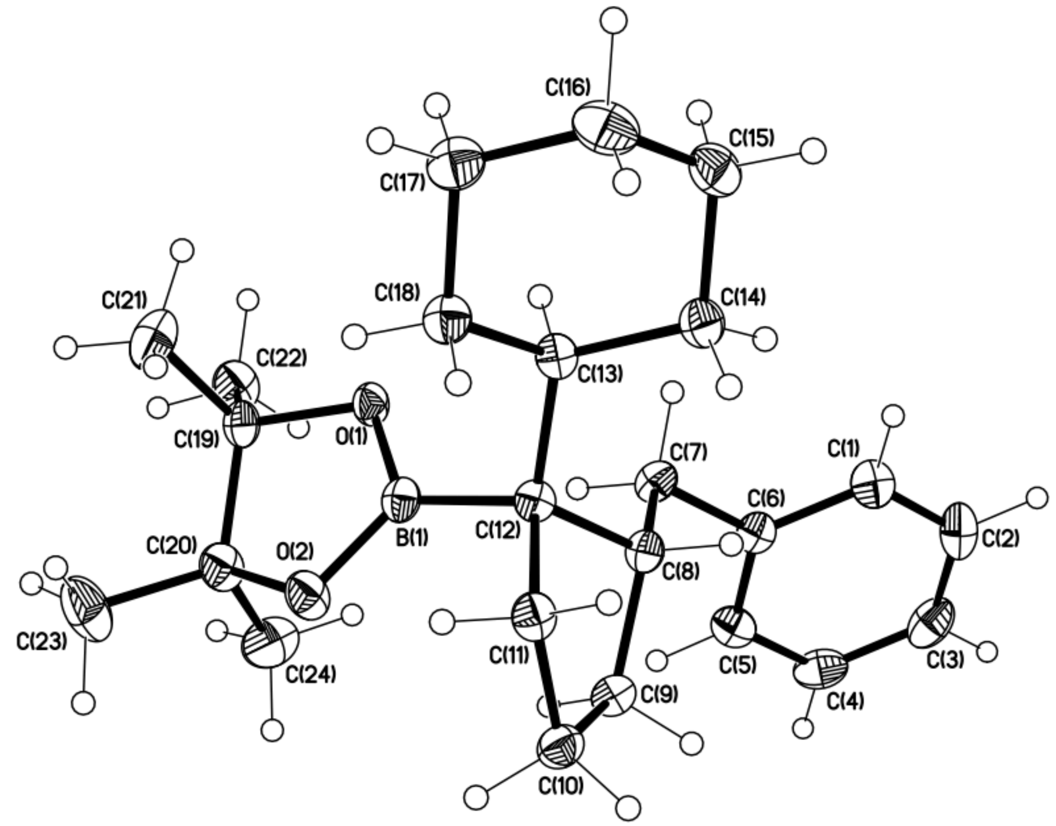
(3-((1*R*,2*R*)-2-benzyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)propoxy)(*tert*-butyl)dimethylsilane (18). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **S2** (58.5 mg, 0.1 mmol), KO*t*-Bu (22.4 mg, 0.2 mmol) and THF (0.5 mL). The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a white solid (30 mg, 65%, > 20:1 dr, crude NMR shows the same diastereoselectivity). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.29 – 7.22 (m, 2H), 7.18 – 7.13 (m, 3H), 3.67 – 3.54 (m, 2H), 2.98 (dd, *J* = 13.2, 3.3 Hz, 1H), 2.33 (dd, *J* = 13.2, 11.6 Hz, 1H), 1.98 (ddd, *J* = 12.5, 8.7, 4.8 Hz, 1H), 1.82 – 1.43 (m, 7H), 1.35 – 1.21 (m, 2H), 1.27 (s, 12H), 1.21 – 1.06 (m, 1H), 0.91 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 143.00, 128.80, 128.07, 125.41, 82.93, 64.26, 53.02, 39.37, 34.41, 34.35, 31.36, 30.94, 26.02, 25.12, 24.89, 22.41, 18.40, -5.17; IR (neat): 2975.9 (w), 2951.9 (m), 2929.1 (m), 2856.3 (m), 1453.9 (w), 1386.9 (m), 1299.6 (m), 1253.8 (m), 1215.5 (w), 1142.3 (s), 1098.6 (m), 990.1 (w), 835.3 (s), 775.1 (m), 698.6 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{27}{}^{1}H_{48}{}^{11}B_{1}{}^{16}O_{3}{}^{28}Si_{1}$ [M+H]$^{+}$: calculated: 459.3466, found: 459.3454.

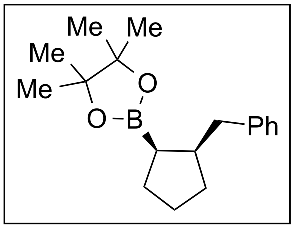


2-((1*R*, 2*R*)-2-benzyl-1-isopropylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (19). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **S3** (90.9 mg, 0.2 mmol), KO*t*-Bu (44.8 mg, 0.4 mmol) and THF (1 mL). The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a white solid (34.5 mg, 52.5%, > 20:1 dr, crude NMR shows the same diastereoselectivity). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.29 – 7.22 (m, 2H), 7.19 – 7.12 (m, *J* = 6.9, 5.7, 1.4 Hz, 3H), 2.97 (dd, *J* = 13.2, 3.1 Hz, 1H), 2.34 (dd, *J* = 13.3, 11.7 Hz, 1H), 2.02 – 1.75 (m, 3H), 1.74 – 1.61 (m, 1H), 1.64 – 1.52 (m, 1H), 1.45 – 1.32 (m, 2H), 1.28 (s, 12H), 1.28 – 1.18 (m, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 143.29, 128.77, 128.07, 125.39, 82.83, 48.45, 39.32, 31.82, 31.14, 29.17, 25.19, 24.93, 22.49, 21.15, 17.15; IR (neat): 2955.3 (m), 2870.1 (w), 1495.1 (w), 1380.1 (m), 1297.7 (m), 1212.7 (w), 1140.6 (s), 982.1 (w), 864.9 (w), 745.6 (w), 699.2 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{21}{}^{1}H_{34}{}^{11}B_{1}{}^{16}O_{2}$ [M+H]$^{+}$: calculated: 329.2652, found: 329.2655.

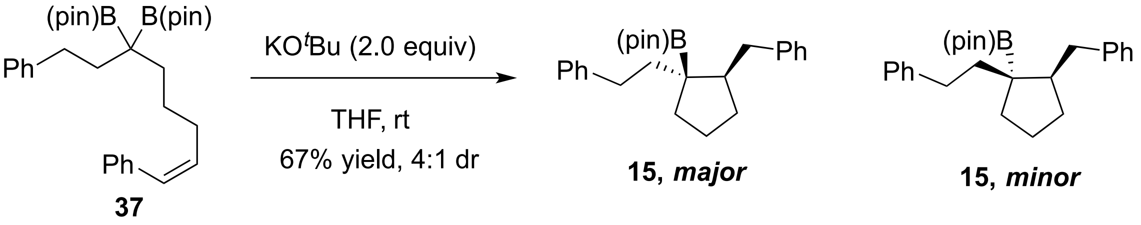


2-((1*R*,2*R*)-2-benzyl-1-cyclohexylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **S4** (98.9 mg, 0.2 mmol), KO*t*-Bu (44.8 mg, 0.4 mmol) and THF (1 mL). The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a white solid (59 mg, 80%, > 20:1 dr, crude NMR shows the same diastereoselectivity). ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.34 – 7.21 (m, 2H), 7.21 – 7.12 (m, 3H), 2.97 (dd, *J* = 13.3, 3.2 Hz, 1H), 2.34 (dd, *J* = 13.3, 11.9 Hz, 1H), 2.00 – 1.91 (m, 1H), 1.84 – 1.76 (m, 1H), 1.79 – 1.67 (m, 3H), 1.66 – 1.58 (m, 3H), 1.61 – 1.50 (m, 2H), 1.45 – 1.31 (m, 2H), 1.33 – 1.19 (m, 14H), 1.22 – 1.17 (m, 2H), 1.17 – 1.08 (m, 1H), 1.09 – 0.95 (m, 1H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 143.30, 128.78, 128.05, 125.36, 82.80, 47.14, 41.83, 39.18, 31.65, 31.56, 30.06, 27.34, 27.12, 27.08, 27.04, 25.22, 24.90, 22.39; IR (neat): 2976.2 (m), 2925.3 (s), 2851.6 (m), 1449.0 (w), 1378.7 (m), 1297.3 (m), 1212.8 (w), 1141.8 (s), 864.2 (w), 746.5 (w), 698.8 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{24}{}^{1}H_{38}{}^{11}B_{1}{}^{16}O_2$ [M+H]$^+$: calculated: 369.2965, found: 369.2967. The relative stereochemistry was assigned by X-ray crystallography.





2-((1*R*,2*R*)-2-benzylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (20). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **S5** (82.4 mg, 0.2 mmol), KO*t*-Bu (44.8 mg, 0.4 mmol) and THF (1 mL). The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a colorless oil (25.7 mg, 45%, > 18:1 dr, crude NMR shows the same diastereoselectivity). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 – 7.21 (m, 2H), 7.20 – 7.12 (m, 3H), 2.78 (dd, J = 13.4, 5.9 Hz, 1H), 2.51 (dd, J = 13.4, 8.6 Hz, 1H), 2.21 – 2.11 (m, 1H), 1.87 – 1.77 (m, 1H), 1.77 – 1.65 (m, 1H), 1.66 – 1.44 (m, 3H), 1.27 (d, J = 4.5 Hz, 1H), 1.18 (s, 6H), 1.17 (s, 6H), 0.99 – 0.86 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.22, 128.98, 128.05, 125.48, 82.72, 45.07, 42.49, 33.51, 28.47, 25.84, 24.72, 24.70; IR (neat): 2956.1 (s), 2932.8 (m), 2919.8 (m), 2876.6 (w), 2861.0 (w), 2361.0 (m), 2163.9 (s), 2013.9 (w), 1728.4 (s), 1379.0 (m), 1290.6 (s), 1316.8 (m), 1145.8 (m), 763.7 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{18}{}^{1}H_{27}{}^{11}B_{1}{}^{16}O_2$ $[M+H]^+$: calculated: 287.2182, found: 287.2194. Relative configuration was determined after oxidation and comparison with reported data.[8] To a 20 mL vial containing 2-((1*R*,2*R*)-2-benzylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10 mg, 0.035mmol), NaOH solution (3M, 1 mL) is added followed by THF (1 mL). The vial is then cooled to 0°C and H_2O_2 (30 wt%, 1 mL) is carefully added. The reaction mixture is then allowed to stir at room temperature for three hours, at which point, the mixture is cooled back to 0°C and saturated, aqueous $Na_2S_2O_3$ (1 mL) is added to degrade excess H_2O_2. The mixture is then extracted with ethyl acetate three times and the combined organics dried over Na_2SO_4, and concentrated *in vacuo*. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.27 (m, 2H), 7.22 – 7.17 (m, 3H), 3.96 – 3.87 (m, 1H), 2.76 (dd, J = 13.6, 6.9 Hz, 1H), 2.55 (dd, J = 13.6, 8.2 Hz, 1H), 2.08 – 2.00 (m, 1H), 1.99 – 1.92 (m, 1H), 1.89 – 1.80 (m, 1H), 1.77 – 1.66 (m, 1H), 1.66 – 1.54 (m, 2H), 1.34 – 1.25 (m, 1H), 1.23 (d, J = 4.1 Hz, 1H).



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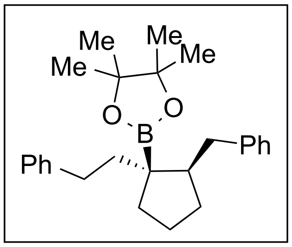
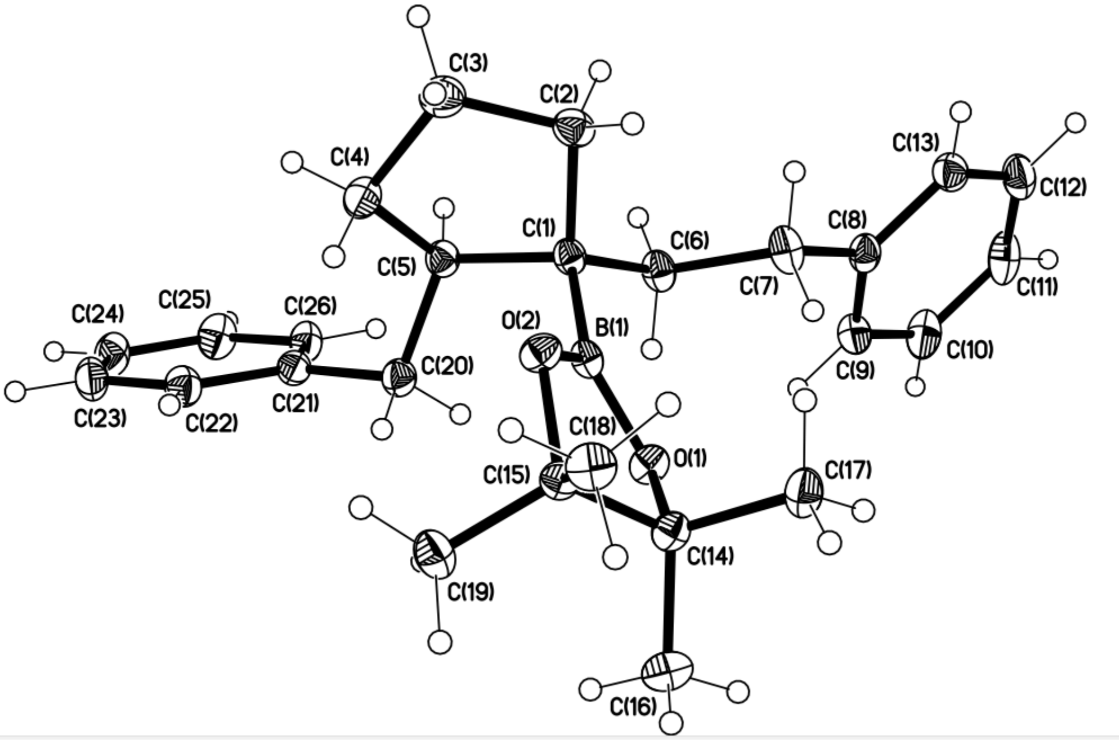
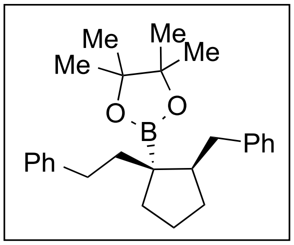
[8] Simpson, A. F.; Bodkin, C. D.; Butts, C. P.; Armitage, M. A.; Gallagher, T. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3047.

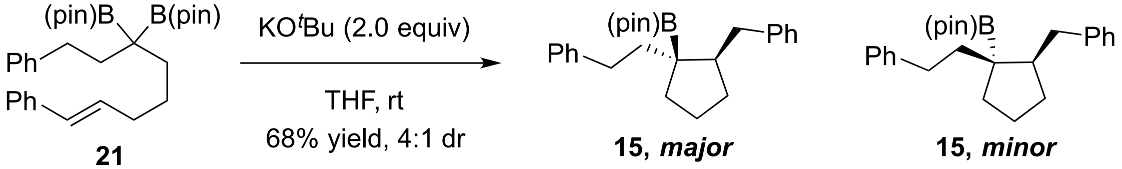


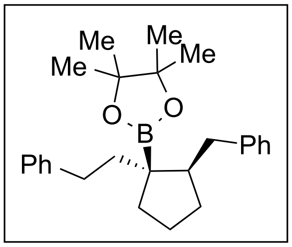
2-((1*R*,2*R*)-2-benzyl-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15, major diastereomer). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **37** (103.3 mg, 0.2 mmol), KO*t*-Bu (44.8 mg, 0.4 mmol) and THF (1 mL). The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a white solid (52.7 mg, 67%, 4:1 dr, crude NMR shows the same diastereoselectivity). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.12 (m, 10H), 3.01 (dd, *J* = 13.2, 3.3 Hz, 1H), 2.62 (ddd, *J* = 10.4, 5.8, 3.5 Hz, 2H), 2.36 (dd, *J* = 13.2, 11.6 Hz, 1H), 2.20 – 2.04 (m, 2H), 1.81 – 1.47 (m, 5H), 1.46 – 1.31 (m, 2H), 1.31 (s, 6H), 1.31 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.76, 142.91, 128.80, 128.34, 128.25, 128.09, 125.50, 125.44, 83.07, 53.06, 41.31, 39.41, 34.42, 34.17, 31.42, 25.28, 24.89, 22.49; ; IR (neat): 2976.2 (m), 2930.8 (m), 2857.6 (w), 1495.3 (w), 1453.6 (m), 1386.7 (m), 1344.8 (w), 1300.7 (m), 1213.8 (m), 1141.2 (s), 1029.5 (w), 967.3 (w), 855.4 (w), 746.9 (m), 697.9 (s) cm^{-1}; HRMS-(DART+) for $^{12}C_{26}{}^{1}H_{39}{}^{11}B_{1}{}^{14}N_{1}{}^{16}O_{2}$ $[M+NH_4]^+$: calculated: 408.3074, found: 408.3091. The relative stereochemistry was assigned by X-ray crystallography.



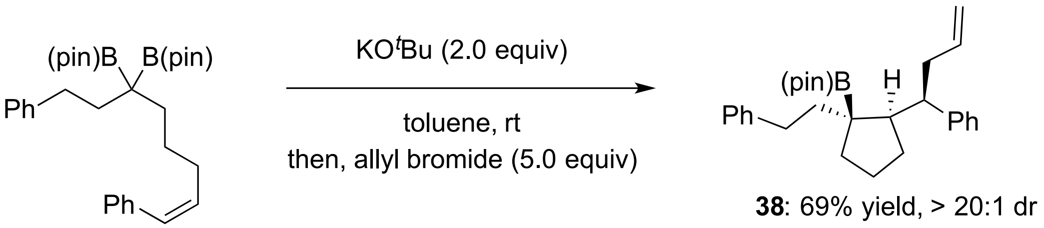


2-((1*S*,2*R*)-2-benzyl-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15, minor diastereomer). <u>^{1}H NMR</u> (600 MHz, CDCl$_3$): δ 7.29 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.16 (m, 4H), 7.19 – 7.07 (m, 4H), 2.96 (dd, *J* = 13.1, 3.3 Hz, 1H), 2.63 – 2.55 (m, 2H), 2.29 (dd, *J* = 13.1, 11.8 Hz, 1H), 2.18 – 2.10 (m, 1H), 1.87 (ddd, *J* = 13.3, 10.4, 6.4 Hz, 2H), 1.74 – 1.64 (m, 2H), 1.61 – 1.44 (m, 3H), 1.38 – 1.27 (m, 1H), 1.31 (s, 6H), 1.31 (s, 6H); <u>^{13}C NMR</u> (150 MHz, CDCl$_3$): δ 143.80, 142.83, 128.81, 128.38, 128.28, 128.11, 125.55, 125.42, 83.05, 48.64, 36.78, 34.07, 33.33, 32.55, 29.80, 24.99, 24.71, 22.71; <u>IR</u> (neat): 2957.0 (s), 2930.9 (s), 2863.3 (m), 1728.6 (m), 1455.6 (w), 1376.6 (m), 1272.7 (m), 1142.1 (s), 1072.5 (w), 747.1 (w), 699.6 (m) cm^{-1}; <u>HRMS</u>-(DART+) for $^{12}C_{26}{}^{1}H_{39}{}^{11}B_{1}{}^{14}N_{1}{}^{16}O_{2}$ [M+NH$_4$]$^+$: calculated: 408.3074, found: 408.3079.



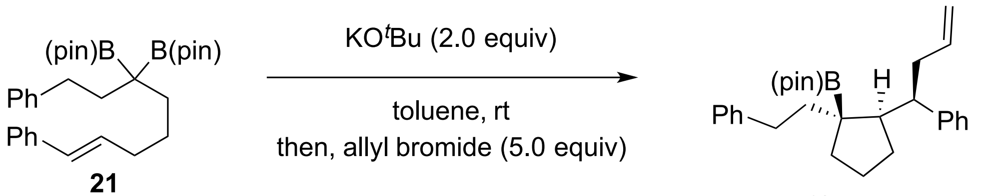


2-((1*R*,2*R*)-2-benzyl-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15, major diastereomer). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **21** (103.3 mg, 0.2 mmol), KO*t*-Bu (44.8 mg, 0.4 mmol) and THF (1 mL). The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a white solid (53.5 mg, 68%, 4:1 dr, crude NMR shows the same diastereoselectivity). The spectra is the same as above.



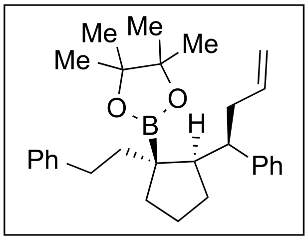
37

38: 69% yield, > 20:1 dr

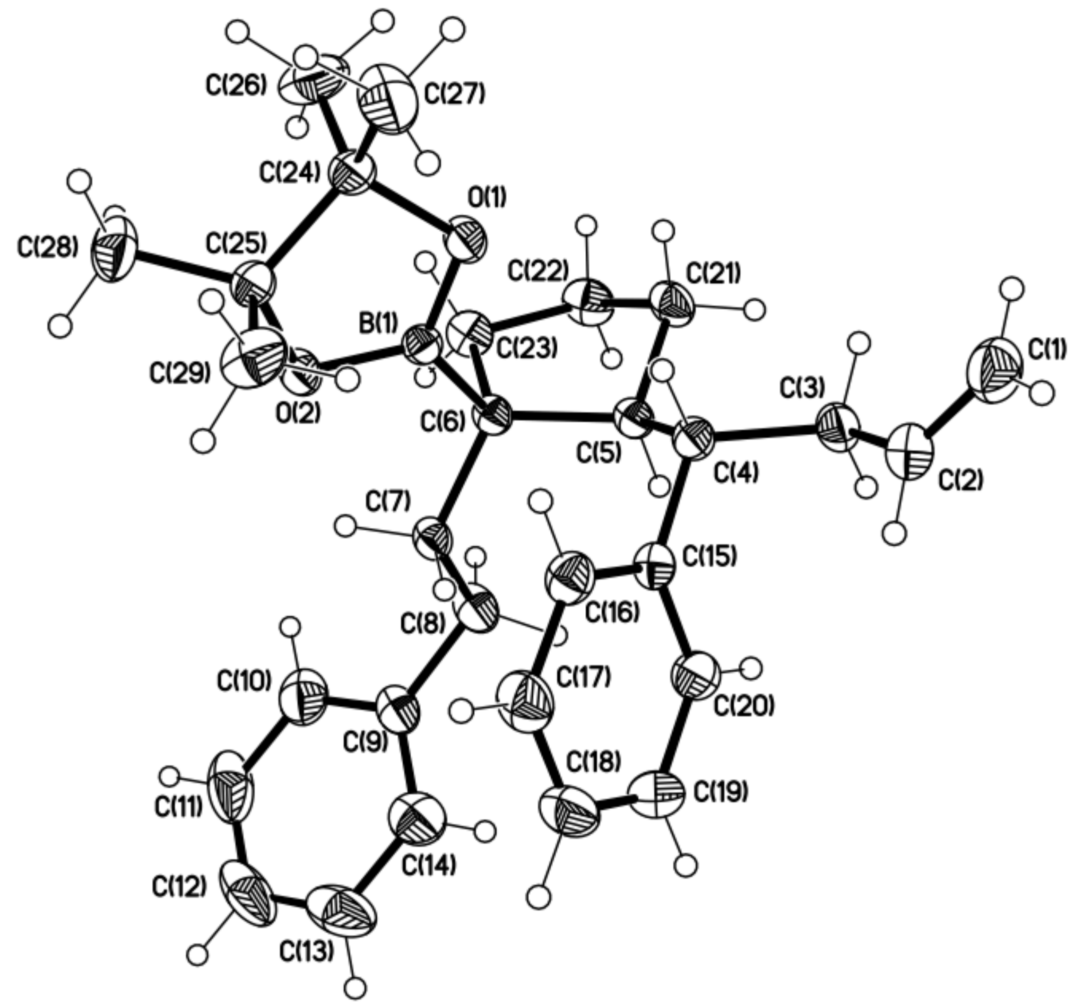


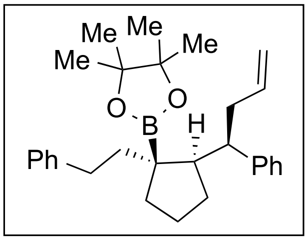
21

38: 76% yield, > 20:1 dr

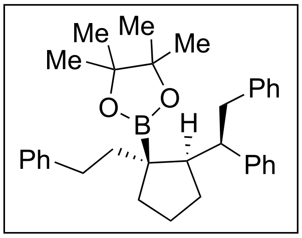


4,4,5,5-tetramethyl-2-((1*R*,2*R*)-1-phenethyl-2-((*R*)-1-phenylbut-3-en-1-yl)cyclopentyl)-1,3,2-dioxaborolane (38). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with (*Z*)-2,2'-(1,8-diphenyloct-7-ene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(37)** (56.13 mg, 0.1 mmol), KO*t*-Bu (22.4 mg, 0.2 mmol) and toluene (0.5 mL). Upon completion, the reaction mixture is quenched with allyl bromide (60.5 mg, 0.5 mmol) and allowed stir an additional two hours. Mixture then diluted with diethyl ether (2 mL) and filtered through a silica gel plug, rinsing with diethyl ether. Filtrate is then concentrated *in vacuo* and the crude residue purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a white solid (30.7 mg, 69%, >10:1 dr, crude NMR shows the same diastereoselectivity). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.30 – 7.18 (m, 4H), 7.19 – 7.11 (m, 3H), 7.14 – 7.04 (m, 1H), 6.91 – 6.85 (m, 2H), 5.50 (dddd, *J* = 18.0, 10.0, 7.4, 6.0 Hz, 1H), 4.85 (dd, *J* = 17.1, 1.7 Hz, 1H), 4.81 – 4.76 (d, *J* = 10.0, 1H), 2.92 (td, *J* = 10.2, 8.8, 3.7 Hz, 1H), 2.59 – 2.47 (m, 1H), 2.40 (td, *J* = 13.2, 4.5 Hz, 1H), 2.36 – 2.25 (m, 2H), 1.97 (td, *J* = 8.9, 8.4, 4.8 Hz, 2H), 1.87 (q, *J* = 8.7 Hz, 1H), 1.73 (p, *J* = 9.9, 8.7 Hz, 1H), 1.66 – 1.49 (m, 2H), 1.43 – 1.31 (m, 2H), 1.29 (s, 6H), 1.28 (s, 6H), 0.83 (td, *J* = 13.0, 5.2 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 145.72, 143.69, 137.68, 128.66, 128.13, 127.90, 127.78, 125.68, 125.13, 115.16, 82.78, 55.13, 48.35, 39.72, 39.16, 35.59, 32.69, 30.42, 25.29, 24.91, 22.08; IR (neat): 2956.9 (s), 2930.5 (s), 2872.6 (m), 1729.4 (s), 1457.5 (m), 1379.2 (m), 1288.9 (s), 1239.1 (w), 1141.6 (s), 1073.0 (m), 755.5 (m), 700.3 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{29}{}^{1}H_{40}{}^{11}B_{1}{}^{6}O_{2}$ [M+H]$^+$: calculated: 431.3121, found: 431.3115. The relative stereochemistry was assigned by X-ray crystallography.

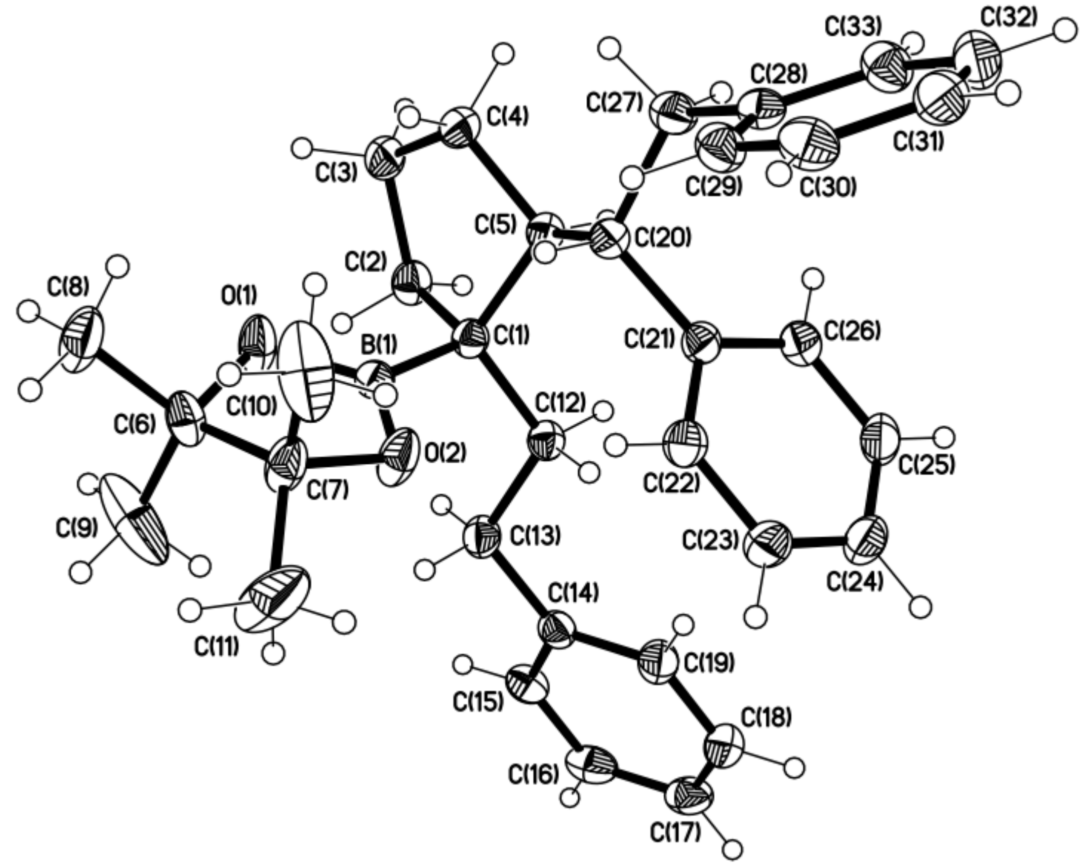


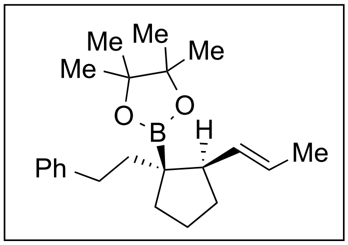


4,4,5,5-tetramethyl-2-((1*R*,2*R*)-1-phenethyl-2-((*R*)-1-phenylbut-3-en-1-yl)cyclopentyl)-1,3,2-dioxaborolane (38). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with (*E*)-2,2'-(1,8-diphenyloct-7-ene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(21)** (56.13 mg, 0.1 mmol), KO*t*-Bu (22.4 mg, 0.2 mmol) and toluene (0.5 mL). Upon completion, the reaction mixture was quenched with allyl bromide (60.5 mg, 0.5 mmol), stir for another two hours, then diluted with diethyl ether (2 mL), filtered through a silica gel plug, rinsed with diethyl ether, and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a white solid (32.7 mg, 76%, >20:1 dr). ^{1}H and ^{13}C NMR spectral data and X-ray crystallographic data identical to that **above**.

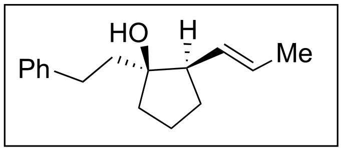


2-((1*R*,2*R*)-2-((*R*)-1,2-diphenylethyl)-1-phenethylcyclopentyl)-4,5,5,5-tetramethyl-1,3,2-dioxaborolane (16). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **37** (103.2 mg, 0.2 mmol), KO*t*-Bu (44.8 mg, 0.4 mmol) and THF (1 mL). Upon completion, the reaction mixture is quenched with benzyl bromide (171 mg, 1.0 mmol) and allowed to stir for an additional two hours. Mixture is then diluted with diethyl ether (2 mL) and filtered through a silica gel plug, rinsing with diethyl ether, and concentrated *in vacuo*. The crude residue is then purified on silica gel (hexanes: ethyl acetate = 100 : 0.8, stain in CAM) to afford the desired product as a white solid (64 mg, 66 %, > 6:1 dr) with unresolved protonated byproduct. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.14 (t, *J* = 7.5 Hz, 2H), 7.12 – 6.98 (m, 9H), 6.86 (d, *J* = 7.6 Hz, 4H), 3.19 (dd, *J* = 13.1, 3.7 Hz, 1H), 3.13 (ddd, *J* = 12.1, 8.6, 3.8 Hz, 1H), 2.69 (dd, *J* = 13.2, 11.6 Hz, 1H), 2.40 (td, *J* = 13.2, 4.5 Hz, 1H), 2.37 – 2.29 (m, 1H), 2.17 – 2.07 (m, 1H), 2.00 (ddd, *J* = 12.5, 8.4, 3.9 Hz, 2H), 1.84 – 1.67 (m, 2H), 1.68 – 1.57 (m, 1H), 1.45 – 1.33 (m, 1H), 1.32 – 1.24 (m, 1H), 1.27 (s, 6H), 1.27 (s, 6H), 0.84 (td, *J* = 12.9, 5.1 Hz, 1H); ^{13}C NMR (150 MHz, CDCl$_3$): δ 145.28, 143.65, 141.22, 129.02, 128.71, 128.36, 128.10, 127.86, 127.58, 127.53, 125.50, 125.12, 125.10, 82.77, 54.97, 50.49, 41.70, 39.54, 35.68, 32.64, 30.95, 25.33, 24.83, 21.93; IR (neat): 3026.1 (w), 2929.9 (m), 2859.7 (w), 1728.7 (w), 1495.2 (w), 1453.2 (w), 1380.2 (m), 1141.5 (s), 967.6 (w), 862.8 (w), 746.1 (w), 697.9 (s) cm^{-1}; HRMS-(DART+) for $^{12}C_{33}{}^{1}H_{42}{}^{11}B_{1}{}^{16}O_{2}$ [M+H]$^+$: calculated: 481.3278, found: 481.3291. The relative stereochemistry was assigned by X-ray crystallography.

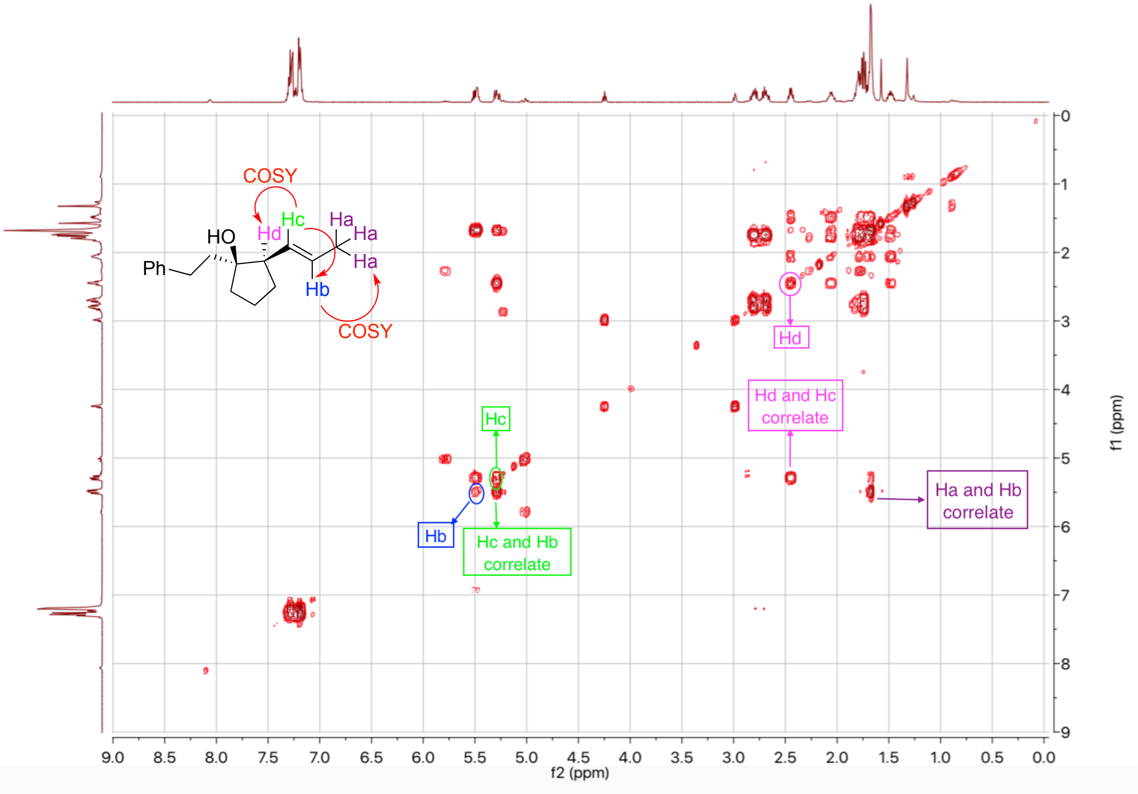


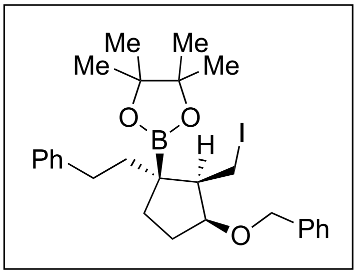


4,4,5,5-tetramethyl-2-((1*R*,2*R*)-1-phenethyl-2-((*E*)-prop-1-en-1-yl)cyclopentyl)-1,3,2-dioxaborolane (**23**). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with 1,1-diboronate ester **22** (46.6 mg, 0.1 mmol), KO*t*-Bu (22.4 mg, 0.2 mmol) and THF (0.5 mL). Upon completion, the reaction mixture is diluted with diethyl ether (2 mL) and filtered through a silica gel plug, rinsing with diethyl ether, and concentrated *in vacuo*. The crude residue is then purified on silica gel (hexanes: diethyl ether = 100 : 1, stain in CAM) to afford the desired product as a colorless oil (18.8 mg, 55%, >20:1 dr, crude NMR shows the same diastereoselectivity). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 – 7.22 (m, 2H), 7.21 – 7.13 (m, 3H), 5.52 – 5.35 (m, 2H), 2.57 (td, *J* = 12.8, 4.9 Hz, 2H), 2.47 (td, *J* = 12.9, 5.0 Hz, 1H), 1.99 – 1.82 (m, 1H), 1.80 – 1.66 (m, 3H), 1.65 (dd, *J* = 4.8, 0.7 Hz, 3H), 1.63 – 1.55 (m, 2H), 1.53 – 1.47 (m, 1H), 1.42 (td, *J* = 12.9, 5.0 Hz, 1H), 1.26 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.93, 132.52, 128.35, 128.16, 125.39, 124.38, 82.99, 49.25, 34.75, 34.01, 33.06, 31.09, 24.86, 24.71, 23.10, 18.08; IR (neat): 2976.5 (m), 2955.3 (m), 2870.6 (m), 1726.8 (w), 1454.8 (w), 1379.3 (s), 1304.3 (m), 1272.9 (m), 1143.3 (s), 968.1 (w), 857.0 (w), 757.3 (s), 699.3 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{22}{}^{1}H_{34}{}^{11}B_{1}{}^{16}O_{2}$ $[M+H]^{+}$: calculated: 341.2652, found: 341.2660.

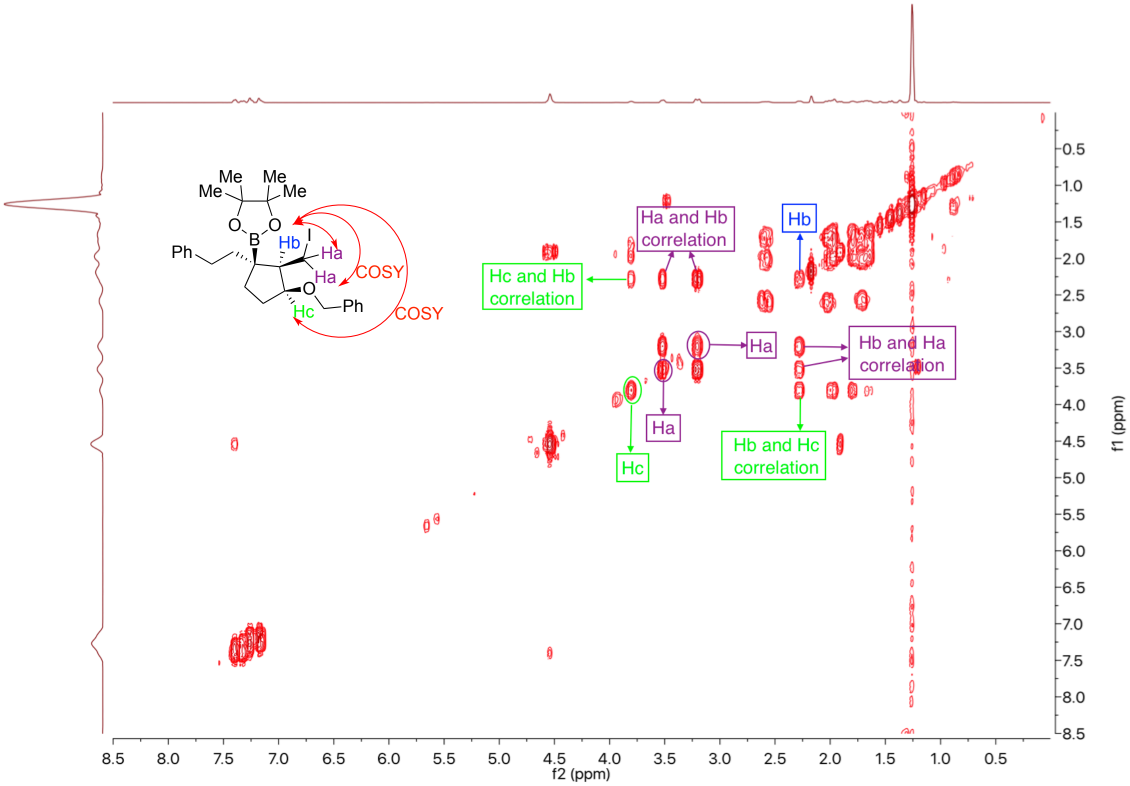


(1*S*,2*R*)-1-phenethyl-2-((*E*)-prop-1-en-1-yl)cyclopentan-1-ol (S33). This reaction was performed to comfirm the structure of compound 4,4,5,5-tetramethyl-2-((1*R*,2*R*)-1-phenethyl-2-((*E*)-prop-1-en-1-yl)cyclopentyl)-1,3,2-dioxaborolane (**23**). To a 20 mL vial containing the compound (**23**) (25 mg, 0.0745 mmol) add THF (1 mL), NaOH (0.6 mL, 3 M, 1.8 mmol), then cool the vial to 0 °C. Add hydrogen peoxide (0.3 mL, 30% in H_2O) into the above mixture dropwise, let the reaction stir for overnight. The reaction was cooled to 0 °C again, and quenched by $Na_2S_2O_3$ (1 mL, saturated solution) slowly, stirred for 30 minutes, then extrated with diethyl ether, dried over Na_2SO_4, and evaporated *in vacuo*. The crude reaction mixture was purified by column chromatography (hexanes: ethyl acetate = 100 : 5 to 100 : 10, stain in CAM) on silica gel to afford desired product (11.8 mg, 70 % yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 5.49 (dqd, *J* = 15.1, 6.4, 0.9 Hz, 1H), 5.29 (ddq, *J* = 15.1, 9.2, 1.6 Hz, 1H), 2.80 (ddd, *J* = 13.4, 9.4, 7.5 Hz, 1H), 2.69 (ddd, *J* = 13.5, 9.6, 7.7 Hz, 1H), 2.51 – 2.40 (m, 1H), 2.10 – 2.02 (m, 1H), 1.84 – 1.71 (m, 5H), 1.70 – 1.65 (m, overlap, 1H), 1.67 (dd, *J* = 6.4, 1.7 Hz, 3H), 1.53 – 1.45 (m, 1H), 1.32 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.99, 131.63, 128.88, 128.37, 125.96, 125.68, 83.62, 54.55, 39.24, 37.23, 30.28, 30.19, 21.02, 18.07. The structure was further confirmed by COSY spectra, shown below.





(1*S*,2*R*,3*S*)-2-(iodomethyl)-3-phenethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl benzoate (14, *major product*). The reaction was performed according to *Representative Procedure for Deborylative cyclization* with diboronate ester **S7** (55 mg, 0.1 mmol), KO*t*-Bu (22.4 mg, 0.20 mmol) and THF (0.5 mL) for overnight. Upon completion, the reaction mixture is quenched with a solution of I_2 (50.8 mg, 0.20 mmol) in anhydrous THF (0.3 mL) and allowed to stir at room temperature for three hours. Reaction mixture is then diluted with diethyl ether (2 mL) and filtered through a silica gel plug, rinsing with diethyl ether. Filtrate is then concentrated *in vacuo* and the crude residue purified by column chromatography on silica gel (100 : 0.8 Hexanes/EtOAc, gradient to 100 : 3 Hexanes/EtOAc, stain in CAM) to afford a colorless oil (29.3 mg, 55%, product **14** : product **S13** = 2.9 : 1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 – 7.38 (m, 2H), 7.36 – 7.30 (m, 2H), 7.29 – 7.24 (m, 3H), 7.20 – 7.14 (m, 3H), 4.55 (d, *J* = 1.9 Hz, 2H), 3.81 (qd, *J* = 4.6, 3.2 Hz, 1H), 3.52 (dd, *J* = 9.8, 4.8 Hz, 1H), 3.21 (t, *J* = 10.1 Hz, 1H), 2.67 – 2.50 (m, 2H), 2.28 (dt, *J* = 10.0, 4.8 Hz, 1H), 2.10 – 1.94 (m, 3H), 1.85 – 1.75 (m, 1H), 1.75 – 1.61 (m, 2H), 1.26 (two sets of singlet, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.05, 138.81, 128.30, 128.26, 128.24, 127.85, 127.36, 125.59, 87.16, 83.41, 71.26, 57.60, 41.33, 33.47, 33.27, 30.50, 25.07, 24.90, 8.22; IR (neat): 2975.4 (w), 2926.7 (w), 2855.7 (w), 1495.8 (w), 1378.8 (m), 1310.9 (m), 1198.9 (m), 1166.4 (s), 1140.4 (s), 1099.2 (m), 1066.9 (m), 856.9 (m), 735.0 (s), 697.3 (s) cm^{-1}; HRMS-(DART+) for $^{12}C_{27}{}^{1}H_{36}{}^{11}B_1{}^{16}O_3{}^{127}I_1{}^{23}Na_1$ [M+Na]$^+$: calculated: 569.1700, found: 569.1707. The relative stereochemistry was assigned by COSY and NOESY spectra, shown below.



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correlation
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Hb and Ha
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Ha
Hc
Hb and Hc
correlation
f1 (ppm)
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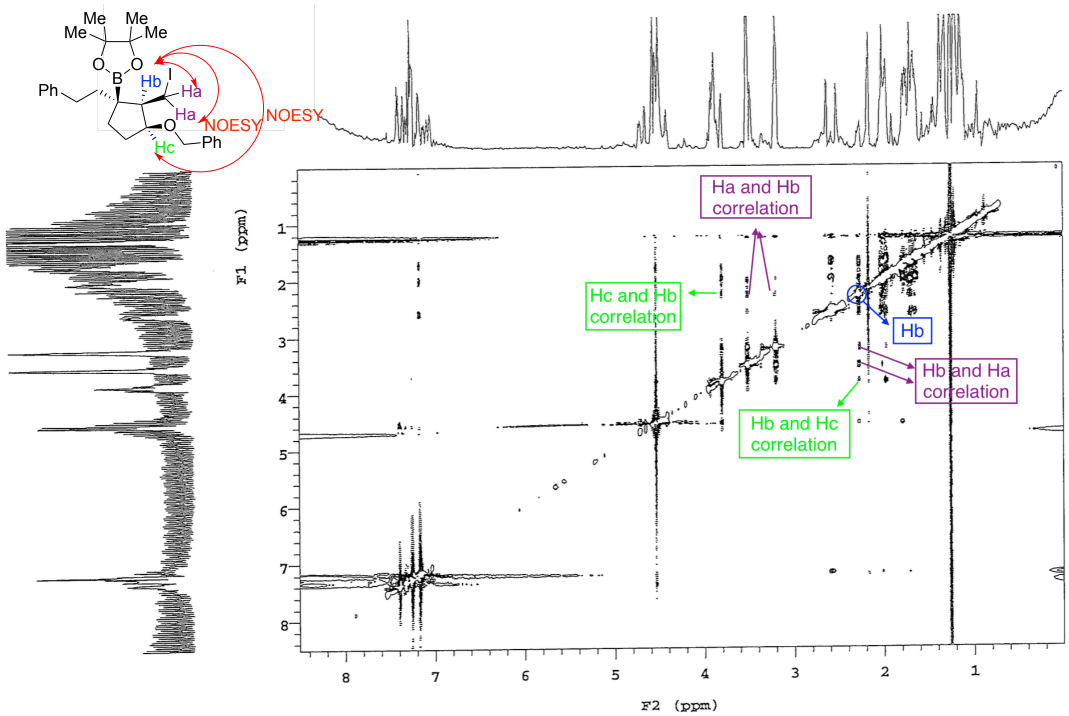

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NOESY
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Ph
Hc
Ha and Hb
correlation
Hc and Hb
correlation
Hb
Hb and Ha
correlation
Hb and Hc
correlation
F1 (ppm)
F2 (ppm)
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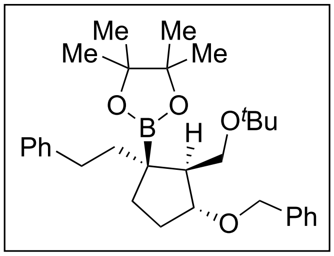
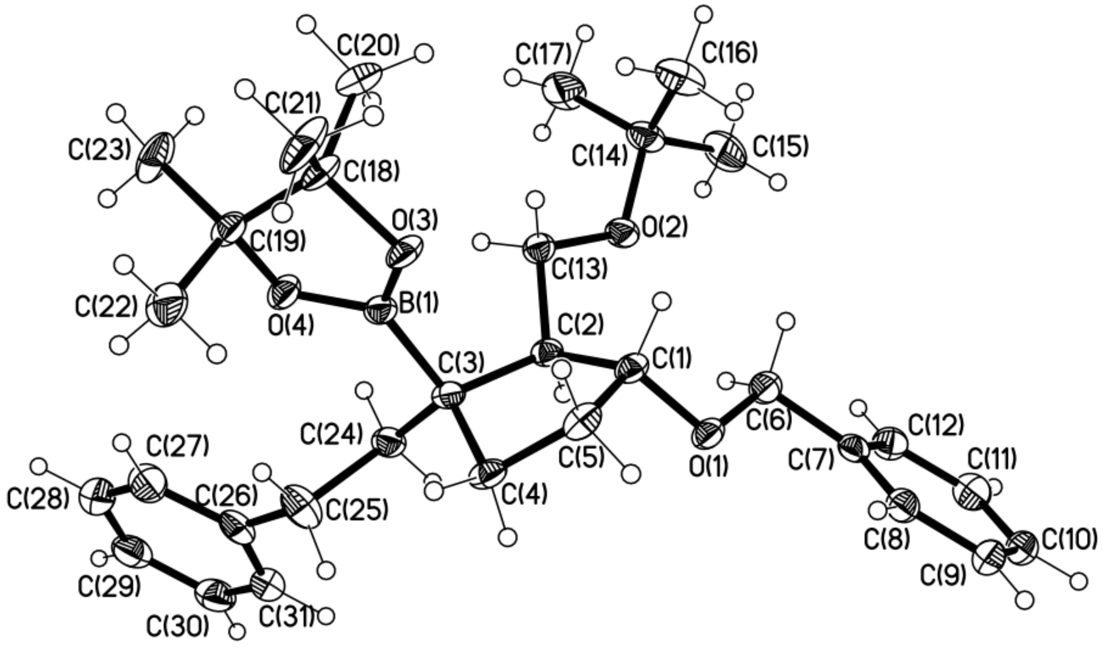
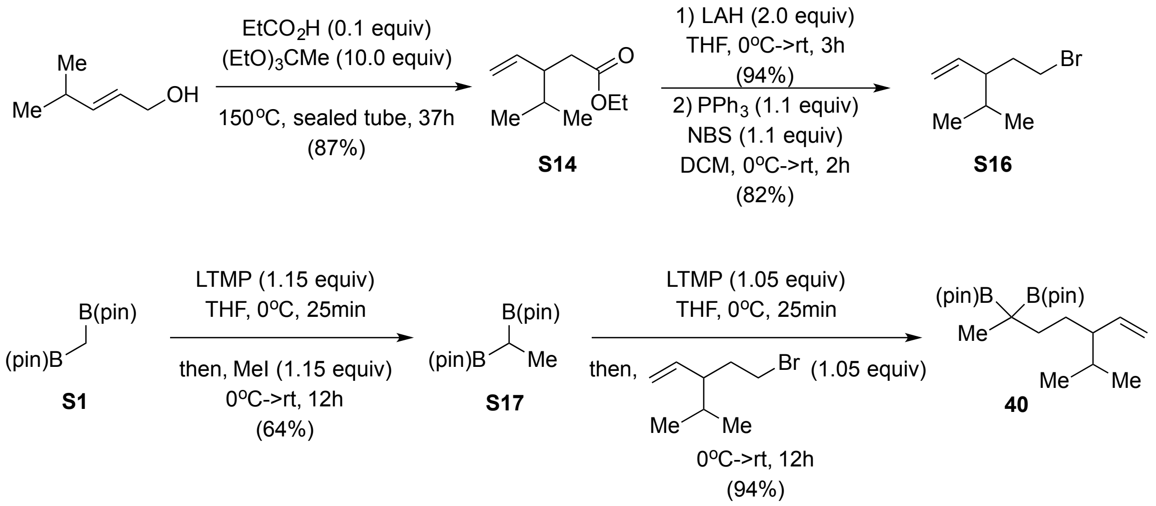
2
3
4
5
6
7
8

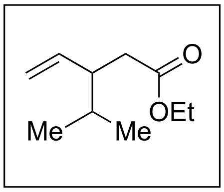


2-((1*S*,2*S*,3*R*)-3-(benzyloxy)-2-(*tert*-butoxymethyl)-1-phenethyl cyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S13, *minor product*). This product was isolated along side the above product **(14)**. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.37 – 7.33 (m, 2H), 7.33 – 7.28 (m, 2H), 7.28 – 7.22 (m, 3H), 7.21 – 7.17 (m, 2H), 7.17 – 7.13 (m, 1H), 4.57 (d, *J* = 12.3 Hz, 1H), 4.50 (d, *J* = 12.3 Hz, 1H), 3.82 (dt, *J* = 6.9, 3.5 Hz, 1H), 3.52 (dd, *J* = 8.8, 5.0 Hz, 1H), 3.18 (dd, *J* = 9.8, 8.8 Hz, 1H), 2.68 – 2.47 (m, 2H), 2.07 – 1.92 (m, 3H), 1.87 (ddd, *J* = 11.5, 7.1, 4.1 Hz, 1H), 1.83 – 1.67 (m, 2H), 1.63 (ddd, *J* = 11.9, 9.5, 7.4 Hz, 1H), 1.26 (s, 12H), 1.16 (s, 9H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 143.68, 139.66, 128.39, 128.17, 128.12, 127.59, 127.00, 125.38, 84.60, 82.99, 72.49, 70.49, 62.86, 56.23, 41.83, 33.73, 32.97, 31.65, 27.66, 25.11, 24.93; IR (neat): 3026.0 (w), 2972.8 (s), 2927.6 (m), 2857.0 (m), 1496.0 (m), 1378.4 (s), 1307.1 (m), 1198.5 (m), 1143.6 (s), 1073.9 (m), 857.5 (w), 698.5 (w) cm^{-1}; HRMS-(DART+) for ${}^{12}C_{31}{}^{1}H_{45}{}^{11}B_{1}{}^{16}O_{4}{}^{23}Na_{1}$ [M+Na]$^{+}$: calculated: 515.3309, found: 515.3320. The relative stereochemistry was assigned by X-ray crystallography, shown below:

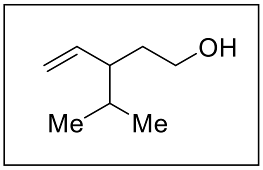


VI. Total Synthesis of Natural Product Aphanamal





Ethyl 3-isopropylpent-4-enoate (S14). A flame dried 150 mL pressure vessel equipped with magnetic stir bar is charged with (*E*)-4-methylpent-2-en-1-ol[9] (3.17 g, 31.6 mmol, 1.0 equiv), triethyl orthoacetate (57.9 mL, 316 mmol, 10 equiv) and propionic acid (239 μL, 3.20 mmol, 0.1 equiv) in succession. The vessel is sealed with a threaded, teflon cap and allowed to stir heated at 150°C for 1.5 days. At this point, the vessel and contents are cooled to 0°C and the excess triethyl orthoacetate consumed by combining the reaction mixture with 50 mL H_2O, 50 mL THF and ca. 20 mg *p*-TsOH•H_2O (this process is exothermic). Organics are then extracted 3x with Et_2O and dried of Na2SO4. Concentration of solution yields clear, yellow oil with fruity fragrence (4.66 g, 27.4 mmol, 87%). No further purification necessary. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.65 (ddd, *J* = 17.1, 10.4, 8.6 Hz, 1H), 5.05 – 4.98 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.44 – 2.35 (m, 2H), 2.32 – 2.24 (m, 1H), 1.68 – 1.61 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 172.94 (s), 138.76 (s), 115.97 (s), 60.15 (s), 46.71 (s), 37.49 (s), 31.29 (s), 20.25 (s), 18.79 (s), 14.25 (s); IR (neat): 2962.8 (m), 2876.7 (m), 1732.2 (s), 1465.7 (w), 1387.4 (w), 1265.6 (m), 1182.5 (m), 1142.6 (m), 1034.6 (w), 914.7 (s), 733.4 (s) cm^{-1}; HRMS-(DART+) for $^{12}C_{10}{}^{1}H_{19}{}^{16}O_2$ $[M+H]^+$: calculated: 171.1385, found: 171.1379.



3-isopropylpent-4-en-1-ol (S15). A flame dried 500 mL round bottom equipped with magnetic stir bar is charged with LAH (1.60 g, 29.2 mmol, 2.0 equiv) inside an argon-filled glovebox. The vessel is sealed with a rubber septum and moved to the fume hood where it is brought to 0°C and charged with anhydrous THF (200 mL). A solution of **S14** (4.66 g, 27.4 mmol, 1.0 equiv) in anhydrous THF (15 mL) is then added to the reaction vessel

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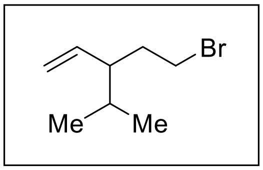
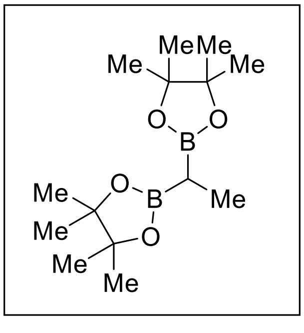
[9] For preparation see: Crimmins, M. T.; Al-awar, R. S.; Vallin, I. M.; Hollis, W. G., Jr.; O'Mahony, R.; Lever J. G.; Bankaitis-Davis, D. M. *J. Am. Chem. Soc.* **1996**, *118*, 7513

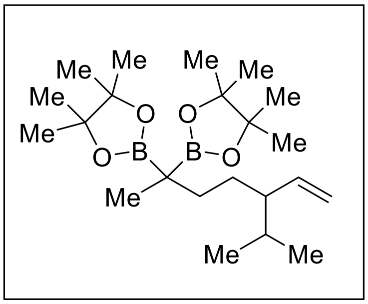
dropwise. The reaction mixture is then allowed to stir for 3h, slowly reaction room temperature. At this point, the vessel and contents are brought back to 0°C and the excess LAH carefully quenched with 1.6 mL H_2O, 1.6 mL 3M NaOH and 4.8 mL H_2O in succession. The grey slurry is then brought to rt and ca. 5 g Na_2SO_4 added. This mixture is allowed to stir for 10 min then passed through a pad of celite, rinsing with Et_2O. Concentration of the filtrate yields a clear, colorless oil (3.31 g, 25.8 mmol, 94%). No further purification necessary. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.60 (ddd, *J* = 17.1, 10.2, 9.5 Hz, 1H), 5.04 (dd, *J* = 10.2, 2.1 Hz, 1H), 5.00 (ddd, *J* = 17.1, 2.1, 0.7 Hz, 1H), 3.67 (ddd, *J* = 10.7, 7.0, 5.5 Hz, 1H), 3.59 (dt, *J* = 10.6, 7.1 Hz, 1H), 1.97 – 1.90 (m, 1H), 1.75 – 1.68 (m, 1H), 1.63 – 1.54 (m, 1H), 1.54 – 1.46 (m, 1H), 1.41 (br s, 1H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 140.56 (s), 115.85 (s), 61.68 (s), 47.52 (s), 34.85 (s), 31.82 (s), 20.45 (s), 18.92 (s); IR (neat): 3325.1 (w, br), 2988.0 (m), 2870.1 (s), 1450.4 (w), 1391.6 (m), 1360.6 (w), 1295.9 (w), 1141.8 (s), 1073.6 (w), 911.4 (w), 734.3 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_8{}^1H_{17}{}^{16}O_1$ $[M+H]^+$: calculated: 129.1279, found: 129.1281.



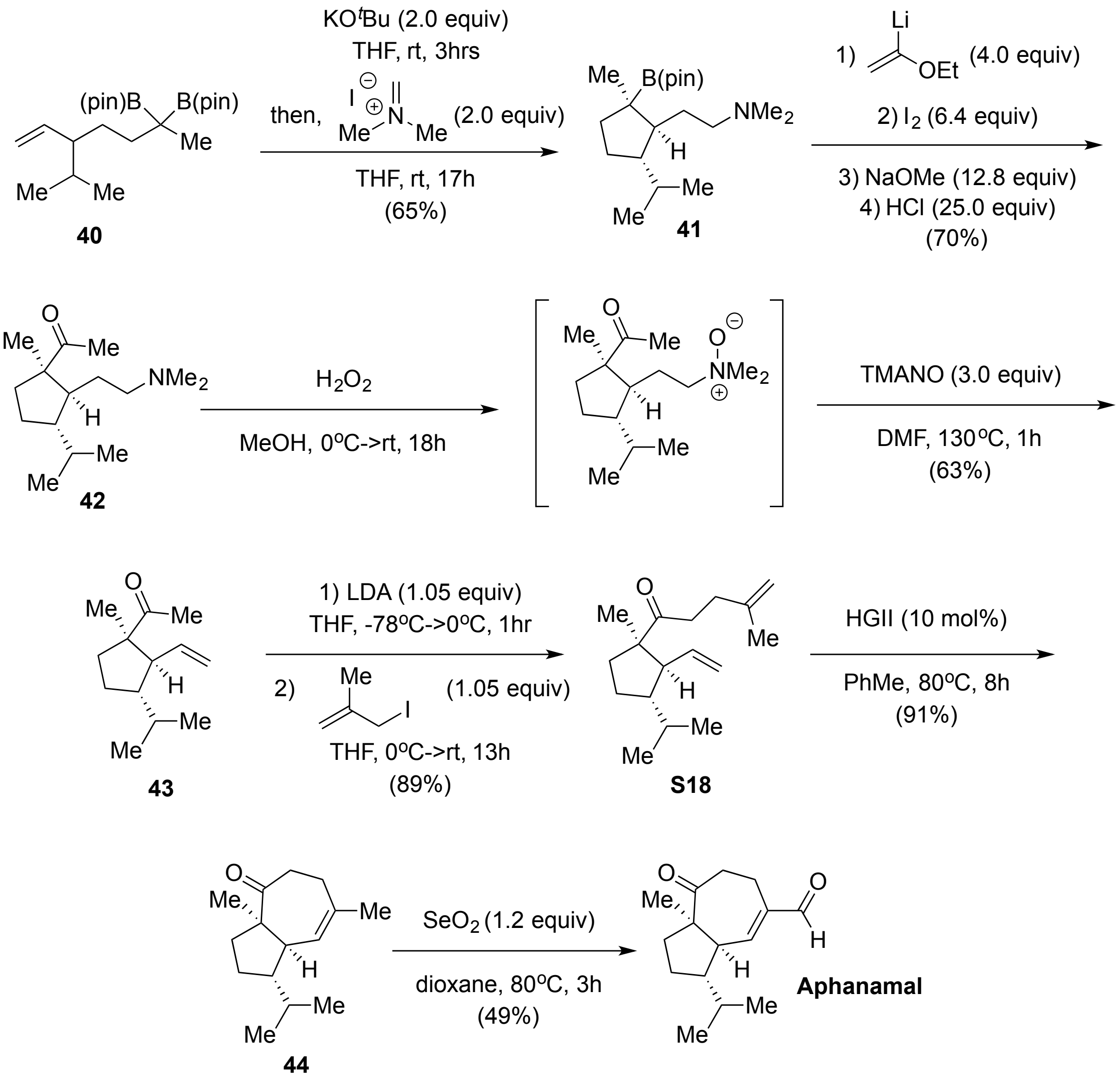
5-bromo-3-isopropylpent-1-ene (S16). A flame dried 100 mL round bottom equipped with magnetic stir bar is charged with PPh_3 (3.41 g, 12.7 mmol, 1.1 equiv) then sealed with a rubber septum. A solution of **S15** (1.47 g, 11.5 mmol, 1.0 equiv) in anhydrous DCM (11.5 mL) is then charged into the reaction vessel. The homogeneous mixture is allowed to stir at 0°C and the vessel temporarily opened to allow for the slow addition of solid NBS (2.25 g, 12.7 mmol, 1.1 equiv; this process is highly exothermic). Vessel is re-sealed and allowed to stir at rt for 3h, at which point it is concentrated *in vacuo* to render crude solid/oil mixutre. Solid is suspended in Pentanes and loaded onto a SiO_2 column. The column is then eluted with 1% Et_2O/Pentane, visualizing the product with $KMnO_4$. Product isolated as clear, colorless oil (1.80 g, 9.42 mmol, 82%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.50 (ddd, *J* = 17.0, 10.3, 9.3 Hz, 1H), 5.09 (dd, *J* = 10.3, 2.1 Hz, 1H), 5.04 (dd, *J* = 17.1, 2.0 Hz, 1H), 3.45 (ddd, *J* = 9.6, 7.7, 4.6 Hz, 1H), 3.29 (m, 1H), 2.03 – 1.93 (m, 2H), 1.82 – 1.74 (m, 1H), 1.60 (m, 1H), 0.90 (d, *J* = 6.7 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 138.85 (s), 116.88 (s), 49.18 (s), 34.98 (s), 32.55 (s), 31.53 (s), 20.43 (s), 19.04 (s); IR (neat): 3076.2 (w), 2959.5 (s), 2929.7 (m), 2873.3 (m), 1638.1 (w), 1465.5 (w), 1368.8 (w), 1256.9 (m), 1212.1 (w), 999.3 (m), 917.4 (s), 639.5 (w), 568.5 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_8{}^1H_{16}{}^{79}Br_1$ $[M+H]^+$: calculated: 191.0435, found: 191.0438.

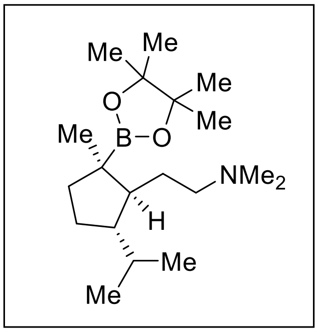


2,2'-(ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (S17). The reaction was performed according to *Representative Procedure (Method C)* with 1,1-diborylmethane (2.68 g, 10.0 mmol, 1.00 equiv), LTMP (1.69 g, 11.5 mmol, 1.15 equiv), Iododmethane (716 µL, 11.5 mmol, 1.15 equiv) and THF (40 mL). The crude reaction mixture was purified by column chromatography on silica gel (0% EtOAc/Hexanes, gradient to 6% EtOAc/Hexanes, visualized with CAM stain) to afford a clear, colorless oil (1.80 g, 6.38 mmol, 64%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 1.21 (s, 12H), 1.21 (s, 12H), 1.02 (d, *J* = 7.2 Hz, 3H), 0.70 (q, *J*= 7.2 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 82.86 (s), 24.80 (s), 24.50 (s), 9.02 (s); IR (neat): 2976.8 (w), 2934.5 (w), 2879.4 (w), 1460.5 (w), 1304.2 (s), 1268.8 (m), 1216.1 (w), 1142.1 (s), 1105.9 (m), 846.1 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{14}{}^{1}H_{29}{}^{11}B_2{}^{16}O_4$ [M+H]$^+$: calculated: 283.2252, found: 283.2265.



2,2'-(5-isopropylhept-6-ene-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (40). The reaction was performed according to *Representative Procedure (Method D)* with diboronate ester **S17** (1.76 g, 6.24 mmol, 1.00 equiv), LTMP (964 mg, 6.55 mmol, 1.05 equiv), alkyl bromide **S16** (1.25 g, 6.55 mmol, 1.05 equiv) and THF (25 mL). The crude reaction mixture was purified by column chromatography on silica gel (1% EtOAc/Hexanes, gradient to 3% EtOAc/Hexanes, visualized with CAM stain) to afford a clear, colorless oil (2.32 g, 5.92 mmol, 94%). ^{1}H NMR (600 MHz, CDCl$_3$): δ 5.56 (ddd, *J* = 17.0, 10.3, 9.0 Hz, 1H), 4.97 (dd, *J* = 10.3, 2.3 Hz, 1H), 4.92 (dd, *J* = 17.1, 2.3 Hz, 1H), 1.78 – 1.69 (m, 1H), 1.60 (ddd, *J* = 13.6, 12.1, 6.8 Hz, 1H), 1.55 – 1.41 (m, 2H), 1.42 – 1.33 (m, 1H), 1.28 – 1.22 (m, 1H), 1.22 – 1.18 (m, 24H), 1.03 (s, 3H), 0.84 (d, *J* = 6.7 Hz, 3H), 0.79 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 141.17 (s), 114.87 (s), 82.82 (s), 82.80 (s), 51.01 (s), 31.82 (s), 31.25 (s), 29.67 (s), 24.73 (s), 24.69 (s), 24.62 (s), 20.58 (s), 18.79 (s), 15.99 (s). IR (neat): 2976.3 (w), 2930.3 (w), 2869.8 (w), 1458.9 (w), 1298.5 (s), 1138.0 (s), 1080.9 (w), 968.3 (w), 848.9 (m), 668.7 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{22}{}^{1}H_{43}{}^{11}B_2{}^{16}O_4$ [M+H]$^+$: calculated: 393.3347, found: 393.3358.





2-((1S,2S,5S)-5-isopropyl-2-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)-N,N-dimethylethan-1-amine (41). A flame-dried, 250mL round bottom equipped with magnetic stirbar is charged with **40** (2.97 g, 7.57 mmol) inside an Argon filled glovebox. A solution is then prepared with anhydrous THF (37.9 mL, 0.2 M). KO*t*Bu (1.70 g, 15.1 mmol, 2 equiv.) is then added to the solution neat, in one portion. The reaction mixture is allowed to stir for 3hrs inside the glovebox at room temperature and gradually becomes clear, pale yellow. At this point, freshly prepared Eschenmoser's Salt[10] (2.80 g, 15.1 mmol, 2 equiv.) is added neat, in one portion; white slurry results. The sealed reaction vessel is then brought to the fume hood where it is allowed to

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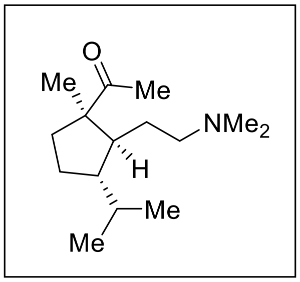
[10] Eschenmoser, A.; Schreiber, J.; Maag, H.; Hashimoto, N. *Angew. Chem. Int. Ed.* **1971**, *10*, 330

stir for 17h at room temperature. Mixture is then diluted with reagent grade Et_2O and passed through a pad of silica, rinsing with 50% EtOAc/1.5% NEt_3/Hexanes. After concentration, ^{1}H NMR suggests ca. 7:1 epimeric ratio (presumably about the isopropyl group). SiO_2 chromatography performed (5% NEt_3/Hexanes, then 5% NEt_3/5% EtOAc/Hexanes), rendering product of acceptable purity as clear, colorless oil **(1.59 g, 4.92 mmol, 65%)**. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.30 – 2.24 (m, 2H), 2.20 (s, 6H), 1.79 – 1.71 (m, 1H), 1.70 – 1.60 (m, 4H), 1.58 – 1.48 (m, 1H), 1.40 – 1.32 (m, 1H), 1.21 (s, 12H), 1.19 – 1.08 (m, 2H), 1.01 (s, 3H), 0.89 (d, J = 6.7 Hz, 3H), 0.78 (d, J = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 82.60 (s), 59.82 (s), 52.54 (s), 51.78 (s), 45.55 (s), 37.69 (s), 31.97 (s), 30.01 (s), 24.87 (s), 24.82 (s), 24.79 (s), 24.76 (s), 22.71 (s), 16.93 (s). IR (neat): 2949.7 (br m), 2867.3 (w), 1460.8 (m), 1379.8 (s), 1369.2 (s), 1300.1 (s), 1142.2 (s), 856.5 (m), 693.4 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{19}{}^{1}H_{39}{}^{11}B_1{}^{14}N_1{}^{16}O_2$ $[M+H]^+$: calculated: 324.3074, found: 324.3063.



1-((1R,2S,3S)-2-(2-(dimethylamino)ethyl)-3-isopropyl-1-methylcyclopentyl)ethan-1-one (42). Adapted from published procedure.[11] A flame-dried, 500mL round bottom equipped with magnetic stirbar is sealed then evacuated/refilled with Nitrogen gas 3x. The vessel is then charged with Ethyl vinyl ether (3.00 mL, 31.3 mmol, 6.4 equiv.) followed by 60 mL anhydrous THF. The solution is allowed to then stir at -78°C, and *t*-BuLi in Pentanes (11.5 mL, 1.7 M, 19.6 mmol, 4.0 equiv.) added across ca. 10min. The resulting mixture is a bright yellow solution. This solution is allowed to stir for 30min at -78°C, then the mixture brought to 0°C, where it is allowed to stir for an additional 30min (mixture becomes clear, colorless during the heating process and a black discoloration of the Teflon stirbar is noted). Mixture is cooled back to -78°C and a solution of **41** (1.58 g, 4.89 mmol, 1.0 equiv) in 60 mL anhydrous THF added across ca. 10min. The mixture is allowed to stir for 30min at -78°C, then brought to room temperature where it is allowed to stir for 5min (warming with a water bath). Mixture is again lowered to -78°C and a solution of I_2 in anhydrous THF (62.6 mL, 0.5 M, 31.3 mmol, 6.4 equiv.) added gradually across ca. 10min. The resulting deep purple mixture is allowed to stir for 30min at -78°C, then brought to room temperature where it is allowed to stir an additional 10min (warming with a water bath). Mixture is cooled back to -78°C and a solution of NaOMe in methanol (62.6 mL, 1.0 M, 62.6 mmol, 12.8 equiv.) is added gradually. The mixture is then allowed to stir overnight at room temperature. Upon return, the mixture is pale yellow. An aqueous solution of HCl is added gradually (122 mL, 1.0 M, 122 mmol, 25 equiv.). Mixture becomes orange. A saturated, aqueous solution of $Na_2S_2O_3$ then added (ca. 30 mL) and the mixture made basic with saturated, aqueous $NaHCO_3$. Organics are then extracted 3x with Et_2O and combined organics washed 2x with H_2O and once with Brine. Organics dried over Na_2SO_4 then concentrated to give crude oil. Crude oil purified by SiO_2 chromatography (10%

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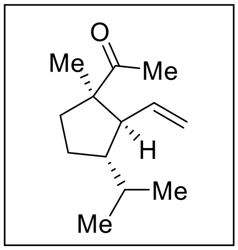
[11] Aggarwal, V. K.; Sonawane, R. P.; Jheengut, V.; Rabalakos, C.; Larouche-Gauthier, R.; Scott, H. K. *Angew. Chem. Int. Ed.* **2011**, *50*, 3760

EtOAc/pentane, then 25% EtOAc/pentane, then 10% EtOAc/5% NEt_3/Pentane, then 25% EtOAc/5% NEt_3/Pentane), visualizing with Cerium Ammonium Molybdate stain. Product isolated as pale yellow oil **(823 mg, 3.44 mmol, 70%)**. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.19 (t, *J* = 7.8 Hz, 2H), 2.16 (s, 6H), 2.13 (s, 3H), 2.03 – 1.95 (m, 1H), 1.77 – 1.58 (m, 3H), 1.55 – 1.48 (m, 1H), 1.48 – 1.31 (m, 4H), 1.21 (s, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.81 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 213.22 (s), 58.80 (s), 58.71 (s), 52.19 (s), 50.52 (s), 45.47 (s), 35.69 (s), 31.09 (s), 30.28 (s), 28.24 (s), 25.27 (s), 24.97 (s), 22.65 (s), 17.64 (s).IR (neat): 2953.9 (br s), 2871.7 (m), 2763.9 (w), 1698.0 (s), 1461.2 (s), 1352.6 (m), 1041.4 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{15}{}^1H_{30}{}^{14}N_1{}^{16}O_1$ $[M+H]^+$: calculated: 240.2327, found: 240.2337.



1-((1R,2S,3S)-3-isopropyl-1-methyl-2-vinylcyclopentyl)ethan-1-one (43). Adapted from published procedure.[12] A 50 mL round bottom equipped with magnetic stirbar is charged with **42** (823 mg, 3.44 mmol) and solution made with reagent grade MeOH (18.8 mL, 0.18 M). The reaction vessel and contents are brought to 0°C and aqueous H_2O_2 (2.96 mL, ca. 30% w/w) added gradually. The mixture is allowed to stir overnight (19.5h), slowly reaching room temperature. Upon return, excess H_2O_2 is degraded by adding two spatula tips (ca. 50 mg) MnO_2 to mixture and stirring for 1h at room temperature (or until bubbling ceases). The mixture is then filtered through a pad of celite, rinsing with MeOH. Filtrate concentrated, then redissolved in DCM and dried over Na_2SO_4. Solution decanted then concentrated to yield crude, N-oxide intermediate as a yellow oil. A 40 mL vial containing N-oxide intermediate and magnetic stirbar is charged with TMANO dihydrate (1.15 g, 10.3 mmol, 3.0 equiv.). The vessel is then charged with 14.5 mL DMF (purchased as anhydrous from Acros, stored over sieves in sealed container with septum). Reaction vessel is sealed and set to stir at 130°C in preheated oil bath for 1h, where the mixture gradually becomes more yellow in color. Reaction removed from oil bath and allowed to cool to room temperature then poured into a separatory funnel and diluted with Et_2O (ca. 50 mL). Organics washed 4x with ca. 10 mL H_2O the once with Brine. Organics dried over Na_2SO_4 then decanted and concentrated to yield yellow oil. Crude yellow oil is purified by SiO_2 chromatography (2% Et_2O/pentane, visualized with $KMnO_4$ stain) to render product as pale yellow oil with pleasant, turpentine-like smell. **(425 mg, 2.19 mmol, 63%).** ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.57 (dt, *J* = 17.0, 10.0 Hz, 1H), 5.03 – 4.96 (m, 2H), 2.16 (m, 1H), 2.06 (s, 3H), 2.01 (m, 1H), 1.82 – 1.73 (m, 2H), 1.63 – 1.54 (m, 1H), 1.45 – 1.35 (m, 1H), 1.35 – 1.29 (m, 1H), 1.26 (s, 3H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.80 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 213.07 (s), 139.95 (s), 115.90 (s), 59.58 (s), 59.52 (s), 51.02 (s), 35.21 (s), 30.36 (s), 28.61 (s), 25.92 (s), 24.41 (s), 21.95 (s), 18.19 (s). IR (neat): 2956.8 (s), 2872.6 (m), 1700.7 (s), 1464.5 (m), 1352.7 (m), 1002.7 (w), 912.2 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{13}{}^1H_{23}{}^{16}O_1$ $[M+H]^+$: calculated: 195.1749, found: 195.1750.

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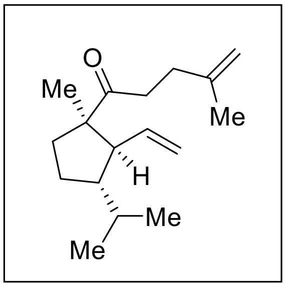
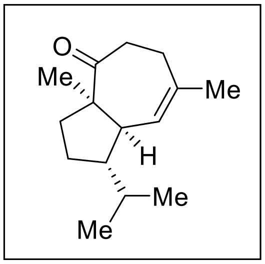
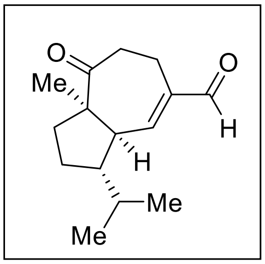
[12] White, J. D.; Ihle, D. C. *Org. Lett.* **2006**, *8*, 1081



1-((1R,2S,3S)-3-isopropyl-1-methyl-2-vinylcyclopentyl)-4-methylpent-4-en-1-one (S18). A flamed dried 20 mL vial equipped with magnetic stirbar is sealed with rubber septum, then evacuated/refilled with N_2 3x. LDA is prepared freshly in the vial at -78°C by slow addition of *n*BuLi in Hexanes (812 μL, 2.5 M, 1.05 equiv.) to a solution of diisopropyl amine (285 μL, 2.03 mmol, 1.05 equiv.) in 0.5 mL anhydrous THF. Mixture is allowed to stir for ca. 15min at -78°C then a solution of **43** (376 mg, 1.93 mmol, 1.0 equiv.) in 1.5 mL anhydrous THF added dropwise. Resulting mixture allowed to stir for 40min at -78°C then 20min at 0°C. At this point, freshly prepared, neat methallyl iodide (218 μL, 2.03 mmol, 1.05 equiv.) charged in at once. Resulting mixture allowed to stir overnight (14h), slowly reaching room temperature. Upon return, mixture is quenched with ca. 1 mL H_2O then extracted 3x with ca. 5 mL Et_2O. Combined organics dried over Na_2SO_4 then decanted and concentrated to render crude oil. Crude oil purified by SiO_2 chromatography (pentane, then 1% Et_2O/pentane, visualized with $KMnO_4$). Product isolated as clear, colorless oil **(428 mg, 1.73 mmol, 89%)**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.54 (ddd, *J* = 17.3, 9.9 Hz, 9.9 Hz, 1H), 5.05 – 4.92 (m, 2H), 4.70 (s, 1H), 4.65 (s, 1H), 2.51 (t, *J* = 7.7 Hz, 2H), 2.31 – 2.07 (m, 3H), 2.02 (t, *J* = 9.1 Hz, 1H), 1.84 – 1.74 (m, 2H), 1.71 (s, 3H), 1.63 – 1.52 (m, 1H), 1.47 – 1.29 (m, 2H), 1.28 (s, 3H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 214.04 (s), 145.19 (s), 140.02 (s), 115.82 (s), 109.87 (s), 59.83 (s), 59.39 (s), 51.10 (s), 38.77 (s), 35.43 (s), 31.44 (s), 30.44 (s), 26.01 (s), 24.15 (s), 22.65 (s), 21.96 (s), 18.27 (s). IR (neat): 2956.4 (s), 2872.7 (m), 1700.0 (s), 1649.7 (w), 1459.4 (m), 1375.9 (w), 1003.2 (m), 911.3 (m), 887,0 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{17}{}^{1}H_{29}{}^{16}O_1$ $[M+H]^+$: calculated: 249.2198, found: 249.2220.



(1S,3aR,8aR)-1-isopropyl-3a,7-dimethyl-2,3,3a,5,6,8a-hexahydroazulen-4(1H)-one (44). A 25 mL, 2-neck round bottom is fixed with a stopcock side-arm and a reflux condenser. The vessel is equipped with a magnetic stirbar then the whole apparatus flame dried. Upon cooling to near room temperature, the vessel is charged with Hoveyda-Grubbs 2nd Generation (94 mg, 0.15 mmol, 10 mol%) then sealed and evacuated/refilled with N_2 3x. A solution of **S18** (368 mg, 1.48 mmol, 1.0 equiv.) in 8.9 mL anhydrous toluene is then transferred to the reaction vessel. The green mixture is then set to stir at 80°C with a steady stream of N_2 blowing across the solution, from the side-arm out the reflux condenser (in order to remove forming ethylene from solution). Reaction is allowed to stir for 8.5h then cooled to room temperature. The reaction solution is then concentrated *in vacuo* and crude oil purified by SiO_2 chromatography (1% Et_2O/Pentane, then 2.5% Et_2O/Pentane, visualized with $KMnO_4$). Clear, colorless oil results **(298 mg, 1.35 mmol, 91%)**. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.22 (d, *J* = 4.2 Hz, 1H), 2.74 (ddd, *J* = 14.6, 5.6, 4.0 Hz, 1H), 2.61 – 2.49 (m, 1H), 2.42 (ddd, *J* = 14.6, 12.0, 5.7 Hz, 1H), 2.27 – 2.18 (m, 1H), 2.09 – 1.98 (m, 2H), 1.79 – 1.73 (m, 1H), 1.71 (s, 3H), 1.61 (ddd, *J* = 14.7, 10.5, 7.4 Hz, 1H), 1.55 (dq, *J* = 13.6, 6.7 Hz, 1H),1.38 – 1.26 (m, 2H), 1.22 (s, 3H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 213.86 (s), 138.28 (s), 131.34 (s), 58.74 (s), 56.24 (s), 51.73 (s), 39.07 (s), 34.54 (s), 33.17 (s), 29.00 (s), 27.14 (s), 24.62 (s), 24.17 (s), 22.03 (s), 20.03 (s). IR (neat): 2953.7 (m), 2869.7 (m), 1698.7 (s), 1459.0 (w), 1446.4 (w), 1384.9 (w), 1072.2 (w), 1006.4 (w), 816.1 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{15}{}^{1}H_{25}{}^{16}O_{1}$ [M+H]$^{+}$: calculated: 221.1905, found: 221.1904.



(3S,3aR,8aR)-3-isopropyl-8a-methyl-8-oxo-1,2,3,3a,6,7,8,8a-octahydroazulene-5-carbaldehyde (Aphanamal). A 20 mL vial containing **44** (294 mg, 1.33 mmol, 1.0 equiv.) was equipped with magnetic stirring bar and charged with SeO$_2$ (177 mg, 1.6 mmol, 1.2 equiv.). The vial was then sealed with a rubber septum and evacuated/refilled with N$_2$ 3x. Anhydrous 1,4-dioxane (6.6 mL, 0.2 M) was then charged in and the resulting, heterogeneous mixture set to stir (ca. 800 rpm) at 80°C in a preheated oil bath. The mixture becomes clear, orange in appearance and homogeneous within 30min of heating. After stirring at 80°C for 3h, the mixture is cooled to room temperature then passed through a pad of SiO$_2$, rinsing with Et$_2$O. The filtrate is concentrated to render crude, orange oil. SiO2 chromatography performed (5% Et$_2$O/Pentane, gradient to 20% Et$_2$O/Pentane). Product isolated as yellow oil **(153 mg, 0.65 mmol, 49%)**. ^{13}C and ^{1}H NMR spectra are in accord with published values.[13] ^{1}H NMR (600 MHz, CDCl$_3$): δ 9.33 (s, 1H), 6.62 (d, J = 5.3 Hz, 1H), 2.80 – 2.75 (m, 1H), 2.73 – 2.67 (m, 1H), 2.52 (dd, J = 8.7, 5.4 Hz, 1H), 2.51 – 2.46 (m, 1H), 2.45 – 2.39 (m, 1H), 2.24 – 2.15 (m, 1H), 1.88 – 1.76 (m, 2H), 1.64 (dq, J = 13.4, 6.7 Hz, 1H), 1.47 – 1.36 (m, 2H), 1.31 (s, 3H), 0.92 (d, J = 6.7 Hz, 6H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 212.06 (s), 192.63 (s), 158.54 (s), 143.71 (s), 59.58 (s), 55.32 (s), 53.10 (s), 38.86 (s), 35.09 (s), 32.30 (s), 26.74 (s), 24.94 (s), 21.91 (s), 19.62 (s), 19.41 (s). IR (neat): 2957.2 (m), 2871.5 (w), 1683.9 (s), 1635.7 (w), 1459.1 (w), 1313.1 (w), 1173.5 (w), 793.5 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{15}{}^{1}H_{23}{}^{16}O_{2}$ [M+H]$^{+}$: calculated: 235.1698, found: 235.1701.

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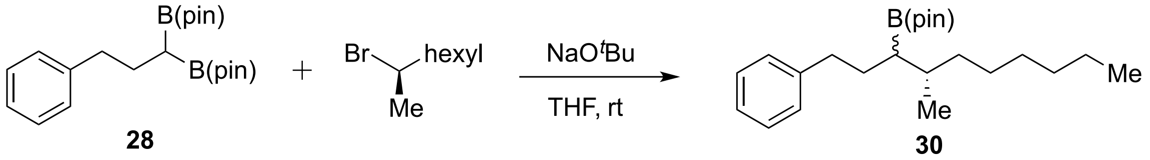
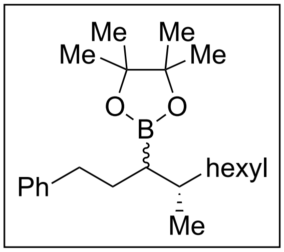
[13] Moriyasu, M.; Takeuchi, S.; Ichimaru, M.; Nakatani, N.; Nishiyama, Y.; Kato, A.; Mathenge, S. G.; Juma, F. D.; ChaloMutiso, P. B. *J. Nat. Med.* **2012**, *66*, 453.

VII. Mechanistic Studies

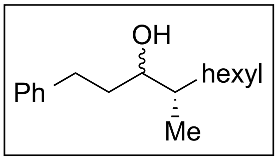
1. Radical Probe Experiment I

Procedure for Deborylative Alkylation Experiment:





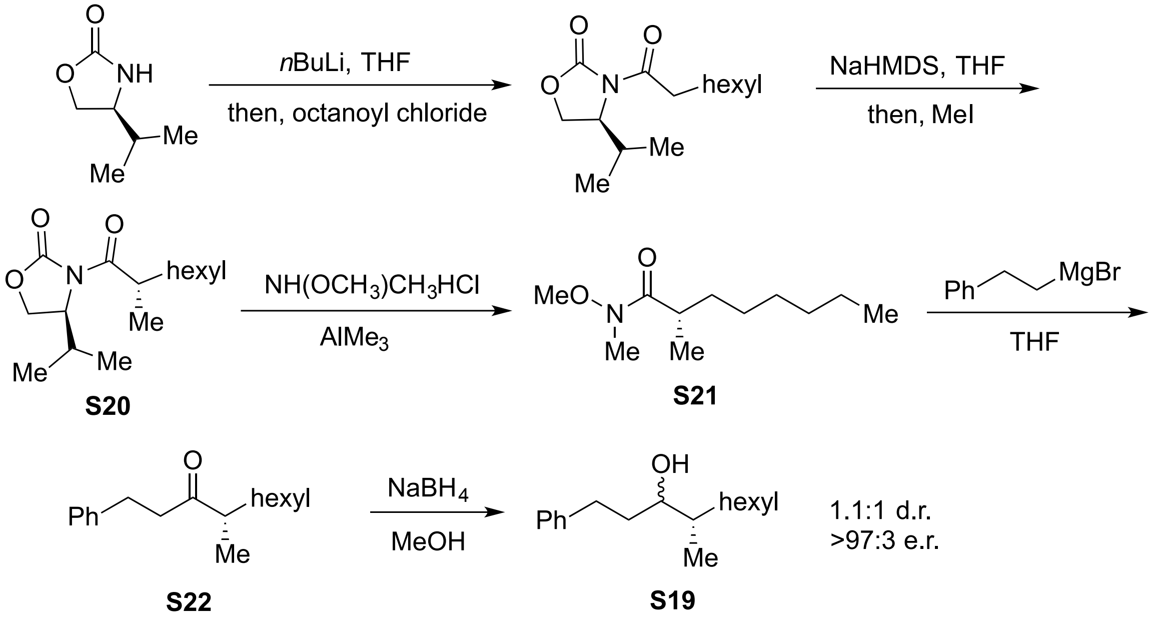
4,4,5,5-tetramethyl-2-((4*S*)-4-methyl-1-phenyldecan-3-yl)-1,3,2-dioxaborolane (30). In the glove box, an oven-dried 2-dram vial equipped with magnetic stir bar is charged with 1,1-diboronate ester **28** (96.8 mg, 0.26 mmol), NaO^{t}Bu (50 mg, 0.52 mmol), and THF (1 mL). The reaction mixture was allowed to stir at room temperature for 15 min, followed by the addition of (*R*)-2-bromooctane (35.1 μL, 0.20 mmol). The vial was sealed with a polypropylene cap, removed from the glove box, and was allowed to stir at room temperature for overnight. Upon completion, the reaction mixture was diluted with diethyl ether (2 mL), filtered through a silica gel plug, rinsed with diethyl ether, and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (hexanes: ethyl acetate = 100:1 to 50:1) to isolate the desired product (35 mg, 49%, 1.1:1 d.r. 98:2 er)(diastereoselectivity was determined based on NMR integration after oxidation). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28 – 7.26 (m, 3H), 7.21 – 7.13 (m, 2H), 2.72 – 2.57 (m, 1H), 2.57 – 2.43 (m, 1H), 1.87 – 1.68 (m, 1H), 1.68 – 1.56 (m, 2H), 1.43 – 1.33 (m, 1H), 1.32 – 1.19 (m, 8 H, overlap), 1.27 (s, 12H), 1.18 – 1.07 (m, 1H), 1.04 - 0.98 (m, 1H), 0.93 – 0.84 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.26, 128.36, 128.17, 125.48, 82.83, 36.42, 36.15, 36.09, 35.91, 34.62, 34.38, 31.89, 31.51, 30.20, 29.58, 29.56, 27.52, 27.25, 25.08, 25.06, 24.79, 22.64, 18.75, 18.44, 14.09; IR (neat): 2956.5 (m), 2926.9 (s), 2856.3 (m), 1729.6 (w), 1456.9 (w), 1379.1 (m), 1313.8 (m), 1270.7 (w), 1143.9 (s), 699.1 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{23}{}^{1}H_{40}{}^{11}B_{1}{}^{16}O_{2}$ [M+H]$^+$: calculated: 359.3121, found: 359.3139.



