Electronic Supporting Information

Total Synthesis of the Originally Assigned Structure of Vannusal B

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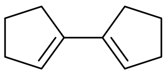
I) Experimental

General Procedures. All reactions were carried out under an argon atmosphere with dry solvent under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF), toluene, benzene, diethyl ether (Et_2O), *N*,*N*-dimethylformamide (DMF), CH_3CN, CH_3OH and methylene chloride (CH_2Cl_2) were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Yields refer to chromatographically and spectroscopically (^1H NMR) homogeneous materials. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated.

Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and an ethanolic solution of phosphomolybdic acid and cerium sulfate, and heat as developing agents. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. NMR spectra were recorded on Bruker DRX-600, DRX-500 or Varian Inova-400 instruments and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, br = broad, td = triple doublet, dt = double triplet, dq = double quartet, pent = pentet.

Infrared (IR) spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a VG ZAB-ZSE mass spectrometer using MALDI (matrix-assisted laser-desorption ionization) or ESI (electrospray ionization).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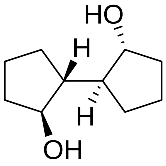
Diene 5: To a stirred solution of commercially available diol **4** (50.0 g, 290.0 mmol) in pyridine (300 mL) at 25 °C in a 1 L 3-neck flask equipped with an internal thermometer was added $POCl_3$ (60.0 mL, 638.0 mmol). The mixture was heated by heat gun until (ca. 70 °C) the reaction mixture began to self-exotherm, at which time the flask was placed into a 25 °C water bath in order to maintain an internal temperature below 100 °C. After the reaction subsided, the flask was placed into an oil bath and heated to 90 °C (30 min), cooled to ambient temperature, and the contents were poured into a vigorously stirred solution of pentane (1 L). From the resulting slurry, the pentane solution was decanted and the remaining solids were quenched with 1 M HCl solution and extracted with pentane (2 × 300 mL). The combined pentane extracts were then washed with 1 M HCl (2 × 400 mL) solution, dried ($MgSO_4$), filtered through a plug of silica gel (eluting with 100 % pentane), and concentrated under reduced pressure (bath temperature was maintained < 20 °C) to afford diene **5** (38.0 g, 281 mmol, 97 %). **5:** $R_f = 0.50$ (silica gel, Et_2O:hexanes, 1:9); IR ν_{max} (film): 2954s, 2844s, 1439, 1294m, 1033m cm^{-1}; ^1H NMR: ($CDCl_3$, 600 MHz) $\delta =$ 5.88 (s, 2 H), 2.49 (dd, $J = 1.2$, 8.4 Hz, 4 H), 2.42 (t, $J = 6.6$ Hz, 4 H), 1.91 (pent, $J = 7.2$ Hz, 4 H) ppm; ^{13}C NMR: ($CDCl_3$, 600 MHz) δ = 140.37, 126.62, 33.01, 32.84, 23.40 ppm; HRMS calcd for $C_{34}H_{64}O_6Si_2Na^+$ [M+Na^+] 647.4133 found 647.4121.

Meso **diol 6:** To a solution of BH_3•THF (1.0 M in THF, 652 mL, 652.0 mmol) at –40 °C was added cyclohexene (66.0 mL, 65.0 mmol, in 500 mL THF) via addition funnel over a period of 30 min. The resulting mixture was stirred at 0 °C (2 h), cooled to –40 °C, and diene **5** (35.0 g, 260 mmol, in 200 mL of THF) was added by addition funnel. The reaction mixture was warmed to 25 °C overnight, after which time it was heated to 50 °C for 30 min and quenched (*carefully!)* at –50 °C with a mixture of 30 % H_2O_2/3 N NaOH (2:1, 1 L). The resulting mixture was warmed to 25 °C and heated to 60 °C for 12 h. After cooling to 25 °C, the reaction mixture was extracted with THF/Et_2O (1:1, 2 × 500 mL). The organic extracts were washed with saturated $Na_2S_2O_4$ solution (1 × 500 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to afford the crude oil. Pure *meso* diol **6** (22.6 g, 132.0 mmol, 50 %) was obtained after precipitation from PhMe as a white solid. **6:** $R_f = 0.5$ (silica gel, acetone/hexanes, 3:2); IR ν_{max} (film): 3279brs, 2941m, 1431w, 1344m, 1028m, 977m cm^{-1}; ^1H NMR: ($CDCl_3$, 600 MHz) δ = 4.01 (t, $J = 4.8$ Hz, 2 H), 1.90 (m, 2 H), 1.87 (m, 2 H), 1.80 – 1.68 (m, 4 H), 1.63 – 1.55 (m, 6 H), 1.40 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 50.97, 35.28, 28.94, 22.41 ppm; HRMS calcd for $C_{10}H_{18}O_2Na^+$ [M+Na^+] 193.1199 found 193.1198.



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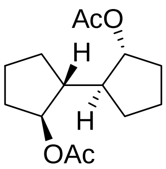
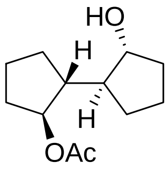
Meso bisacetate 6a: To solution of *meso* diol **6** (18.88 g, 111.0 mmol) in pyridine (300 mL) at 0 °C was added 4-DMAP (0.27 g, 2.2 mmol) and Ac_2O (37.0 mL, 330 mmol). The resulting mixture was warmed to 25 °C (over a period of 8 h), quenched with H_2O (200 mL), and extracted with Et_2O (2 × 250 mL). The ethereal extracts were washed with 1 M HCl solution (3 × 200 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to afford the pure titled compound **6a** (27.9 g, 111.0 mmol, 100 %) as a white solid. **6a:** $R_f = 0.7$ (silica gel, EtOAc/hexanes, 1:1); IR ν_{max} (film): 2957w,



6a

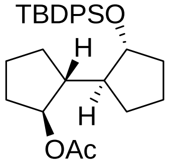
2874w, 1728s, 1439w, 1374m, 1231s, 1024s cm^{-1}; ^{1}H NMR: ($CDCl_3$, 500 MHz) δ = 4.87 (dt, *J* = 4.0, 7.5 Hz, 2 H), 2.00 (s, 6 H), 1.95 – 1.83 (m, 6 H), 1.70 – 1.54 (m, 6 H), 1.32 (m, 2 H) ppm; ^{13}C NMR: ($CDCl_3$, 125 MHz) δ = 170.79, 79.77, 48.11, 32.39, 28.29, 22.91, 21.38 ppm; HRMS calcd for $C_{14}H_{22}O_4Na^+$ [*M*+Na$^+$] 277.141 found 277.1423.

Monoacetate 7: To a solution of *meso* bisacetate **6a** (33.5 g, 132 mmol) in a mixture of acetone/phosphate buffer (pH = 7) (2:1, 1.5 L) was added Lipase Amano PS (100 wt% 33.5 g) and the resulting slurry was vigorously stirred for 36 h at 25 °C. Celite was added and the resulting slurry was filtered and washed with Et_2O. The resulting mixture was diluted with H_2O (1 L) and extracted with Et_2O (3 × 500 mL). The organic extracts were dried ($MgSO_4$), filtered through a silica plug (eluting with 100 % Et_2O), and concentrated under reduced pressure to afford the enantiomerically pure monoacetate **7** (28.0 g, 132 mmol, 100 %, 99 % ee) as a white solid. **7:** R_f = 0.3 (silica gel, EtOAc/hexanes 1:1); $[\alpha]^{25}_{D}$ –19.8 (*c* = 1.0, $CHCl_3$); IR ν_{max} (film): 3414brs, 2953w, 2872w, 1731s, 1713s, 1449w, 1376m, 1238s, 1027m cm^{-1}; ^{1}H NMR: ($CDCl_3$, 600 MHz) δ = 4.95 (dt, *J* = 4.2, 1.2 Hz, 1 H), 3.97 (dd, *J* = 5.4, 6.6 Hz, 1 H), 2.02 (s, 3 H), 1.92, (m, 3 H), 1.84 (m, 3 H), 1.67 (m, 4 H), 1.58 (m, 2 H), 1.39 (dq, *J* = 4.2, 3.6 Hz, 1 H), 1.28 (dq, *J* = 4.8, 9.0 Hz, 1 H) ppm; ^{13}C NMR: ($CDCl_3$, 150 MHz) δ = 171.15, 79.71, 76.78, 50.92, 48.13, 35.31, 32.34, 29.06, 28.75, 22.85, 22.47 ppm; HRMS calcd for $C_{12}H_{20}O_3H^+$ [*M*+H$^+$] 213.1485 found 213.1485.



7

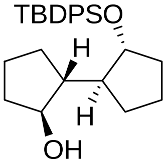
TBDPS silyl ether 7a: To a solution of monoacetate **7** (23.0 g, 107.6 mmol) in CH_2Cl_2 (500 mL) was added imidazole (20.0 g, 293.7 mmol) and TBDPSCl (33.44 mL, 120.0 mmol). The reaction mixture was stirred at 25 °C (12 h), concentrated under reduced pressure, and purified by flash column chromatography (5→10 % Et_2O/hexanes) to afford silyl ether **7a** (45.0 g, 99.9 mmol, 99 %) as a colorless oil. **7a:** R_f = 0.5 (silica gel, Et_2O:hexanes, 4:6); $[\alpha]^{25}_{D}$ +5.43 (*c* = 1.6, $CHCl_3$); IR ν_{max} (film): 2956m, 2857m, 1733s, 1472w, 1427w, 1362w, 1243s, 1110s cm^{-1}; ^{1}H NMR: ($CDCl_3$, 500 MHz) δ = 7.67 (dd, *J* = 1.5, 8.0, 4 H), 7.40 (m, 6 H), 4.83 (dt, *J* = 3.0, 6.0 Hz, 1 H), 4.01 (dt, *J* = 3.5, 5.0 Hz, 1 H), 1.94 (s, 3 H), 1.90 (m, 1 H), 1.80 (m, 2 H), 1.73 (m, 1 H), 1.66 (m, 2 H), 1.61 (m, 2 H), 1.50 (m, 5 H), 1.31 (ddd, *J* = 6.0, 7.0, 13.0 Hz, 1 H), 1.04 (s, 9 H) ppm; ^{13}C NMR: ($CDCl_3$, 150 MHz) δ = 170.68, 135.87, 135.81, 135.26, 134.73, 134.43, 130.01, 129.46, 129.38, 127.67,



7a

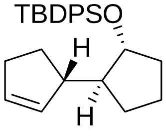
127.45, 127.40, 80.21, 79.06, 51.69, 47.7, 34.46, 32.55, 29.43, 27.86, 26.96, 23.14, 22.47, 21.38 ppm; HRMS calcd for $C_{28}H_{38}O_3SiH^+$ [M+H$^+$] 451.2663 found 451.2656.

Alcohol 7b: To a solution of **7b** (40.0 g, 88.8 mmol) in CH_2Cl_2 (1 L) at –78 °C was added DIBAL-H (1.0 M in hexanes, 220.0 mL, 220.0 mmol) and the mixture was stirred for 30 min. The reaction mixture was quenched with EtOH (20 mL) followed by a saturated Rochelle's salt solution (500 mL). The resulting mixture was vigorously stirred (until the layers separated) and extracted with Et_2O (2 × 400 mL). The organic extracts were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography (10→30 % Et_2O/hexanes), to afford alcohol **7b** (35.1 g, 88.6 mmol, 98 %). **7b:** R_f = 0.3 (silica gel, Et_2O:hexanes, 4:6); $[\alpha]^{25}_D$ +0.52 (c = 2.7, $CHCl_3$); IR ν_{max} (film): 3346brs, 2952m, 2857w, 1472w, 1427m, 1109s cm^{-1}; ^{1}H NMR: ($CDCl_3$, 500 MHz) δ = 7.70 (dd, J = 1.5, 8.0 Hz 2 H), 7.68 (dd, J = 1.5, 8.0 Hz, 2 H), 7.40 (m, 6 H), 4.04 (ddd, J = 2.0, 3.5, 5.5 Hz, 1 H), 3.83 (brs, 1 H), 1.94 (m, 1 H), 1.83 (m, 1 H), 1.76 (m, 1 H), 1.64 (m, 3 H), 1.44 (m, 3 H), 1.35 (ddd, J = 6.0,7.0, 13.0 Hz, 1 H), 1.06 (s, 9 H) ppm; ^{13}C NMR: ($CDCl_3$, 125 MHz) δ = 135.91, 135.87, 134.73, 134.50, 129.53, 129.45, 127.49, 127.43, 78.73, 77.40, 51.61, 50.87, 35.29, 34.64, 29.31, 28.05, 26.99, 2.68, 22.52 ppm; HRMS calcd for $C_{26}H_{36}O_2SiNa^+$ [M+Na$^+$] 431.2377 found 431.2392.



