Stereoselective Chlorination of Acyclic Aliphatic 1,3-*Anti* vs. 1,3-*Syn* Diols with Triphosgene-Pyridine Activation

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SUPPORTING INFORMATION

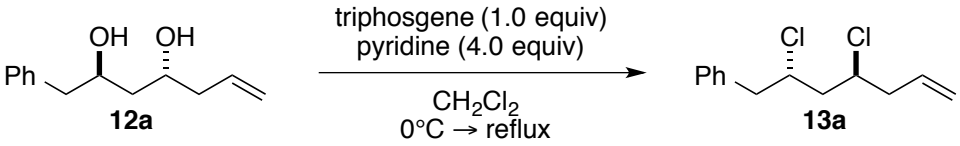
1. GENERAL INFORMATION

All materials, unless otherwise stated, were purchased from commercial sources and utilized without further purification. Anhydrous reactions were conducted in oven-dried glassware, which was then cooled under vacuum and purged with nitrogen gas. Anhydrous solvents (dichloromethane, toluene, acetonitrile, diethyl ether, and tetrahydrofuran) were filtered through activated 4 Å molecular sieves under nitrogen in a solvent purification system. Reactions were monitored either by analytical thin-layer chromatography (TLC silica gel 60 F_{254}, glass plates) and analyzed using 254 nm UV light and anisaldehyde–sulfuric acid or potassium permanganate stains or *via* gas chromatography–mass spectrometry (GC-MS). The column for the GC-MS system was 5% phenyl methyl siloxane, measuring 30 m in length with an internal diameter of 250 μm and film thickness of 0.25 μm. Low and high mass readings were set to 40 to 800 m/z, respectively. Oven, inlet, and detector temperatures were set to 250°C, and helium was used as the inert carrier gas. Column chromatography was completed using silica gel. Unless otherwise noted, all ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C. Chemical shifts (δ) are reported in ppm relative to residual $CHCl_3$ as an internal reference (^{1}H, 7.26 ppm; ^{13}C, 77.00 ppm). Coupling constants (*J*) are reported in hertz (Hz). Peak multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), x (septet), h (heptet), b (broad), and m (multiplet). FT-IR spectra were recorded using thin films, and absorption frequencies are reported in reciprocal centimeters (cm^{-1}). High-resolution mass spectrometry (HRMS) analyses were performed using electron spray ionization–time of flight (ESI-TOF) methods.

2. EXPERIMENTAL SECTION

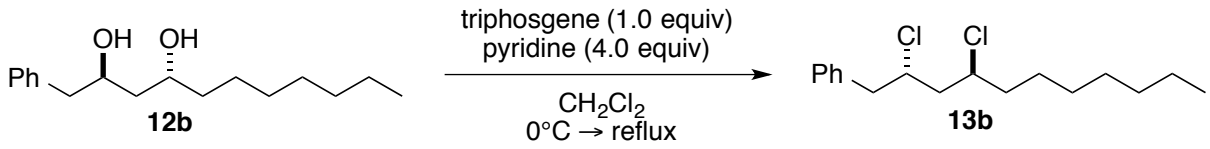
2.1. Dichlorination Procedure for 1,3-*Anti* Diols

Unless otherwise noted, 1,3-*anti* diol starting material was dissolved in anhydrous dichloromethane (~60-100 mM concentration). The solution was then cooled to 0°C. Triphosgene was added in one portion, followed by pyridine *via* syringe. The solution was stirred for 5 min and then warmed to gentle reflux for 3-6 hours. After cooling to room temperature, the reaction mixture was then poured into a separatory funnel containing aqueous HCl solution (1M, 10 mL), and the biphasic mixture was shaken vigorously. Upon separation of layers, the aqueous layer was re-extracted with dichloromethane (2 × 15 mL). Organic extracts were collected, dried over Na_2SO_4, filtered, and concentrated under vacuum. The resulting crude material was purified using flash column chromatography with silica gel as the stationary phase and a mixture of hexanes/ethyl acetate, pentane/diethyl ether, or pentane/dichloromethane as the mobile phase.

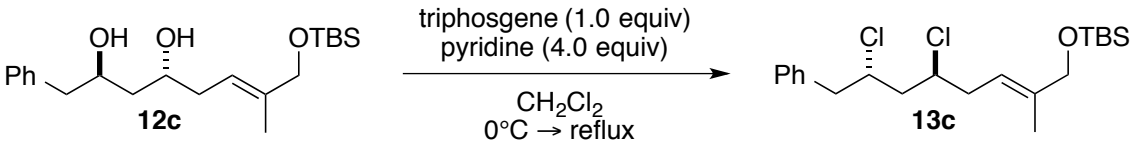


(±)-((2*S*,4*S*)-2,4-dichlorohept-6-en-1-yl)benzene (13a). 1,3-*anti* diol **12a** (50 mg, 0.24 mmol) was dissolved in CH_2Cl_2 (4.0 mL) and treated with triphosgene (71 mg, 0.24 mmol) and pyridine (78 μL, 0.96 mmol) to produce 1,3-*anti* dichloride **13a** in 90% yield as colorless oil (52 mg, 0.21 mmol). The purified product was eluted with 100% hexanes. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.41-7.23 (5H, m), 5.86 (1H, m), 5.19-5.14 (2H, m), 4.50 (1H, p, J = 6.6 Hz), 4.32 (1H, p, J = 6.5 Hz), 3.15 (1H, dd, J = 14.1, 7.4 Hz), 3.07 (1H, dd, J = 14.1, 6.4 Hz), 2.54 (2H, t, J = 6.6 Hz), 2.05-2.02 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 137.16, 133.53,

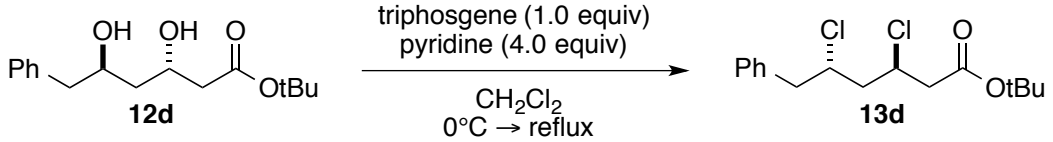
129.34, 128.47, 126.93, 118.39, 60.50, 59.24, 45.57, 44.98, 42.84. IR (cm^{-1}): *f* = 3081, 3065, 3029, 2961, 2926, 2854, 1698, 1643, 1604, 1496, 1454, 1277, 1239, 922, 700. HRMS-ESI: $(M-H_2Cl)^+$ = 205.0779 calculated for $C_{13}H_{14}Cl$, experimental = 205.0789. GC-MS: Rt = 18.72 min; M^+ = 242.1 calculated for $C_{13}H_{16}Cl_2$, experimental = 242.1.



(±)-((2*S*,4*S*)-2,4-dichlorotridecyl)benzene (13b). 1,3-*anti* diol **12b** (97 mg, 0.37 mmol) was dissolved in CH_2Cl_2 (6.0 mL) and treated with triphosgene (110 mg, 0.37 mmol) and pyridine (119 μL, 1.47 mmol) to produce 1,3-*anti* dichloride **13b** in 65% yield as a colorless oil (72 mg, 0.24 mmol). The purified product was eluted with 100% hexanes. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.37-7.24 (5H, m), 4.52 (1H, m), 4.26 (1H, m), 3.14 (1H, dd, J = 13.8, 7.5 Hz), 3.06 (1H, dd, *J* = 14.0, 6.3 Hz), 2.08-1.94 (2H, m), 1.74 (1H, m), 1.54-1.42 (3H, m) 1.31 (3H, s), 0.91 (3H, t, *J* = 6.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 137.21, 129.35, 128.44, 126.89, 60.82, 60.66, 46.33, 45.01, 38.74, 31.73, 29.10, 29.01, 26.38, 22.61, 14.07. IR (cm^{-1}): *f* = 2958, 2929, 2854, 1496, 1455, 750, 699, 612. HRMS-ESI: $(M-HCl_2)^+$ = 229.1951 calculated for $C_{17}H_{25}$, experimental = 229.1948. GC-MS: Rt = 21.92 min; M^+ = 300.1 calculated for $C_{17}H_{26}Cl_2$, experimental = 300.1.

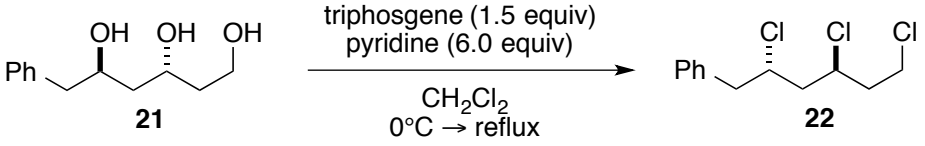


(±)-*tert*-butyl(((5*S*,7*S*,*E*)-5,7-dichloro-2-methyl-8-phenyloct-2-en-1 yl)oxy)dimethylsilane (13c). 1,3-*anti* diol **12c** (55 mg, 0.15 mmol) was dissolved in CH_2Cl_2 (1.5 mL) and treated with triphosgene (45 mg, 0.15 mmol) and pyridine (49 μL, 0.60 mmol) to produce 1,3-*anti* dichloride **13c** in 80% yield as a colorless oil (48 mg, 0.12 mmol). The purified product was eluted with 100% hexanes. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.36-7.21 (5H, m), 5.47 (1H, t, *J* = 8.0 Hz), 4.47 (1H, p, *J* = 8.0 Hz), 4.27 (1H, p, *J* = 8.0 Hz), 4.03 (2H, s), 3.12 (1H, dd, *J* = 16.0, 8.0 Hz), 3.03 (1H, dd, *J* = 16.0, 8.0 Hz), 2.55-2.46 (2H, m), 2.02-1.98 (2H, m), 1.60 (3H, s), 0.92 (9H, s), 0.06 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 137.87, 137.20, 129.36, 128.47, 126.93, 118.85, 68.04, 60.55, 60.04, 45.59, 45.04, 36.73, 25.94, 18.41, 13.78, -5.27. IR (cm^{-1}): *f* = 2954, 2928, 2855, 1252, 1109, 1072, 835, 775, 699. HRMS-ESI: $(M-2Cl+H)^+$ = 329.2295 calculated for $C_{21}H_{33}OSi$, experimental = 329.2289. GC-MS: Rt = 23.58 min; $(M-C_4H_9)^+$ = 343.1 calculated for $C_{17}H_{25}Cl_2OSi$, experimental = 343.1.



(±)-(3*S*,5*S*)-*tert*-butyl 3,5-dichloro-6-phenylhexanoate (13d). 1,3-*anti* diol **12d** (150 mg, 0.54 mmol) was dissolved in CH_2Cl_2 (8.0 mL) and treated with triphosgene (160 mg, 0.54 mmol) and pyridine (175 μL, 2.16 mmol) to produce 1,3-*anti* dichloride **13d** in 73% yield as a colorless oil (125 mg, 0.40 mmol). The purified product was eluted with 90:10 hexanes:EtOAc. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.37-7.24 (5H, m), 4.62 (1H, m), 4.48 (1H, dtd, *J* =

10.0, 6.9, 2.9 Hz), 3.16 (1H, dd, *J* = 14.2, 7.2 Hz), 3.07 (1H, dd, *J* = 14.1, 6.5 Hz), 2.74 (1H, dd, *J* = 15.5, 7.7 Hz), 2.65 (1H, dd, *J* = 15.6, 6.2 Hz), 2.13-2.01 (2H, m), 1.49, (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 168.58, 136.95, 129.30, 128.43, 126.91, 81.44, 59.93, 55.32, 45.41, 44.81, 44.78, 27.95. IR (cm^{-1}): *f* = 2978, 2931, 1728, 1367, 1145, 751, 699. HRMS-ESI: $(M\text{-}H_2Cl_2)^+$ = 244.1463 calculated for $C_{16}H_{20}O_2$, experimental = 244.1957.

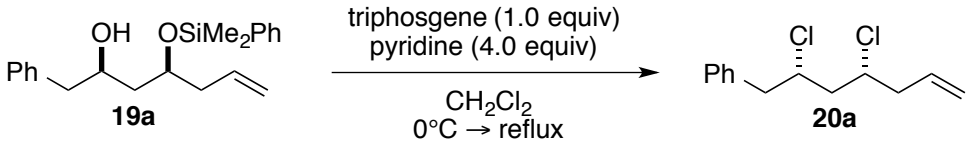


(±)-((2*S*,4*S*)-2,4,6-trichlorohexyl)benzene (22). 1,3,5-*anti* triol **21** (37 mg, 0.175 mmol) was dissolved in CH_2Cl_2 (2.5 mL) and treated with triphosgene (78 mg, 0.27 mmol) and pyridine (85 μL, 1.05 mmol) to produce 1,3,5-*anti* trichloride **22** in 75% yield as a colorless oil (35 mg, 0.13 mmol). The purified product was eluted with 100% hexanes. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.38-7.24 (5H, m), 4.49 (2H, p, *J* = 8.0 Hz), 3.79-3.70 (2H, m), 3.18 (1H, dd, *J* = 12.0, 8.0 Hz), 3.07 (1H, dd, *J* = 12.0, 8.0 Hz), 2.18-1.96 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 136.99, 129.36, 128.53, 127.01, 60.02, 57.27, 46.02, 44.93, 41.26, 41.11. IR (cm^{-1}): *f* = 2964, 2925, 1454, 906, 701. HRMS-ESI: $(M\text{-}Cl+H)^+$ = 229.0545 calculated for $C_{12}H_{15}Cl_2$, experimental = 229.0527. GC-MS: Rt = 20.29 min; M^+ = 264.0 calculated for $C_{12}H_{15}Cl_3$, experimental = 264.0.

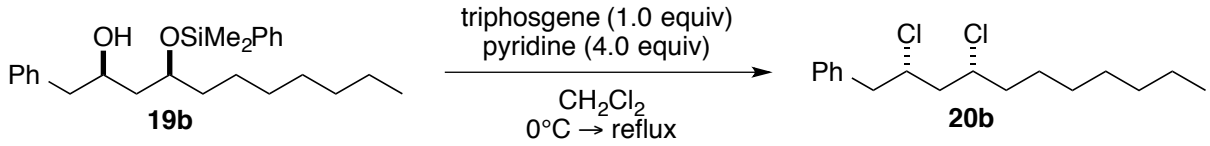
2.2. Dichlorination Procedure for 1,3-*Syn* Diols

Unless otherwise noted, 1,3-*syn* diol monosilylether starting material was dissolved in anhydrous dichloromethane (~500 mM concentration). The solution was then cooled to 0°C. Triphosgene was added in one portion, followed by pyridine *via* syringe. The solution was stirred

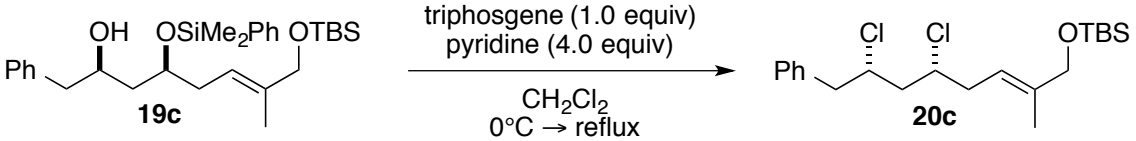
for 5 min and then warmed to gentle reflux for 3-6 hours. After cooling to room temperature, the reaction mixture was then poured into a separatory funnel containing aqueous HCl solution (1M, 10 mL), and the biphasic mixture was shaken vigorously. Upon separation of layers, the aqueous layer was re-extracted with dichloromethane (2 × 15 mL). Organic extracts were collected, dried over Na_2SO_4, filtered, and concentrated under vacuum. The resulting crude material was purified using flash column chromatography with silica gel as the stationary phase and a mixture of hexanes/ethyl acetate, pentane/diethyl ether, or pentane/dichloromethane as the mobile phase.



(±)-((2*S*,4*R*)-2,4-dichlorohept-6-en-1-yl)benzene (20a). 1,3-*syn* diol monosilylether **19a** (114 mg, 0.34 mmol) was dissolved in CH_2Cl_2 (0.68 mL) and treated with triphosgene (101 mg, 0.34 mmol) and pyridine (108 μL, 1.34 mmol) to produce 1,3-*syn* dichloride **20a** in 76% yield as a colorless oil (62 mg, 0.26 mmol). The purified product was eluted with 100% hexanes. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.38-7.24 (5H, m), 5.85 (1H, m), 5.17-5.13 (2H, m), 4.31-4.18 (2H, m), 3.14 (1H, dd, *J* = 14.1, 5.5 Hz), 3.02 (1H, dd, *J* = 14.1, 7.9 Hz), 2.61 (1H, dt, *J* = 14.9, 5.7 Hz), 2.47 (1H, dt, *J* = 14.6, 7.3 Hz), 2.33-2.20 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 137.14, 133.04, 129.37, 128.47, 126.98, 118.65, 59.82, 58.30, 45.37, 44.10, 41.13. IR (cm^{-1}): *f* = 3065, 3029, 2963, 2918, 1434, 923, 749, 699. HRMS-ESI: $(M\text{-}HCl_2)^+$ = 171.1168 calculated for $C_{13}H_{15}$, experimental = 171.1172. GC-MS: Rt = 18.70 min; M^+ = 242.1 calculated for $C_{13}H_{16}Cl_2$, experimental = 242.0.

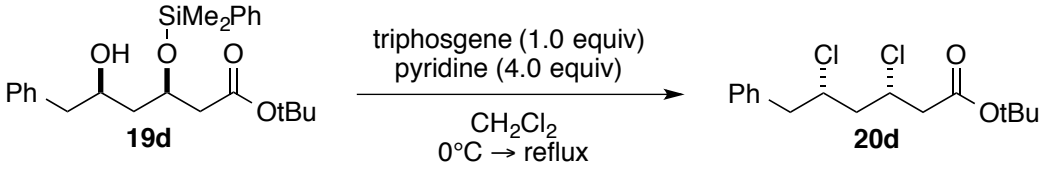


(±)-((2*S*,4*R*)-2,4-dichlorotridecyl)benzene (20b). 1,3-*syn* diol monosilylether **19b** (110 mg, 0.28 mmol) was dissolved in CH_2Cl_2 (0.56 mL) and treated with triphosgene (83 mg, 0.28 mmol) and pyridine (89 μL, 1.10 mmol) to produce 1,3-*syn* dichloride **20b** in 82% yield as a colorless oil (68.5 mg, 0.23 mmol). The purified product was eluted with 100% hexanes. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.41-7.26 (5H, m), 4.29 (1H, tdd, *J* = 8.0, 5.8, 5.8 Hz), 4.26 (1H, m), 3.16 (1H, dd, *J* = 14.0, 5.4 Hz), 3.02 (1H, dd, *J* = 14.1, 8.1 Hz), 2.32 (1H, dt, *J* = 14.7, 7.5 Hz), 2.20 (1H, dt, *J* = 13.7, 6.4 Hz), 1.79 (1H, m), 1.66 (1H, ddt, *J* = 14.0, 14.0, 4.7 Hz), 1.56-1.40 (2H, m), 1.37-1.28 (8H, m), 0.93 (3H, t, *J* = 6.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 137.24, 129.38, 128.45, 126.95, 59.96, 59.94, 46.28, 44.06, 37.08, 31.73, 29.10, 28.96, 25.94, 22.61, 14.08. IR (cm^{-1}): *f* = 3028, 2956, 2926, 2855, 1497, 1455, 1254, 1119, 1059, 831, 791, 699. HRMS-ESI: $(M\text{-}HCl_2)^+$ = 229.1951 calculated for $C_{17}H_{25}$, experimental = 229.1955. GC-MS: Rt = 21.88 min; M^+ = 300.1 calculated for $C_{17}H_{26}Cl_2$, experimental = 300.1.

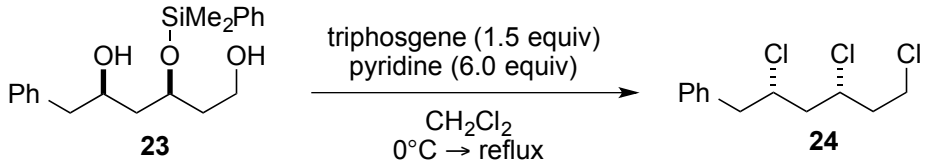


(±)-*tert*-butyl(((5*R*,7*S*,*E*)-5,7-dichloro-2-methyl-8-phenyloct-2-en-1-yl)oxy)dimethylsilane (20c). 1,3-*syn* diol monosilylether **19c** (38 mg, 0.076 mmol) was dissolved in CH_2Cl_2 (0.15 mL) and treated with triphosgene (23 mg, 0.076 mmol) and pyridine (25 μL, 0.31 mmol). The crude was eluted with 100% hexanes → 98:2 hexanes:EtOAc to produce 1,3-*syn* dichloride **20c** in 93% yield as a colorless oil (29 mg, 0.071 mmol). ^{1}H NMR

(400 MHz, $CDCl_3$); δ (ppm) = 7.39-7.24 (5H, m), 5.50 (1H, t, *J* = 8.0 Hz), 4.28 (1H, p, *J* = 8.0 Hz), 4.20 (1H, p, *J* = 8.0 Hz), 4.04 (2H, s), 3.15 (1H, dd, *J* = 16.0, 8.0 Hz), 2.99 (1H, dd, *J* = 16.0, 8.0 Hz), 2.62-2.47 (2H, m), 2.32-2.22 (2H, m), 1.63 (3H, s), 0.95 (9H, s), 0.10 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 138.00, 137.24, 129.40, 128.46, 126.96, 118.47, 68.06, 60.02, 59.20, 45.67, 44.05, 35.19, 25.94, 18.41, 13.79, -5.28. IR (cm^{-1}): *f* = 2954, 2928, 2856, 1253, 1111, 1072, 836, 776, 699. HRMS-ESI: $(M+Na)^+$ = 423.1648 calculated for $C_{21}H_{34}Cl_2NaOSi$, experimental = 423.1676. GC-MS: Rt = 23.58 min; $(M-C_4H_9)^+$ = 343.1 calculated for $C_{17}H_{25}Cl_2OSi$, experimental = 343.1.



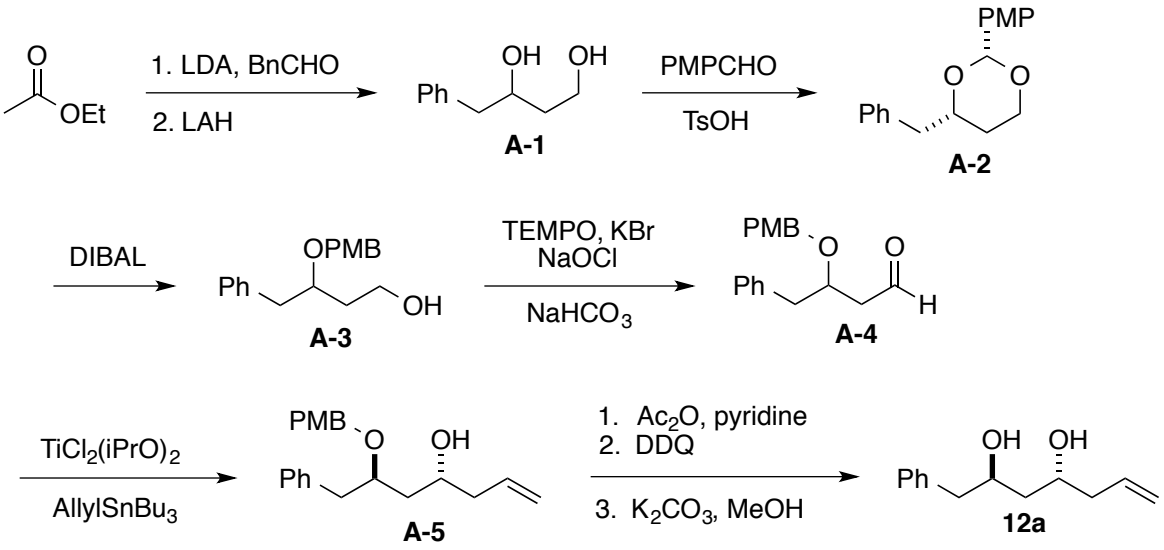
(±)-(3*R*,5*S*)-*tert*-butyl 3,5-dichloro-6-phenylhexanoate (20d). 1,3-*syn* diol monosilylether **19d** (29 mg, 0.070 mmol) was dissolved in CH_2Cl_2 (0.14 mL) and treated with triphosgene (21 mg, 0.070 mmol) and pyridine (23 μL, 0.28 mmol) to produce 1,3-*syn* dichloride **20d** in 92% yield as a colorless oil (20 mg, 0.065 mmol). The purified product was eluted with 100% hexanes, buffered with 1% Et_3N. ^1H NMR (500 MHz, $CDCl_3$); δ (ppm) = 7.38-7.20 (5H, m), 4.47 (1H, m), 4.29-4.23 (1H, m), 3.16 (1H, dd, *J* = 14.2, 5.2 Hz), 2.98 (1H, dd, *J* = 14.2, 8.3 Hz), 2.72 (1H, dd, *J* = 15.8, 5.1 Hz), 2.63 (1H, dd, *J* = 15.8, 8.4 Hz), 2.34-2.24 (2H, m), 1.46 (9H, s). ^{13}C NMR (125 MHz, $CDCl_3$); δ (ppm) = 168.86, 137.08, 129.40, 128.48, 127.00, 81.60, 59.46, 54.65, 45.58, 43.87, 43.61, 28.05. IR (cm^{-1}): *f* = 2977, 2927, 2854, 1715, 1368, 1296, 1255, 1148, 700. HRMS-ESI: $(M+Na)^+$ = 339.0889 calculated for $C_{16}H_{22}Cl_2NaO_2$, experimental = 339.0891.



(±)-((2*S*,4*R*)-2,4,6-trichlorohexyl)benzene (24). 1,3,5-*syn* triol monosilylether **23** (60 mg, 0.17 mmol) was dissolved in CH_2Cl_2 (0.34 mL) and treated with triphosgene (77 mg, 0.26 mmol) and pyridine (82 μL, 1.02 mmol) to produce 1,3,5-*syn* trichloride **24** in 55% yield as a colorless oil (25 mg, 0.09 mmol). The purified product was eluted with 100% hexanes, buffered with 1% Et_3N. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.37-7.24 (5H, m), 4.37 (1H, dtd, *J* = 10.0, 7.0, 3.0 Hz), 4.30 (1H, ddd, *J* = 13.8, 7.8, 6.0 Hz), 3.78-3.68 (2H, m), 3.15 (1H, dd, *J* = 14.1, 5.5 Hz), 3.03 (1H, dd, *J* = 14.2, 7.9 Hz), 2.34 (1H, dt, *J* = 14.5, 7.6 Hz), 2.26-2.18 (2H, m), 2.07 (1H, ddt, *J* = 10.7, 9.8, 5.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 136.94, 129.40, 128.52, 127.06, 59.29, 56.38, 45.95, 43.98, 41.26, 39.77. IR (cm^{-1}): *f* = 3029, 2964, 2923, 2852, 1497, 1454, 1438, 1311, 1247, 749, 700. HRMS-ESI: $(M\text{-}Cl)^+$ = 229.0545 calculated for $C_{12}H_{15}Cl_2$, experimental = 229.0543. GC-MS: Rt = 20.25 min; M^+ = 264.0 calculated for $C_{12}H_{15}Cl_3$, experimental = 264.0.

2.3. Synthesis of 1,3-*Anti* Diols

Preparation of 1,3-Anti Diol **12a**



(±)-4-phenylbutane-1,3-diol (A-1). A solution of LDA in THF (300 mL) was prepared by dissolving diisopropylamine (37.6 mL, 266.00 mmol) in THF while cooling to -78°C. *n*-BuLi (106.5 mL, 266.00 mmol) was slowly added. The mixture was allowed to stir for 15 minutes before ethyl acetate (26 mL, 266.00 mmol) was added dropwise. After stirring the resulting mixture for 20 minutes, phenylacetaldehyde (18.6 mL, 166.40 mmol) was added. The mixture was allowed to stir until complete consumption of aldehyde and then quenched with a half-saturated NH_4Cl (150 mL) solution. Upon separation of layers, the aqueous layer was extracted with EtOAc (3 x 50 mL). Organic layers were combined and dried over $MgSO_4$ and concentrated in vacuo.

The resulting crude material was then dissolved in Et_2O (20 mL). The solution was then added dropwise *via* cannula to a cooled (0°C) suspension of lithium aluminum hydride (7.0 g, 183.00 mmol) in Et_2O (500 mL). After stirring for one hour, the reaction was quenched by the

slow addition of deionized water (7.0 mL), which was followed by addition of a 15% aqueous sodium hydroxide solution (7.0 mL), and then deionized water (21.0 mL). This workup sequence resulted in the formation of white precipitates. After further stirring for one hour, the filtrate was collected using vacuum filtration and concentrated in vacuo. The crude material was then purified in 30:70 → 20:80 hexanes:EtOAc to give 1,3-diol **A-1** with a yield of 56% (15.49 g, 93.26 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.36-7.23 (5H, m), 3.91-3.84 (2H, m), 2.87-2.76 (2H, m), 2.42-2.37 (2H, bs), 1.82-1.75 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) =138.08, 129.36, 128.51, 126.47, 72.77, 61.43, 44.26, 37.70. Compound **A-1** is known (CAS #74578-77-1).

(±)-4-benzyl-2-(4-methoxyphenyl)-1,3-dioxane (A-2). 1,3-Diol **A-1** (15.49 g, 93.26 mmol) was dissolved in toluene (300 mL) and *p*-anisaldehyde (17.0 mL, 136.20 mmol) and TsOH (177 mg, 0.93 mmol) were added. The resulting mixture was heated to reflux using a dean stark apparatus. After stirring overnight, the reaction was quenched by the addition of solid $NaHCO_3$ (300 mg), and the mixture was then concentrated in vacuo. In order to create better chromatographic separation between the product and residual *p*-anisaldehyde, the crude material was dissolved in MeOH (200 mL) and carefully treated with $NaBH_4$ (5.29 g, 139.90 mmol). The mixture was stirred until *p*-anisaldehyde was fully consumed. After removing the organic solvent under vacuum, the crude material was then quenched with a half-saturated NH_4Cl solution (100 mL) and then extracted with EtOAc (3 x 100 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude material was purified with 80:20 hexanes:EtOAc to give acetal **A-2** with a yield of 97% (25.59 g, 90.10 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.43 (2H, d, J = 8.2 Hz), 7.35-7.24 (5H, m), 6.90 (2H, d, J = 8.4 Hz), 5.48 (1H, s),

4.24 (1H, m), 3.95 (1H, m), 3.81 (3H, s), 3.09 (1H, dd, J = 13.5, 6.3 Hz), 2.80 (1H, dd, J = 13.6, 6.9 Hz), 1.84 (1H, m), 1.49 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 159.85, 137.74, 131.35, 129.54, 128.29, 127.32, 126.35, 113.58, 101.06, 77.99, 66.95, 55.28, 42.60, 30.77. IR (cm^{-1}): f = 2953, 2840, 1614, 1516, 1247, 1171, 1103, 1031, 907, 825, 726, 699, 532. HRMS-ESI: $(M+)^+$ = 285.1485 calculated for $C_{18}H_{21}O_3$, experimental = 285.1484.

(±)-3-((4-methoxybenzyl)oxy)-4-phenylbutan-1-ol (A-3). Acetal **A-2** (9.46 g, 33.30 mmol) was dissolved in CH_2Cl_2 (200 mL) and cooled to -78°C. DIBAL (48.3 mL, 48.30 mmol, 1M solution in toluene) was added dropwise. The reaction was allowed to stir at -78°C for two hours before being allowed to slowly warm to room temperature overnight. After cooling back to 0°C, the reaction mixture was slowly quenched with a saturated aqueous solution of Rochelle's salt (150 mL) and vigorously stirred for two hours. Upon separation of layers, the aqueous layer was then extracted with CH_2Cl_2 (3 x 100 mL). The organic layers were collected, dried over Na_2SO_4, and concentrated in vacuo. The crude mixture was purified in 70:30 → 60:40 hexanes:EtOAc to give alcohol **A-3** with a yield of 80% (7.29 g, 25.48 mmol) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.35-7.20 (7H, m), 6.89 (2H, d, J = 8.6 Hz), 4.54 (1H, d, J = 11.0 Hz), 4.43 (1H, d, J = 11.0 Hz), 3.89-3.68 (3H, m), 3.83 (3H, s), 3.05 (1H, dd, J = 13.5, 5.8 Hz), 2.80 (1H, d, J = 13.6, 7.0 Hz), 2.43 (1H, bs), 1.83-1.67 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 159.25, 138.38, 130.13, 129.52, 129.45, 128.34, 126.23, 113.84, 79.23, 71.15, 60.62, 55.22, 40.46, 36.02. IR (cm^{-1}): f = 3409, 3029, 2936, 2866, 1612, 1513, 1247, 1173, 1033, 906, 822, 725, 700, 647, 513. HRMS-ESI: $(M+Na)^+$ = 309.1461 calculated for $C_{18}H_{22}NaO_3$, experimental = 309.1471.

(±)-3-((4-methoxybenzyl)oxy)-4-phenylbutanal (A-4). Alcohol **A-3** (7.29 g, 25.48 mmol) was dissolved in CH_2Cl_2 (250 mL) and cooled to 0°C. TEMPO (399 mg, 2.55 mmol) and KBr (1.3 mL, 2.55 mmol, 2M solution) were then added to the solution. A bleach solution containing NaOCl (35 mL, 28.03 mmol, Clorox brand) and $NaHCO_3$ (519 mg, 15 mg per 1 mL of bleach) was added slowly to maintain the internal reaction temperature near 0°C. Upon completion, the biphasic layers were separated. The aqueous layer reaction was then extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers were then washed with $Na_2S_2O_3$, followed by a saturated $NaHCO_3$ solution, and then dried over Na_2SO_4 and concentrated in vacuo. The crude mixture was purified in 80:20 → 70:30 hexane:EtOAc to give aldehyde **A-4** with a yield of 69% (5.00 g, 17.60 mmol) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 9.71 (1H, t, *J* = 2.1 Hz), 7.33-7.17 (7H, m), 6.86 (2H, d, *J* = 8.6 Hz), 4.47 (2H, q, *J* = 11.1, 4.4 Hz), 4.19-4.13 (1H, m), 3.81 (3H, s), 3.03 (1H, dd, *J* = 13.6, 6.0 Hz), 2.81 (1H, dd, *J* = 13.6, 6.8 Hz), 2.63 (1H, ddd, *J* = 16.6, 7.7, 2.5 Hz), 2.51 (1H, ddd, *J* = 16.5, 4.4, 1.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 201.31, 159.27, 137.60, 130.01, 129.53, 129.46, 128.48, 126.56, 113.81, 75.07, 71.33, 55.26, 48.04, 40.59. IR (cm^{-1}): *f* = 2975, 2850, 1719, 1612, 1513, 1248, 1087, 1033, 702. HRMS-ESI: $(M+Na)^+$ = 307.1310 calculated for $C_{18}H_{20}O_3Na$, experimental = 307.1308.

(±)-(4*R*,6*R*)-6-((4-methoxybenzyl)oxy)-7-phenylhept-1-en-4-ol (A-5). PMB aldehyde **A-4** (1.50 g, 5.28 mmol) was dissolved in CH_2Cl_2 (25 mL) in a round bottom flask containing 4Å molecular sieves. After cooling the mixture to -78°C, freshly prepared $TiCl_2(OiPr)_2$ (10.3 mL, 7.92 mmol, 0.77M in CH_2Cl_2) was then added and allowed to stir for 10 minutes. Tributylallylstannane (2.50 mL, 7.92 mmol) was added dropwise. The reaction was stirred until

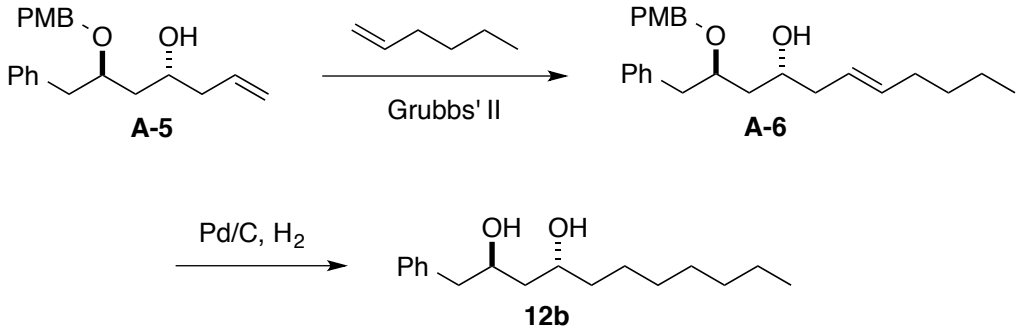
completion and then quenched with a saturated $NaHCO_3$ solution (25 mL) and allowed to warm to room temperature. The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were then dried over Na_2SO_4 and concentrated in vacuo. The crude mixture was purified in 80:20 → 70:30 hexanes:EtOAc to give alcohol **A-5** in 95% yield (1.63 g, 5.00 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.35-7.20 (7H, m), 6.88 (2H, d, *J* = 8.2 Hz), 5.81 (1H, m), 5.09 (2H, d, *J* = 13.2 Hz), 4.45 (2H, dd, *J* = 15.8, 10.8 Hz), 4.03-3.93 (2H, m), 3.81 (3H, s), 3.03 (1H, dd, *J* = 13.8, 6.4 Hz), 2.80 (1H, dd, *J* = 13.7, 6.7 Hz), 2.66 (1H, d, *J* = 3.3 Hz), 2.20 (2H, t, *J* = 6.7 Hz), 1.68-1.59 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 159.16, 138.50, 134.80, 130.15, 129.49, 129.39, 128.25, 126.13, 117.43, 113.73, 77.53, 71.38, 67.51, 55.14, 42.08, 40.41, 39.73. IR (cm^{-1}): *ƒ* = 3359, 3064, 3027, 2917, 2859, 1496, 1434, 1247, 1081, 1032, 909, 730, 699. HRMS-ESI: $(M+Na)^+$ = 349.1774 calculated for $C_{21}H_{26}NaO_3$, experimental = 349.1768.

(±)-(2*R*,4*R*)-1-phenylhept-6-ene-2,4-diol (12a). Alcohol **A-5** (150 mg, 0.46 mmol) was dissolved in CH_2Cl_2 (10 mL). DMAP (56 mg, 0.46 mmol) was added to the reaction mixture, followed by addition of acetic anhydride (0.22 mL, 2.30 mmol) and pyridine (0.40 mL, 4.60 mmol). Upon completion, the reaction was quenched with a 2M HCl solution (15 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum to give the crude acetate protected alcohol.

The resulting crude product was then dissolved in a mixture of CH_2Cl_2:H_2O (8 mL:few drops) and treated with DDQ (157 mg, 0.69 mmol). Upon completion, the reaction was quenched with a saturated $NaHCO_3$ solution (15 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum.

The crude monoprotected alcohol was then dissolved in MeOH (5 mL) and treated with K_2CO_3 (127 mg, 0.92 mmol). Upon completion, the reaction was quenched with a half saturated NH_4Cl solution (15 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude mixture was purified in 70:30 → 60:40 hexanes:EtOAc to give 1,3-*anti* diol **12a** in 62% yield (59 mg, 0.28 mmol) over three steps, as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.35-7.21 (5H, m), 5.81 (1H, m), 5.16-5.10 (2H, m), 4.19 (1H, p, *J* = 6.1 Hz), 4.03 (1H, p, *J* = 5.9 Hz), 2.84-2.75 (2H, m), 2.35 (1H, bs), 2.29-2.24 (3H, m), 1.69 (2H, dd, *J* = 6.0, 5.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 138.26, 134.60, 129.35, 128.59, 126.54, 70.04, 68.08, 44.04, 41.99, 41.52. IR (cm^{-1}): *f* = 3335, 3076, 3028, 2914, 1496, 1433, 1327, 1080, 995, 914, 743, 698, 489. HRMS-ESI: $(M+H)^+$ = 207.1380 calculated for $C_{13}H_{19}O_2$, experimental = 207.1381.

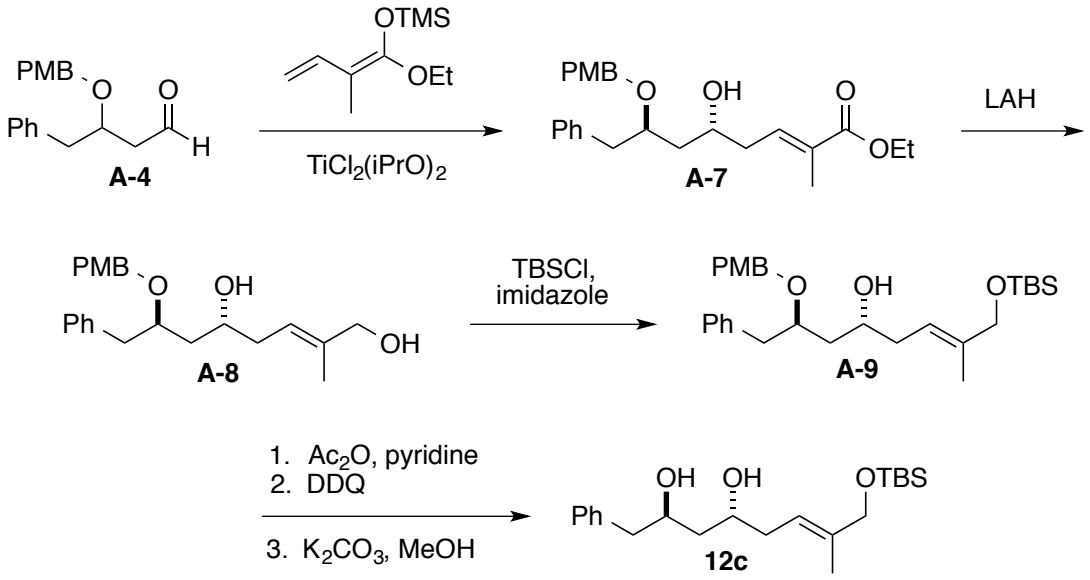
Preparation of 1,3-Anti Diol **12b**



(±)-(2*R*,4*R*)-1-phenylundecane-2,4-diol (12b). Grubb's II catalyst (24 mg, 0.028mmol) was dissolved in CH_2Cl_2 (8 mL). Allylic alcohol **A-5** (178 mg, 0.55 mmol) and 1-hexene (0.70 mL, 5.50 mmol) were then added, and the reaction mixture was heated to reflux. Upon completion, the reaction mixture was cooled to room temperature and concentrated in vacuo to afford alkene **A-6**. The crude mixture was then introduced into a round bottom flask under

vacuum. 10% Pd/C (300 mg, 0.28 mmol) was added carefully, followed by the addition of MeOH (5 mL). The black suspension was then purged and bubbled with a balloon of H_2 gas overnight. Upon completion, the reaction mixture was filtered through a pad of celite via vacuum filtration. The solid residue was rinsed with EtOAc (3 x 10 mL), and the filtrate was concentrated in vacuo. The crude mixture was purified in 60:40 hexanes:EtOAc to give aliphatic chain **12b** in 67% yield (97 mg, 0.37mmol) over two steps, as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.37-7.24 (5H, m), 4.20 (1H, t, *J* = 5.8 Hz), 3.97 (1H, t, *J* = 5.5 Hz), 2.82 (2H, d, *J* = 6.6 Hz), 2.67 (2H, s), 1.67 (2H, t, *J* = 5.7 Hz), 1.59-1.43 (2H, m), 1.32 (10H, bs), 0.93 (3H, t, *J* = 6.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 138.43, 129.40, 128.57, 126.50, 70.13, 69.22, 44.06, 41.91, 37.46, 31.83, 29.61, 29.28, 25.78, 22.67, 14.11. IR (cm^{-1}): *f* = 3434, 3325, 2925, 2854, 1496, 1454, 1130, 1081, 836, 746, 699, 606, 504. HRMS-ESI: $(M+H)^+$ = 265.2162 calculated for $C_{17}H_{29}O_2$, experimental = 265.2162.

Preparation of 1,3-Anti Diol **12c**



(±)-ethyl(5*R*,7*R*,*E*)-5-hydroxy-7-((4-methoxybenzyl)oxy)-2-methyl-8-phenyloct-2-enoate (A-7). Aldehyde **A-4** (1.46 g, 5.12 mmol) was dissolved in CH_2Cl_2 (40 mL) and cooled to -78°C. A freshly prepared solution of $TiCl_2(OiPr)_2$ (2.5 mL, 7.69 mmol, 3M in CH_2Cl_2) was added dropwise, and the mixture was stirred for 20 minutes. A solution of (*Z*)-((1-ethoxy-2-methylbuta-1,3-dien-1-yl)oxy)trimethylsilane (1.54 g, 7.69 mmol) in CH_2Cl_2 (3 x 3 mL) was then added slowly *via* cannula. After reaching completion, the reaction was quenched with pH 7 phosphate buffer (50 mL) and a saturated Rochelle's salt solution (50 mL). The biphasic layers were allowed to warm to room temperature while stirring vigorously. Upon separation of layers, the aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL). The organic layers were then combined, dried over Na_2SO_4, and concentrated under vacuum. The crude mixture was purified in 80:20 → 70:30 hexanes:EtOAc to give ester **A-7** with a yield of 58% (1.22 g, 2.96 mmol) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.31-7.17 (7H, m), 6.86 (2H, d, *J* = 8.6 Hz), 6.76 (1H, t, *J* = 6.3 Hz), 4.47 (1H, d, *J* = 11.1 Hz), 4.40 (1H, d, *J* = 11.1 Hz), 4.18 (2H, q, *J* = 14.1, 7.0 Hz), 4.09 (1H, m), 3.92 (1H, m), 3.79 (3H, s), 3.03 (1H, dd, *J* = 13.6, 6.1 Hz), 2.87 (1H, bs), 2.77 (1H, dd, *J* = 13.5, 6.9 Hz), 2.37-2.21 (2H, m), 1.80 (3H, s), 1.69-1.56 (2H, m), 1.27 (3H, dt, *J* = 12.7, 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 167.83, 159.26, 138.29, 137.79, 129.93, 129.58, 129.55, 129.35, 128.33, 126.23, 113.81, 77.47, 71.30, 67.67, 60.39, 55.17, 40.10, 39.57, 36.80, 14.21, 12.57. IR (cm^{-1}): *f* = 3479, 2936, 2871, 1706, 1496, 1249, 1081, 1034, 702. HRMS-ESI: $(M+Na)^+$ = 435.2142 calculated for $C_{25}H_{32}NaO_5$, experimental = 435.2140.

(±)-(5*R*,7*R*,*E*)-7-((4-methoxybenzyl)oxy)-2-methyl-8-phenyloct-2-ene-1,5-diol (A-8). Ester **A-7** (1.10 g, 2.67 mmol) was dissolved in Et_2O (10 mL) and added slowly via cannula to a

cooled (0°C) suspension of lithium aluminum hydride (152 mg, 4.00 mmol) in Et_2O (90 mL). After complete consumption of the starting material, the reaction was quenched by the slow addition of deionized water (0.2 mL), followed by addition of a 15% aqueous sodium hydroxide solution (0.2 mL), and then deionized water (0.6 mL). This workup sequence resulted in the formation of white precipitates. After further stirring for one hour, the filtrate was collected using vacuum filtration and concentrated under vacuum. The crude material was then purified in 60:40 → 50:50 hexanes:EtOAc → 100% EtOAc to give diol **A-8** with a yield of 67% (662 mg, 1.79 mmol) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.33-7.19 (7H, m), 6.88 (2H, d, *J*= 8.3 Hz), 5.41 (1H, t, *J* = 7.5 Hz), 4.46 (2H, q, *J* = 11.0 Hz), 3.99 (2H, s), 3.96-3.92 (2H, m), 3.82 (3H, s), 3.05 (1H, dd, *J* = 13.5, 6.2 Hz), 2.79 (1H, dd, *J* = 13.6, 7.0 Hz), 2.71 (1H, bs), 2.24 (1H, dt, *J* = 14.4, 7.1 Hz), 2.14 (1H, dt, *J* = 14.2, 6.8 Hz), 1.65 (3H, s), 1.63-1.59 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 159.08, 138.44, 137.13, 130.06, 129.44, 129.35, 128.19, 126.09, 121.49, 113.69, 77.56, 71.39, 68.25, 68.20, 55.08, 40.43, 40.36, 39.83, 35.78, 13.82. IR (cm^{-1}): *f* = 3383, 2934, 2912, 2861, 1513, 1247, 1174, 1032, 821, 701. HRMS-ESI: $(M+H)^+$ = 371.2217 calculated for $C_{23}H_{31}O_4$, experimental = 371.2205.

(±)-(2*R*,4*R*,*E*)-8-((*tert*-butyldimethylsilyl)oxy)-2-((4-methoxybenzyl)oxy)-7-methyl-1-phenyloct-6-en-4-ol (A-9). Diol **A-8** (728 mg, 1.97 mmol) was dissolved in CH_2Cl_2 (100 mL) and cooled to 0^{o}C. Imidazole (268 mg, 3.94 mmol) was then added, followed by TBSCl (445 mg, 2.95 mmol). White precipitate was observed after the addition of TBSCl. The reaction mixture was then warmed to room temperature and stirred overnight. 2M aqueous HCl solution (50 mL) was added to quench the reaction, and the aqueous layer was then extracted with CH_2Cl_2 (3 x 25 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated

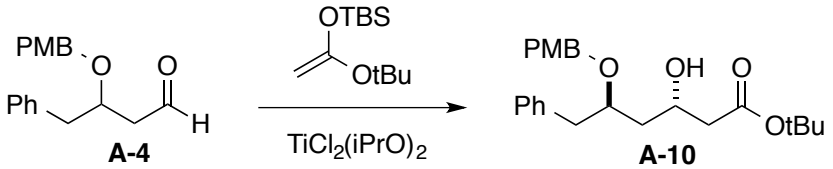
under vacuum. The crude mixture was purified in 80:20 hexane:EtOAc to give alcohol **A-9** with a yield of 97% (923 mg, 1.91 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.34-7.19 (7H, m), 6.87 (2H, d, *J* = 8.6 Hz), 5.41 (1H, t, *J* = 6.9 Hz), 4.44 (2H, q, *J* = 11.4 Hz), 4.02 (2H, s), 4.01-3.90 (2H, m), 3.83 (3H, s), 3.02 (1H, dd, *J* = 13.6, 6.6 Hz), 2.80 (1H, dd, *J* = 13.5, 6.7 Hz), 2.56 (1H, bs), 2.27-2.12 (2H, m), 1.66-1.61 (2H, m), 1.59 (3H, s), 0.94 (9H, s), 0.09 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 159.22, 138.57, 137.21, 130.26, 129.62, 129.47, 128.34, 126.19, 120.12, 113.91, 77.69, 71.47, 68.45, 68.35, 55.24, 40.52, 39.84, 35.83, 25.94, 18.39, 13.66, -5.28. IR (cm^{-1}): *f* = 3449, 2951, 2928, 2855, 1513, 1248, 1066, 835, 776, 668. HRMS-ESI: $(M+Na)^+$ = 507.2901 calculated for $C_{29}H_{44}NaO_4Si$, experimental = 507.2897.

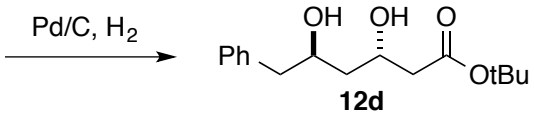
(±)-(2*R*,4*R*,*E*)-8-((*tert*-butyldimethylsilyl)oxy)-2-((4-methoxybenzyl)oxy)-7-methyl-1-phenyloct-6-en-4-ol (12c). Alcohol **A-9** (128 mg, 0.26 mmol) was dissolved in CH_2Cl_2 (20 mL). DMAP (32 mg, 0.26 mmol) was then added, followed by acetic anhydride (125 μL, 1.32 mmol), and pyridine (214 μL, 2.64 mmol). The reaction was stirred at room temperature until all starting material was fully consumed, and then quenched with 2M HCl (20 mL). The aqueous layer was then extracted with CH_2Cl_2 (3 x 10 mL). The organic layers were then combined, dried over Na_2SO_4, and concentrated under vacuum.

The resulting crude material was dissolved in CH_2Cl_2 (50 mL). 10 drops of H_2O and DDQ (90 mg, 0.40 mmol) were sequentially added. After the disappearance of starting material, the reaction was quenched with a saturated $NaHCO_3$ solution (30 mL) and extracted with CH_2Cl_2 (4 x 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum.

The resulting crude material was dissolved in MeOH (50 mL) and K_2CO_3 (183 mg, 1.32 mmol) was then added. Upon completion, the reaction mixture was quenched with a half saturated NH_4Cl solution (30 mL) and extracted with EtOAc (4 x 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude mixture was purified in 85:15 → 80:20 hexanes:EtOAc to give diol **12c** with a yield of 58% (55 mg, 0.15 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.35-7.23 (5H, m), 5.45 (1H, t, *J* = 6.8 Hz), 4.20 (1H, p, *J* = 6.1 Hz), 4.04 (2H, s), 4.02 (1H, m), 2.81 (2H, d, *J* = 6.4 Hz), 2.46 (1H, bs), 2.33 (1H, dt, *J* = 14.8, 7.7 Hz), 2.22 (1H, dt, *J* = 13.0, 5.8 Hz), 1.72 (2H, t, *J* = 5.8 Hz), 1.64 (3H, s), 0.94 (9H, s), 0.09 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 138.36, 137.88, 129.35, 128.54, 126.46, 119.60, 70.08, 68.98, 68.29, 44.06, 41.49, 35.68, 25.93, 18.40, 13.71, -5.29. IR (cm^{-1}): *f* = 3375, 2928, 2856, 1327, 939, 775. HRMS-ESI: $(M+H)^+$ = 365.2506 calculated for $C_{21}H_{37}O_3Si$, experimental = 365.2509.

Preparation of 1,3-Anti Diol **12d**





(±)-(3*S*,5*R*)-tert-butyl 3-hydroxy-5-((4-methoxybenzyl)oxy)-6-phenylhexanoate. (A-10). Aldehyde **A-4** (1.46 g, 5.12 mmol) was dissolved in CH_2Cl_2 (40 mL) and cooled to -78°C. $TiCl_2(O^iPr)_2$ was added dropwise and the reaction mixture was stirred for 20 minutes. A solution of ketene acetal (1.54 g, 7.69 mmol) was then added slowly in 3 portions with 3 mL of CH_2Cl_2.

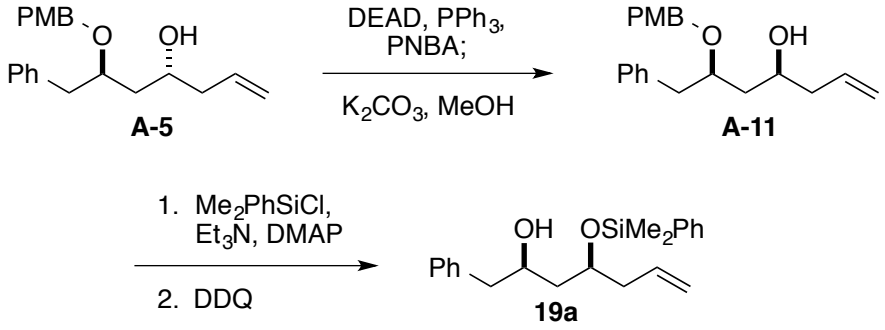
The reaction was quenched with a solution of pH 7 phosphate buffer (30 mL) and Rochelle's salt (25 mL). The mixture was allowed to stir to room temperature and extracted with CH_2Cl_2 (3 x 50 mL). The organic layers were then dried over Na_2SO_4 and concentrated under vacuum. The crude mixture was purified in 80:20 → 70:30 hexane:EtOAc to give **A-10** with a yield of 58% (1.22 g, 2.96 mmol) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.30-7.18 (8H, m), 6.87-6.83 (2H, m), 4.41 (2H, d, *J* = 2.2 Hz), 4.24 (1H, m), 3.95 (1H, dtd, *J* = 9.0, 6.2, 3.1 Hz), 3.79 (3H, s), 3.25 (1H, d, *J* = 3.8 Hz), 2.96 (1H, dd, *J* = 13.6, 6.2 Hz), 2.78 (1H, dd, *J* = 13.6, 6.5 Hz), 2.34-2.31 (2H, m), 1.62 (1H, m), 1.52 (1H, ddd, *J* = 14.4, 8.9, 3.0 Hz), 1.43 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 172.05, 159.21, 138.55, 130.44, 129.62, 129.54, 128.40, 128.32, 126.20, 113.80, 81.02, 71.79, 65.11, 55.26, 42.84, 40.84, 40.59, 28.08. IR (cm^{-1}): *f* = 3491, 2976, 2934, 1724, 1514, 1248, 1150, 822, 701. HRMS-ESI: $(M+Na)^+$ = 423.2142 calculated for $C_{24}H_{32}NaO_5$, experimental = 423.2125.

(±)-(3*S*,5*R*)-tert-butyl 3,5-dihydroxy-6-phenylhexanoate (12d). PMB alcohol **A-10** (300 mg, 0.75 mmol) was placed under vacuum and treated with Pd/C (80 mg, 0.075 mmol) then dissolved in MeOH (10 mL) while being bubbled with H_2 gas via balloon. Upon completion, the reaction mixture was filtered thru a celite cake and rinsed with EtOAc (3x10 mL). The crude mixture was purified in 80:20 → 65:35 hexanes:EtOAc to give tert-butyl ester diol **12d** in 88% yield (185 mg, 0.66 mmol) as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.33-7.22 (5H, m), 4.34 (1H, ddd, *J* = 15.8, 7.9, 4.0 Hz), 4.17 (1H, dd, *J* = 14.2, 7.4 Hz), 3.65 (1H, d, *J* = 3.8 Hz), 2.80 (2H, d, *J* = 6.7 Hz), 2.74 (1H, bs), 2.48-2.36 (2H, m), 1.65 (2H, dddd, *J* = 32.3, 14.4, 8.3, 2.8 Hz), 1.47 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 172.24, 138.33, 129.32, 128.45, 126.36, 81.28, 69.52, 68.96, 65.61, 44.01, 42.23, 41.48, 28.03. IR (cm^{-1}): *f* = 3041, 2977,

2933, 1707, 1454, 1367, 1254, 1146, 1080, 954, 843, 747, 700. HRMS-ESI: $(M+Na)^+$ = 303.1567 calculated for $C_{16}H_{24}NaO_4$, experimental = 303.1556.

2.4. Synthesis of 1,3-*Syn* Diol Monosilylethers

Preparation of 1,3-Syn Diol Monosilylether **19a**



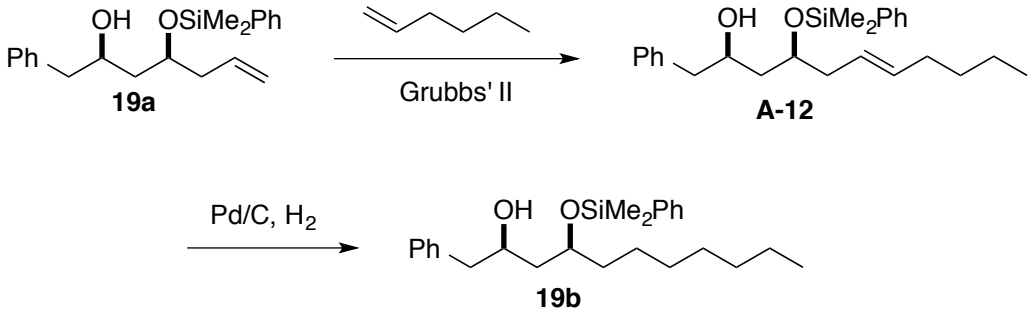
(±)-(4*S*,6*R*)-6-((4-methoxybenzyl)oxy)-7-phenylhept-1-en-4-ol (A-11). Alcohol **A-5** (1.14 g, 3.49 mmol) was dissolved in toluene (125 mL). PPh_3 (2.56 g, 9.77 mmol) and *p*-nitrobenzoic acid (1.63 g, 9.77 mmol) were added and the reaction was stirred for 5 minutes before the dropwise addition of diethylazodicarboxylate (1.53 mL, 9.77 mmol). The reaction mixture was stirred at room temperature overnight then concentrated in vacuo. The crude mixture was then dissolved in MeOH (100 mL) and K_2CO_3 (2.70 g, 19.54 mmol) was added and stirred for two hours. The reaction was quenched with deionized water (100 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude mixture was purified in 80:20 → 70:30 hexanes:EtOAc to give alcohol **A-11** in 67% yield (767 mg, 2.35 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.35-7.20 (7H, m), 6.91-6.87 (2H, m), 4.29 (1H, m), 5.11-5.04 (2H, m), 4.58 (1H, d, *J* = 10.8 Hz), 4.43 (1H, d, *J* = 10.8 Hz), 3.88 (1H, ddt, *J* = 7.6, 7.5, 5.2 Hz), 3.82 (3H, s), 3.78 (1H, dd, *J* = 12.2, 6.5

Hz), 3.53 (1H, bs), 3.04 (1H, dd, *J* = 13.6, 5.1 Hz), 2.79 (1H, dd, *J* = 13.6, 7.2 Hz), 2.22-2.11 (2H, m), 1.64-1.61 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 159.28, 138.02, 134.79, 129.68, 129.59, 129.44, 128.34, 126.27, 117.14, 113.87, 80.50, 70.90, 70.57, 55.17, 41.89, 40.55, 40.27. IR (cm^{-1}): *f* = 3464, 3027, 2935, 2912, 2865, 1709, 1612, 1513, 1247, 1079, 1033, 821, 746, 701. HRMS-ESI: $(M+Na)^+$ =349.1774 calculated for $C_{21}H_{26}NaO_3$, experimental = 349.1768.