(4*S*)-4-methyl-1-phenyldecan-3-ol (S19). To a 20 mL vial containing the compound **30** and THF (1 mL), aqueous NaOH (0.6 mL, 3 M, 1.8 mmol) is added then the vial is cooled 0 °C. Aqueous Hydrogen Peroxide (0.3 mL, 30% in H_2O) is then slowly added to the reaction vessel and reaciton allowed to stir overnight. Upon return, the vessel is cooled back to 0 °C and quenched slowly with saturated, aqueous $Na_2S_2O_3$ (1 mL), stirred for 30 minutes, then extrated with diethyl ether. Combined extracts are then dried over Na_2SO_4 and concentrated *in vacuo*. The crude residue is then purified by column chromatography on silica gel. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32 – 7.27 (m, 4H), 7.24 – 7.16 (m, 6H), 3.54 (dt, *J* = 10.6, 5.5 Hz, 1H), 3.48 (dtd, *J* = 9.8, 5.1, 2.9 Hz, 1H), 2.95 – 2.78 (m, 2H), 2.73 – 2.59 (m, 2H), 1.84 – 1.73 (m, 4H), 1.57 – 1.47 (m, 2H), 1.46 – 1.38 (m, 2H), 1.38 – 1.22 (m, 17H), 1.21 –1.14 (m, 2H), 1.14 – 1.05 (m, 1H), 0.95 – 0.84 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 142.36, 142.31, 128.42, 128.36, 125.76, 75.44, 74.72, 39.01, 38.45, 36.26, 35.19, 33.23, 32.69, 32.56, 31.92, 31.84, 29.69, 29.60, 29.58, 27.31, 27.25, 22.65, 15.20, 14.08, 13.69; IR (neat): 3357.0 (w), 2956.7 (m), 2927.8 (s), 2855.0 (m), 1724.7 (m), 1455.3 (w), 1275.3 (w), 1131.9 (w), 751.2 (m), 698.4 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{17}{}^{1}H_{27}$ [M+H-H$_2$O]$^+$: calculated: 231.2113, found: 231.2118.

Proof of Stereochemistry:

The same title compound was prepared from Evans Alkylation as shown below:



(*R*)-4-isopropyl-3-((*S*)-2-methyloctanoyl)oxazolidin-2-one **(S20)** prepared according to the literature procedure.[14] The product is obtained as a colorless oil (78%, d.r. = 88:12). The NMR spectra are in accord with previously reported data. [15] Preparation of (*S*)-*N*-methoxy-*N*,2-dimethyloctanamide **S21** adapted from literature procedure.[16] To a stirred solution of *N*,*O*-Dimethylhydroxylamine hydrochloride (312.1 mg, 3.2 mmol) in CH_2Cl_2 (5 ml) at 0 °C, neat $AlMe_3$ (307 µL, 3.2 mmol) is carefully added. The reaction mixture is stirred at 0 °C for 10 min and then one hour at room temperature. The mixture is then cooled back to 0 °C and a solution of oxazolidone **S20** (227 mg, 0.8 mmol) in CH_2Cl_2 (5 ml) is added to the reaction vessel. The resulting mixture is then allowed to stir overnight, gradually reaching room temperature. Upon return, the reaction solution is diluted with CH_2Cl_2 (10 mL) and poured into a separatory funnel containing ice-cold aqueous 0.5 N HCl (25 ml) and organics are extracted 3x with CH_2Cl_2. The combined extracts are then washed with saturated, aqueous $NaHCO_3$ and saturated, aqueous

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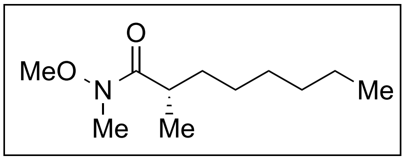
[14] Evans, D. A.; Ennis, M. D.; Le, T. *J. Am. Chem. Soc.* **1984**, *106*, 1155

[15] Minko, Y.; Pasco, M.; Lercher, L.; Botoshansky, M.; Marek, I. *Nature* **2012**, *490*, 522

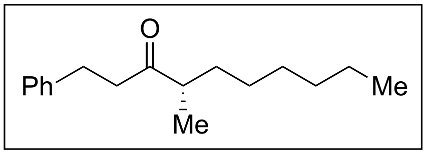
[16] Micalizio, G. C.; Pinchuk, A. N.; Roush, W. R. *J. Org. Chem.* **2000**, *65*, 8730

NaCl, in succession, then dried over Na_2SO_4. Volatiles are then removed *in vacuo* and the crude, colorless oil is then purified by silica gel chromatography (8:2 pentane/Et_2O, gradient to 7:3 pentane/Et_2O) to afford (*S*)-*N*-methoxy-*N*,2-dimethyloctanamide **S21** as a colorless oil (38.2 mg, 22 %).



(*S*)-*N*-methoxy-*N*,2-dimethyloctanamide (S21). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.68 (s, 3H), 3.19 (s, 3H), 2.86 (s, 1H), 1.67 (ddd, *J* = 13.2, 8.3, 5.3 Hz, 1H), 1.32 – 1.18 (m, 9H), 1.11 (d, *J* = 6.8 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 61.40, 35.09, 33.83, 31.73, 29.68, 29.31, 27.50, 22.61, 17.45, 14.04; IR (neat): 2964.0 (m), 2930.4 (m), 2871.7 (m), 1779.3 (s), 1699.3 (m), 1385.5 (m), 1300.8 (w), 1204.9 (m), 1141.6 (m), 911.6 (w), 733.4 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{11}{}^1H_{24}{}^{14}N_1{}^{16}O_2$ $[M+H]^+$: calculated: 202.1807, found: 202.1797.

To a dried flask fitted with magnetic stir bar and charged with Mg^0 (36.5 mg, 1.5 mmol) and anhydrous THF (5 mL), (2-bromoethyl)benzene (0.17 mL, 1.25 mmol) is added slowly under N_2. Mixture is then stirred at 60 °C for two hours and the resulting Grignard solution is cooled back to room temperature where it is added to a solution of amide **S21** (38.2 mg, 0.177 mmol) in anhydrous THF (1 mL) drop wise at 0 °C. The reaction mixture is allowed to stir for 3h, gradually warming to room temperature. Upon completion, reaction is cooled to 0 °C and quenched with saturated, aqueous NH_4Cl (1 mL). Organics are then extracted with diethyl ether (3 × 3 mL) and the combined extracts washed with brine and dried over anhydrous Na_2SO_4. Volatiles are then removed *in vacuo* and the crude residue was purified on silica gel (hexane: ethyl acetate= 100:1, gradient to 20:1) to afford compound **S22** as an colorless oil (34 mg, 78%).



(*S*)-4-methyl-1-phenyldecan-3-one (S22). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.26 (m, 2H), 7.21 – 7.16 (m, 3H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.78 – 2.70 (m, 2H), 2.48 (h, *J* = 6.9 Hz, 1H), 1.65 – 1.56 (m, 1H), 1.35 – 1.12 (m, 9H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 213.81, 141.35, 128.41, 128.33, 126.00, 46.54, 42.65, 32.94, 31.63, 29.74, 29.30, 27.18, 22.56, 16.16, 14.03; IR (neat): 2958.0 (s), 2928.3 (s), 2858.2 (m), 1728.0 (s), 1462.1 (m), 1272.6 (s), 1122.5 (m), 1072.6 (m), 744.7 (w), 699.4 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{17}{}^1H_{27}{}^{16}O_1$ $[M+H]^+$: calculated: 247.2062, found: 247.2053.

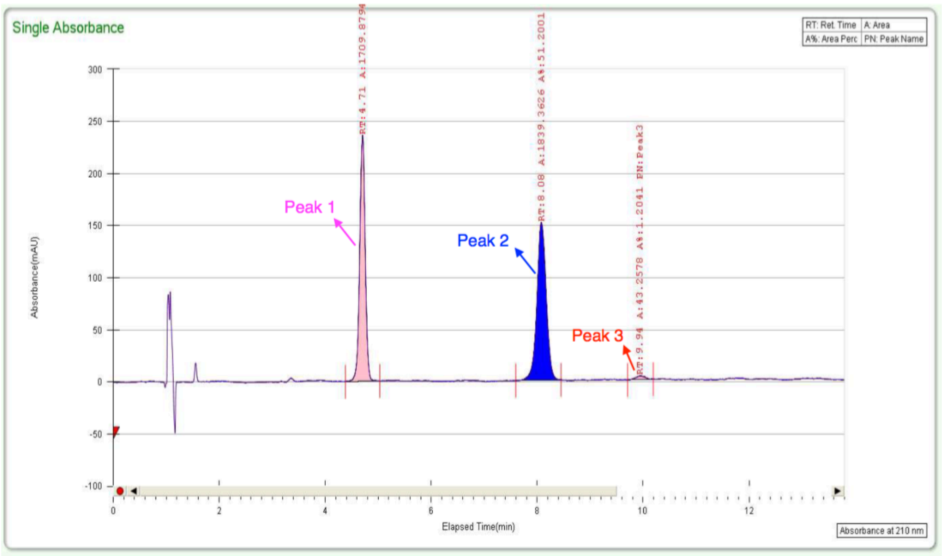
To a vial containing a solution of (*S*)-4-methyl-1-phenyldecan-3-one **S22** (34 mg, 0.14 mmol) in MeOH (1 mL), $NaBH_4$ (10.6 mg, 0.28 mmol) is added at 0 °C. The reaction mixture is then allowed to stir for 20 min at room temperature, then quenched with saturated aqueous NH_4Cl (1 mL). Organics are then extracted with diethyl ether (3 × 3 mL) and the combined organic layers washed with brine and dried over anhydrous Na_2SO_4. Volatiles are then removed *in vacuo* and the crude residue purified on silica gel (hexane: ethyl acetate = 10:1) to yield

(4*S*)-4-methyl-1-phenyldecan-3-ol **S19** as an colorless oil (32 mg, 92%, 1.1:1 d.r., 97:3 er). (diastereoselectivity was determined based on NMR integration). The spectra data is the same as shown above.

Analysis of Stereochemistry

The enantioselectivity was determined by SFC analysis of the reaction product shown below.

SFC trace of base promoted deborylative alkylation product compound **30** (after oxidation):



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Report By      current_User
Report Date    4/10/2017
Method Name    potterbo.met
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Injection Info                                      Temp           34.8
Inj Vol          10                                 Flow           3
Solvent          IPA                                % Modifier     10
Column           OD-H                               Pressure       100
Sample           xl-4-098-fineagain
Well location    P1: 1A

Peak Info
Peak No     % Area      Area        RT (min)            Height (mV)       K'
1           47.5958     1709.8794   4.71                236.3671          0.0042
2           51.2001     1839.3626   8.08                151.5557          0.0073
3           1.2041      43.2578     9.94                3.6284            0.009
Total:      100         3592.4998
```

Diastereoselectivity = Area of Peak1/ Area of (Peak 2 + Peak 3)

= 1709.8794/ (1839.3626 + 43.2578)

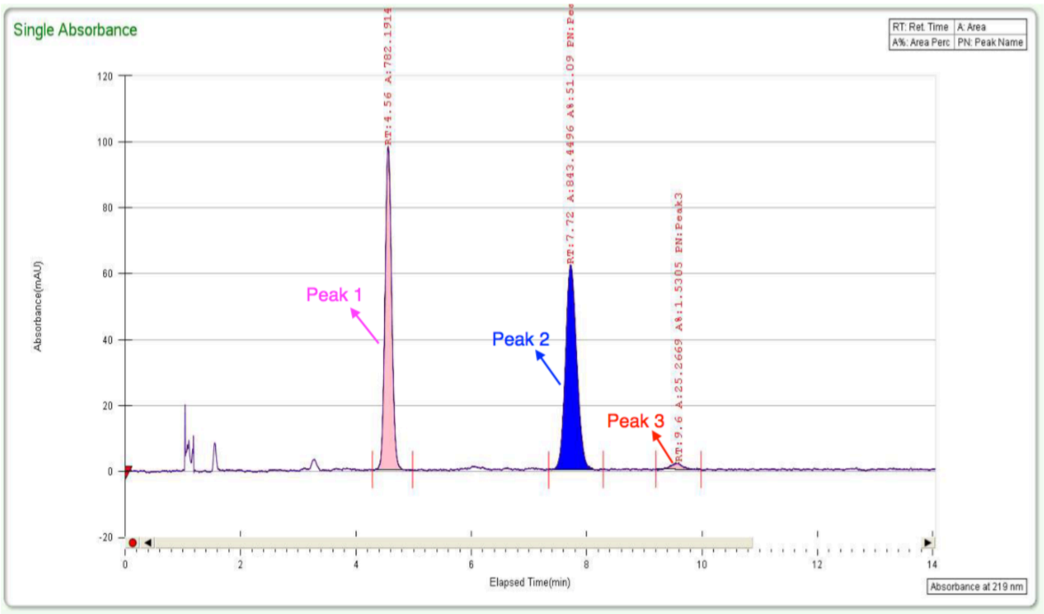
= 1/1.1

Enantioselectivity = Area of (Peak 2 - Peak 3)/ Area of (Peak 2 + Peak 3)

= (1839.3626 - 43.2578)/ (1839.3626 + 43.2578)

= 95 %

SFC trace of authentic product prepared from Evans alkylation compound **S19**:



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Log Date        10/19/2015 5:12:06 PM
Report By       current_User
Report Date     4/10/2017
Method Name     potterbo.met
Notes           ODH, 100 bar,  10% iPA, 3 mL/min, 35 deg C

Injection Info
Inj Vol           10
Solvent           IPA
Column            OD-H
Sample            xl-4-271-finediluteagain
Well location     P1: 3A
Temp              35
Flow              3
% Modifier        10
Pressure          101

Peak Info
Peak No     % Area      Area        RT (min)            Height (mV)     K'
1           47.3795     782.1914    4.56                97.939          0.0044
2           51.09       843.4496    7.72                62.1709         0.0075
3           1.5305      25.2669     9.6                 1.8841          0.0093
Total:      100         1650.9079
```
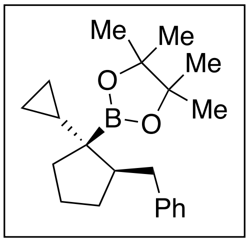

Diastereoselectivity = Area of Peak1/ Area of (Peak 2 + Peak 3)
= 782.1914/ (843.4496 + 25.2669)
= 1/1.1

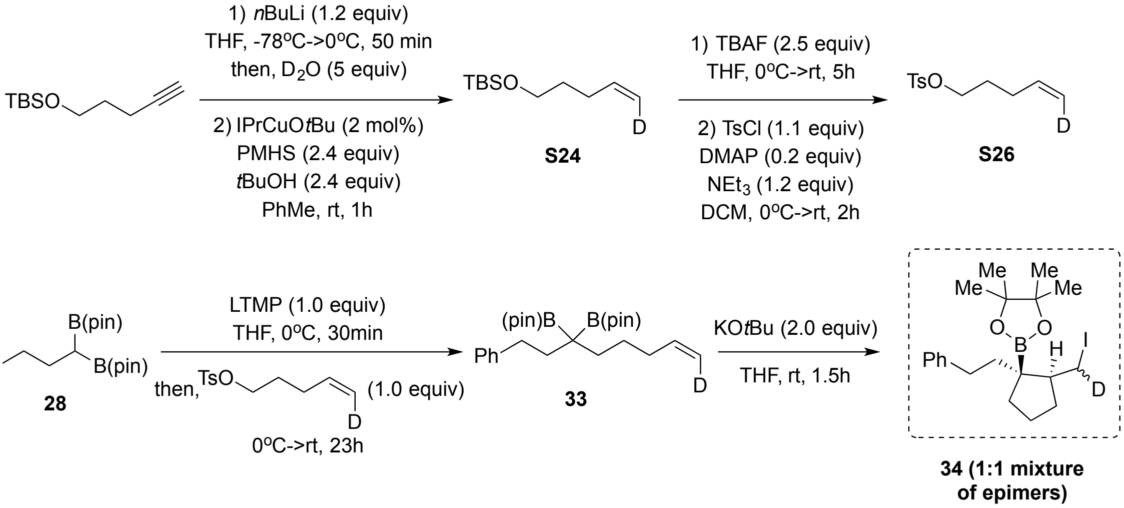
Enantioselectivity = Area of (Peak 2 - Peak 3)/ Area of (Peak 2 + Peak 3)
= (843.4496 - 25.2669)/ (843.4496 + 25.2669)
= 94 %

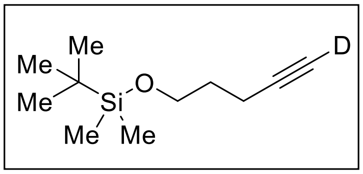
2. Radical Probe Experiment II



2-((1*R*,2*R*)-2-benzyl-1-cyclopropylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (32). The reaction was performed according to *Representative Procedure for Deborylative cyclization* with diboronate ester **31** (45.2 mg, 0.1 mmol), KO*t*-Bu (22.4 mg, 0.2 mmol), and THF (0.5 mL) for 6 hours. The crude reaction mixture was purified by column chromatography on silica gel (100:0.8 hexanes/ethyl acetate, stain in CAM) to afford a colorless oil (15 mg, 46 %, d.r. > 20:1, crude NMR shows the same diastereoselectivity). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 – 7.22 (m, 2H), 7.24 – 7.12 (m, 3H), 3.07 (dd, *J* = 13.2, 3.5 Hz, 1H), 2.43 (dd, *J* = 13.2, 11.7 Hz, 1H), 1.87 (tdd, *J* = 9.0, 6.6, 3.5 Hz, 1H), 1.76 – 1.62 (m, 1H), 1.66 – 1.57 (m, 2H), 1.52 – 1.40 (m, 1H), 1.35 – 1.19 (m, 1H), 1.26 (s, 12H), 1.15 – 1.02 (m, 1H), 0.86 (ddt, *J* = 11.3, 8.6, 3.7 Hz, 1H), 0.44 – 0.26 (m, 1H), 0.29 – 0.16 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.17, 128.89, 128.04, 125.35, 82.84, 52.53, 39.16, 30.96, 30.57, 24.92, 24.83, 22.42, 16.75, 2.07, 0.29; IR (neat): 2976.4 (w), 2954.8 (w), 2866.4 (w), 1495.0 (w), 1387.8 (m), 1299.9 (m), 1214.2 (w), 1141.6 (s), 1013.6 (w), 967.5 (w), 862.4 (w), 744.8 (w), 699.3 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{21}{}^{1}H_{32}{}^{11}B_{1}{}^{16}O_{2}$ $[M+H]^+$: calculated: 327.2495, found: 327.2492.

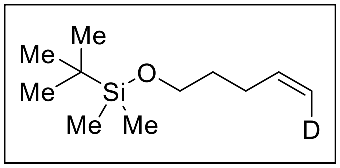
3. ^{2}D-Labeled Experiment



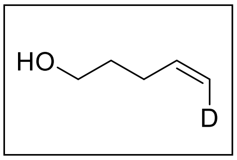


***tert*-butyldimethyl((pent-4-yn-1-yl-5-*d*)oxy)silane (S23).** A flame dried 20 mL vial equipped with stir bar is charged with *tert*-butyldimethyl(pent-4-yn-1-yloxy)silane (1.87 g, 9.43 mmol, 1.0 equiv), then sealed and evacuated/backfilled with N_2 3x. Anhydrous THF (9.4 mL) is then charged in the vessel and the clear colorless solution set to stir at -78°C. A solution of *n*BuLi in Hexanes (4.20 mL, 2.70 M, 11.3 mmol, 1.2 equiv) is then added dropwise, resulting in a clear, yellow solution. After stirring for 30min at -78°C, the mixture is brought to 0°C and allowed to stir an additional 20min.

At this point, the reaction is quenched by slow addition of D_2O (853 µL, 47.2 mmol, 5.0 equiv), resulting in a white slurry. The resulting mixture is allowed to stir for 4h, then directly dried over Na_2SO_4 and passed through a pad of SiO_2, rinsing with Et_2O. Filtrate is then concentration to yield clear, colorless oil (1.88 g, 9.43 mmol, quantitative). No further purification necessary. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.70 (t, *J* = 6.0 Hz, 2H), 2.27 (t, *J* = 7.1 Hz, 2H), 1.78 – 1.68 (m, 2H), 0.89 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 61.41, 31.51, 25.90, 18.29, 14.79, -5.39; IR (neat): 2988.3 (s), 2946.7 (w), 2870.2 (s), 1393.6 (w), 1142.5 (s) cm^{-1}; HRMS-(DART+) for $^{12}C_{11}{}^{1}H_{22}{}^{2}D_{1}{}^{29}Si_{1}{}^{16}O_{1}$ $[M+H]^+$: calculated: 200.1581, found: 200.1572.



(*Z*)-*tert*-butyldimethyl((pent-4-en-1-yl-5-*d*)oxy)silane (S24). Adapted from published procedure.[17] A flame dried 250 mL round bottom equipped with magnetic stir bar is charged with **S23** (1.43 g, 7.2 mmol, 1.0 equiv) inside an argon-filled glovebox. *t*BuOH (990 mg, 13.4 mmol, 2.4 equiv) is then added to the vessel, followed by toluene (60 mL) then Polymethylhydrosiloxane (979 µL, 17.3 mmol (monomer), 2.4 equiv). The mixture is set to stir, then IPrCuO*t*Bu[18] (75.6 mg, 0.14 mmol, 2 mol%) is added, at which point bubbling is observed. The vessel is sealed with a rubber septum, then moved to the fume hood where it is allowed to stir for 1h at room temperature. At this point, the reaction mixture turns dark brown and it is passed through a pad of silica gel, rinsing with Et_2O. The filtrate is concentrated then SiO_2 chromatography performed (0% Et_2O/Pentanes, gradient to 2.5% Et_2O/Pentanes, visualizing with $KMnO_4$). Product coelutes with PMHS and yield is carried across two steps. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.85 – 5.77 (m, 1H), 4.94 (d, *J* = 10.2 Hz, 1H), 3.62 (t, *J* = 6.5 Hz, 2H), 2.10 (td, *J* = 7.6, 0.9 Hz, 2H), 1.64 – 1.58 (m, 2H), 0.90 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): 138.45 (s), 114.19 (t, *J*=23.5 Hz), 62.53 (s), 31.99 (s), 29.97 (s), 25.95 (s), 18.34 (s), -5.30 (s); IR (neat): 2987.3 (m), 2871.0 (m), 1142.4 (s) cm^{-1}; HRMS-(DART+) for $^{12}C_{11}{}^{1}H_{24}{}^{2}D_{1}{}^{29}Si_{1}{}^{16}O_{1}$ $[M+H]^+$: calculated: 202.1737, found: 202.1741.



(*Z*)-pent-4-en-5-*d*-1-ol (S25). A 50 mL round bottom equipped with magnetic stir bar is charged with a solution of **S24** (1.36 g, 6.75 mmol, 1.0 equiv; mixed with PMHS, see above) in anhydrous THF (6.75 mL). The vessel and contents are then brought to 0°C, at which point TBAF solution in THF (16.8 mL, 1 M, 16.8 mmol, 2.5 equiv) is added dropwise (exothermic process). After addition, the mixture is allowed to stir at room temperature for 5h. The reaction mixture is then poured into a seperatory funnel containing ca. 10 mL brine and the organics are extracted 3x with ca. 10 mL Et_2O. Combined organics are then dried over Na_2SO_4 and concentrated to yield crude oil. Oil is purified by SiO_2 chromatography (2.5% Et_2O/Pentanes, gradient to 10% Et_2O/Pentanes, visualized with $KMnO_4$ to yield clear, colorless oil (343.9 mg, 3.95 mmol, 55%

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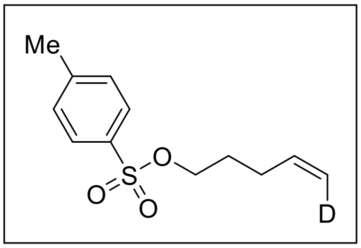
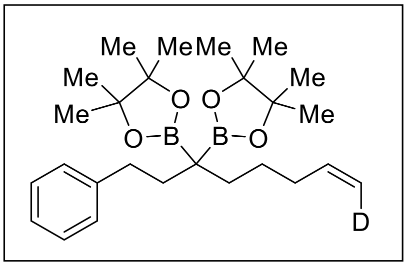
[17] Lalic, G.; Whittaker, A. M. *Org. Lett.*, **2013**, *15*, 1112

[18] For preparation see: Sadighi, J. P.; Mankad, N. P.; Laitar, D. S. *Organometallics*, **2004**, *23*, 3369

across 2 steps). ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.87 – 5.79 (m, 1H), 4.97 (d, *J* = 10.2 Hz, 1H), 3.67 (t, *J* = 6.5 Hz, 2H), 2.15 (td, *J* = 7.6, 0.8 Hz, 2H), 1.71 – 1.64 (m, 2H), 1.57 (br s, 1H); ^{13}C NMR (150 MHz, CDCl$_3$): δ 138.15 (s), 114.65 (t, *J*=23.5 Hz), 62.50 (s), 31.80 (s), 30.04 (s); IR (neat): 2988.5 (w), 2869.8 (w), 1141.9 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_5{}^1H_{10}{}^2D_1{}^{16}O_1$ [M+H]$^+$: calculated: 88.0873, found: 88.0870.

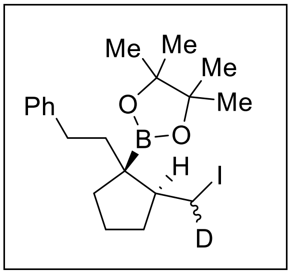


(*Z*)-pent-4-en-1-yl-5-*d* 4-methylbenzenesulfonate (S26). A flame dried 20 mL vial equipped with magnetic stir bar is charged with TsCl (904 mg, 4.74 mmol, 1.10 equiv) followed by DMAP (105 mg, 0.86 mmol, 0.20 equiv). The vial is sealed and evacuated/refilled with N$_2$ 3x, then a solution of **S25** (375 mg, 4.31 mmol, 1.0 equiv) in anhydrous DCM (21.6 mL) is charged in. The mixture is brought to 0°C then reagent grade NEt$_3$ (720 µL, 5.17 mmol, 1.2 equiv) is added dropwise. The reaction is then allowed to stir at room temperature for 2h. At this point, the reaction mixture is treated with ca. 5 mL H$_2$O and the organics are extracted 3x with ca. 5 mL DCM. Combined organics are dried over Na$_2$SO$_4$ then concentrated to yield crude oil. Crude material is purified by SiO$_2$ chromatography (2.5% Et$_2$O/Pentanes, gradient to 10% Et$_2$O/Pentanes, visualized with CAM stain) to render clear, colorless oil (666 mg, 2.76 mmol, 64%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.79 (d, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 5.72 – 5.64 (m, 1H), 4.94 (d, *J* = 10.1 Hz, 1H), 4.04 (t, *J* = 6.4 Hz, 2H), 2.45 (s, 3H), 2.08 (q, *J* = 7.1 Hz, 2H), 1.74 (p, *J* = 6.9 Hz, 2H); ^{13}C NMR (150 MHz, CDCl$_3$): δ 144.66 (s), 136.51 (s), 133.19 (s), 129.80 (s), 127.89 (s), 115.56 (t, *J*=23.6 Hz), 69.78 (s), 29.32 (s), 27.99 (s), 21.63 (s); IR (neat): 2957.1 (w), 1598.4 (w), 1359.0 (s), 1188.7 (s), 1097.8 (w), 928.0 (m), 810.6 (m), 664.2 (m), 554.6 (s) cm^{-1}; HRMS-(DART+) for $^{12}C_{12}{}^1H_{15}{}^2D_1{}^{32}S_1{}^{16}O_3{}^{23}Na_1$ [M+Na]$^+$: calculated: 264.0781, found: 264.0780.

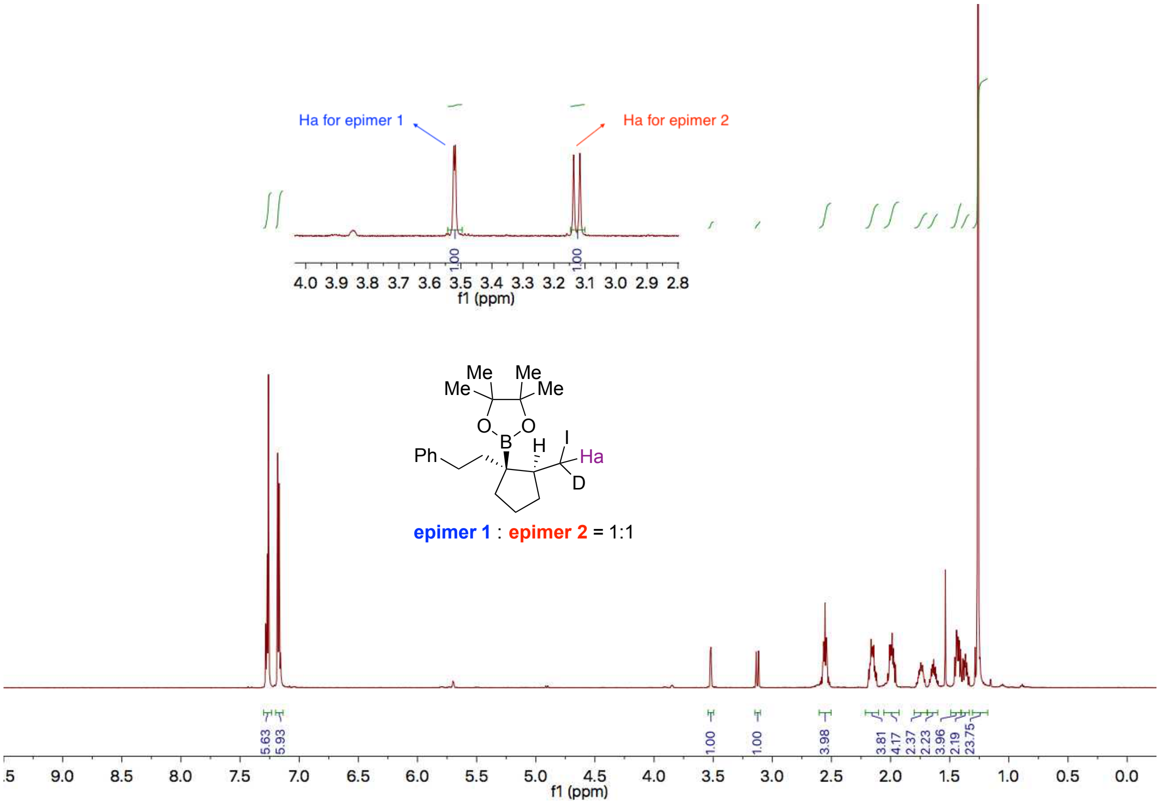


(*Z*)-2,2'-(1-phenyloct-7-ene-3,3-diyl-8-*d*)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (33). A flame dried 20 mL vial equipped with magnetic stir bar is charged with LTMP (405 mg, 2.75 mmol, 1.0 equiv) inside an argon-filled glovebox. The vial is sealed then moved to the hood where it is charged with anhydrous THF (9 mL). The orange solution is set to stir at 0°C then charged with a solution of **28** (1.02 g, 2.75 mmol, 1.0 equiv) in anhydrous THF (2 mL) where it is allowed to stir for 30 min. At this point, a solution of **S26** (663 mg, 2.75 mmol, 1.0 equiv) in anhydrous THF (2 mL) is added gradually. The mixture is brought to room temperature and allowed to stir overnight (23h). Upon return, the reaction mixture is diluted with Et$_2$O and passed through a pad of silica gel, rinsing with Et$_2$O. Filtrate is concentrated to render crude solid. Solid is purified by SiO$_2$ chromatography (0% EtOAc/Hexanes, gradient to 3% EtOAc/Hexanes, visualized with CAM stain). Product isolated as a white solid (938 mg, 2.13 mmol, 77%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.25 – 7.21 (m, 2H), 7.22 – 7.16 (m, 2H), 7.16 – 7.10 (m, 1H), 5.89 – 5.80 (m, 1H), 4.92 (d, *J* =

10.3 Hz, 1H), 2.54 – 2.46 (m, 2H), 2.08 (q, *J* = 7.0 Hz, 2H), 1.93 – 1.86 (m, 2H), 1.75 – 1.69 (m, 2H), 1.42 – 1.34 (m, 2H), 1.23 (s, 24H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.93 (s), 139.40 (s), 128.63 (s), 128.24 (s), 125.50 (s), 113.85 (t, *J*=23.5 Hz), 83.13 (s), 34.65 (s), 33.98 (s), 32.03 (s), 28.82 (s), 26.80 (s), 24.95 (s), 24.86 (s); IR (neat): 2978.5 (m), 2931.5 (w), 2858.9 (w), 1456.2 (w), 1378.6 (m), 1309.7 (s), 1255.2 (w), 1138.6 (s), 968.9 (w), 909.9 (m), 853.4 (m), 733.1 (s), 699.4 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{26}{}^{1}H_{42}{}^{2}D_{1}{}^{11}B_{2}{}^{16}O_{4}$ [M+H]$^+$: calculated: 442.3410, found: 442.3422.

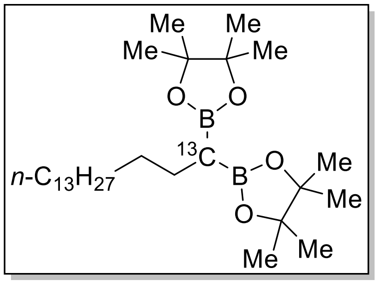


2-((1*R*,2*S*)-2-(iodomethyl-*d*)-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (34). The reaction was performed according to *Representative Procedure for Deborylative Cyclization* with **33** (88.2 mg, 0.2 mmol, 1.00 equiv), KO*t*Bu (44.9 mg, 0.4 mmol, 2.0 equiv) in THF (1 mL) for 1h 30min. Yellow reaction mixture was then quenched with an I_2 solution in anhydrous THF (0.8 mL, 0.5 M, 0.4 mmol, 2.0 equiv), where the reaction turns white, then purple. The crude reaction mixture was purified by SiO_2 chromatography (0% EtOAc/Hexanes, gradient to 1% EtOAc/Hexanes, visualized with CAM stain) to afford a white solid (60.0 mg, 0.136 mmol, 68%; 1:1 mixture of epimers). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 – 7.25 (m, 2H), 7.20 – 7.15 (m, 3H), 3.52 (d, *J* = 3.1 Hz, 0.5H), 3.13 (d, *J* = 12.1 Hz, 0.5H), 2.60 – 2.51 (m, 2H), 2.20 – 2.11 (m, 2H), 2.03 – 1.94 (m, 2H), 1.79 – 1.70 (m, 1H), 1.68 – 1.59 (m, 1H), 1.47 – 1.40 (m, 2H), 1.40 – 1.33 (m, 1H), 1.26 (s, 12H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.11 (s), 128.37 (s), 128.22 (s), 125.64 (s), 83.30 (s), 53.87 (s), 53.84 (s), 41.19 (s), 41.17 (s), 36.11 (s), 36.08 (s), 33.91 (s), 33.88 (s), 25.12 (s), 24.82 (s), 21.86 (s), 21.84 (s), 11.49 (t, *J*=22.9 Hz), 11.47 (t, *J*=22.9 Hz); IR (neat): 2976.1 (m), 2930.8 (m), 2867.2 (w), 1454.0 (w), 1380.7 (s), 1311.3 (s), 1199.0 (w), 1141.5 (s), 966.9 (w), 853.6 (w), 748.3 (w), 698.5 (m) cm^{-1}; HRMS-(DART+) for $^{12}C_{20}{}^{1}H_{29}{}^{2}D_{1}{}^{11}B_{1}{}^{16}O_{2}{}^{127}I_{1}{}^{23}Na_{1}$ [M+Na]$^+$: calculated: 464.1344, found: 464.1339.

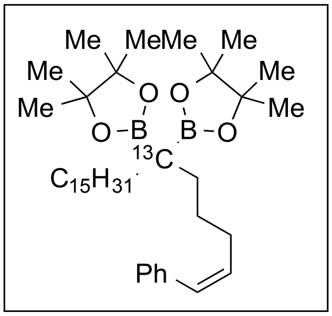


4. Analysis of Reaction Intermediates by ^{13}C-Labeled Experiments I

a) Preparation of ^{13}C-Labeled *geminal*-Diboronate Ester:



2,2'-(hexadecane-1,1-diyl-1-13C)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S27). Prepared from palmitic acid-1-^{13}C according to the literature procedure. The ^{1}H and ^{13}C NMR spectra were in accord with previously reported data.[19] ^{1}H NMR (500 MHz, CDCl$_3$): δ 1.55-1.53 (m, 2H), 1.31-1.22 (m, 50H), 0.88 (t, *J* = 6.9 Hz, 3H), 0.71 (2dt, *J* = 111.5, 7.8 Hz, 1H).



(*Z*)-2,2'-(1-phenylhenicos-1-ene-6,6-diyl-6-^{13}*C*)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (24). Prepared according to *Representative Procedure for Preparation of geminal-Diboronate Esters (Method D)* with **S27** (250 mg, 0.52 mmol), LTMP (92 mg, 0.624 mmol), (*Z*)-(5-bromopent-1-en-1-yl)benzene (141 mg, 0.624mmol) and THF (2.5 mL). The crude reaction mixture was purified by column chromatography on silica gel (100:1

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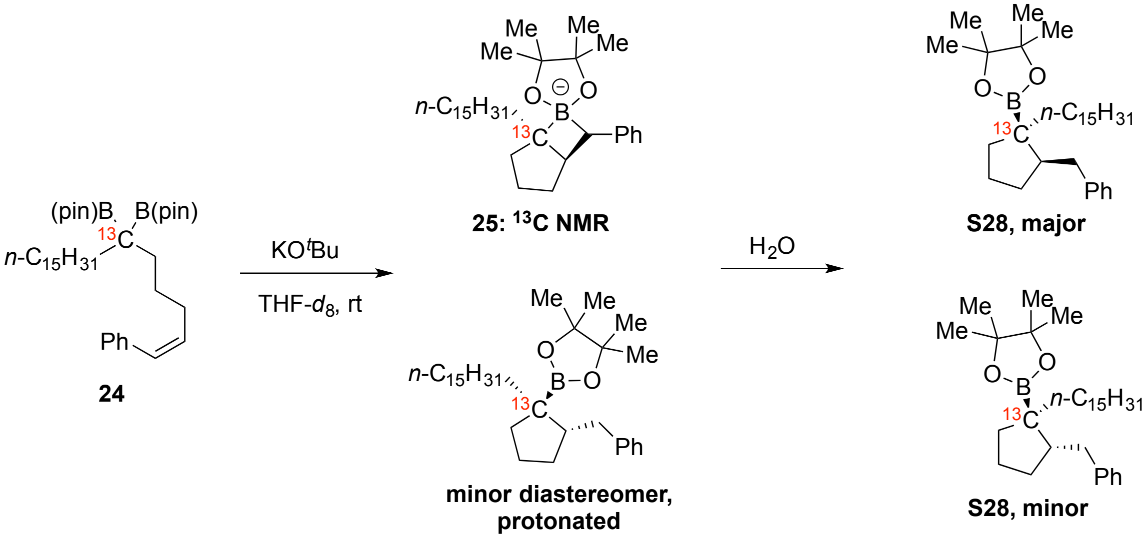
[19] K. Hong, X. Liu, and J. P. Morken *J. Am. Chem. Soc.* **2014**, *136,* 10581.

hexanes/ethyl acetate, stain in CAM) to afford a colorless oil (191 mg, 59%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 – 7.24 (m, 4H), 7.19 (t, *J* = 7.0 Hz, 1H), 6.36 (d, *J* = 11.7 Hz, 1H), 5.70 (dt, *J* = 11.8, 7.2 Hz, 1H), 2.60 – 2.22 (m, 2H), 1.71 – 1.63 (m, 2H), 1.59 (dt, *J* = 7.8, 4.1 Hz, 2H), 1.37 (t, *J* = 7.9 Hz, 2H), 1.31 – 1.22 (m, 26H), 1.21 (s, 24H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{1}H NMR (500 MHz, THF-d_8): δ 7.38 – 7.20 (m, 4H), 7.20 – 7.11 (m, 1H), 6.48 – 6.25 (d, *J* = 11.8 Hz, 1H), 5.71 – 5.58 (m, 1H), 2.36 – 2.22 (m, 2H), 1.67 – 1.52 (m, 4H), 1.48 – 1.37 (m, 2H), 1.29 (d, *J* = 2.6 Hz, 26H), 1.22 – 1.11 (m, 24H), 0.93 – 0.84 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.87, 133.55, 128.72, 128.34, 128.01, 126.26, 82.84, 31.91, 30.40, 30.36, 29.71, 29.69, 29.66, 29.65, 29.60, 29.34, 29.01, 28.94, 28.78, 28.70, 27.67, 27.12, 24.72, 22.67, 19.29, 14.09; ^{13}C NMR (125 MHz, THF-d_8): δ 139.00, 134.07, 129.71, 129.61, 128.94, 127.25, 83.55, 33.05, 31.73, 30.84, 30.78, 30.76, 30.48, 30.36, 28.81, 28.16, 23.73, 20.13(br, ***C***-B), 14.60; IR (neat): 2958.2 (m), 2924.6 (s), 2854.5 (m), 1729.3 (m), 1463.0 (w), 1377.4 (w), 1344.6 (w), 1288.6 (s), 1269.5 (s), 1138.7 (s), 1072.3 (w), 854.8 (w), 700.0 (w) cm^{-1}; HRMS-(DART+) for $^{12}C_{38}{}^{13}C_{1}{}^{1}H_{68}{}^{11}B_{2}{}^{16}O_{4}$ $[M+H]^{+}$: 624.5416, found: 624.5418.

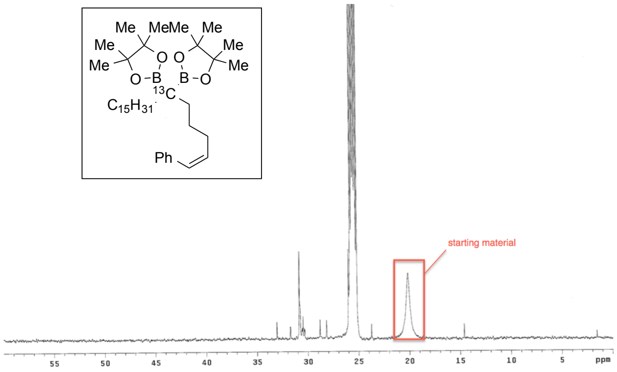
b) ^{13}C NMR Experiments



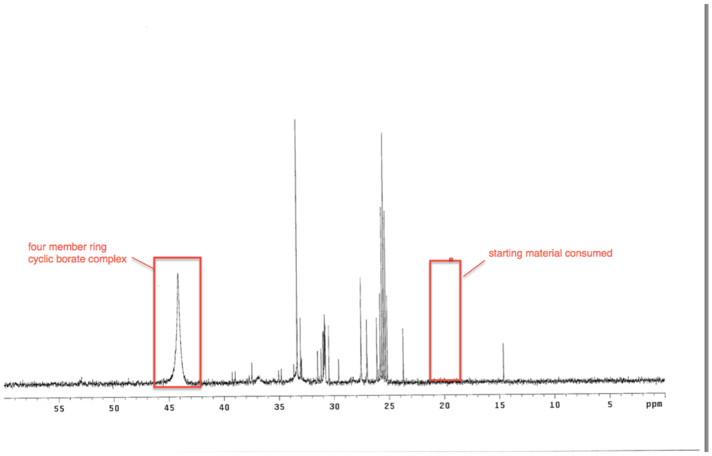
In the glove box, an oven-dried NMR tube is charged with diboronate ester **24** (31.2 mg, 0.05mmol), KO*t*-Bu (11.2 mg, 0.1 mmol) and THF-d_8 (0.60 mL). The NMR tube is then sealed with a rubber septum, removed from the glove box, and monitored by ^{13}C NMR at 25 °C. After 7 hours, water (2.7 μL, 0.15 mmol) is added via syringe, and the mixture again observed by ^{13}C NMR. At this point, the reaction mixture is diluted with diethyl ether, filtered through a silica gel plug, rinsed with diethyl ether, and concentrated *in vacuo*. The crude reaction mixture is purified on silica gel (hexanes: ethyl acetate = 100:0.6) to afford the desired product **S28** (19.6 mg, 79% yield, d.r. > 10:1) together with protodeborylation byproduct (2.1 mg).

^{13}C NMR Spectra of the Reaction Mixture (125 MHz, THF-d_8, δ 10–60 ppm):

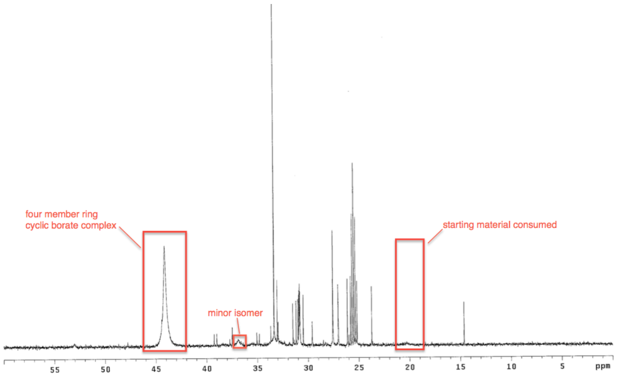
i. Diboronate ester **24**



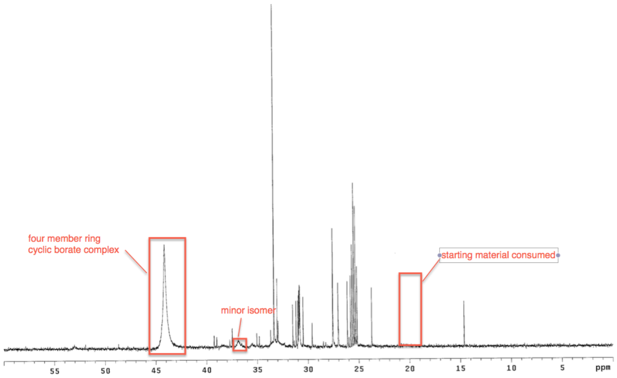
ii. **24** and KO*t*-Bu for 30 minutes



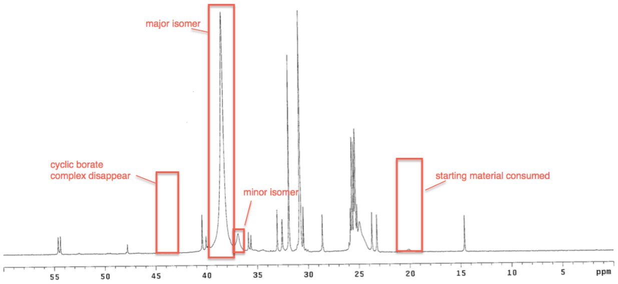
iii. **24** and KO*t*-Bu for 180 minutes



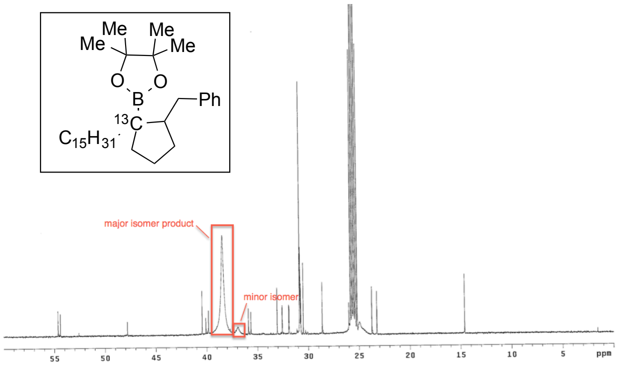
iv. **24** and KO*t*-Bu for 7 hours

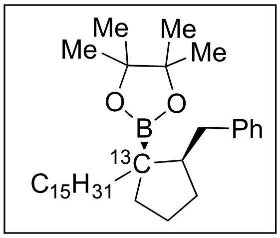


v. 1 minute after H_2O was added



vi. Isolated product, **S28**

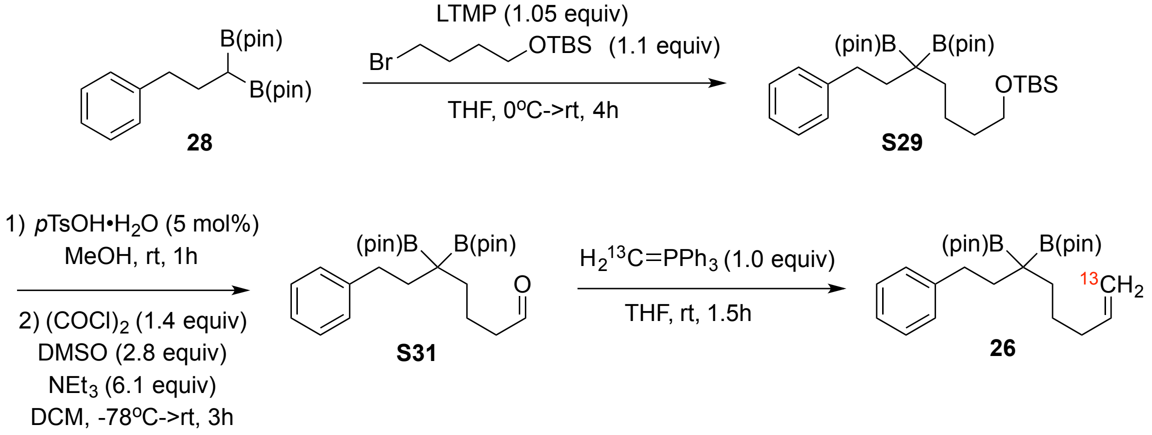


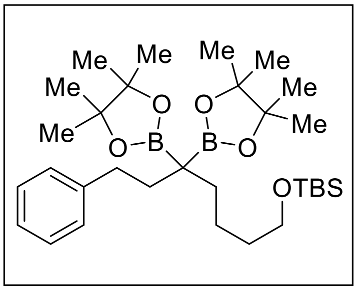


2-(2-benzyl-1-pentadecylcyclopentyl-1-^{13}*C*)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. (**S28,** ***major diastereomer***) ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 – 7.22 (m, 2H), 7.17 – 7.13 (m, 3H), 2.99 (dt, *J* = 13.4, 2.4 Hz, 1H), 2.32 (ddd, *J* = 13.1, 11.5, 1.4 Hz, 1H), 1.97 (dddd, *J* = 12.5, 8.7, 4.7, 1.5 Hz, 1H), 1.82 – 1.74 (m, 1H), 1.73 – 1.56 (m, 3H), 1.52 – 1.41 (m, 1H), 1.35 – 1.18 (m, 40H), 1.12 – 1.03 (m, 1H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{1}H NMR (500 MHz, THF-d_8): δ 7.21 – 7.16 (m, 2H), 7.13 – 7.06 (m, 3H), 2.98 (dt, *J* = 13.5, 2.6 Hz, 1H), 2.41 – 2.28 (m, 1H), 2.08 – 1.96 (m, 1H), 1.90 – 1.78 (m, 1H), 1.67 – 1.52 (m, 2H), 1.51 – 1.41 (m, 2H), 1.37 – 1.23 (m, 38H), 1.22 – 1.14 (m, 2H), 1.11 – 1.02 (m, 1H), 0.89 (td, *J* = 6.9, 2.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.10, 128.82, 128.04, 125.36, 82.88, 53.07, 52.83, 46.76, 39.39, 38.80, 38.54, 37.36, 34.42, 34.17, 31.92, 31.33, 31.31, 30.72, 30.68, 29.72, 29.70, 29.65, 29.64, 29.36, 27.47, 25.16, 24.85, 24.81, 22.68, 22.40, 14.12; ^{13}C NMR (125 MHz, THF-d_8): δ 144.03, 144.00, 129.70, 129.64, 128.98, 128.95, 126.32, 83.89, 54.63, 54.40, 47.80, 40.44, 40.08, 39.81, 38.41, 35.89, 35.64, 33.06, 32.58, 32.55, 31.92, 31.88, 30.84, 30.80, 30.76, 30.74, 30.49, 28.63, 23.74, 23.25, 14.61; IR (neat): 2956.4 (m), 2923.6 (s), 2853.7 (m), 1728.8 (m), 1462.6 (w), 1378.0 (w), 1287.5 (m), 1141.5 (m), 1072.2 (w), 743.0 (w), 699.7 (w) cm^{-1}; HRMS-(DART+) for ${}^{12}C_{32}{}^{13}C_1{}^1H_{58}{}^{11}B_1{}^{16}O_2$ $[M+H]^+$: calculated: 498.4563, found: 498.4574.

5. Analysis of Reaction Intermediates by ^{13}C-Labeled Experiments II

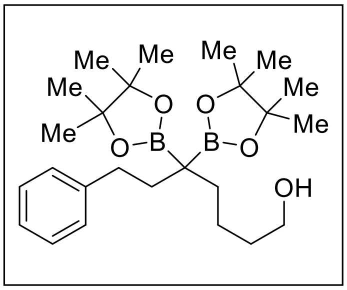
a) Preparation of ^{13}C-Labeled Alkene of *geminal*-Diboronate Ester



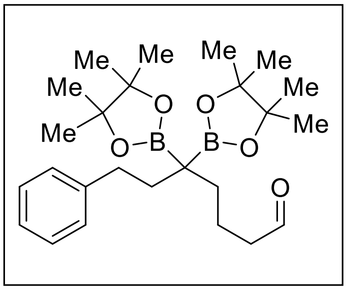


***tert*-butyldimethyl((7-phenyl-5,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)oxy)silane (S29).** The reaction was performed according to *Representative Procedure (Method D)* with diboronate ester **28** (372.3 mg, 1.0 mmol), LTMP (155 mg, 1.05 mmol), (4-bromobutoxy)(*tert*-butyl)dimethylsilane

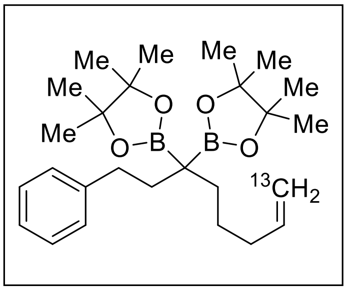
(294.0 mg, 1.10 mmol) and THF (4 mL). The crude reaction mixture was purified by column chromatography on silica gel (1% EtOAc/Hexanes, gradient to 3% EtOAc/Hexanes, visualized with CAM stain) to afford a clear, colorless oil (522.9 mg, 94%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 – 7.21 (m, 2H), 7.21 – 7.17 (m, 2H), 7.16 – 7.10 (m, 1H), 3.62 (t, *J* = 6.5 Hz, 2H), 2.55 – 2.45 (m, 2H), 1.94 – 1.84 (m, 2H), 1.76 – 1.66 (m, 2H), 1.58 – 1.49 (m, 2H), 1.38 – 1.27 (m, 2H), 1.23 (s, 24H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.83 (s), 128.50 (s), 128.07 (s), 125.32 (s), 82.95 (s), 63.52 (s), 33.88 (s), 33.84 (s), 31.91 (s), 29.01 (s), 26.00 (s), 24.81 (s), 24.70 (s), 23.63 (s), 18.34 (s), -5.22 (s); IR (neat): 2977.0 (w), 2928.8 (m), 2857.4 (w), 1349.2 (m), 1306.0 (m), 1253.9 (m), 1138.3 (s), 1101.4 (m), 850.4 (m), 835.8 (m), 775.0 (m), 699.0 (m) cm^{-1}. HRMS-(DART+) for $^{12}C_{31}{}^1H_{57}{}^{11}B_2{}^{16}O_5{}^{28}Si_1$ [M+H]: calculated: 559.4161, found: 559.4183.



7-phenyl-5,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptan-1-ol (S30). A 20 mL vial containing **S29** (482 mg, 0.86 mmol, 1.0 equiv) and magnetic stirbar is loaded with reagent grade MeOH (6.9 mL, 0.125 M). The heterogeneous mixture is set to stir at room temperature, then *p*-TsOH monohydrate added (8.2 mg, 0.04 mmol, 0.05 equiv). The mixture almost immediately becomes homogeneous. Allowed to stir 1h at rt then volatile components removed *in vacuo*. Resulting crude oil is then purified by SiO_2 chromatography (5% EtOAc/Hexanes, gradient to 25% EtOAc/Hexanes, visualized with $KMnO_4$ stain). Product isolated as white solid (356.3 mg, 93%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 – 7.22 (m, 2H), 7.22 – 7.17 (m, 2H), 7.16 – 7.11 (m, 1H), 3.73 – 3.65 (m, 2H), 2.56 – 2.48 (m, 2H), 1.93 – 1.85 (m, 2H), 1.75 – 1.64 (m, 3H), 1.64 – 1.56 (m, 2H), 1.44 – 1.31 (m, 2H), 1.23 (s, 24H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.67 (s), 128.45 (s), 128.11 (s), 125.40 (s), 83.07 (s), 62.33 (s), 33.84 (s), 32.72 (s), 32.13 (s), 27.98 (s), 24.79 (s), 24.66 (s), 23.03 (s); IR (neat): 3457.7 (w, br), 2977.0 (w), 2929.0 (w), 2861.0 (w), 1348.8 (m), 1307.5 (s), 1250.7 (m), 1137.6 (s), 853.2 (m), 699.8 (w) cm^{-1}. HRMS-(DART+) for $^{12}C_{25}{}^1H_{43}{}^{11}B_2{}^{16}O_5$ [M+H]: calculated: 445.3297, found: 445.3286.

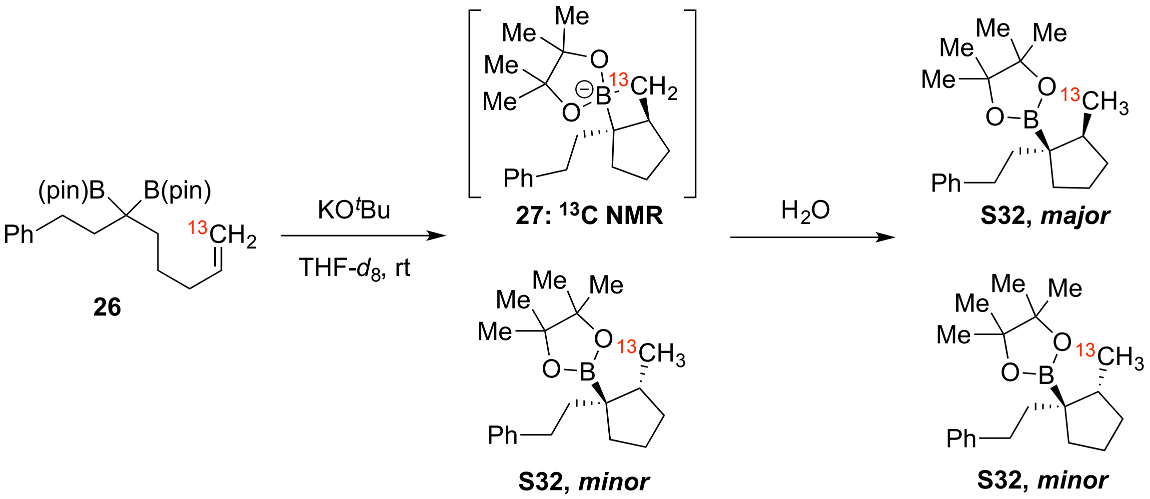


7-phenyl-5,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) heptanal (S31). A flame dried 20 mL vial equipped with magnetic stirbar is sealed with rubber septum then evacuated/backfilled with N_2 3x. The vial is then charged with $(COCl)_2$ (71.1 µL, 0.84 mmol, 1.4 equiv) followed by anhydrous DCM (0.3 mL). The solution is then set to stir at -78°C and anhydrous DMSO (119 µL, 1.67 mmol, 2.8 equiv) was added dropwise, significant gas evolution noted. The mixture was allowed to stir at -78°C for ca. 10min. A solution of **S30** in anhydrous DCM (0.3 mL) is then added dropwise, followed immediately by the slow addition of freshly distilled NEt_3 (507 µL, 3.64 mmol, 6.1 equiv; salt formation observed). The vessel and contents were then allowed to warm to room temperature and stir an additional 3h. Volatiles were then removed by high vacuum and the organics redissolved in EtOAc. Organics were washed with a saturated, aqueous Na_2CO_3 solution then concentrated to yield crude oil. Oil purified by SiO_2 chromatography (5% EtOAc/Hexanes, gradient to 10% EtOAc/Hexanes, visualized with CAM stain). Product isolated as white solid (232 mg, 0.52 mmol, 88%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.77 (s, 1H), 7.27 – 7.22 (m, 2H), 7.22 – 7.18 (m, 2H), 7.18 – 7.11 (m, 1H), 2.55 – 2.49 (m, 2H), 2.46 – 2.40 (m, 2H), 1.95 – 1.89 (m, 2H), 1.75 – 1.69 (m, 2H), 1.66 – 1.59 (m, 2H), 1.23 (s, 24H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 203.07 (s), 143.53 (s), 128.48 (s), 128.14 (s), 125.45 (s), 83.12 (s), 44.61 (s), 33.83 (s), 31.89 (s), 28.98 (s), 24.81 (s), 24.72 (s), 19.86 (s); IR (neat): 2977.3 (w), 2931.7 (w), 1708.3 (m), 1454.9 (w), 1310.4 (m), 1252.4 (m), 1137.5 (s), 853.9 (w) cm^{-1}. HRMS-(DART+) for $^{12}C_{25}{}^{1}H_{41}{}^{11}B_2{}^{16}O_5$ [M+H]: calculated: 443.3140, found: 443.3138.



2,2'-(1-phenyloct-7-ene-3,3-diyl-8-^{13}*C*)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (26). A flame dried, 20 mL vial equipped with magnetic stirbar is charged with Methyl-^{13}*C*-triphenylphosphonium iodide (212 mg, 0.52 mmol, 1 equiv) and KO*t*-Bu (59 mg, 0.52 mmol, 1 equiv) inside an argon-filled glovebox. Anhydrous THF is then charged into the vessel (1.5 mL) to give a vivid yellow solution. Vessel is sealed with a rubber septum and moved to the fume hood where it is allowed to stir for 1h at room temperature. A solution of **S31** (231 mg, 0.52 mmol, 1 equiv) in anhydrous THF (1.5 mL) is then added to the reaction vessel. The yellow color fades and a white suspension remains. The suspension is allowed to stir for 1.5h at room temperature at which point it is passed through a pad of SiO_2, rinsing with Et_2O. The resulting clear, colorless solution is concentrated to give a white solid. Product is isolated by SiO_2 chromatography (1% EtOAc/Hexanes, gradient to 5% EtOAc/Hexanes, visualized by CAM stain) to give white solid (208 mg, 0.47 mmol, 91%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.26 – 7.22 (m, 2H), 7.22 – 7.18 (m, 2H), 7.16 – 7.09 (m, 1H), 5.86 (ddt, J = 16.8, 10.2, 6.6 Hz, 1H), 5.01 (ddd, J = 153.4, 17.2, 1.8 Hz, 1H), 4.93 (ddd, J = 156.8, 10.2, 2.0 Hz, 1H), 2.54 – 2.47 (m, 2H), 2.11 – 2.04 (m, 2H), 1.93 – 1.85 (m, 2H), 1.75 – 1.69 (m, 2H), 1.43 – 1.34 (m, 2H), 1.23 (s, 24H); ^{13}C NMR δ 143.78 (s), 139.33 (d, J = 69.2 Hz), 128.49 (s), 128.09 (s), 125.35 (s), 113.98 (s, ^{13}*C*), 82.98 (s), 34.55 (s), 33.83 (s), 31.88 (s), 28.66 (s), 26.65 (d, J = 3.6 Hz), 24.80 (s), 24.71 (s); IR (neat): 2977.9 (w), 2927.4 (w), 2858.9 (w), 1352.9 (w), 1307.7 (2), 1255.5 (w), 1139.2 (m), 855.6 (w) cm^{-1}. HRMS-(DART+) for $^{12}C_{25}{}^{13}C_1{}^{1}H_{43}{}^{11}B_2{}^{16}O_4$ [M+H]: calculated: 442.3381, found: 442.3388.

b) ^{13}C NMR Experiments of ^{13}C-Labeled *geminal*-Diboronate Ester



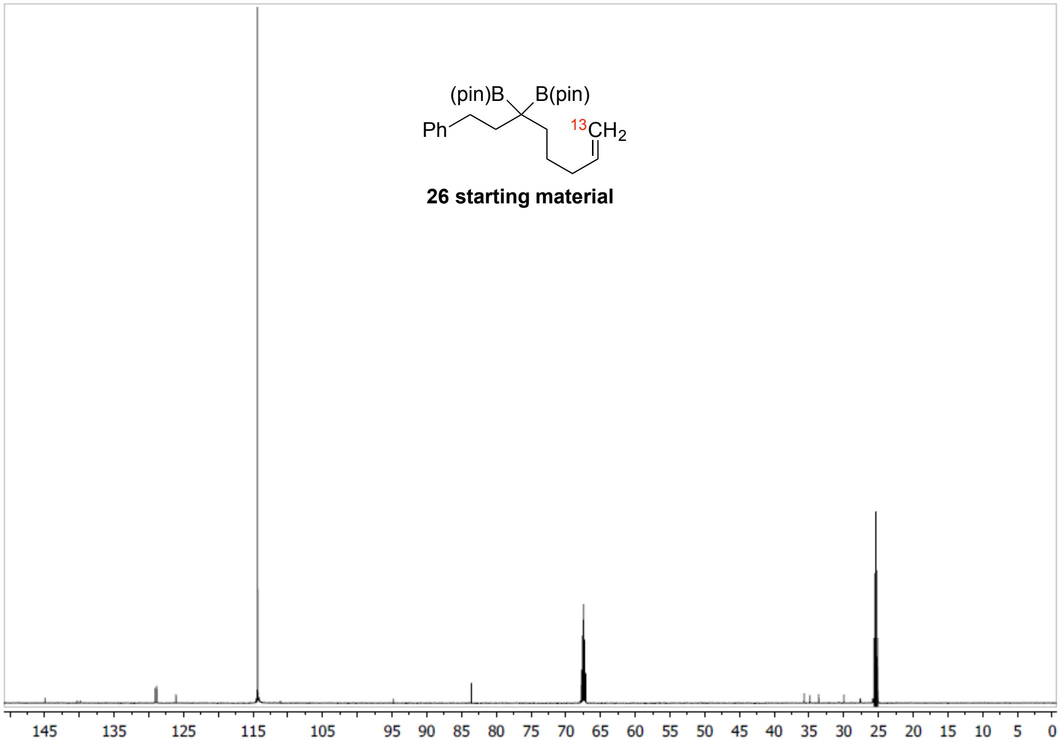


Figure 1 - ^{13}C labeled starting material **(26)** in d_8-THF

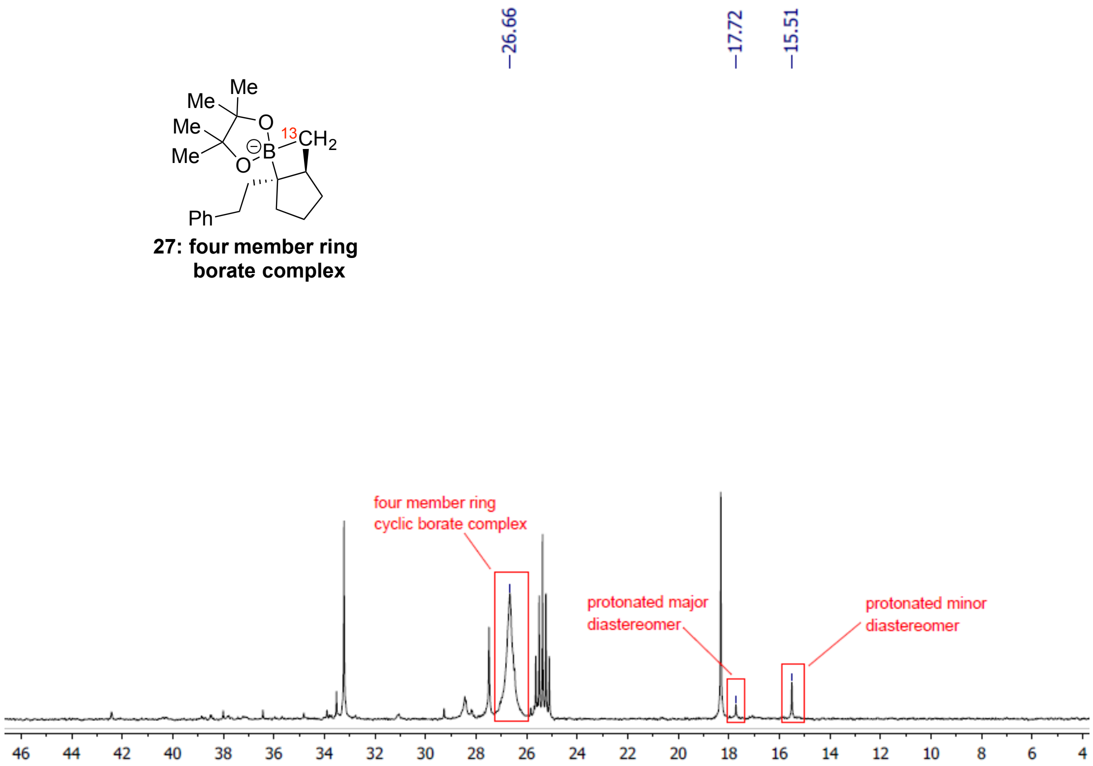

27: four member ring borate complex

Figure 2 – **26** with KO*t*-Bu for 20 minutes in *d₈*-THF (zoomed in on significant region for clarity)

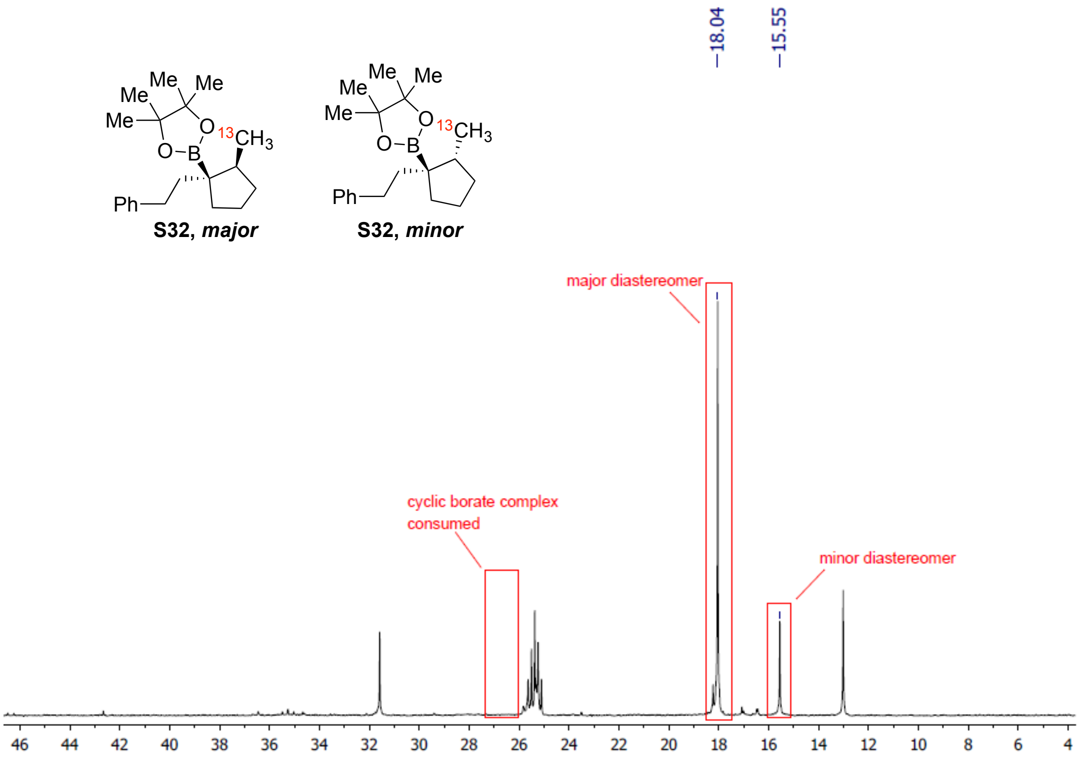

S32, *major* **S32, *minor***

Figure 3 – 1 minute after addition of H_2O

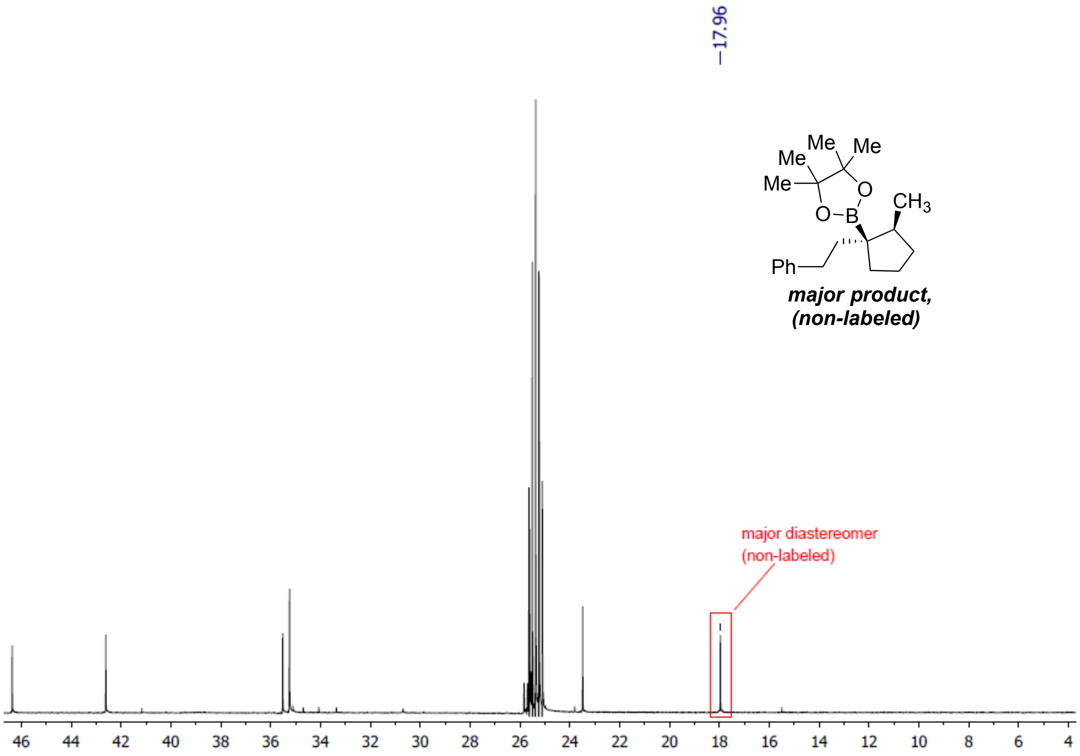


Figure 4 - Isolated major product (non-^{13}C labeled) in d_8-THF

X-ray crystallographic data

X-ray crystallographic data for **2-((1*R*,2*S*)-2-(iodomethyl)-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound 9).**

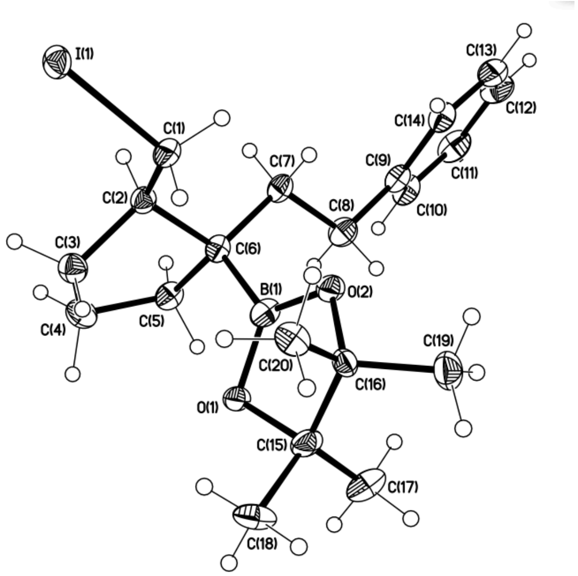


Table S2.

Crystal data and structure refinement for **2-((1*R*,2*S*)-2-(iodomethyl)-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane**. **(Compound 12).**

Identification code	C20H30BIO2	
Empirical formula	C20 H30 B I O2	
Formula weight	440.15	
Temperature	100(2) K	
Wavelength	0.71073 ≈	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.5129(8) ≈	α= 99.987(2)∞.
	b = 13.4237(16) ≈	β= 95.992(2)∞.
	c = 23.452(3) ≈	γ = 96.163(2)∞.
Volume	1991.7(4) ≈^{3}	
Z	4	
Density (calculated)	1.468 Mg/m^{3}	
Absorption coefficient	1.617 mm^{-1}	
F(000)	896	
Crystal size	0.400 x 0.210 x 0.150 mm^{3}	
Theta range for data collection	1.639 to 28.450∞.	
Index ranges	-8<=h<=8, -17<=k<=17, -31<=l<=31	
Reflections collected	38081	
Independent reflections	10019 [R(int) = 0.0443]	
Completeness to theta = 25.242∞	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6368	
Refinement method	Full-matrix least-squares on F^{2}	
Data / restraints / parameters	10019 / 1 / 500	
Goodness-of-fit on F^{2}	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.0315, wR2 = 0.0648	
R indices (all data)	R1 = 0.0501, wR2 = 0.0718	
Extinction coefficient	na	
Largest diff. peak and hole	1.372 and -0.705 e.≈$^{-3}$	

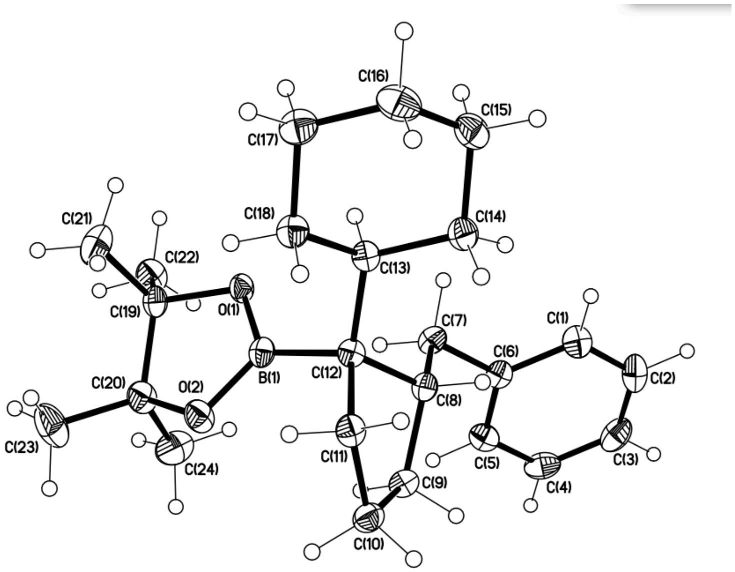
Table S3.

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (≈^{2}x 10^3) for C20H30BIO2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	-2688(1)	8964(1)	2686(1)	22(1)
O(2)	53(3)	6298(1)	3911(1)	20(1)
B(1)	1532(5)	7128(2)	4056(1)	21(1)
C(1)	-1455(4)	8104(2)	3314(1)	20(1)
C(2)	292(4)	8747(2)	3743(1)	18(1)
C(3)	2305(4)	8995(2)	3486(1)	22(1)
C(4)	3922(4)	9401(2)	4024(1)	24(1)
C(5)	3035(4)	8990(2)	4538(1)	20(1)
C(6)	1022(4)	8255(2)	4272(1)	17(1)
C(7)	-613(4)	8255(2)	4702(1)	20(1)
C(8)	141(4)	7877(2)	5255(1)	24(1)
C(9)	-1343(4)	7918(2)	5712(1)	20(1)
C(10)	-665(4)	8360(2)	6286(1)	26(1)
C(11)	-1990(5)	8377(2)	6714(1)	30(1)
C(12)	-4042(5)	7939(2)	6566(1)	31(1)
C(13)	-4752(4)	7494(2)	5993(1)	28(1)
C(14)	-3424(4)	7487(2)	5567(1)	22(1)
O(1)	3490(10)	6911(6)	3899(3)	18(1)
C(15)	3369(4)	5794(2)	3800(1)	24(1)
C(16)	971(8)	5454(4)	3569(3)	17(1)
C(17)	4185(11)	5443(5)	4300(3)	28(2)
C(18)	4715(9)	5507(5)	3275(3)	26(1)
C(19)	138(11)	4472(5)	3748(3)	29(2)
C(20)	314(7)	5426(4)	2926(2)	22(1)
O(1X)	3508(11)	6877(7)	4129(3)	18(1)
C(15X)	3369(4)	5794(2)	3800(1)	24(1)
C(16X)	1111(8)	5382(4)	3915(3)	21(1)
C(17X)	5083(10)	5330(6)	4167(4)	27(2)
C(18X)	3761(13)	5791(6)	3223(3)	33(2)

C(19X)	925(10)	5039(5)	4499(3)	31(2)
C(20X)	69(12)	4557(6)	3430(4)	37(2)
I(2)	1188(1)	-112(1)	1601(1)	24(1)
O(3)	7717(3)	2663(1)	800(1)	22(1)
O(4)	4297(3)	2481(1)	432(1)	21(1)
B(2)	5722(4)	2670(2)	924(1)	15(1)
C(21)	2576(4)	1186(2)	1285(1)	20(1)
C(22)	4214(4)	1849(2)	1738(1)	17(1)
C(23)	6177(4)	1364(2)	1884(1)	24(1)
C(24)	7890(4)	2260(2)	2137(1)	27(1)
C(25)	6965(4)	3230(2)	2028(1)	22(1)
C(26)	5057(4)	2869(2)	1558(1)	16(1)
C(27)	3411(4)	3617(2)	1599(1)	18(1)
C(28)	4219(4)	4659(2)	1471(1)	21(1)
C(29)	2722(4)	5441(2)	1529(1)	18(1)
C(30)	3393(4)	6433(2)	1827(1)	21(1)
C(31)	2049(4)	7166(2)	1876(1)	25(1)
C(32)	-7(4)	6927(2)	1629(1)	26(1)
C(33)	-689(4)	5951(2)	1328(1)	26(1)
C(34)	644(4)	5209(2)	1282(1)	23(1)
C(35)	7617(4)	2262(2)	171(1)	24(1)
C(36)	5453(4)	2521(2)	-69(1)	19(1)
C(37)	7693(5)	1120(2)	109(1)	40(1)
C(38)	9428(4)	2782(3)	-62(1)	43(1)
C(39)	5514(5)	3600(2)	-188(1)	33(1)
C(40)	4339(4)	1753(2)	-595(1)	30(1)

X-ray crystallographic data for compound **2-((1*R*,2*R*)-2-benzyl-1-cyclohexylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane**



(Compound 17).

Table S4.

Crystal data and structure refinement for **2-((1*R*,2*R*)-2-benzyl-1-cyclohexylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound 17).**

Identification code	C24H37BO2	
Empirical formula	C24 H37 B O2	
Formula weight	368.34	
Temperature	100(2) K	
Wavelength	0.71073 ≈	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 9.6816(10) ≈	α= 90∞.
	b = 18.2436(19) ≈	β= 106.083(2)∞.
	c = 12.6856(13) ≈	γ = 90∞.
Volume	2152.9(4) ≈^{3}	
Z	4	
Density (calculated)	1.136 Mg/m^3	
Absorption coefficient	0.069 mm^{-1}	
F(000)	808	
Crystal size	0.400 x 0.250 x 0.180 mm^3	
Theta range for data collection	1.671 to 28.339∞.	
Index ranges	-12<=h<=12, -24<=k<=24, -16<=l<=16	

Reflections collected	38756
Independent reflections	10716 [R(int) = 0.0408]
Completeness to theta = 25.242∞	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6888
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10716 / 1 / 496
Goodness-of-fit on F^2	1.057
Final R indices [I>2sigma(I)]	R1 = 0.0443, wR2 = 0.0949
R indices (all data)	R1 = 0.0609, wR2 = 0.1035
Extinction coefficient	na
Largest diff. peak and hole	0.249 and -0.204 e.≈$^{-3}$

Table S5.

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (≈^{2}x 10^3) for c24h37bo2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	6063(2)	4076(1)	7419(1)	19(1)
O(2)	6763(2)	5252(1)	7239(1)	24(1)
B(1)	6938(3)	4526(2)	7027(2)	18(1)
C(1)	11365(3)	2530(1)	8609(2)	25(1)
C(2)	12672(3)	2314(2)	9307(2)	29(1)
C(3)	13283(3)	2698(2)	10260(2)	29(1)
C(4)	12581(3)	3300(2)	10513(2)	28(1)
C(5)	11273(3)	3523(1)	9810(2)	23(1)
C(6)	10647(2)	3139(1)	8850(2)	19(1)
C(7)	9233(2)	3383(1)	8077(2)	21(1)
C(8)	9426(2)	3951(1)	7244(2)	18(1)
C(9)	10151(2)	4665(1)	7754(2)	20(1)
C(10)	9808(2)	5230(1)	6811(2)	23(1)
C(11)	8642(2)	4870(1)	5868(2)	20(1)
C(12)	8029(2)	4227(1)	6396(2)	17(1)
C(13)	7216(2)	3644(1)	5562(2)	18(1)
C(14)	8149(3)	3167(1)	5037(2)	23(1)
C(15)	7238(3)	2616(1)	4224(2)	27(1)
C(16)	6051(3)	2994(2)	3343(2)	31(1)
C(17)	5109(3)	3456(1)	3861(2)	26(1)
C(18)	6018(2)	4008(1)	4658(2)	21(1)
C(19)	5048(2)	4539(1)	7778(2)	21(1)
C(20)	5866(3)	5281(1)	7999(2)	24(1)
C(21)	3694(3)	4582(2)	6819(2)	33(1)
C(22)	4731(3)	4186(1)	8765(2)	28(1)
C(23)	4945(3)	5960(2)	7749(2)	38(1)
C(24)	6899(3)	5330(2)	9148(2)	35(1)
O(3)	1073(2)	6054(1)	2477(1)	20(1)
O(4)	1855(2)	4917(1)	2164(1)	23(1)

B(2)	1950(3)	5655(1)	2006(2)	18(1)
C(25)	6537(3)	7496(1)	3698(2)	26(1)
C(26)	7861(3)	7636(2)	4440(2)	33(1)
C(27)	8243(3)	7291(2)	5448(2)	32(1)
C(28)	7300(3)	6804(1)	5718(2)	29(1)
C(29)	5981(3)	6663(1)	4973(2)	24(1)
C(30)	5581(2)	7007(1)	3951(2)	20(1)
C(31)	4174(2)	6830(1)	3121(2)	20(1)
C(32)	4379(2)	6281(1)	2263(2)	18(1)
C(33)	5108(2)	5562(1)	2723(2)	22(1)
C(34)	4916(3)	5073(1)	1708(2)	24(1)
C(35)	3644(2)	5405(1)	814(2)	20(1)
C(36)	2997(2)	6011(1)	1393(2)	16(1)
C(37)	2178(2)	6619(1)	607(2)	17(1)
C(38)	3124(3)	7113(1)	117(2)	22(1)
C(39)	2237(3)	7686(1)	-658(2)	28(1)
C(40)	1044(3)	7337(2)	-1563(2)	32(1)
C(41)	82(3)	6861(2)	-1076(2)	28(1)
C(42)	968(3)	6282(1)	-312(2)	22(1)
C(43)	556(2)	5554(1)	3189(2)	22(1)
C(44)	711(3)	4793(1)	2691(2)	23(1)
C(45)	-962(3)	5768(2)	3167(2)	31(1)
C(46)	1562(3)	5657(2)	4346(2)	33(1)
C(47)	-614(3)	4567(2)	1789(2)	36(1)
C(48)	1180(3)	4174(2)	3511(2)	35(1)

X-ray crystallographic data for compound **2-((1*R*,2*R*)-2-benzyl-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound 15, major diastereomer).**

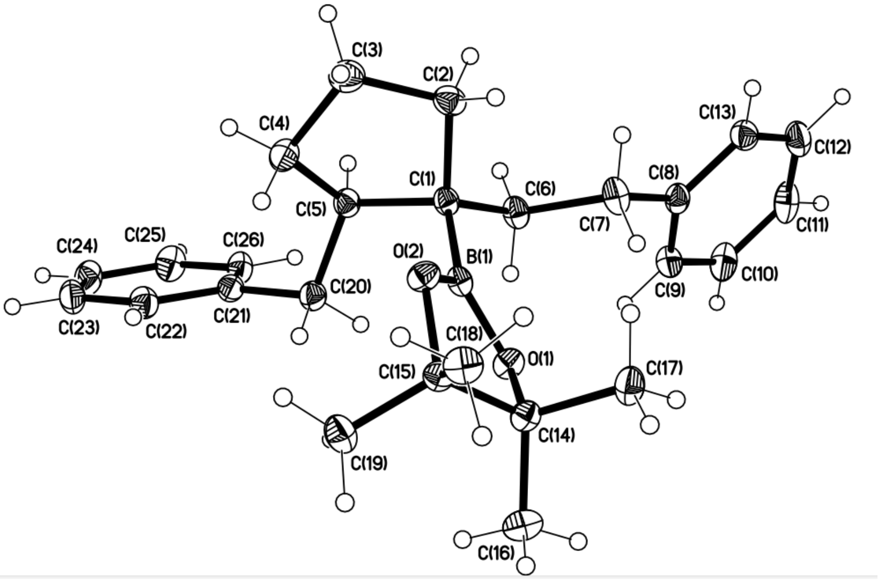


Table S6.

Crystal data and structure refinement for **2-((1*R*,2*R*)-2-benzyl-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound 15, major diastereomer).**

Identification code	C26H35BO2	
Empirical formula	C26 H35 B O2	
Formula weight	390.35	
Temperature	100(2) K	
Wavelength	0.71073 ≈	
Crystal system	Monoclinic	
Space group	P2$_1$/n	
Unit cell dimensions	a = 11.0652(19) ≈	α= 90∞.
	b = 17.228(3) ≈	β= 98.660(3)∞.
	c = 11.842(2) ≈	γ = 90∞.
Volume	2231.7(7) ≈^{3}	
Z	4	
Density (calculated)	1.162 Mg/m^3	
Absorption coefficient	0.070 mm^{-1}	

F(000)	848
Crystal size	0.530 x 0.400 x 0.220 mm^3
Theta range for data collection	2.103 to 28.324∞.
Index ranges	-14<=h<=14, -22<=k<=20, -15<=l<=15
Reflections collected	43822
Independent reflections	5557 [R(int) = 0.0352]
Completeness to theta = 25.242∞	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.7070
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5557 / 0 / 266
Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR2 = 0.0983
R indices (all data)	R1 = 0.0474, wR2 = 0.1046
Extinction coefficient	na
Largest diff. peak and hole	0.390 and -0.188 e.≈$^{-3}$

Table S7.