7b

Olefin 8: To a solution of alcohol **7b** (90 mg, 0.22 mmol) in CH_2Cl_2 (2 mL) at 25 °C were sequentially added Et_3N (150 μL, 1.1 mmol) and Martins' sulfurane (0.2 g, 0.264 mmol) in CH_2Cl_2 (1 mL). The resulting reaction mixture was stirred for 18 h and then quenched with saturated $NaHCO_3$ solution (20 mL). The resulting mixture was extracted with hexanes (2 x 10 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography (silica gel, 2 % Et_2O/hexanes) to afford olefin **8** (79 mg, 0.20 mmol, 91 %) as a colorless oil. **8:** R_f = 0.70 (silica gel, Et_2O/hexanes, 1:19); $[\alpha]^{25}_D$ –44.33 (c = 2.1, $CHCl_3$); IR ν_{max} (film): 2953m, 2856m, 1472w, 1427m, 1109s cm^{-1}; ^{1}H NMR: ($CDCl_3$, 600 MHz) δ = 7.74 (m, 4 H), 7.47 – 7.40 (m, 6 H), 5.72 (m, 1 H), 5.48 (m, 1 H), 4.03 (dd, J = 4.2, 9.6 Hz, 1 H), 2.57 (m, 1 H), 2.22 (m, 2 H), 1.93 (m, 1 H), 1.86 (m, 2 H), 1.77 (m, 1 H), 1.64 (m, 1 H), 1.53 (m, 2



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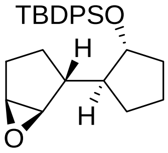
H), 1.34 (ddd, $J = 5.4, 6.6, 13.2$ Hz, 1 H), 1.25 (ddd, $J = 7.2, 12.0, 14.4$ Hz, 1 H) ppm; ^{1}H NMR: ($CDCl_3$, 150 MHz) $\delta = 135.84, 135.88, 134.83, 134.51, 132.98, 131.17, 129.41, 129.37, 127.44, 127.40, 78.91, 53.25, 47.71, 34.81, 32.08, 28.50, 27.03, 26.75, 22.30, 19.19$ ppm; HRMS calcd for $C_{26}H_{34}O_2SiH^+$ [M+H$^+$] 407.2401 found 407.2397.



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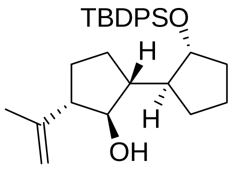
Epoxide 9: To a stirred solution of olefin **8** (34.9 g, 85.9 mmol) in THF/H_2O (4:1, 750 mL) at 0 °C was added NIS (30.0 g, 133.0 mmol) portionwise over 5 min. The reaction mixture was stirred at this temperature for 30 min, and then warmed to 25 °C (1 h). To the resulting mixture were then added MeOH (600 mL) and K_2CO_3 (30.7 g, 220.0 mmol) and the mixture was stirred for 12 h. The reaction mixture was quenched with H_2O (1 L), extracted with Et_2O (2 × 300 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give an oil (15:1 dr based on crude NMR). The crude residue was purified by flash column chromatography (silica gel, 2→20 %, Et_2O/hexanes) to afford epoxide **9** (32.9 g, 80.9 mmol, 90 %) as a single diastereoisomer. **9:** $R_f = 0.50$ (silica gel, Et_2O/hexanes, 1:5); $[\alpha]^{25}_{D}$ 0.0 ($c = 2.6$, $CHCl_3$); IR ν_{max} (film): 2955m, 2931w, 2857m, 1589w, 1472w, 1427m, 1109s cm^{-1}; ^{1}H NMR: ($CDCl_3$, 600 MHz) $\delta = 7.67$ (t, $J = 6.6$ Hz, 4 H), 7.43 (m, 2 H), 7.38 (t, $J = 6.6$ Hz, 4 H), 3.99 (dd, $J = 3.6, 9.0$ Hz, 1 H), 3.36 (d, $J = 1.8$ Hz, 1 H), 3.13 (d, $J = 2.4$ Hz, 1 H), 1.93 (m, 2 H), 1.80 (dd, $J = 7.8, 13.8$ Hz, 1 H), 1.74 (m, 2 H), 1.61 (ddd, $J = 3.6, 8.4, 12.0$ Hz, 1 H), 1.55 (m, 1 H), 1.48 (m, 1 H), 1.42 (m, 1 H), 1.35 – 1.20 (m, 2 H), 1.05 (s, 9 H); ^{13}C NMR: ($CDCl_3$, 150 MHz) $\delta = 135.84, 134.57, 134.26, 129.58, 127.54, 127.47, 78.95, 59.42, 57.37, 49.41, 41.46, 34.50, 27.93, 26.99, 25.95$ ppm; HRMS calcd for $C_{26}H_{34}O_2SiH^+$ [M+H$^+$] 407.2401 found 407.2397.

Hydroxy olefin 10: To a stirred solution of 2-bromopropene (2.83 ml, 32.4 mmol) in THF (120 mL) at –78 °C was added *t*BuLi (1.7 M in pentane, 38.0 mL, 64.0 mmol). The mixture which developed a light yellow color, was stirred for 2 min, after which time an additional portion of 2-bromopropene (0.3 mL, 3.4 mmol) was added to ensure the disappearance of any remaining *t*BuLi (and yellow color). Immediately following this addition, $BF_3 \cdot Et_2O$ (2.04 mL, 16.2 mmol) was added followed by cannulation of a solution of epoxide **9** (3.30 g, 8.11 mmol) in THF (30 mL) at –78 °C. The mixture was stirred for 20 min a –78 °C and then placed into a –40 °C bath and stirred for 30 min. The reaction mixture was quenched by the addition of saturated $NaHCO_3$



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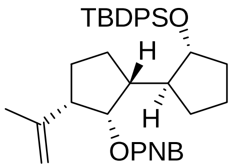
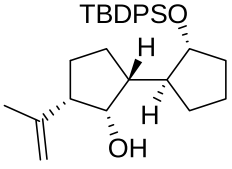
solution (50 mL). The resulting mixture was extracted with Et_2O (2 × 100 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (silica gel, 5→10 % Et_2O/hexanes) to afford alcohol **10** (3.01 g, 6.68 mmol, 83 %) as a colorless oil. **10**: R_f = 0.50 (silica gel, Et_2O/hexanes, 3:7); $[\alpha]^{25}_{D}$ +1.93 (*c* = 1.4, $CHCl_3$); IR ν_{max} (film): 3453brs, 2955s, 2858m, 1472w, 1427w, 1110s, 1044s cm^{-1}; ^1H NMR: ($CDCl_3$, 600 MHz) δ = 7.71 (m, 4 H), 7.40 (m, 6 H), 4.77(s, 1 H), 4.74, (s, 1 H), 4.08 (dt, *J* = 2.4, 3.0 Hz, 1 H), 3.54 (t, *J* = 8.4 Hz, 1 H), 2.24 (q, *J* = 8.4 Hz, 1 H), 2.00, (m, 1 H), 1.98 (m, 1 H), 1.80 (m, 1 H), 1.67 (s, 3 H), 1.64 (m, 4 H), 1.53 (m, 5 H), (dq, *J* = 4.2, 6.0 Hz, 1 H), 1.11 (m, 1 H), 1.05 (s, 9 H) ppm; ^{13}C NMR: ($CDCl_3$, 150 MHz) δ = 145.93, 135.90, 135.87, 134.78, 134.59, 129.47, 129.41, 127.46, 127.42, 110.74, 79.32, 78.63, 55.58, 52.02, 47.65, 34.90, 27.63, 27.00, 26.44, 26.18, 22.65, 19.78 ppm; HRMS calcd for $C_{29}H_{40}O_2SiH^+$ [*M*+H^+] 449.2870 found 449.2864.

***P*-nitrobenzoate 10a:** To a stirred solution of alcohol **10** (7.25 g, 16.0 mmol) in benzene (200 mL) at 25 °C was added *p*NO_2-$C_6H_4CO_2H$ (4.0 g, 24.0 mmol), Ph_3P (7.55 g, 28.8 mmol), and DEAD (4.2 mL, 24.0 mmol). The resulting solution was stirred at ambient temperature for 16 h. The reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (silica gel, 2→5 % Et_2O/hexanes) to afford *p*-nitrobenzoate **10a** (9.01 g, 15.0 mmol, 94 %) as a yellow foam. **10a:** R_f = 0.40 (silica gel, Et_2O/hexanes, 1:9); $[\alpha]^{25}_{D}$ +3.33 (*c* = 1.2, $CHCl_3$); IR ν_{max} (film): 2958m, 2850w, 1724s, 1530s, 1346m, 1271s, 1111s cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ = 8.30 (d, *J* = 8.4 Hz, 2 H), 8.10 (d, *J* = 8.4 Hz, 2 H), 7.64 (dd, *J* = 3.0, 6.6 Hz, 4 H), 7.43 (t, *J* = 7.2 Hz, 1 H), 7.41 (d, *J* = 7.2 Hz, 1 H), 7.37 (t, *J* = 7.2 Hz, 2 H), 7.32 (t, *J* = 7.2 Hz, 2 H), 5.62 (t, *J* = 3.5 Hz, 1 H), 4.71 (s, 1 H), 4.66 (s, 1 H), 4.05 (dd, *J* = 1.8, 2.4 Hz, 1 H), 2.48 (t, *J* = 9.0 Hz, 1 H), 1.90 – 1.81 (m, 3 H), 1.76 (s, 3 H), 1.64 (m, 2 H), 1.51 (m, 2 H), 1.34 (m, 1 H), 1.27 (m, 1 H), 1.00 (s, 9 H) ppm; ^{13}C NMR: ($CDCl_3$, 150 MHz) δ = 163.61, 150.29, 142.94, 135.96, 135.79, 133.74, 133.61, 130.52, 129.48, 129.45, 127.42, 127.37, 123.49, 111.36, 79.12, 78.56, 51.21, 49.38, 47.96, 34.16, 28.82, 26.90, 26.78, 25.72, 23.67, 22.38 ppm; HRMS calcd for $C_{36}H_{43}NO_5SiH^+$ [*M*+H^+] 620.2803 found 620.2805.

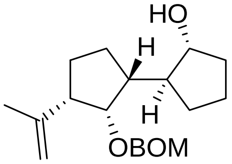


10a



11

Hydroxy olefin 11: To a stirred solution of **10a** (9.01 g, 15.0 mmol) in CH_2Cl_2 (200 mL) at –78 °C was added DIBAL-H (1.0 M in hexanes, 45.0 mL, 45.0 mmol). The resulting mixture was stirred for 30 min at this temperature and then quenched carefully with EtOH (5 mL) and saturated Rochelle's salt solution (200 mL). The mixture was warmed to 25 °C and stirred until the layers had separated. The resulting mixture was extracted with CH_2Cl_2 (200 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (silica gel, 2→10 % Et_2O/hexanes) to furnish hydroxy olefin **11** (6.47 g, 14.4 mmol, 96 %) as a colorless oil. **11:** R_f = 0.30 (silica gel, Et_2O/hexanes, 1:9); $[\alpha]^{25}_{D}$ +4.46 (*c* = 1.3, $CHCl_3$); IR ν_{max} (film): 3539br, 2957m, 2857m, 1645w, 1472w, 1427m, 1110s cm^{-1}; ^1H NMR: ($CDCl_3$, 600 MHz) δ = 7.69 (dd, *J* = 1.2, 7.2 Hz, 4 H), 7.42 – 7.36 (m, 6 H), 4.99 (d, *J* = 1.2 Hz, 1 H), 4.83 (s, 1 H), 4.03 (m, 1 H), 3.96 (t, *J* = 3.6 Hz, 1 H), 2.36 (m, 1 H), 2.11 (m, 1 H), 1.80 (s, 3 H), 1.78 (m, 2 H), 1.59 (m, 3 H), 1.51 (m, 1 H), 1.48 – 1.25 (m, 6 H), 1.04 (s, 9 H) ppm; ^{13}C NMR: ($CDCl_3$, 150 MHz) δ = 144.30, 135.96, 135.88, 135.03, 134.50, 129.39, 129.32, 127.42, 127.37, 111.72, 79.52, 73.33, 52.55, 49.28, 48.84, 34.29, 28.82, 27.01, 26.77, 24.99, 23.68, 22.38 ppm; HRMS calcd for $C_{21}H_{30}O_3SiH^+$ [M+H^+] 449.287 found 449.286.