(±)-(2*R*,4*S*)-4-((dimethyl(phenyl)silyl)oxy)-1-phenylhept-6-en-2-ol (19a). Allylic alcohol **A-11** (1.12 g, 3.43 mmol) was dissolved in CH_2Cl_2 (40 mL). Et_3N (0.86 mL, 6.17 mmol) was added along with DMAP (18 mg, 0.27 mmol) and stirred for five minutes. $Me_2PhSiCl$ (0.7 mL, 4.12 mmol) was then added and the reaction was stirred overnight. The reaction was quenched with a half saturated NH_4Cl solution (40 mL) and extracted with CH_2Cl_2 (3 x 30 mL). The organic layers were collected and concentrated in vacuo. The crude mixture was then dissolved in a mixture of CH_2Cl_2:H_2O (30 mL:few drops) and DDQ (1.2 g, 5.15 mmol) was added. Upon completion, the reaction was diluted with CH_2Cl_2 (40 mL) and vacuum filtered. The mixture was then washed with a saturated $NaHCO_3$ solution (50 mL), dried over Na_2SO_4 and concentrated in vacuo. The crude mixture was purified in 90:10 → 80:20 hexanes:EtOAc to give monoprotected alcohol **19a** in 80% yield over two steps (936 mg, 2.75 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.60-7.56 (2H, m), 7.39-7.10 (8H, m), 5.66 (1H, ddt, *J* = 17.2, 10.4, 6.8 Hz), 4.99-4.92 (2H, m), 4.05-3.89 (2H, m), 2.98 (1H, s), 2.75-2.62 (2H, m), 2.24-2.11 (2H, m), 1.65-1.53 (2H, m), 0.41 (6H, q, *J* = 4.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 138.45, 137.33, 133.98, 133.51, 129.82, 129.44, 128.36, 127.92, 126.25, 117.55, 72.63, 71.69, 44.09, 42.17, 42.07, -1.00, -1.14. IR (cm^{-1}): *f* = 3443, 3069, 3026, 2941, 1428, 1251, 1116, 1065,

913, 823, 783, 738, 697. HRMS-ESI: $(M+H)^+$ = 341.1931 calculated for $C_{21}H_{29}O_2Si$, experimental = 341.1925.

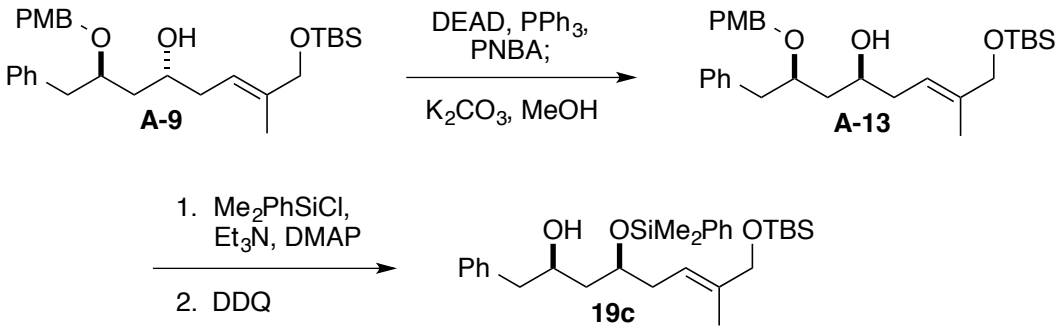
Preparation of 1,3-Syn Diol Monosilylether **19b**



(±)-(2*R*,4*S*)-4-((dimethyl(phenyl)silyl)oxy)-1-phenylundecan-2-ol (19b). Alcohol **19a** (145 mg, 0.43 mmol) along with 1-hexene (0.53 mL, 4.30 mmol) were added simultaneously to a round bottom flask containing Grubb's 2nd generation catalyst (74 mg, 0.0086 mmol) dissolved in CH_2Cl_2 (6 mL). The reaction mixture was then heated to reflux overnight. Upon completion, the reaction was concentrated in vacuo to give crude intermediate **A-12**, which was then placed under vacuum and treated with Pd/C (46 mg, 0.043 mmol) and dissolved in EtOAc (5 mL). The reaction was then bubbled with H_2 gas until completion. It was then filtered through celite via vacuum filtration, rinsed with EtOAc (3 x 10 mL) and concentrated in vacuo. The crude mixture was purified with 90:10 → 80:20 hexanes:EtOAc to give **19b** in 66% yield over two steps (113 mg, 0.28 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.66 (2H, d, *J* = 6.2 Hz), 7.47-7.24 (8H, m), 4.05-3.94 (2H, m), 3.18 (1H, s), 2.82 (1H, dd, *J* = 13.6, 6.6 Hz), 2.75 (1H, dd, *J* = 13.7, 5.8 Hz), 1.71-1.61 (2H, m), 1.48 (2H, q, *J* = 7.0 Hz), 1.37-1.22 (10H, m), 0.95 (3H, t, *J* = 6.9 Hz), 0.50 (6H, d, *J* = 2.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 138.50, 137.54, 133.45, 129.68, 129.41, 128.30, 127.83, 126.18, 72.32, 71.85, 44.13, 42.21, 37.60, 31.71, 29.55, 29.12, 24.61, 22.58, 14.05, -1.00, -1.20. IR (cm^{-1}): *f* = 3383, 3068, 3027, 2927, 2856,

1455, 1428, 1252, 1118, 1084, 829, 785, 742, 700. HRMS-ESI: $(M+H)^+$ = 399.2714 calculated for $C_{25}H_{39}O_2Si$, experimental = 399.2709.

Preparation of 1,3-Syn Diol Monosilylether **19c**



(±)-(2*R*,4*S*,*E*)-8-((*tert*-butyldimethylsilyl)oxy)-2-((4-methoxybenzyl)oxy)-7-methyl-1-phenyloct-6-en-4-ol (A-13). Alcohol **A-9** (923 mg, 1.91 mmol) was dissolved in THF (100 mL). PPh_3 (1.50 g, 5.72 mmol) was then added, followed by *p*-nitrobenzoic acid (637 mg, 3.82 mmol), and then diethylazodicarboxylate (0.90 mL, 5.72 mmol). The reaction mixture was allowed to stir overnight at room temperature and then concentrated under vacuum. The resulting crude material was dissolved in MeOH (60 mL) and K_2CO_3 (1.37 g, 11.43 mmol) was then added. The reaction mixture was then concentrated under vacuum, quenched with deionized H_2O (20 mL), and extracted with EtOAc (4 x 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude material was purified in 90:10 → 80:20 hexanes:EtOAc to give alcohol **A-13** with a yield of 57% (527 mg, 1.09 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.35-7.28 (2H, m), 7.28-7.19 (5H, m), 6.89 (2H, d, *J* = 8.0 Hz), 5.39 (1H, t, *J* =6.5 Hz), 4.57 (1H, d, *J* = 10.7 Hz), 4.43 (1H, d, *J* = 10.7 Hz), 4.00 (2H, s), 3.87 (1H, m), 3.82 (3H, s), 3.76 (1H, m), 3.49 (1H, bs), 3.02 (1H, dd, *J* = 13.7, 5.2 Hz), 2.80 (1H, dd, *J* = 13.7, 6.8 Hz), 2.20 (1H, dt, *J* = 14.1, 6.6 Hz), 2.11 (1H, dt, *J* = 14.8, 7.3 Hz), 0.92

(9H, s), 0.06 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 159.34, 138.12, 136.90, 129.80, 129.64, 129.52, 128.39, 126.33, 120.09, 113.93, 80.71, 71.34, 71.01, 68.49, 55.26, 40.72, 40.40, 35.65, 25.95, 18.40, 13.63, -5.27. IR (cm^{-1}): *f* = 3470, 2951, 2928, 2855, 1514, 1249, 1068, 836, 700.

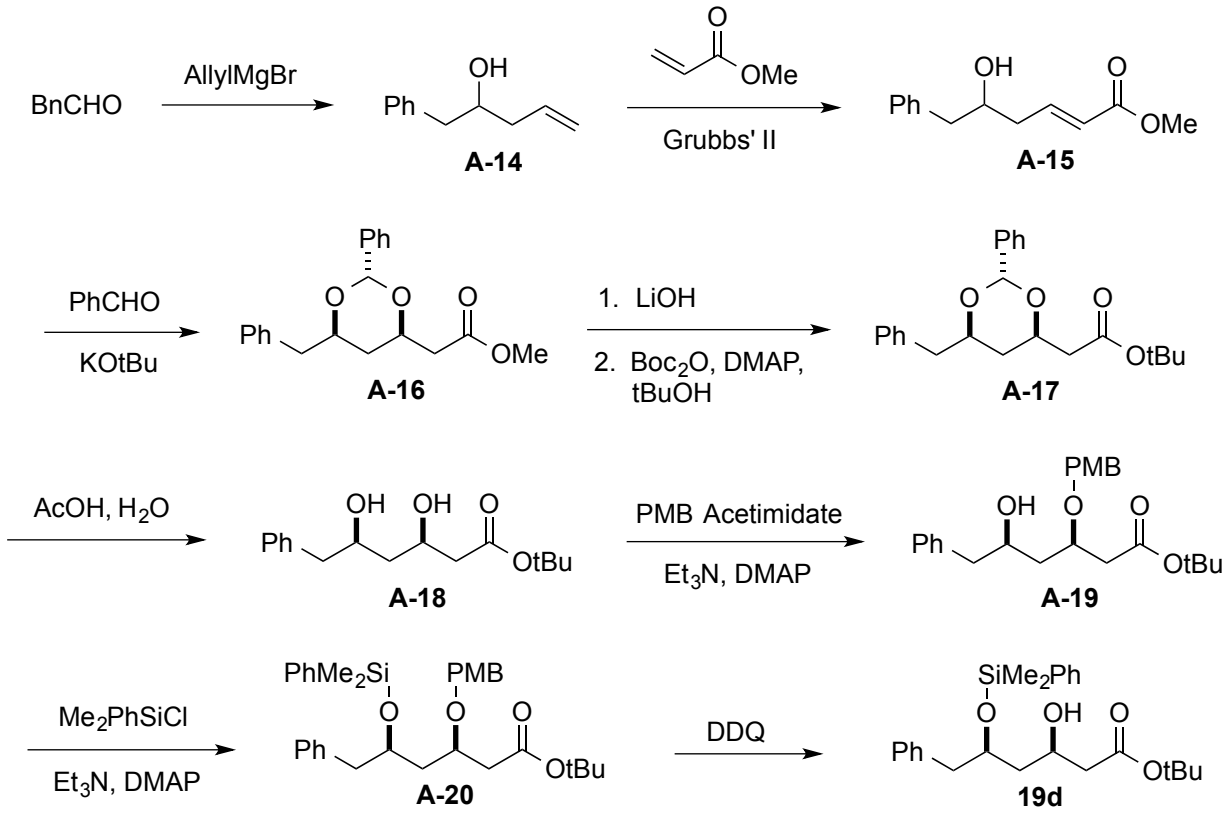
(±)-(2*R*,4*S*,*E*)-8-((*tert*-butyldimethylsilyl)oxy)-4-((dimethyl(phenyl)silyl)oxy)-7-methyl-1-phenyloct-6-en-2-ol (19c). Alcohol **A-13** (508 mg, 1.05 mmol) was dissolved in CH_2Cl_2 (40 mL). Et_3N (263 μL, 1.89 mmol) was then added, followed by DMAP (10 mg, 0.08 mmol), and $Me_2PhSiCl$ (211 μL, 1.26 mmol). Upon completion, the reaction was quenched with a half saturated NH_4Cl solution (25 mL) and extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum.

The resulting crude material was then dissolved in CH_2Cl_2 (50 mL). Then, 5 drops of H_2O and DDQ (358 mg, 1.58 mmol) were sequentially added. After stirring for an hour, the reaction was poured into a separatory funnel containing a saturated $NaHCO_3$ solution (50 mL). The mixture was then extracted with CH_2Cl_2 (4 x 30 mL), the organic layers combined and dried over Na_2SO_4, and concentrated under vacuum.

In order to create better chromatographic separation between the product and residual *p*-anisaldehyde, the crude material was dissolved in CH_2Cl_2 (50 mL) and cooled to -78°C. DIBAL (2.1 mL, 2.10 mmol, 1M in toluene) was then added dropwise. The reaction mixture was stirred until *p*-anisaldehyde was fully consumed. The reaction was quenched with a saturated Rochelle's salt solution (40 mL) and the mixture was allowed to stir vigorously for 2 hours. Upon separation of layers, the aqueous layer was then extracted with CH_2Cl_2 (3 x 30 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under vacuum. The crude material was

purified in 100% hexanes and 99:1→ 90:10 hexanes:EtOAc to give 1,3-*syn* diol monosilylether **19c** with a yield of 18% (96 mg, 0.19 mmol) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.59 (2H, d, *J*= 8.0 Hz), 7.42-7.35 (3H, m), 7.29 (2H, d, *J* = 8.0 Hz), 7.22-7.15 (3H, m), 5.30 (1H, t, *J* = 7.2 Hz), 3.94 (3H, s), 3.91 (1H, m), 3.12 (1H, bs), 2.70 (2H, qd, *J* = 13.6, 6.4 Hz), 2.23-2.10 (2H, m), 1.64-1.54 (2H, m), 1.47 (3H, s), 0.90 (9H, s), 0.43 (6H, d, *J* = 3.6 Hz), 0.04 (6H, d, *J* = 1.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 138.52, 137.39, 136.75, 133.53, 129.78, 129.45, 128.33, 127.92, 126.22, 119.29, 73.34, 71.91, 68.28, 44.11, 42.23, 36.06, 25.94, 18.40, 13.58, -0.97, -1.14, -5.28. IR (cm^{-1}): *f* = 3452, 2953, 2855, 1251, 1063, 777, 740, 699. HRMS-ESI: $(M+Na)^+$ = 521.2878 calculated for $C_{29}H_{46}NaO_3Si_2$, experimental = 521.2868.

Preparation of 1,3-Syn Diol Monosilylether **19d**



1-phenylpent-4-en-2-ol (A-14). Phenylacetaldehyde (5.6 mL, 49.92 mmol) was dissolved in THF (200 mL) and cooled to -78°C. Allyl magnesium bromide (55 mL, 54.91 mmol, 1M in diethyl ether) was added to the reaction mixture dropwise using an addition funnel. Upon completion, the reaction mixture was quenched with a half saturated NH_4Cl solution (100 mL), extracted with ethyl acetate (3 x 50 mL). The organic layers were combined and dried over Na_2SO_4, and concentrated under vacuum. The crude mixture was purified in 100% CH_2Cl_2 → 90:10 CH_2Cl_2:EtOAc to give allylic alcohol **A-14** in 62% yield (5.03 g, 31.03 mmol) as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.37-7.24 (5H, m), 5.90 (1H, m), 5.20 (1H, m), 5.17 (1H t, *J* = 1.2 Hz), 3.92 (1H, dddd, *J* = 12.6, 7.9, 4.7, 3.1 Hz), 2.86 (1H, dd, *J* = 13.6, 4.9 Hz), 2.76 (1H, dd, *J* = 13.6, 8.0 Hz), 2.37 (1H, dddt, *J* = 14.0, 6.4, 4.9, 1.1 Hz), 2.26 (1H, m), 1.73 (1H, t, *J* = 3.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 138.36, 134.66, 129.40, 128.52, 126.47, 118.13, 71.66, 43.28, 41.18. IR (cm^{-1}): *f* = 3395, 3076, 3028, 2918, 1640, 1495, 1454, 1078, 1031, 997, 914, 744, 699. Compound **A-14** is known (CAS #61077-65-4).

(±)-(*E*)-methyl 5-hydroxy-6-phenylhex-2-enoate (A-15). Grubb's 2nd generation catalyst (263 mg, 0.31 mmol) was dissolved in CH_2Cl_2 (60 mL). Allylic alcohol **A-14** (4.96 g, 30.60 mmol) and methyl acrylate (14.0 mL, 153.00 mmol) were added simultaneously to the reaction mixture and brought to reflux overnight. Upon completion, the reaction was cooled then concentrated under vacuum. The crude mixture was purified in 80:20 → 70:30 hexanes:EtOAc to give methyl ester alcohol **A-15** in 43% yield (2.90 g, 13.16 mmol) as a dark oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.34-7.20 (5H, m), 7.03 (1H, dt, *J* = 15.7, 7.3 Hz), 5.93 (1H, dt, *J* = 15.6, 1.4 Hz), 3.98 (1H, tq, *J* = 8.0, 4.1 Hz), 3.73 (3H, s), 2.84 (1H, dd, *J* = 13.6, 4.7 Hz), 2.72 (1H, dd, *J* = 13.6, 8.2 Hz), 2.50-2.35 (2H, m), 1.74 (1H, d, *J* = 2.4 Hz). ^{13}C NMR (100 MHz,

$CDCl_3$); δ (ppm) = 166.70, 145.25, 137.69, 129.36, 128.67, 126.72, 123.52, 71.29, 51.48, 43.59, 39.33. IR (cm^{-1}): *f* = 3436, 3027, 2949, 2848, 1704, 1656, 1436, 1321, 1271, 1212, 1160, 1033, 746, 699. HRMS-ESI: $(M+H)^+$ = 221.1172 calculated for $C_{13}H_{17}O_3$, experimental = 221.1178.

(±)-methyl 2-((2*S*,4*R*,6*R*)-6-benzyl-2-phenyl-1,3-dioxane-4-yl)acetate (A-16). Methyl ester alcohol **A-15** (1.7 g, 7.72 mmol) was dissolved in THF (40 mL) and cooled to 0°C. Freshly distilled benzaldehyde (0.9 mL, 8.50 mmol) followed by *t*-BuOK (86 mg, 0.77 mmol) was added to the reaction mixture and the resulting yellow solution was stirred for 15 minutes at 0°C. This sequence of addition and stirring was repeated three times and the reaction mixture was quenched with a solution of pH 7 phosphate buffer (40 mL) and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The crude mixture was purified in 80:20 hexanes:EtOAc to afford methyl ester benzylidene acetal **A-16** in 67% yield (1.68 g, 5.15 mmol) as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.51-7.49 (2H, m), 7.36-7.20 (8H, m), 5.53 (1H, s), 4.24 (1H, m), 4.02 (1H, dtd, *J* = 11.0, 6.4, 2.3 Hz), 3.63 (3H, s), 3.05 (1H, dd, *J* = 13.7, 6.6 Hz), 2.77 (1H, dd, *J* = 13.7, 6.4 Hz), 2.69 (1H, dd, *J* = 15.7, 7.3 Hz), 2.45 (1H, dd, *J* = 15.7, 5.7 Hz), 1.62 (1H, dt, *J* = 13.0, 2.5 Hz), 1.45 (1H, dt, *J* = 13.1, 11.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 170.68, 138.20, 137.28, 129.25, 128.30, 128.04, 127.81, 126.15, 125.80, 100.17, 77.02, 72.82, 51.33, 42.04, 40.36, 35.60. IR (cm^{-1}): *f* = 3063, 3030, 2950, 2915, 2850, 1735, 1437, 1403, 1346, 1200, 1109, 1056, 1043, 1009, 751, 698. HRMS-ESI: $(M+H)^+$ = 327.1591 calculated for $C_{20}H_{23}O_4$, experimental = 327.1585.

(±)-tert-butyl 2-((2*S*,4*R*,6*R*)-6-benzyl-2-phenyl-1,3-dioxan-4-yl)acetate (A-17). Methyl ester benzylidene acetal **A-16** (1.5 g, 4.60 mmol) was dissolved in a 1:1 mixture THF:H_2O (20 mL) and LiOH (965 mg, 23.00 mmol) was subsequently added and stirred. Upon completion the reaction mixture was quenched with 1M HCl (20 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under vacuum to give the carboxylic acid.

The crude carboxylic acid was then dissolved in tert-butanol (20 mL). Di-*tert*-butyl dicarbonate (2.0 g, 9.20 mmol) and DMAP (169 mg, 1.38 mmol) were then added to the reaction mixture. Through TLC monitoring, the completed reaction was concentrated under vacuum and the crude reaction mixture was purified in 95:5 → 90:10 hexanes:EtOAc to give the *tert*-butyl ester benzylidene acetal **A-17** in 69% yield (1.17 g, 3.17 mmol) as a clear oil over two steps. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.49-7.47 (2H, m), 7.36-7.19 (8H, m), 5.54 (1H, s), 4.20 (1H, dddd, *J* = 11.3, 7.4, 6.0, 2.5 Hz), 4.04 (1H, dtd, *J* = 11.1, 6.5, 2.4 Hz), 3.07 (1H, dd, *J* = 13.7, 6.5 Hz), 2.78 (1H, dd, *J* = 13.7, 6.5 Hz), 2.60 (1H, dd, *J* = 15.2, 7.2 Hz), 2.39 (1H, dd, *J* = 15.2, 6.0 Hz), 1.64 (1H, dt, *J* = 13.0, 2.3 Hz), 1.42 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 169.89, 138.42, 137.53, 129.44, 128.43, 128.21, 127.99, 126.32, 125.91, 100.30, 80.63, 77.34, 73.49, 42.27, 42.12, 35.83, 27.98. IR (cm^{-1}): *f* = 3064, 3031, 2977, 2927, 2868, 1727, 1454, 1367, 1345, 1145, 1110, 1018, 750, 698. HRMS-ESI: $(M+H)^+$ = 369.2060 calculated for $C_{23}H_{29}O_4$, experimental = 369.2062.

(±)-(3*R*,5*R*)-tert-butyl 3,5-dihydroxy-6-phenylhexanoate (A-18). *Tert*-butyl ester benzylidene acetal **A-17** (180 mg, 0.49 mmol) was dissolved in a 1:1 mixture of AcOH:H_2O (5 mL) and heated to 40^{o}C on a sand bath for 48 hours. Upon completion, the reaction was cooled

and concentrated under vacuum and purified in 90:10 → 80:20 hexanes:EtOAc to afford *tert*-butyl ester diol **A-18** in 61% yield (84 mg, 0.30 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.30-7.18 (5H, m), 4.17 (1H, tt, *J* = 8.2, 4.4 Hz), 4.08 (1H, m), 2.82 (1H, dd, *J* = 13.5, 6.8 Hz), 2.70 (1H, dd. *J* = 13.5, 6.3 Hz), 2.41-2.30 (2H, m) 1.61-1.53 (2H, m), 1.42 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 171.67, 138.06, 129.30, 128.29, 126.22, 81.12, 72.91, 68.82, 44.05, 42.63, 41.17, 27.91. IR (cm^{-1}): *f* = 3403, 3028, 2878, 2934, 1720, 1367, 1257, 1146, 1087, 843, 733, 700. HRMS-ESI: $(M+Na)^+$ = 303.1567 calculated for $C_{16}H_{24}NaO_4$, experimental = 303.1575.

(±)-(3*R*,5*R*)-tert-butyl 5-hydroxy-3-((4-methoxybenzyl)oxy)-6-phenylhexanoate (A-19). *Tert*-butyl ester diol **A-18** (118 mg, 0.42 mmol) was dissolved in CH_2Cl_2 (2.5 mL) and cooled to 0^{o}C. PMB acetimidate (95 μL, 0.46 mmol) and PTSA (10 mg, 0.053 mmol) were added to the reaction mixture and stirred to completion. The reaction was quenched with H_2O (5 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude mixture was purified 90:10 → 86:14 → 82:18 hexanes:diethyl ether to give monobenzyl ether protected *tert*-butyl ester diol **A-19** in 45% yield (75 mg, 0.19 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.34-7.21 (7H, m), 6.90-6.87 (2H, m), 4.55 (1H, d, *J* = 11.0 Hz), 4.44 (1H, d, *J* = 11.0 Hz), 4.13 (1H, m), 3.88 (1H, m), 3.82 (3H, s), 3.72 (1H, d, *J* = 2.2 Hz), 3.02 (1H, dd, *J* = 13.6, 5.6 Hz), 2.81 (1H, dd, *J* = 13.6, 6.8 Hz), 2.35 (1H, dd, *J* = 15.7, 7.6 Hz), 2.27 (1H, dd, *J* = 15.7, 5.1 Hz), 1.77-1.58 (2H, m), 1.42 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 171.46, 159.27, 138.14, 129.92, 129.56, 129.49, 128.39, 126.30, 113.87, 80.82, 79.40, 70.86, 67.43, 55.24, 42.83, 40.46, 40.26, 28.02. IR

(cm^{-1}): *f* = 3467, 3029, 2978, 2934, 1721, 1612, 1513, 1367, 1247, 1079, 1032, 909, 729, 700. HRMS-ESI: $(M+Na)^+$ = 423.2142 calculated for $C_{24}H_{32}NaO_5$, experimental = 423.2153.

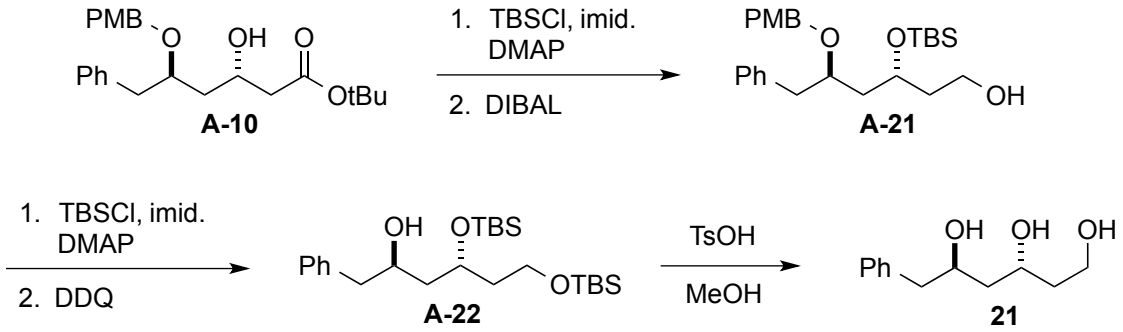
(±)-(3*R*,5*R*)-tert-butyl 5-((dimethyl(phenyl)silyl)oxy)-3-((4-methoxybenzyl)oxy)-6-phenylhexanoate (A-20). Monobenzyl ether protected *tert*-butyl ester diol **A-19** (162 mg, 0.40 mmol) was dissolved in CH_2Cl_2 (4 mL). Et_3N (0.1 mL, 0.72 mmol) and DMAP (2 mg, 0.032 mmol) were added, followed by addition of dimethylphenylsilyl chloride (0.1 mL, 0.60 mmol). Upon completion, the reaction was quenched with a half saturated NH_4Cl solution (5 mL), and extracted with CH_2Cl_2 (3 x 10 mL). The organic layers were combined and washed with a saturated $NaHCO_3$ solution, dried over Na_2SO_4, and concentrated under vacuum to afford diprotected tert-butyl ester diol **A-20** in 83% yield (178 mg, 0.33 mmol) as a colorless oil. HRMS-ESI: $(M+H)^+$ = 535.2874 calculated for $C_{32}H_{43}O_5Si$, experimental = 535.2895.

(±)-(3*R*,5*R*)-tert-butyl 5-((dimethyl(phenyl)silyl)oxy)-3-hydroxy-6-phenylhexanoate (19d). Diprotected *tert*-butyl diol **A-20** (40 mg, 0.070 mmol) was dissolved in a mixture of CH_2Cl (2 mL) and a few droplets of H_2O. To this solution was added DDQ (25 mg, 0.11 mmol) and the reaction was stirred vigorously. Upon completion, the reaction was quenched with a saturated $NaHCO_3$ solution (5 mL) and extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude mixture was purified in 100% CH_2Cl_2 to afford the monosilylated *tert*-butyl ester diol **19d** in 66% yield (19 mg, 0.046 mmol) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.60-7.57 (10H, m), 4.29 (1H, p, *J* = 6.4 Hz), 3.94 (1H, dt, *J* = 11.2, 7.1 Hz), 2.78 (1H, s), 2.73 (1H, dd, *J* = 13.0, 6.6 Hz), 2.66 (1H, dd, *J* = 13.5, 5.9 Hz), 2.42 (1H, dd, *J* = 14.9, 5.4 Hz), 2.35 (1H, dd, *J* = 15.1, 7.0 Hz), 1.68-

1.64 (2H, m), 1.36 (9H, s), 0.43 (6H, d, J = 3.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 170.40, 138.28, 137.37, 133.46, 129.81, 129.41, 128.40, 127.92, 126.31, 80.66, 71.03, 69.51, 44.04, 44.00, 42.87, 28.00, -1.21, -1.31. IR (cm^{-1}): f = 3437, 3069, 3027, 2932, 1724, 1368, 1254, 1152, 905, 730, 702. HRMS-ESI: $(M+Na)^+$ = 437.2119 calculated for $C_{24}H_{34}NaO_4Si$, experimental = 437.2129.

2.5. Synthesis of 1,3,5-Triols

Preparation of 1,3,5-Anti Triol **21**



(±)-(3*R*,5*R*)-3-((*tert*-butyldimethylsilyl)oxy)-5-((4-methoxybenzyl)oxy)-6-phenylhexan-1-ol (A-21). Alcohol **A-10** (397 mg, 0.99 mmol) was dissolved in CH_2Cl_2 (12 mL) and cooled to 0^{o}C. Imidazole (337 mg, 4.95 mmol) was then added, followed by TBSCl (299 mg, 1.98 mmol), and DMAP (24 mg, 0.19 mmol). The reaction was stirred to room temperature overnight, quenched with 2M HCl (20 mL), and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude mixture was purified in 95:5 → 90:10 hexanes:EtOAc to give the TBS ether with 71% yield (360 mg, 0.70 mmol) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.32-7.28 (2H, m), 7.24-7.19 (5H, m), 6.87 (2H, d, J = 8.7 Hz), 4.51 (1H, d, J = 11.0 Hz), 4.42 (1H, d, J = 11.0 Hz),

4.27 (1H, t, J = 5.6 Hz), 3.82 (1H, m), 3.82 (3H, s), 2.99 (1H, dd, J = 13.6, 5.2 Hz), 2.78 (1H, dd, J = 13.8, 6.2 Hz), 2.39 (2H, d, J = 5.6 Hz), 1.73-1.68 (2H, m), 1.42 (9H, s), 0.85 (9H, s), 0.02 (6H, d, J = 6.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 170.61, 159.01, 138.64, 130.85, 129.53, 129.11, 128.25, 126.08, 113.71, 80.24, 77.27, 70.63, 67.11, 55.26, 44.78, 42.56, 40.69, 28.09, 25.85, 17.95, -4.28, -4.60. IR (cm^{-1}): f = 2929, 2856, 1729, 1514, 1248, 1081, 834, 775, 700. HRMS-ESI: $(M+H)^+$ = 515.3187 calculated for $C_{30}H_{47}O_5Si$, experimental = 515.3180.

The purified TBS ether (97 mg, 0.19 mmol) was dissolved in CH_2Cl_2 (5 mL) and cooled to -78°C. DIBAL (1.1 mL, 1.13 mmol, 1M in toluene) was then added dropwise. After one hour, the reaction was slowly warmed to room temperature and stirred until completion. The reaction was cooled back to 0°C, quenched with a saturated solution of Rochelle's salt (5 mL), and stirred vigorously for 2 hours. The aqueous layer was then extracted with CH_2Cl_2 (4 x 5 mL); the organic layers were dried over Na_2SO_4 and concentrated under vacuum. The resulting crude mixture was purified in 85:15 → 80:20 hexanes:EtOAc to give alcohol **A-21** with a yield of 47% (38 mg, 0.09 mmol) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.31 (2H, q, J = 7.6, 3.6 Hz), 7.23 (5H, d, J = 8.1 Hz), 6.89 (2H, d, J = 8.0 Hz), 4.53 (1H, d, J = 10.9 Hz), 4.41 (1H, d, J = 10.8 Hz), 4.03 (1H, p, J = 5.7 Hz), 3.83 (3H, s), 3.78 (1H, m), 3.72-3.61 (2H, m), 3.00 (1H, dd, J = 13.8, 5.4 Hz), 2.78 (1H, dd, J = 13.7, 6.7 Hz), 2.36 (1H, bs), 1.86 (1H, m), 1.81-1.63 (3H, m), 0.87 (9H, s), 0.05 (3H, s), 0.01 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 159.14, 138.43, 130.49, 129.48, 129.29, 128.33, 126.20, 113.71, 77.49, 70.72, 69.41, 59.82, 55.26, 41.79, 40.61, 38.97, 25.79, 17.88, -4.43, -4.60. IR (cm^{-1}): f = 3410, 2928, 2855, 1513, 1248, 1079, 1034, 834, 775, 700. HRMS-ESI: $(M+H)^+$ = 445.2769 calculated for $C_{26}H_{41}O_4Si$, experimental = 445.2763.

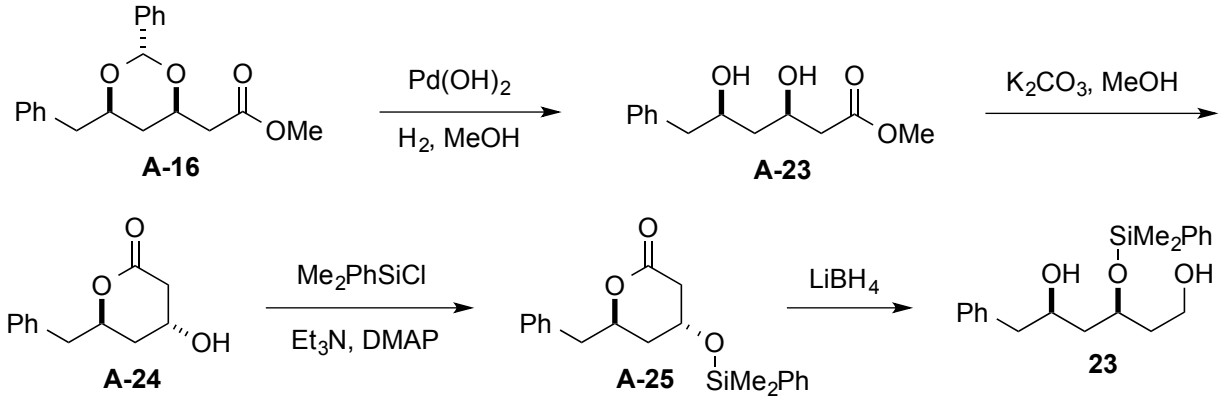
(±)-(2*R*,4*R*)-4,6-bis((*tert*-butyldimethylsilyl)oxy)-1-phenylhexan-2-ol (A-22). Alcohol **A-21** (114 mg, 0.26 mmol) was dissolved in CH_2Cl_2 (20 mL) and cooled to 0°C. Imidazole (70 mg, 1.04 mmol) was then added, followed by TBSCl (78 mg, 0.52 mmol), and DMAP (6 mg, 0.05 mmol). The reaction was stirred to room temperature overnight. The mixture was quenched with 2M HCl (20 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum.

The crude mixture was dissolved in CH_2Cl_2:H_2O (15 mL:10 drops) and DDQ (59 mg, 0.26 mmol) was added. After 30 minutes, the reaction was quenched with a saturated $NaHCO_3$ solution (20 mL) and extracted with CH_2Cl_2 (4 x 15 mL). The combined organic layers were dried over $NaSO_4$ and concentrated under vacuum. The resulting crude mixture was purified with 100% hexanes and 98:2 → 95:5 hexanes:EtOAc to give **A-22** with a 50% yield (59 mg, 0.13 mmol) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.33-7.28 (2H, m), 7.24 (3H, d, *J* = 6.9 Hz), 4.24-4.15 (2H, m), 3.67-3.48 (3H, m), 2.87 (1H, dd, *J* = 13.4, 6.8 Hz), 2.69 (1H, dd, *J* = 13.4, 6.3 Hz), 1.86 (1H, dq, *J* = 12.9, 6.4 Hz), 1.75-1.62 (2H, m), 0.92 (9H, s), 0.89 (9H, s), 0.11 (3H, s), 0.10 (3H, s), 0.03 (3H, s), 0.01 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 138.67, 129.35, 128.36, 126.21, 69.63, 68.71, 59.54, 44.43, 40.97, 38.98, 25.89, 25.82, 18.21, 17.94, -4.74, -5.44. IR (cm^{-1}): *f* = 3495, 2928, 2856, 1254, 835, 775, 700. HRMS-ESI: $(M+H)^+$ = 439.3058 calculated for $C_{24}H_{47}O_3Si_2$, experimental = 439.3056.

(±)-(3*R*,5*R*)-6-phenylhexane-1,3,5-triol (21). *p*-toluenesulfonic acid (54 mg, 0.28 mmol) was added into a round bottom flask containing alcohol **A-22** (62 mg, 0.14 mmol). MeOH (2 mL) was then added and the reaction was allowed to stir overnight. Upon completion, the reaction was quenched with Et_3N (1 mL) and then concentrated under vacuum. The resulting

crude was purified in 10:90 hexanes:EtOAc → 100% EtOAc → 95:5 EtOAc:MeOH to give triol **21** with a yield of 98% (29 mg, 0.14 mmol) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.38-7.24 (5H, m), 4.54-4.45 (2H, m), 3.79-3.70 (2H, m), 3.17 (1H, dd, *J* = 14.2, 7.1 Hz), 3.07 (1H, dd, *J* = 14.1, 6.6 Hz), 2.15 (2H, q, *J* = 13.2, 6.5 Hz), 2.08 (1H, d, *J* = 11.8 Hz), 2.01 (1H, d, *J* = 11.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 138.11, 129.35, 128.66, 126.62, 70.22, 69.75, 61.97, 44.00, 42.09, 38.19. IR (cm^{-1}): *f* = 3327, 2939, 1453, 1062, 748, 700. HRMS-ESI: $(M+H)^+$ = 211.1329 calculated for $C_{12}H_{19}O_3$, experimental = 211.1332.

Preparation of 1,3,5-Syn Triol Monosilylether **23**



(±)-methyl (3*R*,5*R*)-3,5-dihydroxy-6-phenylhexanoate (A-23). Methyl ester **A-16** (2.20 g, 6.75 mmol) was dissolved in MeOH (60 mL) and then $Pd(OH)_2$ (1.90 g, 13.49 mmol) was added. The reaction was then purged and bubbled with H_2 gas via balloon and stirred to completion. The mixture was then filtered through celite via vacuum filtration, rinsed with EtOAc (3 x 20 mL) and concentrated in vacuo. The crude mixture was purified in 60:40 → 50:50 hexanes:EtOAc to give 1,3-*syn* diol **A-23** in 58% yield (0.93 g, 3.92 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.30-7.18 (5H, m), 4.21 (1H, bs), 4.16 (1H, d, *J* = 2.7 Hz), 4.05 (1H, m), 3.71 (1H, d, *J* = 2.7 Hz), 3.65 (3H, s), 2.78 (1H, dd, *J* = 13.6, 7.0 Hz), 2.71 (1H,

dd, *J* = 13.5, 6.0 Hz), 2.49-2.37 (2H, m), 1.63-1.53 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 172.34, 137.85, 129.19, 128.17, 126.13, 72.60, 68.34, 51.45, 43.98, 41.46, 41.23. IR (cm^{-1}): *f* =3428, 3060, 3028, 2951, 2917, 1729, 1438, 1266, 1198, 1081, 910, 731, 700. HRMS-ESI: $(M+H)^+$ = 239.1278 calculated for $C_{13}H_{19}O_4$, experimental 239.1279.

(±)-(4*R*,6*R*)-6-Benzyl-4-hydroxytetrahydro-2*H*-pyran-2-one (A-24). Diol **A-23** (877 mg, 3.68 mmol) was dissolved in MeOH:H_2O (10:1, 33 mL) and K_2CO_3 (1.00 g, 7.37 mmol) was added and stirred at room temperature. Upon consumption of starting material, the reaction was quenched with a 1M HCl solution (50 mL) and extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude mixture was purified in 50:50 → 40:60 hexanes:EtOAc to give **A-24** in 75% yield (567 mg, 2.75 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.30-7.19 (5H, m), 4.91 (1H, dtd, *J* = 11.5, 6.3, 2.9 Hz), 4.17 (1H, p, *J* = 3.8 Hz), 3.71 (1H, bs), 2.99 (1H, dd, *J* = 14.0, 6.3 Hz), 2.88 (1H, dd, *J* = 14.0, 6.3 Hz), 2.51 (2H, d, *J* = 4.1 Hz), 1.87 (1H, dt, *J* = 14.5, 3.5 Hz), 1.59 (1H, ddd, *J* = 14.5, 11.5, 3.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) = 171.29, 135.99, 129.31, 128.22, 126.53, 76.39, 61.72, 41.26, 38.08, 34.46. IR (cm^{-1}): *f* = 3420, 3029, 2923, 1705, 1496, 1389, 1252, 1066, 1041, 755, 702. HRMS-ESI: $(M+H)^+$ = 207.1016 calculated for $C_{12}H_{15}O_3$, experimental = 207.1014.

(±)-(4*R*,6*R*)-6-benzyl-4-((dimethyl(phenyl)silyl)oxy)tetrahydro-2*H*-pyran-2-one (A-25). Alcohol **A-24** (390 mg, 1.89 mmol) was dissolved in CH_2Cl_2 (8 mL). Et_3N (0.50 mL, 3.40 mmol) and DMAP (10 mg, 0.08 mmol) were added and stirred for 5 minutes. $Me_2PhSiCl$ (0.50 mL, 2.84 mmol) was then added and stirred at room temperature. Upon completion, the reaction

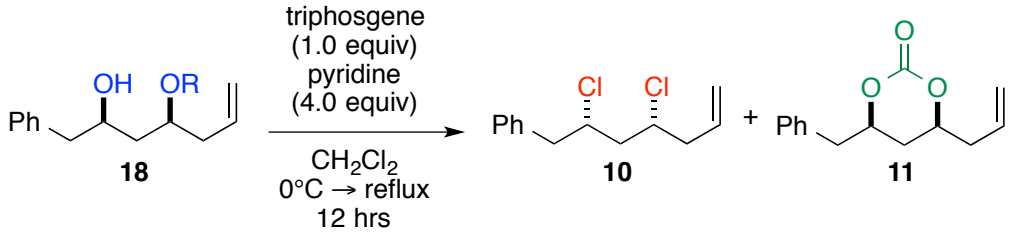
was quenched with a half saturated NH_4Cl solution (15 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed with $NaHCO_3$, dried over Na_2SO_4 and concentrated in vacuo. The crude mixture was purified in 80:20 → 70:30 hexanes:EtOAc to give **A-25** in 83% yield (537 mg, 1.58 mmol) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.52-7.21 (10H, m), 4.97 (1H, dtd, *J* = 11.3, 6.3, 3.0 Hz) 4.24 (1H, p, *J* = 3.8 Hz), 3.06 (1H, dd, *J* = 13.9, 5.9 Hz), 2.91 (1H, dd, *J* = 13.9, 6.6 Hz), 2.57 (1H, dq, *J* = 17.5, 1.6 Hz), 2.51 (1H, dd, *J* = 17.5, 4.4 Hz), 1.78 (1H, m), 1.58 (1H, ddd, *J* = 14.2, 11.3, 2.9 Hz), 0.37 (6H, d, *J* = 10.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$);δ (ppm) = 170.16, 136.89, 136.23, 133.27, 129.92, 129.55, 128.46, 127.99, 126.75, 76.24, 63.48, 41.52, 39.02, 35.24, -1.47, -1.65. IR (cm^{-1}): *f* = 3395, 3067, 3028, 2956, 2923, 1706, 1496, 1427, 1389, 1252, 1118, 1064, 1040, 830, 790, 699. HRMS-ESI: $(M+H)^+$ = 341.1567 calculated for $C_{20}H_{25}O_3Si$, experimental = 341.1569.

(±)-(3S,5R)-3-((dimethyl(phenyl)silyl)oxy)-6-phenylhexane-1,5-diol (23). Lactone **A-25** (200 mg, 0.59 mmol) was dissolved in THF (5 mL) and cooled to -78°C. $LiBH_4$ (26 mg, 1.18 mmol) was then added and the reaction was stirred to completion. The reaction was quenched with deionized H_2O (10 mL) and extracted with ether (3 x 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude mixture was purified in 70:30 → 60:40 → 50:50 hexanes:EtOAc to give **23** in 34% yield (70 mg, 0.20 mmol) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$); δ (ppm) = 7.63-7.17 (10H, m), 4.16 (1H, p, *J* = 6.4 Hz), 3.92 (1H, p, *J* = 6.7 Hz), 3.71-3.60 (2H, m), 2.71 (2H, d, *J* = 6.4 Hz), 1.79 (1H, dt, *J* = 13.3, 7.3 Hz), 1.71-1.65 (4H, m), 1.28 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$);δ (ppm) = 138.12, 137.31, 133.49, 129.90, 129.40, 128.48, 127.97, 126.44, 70.62, 70.44, 59.63, 44.38, 42.97, 38.76, -1.26, -1.36. IR (cm^{-1}):

f = 3372, 3337, 3026, 2923, 2852, 1454, 1081, 700. HRMS-ESI: $(M+H)^+$ = 345.1886 calculated for $C_{20}H_{29}O_3Si$, experimental = 345.1871.

3. GC-MS DATA FOR TABLE 2

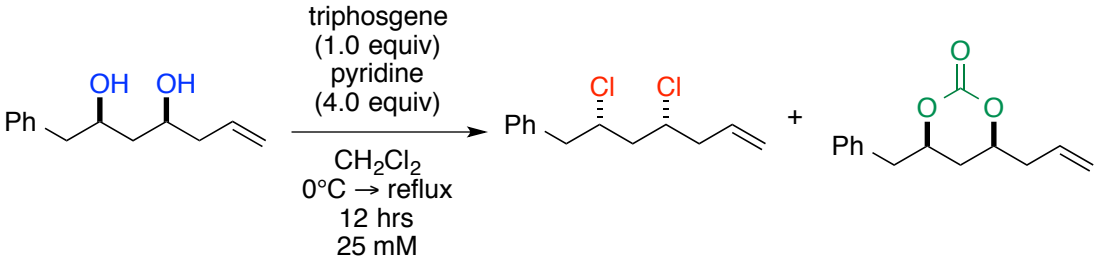
Table 2. Screening and Reaction Optimization with 1,3-*syn* Diol Monosilylether.

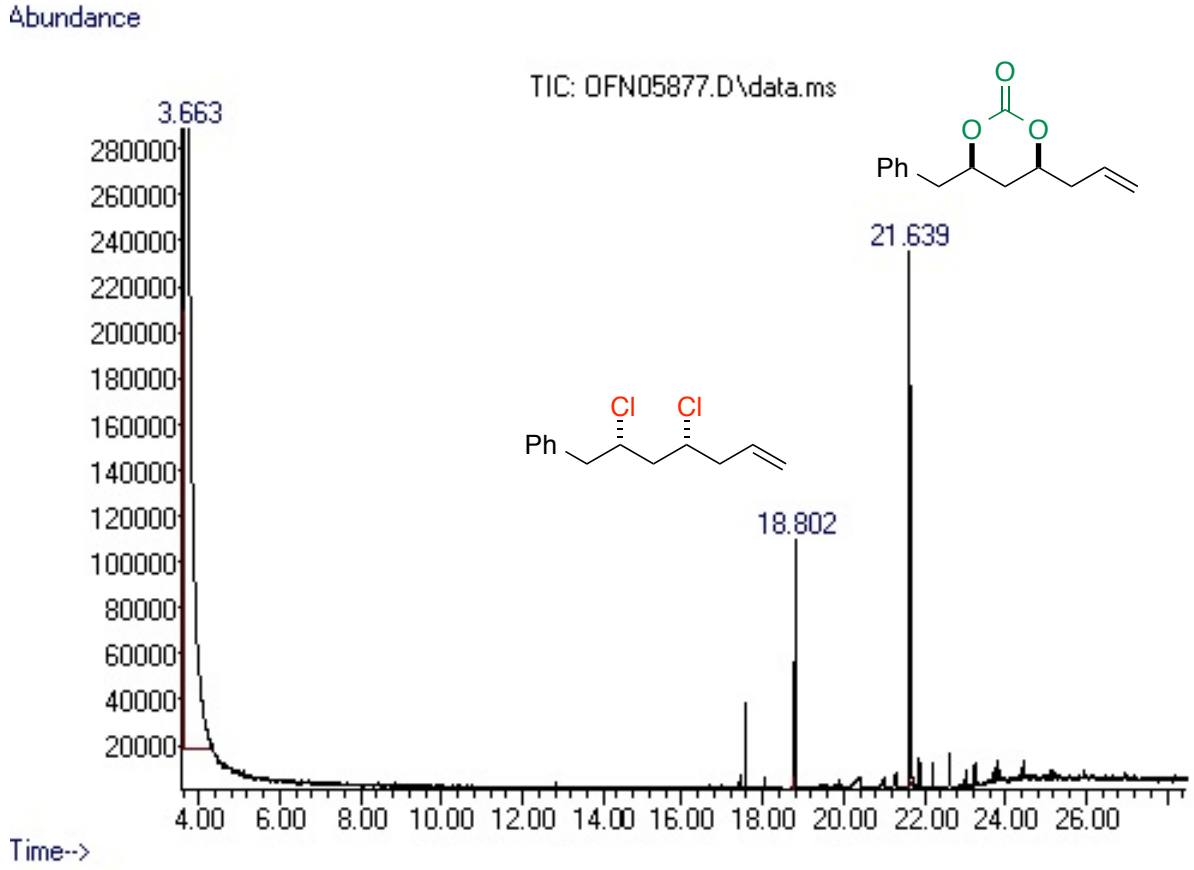


entry	-R	conc. (mM)[a]	dichloride **10** : carbonate **11**[b]
1	-H	25	34 : 66
2	-$SiMe_3$	25	65 : 35
3	-$SiEt_3$	25	32 : 68
4	**-$SiMe_2Ph$**	**25**	**80 : 20**
5	-$SiMePh_2$	25	65 : 35
6	-$SiMe_2Ph$	5	69 : 31
7	-$SiMe_2Ph$	100	80 : 20
8	**-$SiMe_2Ph$**	**500**	**99 : 1**

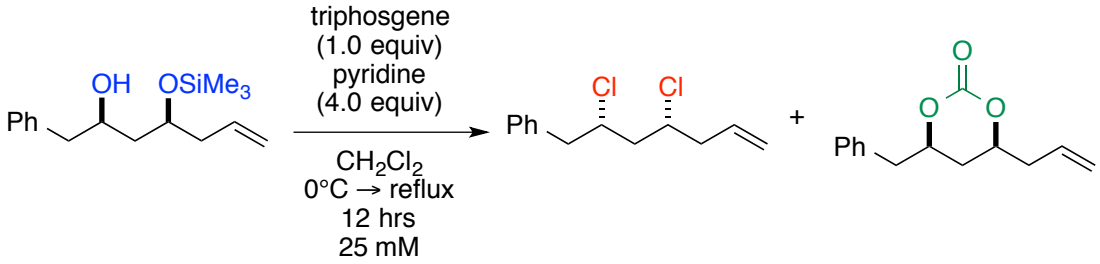
[a] Concentration was based on starting material **18**. [b] The ratio of dichloride **10** and cyclic carbonate **11** was determined via GC-MS analyses of the crude reaction mixtures.