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (≈^{2}x 10^3) for C26H35BO2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	3744(1)	6957(1)	6459(1)	16(1)
C(1)	4240(1)	6174(1)	6004(1)	16(1)
C(2)	3572(1)	5462(1)	6436(1)	20(1)
C(3)	4263(1)	5252(1)	7628(1)	25(1)
C(4)	5459(1)	5724(1)	7780(1)	21(1)
C(5)	5581(1)	6018(1)	6580(1)	17(1)
C(6)	4146(1)	6187(1)	4692(1)	19(1)
C(7)	2834(1)	6200(1)	4049(1)	22(1)
C(8)	2736(1)	6139(1)	2762(1)	19(1)
C(9)	3493(1)	6557(1)	2143(1)	24(1)
C(10)	3359(1)	6505(1)	960(1)	28(1)
C(11)	2472(1)	6028(1)	371(1)	28(1)
C(12)	1717(1)	5606(1)	971(1)	26(1)
C(13)	1848(1)	5658(1)	2154(1)	21(1)
C(14)	2901(1)	8165(1)	6432(1)	17(1)
C(15)	3167(1)	7859(1)	7684(1)	17(1)
C(16)	3325(1)	8988(1)	6262(1)	25(1)
C(17)	1568(1)	8068(1)	5898(1)	23(1)
C(18)	2107(1)	7938(1)	8356(1)	22(1)
C(19)	4338(1)	8192(1)	8354(1)	24(1)
C(20)	6468(1)	6702(1)	6570(1)	19(1)
C(21)	7791(1)	6466(1)	6917(1)	18(1)
C(22)	8387(1)	6573(1)	8030(1)	22(1)
C(23)	9608(1)	6368(1)	8336(1)	25(1)
C(24)	10256(1)	6054(1)	7529(1)	26(1)
C(25)	9672(1)	5936(1)	6420(1)	26(1)
C(26)	8448(1)	6137(1)	6121(1)	22(1)
O(1)	3615(1)	7630(1)	5831(1)	18(1)
O(2)	3387(1)	7033(1)	7515(1)	18(1)

X-ray crystallographic data for **4,4,5,5-tetramethyl-2-((1*R*,2*R*)-1-phenethyl-2-((*R*)-1-phenylbut-3-en-1-yl)cyclopentyl)-1,3,2-dioxaborolane (Compound 38).**

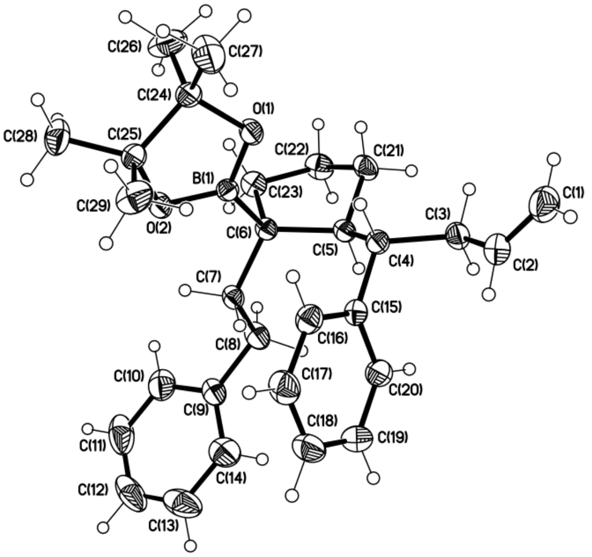


Table S8.

Crystal data and structure refinement for **4,4,5,5-tetramethyl-2-((1*R*,2*R*)-1-phenethyl-2-((*R*)-1-phenylbut-3-en-1-yl)cyclopentyl)-1,3,2-dioxaborolane (Compound 38).**

Identification code	C29H39BO2	
Empirical formula	C29 H39BO2	
Formula weight	430.41	
Temperature	173(2) K	
Wavelength	1.54178 ≈	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.9886(5) ≈	α= 69.073(2)∞.
	b = 10.2525(5) ≈	β= 84.917(2)∞.
	c = 13.6756(7) ≈	γ = 76.535(2)∞.
Volume	1272.13(11) ≈^{3}	
Z	2	
Density (calculated)	1.124 Mg/m^3	
Absorption coefficient	0.516 mm^{-1}	

F(000)	468
Crystal size	0.520 x 0.400 x 0.080 mm^3
Theta range for data collection	3.460 to 66.686∞.
Index ranges	-11<=h<=11, -12<=k<=12, -16<=l<=16
Reflections collected	24493
Independent reflections	4448 [R(int) = 0.0249]
Completeness to theta = 66.750∞	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.6785
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4448 / 0 / 293
Goodness-of-fit on F^2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0393, wR2 = 0.0981
R indices (all data)	R1 = 0.0407, wR2 = 0.0993
Extinction coefficient	na
Largest diff. peak and hole	0.313 and -0.208 e.$≈^{-3}$

Table S9.

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (≈^{2}x 10^3) for C29H39BO2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	1652(1)	3532(1)	4221(1)	33(1)
O(2)	3289(1)	1550(1)	4287(1)	28(1)
B(1)	2635(1)	2887(1)	3680(1)	22(1)
C(1)	2312(2)	9366(2)	2921(1)	47(1)
C(2)	3111(1)	8405(1)	2586(1)	38(1)
C(3)	2640(1)	7591(1)	2017(1)	31(1)
C(4)	3085(1)	5954(1)	2560(1)	25(1)
C(5)	2623(1)	5150(1)	1936(1)	24(1)
C(6)	2891(1)	3481(1)	2455(1)	23(1)
C(7)	4324(1)	2676(1)	2218(1)	25(1)
C(8)	4718(1)	2968(1)	1061(1)	36(1)
C(9)	6021(1)	1925(1)	966(1)	34(1)
C(10)	5970(2)	619(2)	909(1)	47(1)
C(11)	7174(2)	-372(2)	882(1)	66(1)
C(12)	8432(2)	-70(2)	912(1)	70(1)
C(13)	8499(2)	1219(2)	968(1)	62(1)
C(14)	7301(2)	2214(2)	996(1)	45(1)
C(15)	4629(1)	5496(1)	2730(1)	26(1)
C(16)	5180(1)	4679(1)	3714(1)	32(1)
C(17)	6591(1)	4191(2)	3858(1)	42(1)
C(18)	7480(1)	4540(2)	3019(1)	44(1)
C(19)	6948(1)	5389(2)	2037(1)	41(1)
C(20)	5542(1)	5858(1)	1894(1)	33(1)
C(21)	1088(1)	5601(1)	1657(1)	31(1)
C(22)	902(1)	4471(1)	1239(1)	35(1)
C(23)	1712(1)	3076(1)	1998(1)	30(1)
C(24)	1417(1)	2419(1)	5208(1)	32(1)
C(25)	2800(1)	1298(1)	5365(1)	27(1)
C(26)	222(1)	1858(2)	5013(1)	58(1)

C(27)	1065(2)	3067(2)	6056(1)	59(1)
C(28)	2684(2)	-255(1)	5849(1)	43(1)
C(29)	3884(1)	1544(2)	5945(1)	43(1)

X-ray crystallographic data for compound **2-((1*R*,2*R*)-2-((*R*)-1,2-diphenylethyl)-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound 16).**

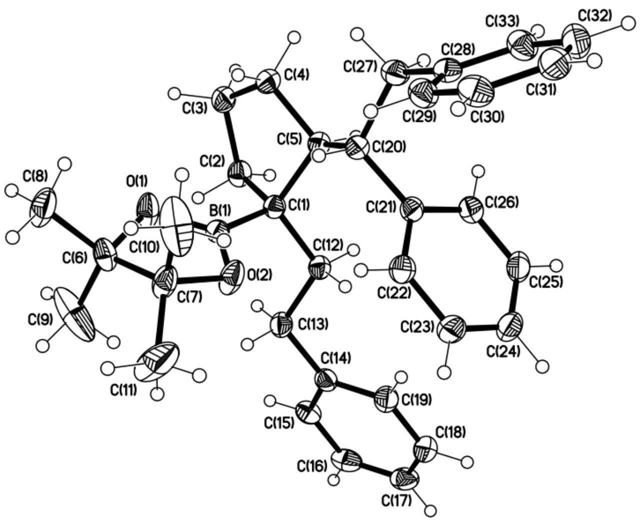


Table S10.

Crystal data and structure refinement for **2-((1*R*,2*R*)-2-((*R*)-1,2-diphenylethyl)-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound 16).**

Identification code	C33H41BO2	
Empirical formula	C33 H41BO2	
Formula weight	480.47	
Temperature	100(2) K	
Wavelength	0.71073 ≈	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 13.8342(16) ≈	α= 90∞.
	b = 17.292(2) ≈	β= 90∞.
	c = 23.666(3) ≈	γ = 90∞.

Volume	5661.4(11) ≈^{3}
Z	8
Density (calculated)	1.127 Mg/m^3
Absorption coefficient	0.067 mm^{-1}
F(000)	2080
Crystal size	0.550 x 0.380 x 0.180 mm^3
Theta range for data collection	1.721 to 28.335∞.
Index ranges	-18<=h<=18, -23<=k<=22, -31<=l<=31
Reflections collected	94700
Independent reflections	7044 [R(int) = 0.0525]
Completeness to theta = 25.242∞	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.7017
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7044 / 821 / 406
Goodness-of-fit on F^2	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0439, wR2 = 0.1041
R indices (all data)	R1 = 0.0649, wR2 = 0.1172
Extinction coefficient	na
Largest diff. peak and hole	0.320 and -0.237 e.≈$^{-3}$

Table S11.

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (≈^{2}x 10^3) for C33H41BO2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	5645(1)	1765(1)	4124(1)	33(1)
O(2)	5909(1)	2977(1)	4455(1)	33(1)
C(6)	5676(1)	1686(1)	4741(1)	27(1)
C(7)	5546(1)	2534(1)	4940(1)	31(1)
C(8)	4873(2)	1142(1)	4932(1)	42(1)
C(9)	6661(2)	1356(2)	4881(1)	72(1)
C(10)	4480(2)	2753(1)	5008(1)	57(1)
C(11)	6116(3)	2768(2)	5452(1)	75(1)
O(1X)	5206(10)	1976(8)	4159(4)	36(3)
O(2X)	6309(10)	2822(9)	4479(5)	32(3)
C(6X)	5140(10)	1968(9)	4782(5)	43(3)
C(7X)	6040(10)	2389(9)	4986(5)	37(3)
C(8X)	4178(15)	2328(17)	4931(12)	84(7)
C(9X)	5248(19)	1109(11)	4917(13)	53(6)
C(10X)	5920(30)	2950(18)	5468(12)	49(5)
C(11X)	6951(15)	1978(16)	5134(11)	82(6)
B(1)	5869(1)	2514(1)	3994(1)	21(1)
C(1)	6077(1)	2810(1)	3372(1)	20(1)
C(2)	6219(1)	2117(1)	2963(1)	25(1)
C(3)	5199(1)	1834(1)	2804(1)	29(1)
C(4)	4509(1)	2497(1)	2966(1)	26(1)
C(5)	5157(1)	3196(1)	3107(1)	21(1)
C(12)	6954(1)	3358(1)	3365(1)	21(1)
C(13)	7903(1)	2997(1)	3563(1)	24(1)
C(14)	8758(1)	3546(1)	3539(1)	22(1)
C(15)	9683(1)	3258(1)	3433(1)	26(1)
C(16)	10479(1)	3747(1)	3407(1)	31(1)
C(17)	10366(1)	4538(1)	3484(1)	32(1)
C(18)	9455(1)	4833(1)	3593(1)	31(1)

C(19)	8658(1)	4343(1)	3621(1)	28(1)
C(20)	4625(1)	3832(1)	3443(1)	22(1)
C(21)	5249(1)	4538(1)	3565(1)	22(1)
C(22)	5498(1)	4731(1)	4119(1)	25(1)
C(23)	6105(1)	5355(1)	4232(1)	30(1)
C(24)	6456(1)	5803(1)	3793(1)	32(1)
C(25)	6198(1)	5629(1)	3242(1)	30(1)
C(26)	5598(1)	5003(1)	3128(1)	26(1)
C(27)	3697(1)	4073(1)	3121(1)	27(1)
C(28)	3181(1)	4766(1)	3368(1)	25(1)
C(29)	2927(1)	4793(1)	3938(1)	28(1)
C(30)	2451(1)	5429(1)	4162(1)	32(1)
C(31)	2214(1)	6049(1)	3818(1)	33(1)
C(32)	2465(1)	6032(1)	3253(1)	34(1)
C(33)	2947(1)	5397(1)	3030(1)	31(1)

X-ray crystallographic data for **2-((1*S*,2*S*,3*R*)-3-(benzyloxy)-2-(*tert*-butoxymethyl)-1-phenethylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound S13).**

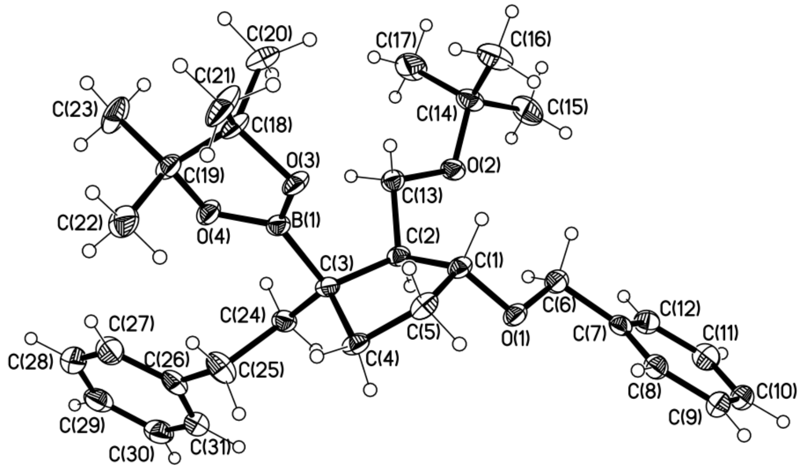


Table S12.

Crystal data and structure refinement for **2-((1*S*,2*S*,3*R*)-3-(benzyloxy)-2-(*tert*-butoxymethyl)-1-phenethylcyclopentyl)-4,4,5,5-tetramet**

hyl-1,3,2-dioxaborolane (Compound S13).

Identification code	C31H45BO4	
Empirical formula	C31 H45 B O4	
Formula weight	492.48	
Temperature	100(2) K	
Wavelength	1.54178 ≈	
Crystal system	Orthorhombic	
Space group	$Pna2_1$	
Unit cell dimensions	a = 26.2433(11) ≈	α= 90∞.
	b = 17.5408(7) ≈	β= 90∞.
	c = 6.2731(3) ≈	γ = 90∞.
Volume	2887.7(2) $≈^3$	
Z	4	
Density (calculated)	1.133 Mg/m^3	
Absorption coefficient	0.564 mm^{-1}	
F(000)	1072	
Crystal size	0.360 x 0.240 x 0.180 mm^3	
Theta range for data collection	3.030 to 69.934∞.	
Index ranges	-31<=h<=31, -21<=k<=18, -6<=l<=7	
Reflections collected	22546	
Independent reflections	4866 [R(int) = 0.0631]	
Completeness to theta = 67.679∞	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.5608	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4866 / 393 / 401	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0352, wR2 = 0.0899	
R indices (all data)	R1 = 0.0368, wR2 = 0.0912	
Absolute structure parameter	0.06(12)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.189 and -0.169 e.$≈^{-3}$	

Table S13.

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (≈^{2}x 10^3) for C31H45BO4. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	3636(1)	6170(1)	3554(2)	21(1)
O(2)	3680(1)	4596(1)	7018(2)	22(1)
B(1)	2301(1)	4380(1)	3302(4)	20(1)
C(1)	3375(1)	5467(1)	3104(3)	19(1)
C(2)	3037(1)	5197(1)	4987(3)	18(1)
C(3)	2474(1)	5196(1)	4159(3)	18(1)
C(4)	2499(1)	5778(1)	2310(3)	21(1)
C(5)	3011(1)	5617(1)	1255(3)	22(1)
C(6)	4045(1)	6079(1)	5011(4)	22(1)
C(7)	4374(1)	6783(1)	5004(3)	20(1)
C(8)	4436(1)	7217(1)	3181(4)	22(1)
C(9)	4763(1)	7844(1)	3176(4)	26(1)
C(10)	5036(1)	8028(1)	5001(4)	27(1)
C(11)	4976(1)	7596(1)	6831(4)	28(1)
C(12)	4643(1)	6977(1)	6840(4)	24(1)
C(13)	3210(1)	4446(1)	5971(3)	20(1)
C(14)	3998(1)	3956(1)	7578(4)	26(1)
C(15)	4426(1)	4324(1)	8857(4)	38(1)
C(16)	4212(1)	3580(1)	5589(4)	38(1)
C(17)	3708(1)	3388(1)	8954(5)	39(1)
O(3)	2500(2)	4007(2)	1709(8)	22(1)
C(18)	2256(2)	3251(2)	1658(8)	25(1)
C(19)	1744(2)	3408(2)	2781(6)	22(1)
O(4)	1884(2)	4016(2)	4264(6)	22(1)
C(20)	2606(3)	2722(5)	2866(16)	36(2)
C(21)	2217(8)	3017(12)	-680(20)	43(4)
C(22)	1342(2)	3742(3)	1316(12)	35(1)
C(23)	1527(7)	2728(7)	3990(30)	36(3)
O(3X)	2323(2)	4150(2)	1138(7)	24(1)

C(18X)	2014(2)	3453(2)	974(8)	26(1)
C(19X)	2053(2)	3127(2)	3272(7)	22(1)
O(4X)	2122(2)	3817(2)	4544(5)	18(1)
C(20X)	2218(9)	2932(12)	-710(20)	32(3)
C(21X)	1480(3)	3709(4)	370(12)	36(2)
C(22X)	1582(6)	2724(7)	4070(20)	28(3)
C(23X)	2525(3)	2630(5)	3601(14)	26(2)
C(24)	2109(1)	5444(1)	5954(3)	21(1)
C(25)	1567(1)	5633(1)	5174(4)	33(1)
C(26)	1199(1)	5684(1)	7013(4)	27(1)
C(27)	842(1)	5110(1)	7365(4)	32(1)
C(28)	530(1)	5128(1)	9155(5)	36(1)
C(29)	566(1)	5715(1)	10595(4)	32(1)
C(30)	912(1)	6299(1)	10249(4)	32(1)
C(31)	1223(1)	6281(1)	8467(4)	29(1)

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Computational Studies

All geometries were optimized using the m062x/6-31+G* method. The geometry optimizations were carried out in THF solvent simulated by the polarizable dielectric continuum solvation method PCM. Frequency calculations were carried out using the m062x/6-31+G* method on all optimized geometries to make sure that the stationary point geometries either have all real normal mode frequencies (minima) or one imaginary normal mode frequency (transition states). Gibbs free energies were computed using the unscaled normal mode frequencies at 1.0 atm and 298.15 K. All calculations were carried out with the Gaussian 09 computer program[1].

GS

```
---------------------------------------
 Cartesian coordinates (Angstroms):
---------------------------------------

37

H   -1.383   -1.687   -0.872
H   -2.532   -3.010   -0.574
C   -1.488   -2.776   -0.812
H   -2.042   -1.802   -3.228
H   -0.851   -3.138    0.002
H    4.283   -0.746   -0.967
H    1.550   -1.782   -0.121
C   -1.972   -2.894   -3.262
H   -2.982   -3.305   -3.145
C   -1.053   -3.384   -2.150
O    0.281   -2.964   -2.416
C    2.170    1.091    1.237
C    3.583   -1.561   -0.725
H   -1.588   -3.182   -4.244
C    2.265   -0.954   -0.235
H   -1.868   -5.285   -0.155
B    1.177   -3.932   -1.847
H   -2.950   -5.444   -1.559
C    2.406   -0.211    1.058
C   -1.934   -5.629   -1.190
C   -0.900   -4.935   -2.067
```

H	1.858	-0.286	-1.008
O	0.391	-5.080	-1.484
C	3.378	-2.486	-1.947
H	2.857	-1.888	-2.713
C	2.623	-3.768	-1.680
H	-1.760	-6.711	-1.201
H	-1.867	-5.554	-3.934
H	4.379	-2.688	-2.366
C	-0.881	-5.584	-3.455
H	-0.158	-5.082	-4.106
H	-0.580	-6.632	-3.351
H	4.039	-2.145	0.089
H	3.222	-4.582	-1.260
H	2.748	-0.804	1.910
H	1.834	1.721	0.415
H	2.303	1.571	2.203

```
          1                      2                      3
                 A                      A                      A
 Frequencies --    24.6824                36.8523                69.5065
 Red. masses --     3.8973                 3.7105                 3.2201
 Zero-point correction=                           0.326180 (Hartree/Particle)
 Thermal correction to Energy=                    0.343179
 Thermal correction to Enthalpy=                  0.344123
 Thermal correction to Gibbs Free Energy=         0.281779
 Sum of electronic and zero-point Energies=          -645.375869
 Sum of electronic and thermal Energies=             -645.358870
 Sum of electronic and thermal Enthalpies=           -645.357926
 Sum of electronic and thermal Free Energies=        -645.420270

       Item               Value     Threshold  Converged?
 Maximum Force            0.000051     0.000450     YES
 RMS     Force            0.000008     0.000300     YES
```

TS1_SYN

```
-----------------------------------------
 Cartesian coordinates (Angstroms):
```

```
----------------------------------------

37

H    -2.269    -2.822    -0.473
H    -3.568    -1.638    -0.738
C    -2.482    -1.780    -0.733
H    -2.294    -2.216     1.888
H    -2.099    -1.595    -1.743
H     4.402    -0.965    -1.084
H     4.394    -0.380     1.321
C    -2.343    -1.142     1.678
H    -3.390    -0.827     1.750
C    -1.792    -0.869     0.286
O    -0.394    -1.180     0.258
C     1.946     1.200     1.528
C     3.745    -1.532    -0.407
H    -1.764    -0.616     2.442
C     3.462    -0.695     0.833
H    -3.106     0.479    -1.886
B     0.229    -0.303    -0.646
H    -3.961     0.866    -0.375
C     2.635     0.535     0.489
C    -3.044     1.039    -0.950
C    -1.818     0.636    -0.140
H     2.902    -1.294     1.567
O    -0.652     0.744    -0.968
C     2.384    -1.752    -1.081
H     2.515    -2.204    -2.077
C     1.650    -0.426    -1.106
H    -2.989     2.106    -1.191
H    -2.548     1.603     1.676
H     1.816    -2.480    -0.483
C    -1.652     1.589     1.045
H    -0.783     1.309     1.647
H    -1.483     2.600     0.660
H     4.258    -2.473    -0.167
H     3.149     1.201    -0.210
H     1.452     2.144     1.298
H     1.404     0.583     2.251
H     1.960     0.239    -1.919
```

```
                 1                      2                      3
                 A                      A                      A
 Frequencies --  -465.7393              66.9673                74.3594
 Red. masses --     4.8610               3.3862                 3.0315
 Zero-point correction=                           0.326377 (Hartree/Particle)
 Thermal correction to Energy=                     0.341865
 Thermal correction to Enthalpy=                   0.342809
 Thermal correction to Gibbs Free Energy=           0.285551
 Sum of electronic and zero-point Energies=             -645.346421
 Sum of electronic and thermal Energies=                -645.330933
 Sum of electronic and thermal Enthalpies=              -645.329989
 Sum of electronic and thermal Free Energies=           -645.387247

        Item               Value     Threshold  Converged?
 Maximum Force            0.000032     0.000450     YES
 RMS     Force            0.000004     0.000300     YES
```

INT_SYN

```
-----------------------------------------
 Cartesian coordinates (Angstroms):
-----------------------------------------

37

H   -2.034   -2.843   -0.420
H   -3.401   -1.759   -0.756
C   -2.309   -1.821   -0.698
H   -2.235   -2.234    1.928
H   -1.892   -1.612   -1.689
H    4.457   -1.276   -0.990
H    4.324   -0.576    1.388
C   -2.340   -1.165    1.715
H   -3.407   -0.916    1.735
C   -1.746   -0.858    0.349
O   -0.321   -1.073    0.392
C    2.091    1.321    1.370
C    3.644   -1.703   -0.387
H   -1.832   -0.606    2.504
```

C	3.409	-0.824	0.840
H	-3.024	0.392	-1.897
B	0.281	-0.124	-0.416
H	-3.980	0.747	-0.440
C	2.713	0.434	0.297
C	-3.044	0.965	-0.967
C	-1.847	0.640	-0.086
H	2.730	-1.333	1.543
O	-0.637	0.817	-0.849
C	2.310	-1.598	-1.146
H	2.417	-1.804	-2.217
C	1.782	-0.164	-0.856
H	-3.035	2.030	-1.219
H	-2.705	1.568	1.691
H	1.614	-2.347	-0.745
C	-1.787	1.608	1.096
H	-0.929	1.385	1.737
H	-1.665	2.624	0.709
H	3.916	-2.739	-0.152
H	3.492	1.012	-0.229
H	1.603	2.191	0.891
H	1.282	0.756	1.871
H	1.889	0.472	-1.745

```
                 1                   2                   3
                 A                   A                   A
 Frequencies --   27.7672              58.2730              82.3290
 Red. masses --    2.6544               3.4536               3.6358
 Zero-point correction=                           0.328923 (Hartree/Particle)
 Thermal correction to Energy=                     0.344508
 Thermal correction to Enthalpy=                   0.345453
 Thermal correction to Gibbs Free Energy=          0.287175
 Sum of electronic and zero-point Energies=          -645.361118
 Sum of electronic and thermal Energies=             -645.345532
 Sum of electronic and thermal Enthalpies=           -645.344588
 Sum of electronic and thermal Free Energies=        -645.402866

        Item               Value     Threshold  Converged?
 Maximum Force            0.000014     0.000450     YES
 RMS     Force            0.000004     0.000300     YES
```

```
TS2_SYN

----------------------------------------
 Cartesian coordinates (Angstroms):
----------------------------------------

37

H   -1.927   -2.791   -0.438
H   -3.288   -1.716   -0.825
C   -2.199   -1.766   -0.710
H   -2.267   -2.221    1.913
H   -1.731   -1.532   -1.672
H    4.440   -1.296   -1.073
H    4.393   -0.464    1.277
C   -2.370   -1.151    1.706
H   -3.440   -0.912    1.668
C   -1.695   -0.819    0.382
O   -0.282   -1.020    0.501
C    1.799    1.136    1.216
C    3.673   -1.715   -0.405
H   -1.915   -0.598    2.532
C    3.463   -0.776    0.784
H   -2.938    0.458   -1.871
B    0.380   -0.017   -0.245
H   -3.925    0.778   -0.425
C    2.678    0.416    0.207
C   -2.981    1.014   -0.931
C   -1.793    0.684   -0.038
H    2.844   -1.281    1.541
O   -0.583    0.865   -0.782
C    2.301   -1.690   -1.103
H    2.356   -2.002   -2.153
C    1.803   -0.236   -0.916
H   -2.978    2.084   -1.165
H   -2.708    1.590    1.727
H    1.625   -2.391   -0.595
C   -1.769    1.632    1.164
H   -0.936    1.393    1.832
H   -1.628    2.655    0.798
H    3.995   -2.724   -0.122
```

```
H    3.411    1.104   -0.248
H    1.256    2.019    0.881
H    1.292    0.522    1.959
H    1.879    0.332   -1.855

                1                  2                  3
                A                  A                  A
 Frequencies --  -550.9388            49.2730            57.0464
 Red. masses --     2.9417             2.8077             3.5391
 Zero-point correction=                      0.326555 (Hartree/Particle)
 Thermal correction to Energy=                0.341917
 Thermal correction to Enthalpy=              0.342861
 Thermal correction to Gibbs Free Energy=       0.285668
 Sum of electronic and zero-point Energies=         -645.354602
 Sum of electronic and thermal Energies=           -645.339240
 Sum of electronic and thermal Enthalpies=         -645.338296
 Sum of electronic and thermal Free Energies=       -645.395489

       Item             Value     Threshold  Converged?
 Maximum Force           0.000031     0.000450     YES
 RMS     Force          0.000004     0.000300     YES
```

PDT_SYN

```
-----------------------------------------
 Cartesian coordinates (Angstroms):
-----------------------------------------

37

H   -1.242   -2.674   -0.381
H   -2.681   -1.821   -0.981
C   -1.634   -1.695   -0.681
H   -2.079   -2.263    1.889
H   -1.055   -1.345   -1.542
H    4.212   -1.690   -1.028
H    4.221   -0.775    1.283
C   -2.324   -1.217    1.670
H   -3.395   -1.159    1.440
C   -1.480   -0.724    0.498
O   -0.123   -0.666    0.885
```

C	1.751	1.215	0.868
C	3.343	-1.921	-0.396
H	-2.126	-0.628	2.570
C	3.270	-0.904	0.750
H	-2.733	0.394	-1.842
B	0.557	0.375	0.060
H	-3.866	0.503	-0.473
C	2.777	0.379	0.066
C	-2.939	0.907	-0.898
C	-1.771	0.750	0.073
H	2.518	-1.238	1.479
O	-0.570	1.127	-0.567
C	2.039	-1.661	-1.180
H	2.133	-1.960	-2.233
C	1.753	-0.156	-0.982
H	-3.100	1.969	-1.115
H	-2.964	1.467	1.778
H	1.229	-2.262	-0.746
C	-1.998	1.655	1.293
H	-1.198	1.509	2.026
H	-1.977	2.699	0.962
H	3.449	-2.958	-0.054
H	3.643	0.930	-0.338
H	1.857	1.157	1.964
H	1.786	2.275	0.578
H	1.784	0.407	-1.925

```
                 1                   2                   3
                 A                   A                   A
 Frequencies --    63.8222              71.6321              89.0193
 Red. masses --     3.0676               3.1689               3.4432
 Zero-point correction=                           0.328434 (Hartree/Particle)
 Thermal correction to Energy=                     0.343345
 Thermal correction to Enthalpy=                   0.344289
 Thermal correction to Gibbs Free Energy=           0.288438
 Sum of electronic and zero-point Energies=            -645.397903
 Sum of electronic and thermal Energies=               -645.382991
 Sum of electronic and thermal Enthalpies=             -645.382047
 Sum of electronic and thermal Free Energies=           -645.437898

        Item               Value     Threshold  Converged?
```

```
 Maximum Force            0.000019     0.000450     YES
 RMS     Force            0.000004     0.000300     YES
```

TS1_ANTI

```
---------------------------------------
 Cartesian coordinates (Angstroms):
---------------------------------------

37

H    -2.147    -2.703    -0.607
H    -3.402    -1.446    -0.612
C    -2.331    -1.632    -0.744
H    -1.932    -2.309     1.799
H    -2.051    -1.365    -1.769
H     4.341    -2.421    -0.135
H     4.680     0.028    -0.627
C    -1.917    -1.220     1.686
H    -2.924    -0.840     1.895
C    -1.491    -0.855     0.271
O    -0.120    -1.227     0.076
C     3.004     2.056    -0.002
C     3.509    -1.707    -0.071
H    -1.226    -0.807     2.425
C     3.985    -0.281     0.170
H    -3.001     0.768    -1.556
B     0.457    -0.301    -0.820
H    -3.593     1.067     0.096
C     2.805     0.677     0.191
C    -2.760     1.234    -0.597
C    -1.464     0.678    -0.024
H     4.533    -0.203     1.119
O    -0.427     0.779    -1.007
C     2.653    -1.678    -1.351
H     3.324    -1.719    -2.221
C     1.850    -0.387    -1.357
H    -2.659     2.313    -0.755
H    -1.818     1.521     1.962
```

```
H    2.027   -2.581   -1.399
C   -1.038    1.501    1.194
H   -0.120    1.099    1.635
H   -0.838    2.528    0.871
H    2.881   -2.013    0.778
H    2.133    0.334   -2.123
H    3.698    2.376   -0.784
H    2.175    2.741    0.179
H    2.099    0.421    0.987
```

```
                 1                      2                      3
                 A                      A                      A
 Frequencies --  -455.1548               49.2056                72.5751
 Red. masses --     5.9965                2.8683                 3.3171
 Zero-point correction=                           0.326380 (Hartree/Particle)
 Thermal correction to Energy=                     0.341995
 Thermal correction to Enthalpy=                   0.342939
 Thermal correction to Gibbs Free Energy=          0.285215
 Sum of electronic and zero-point Energies=          -645.347479
 Sum of electronic and thermal Energies=             -645.331865
 Sum of electronic and thermal Enthalpies=           -645.330920
 Sum of electronic and thermal Free Energies=        -645.388645
```

```
        Item             Value     Threshold  Converged?
 Maximum Force           0.000035     0.000450     YES
 RMS     Force           0.000006     0.000300     YES
```

PDT_ANTI

```
-----------------------------------------
 Cartesian coordinates (Angstroms):
-----------------------------------------
```

37

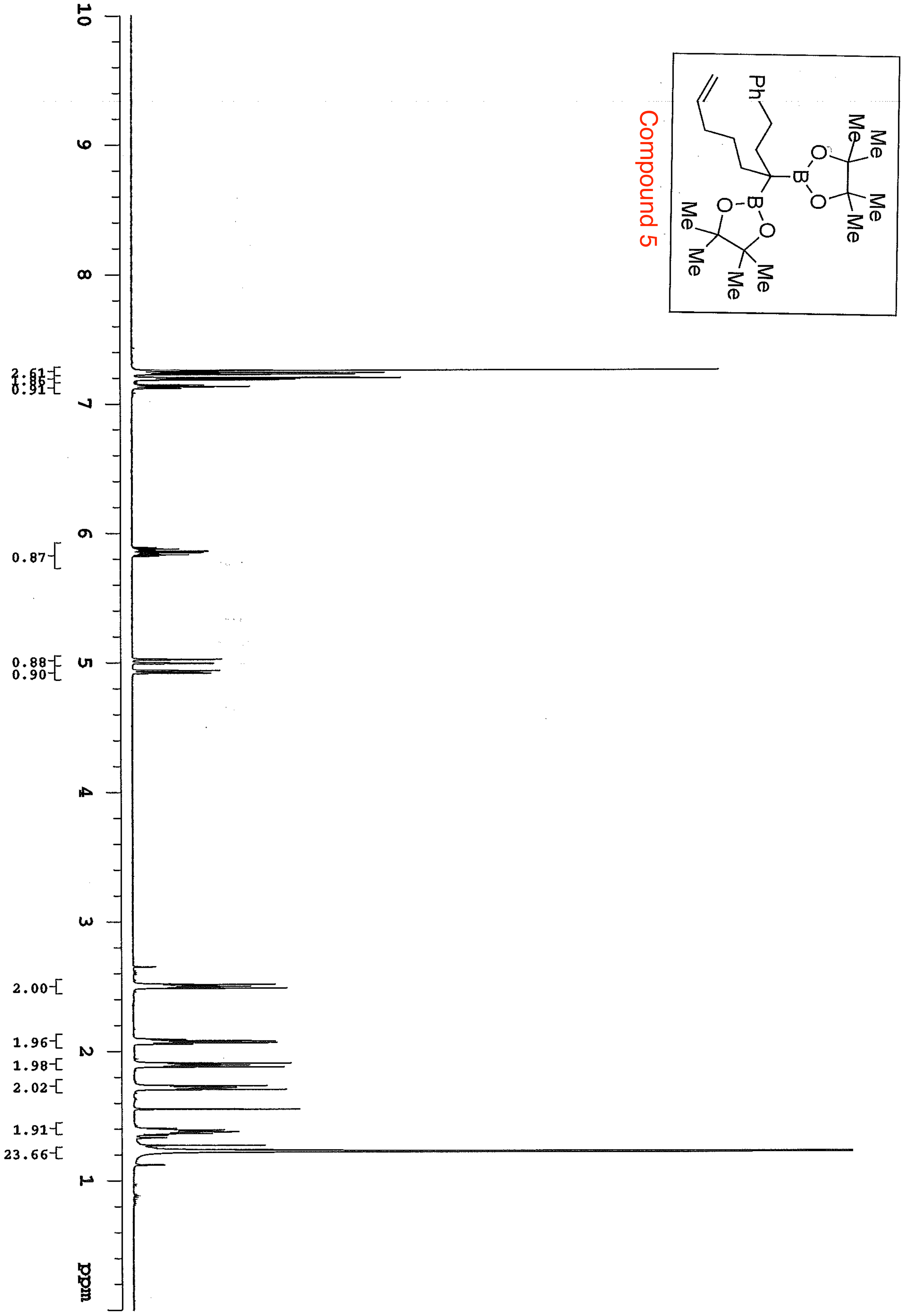
```
C    2.641    0.327    0.218
H    2.244   -0.164    1.124
H   -1.458   -2.009    0.002
H   -2.651   -1.422   -1.178
C   -1.655   -1.243   -0.756
```

H	-2.586	-0.576	1.657
H	-0.906	-1.345	-1.548
H	4.587	-1.823	-1.278
H	4.588	0.477	-0.717
C	-2.625	0.280	0.973
H	-3.624	0.307	0.520
C	-1.544	0.139	-0.094
O	-0.269	0.267	0.502
C	1.918	1.683	0.088
C	3.901	-1.603	-0.451
H	-2.481	1.191	1.560
C	4.091	-0.130	0.052
H	-2.243	0.190	-2.889
B	0.674	0.737	-0.551
H	-3.536	0.974	-1.947
C	-2.506	1.080	-2.311
C	-1.533	1.285	-1.154
H	4.705	-0.087	0.961
O	-0.204	1.241	-1.637
C	2.402	-1.746	-0.914
H	2.328	-2.297	-1.860
C	1.921	-0.298	-0.971
H	-2.471	1.944	-2.984
H	-2.827	2.779	-0.189
H	1.833	-2.314	-0.164
C	-1.785	2.654	-0.507
H	-1.130	2.790	0.360
H	-1.553	3.435	-1.240
H	4.136	-2.318	0.347
H	1.795	2.268	1.011
H	2.400	2.315	-0.674
H	2.383	0.166	-1.867

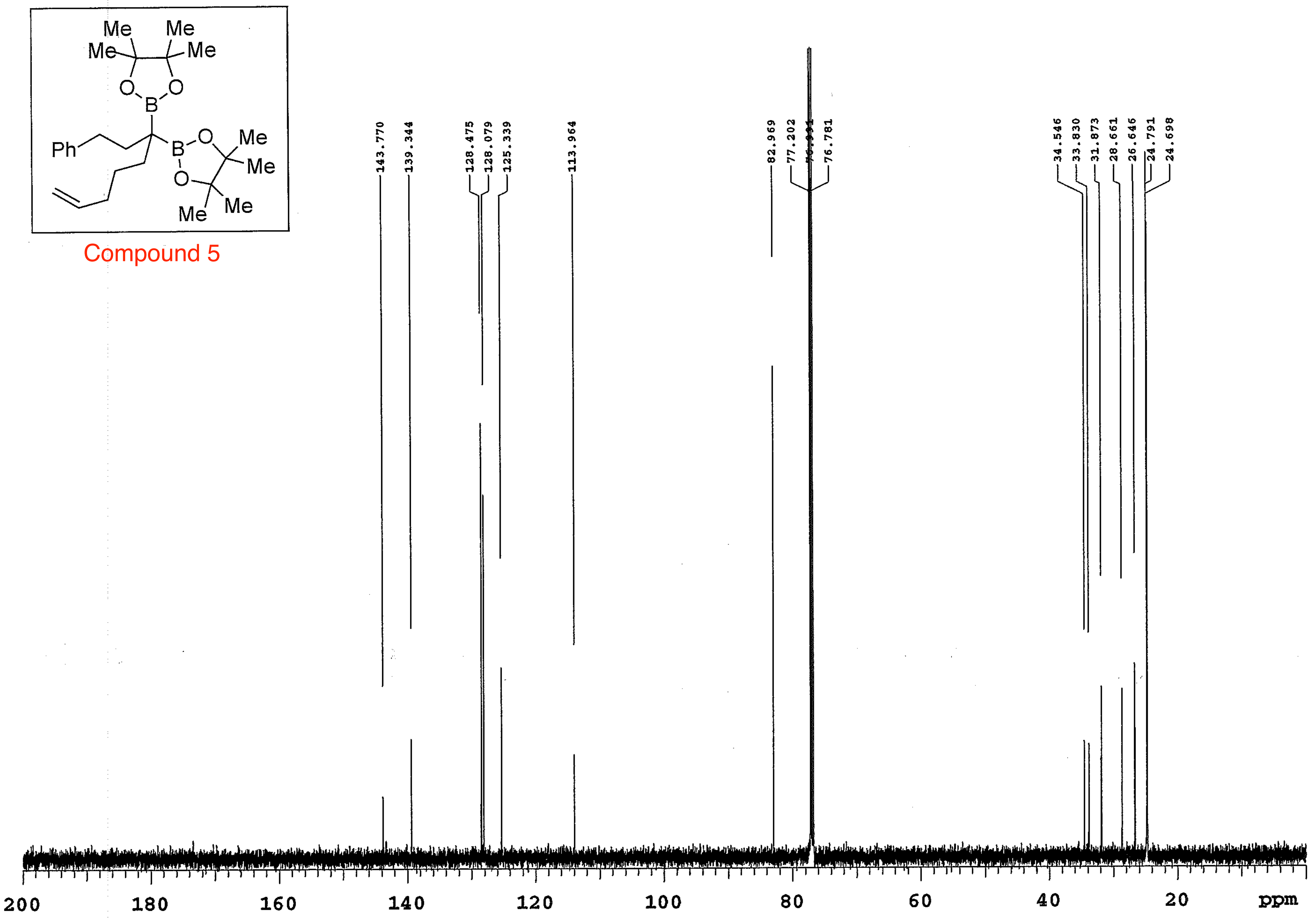
```
                    1                      2                      3
                    A                      A                      A
Frequencies --    62.0776                68.8159                98.9517
Red. masses --     3.7307                 3.0379                 2.7455
Zero-point correction=                           0.328127 (Hartree/Particle)
Thermal correction to Energy=                     0.343269
Thermal correction to Enthalpy=                   0.344213
Thermal correction to Gibbs Free Energy=          0.287716
```

```
Sum of electronic and zero-point Energies=         -645.377943
Sum of electronic and thermal Energies=            -645.362802
Sum of electronic and thermal Enthalpies=          -645.361857
Sum of electronic and thermal Free Energies=       -645.418355

       Item             Value     Threshold  Converged?
Maximum Force          0.000037     0.000450     YES
RMS     Force          0.000008     0.000300     YES
    Gaussian 09, Revision A.02,
     M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,
     M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci,
     G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian,
     A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada,
     M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima,
     Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr.,
     J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers,
     K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand,
     K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi,
     M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross,
     V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann,
     O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski,
     R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth,
     P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels,
     O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski,
      and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
```

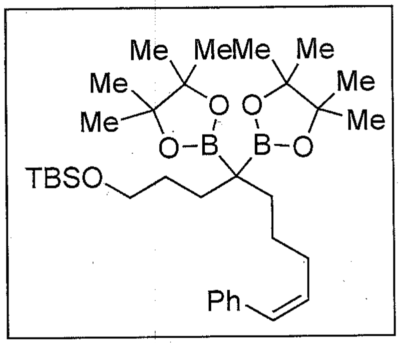

Me
Me
O
B
O
Me
Me
Ph
B
O
O
Me
Me
Me
Me
10
9
8
7
6
5
4
3
2
1
ppm
2.61
1.86
0.91
0.87
0.88
0.90
2.00
1.96
1.98
2.02
1.91
23.66

Compound 5

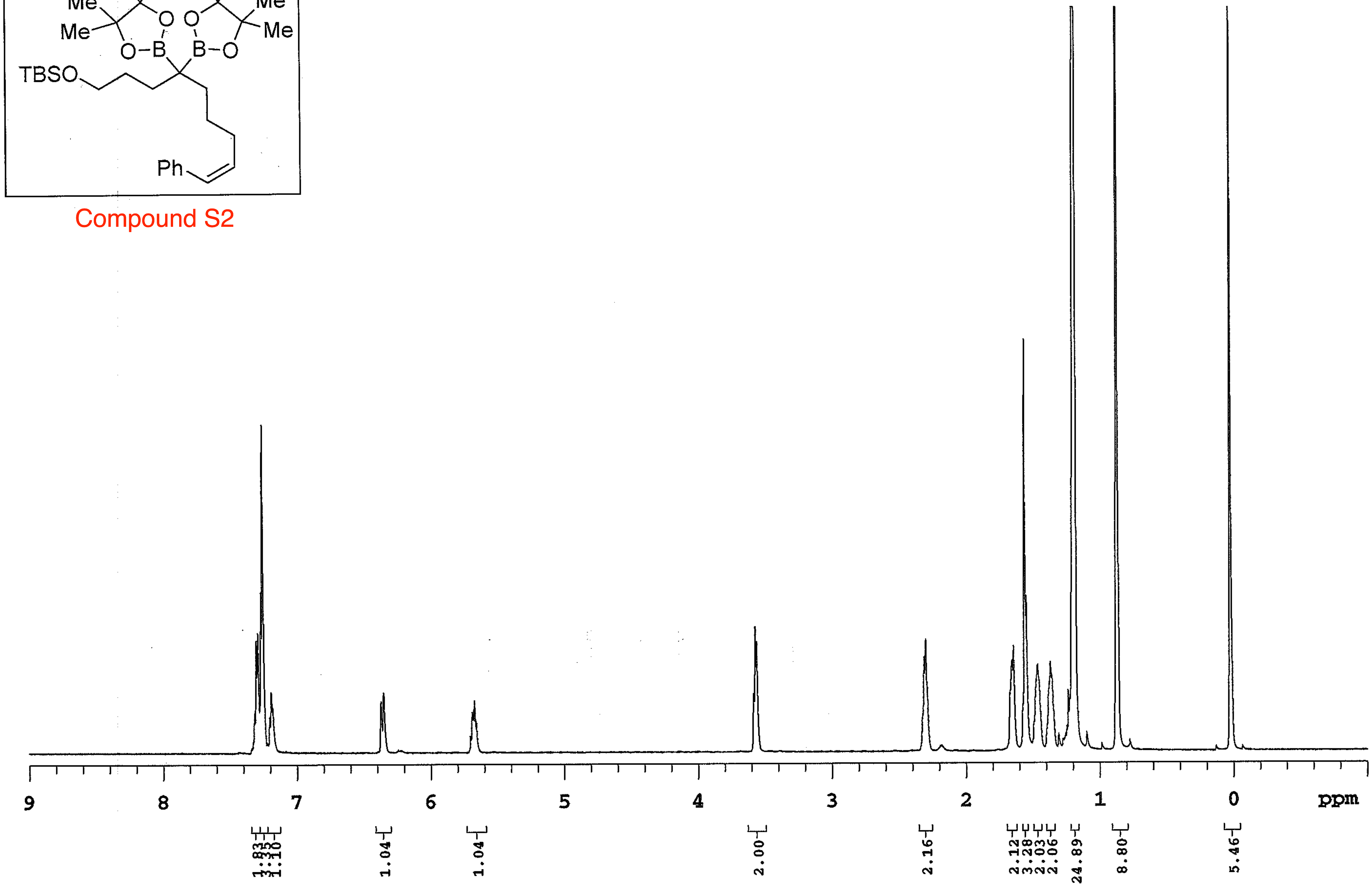

Me
Me
Me
Me
O
B
O
Ph
B
O
O
Me
Me
Me
Me

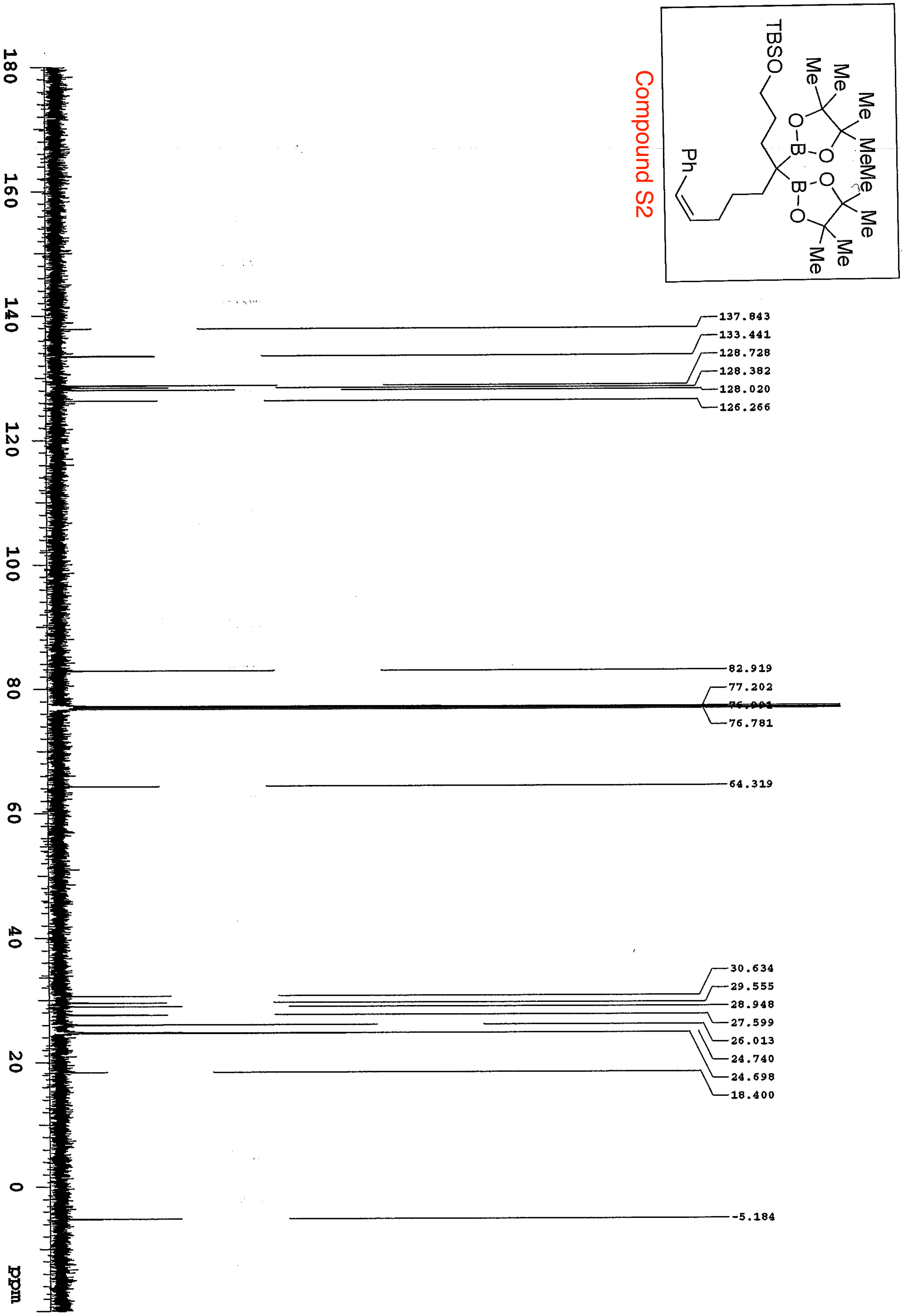
Compound 5

143.770
139.344
128.475
128.079
125.339
113.964
82.969
77.202
76.991
76.781
34.546
33.830
31.873
28.661
26.646
24.791
24.698
200
180
160
140
120
100
80
60
40
20
ppm

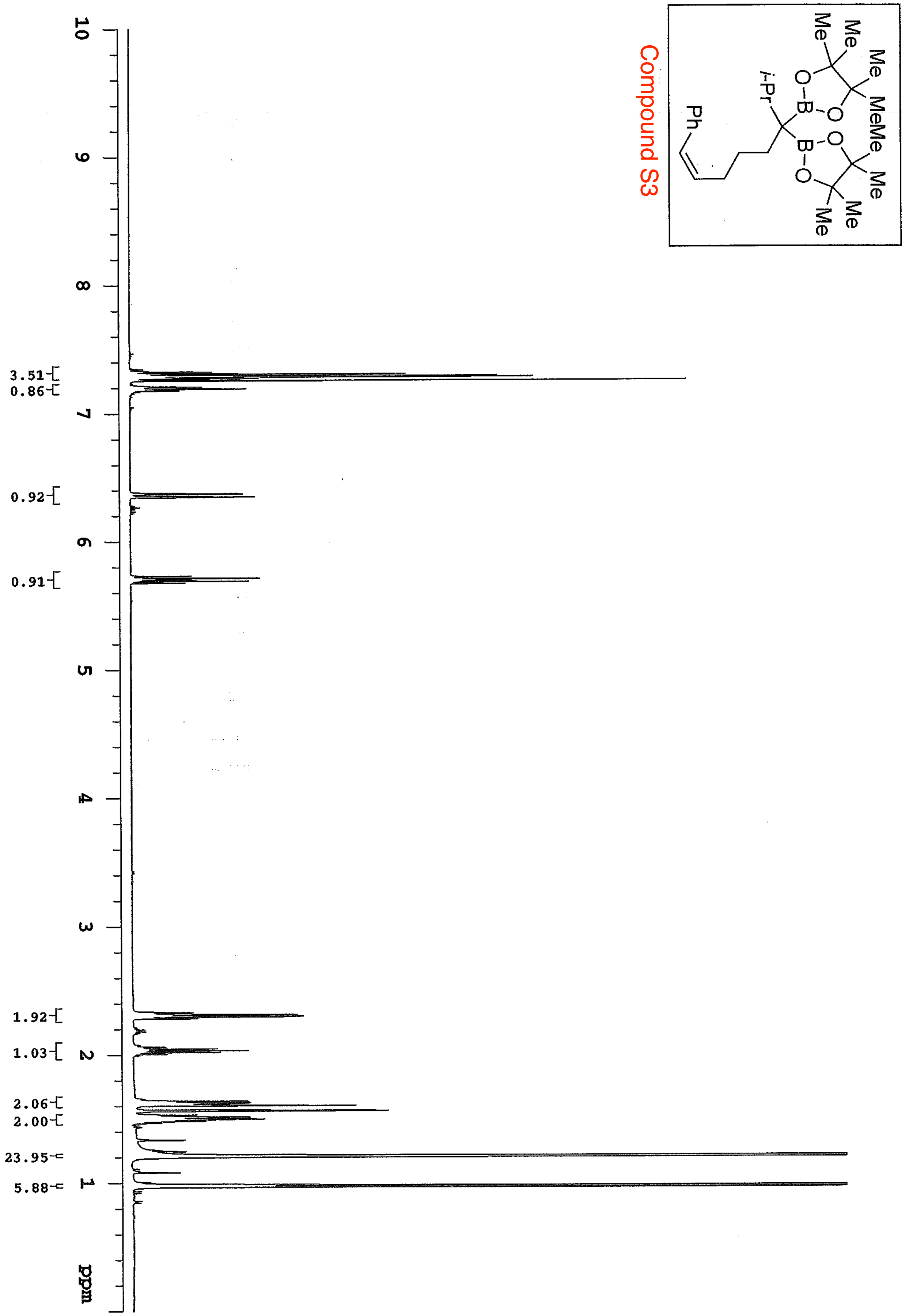

Me
MeMe
Me
Me
Me
Me
Me
O
O
O-B
B-O
TBSO
Ph

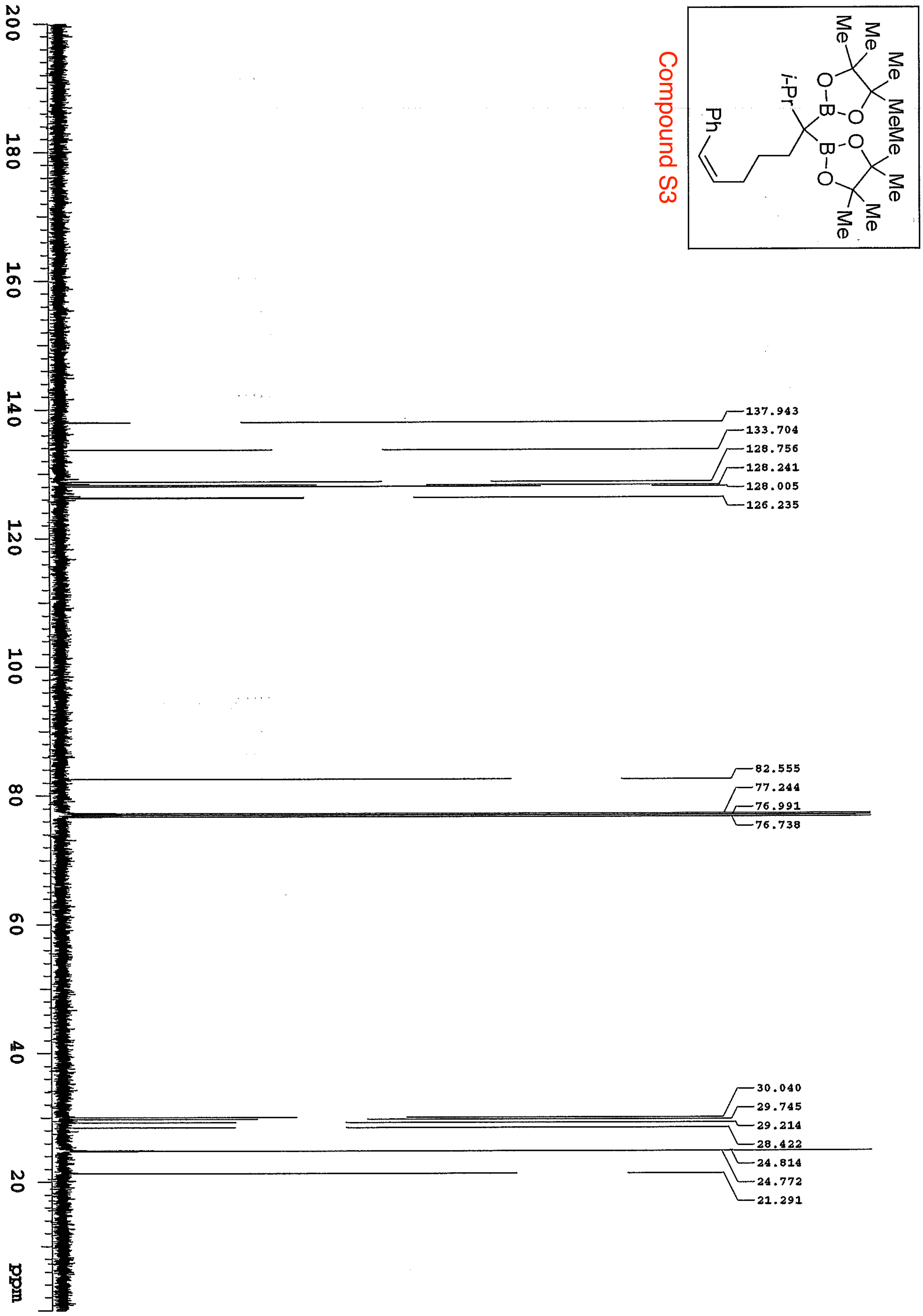
Compound S2


9
8
7
6
5
4
3
2
1
0
ppm
1.83
3.35
1.10
1.04
1.04
2.00
2.16
2.12
3.28
2.03
2.06
24.89
8.80
5.46

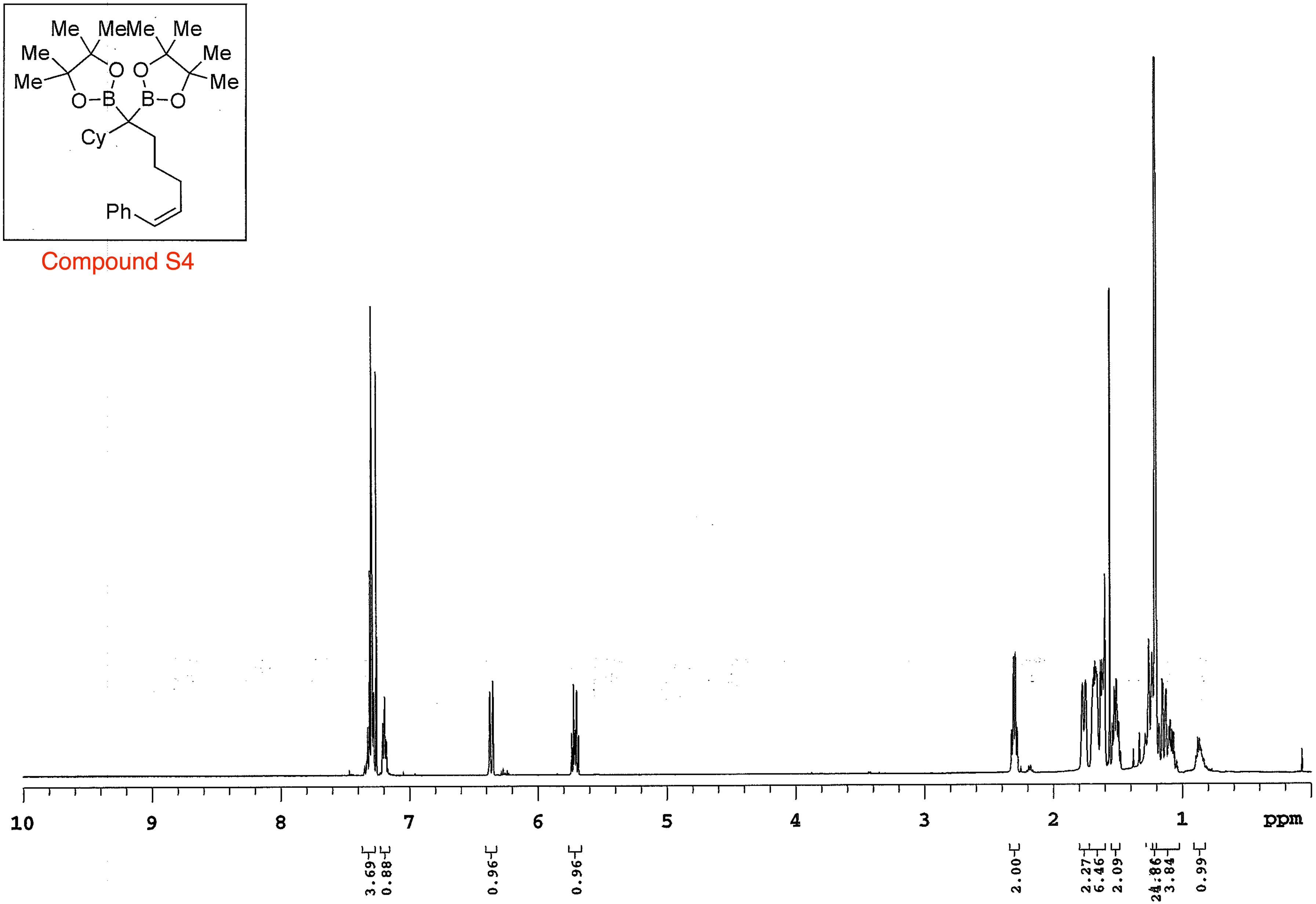

Compound S2

TBSO
Me
Me
Me
MeMe
Me
Me
Me
O-B
O
B-O
O
Ph
137.843
133.441
128.728
128.382
128.020
126.266
82.919
77.202
76.991
76.781
64.319
30.634
29.555
28.948
27.599
26.013
24.740
24.698
18.400
-5.184
180
160
140
120
100
80
60
40
20
0
ppm


Compound S3
Me
Me
Me
MeMe
Me
Me
Me
O
O
O
O
O–B
B–O
i-Pr
Ph
10
9
8
7
6
5
4
3
2
1
ppm
3.51
0.86
0.92
0.91
1.92
1.03
2.06
2.00
23.95
5.88

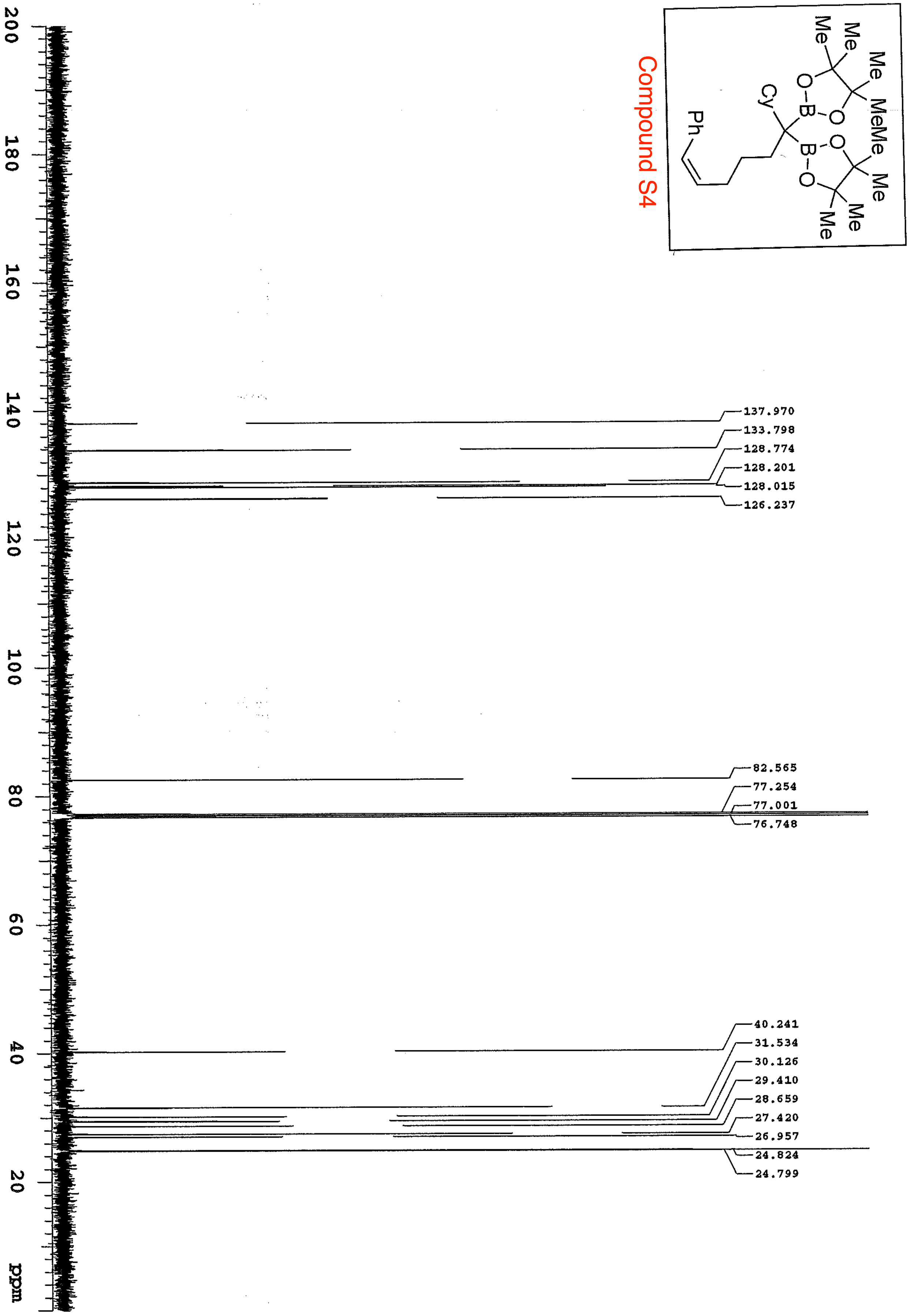

200
180
160
140
120
100
80
60
40
20
ppm
137.943
133.704
128.756
128.241
128.005
126.235
82.555
77.244
76.991
76.738
30.040
29.745
29.214
28.422
24.814
24.772
21.291
Me
Me
Me
MeMe
Me
Me
Me
O
O
O
O
B
B
i-Pr
Ph

Compound S3

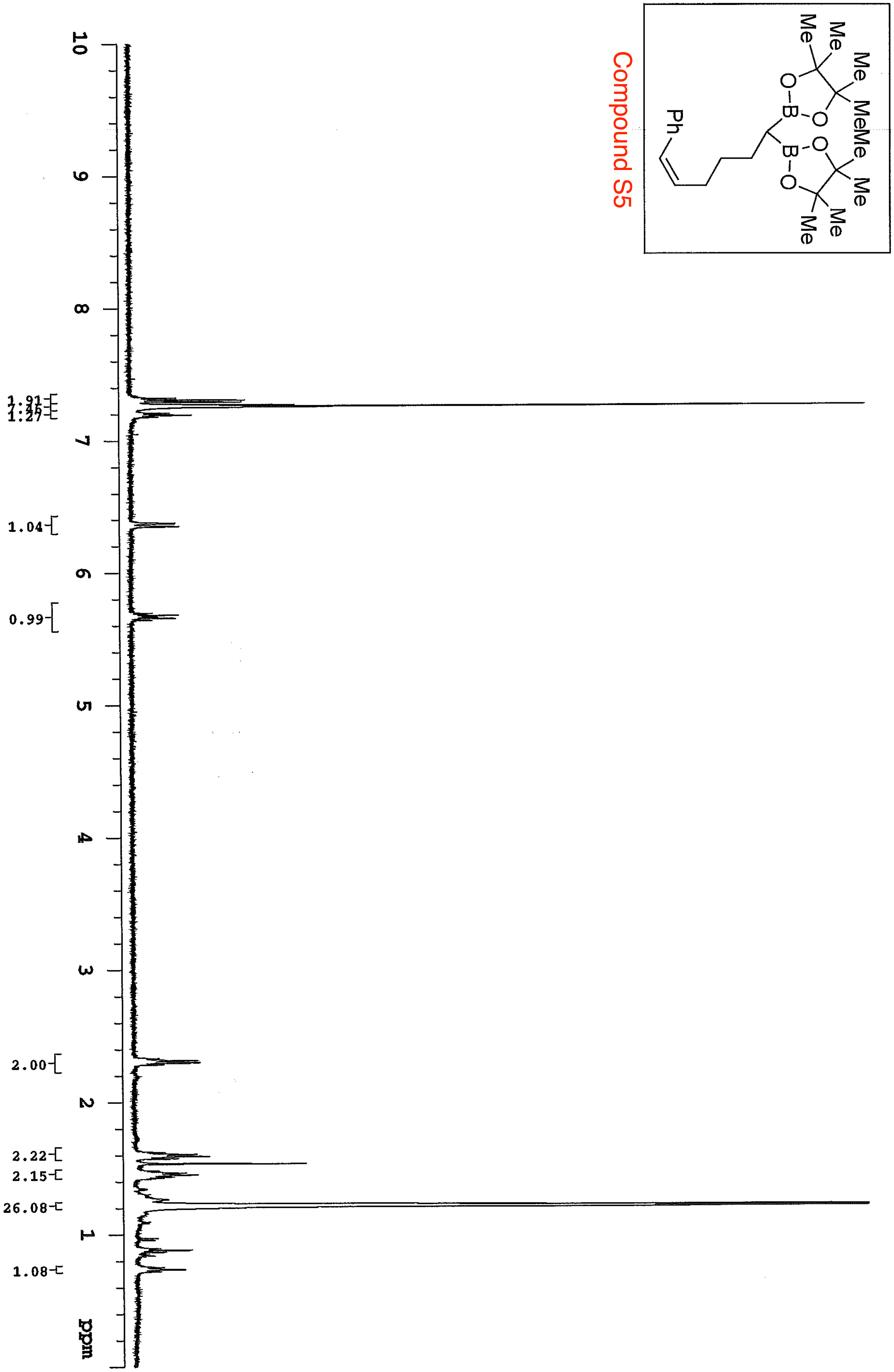

Me
MeMe
Me
Me
Me
Me
Me
O
O
O
O
B
B
Cy
Ph

Compound S4

10
9
8
7
6
5
4
3
2
1
ppm
3.69
0.88
0.96
0.96
2.00
2.27
6.46
2.09
24.86
3.84
0.99

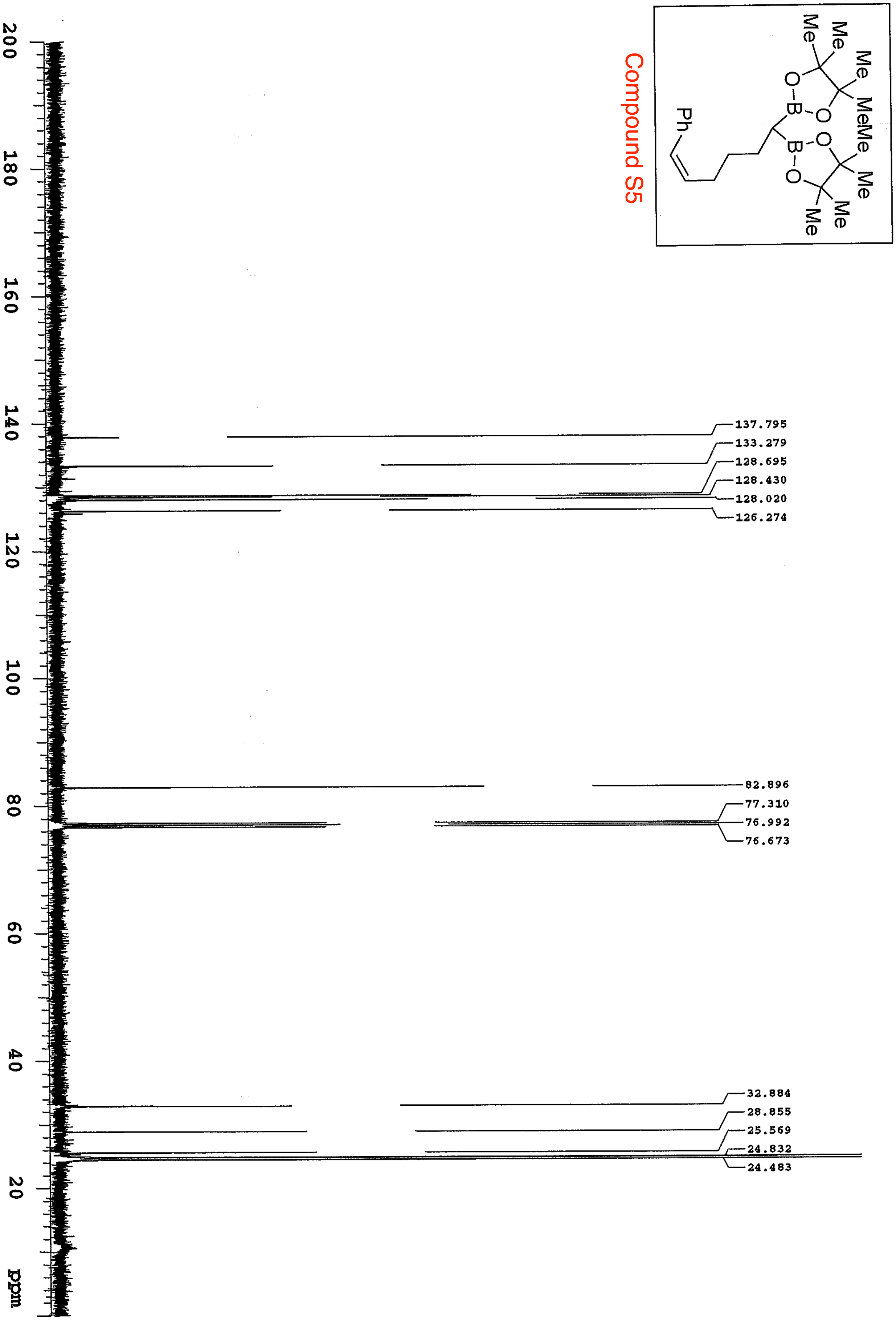

Me
Me
Me
MeMe
Me
Me
Me
O
O
O
O
B
B
Cy
Ph
137.970
133.798
128.774
128.201
128.015
126.237
82.565
77.254
77.001
76.748
40.241
31.534
30.126
29.410
28.659
27.420
26.957
24.824
24.799
200
180
160
140
120
100
80
60
40
20
ppm

Compound S4



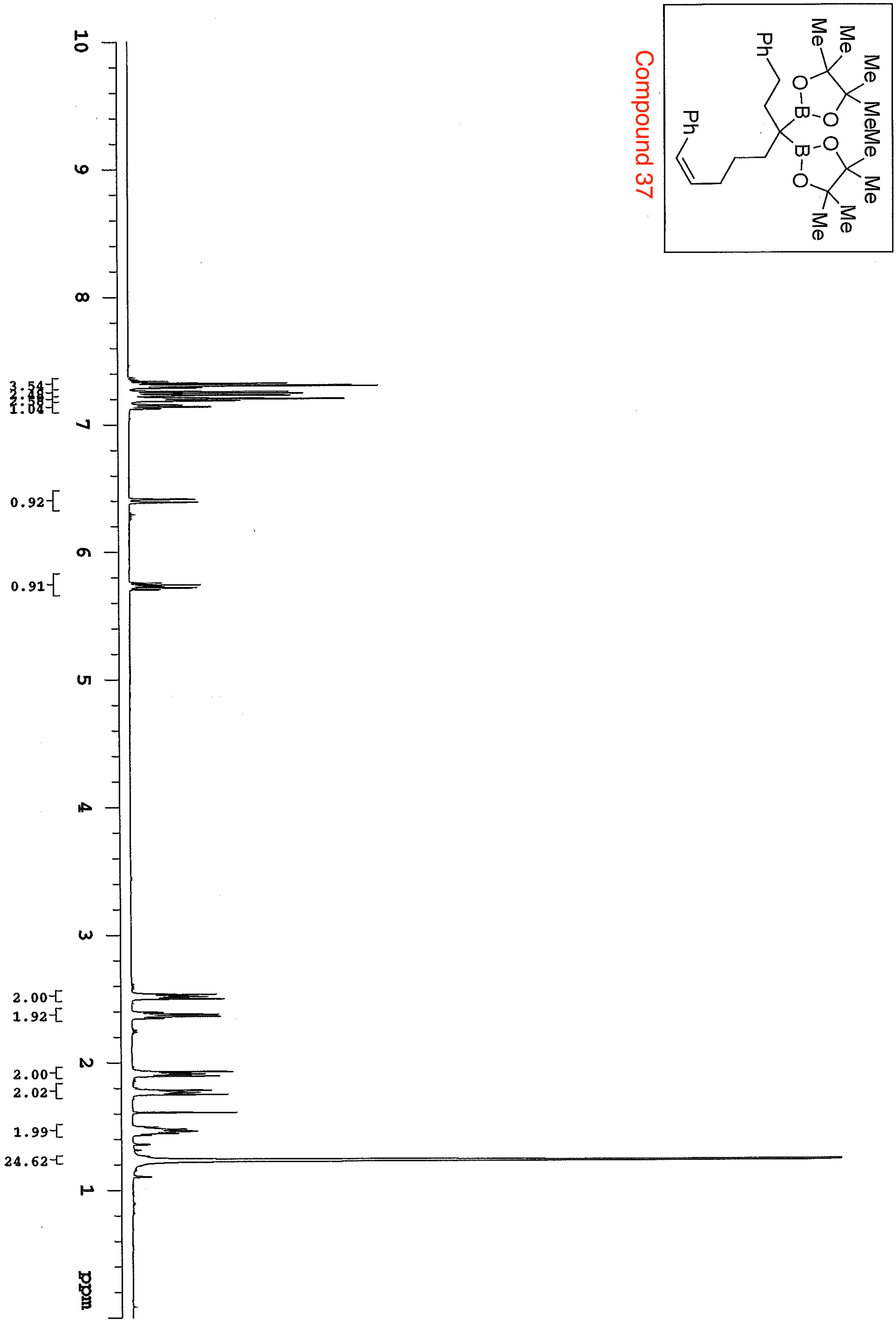
Compound S5

Me
Me
Me
MeMe
Me
Me
Me
O–B
O
B–O
O
Ph
10
9
8
7
6
5
4
3
2
1
ppm
1.91
1.27
1.04
0.99
2.00
2.22
2.15
26.08
1.08


Me
Me
Me
MeMe
Me
Me
Me
O
O
O
O
B
B
Ph

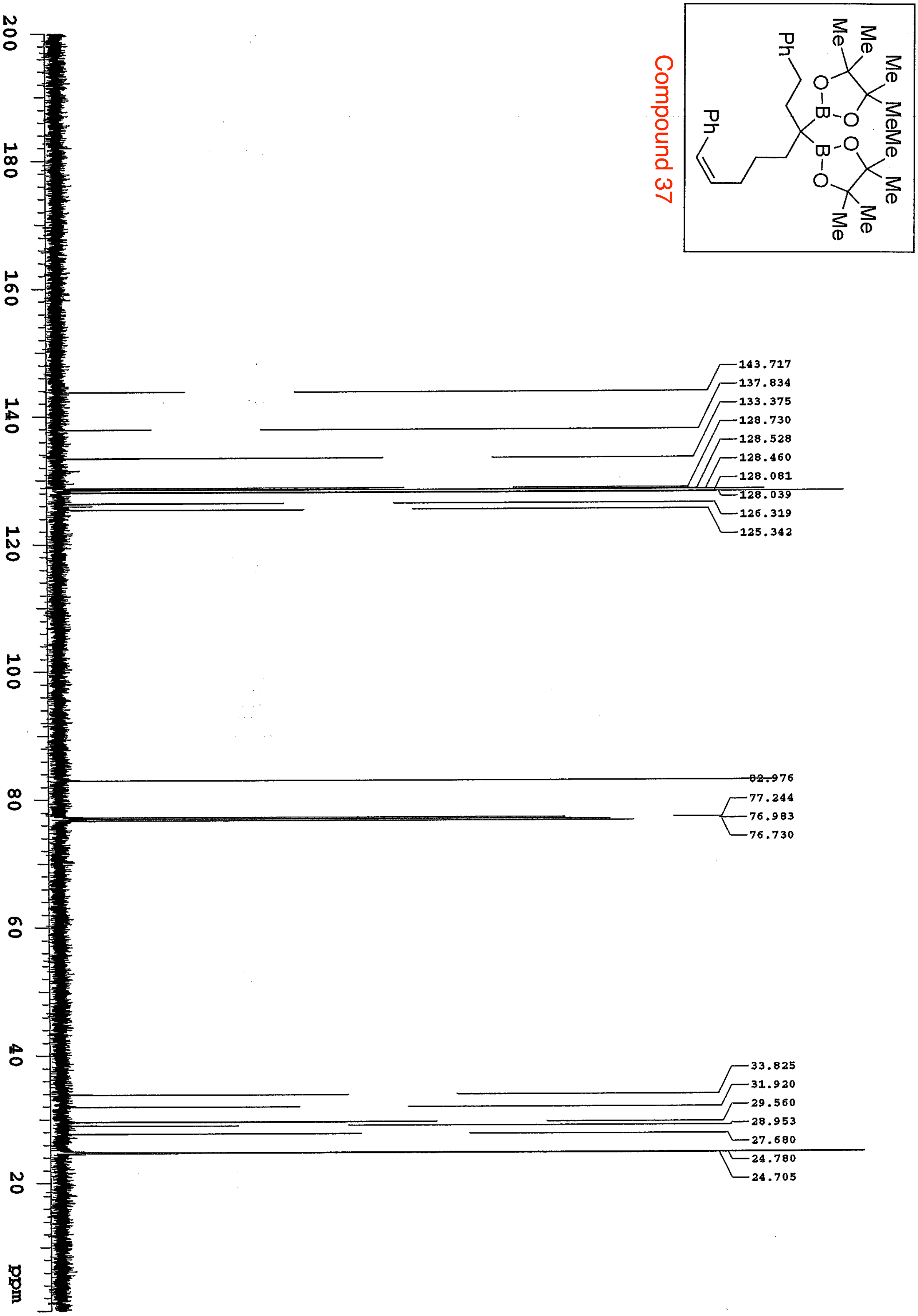
Compound S5

137.795
133.279
128.695
128.430
128.020
126.274
82.896
77.310
76.992
76.673
32.884
28.855
25.569
24.832
24.483
200
180
160
140
120
100
80
60
40
20
ppm


Me
Me
Me
MeMe
Me
Me
Me
O
B
O
O
B
O
Ph
Ph

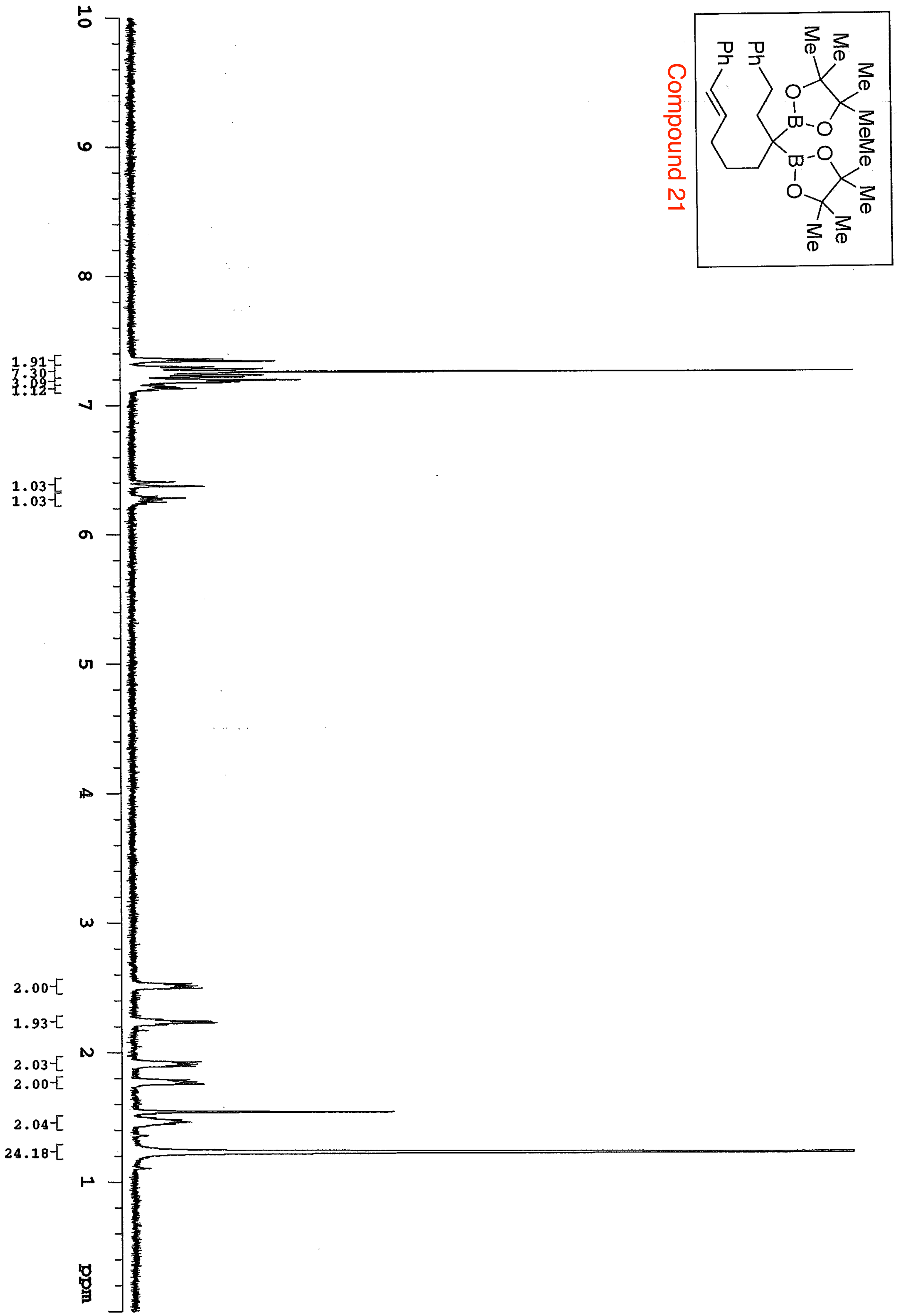
Compound 37

10
9
8
7
6
5
4
3
2
1
ppm
3.54
1.04
0.92
0.91
2.00
1.92
2.00
2.02
1.99
24.62

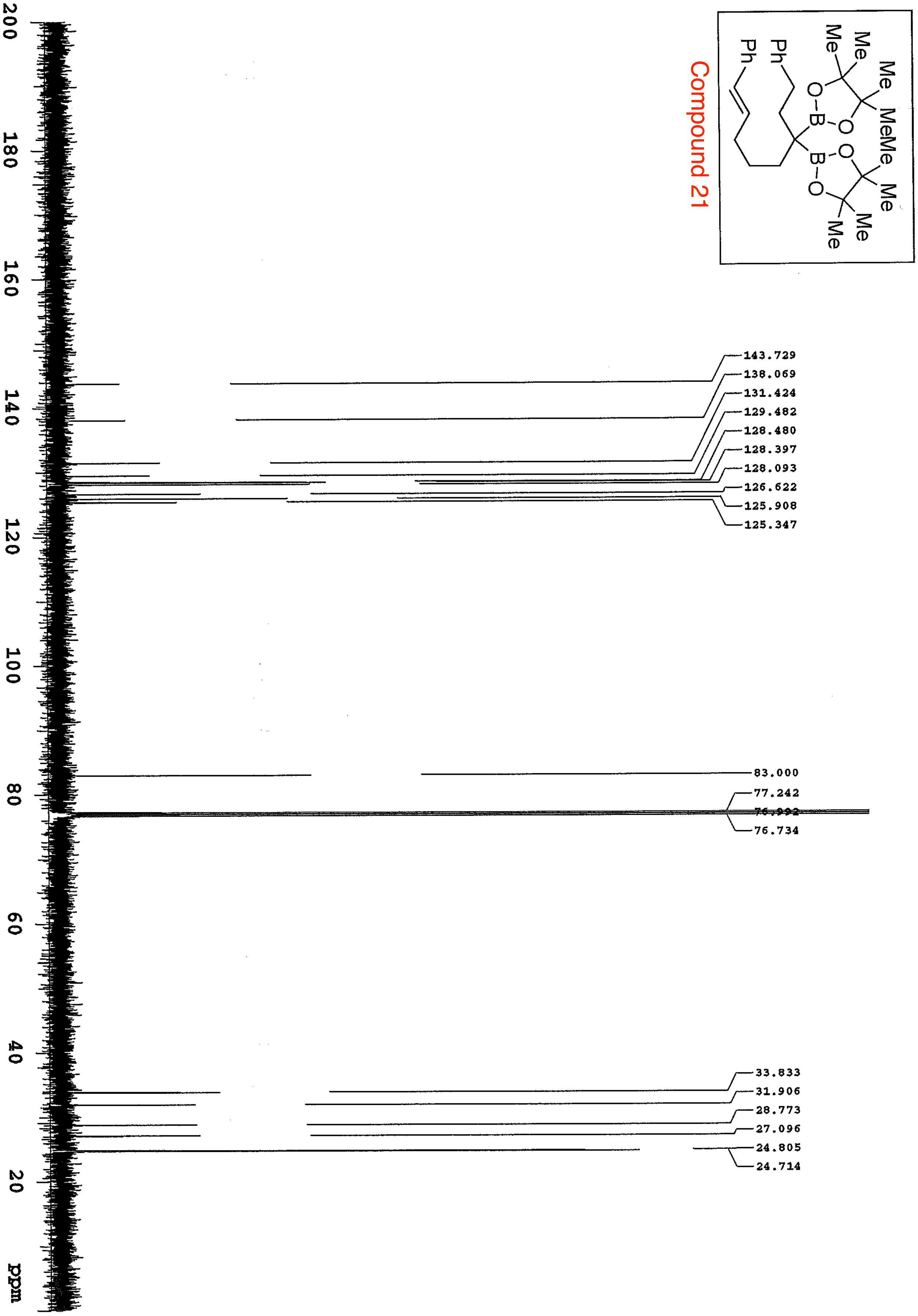

Me
Me
MeMe
Me
Me
Me
O-B
O
O
B-O
Ph
Ph

Compound 37

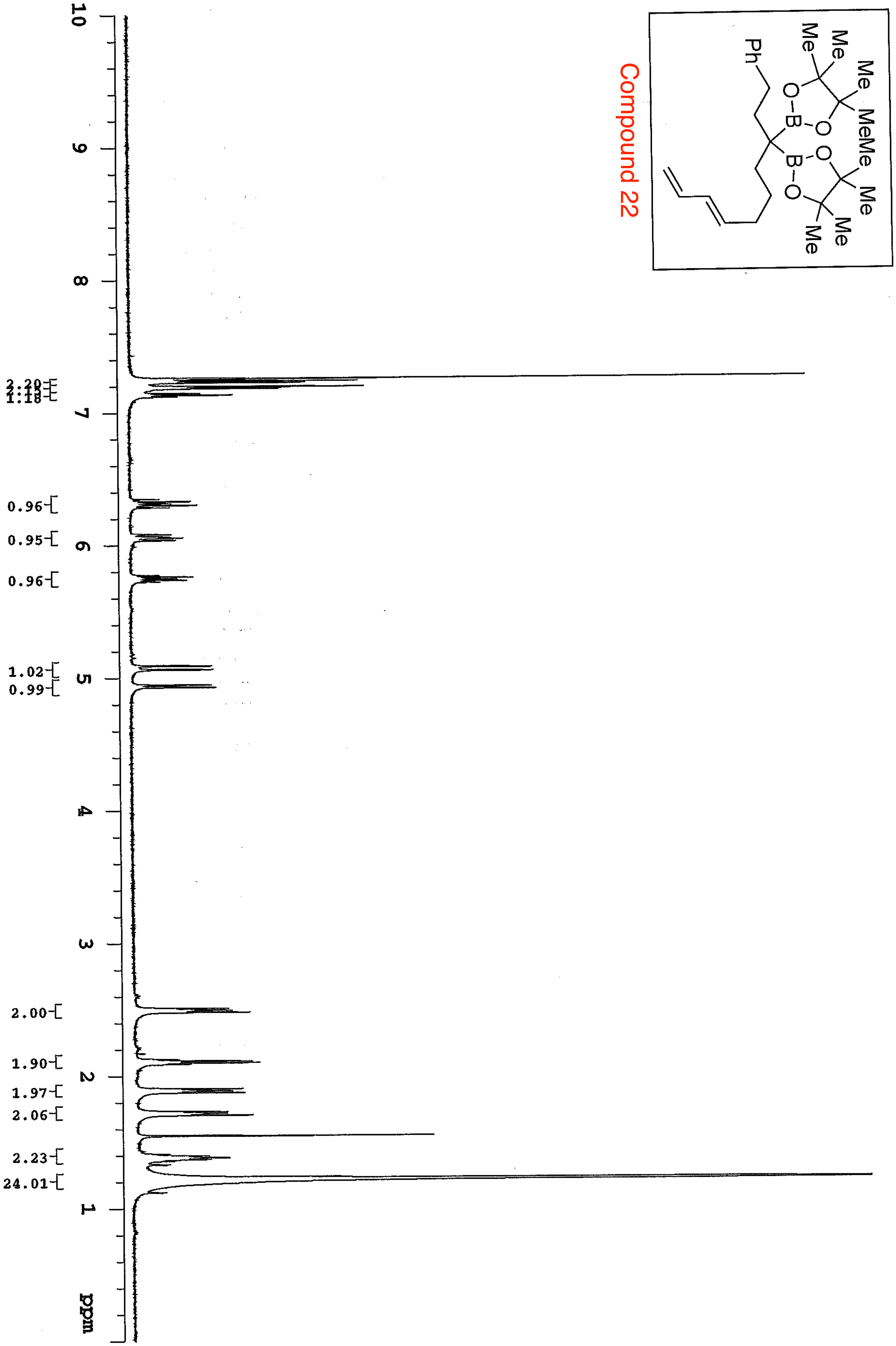
143.717
137.834
133.375
128.730
128.528
128.460
128.081
128.039
126.319
125.342
82.976
77.244
76.983
76.730
33.825
31.920
29.560
28.953
27.680
24.780
24.705
200
180
160
140
120
100
80
60
40
20
ppm