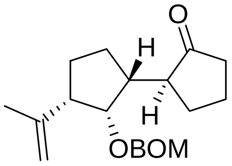


12

Alcohol 12: To a stirred solution of hydroxyl olefin **11** (6.47 g, 14.4 mmol) in PhMe (150 mL) was added *n*Bu_4NI (5.0 g, 14.4 mmol), *i*Pr_2NEt (25 mL, 144 mmol), and BOMCl (6.7 mL, 43.0 mmol). The resulting mixture was heated to 90 °C for 12 h. After cooling to 25 °C, the reaction mixture was quenched by the addition of saturated $NaHCO_3$ solution (50 mL), extracted with Et_2O (2 × 100 mL), dried ($MgSO_4$), and concentrated under reduced pressure. To the crude residue was added TBAF (1.0 M in THF, 150 mL, 15.0 mmol) and the resulting mixture was heated to 70 °C for 8 h. The mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel, 5→40 % EtOAc/hexanes) to furnish alcohol **12** (4.62 g, 13.9 mmol, 95 %). **12:** R_f = 0.30 (silica gel, EtOAc/hexanes, 3:7); $[\alpha]^{25}_{D}$ –41.00 (*c* = 1.1, $CHCl_3$); IR ν_{max} (film): 3399brs, 2952m, 2871m, 1647w, 1453w, 1160w, 1026s cm^{-1}; ^1H NMR: ($CDCl_3$, 600 MHz) δ = 7.34 (m, 4 H), 7.28 (m, 1 H), 4.88 (s, 1 H), 4.86 (s, 1 H), 4.72 (d, *J* = 6.6 Hz, 1 H), 4.69 (d, *J* = 6.6 Hz, 1 H), 4.64 (d, *J* = 12.0 Hz, 1 H), 4.57 (d, *J* =

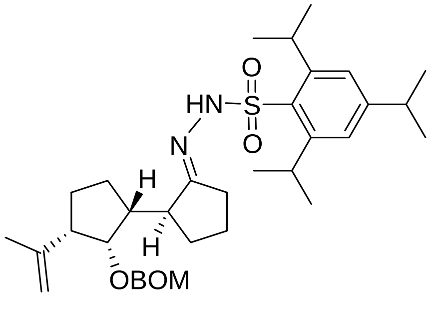
12.0 Hz, 1 H), 4.12 (t, *J* = 2.4 Hz, 1 H), 4.03 (m, 1 H), 2.37 (t, *J* = 9.6 Hz, 1 H), 2.02 (m, 2 H), 1.95 (m, 1 H), 1.87 (m, 2 H), 1.84 (s, 3 H), 1.78 (d, *J* = 3.6 Hz, 1 H), 1.76 – 1.68 (m, 4 H), 1.63 – 1.54 (m, 2 H), 1.35 (dt, *J* = 7.8, 12.6 Hz, 1 H) ppm; ^{13}C NMR: ($CDCl_3$, 150 MHz) δ = 144.04, 138.05, 128.33, 127.67, 127.53, 111.51, 94.89, 82.08, 77.45, 70.00, 52.02, 49.60, 48.87, 34.97, 30.61, 25.88, 25.23, 23.69, 22.32 ppm; HRMS calcd for $C_{21}H_{30}O_3SiNa^+$ [*M*+Na$^+$] 353.2087 found 353.2090.

Ketone 12a: To a stirred solution of alcohol **12** (35.1 g, 85.9 mmol) in CH_2Cl_2/CH_3CN (9:1, 500 mL) was added freshly dried 4 Å MS and NMO (15.12 g, 129.0 mmol). The mixture was stirred for 10 min before TPAP (1.0 g, 2.5 mmol) was added, and the resulting reaction mixture was stirred 12 h at 25 °C. The reaction mixture was quenched by the addition of celite and hexanes (150 mL) and the resulting slurry was filtered through a plug of silica gel (eluting with hexanes/Et_2O, 1:1), concentrated under reduced pressure, and purified by flash column chromatography (2→10 % Et_2O/hexanes) to afford ketone **12a** (33.5 g, 82.5 mmol, 90 %) as a colorless oil. **12a:** R_f = 0.30 (silica gel, Et_2O/hexanes, 3:7); $[\alpha]^{25}_D$ –90.90 (*c* = 1.1, $CHCl_3$); IR ν_{max} (film): 2960w, 1734s, 1647w, 1454w, 1102w, 1039m cm^{-1}; ^{1}H NMR: (C_6D_6, 600 MHz) δ = 7.26 (d, *J* = 7.8 Hz, 2 H), 7.17 (d, *J* = 7.8 Hz, 2 H), 7.08 (t, *J* = 7.8 Hz, 1 H), 4.90 (s, 1 H), 4.86 (s, 1 H), 4.58 (d, *J* = 7.2 Hz, 1 H), 4.56 (d, *J* = 7.2 Hz, 1 H), 4.51 (d, *J* = 12.0 Hz, 1 H), 4.36 (d, *J* = 12.0 Hz, 1 H), 3.90 (t, *J* = 2.4 Hz, 1 H), 2.28 (dd, *J* = 9.6, 17.4 Hz, 1 H), 2.16 (dd, *J* = 7.8, 17.4 Hz, 1 H), 2.06 (m, 4 H), 1.94 (m, 1 H), 1.83 (q, *J* = 9.0 Hz, 1 H), 1.69 (s, 3 H), 1.61 (m, 2 H), 1.48 (m, 1 H), 1.28 (m, 2 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 218.61, 144.17, 138.76, 128.52, 127.63, 111.87, 95.22, 82.77, 69.96, 51.94, 49.76, 46.83, 38.19, 29.62, 26.84, 25.65, 23.66, 20.79 ppm; HRMS calcd for $C_{21}H_{28}O_3SiNa^+$ [*M*+Na$^+$] 351.1931 found 351.1937.

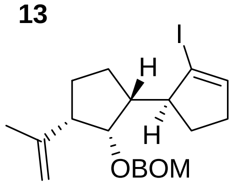


12a

Hydrazone 13 and Vinyl iodide 2: To a solution of ketone **12a** (0.49 g, 1.49 mmol) in THF (8 mL) was added $TrisNHNH_2$ (0.67g, 2.23 mmol). The resulting mixture was stirred at 25 °C for 5 h. PhMe (5 mL) was added and the mixture was concentrated under reduced pressure. The crude residue was directly purified by flash column chromatography (2→10 % EtOAc/hexanes) to afford hydrazone **13** (0.72 g, 1.15 mmol, 80 %). **13:** R_f = 0.30 (silica gel, Et_2O/hexanes, 3:7). Hydrazone **13** was dried overnight under high vacuum and over P_2O_5 before use in the next step.



13

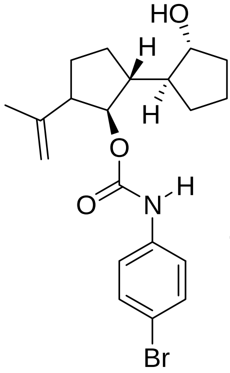


2

To a solution of hydrazone **13** (1.15 g, 1.89 mmol) in THF (40 mL) at –78 °C was added *n*BuLi (2.5 M in hexanes, 1.60 mL, 3.97 mmol). The flask containing the resulting dark orange solution was placed in a –30 °C bath and allowed to slowly warm to –25 °C (15 min), during which time the color of the solution changed from dark orange to light yellow as nitrogen gas was evolved. Upon the completion of gas evolution, the reaction mixture was stirred an additional 5 min before cooling to –78 °C and adding a solution of I_2 (1.35 g, 5.67 mmol) in THF (5 mL). The resulting mixture was warmed to –25 °C and quenched by the addition of saturated $Na_2S_2O_4$ solution (50 mL). The resulting mixture was extracted with hexanes (2 × 50 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (1→3 % Et_2O/hexanes) to afford vinyl iodide **2** (0.71 g, 1.62 mmol, 90 %) as a light yellow oil. **2:** $R_f = 0.75$ (silica gel, Et_2O:hexanes, 1:9); $[\alpha]^{25}_D$ –26.6 (c = 0.5, $CHCl_3$); IR ν_{max} (film): 2939m, 2868m, 1454w, 1159w, 1105w, 1041s cm^{-1}; ^1H NMR: (C_6D_6, 600 MHz) δ = 7.21 (d, J = 7.2 Hz, 2H), 7.10 (m, 2H), 7.01 (m, 1 H), 5.95 (s, 1 H), 4.86 (s, 1 H), 4.81 (s, 1 H), 4.53 (d, J = 6.6 Hz, 1 H), 4.81 (d, J = 6.6 Hz, 1 H), 4.44 (d, J = 12.0 Hz, 1 H), 4.36 (d, J = 12.0 Hz, 1 H), 3.99 (t, J = 2.4 Hz, 1 H), 2.85 (m, 1 H), 2.10 – 2.00 (m, 3 H), 1.98 (m, 1H), 1.93 – 1.88 (m, 1 H), 1.80 (m, 1 H), 1.73 – 1.60 (m, 3 H), 1.66 (s, 3 H), 1.52 (m, 1 H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 143.86, 141.80, 137.99, 128.31, 127.59, 127.51, 111.53, 97.95, 94.76, 82.65, 69.94, 52.61, 51.16, 49.67, 32.59, 29.67, 27.28, 25.62, 23.83; HRMS calcd for $C_{21}H_{27}O_2INa^+$ [M+Na^+] 461.0948 found 461.0945.

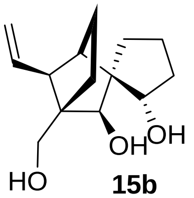
***P*-phenylcarbamate 14**: To a solution of alcohol **10** (15 mg, 0.033 mmmol) in CH_2Cl_2 (1.0 mL) at 25 °C was added Et_3N (28 μL, 0.20 mmol), 4-bromophenyl isocyanate (26 mg, 0.134 mmol), and 4-DMAP (1 mg, 0.008 mmol). The reaction mixture was stirred for 3 h, quenched with saturated $NaHCO_3$ solution (5 mL), and extracted with Et_2O (2 × 10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, concentrated in vacuo. The crude residue was purified by preparative TLC (12 % EtOAc/hexanes) to afford the desired carbamate **10b** (18 mg, 81 %). The so-formed carbamate **10b** was taken up in THF (0.5 mL), and TBAF (0.27 mL, 1.0

M in THF) was added. The reaction mixture was stirred at 25 °C for 1 h, quenched with saturated NH_4Cl solution (5 mL), and extracted with EtOAc (2 × 5 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (20→30 % EtOAc/hexanes) to furnish hydroxy carbamate **14** (10 mg, 91%), which recrystallized from EtOAc/hexanes to afford colorless crystals (mp 136 – 138m °C). **14:** R_f = 0.40 (silica gel, Et_2O:hexanes, 4:6); $[\alpha]^{25}_D$ –8.5 (*c* = 0.4, $CHCl_3$); IR ν_{max} (film): 3407brs, 3314brs, 2955m, 2875m, 1698s, 1594m, 1535m, 1490m, 1397m, 1307m, 1225s cm^{-1}; ^1H NMR: ($CDCl_3$, 600 MHz) δ = 7.40 (dd, *J* = 1.8, 9.0 Hz, 2 H), 7.28 (brs, 1 H), 6.62 (brs, 1 H), 5.09 (t, *J* = 9.0 Hz, 1 H), 4.77 (dd, *J* = 1.8, 9.0 Hz, 2 H), 4.08 (m, 1 H), 2.65 (dd, *J* = 9.0, 18.6 Hz, 1 H), 2.10 (m, 1 H), 1.93 – 1.80 (m, 4 H), 1.77 (m, 1 H), 1.75 (s, 3 H), 1.68 (m, 2 H), 1.60 (m, 2 H), 1.48 (m, 2 H), 1.25 (m, 2 H) ppm; ^{13}C NMR: ($CDCl_3$, 150 MHz) δ = 144.76, 136.74, 131.96, 120.21, 111.21, 80.85, 75.12, 51.92, 49.93, 46.60, 36.08, 30.45, 29.69, 26.59, 24.18, 23.51, 19.96 ppm; HRMS calcd for $C_{20}H_{26}BrNO_3H^+$ $[M{+}H^+]$ 408.1169 found 408.1171.