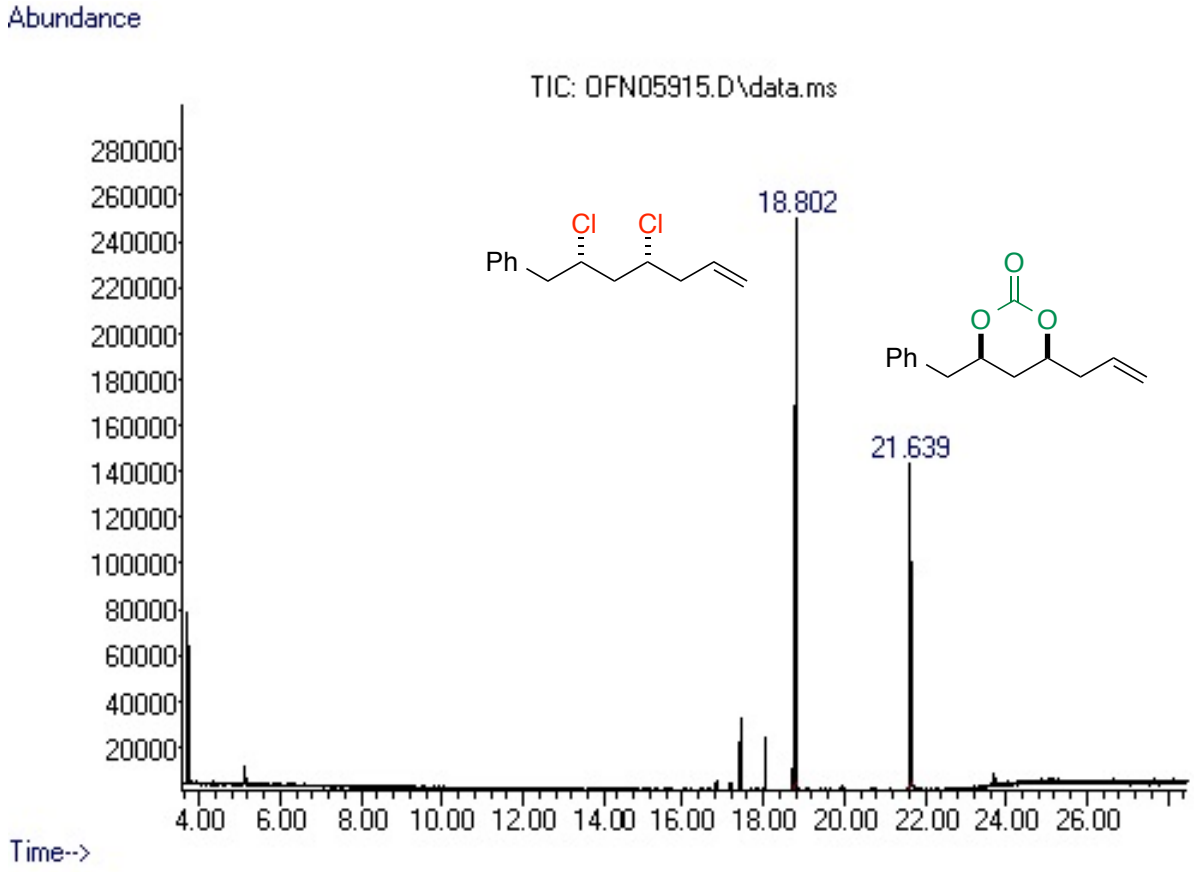
Entry #1


triphosgene
(1.0 equiv)
pyridine
(4.0 equiv)
CH_2Cl_2
0°C → reflux
12 hrs
25 mM
OH
OH
Ph
Cl
Cl
Ph
+
O
O
O
Ph

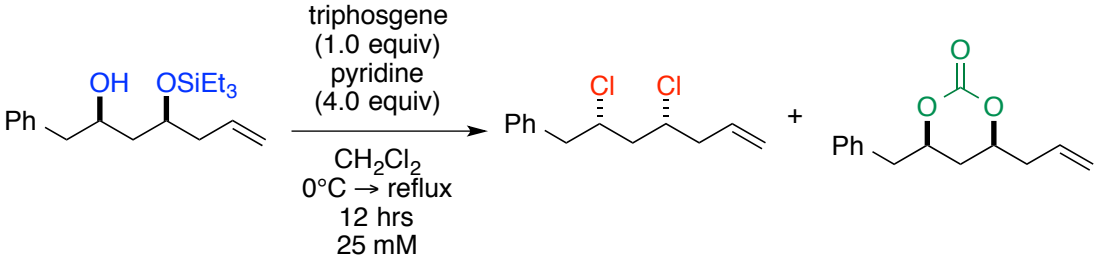

Abundance
TIC: OFN05877.D\data.ms
3.663
21.639
18.802
Cl
Cl
Ph
O
O
O
Ph
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
Time-->

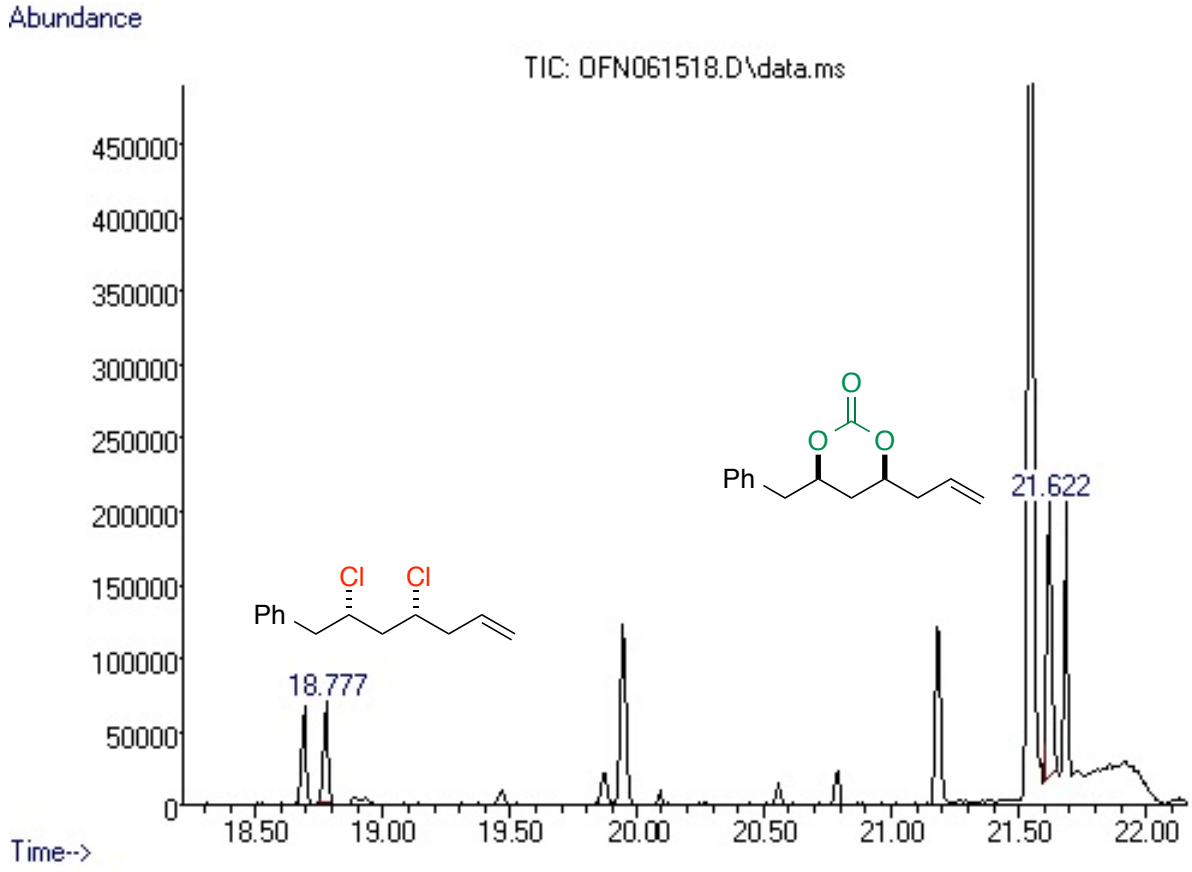
Entry #2


OH
OSiMe3
Ph
triphosgene
(1.0 equiv)
pyridine
(4.0 equiv)
CH2Cl2
0°C → reflux
12 hrs
25 mM
Cl
Cl
Ph
+
O
O
O
Ph

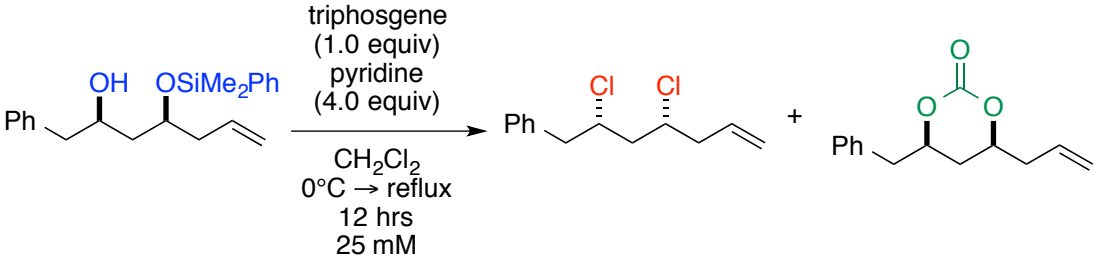

Abundance
TIC: OFN05915.D\data.ms
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
18.802
21.639
Cl
Cl
Ph
O
O
O
Ph
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
Time-->

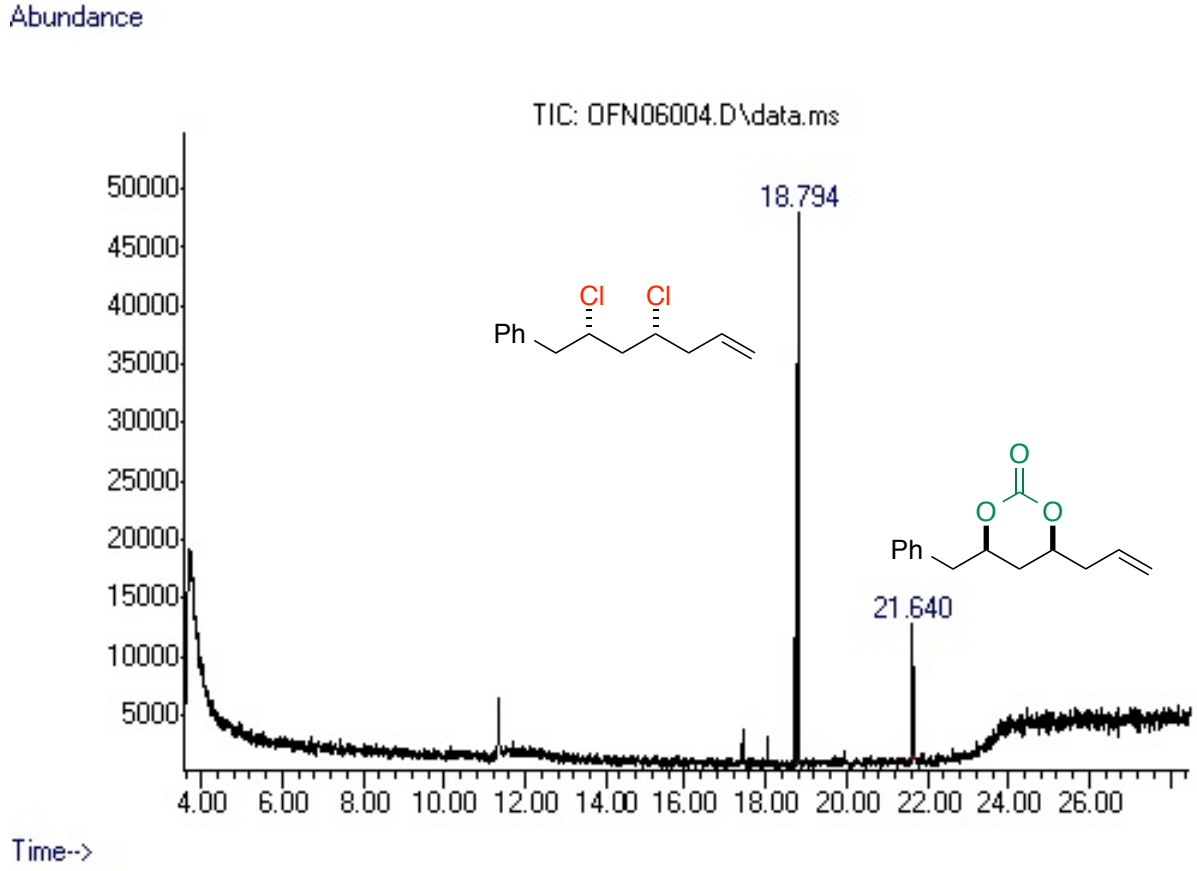
Entry #3


OH
OSiEt3
Ph
triphosgene
(1.0 equiv)
pyridine
(4.0 equiv)
CH2Cl2
0°C → reflux
12 hrs
25 mM
Cl
Cl
Ph
+
O
O
O
Ph

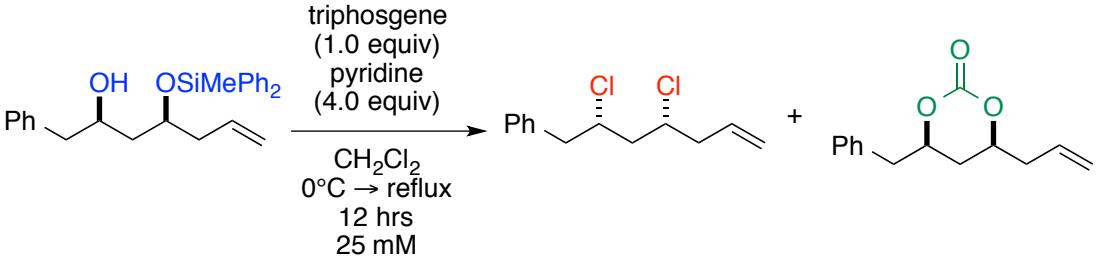

Abundance
TIC: OFN061518.D\data.ms
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
18.50
19.00
19.50
20.00
20.50
21.00
21.50
22.00
Time-->
Cl
Cl
Ph
18.777
O
O
O
Ph
21.622

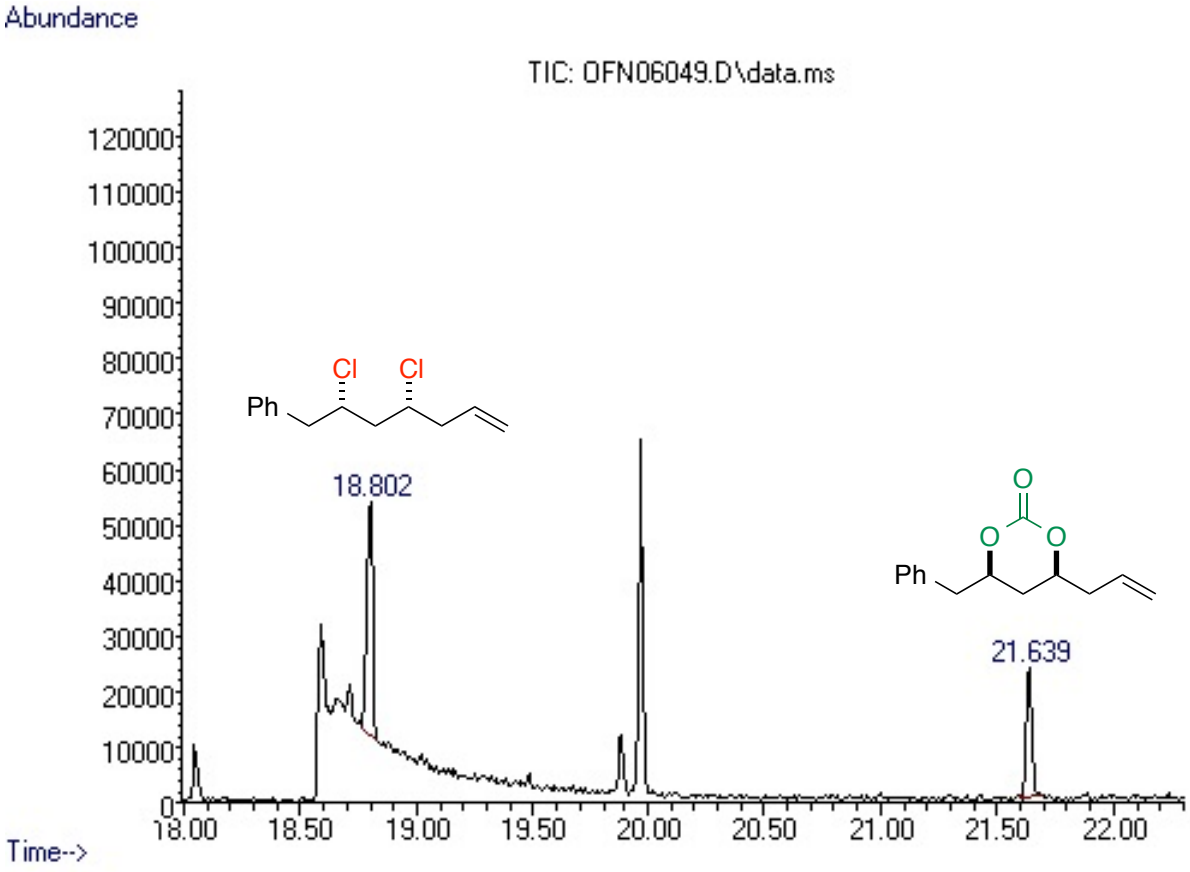
Entry #4


triphosgene
(1.0 equiv)
pyridine
(4.0 equiv)
CH2Cl2
0°C → reflux
12 hrs
25 mM
OH
OSiMe2Ph
Ph
Cl
Cl
Ph
+
O
O
O
Ph

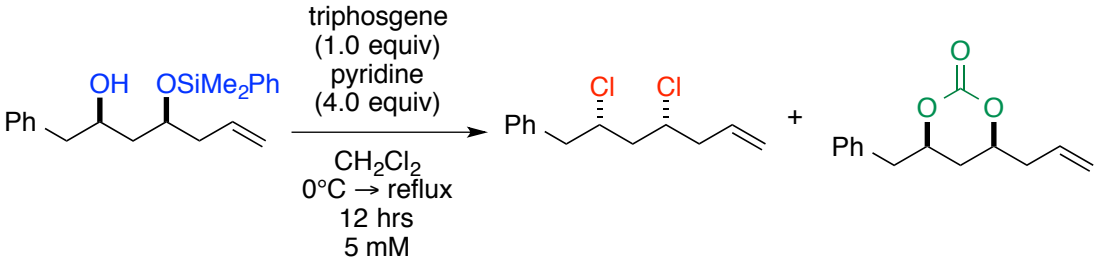

Abundance
TIC: OFN06004.D\data.ms
18.794
21.640
Cl
Cl
Ph
O
O
O
Ph
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
Time-->

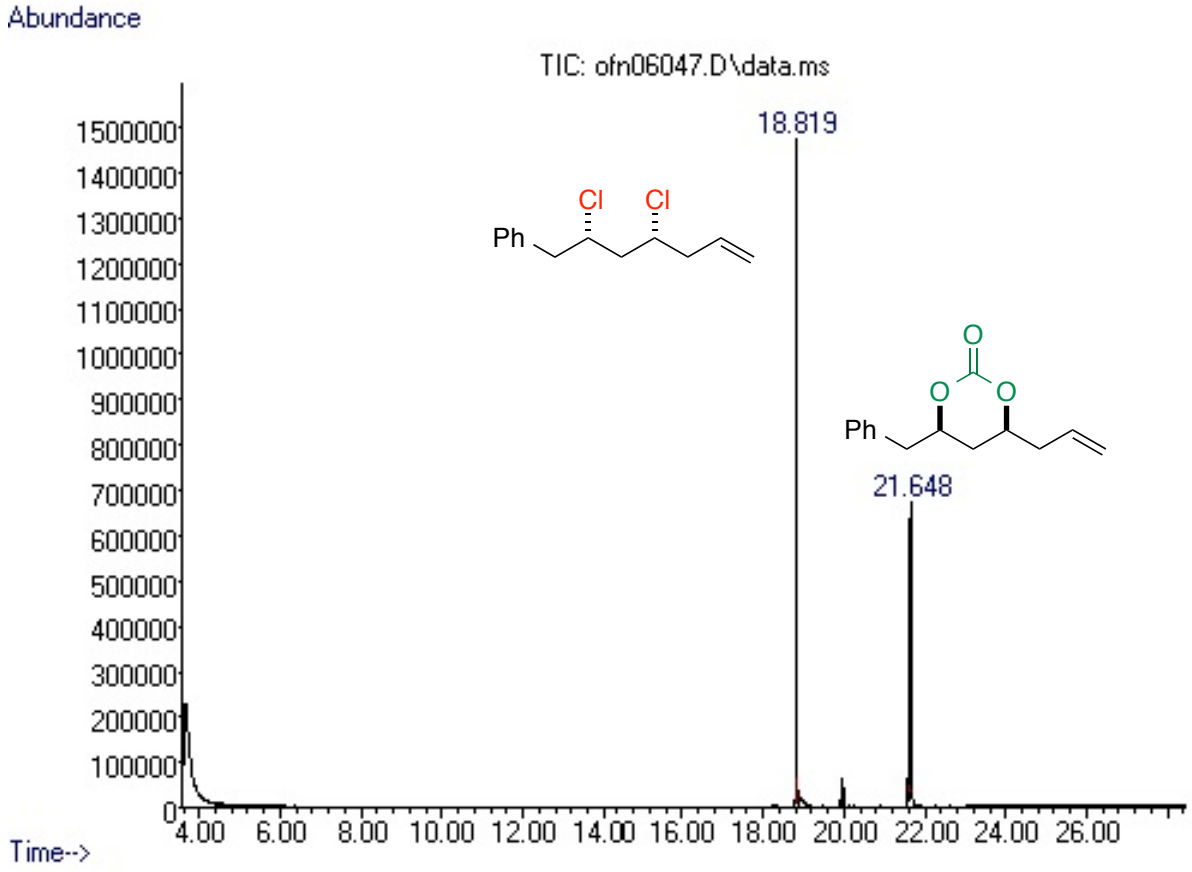
Entry #5


triphosgene
(1.0 equiv)
pyridine
(4.0 equiv)
CH_2Cl_2
0°C → reflux
12 hrs
25 mM
OH
OSiMePh2
Ph
Cl
Cl
Ph
O
O
O
Ph

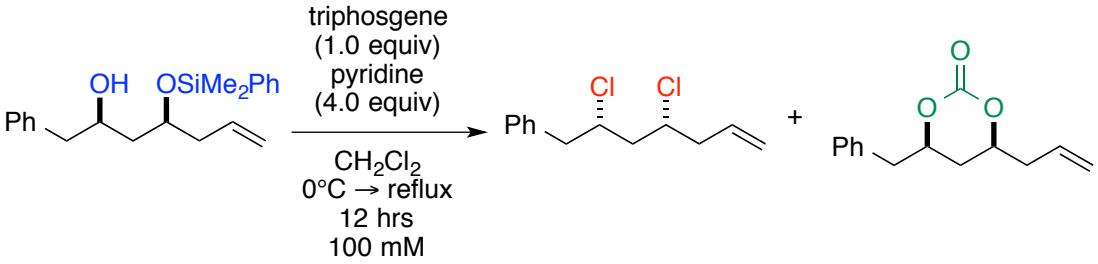

Abundance
TIC: OFN06049.D\data.ms
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
Cl
Cl
Ph
18.802
O
O
O
Ph
21.639
18.00
18.50
19.00
19.50
20.00
20.50
21.00
21.50
22.00
Time-->

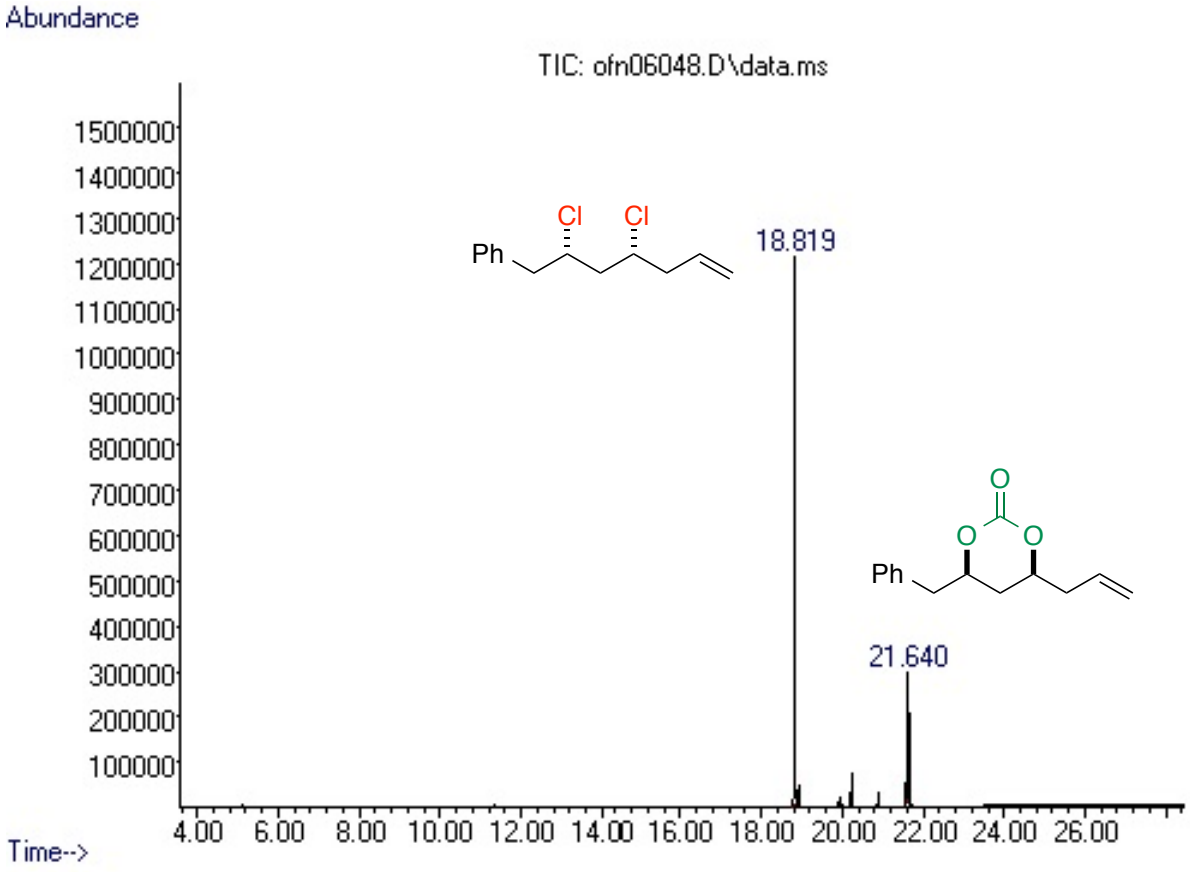
Entry #6


triphosgene
(1.0 equiv)
pyridine
(4.0 equiv)
CH2Cl2
0°C → reflux
12 hrs
5 mM
OH
OSiMe2Ph
Ph
Cl
Cl
Ph
+
O
O
O
Ph

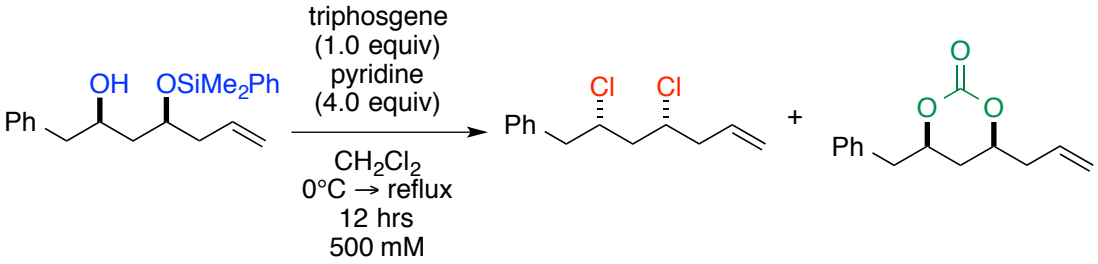

Abundance
TIC: ofn06047.D\data.ms
18.819
21.648
Cl
Cl
Ph
O
O
O
Ph
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
Time-->

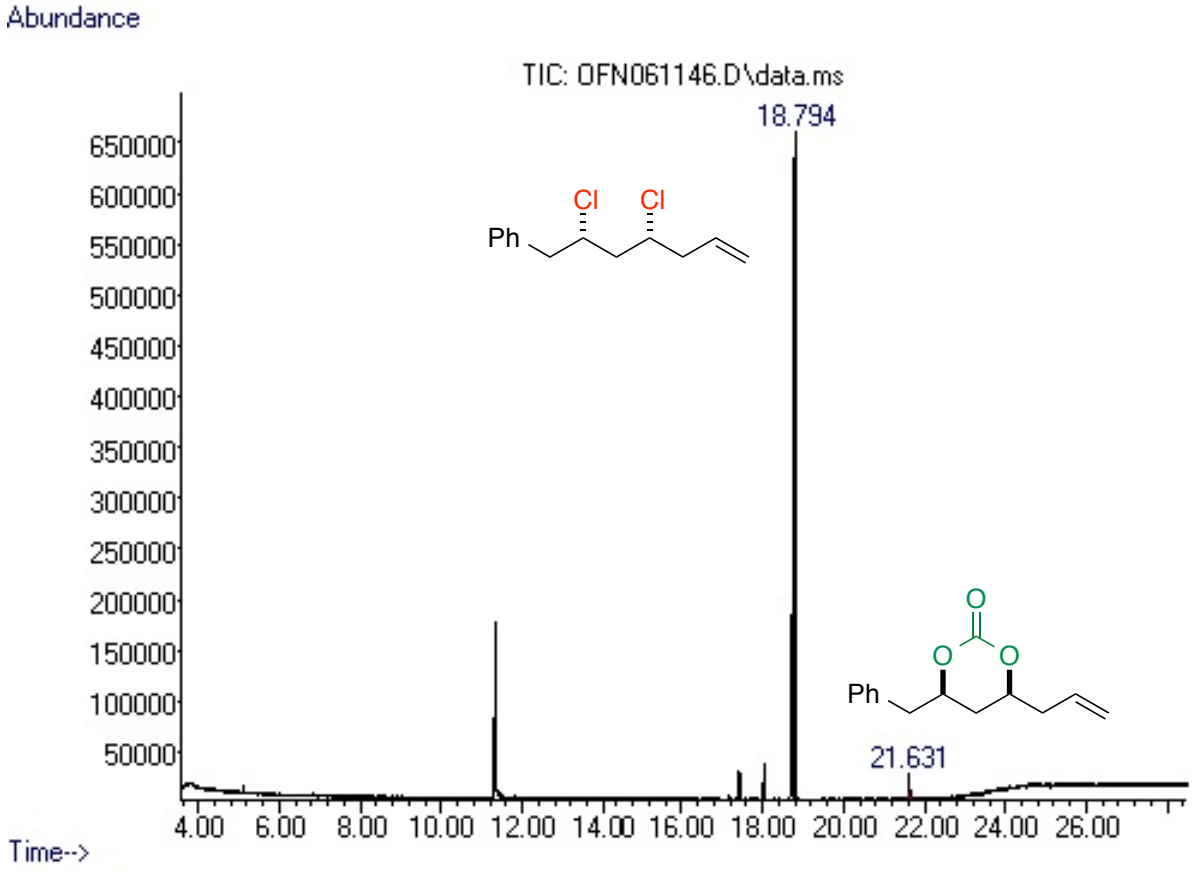
Entry #7


triphosgene
(1.0 equiv)
pyridine
(4.0 equiv)
CH2Cl2
0°C → reflux
12 hrs
100 mM
OH
OSiMe2Ph
Ph
Cl
Cl
O
O
O
+

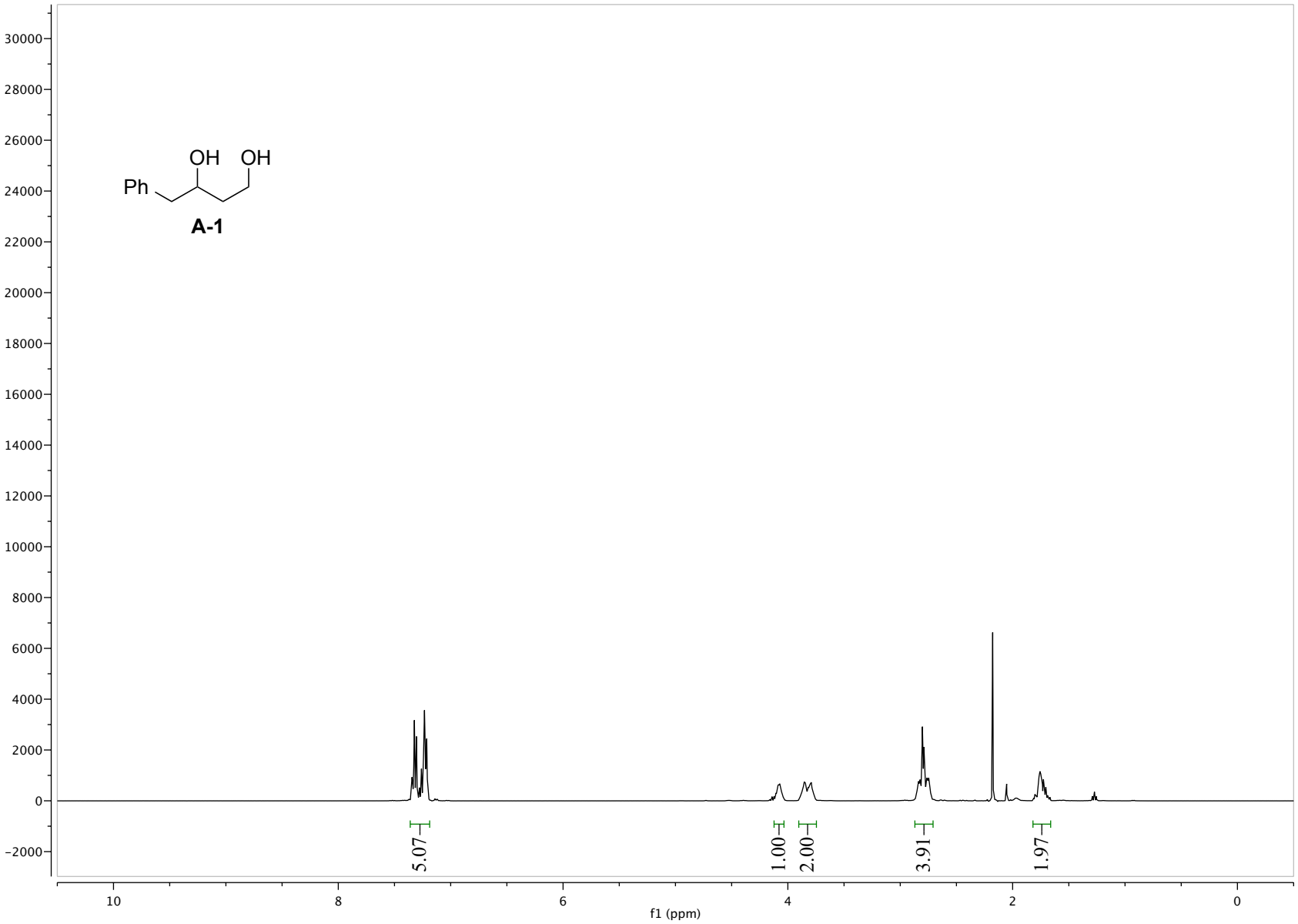

Abundance
TIC: ofn06048.D\data.ms
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
18.819
21.640
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
Time-->

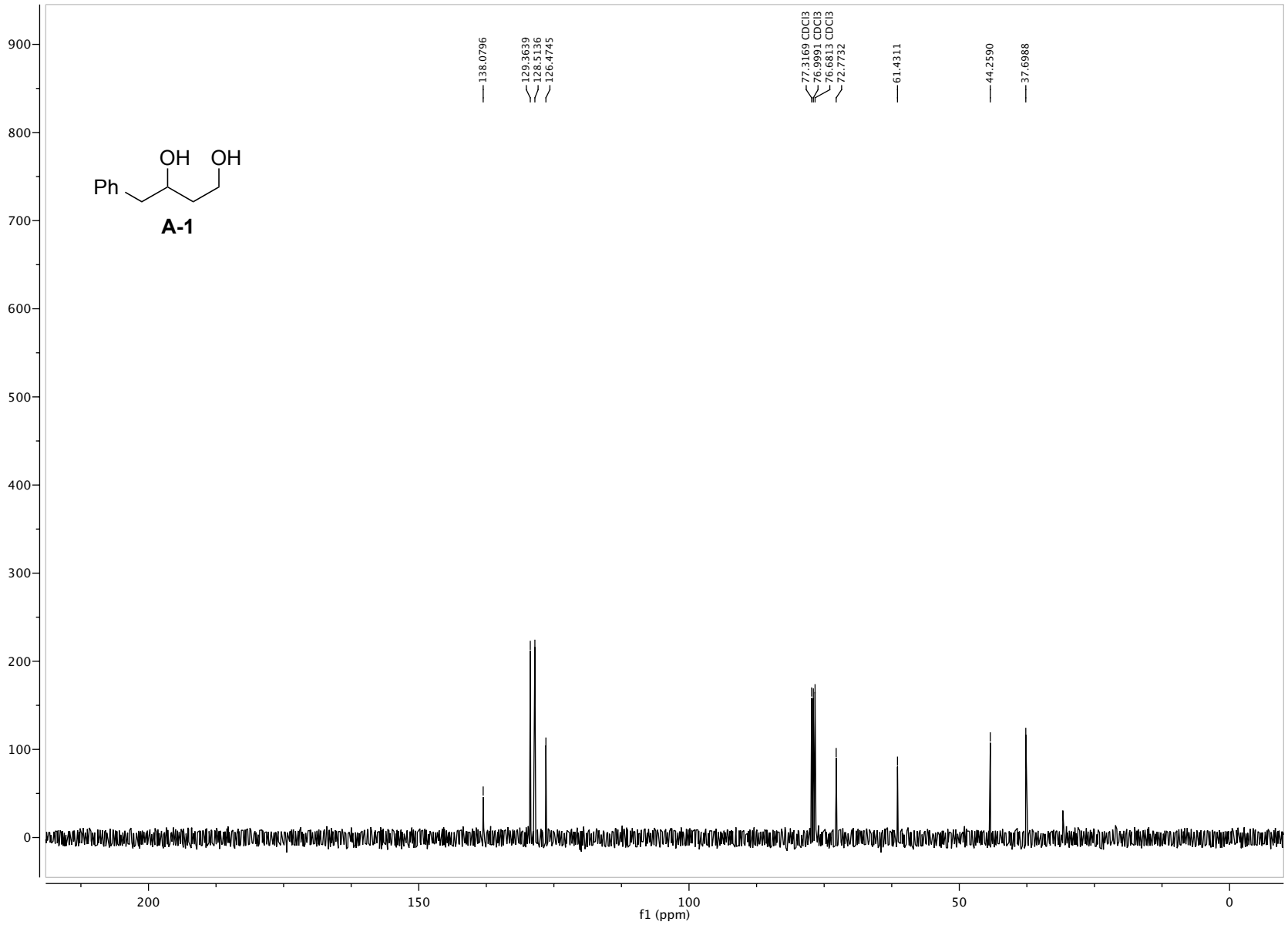
Entry #8

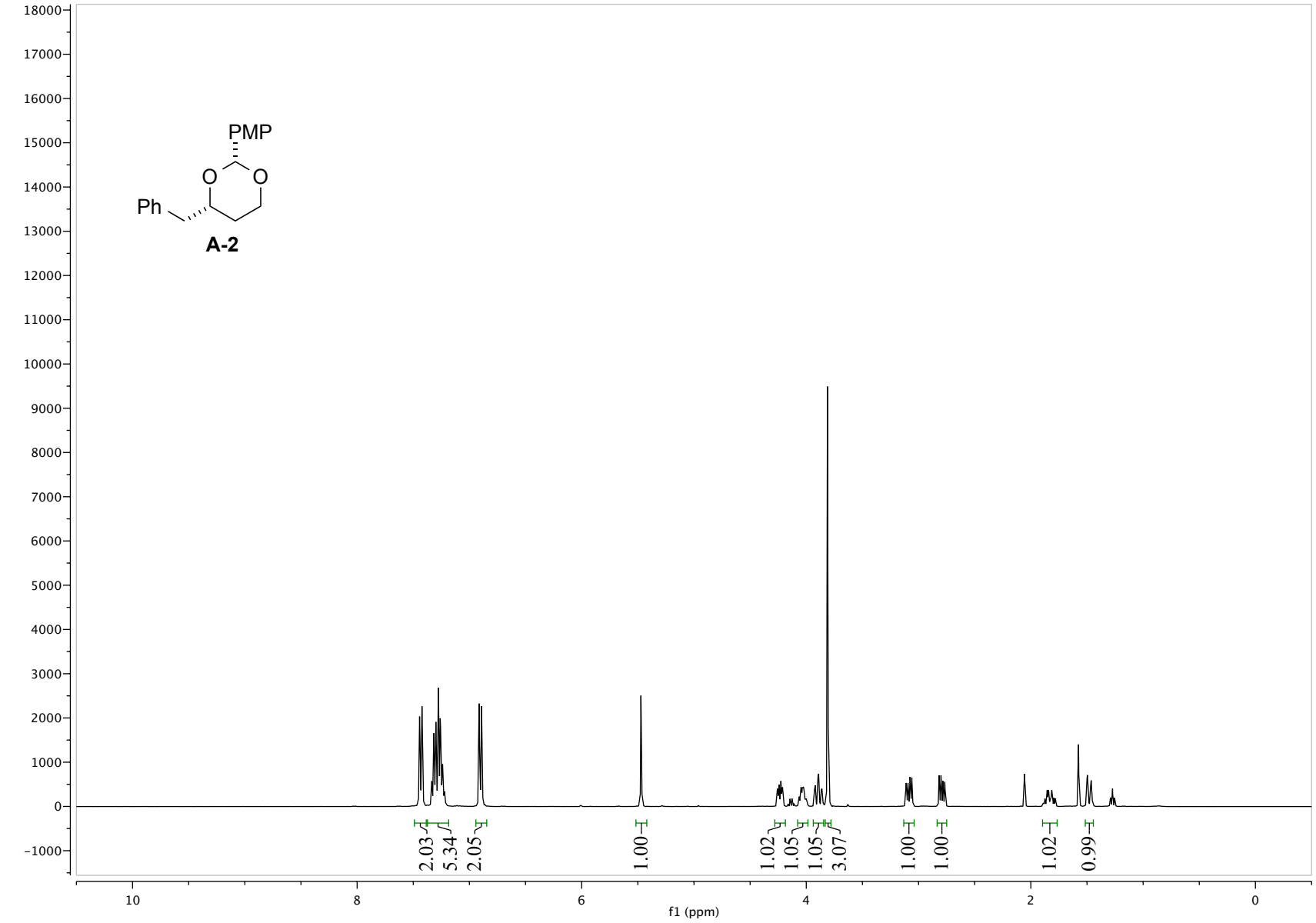


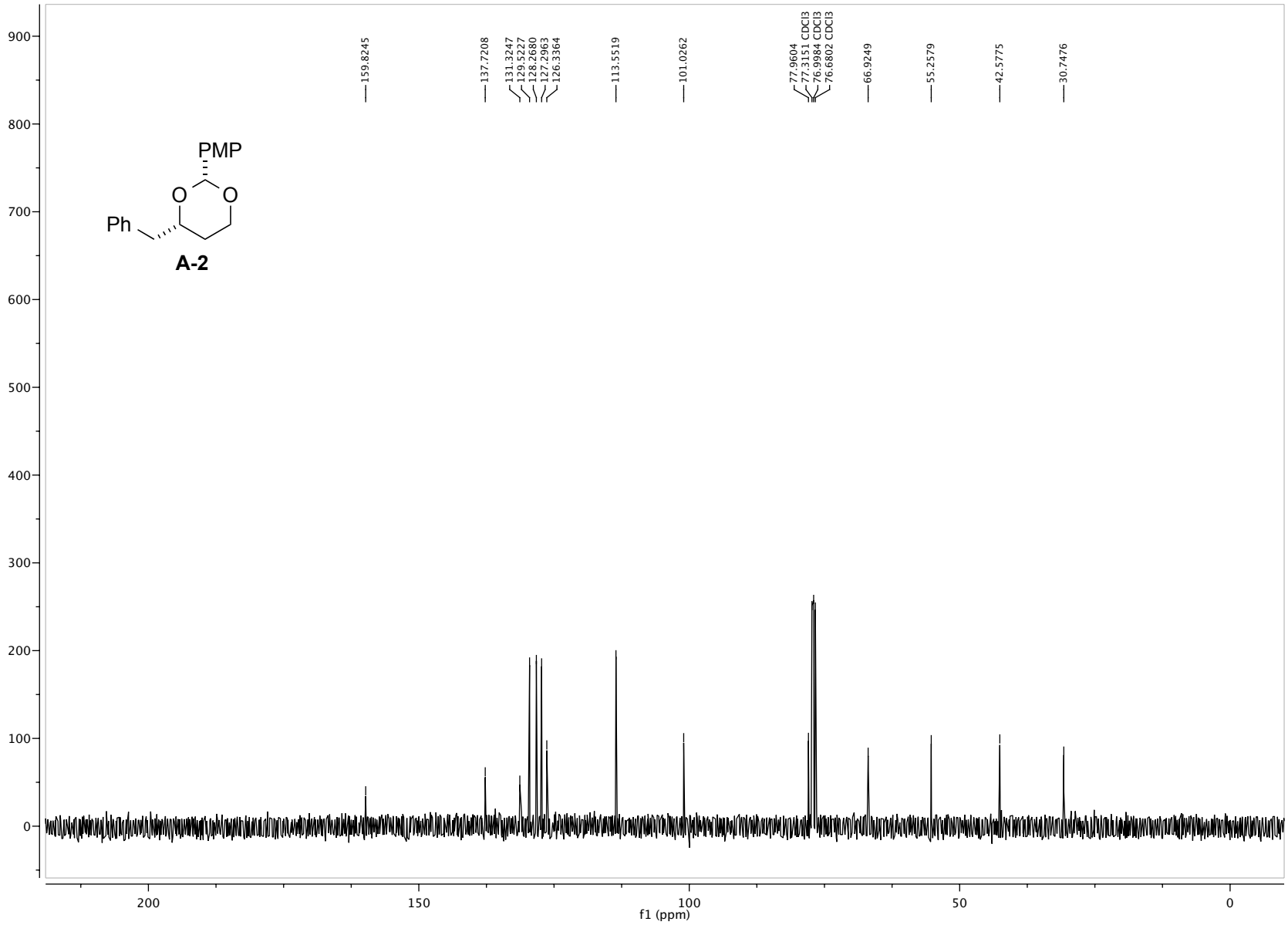


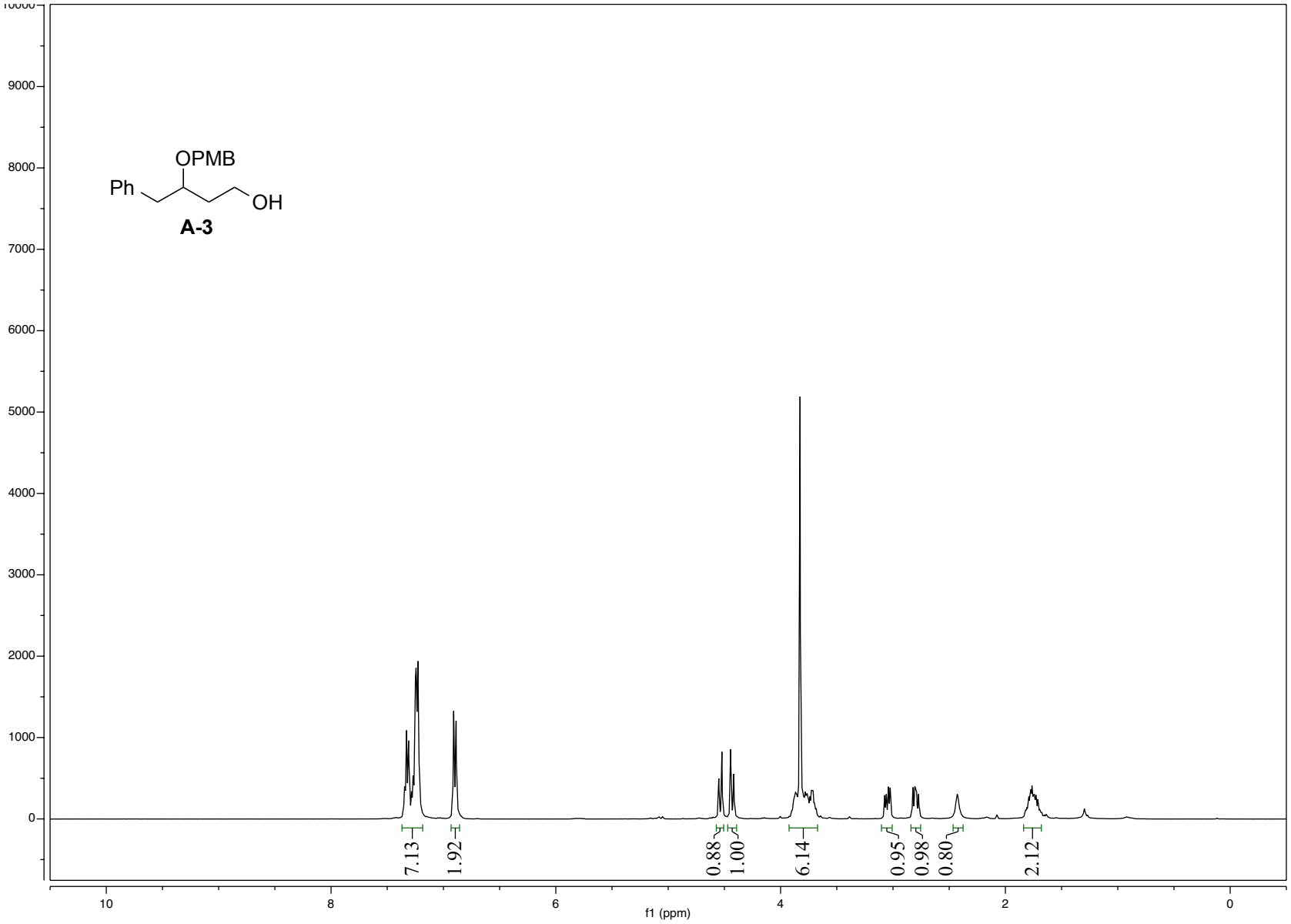
4. ^{1}H AND ^{13}C NMR SPECTRA

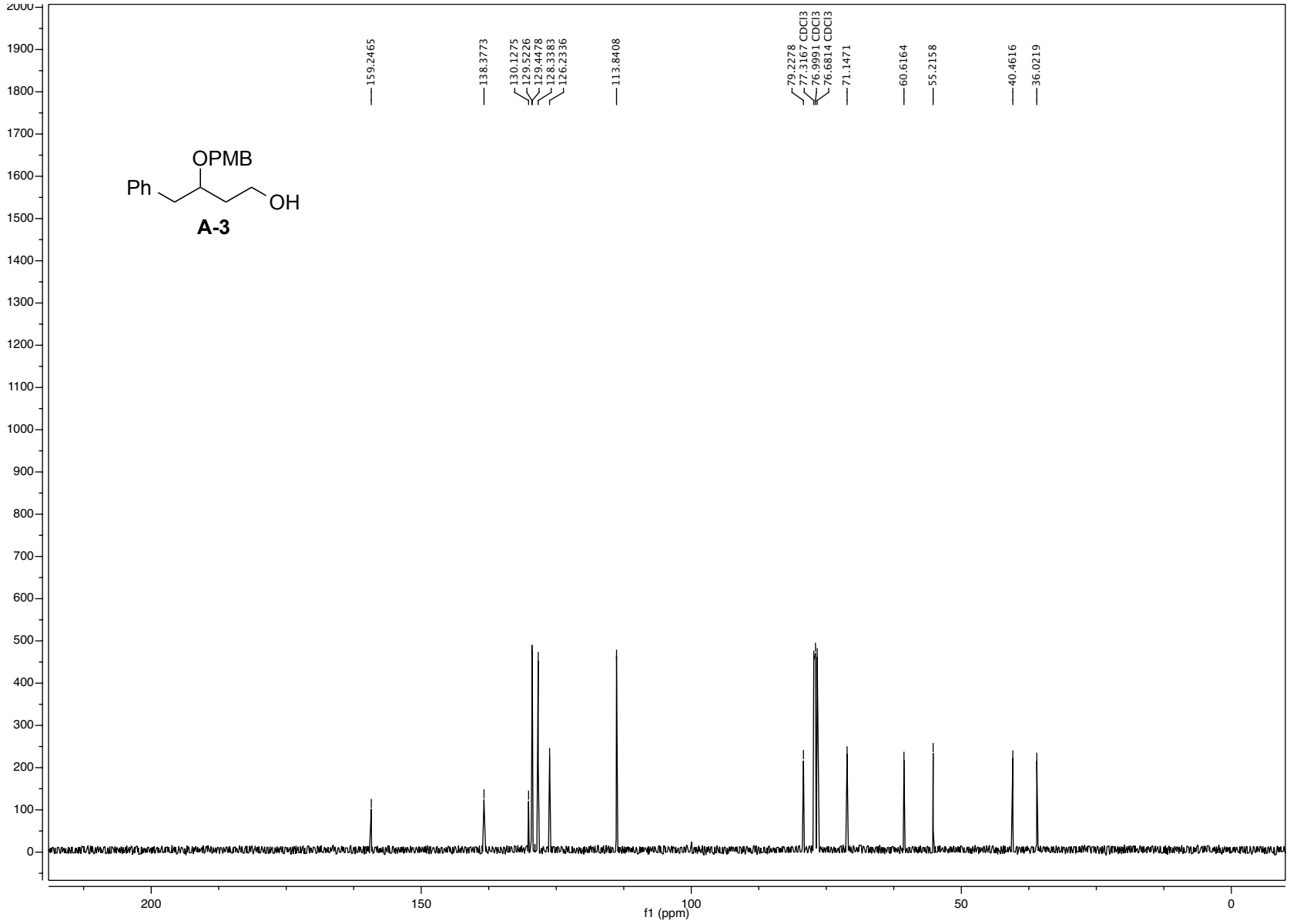

OH
OH
Ph
A-1
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
−2000
5.07
1.00
2.00
3.91
1.97
10
8
6
4
2
0
f1 (ppm)

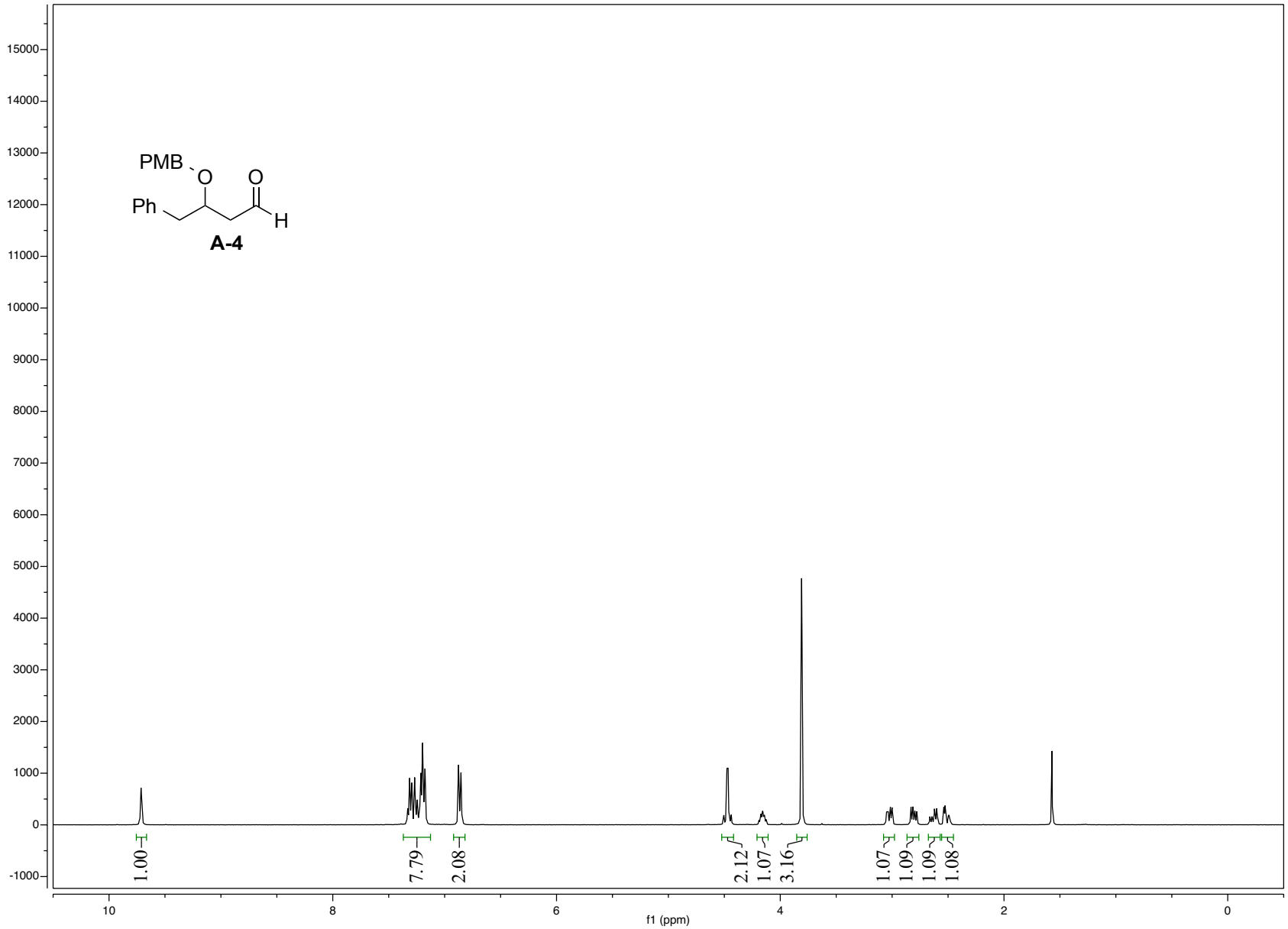

138.0796
129.3639
128.5136
126.4745
77.3169 CDCl3
76.9991 CDCl3
76.6813 CDCl3
72.7732
61.4311
44.2590
37.6988
OH
OH
Ph
A-1
f1 (ppm)

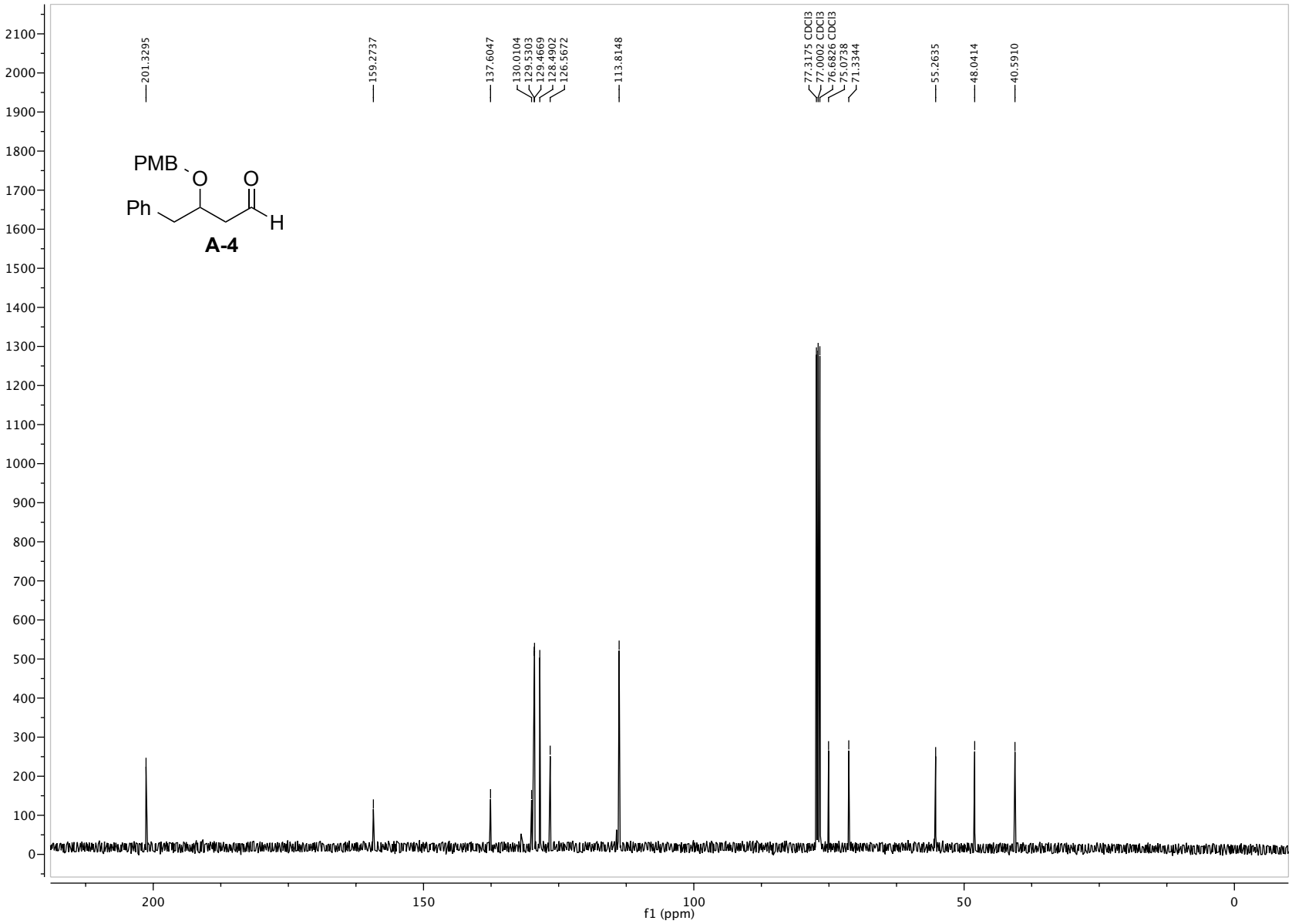

PMP
O
O
Ph
A-2
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
2.03
5.34
2.05
1.00
1.02
1.05
1.05
3.07
1.00
1.00
1.02
0.99
10
8
6
4
2
0
f1 (ppm)

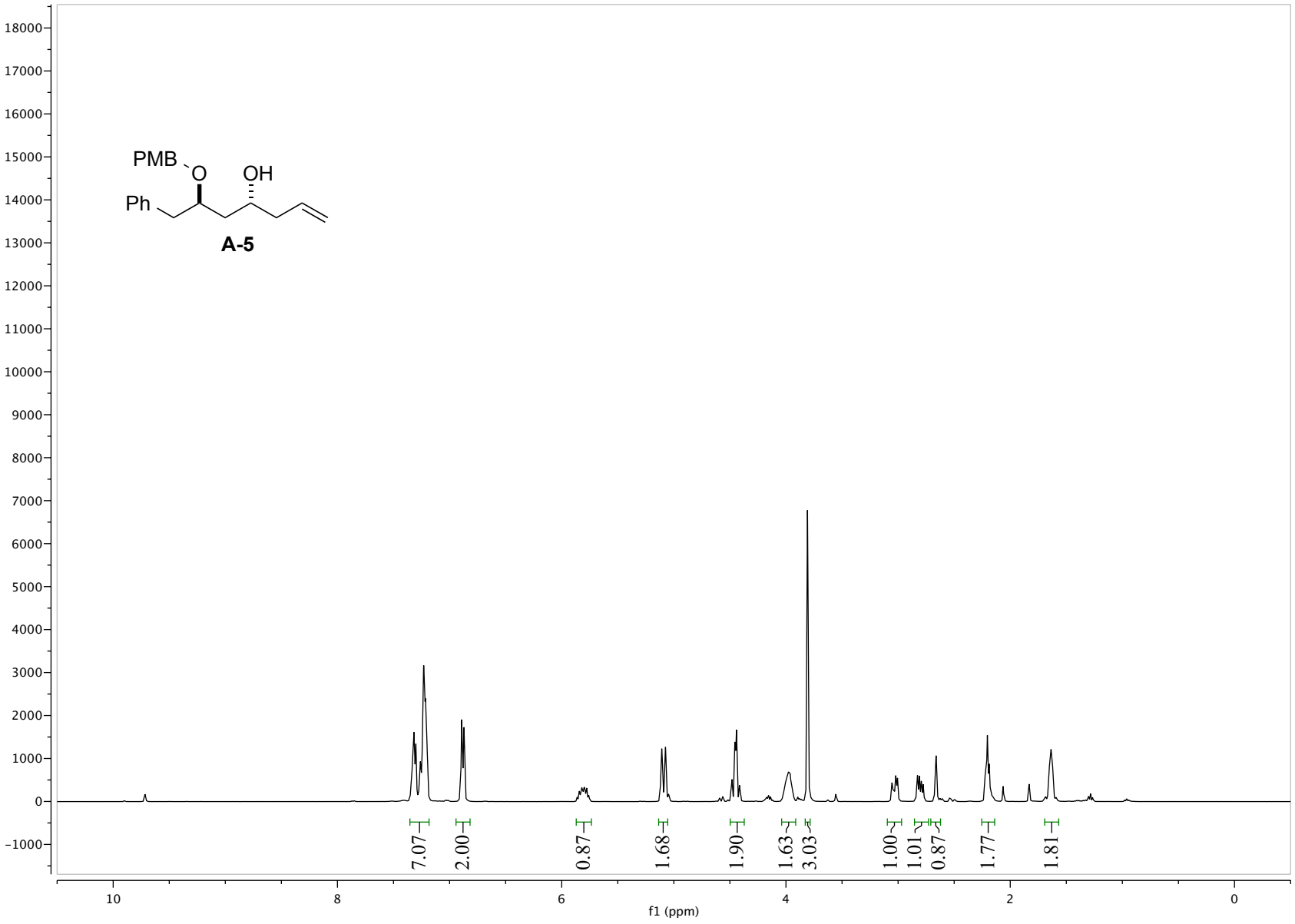

159.8245
137.7208
131.3247
129.5227
128.2680
127.2963
126.3364
113.5519
101.0262
77.9604
77.3151 CDCl3
76.9984 CDCl3
76.6802 CDCl3
66.9249
55.2579
42.5775
30.7476
PMP
O
O
Ph
A-2
900
800
700
600
500
400
300
200
100
0
200
150
100
50
0
f1 (ppm)

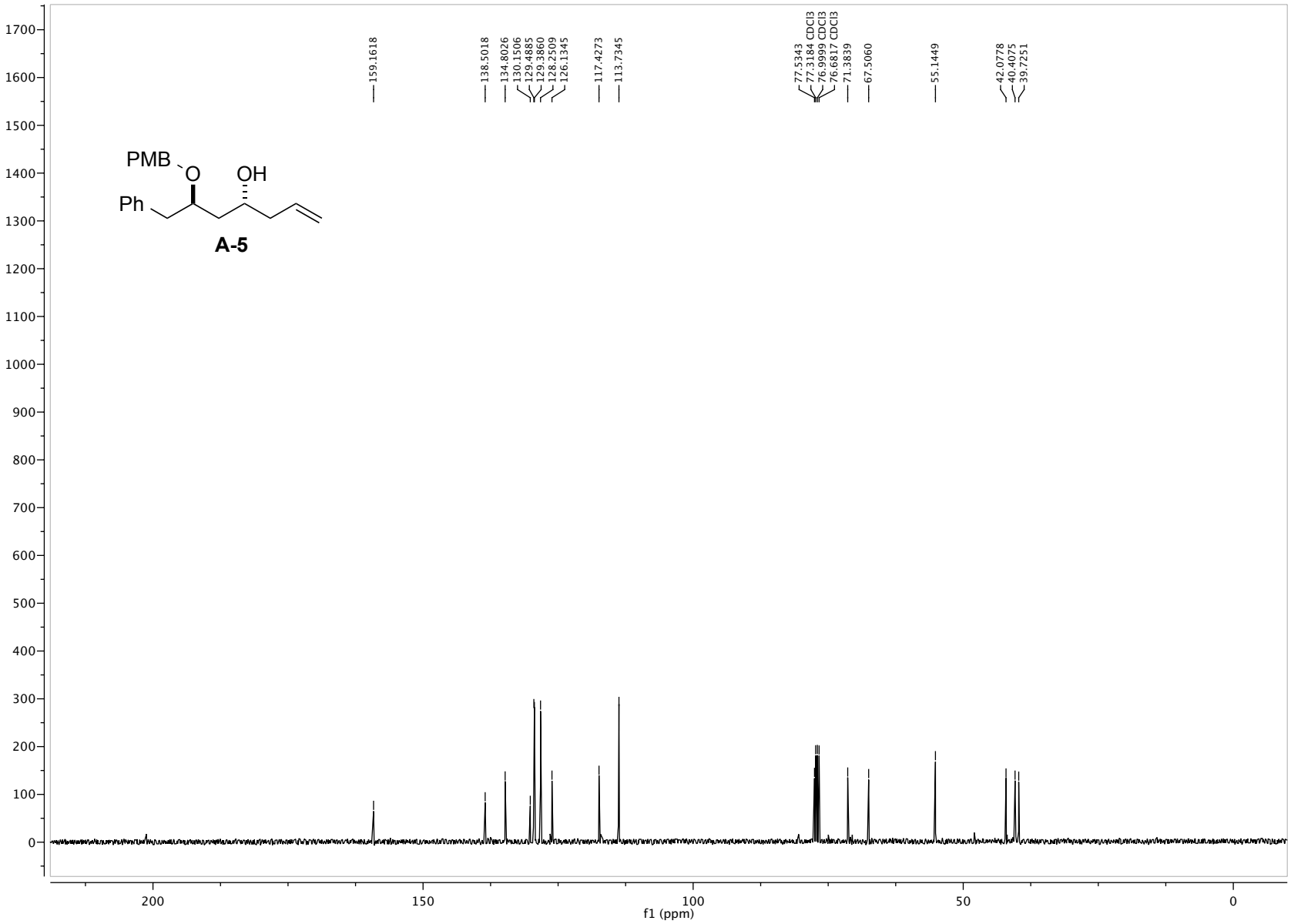

OPMB
Ph
OH
A-3
7.13
1.92
0.88
1.00
6.14
0.95
0.98
0.80
2.12
f1 (ppm)