10
9
8
7
6
5
4
3
2
1
ppm
1.91
7.30
3.09
1.12
1.03
1.03
2.00
1.93
2.03
2.00
2.04
24.18
Me
Me
MeMe
Me
Me
Me
Me
O
B
O
O
B
O
Ph
Ph

Compound 21

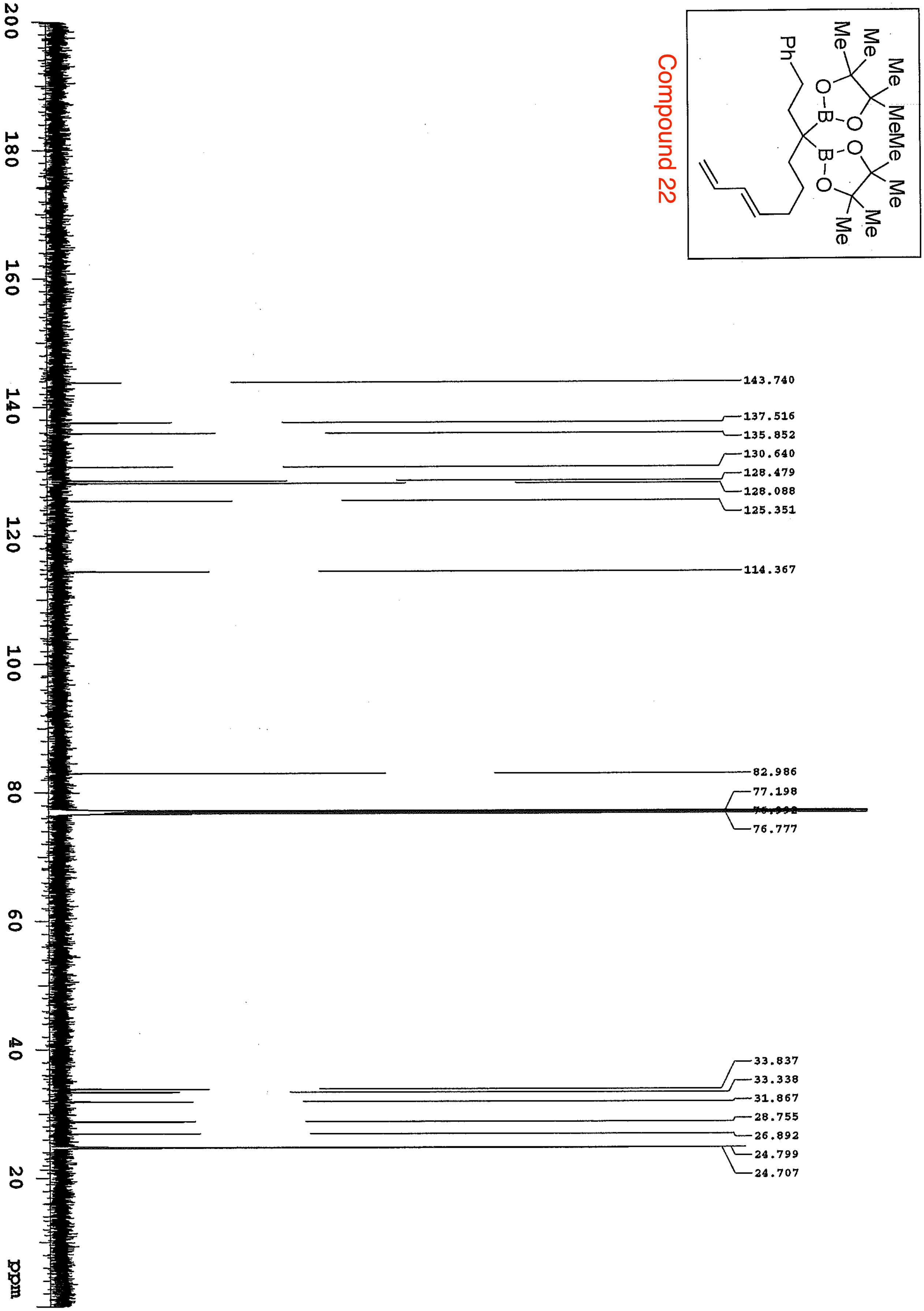

Me
Me
MeMe
Me
Me
Me
Me
O
O
O
O
B
B
Ph
Ph
143.729
138.069
131.424
129.482
128.480
128.397
128.093
126.622
125.908
125.347
83.000
77.242
76.992
76.734
33.833
31.906
28.773
27.096
24.805
24.714
200
180
160
140
120
100
80
60
40
20
ppm

Compound 21


Me
Me
Me
MeMe
Me
Me
Me
O
B
O
O
B
O
Ph

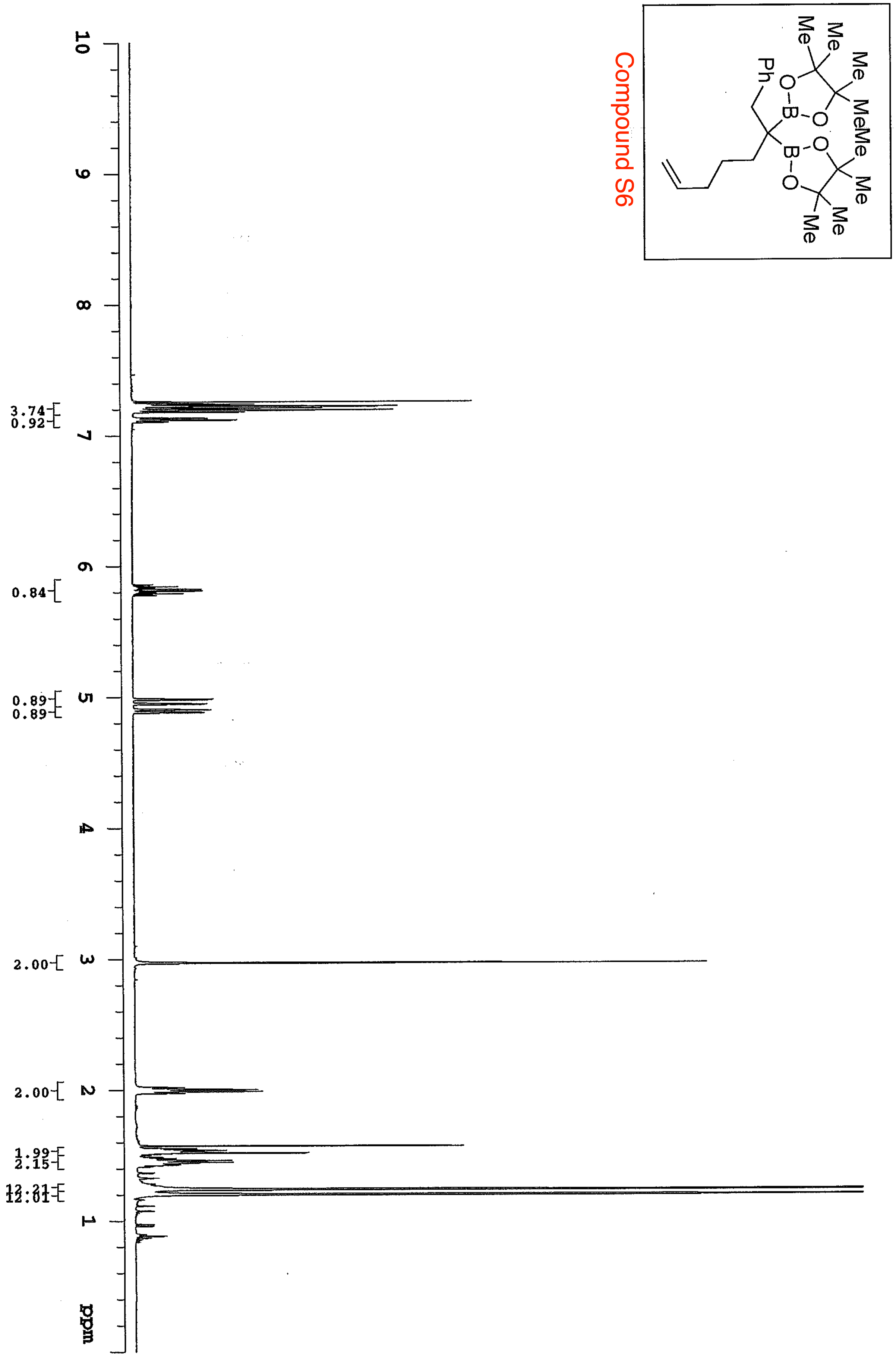
Compound 22

10
9
8
7
6
5
4
3
2
1
ppm
2.20
1.18
0.96
0.95
0.96
1.02
0.99
2.00
1.90
1.97
2.06
2.23
24.01

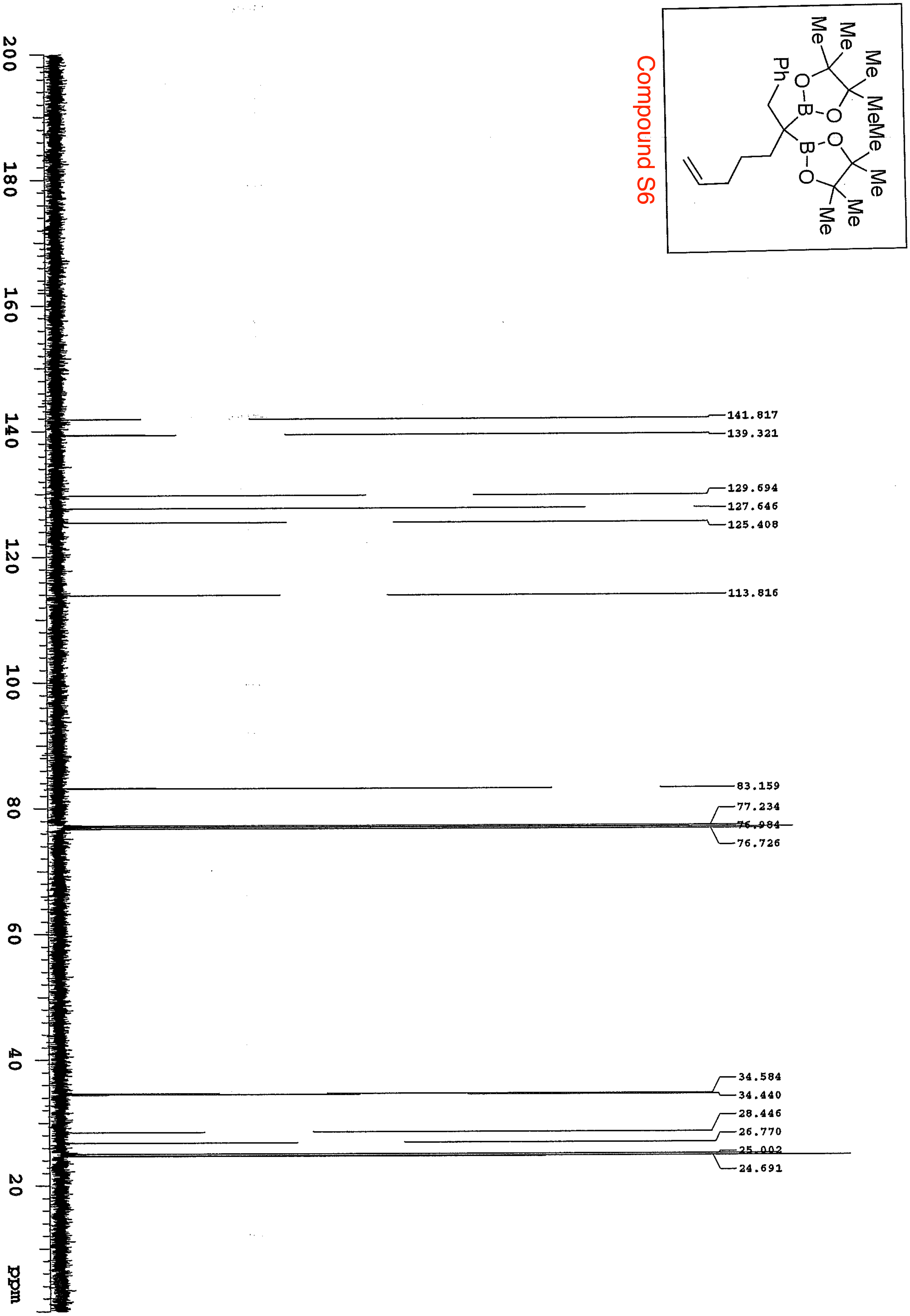


Compound 22

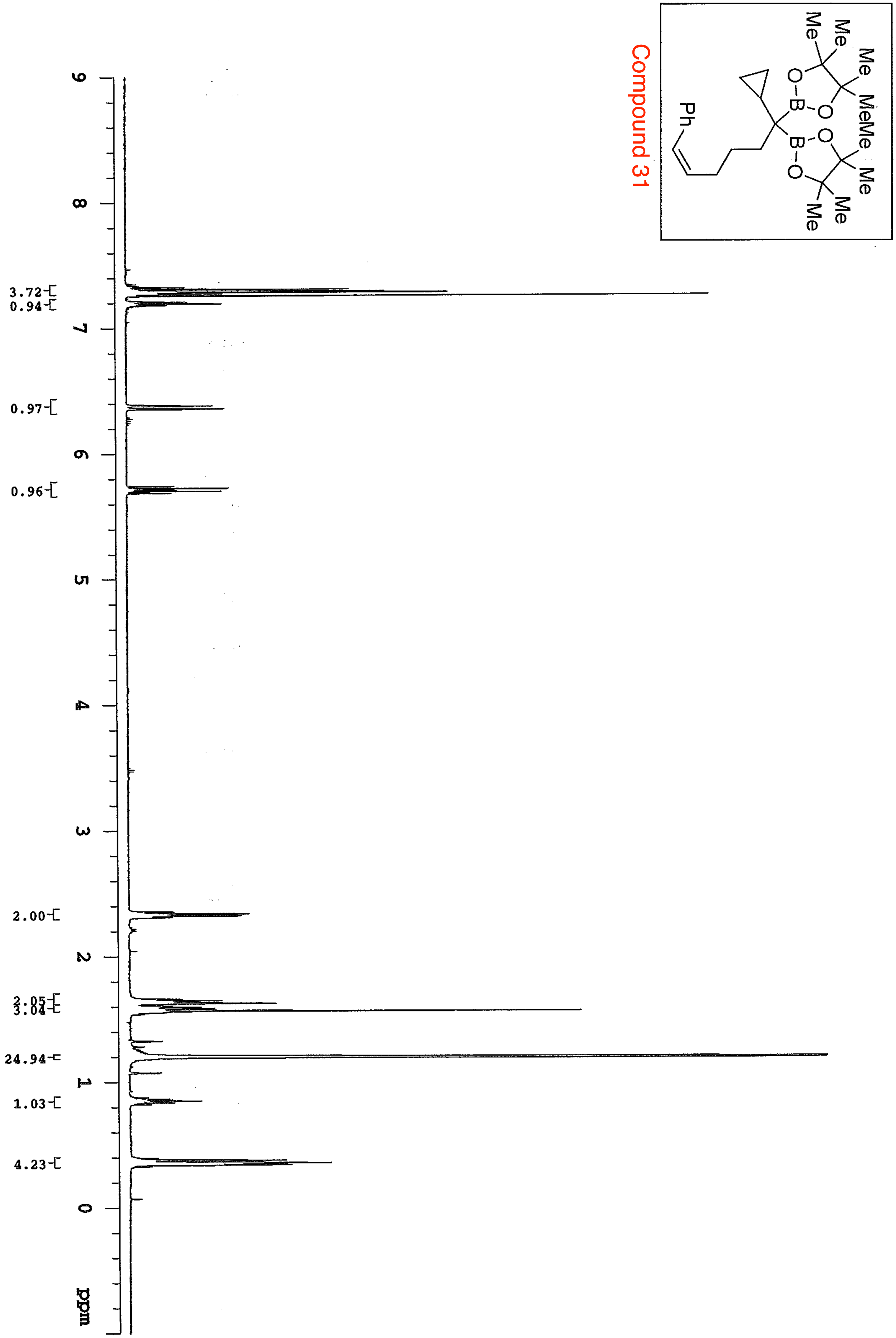
Me
Me
Me
MeMe
Me
Me
Me
O
O
O
O
B
B
Ph
200
180
160
140
120
100
80
60
40
20
ppm
143.740
137.516
135.852
130.640
128.479
128.088
125.351
114.367
82.986
77.198
76.992
76.777
33.837
33.338
31.867
28.755
26.892
24.799
24.707


10
9
8
7
6
5
4
3
2
1
ppm
3.74
0.92
0.84
0.89
0.89
2.00
2.00
1.99
2.15
12.21
12.01
Me
Me
MeMe
Me
Me
Me
Me
O
O
O
O
B
B
Ph

Compound S6

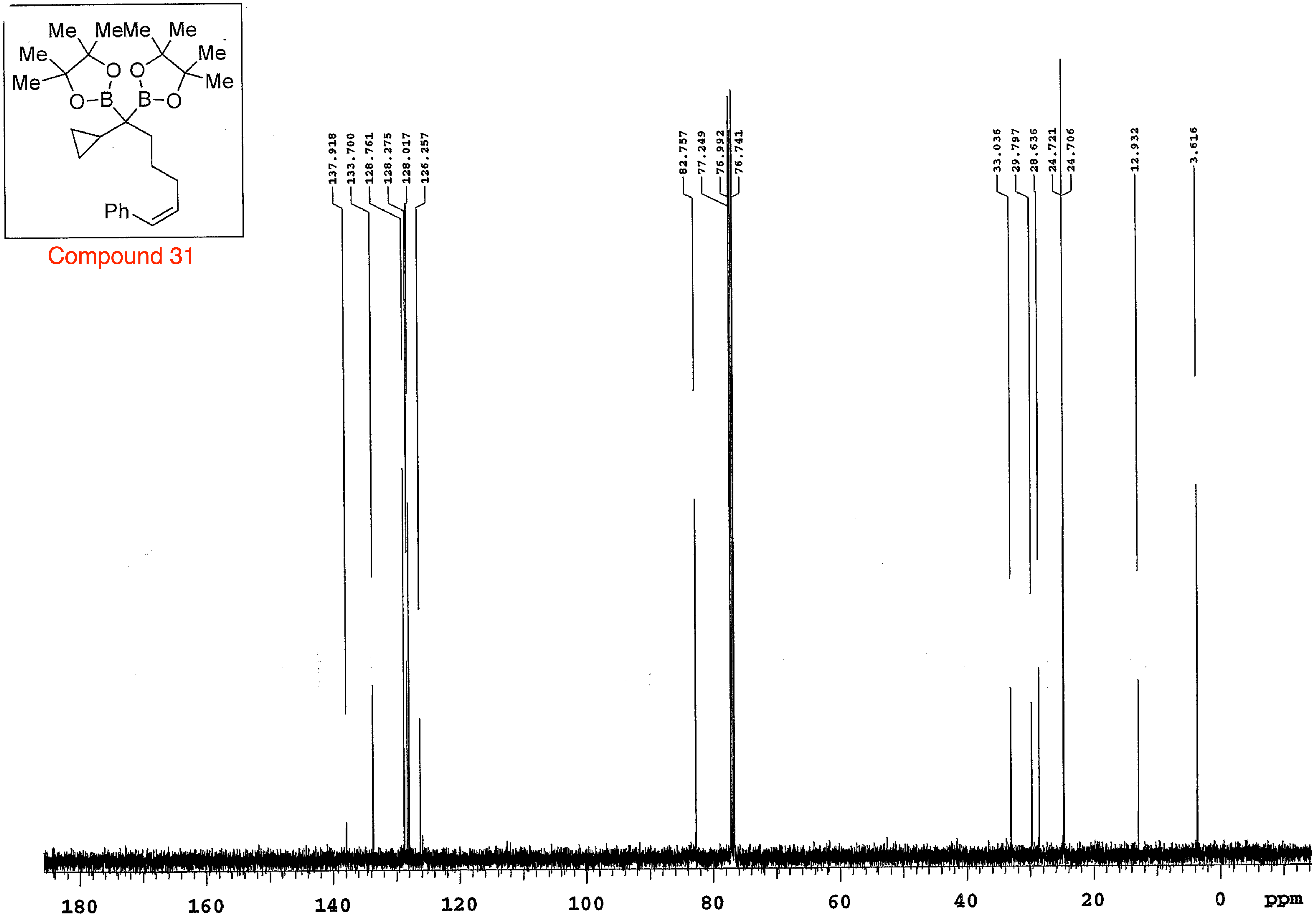

141.817
139.321
129.694
127.646
125.408
113.816
83.159
77.234
76.984
76.726
34.584
34.440
28.446
26.770
25.002
24.691
200
180
160
140
120
100
80
60
40
20
ppm
Me
Me
Me
MeMe
Me
Me
Me
O
B
O
O
B
O
Ph

Compound S6


Me
Me
Me
MeMe
Me
Me
Me
O-B
O
O
B-O
Ph

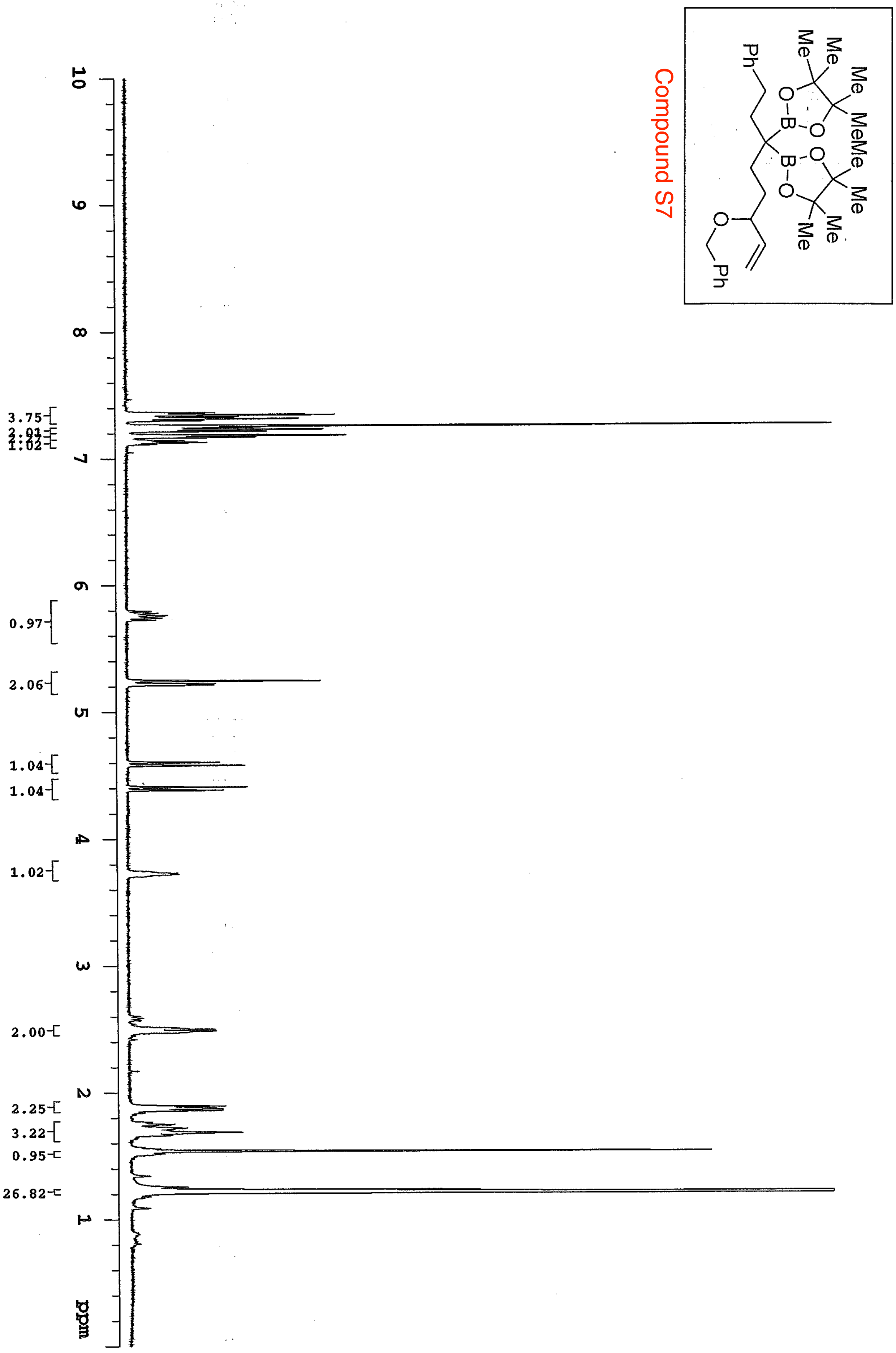
Compound 31

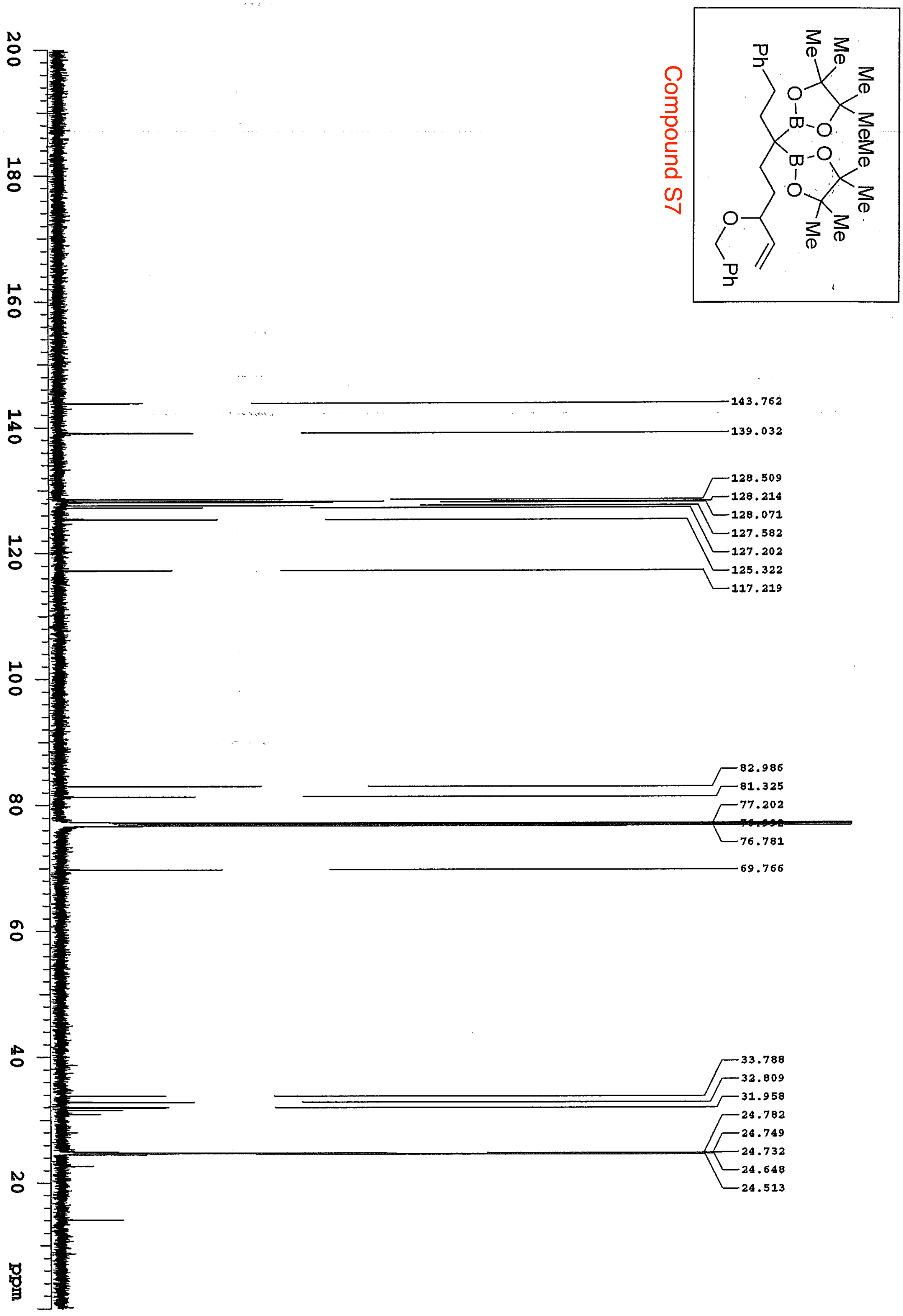
9
8
7
6
5
4
3
2
1
0
ppm
3.72
0.94
0.97
0.96
2.00
2.05
3.04
24.94
1.03
4.23


Me
MeMe
Me
Me
Me
Me
Me
O
O
O-B
B-O
Ph

Compound 31

137.918
133.700
128.761
128.275
128.017
126.257
82.757
77.249
76.992
76.741
33.036
29.797
28.636
24.721
24.706
12.932
3.616
180
160
140
120
100
80
60
40
20
0
ppm

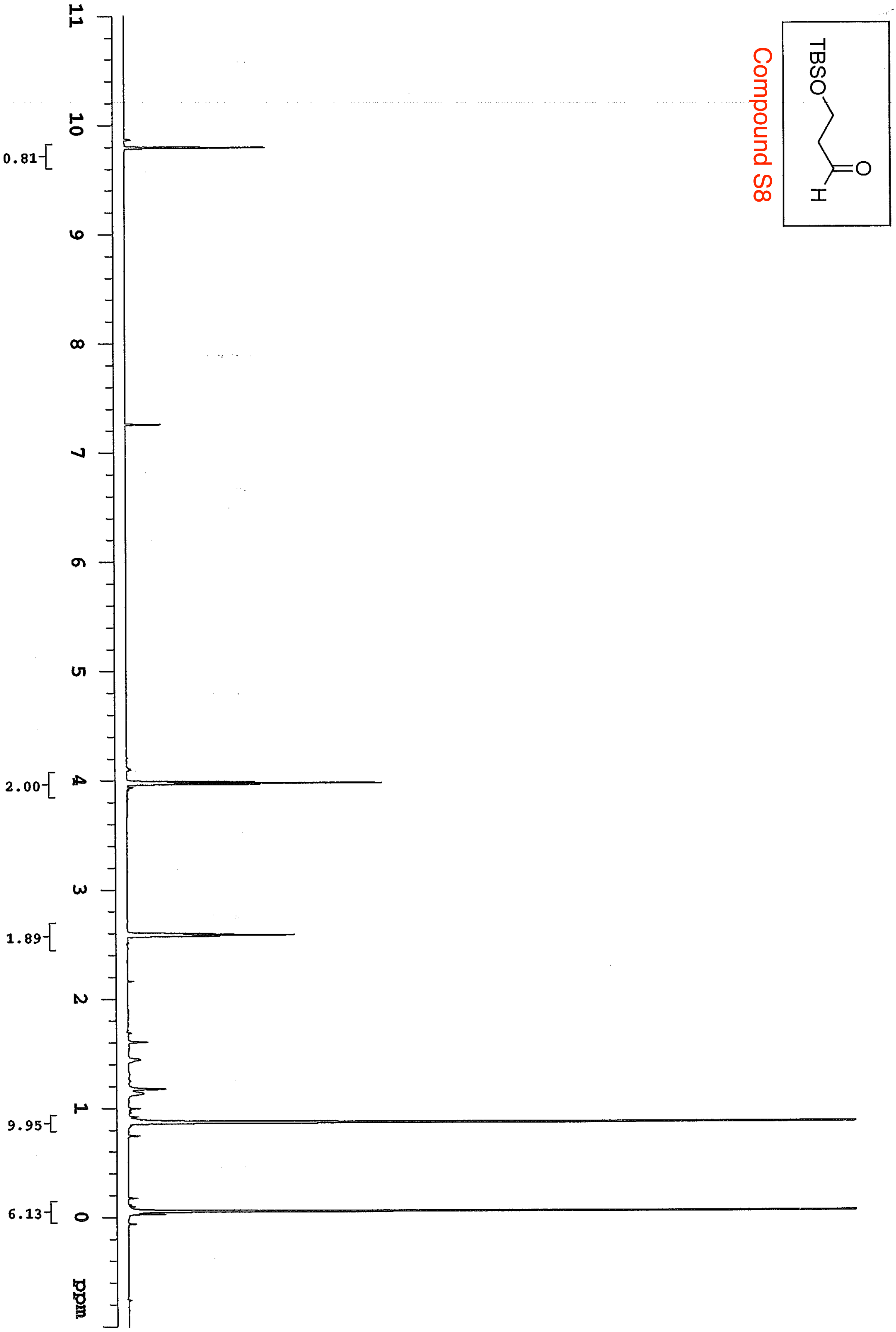

Compound S7
Me
Me
MeMe
Me
Me
Me
Me
O
B
O
O
B
O
Ph
O
Ph
10
9
8
7
6
5
4
3
2
1
ppm
3.75
2.01
2.02
1.02
0.97
2.06
1.04
1.04
1.02
2.00
2.25
3.22
0.95
26.82

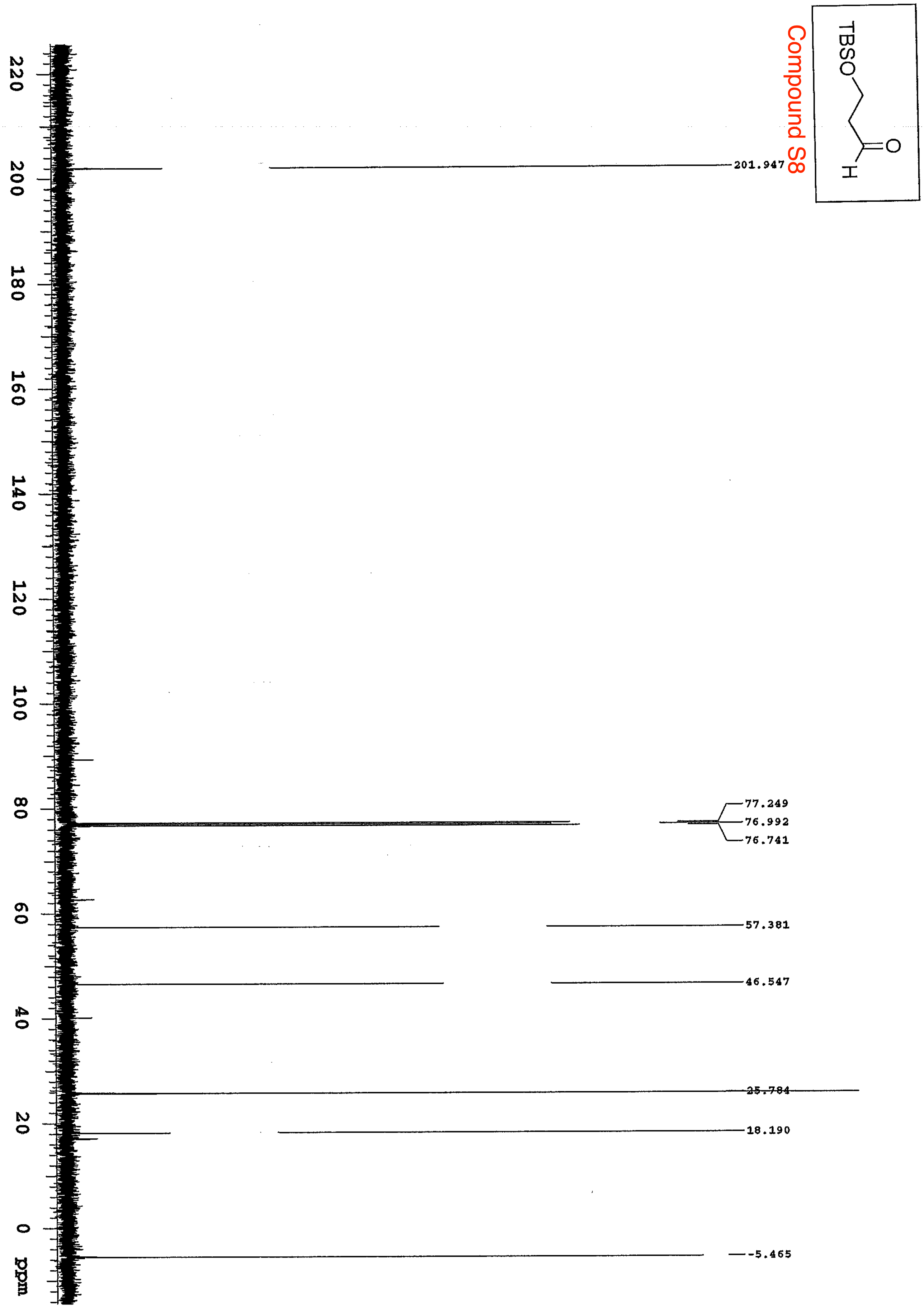


Me
Me
Me
MeMe
Me
Me
Me
O
O
O
O
B
B
Ph
Ph
O
143.762
139.032
128.509
128.214
128.071
127.582
127.202
125.322
117.219
82.986
81.325
77.202
76.992
76.781
69.766
33.788
32.809
31.958
24.782
24.749
24.732
24.648
24.513
200
180
160
140
120
100
80
60
40
20
ppm

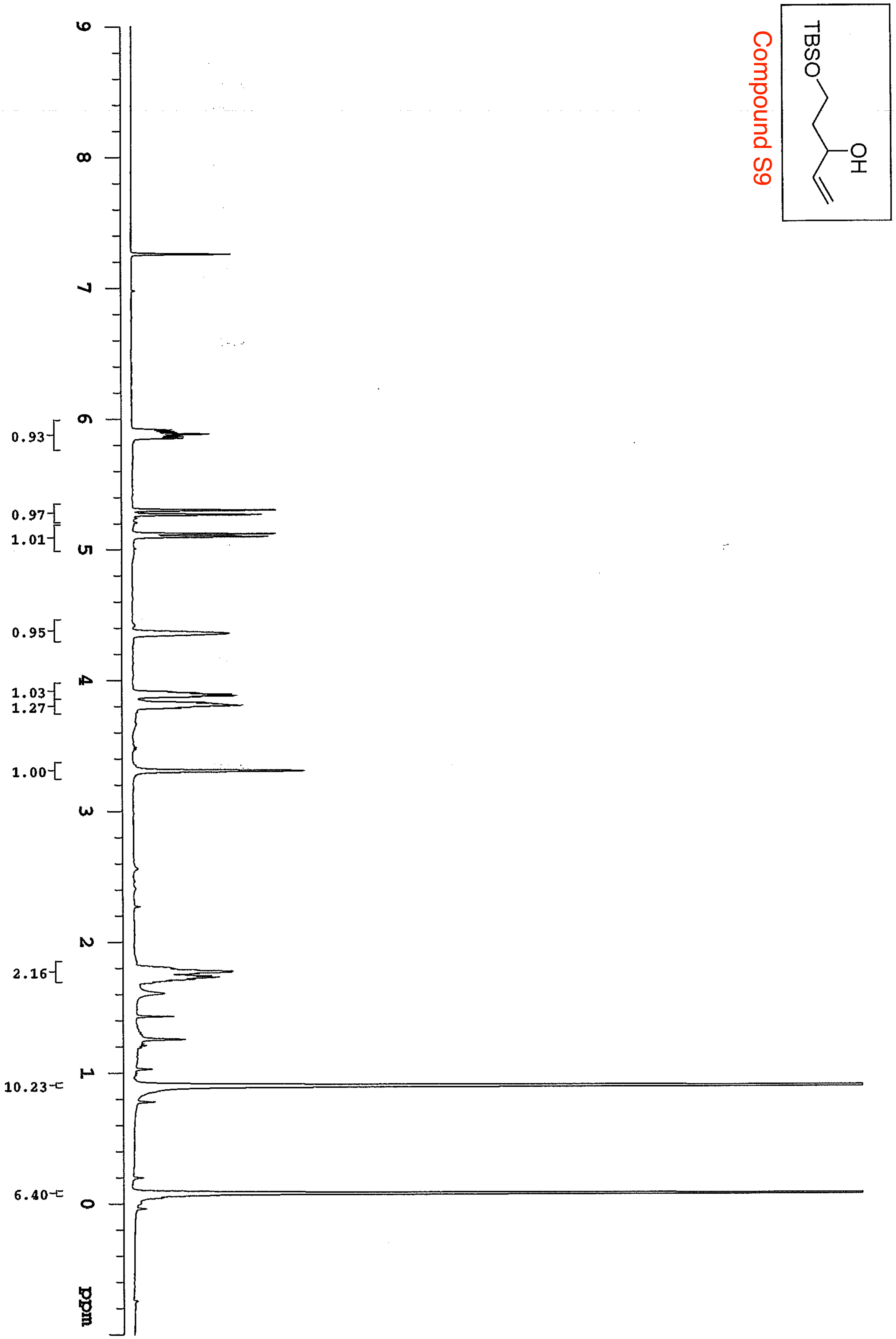
Compound S7

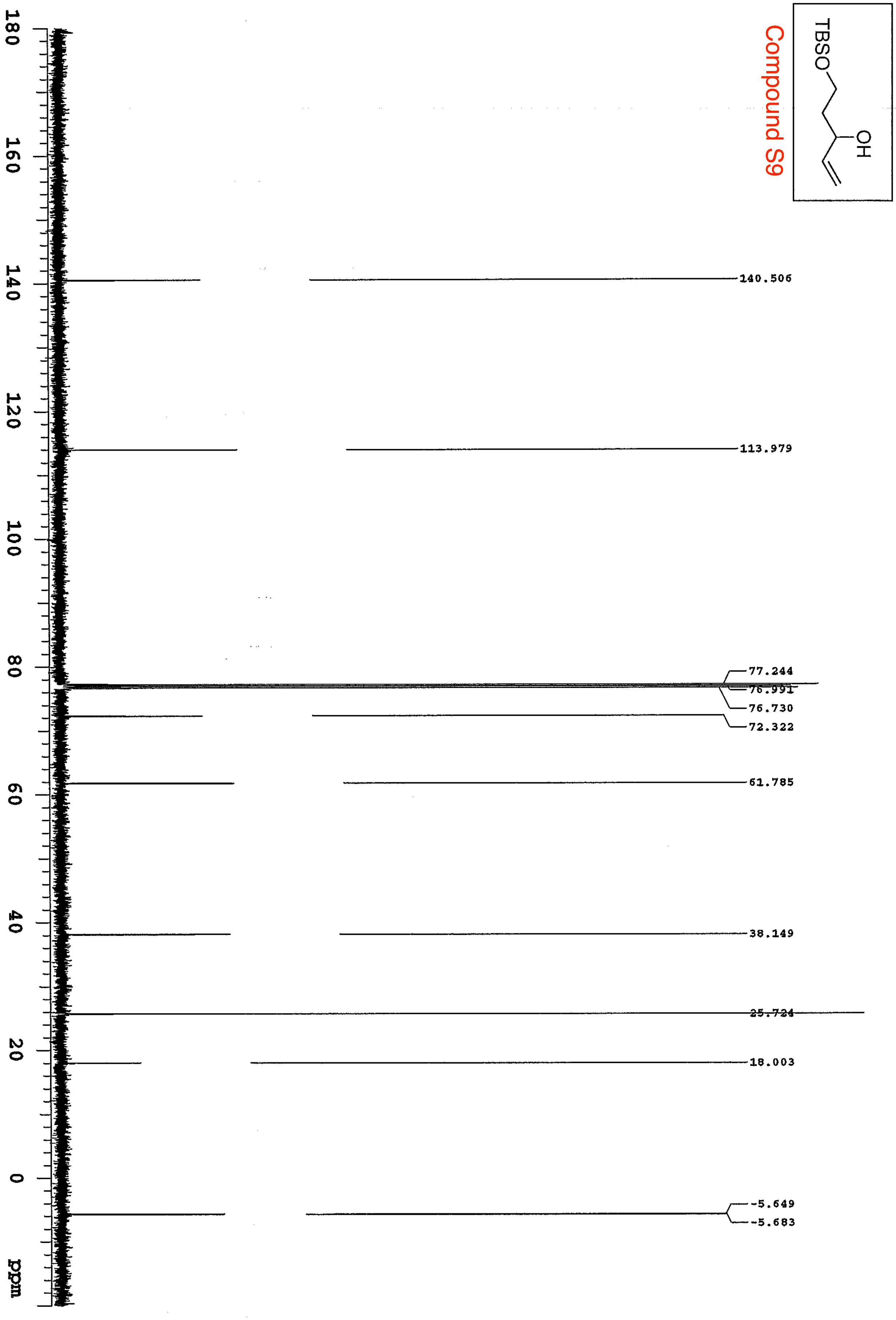
Compound S8

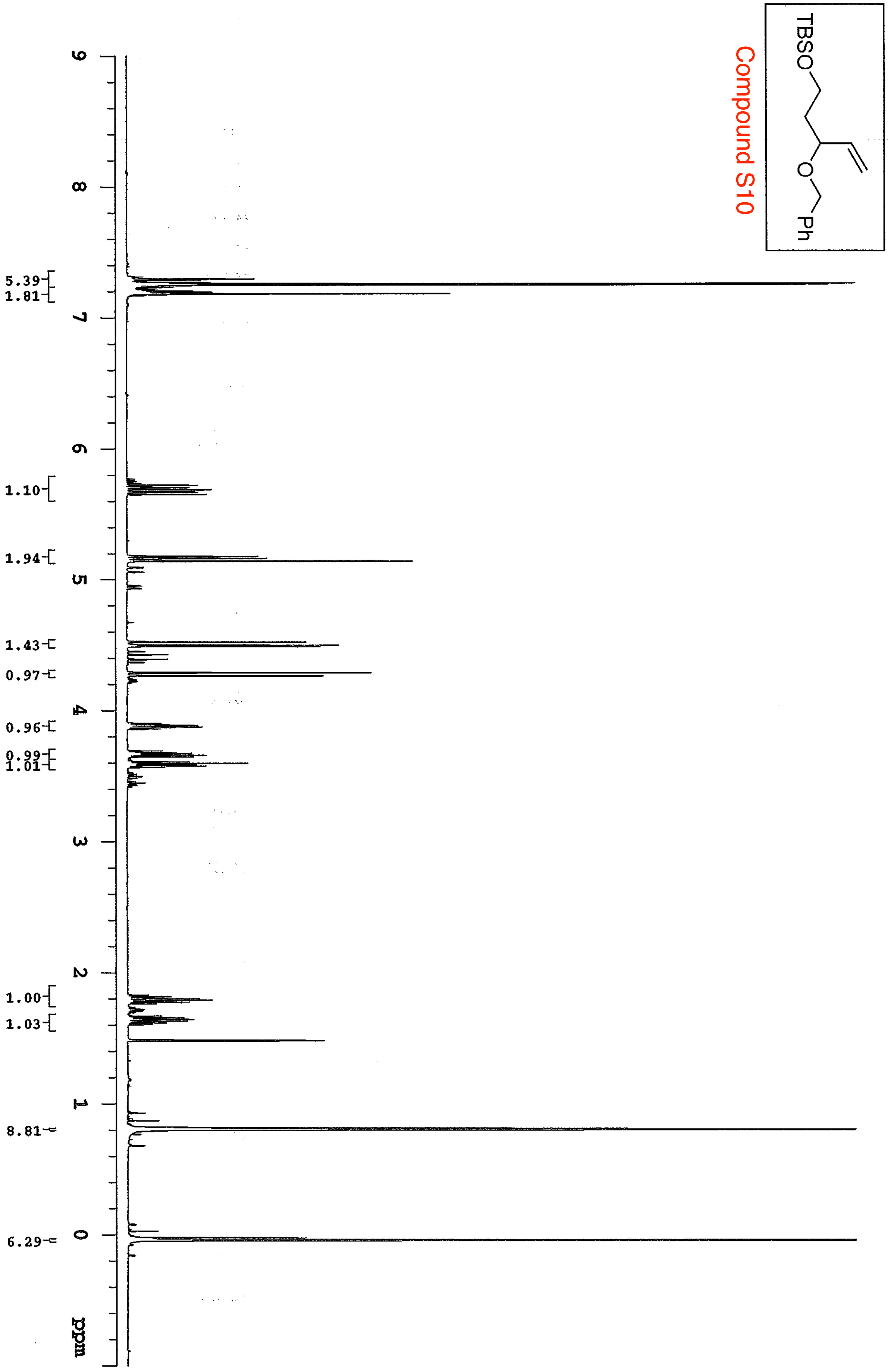



TBSO
O
H
201.947
77.249
76.992
76.741
57.381
46.547
25.784
18.190
-5.465
220
200
180
160
140
120
100
80
60
40
20
0
ppm

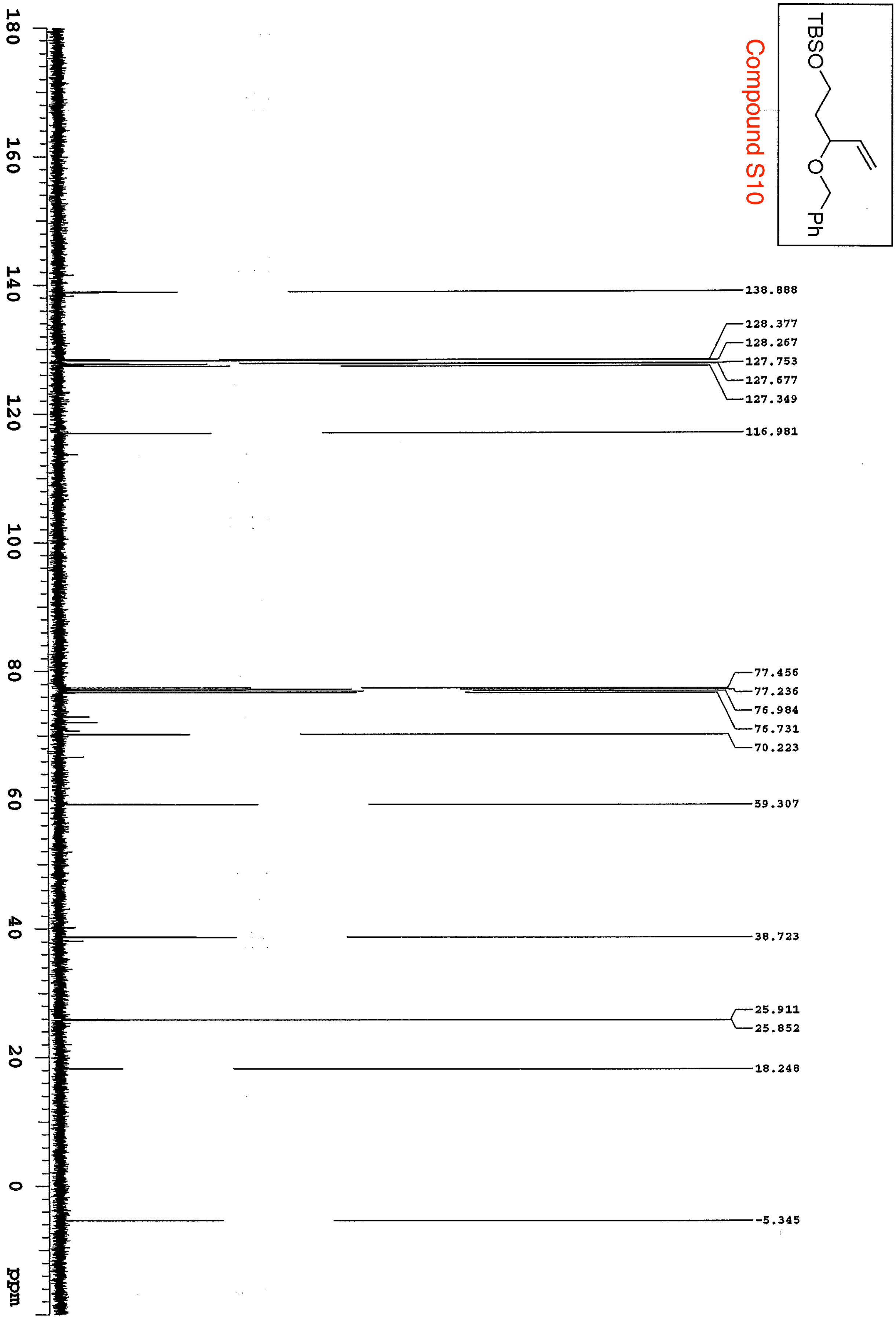
Compound S8

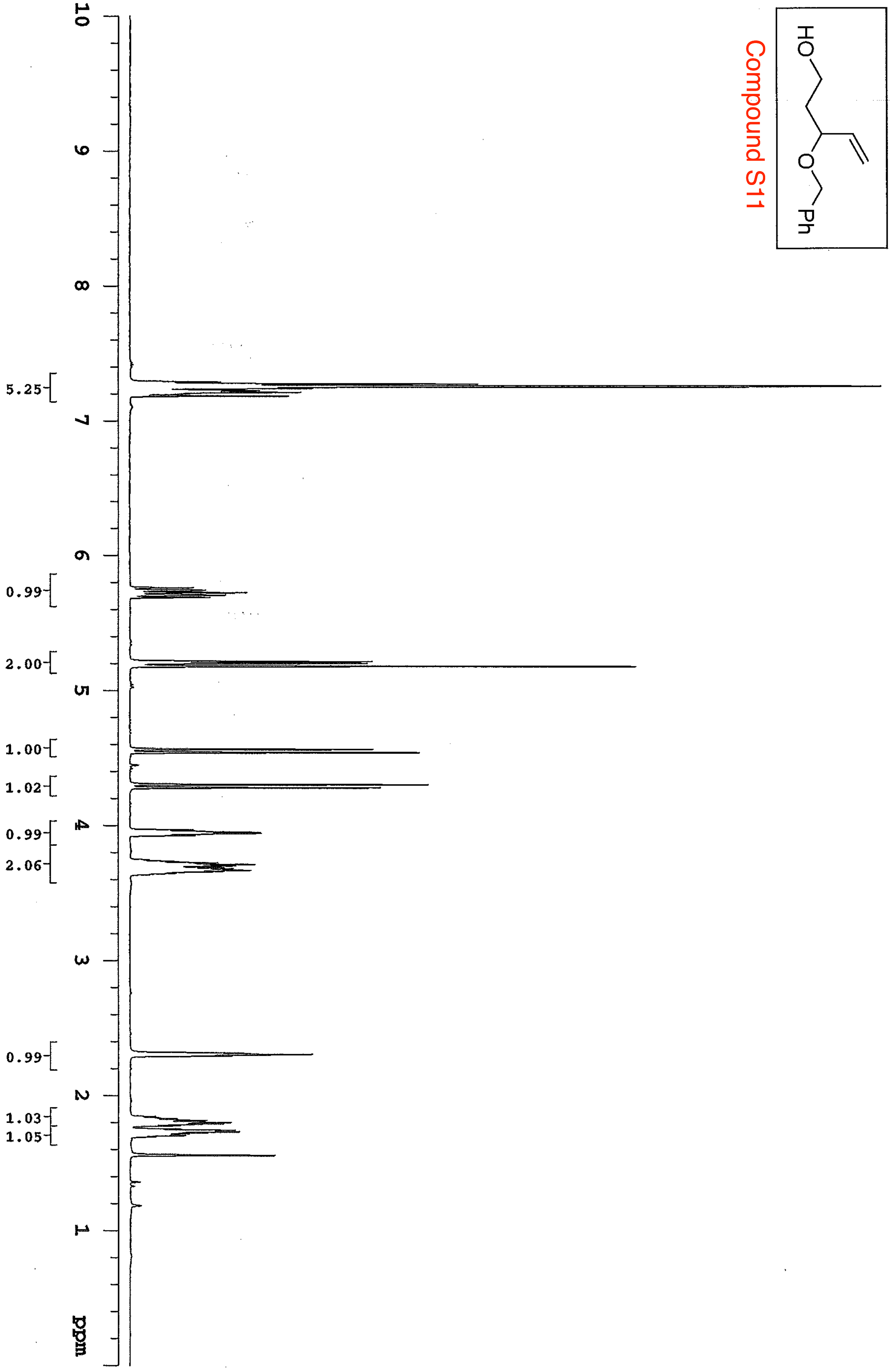

Compound S9
TBSO
OH
9
8
7
6
5
4
3
2
1
0
ppm
0.93
0.97
1.01
0.95
1.03
1.27
1.00
2.16
10.23
6.40


Compound S9
TBSO
OH
140.506
113.979
77.244
76.991
76.730
72.322
61.785
38.149
25.724
18.003
-5.649
-5.683
180
160
140
120
100
80
60
40
20
0
ppm

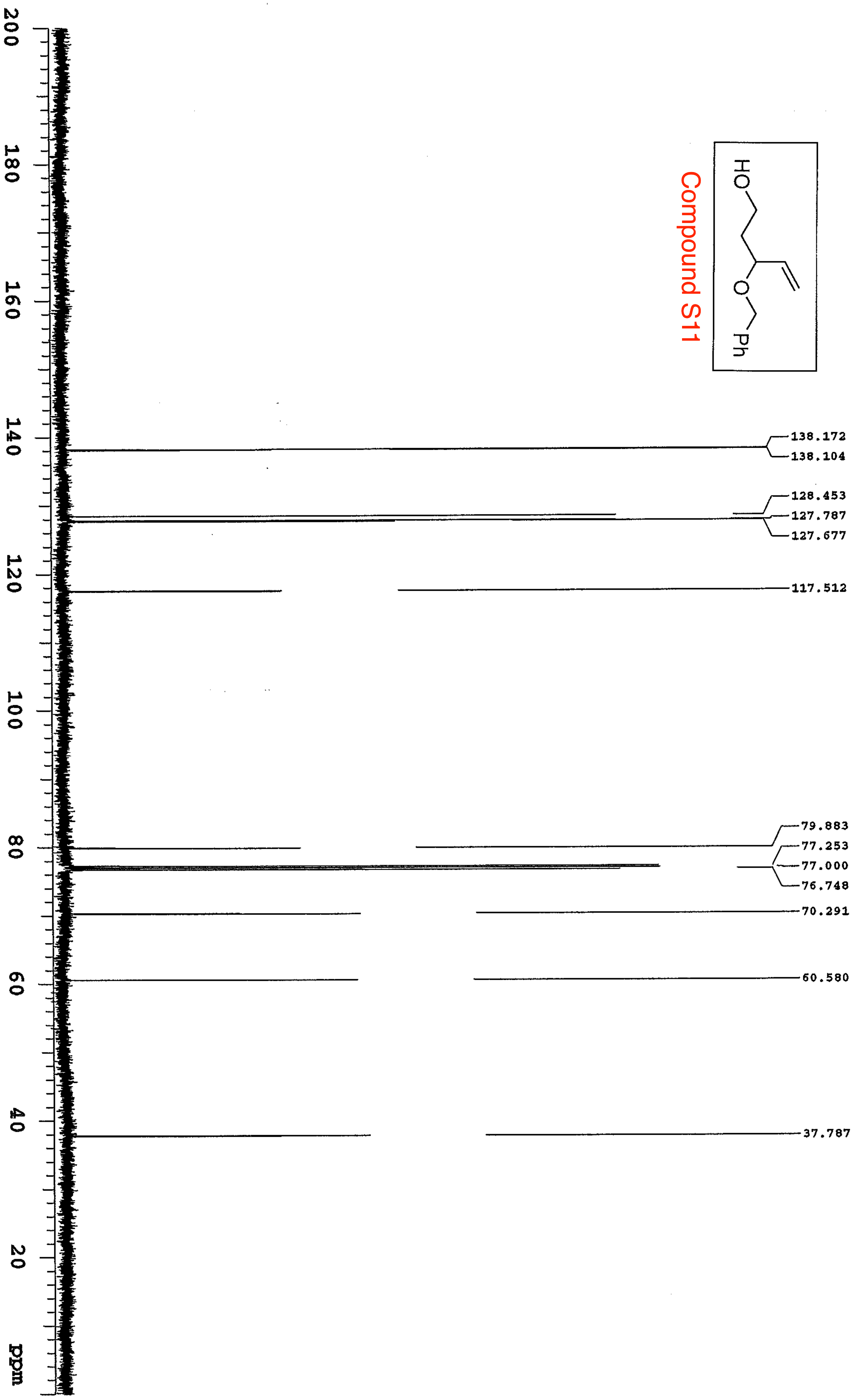


Compound S10

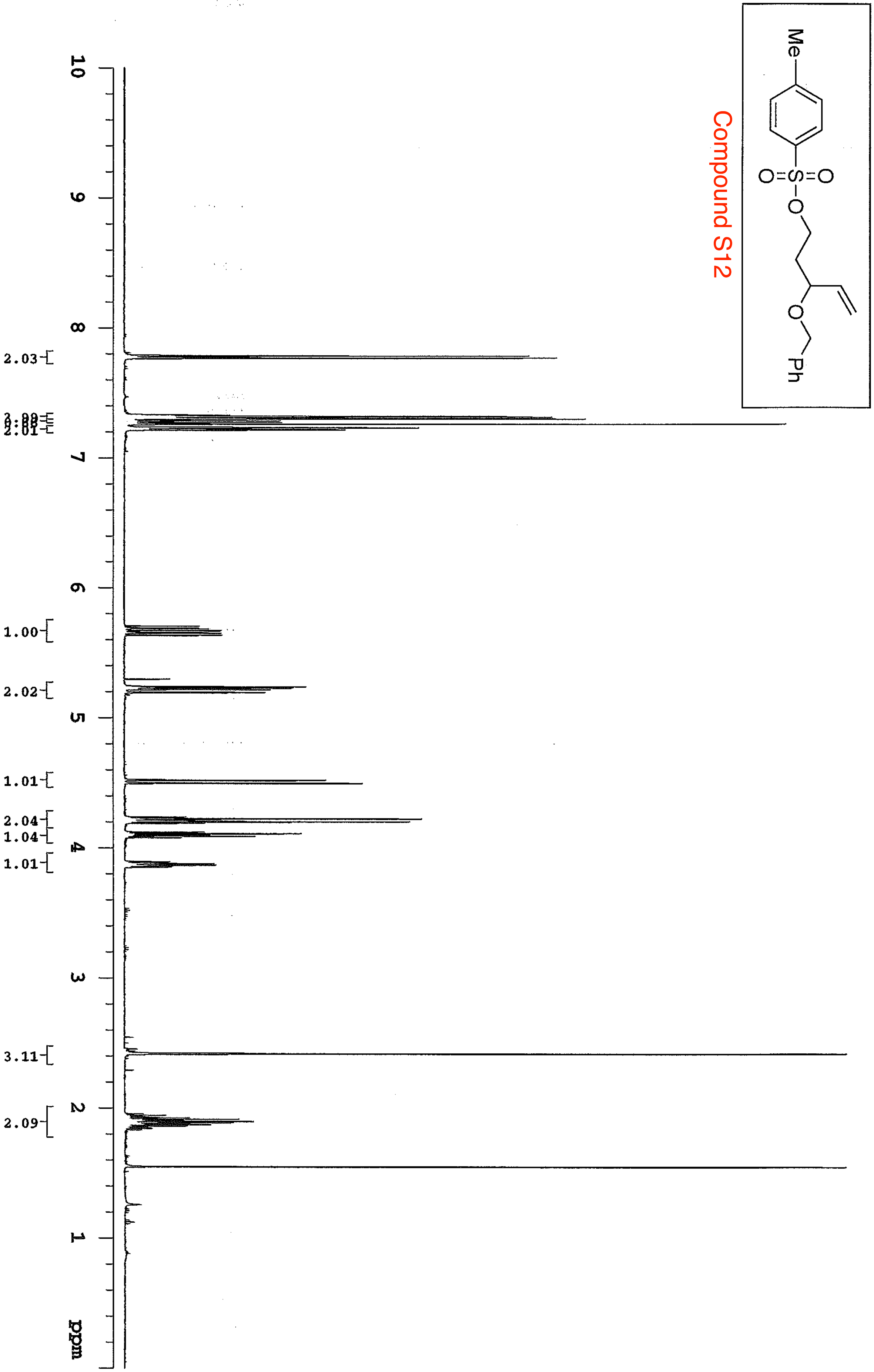

Compound S10



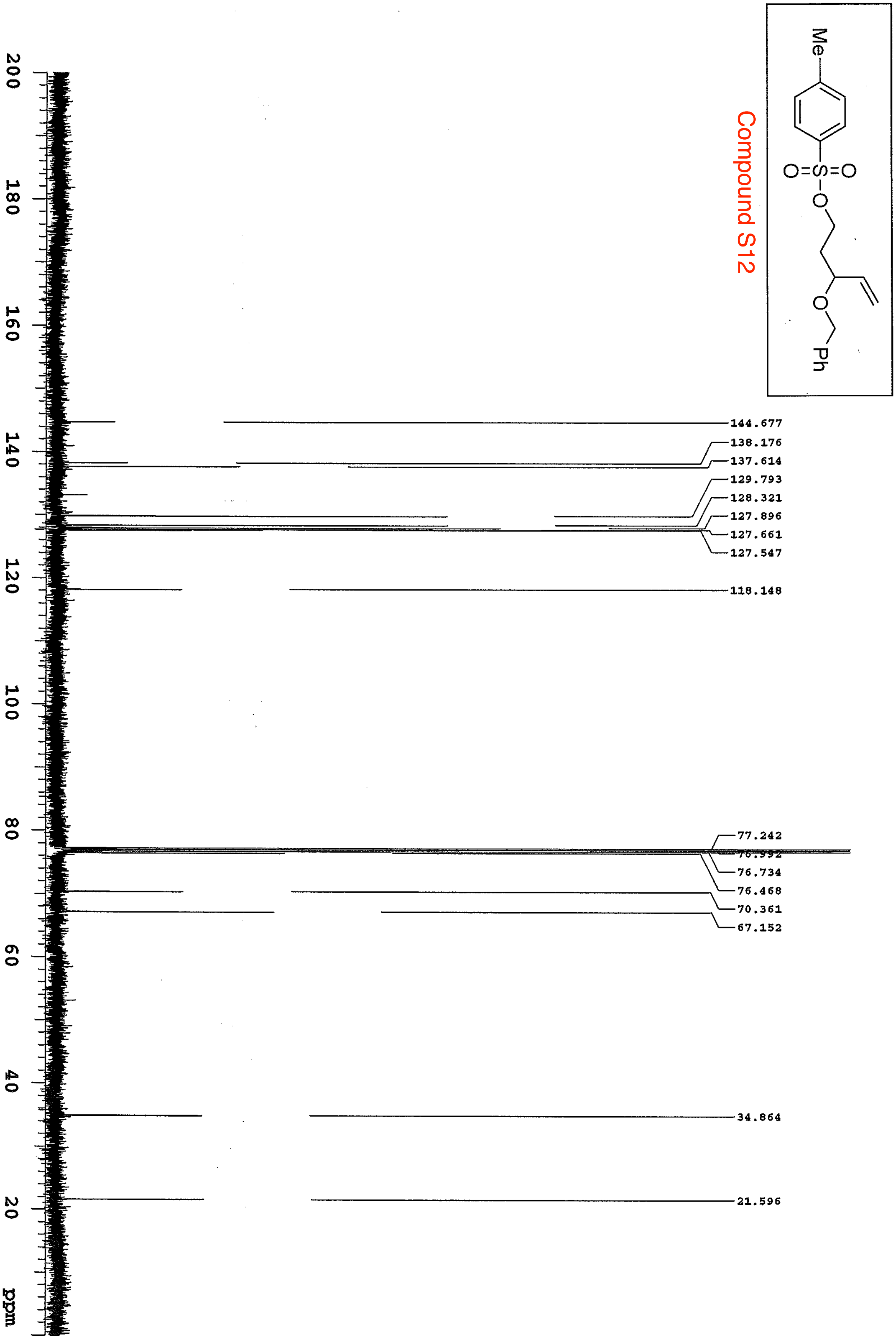
Compound S11

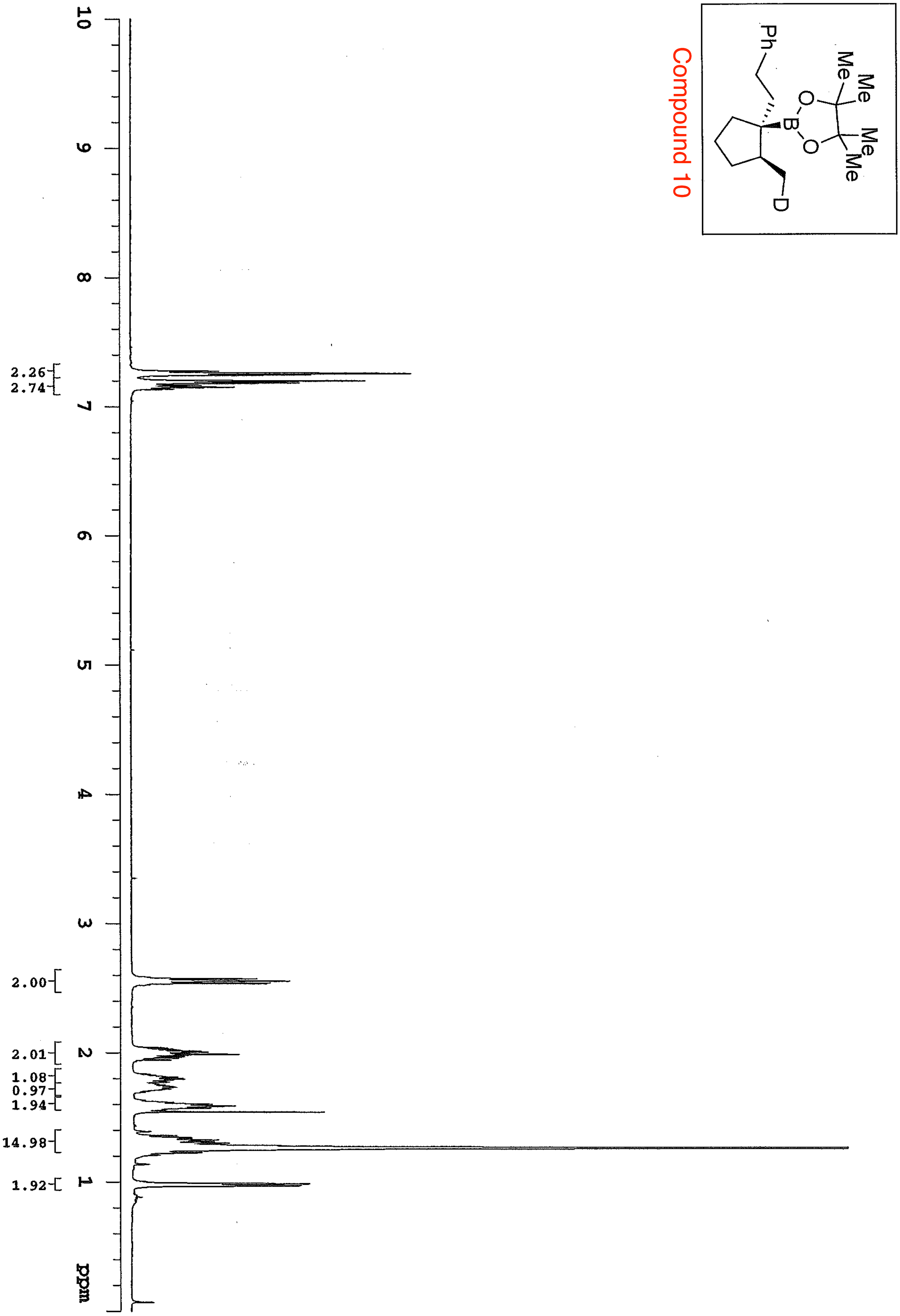


Compound S11



Compound S12

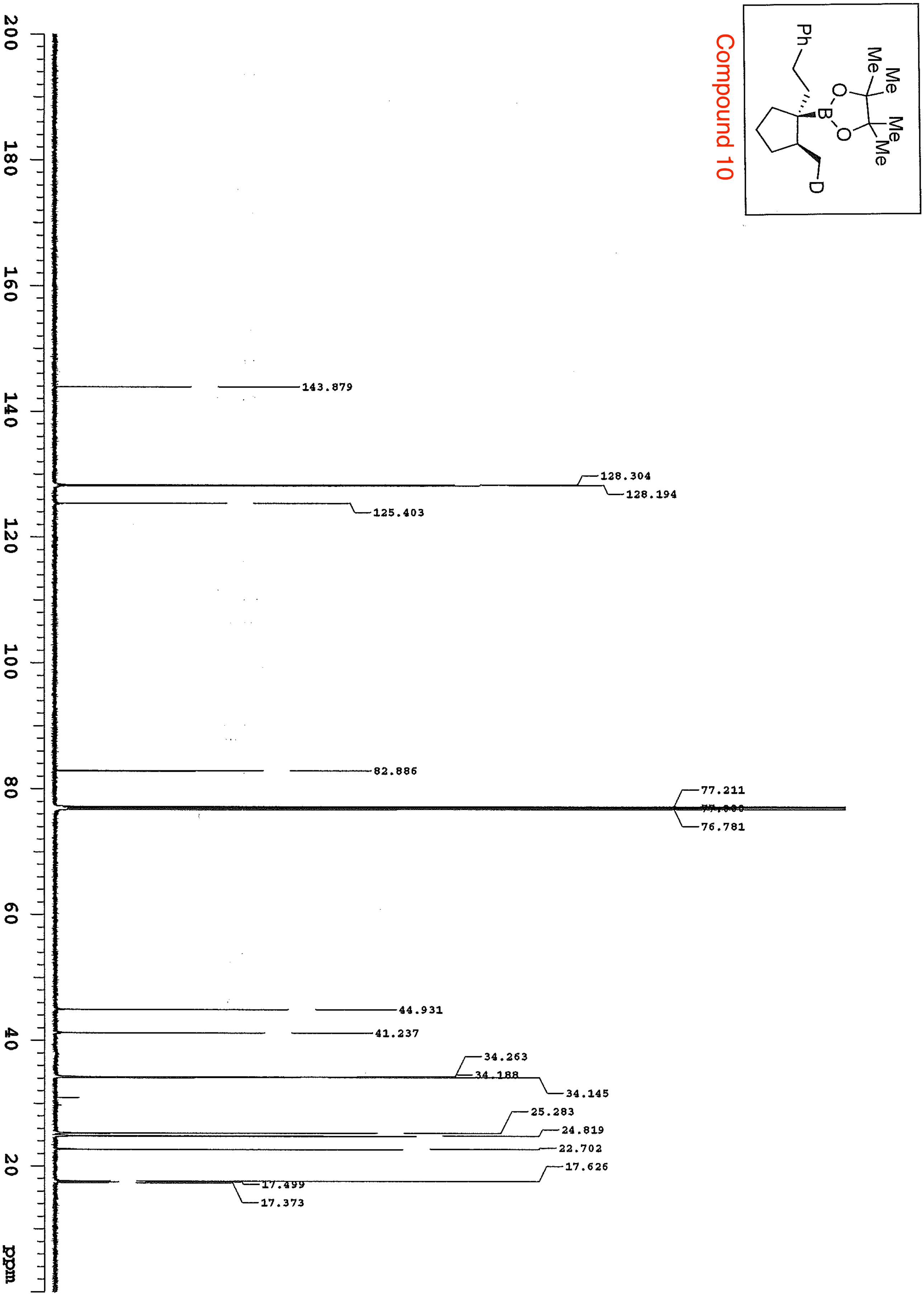

Compound S12


Me
Me
Me
Me
O
B
O
Ph
D
10
9
8
7
6
5
4
3
2
1
ppm
2.26
2.74
2.00
2.01
1.08
0.97
1.94
14.98
1.92

Compound 10

Me
Me
Me
Me
O
B
O
Ph
D

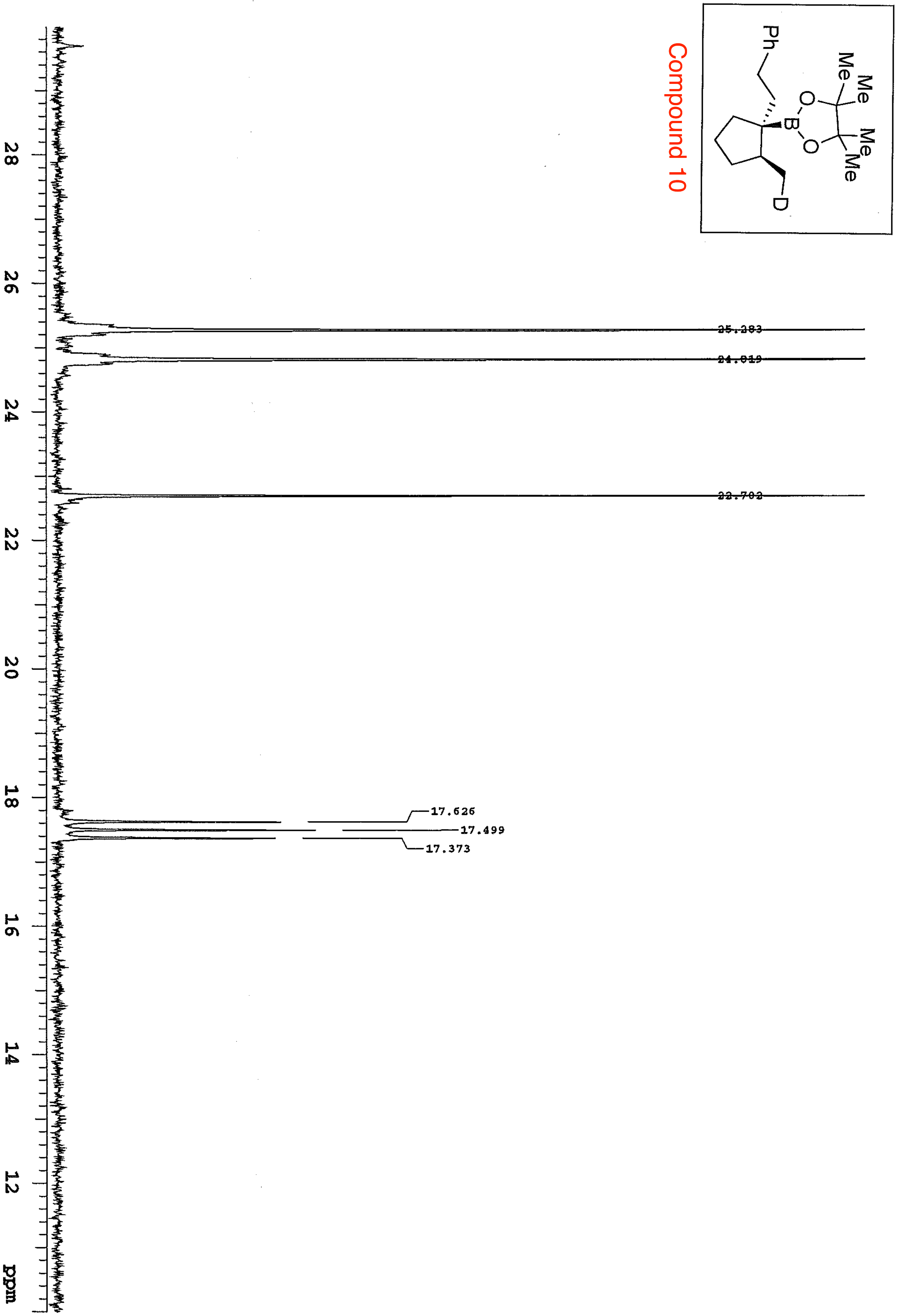
Compound 10

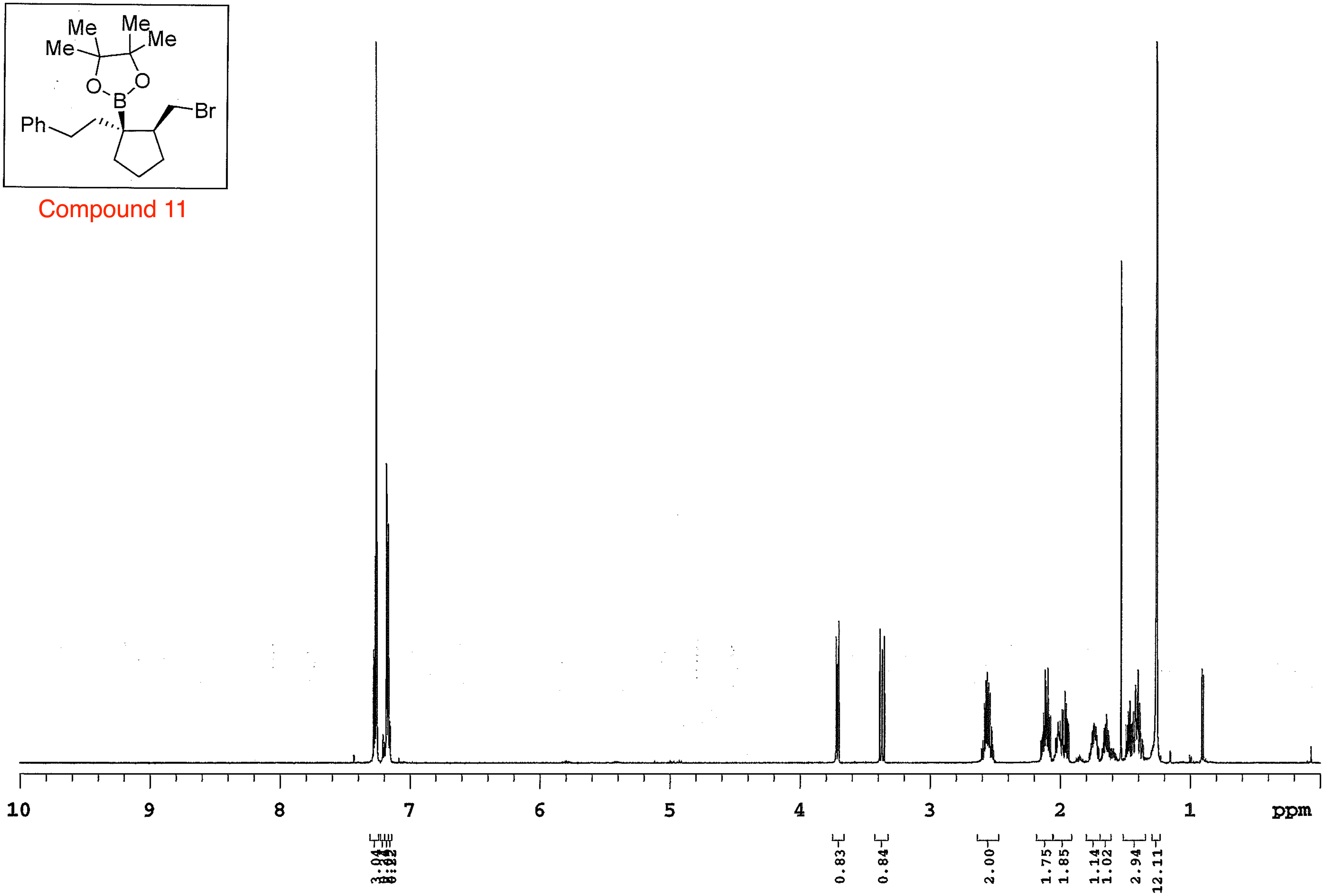


143.879
128.304
128.194
125.403
82.886
77.211
77.000
76.781
44.931
41.237
34.263
34.188
34.145
25.283
24.819
22.702
17.626
17.499
17.373
200
180
160
140
120
100
80
60
40
20
ppm

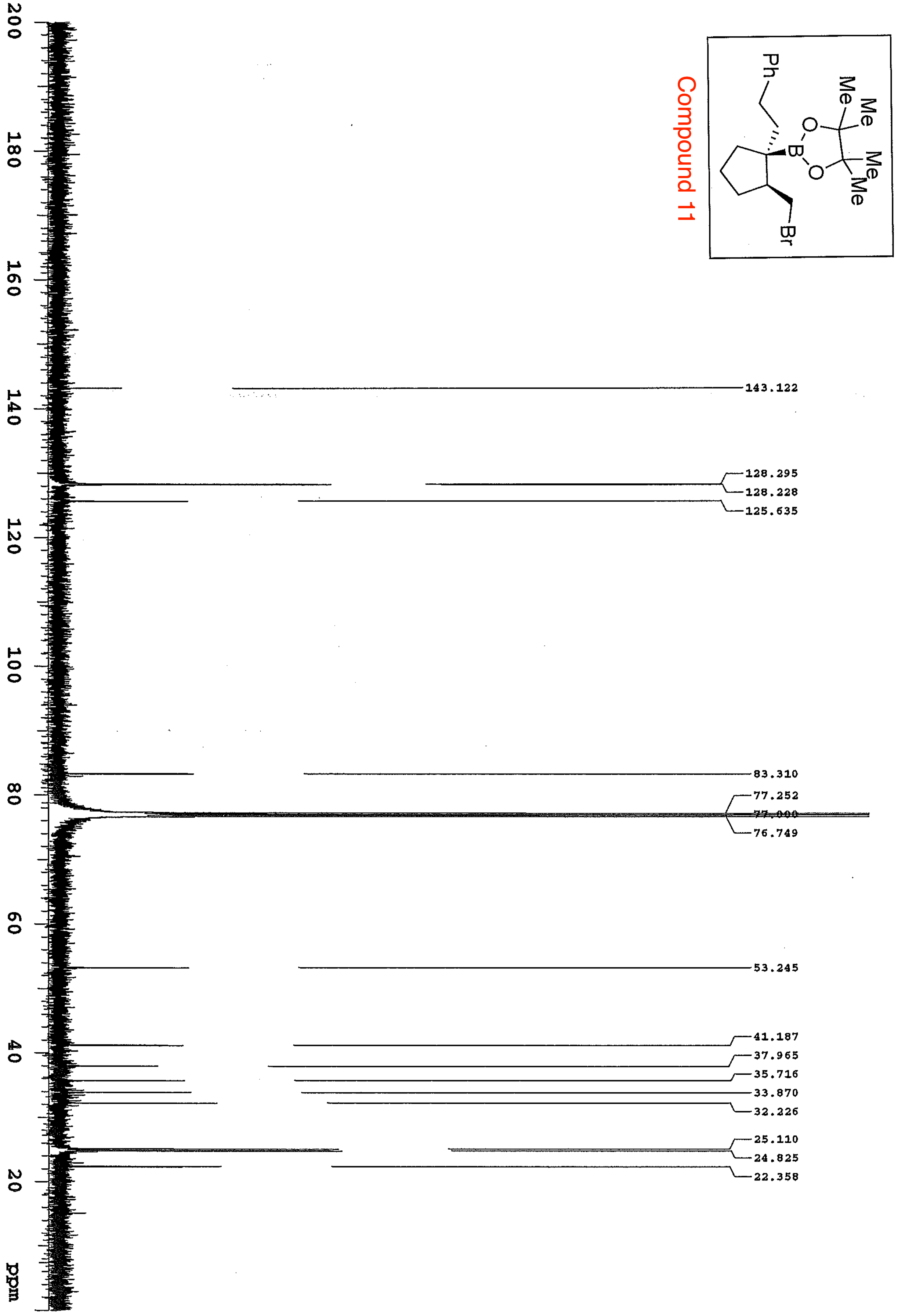
Me
Me
Me
Me
O
B
O
Ph
D

Compound 10


25.283
24.819
22.702
17.626
17.499
17.373
28
26
24
22
20
18
16
14
12
ppm

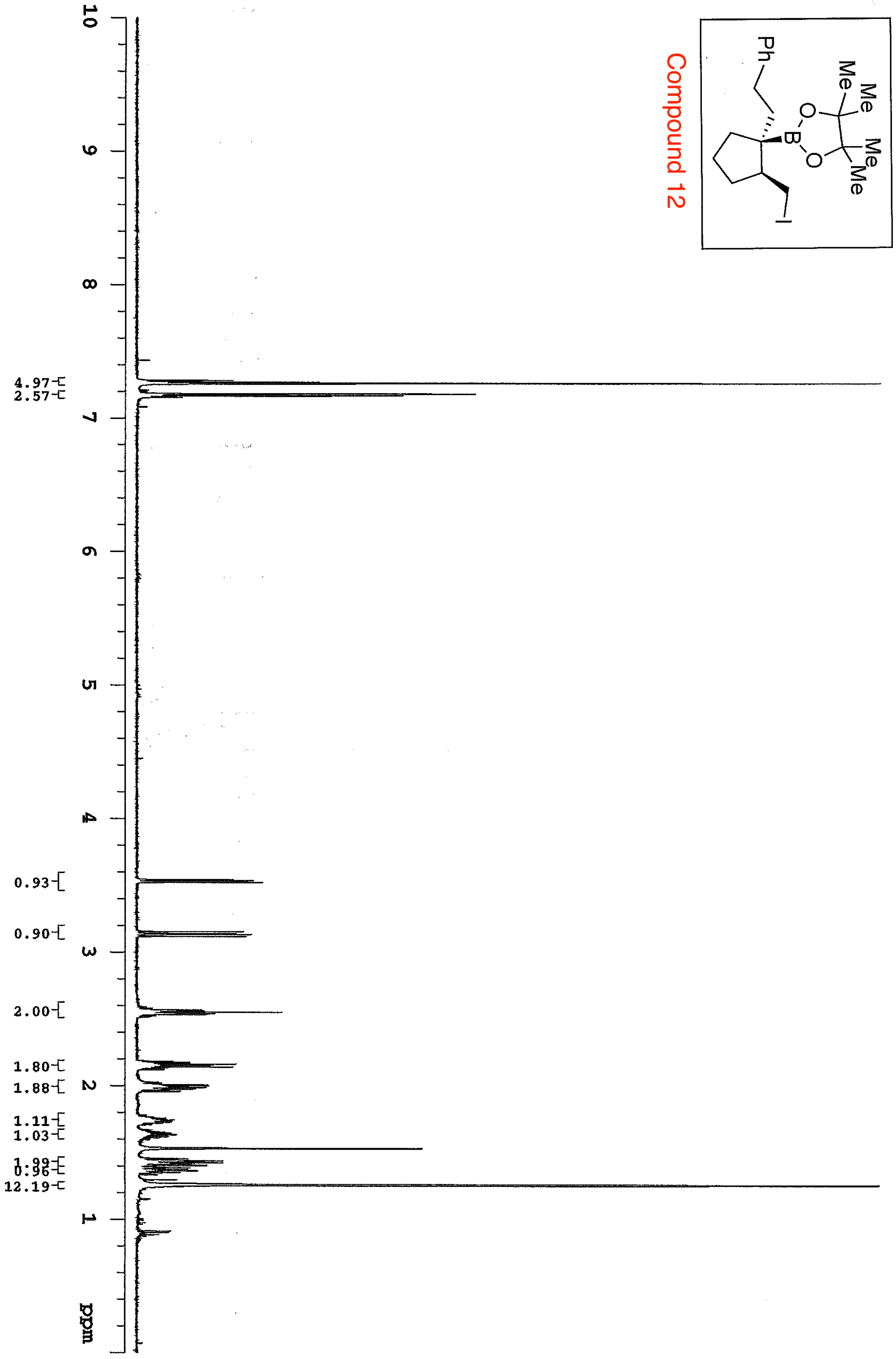


Compound 11



Compound 11

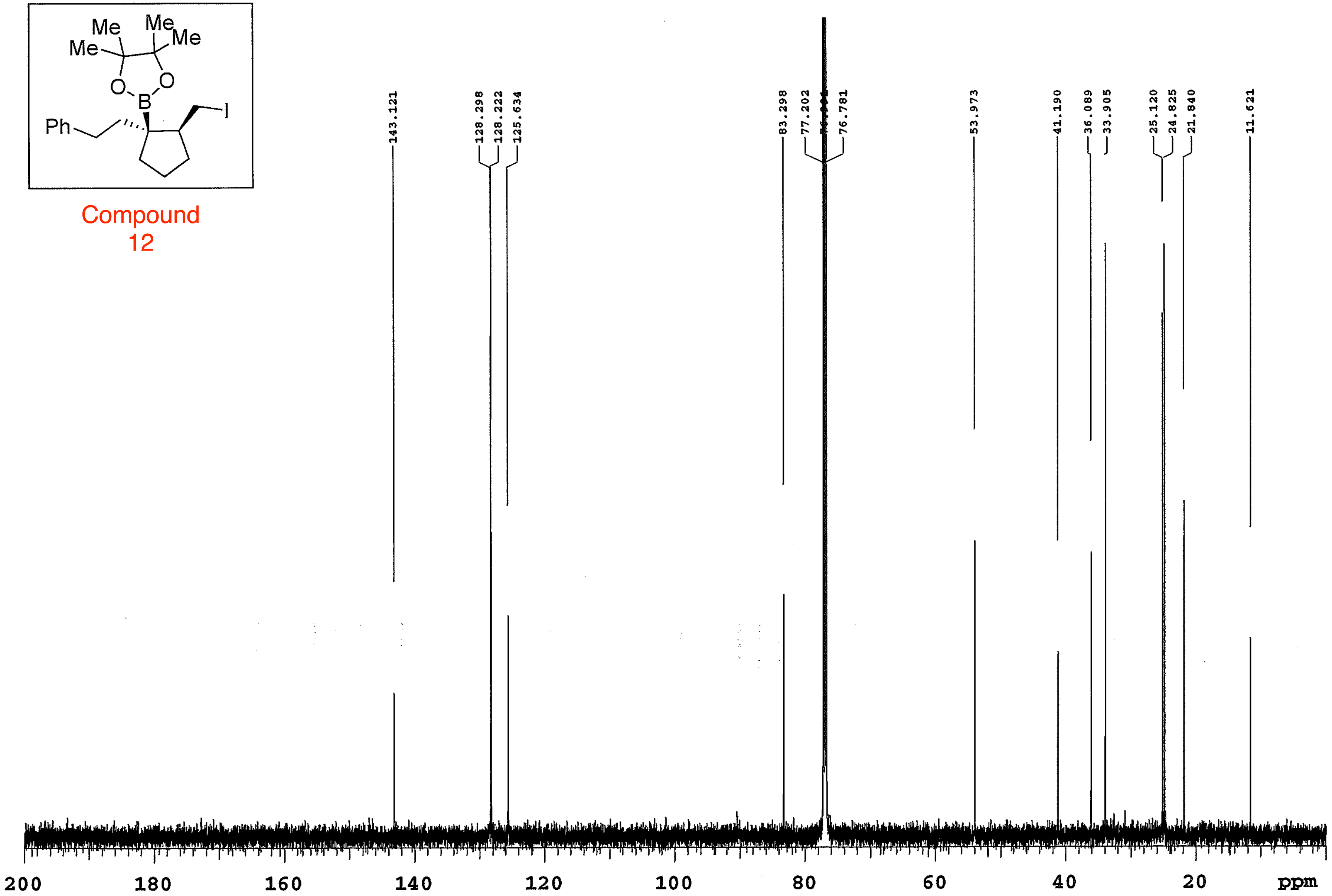
Me
Me
Me
Me
O
B
O
Ph
Br
143.122
128.295
128.228
125.635
83.310
77.252
77.000
76.749
53.245
41.187
37.965
35.716
33.870
32.226
25.110
24.825
22.358
200
180
160
140
120
100
80
60
40
20
ppm