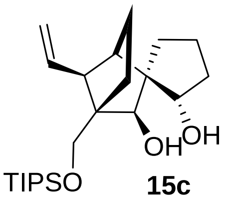


14

TIPS-ether 15c: To a stirred solution of Br-catecholborane (10.6 g, 53.0 mmol) in CH_2Cl_2 (100 mL) at 25 °C was added a CH_2Cl_2 solution (50 mL) of dihydroxy methyl ether **15**[1] (3.84 g, 15.30 mmol) and the resulting mixture was stirred at reflux for 3 h. After cooling to ambient temperature, the reaction mixture was quenched with brine solution (50 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were dried ($MgSO_4$), filtered, concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography eluding first with Et_2O/CH_2Cl_2, 20 %, and then with $MeOH/CH_2Cl_2$, 10→20 %, to furnish the demethylated triol (**15b**) as a dark brown hard glass that was pure enough to be carried forward. To a stirred solution of this triol intermediate in DMF (80 mL) at 25 °C was added imidazole (5.20 g, 76.0 mmol) and TIPSCl (5.8 mL, 30.6 mmol) successively, and stirring was continued at this temperature for 24 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (50 mL), and the resulting mixture was extracted with Et_2O (2 × 100 mL), dried ($MgSO_4$), and



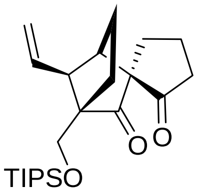
15b



15c

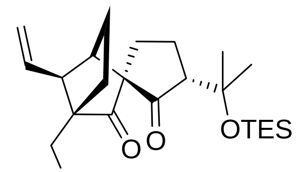
concentrated in vacuo. The crude residue was purified by flash column chromatography (Et_2O/hexanes, 5→30 %) to furnish **15c** (4.03 g, 10.2 mmol, 70 % for the two steps). **15c:** R_f = 0.40 (silica gel, Et_2O:hexanes, 4:6); IR ν_{max} (film): 3508brs, 3346brs, 2946s, 2865s, 1463m, 1403w, 1100m cm^{-1}; ^{1}H NMR: (C_6D_6, 600 MHz) δ = 5.68 (m, 1 H), 5.03 (dd, J = 1.8, 16.8 Hz, 1 H), 4.98 (dd, J = 1.8, 10.2 Hz, 1 H), 4.43 (s, 1 H), 4.15 (s, 1 H), 3.79 (s, 1 H), 3.77 (d, J = 6.6 Hz, 1 H), 3.72 (d, J = 6.6 Hz, 1 H), 3.53 (s, 1 H), 2.39 (ddd, J = 5.4, 9.6, 13.8 Hz, 1 H), 2.18 (d, J = 8.4 Hz, 1 H), 2.09 (dt, J = 6.6, 11.4 Hz, 1 H), 1.96 (m, 1 H), 1.89 (t, J = 11.4 Hz, 1 H), 1.79 (m, 1 H), 1.56 – 1.43 (m, 4 H), 1.22 (m, 2 H), 1.14 (m, 2 H), 1.03 (d, J = 1.8 Hz, 18 H), 0.96 (m, 3 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 135.38, 117.08, 84.25, 75.69, 68.91, 55.40, 55.18, 52.07, 50.87, 37.48, 32.18, 21.84, 20.32, 18.10, 12.01 ppm; HRMS calcd for $C_{23}H_{42}O_3SiH^+$ [M+H$^+$] 395.2976 found 395.2983.

Diketone 16: To a solution of **15c** (3.50 g, 8.87 mmol) in DMSO (100 mL) at 25 °C was added IBX (7.30 g, 26.0 mmol) and the resulting mixture was heated to 50 °C for 4 h. The reaction mixture was quenched by pouring into a vigorously stirred mixture of saturated $NaHCO_3/Na_2S_2O_4$ solution (1:1, 200 mL) and extracted with Et_2O (2 × 100 mL). The ethereal layer was dried ($MgSO_4$), concentrated in vacuo, and the residue was purified via flash column chromatography (silica gel, 5→10 % Et_2O/hexanes) to furnish diketone **16** (3.15 g, 7.98 mmol, 90 %). **16**: R_f = 0.60 (silica gel, Et_2O/hexanes, 4:6); IR ν_{max} (film): 2943, 2865, 1756, 1723, 1464, 1142, 1105, 1013 cm^{-1}; ^{1}H NMR: (C_6D_6, 600 MHz) δ = 5.68 (m, 1 H), 5.26 (d, J = 16.8 Hz, 1 H), 5.12 (dd, J = 1.2, 10.2 Hz, 1 H), 4.10 (d, J = 10.2 Hz, 1 H), 3.53 (d, J = 10.2 Hz, 1 H), 2.76 (d, J = 7.8 Hz, 1 H), 2.28 (m, 1 H), 2.02 (ddd, J = 7.2, 10.2, 13.2 Hz, 1 H), 1.98 (d, J = 6.0 Hz, 1 H), 1.87 (pent, J = 9.0 Hz, 1 H), 1.78 (ddd, J = 4.2, 8.4, 18.6 Hz, 1 H), 1.59 – 1.38 (m, 5 H), 1.20 (m, 1 H), 1.15 – 1.10 (m, 21 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 214.60, 212.46, 133.53, 118.58, 67.33, 63.87, 60.36, 52.36, 48.17, 39.38, 34.03, 23.68, 21.23, 19.89, 18.28, 12.65 ppm; HRMS calcd for $C_{23}H_{38}O_3SiH^+$ [M+H$^+$] 391.2663 found 391.2678.

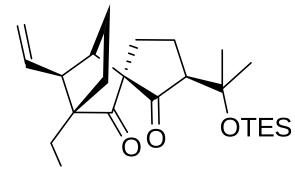


16

Bis(silyl) ether 17: To solution of diketone **16** (3.95 g, 9.86 mmol) in CH_2Cl_2 (200 mL) at –78 °C were added sequentially Et_3N (4.15 mL, 29.0 mmol) and $TiCl_4$ (1.0 M in CH_2Cl_2, 11.8 mL, 11.8 mmol). The resulting solution was stirred at –78 °C (10 min), warmed to –40 °C (30 min),



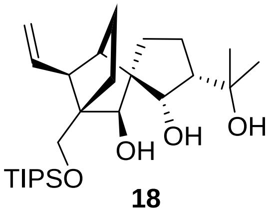
17



17a

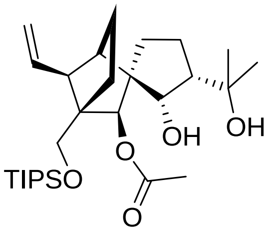
and cooled to –92 °C before dropwise addition of acetone (neat, 1.62 mL, 28.0 mmol). The reaction mixture was maintained below –90 °C for 12 h and quenched with saturated $NaHCO_3$ solution (100 mL). Celite was then added and the resulting slurry was filtered to remove the solids. The layers were separated and the aqueous phase was washed with CH_2Cl_2 (2 × 50 mL). The combined organic extractions were dried ($MgSO_4$), filtered, and concentrated under reduced pressure to provide the crude oil containing a mixture of diastereomeric products (dr = 9:1, **17:17a** based on crude NMR). The residue was then dissolved into CH_2Cl_2 (200 mL) and cooled to –78 °C. To this solution was added 2,6-lut. (7.0 mL, 59.0 mmol) and TESOTf (7.0 mL, 24.6 mmol). The reaction mixture was stirred at –78 °C (20 min) and then warmed to –40 °C (20 min). The reaction mixture was quenched with saturated $NaHCO_3$ solution (50 mL), extracted with CH_2Cl_2 (50 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, Et_2O/hexanes, 1→3 %) to furnish **17** (4.50 g, 8.00 mmol, 81 %) and **17a** (0.41 g, 0.69 mmol, 7 %). (**17**: $R_f = 0.40$ (silica gel, Et_2O:hexanes, 1:50); IR ν_{max} (film): 2954s, 2868s, 1754s, 1718s, 1463m, 1382m, 1238w, 1103m, 1014s cm^{-1}; ^1H NMR: (C_6D_6, 600 MHz) δ = 5.69 (m, 1 H), 5.28 (d, J = 16.8 Hz, 1H), 5.13 (dd, J = 1.2, 10.2 Hz, 1 H), 4.09 (d, J = 10.2 Hz, 1H), 3.50 (d, J = 10.2 Hz, 1 H), 2.84 (d, J = 7.8 Hz, 1 H), 2.42 (m, 1 H), 1.54 (m, 2 H), 1.47 (s, 3 H), 1.45 – 1.36 (m, 2 H), 1.34 (s, 3 H), 1.15 – 1.05 (m, 21 H), 1.01 (t, J = 7.8 Hz, 9 H), 0.60 (q, J = 7.8 Hz, 6 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 214.08, 212.00, 133.55, 118.63, 74.96, 67.99, 63.96, 61.32, 60.28, 58.64, 51.95, 50.22, 31.49, 30.40, 30.21, 26.24, 23.92, 21.12, 18.27, 12.33, 7.41, 7.15 ppm; HRMS calcd for $C_{32}H_{58}O_4Si_2Na^+$ [M+Na^+] 585.3766 found 585.3758; **17a:** $R_f = 0.25$ (silica gel, Et_2O:hexanes, 1:50); IR ν_{max} (film): 2954s, 2868s, 1754s, 1718s, 1463m, 1382m, 1238w, 1103m, 1014s cm^{-1}; ^1H NMR: (C_6D_6, 600 MHz) δ = 5.75 (m, 1 H), 5.31 (d, J = 17.4 Hz, 1 H), 5.13 (d, J = 10.2 Hz, 1 H), 4.14 (d, J = 10.2 Hz, 1 H), 3.58 (d, J = 10.2 Hz, 1 H), 2.84 (d, J = 7.8 Hz, 1 H), 2.34 (d, J = 3.6 Hz, 1 H), 2.15 (ddd, J = 3.6, 9.6, 12.6 Hz, 1 H), 1.95 (m, 1 H), 1.85 – 1.62 (m, 6 H), 1.46 (dd, J = 3.0, 12.0 Hz, 1H), 1.40 (s, 3 H), 1.73 – 1.10 (m, 21 H), 1.04 (s, 3 H), 0.97 (t, J = 7.8 Hz, 9 H), 0.54 (q, J = 7.8 Hz, 6 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 214.14, 212.54, 133.74, 118.50, 74.84, 69.76, 63.84, 60.53, 60.48, 52.18, 46.89, 31.18, 30.22, 27.86, 23.43, 23.32, 21.95, 18.31, 18.27, 12.36, 7.36, 7.01 ppm; HRMS calcd for $C_{32}H_{58}O_4Si_2Na^+$ [M+Na$^+$] 585.3766 found 585.3758.

Triol 18: To a stirred solution of **18** (4.50 g, 8.20 mmol) in THF/MeOH (1:1, 40 mL) at –10 °C was added $NaBH_4$ (3.00 g, 82.0 mmol). The resulting mixture was maintained at this temperature for 30 min and then warmed to 25 °C. After stirring for 4 h at ambient temperature, the reaction mixture was quenched with saturated NH_4Cl solution (50 mL), extracted with Et_2O (2 × 100 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude residue was dissolved in EtOH (100 mL), and PPTS (0.40 g, 1.59 mmol) was added. The mixture was stirred at 25 °C for 3 h and was quenched with saturated $NaHCO_3$ solution (50 mL), extracted with Et_2O (2 × 100 mL), dried ($MgSO_4$), filtered, concentrated in vacuo. The resulting residue was purified by flash column chromatography (10→30 % Et_2O/hexanes) to furnish **18** (3.05 g, 6.74 mmol, 82 %). **18**: $R_f = 0.35$ (silica gel, Et_2O:hexanes, 2:3); IR ν_{max} (film): 3478brs, 3382brs, 2941s, 2865s, 1464m, 1411m, 1153m, 1062s cm^{-1}; ^{1}H NMR: (C_6D_6, 600 MHz) δ = 5.66 (m, 1 H), 5.03 (d, J = 16.8 Hz, 1 H), 4.03 (s, 1 H), 3.73 (d, J = 9.6 Hz, 1 H), 3.70 (d, J = 9.6 Hz, 1 H), 3.60 (s, 1 H), 2.39 (m, 1 H), 2.32 (ddd, J = 7.2, 9.0, 13.8 Hz, 1 H), 2.13 (s, 1 H), 1.60 – 1.45 (m, 5 H), 1.51 (s, 3 H), 1.23 (s, 3 H), 1.01 (d, J = 6.6 Hz, 18 H), 0.97 (m, 3 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 135.17, 117.27, 84.18, 77.32, 71.43, 68.74, 55.46, 55.10, 51.70, 50.76, 50.69, 37.42, 30.32, 29.49, 21.79, 21.62, 21.35, 18.10, 12.00 ppm; HRMS calcd for $C_{26}H_{48}O_4SiH^+$ [M+H$^+$] 453.3394 found 453.3389.