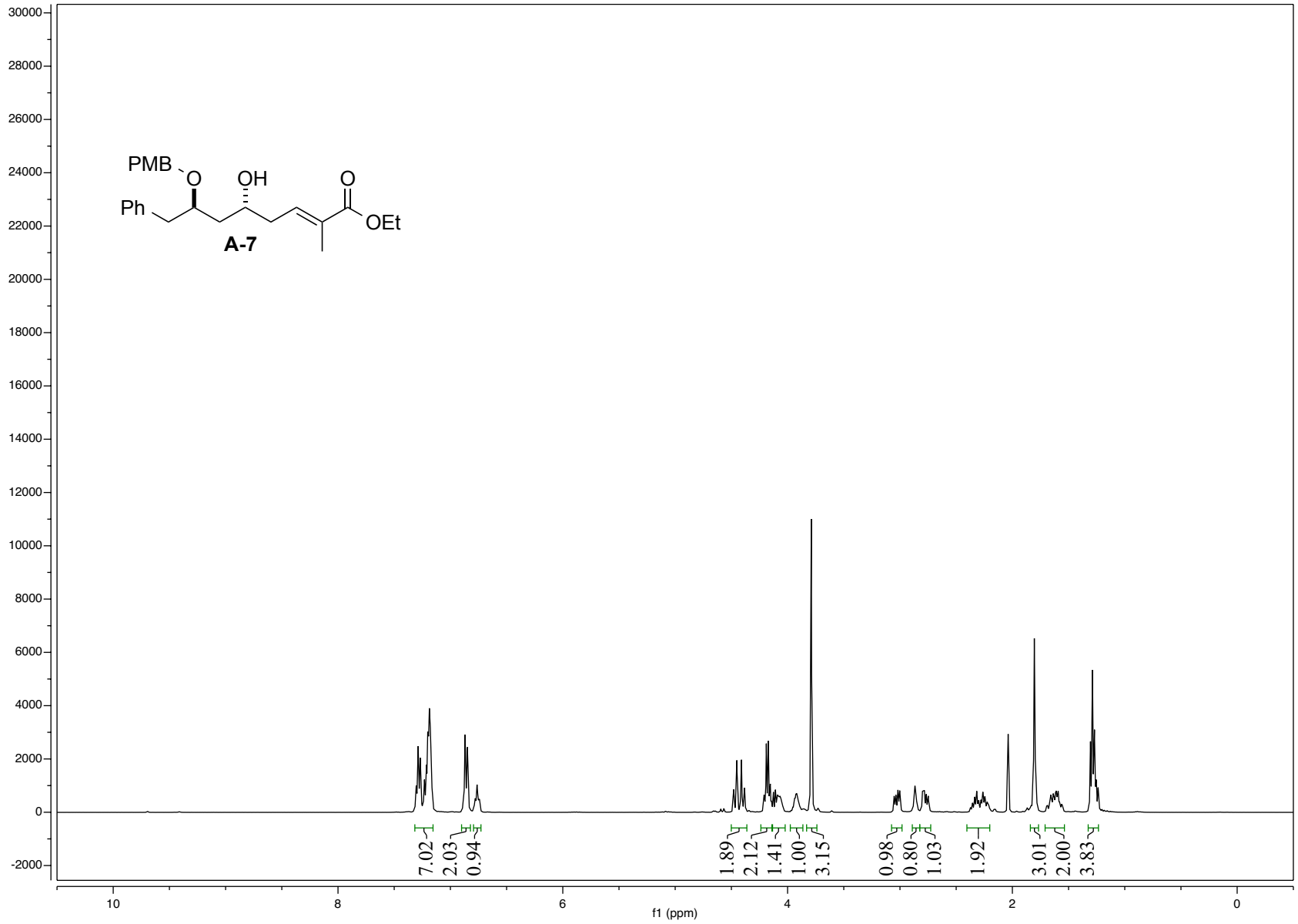

159.2465
138.3773
130.1275
129.5226
129.4478
128.3383
126.2336
113.8408
79.2278
77.3167 CDCl3
76.9991 CDCl3
76.6814 CDCl3
71.1471
60.6164
55.2158
40.4616
36.0219
OPMB
Ph
OH
A-3
f1 (ppm)

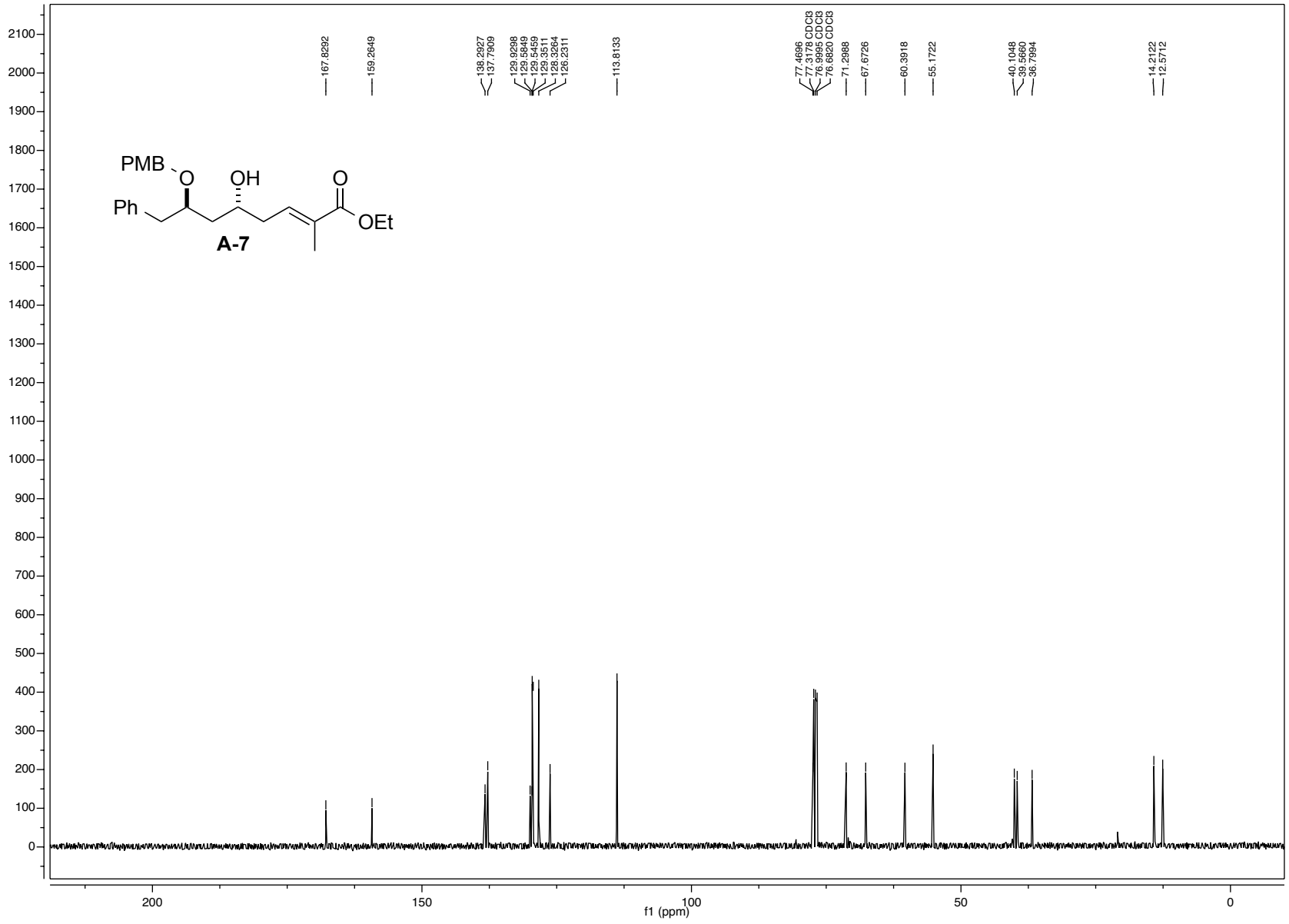

PMB
O
O
Ph
H
A-4
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
1.00
7.79
2.08
2.12
1.07
3.16
1.07
1.09
1.09
1.08
10
8
6
4
2
0
f1 (ppm)

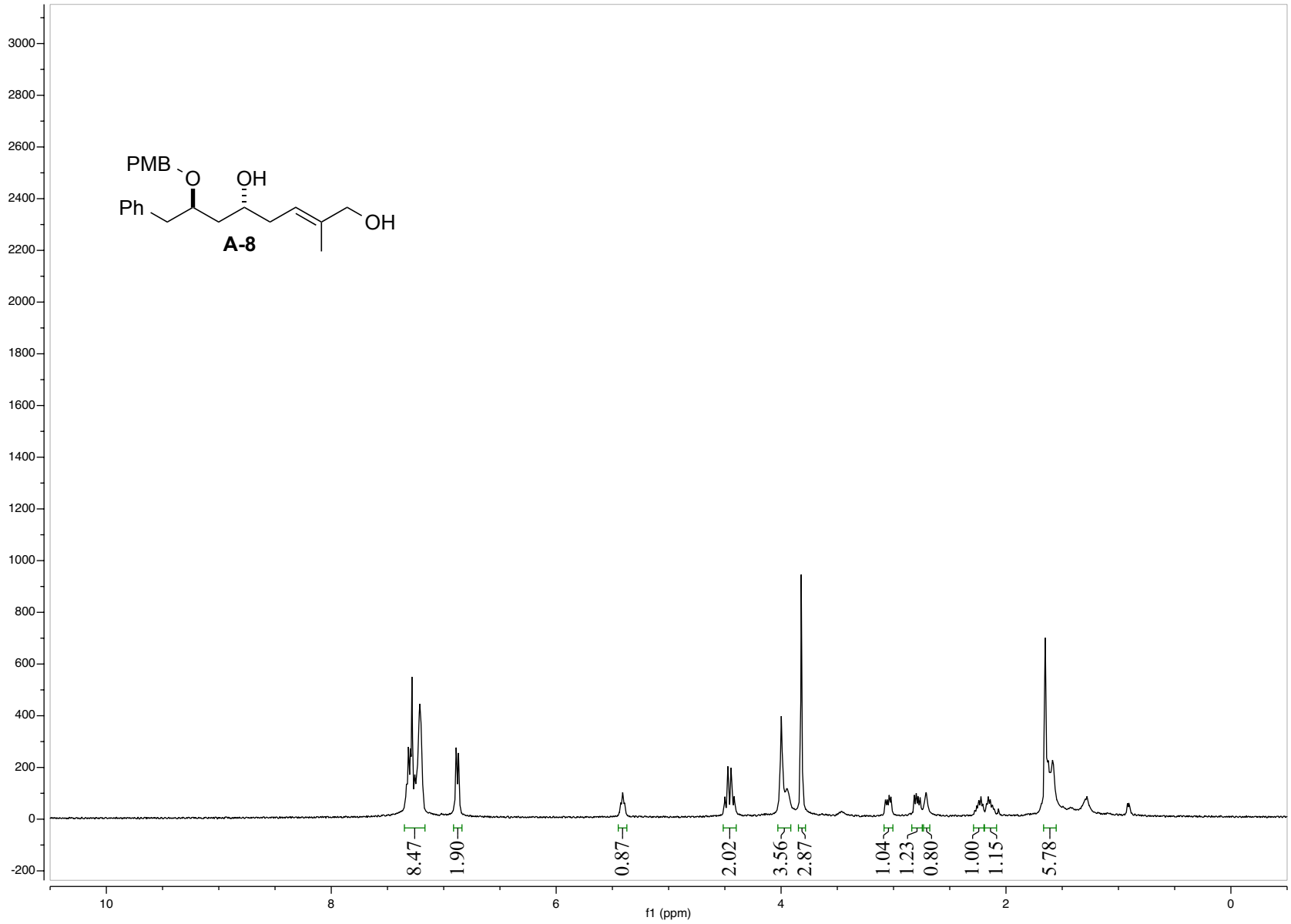

201.3295
159.2737
137.6047
130.0104
129.5303
129.4669
128.4902
126.5672
113.8148
77.3175 CDCl3
77.0002 CDCl3
76.6826 CDCl3
75.0738
71.3344
55.2635
48.0414
40.5910
PMB
O
O
Ph
H
A-4
f1 (ppm)

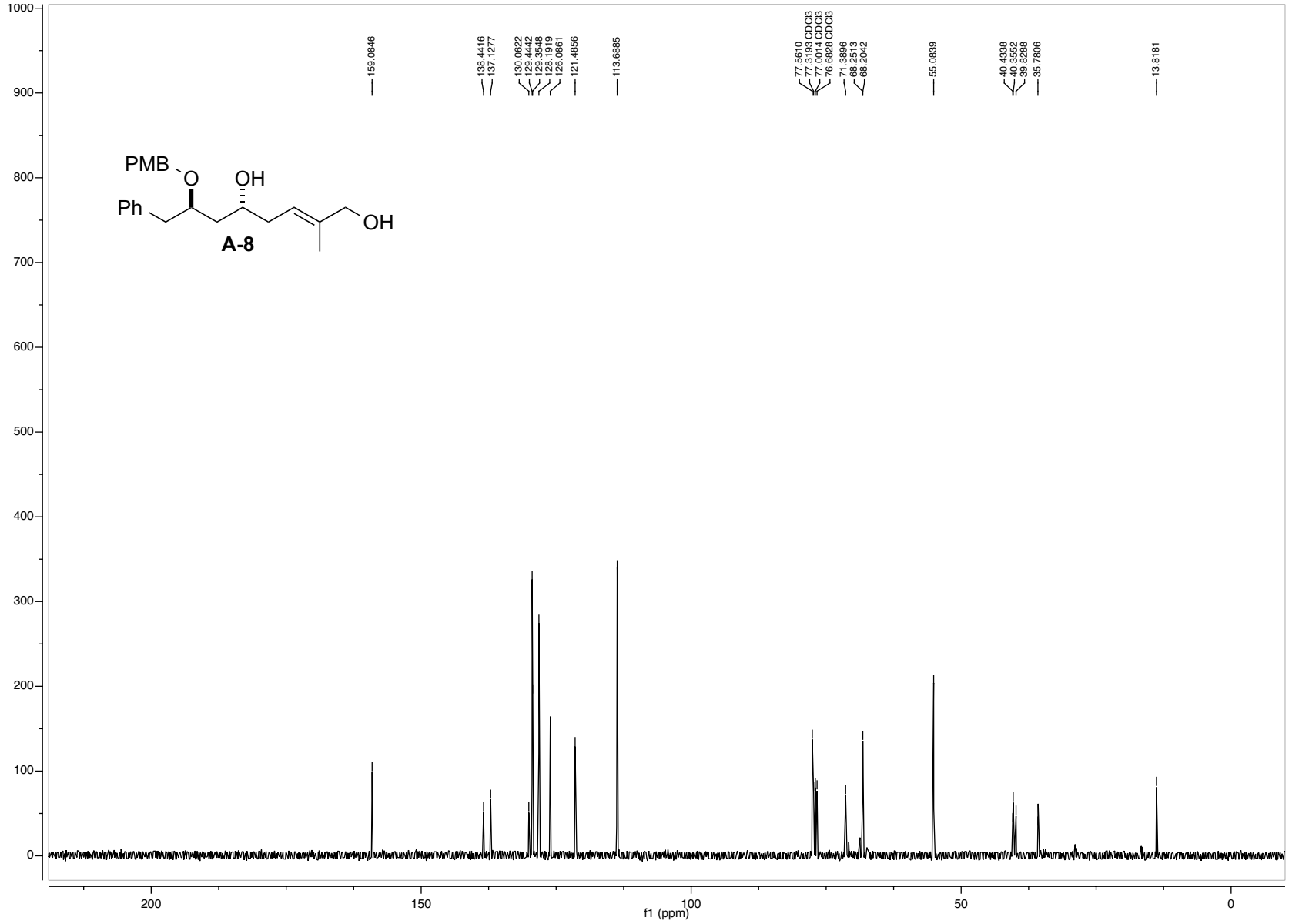

PMB
O
OH
Ph
A-5
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
7.07
2.00
0.87
1.68
1.90
1.63
3.03
1.00
1.01
0.87
1.77
1.81
10
8
6
4
2
0
f1 (ppm)

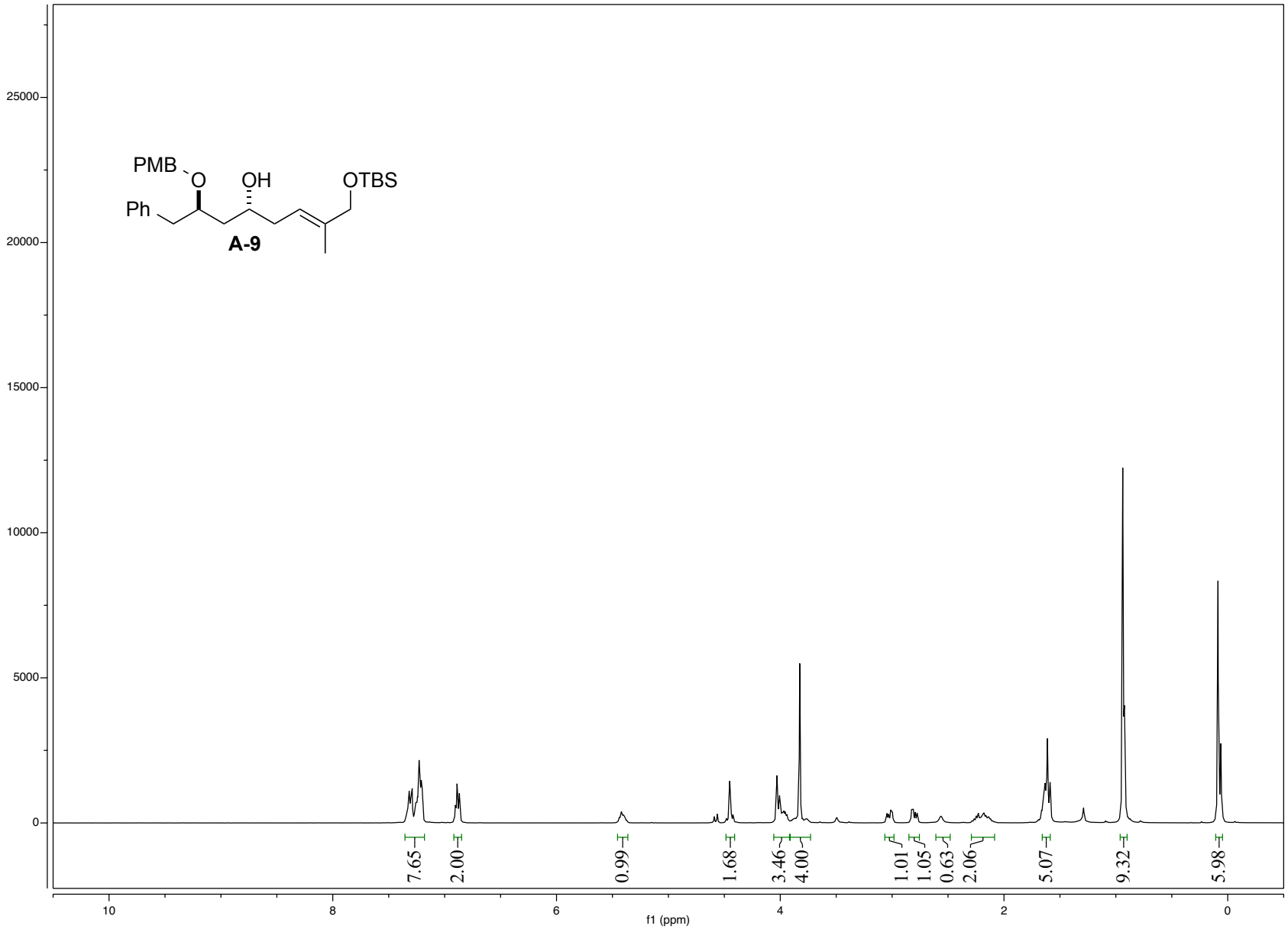

159.1618
138.5018
134.8026
130.1506
129.4885
129.3860
128.2509
126.1345
117.4273
113.7345
77.5343
77.3184 CDCl3
76.9999 CDCl3
76.6817 CDCl3
71.3839
67.5060
55.1449
42.0778
40.4075
39.7251
PMB
O
OH
Ph
A-5
f1 (ppm)

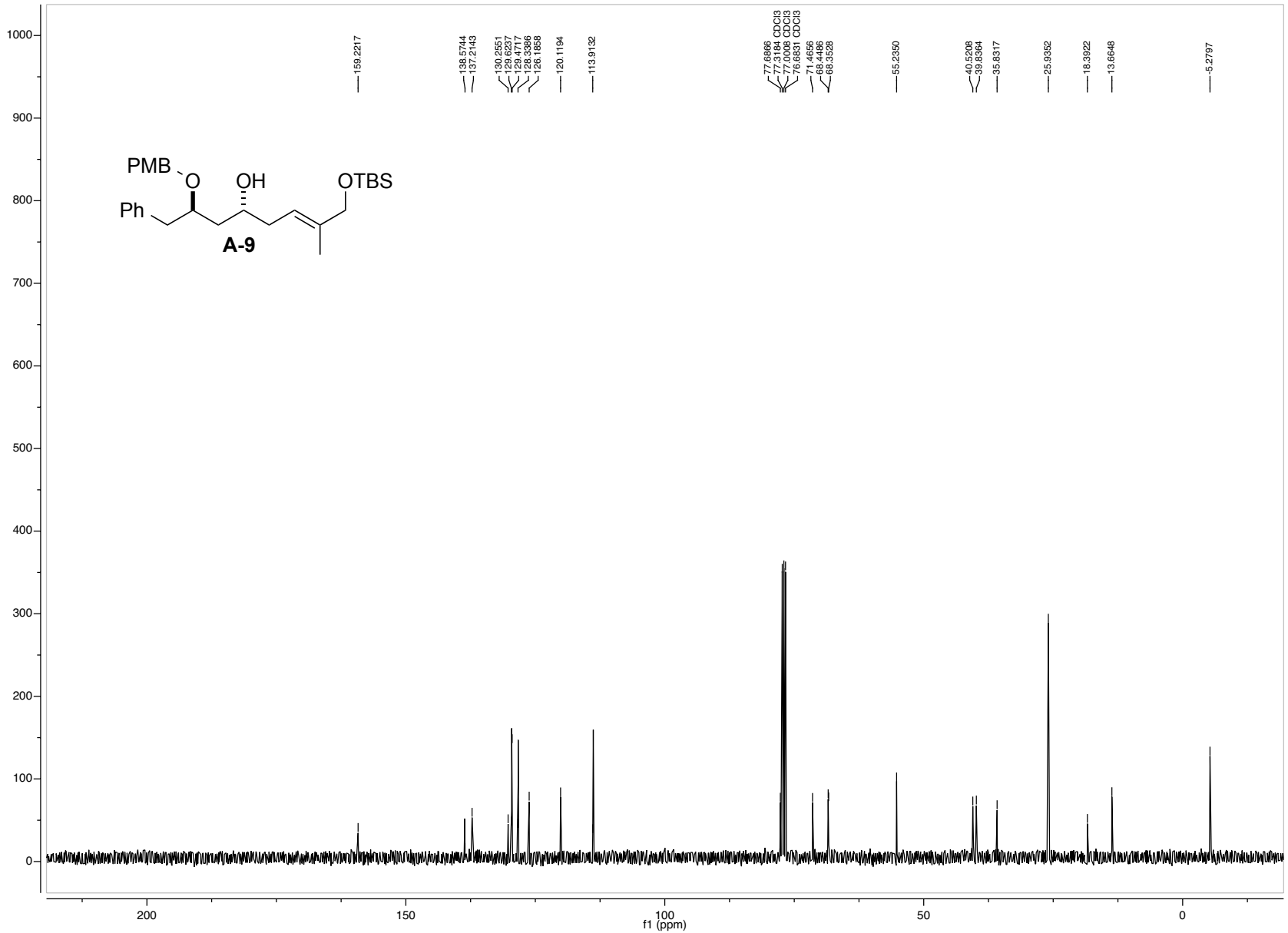

PMB
O
OH
O
Ph
OEt
A-7
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
7.02
2.03
0.94
1.89
2.12
1.41
1.00
3.15
0.98
0.80
1.03
1.92
3.01
2.00
3.83
10
8
6
4
2
0
f1 (ppm)


167.8292
159.2649
138.2927
137.7909
129.9298
129.5849
129.5459
129.3511
128.3264
126.2311
113.8133
77.4696
77.3178 CDCl3
76.9995 CDCl3
76.6820 CDCl3
71.2988
67.6726
60.3918
55.1722
40.1048
39.5660
36.7994
14.2122
12.5712
PMB
O
OH
O
Ph
OEt
A-7
f1 (ppm)


PMB
O
OH
Ph
OH
A-8
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
8.47
1.90
0.87
2.02
3.56
2.87
1.04
1.23
0.80
1.00
1.15
5.78
10
8
6
4
2
0
f1 (ppm)


159.0846
138.4416
137.1277
130.0622
129.4442
129.3548
128.1919
126.0861
121.4856
113.6885
77.5610
77.3193 CDCl3
77.0014 CDCl3
76.6828 CDCl3
71.3896
68.2513
68.2042
55.0839
40.4338
40.3552
39.8288
35.7806
13.8181
PMB
O
OH
Ph
OH
A-8
f1 (ppm)


PMB
O
OH
OTBS
Ph
A-9
25000
20000
15000
10000
5000
0
7.65
2.00
0.99
1.68
3.46
4.00
1.01
1.05
0.63
2.06
5.07
9.32
5.98
10
8
6
4
2
0
f1 (ppm)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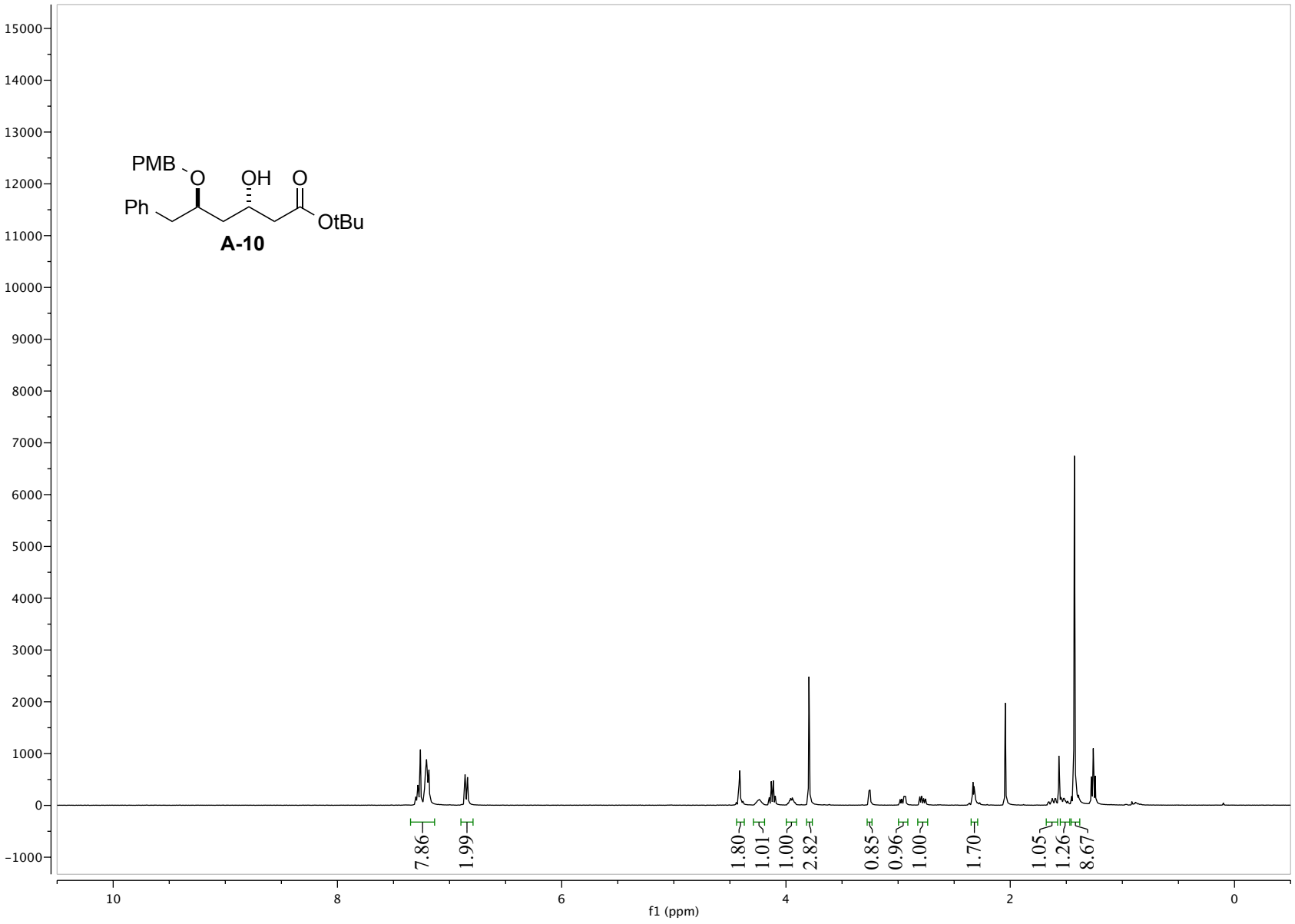
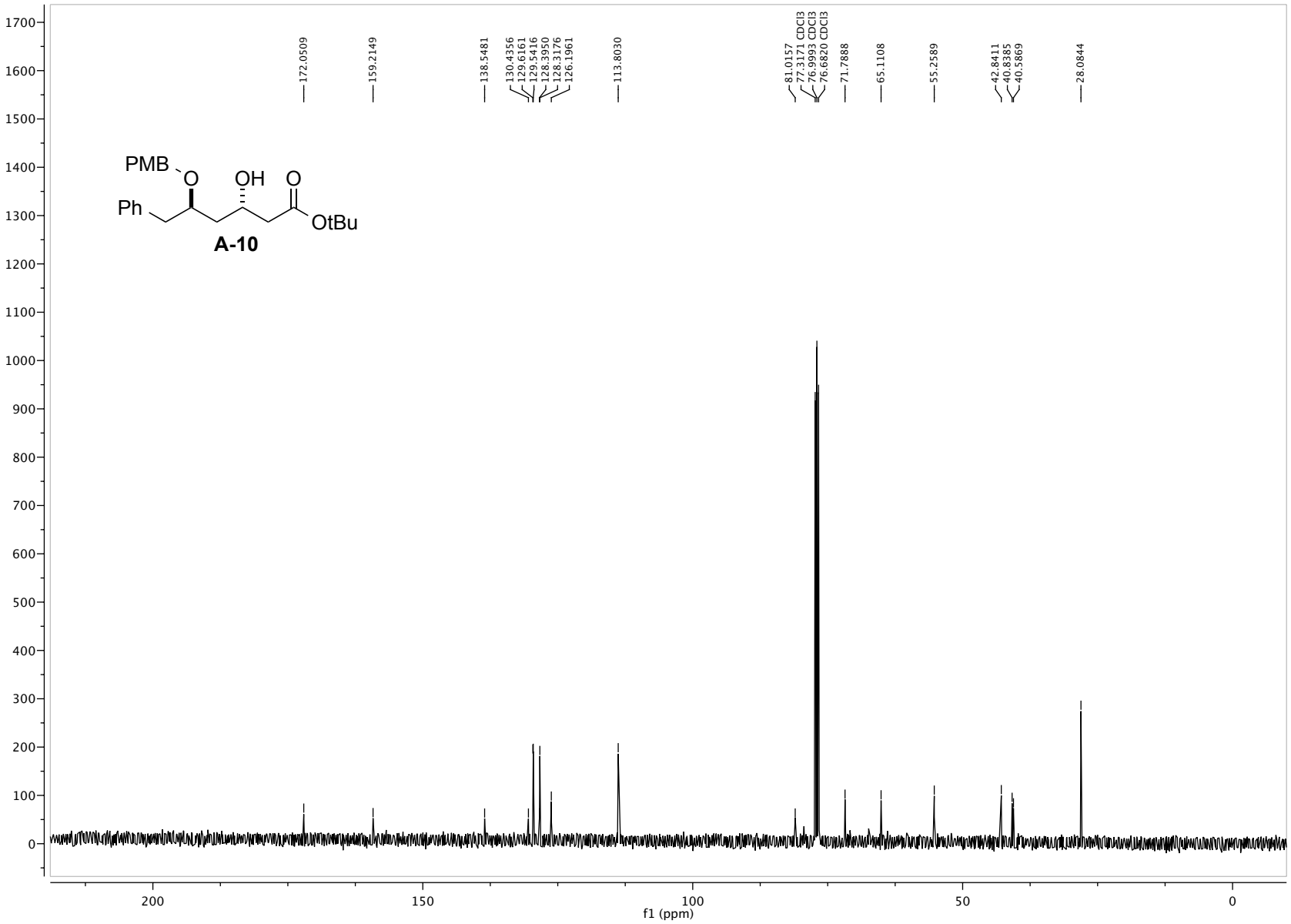
138.5744
137.2143
130.2551
129.6227
129.4717
128.3386
126.1858
120.1194
113.9132
77.6866
77.3184 CDCl3
77.0008 CDCl3
76.6831 CDCl3
71.4656
68.4486
68.3528
55.2350
40.5208
39.8364
35.8317
25.9352
18.3922
13.6648
-5.2797
PMB
O
OH
OTBS
Ph
A-9
f1 (ppm)


PMB
O
OH
O
Ph
OtBu
A-10
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
7.86
1.99
1.80
1.01
1.00
2.82
0.85
0.96
1.00
1.70
1.05
1.26
8.67
10
8
6
4
2
0
f1 (ppm)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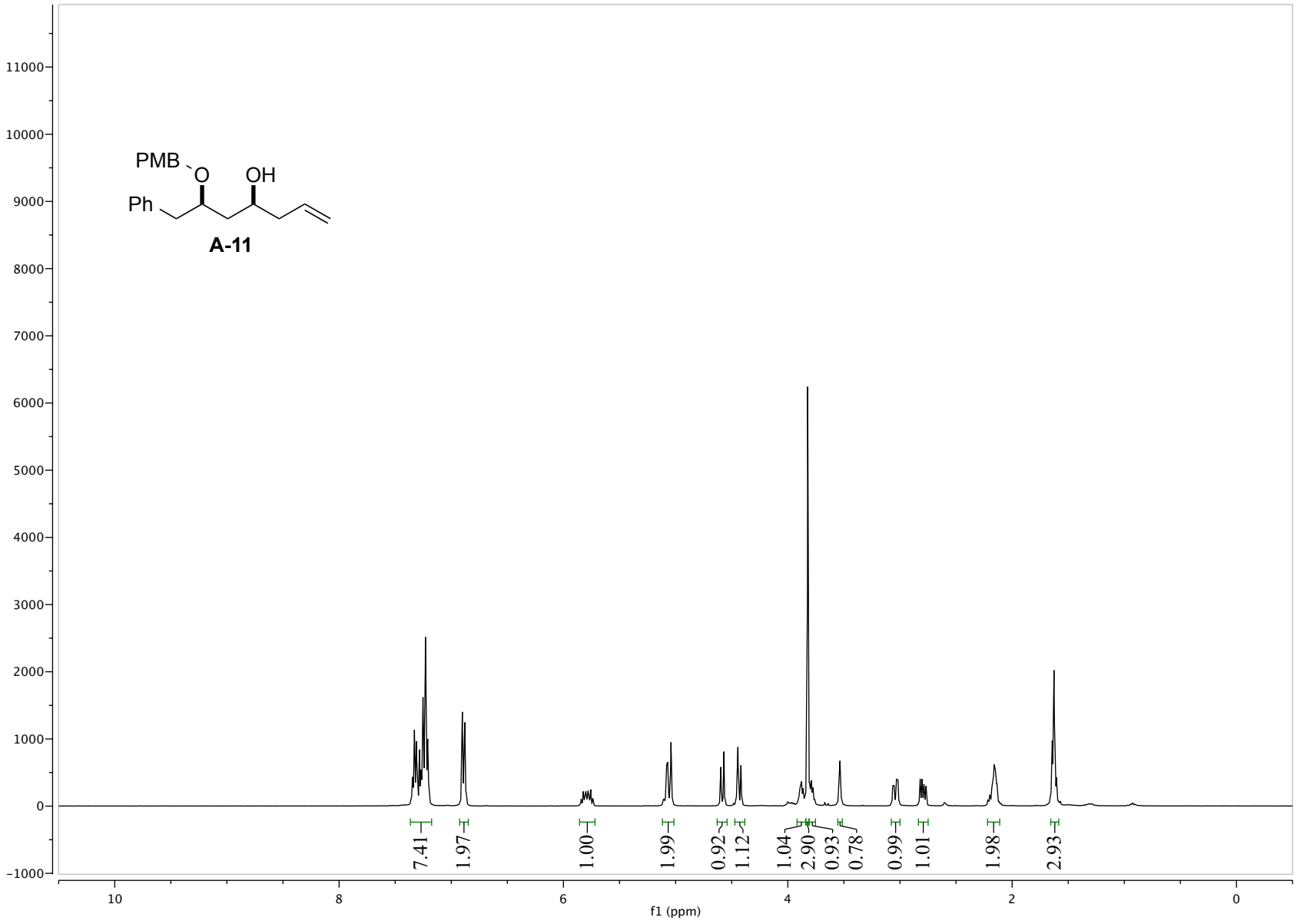
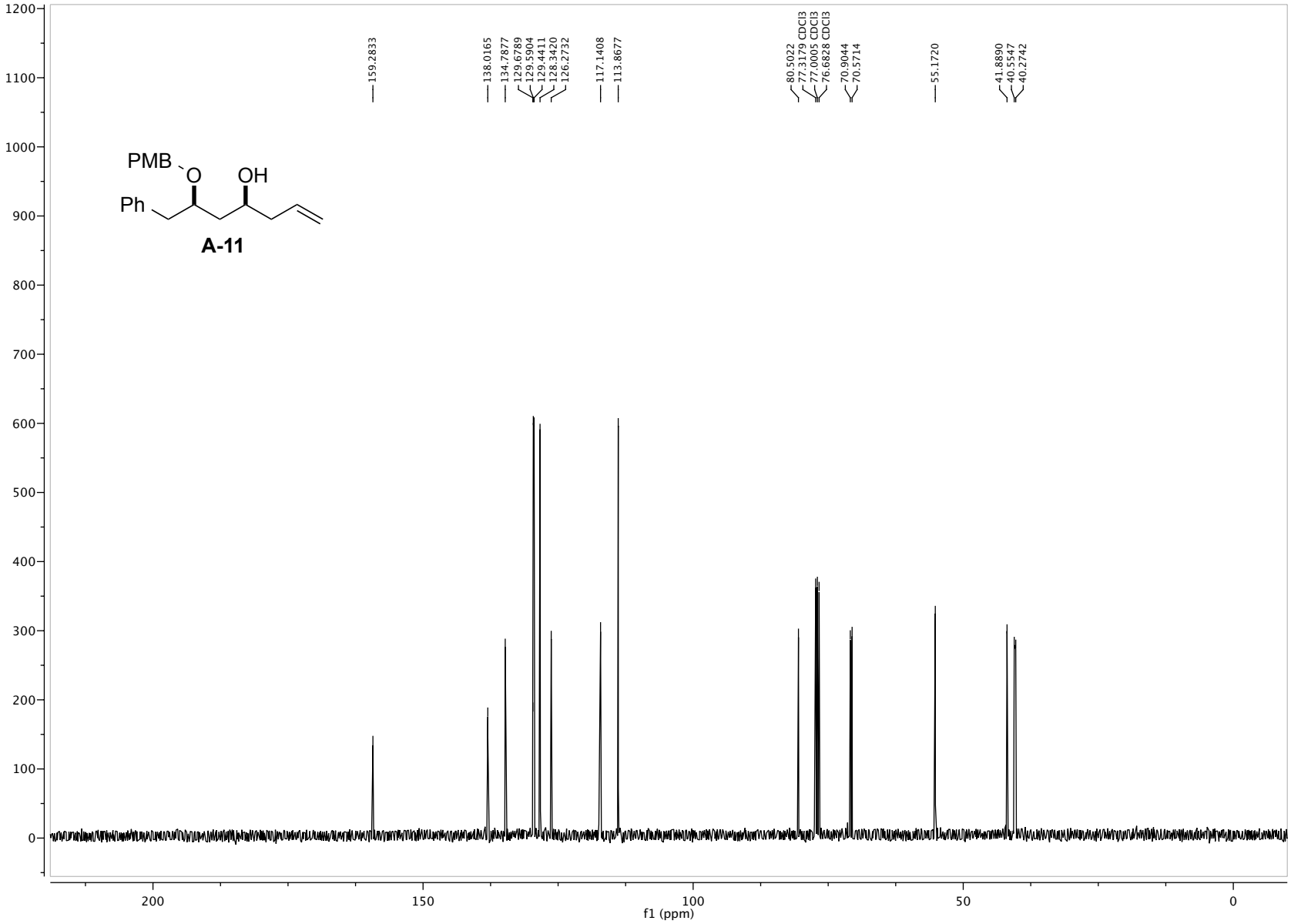
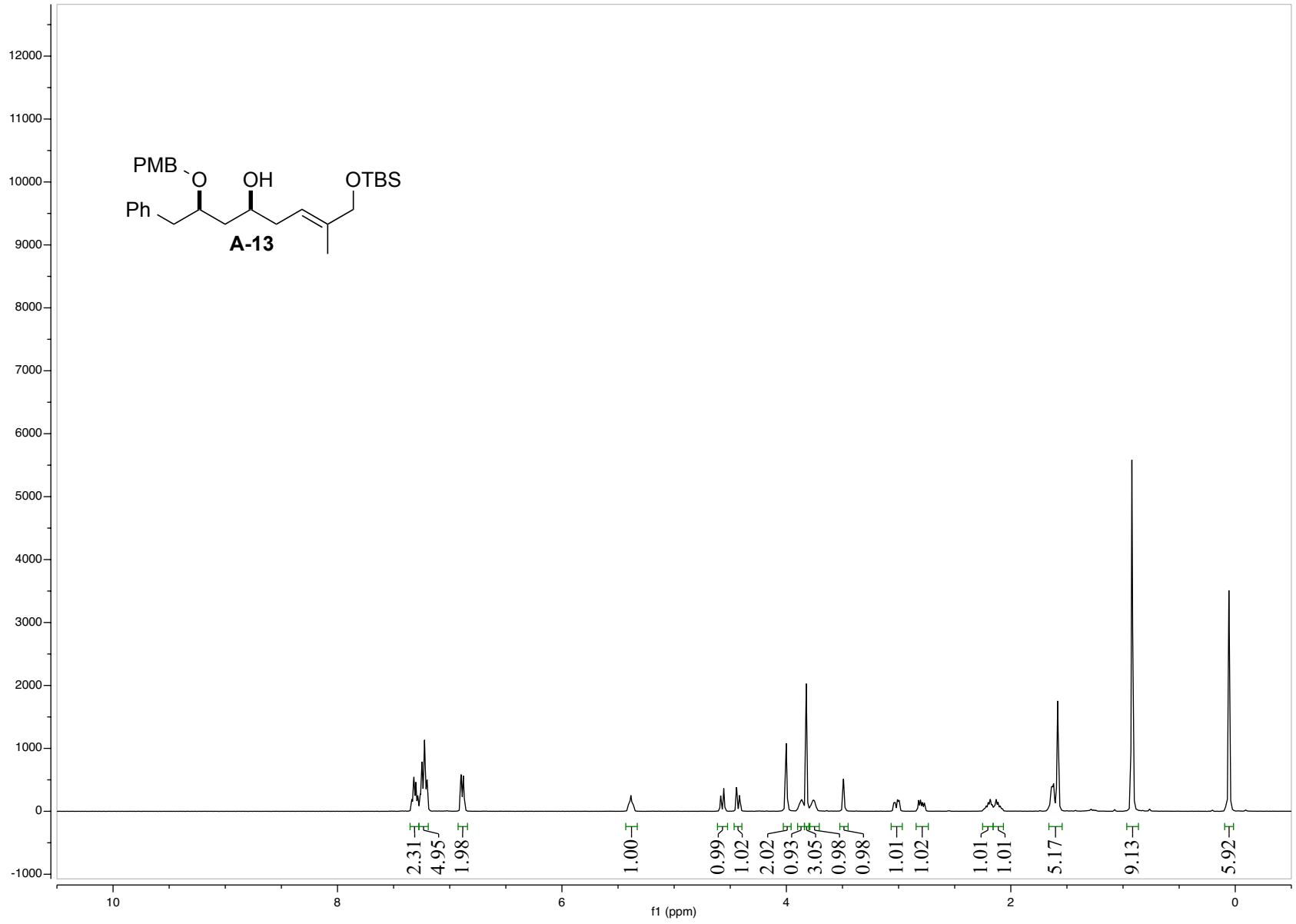
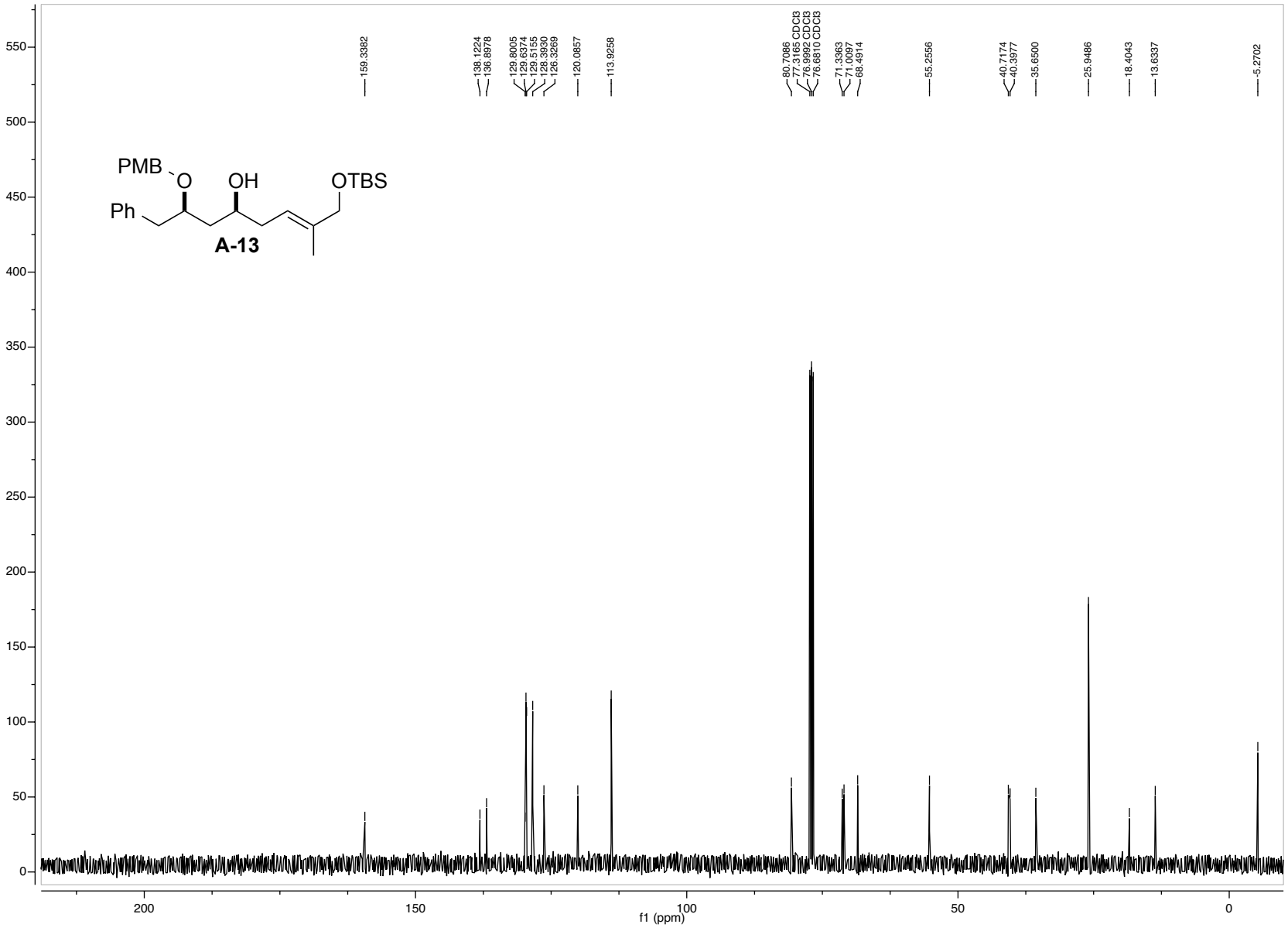
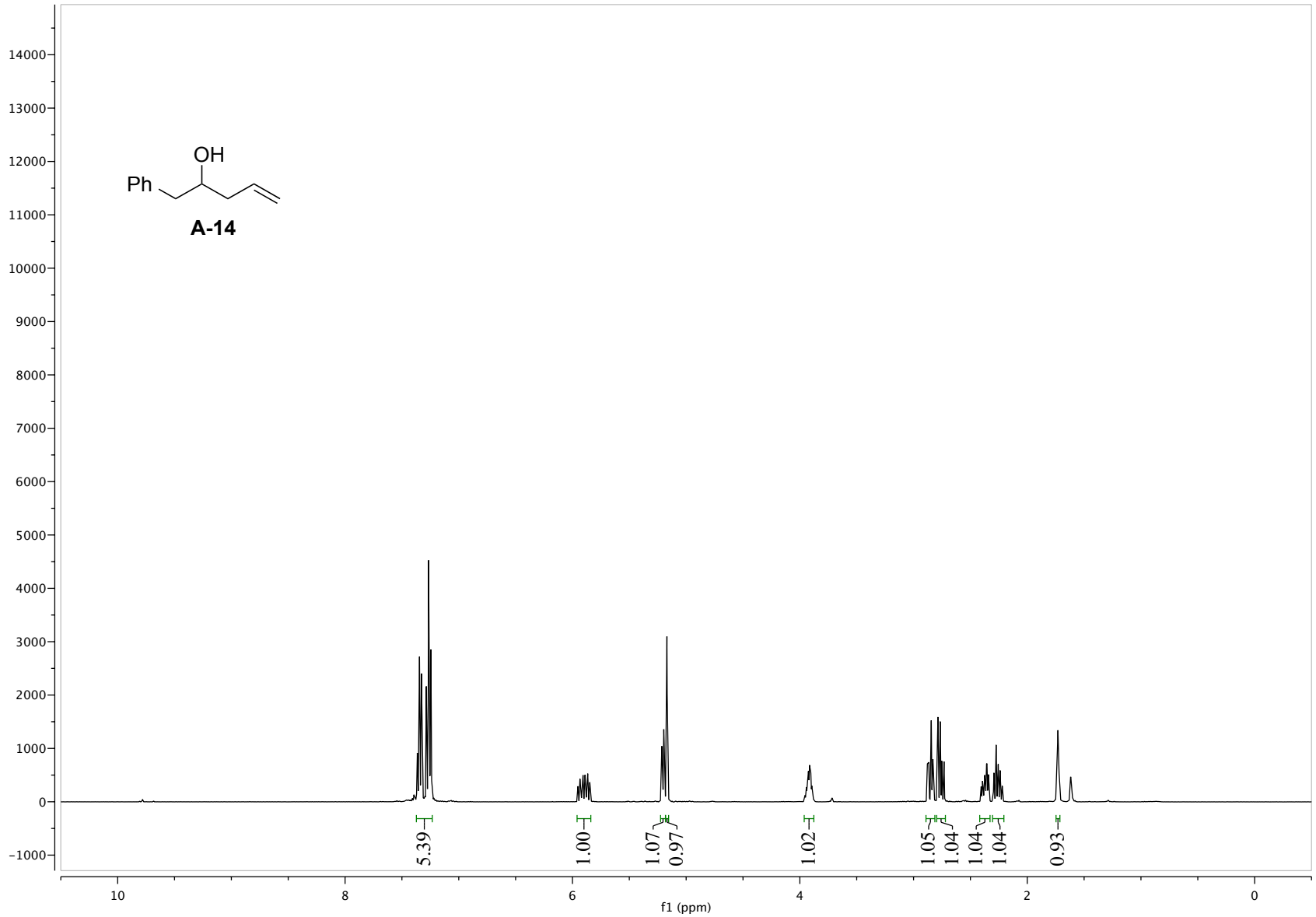
138.5481
130.4356
129.6161
129.5416
128.3950
128.3176
126.1961
113.8030
81.0157
77.3171 CDCl3
76.9993 CDCl3
76.6820 CDCl3
71.7888
65.1108
55.2589
42.8411
40.8385
40.5869
28.0844
PMB
O
OH
O
Ph
OtBu
A-10
f1 (ppm)

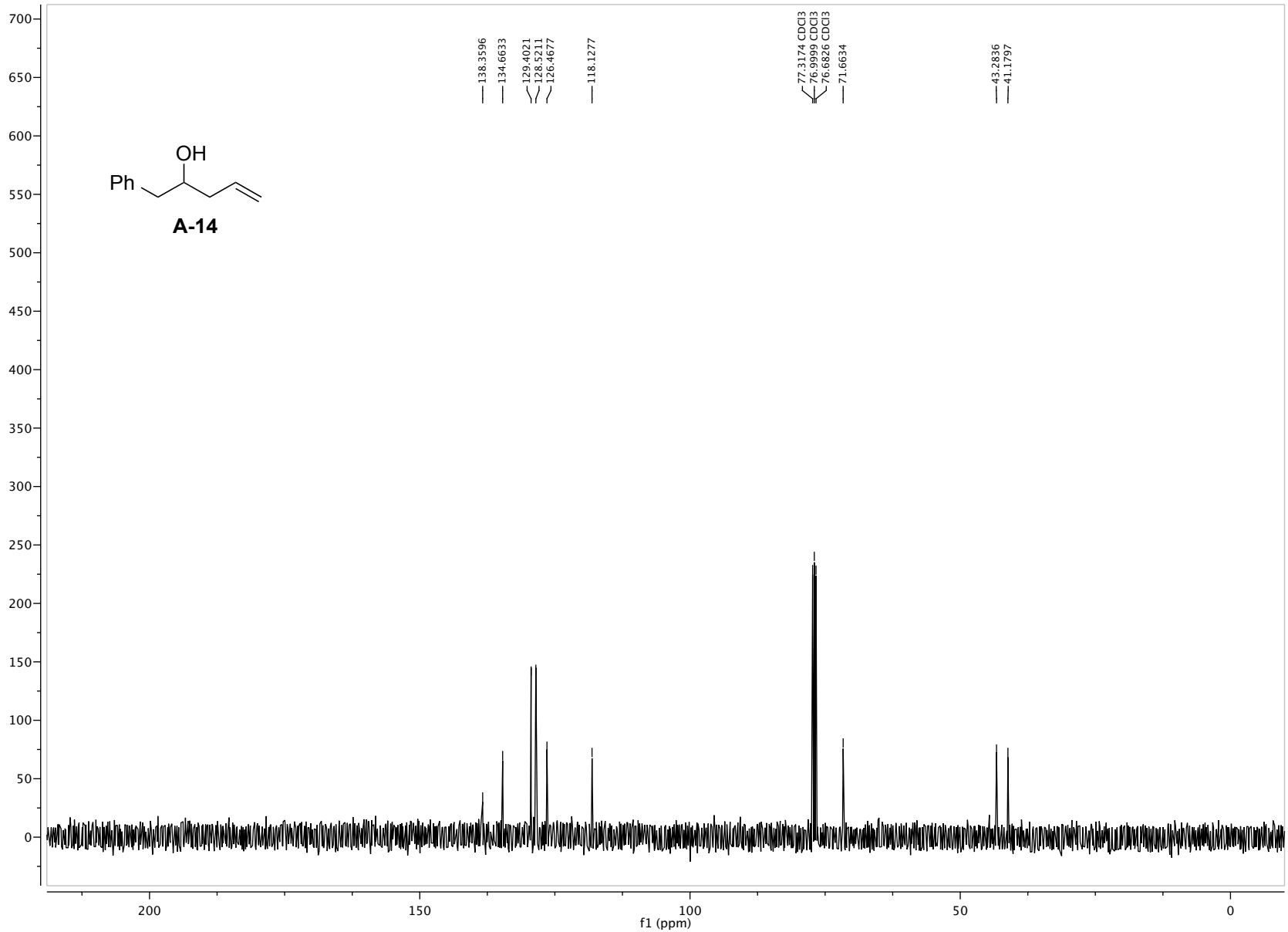

PMB
O
OH
Ph
A-11
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
7.41
1.97
1.00
1.99
0.92
1.12
1.04
2.90
0.93
0.78
0.99
1.01
1.98
2.93
10
8
6
4
2
0
f1 (ppm)

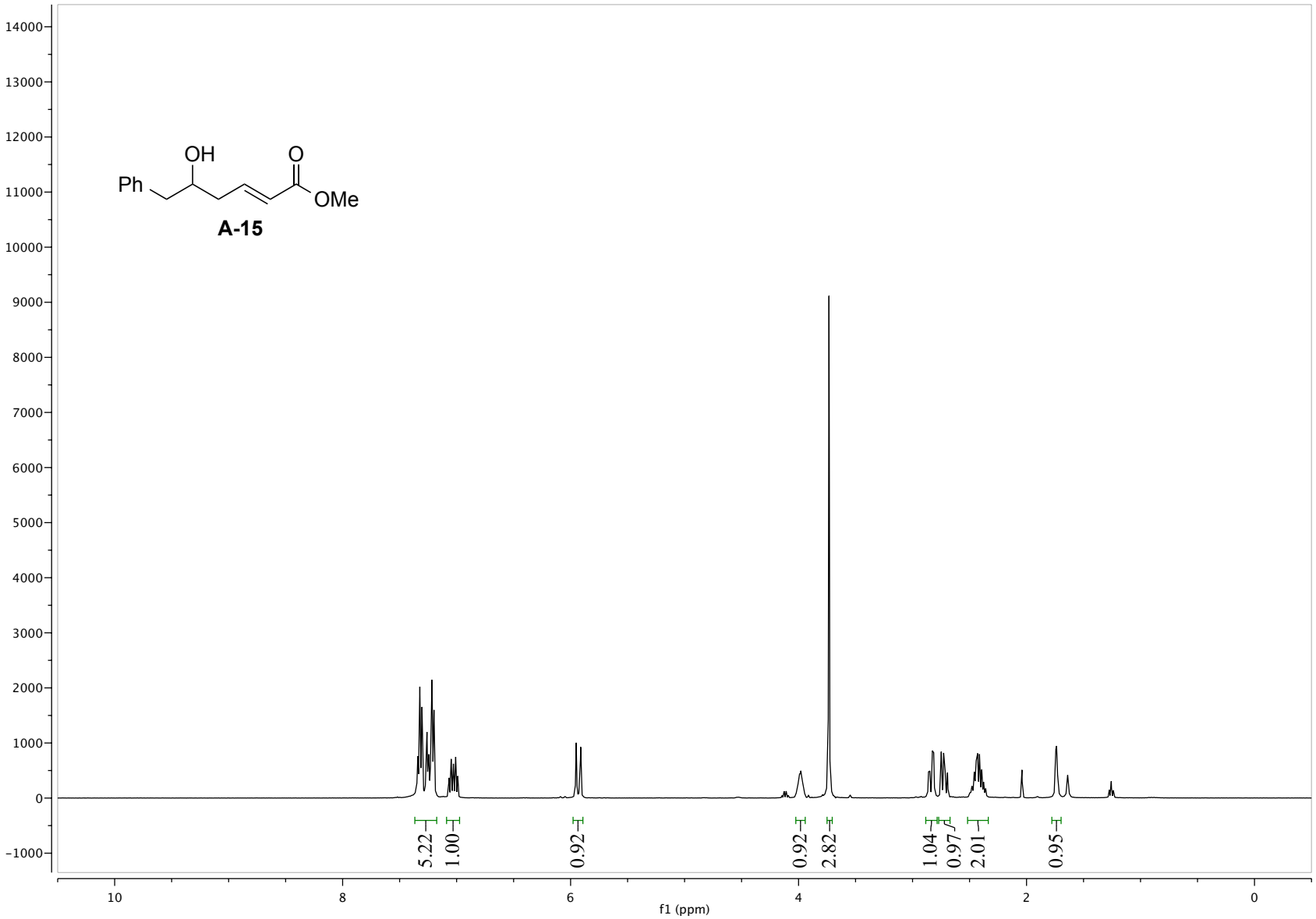

159.2833
138.0165
134.7877
129.6789
129.5904
129.4411
128.3420
126.2732
117.1408
113.8677
80.5022
77.3179 CDCl3
77.0005 CDCl3
76.6828 CDCl3
70.9044
70.5714
55.1720
41.8890
40.5547
40.2742
PMB
O
OH
Ph
A-11
f1 (ppm)