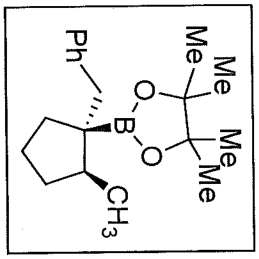

Me
Me
Me
Me
O
B
O
Ph
I
10
9
8
7
6
5
4
3
2
1
ppm
4.97
2.57
0.93
0.90
2.00
1.80
1.88
1.11
1.03
1.99
0.96
12.19

Compound 12

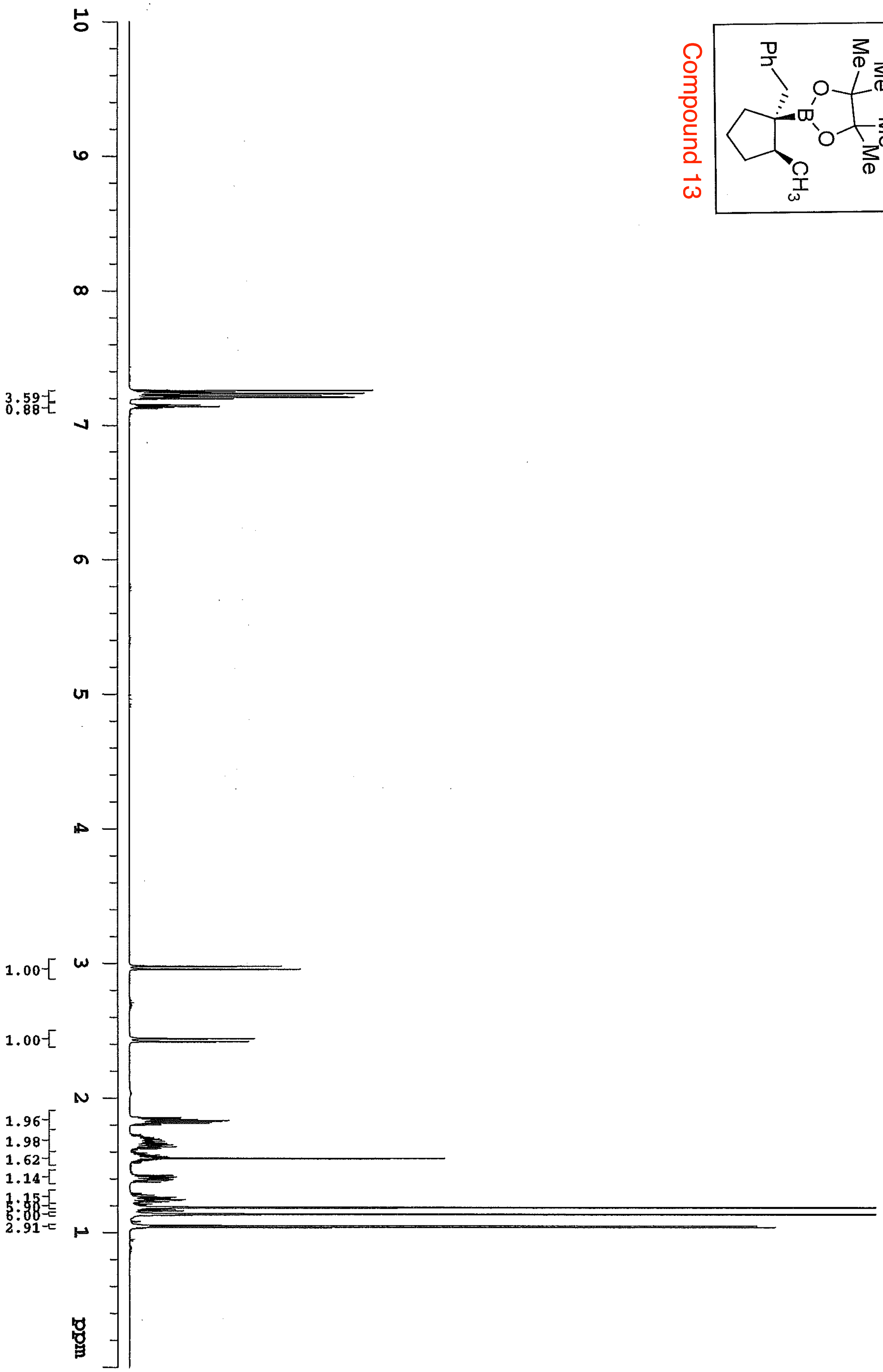
Me
Me
Me
Me
O
B
O
Ph
I

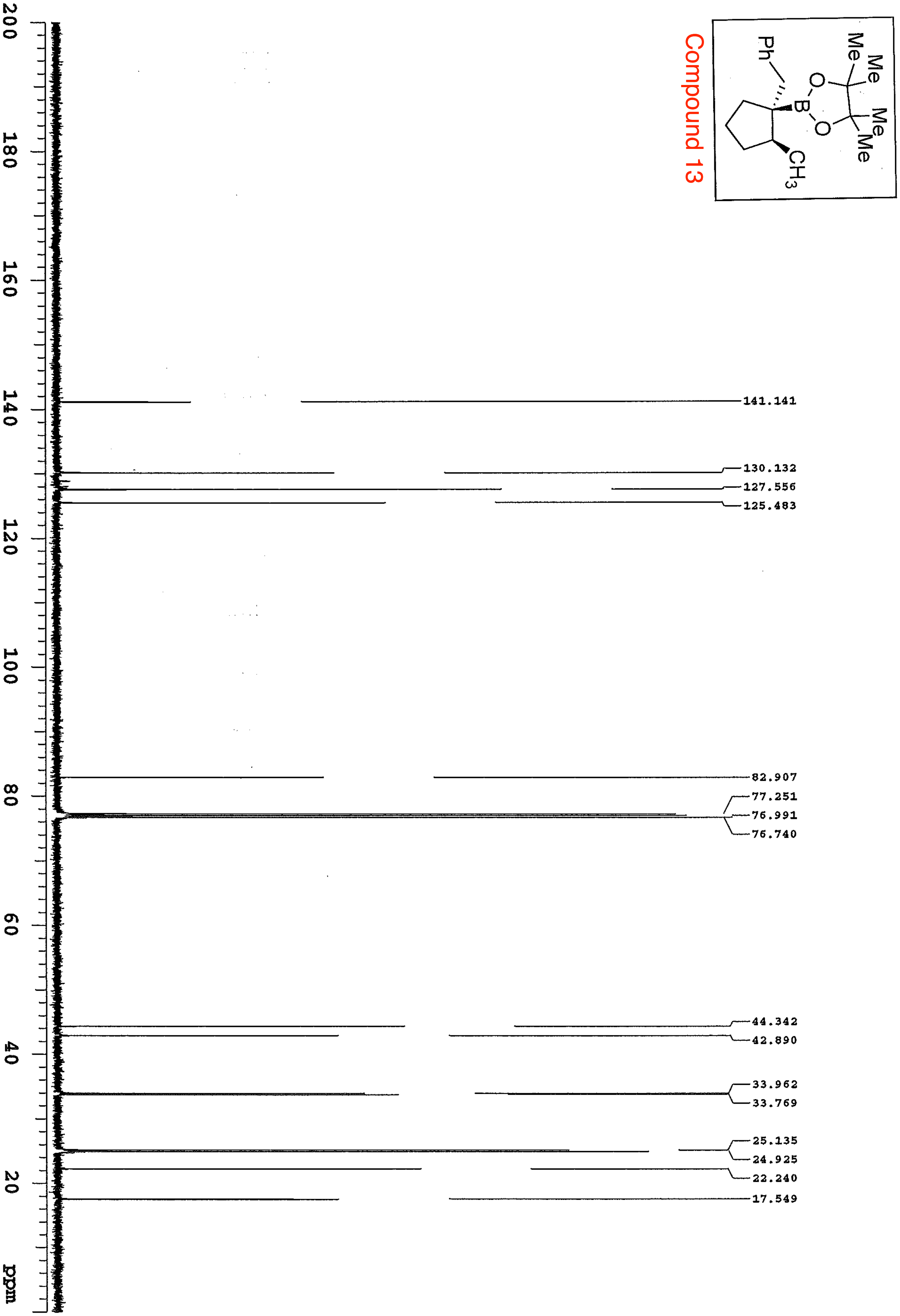
Compound
12


143.121
128.298
128.222
125.634
83.298
77.202
[illegible]
76.781
53.973
41.190
36.089
33.905
25.120
24.825
21.840
11.621
200
180
160
140
120
100
80
60
40
20
ppm

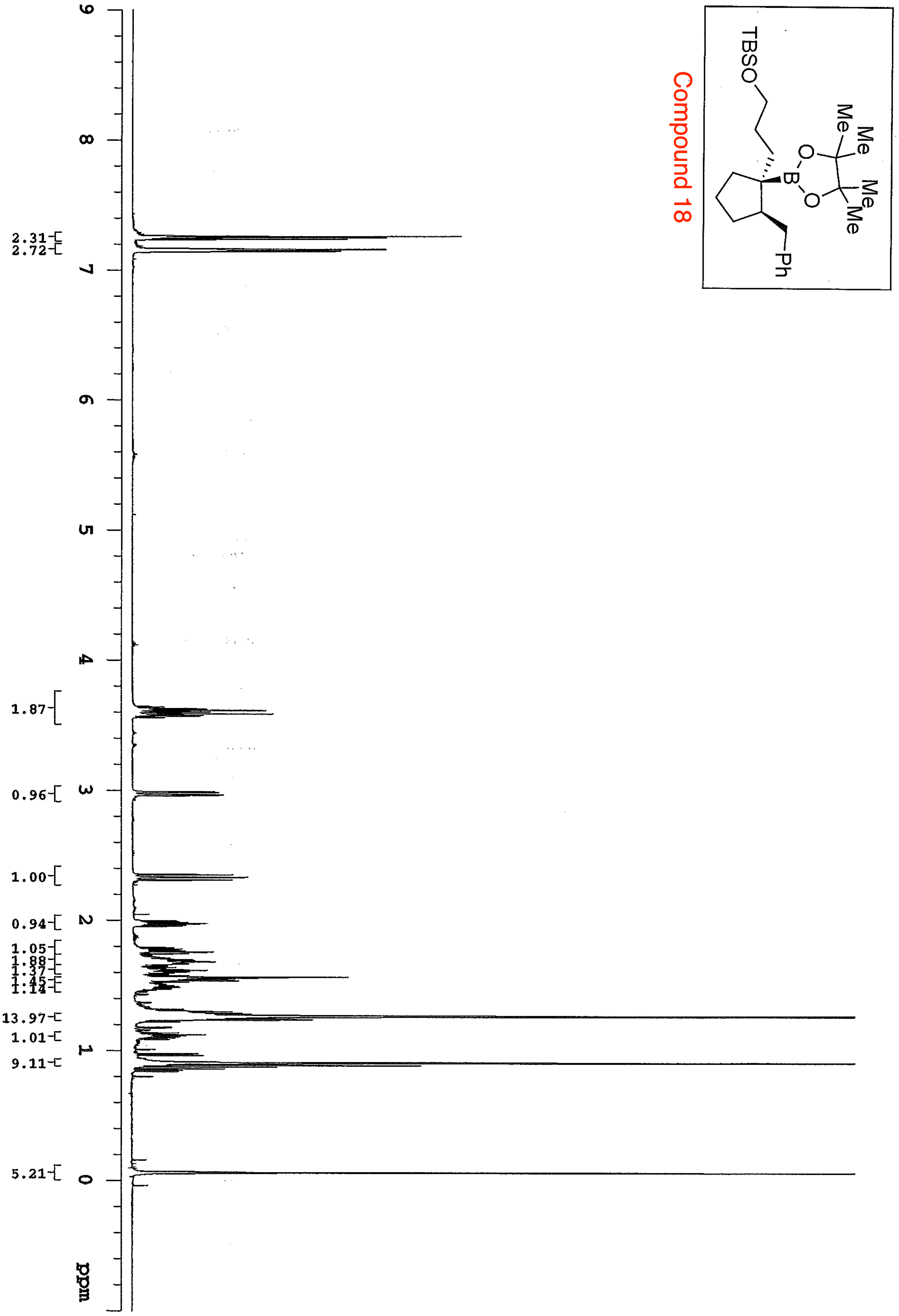

Me
Me
Me
Me
O
B
O
Ph
CH3

Compound 13

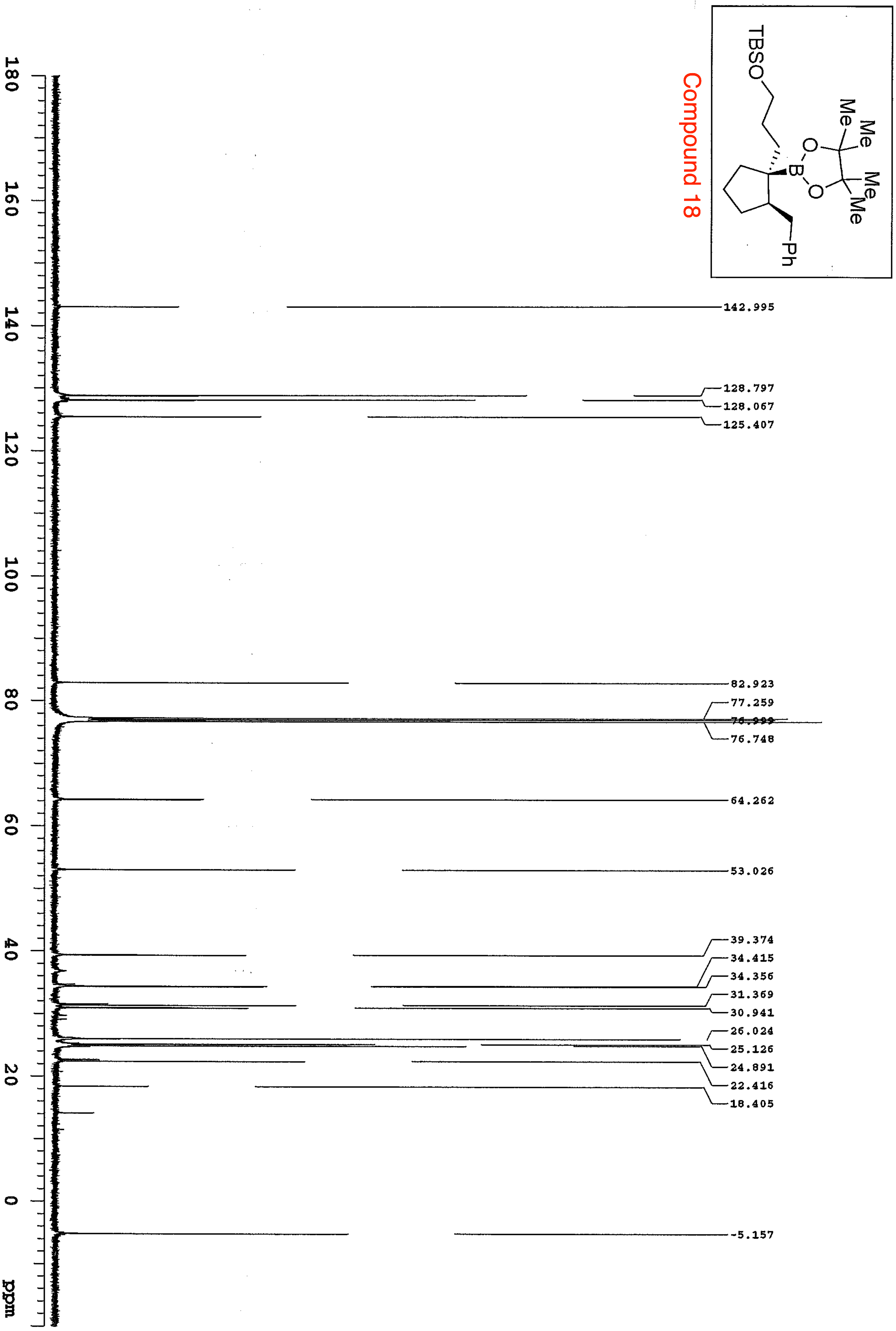

10
9
8
7
6
5
4
3
2
1
ppm
3.59
0.88
1.00
1.00
1.96
1.98
1.62
1.14
1.15
5.90
6.00
2.91


Compound 13

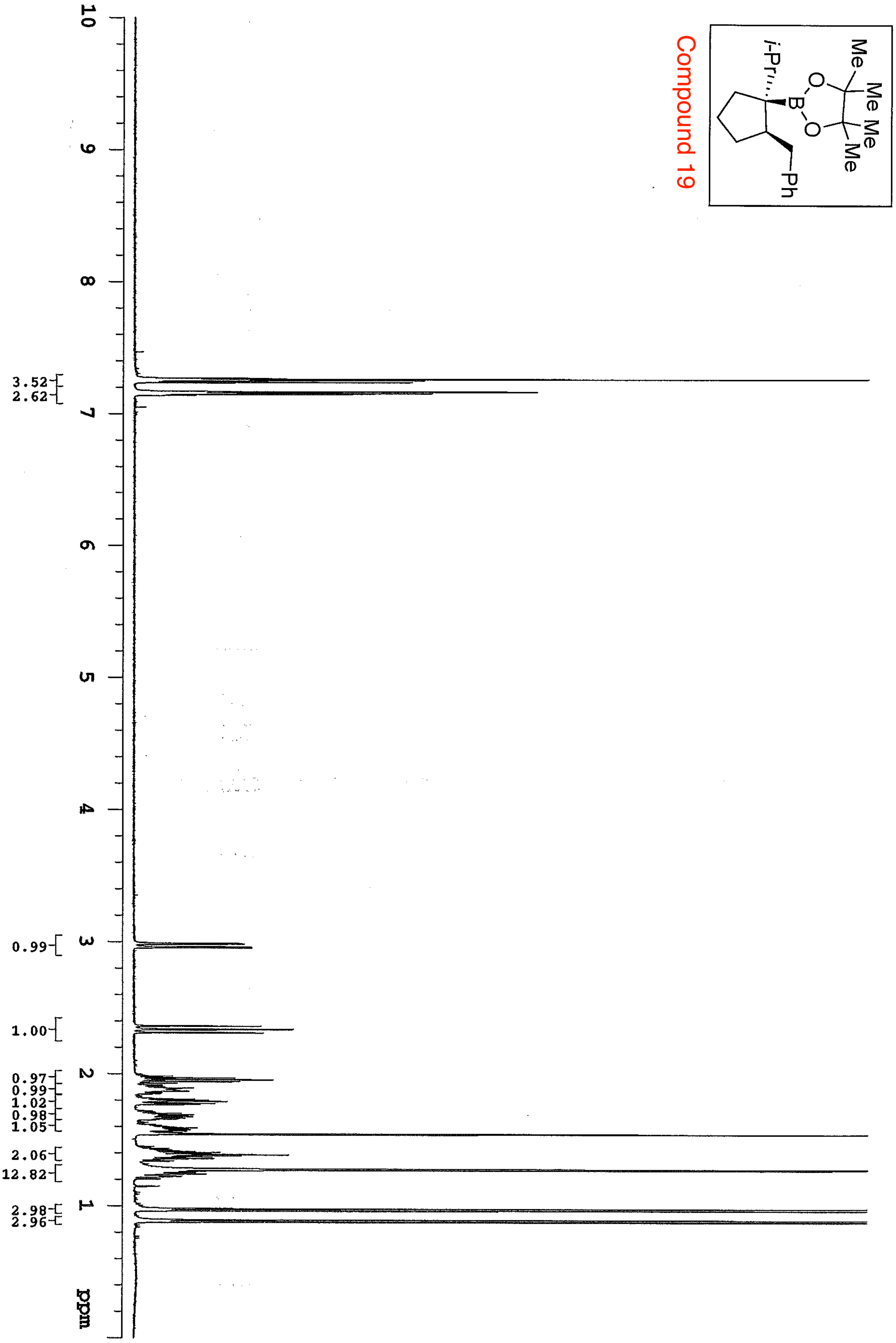
Me
Me
Me
Me
O
B
O
Ph
CH3
141.141
130.132
127.556
125.483
82.907
77.251
76.991
76.740
44.342
42.890
33.962
33.769
25.135
24.925
22.240
17.549
200
180
160
140
120
100
80
60
40
20
ppm


TBSO
Me
Me
Me
Me
O
B
O
Ph
9
8
7
6
5
4
3
2
1
0
ppm
2.31
2.72
1.87
0.96
1.00
0.94
1.05
1.88
1.37
1.45
1.14
13.97
1.01
9.11
5.21

Compound 18


TBSO
Me
Me
Me
Me
O
B
O
Ph
180
160
140
120
100
80
60
40
20
0
ppm
142.995
128.797
128.067
125.407
82.923
77.259
76.999
76.748
64.262
53.026
39.374
34.415
34.356
31.369
30.941
26.024
25.126
24.891
22.416
18.405
-5.157

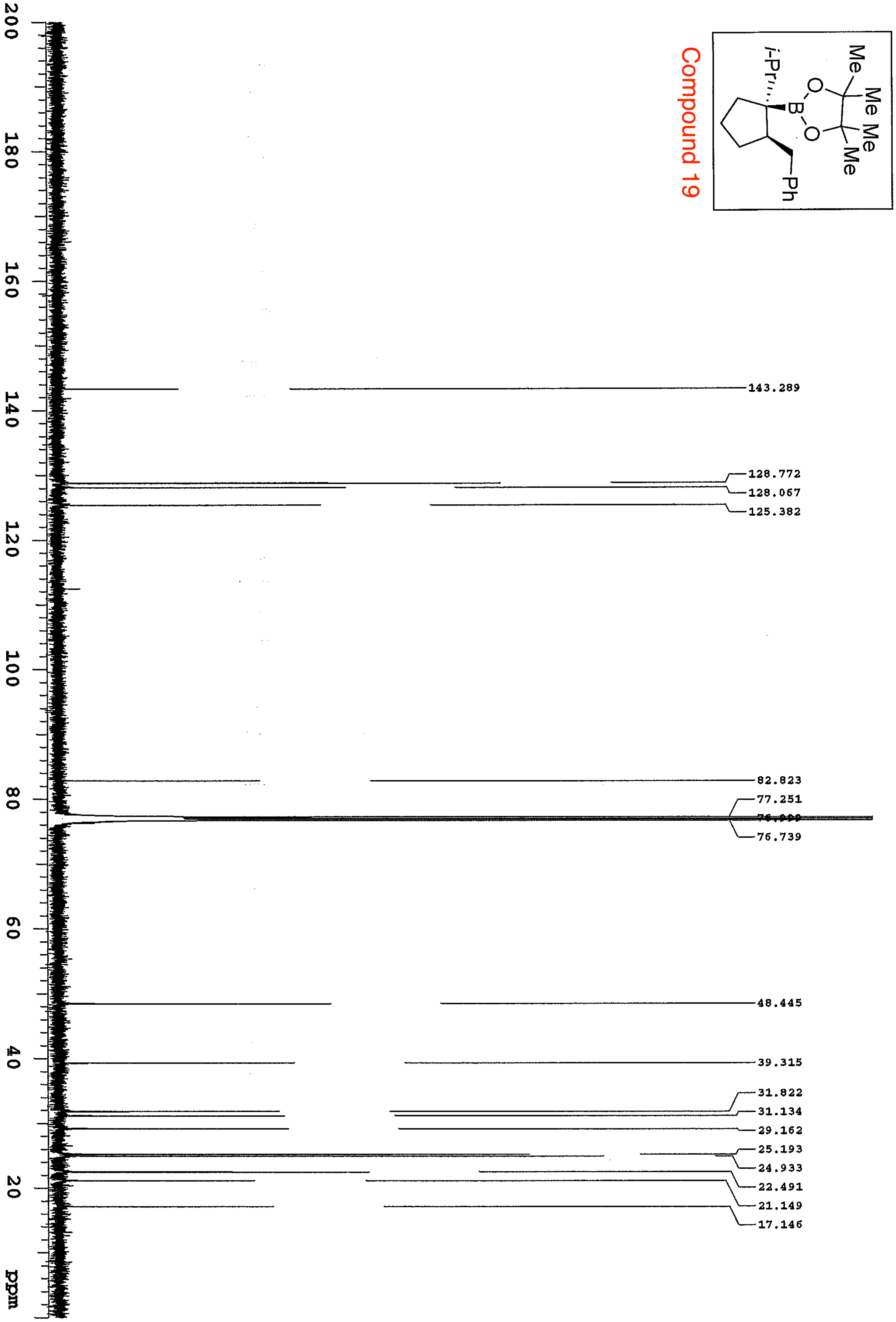
Compound 18


Me
Me Me
Me
O
B
O
i-Pr
Ph
3.52
2.62
0.99
1.00
0.97
0.99
1.02
0.98
1.05
2.06
12.82
2.98
2.96
10
9
8
7
6
5
4
3
2
1
ppm

Compound 19

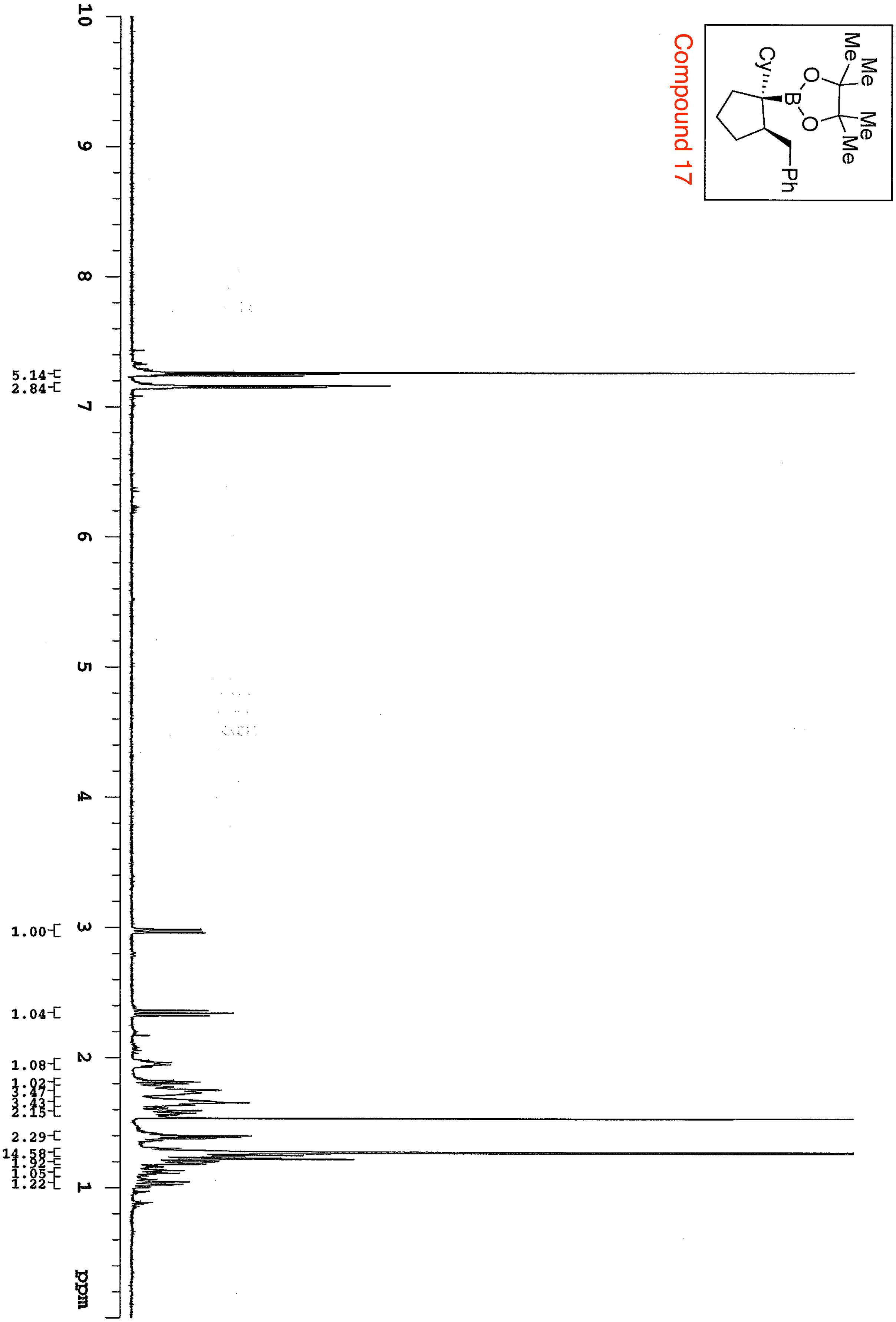
Me
Me
Me
Me
O
B
O
i-Pr
Ph

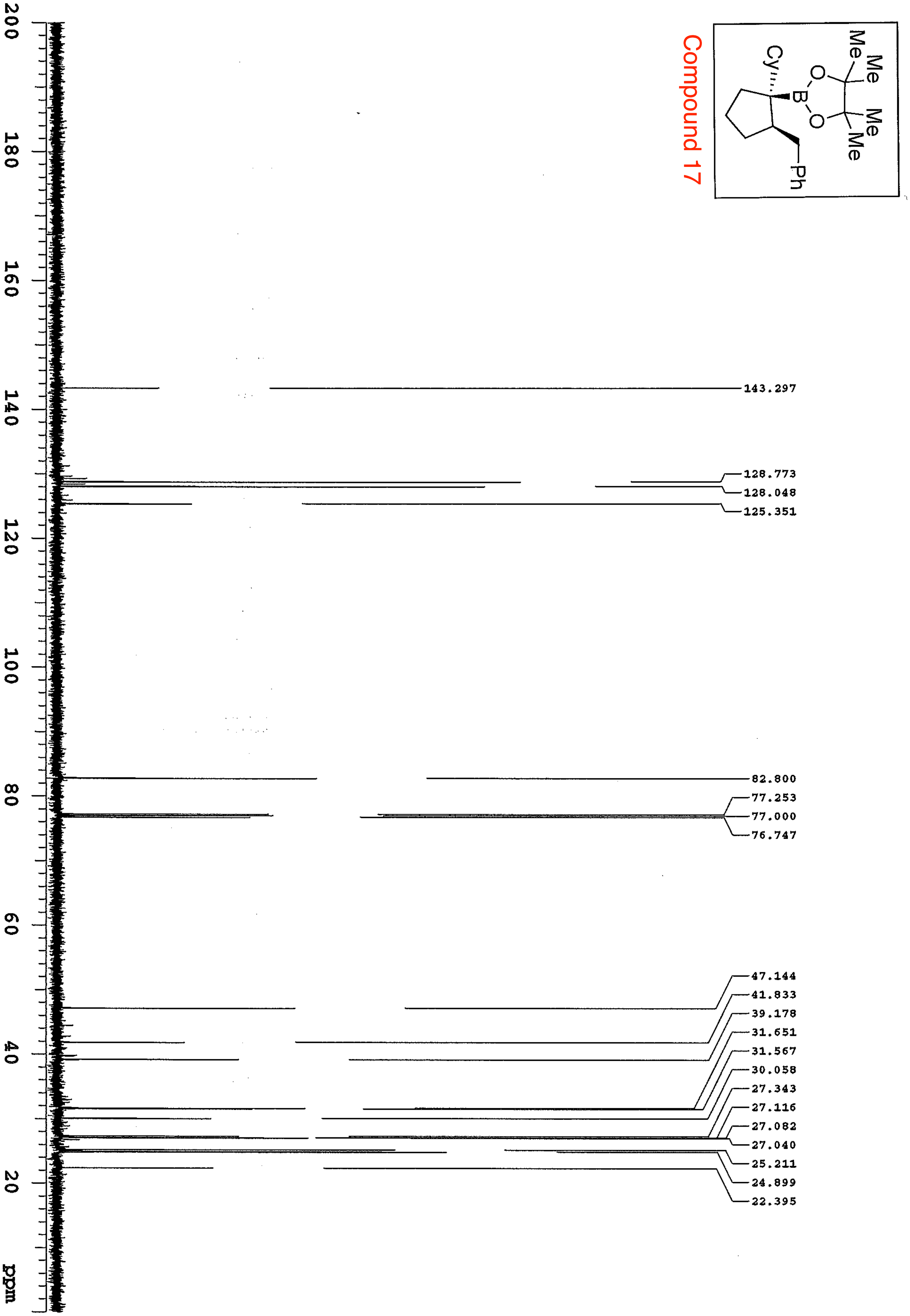
Compound 19


143.289
128.772
128.067
125.382
82.823
77.251
76.739
48.445
39.315
31.822
31.134
29.162
25.193
24.933
22.491
21.149
17.146
200
180
160
140
120
100
80
60
40
20
ppm

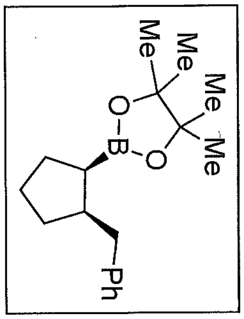
Me
Me
Me
Me
O
B
O
Cy
Ph

Compound 17

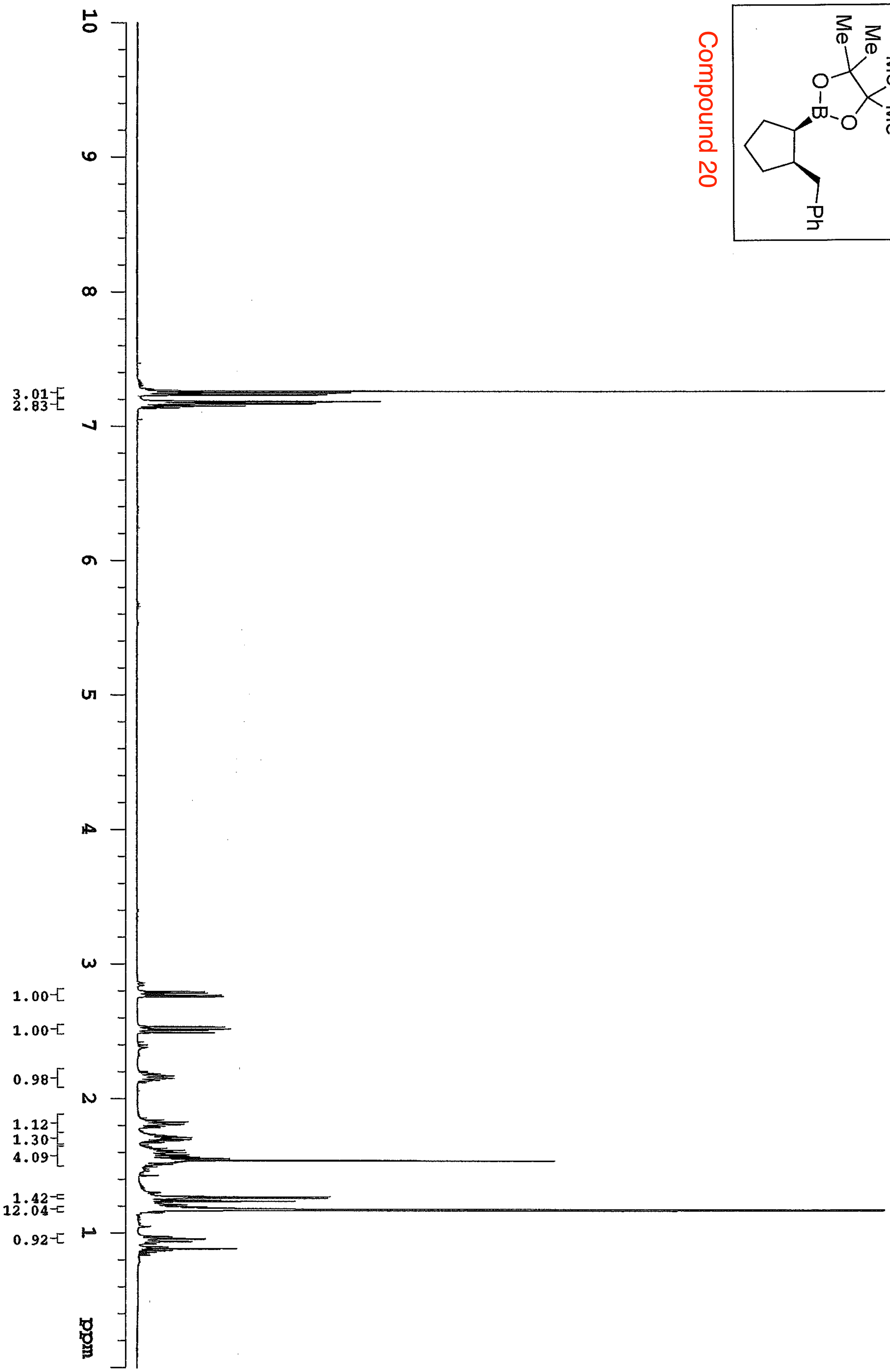

10
9
8
7
6
5
4
3
2
1
ppm
5.14
2.84
1.00
1.04
1.08
1.02
3.47
3.43
2.15
2.29
14.58
1.92
1.05
1.22

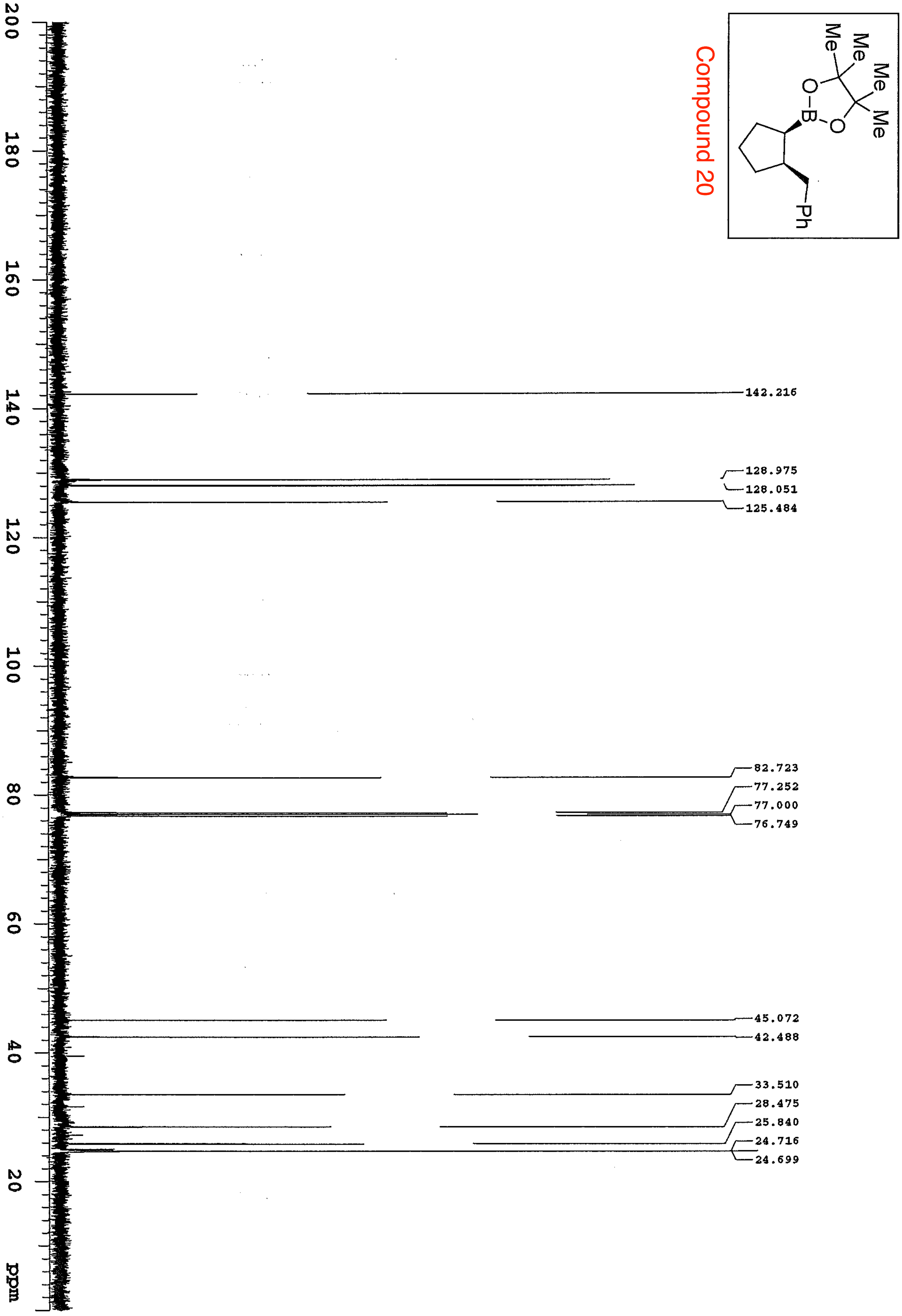

Me
Me
O
B
O
Me
Me
Cy
Ph
143.297
128.773
128.048
125.351
82.800
77.253
77.000
76.747
47.144
41.833
39.178
31.651
31.567
30.058
27.343
27.116
27.082
27.040
25.211
24.899
22.395
200
180
160
140
120
100
80
60
40
20
ppm

Compound 17

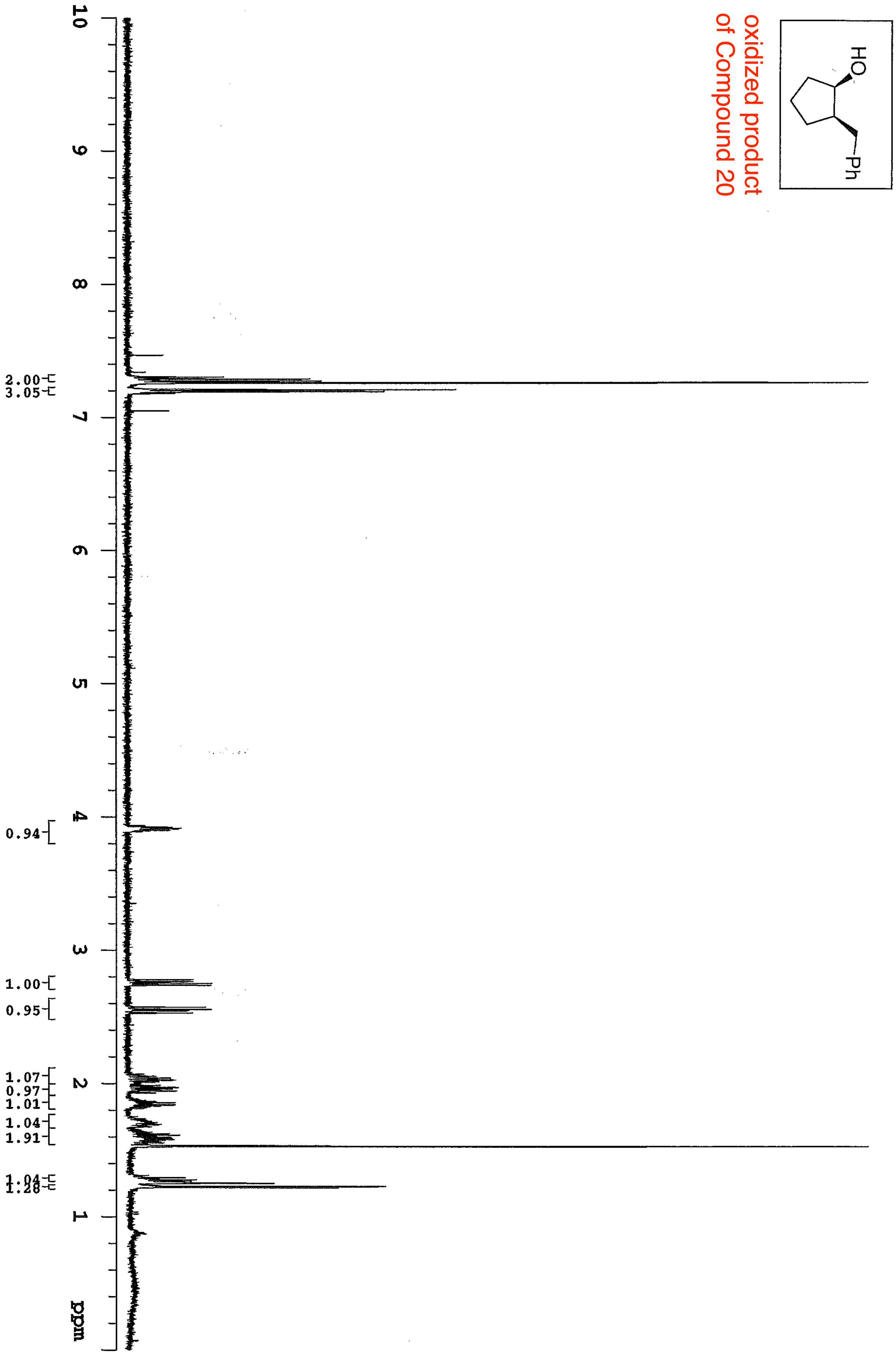

Me
Me
Me
Me
O
B
O
Ph

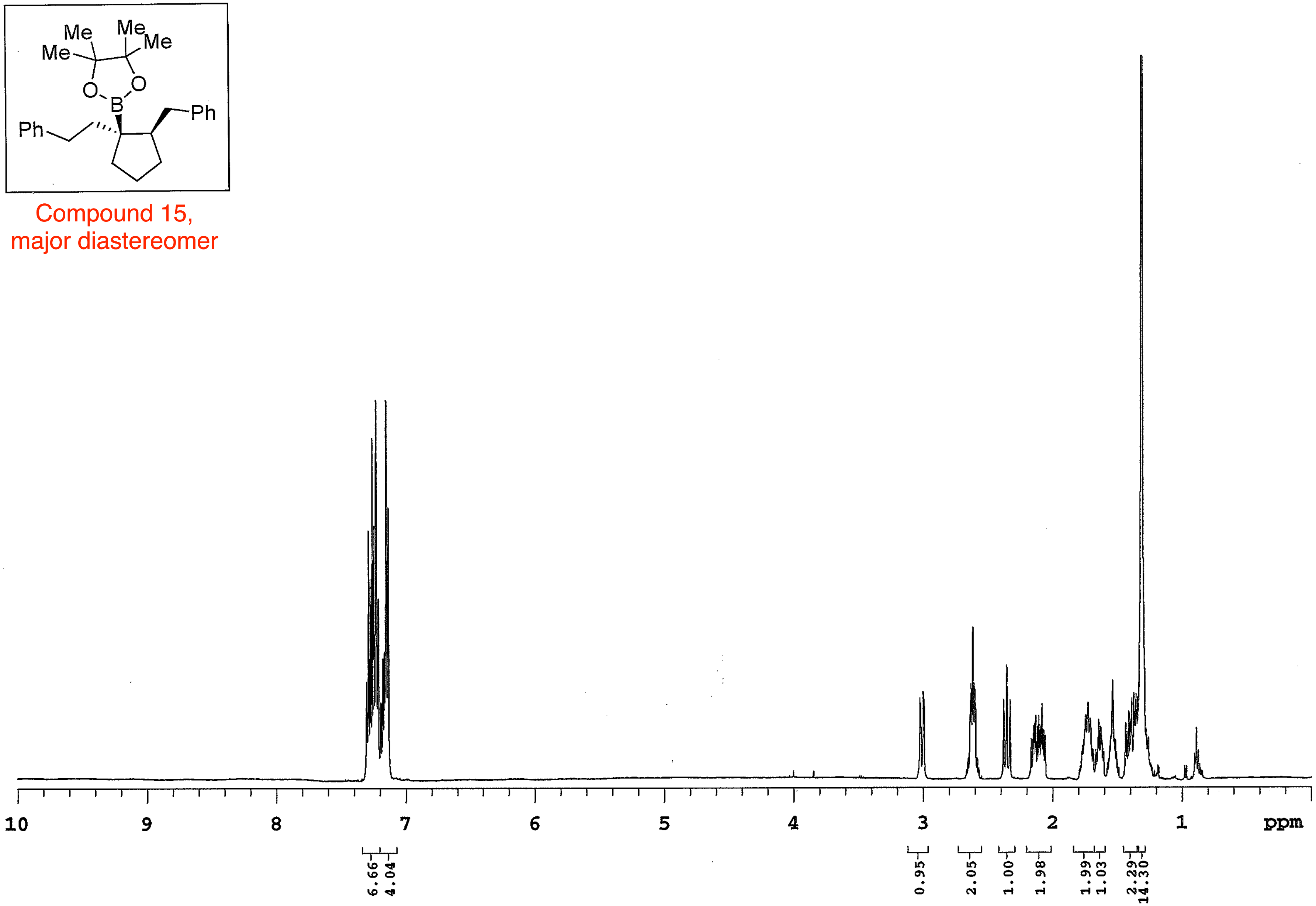
Compound 20


10
9
8
7
6
5
4
3
2
1
ppm
3.01
2.83
1.00
1.00
0.98
1.12
1.30
4.09
1.42
12.04
0.92


Compound 20
Me
Me
Me
Me
O
B
O
Ph
142.216
128.975
128.051
125.484
82.723
77.252
77.000
76.749
45.072
42.488
33.510
28.475
25.840
24.716
24.699
200
180
160
140
120
100
80
60
40
20
ppm

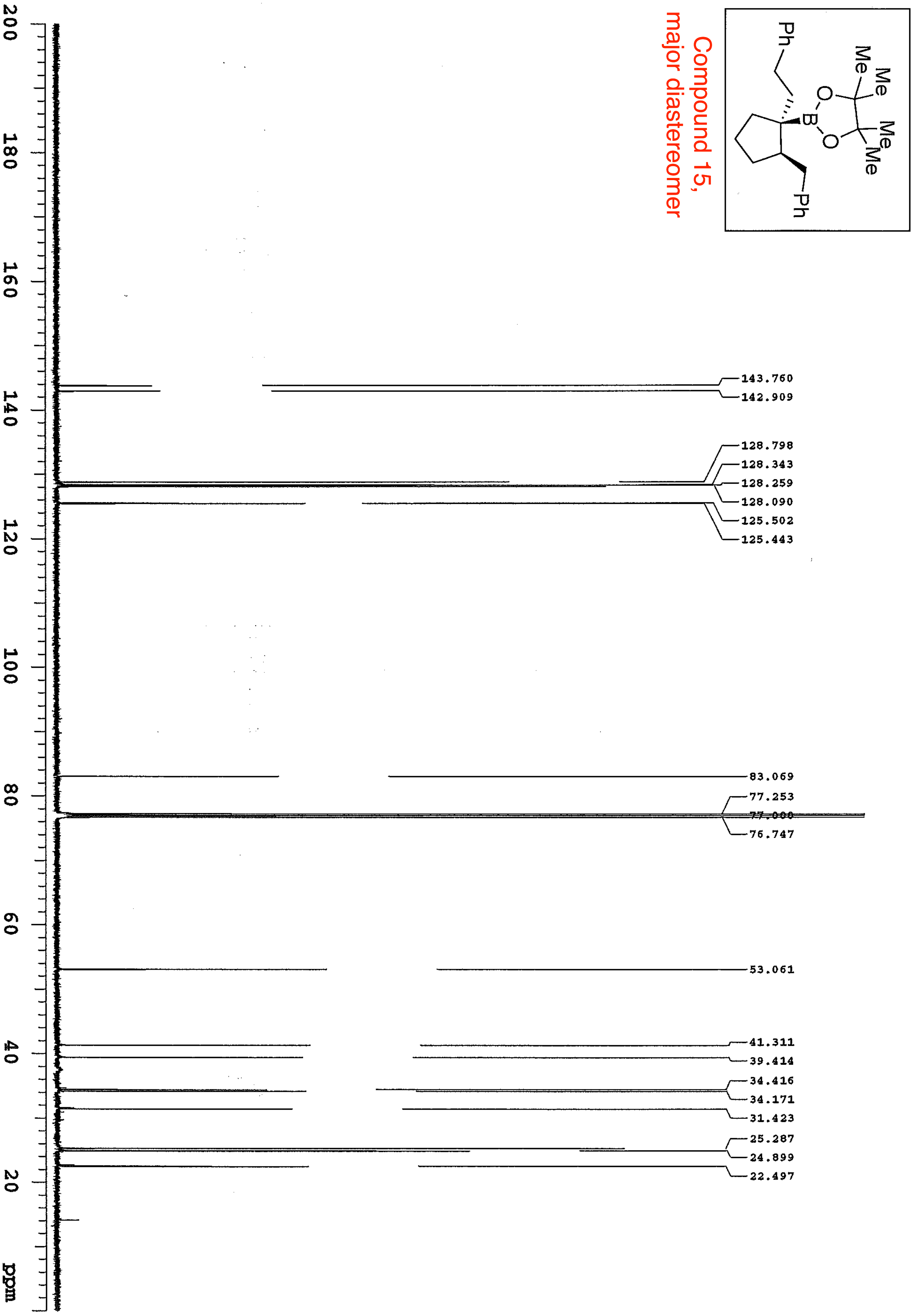
oxidized product of Compound 20

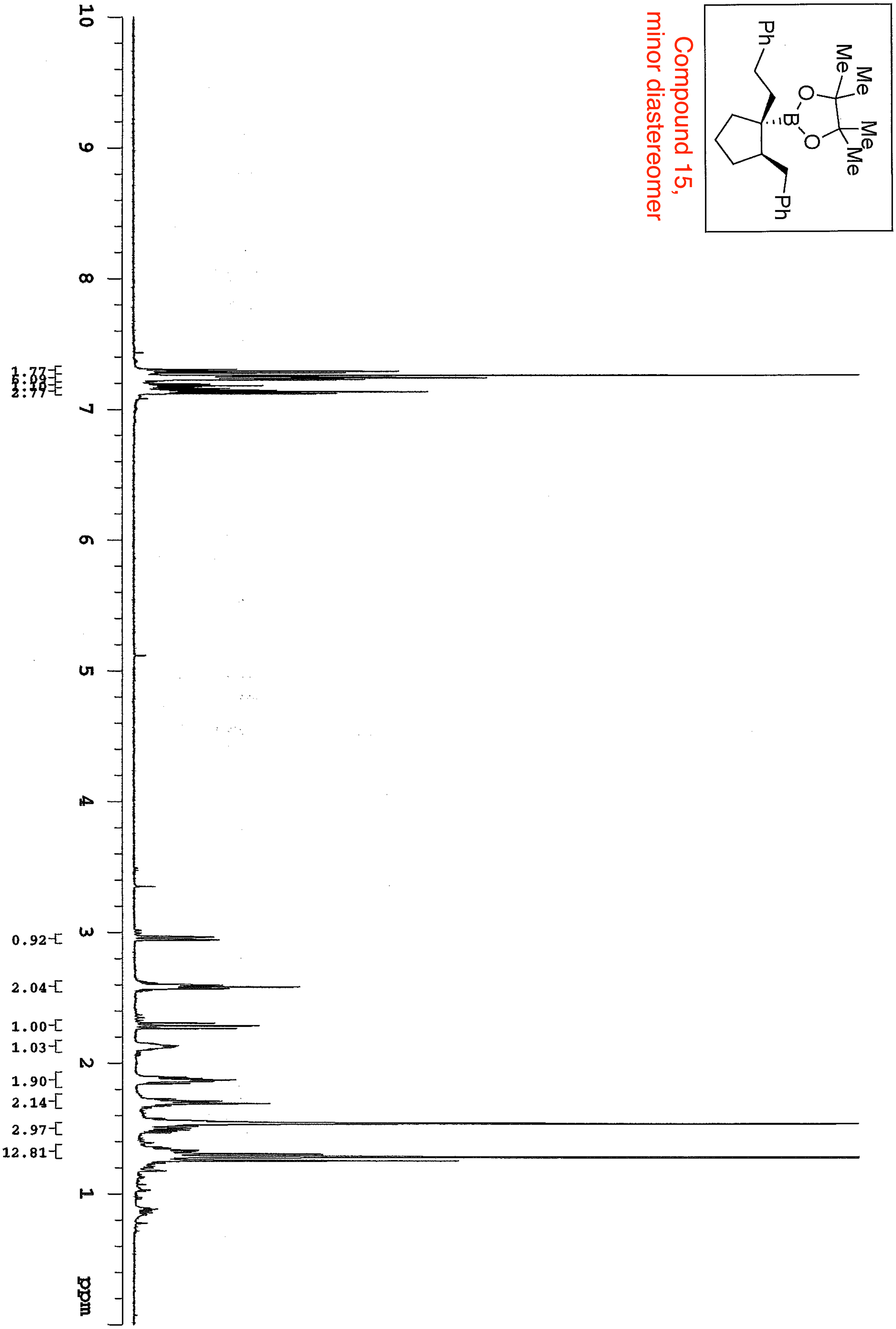


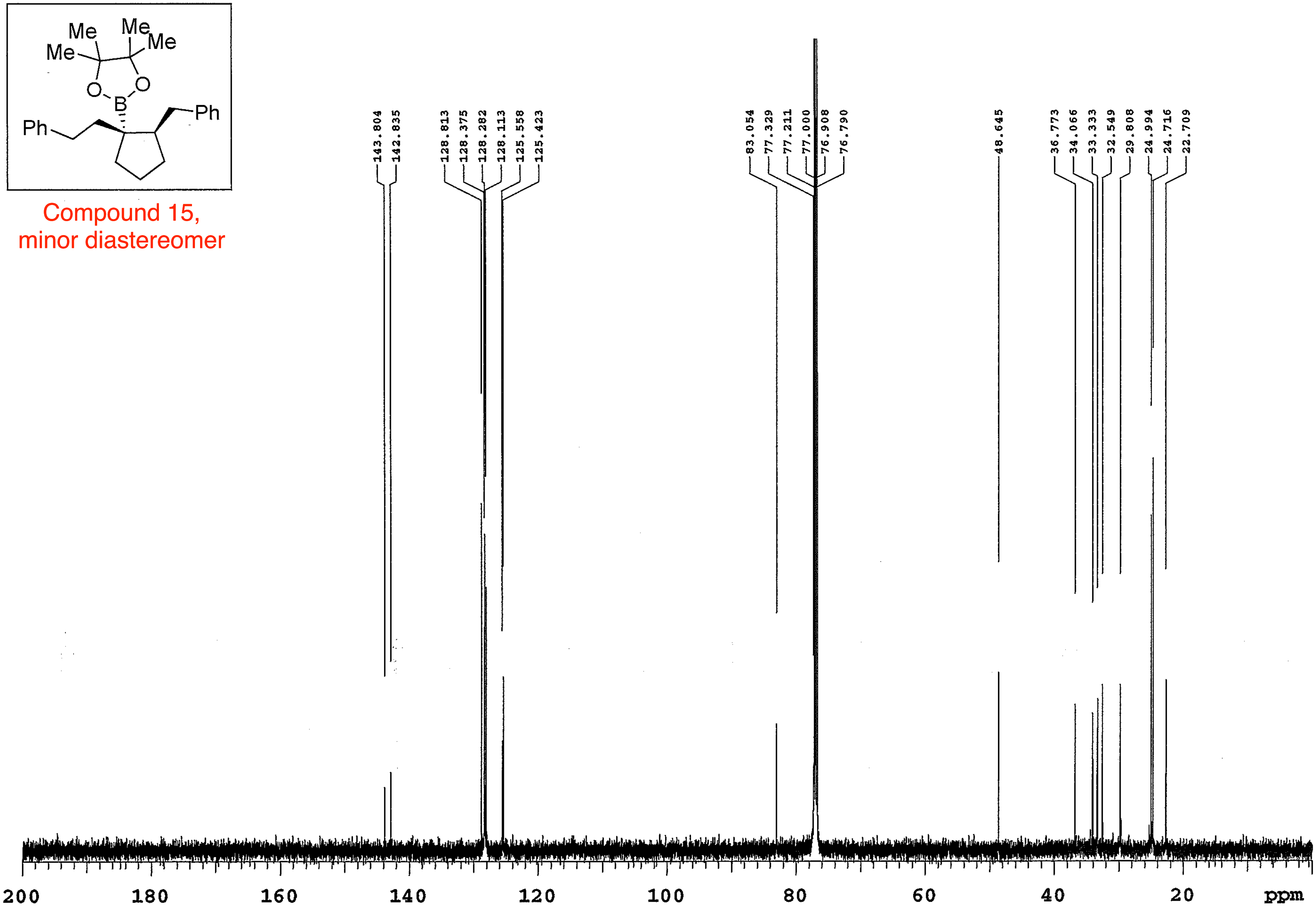


Compound 15,
major diastereomer

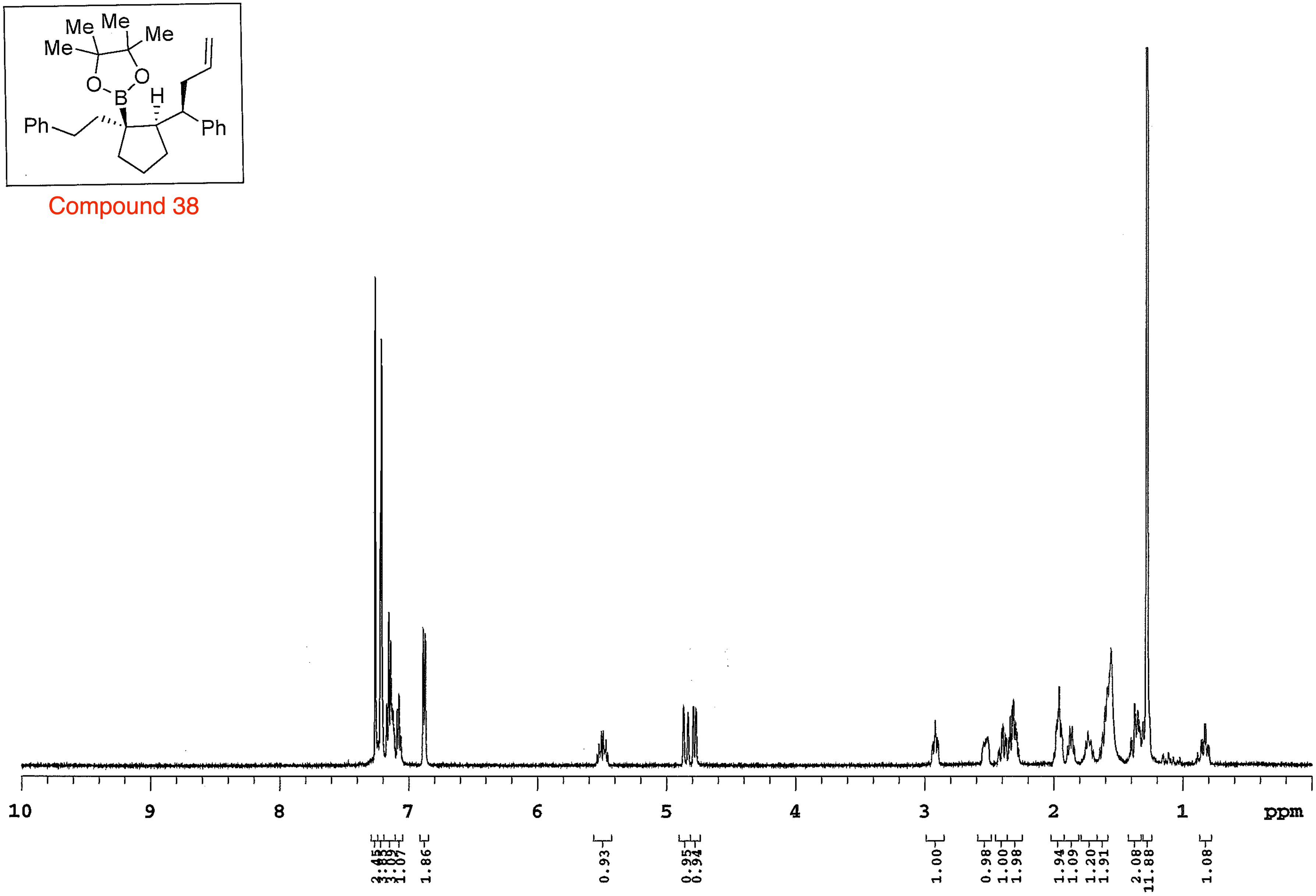
Compound 15, major diastereomer

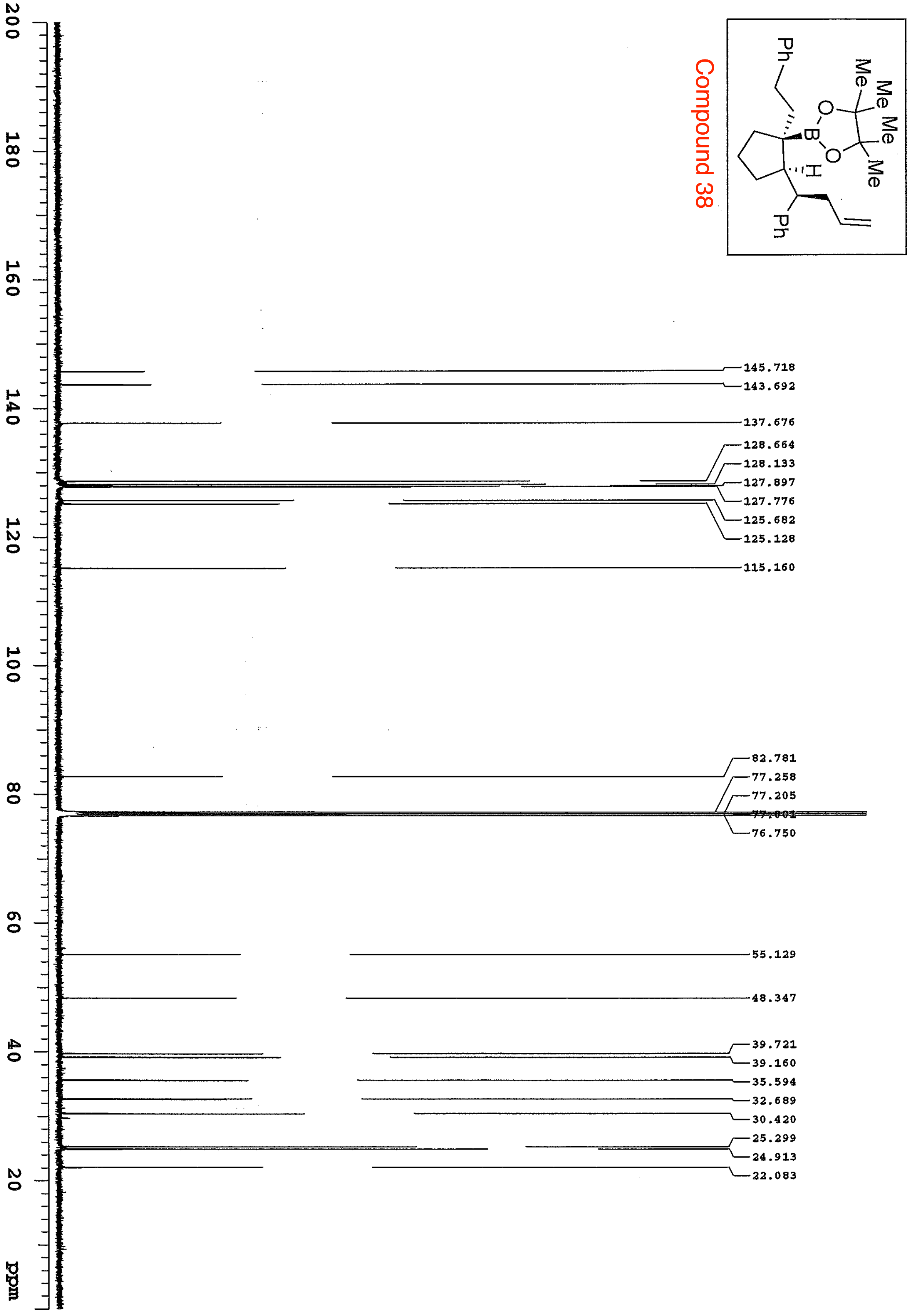



Compound 15, minor diastereomer

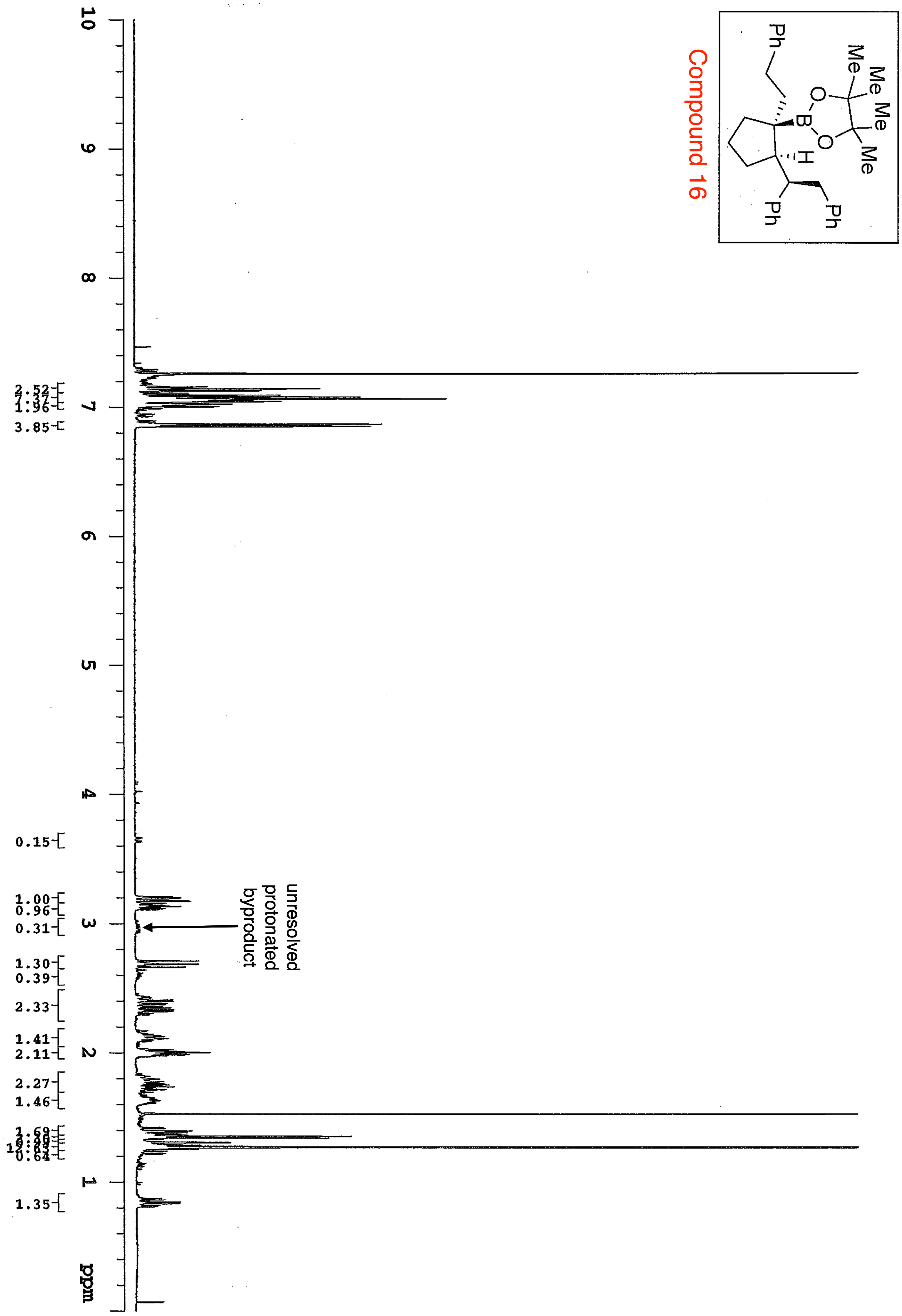


Compound 15,
minor diastereomer

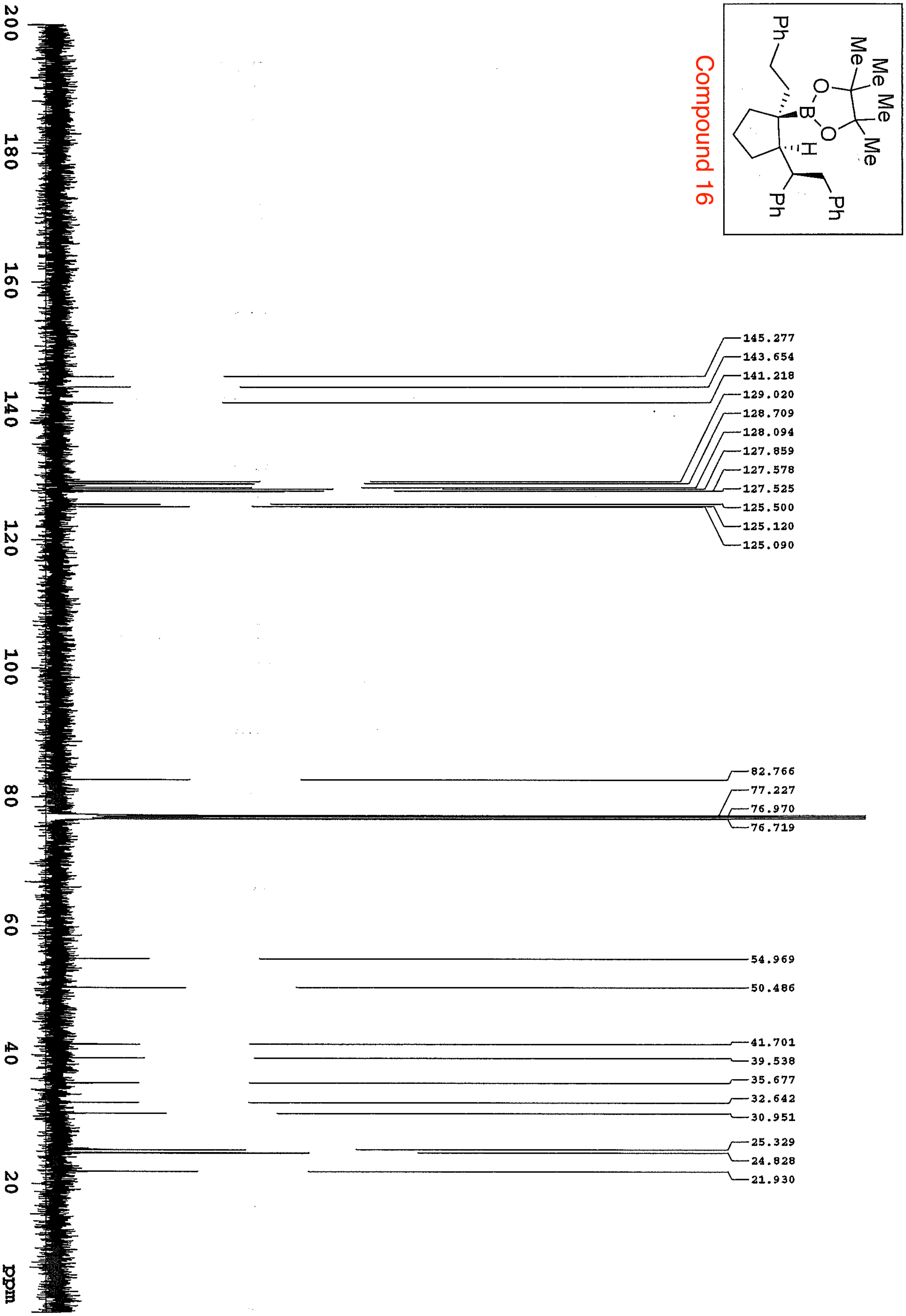

Compound 38
Me
Me
Me
Me
O
B
O
H
Ph
Ph
10
9
8
7
6
5
4
3
2
1
ppm
2.45
3.85
3.09
1.07
1.86
0.93
0.95
0.94
1.00
0.98
1.00
1.98
1.94
1.09
1.20
1.91
2.08
11.88
1.08


Me
Me
Me
Me
O
B
O
H
Ph
Ph
145.718
143.692
137.676
128.664
128.133
127.897
127.776
125.682
125.128
115.160
82.781
77.258
77.205
77.001
76.750
55.129
48.347
39.721
39.160
35.594
32.689
30.420
25.299
24.913
22.083
200
180
160
140
120
100
80
60
40
20
ppm

Compound 38

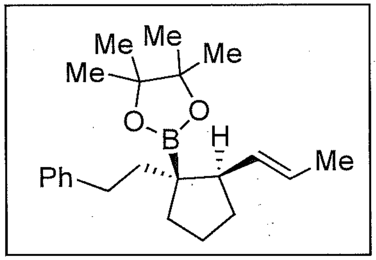

Me
Me
Me
Me
O
B
O
H
Ph
Ph
Ph
unresolved protonated byproduct
10
9
8
7
6
5
4
3
2
1
ppm
2.52
7.37
1.96
3.85
0.15
1.00
0.96
0.31
1.30
0.39
2.33
1.41
2.11
2.27
1.46
1.69
12.83
0.64
1.35

Compound 16

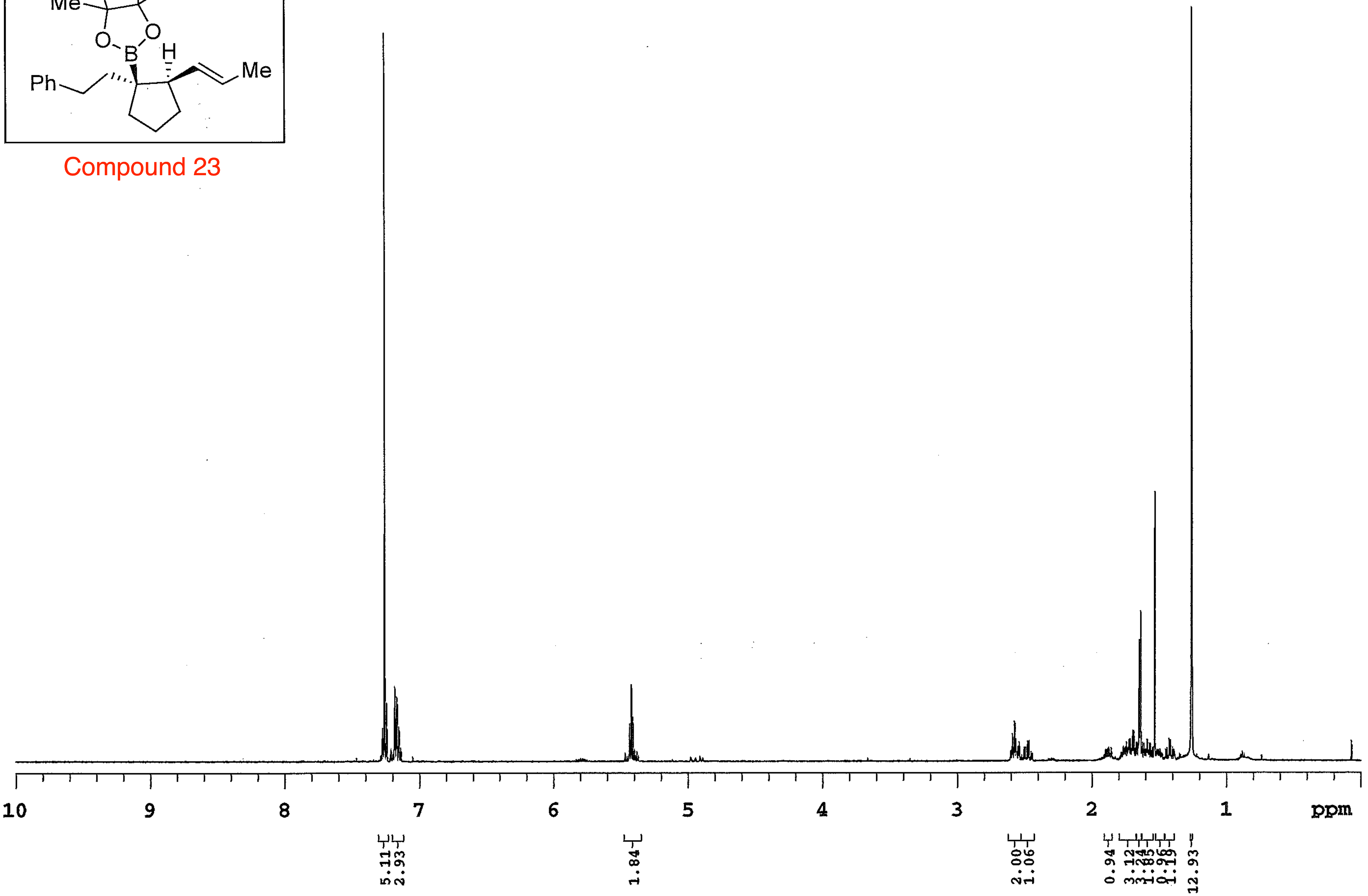


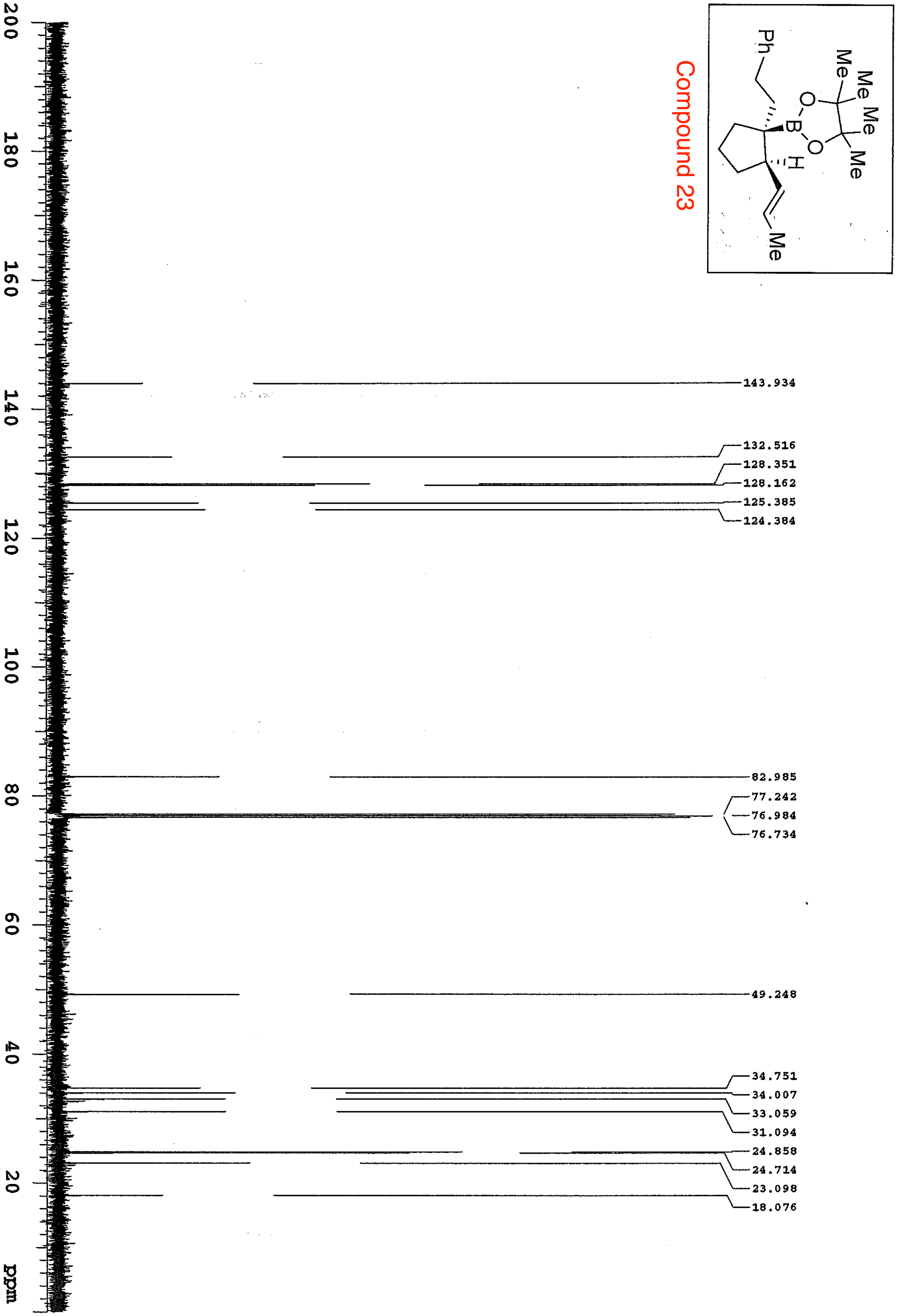
Compound 16

Me
Me
Me
Me
O
B
O
H
Ph
Ph
Ph
145.277
143.654
141.218
129.020
128.709
128.094
127.859
127.578
127.525
125.500
125.120
125.090
82.766
77.227
76.970
76.719
54.969
50.486
41.701
39.538
35.677
32.642
30.951
25.329
24.828
21.930
200
180
160
140
120
100
80
60
40
20
ppm

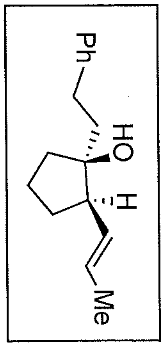

Me
Me
Me
Me
O
O
B
H
Ph
Me

Compound 23

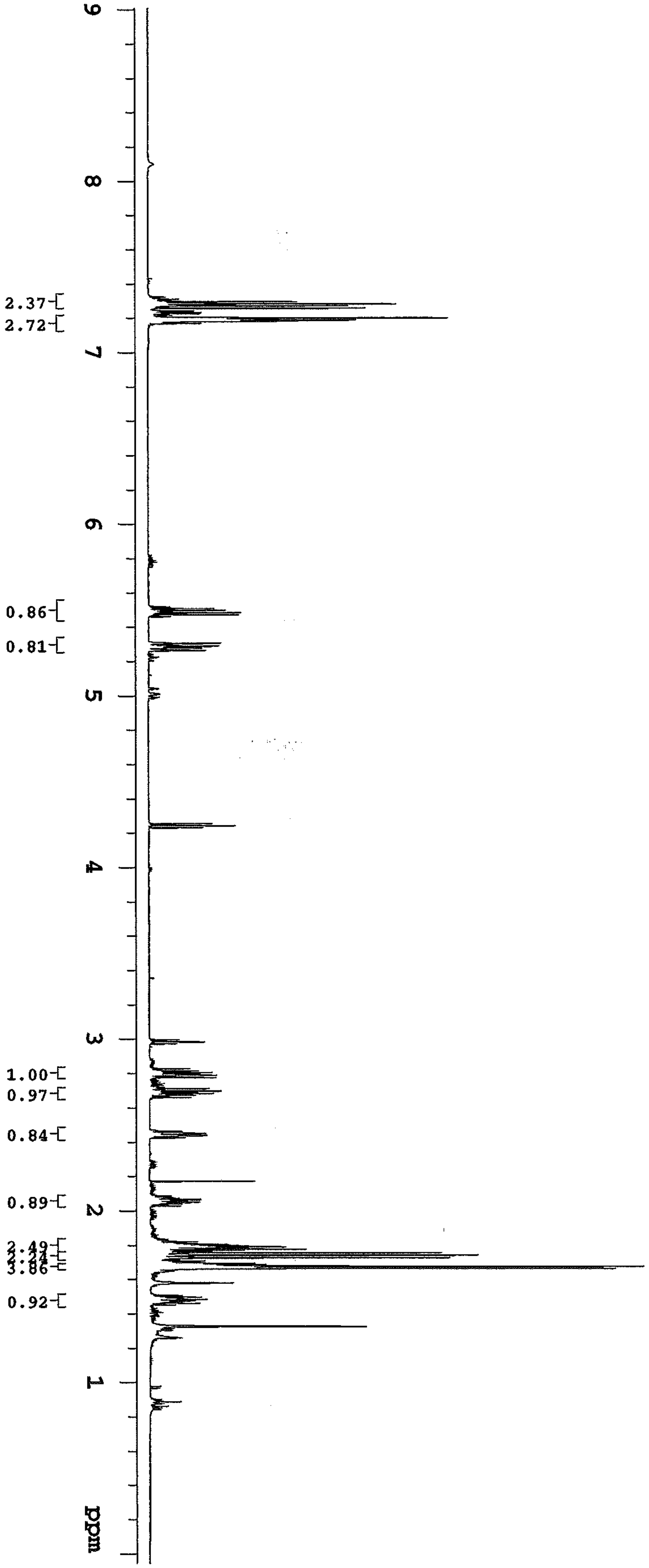

10
9
8
7
6
5
4
3
2
1
ppm
5.11
2.93
1.84
2.00
1.06
0.94
3.12
3.24
1.85
0.96
1.19
12.93