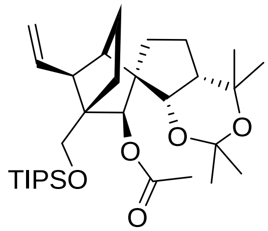
18

Acetate 18a: To a solution of triol **18** (2.34 g, 5.26 mmol) in CH_2Cl_2 (250 mL) at 25 °C was added Et_3N (14.5 mL, 103.4 mmol), Ac_2O (1.3 mL, 103.4 mmol), and 4-DMAP (0.63 g, 1.5 mmol). The resulting mixture was stirred for 24 h at this temperature and then quenched sequentially with EtOH (5 mL) and saturated $NaHCO_3$ solution (200 mL). The mixture was extracted with CH_2Cl_2 (2 × 50 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude residue was purified by flash column chromatography (Et_2O/hexanes, 20→90 %) to furnish **19** (2.05 g, 4.15 mmol, 79 %), which was recrystallized from hexanes. Colorless solid, mp 131 – 133 °C; **19:** $R_f = 0.40$ (silica gel, Et_2O:hexanes, 7:3); IR ν_{max}

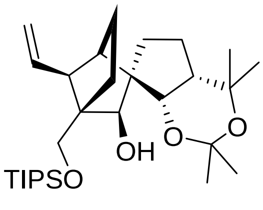


19

(film): 3401brs, 2942s, 2865s, 1722s, 1463m, 1368m, 1261m, 1103m, 1067s cm^{-1}; ^{1}H NMR: (C_6D_6, 500 MHz) δ = 5.78 (m, 1 H), 5.54 (d, J = 1.5 Hz, 1 H), 5.25 (dd, J = 2.0, 17.0 Hz, 1 H), 5.15 (dd, J = 2.0, 10.0 Hz, 1 H), 4.46 (d, J = 2.5 Hz, 1 H), 3.67 (d, J = 6.6 Hz, 1 H), 3.59 (d, J = 6.6 Hz, 1 H), 2.65 (d, J = 8.5 Hz, 1 H), 2.32 (dt, J = 7.5, 12.0 Hz, 1 H), 1.98 (m, 2 H), 1.90 (s, 3H), 1.70 – 1.51 (m, 5 H), 1.50 – 1.38 (m, 2 H), 1.31 (s, 3 H), 1.22 (dd, J = 2.5, 12.5 Hz, 1 H), 1.16 – 1.10 (m, 21 H), 1.04 (s, 3 H) ppm; ^{13}C NMR: (C_6D_6, 125 MHz) δ = 170.97, 135.18, 117.86, 77.51, 76.06, 72.17, 62.36, 56.50, 55.18, 50.78, 50.48, 50.39, 36.08, 30.45, 29.76, 29.52, 21.37, 21.09, 20.76, 18.38, 18.34, 12.45 ppm; HRMS calcd for $C_{28}H_{50}O_5SiNa^+$ [M+Na$^+$] 517.3320 found 517.3345.



19a

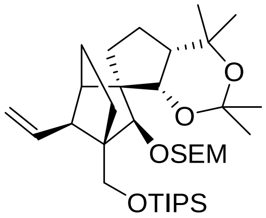


19b

Acetoxy acetonide 19a and alcohol 19b: To a stirred solution of acetate **19** (1.95 g, 4.09 mmol) in CH_2Cl_2 (100 mL) at –78 °C was added 2-methoxypropene (7.86 mL, 81.8 mmol) and a solution of CSA (1.3 g, 4.09 mmol) in THF (5 mL). The resulting mixture was warmed to –30 °C over a period of 2 h and then quenched with saturated $NaHCO_3$ solution (100 mL). The mixture was extracted with CH_2Cl_2 (2 × 50 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude residue was purified by flash column chromatography (Et_2O/hexanes, 2→20 %) to furnish **19a** (1.73 g, 3.34 mmol, 82 %); **19a:** R$_f$ = 0.20 (silica gel, Et_2O:hexanes, 1:9); ^{1}H NMR: (C_6D_6, 500 MHz) δ = 5.80 (m, 1 H), 5.61 (d, J = 1.8 Hz, 1 H), 5.28 (dd, J = 1.8, 16.8 Hz, 1 H), 5.17 (dd, J = 1.8, 10.2 Hz, 1 H), 4.24 (d, J = 1.8 Hz, 1 H), 3.67 (d, J = 10.2 Hz, 1 H), 3.59 (d, J = 10.2 Hz, 1 H), 2.65 (d, J = 8.4 Hz, 1 H), 2.38 (dd, J = 5.4, 12.0 Hz, 1 H), 2.00 – 1.88 (m, 2 H), 1.84 (s, 3 H), 1.65 – 1.55 (m, 4 H), 1.42 (s, 3 H), 1.33 (s, 3 H), 1.30 (m, 1 H), 1.25 (m, 1 H), 1.23 (s, 3 H), 1.15 – 1.10 (m, 21 H), 1.07 (s, 3 H) ppm. To a solution of acetoxy acetonide **19a** (1.60 g, 3.09 mmol) in PhMe (50 mL) at 25 °C was added MeMgBr (3.0 M in Et_2O, 51.6 mL, 154 mmol). The resulting mixture was heated at 50 °C for 8 h, cooled to 0 °C, and quenched by careful addition of saturated NH_4Cl solution (100 mL). The resulting mixture was extracted with Et_2O (2 x 50 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude residue was purified by flash column chromatography (Et_2O/hexanes, 2→10 %) to furnish alcohol **19b** (1.42 g, 2.88 mmol, 94 %) **19b:** R$_f$ = 0.25 (silica gel, Et_2O:hexanes, 1:9); IR ν_{max} (film): 3524brs, 2946s, 2865s, 1466m, 1374m, 1261m, 1196m, 1064m cm^{-1}; ^{1}H

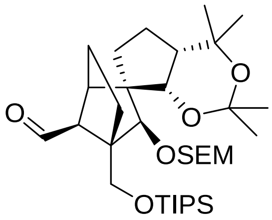
NMR: (C_6D_6, 600 MHz) δ = 5.91 (m, 1 H), 5.35 (dd, *J* = 1.8, 17.4 Hz, 1 H), 5.21 (dd, *J* = 2.4, 10.2 Hz, 1 H), 4.47 (d, *J* = 1.8 Hz, 1 H), 4.42 (s, 1 H), 4.04 (d, *J* = 9.6 Hz, 1 H), 4.00 (s, 1 H), 3.70 (d, *J* = 9.6 Hz, 1 H), 2.65 (d, *J* = 8.4 Hz, 1 H), 2.34 (ddd, *J* = 6.0, 9.6, 13.8 Hz, 1 H), 2.09 (dd, *J* = 4.8, 12.0 Hz, 1 H), 1.9 (m, 1 H), 1.68 – 1.60 (m, 3 H), 1.57 (d, *J* = 3.6 Hz, 1 H), 1.40 – 1.30 (m, 2 H), 1.27 (s, 3 H), 1.22 (s, 3 H), 1.18 (s, 3 H), 1.17 – 1.15 (m, 21 H), 1.11 –1.10 (m, 1 H), 1.04 (s, 3 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 135.87, 117.45, 97.90, 77.82, 73.91, 71.34, 62.21, 57.39, 54.87, 50.33, 50.17, 44.92, 38.42, 32.04, 30.02, 29.48, 24.67, 22.29, 21.80, 20.19, 18.38, 18.6, 12.40 ppm; HRMS calcd for $C_{29}H_{52}O_4SiNa^+$ [*M*+Na$^+$] 515.3533 found 515.3522.

SEM ether 20: To a solution of hydroxyl compound **19b** (1.30 g, 2.64 mmol) in CH_2Cl_2 (30 mL) at 25 °C was added *i*Pr_2NEt (13.8 mL, 79.2 mmol), *n*Bu_4NI (0.96 g, 2.64 mmol), and SEMCl (4.38 mL, 26.4 mmol). The resulting mixture was refluxed for 48 h, cooled to ambient temperature, and quenched with saturated $NaHCO_3$ solution (100 mL). The mixture was extracted with Et_2O (2 × 50 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude residue was purified by flash column chromatography (Et_2O/hexanes, 2→5 %) to furnish SEM ether **20** (1.57 g, 2.52 mmol, 96 %) **20:** R$_f$ = 0.65 (silica gel, Et_2O:hexanes, 1:9); IR ν_{max} (film): 2945s, 2860s, 1466w, 1374m, 1249m, 1196m, 1107m, 1059s, 1031s cm^{-1}; ^{1}H NMR: (C_6D_6, 600 MHz) δ = 6.00 (m, 1 H), 5.26 (dd, *J* = 1.8, 17.4 Hz, 1 H), 5.17 (dd, *J* = 2.4, 10.2 Hz, 1 H), 4.90 (d, *J* = 6.6 Hz, 1 H), 4.88 (d, *J* = 6.6 Hz, 1 H), 4.42 (s, 1 H), 4.01 (d, *J* = 9.6 Hz, 1 H), 3.94 (m, 2 H), 3.78 (d, J = 9.6 Hz, 1 H), 3.60 (m, 1 H), 2.60 (d, *J* = 7.8 Hz, 1 H), 2.18 (m, 1 H), 2.02 (dd, *J* = 4.8, 11.4 Hz, 1 H), 1.95 (m, 1 H), 1.66 (m, 3 H), 1.60 (s, 1 H), 1.47 (s, 3 H), 1.42 (s, 3 H), 1.40 – 1.37 (m, 2 H), 1.31 (m, 1 H), 1.26 (s, 3 H), 1.20 (m, 21 H), 1.10 (s, 3 H), 1.06 (m, 2 H), 0.03 (s, 9 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 136.42, 116.69, 98.00, 97.30, 85.02, 71.90, 71.04, 65.60, 63.00, 57.57, 56.42, 50.66, 50.54, 44.59, 38.24, 32.28, 30.23, 29.74, 18.53, 18.51, 18.35 ppm; HRMS calcd for $C_{35}H_{66}O_5Si_2Na^+$ [*M*+Na$^+$] 645.4341 found 645.4344.



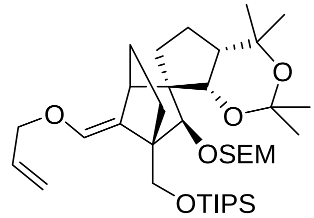
20

Aldehyde 20a: To a solution of olefin **20** (0.95 g, 1.52 mmol) in MeOH/CH_2Cl_2 (1:1, 40 mL) at –78 °C was added pyridine (0.1 mL, 1.26 mmol). Ozone was gently bubbled into the reaction mixture until the solution took on a light blue color. The reaction mixture was stirred for 2 min and then purged with oxygen until the solution became colorless once again. Ph_3P (2.0 g, 7.62 mmol) was added and the reaction mixture was warmed to 25 °C, stirred an additional 30 min at this temperature, and concentrated under reduced pressure. The crude residue was directly purified by flash column chromatography (Et_2O/hexanes, 2→20 %) to furnish aldehyde **20a** (0.93 g, 1.48 mmol, 96 %). **20a**: R_f = 0.50 (silica gel, Et_2O:hexanes, 1:9); IR ν_{max} (film): 2944s, 2866s, 1717s, 1464m, 1374m, 1249m, 1196s, 1062s cm^{-1}; ^{1}H NMR: (C_6D_6, 600 MHz) δ = 10.05 (d, *J* = 2.4 Hz, 1 H), 4.86 (d, *J* = 7.2 Hz, 1 H), 4.70 (d, *J* = 7.2 Hz, 1 H), 4.33 (s, 1 H), 4.07 (d, *J* = 10.2 Hz, 1 H), 4.03 (d, *J* = 10.2 Hz, 1 H), 3.89 (dt, *J* = 6.0, 10.2 Hz, 1 H), 3.68 (s, 1 H), 3.51 (dt, *J* = 6.0, 10.2 Hz, 1 H), 2.38 (s, 1 H), 2.22 (m, 1 H), 1.91 – 1.83 (m, 3 H), 1.80 (d, *J* = 3.6 Hz, 1H), 1.75 (m, 1 H), 1.61 (m, 1 H), 1.42 (s, 3 H), 1.38 (s, 3 H), 1.37 (m, 1 H), 1.30 (m, 1 H), 1.22 (s, 3 H), 1.16 (m, 21 H), 1.09 (s, 3 H), 1.10 – 1.05 (m, 2 H) 0.02 (s, 9 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 201.57, 97.48, 97.26, 85.60, 71.30, 70.99, 65.62, 64.02, 59.39, 58.49, 56.61, 48.02, 44.39, 38.05, 32.20, 30.14, 29.67, 24.79, 22.15, 20.77, 18.40, 18.36, 18.33, 12.34 ppm; HRMS calcd for $C_{34}H_{64}O_6Si_2Na^+$ [M+Na$^+$] 647.4133 found 647.4121.