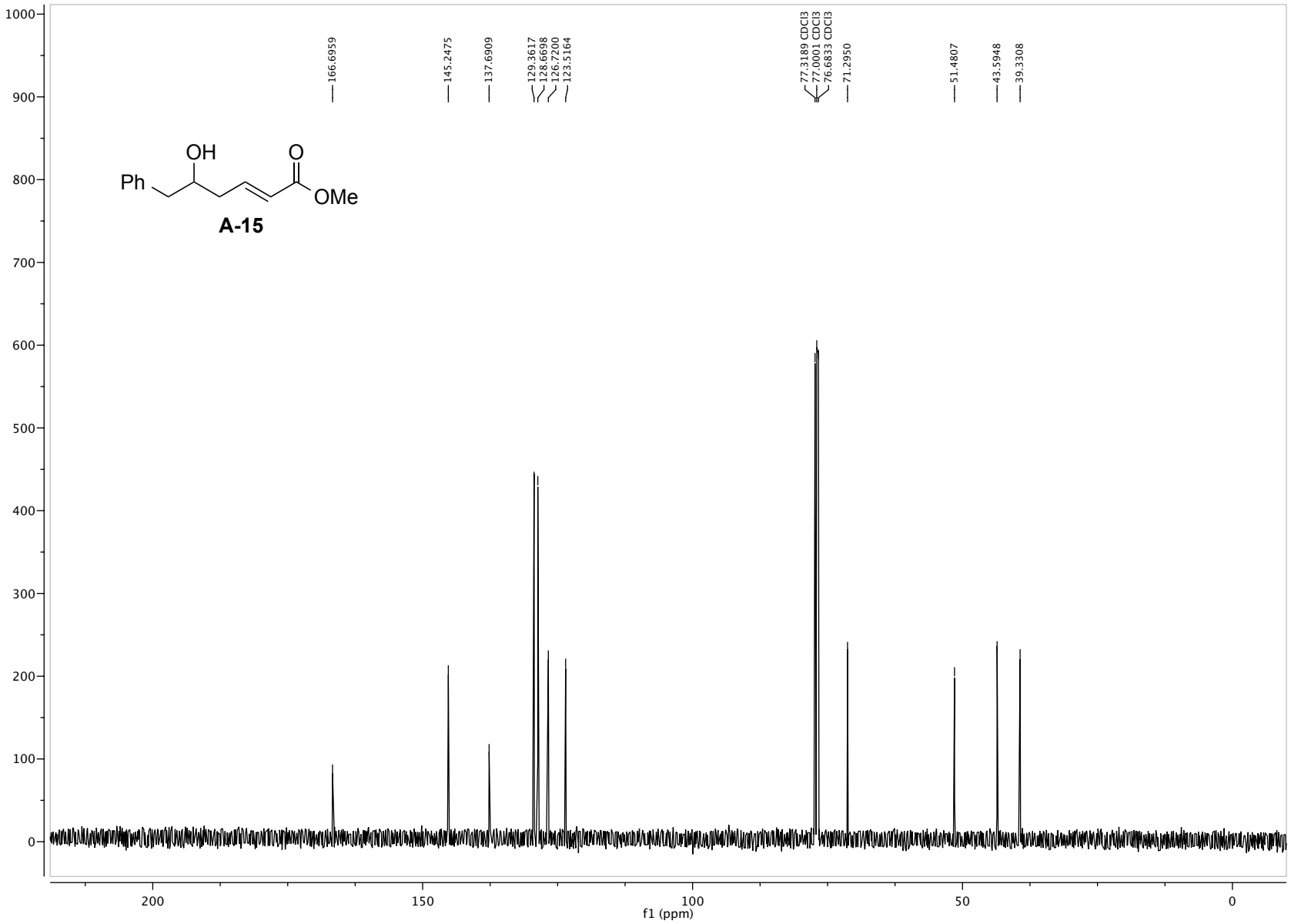

PMB
O
OH
OTBS
Ph
A-13
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
2.31
4.95
1.98
1.00
0.99
1.02
2.02
0.93
3.05
0.98
0.98
1.01
1.02
1.01
1.01
5.17
9.13
5.92
10
8
6
4
2
0
f1 (ppm)

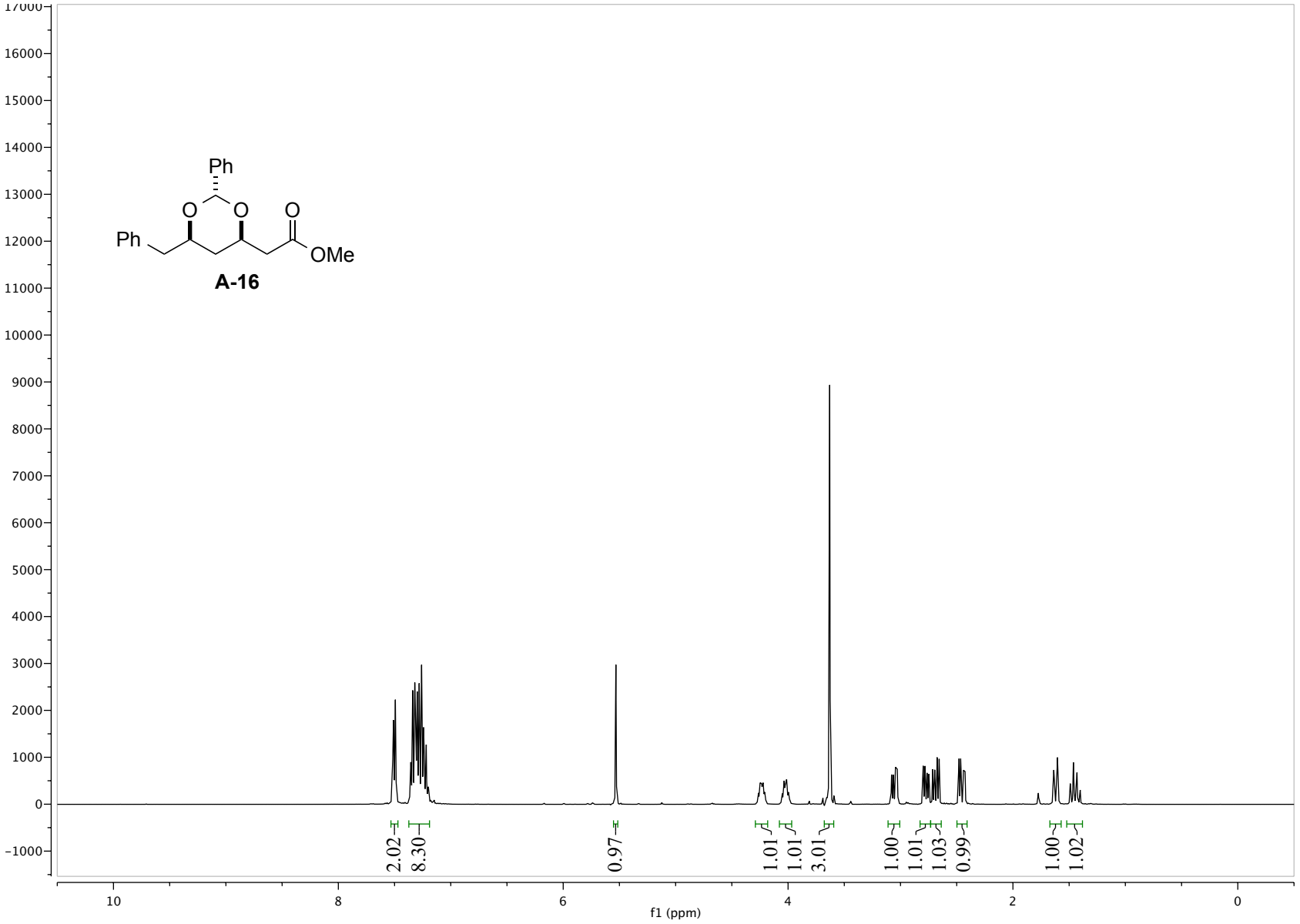

159.3382
138.1224
136.8978
129.8005
129.6374
129.5155
128.3930
126.3269
120.0857
113.9258
80.7086
77.3663 CDCl3
77.0000 CDCl3
76.6310 CDCl3
71.3363
71.0097
68.4914
55.2556
40.7174
40.3977
35.6500
25.9486
18.4043
13.6337
-5.2702
PMB
O
OH
OTBS
Ph
A-13
550
500
450
400
350
300
250
200
150
100
50
0
200
150
100
50
0
f1 (ppm)

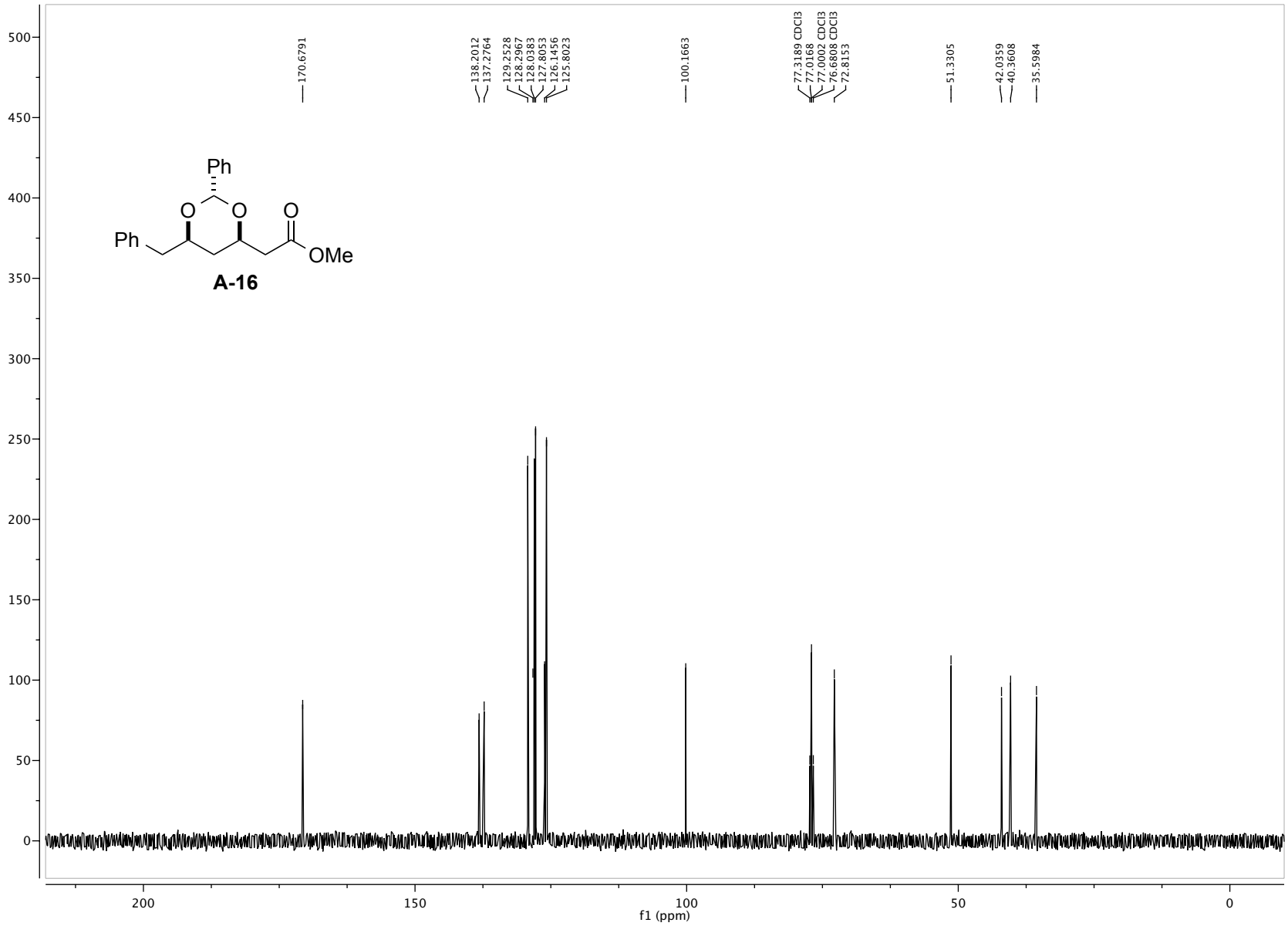

OH
Ph
A-14
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
5.39
1.00
1.07
0.97
1.02
1.05
1.04
1.04
1.04
0.93
10
8
6
4
2
0
f1 (ppm)

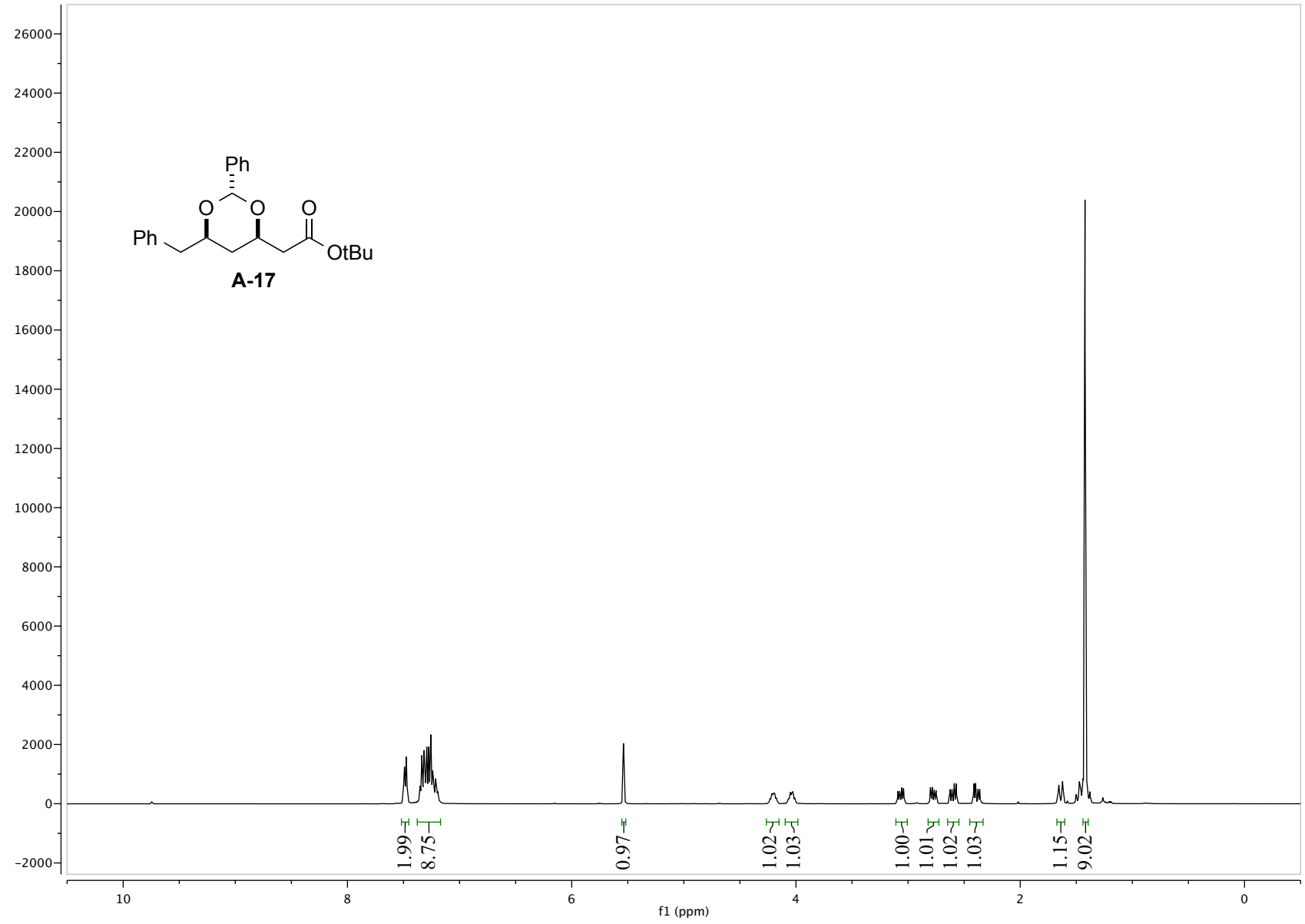

138.3596
134.6633
129.4021
128.5211
126.4677
118.1277
77.3174 CDCl3
76.9999 CDCl3
76.6826 CDCl3
71.6634
43.2836
41.1797
OH
Ph
A-14
f1 (ppm)

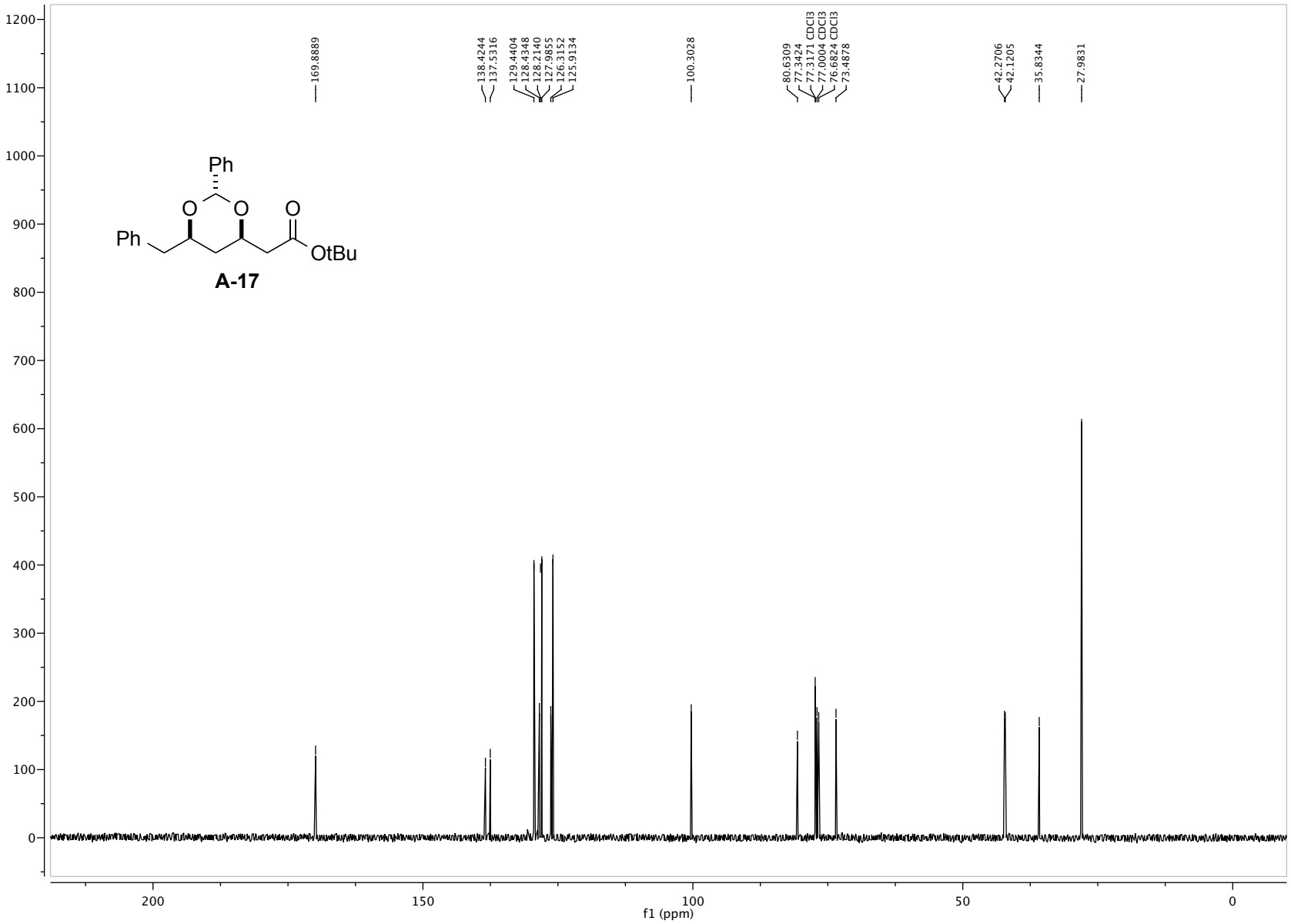

OH
O
Ph
OMe
A-15
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
5.22
1.00
0.92
0.92
2.82
1.04
0.97
2.01
0.95
10
8
6
4
2
0
f1 (ppm)


166.6959
145.2475
137.6909
129.3617
128.6698
126.7200
123.5164
77.3189 CDCl3
77.0001 CDCl3
76.6833 CDCl3
71.2950
51.4807
43.5948
39.3308
OH
O
Ph
OMe
A-15
f1 (ppm)

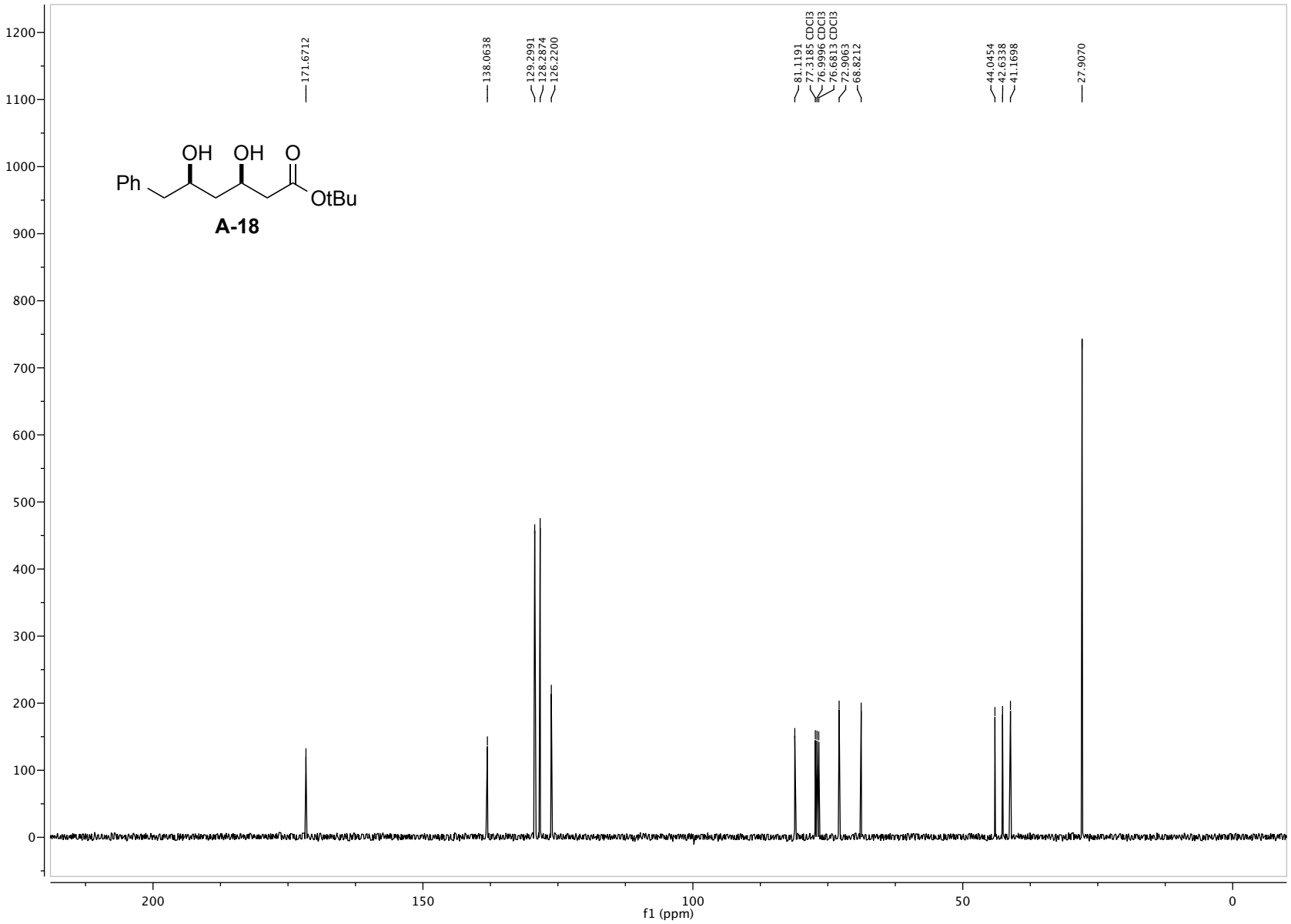

Ph
O
O
O
Ph
OMe
A-16
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
2.02
8.30
0.97
1.01
1.01
3.01
1.00
1.01
1.03
0.99
1.00
1.02
10
8
6
4
2
0
f1 (ppm)

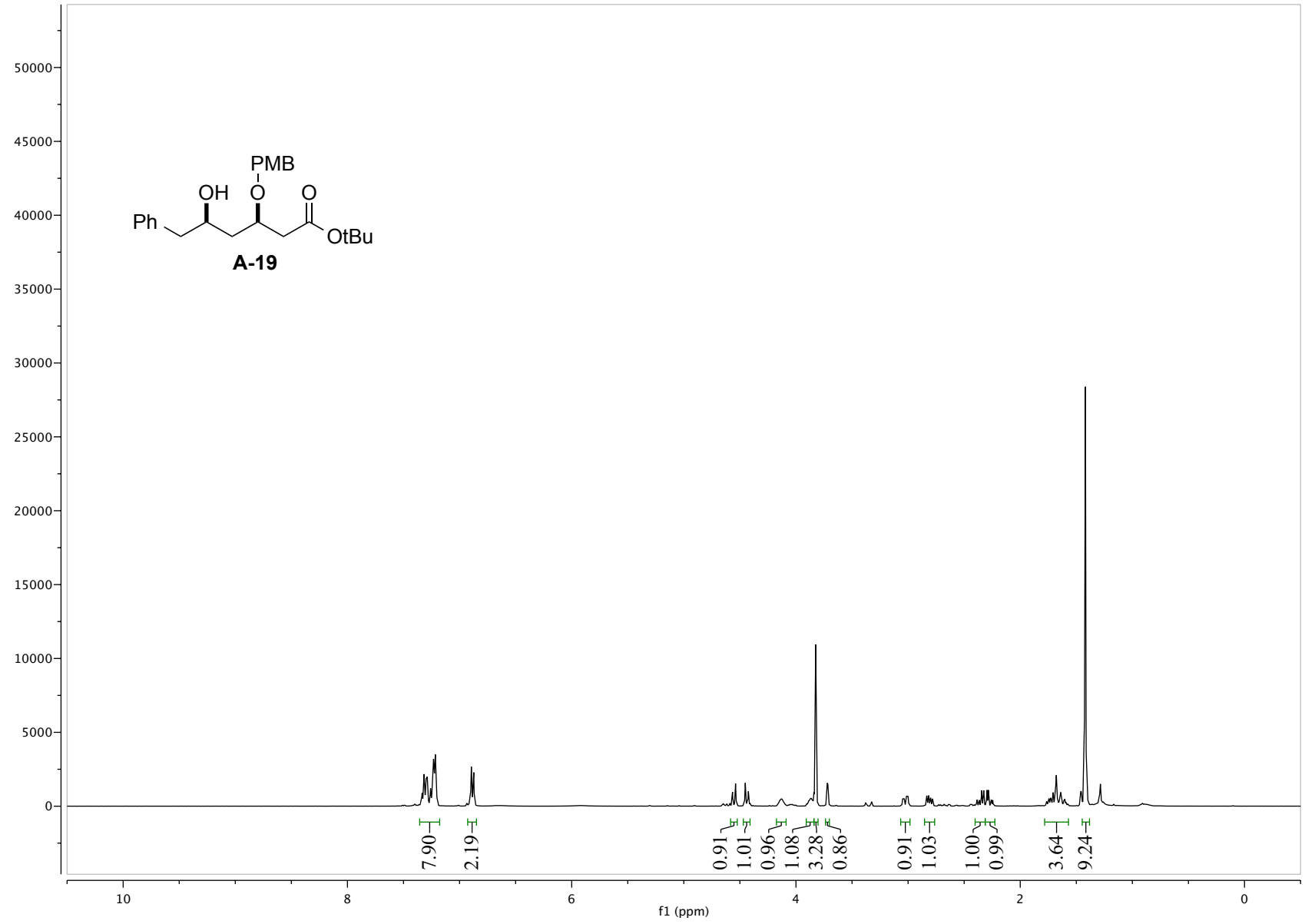

170.6791
138.2012
137.2764
129.2528
128.2967
128.0383
127.8053
126.1456
125.8023
100.1663
77.3189 CDCl3
77.0168
77.0002 CDCl3
76.6808 CDCl3
72.8153
51.3305
42.0359
40.3608
35.5984
Ph
O
O
O
Ph
OMe
A-16
f1 (ppm)

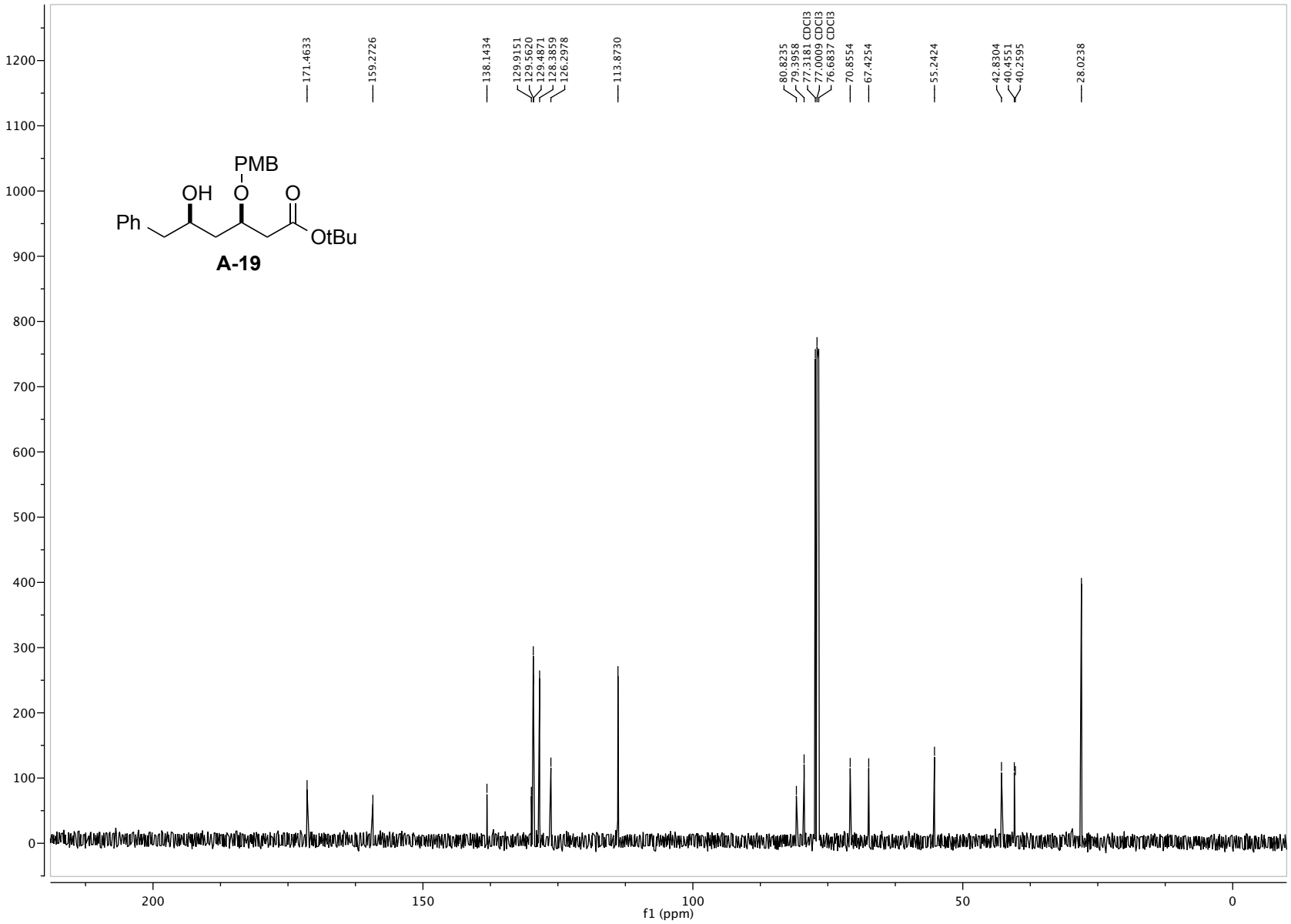

Ph
O
O
O
Ph
OtBu
A-17
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
−2000
1.99
8.75
0.97
1.02
1.03
1.00
1.01
1.02
1.03
1.15
9.02
10
8
6
4
2
0
f1 (ppm)

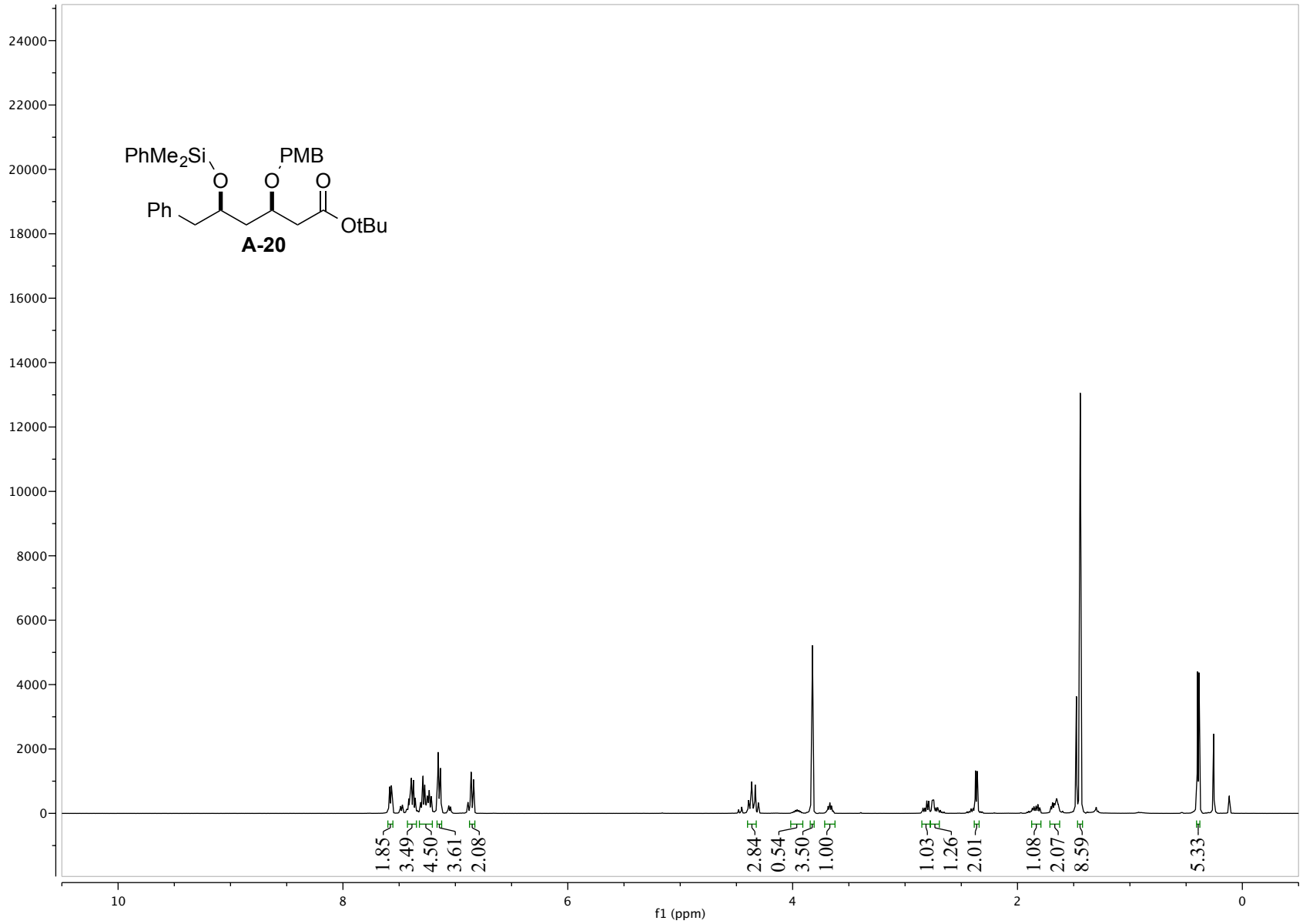

169.8889
138.4244
137.5316
129.4404
128.4348
128.2140
127.9855
126.3152
125.9134
100.3028
80.6309
77.3424
77.3171 CDCl3
77.0004 CDCl3
76.6824 CDCl3
73.4878
42.2706
42.1205
35.8344
27.9831
Ph
O
O
O
Ph
OtBu
A-17
f1 (ppm)

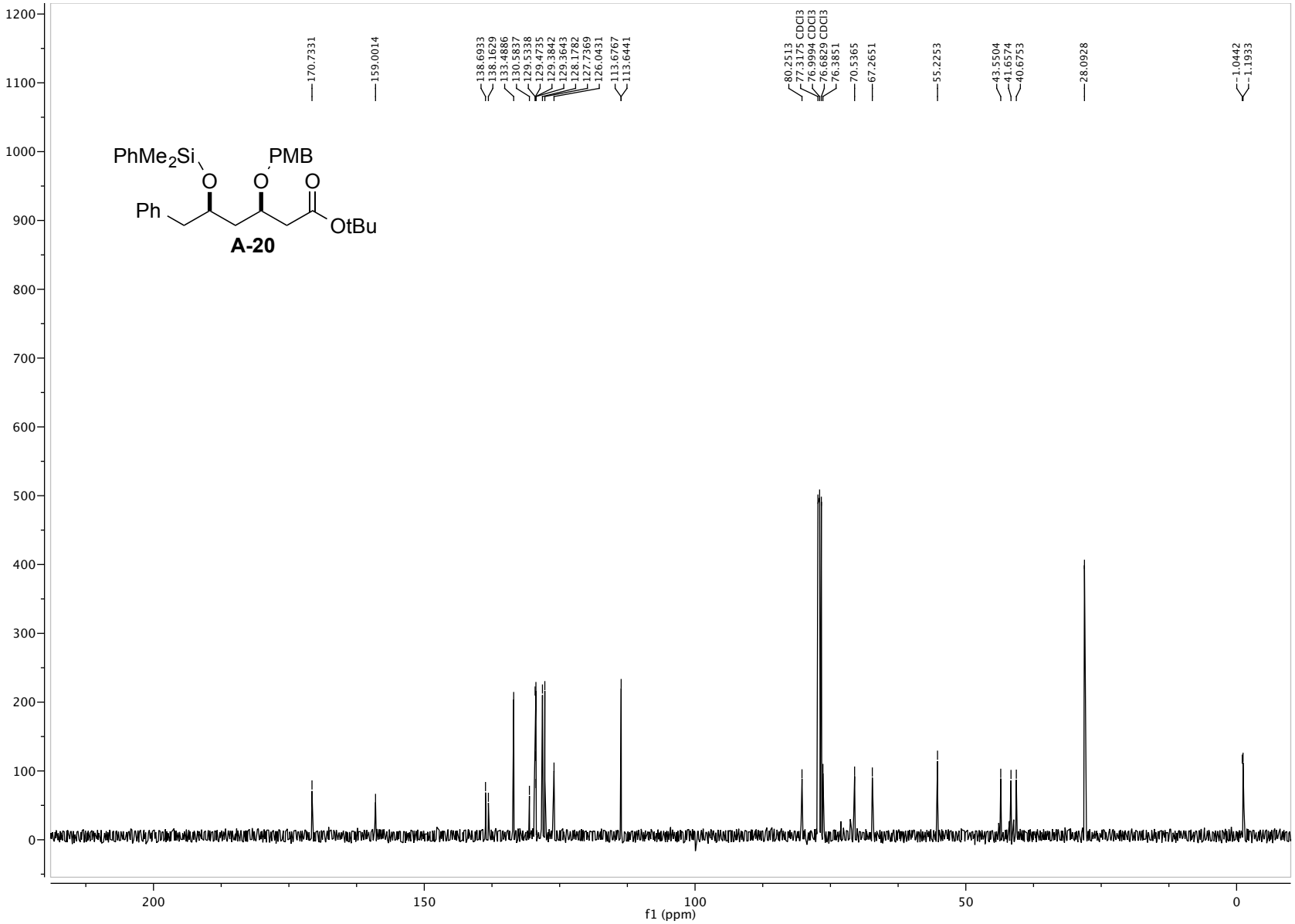

OH
OH
O
Ph
OtBu
A-18
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
−5000
5.02
1.09
1.30
1.00
1.01
2.02
1.97
8.90
10
8
6
4
2
0
f1 (ppm)

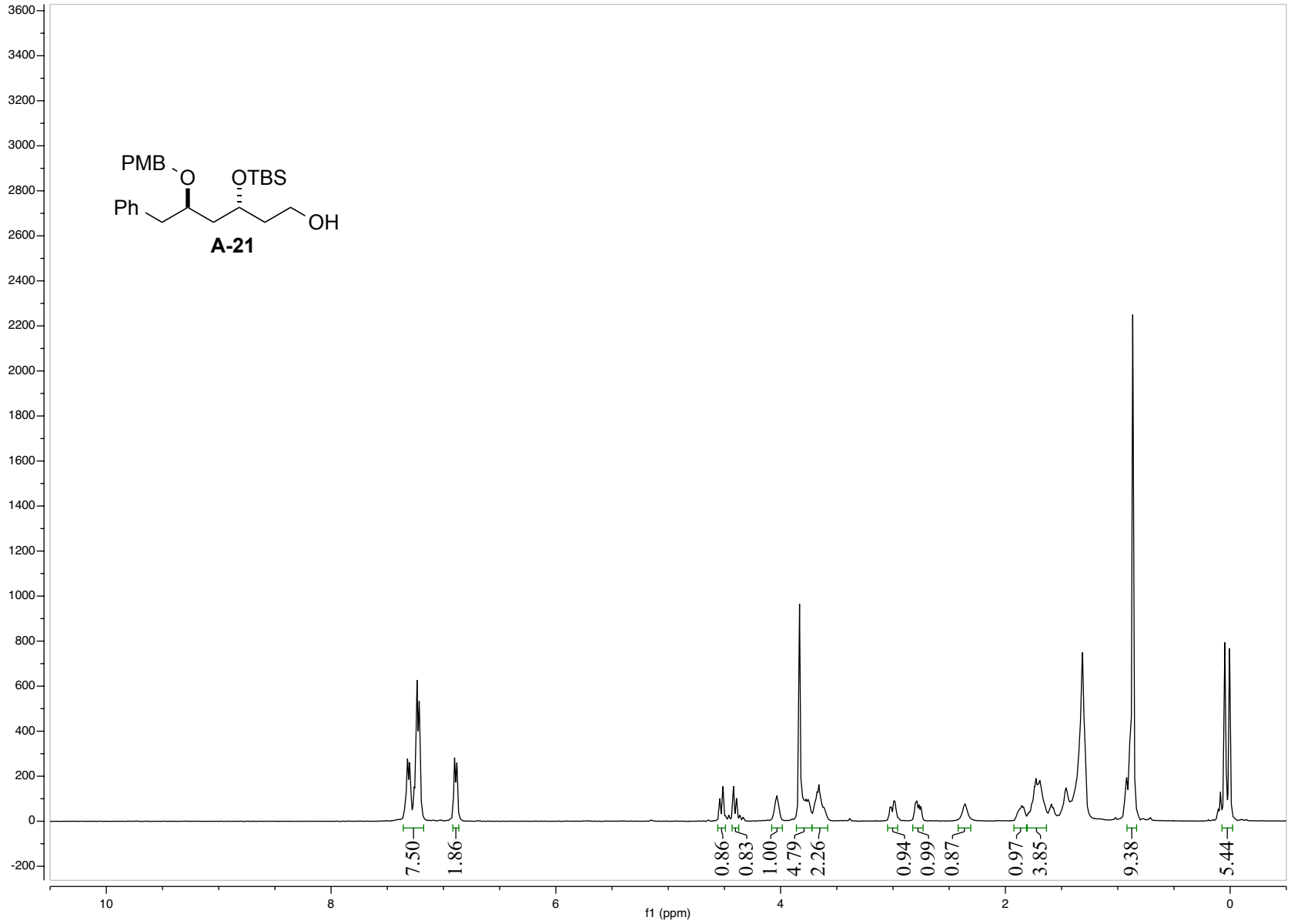

171.6712
138.0638
129.2991
128.2874
126.2200
81.1191
77.3185 CDCl3
76.9996 CDCl3
76.6813 CDCl3
72.9063
68.8212
44.0454
42.6338
41.1698
27.9070
OH
OH
O
Ph
OtBu
A-18
f1 (ppm)

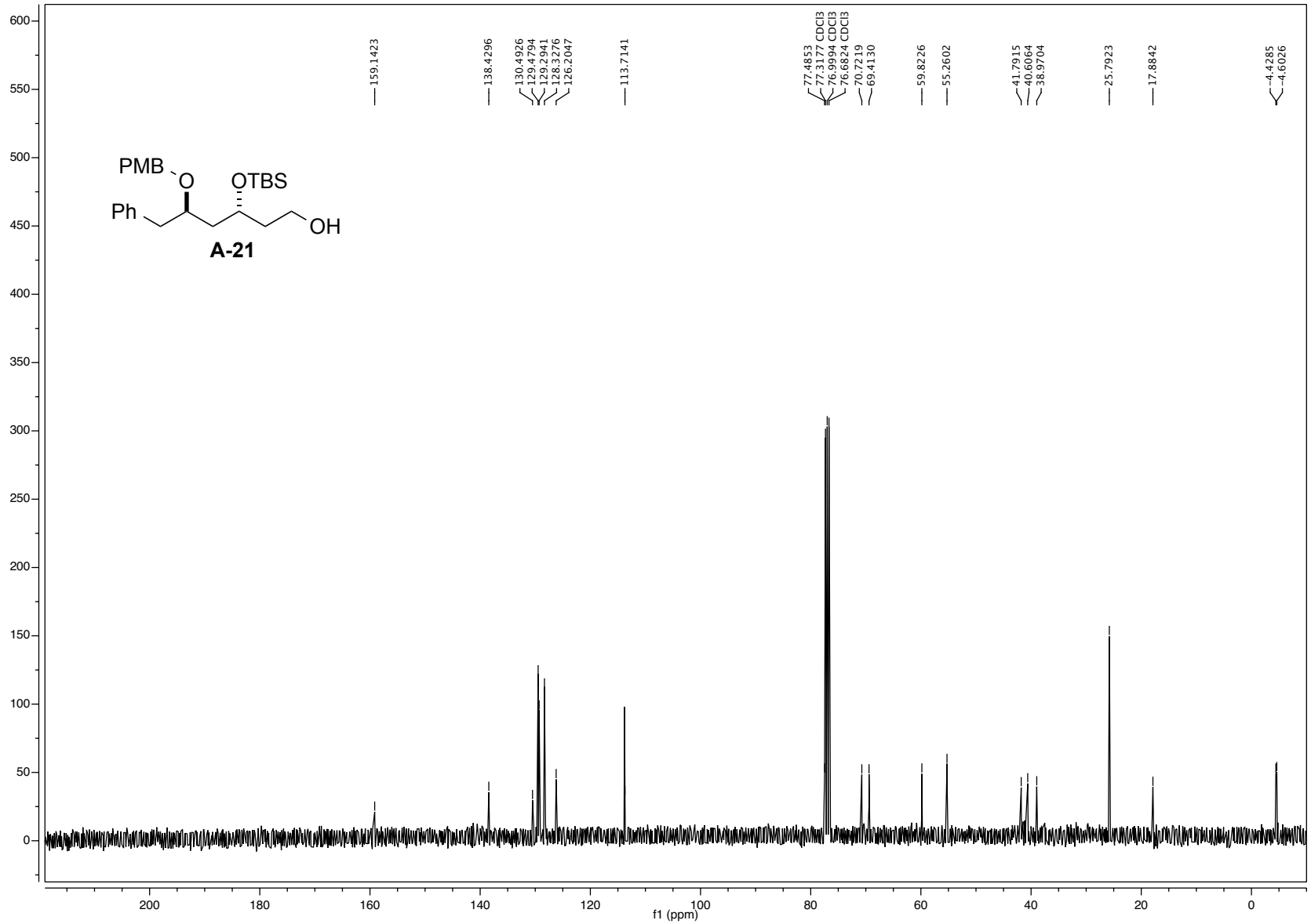

PMB
OH
O
O
Ph
OtBu
A-19
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
7.90
2.19
0.91
1.01
0.96
1.08
3.28
0.86
0.91
1.03
1.00
0.99
3.64
9.24
10
8
6
4
2
0
f1 (ppm)

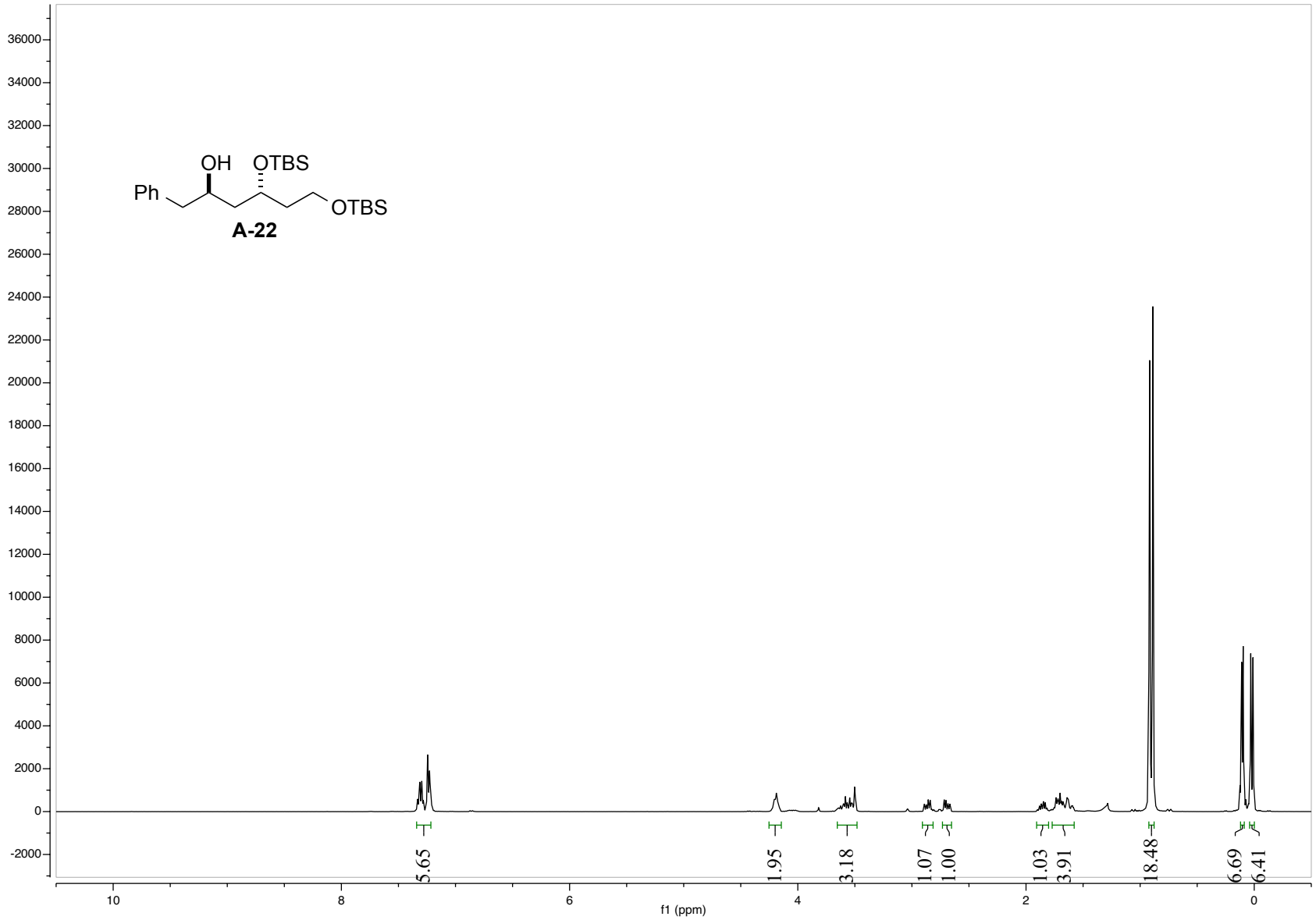

171.4633
159.2726
138.1434
129.9151
129.5620
129.4871
128.3859
126.2978
113.8730
80.8235
79.3958
77.3181 CDCl3
77.0009 CDCl3
76.6837 CDCl3
70.8554
67.4254
55.2424
42.8304
40.4551
40.2595
28.0238
PMB
OH
O
O
Ph
OtBu
A-19
f1 (ppm)

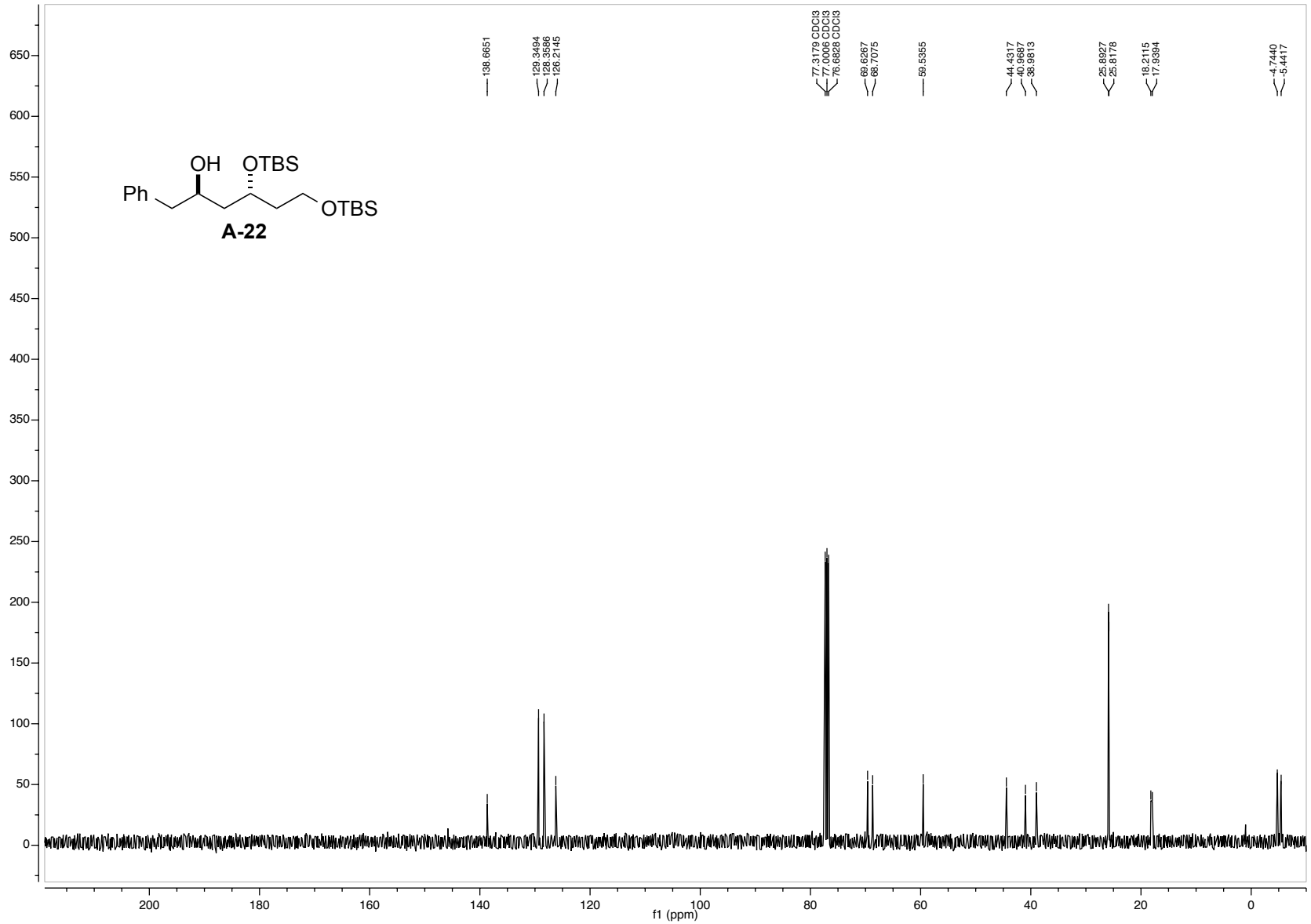

PhMe2Si
PMB
O
O
O
Ph
OtBu
A-20
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
1.85
3.49
4.50
3.61
2.08
2.84
0.54
3.50
1.00
1.03
1.26
2.01
1.08
2.07
8.59
5.33
10
8
6
4
2
0
f1 (ppm)

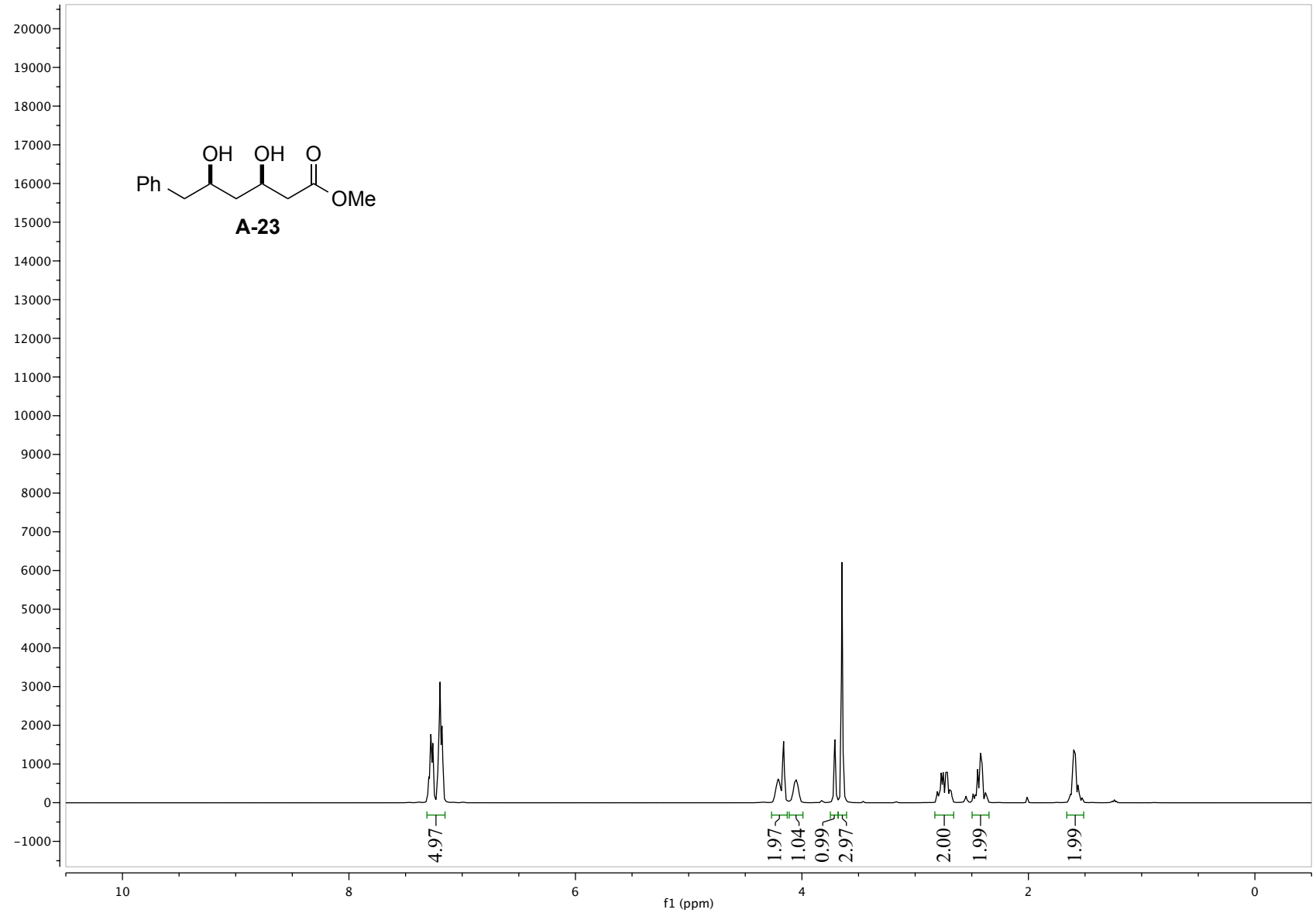

170.7331
159.0014
138.6933
138.1629
133.4886
130.5837
129.5338
129.4735
129.3842
129.3643
128.1782
127.7369
126.0431
113.6767
113.6441
80.2513
77.3175 CDCl3
76.9994 CDCl3
76.6829 CDCl3
76.3851
70.5365
67.2651
55.2253
43.5504
41.6574
40.6753
28.0928
-1.0442
-1.1933
PhMe2Si
PMB
O
O
O
Ph
OtBu
A-20
f1 (ppm)