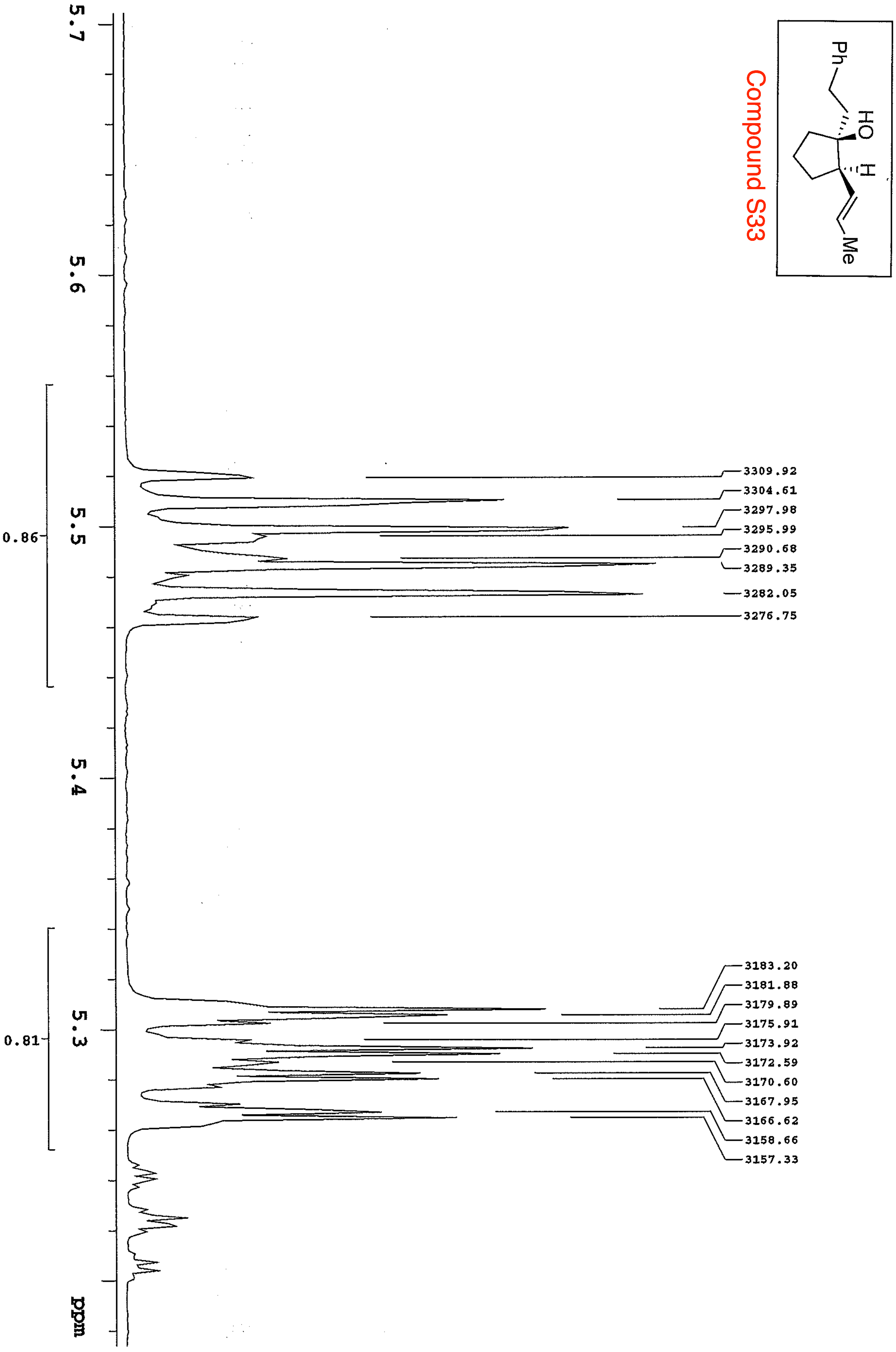

Compound 23

Me
Me
Me
Me
O
B
O
H
Ph
Me
143.934
132.516
128.351
128.162
125.385
124.384
82.985
77.242
76.984
76.734
49.248
34.751
34.007
33.059
31.094
24.858
24.714
23.098
18.076
200
180
160
140
120
100
80
60
40
20
ppm

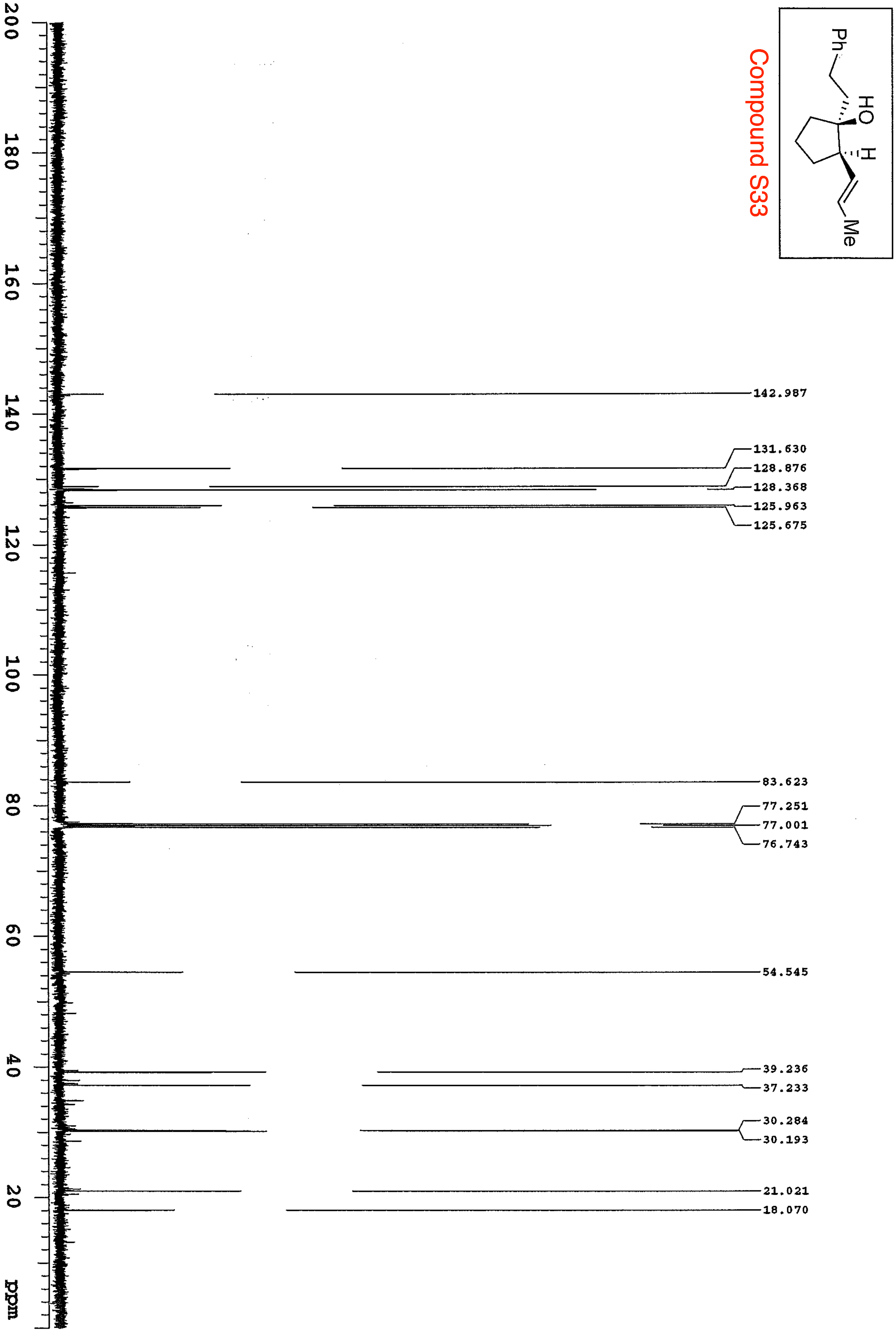


Compound S33

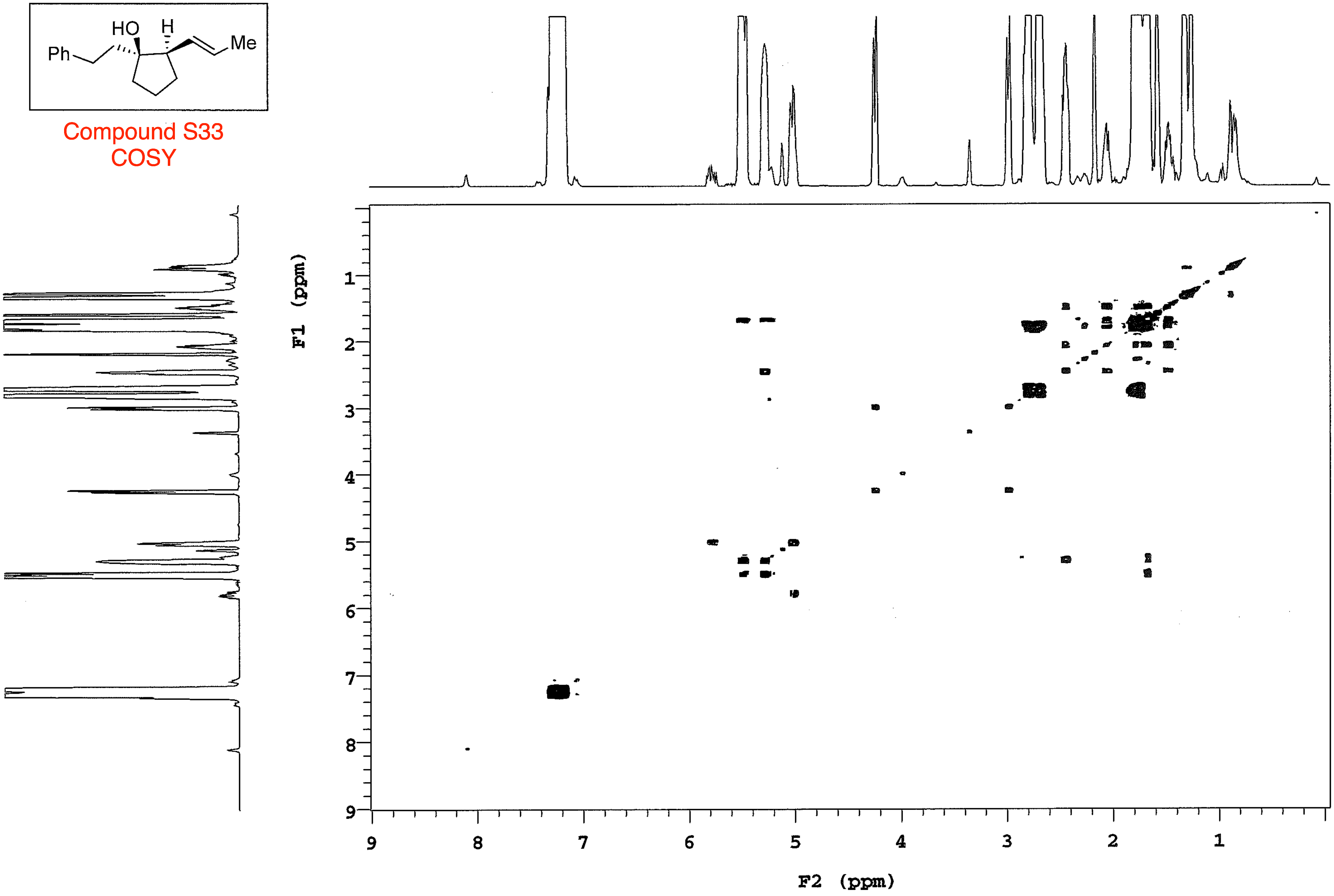




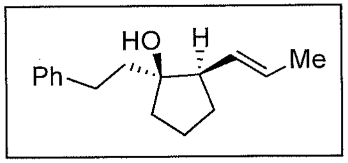
Compound S33



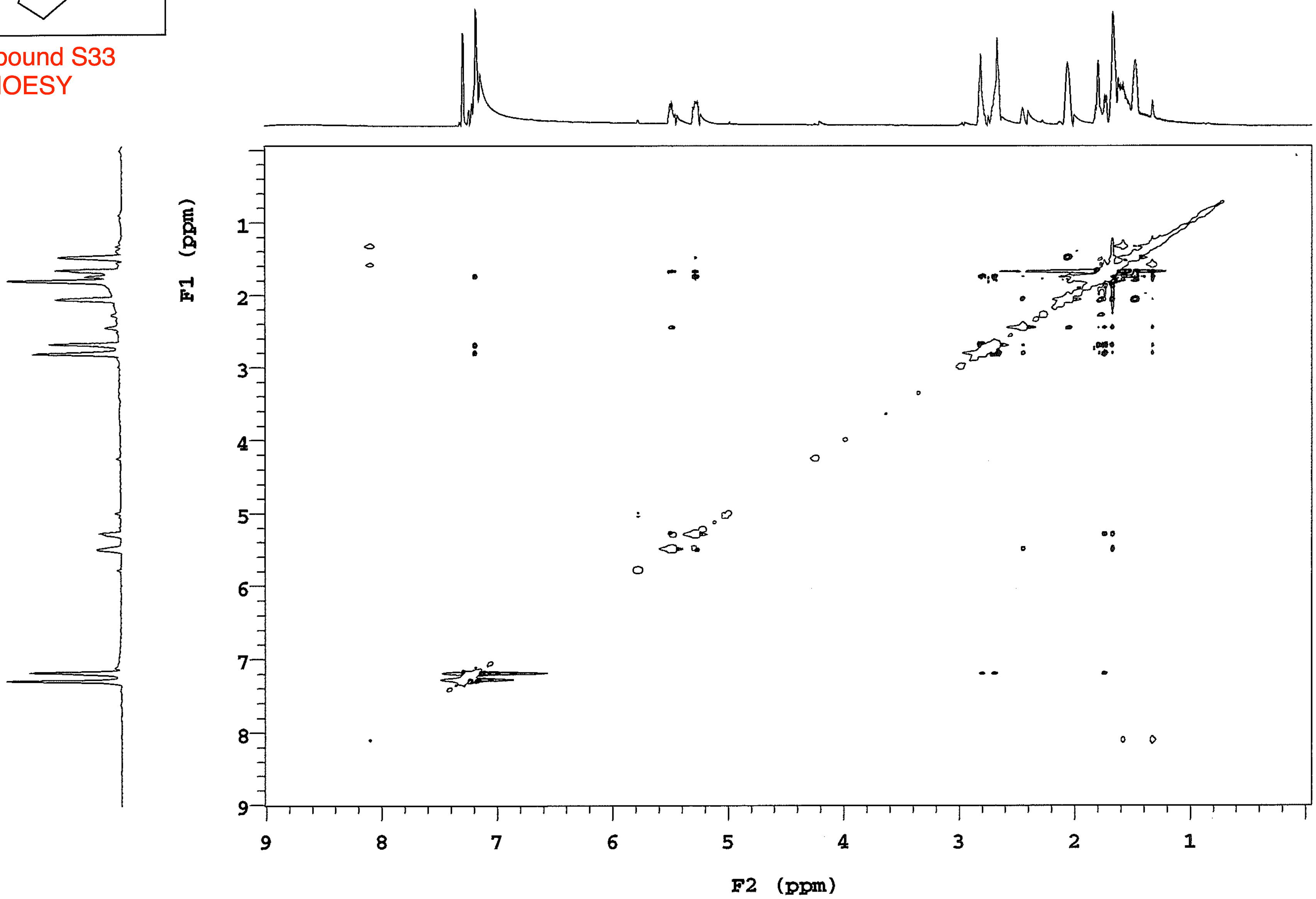
Compound S33

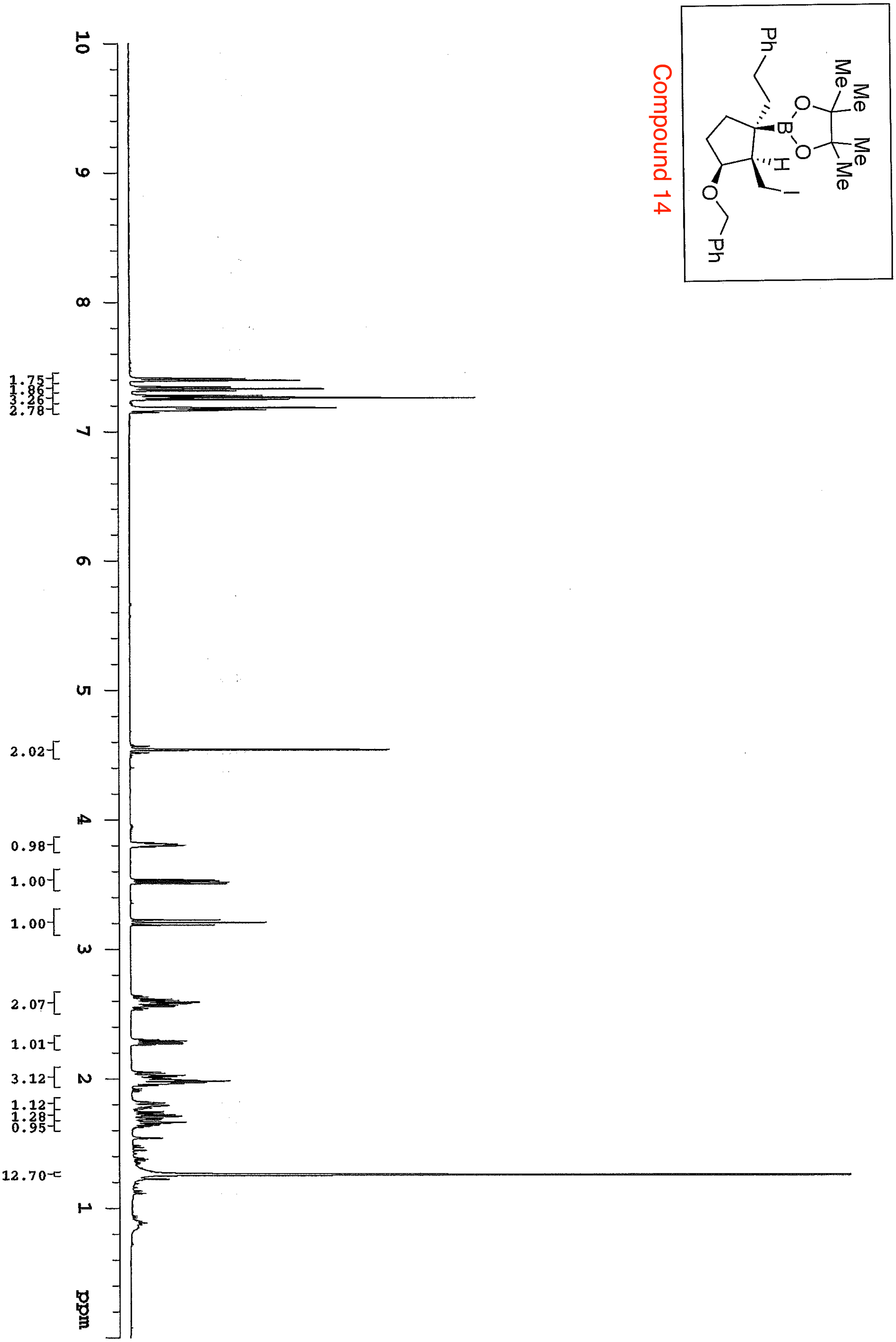


Compound S33
COSY



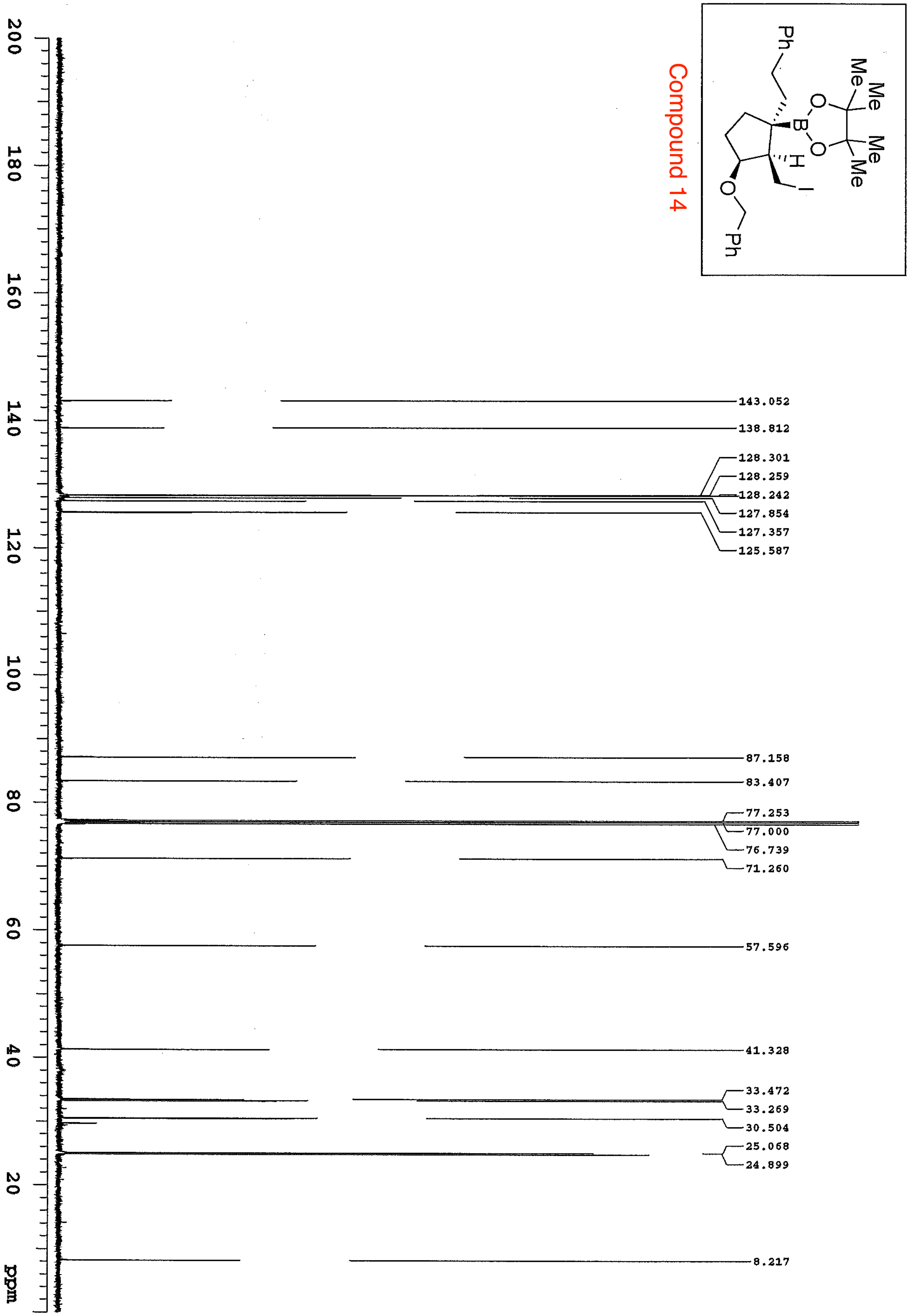
Compound S33
NOESY




Me
Me
Me
Me
O
B
O
H
I
Ph
O
Ph

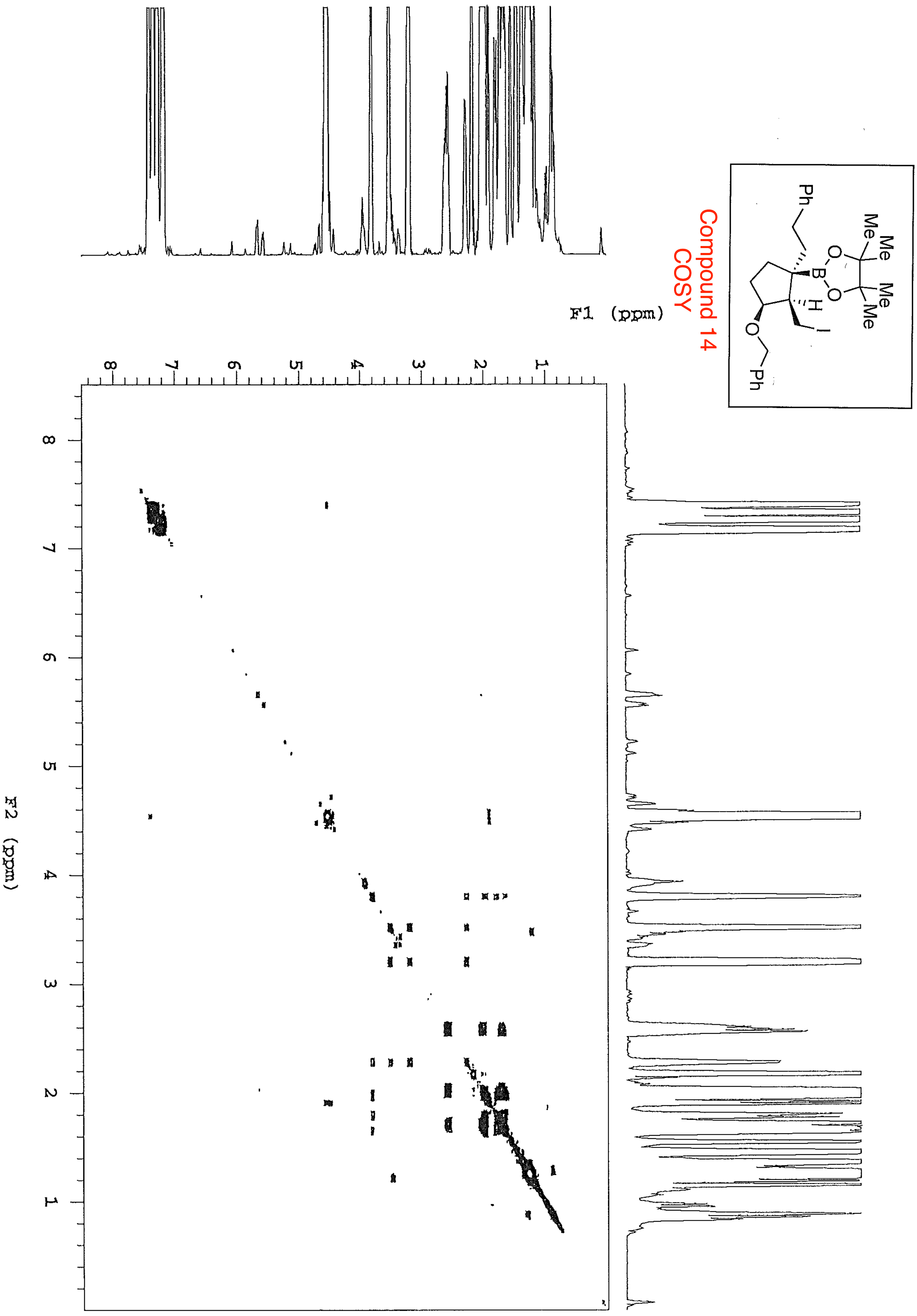
Compound 14

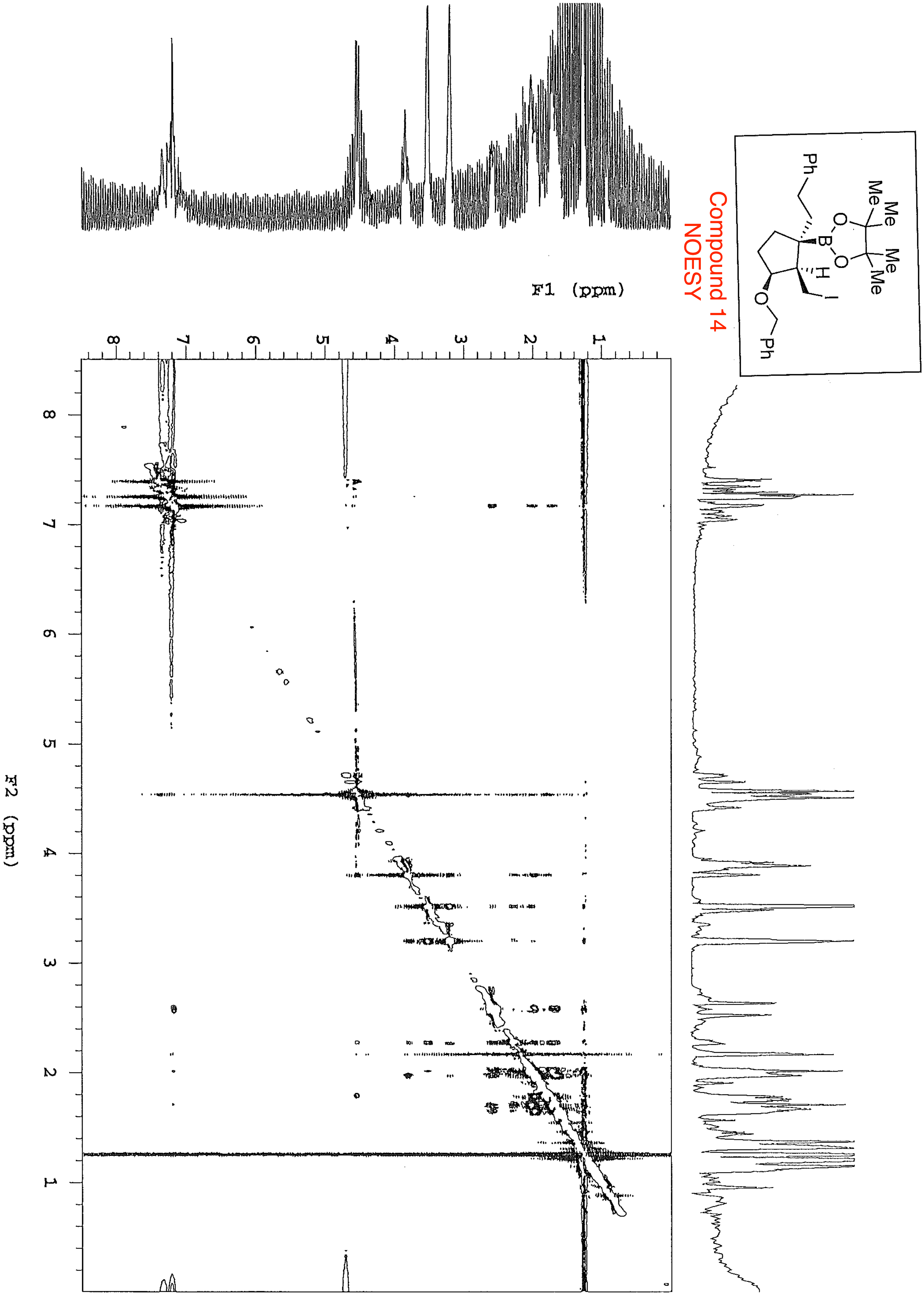
10
9
8
7
6
5
4
3
2
1
ppm
1.75
1.86
3.26
2.78
2.02
0.98
1.00
1.00
2.07
1.01
3.12
1.12
1.28
0.95
12.70


Compound 14

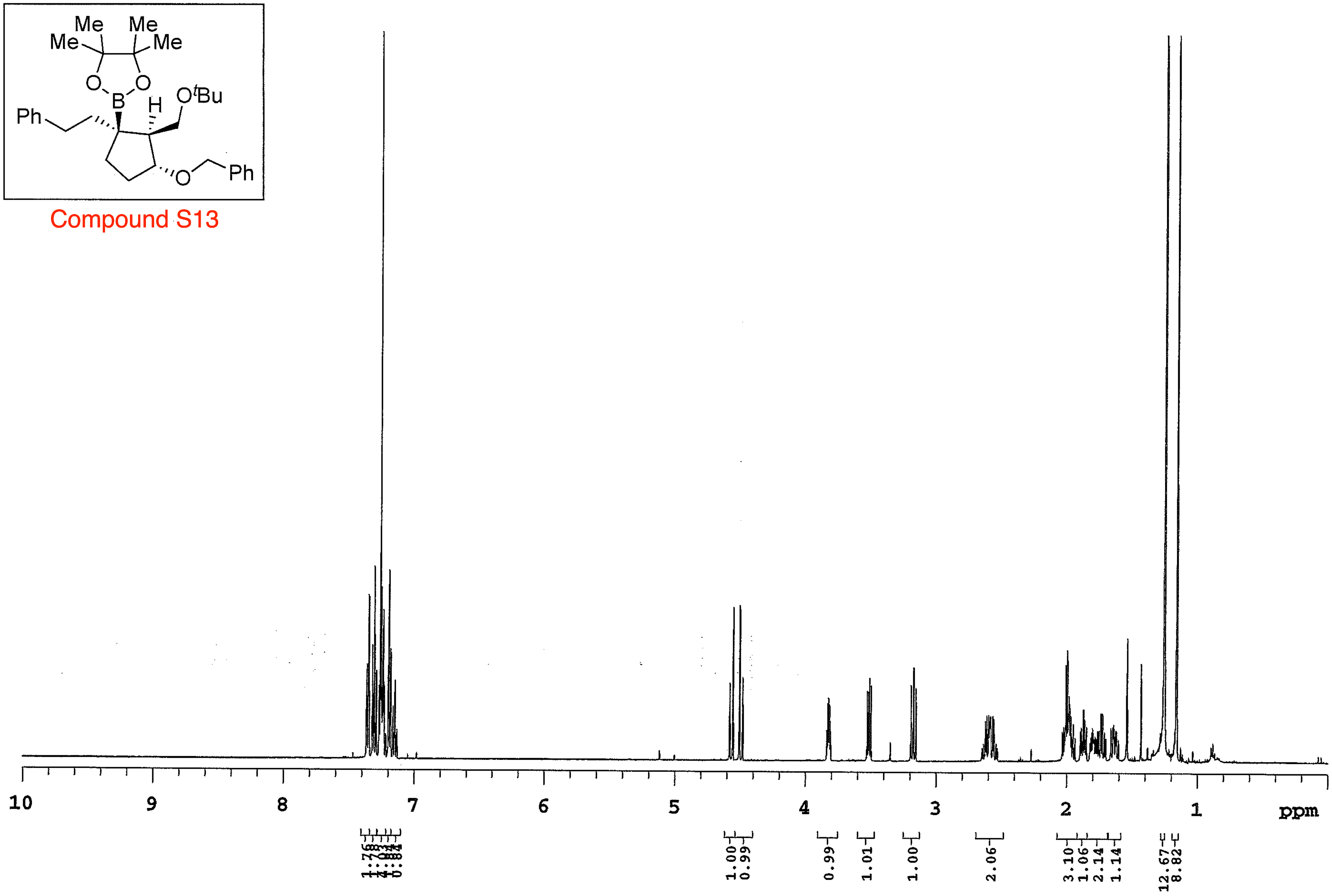
Me
Me
Me
Me
O
B
O
H
I
Ph
O
Ph
143.052
138.812
128.301
128.259
128.242
127.854
127.357
125.587
87.158
83.407
77.253
77.000
76.739
71.260
57.596
41.328
33.472
33.269
30.504
25.068
24.899
8.217
200
180
160
140
120
100
80
60
40
20
ppm

Compound 14
COSY

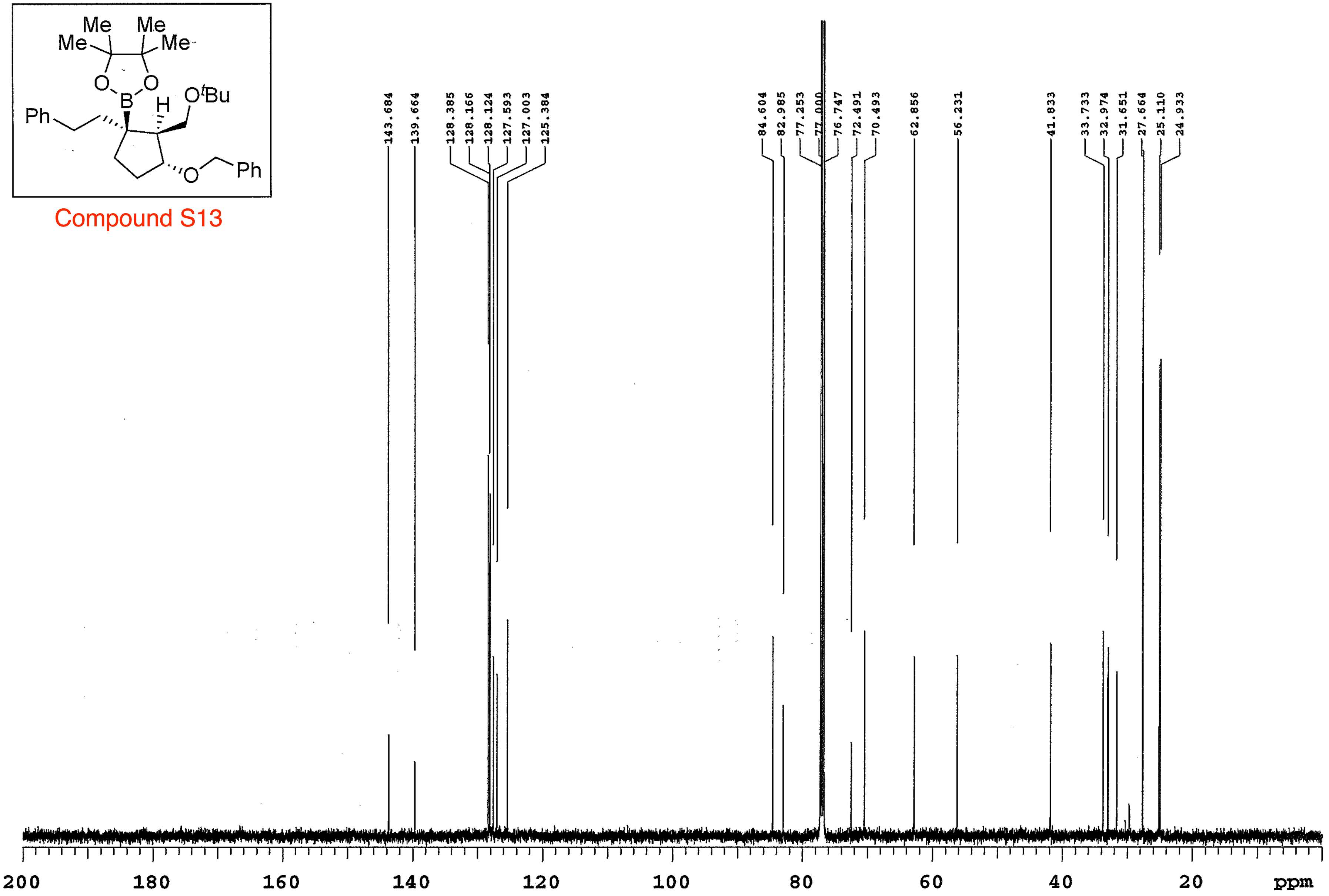


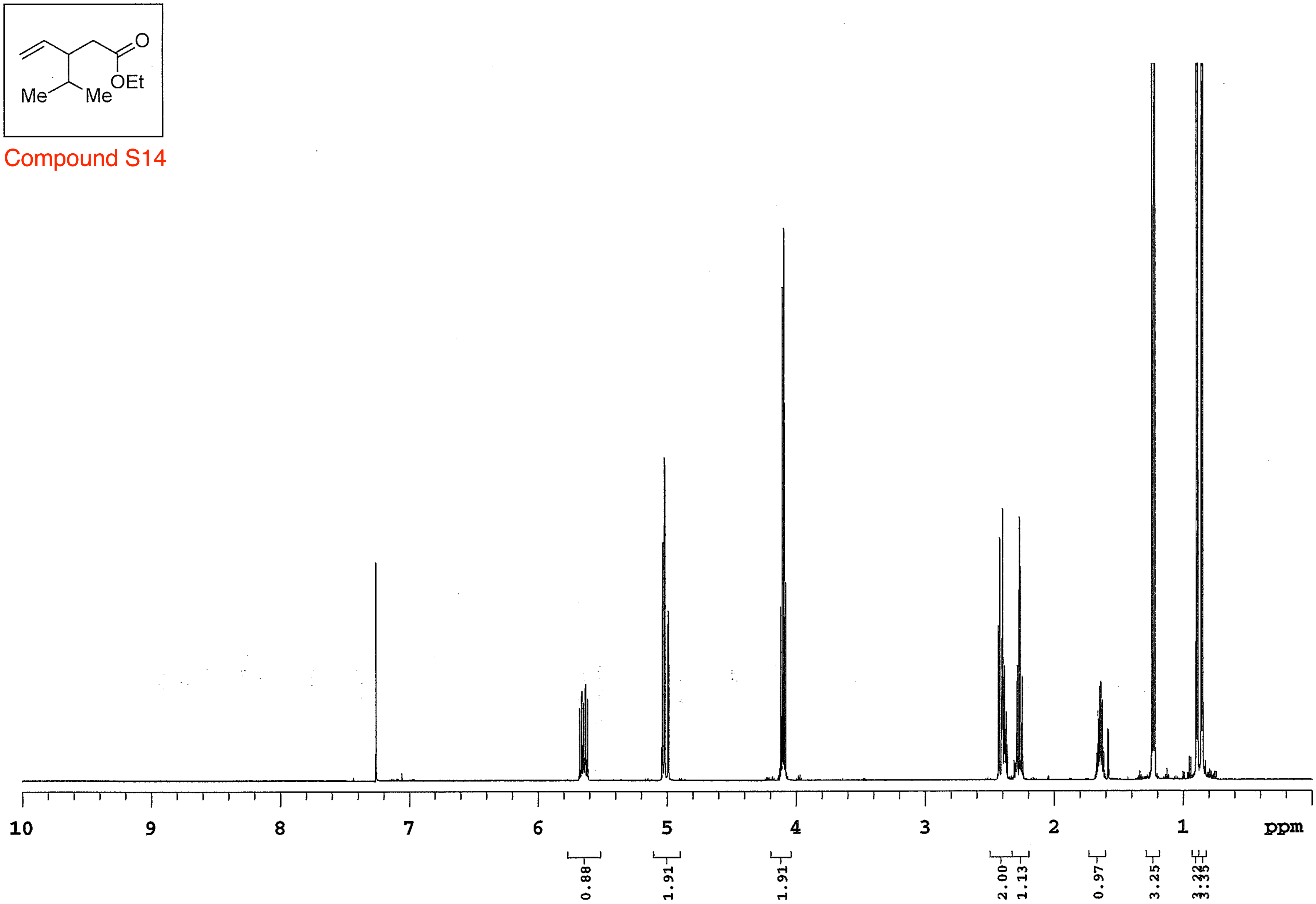


Compound 14
NOESY



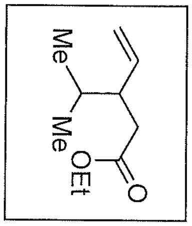
Compound S13

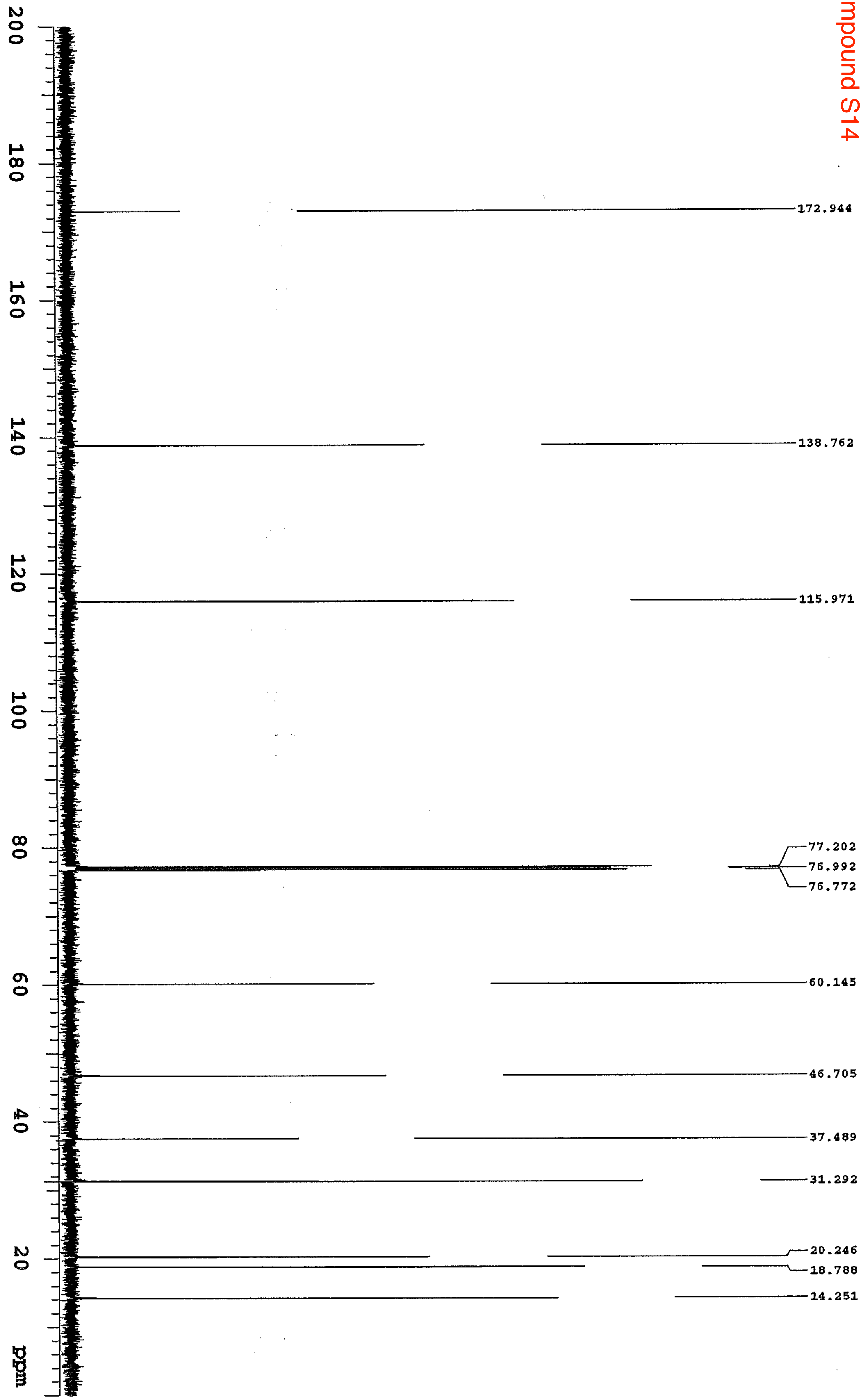


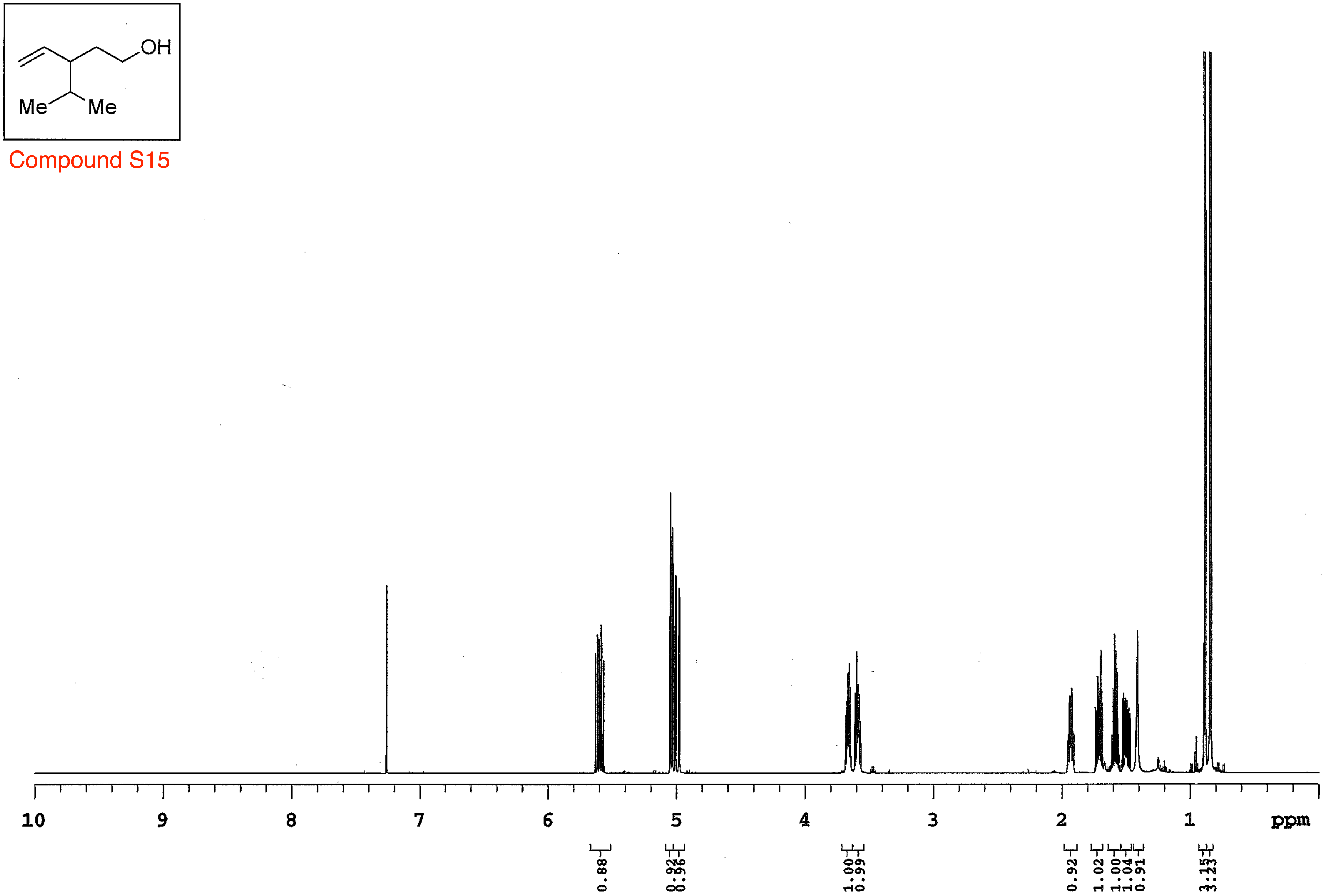


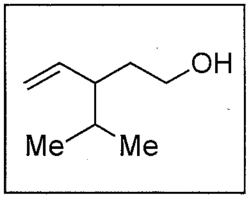
Compound S14

Compound S14

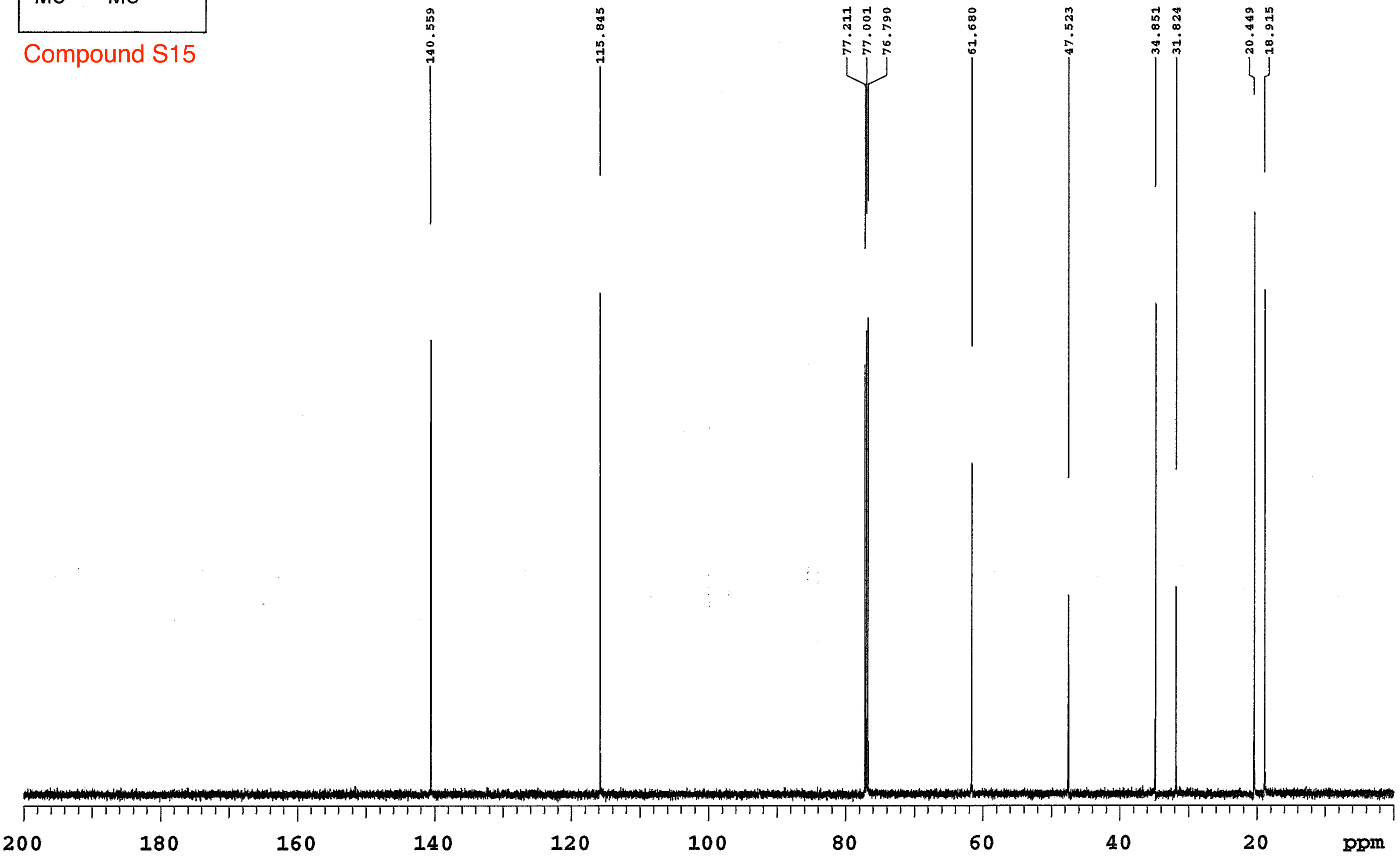


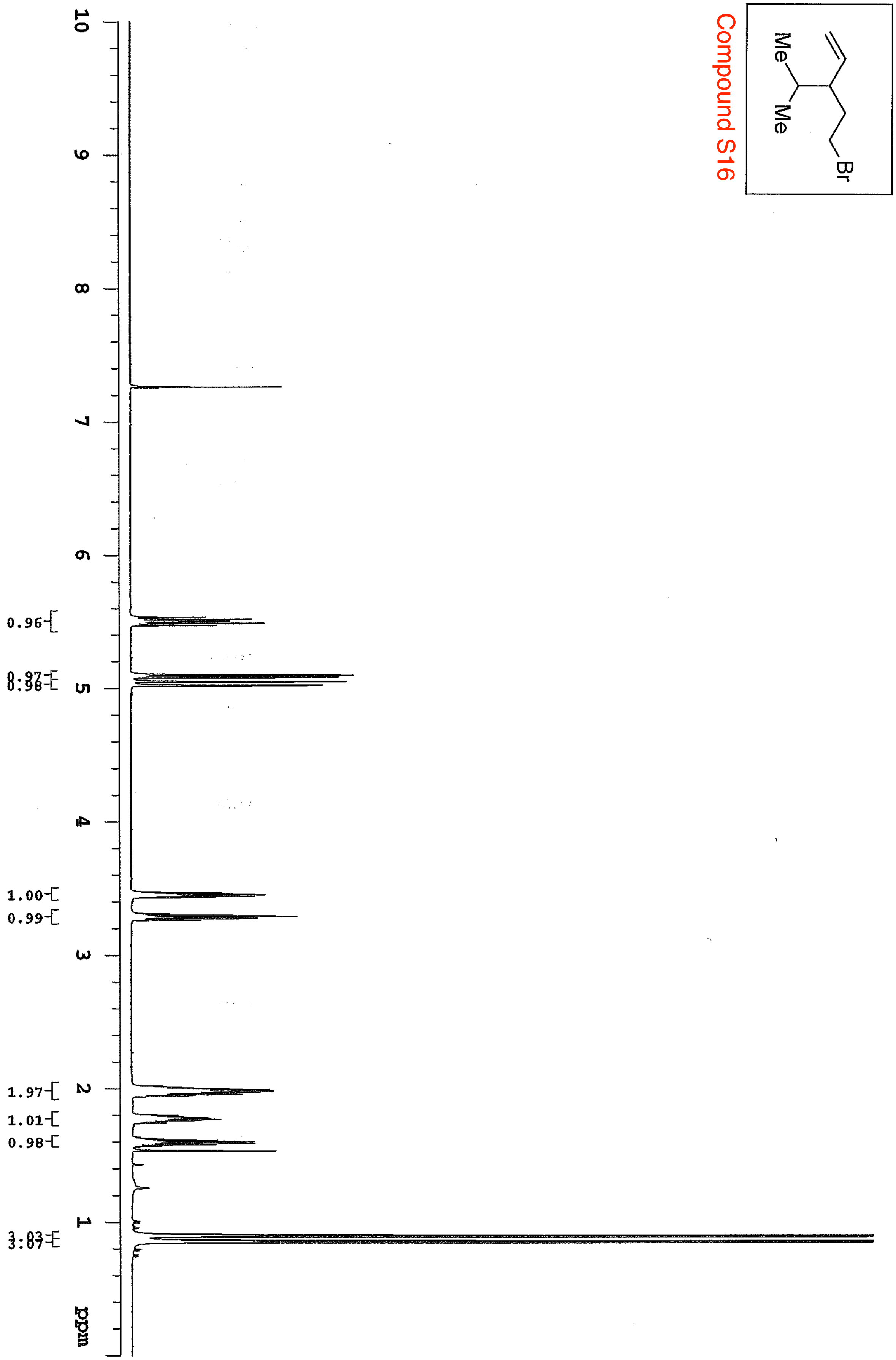



Compound S15

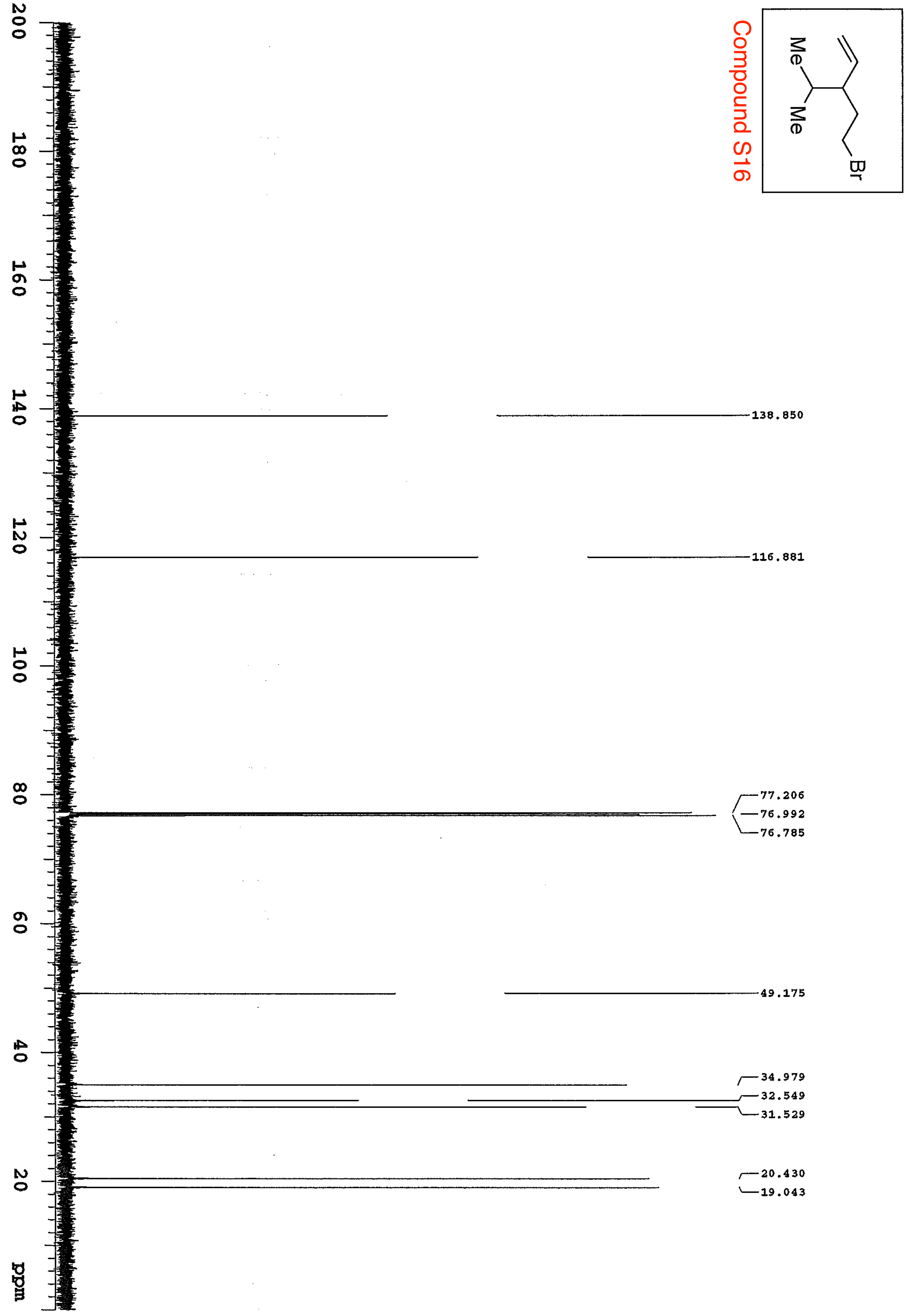


Compound S15

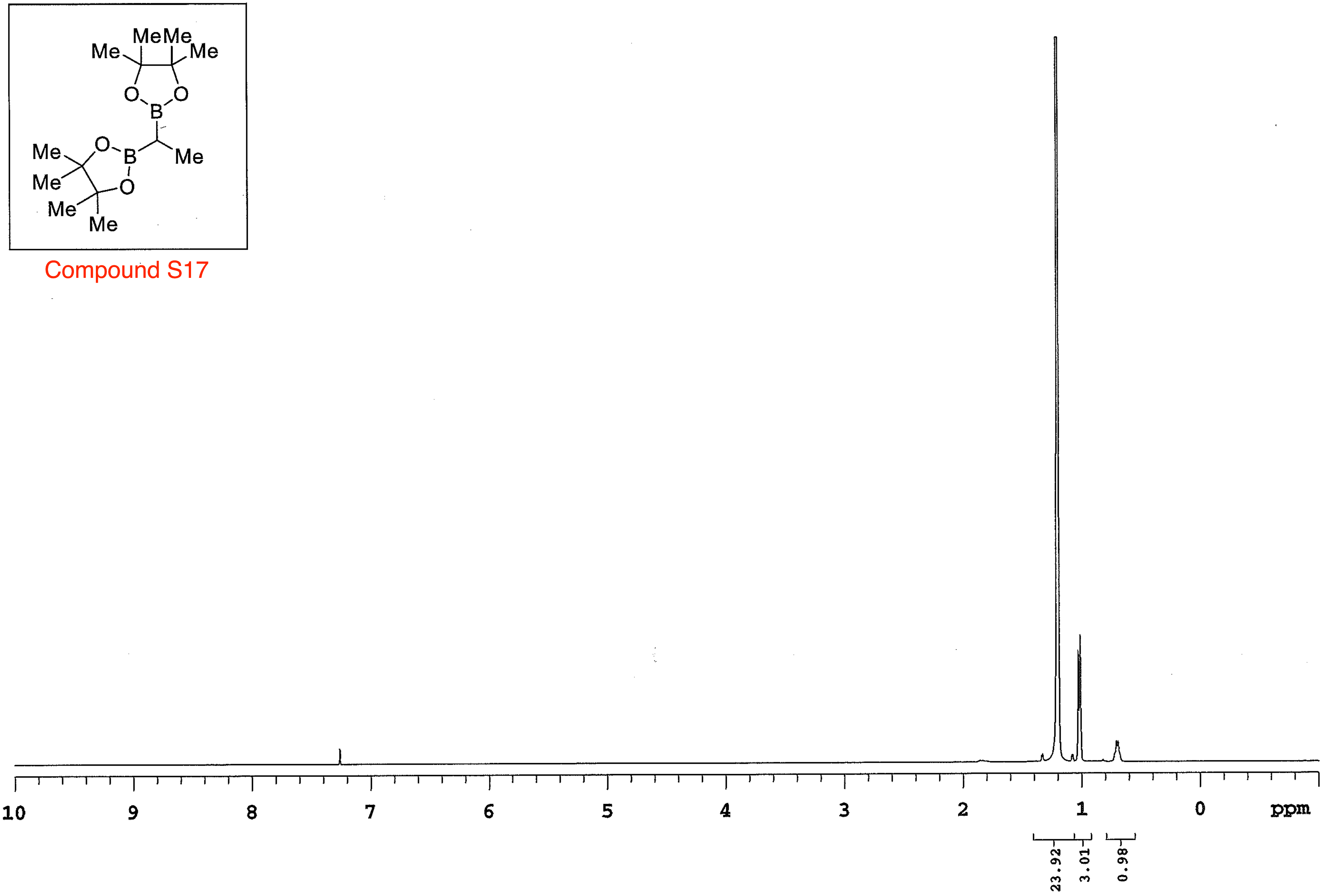




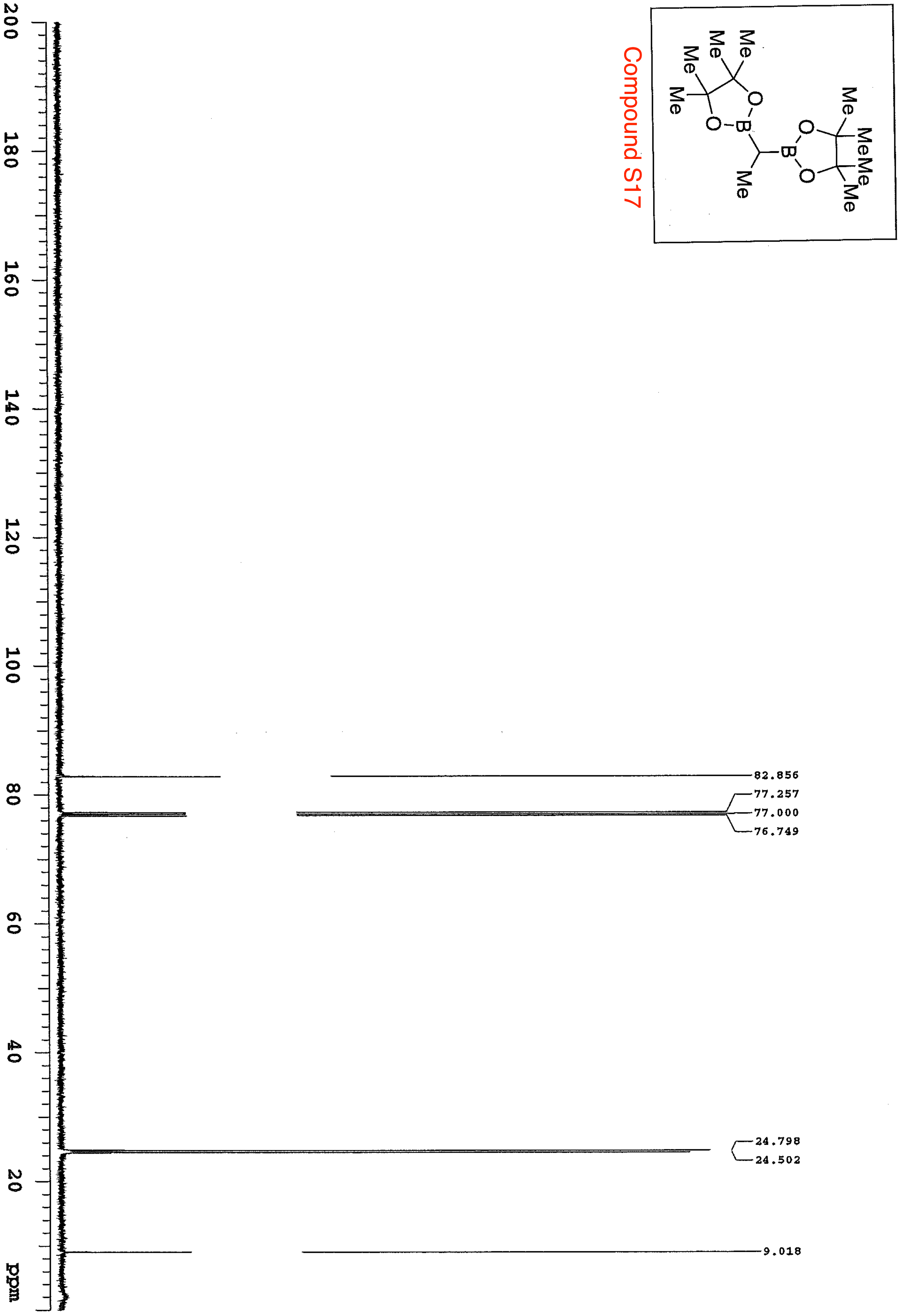
Compound S16

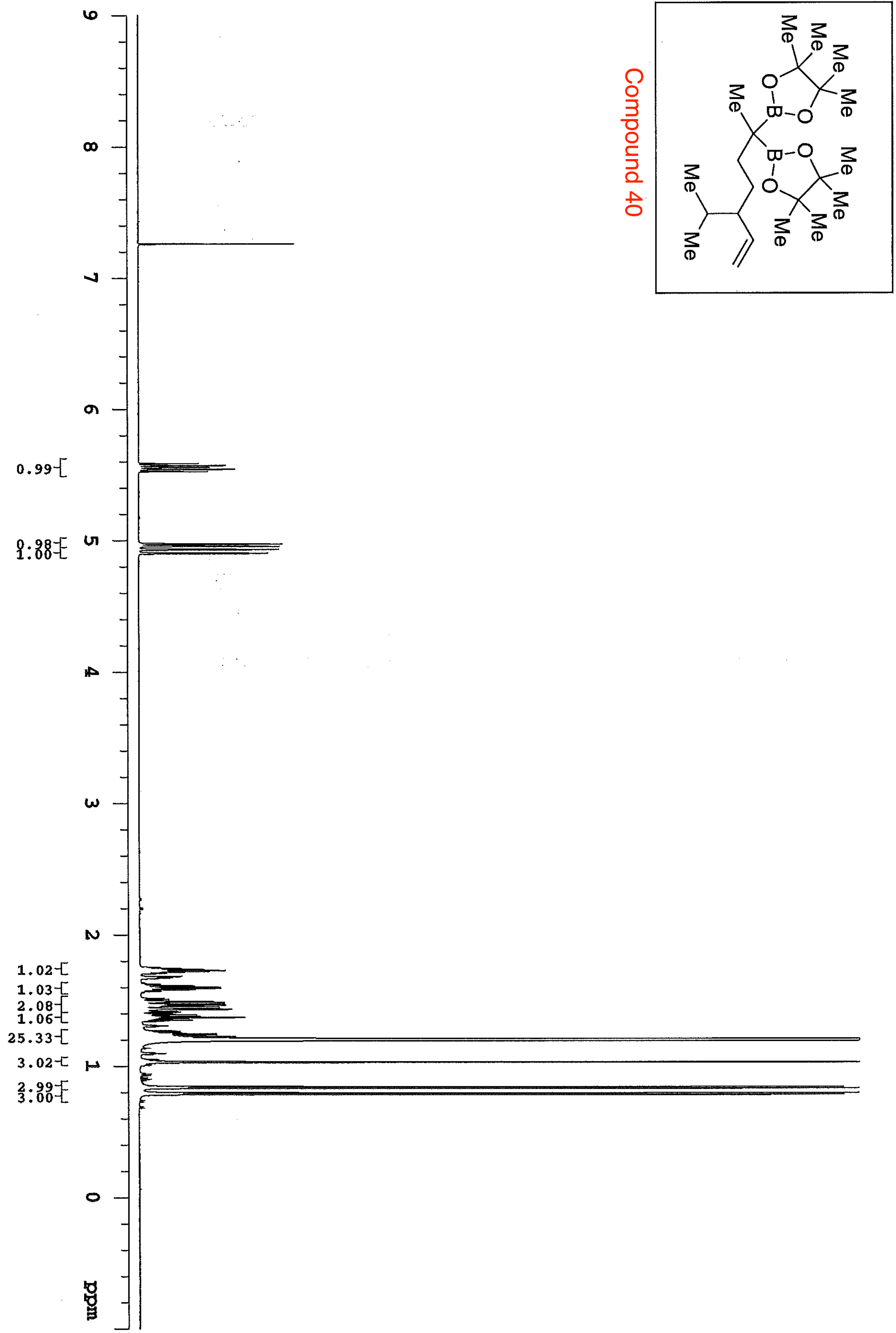


Compound S16

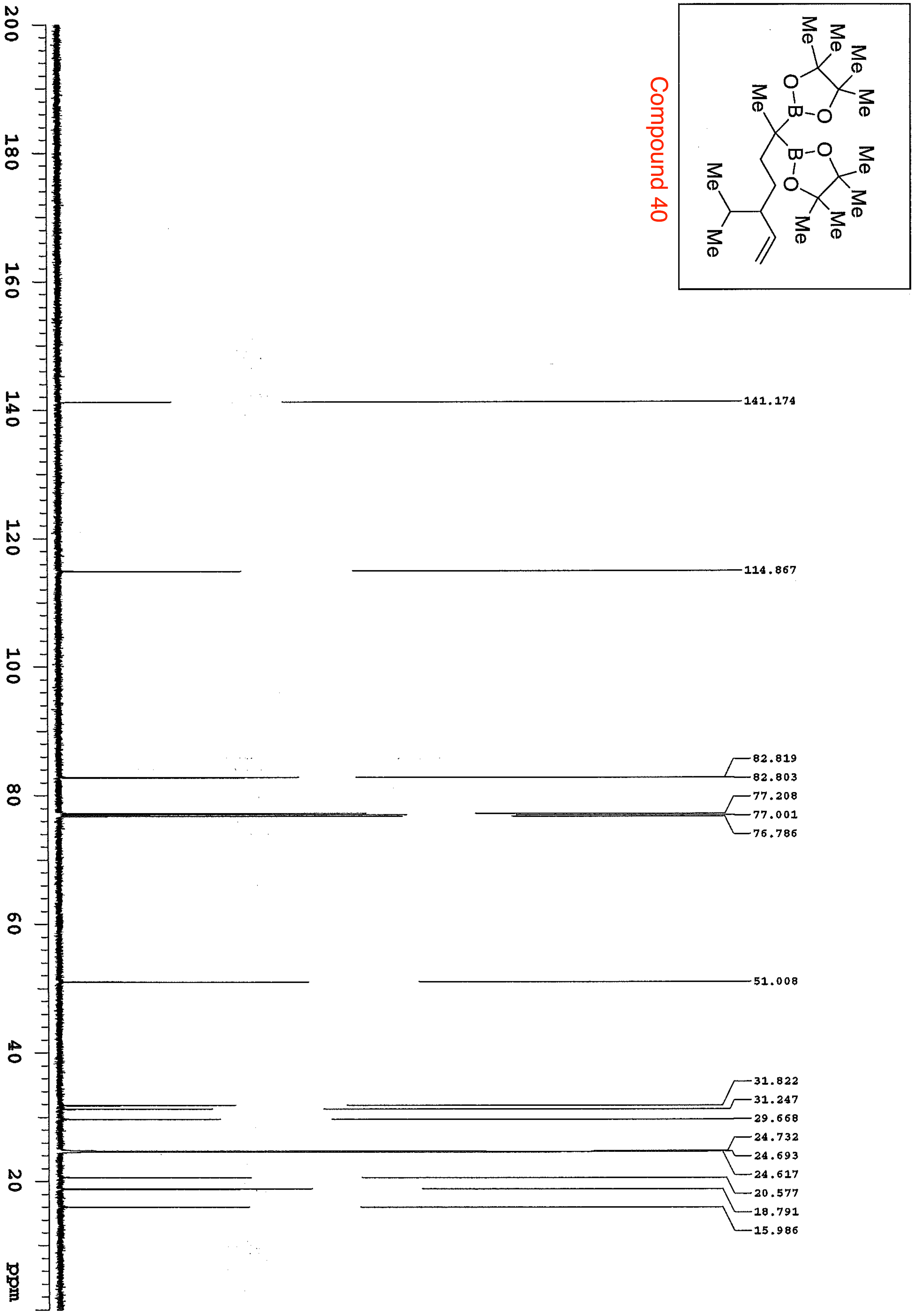


Compound S17

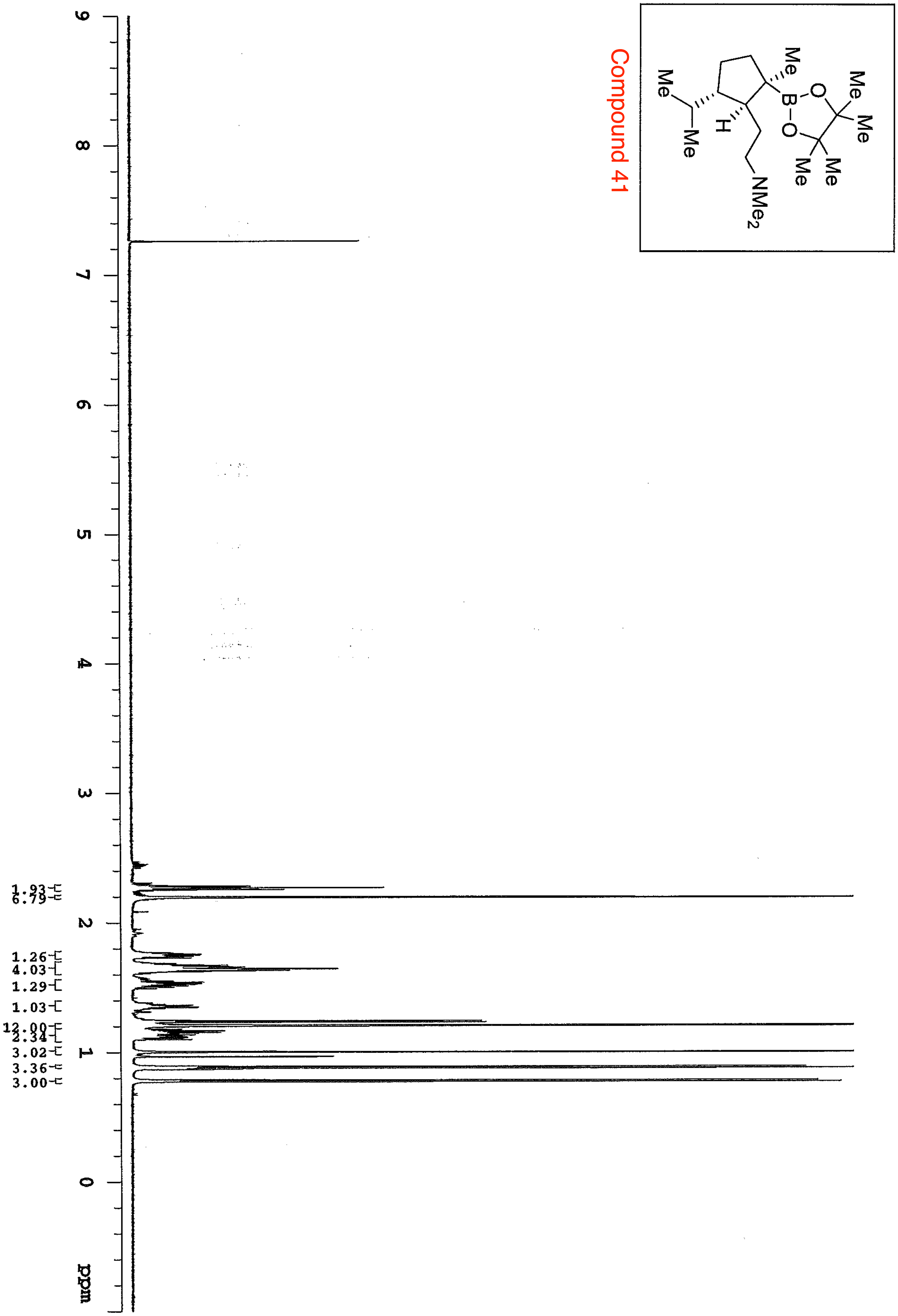

Compound S17



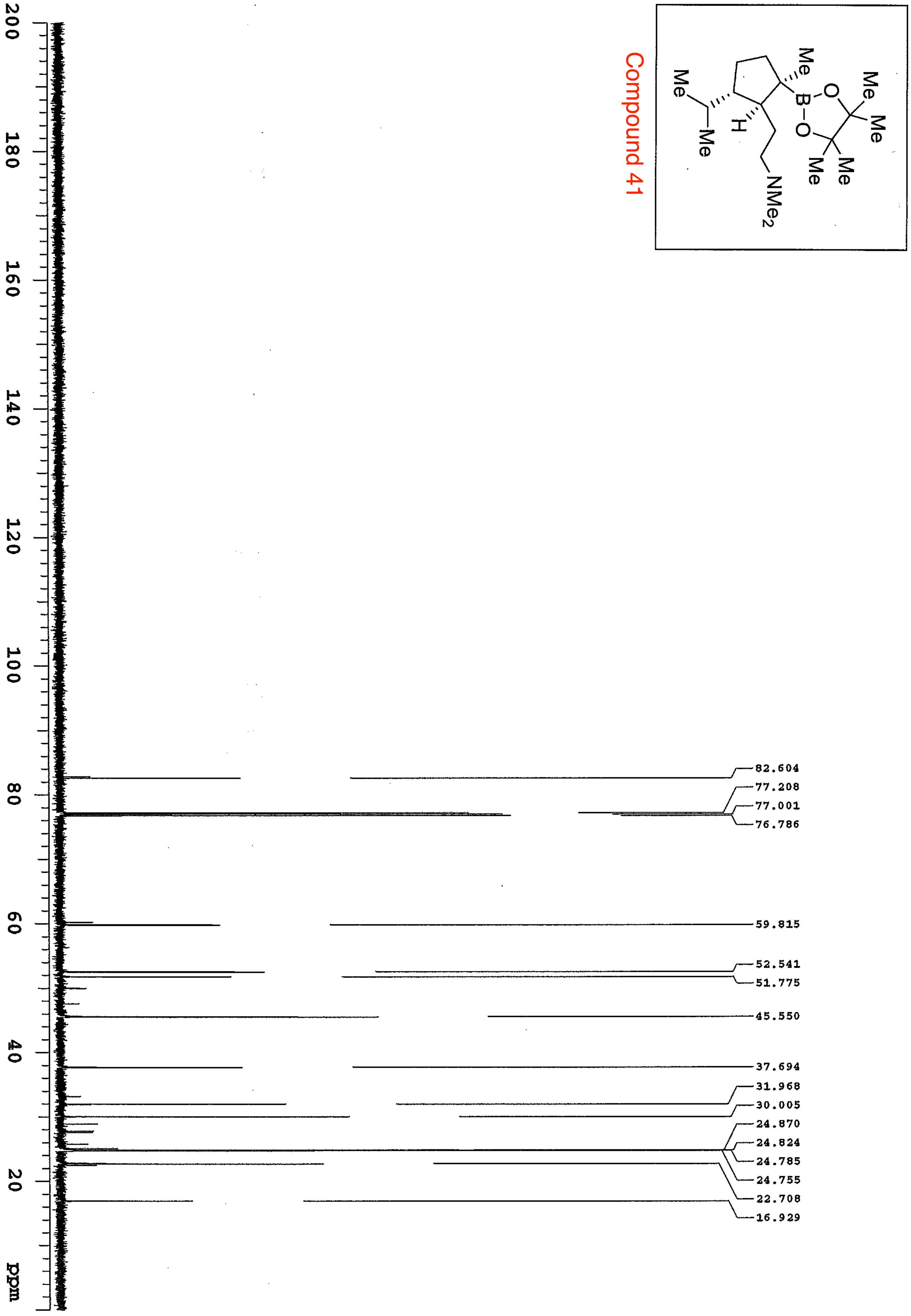
Compound 40


200
180
160
140
120
100
80
60
40
20
ppm
141.174
114.867
82.819
82.803
77.208
77.001
76.786
51.008
31.822
31.247
29.668
24.732
24.693
24.617
20.577
18.791
15.986
Me
Me
Me
Me
O
O
B
Me
B
O
O
Me
Me
Me
Me
Me
Me

Compound 40

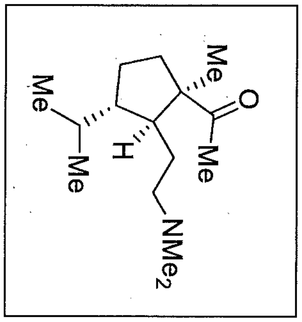

Me
Me
O
B
O
Me
Me
Me
H
NMe$_2$
Me
Me
9
8
7
6
5
4
3
2
1
0
ppm
1.93
6.79
1.26
4.03
1.29
1.03
12.00
2.34
3.02
3.36
3.00

Compound 41

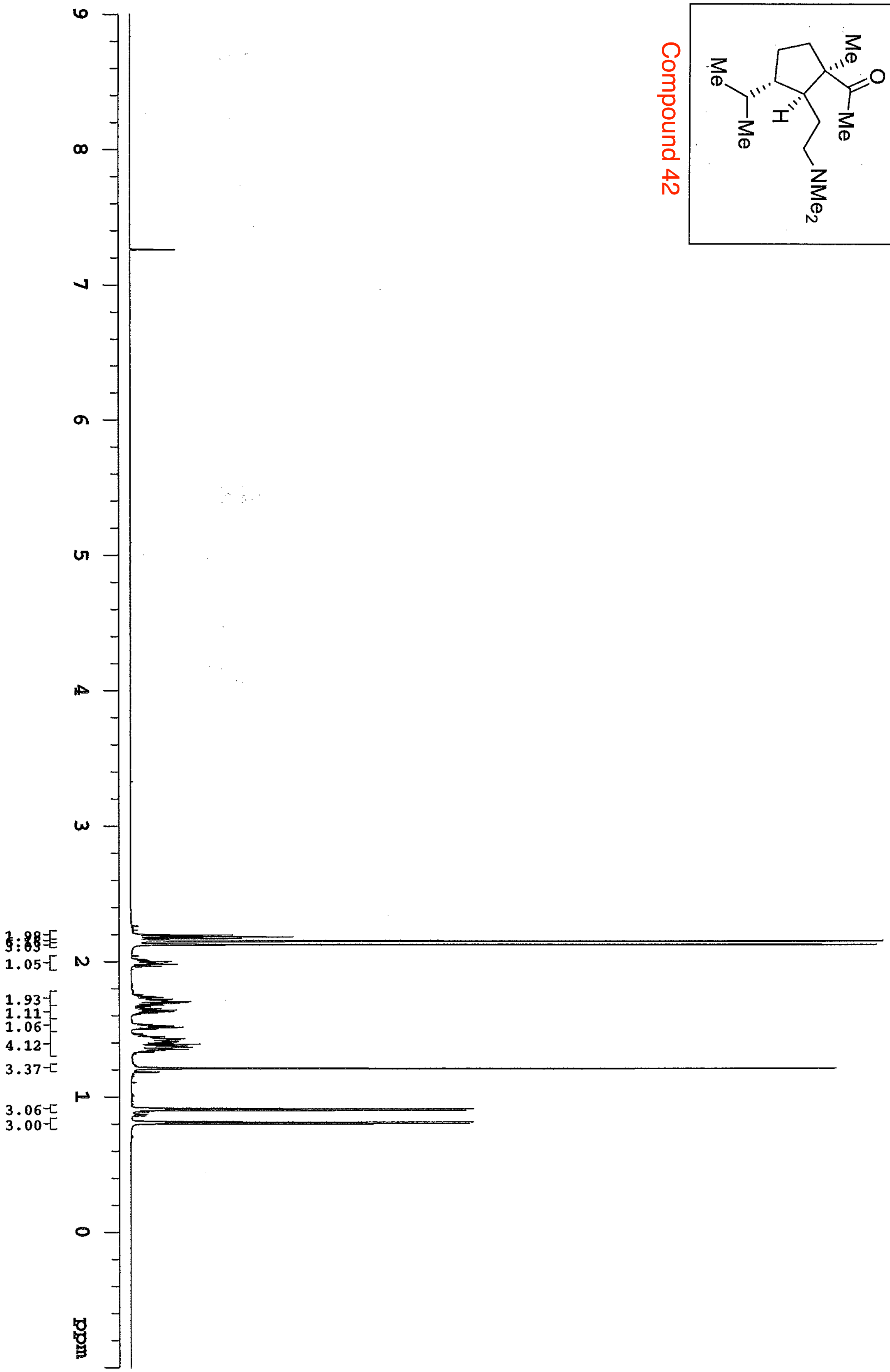


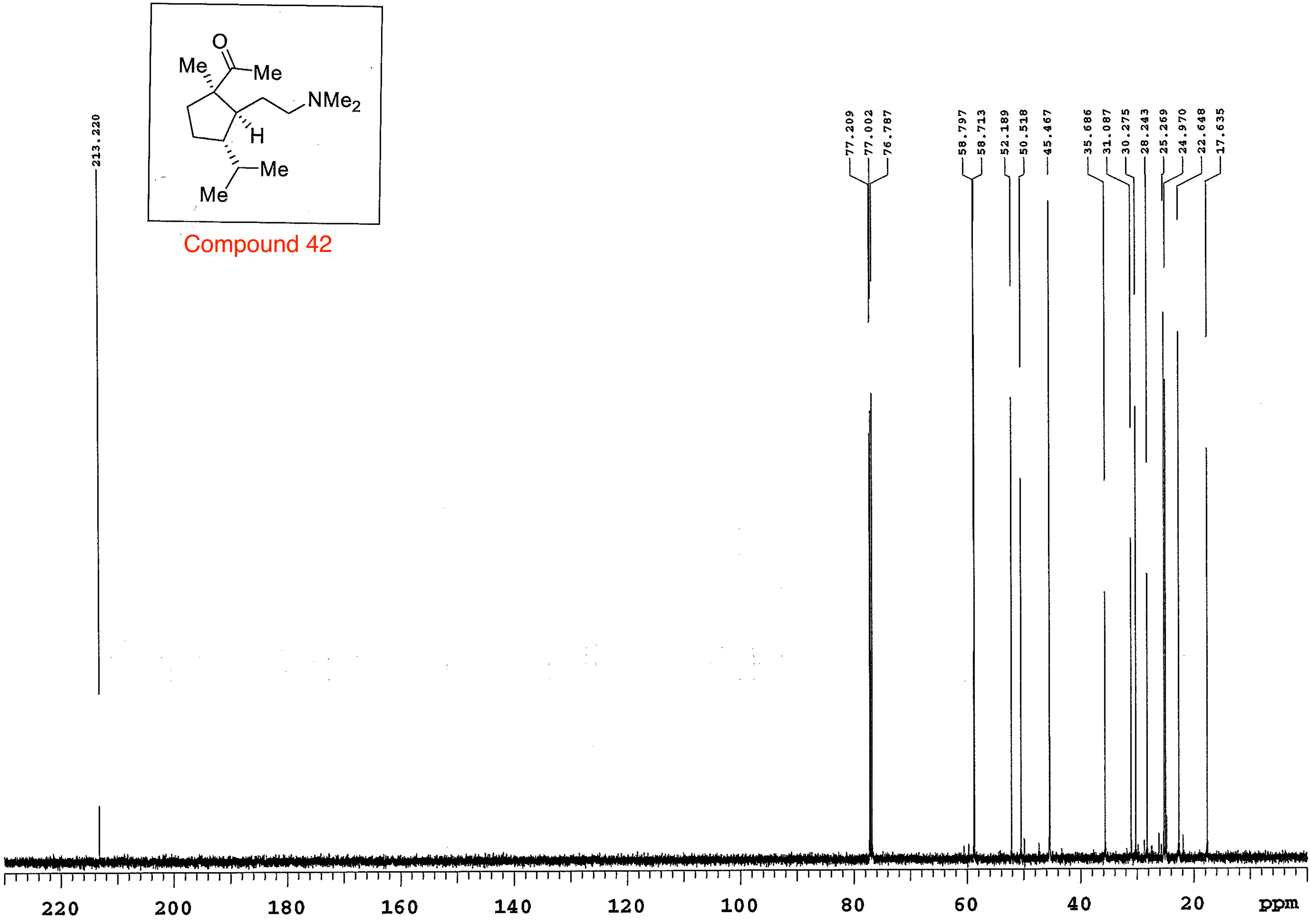
Compound 41

Me
Me
O
B
O
Me
Me
Me
H
NMe2
Me
Me
200
180
160
140
120
100
80
60
40
20
ppm
82.604
77.208
77.001
76.786
59.815
52.541
51.775
45.550
37.694
31.968
30.005
24.870
24.824
24.785
24.755
22.708
16.929