20a

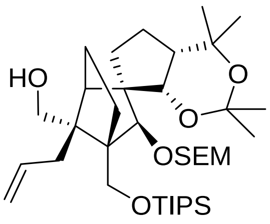
Allyl enol ether 21: To KH (1.97 g, 14.8 mmol, 30 % in mineral oil, washed with hexanes) in DME (20 mL) at –10 °C was added HMPA (2.65 mL, 14.8 mmol), aldehyde **20a** (0.93 g, 1.48 mmol, dissolved into 10 mL DME), and allylchloride (2.3 mL, 30.0 mmol). The reaction mixture was stirred at this temperature for 30 min and then warmed to 25 °C and stirred for an additional 8 h. The reaction mixture was quenched by cannulation into phosphate buffer solution (pH = 7, 100 mL). The resulting mixture was extracted with Et_2O (2 × 100 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude residue was purified by flash column chromatography (Et_2O/hexanes, 2→5 %) to furnish allyl enol ether **21** (0.92 g, 1.38 mmol, 92 %) **21:** R_f = 0.60 (silica gel, Et_2O:hexanes, 1:9); IR ν_{max} (film): 2943m, 1573m, 1456s, 1434s, 1126m, 1034s cm^{-1}; ^{1}H NMR: (C_6D_6, 600 MHz) δ = 6.32 (s, 1 H), 5.83 (m, 1 H), 5.25 (dd, *J* = 1.8, 17.4 Hz, 1 H), 5.05 (dd, *J* = 1.2, 10.2 Hz, 1 H), 4.98 (d, *J* = 7.2 Hz, 1 H), 4.78 (d, *J* = 7.2 Hz, 1 H), 4.45 (d, *J* = 1.8 Hz, 1 H), 4.17 (d, *J* = 10.2



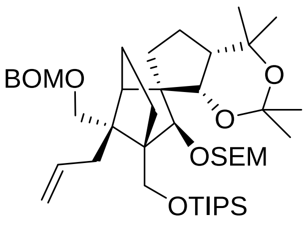
21

Hz, 1 H), 4.13 – 4.11 (m, 3 H), 3.96 (dt, *J* = 5.4, 9.6 Hz, 1 H), 3.74 (s, 1 H), 3.55 (dt, *J* = 5.4, 9.6 Hz, 1 H), 2.73 (d, *J* = 4.2 Hz, 1 H), 2.32 (m, 1 H), 1.99 (m, 1 H), 1.97 (d, *J* = 8.4 Hz, 1 H), 1.92 – 1.87 (m, 2 H), 1.80 (ddd, *J* = 4.2, 9.0, 12.6 Hz, 1 H), 1.65 (m, 1 H), 1.54 (m, 1 H), 1.45 (s, 3 H), 1.40 (s, 3 H), 1.40 (m, 1 H), 1.25 (s, 3 H), 1.20 (m, 21 H), 1.09 (s, 3 H), 0.04 (s, 9 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 134.88, 134.40, 116.85, 97.52, 97.21, 86.15, 72.69, 71.69, 71.14, 65.47, 63.13, 57.79, 54.59, 44.87, 44.83, 38.22, 32.28, 30.3, 29.67, 24.93, 23.12, 22.37, 18.47, 18.42, 12.43, –1.31 ppm; HRMS calcd for $C_{37}H_{68}O_6Si_2Na^+$ [*M*+Na$^+$] 687.4446 found 687.4438.

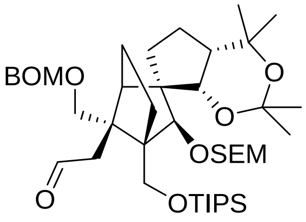
Alcohol 22: A solution of allyl enol ether **21** (0.93 g, 1.39 mmol) and *i*Pr$_2$NEt (0.2 mL, 1.50 mmol) in 1,2-dichlorobenzene (24 mL) was heated under microwave irradiation at 200 °C for 20 min. The resulting solution was cooled to 25 °C and diluted with MeOH (24 mL). NaBH$_4$ (1.0 g, 27.8 mmol) was added and the reaction mixture was stirred for 2 h at that temperature. The reaction mixture was quenched by careful addition of saturated NH$_4$Cl solution (100 mL). The resulting mixture was extracted with CH$_2$Cl$_2$ (2 x 50 mL), dried (MgSO$_4$), and concentrated in vacuo until only 1,2-dichlorobenzene remained. The resulting crude solution was purified by flash column chromatography (Et$_2$O/hexanes, 2→30 %) to furnish alcohol **22** (0.82 g, 1.23 mmol, 88 %). **22**: R$_f$ = 0.30 (silica gel, Et$_2$O:hexanes, 2:8); IR ν_{max} (film): 3457brs, 2944s, 2866s, 1464m, 1373m, 1249m, 1194s, 1054s, 1029s cm^{-1}; ^{1}H NMR: (C_6D_6, 600 MHz) δ = 6.12 (m, 1 H), 5.24 (dd, *J* = 1.2, 16.8 Hz, 1 H), 5.09 (dd, *J* = 2.4, 10.2 Hz, 1 H), 4.93 (d, *J* = 6.0 Hz, 1 H), 4.86 (d, *J* = 6.0 Hz, 1 H), 4.40 (s, 1 H), 4.17 (s, 1 H), 4.03 (d, *J* = 10.2 Hz, 1 H), 3.94 (dd, *J* = 3.0, 12.0 Hz, 1 H), 3.90 (dt, *J* = 6.6, 10.2 Hz, 1 H), 3.76 (d, *J* = 10.2 Hz, 1 H), 3.71 – 3.64 (m, 1 H), 2.98 (dd, *J* = 1.8, 14.4 Hz, 1 H), 2.66 (dd, *J* = 3.0, 9.6 Hz, 1 H), 2.27 (m, 2 H), 2.00 – 1.90 (m, 2 H), 1.83 (dt, *J* = 2.4, 6.6 Hz, 1 H), 1.70 (d, *J* = 3.6 Hz, 1 H), 1.60 – 1.55 (m, 1 H), 1.53 (s, 3 H), 1.50 (m, 1 H), 1.47 (s, 3 H), 1.42 – 1.37 (m, 1 H), 1.28 (m, 2 H), 1.25 (s, 3 H), 1.20 (m, 21 H), 1.13 (m, 1 H), 1.08 (s, 3 H), 1.04 (m, 2 H), 0.03 (s, 9 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 136.92, 116.61, 98.13, 97.44, 83.94, 73.68, 71.10, 66.16, 63.73, 62.72, 56.97, 55.22, 54.36, 50.04, 44.14, 37.19, 34.38, 32.24, 31.92, 30.07, 29.63, 24.76, 22.79, 22.65, 20.81, 18.54, 18.43, 12.41, –1.31 ppm; HRMS calcd for $C_{37}H_{70}O_6Si_2Na^+$ [*M*+Na$^+$] 689.4603 found 689.4605.



22


22a

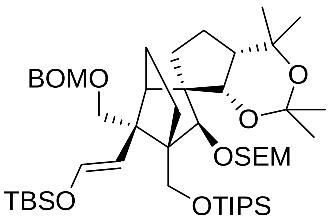
BOM ether 22a: To a solution of alcohol **22** (0.81 g, 1.21 mmol) in CH_2Cl_2 (25 mL) at 25 °C was added *i*Pr_2NEt (3.20 mL, 18.0 mmol), *n*Bu_4NI (0.45 g, 1.21 mmol), and BOMCl (0.76 mL, 5.0 mmol). The resulting mixture was refluxed for 8 h, cooled to ambient temperature, and quenched with saturated $NaHCO_3$ solution (100 mL). The resulting mixture was extracted with Et_2O (2 × 50 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude residue was purified by flash column chromatography (Et_2O/hexanes, 2→10 %) to afford BOM ether **22a**. **22a:** R_f = 0.45 (silica gel, Et_2O:hexanes, 1:9); IR ν_{max} (film): 2943s, 2860s, 1464m, 1374m, 1246m, 1195s, 1097s, 1041s cm^{-1}; ^1H NMR: (C_6D_6, 600 MHz) δ = 7.40 (d, *J* = 7.2 Hz, 2 H), 7.20 (t, *J* = 7.8 Hz, 2 H), 7.10 (t, *J* = 7.2 Hz, 1 H), 6.35 (m, 1 H), 5.20 (dd, *J* = 1.2, 16.8 Hz, 1 H), 5.13 (dd, *J* = 2.4, 10.2 Hz, 1 H), 4.95 (d, *J* = 7.2 Hz, 1 H), 4.80 (d, *J* = 7.2 Hz, 1 h), 4.70 (d, *J* = 6.6 Hz, 1 H), 4.67 (d, *J* = 12.0 Hz, 1 H) 4.65 (d, *J* = 6.6 Hz, 1 H), 4.59 (d, *J* = 12.0 Hz, 1 H), 4.44 (s, 1 H), 4.20 (d, *J* = 10.2 Hz, 1 H), 4.11 (s, 1 H), 3.98 (t, *J* = 4.8 Hz, 2 H), 3.94 (m, 1 H), 3.76 (d, *J* = 10.2 Hz, 1 H), 3.60 (dt, *J* = 6.6, 10.2 Hz, 1 H), 2.92 (dd, *J* = 5.4, 15.6 Hz, 1 H), 2.68 (dd, *J* = 9.0, 15.0 Hz, 1 H), 2.31 (m, 1 H), 2.06 (t, *J* = 12.0 Hz, 1 H), 2.00 – 1.87 (m, 3 H), 1.86 (d, *J* = 3.6 Hz, 1 H), 1.75 (m, 1 H), 1.54 (m, 1 H), 1.50 (s, 3 H), 1.33 (t, *J* = 7.2 Hz, 1 H), 1.23 (s, 3 H), 1.21 (m, 21 H), 1.15 (d, *J* = 4.2 Hz, 1 H), 1.07 (s, 3 H), 1.06 (m, 2 H), 0.03 (s, 9 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 138.64, 13786, 115.83, 97.66, 97.36, 95.22, 85.33, 73.59, 71.72, 71.12, 69.82, 65.94, 63.44, 56.98, 54.61, 53.32, 50.06, 44.21, 50.05, 44.21, 37.80, 37.06, 32.23, 30.05, 29.61, 24.81, 22.93, 21.35, 20.78, 18.48, 18.44, 12.41, –1.32 ppm; HRMS calcd for $C_{45}H_{78}O_7Si_2Na^+$ [*M*+Na^+] 809.5178 found 809.5198.


23

Aldehyde 23: To a solution of intermediate olefin **22a** (ca. 0.96g, 1.21 mmol) in MeOH/CH_2Cl_2 (1:1, 40 mL) at –78 °C was added pyridine (0.1 mL, 1.26 mmol). Ozone was gently bubbled into the reaction mixture until the solution took on a light blue color. The reaction mixture was stirred for 2 min and then purged with oxygen until the solution became colorless. Ph_3P (1.61 g, 6.14 mmol) was added and the reaction mixture was warmed to 25 °C, stirred an additional 30 min at that temperature, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (Et_2O/hexanes, 2→30 %) to furnish **23** (0.89 g, 1.12 mmol, 88 % for the two steps). **23:** R_f = 0.45 (silica gel,

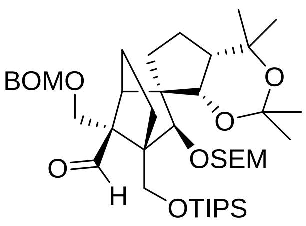
Et_2O:hexanes, 3:7); IR ν_{max} (film): 2944m, 2866m, 1716s, 1463w, 1374m, 1194m, 1096s, 1021s cm^{-1}; ^1H NMR: (C_6D_6, 600 MHz) δ = 9.99 (q, *J* = 2.4 Hz, 1 H), 7.38 (d, *J* = 7.8 Hz, 2 H), 7.19 (t, *J* = 7.2 Hz, 2 H), 7.10 (t, *J* = 7.2 Hz, 1 H), 4.87 (d, *J* = 7.2 Hz, 1 H), 4.74 (d, *J* = 7.2 Hz, 1 H), 4.57 (d, *J* = 12.0 Hz, 1 H), 4.56 (d, *J* = 6.6 Hz, 1 H), 4.53 (d, *J* = 6.6 Hz, 1 H), 4.48 (d, *J* = 12.0 Hz, 1 H), 4.38 (s, 1 H), 3.96 (d, *J* = 11.4 Hz, 1 H), 3.94 (s, 1 H), 3.88 (m, 1 H), 3.87 (d, *J* = 10.2 Hz, 1 H), 3.84 (d, *J* = 11.4 Hz, 1 H), 3.72 (d, *J* = 10.2 Hz, 1 H), 3.55 (dt, *J* = 6.0, 9.6 Hz, 1 H), 2.78 (dd, *J* = 3.6, 16.2 Hz, 1 H), 2.72 (d, *J* = 16.2 Hz, 1 H), 2.24 (m, 1 H), 2.20 (s, 1 H), 2.00 – 1.87 (m, 3 H), 1.78 (m, 1 H), 1.55 (m, 1 H), 1.48 (s, 3 H), 1.42 (s, 3 H), 1.30 (t, *J* = 9.0 Hz, 1 H), 1.25 (s, 3 H), 1.15 (s, 21 H), 1.09 (s, 3 H), 1.04 (m, 2 H), 0.01 (s, 9 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 201.62, 138.39, 128.57, 128.53, 127.77, 97.66, 97.37, 94.85, 84.48, 73.53, 71.65, 71.09, 69.96, 65.96, 62.97, 57.32, 54.83, 52.96, 49.25, 48.24, 44.21, 36.80, 32.21, 30.04, 29.63, 24.76, 22.94, 20.91, 20.81, 18.51,18.43, 18.40, 12.28, –1.34 ppm; HRMS calcd for $C_{44}H_{76}O_8Si_2Na^+$ [*M*+Na$^+$] 811.4971 found 811.4977.