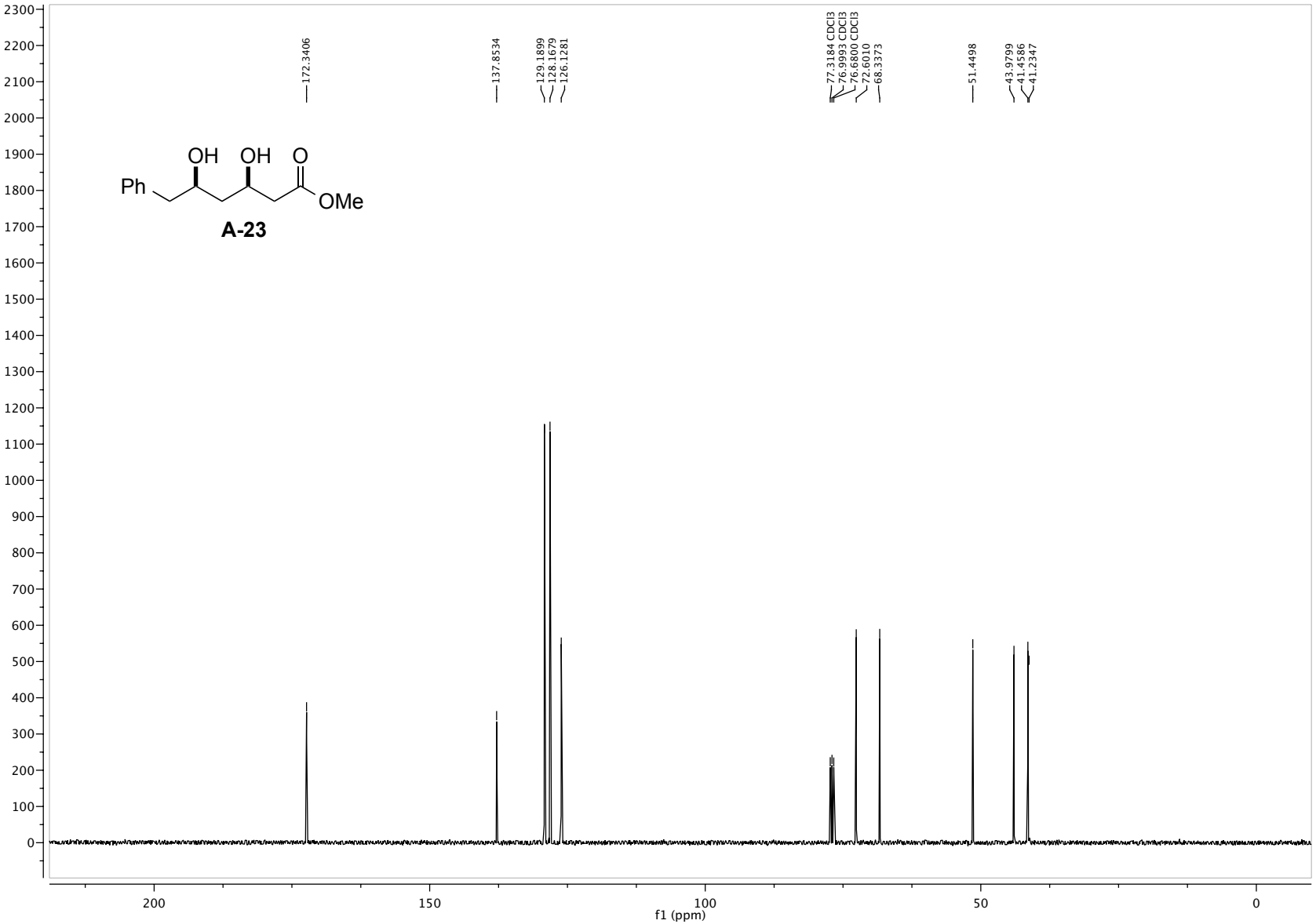

PMB
O
OTBS
Ph
OH
A-21
7.50
1.86
0.86
0.83
1.00
4.79
2.26
0.94
0.99
0.87
0.97
3.85
9.38
5.44
f1 (ppm)

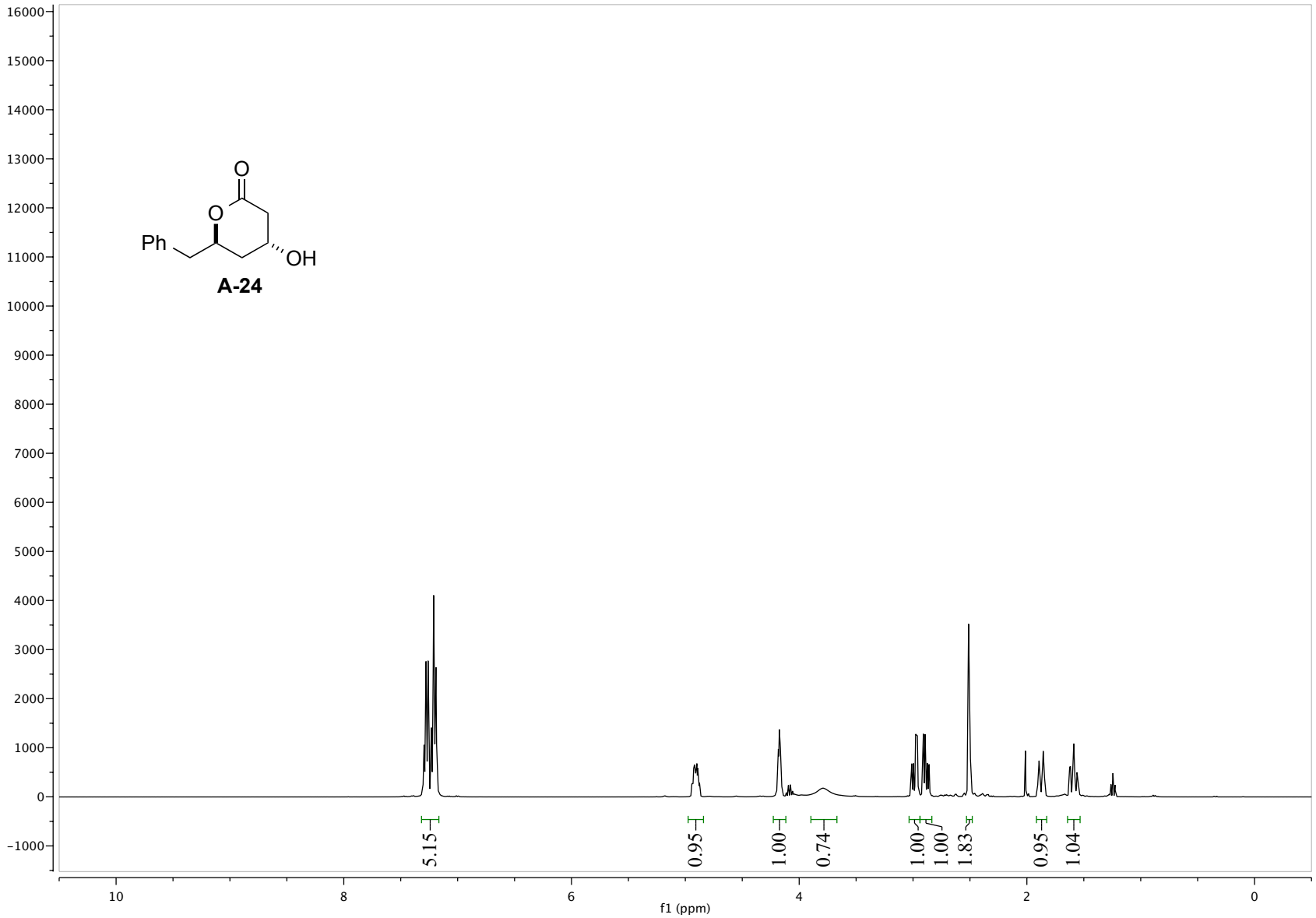

PMB
O
OTBS
Ph
OH
A-21
159.1423
138.4296
130.4926
129.4794
129.2941
128.3276
126.2047
113.7141
77.4853
77.3177 CDCl3
76.9994 CDCl3
76.6824 CDCl3
70.7219
69.4130
59.8226
55.2602
41.7915
40.6064
38.9704
25.7923
17.8842
-4.4285
-4.6026
f1 (ppm)

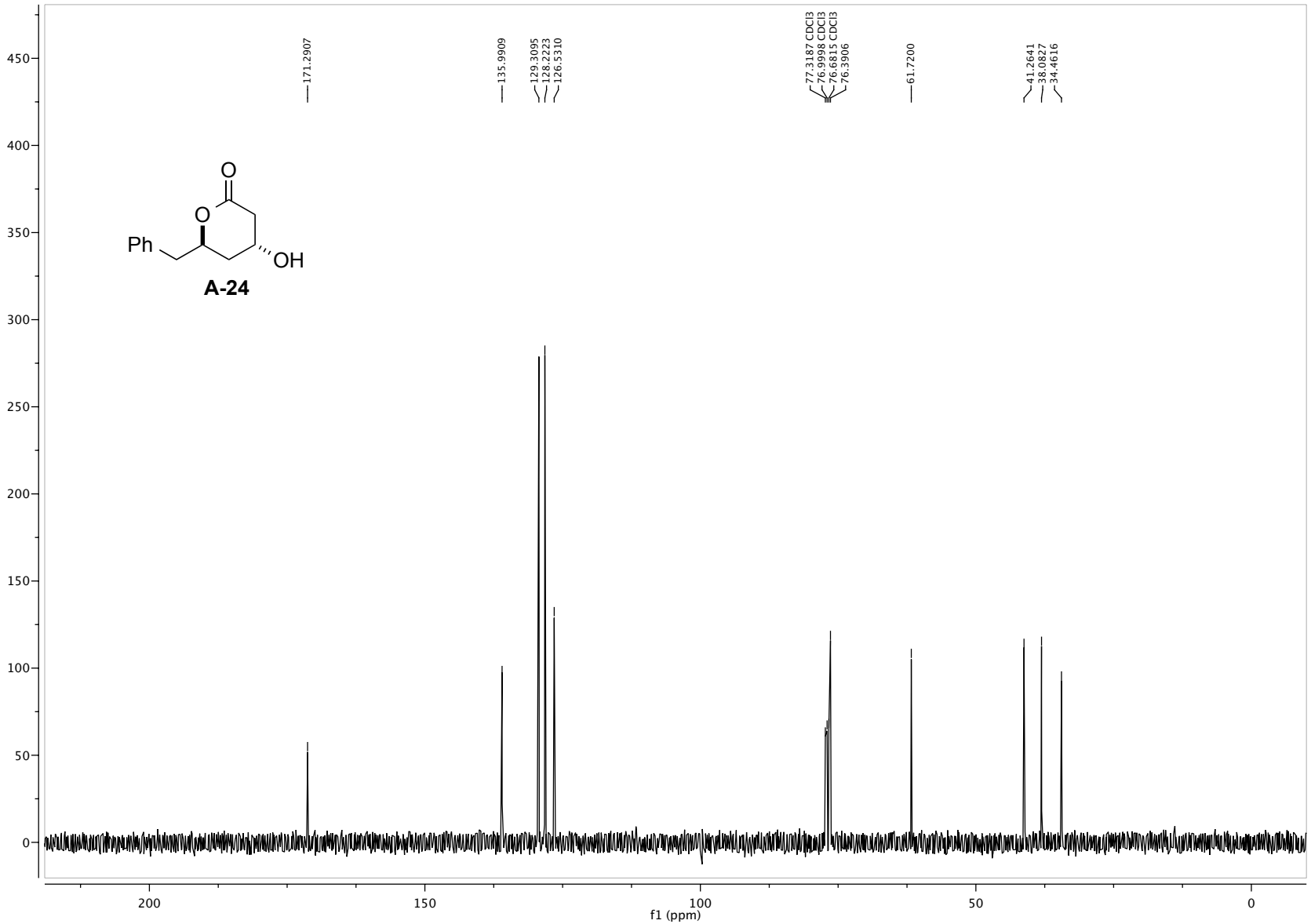

OH
OTBS
Ph
OTBS
A-22
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
5.65
1.95
3.18
1.07
1.00
1.03
3.91
18.48
6.69
6.41
10
8
6
4
2
0
f1 (ppm)

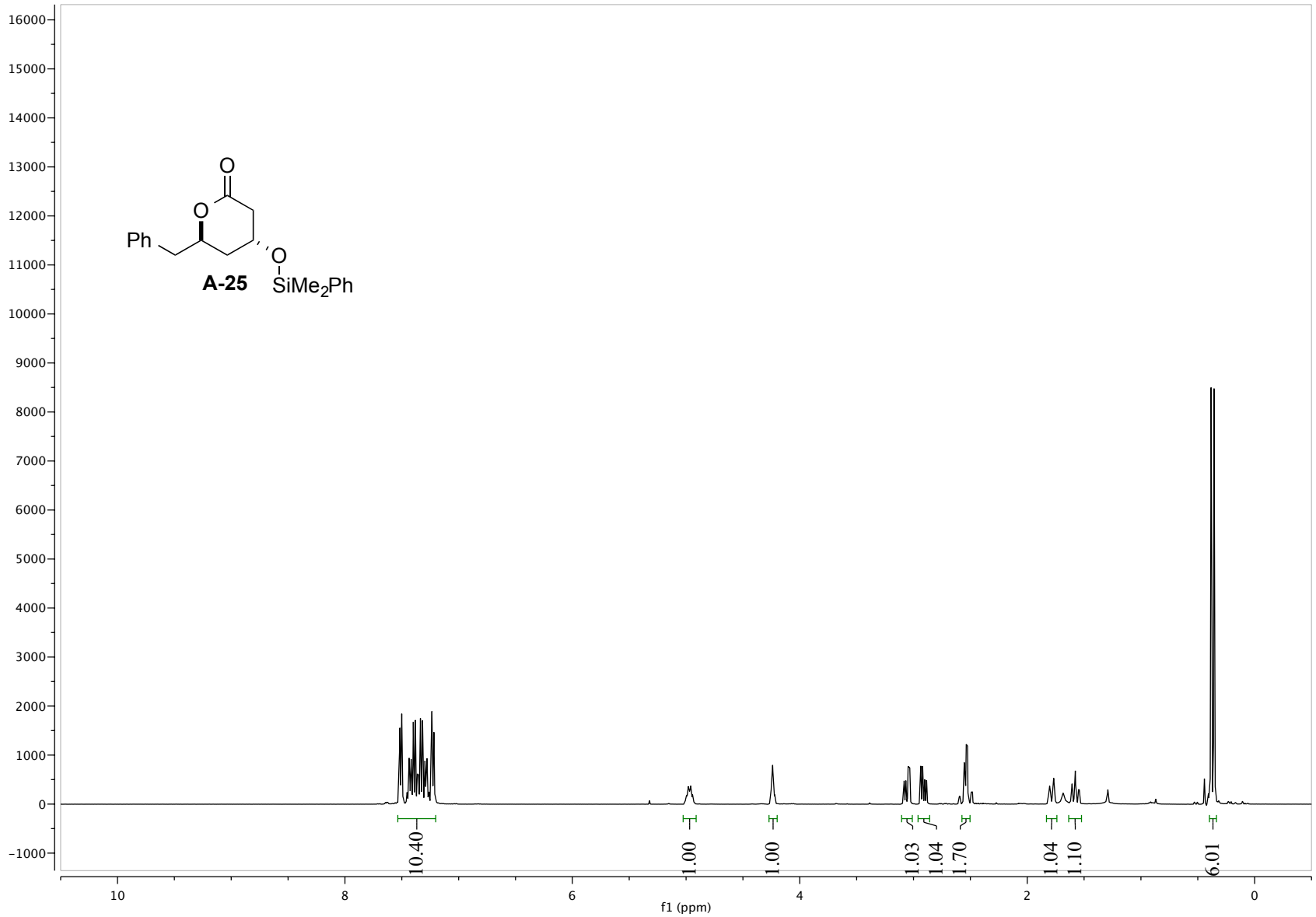

138.6651
129.3494
128.3586
126.2145
77.3179 CDCl3
77.0006 CDCl3
76.6828 CDCl3
69.6267
68.7075
59.5355
44.4317
40.6897
38.9813
25.8927
25.8178
18.2115
17.9394
-4.7440
-5.4417
OH
OTBS
Ph
OTBS
A-22
f1 (ppm)

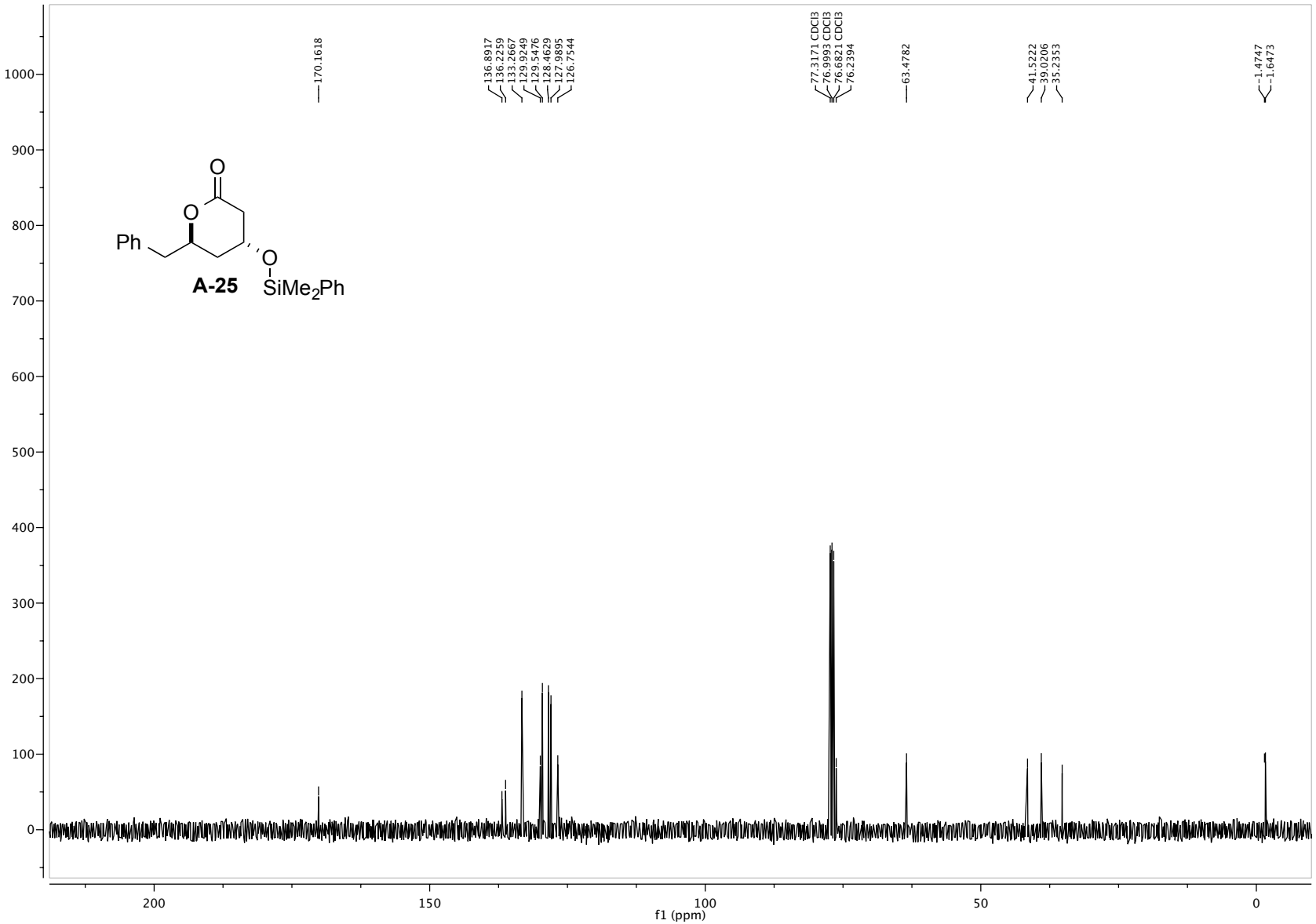

OH
OH
O
Ph
OMe
A-23
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
4.97
1.97
1.04
0.99
2.97
2.00
1.99
1.99
10
8
6
4
2
0
f1 (ppm)

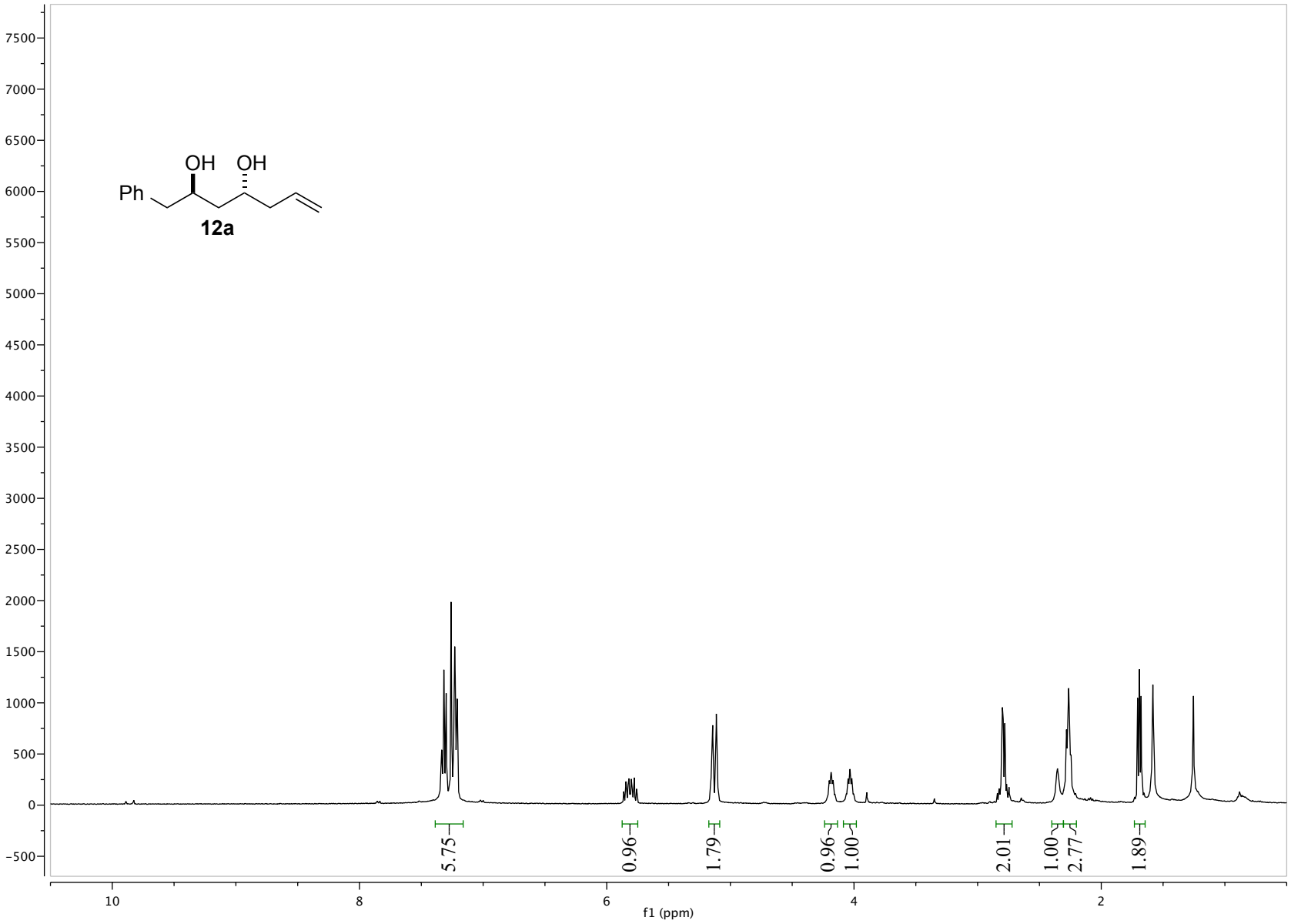

172.3406
137.8534
129.1899
128.1679
126.1281
77.3184 CDCl3
76.9993 CDCl3
76.6800 CDCl3
72.6010
68.3373
51.4498
43.9799
41.4586
41.2347
OH
OH
O
Ph
OMe
A-23
f1 (ppm)

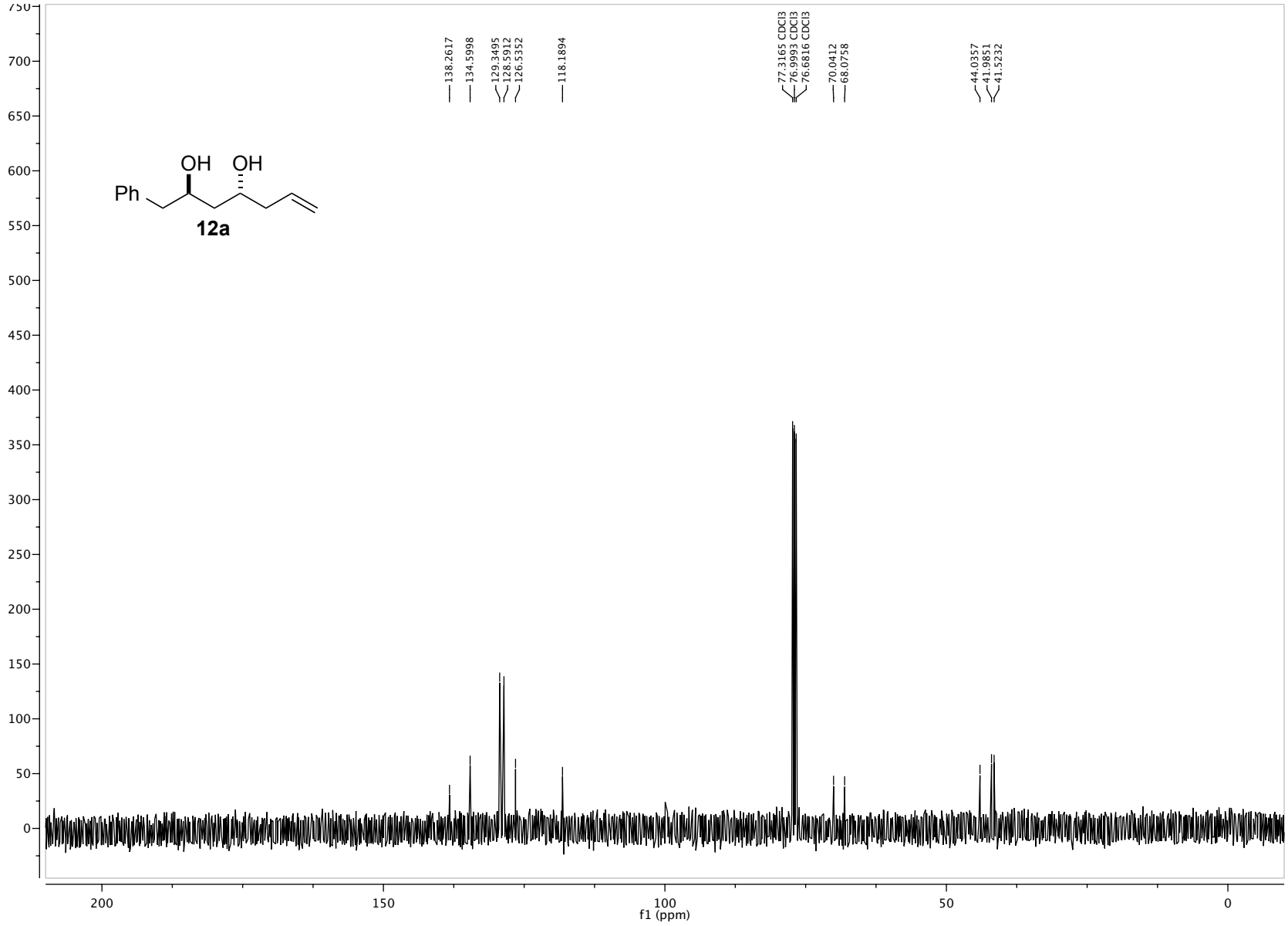

O
O
Ph
OH
A-24
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
5.15
0.95
1.00
0.74
1.00
1.00
1.83
0.95
1.04
10
8
6
4
2
0
f1 (ppm)

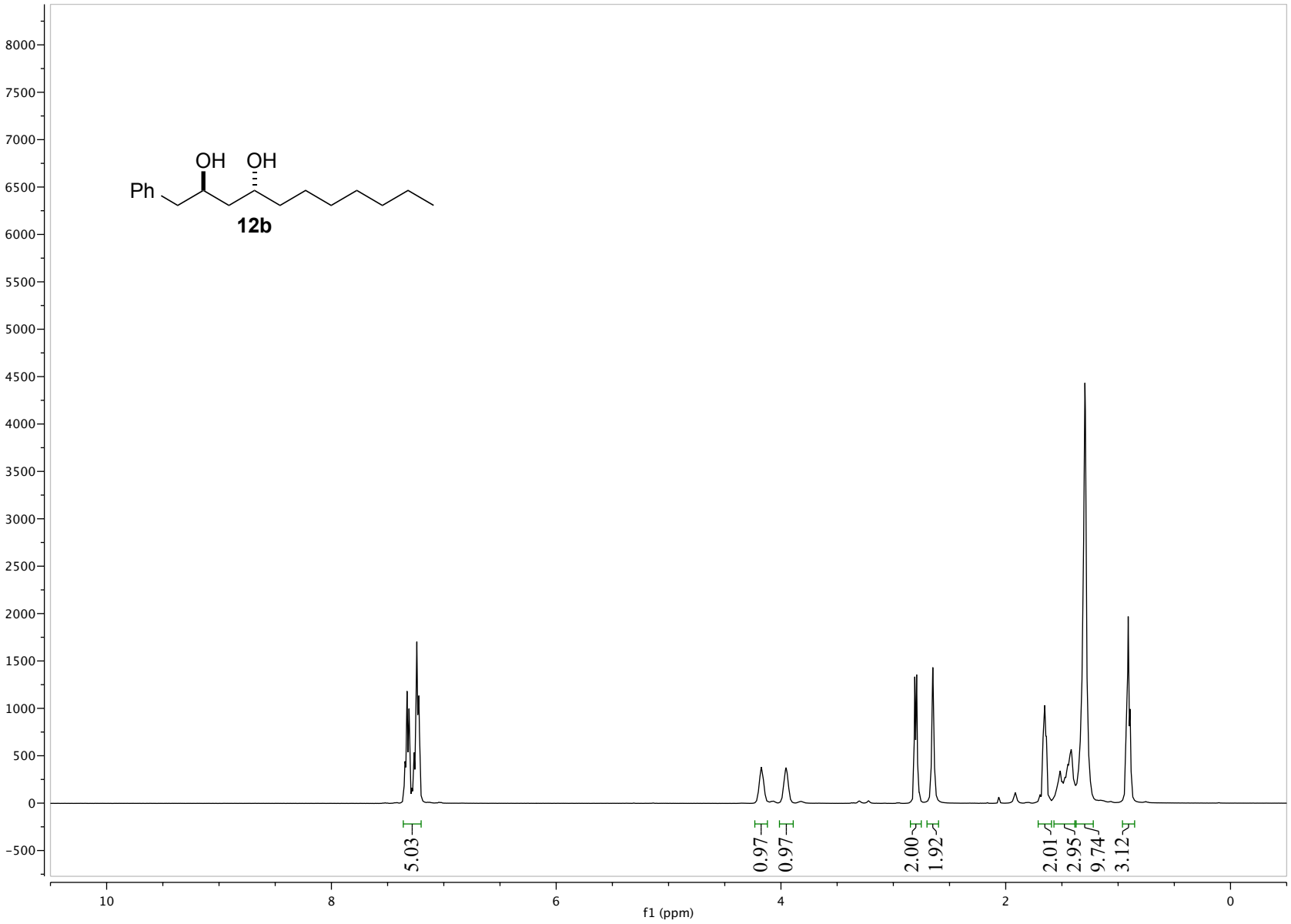

171.2907
135.9909
129.3095
128.2223
126.5310
77.3187 CDCl3
76.9998 CDCl3
76.6815 CDCl3
76.3906
61.7200
41.2641
38.0827
34.4616
O
O
Ph
OH
A-24
450
400
350
300
250
200
150
100
50
0
200
150
100
50
0
f1 (ppm)

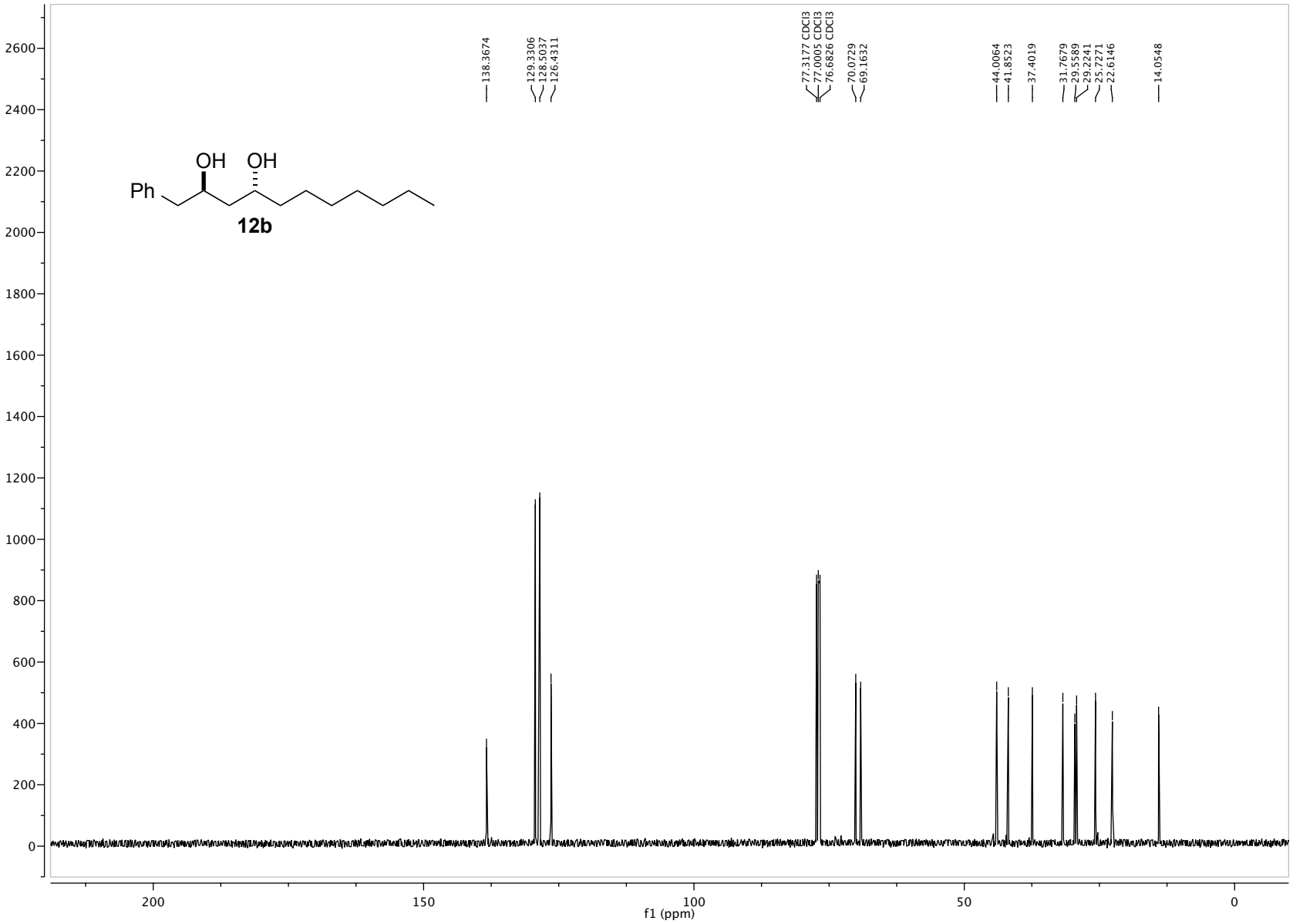

O
O
Ph
O
SiMe2Ph
A-25
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.40
1.00
1.00
1.03
1.04
1.70
1.04
1.10
6.01
10
8
6
4
2
0
f1 (ppm)

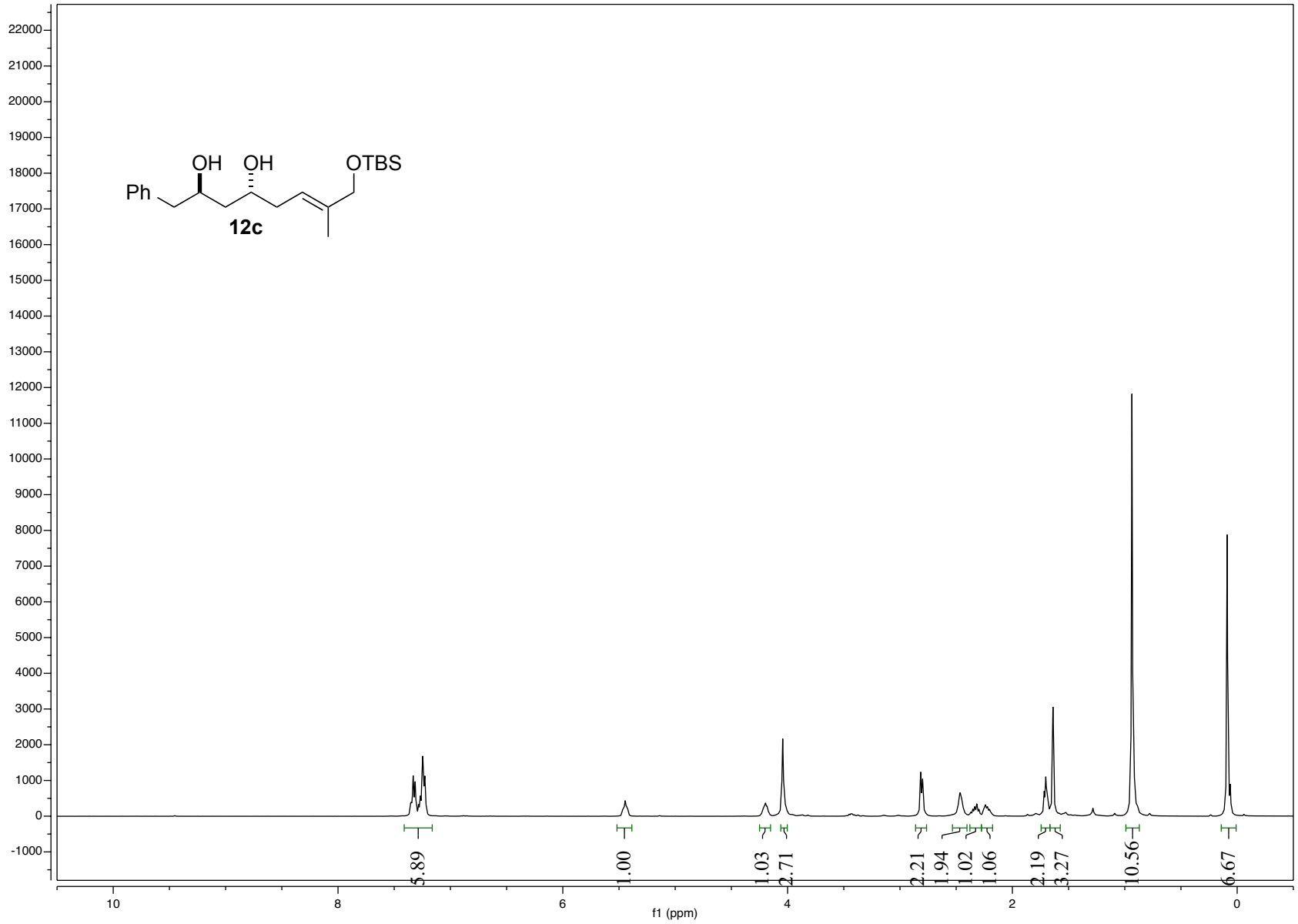

170.1618
136.8917
136.2259
133.2667
129.9249
129.5476
128.4629
127.9895
126.7544
77.3171 CDCl3
76.9993 CDCl3
76.6821 CDCl3
76.2394
63.4782
41.5222
39.0206
35.2353
-1.4747
-1.6473
Ph
O
O
O
SiMe2Ph
A-25
1000
900
800
700
600
500
400
300
200
100
0
200
150
100
50
0
f1 (ppm)

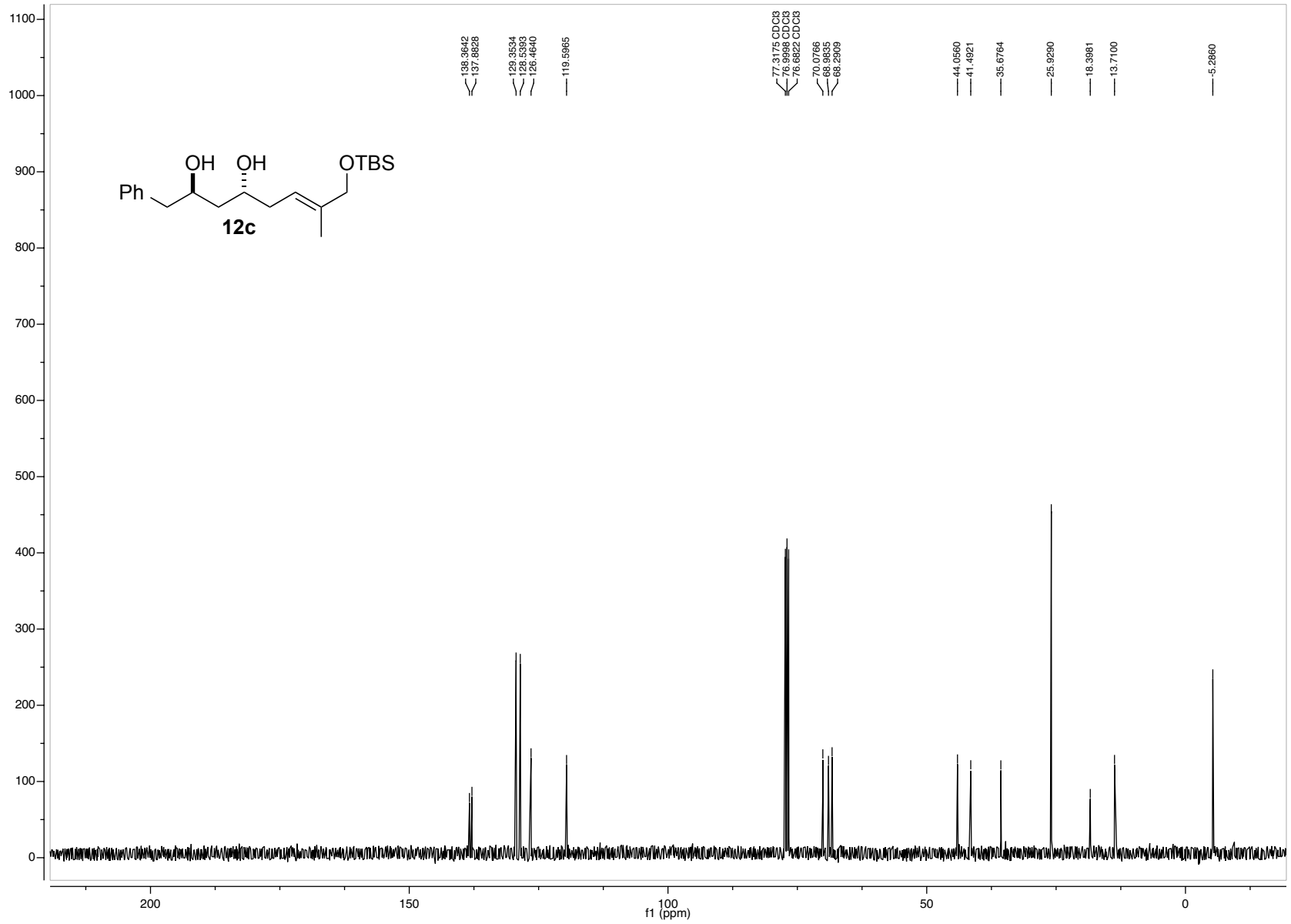

OH
OH
Ph
12a
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
5.75
0.96
1.79
0.96
1.00
2.01
1.00
2.77
1.89
10
8
6
4
2
f1 (ppm)

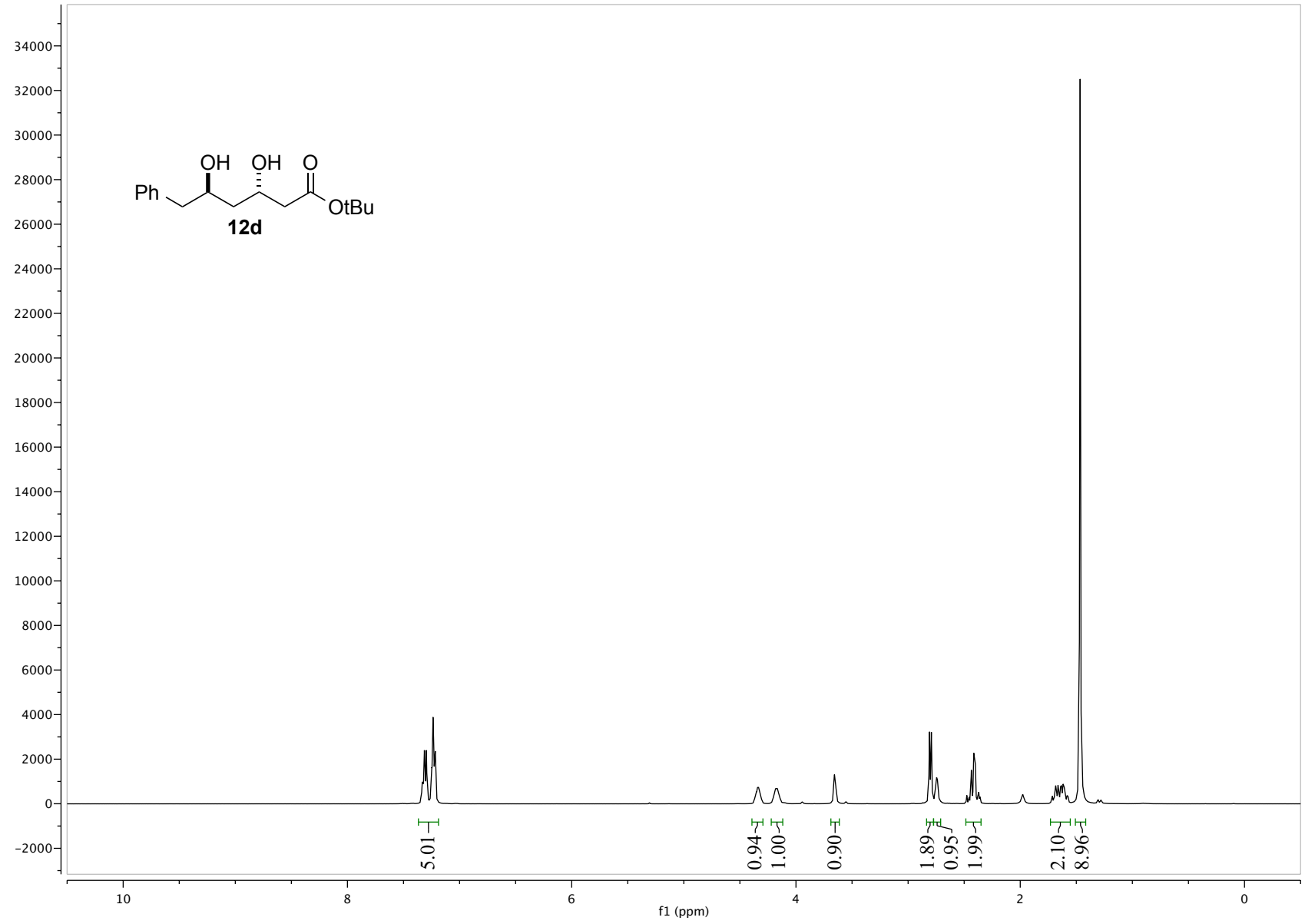

138.2617
134.5998
129.3495
128.5912
126.5352
118.1894
77.3165 CDCl3
76.9993 CDCl3
76.6816 CDCl3
70.0412
68.0758
44.0357
41.9851
41.5232
OH
OH
Ph
12a
f1 (ppm)

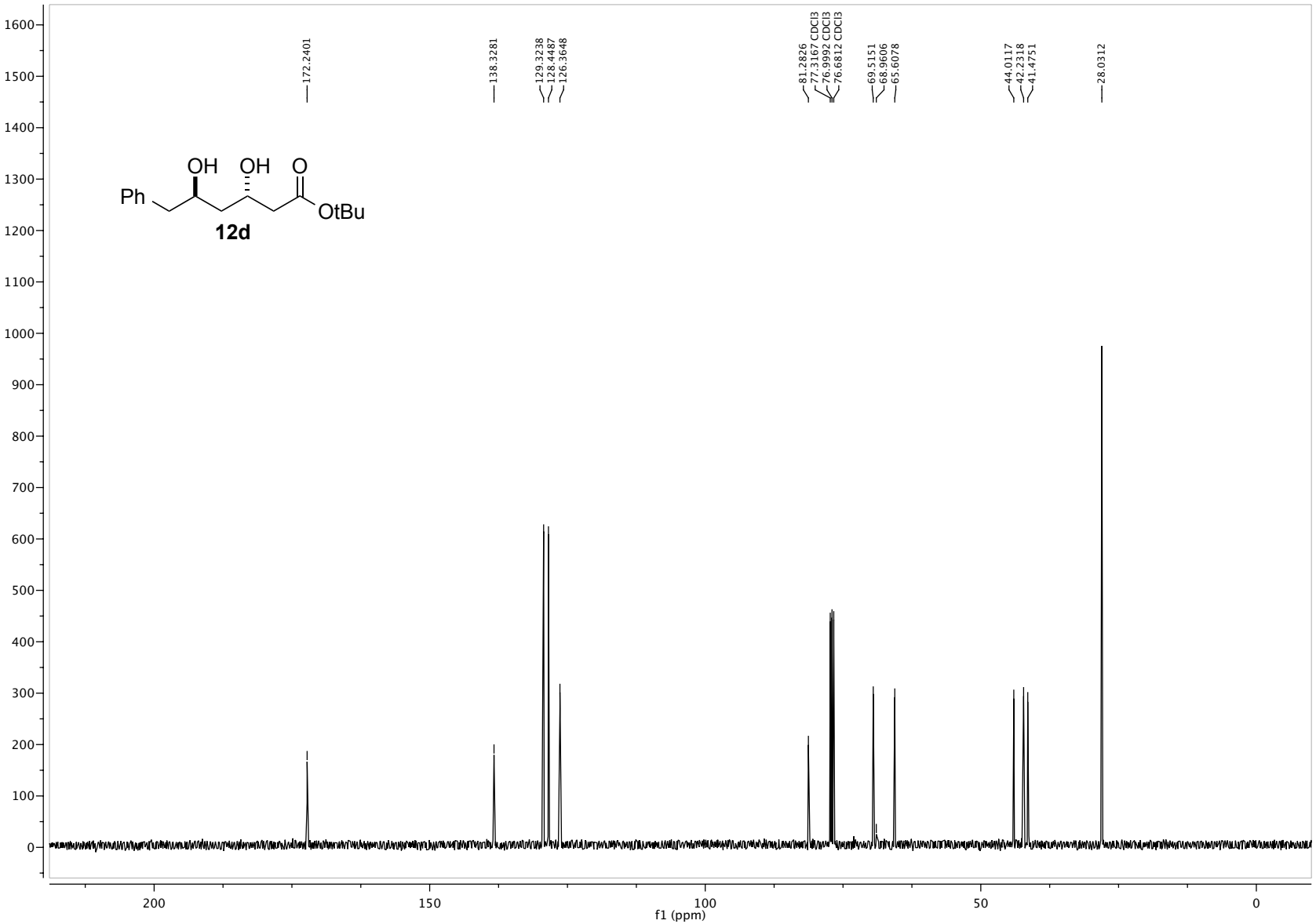

OH
OH
Ph
12b
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
5.03
0.97
0.97
2.00
1.92
2.01
2.95
9.74
3.12
10
8
6
4
2
0
f1 (ppm)

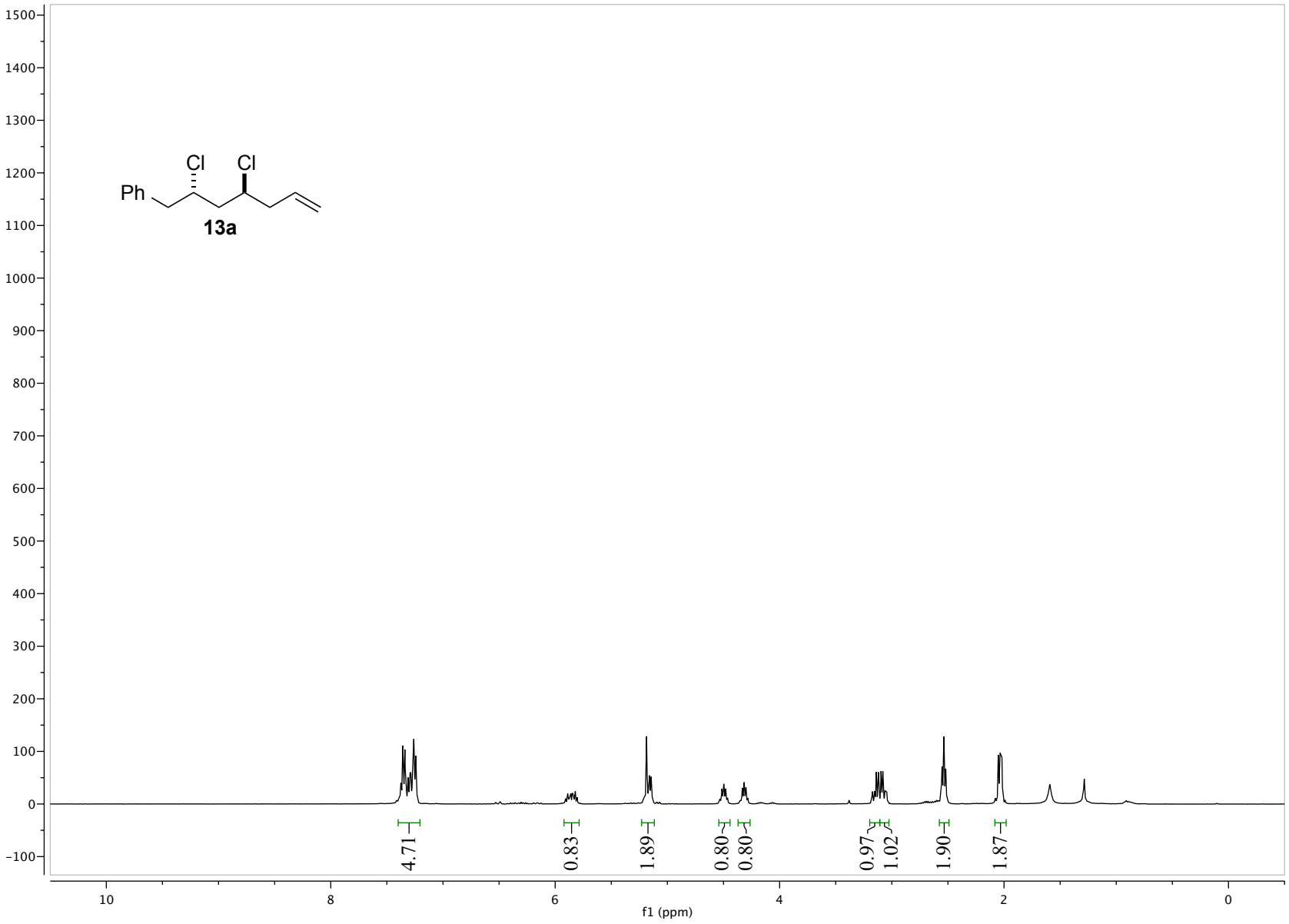

138.3674
129.3306
128.5037
126.4311
77.3177 CDCl3
77.0005 CDCl3
76.6826 CDCl3
70.0729
69.1632
44.0064
41.8523
37.4019
31.7679
29.5589
29.2241
25.7271
22.6146
14.0548
OH
OH
Ph
12b
f1 (ppm)

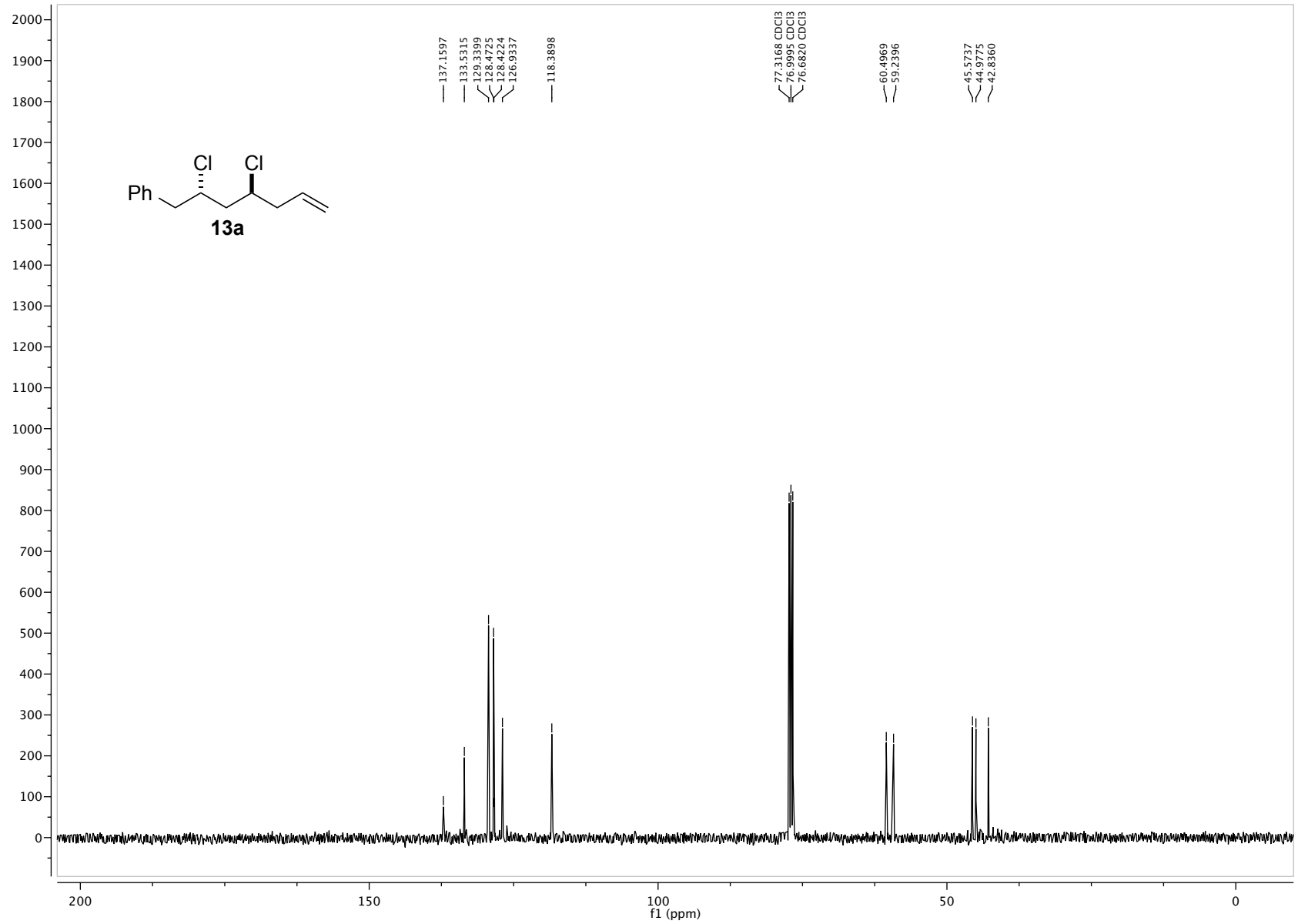

OH
OH
OTBS
Ph
12c
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
5.89
1.00
1.03
2.71
2.21
1.94
1.02
1.06
2.19
3.27
10.56
6.67
10
8
6
4
2
0
f1 (ppm)