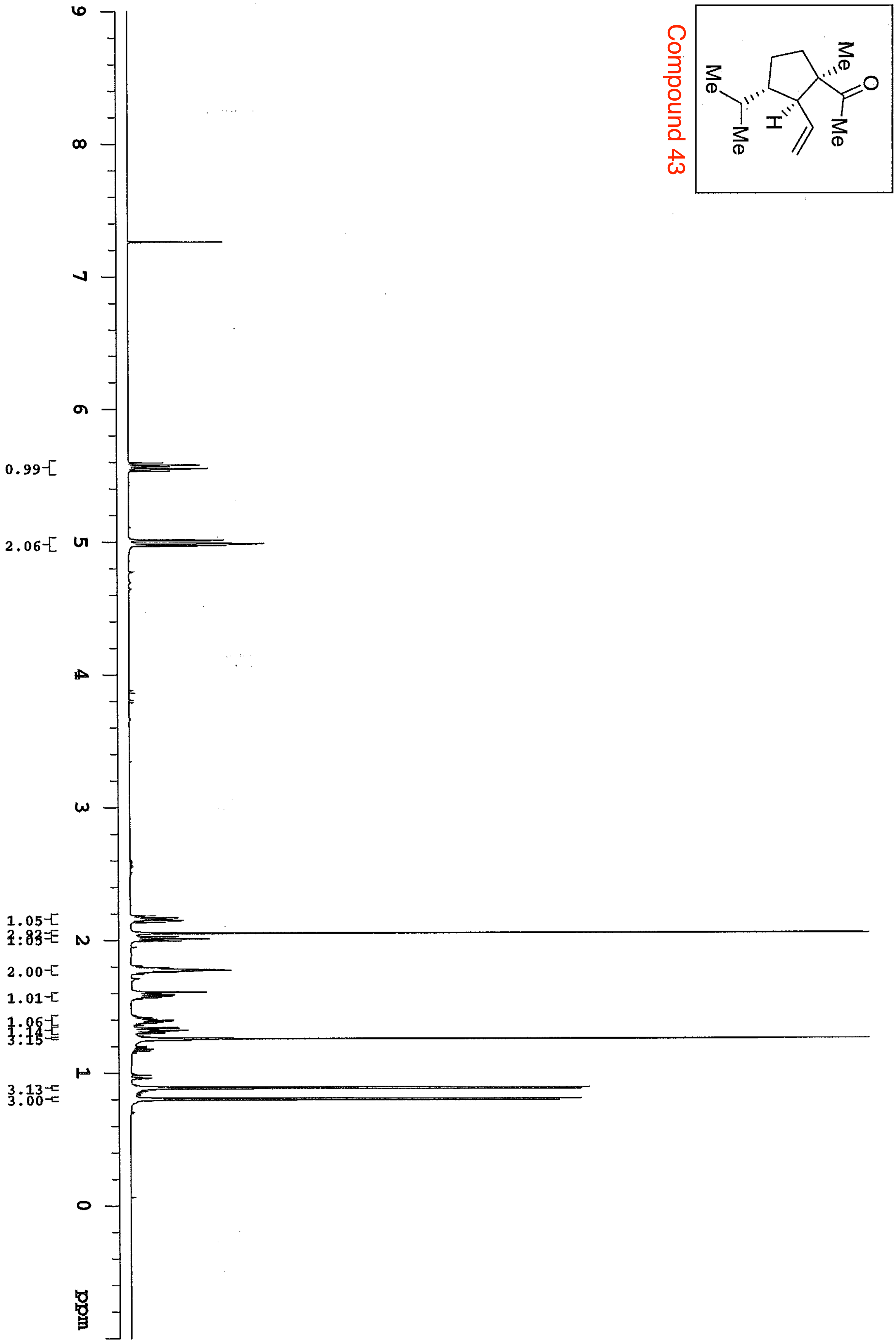

Me
O
Me
H
Me
Me
NMe$_2$

Compound 42

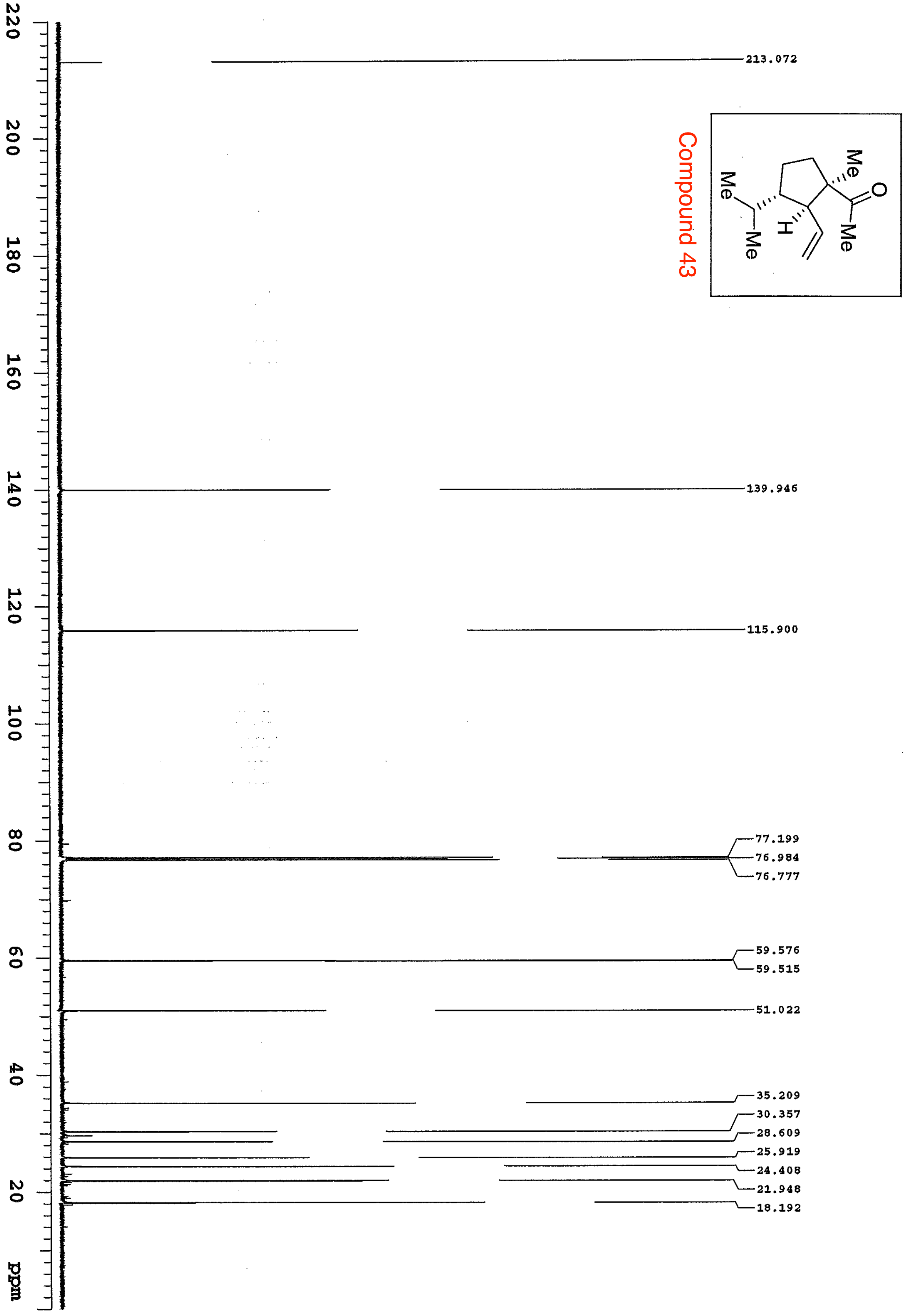

9
8
7
6
5
4
3
2
1
0
ppm
1.98
3.03
1.05
1.93
1.11
1.06
4.12
3.37
3.06
3.00


213.220
77.209
77.002
76.787
58.797
58.713
52.189
50.518
45.467
35.686
31.087
30.275
28.243
25.269
24.970
22.648
17.635
220
200
180
160
140
120
100
80
60
40
20
ppm
Me
O
Me
NMe2
H
Me
Me

Compound 42

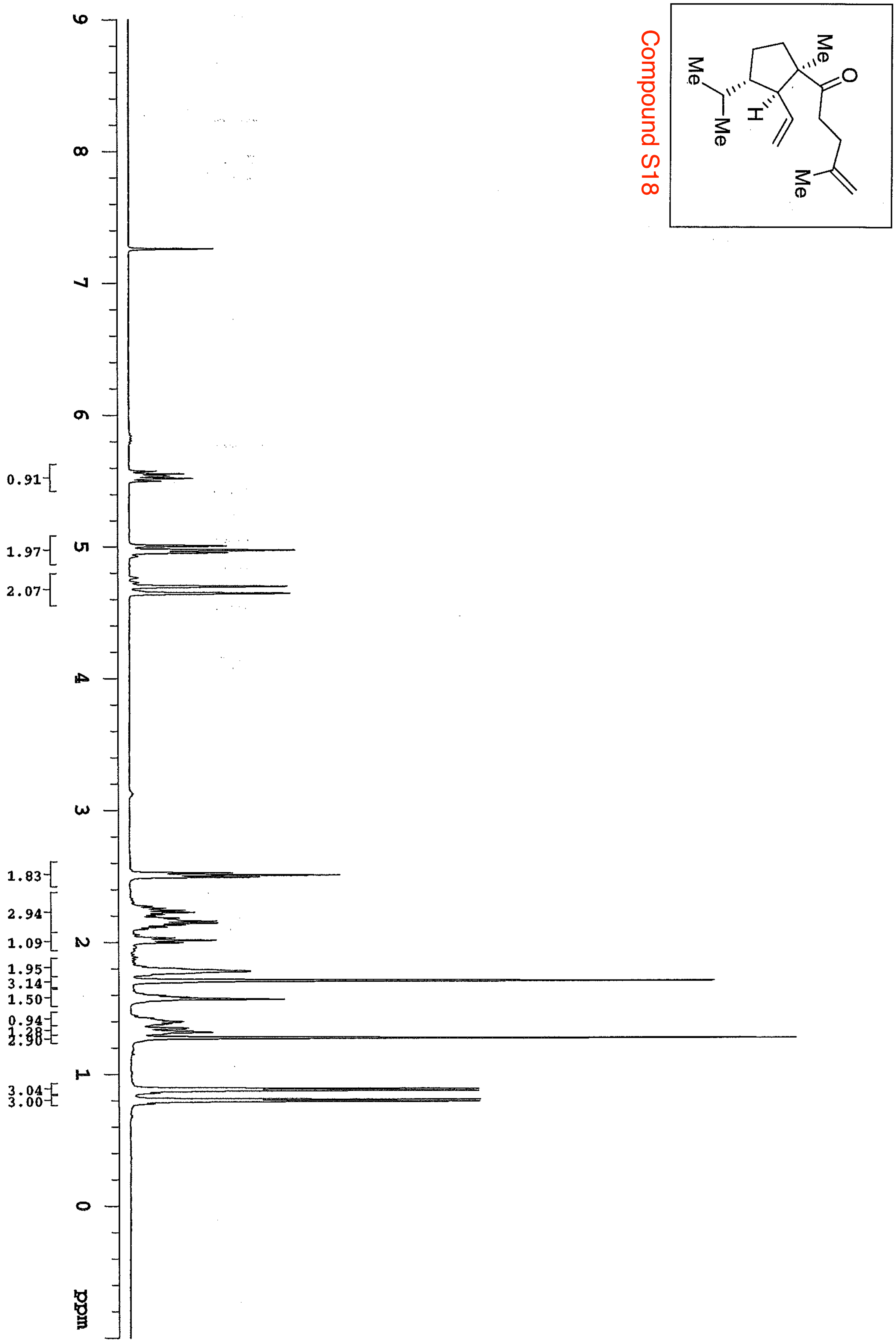

9
8
7
6
5
4
3
2
1
0
ppm
0.99
2.06
1.05
2.92
1.03
2.00
1.01
1.06
1.14
3.15
3.13
3.00
O
Me
Me
H
Me
Me

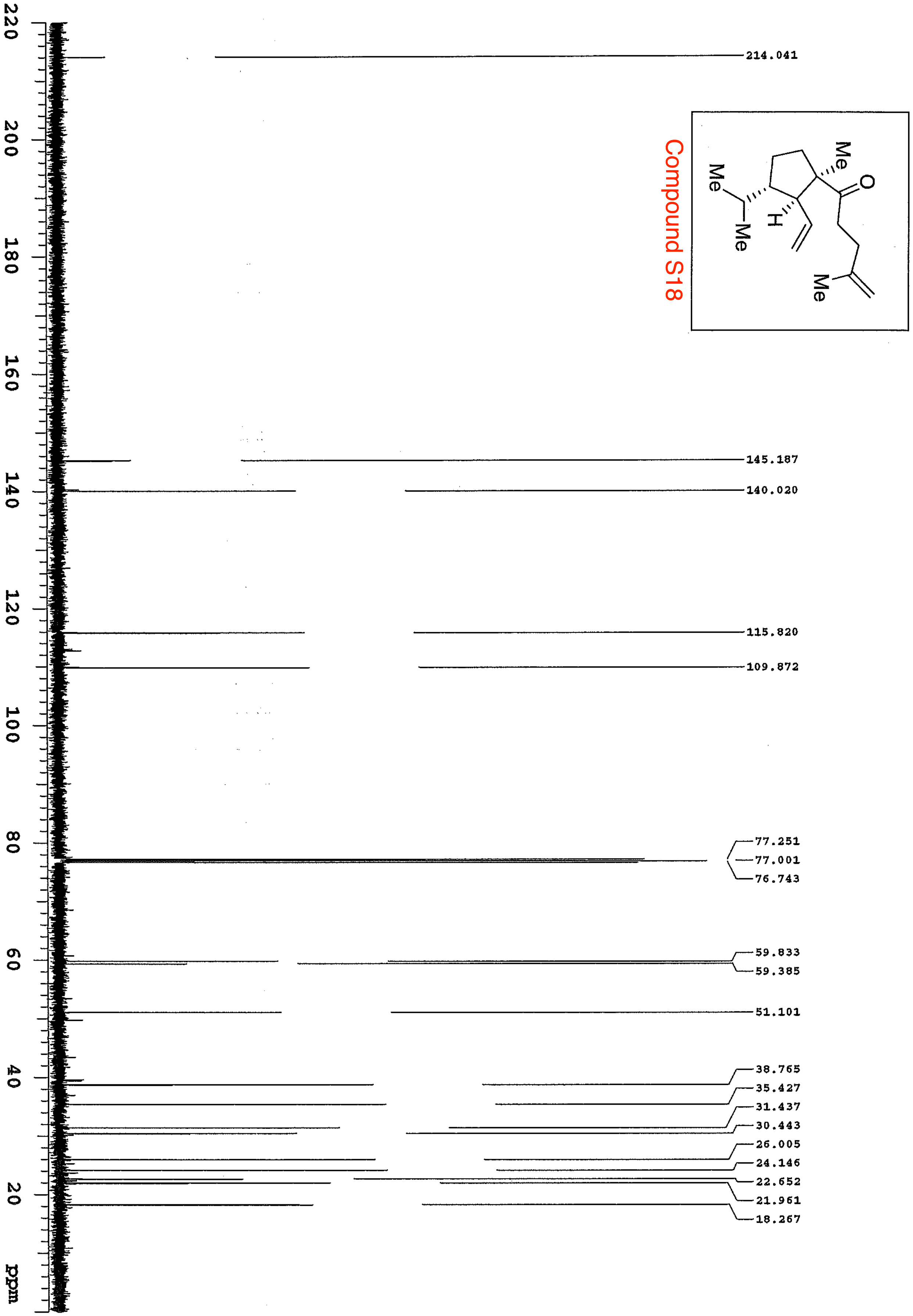
Compound 43

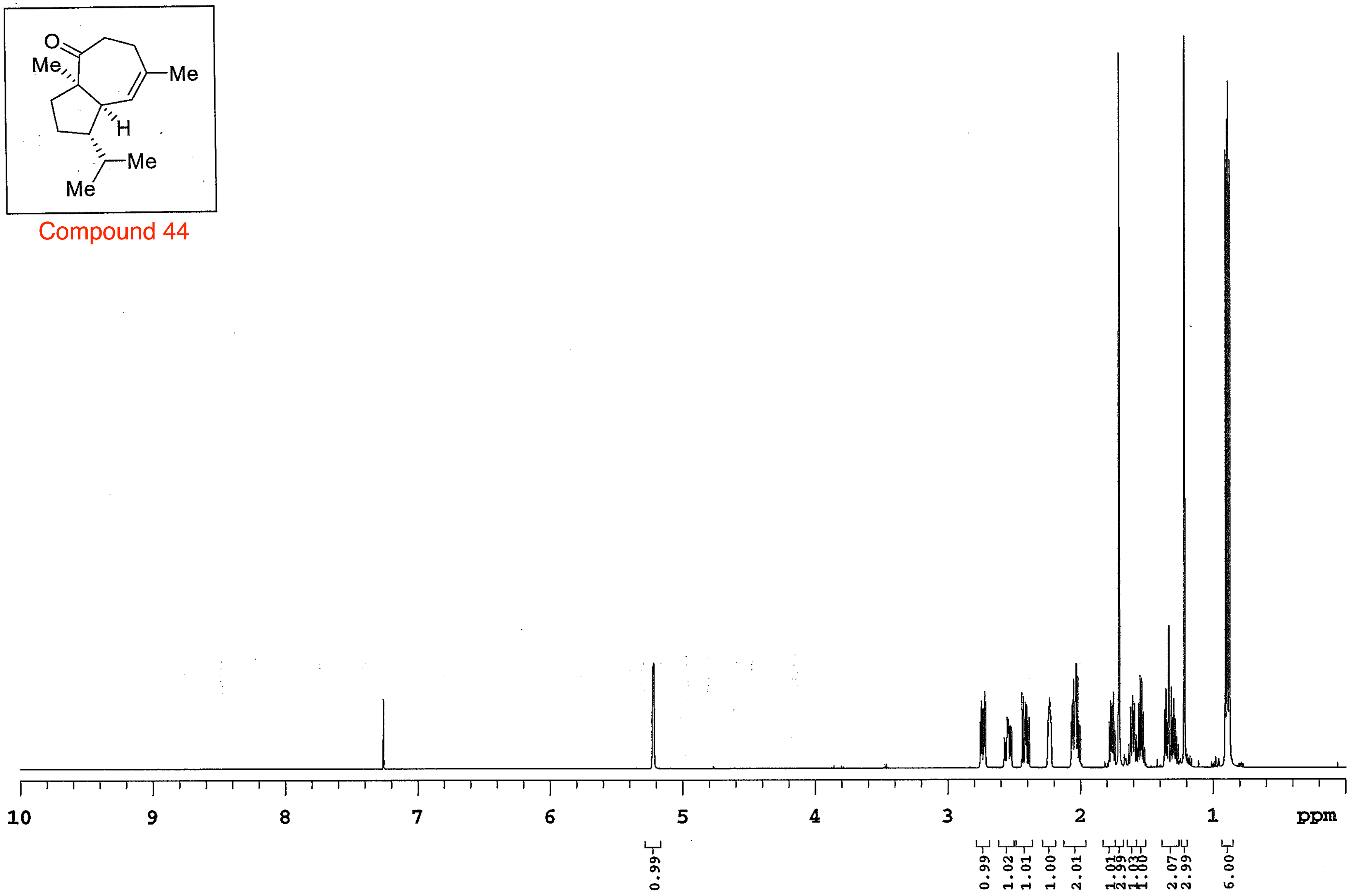

220
200
180
160
140
120
100
80
60
40
20
ppm
213.072
139.946
115.900
77.199
76.984
76.777
59.576
59.515
51.022
35.209
30.357
28.609
25.919
24.408
21.948
18.192
Me
O
Me
H
Me
Me

Compound 43

Compound S18

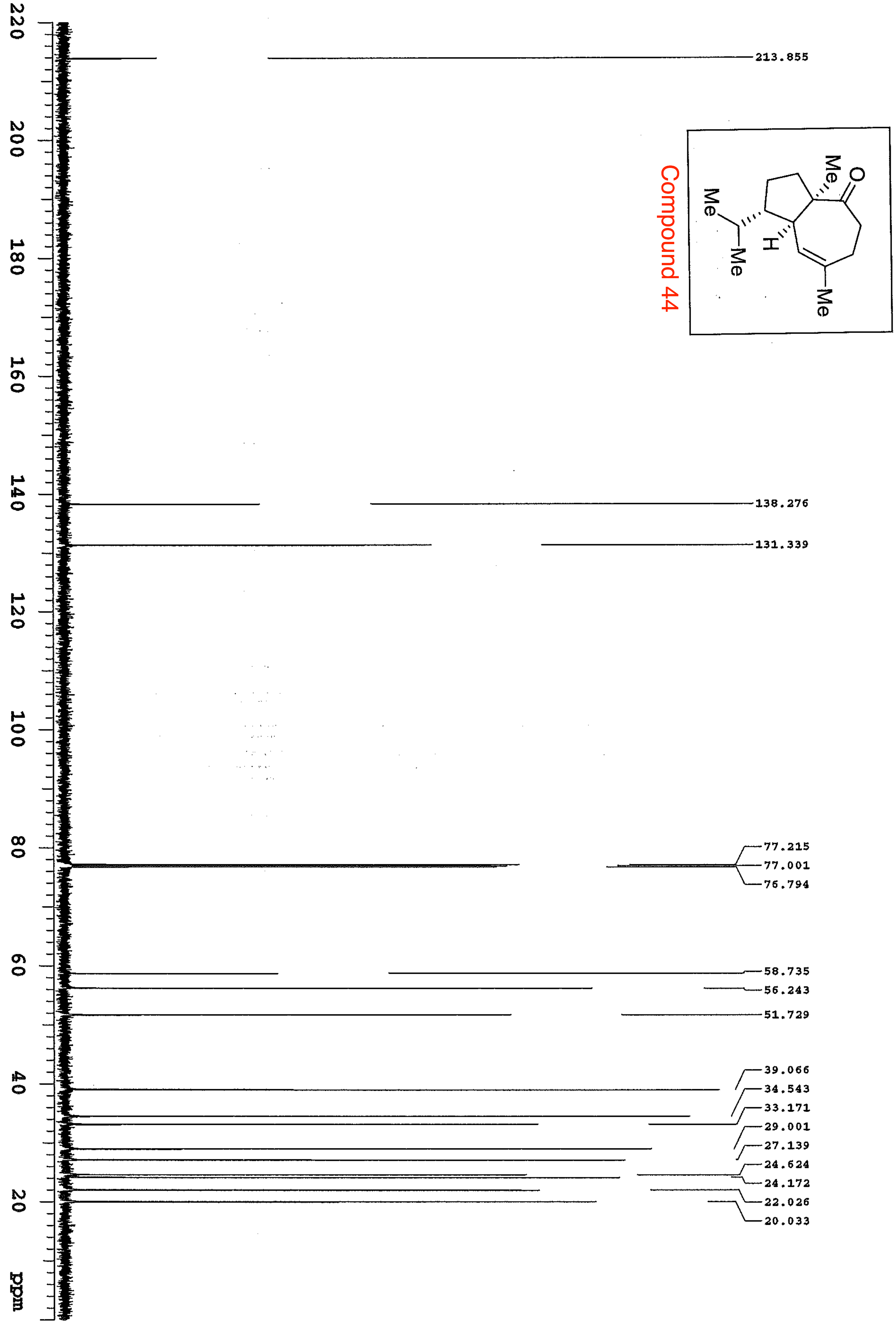


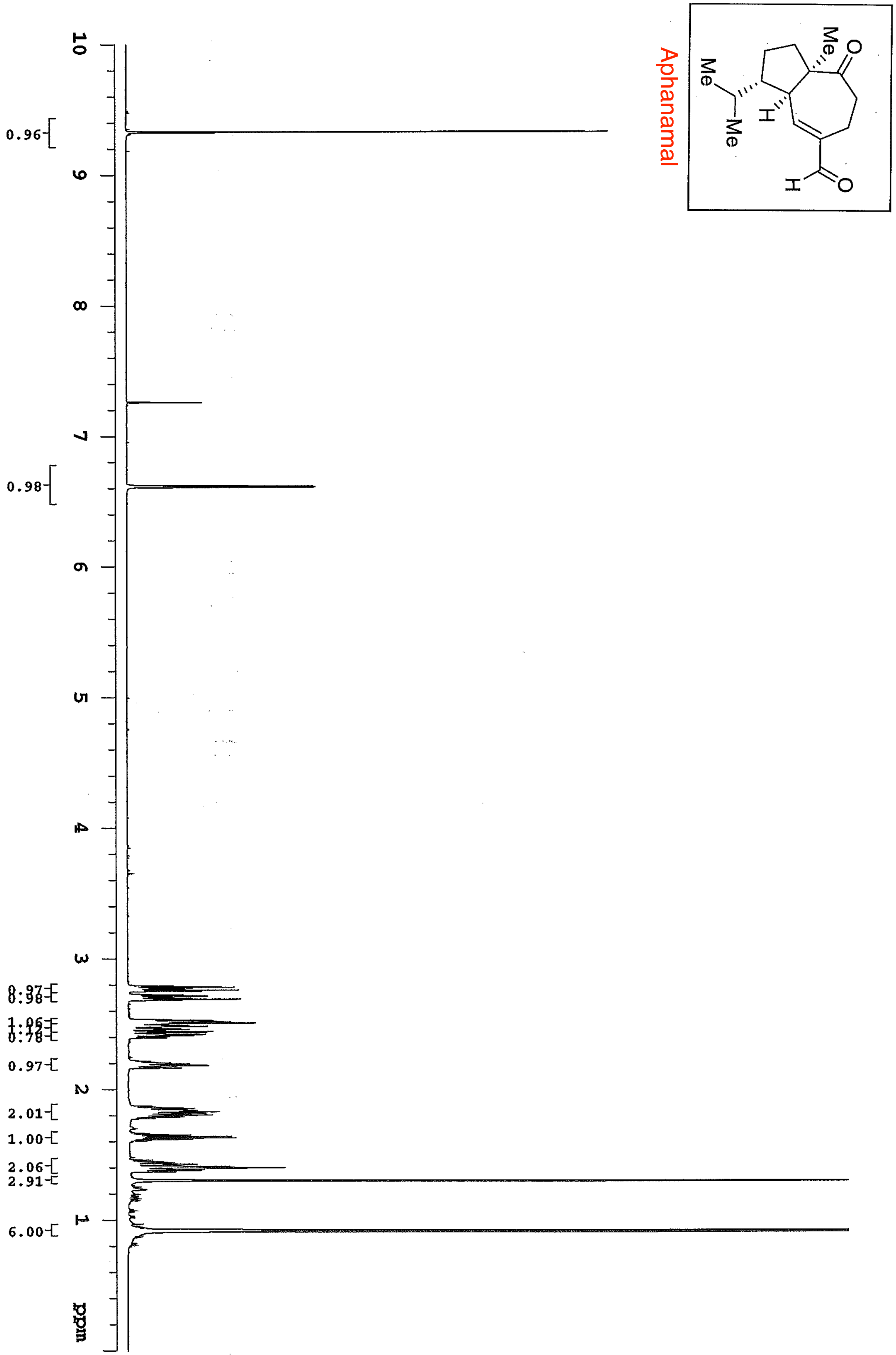

Compound S18



Compound 44

O
Me
Me
H
Me
Me
10
9
8
7
6
5
4
3
2
1
ppm
0.99
0.99
1.02
1.01
1.00
2.01
1.01
2.99
1.03
1.00
2.07
2.99
6.00

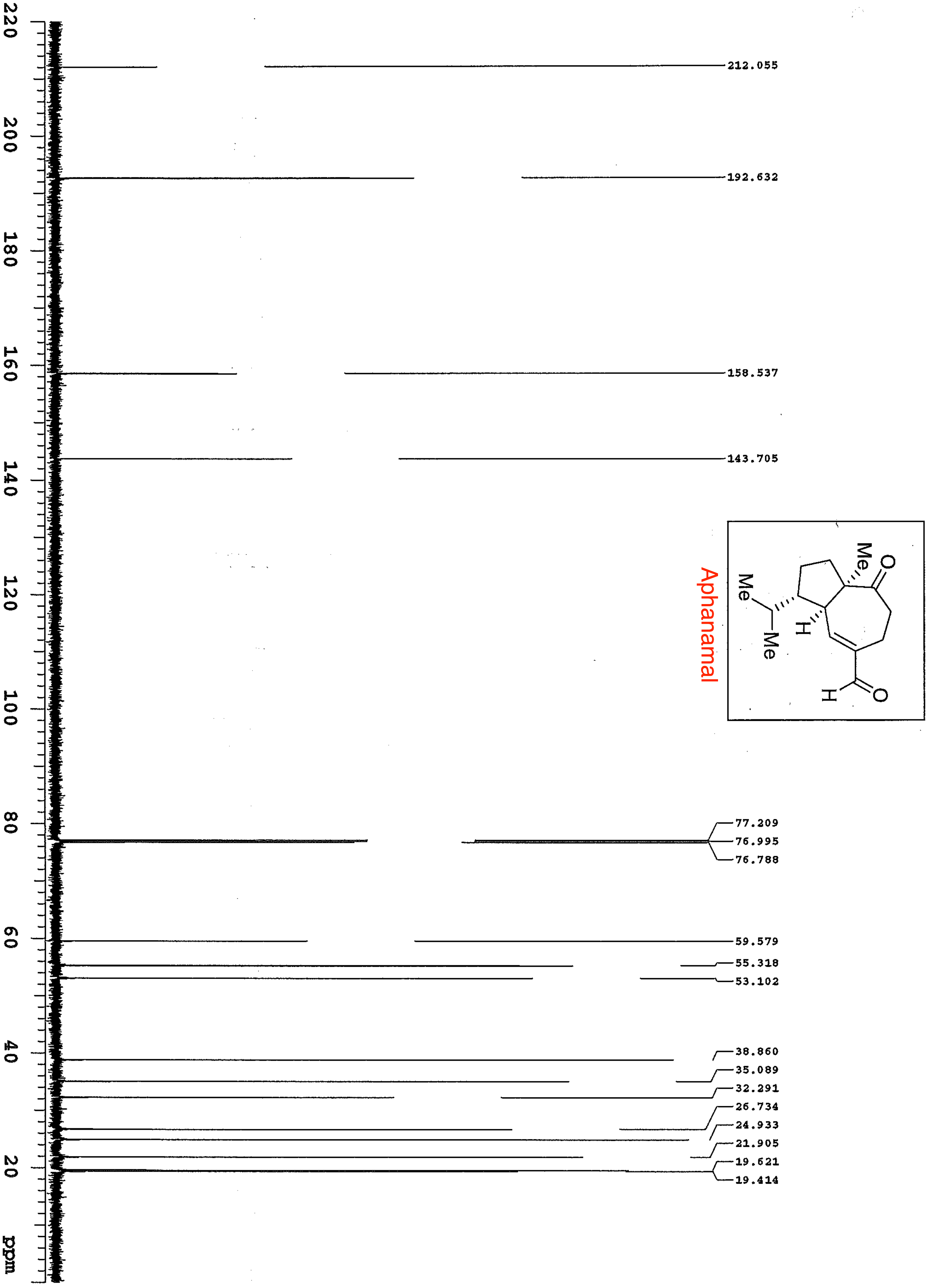

Compound 44
Me
O
Me
H
Me
Me
Me
213.855
138.276
131.339
77.215
77.001
76.794
58.735
56.243
51.729
39.066
34.543
33.171
29.001
27.139
24.624
24.172
22.026
20.033
220
200
180
160
140
120
100
80
60
40
20
ppm

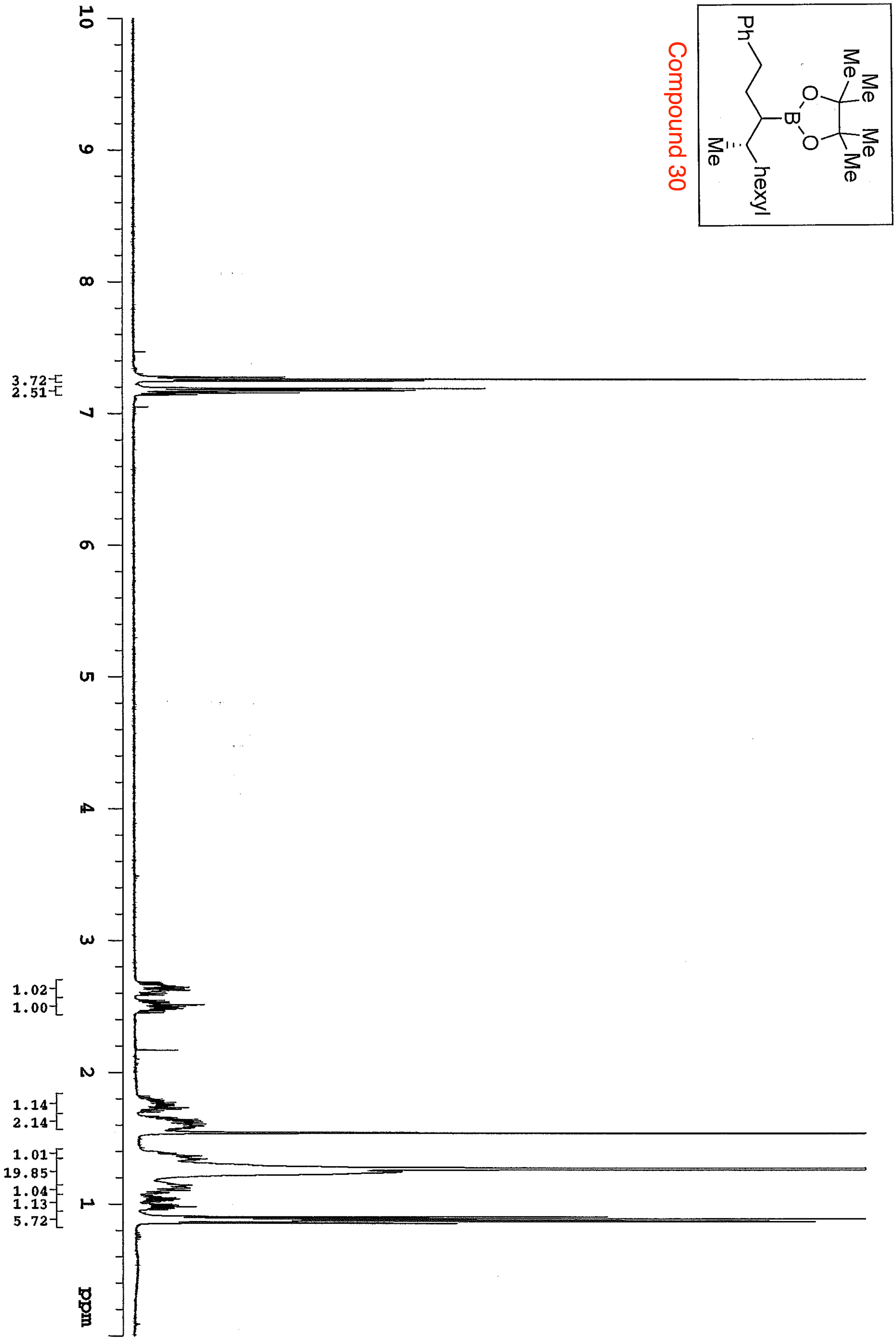


O
Me
H
Me
Me
H
O

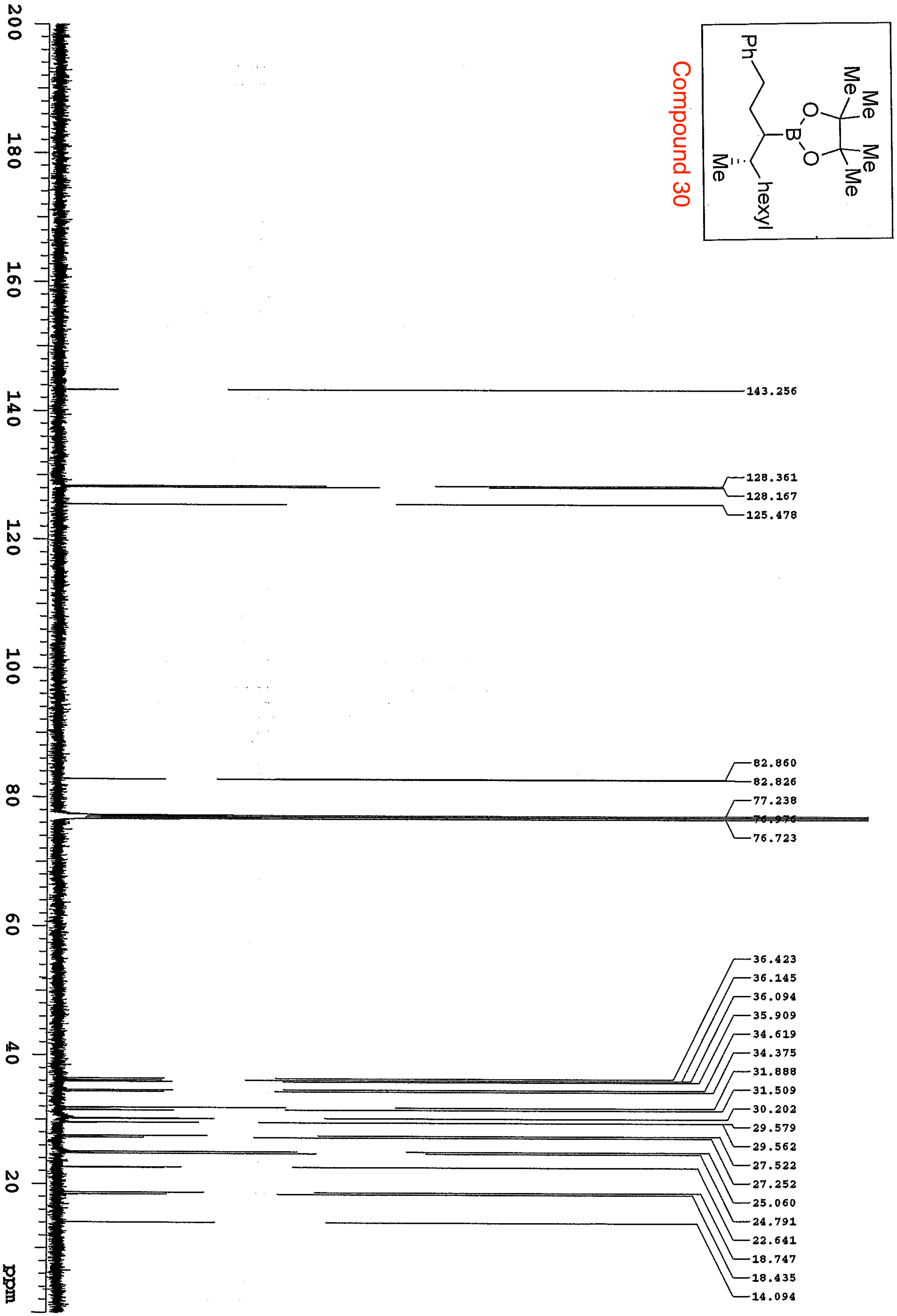
Aphanamal

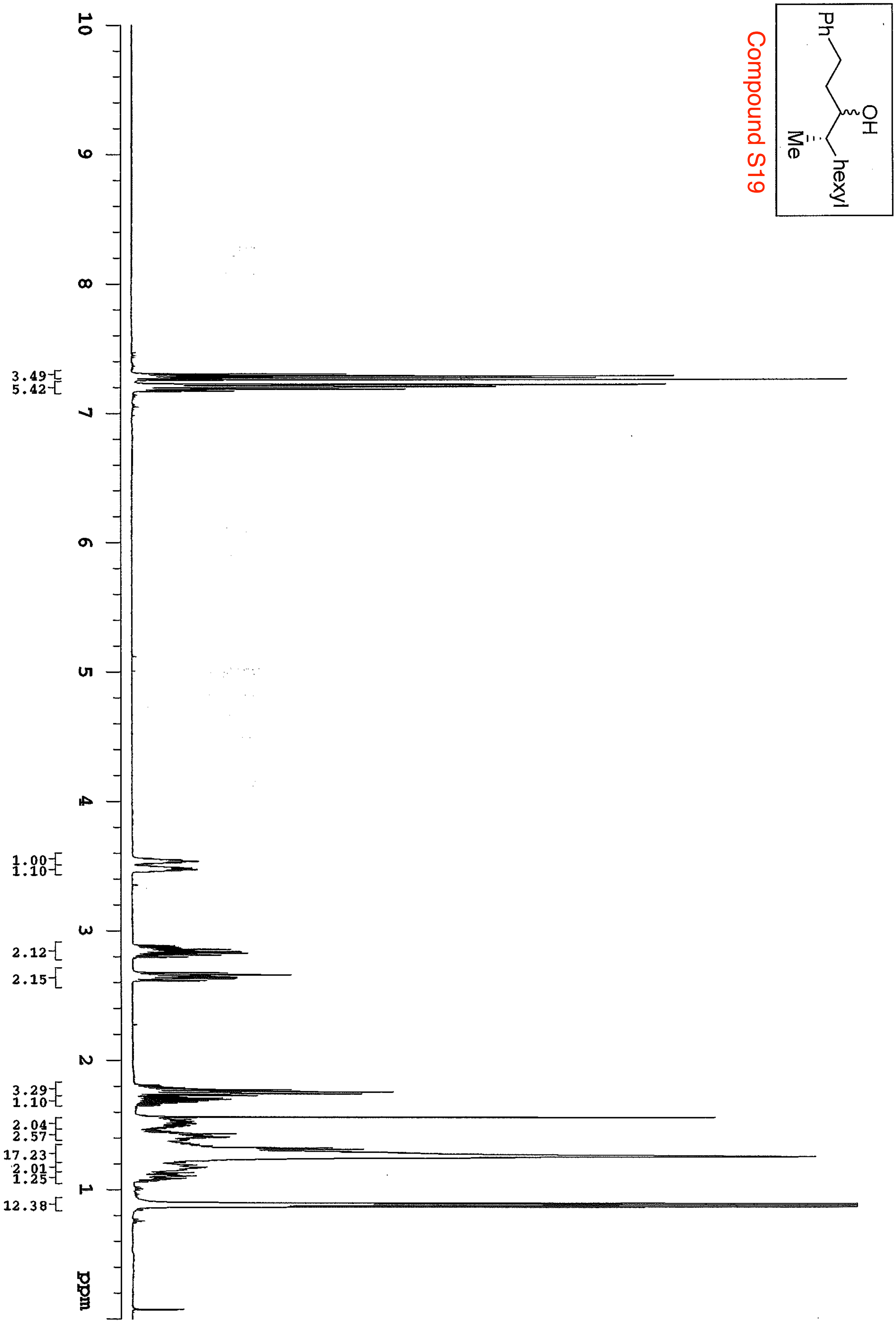
10
9
8
7
6
5
4
3
2
1
ppm
0.96
0.98
0.97
0.98
1.06
0.78
0.97
2.01
1.00
2.06
2.91
6.00


Aphanamal
Me
O
Me
Me
H
H
O
220
200
180
160
140
120
100
80
60
40
20
ppm
212.055
192.632
158.537
143.705
77.209
76.995
76.788
59.579
55.318
53.102
38.860
35.089
32.291
26.734
24.933
21.905
19.621
19.414

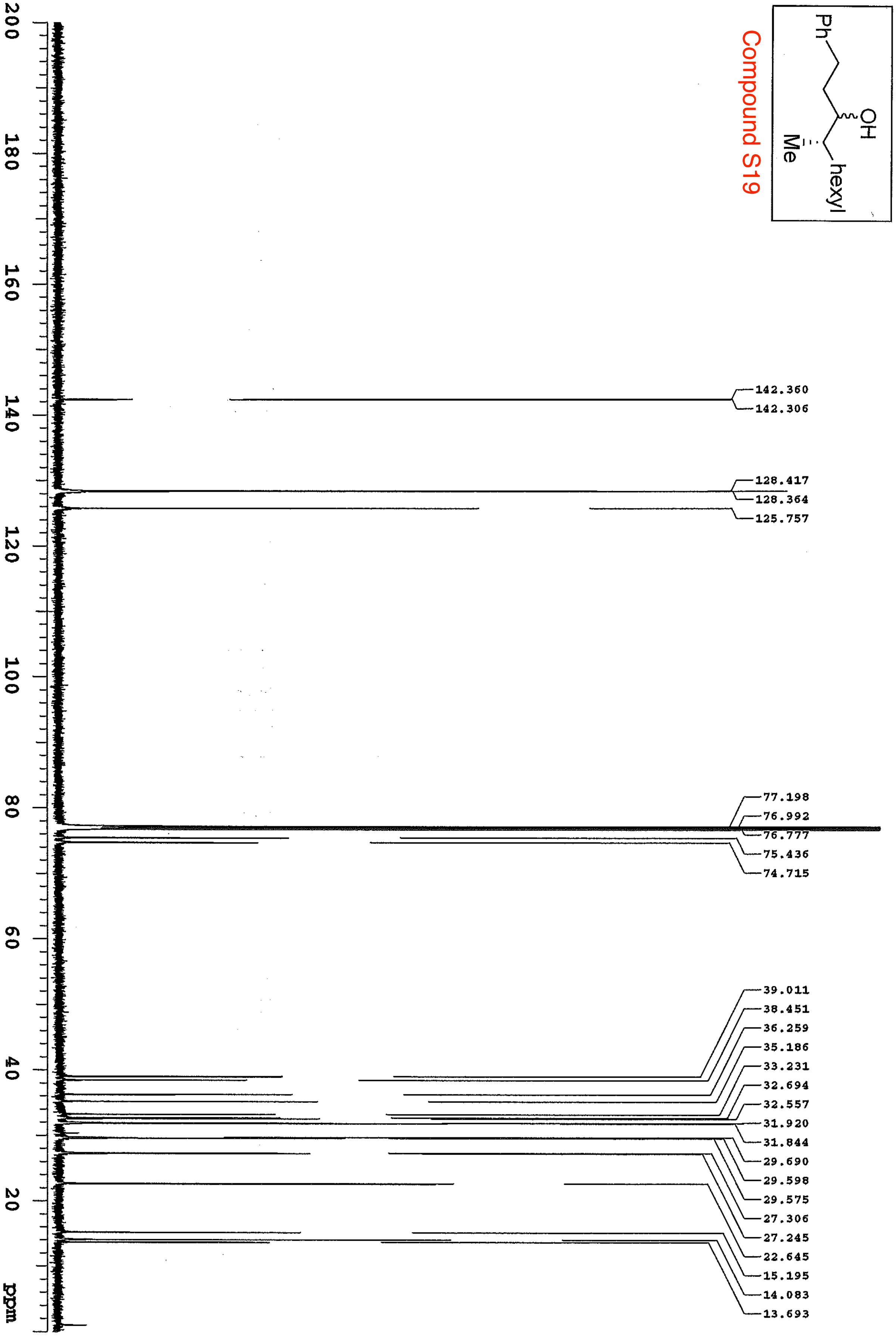

Me
Me
Me
Me
O
B
O
Ph
hexyl
Me
10
9
8
7
6
5
4
3
2
1
ppm
3.72
2.51
1.02
1.00
1.14
2.14
1.01
19.85
1.04
1.13
5.72

Compound 30

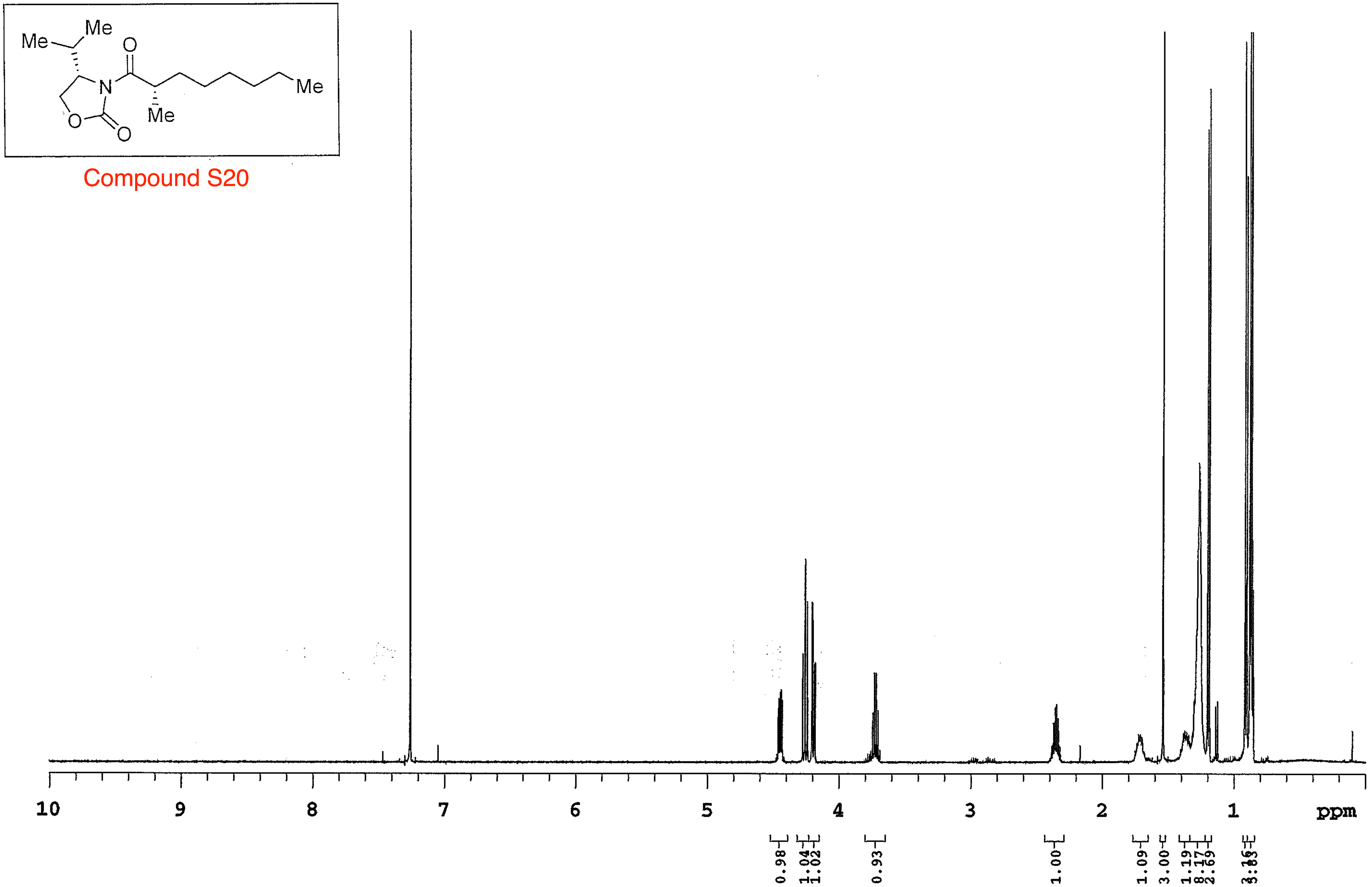

Me
Me
Me
Me
O
B
O
Ph
hexyl
Me
Compound 30
143.256
128.361
128.167
125.478
82.860
82.826
77.238
76.976
76.723
36.423
36.145
36.094
35.909
34.619
34.375
31.888
31.509
30.202
29.579
29.562
27.522
27.252
25.060
24.791
22.641
18.747
18.435
14.094
200
180
160
140
120
100
80
60
40
20
ppm



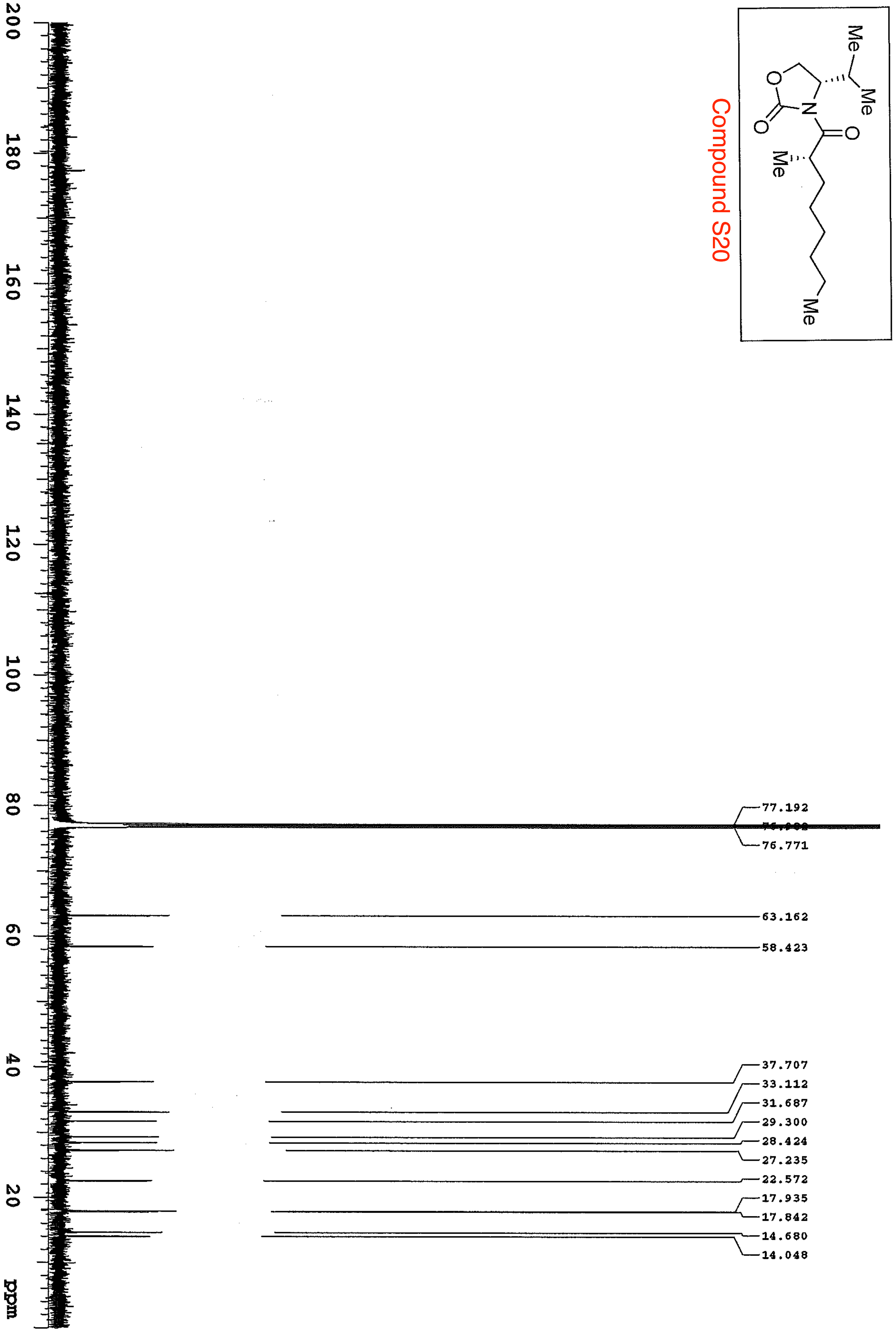
Compound S19



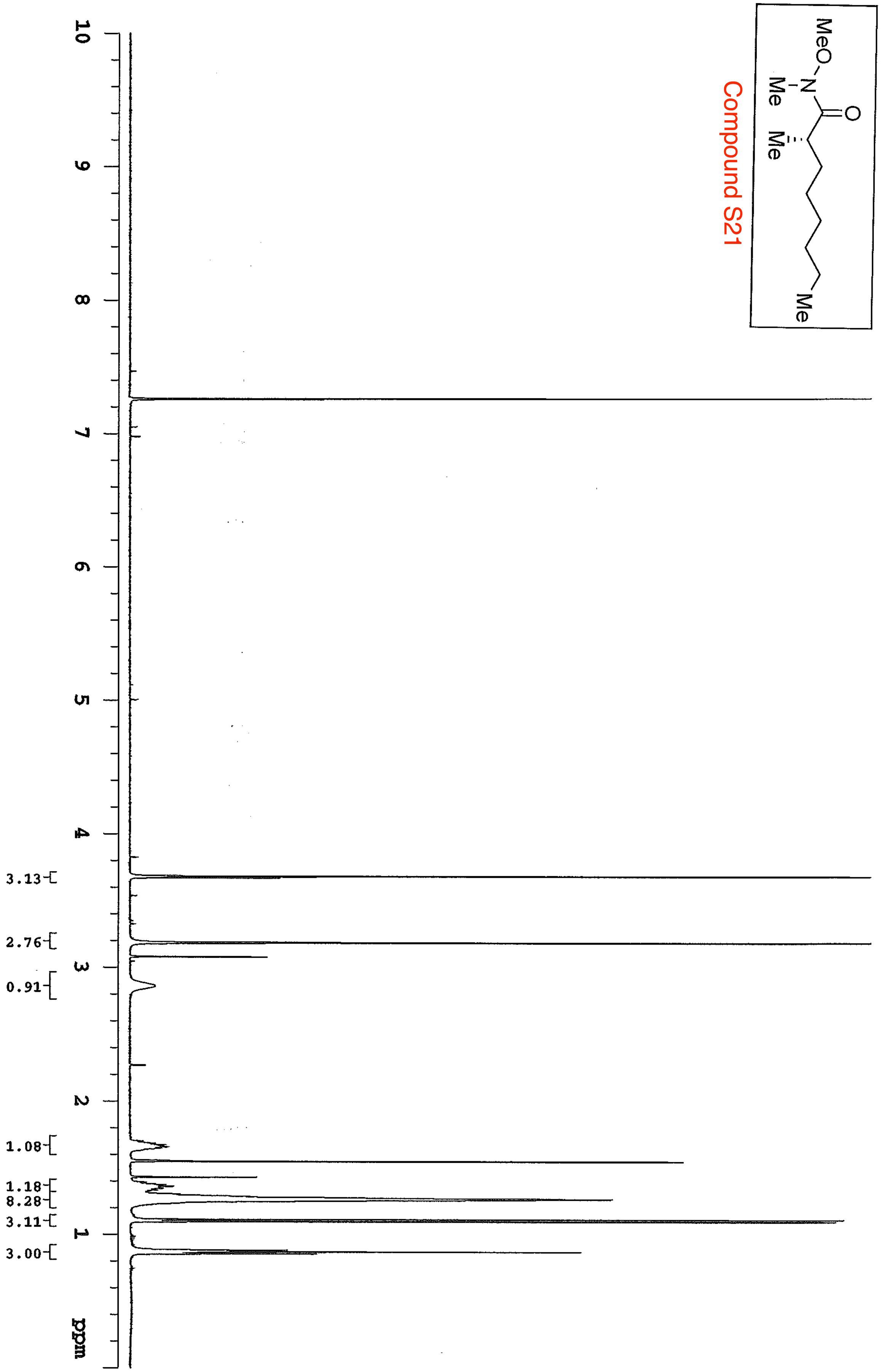
Compound S19



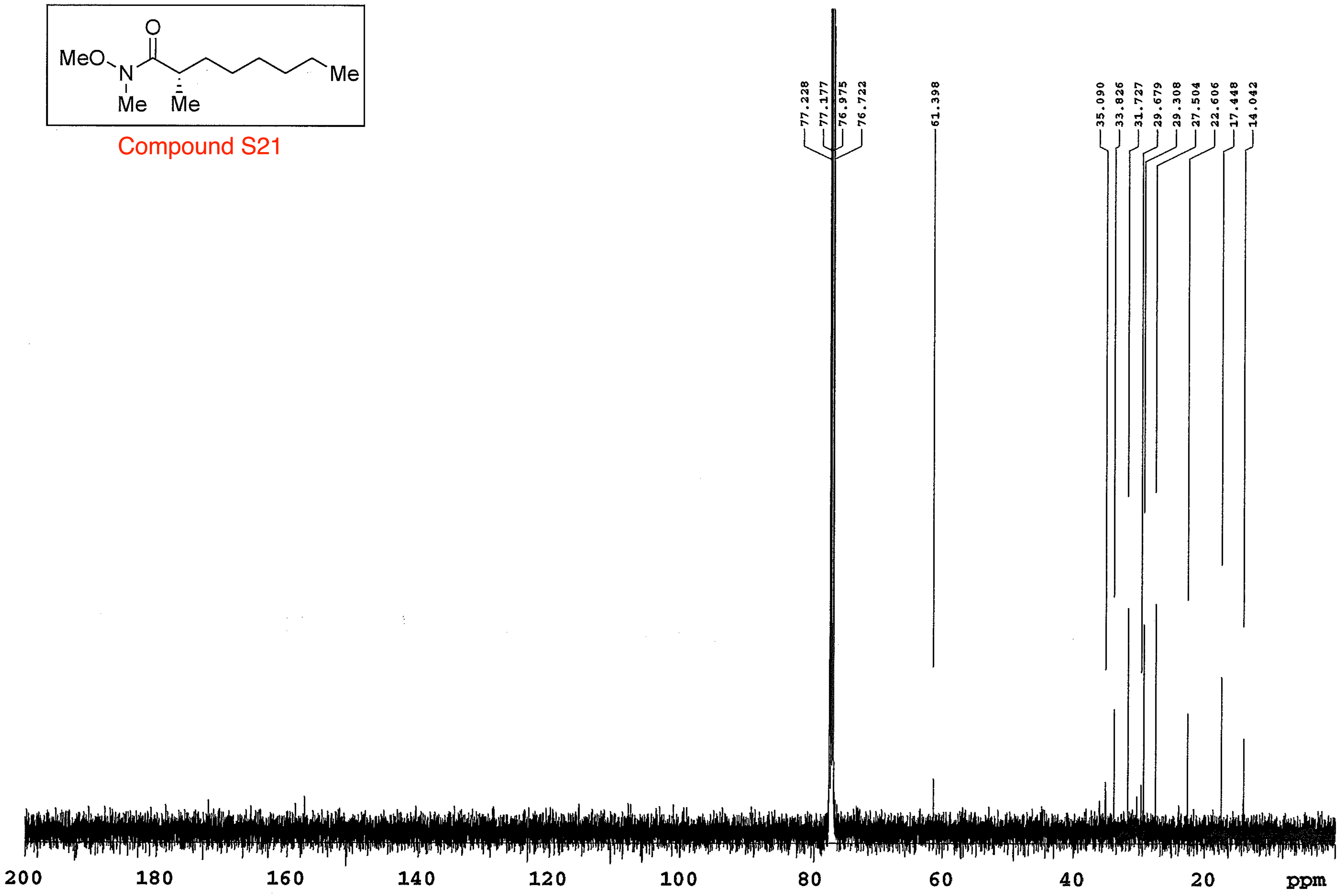
Compound S20



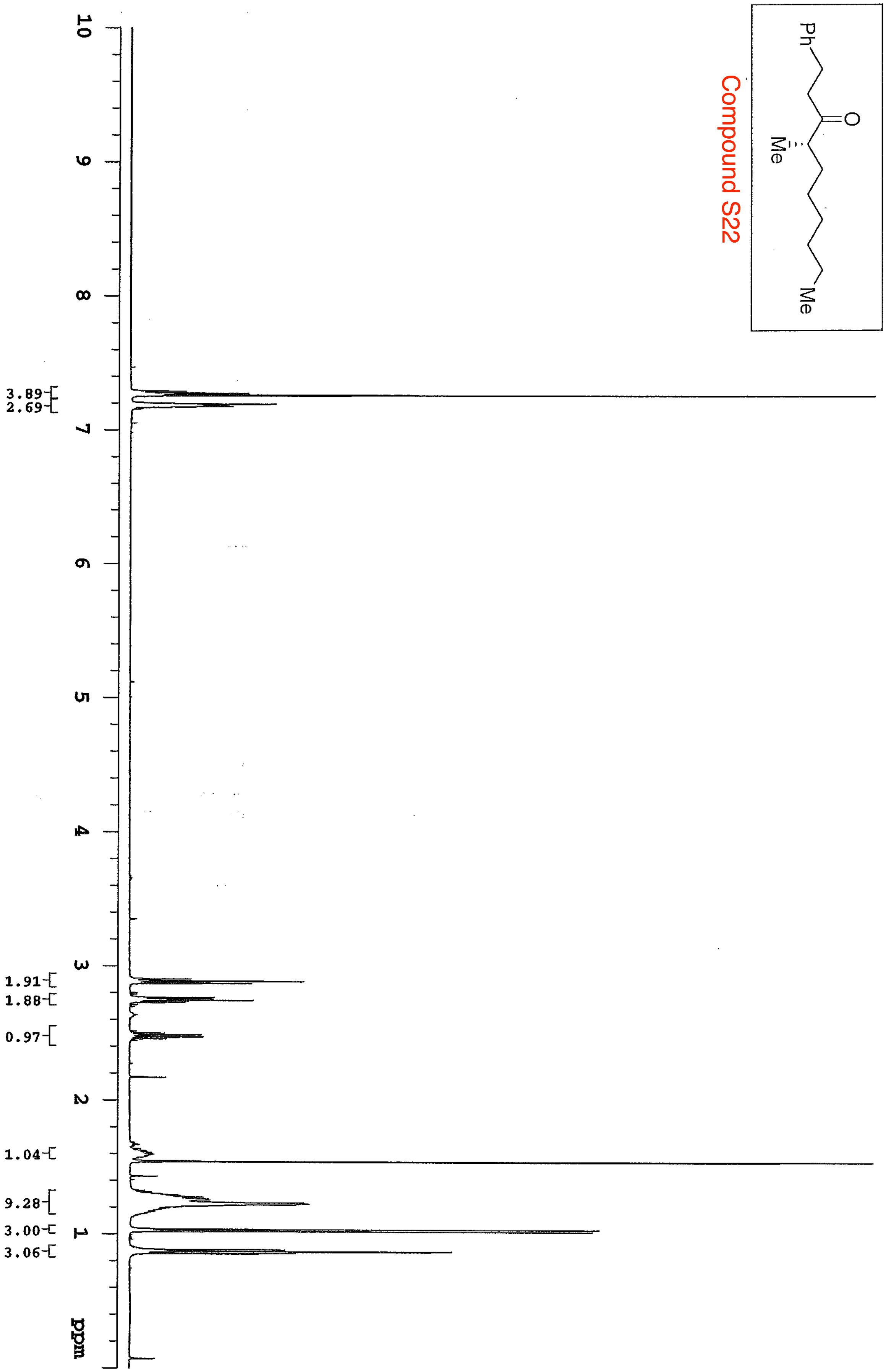
Compound S20



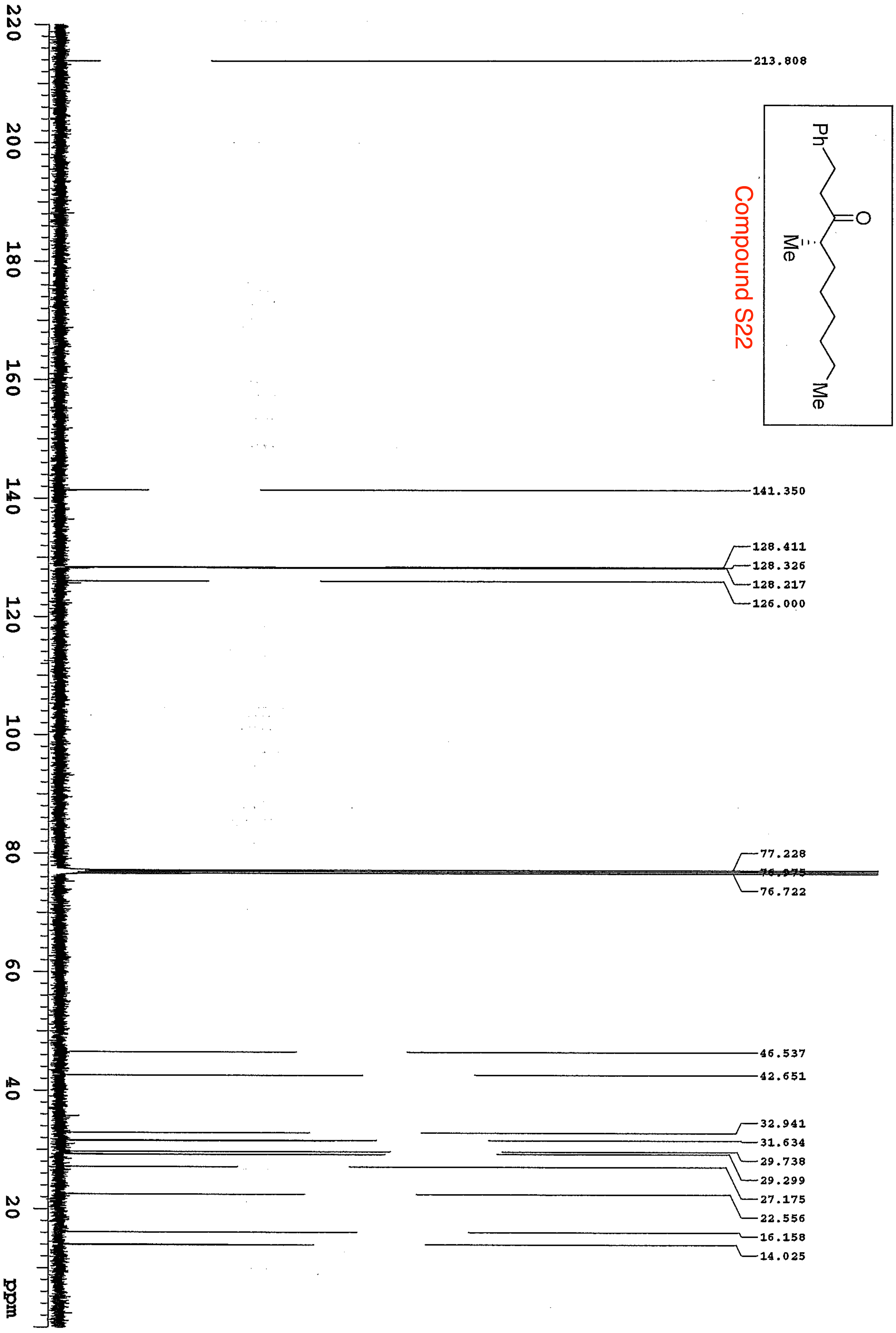
Compound S21



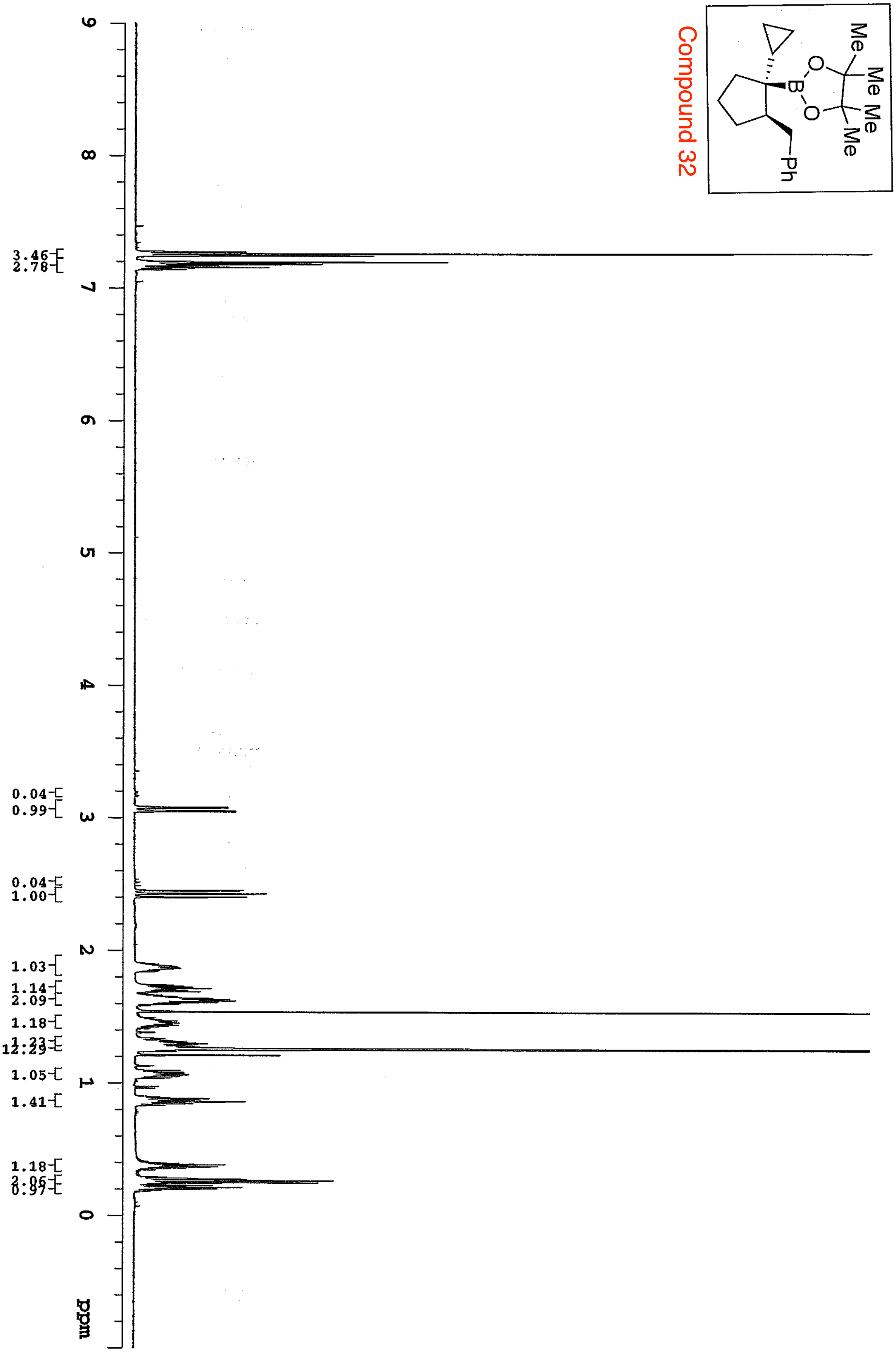
Compound S21



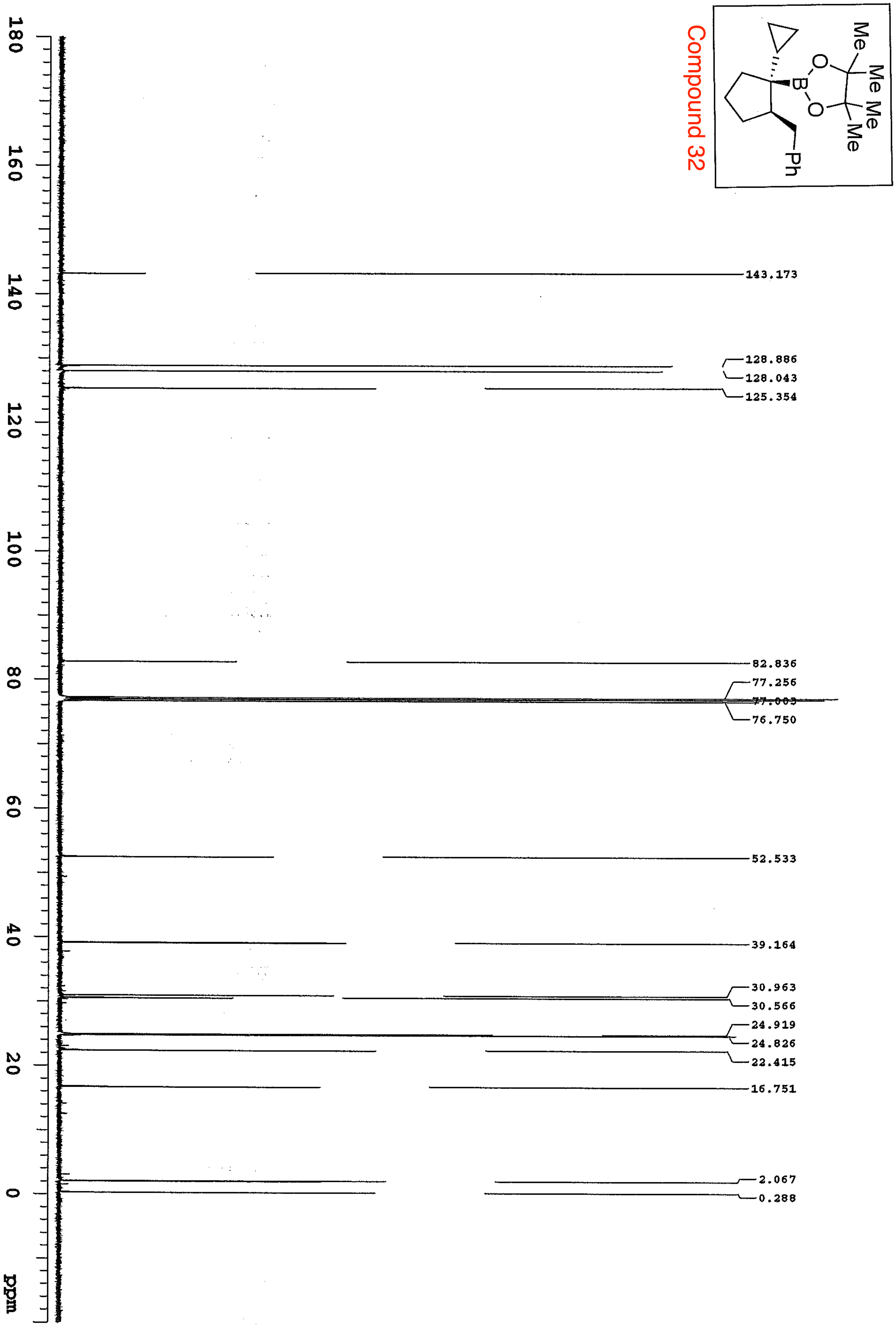
Compound S22



Compound S22

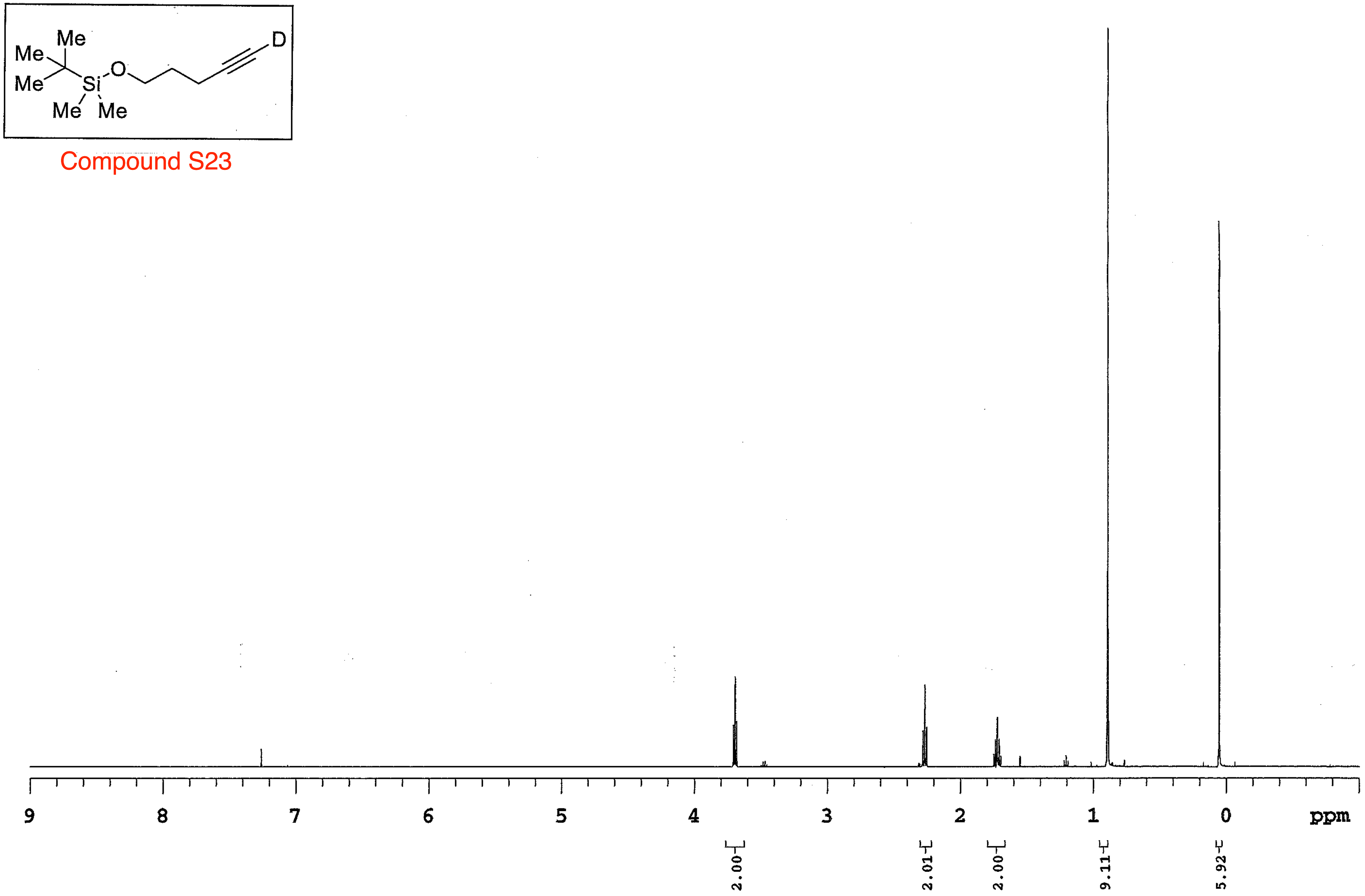

Me
Me
Me
Me
O
B
O
Ph
9
8
7
6
5
4
3
2
1
0
ppm
3.46
2.78
0.04
0.99
0.04
1.00
1.03
1.14
2.09
1.18
1.23
12.29
1.05
1.41
1.18
2.05
0.97

Compound 32

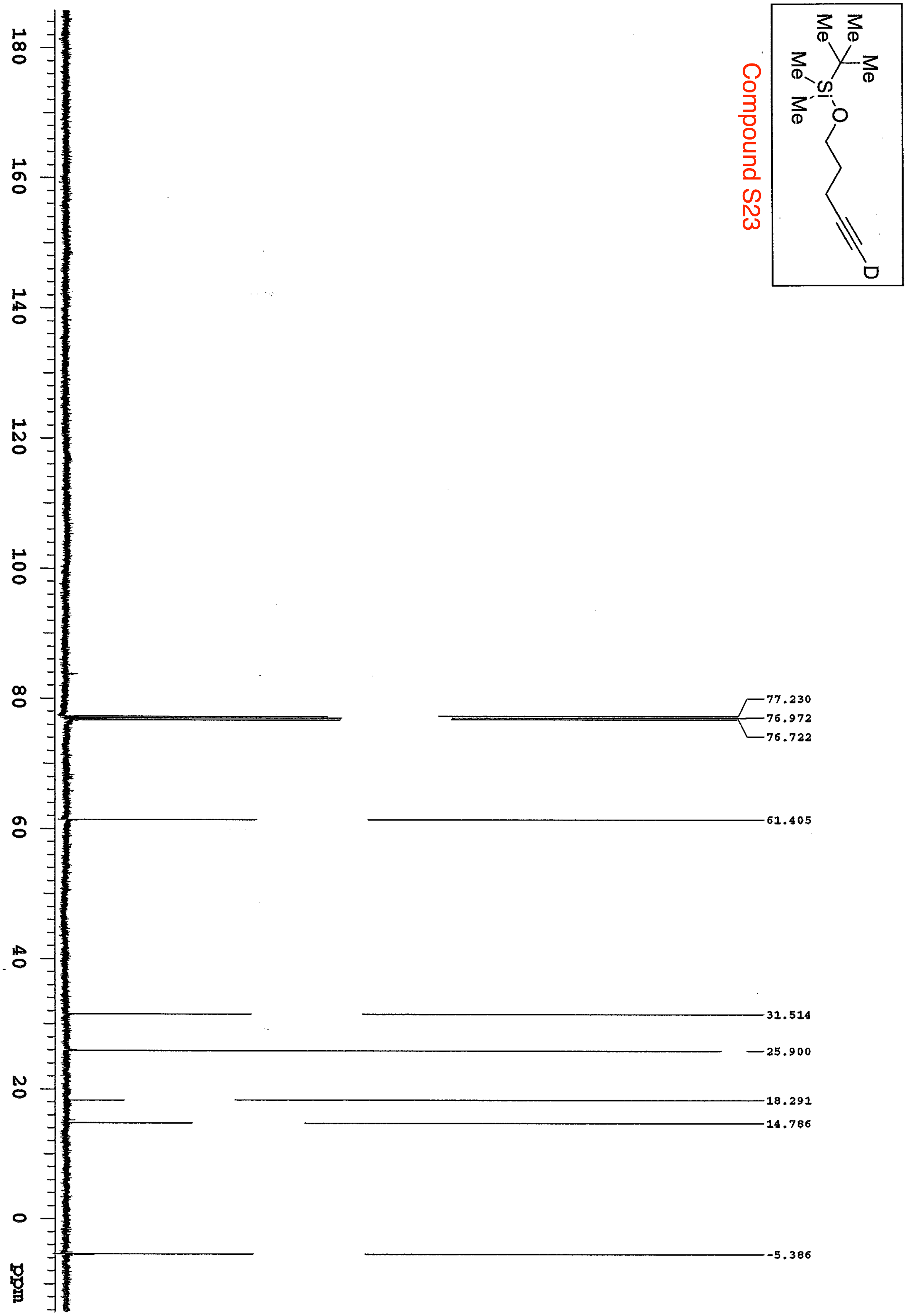


Compound 32

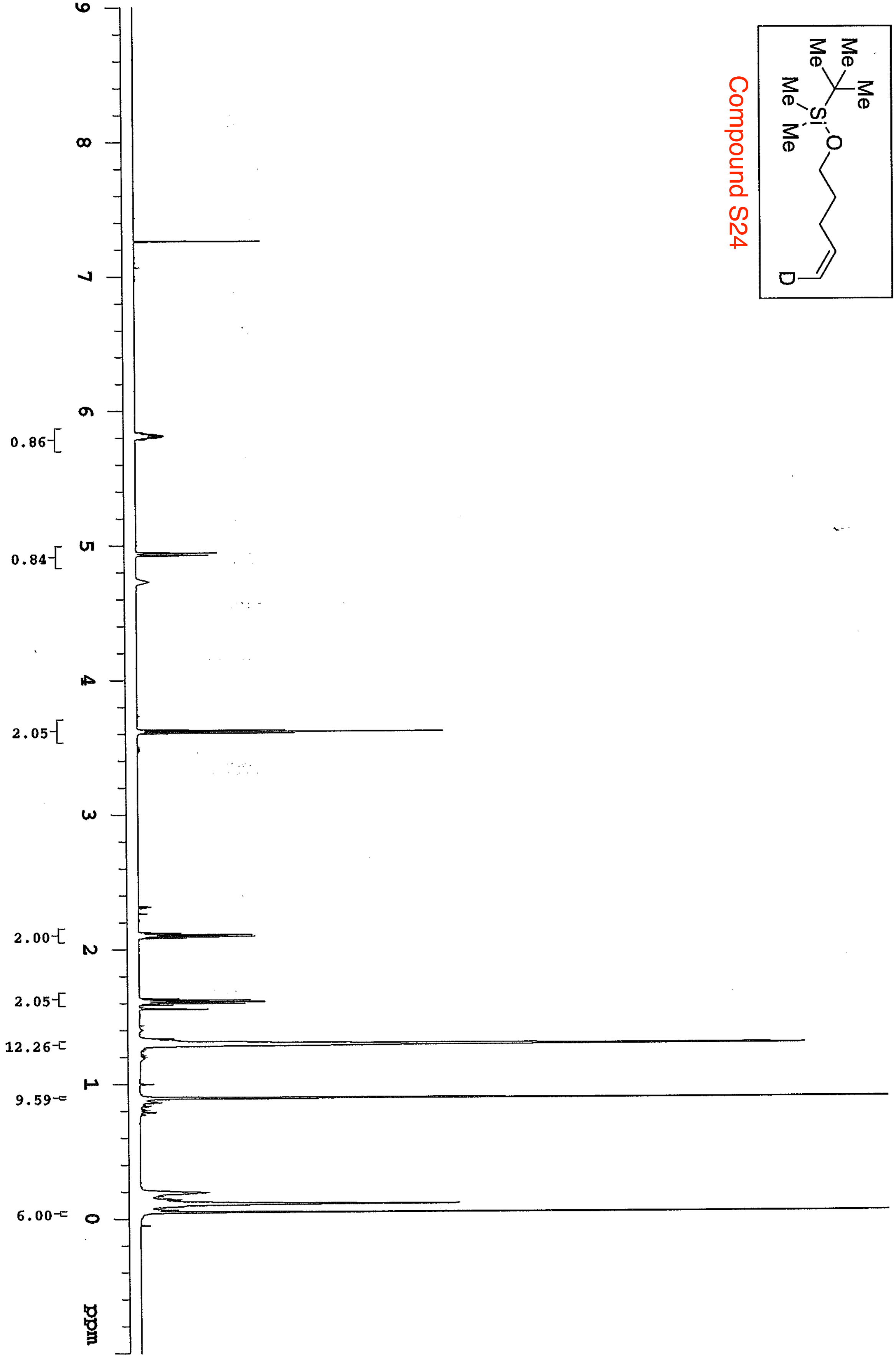
Me
Me
Me
Me
O
B
O
Ph
143.173
128.886
128.043
125.354
82.836
77.256
77.003
76.750
52.533
39.164
30.963
30.566
24.919
24.826
22.415
16.751
2.067
0.288
180
160
140
120
100
80
60
40
20
0
ppm