Silyl enol ether 23a: To a solution of aldehyde **23** (0.94 g, 1.26 mmol) in CH_2Cl_2 (30 mL) at 25 °C was added DBU (6.0 mL, 3.94 mmol) and TBSCl (3.0 g, 19.2 mmol). The resulting mixture was stirred for 48 h at that temperature and quenched with saturated $NaHCO_3$ solution (100 mL). The resulting mixture was extracted with Et_2O (2 × 50 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude residue was purified by flash column chromatography (Et_2O/hexanes, 5→10 %) to furnish **23a** (1.08 g, 1.26 mmol, 100 %). **23a:** R$_f$ = 0.65 (silica gel, Et_2O:hexanes, 2:8); IR ν_{max} (film): 2946s, 2866s, 1652m, 1463m, 1373m, 1250m, 1195m, 1173m, 1094s, 1046s cm^{-1}; ^1H NMR: (C_6D_6, 600 MHz) δ = 7.42 (d, *J* = 7.2 Hz, 2 H), 7.21 (t, *J* = 7.8 Hz, 2 H), 7.11 (t, *J* = 7.2 Hz, 1 H), 4.90 (m, 2 H), 4.77 (d, *J* = 6.0 Hz, 1 H) 4.75 (d, *J* = 6.0 Hz, 1 H), 4.70 (d, *J* = 12.0 Hz, 1 H), 4.61 (d, *J* = 12.0 Hz, 1 H), 4.52 (s, 1 H), 4.15 (s, 1 H), 4.03 (d, *J* = 10.8 Hz, 1 H), 3.93 (d, *J* = 10.8 Hz, 1 H), 3.91 (m, 1 H), 3.86 (d, *J* = 10.2 Hz, 1 H), 3.79 (d, *J* = 10.2 Hz, 1 H), 3.65 (dt, *J* = 6.6, 10.2 Hz, 1 H), 2.32 (dt, *J* = 2.4, 11.4 Hz, 1 H), 2.26 – 2.23 (m, 1 H), 2.22 (d, *J* = 3.6 Hz, 1 H), 2.10 – 1.95 (m, 3 H), 1.72 – 1.55 (m, 3 H), 1.51 (s, 3 H), 1.46 (s, 3 H), 1.42 (t, *J* = 9.0 Hz, 1 H), 1.25 (s, 3 H), 1.19 (m, 21 H), 1.12 (m, 1 H), 1.10 (s, 3 H), 1.05 (m, 2 H), 0.97 (s, 9 H), 0.14 (s, 3 H), 0.13 (s, 3 H), 0.03 (s, 9 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 142.84, 138.71, 128.51, 128.29,



23a

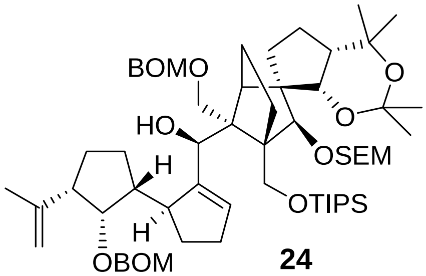
127.70, 114.08, 98.16, 97.44, 95.29, 84.67, 73.80, 71.13, 70.42, 69.83, 66.02, 62.89, 57.65, 55.02, 50.70, 44.30, 36.24, 32.29, 30.10, 29.70, 25.85, 24.85, 23.13, 22.05, 21.53, 18.56, 12.41, –1.29, –4.87, –4.95 ppm; HRMS calcd for $C_{50}H_{90}O_8Si_3Na^+$ [M+Na^+] 925.5835 found 925.5851.



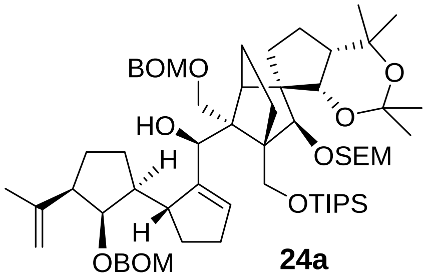
3

Aldehyde 3: To a solution of enol ether **23a** (1.05 g, 1.26 mmol) in MeOH/CH_2Cl_2 (1:1, 40 mL) at –78 °C was added pyridine (0.1 mL, 1.26 mmol). Ozone was gently bubbled into the reaction mixture until the solution took on a light blue color. The reaction mixture was stirred for 2 min and then purged with oxygen until it became colorless. Ph_3P (1.65 g, 6.29 mmol) was added and the reaction mixture was warmed to 25 °C, stirred an additional 30 min at this temperature, and then concentrated under reduced pressure. The crude residue was purified by flash column chromatography (Et_2O/hexanes, 5→20 %) to furnish **3** (0.94 g, 1.22 mmol, 97 %). **3:** R_f = 0.30 (silica gel, Et_2O:hexanes, 2:8); IR ν_{max} (film): 2944s, 2865s, 1723m, 1464m, 1374m, 1249m, 1196m, 1097s, 1036s cm^{-1}; ^1H NMR: (C_6D_6, 600 MHz) δ = 10.33 (s, 1 H), 7.37 (d, J = 7.2 Hz, 2 H), 7.19 (t, J = 7.8 Hz, 2 H), 7.09 (t, J = 7.2 Hz, 1 H), 4.92 (d, J = 7.2 Hz, 1 H), 4.75 (d, J = 7.2 Hz, 1 H), 4.57 (d, J = 6.6 Hz, 1 H), 4.56 (d, J = 6.6 Hz, 1 H), 4.40 (s, 1 H), 4.17 (d, J = 10.8 Hz, 1 H), 4.14 (s, 2 H), 3.99 (s, 1 H), 3.92 (dt, J = 6.6, 10.2 Hz, 1 H), 3.83 (d, J = 10.8 Hz, 1 H), 3.55 (dt, J = 6.6, 10.2 Hz, 1 H), 2.32 (d, J = 3.5 Hz, 1 H), 2.28 (m, 1 H), 1.95 (m, 2 H), 1.87 (m, 2 H), 1.56 (m, 1 H), 1.47 (s, 3 H), 1.43 (s, 3 H), 1.21(s, 3 H), 1.17 (m, 21 H), 1.09 (s, 3 H), 1.05 (m, 2 H), 0.03 (s, 9 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 203.76, 138.35, 97.61, 97.37, 94.74, 84.95, 72.86, 71.10, 69.81, 66.45, 65.98, 65.53, 63.21, 58.04, 54.98, 49.09, 44.04, 36.67, 32.22, 24.78, 22.82, 21.29, 20.56, 8.37, 18.34, 12.35, –1.37 ppm; HRMS calcd for $C_{43}H_{74}O_8Si_2Na^+$ [M+Na^+] 797.4814 found 797.4822.

Allylic alcohols 24 and 24a: To a solution of vinyl iodide **2** (0.389 g, 0.89 mmol) in THF (6.8 mL) at –78 °C was added *t*BuLi (1.7 M in pentane, 1.05 mL, 1.78 mmol). The reaction mixture was stirred at –78 °C for 20 min and then slowly warmed up to –40 °C over 30 min. A solution of aldehyde **3** (0.53 g, 0.68 mmol) in THF (3.4 mL) was added and the resultant reaction mixture was warmed to 0 °C over 20 min. The reaction mixture was quenched with saturated NH_4Cl solution (20 mL), extracted with Et_2O (2 × 50 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude residue was purified by flash column chromatography (EtOAc/hexanes, 5→20 %) to



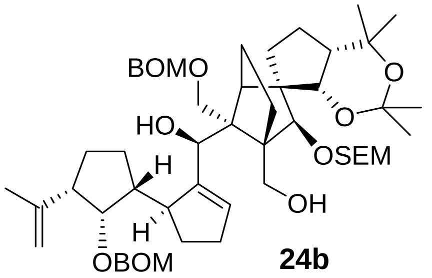
24



24a

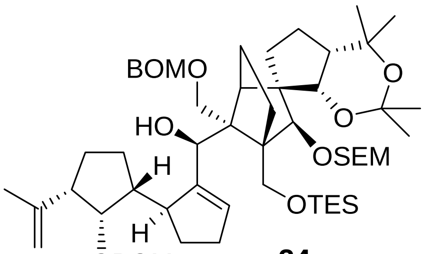
furnish hydroxyl compounds **24** (0.30 g, 0.276 mmol, 40 %) and **24a** (0.30 g, 0.276 mmol, 40 %). **24:** R_f = 0.50 (silica gel, EtOAc:hexanes, 2:8); $[\alpha]^{25}_{D}$ –40.00 (*c* = 0.4, $CHCl_3$); IR ν_{max} (film): 3417brs, 2945s, 2865s, 1458m, 1373m, 1246m, 1196m, 1039s cm^{-1}; ^{1}H NMR: (C_6D_6, 600 MHz) δ = 7.44 (d, *J* = 7.2 Hz, 2 H), 7.34 (d, *J* = 7.8 Hz, 2 H), 7.19 (t, *J* = 7.2 Hz, 2 H), 7.15 (m, 2 H), 7.10 (t, *J* = 7.2 Hz, 1 H), 7.06 (t, *J* = 7.2 Hz, 1 H), 6.44 (s, 1 H), 4.96 (s, 1 H), 4.95 (s, 1 H), 4.94 (brs, 1 H), 4.90 (s, 1 H), 4.85 (d, *J* = 3.0 Hz, 1 H), 4.78 – 4.70 (m, 9 H), 4.56 (d, *J* = 10.2 Hz, 1 H), 4.54 (s, 1 H), 4.52 (d, *J* = 12.0 Hz, 1 H), 4.25 (t, *J* = 3.0 Hz, 1 H), 4.16 (d, *J* = 10.8 Hz, 1 H), 4.13 (s, 1 H), 4.09 (d, *J* = 10.8 Hz, 1 H), 3.91 (m, 1 H), 3.89 (d, *J* = 10.2 Hz, 1 H), 3.57 (dt, *J* = 6.0, 10.2 Hz, 1 H), 3.05 (t, *J* = 8.4 Hz, 1 H), 2.50 – 2.39 (m, 3 H), 2.31 (t, *J* = 12.0 Hz, 1 H), 2.26 – 2.10 (m, 8 H), 2.0 (m, 4 H), 1.77 (m, 1 H), 1.75 (s, 3 H), 1.58 (m, 1 H), 1.48 (s, 3 H), 1.44 (m, 2 H), 1.42 (s, 3 H), 1.22 (s, 3 H), 1.19 (m, 21 H), 1.17 (s, 3 H), 1.05 (m, 2 H), 0.02 (s, 9 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 148.99, 144.68, 138.94, 138.77, 128.67, 128.58, 128.54, 128.29, 127.64, 111.58, 97.80, 97.33, 95.46, 95.18, 85.84, 83.22, 73.35, 71.09, 70.25, 70.02, 68.50, 65.96, 65.80, 63.32, 59.19, 58.83, 55.39, 51.51, 50.51, 50.14, 47.58, 44.35, 36.30, 34.93, 32.23, 31.92, 31.24, 30.45, 30.07, 29.37, 27.03, 25.86, 24.88, 23.77, 22.87, 21.21, 20.83, 18.62, 18.27, 18.16, 12.29, –1.34 ppm; HRMS calcd for $C_{64}H_{102}O_{10}Si_2Na^+$ [*M*+Na$^+$] 1109.6903 found 1109.6908. **24a:** R_f = 0.55 (silica gel, EtOAc:hexanes, 2:8); $[\alpha]^{25}_{D}$ +2.94 (*c* = 1.7, $CHCl_3$); IR ν_{max} (film): 3417brs, 2945s, 2865s, 1458m, 1373m, 1246m, 1196m, 1039s cm^{-1}; ^{1}H NMR: (C_6D_6, 600 MHz) δ = 7.49 (d, *J* = 7.2 Hz, 2 H), 7.27 (d, *J* = 7.8 Hz, 2 H), 7.20 (t, *J* = 7.2 Hz, 2 H), 7.15 (m, 2 H), 7.09 (t, *J* = 7.2 Hz, 1 H), 7.06 (t, *J* = 7.2 Hz, 1 H), 6.41 (s, 1 H), 5.03 (s, 1 H), 4.97 (d, *J* = 7.2 Hz, 1 H), 4.96 (brs, 1 H), 4.92 (s, 1 H), 4.86 (m, 2 H), 4.80 (d, *J* = 12.0 Hz, 1 H), 4.76 (d, *J* = 6.6 Hz, 1 H), 4.73 (s, 2 H), 4.70 (d, *J* = 3.6 Hz, 1 H), 4.67 (d, *J* = 6.6 Hz, 1 H), 4.64 (d, *J* = 12.0 Hz, 1 H), 4.61 (d, *J* = 12.0 Hz, 1 H), 4.50 (d, *J* = 12.0 Hz, 1 H), 4.50 (s, 1 H), 4.32 (t, *J* = 2.4 Hz, 1 H), 4.06 (m, 3 H), 3.90 (dt, *J* = 6.0, 10.2 Hz, 1 H), 3.59 (m, 3 H), 2.56 (s, 1 H), 2.50 – 2.22 (m, 9 H), 2.18 (m, 1 H), 2.10 (m, 2 H), 2.02 (m, 2 H), 1.82 (m, 1 H), 1.81 (s, 3 H), 1.74 (m, 2 H), 1.62 (m, 1 H), 1.49 (s, 3 H), 1.44 (s, 3 H), 1.42 (m, 1 H), 1.25 (s, 3 H), 1.17 (m, 21 H), 1.16 (s, 3 H), 1.11 – 1.00 (m, 2 H), 1.06 (s, 3 H), 0.02 (s, 9 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 148.16, 144.68, 139.17, 139.02, 128.50, 128.39, 128.29, 127.61, 127.37, 111.54, 97.72, 97.33, 94.83, 94.72, 85.86, 83.25, 85.68, 83.25, 73.1671.13, 69.85, 69.48, 68.01, 65.94, 65.03, 62.93, 58.81, 58.24, 55.20, 51.91, 50.83, 55. 20, 51.91, 50.83, 50.49, 47.02, 44.30, 36.36, 32.26, 31.43, 30.85, 30.03, 29.54, 27.58, 26.22, 24.89, 23.80, 22.93, 21.23, 20.84, 18.62, 18.25, 18.12, 12.32, –1.35 ppm; HRMS calcd for $C_{64}H_{102}O_{10}Si_2Na^+$ [M+Na^+] 1109.6903 found 1109.6909.