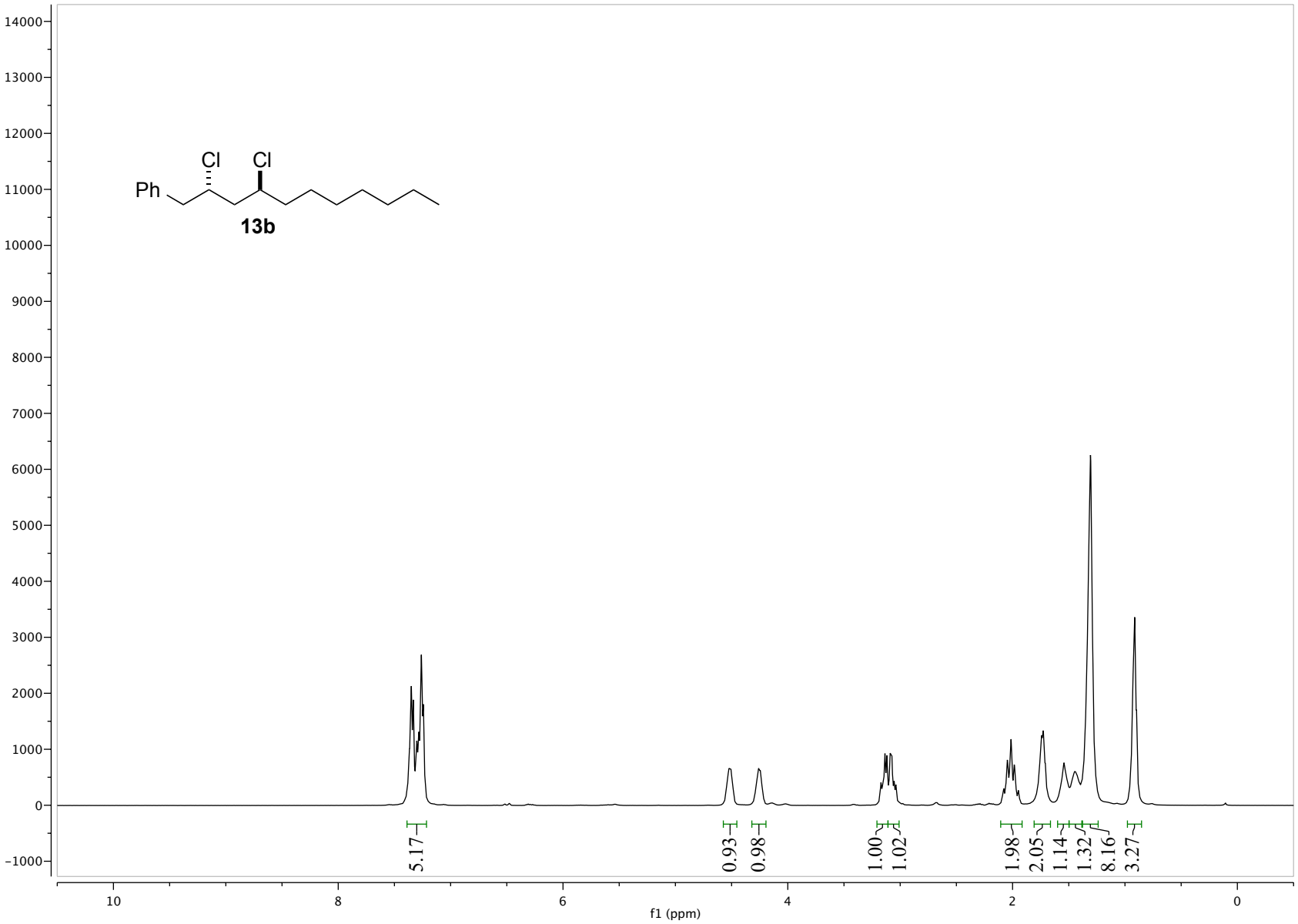

138.3642
137.8828
129.3534
128.5393
128.4640
119.5965
77.3175 CDCl3
76.9998 CDCl3
76.6822 CDCl3
70.0766
68.9835
68.2909
44.0560
41.4921
35.6764
25.9290
18.3981
13.7100
-5.2860
OH
OH
OTBS
Ph
12c
f1 (ppm)

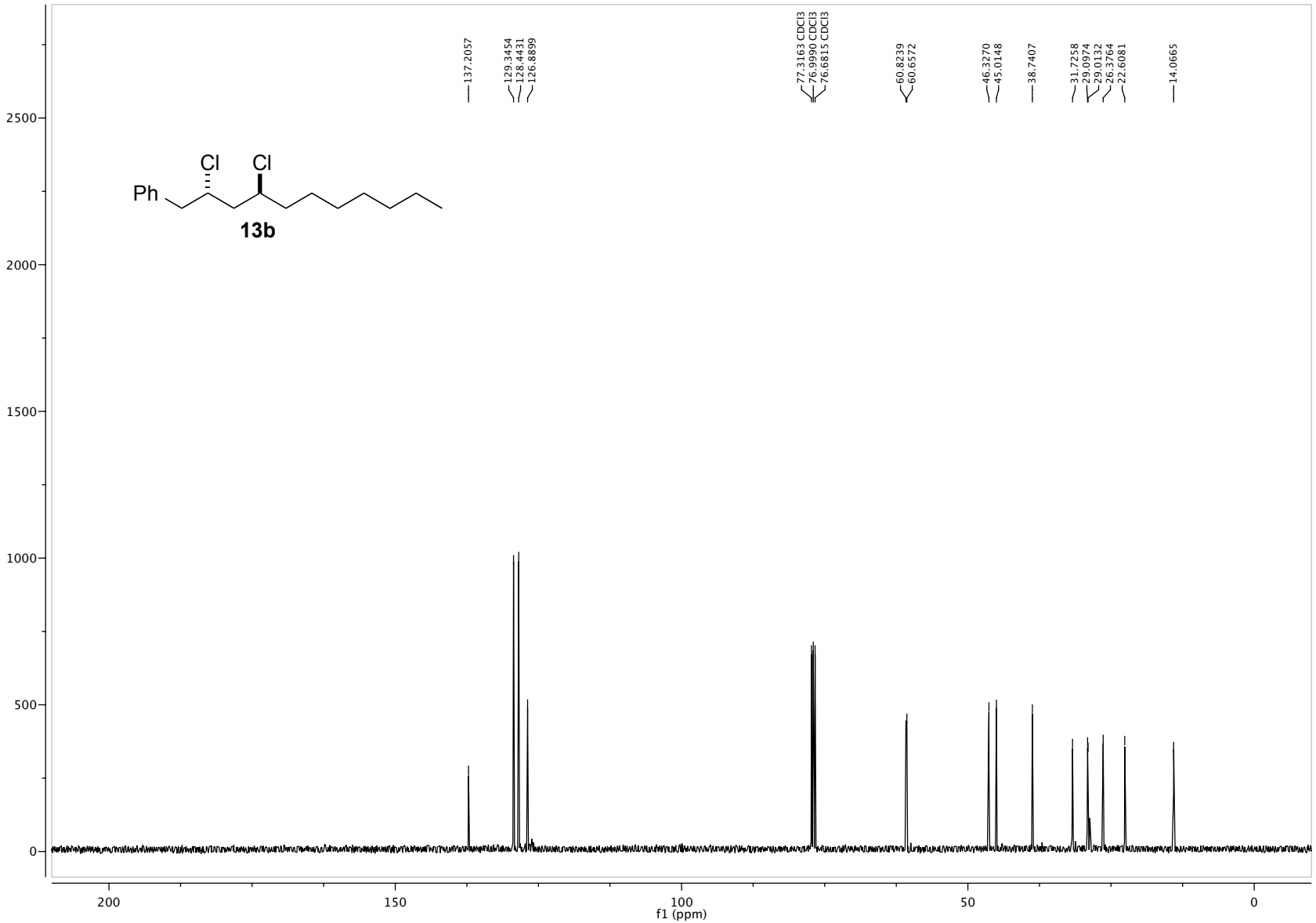

OH
OH
O
Ph
OtBu
12d
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
−2000
5.01
0.94
1.00
0.90
1.89
0.95
1.99
2.10
8.96
10
8
6
4
2
0
f1 (ppm)

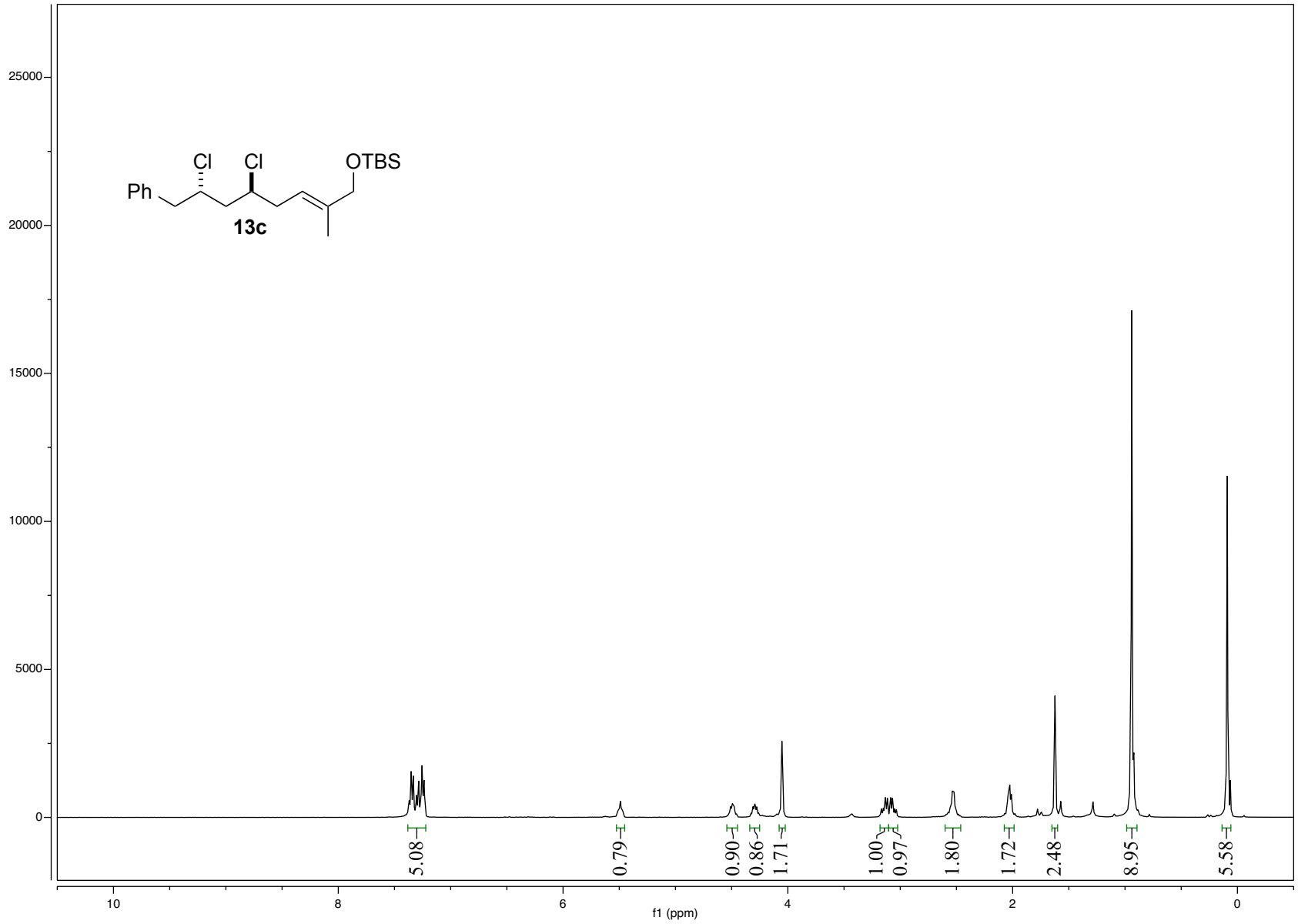

172.2401
138.3281
129.3238
128.4487
126.3648
81.2826
77.3167 CDCl3
76.9992 CDCl3
76.6812 CDCl3
69.5151
68.9606
65.6078
44.0117
42.2318
41.4751
28.0312
OH
OH
O
Ph
OtBu
12d
f1 (ppm)

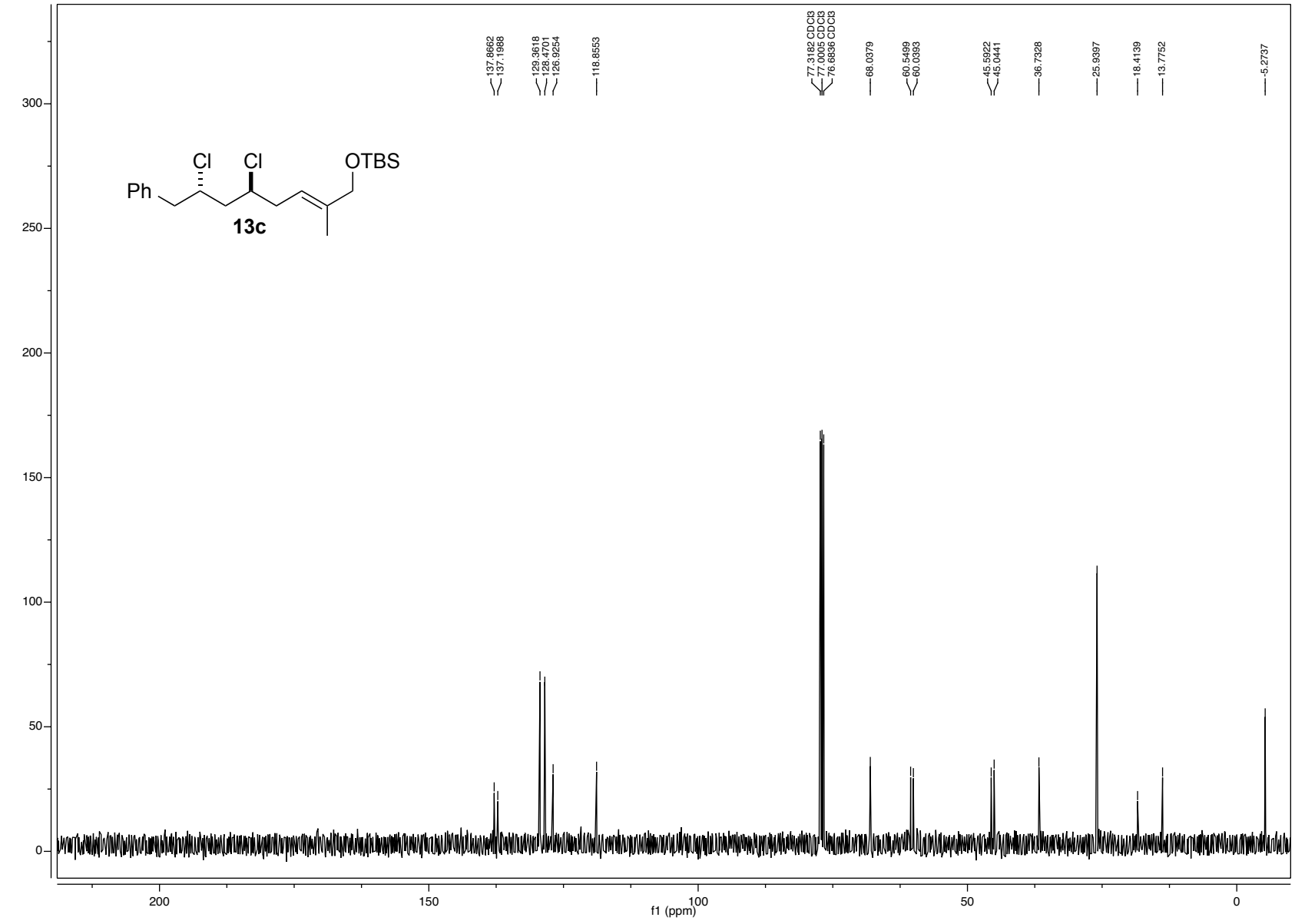

Cl
Cl
Ph
13a
4.71
0.83
1.89
0.80
0.80
0.97
1.02
1.90
1.87
f1 (ppm)

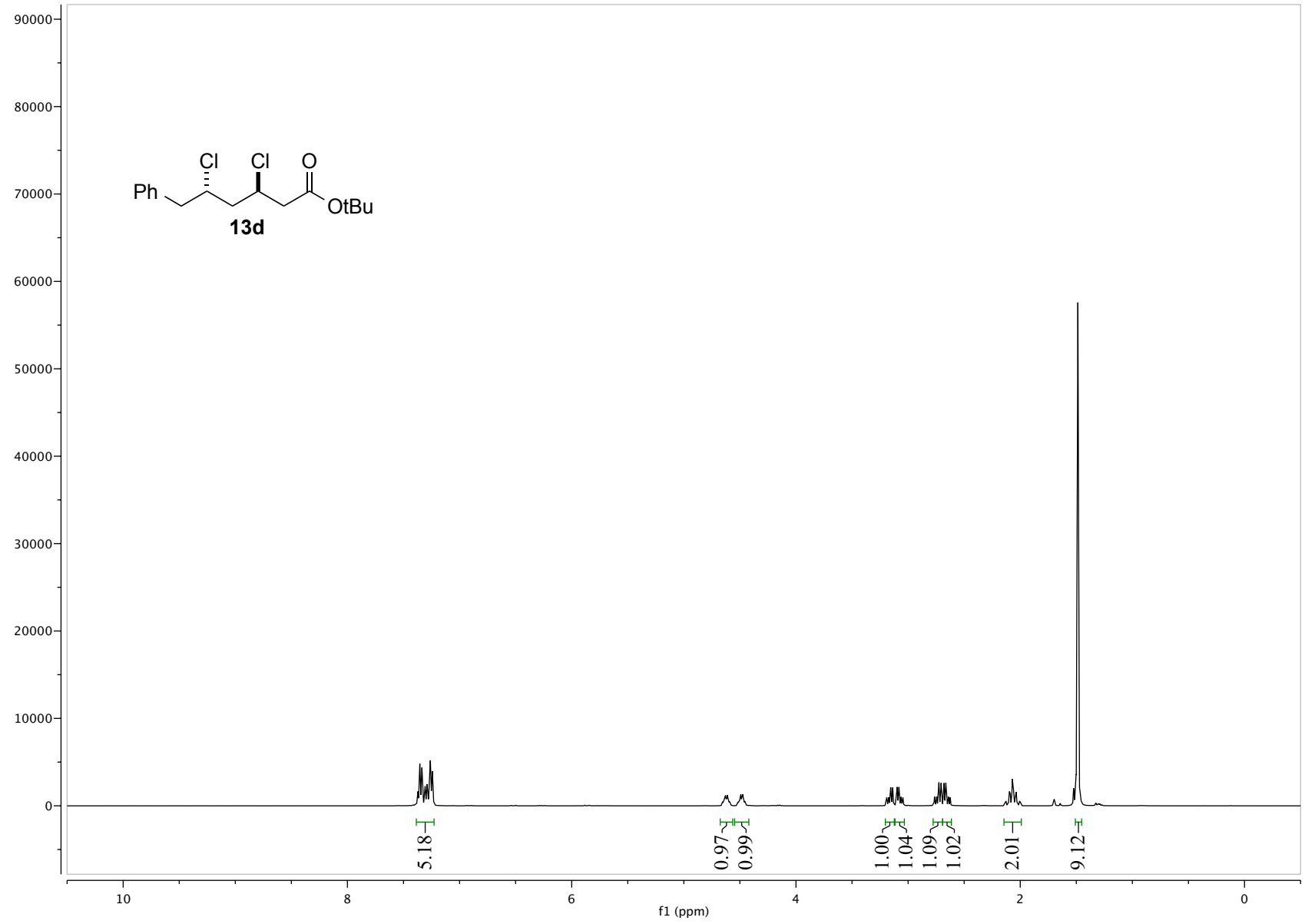

137.1597
133.5315
129.3399
128.4725
128.4224
126.9337
118.3898
77.3168 CDCl3
76.9995 CDCl3
76.6820 CDCl3
60.4969
59.2396
45.5737
44.9775
42.8360
Cl
Cl
Ph
13a
f1 (ppm)

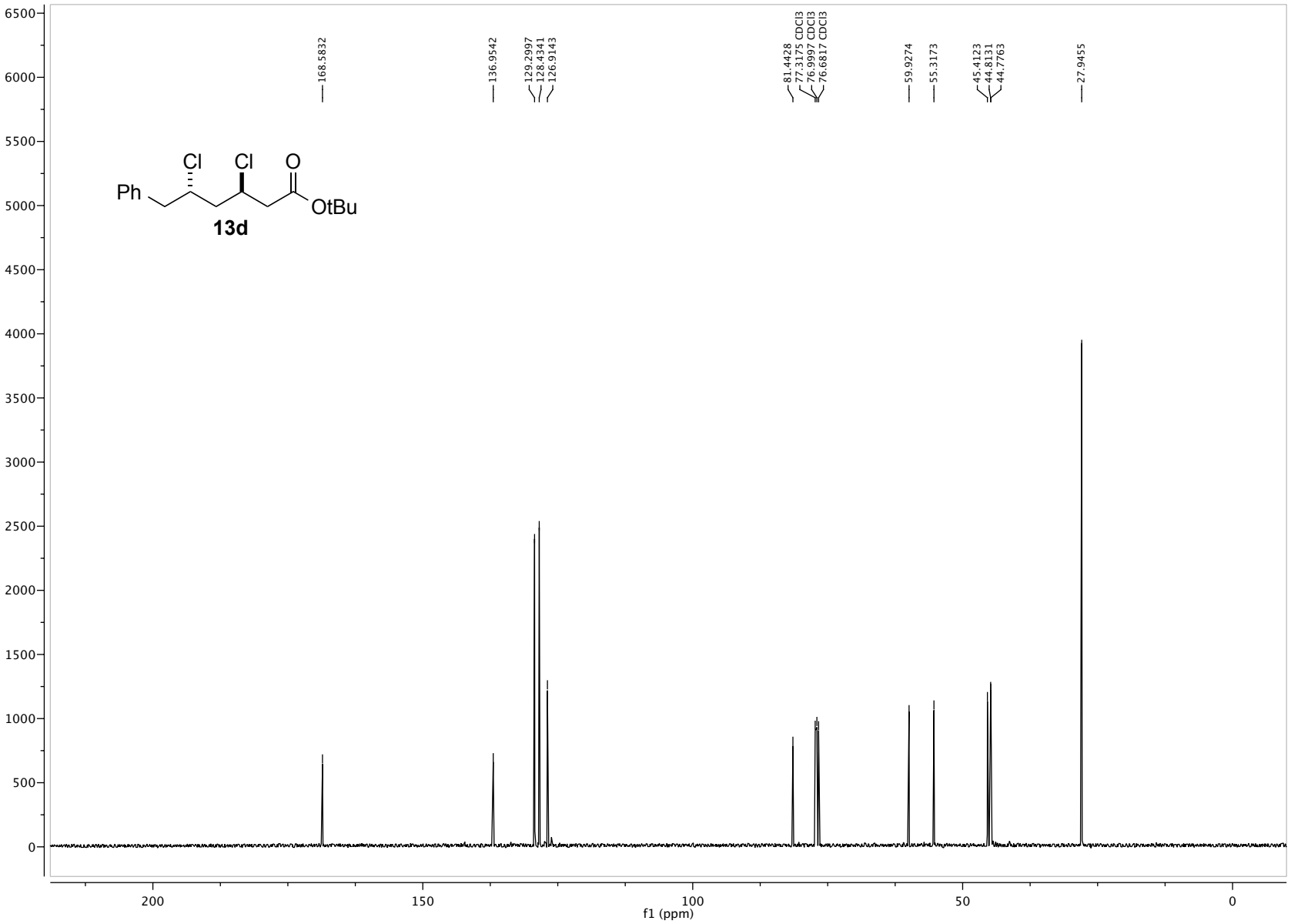

Cl
Cl
Ph
13b
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
5.17
0.93
0.98
1.00
1.02
1.98
2.05
1.14
1.32
8.16
3.27
10
8
6
4
2
0
f1 (ppm)

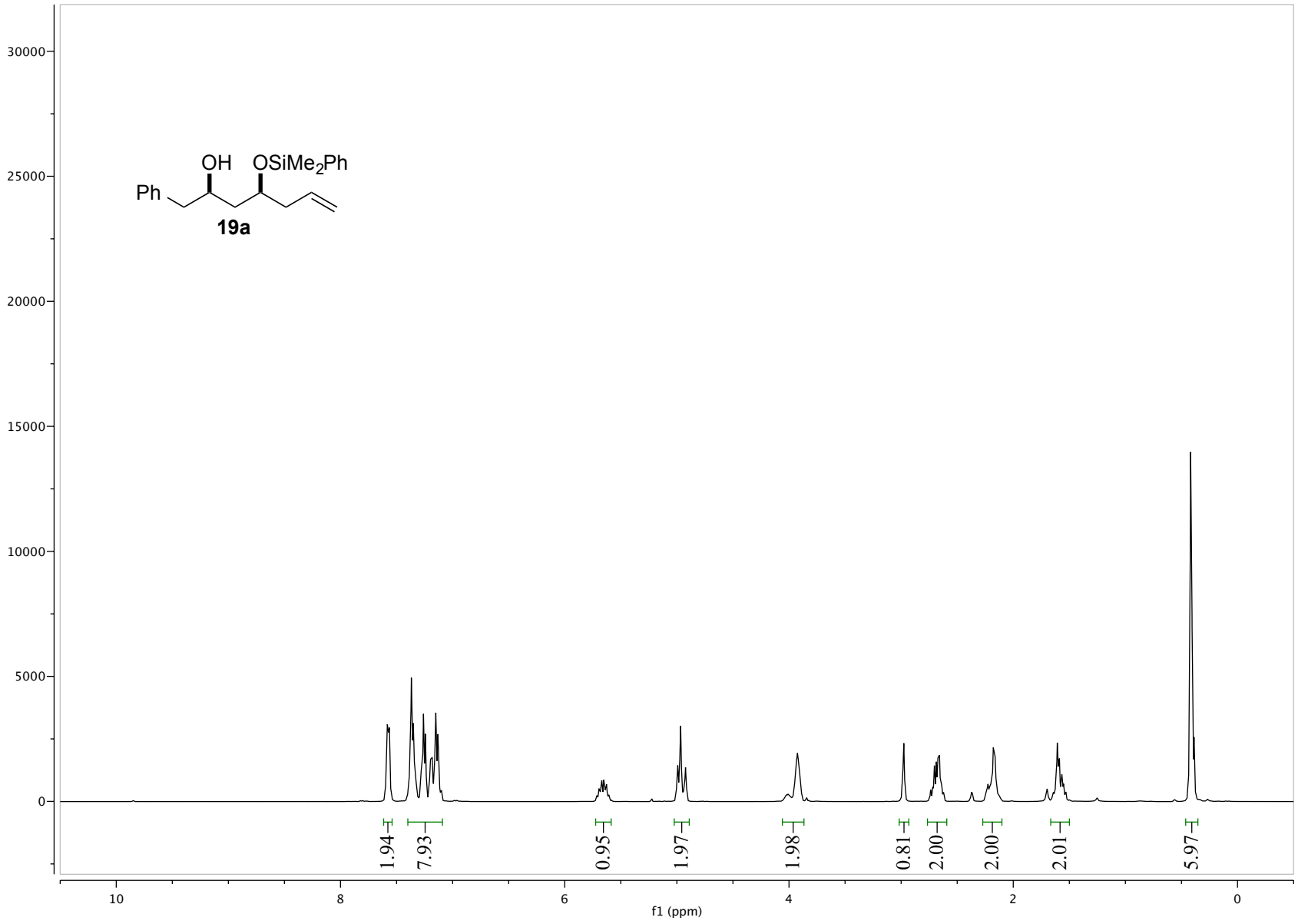

137.2057
129.3454
128.4431
126.8899
77.3163 CDCl3
76.9990 CDCl3
76.6815 CDCl3
60.8239
60.6572
46.3270
45.0148
38.7407
31.7258
29.0974
29.0132
26.3764
22.6081
14.0665
Cl
Cl
Ph
13b
2500
2000
1500
1000
500
0
200
150
100
50
0
f1 (ppm)

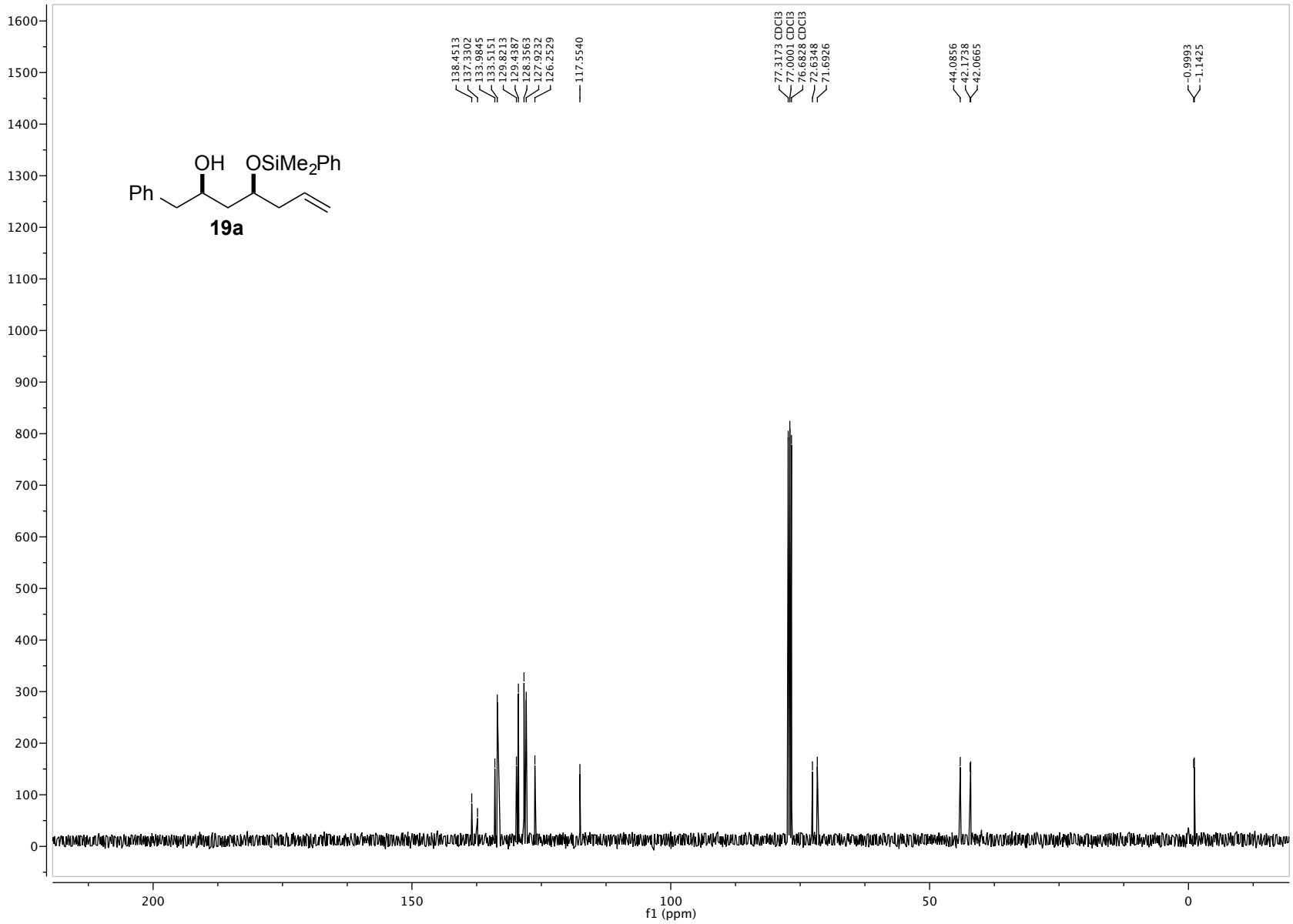

Cl
Cl
OTBS
Ph
13c
25000
20000
15000
10000
5000
0
5.08
0.79
0.90
0.86
1.71
1.00
0.97
1.80
1.72
2.48
8.95
5.58
10
8
6
4
2
0
f1 (ppm)

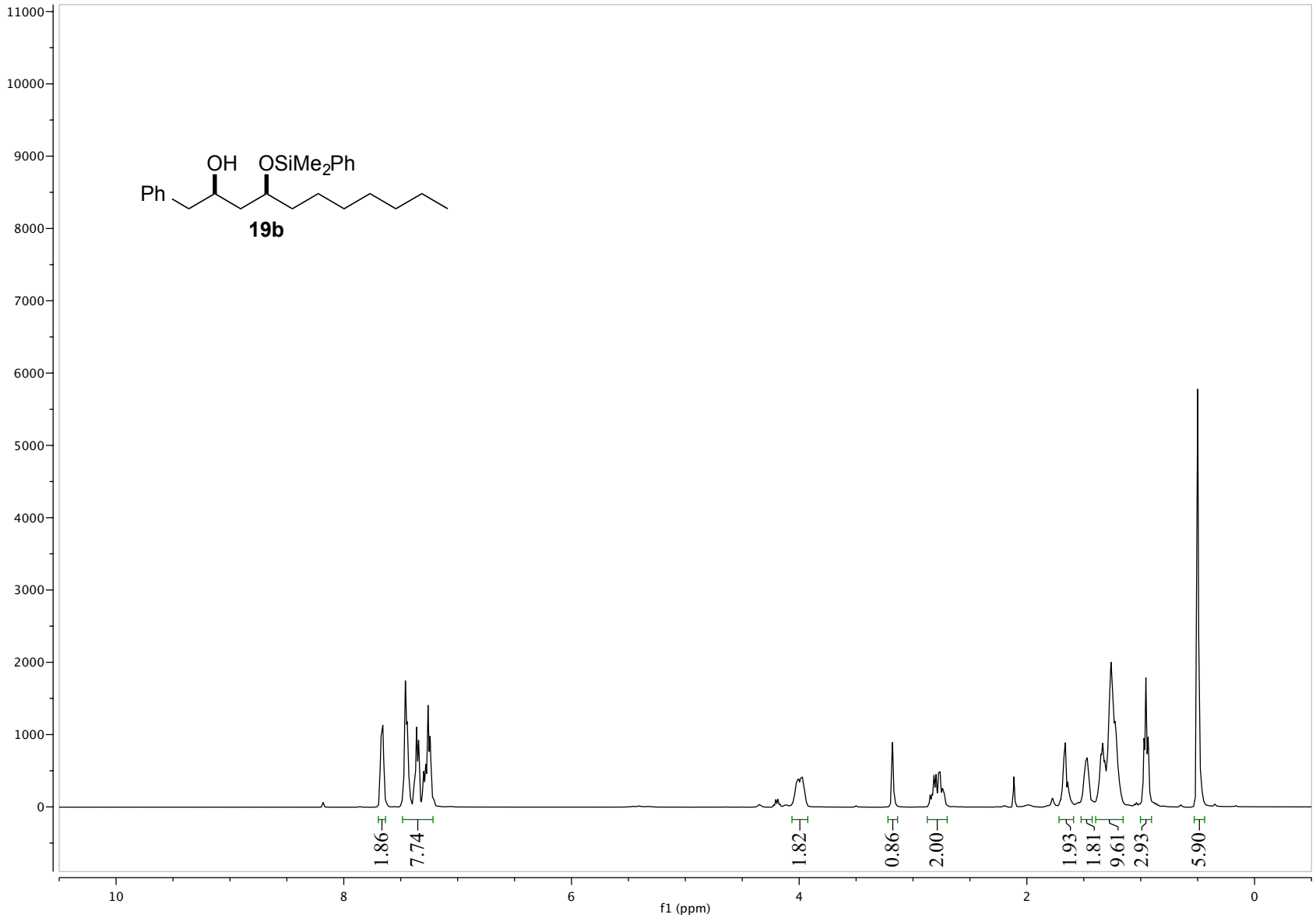

137.8662
137.1988
129.3618
128.4701
126.9254
118.8553
77.3182 CDCl3
77.0005 CDCl3
76.6836 CDCl3
68.0379
60.5499
60.0393
45.5922
45.0441
36.7328
25.9397
18.4139
13.7752
-5.2737
Cl
Cl
OTBS
Ph
13c
300
250
200
150
100
50
0
200
150
100
50
0
f1 (ppm)

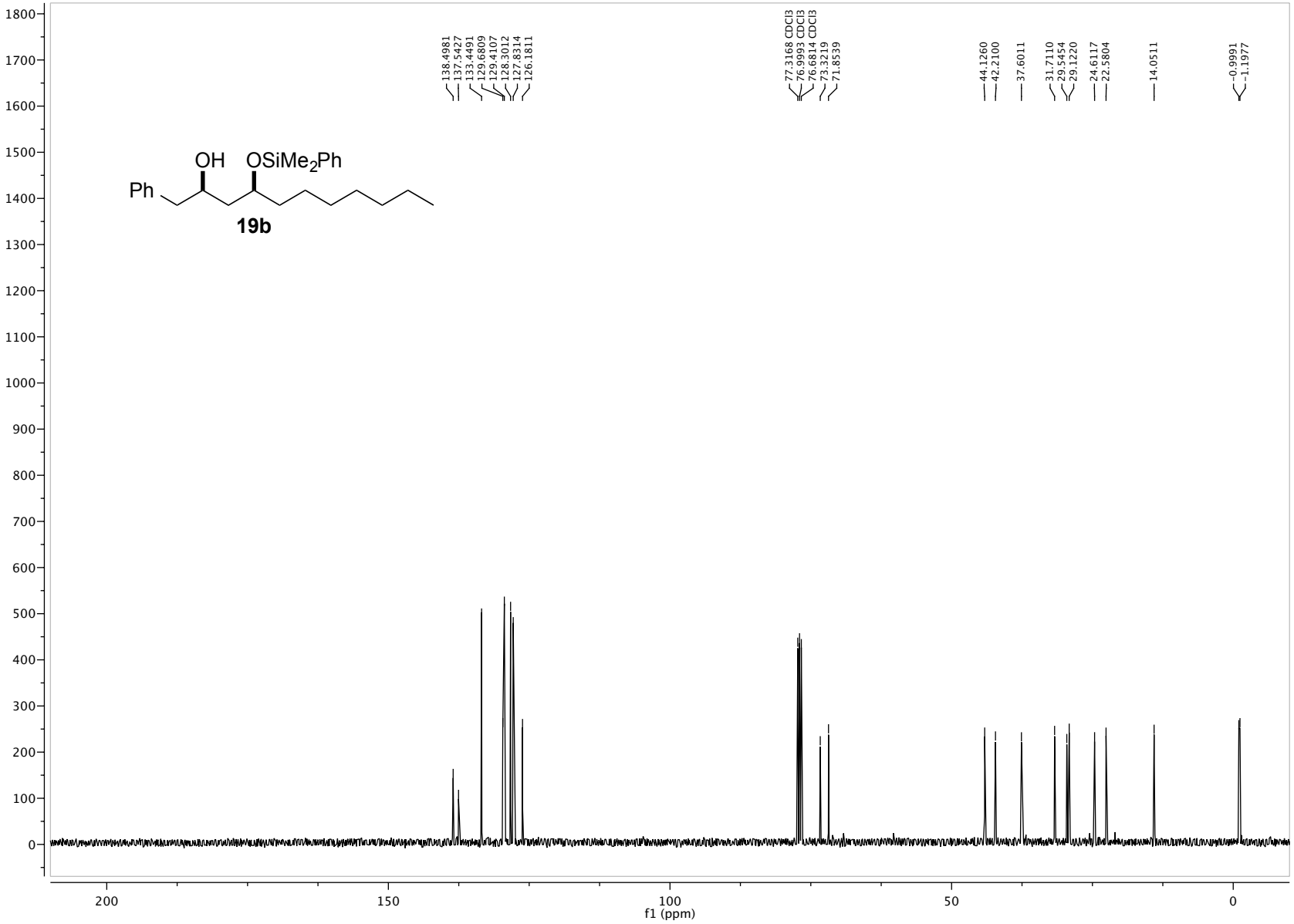

Cl
Cl
O
Ph
OtBu
13d
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
5.18
0.97
0.99
1.00
1.04
1.09
1.02
2.01
9.12
10
8
6
4
2
0
f1 (ppm)

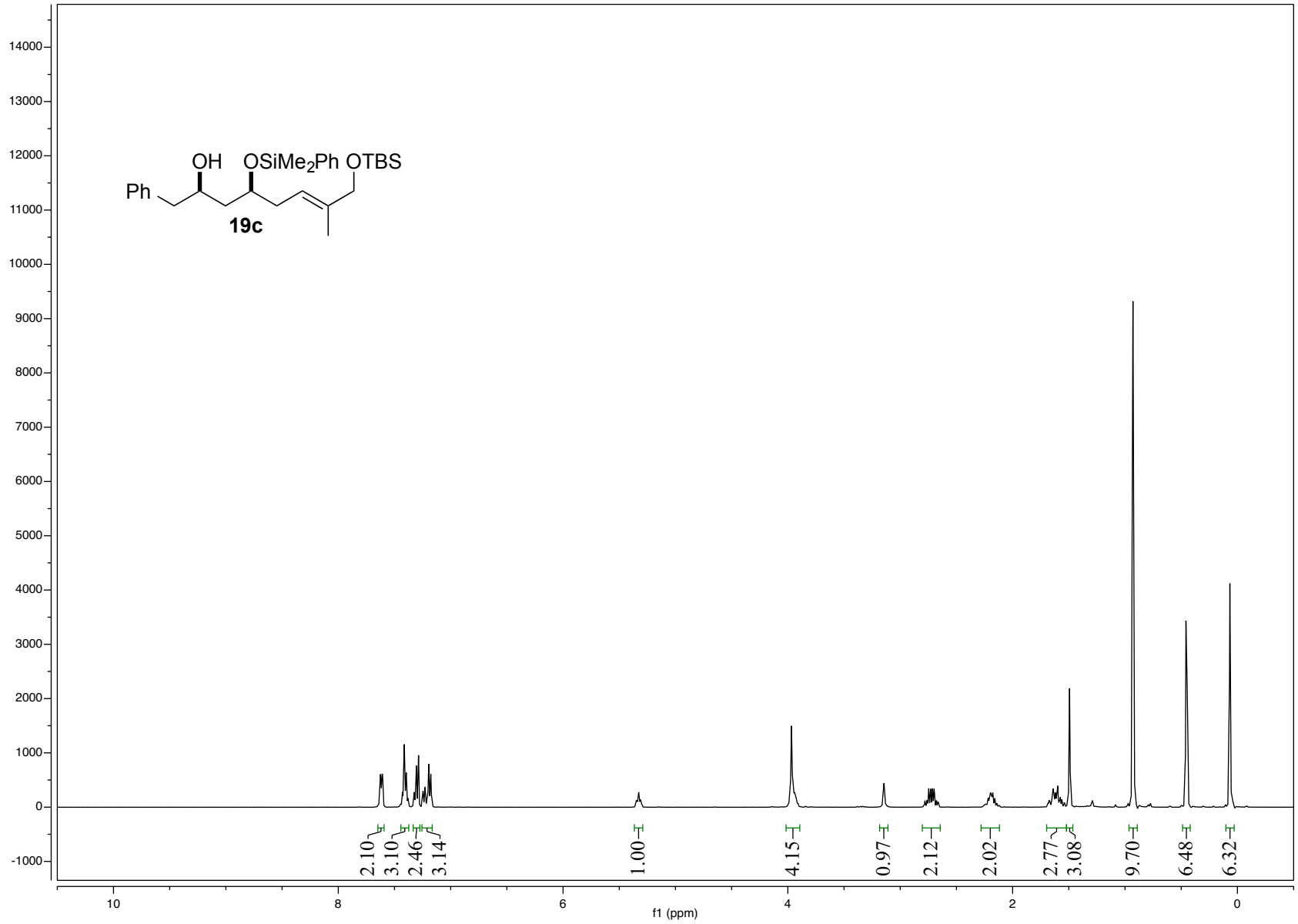

168.5832
136.9542
129.2997
128.4341
126.9143
81.4428
77.3175 CDCl3
76.9997 CDCl3
76.6817 CDCl3
59.9274
55.3173
45.4123
44.8131
44.7763
27.9455
Cl
Cl
O
Ph
OtBu
13d
f1 (ppm)

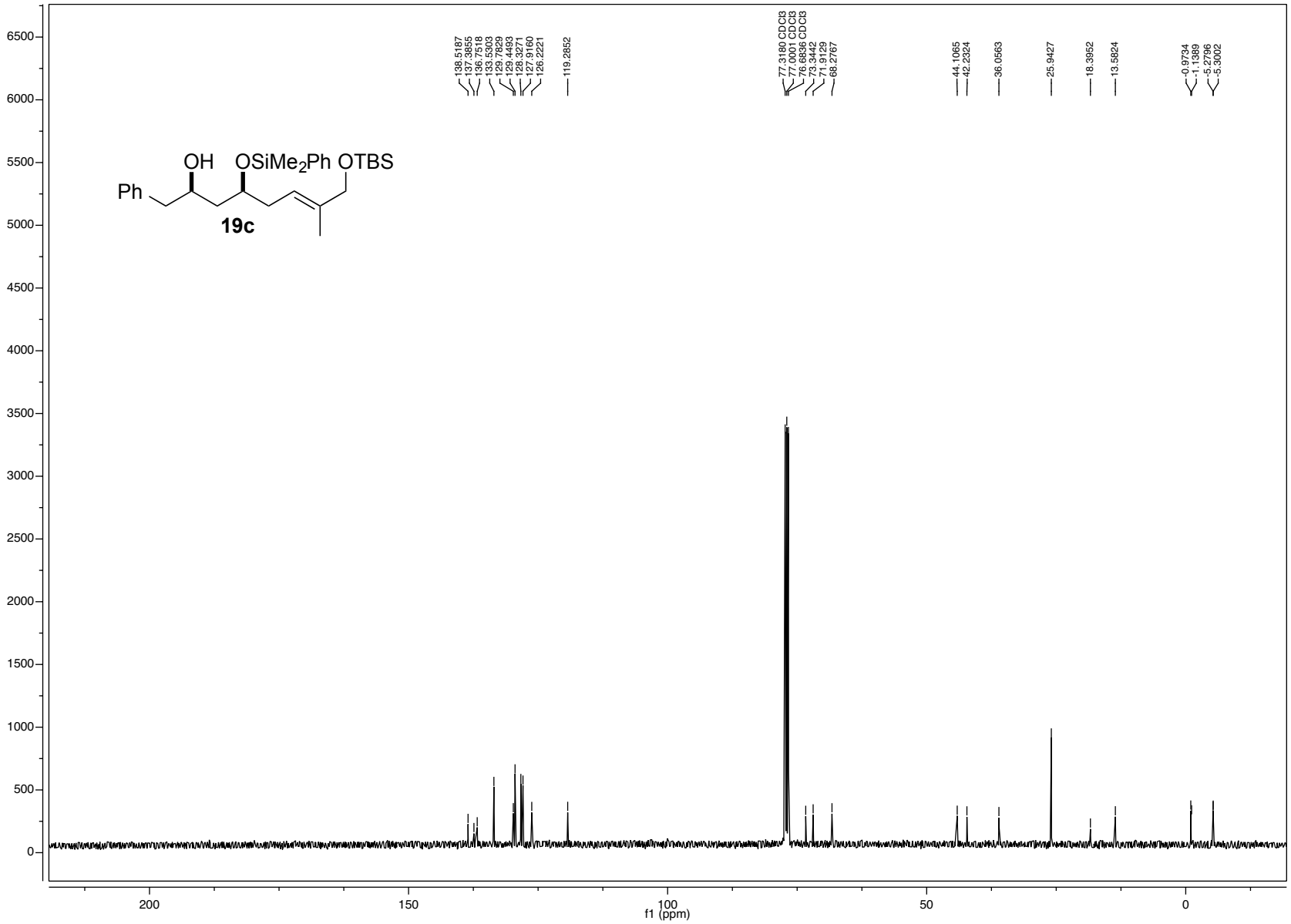

OH
OSiMe2Ph
Ph
19a
30000
25000
20000
15000
10000
5000
0
1.94
7.93
0.95
1.97
1.98
0.81
2.00
2.00
2.01
5.97
10
8
6
4
2
0
f1 (ppm)

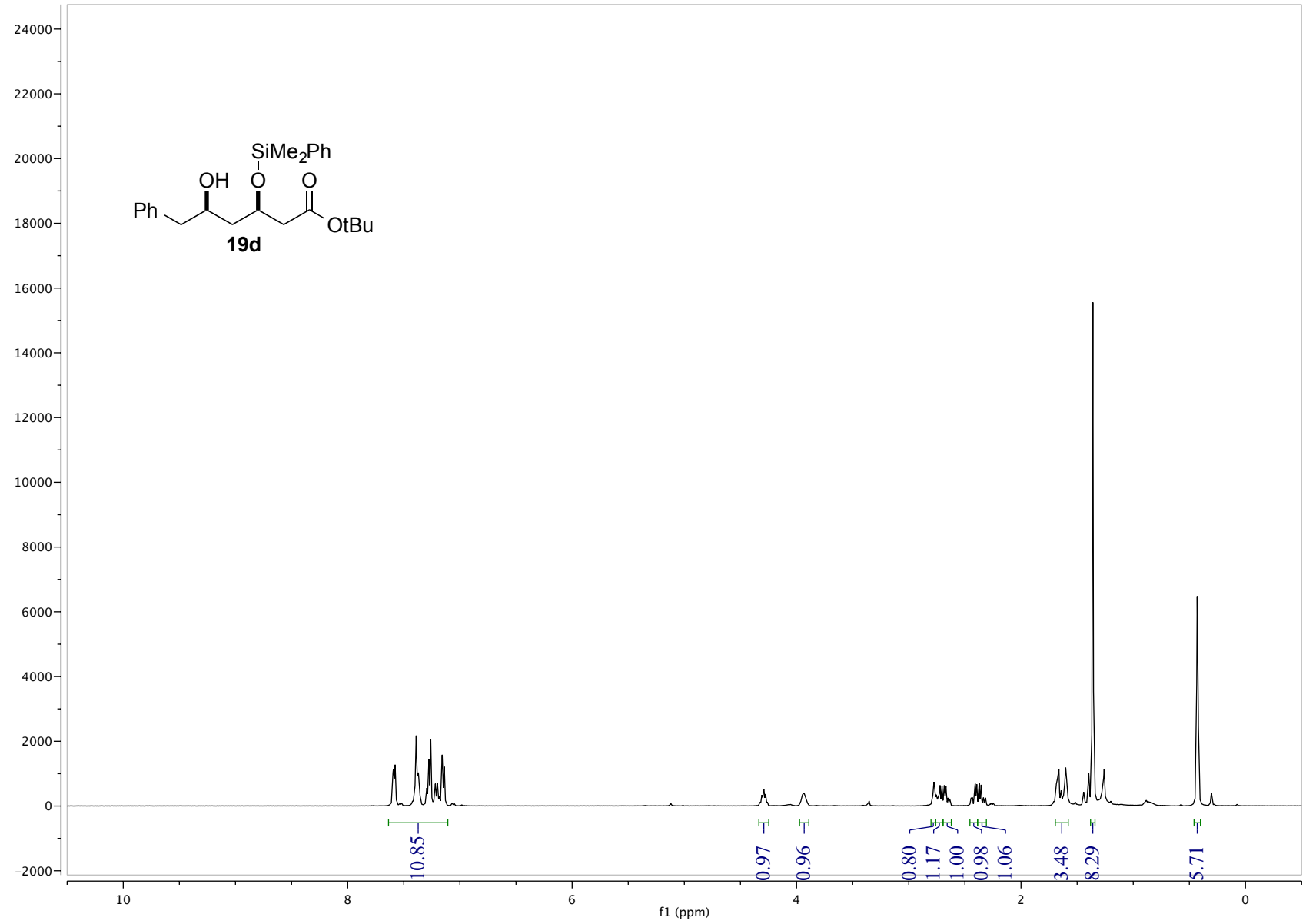

138.4513
137.3302
133.9845
133.5151
129.8213
129.4387
128.3563
127.9232
126.2529
117.5540
77.3173 CDCl3
77.0001 CDCl3
76.6828 CDCl3
72.6348
71.6926
44.0856
42.1738
42.0665
-0.9993
-1.1425
OH
OSiMe2Ph
Ph
19a
f1 (ppm)

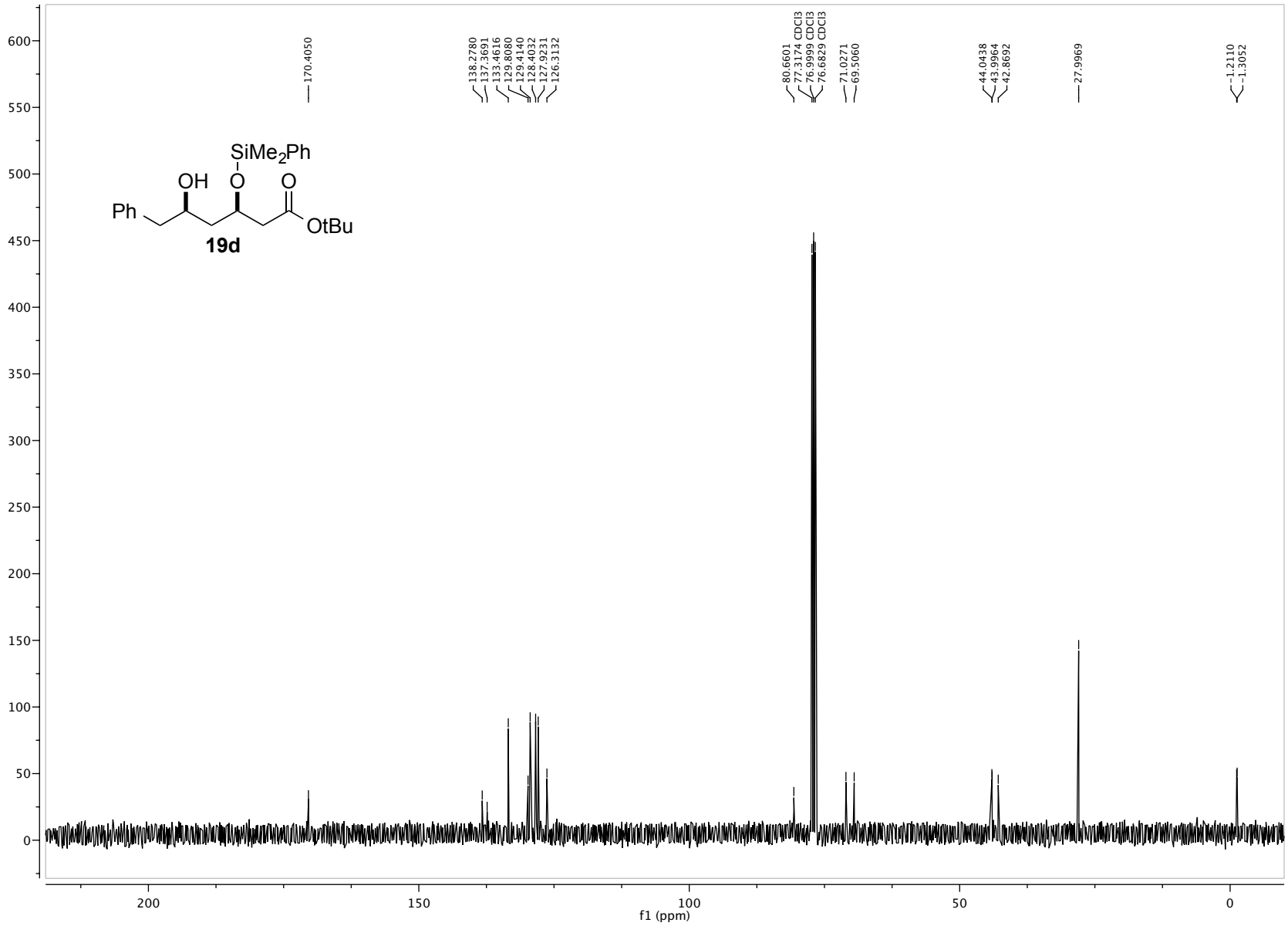

OH
OSiMe2Ph
Ph
19b
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
1.86
7.74
1.82
0.86
2.00
1.93
1.81
9.61
2.93
5.90
10
8
6
4
2
0
f1 (ppm)

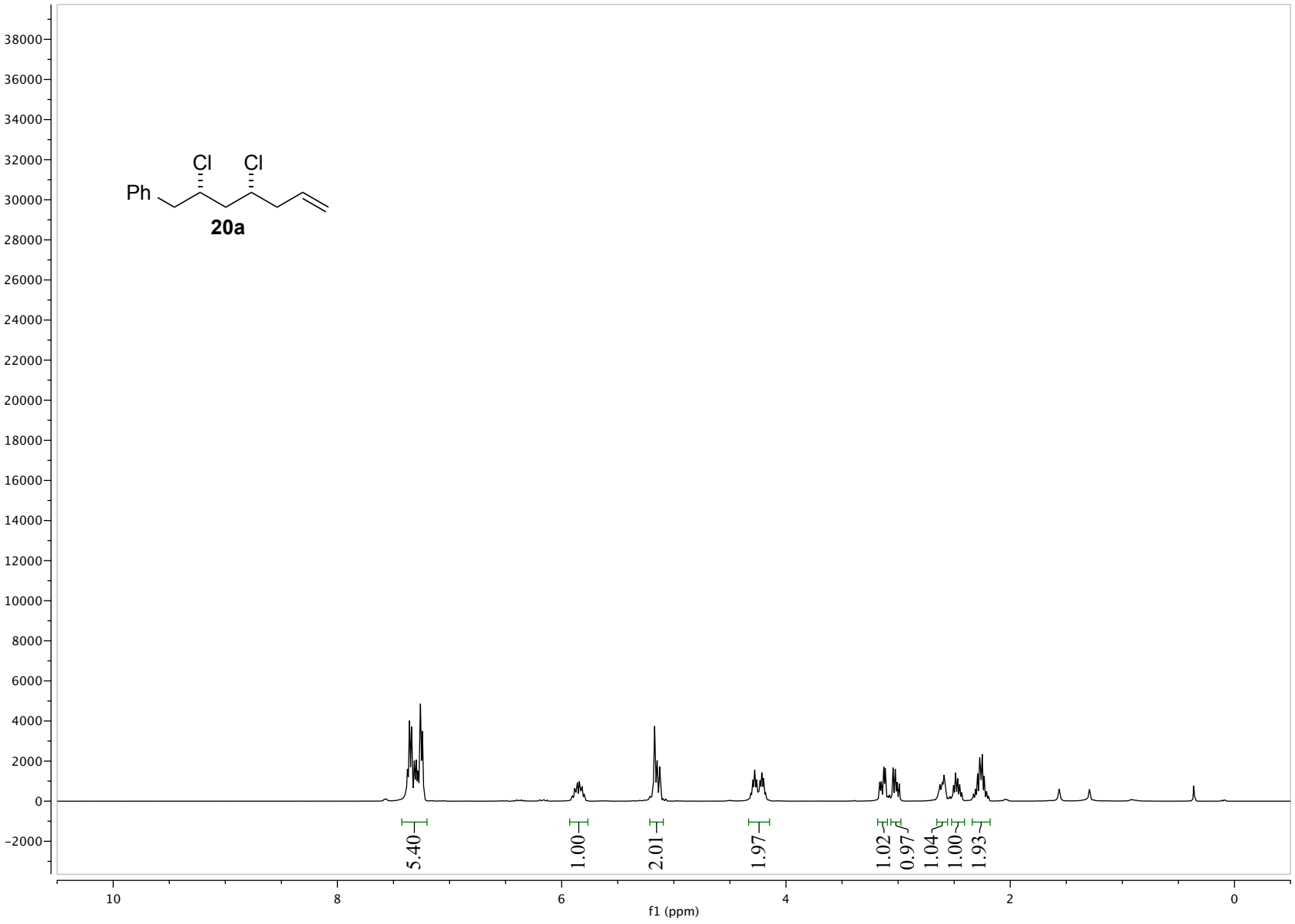

OH
OSiMe2Ph
Ph
19b
138.4981
137.5427
133.4491
129.6809
129.4107
128.3012
127.8314
126.1811
77.3168 CDCl3
76.9993 CDCl3
76.6814 CDCl3
73.3219
71.8539
44.1260
42.2100
37.6011
31.7110
29.5454
29.1220
24.6117
22.5804
14.0511
-0.9991
-1.1977
f1 (ppm)