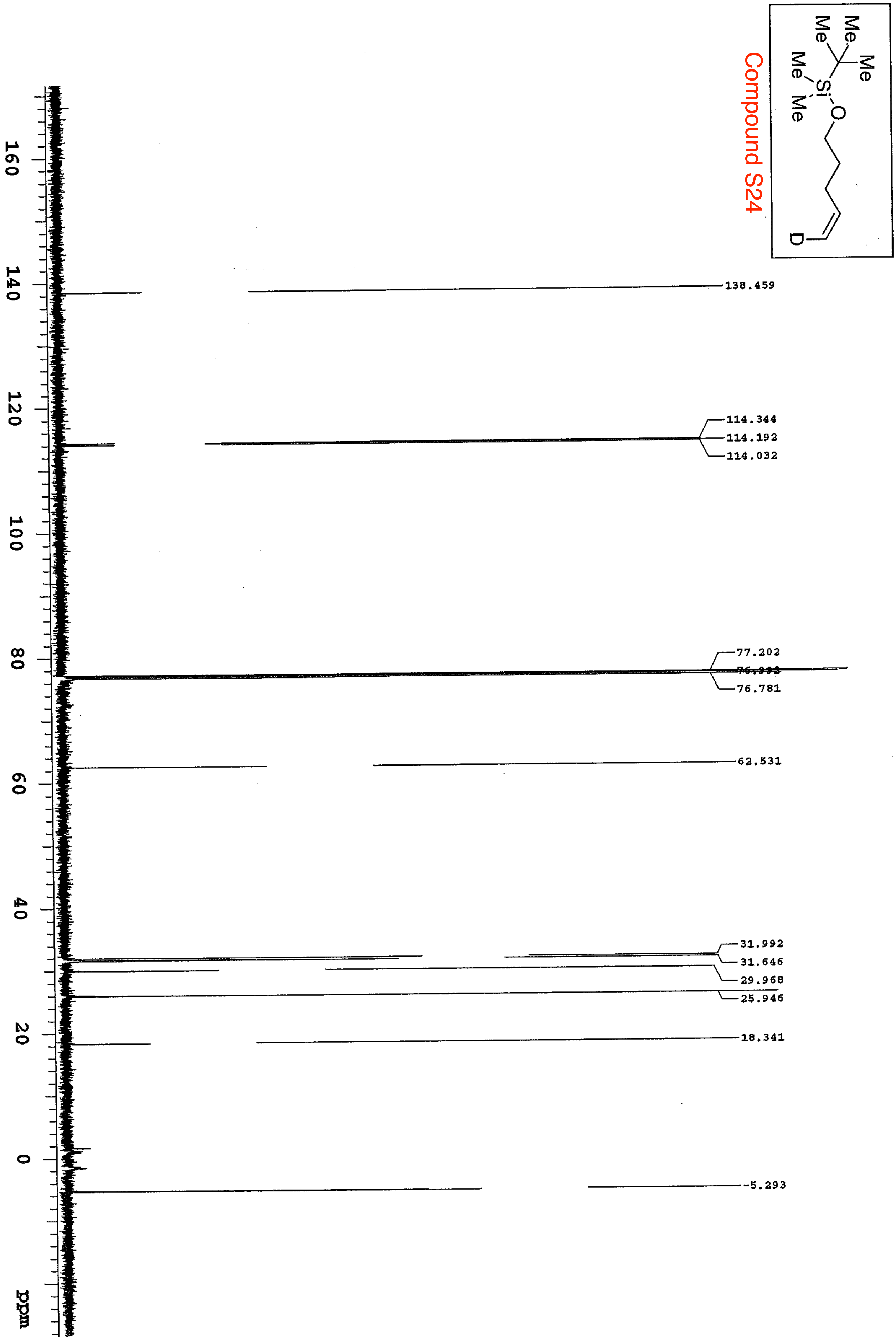


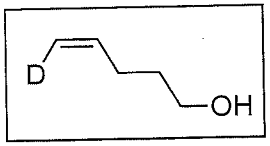
Compound S23



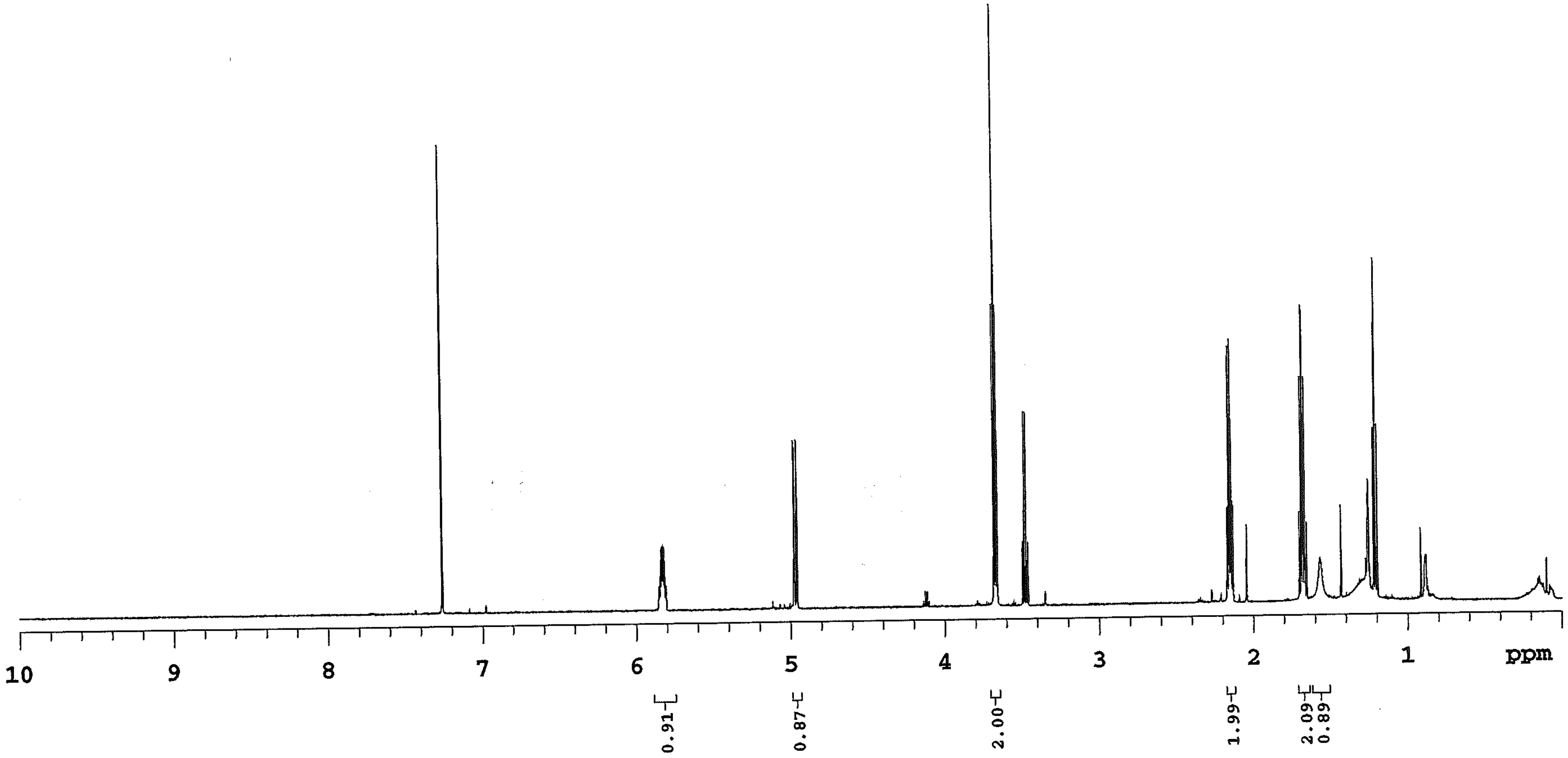
Compound S23


Compound S24

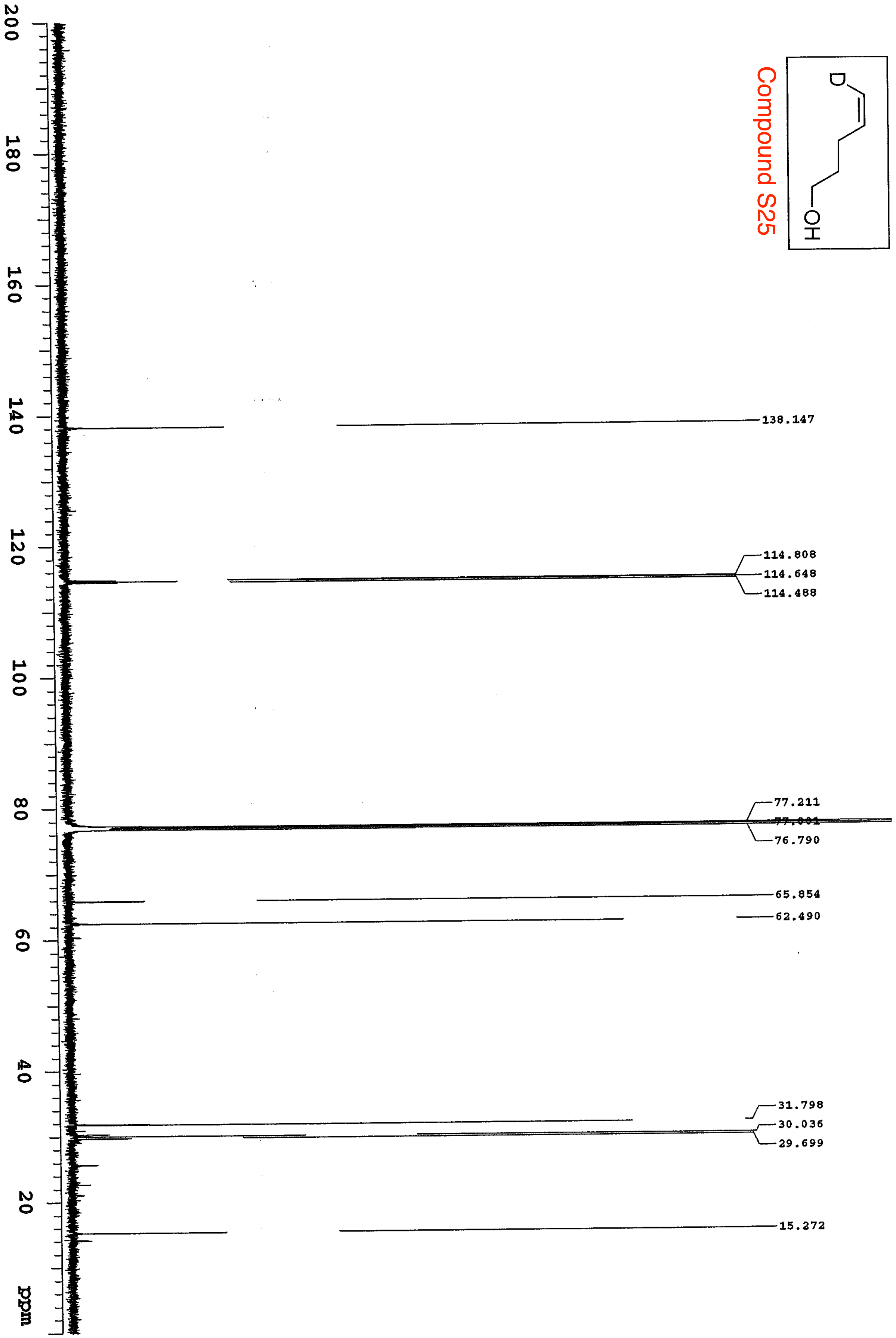

Compound S24

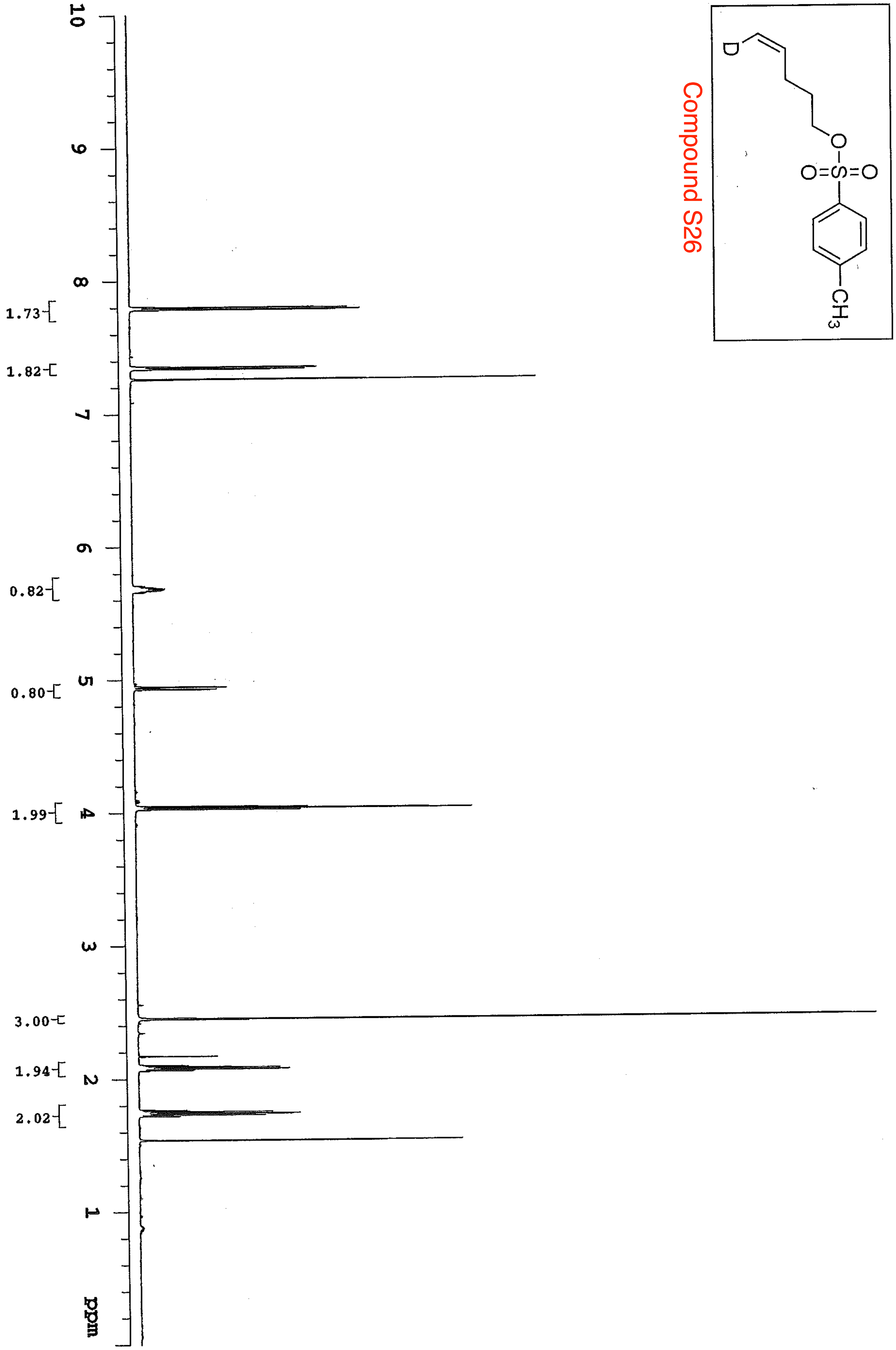


Compound S25

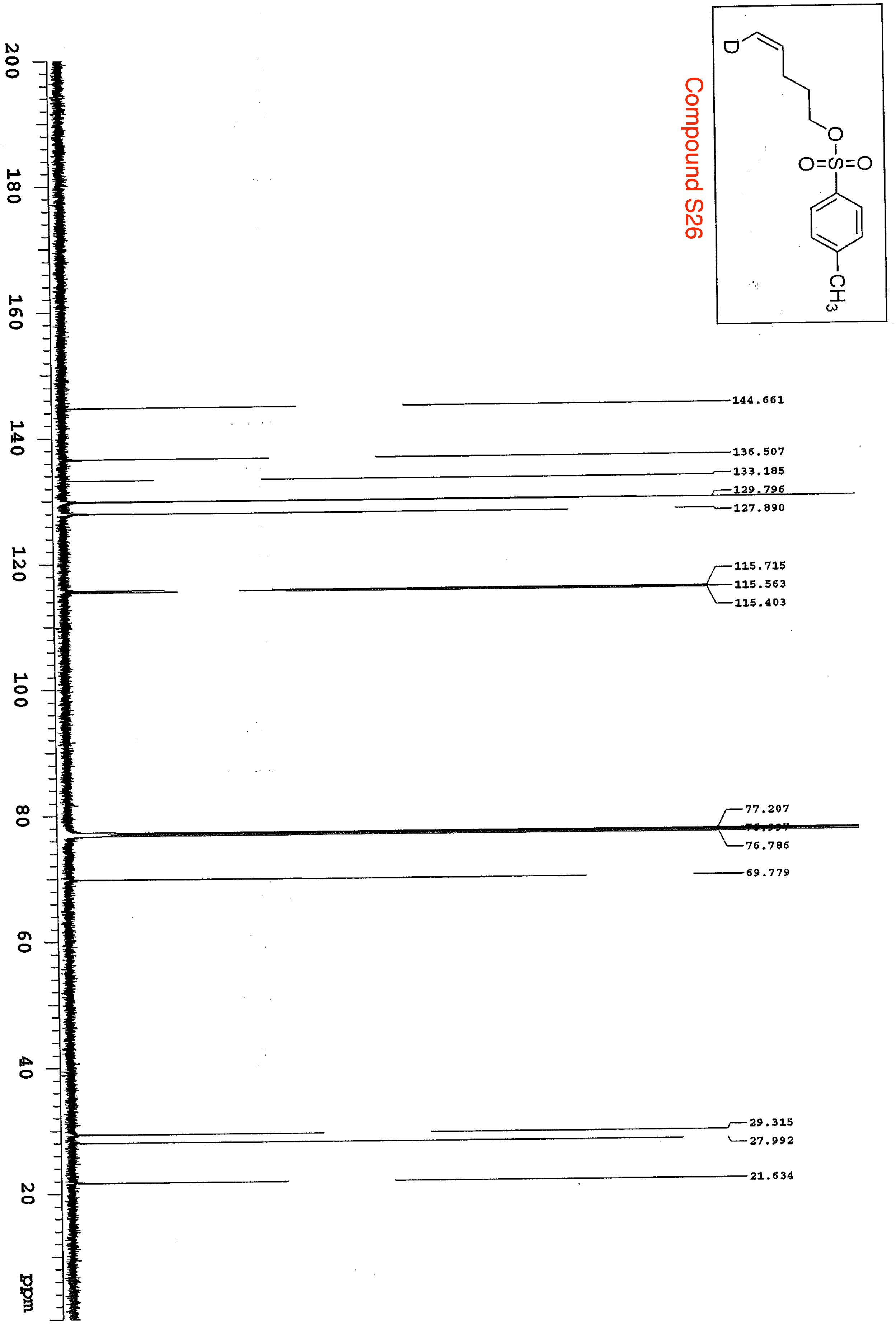


Compound S25

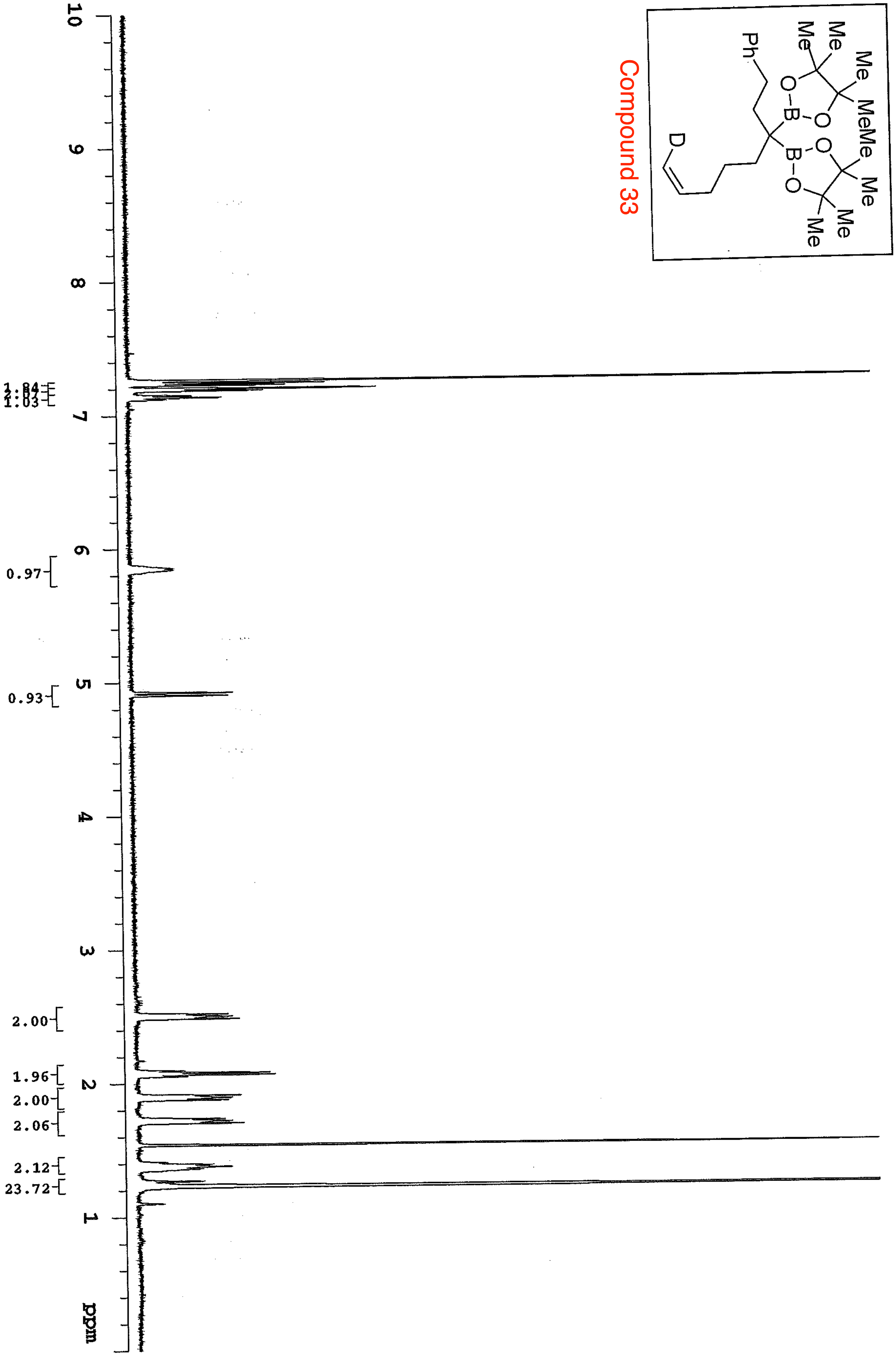




Compound S26

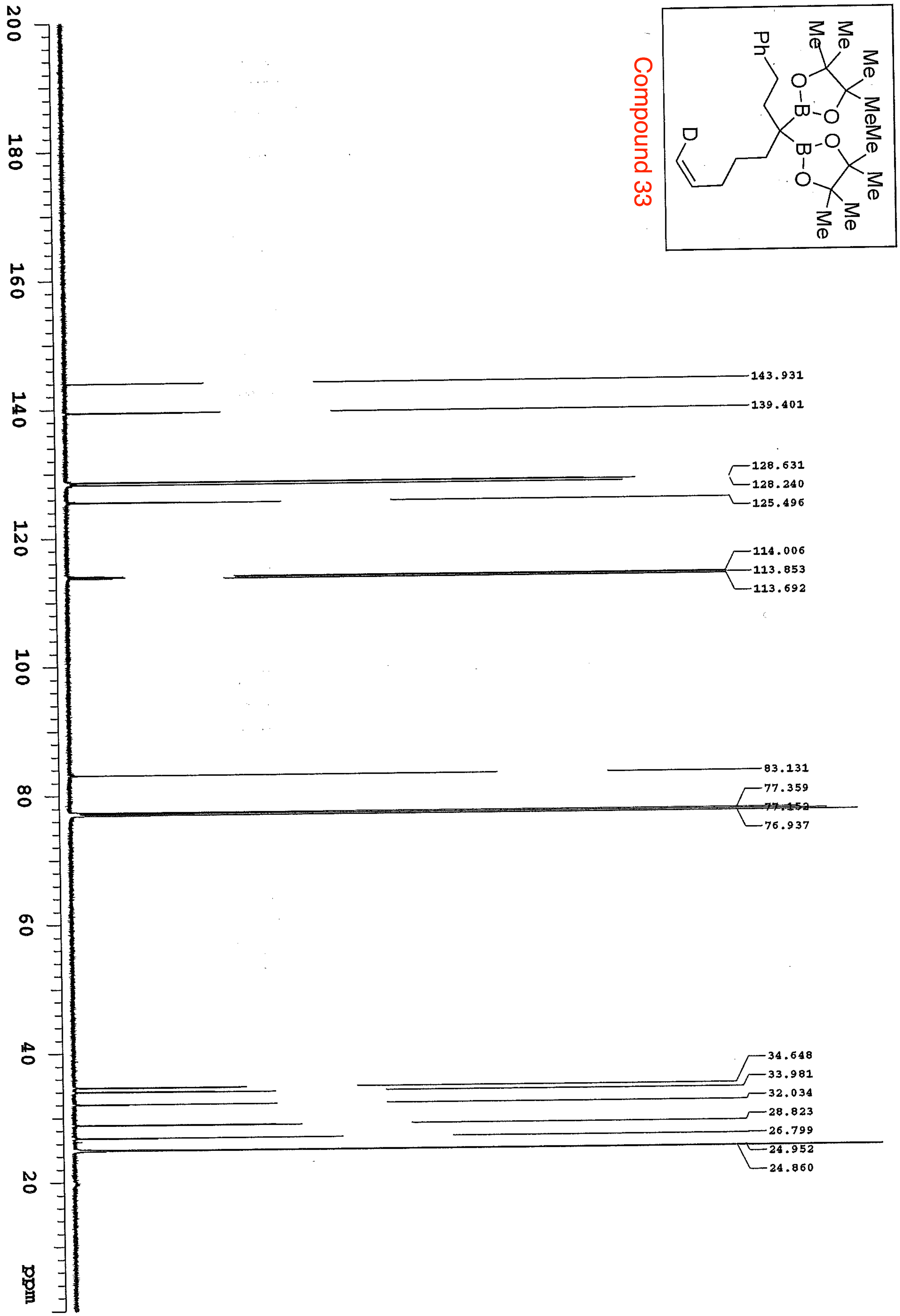


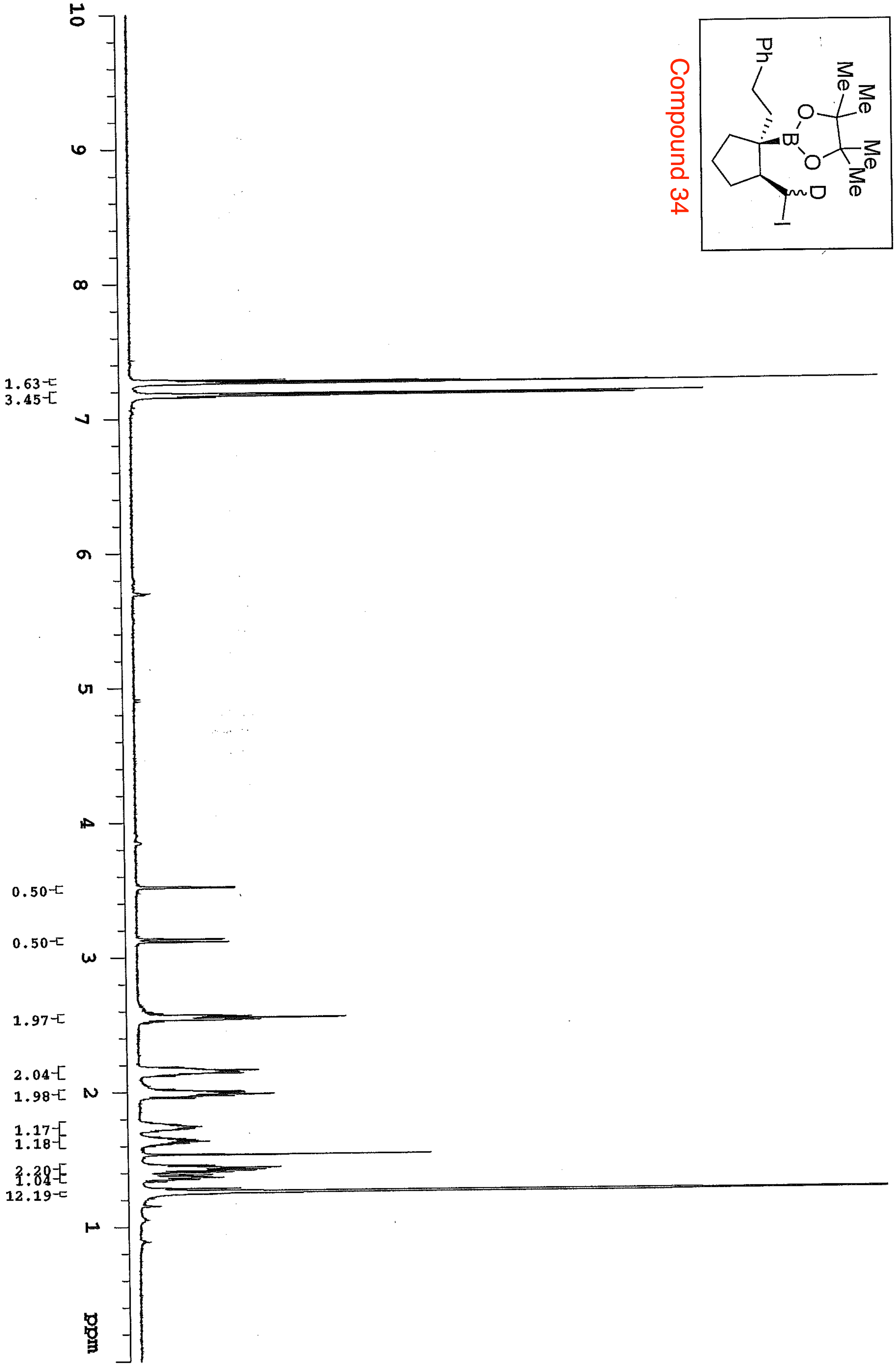
Compound S26


Me
Me
Me
MeMe
Me
Me
Me
O
B
O
O
B
O
Ph
D

Compound 33

10
9
8
7
6
5
4
3
2
1
ppm
1.84
2.07
1.03
0.97
0.93
2.00
1.96
2.00
2.06
2.12
23.72


Compound 33
Me
Me
Me
MeMe
Me
Me
Me
O
O
O
O
O-B
B-O
Ph
D
143.931
139.401
128.631
128.240
125.496
114.006
113.853
113.692
83.131
77.359
77.152
76.937
34.648
33.981
32.034
28.823
26.799
24.952
24.860
200
180
160
140
120
100
80
60
40
20
ppm

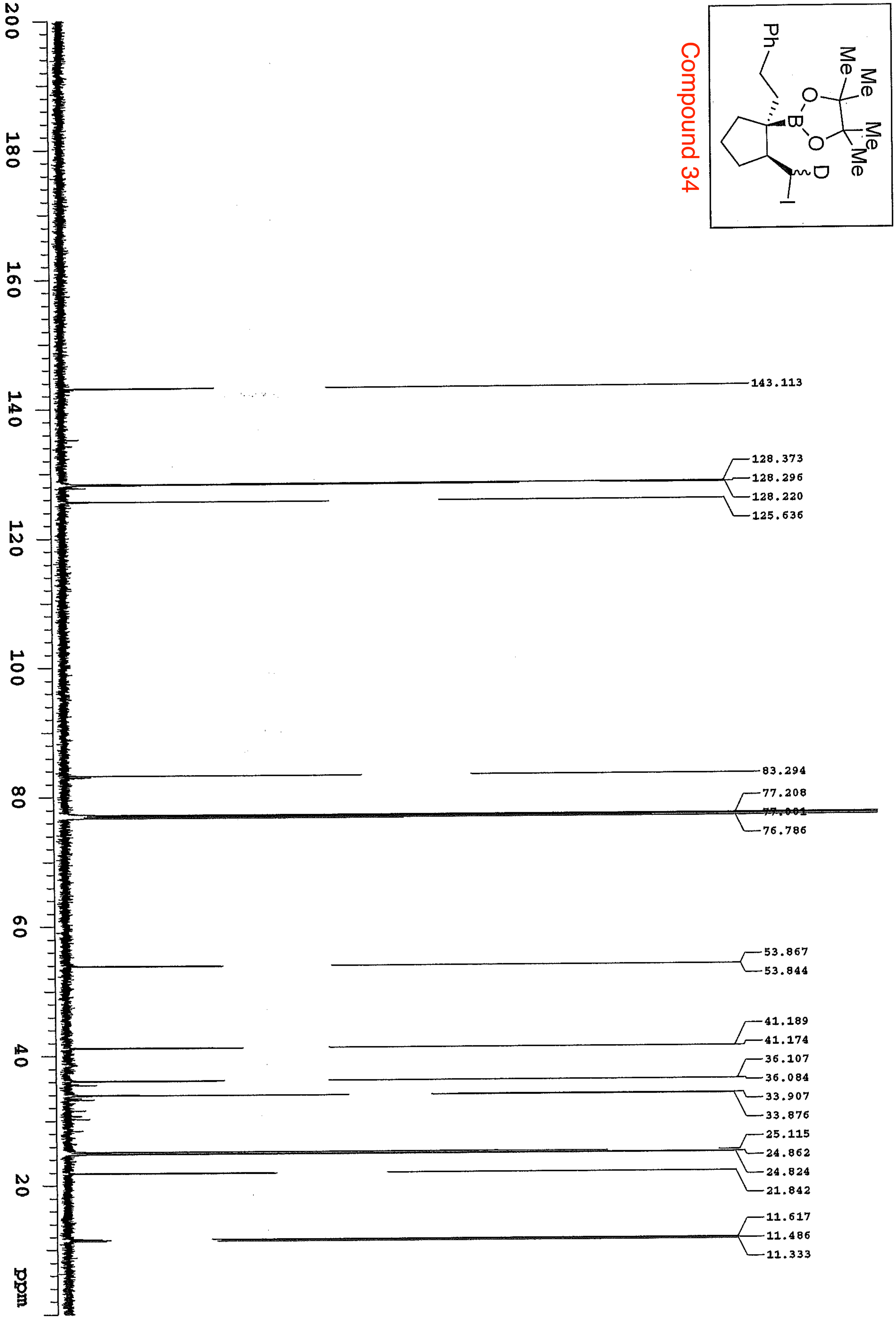


Compound 34

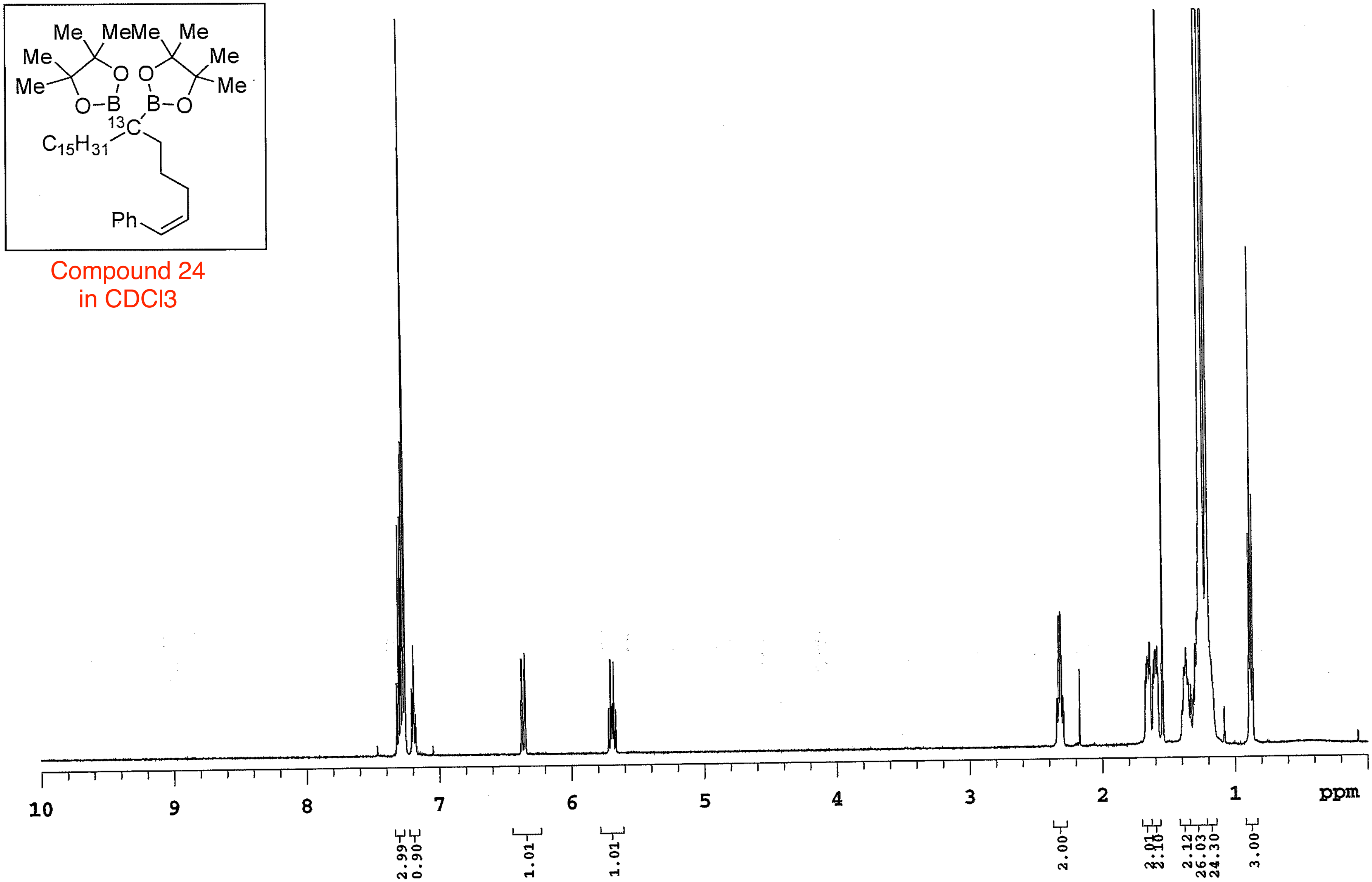
Me
Me
Me
Me
O
B
O
Ph
D
I
10
9
8
7
6
5
4
3
2
1
ppm
1.63
3.45
0.50
0.50
1.97
2.04
1.98
1.17
1.18
2.20
1.04
12.19

Me
Me
Me
Me
O
B
O
D
I
Ph

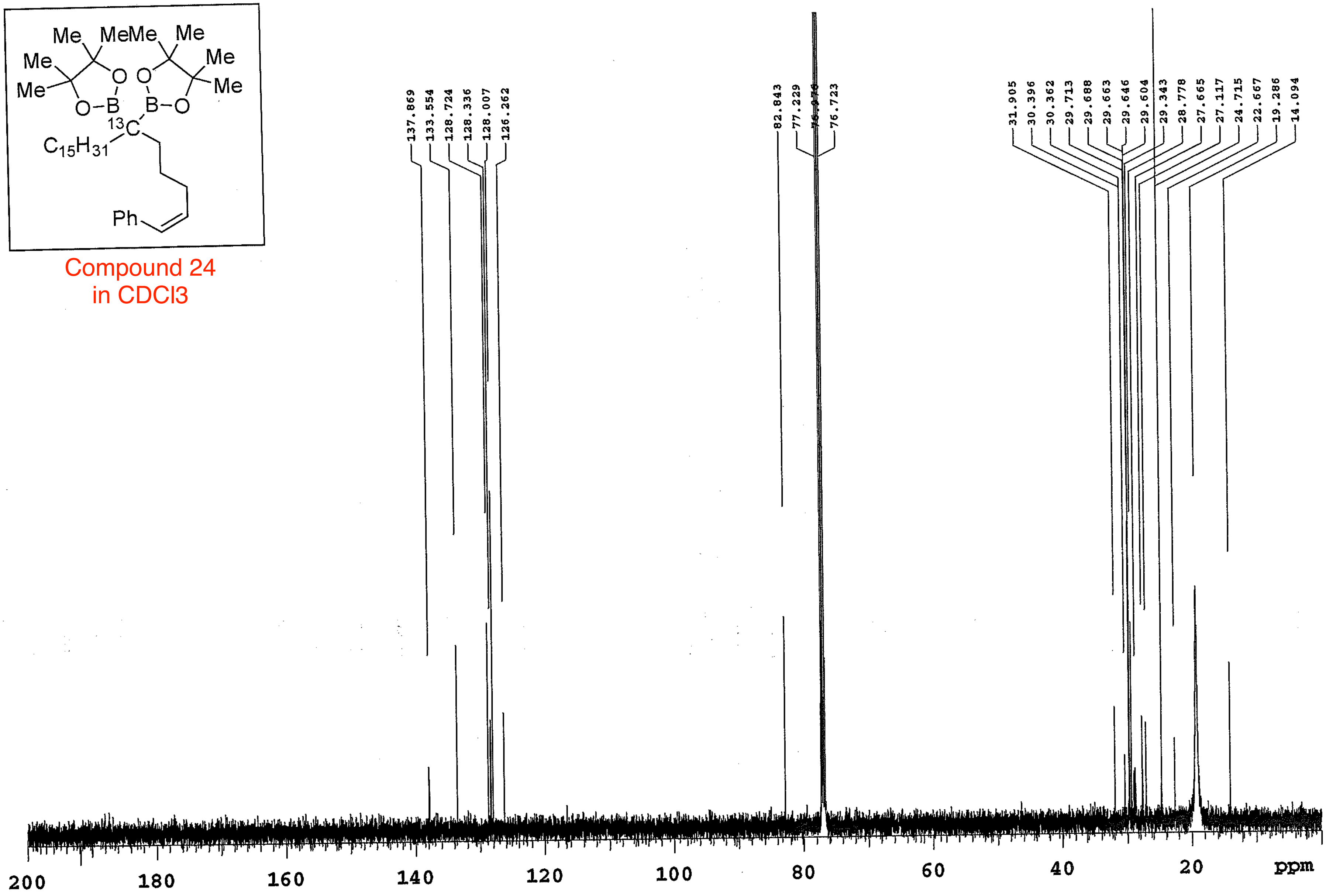
Compound 34



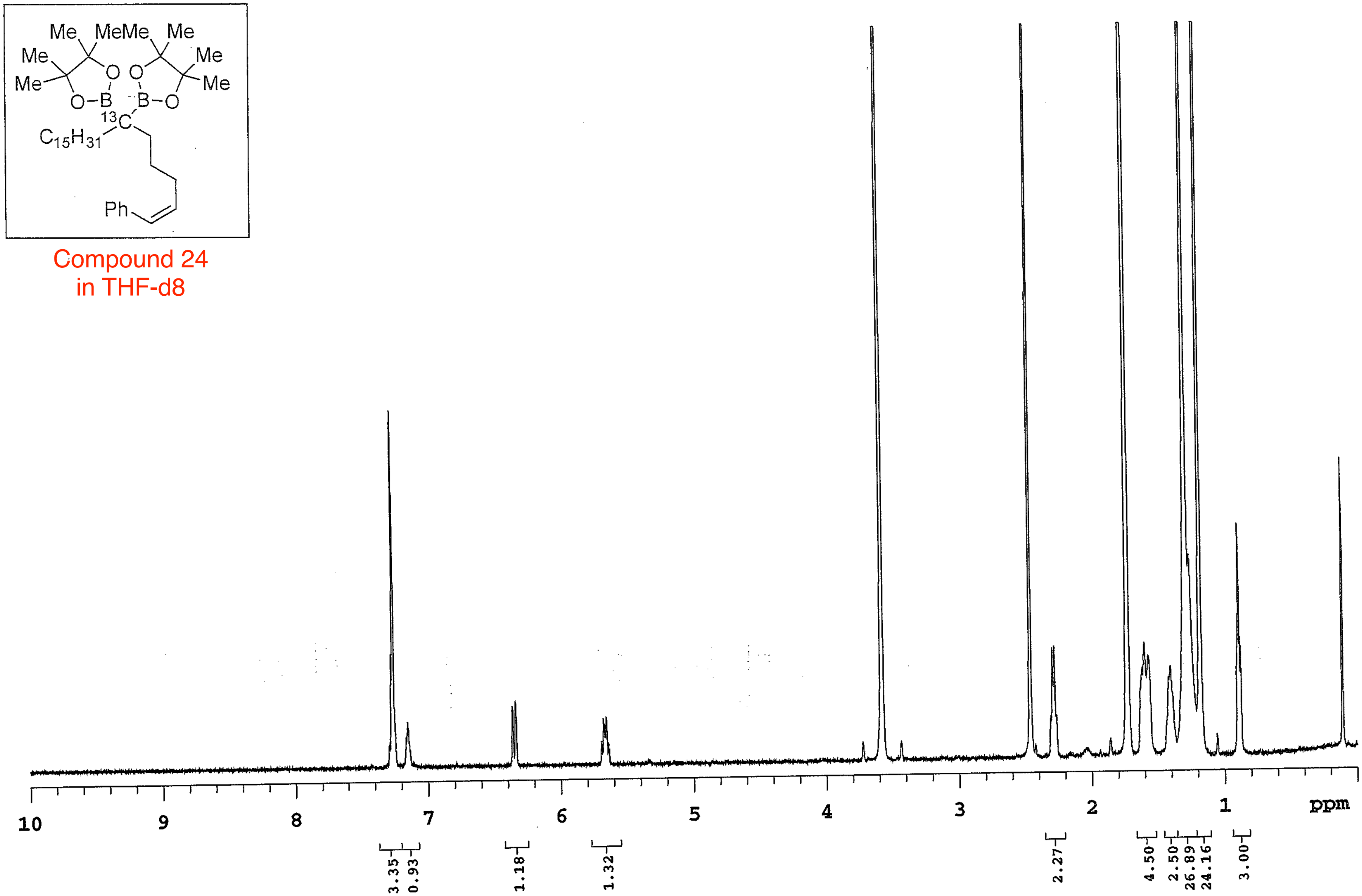
143.113
128.373
128.296
128.220
125.636
83.294
77.208
77.001
76.786
53.867
53.844
41.189
41.174
36.107
36.084
33.907
33.876
25.115
24.862
24.824
21.842
11.617
11.486
11.333
200
180
160
140
120
100
80
60
40
20
ppm



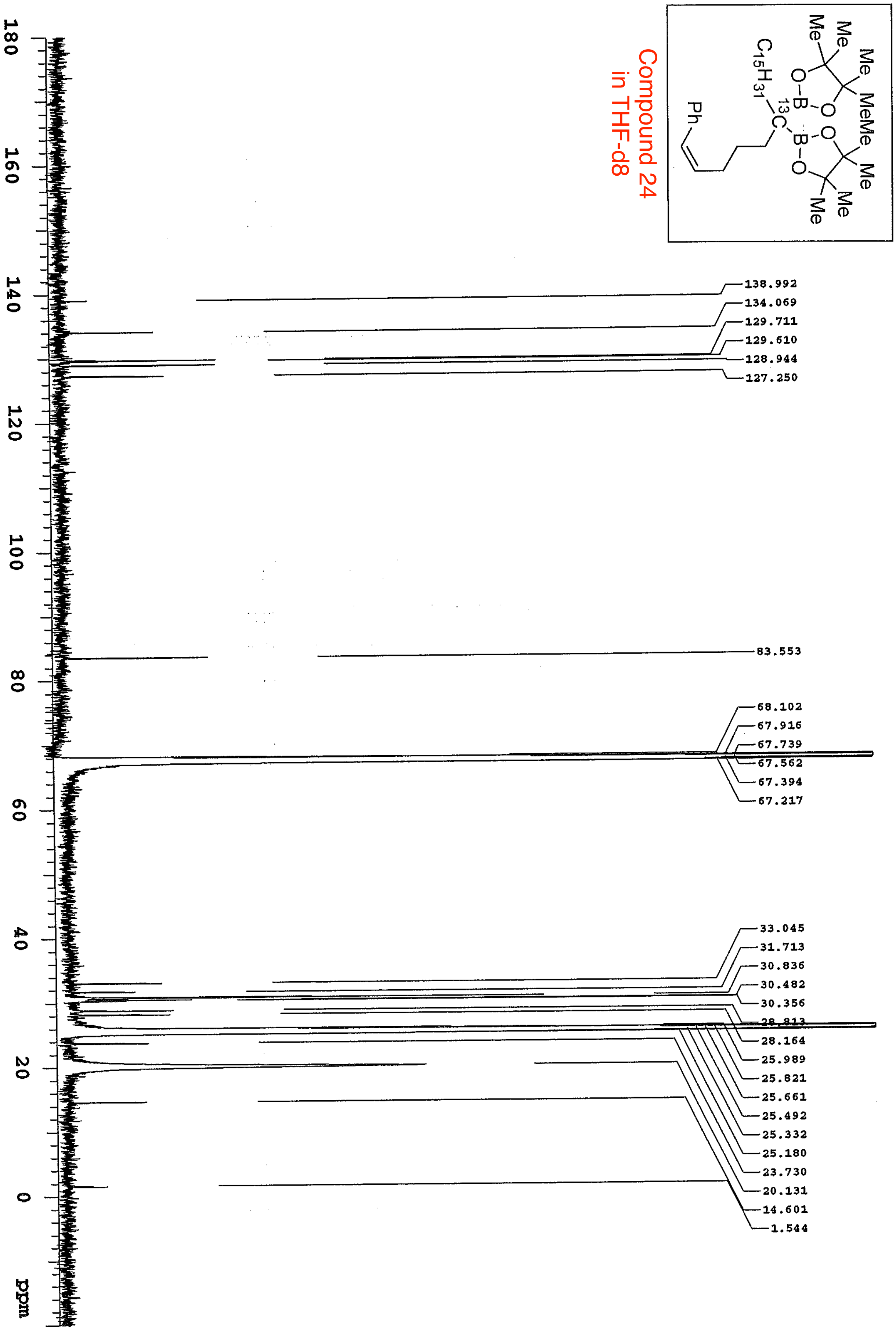
Compound 24
in CDCl3



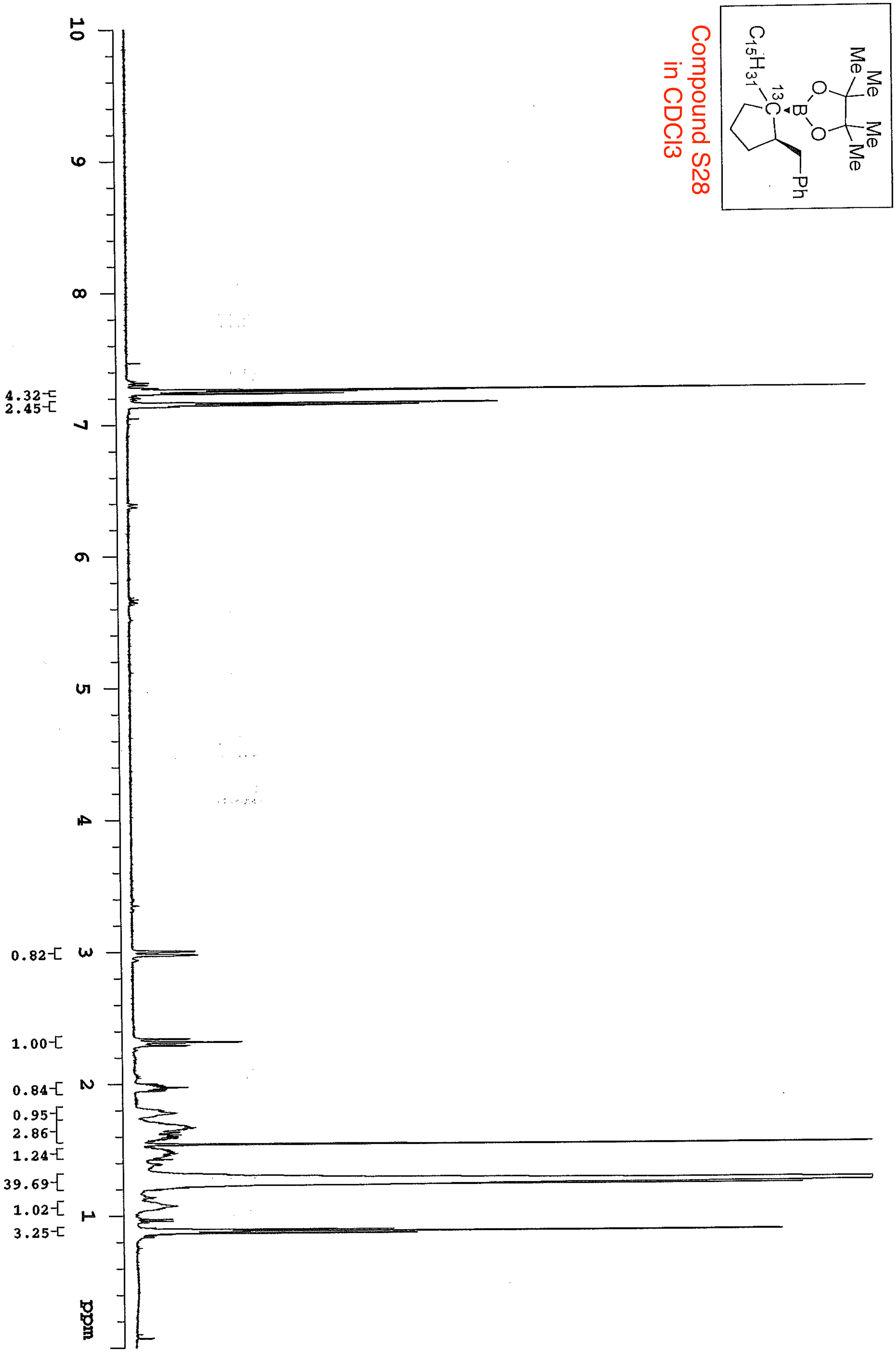
Compound 24
in CDCl3



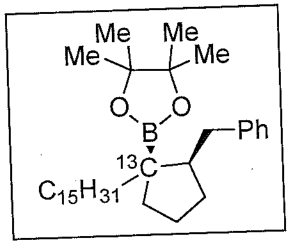
Compound 24
in THF-d8



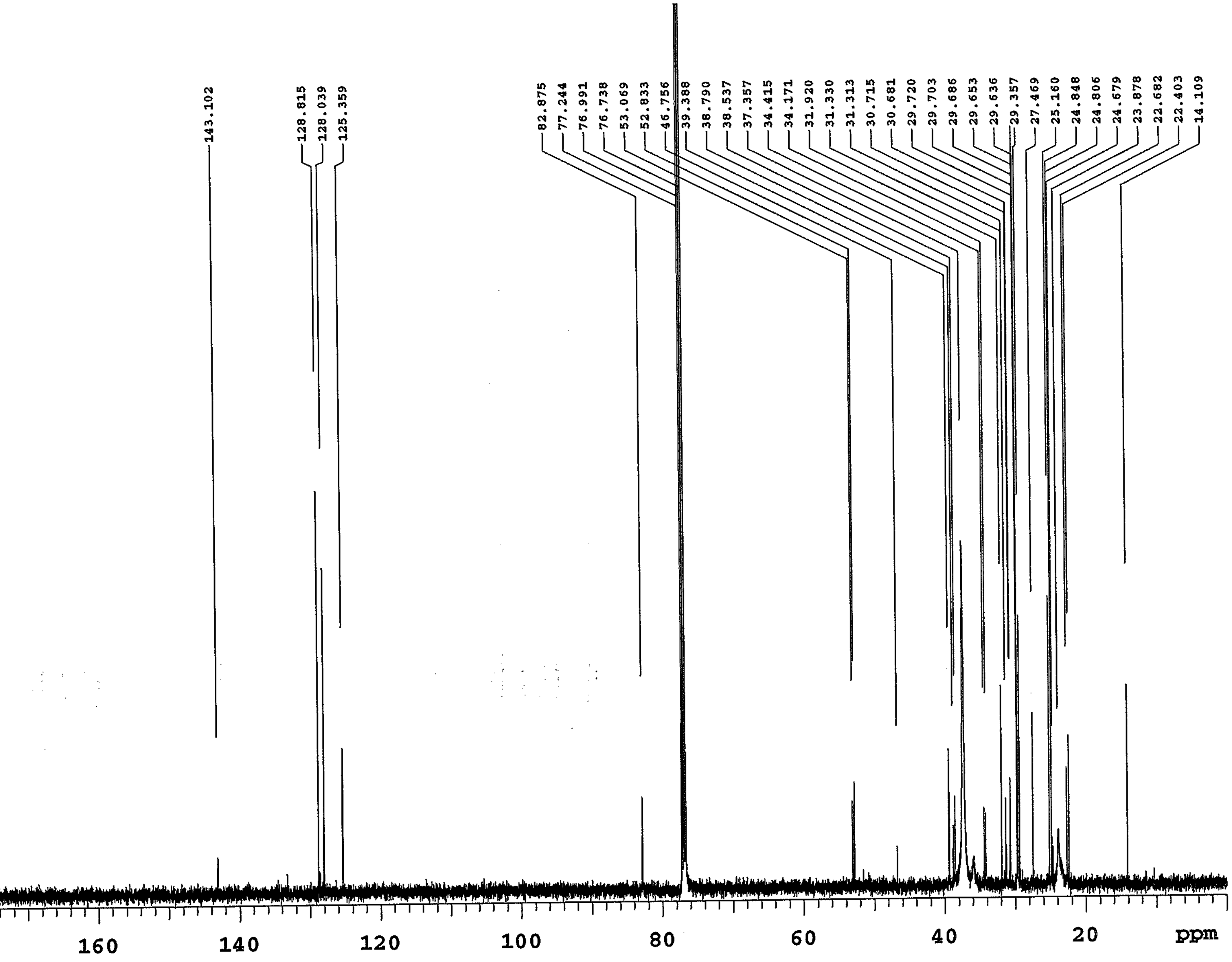
Compound 24 in THF-d8

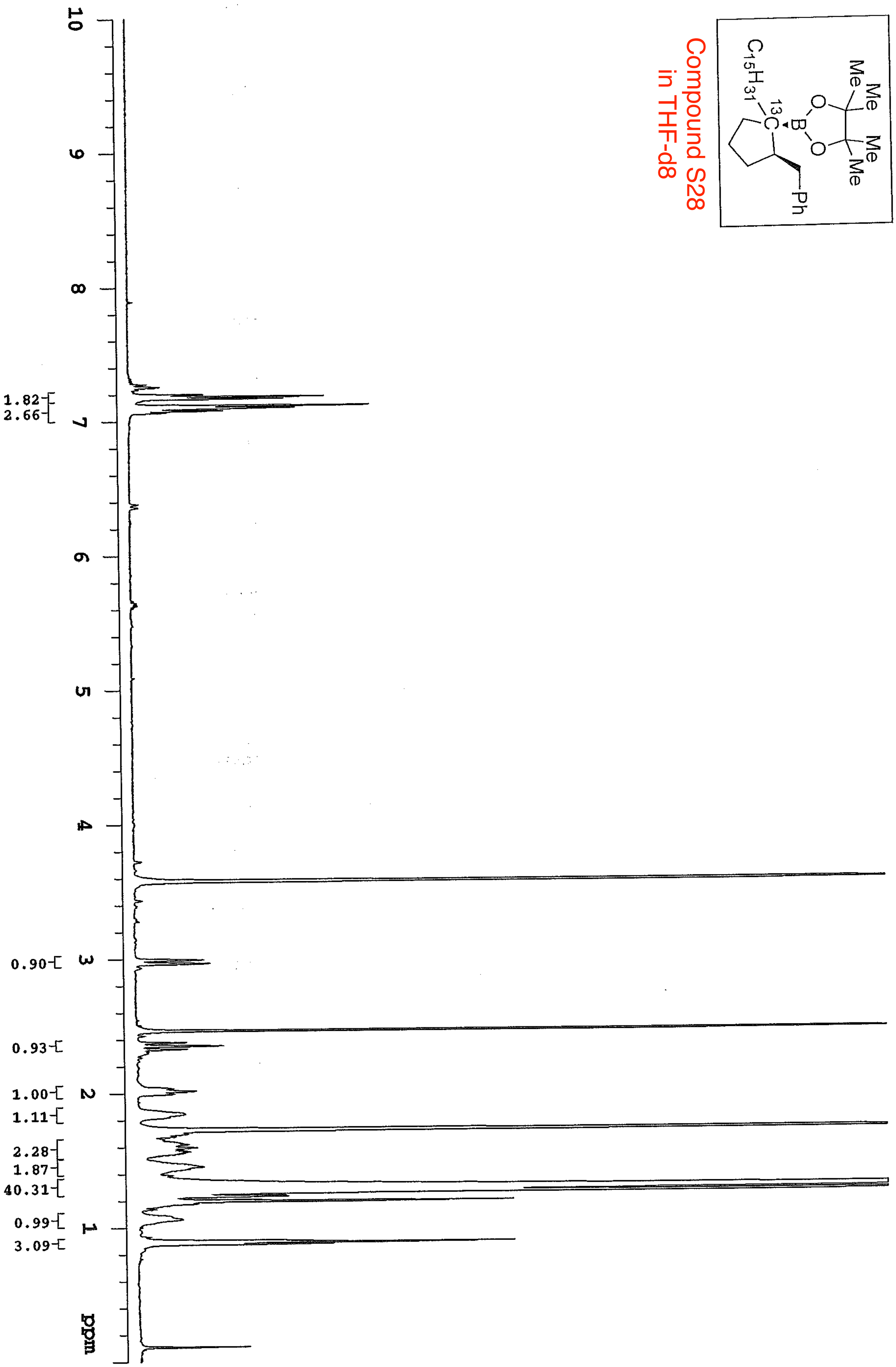


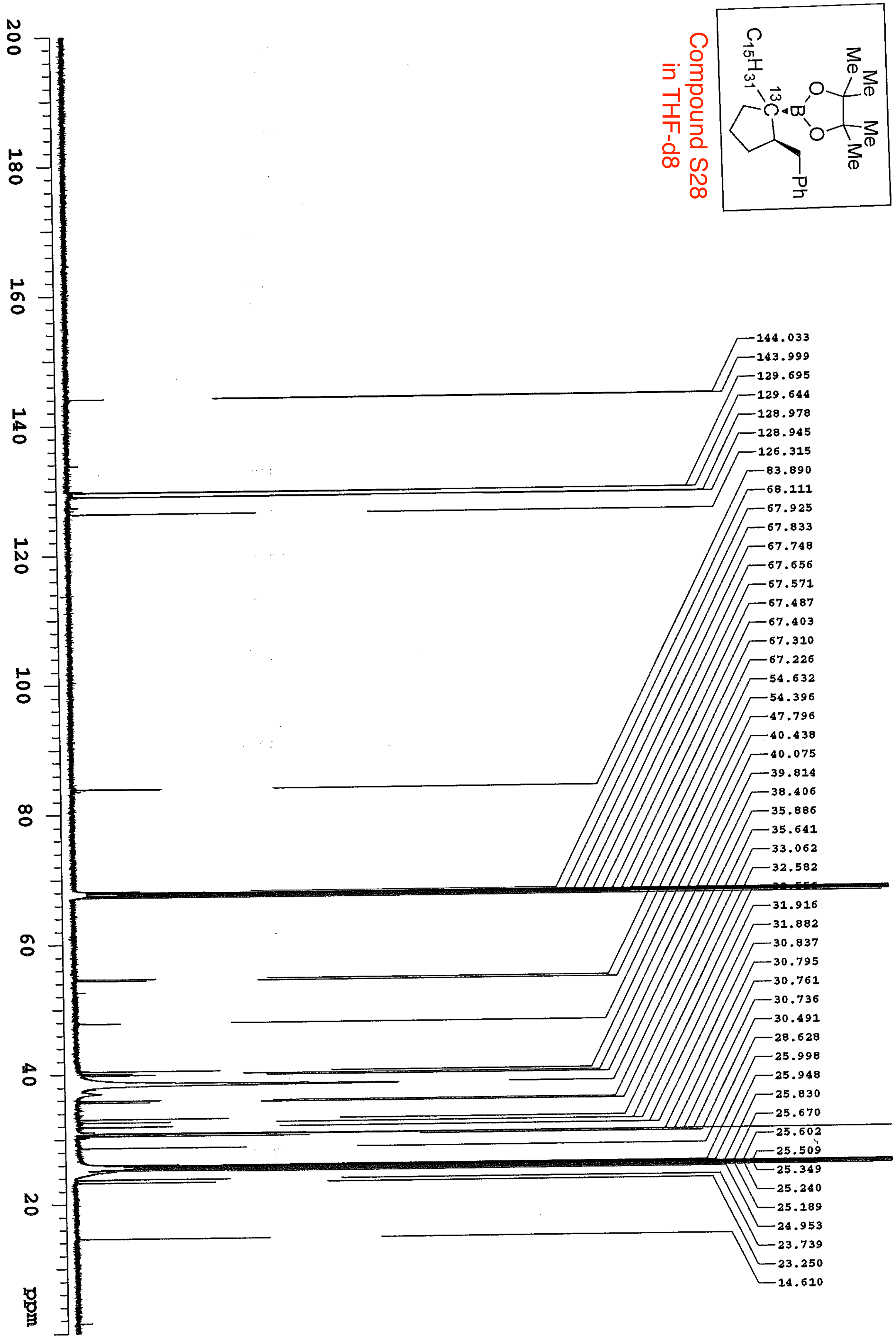
Compound S28 in CDCl3



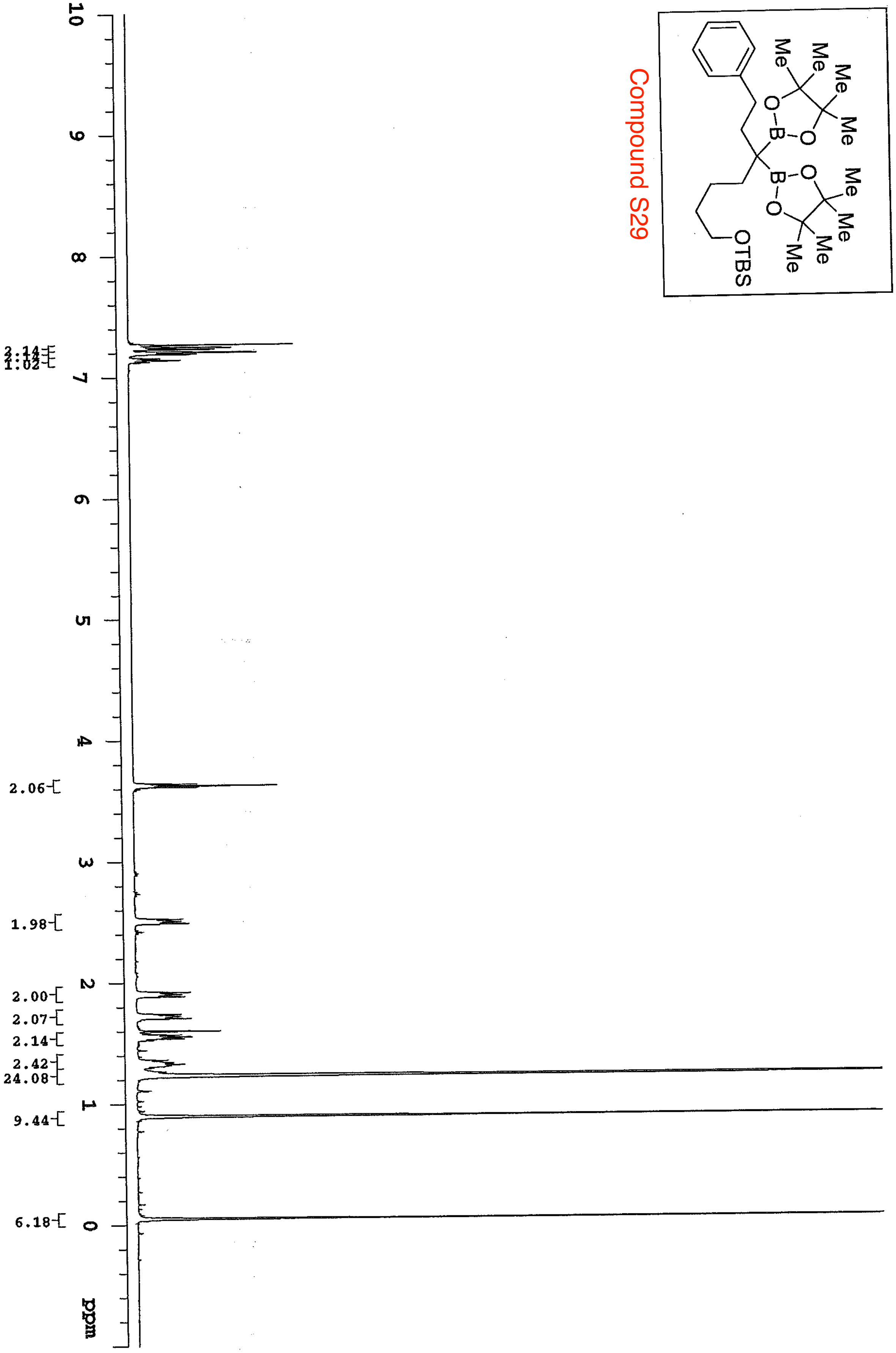
Compound S28
in CDCl3



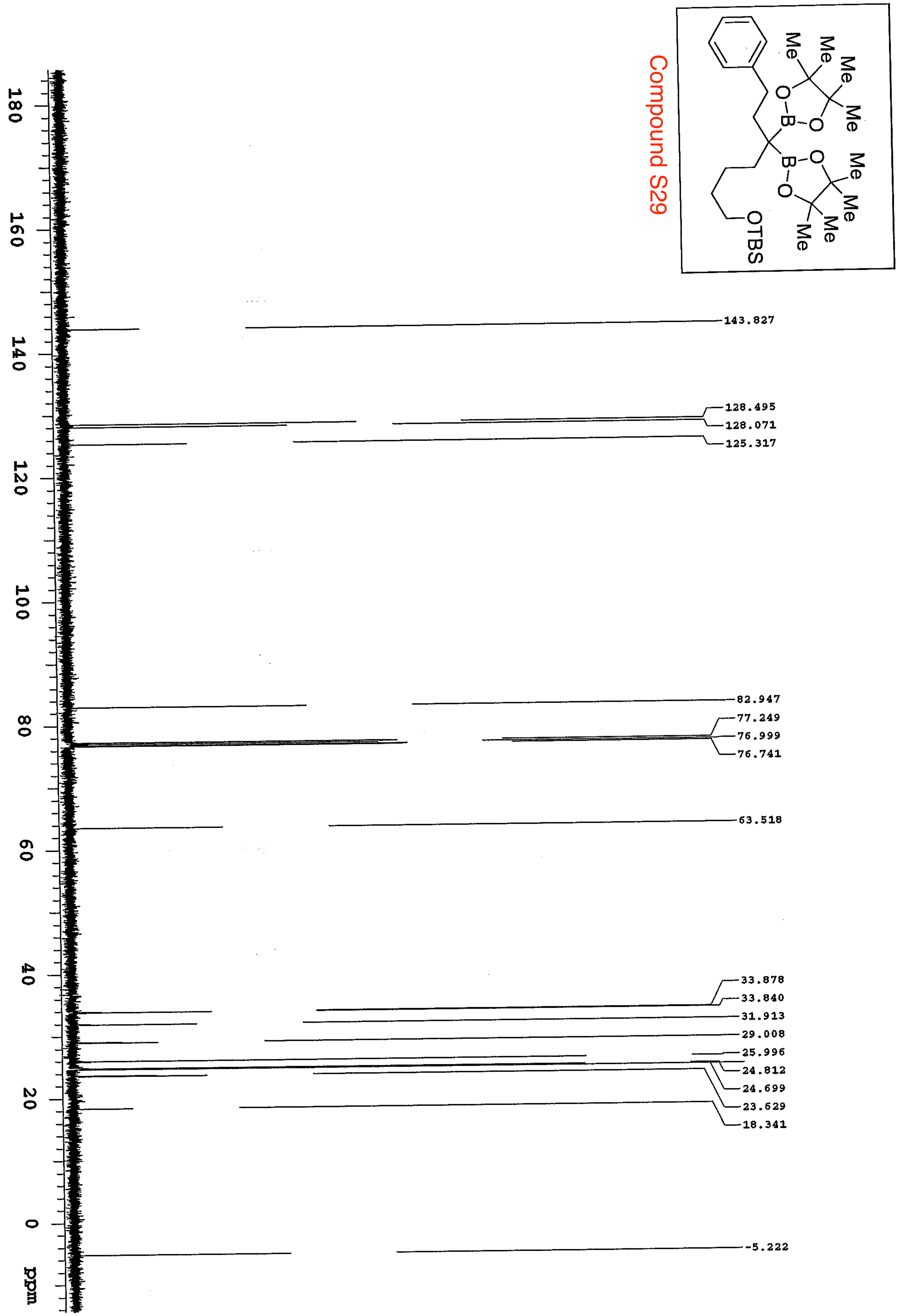

Compound S28
in THF-d8



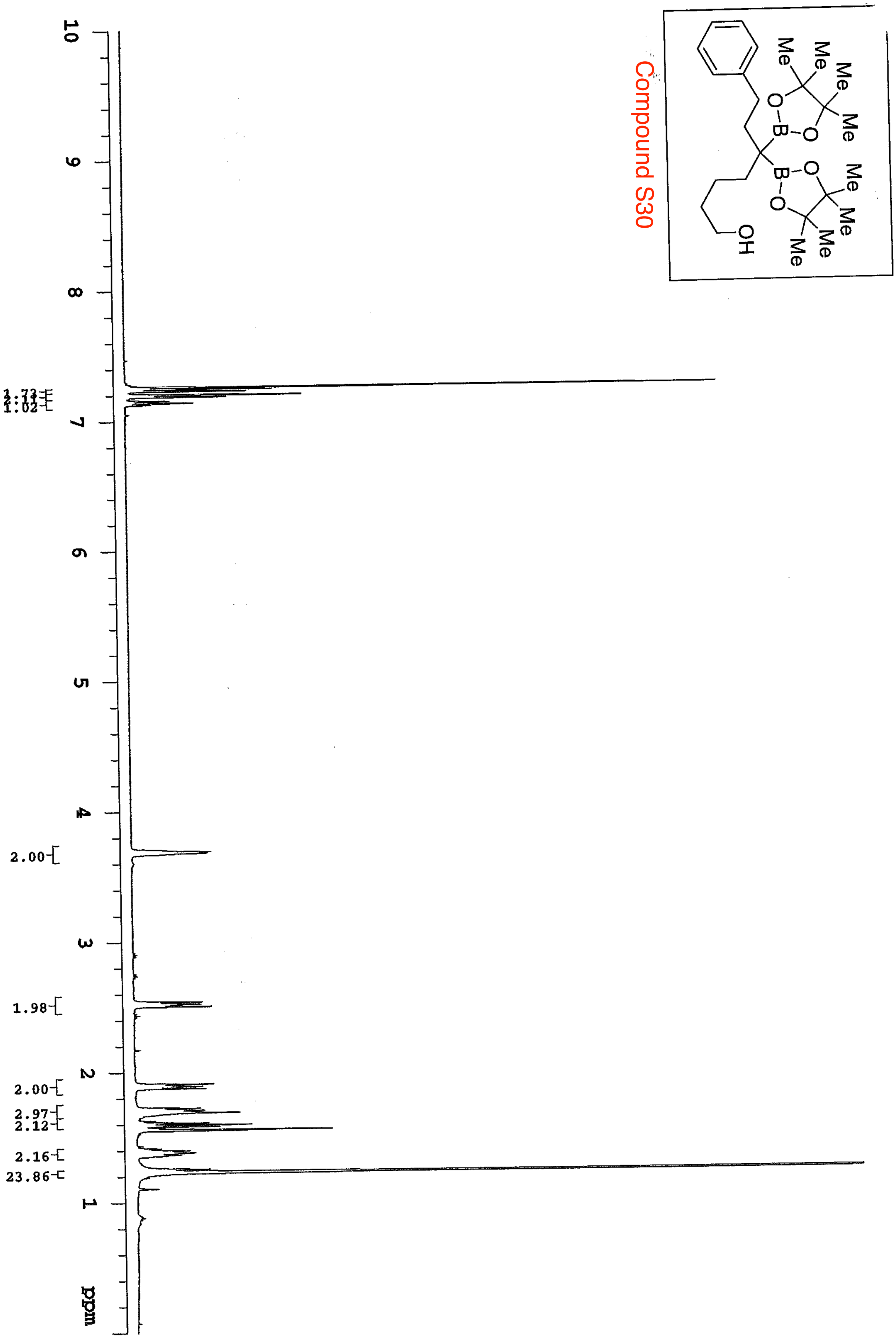
Compound S28
in THF-d8



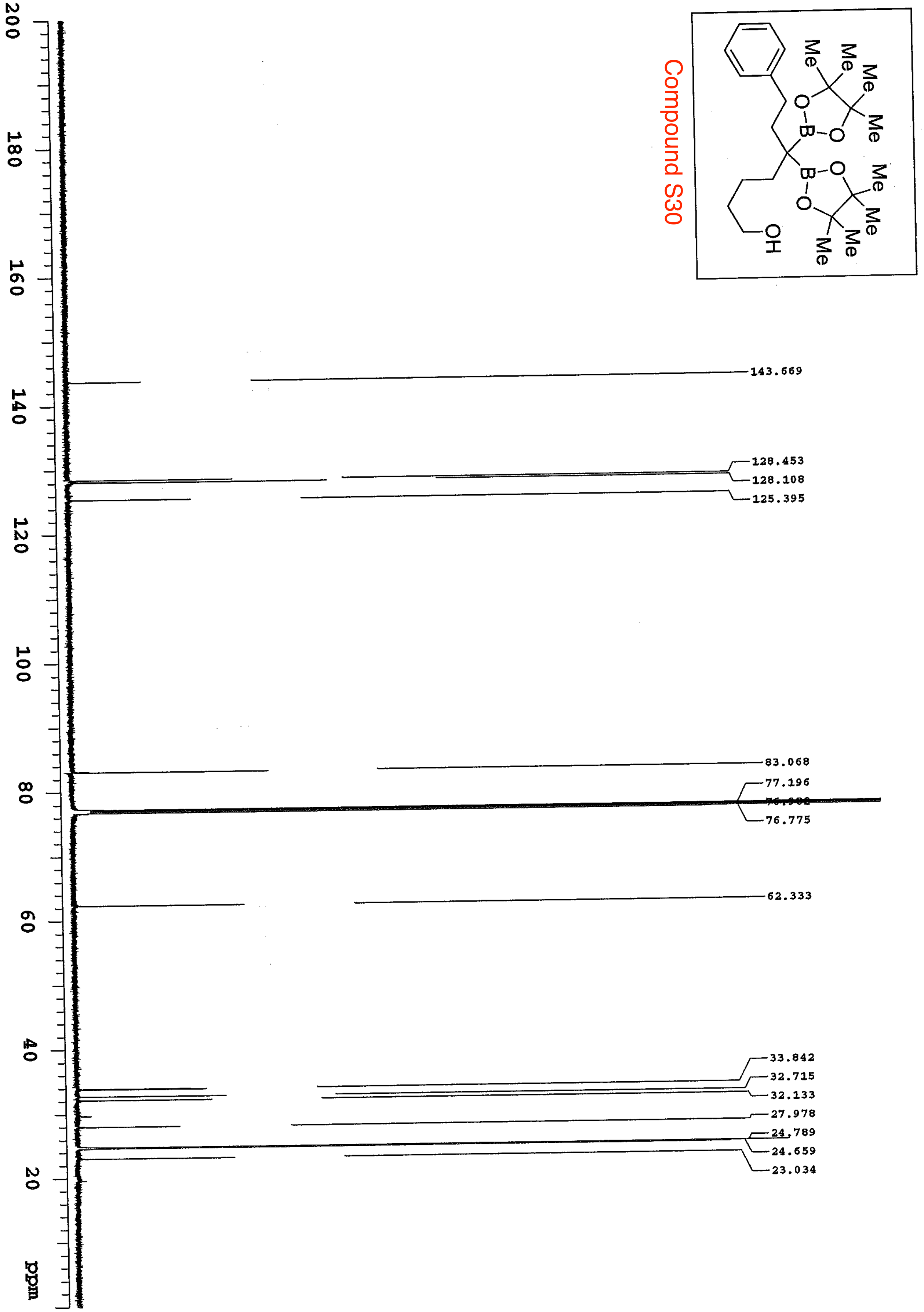
Compound S29



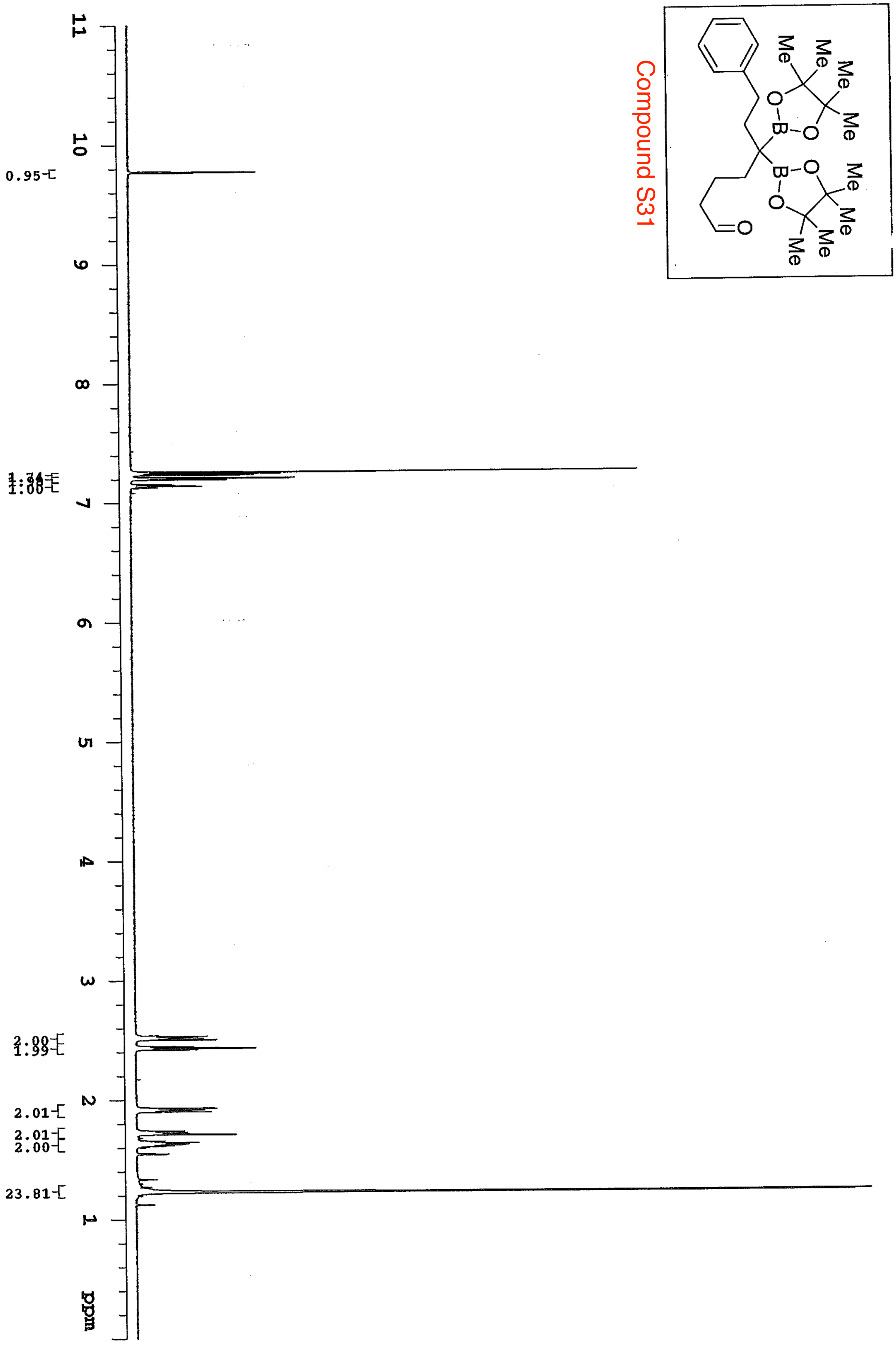
Compound S29



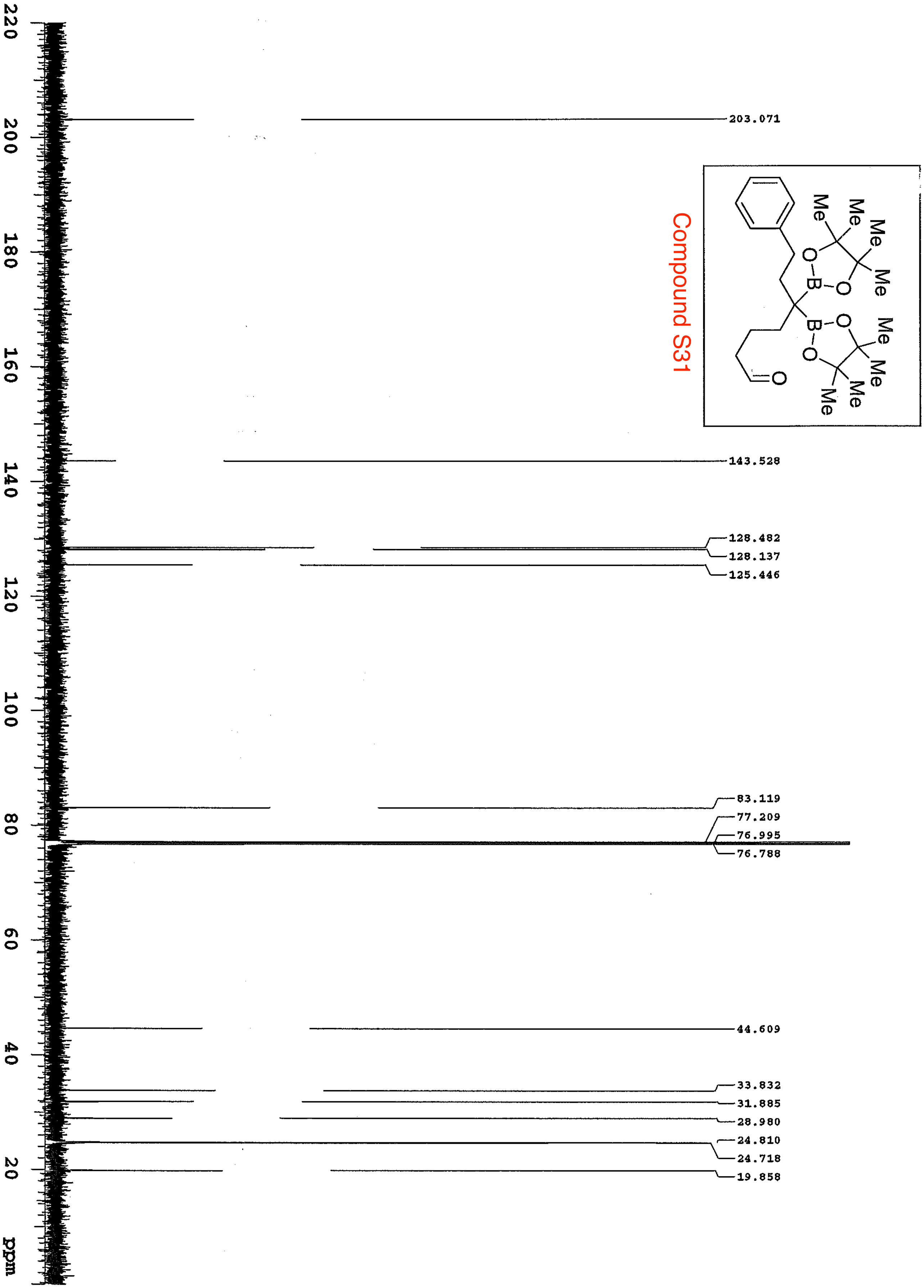
Compound S30



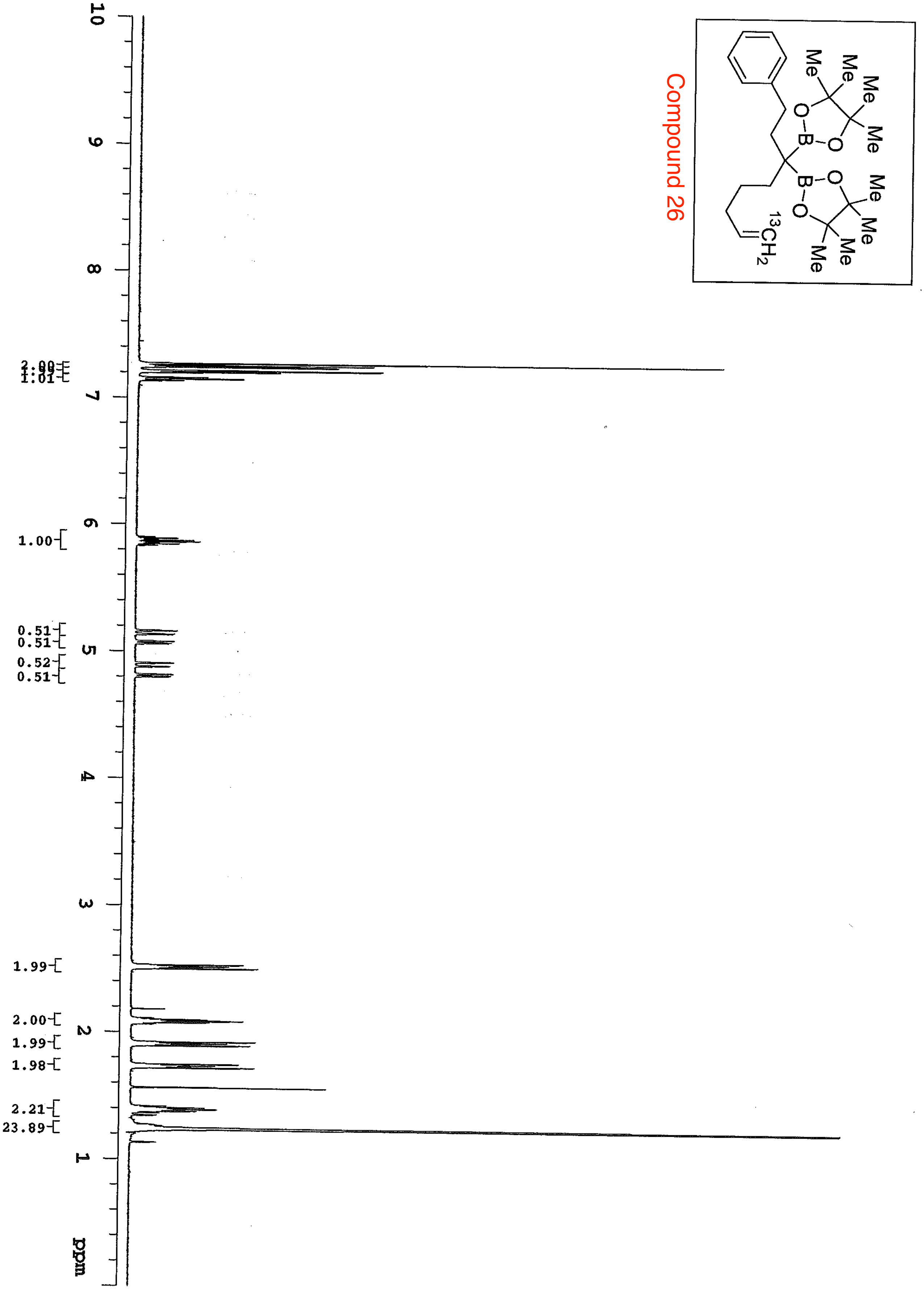
Compound S30



Compound S31

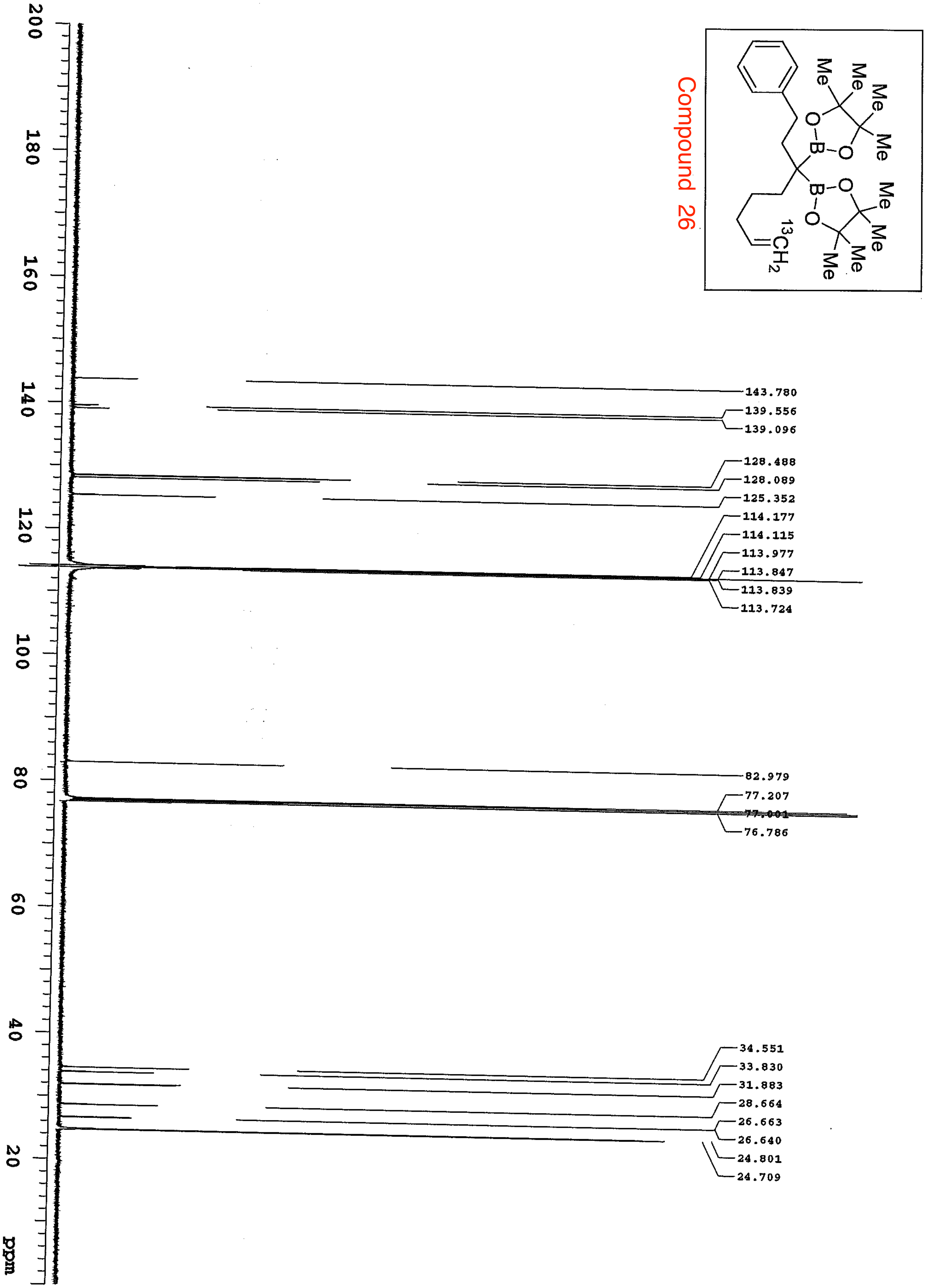


Compound S31



Me
Me
Me
Me
Me
Me
Me
Me
O
B
O
O
B
O
$^{13}CH_2$
2.00
1.99
1.01
1.00
0.51
0.51
0.52
0.51
1.99
2.00
1.99
1.98
2.21
23.89
10
9
8
7
6
5
4
3
2
1
ppm

Compound 26


Me
Me
Me
Me
Me
Me
Me
Me
O
O
O
O
B
B
$^{13}CH_2$
143.780
139.556
139.096
128.488
128.089
125.352
114.177
114.115
113.977
113.847
113.839
113.724
82.979
77.207
77.001
76.786
34.551
33.830
31.883
28.664
26.663
26.640
24.801
24.709
200
180
160
140
120
100
80
60
40
20
ppm

Compound 26