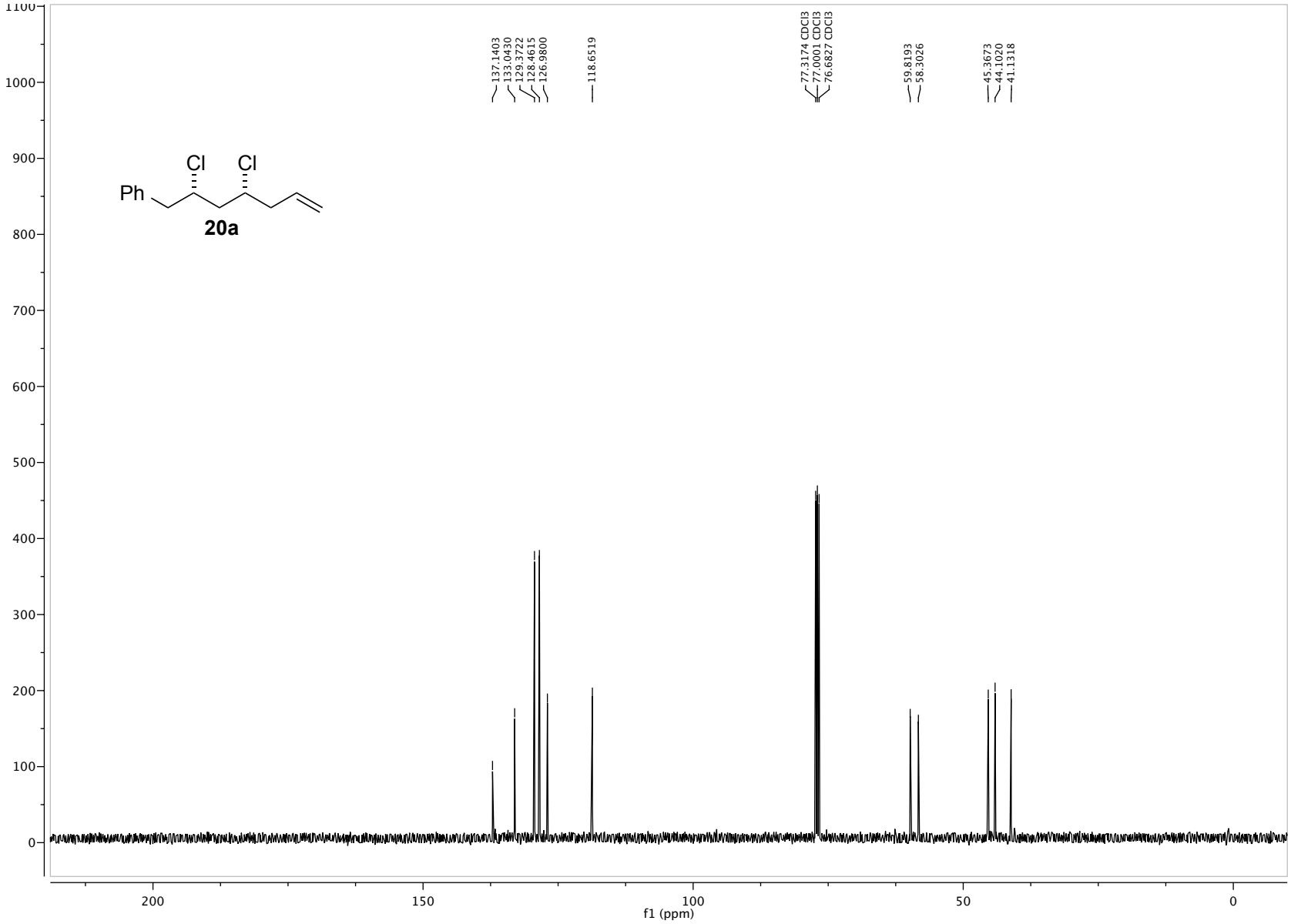

OH
OSiMe2Ph
OTBS
Ph
19c
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
2.10
3.10
2.46
3.14
1.00
4.15
0.97
2.12
2.02
2.77
3.08
9.70
6.48
6.32
10
8
6
4
2
0
f1 (ppm)

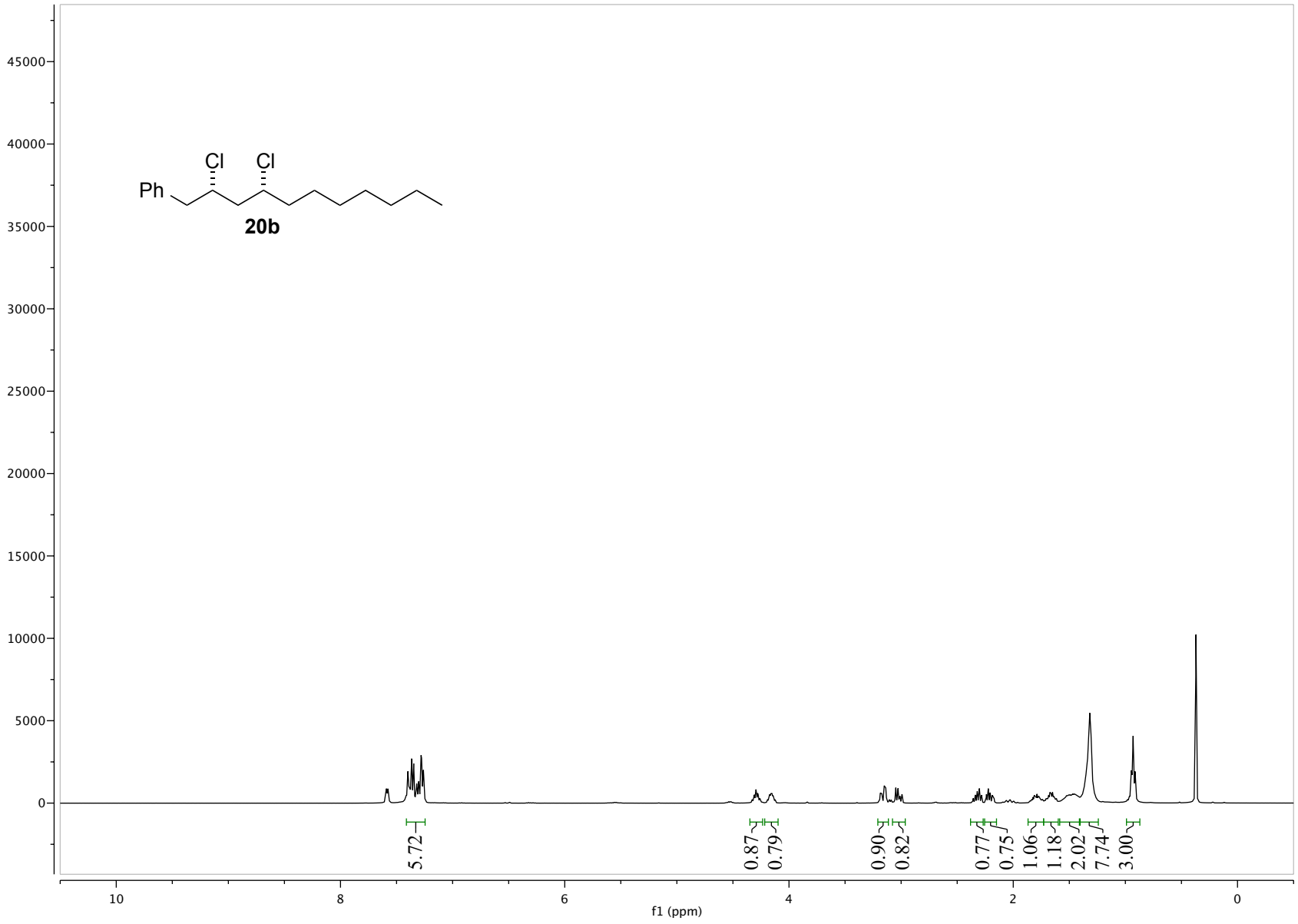

138.5187
137.3855
136.7518
133.5303
129.7629
129.4459
128.3271
127.9160
126.2221
119.2852
77.3180 CDCl3
77.0001 CDCl3
76.6836 CDCl3
73.3442
71.9129
68.2767
44.1065
42.2324
36.0563
25.9427
18.3952
13.5824
-0.9734
-1.1389
-5.2796
-5.3002
OH
OSiMe2Ph
OTBS
Ph
19c
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
200
150
100
50
0
f1 (ppm)

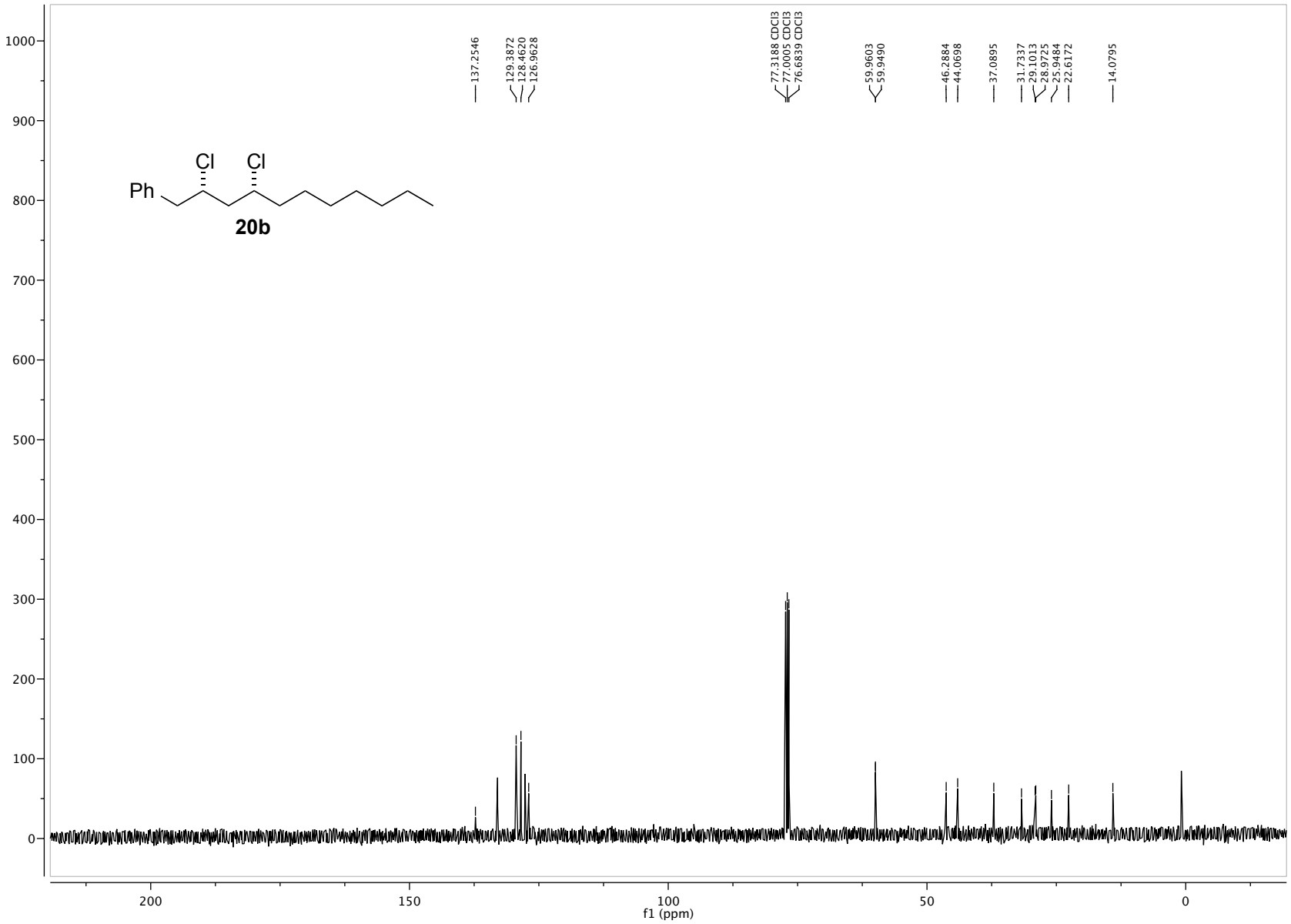

SiMe2Ph
OH
O
O
Ph
OtBu
19d
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10.85
0.97
0.96
0.80
1.17
1.00
0.98
1.06
3.48
8.29
5.71
10
8
6
4
2
0
f1 (ppm)

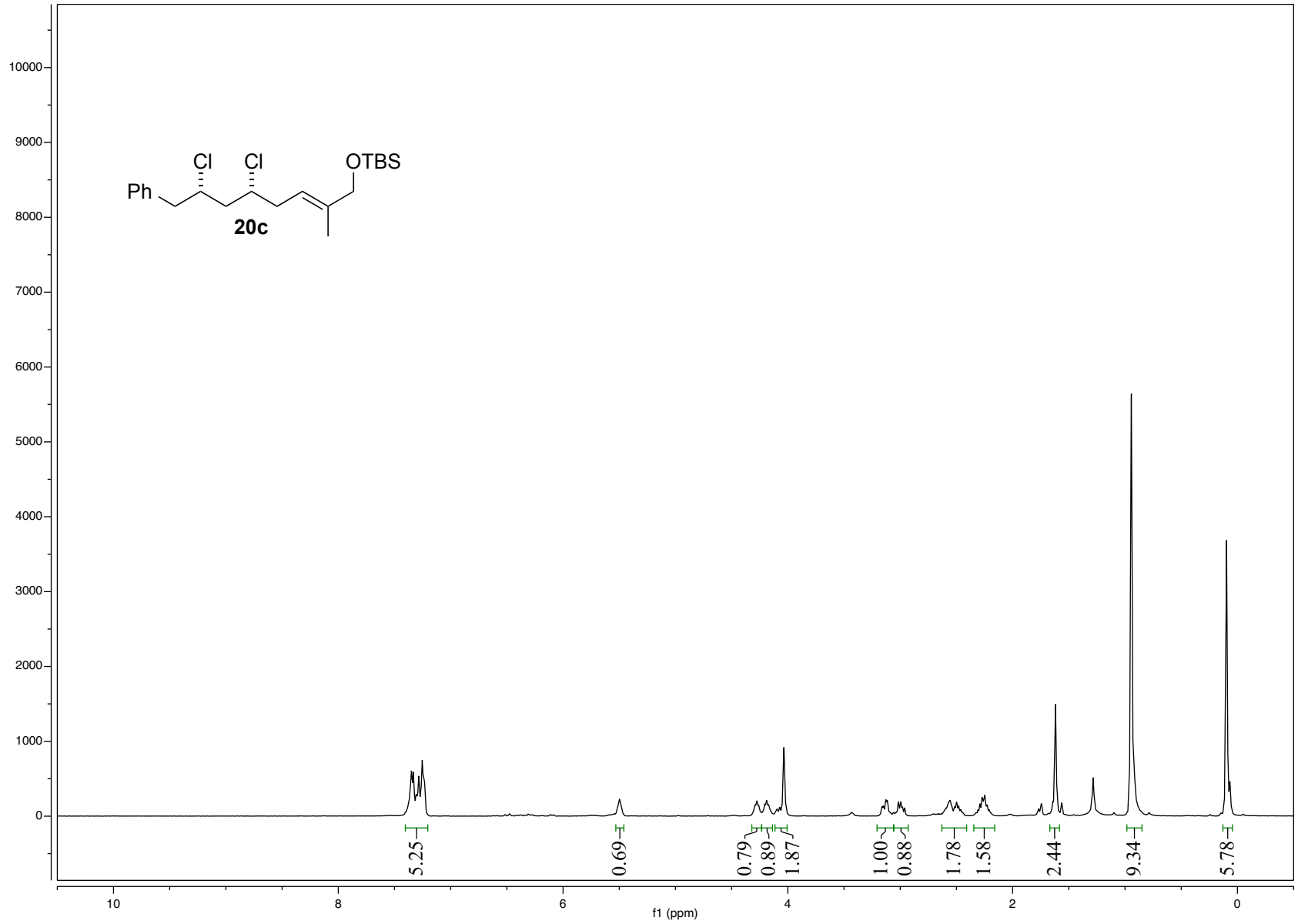

170.4050
138.2780
137.3691
133.4616
129.8080
129.4140
128.4032
127.9231
126.3132
80.6601
77.3174 CDCl3
76.9999 CDCl3
76.6829 CDCl3
71.0271
69.5060
44.0438
43.9964
42.8692
27.9969
-1.2110
-1.3052
SiMe2Ph
OH
O
O
Ph
OtBu
19d
f1 (ppm)

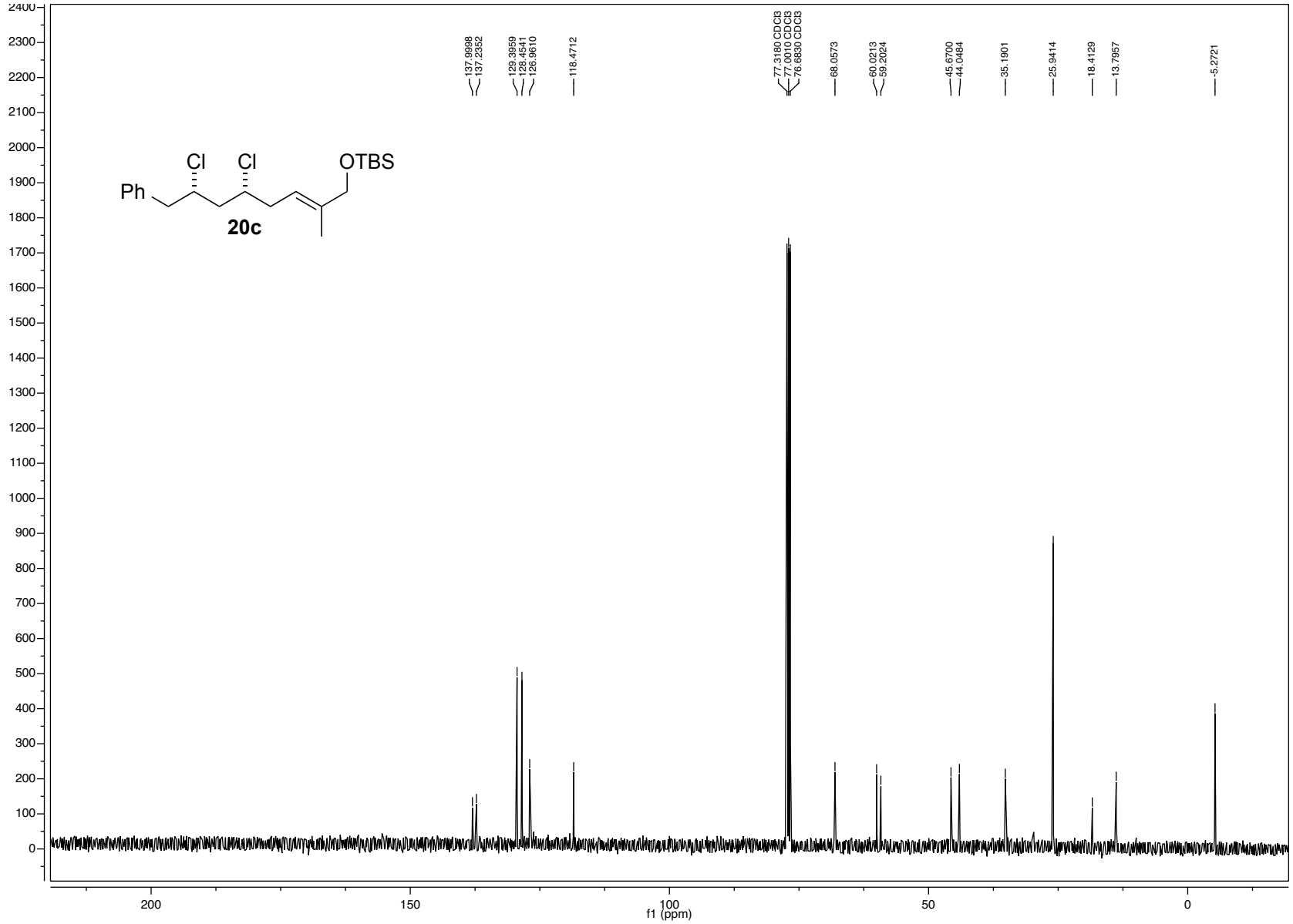

Cl
Cl
Ph
20a
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
−2000
5.40
1.00
2.01
1.97
1.02
0.97
1.04
1.00
1.93
10
8
6
4
2
0
f1 (ppm)

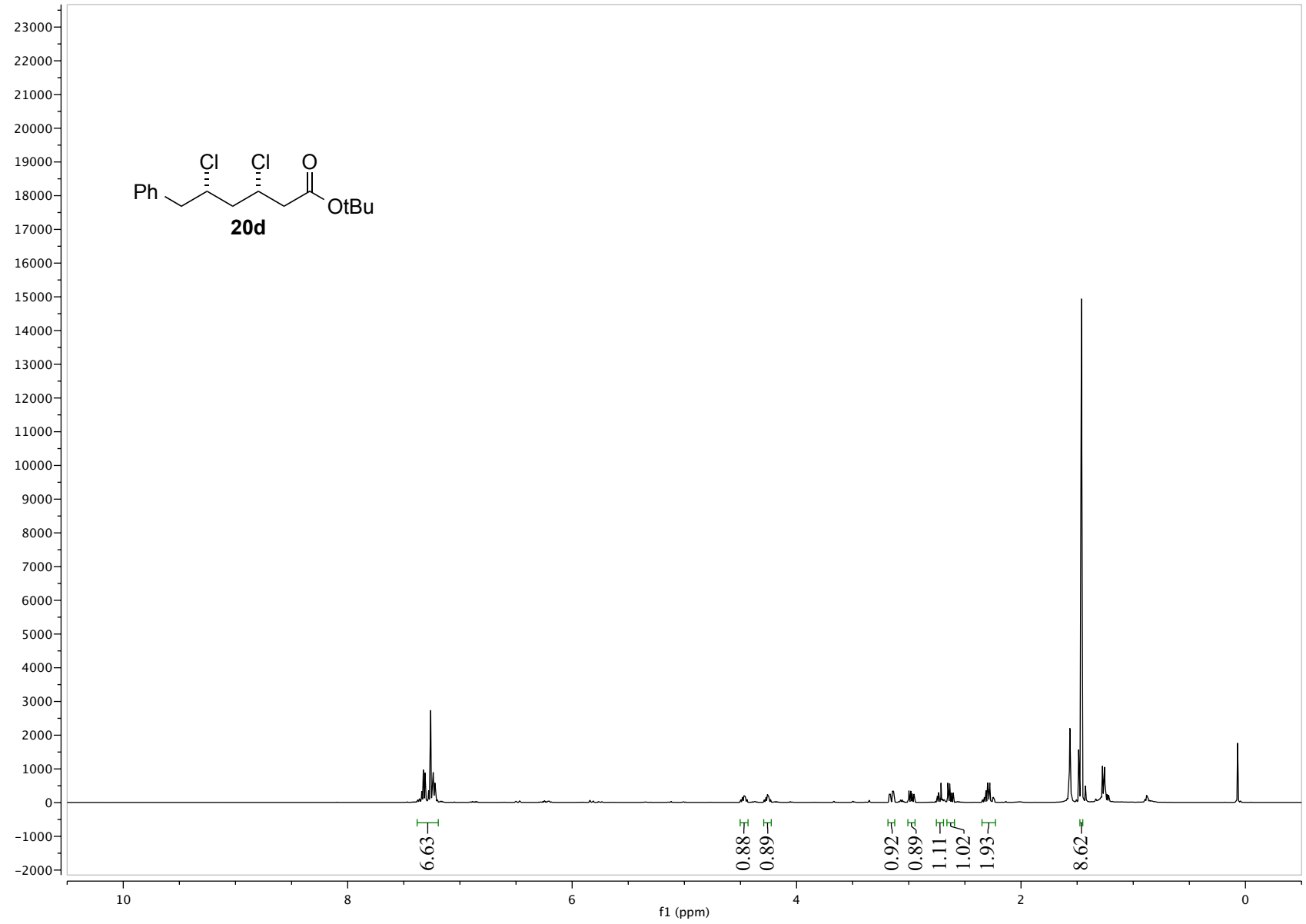

137.1403
133.0430
129.3722
128.4615
126.9800
118.6519
77.3174 CDCl3
77.0001 CDCl3
76.6827 CDCl3
59.8193
58.3026
45.3673
44.1020
41.1318
Cl
Cl
Ph
20a
f1 (ppm)

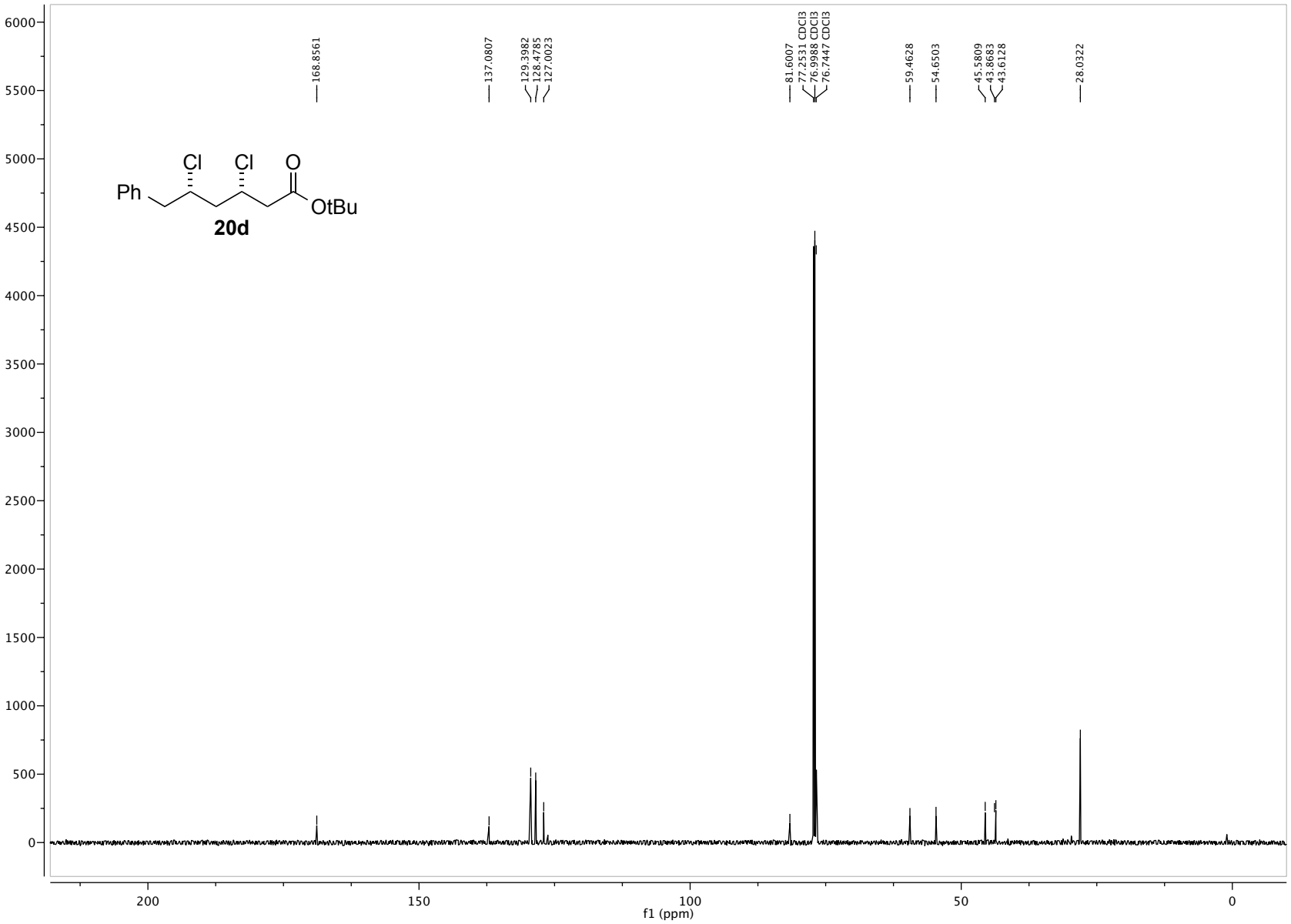

Cl
Cl
Ph
20b
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
5.72
0.87
0.79
0.90
0.82
0.77
0.75
1.06
1.18
2.02
7.74
3.00
10
8
6
4
2
0
f1 (ppm)

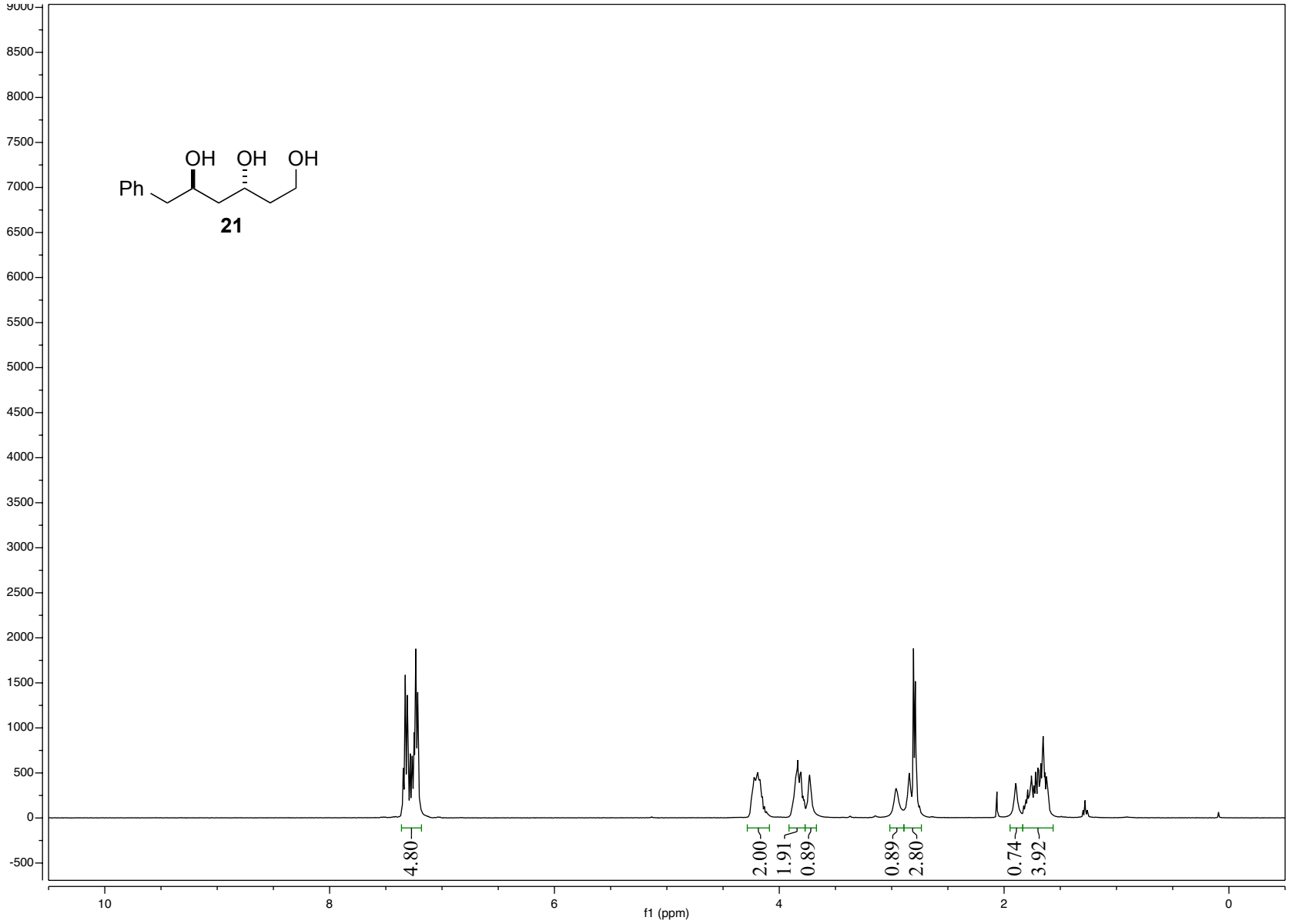

137.2546
129.3872
128.4620
126.9628
77.3188 CDCl3
77.0005 CDCl3
76.6839 CDCl3
59.9603
59.9490
46.2884
44.0698
37.0895
31.7337
29.1013
28.9725
25.9484
22.6172
14.0795
Cl
Cl
Ph
20b
f1 (ppm)

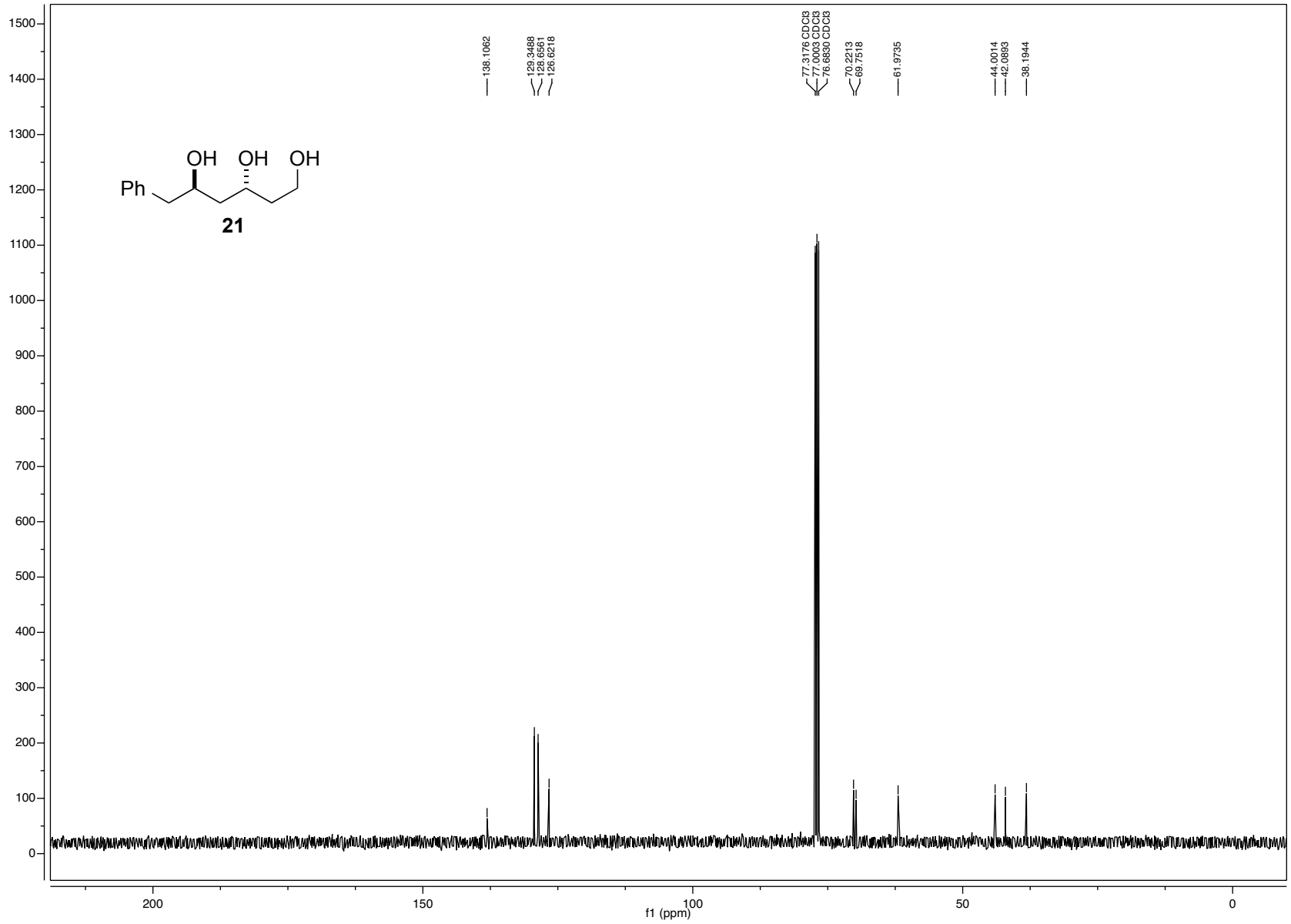

Cl
Cl
OTBS
Ph
20c
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
5.25
0.69
0.79
0.89
1.87
1.00
0.88
1.78
1.58
2.44
9.34
5.78
10
8
6
4
2
0
f1 (ppm)

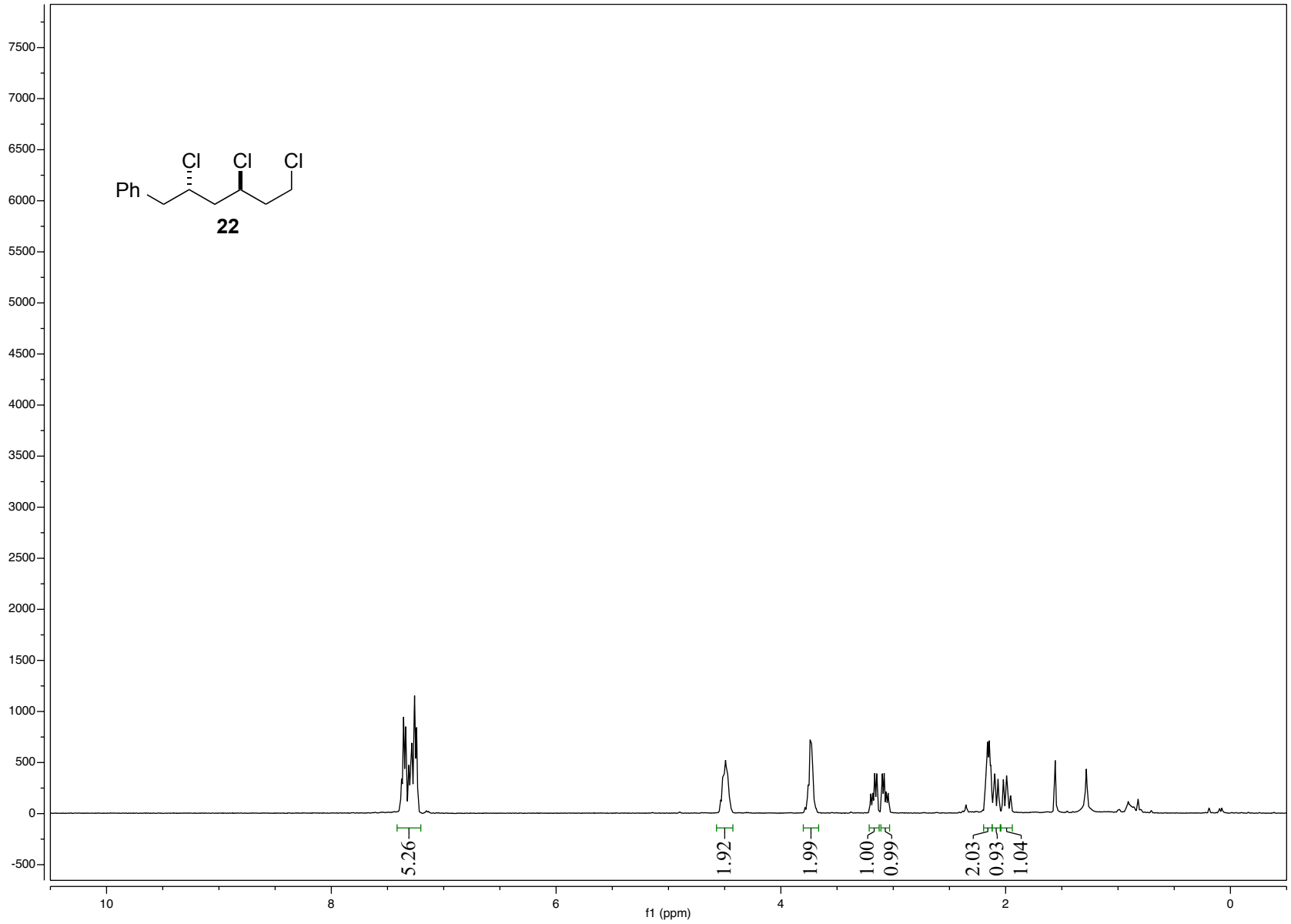

137.9998
137.2352
129.3959
128.4541
126.9610
118.4712
77.3180 CDCl3
77.0010 CDCl3
76.6830 CDCl3
68.0573
60.0213
59.2024
45.6700
44.0484
35.1901
25.9414
18.4129
13.7957
-5.2721
Cl
Cl
OTBS
Ph
20c
f1 (ppm)

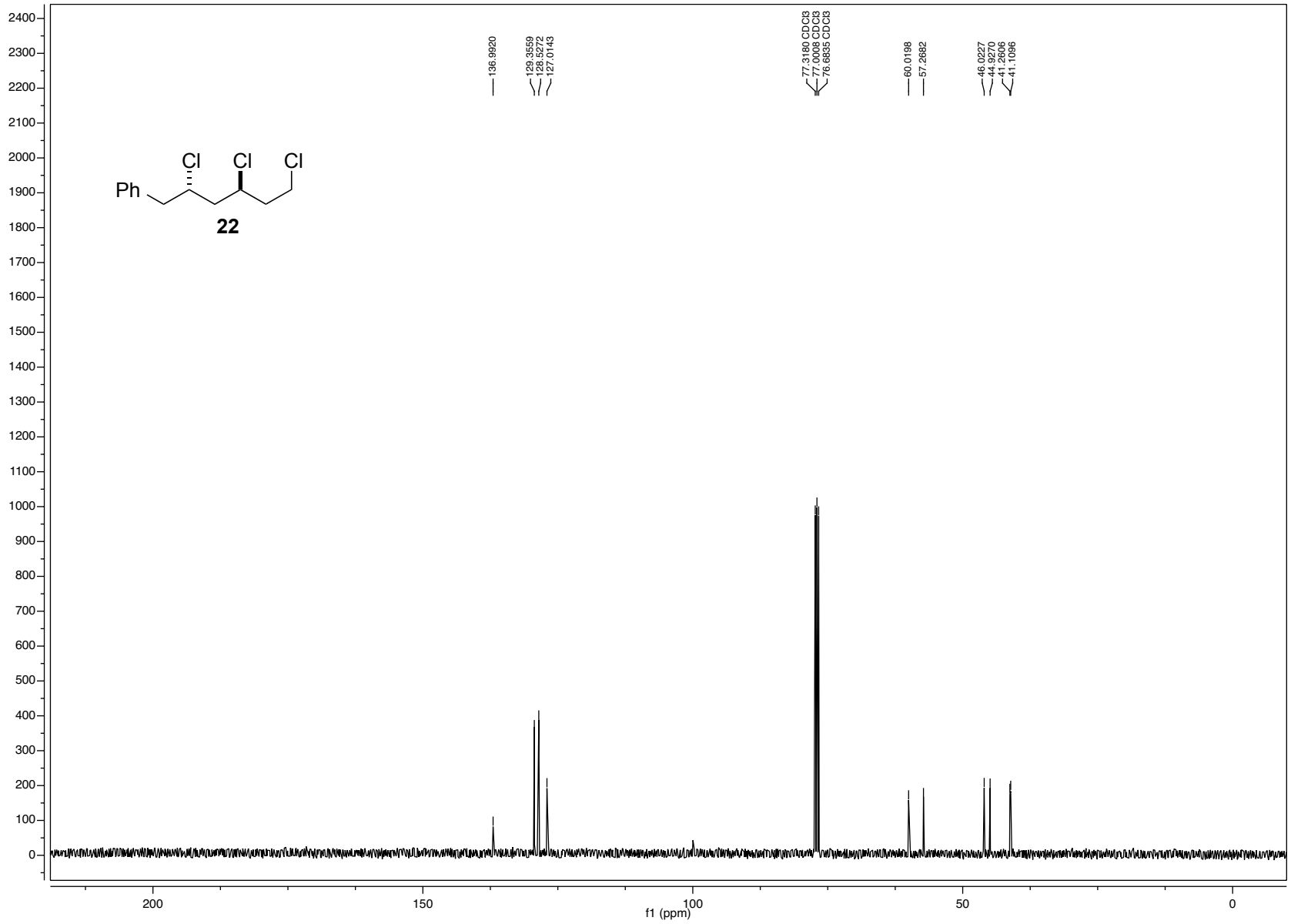

Cl
Cl
O
Ph
OtBu
20d
6.63
0.88
0.89
0.92
0.89
1.11
1.02
1.93
8.62
f1 (ppm)

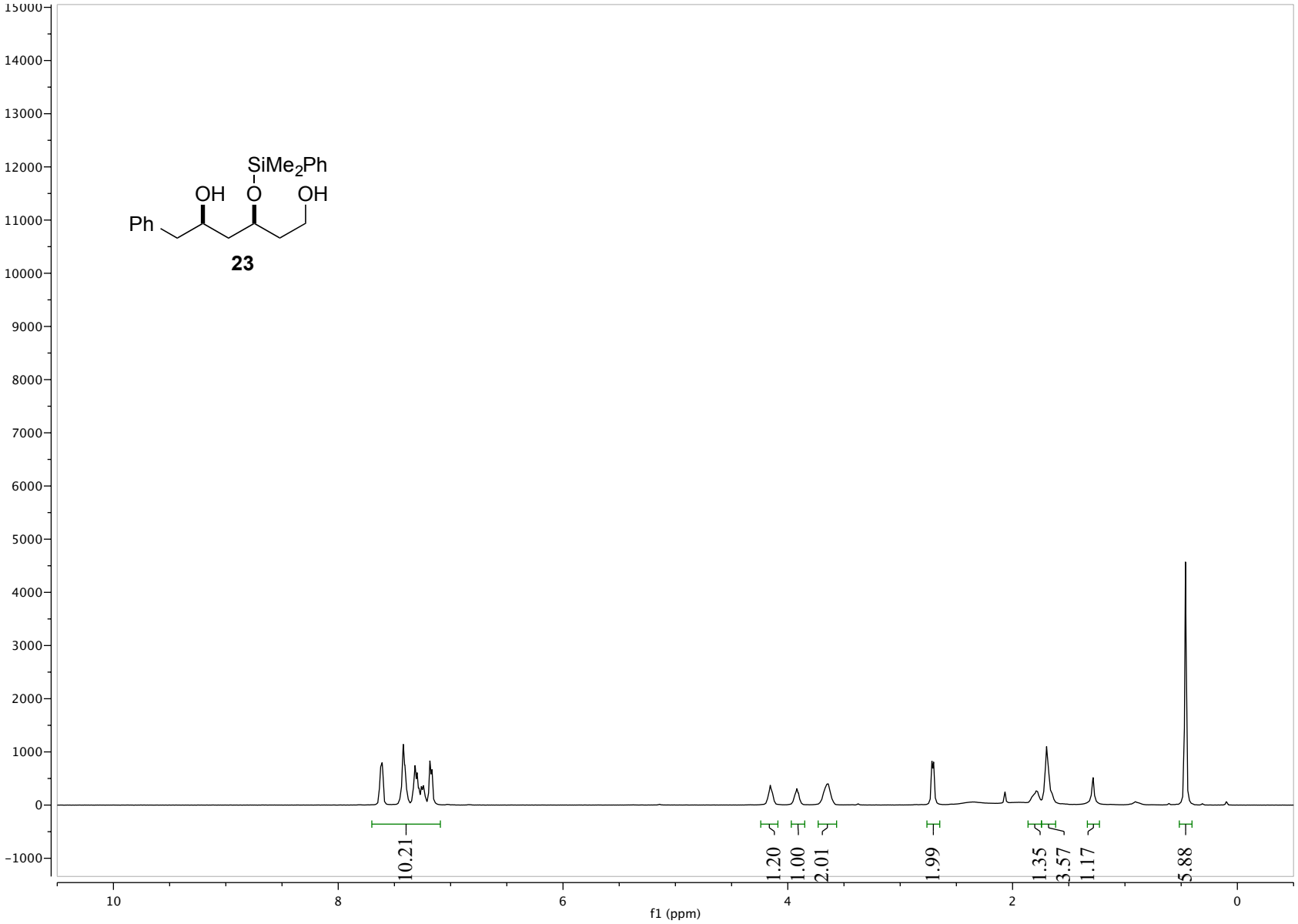

168.8561
137.0807
129.3982
128.4785
127.0023
81.6007
77.2531 CDCl3
76.9988 CDCl3
76.7447 CDCl3
59.4628
54.6503
45.5809
43.8683
43.6128
28.0322
Cl
Cl
O
Ph
OtBu
20d
f1 (ppm)

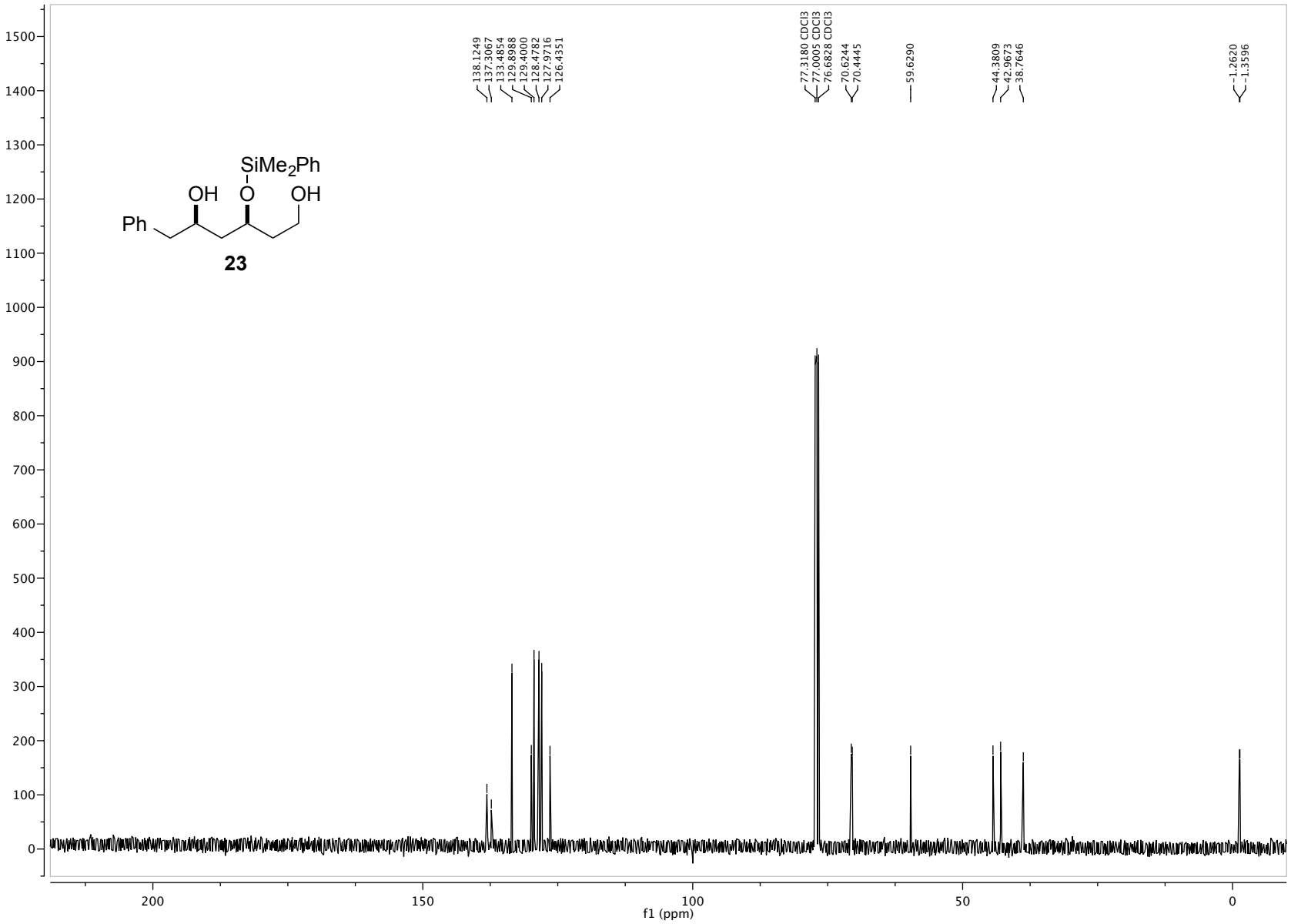

OH
OH
OH
Ph
21
4.80
2.00
1.91
0.89
0.89
2.80
0.74
3.92
f1 (ppm)

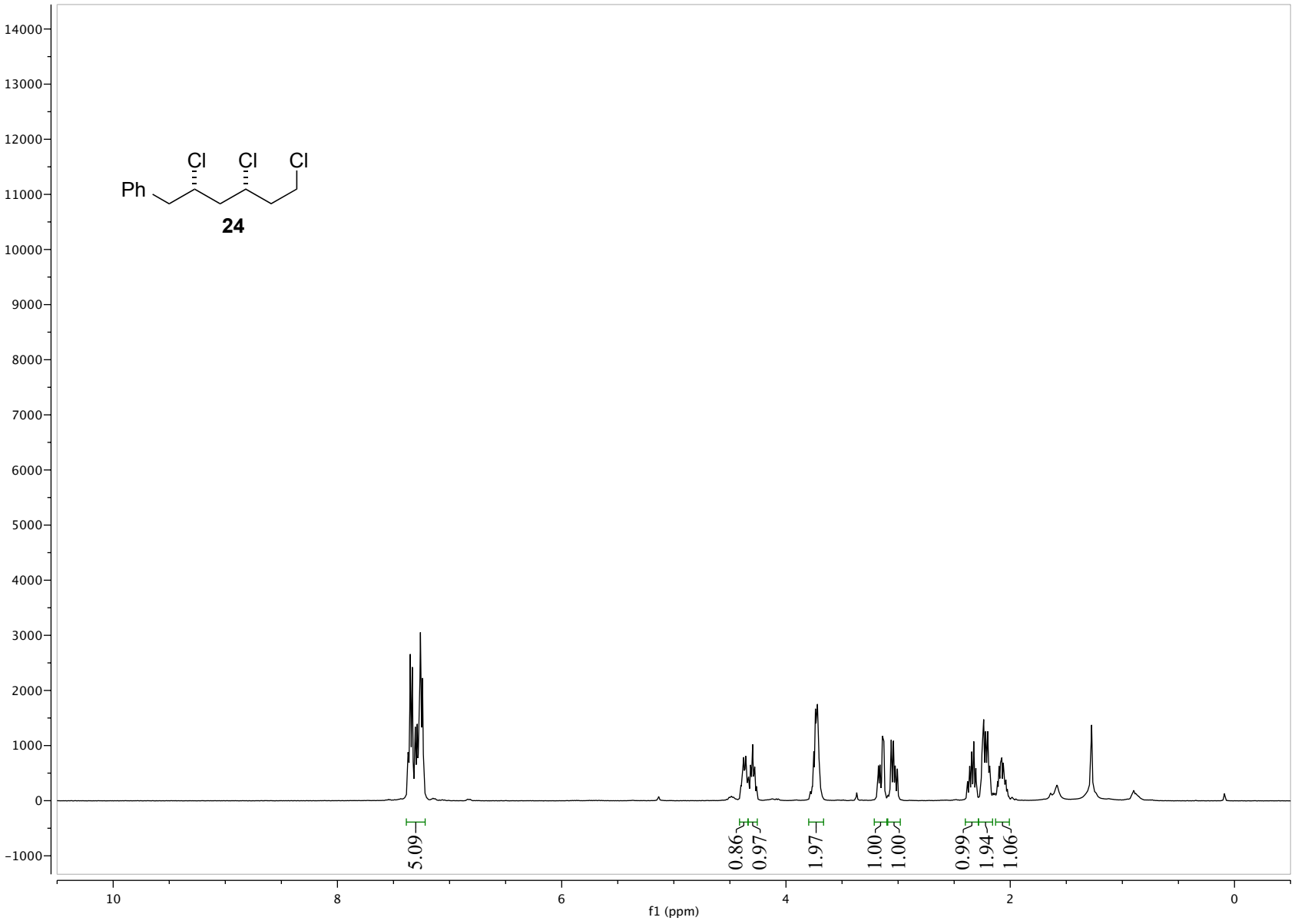

138.1062
129.3488
128.6561
126.6218
77.3176 CDCl3
77.0003 CDCl3
76.6830 CDCl3
70.2213
69.7518
61.9735
44.0014
42.0883
38.1944
OH
OH
OH
Ph
21
f1 (ppm)

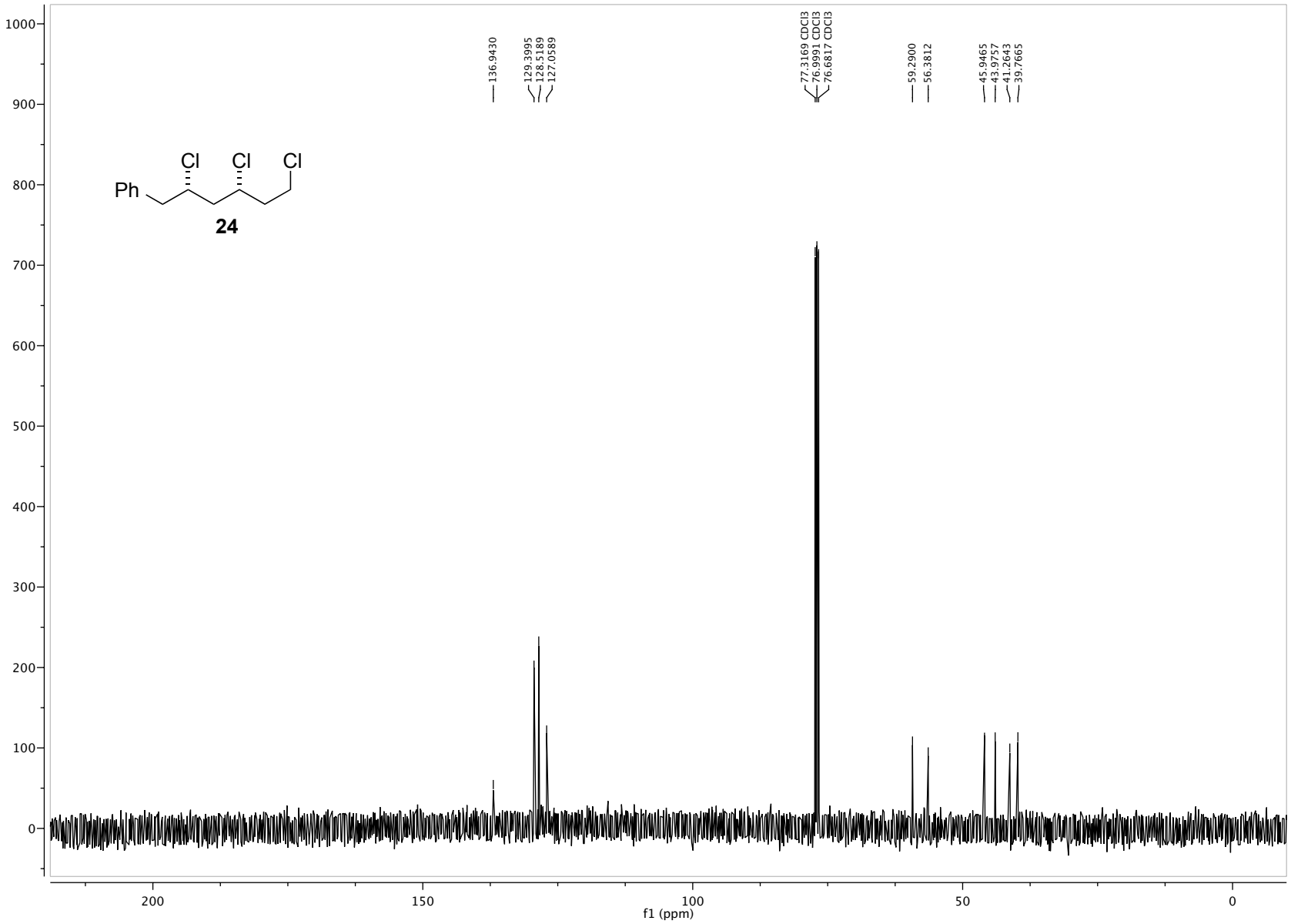

Cl
Cl
Cl
Ph
22
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
5.26
1.92
1.99
1.00
0.99
2.03
0.93
1.04
10
8
6
4
2
0
f1 (ppm)


136.9920
129.3559
128.5272
127.0143
77.3180 CDCl3
77.0008 CDCl3
76.6835 CDCl3
60.0198
57.2682
46.0227
44.9270
41.2606
41.1096
Cl
Cl
Cl
Ph
22
f1 (ppm)


SiMe2Ph
OH
O
OH
Ph
23
10.21
1.20
1.00
2.01
1.99
1.35
3.57
1.17
5.88
f1 (ppm)


SiMe2Ph
OH
O
OH
Ph
23
138.1249
137.3067
133.4854
129.8988
129.4000
128.4782
127.9716
126.4351
77.3180 CDCl3
77.0005 CDCl3
76.6828 CDCl3
70.6244
70.4445
59.6290
44.3809
42.9673
38.7646
-1.2620
-1.3596
f1 (ppm)


Cl
Cl
Cl
Ph
24
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
5.09
0.86
0.97
1.97
1.00
1.00
0.99
1.94
1.06
10
8
6
4
2
0
f1 (ppm)


136.9430
129.3995
128.5189
127.0589
77.3169 CDCl3
76.9991 CDCl3
76.6817 CDCl3
59.2900
56.3812
45.9465
43.9757
41.2643
39.7665
Cl
Cl
Cl
Ph
24
f1 (ppm)