Diol 24b: To a stirred solution of allylic alcohol **24** (275 mg, 0.25 mmol) in THF (10 mL) at 25 °C was added TBAF (1.0 M in THF, 1.3 mL, 1.3 mmol). The resulting mixture was stirred for 30 min at 25 °C and then concentrated under reduced pressure. The resulting crude residue was purified directly by flash column chromatography (EtOAc/hexanes, 5→20 %) to furnish diol **24b** (228 mg, 0.245 mmol, 98 %). **24b:** R_f = 0.45 (silica gel, Et_2O:hexanes, 1:1); $[\alpha]^{25}_{D}$ –48.00 (c = 1.0, $CHCl_3$); IR ν_{max} (film): 3392brs, 2949s, 2886s, 1454m, 1374m, 1249m, 1195m, 1039s cm^{-1}; ^{1}H NMR: (C_6D_6, 600 MHz) δ = 7.39 (d, J = 7.2 Hz, 2 H), 7.30 (d, J = 7.8 Hz, 2 H), 7.22 (t, J = 7.2 Hz, 2 H), 7.15 (m, 2 H), 7.10 (t, J = 7.2 Hz, 1 H), 7.06 (t, J = 7.2 Hz, 1 H), 5.93 (s, 1 H), 5.13 (brs, 1 H), 5.01 (brs, 1 H), 4.98 (d, J = 7.8 Hz, 1 H), 4.94 (s, 1 H), 4.88 (s, 1 H), 4.72 (d, J = 7.8 Hz, 1 H), 4.69 – 4.64 (m, 3 H), 4.60 (d, J = 11.4 Hz, 1 H), 4.45 – 4.40 (m, 4 H), 4.38 (d, J = 6.6 Hz, 1 H), 4.37 (d, J = 6.6 Hz, 1 H), 4.30 (m, 1 H), 4.27 (s, 1 H), 4.14 (t, J = 3.0 Hz, 1 H), 4.07 (dt, J = 7.2, 9.6 Hz, 1 H), 4.02 (d, J = 10.2 Hz, 1 H), 3.54 (dt, J = 7.2, 9.6 Hz, 1 H), 2.90 (t, J = 9.0 Hz, 1 H), 2.48 (t, J = 7.2 Hz, 2 H), 2.39 (m, 1 H), 2.20 – 2.11 (m, 3 H), 2.10 – 1.92 (m, 4 H), 1.82 – 1.90 (m, 3 H), 1.72 (s, 3 H), 1.62 (d, J = 3.0 Hz, 1 H), 1.60 (m , 1 H), 1.54 (m , 1 H), 1.45 (s, 3 H), 1.39 (s, 3 H), 1.35 (m, 1 H), 1.26 (dd, J = 1.8, 7.8 Hz, 2 H), 1.21 (m, 1 H), 1.14 (s, 3 H), 1.08 (m, 2 H), 0.84 (s, 3 H), 0.01 (s, 9 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 150.70, 144.31, 138.58, 137.95, 128.74, 128.64, 111.92, 97.62, 97.40, 95.18, 95.00, 84.91, 83.33, 73.45, 71.67, 70.94, 70.52, 70.12, 69.72, 66.01, 61.92, 59.43, 57.39, 54.78, 52.32, 51.19, 50.14, 47.55, 44.15, 37.66, 34.93, 32.13, 31.79, 30.39, 29.94, 29.25, 26.91, 25.94, 25.60, 24.66, 23.65, 22.89, 21.47, 20.92, 18.44, –1.33 ppm; HRMS calcd for $C_{64}H_{102}O_{10}Si_2Na^+$ [M+Na^+] 953.5569 found 953.5541.



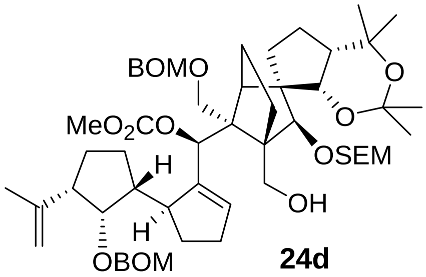
24b

TES ether 24c: To a stirred solution of diol **24b** (228 mg, 0.245 mmol) in CH_2Cl_2 (10 mL) at 25 °C was added imidazole (89 mg, 1.3 mmol) and TESCl (68 μL, 0.437 mmol). The resulting mixture was stirred at this temperature for 30 min, concentrated under reduced pressure, and purified directly by flash column chromatography (EtOAc/hexanes, 5→20 %) to afford **24c** (250 mg, 0.242 mmol, 99 %). **24b:** R_f = 0.5 (silica gel, Et_2O:hexanes, 3:7); $[\alpha]^{25}_{D}$ –35.93 (c = 3.0, $CHCl_3$); IR ν_{max} (film): 3399brs, 2953s, 2877s, 1455m, 1374m, 1249m, 1195m, 1039s cm^{-1}; ^{1}H NMR: (C_6D_6, 600 MHz) δ = 7.44 (d, J = 7.2 Hz, 2 H), 7.32 (d, J = 7.8 Hz, 2 H), 7.19 (t, J = 7.2 Hz, 2 H), 7.14 (m, 2 H), 7.09 (t, J = 7.2 Hz, 1 H), 7.06 (t, J = 7.2 Hz, 1 H), 6.54 (s, 1 H), 4.97 (m, 2 H), 4.90 (d, J = 2.4 Hz, 1 H), 4.89 (s, 1 H), 4.81 (d, J = 6.0 Hz, 1 H), 4.77 – 4.71 (m, 8 H), 4.59 (d, J = 10.2 Hz, 1 H), 4.54 (d, J = 10.2 Hz, 1 H), 4.52 (s, 1 H), 4.23 (t, J = 3.0 Hz, 1 H), 4.11 (s, 1 H), 4.00 (d, J = 11.4 Hz, 1 H), 3.97 (d, J = 11.4 Hz, 1 H), 3.91 (dt, J = 6.0, 10.2 Hz, 1 H), 3.80 (d, J = 10.8 Hz, 1 H), 3.55 (dt, J = 6.0, 10.2 Hz, 1 H), 3.07 (m, 1 H), 2.52 – 2.30 (m, 4 H), 2.30 – 2.08 (m, 8 H), 2.00 (m, 4 H), 1.77 (m, 1 H), 1.74 (s, 3 H), 1.60 (m, 1 H), 1.49 (s, 3 H), 1.45 (m, 1 H), 1.43 (s, 3 H), 1.19 (s, 3 H), 1.07 (m, 1 H), 1.06 (t, J = 7.8 Hz, 9 H), 0.95 (s, 3 H), 0.94 (m, 2 H), 0.69 (q, J = 7.8 Hz, 6 H), 0.03 (s, 9 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 148.71, 144.69, 138.92, 138.82, 129.15, 128.54, 128.29, 111.54, 97.75, 97.32, 95.29, 95.20, 86.12, 83.45, 73.30, 71.10, 70.21, 69.92, 68.23, 65.95, 65.67, 62.57, 59.05, 58.41, 55.38, 51.55, 50.80, 50.42, 48.62, 44.33, 36.29, 32.24, 31.50, 30.70, 30.06, 29.41, 27.24, 25.88, 24.86, 23.78, 22.91, 21.09, 20.90, 18.64, 6.97, 4.58, –1.30 ppm; HRMS calcd for $C_{61}H_{96}O_{10}Si_2Na^+$ [M+Na^+] 1067.6434 found 1067.6457.



24c

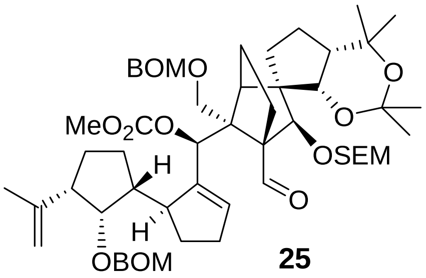
Carbonate 24d: To a solution of **24c** (250 mg, 0.242 mmol) in THF (10 mL) at –78 °C was added KHMDS (0.5 M in PhMe, 1.20 mL, 0.6 mmol), Et_3N (130 μL, 0.956 mmol), and $ClCO_2Me$ (90 μL, 0.956 mmol). The resulting mixture was warmed to 25 °C (30 min) and then quenched with saturated NH_4Cl solution (20 mL). The resulting mixture was extracted with Et_2O (2 × 20 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude residue was then dissolved into THF (2 mL) and added dropwise to a stirred mixture of HF•py/py (1:4, 5 mL) at 0 °C. After warming to 25 °C, the resulting solution was stirred for 12 h and then quenched by carefully pouring the reaction mixture into saturated $NaHCO_3$ solution (50 mL). The resulting mixture was



24d

extracted with Et_2O (2 × 20 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude residue was purified by flash column chromatography (Et_2O/hexanes, 10→40 %) to furnish carbonate **24d** (211 mg, 0.213 mmol, 92 %). **24d:** $R_f = 0.55$ (silica gel, EtOAc:hexanes, 1:1); $[\alpha]^{25}_{D}$ –46.54 (*c* = 1.3, $CHCl_3$); IR ν_{max} (film): 3508brs, 2953s, 2881s, 1746s, 1441w, 1374m, 1267m, 1195m, 1039s cm^{-1}; ^1H NMR: (C_6D_6, 600 MHz) δ = 7.40 (d, *J* = 7.2 Hz, 2 H), 7.37 (d, *J* = 7.8 Hz, 2 H), 7.19 (d, *J* = 7.2 Hz, 2 H), 7.16 (d, *J* = 7.2 Hz, 2 H), 7.09 – 7.05 (m, 2 H), 6.08 (s, 1 H), 5.91 (s, 1 H), 4.98 (d, *J* = 7.2 Hz, 1 H), 4.87 (s, 1 H), 4.84 (s, 1 H), 4.72 (d, *J* = 12.0 Hz, 1 H), 4.70 (m, 1 H), 4.69 (d, *J* = 7.2 Hz, 1 H), 4.68 (d, *J* = 7.2 Hz, 1 H), 4.65 (d, *J* = 12.0 Hz, 1 H), 4.61 (d, *J* = 12.0 Hz, 1 H), 4.59 (s, 1 H), 4.56 (d, *J* = 6.0 Hz, 1 H), 4.52 (d, *J* = 6.0 Hz, 1 H), 4.51 (m, 2 H), 4.27 (d, *J* = 12.0 Hz, 1 H), 4.18 (t, *J* = 3.0 Hz, 1 H), 4.12 (dd, *J* = 6.6, 12.6 Hz, 1 H), 4.02 (dd, *J* = 7.8, 12.6 Hz, 1 H), 3.97 (d, *J* = 11.4 Hz, 1 H), 3.89 (m, 1 H), 3.48 (m, 1 H), 3.34 (s, 3 H), 3.12 (dd, *J* = 7.2, 0.0 Hz, 1 H), 2.98 (t, *J* = 10.2 Hz, 1 H), 2.65 (m, 1 H), 2.59 (t, *J* = 9.0 Hz, 1 H), 2.44 (m ,1 H), 2.41 (d, *J* = 3.6 Hz, 1 H), 2.30 (m, 2 H), 2.20 – 1.90 (m, 9 H), 1.81 (m ,1 H), 1.74 (m ,1 H), 1.70 (s, 3 H), 1.66 (m, 1 H), 1.58 (m, 1 H), 1.47 (s, 3 H), 1.42 (s, 3 H), 1.25 (m, 1 H), 1.18 (s, 3 H), 1.04 (m, 2 H), 0.97 (s, 3 H), 0.03 (s, 9 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 155.83, 148.72, 144.35, 138.72, 138.66, 128.64, 128.29, 126.50, 111.80, 97.95, 97.36, 95.61, 94.96, 83.47, 83.24, 78.26, 73.72, 71.06, 70.54, 70.03, 67.08, 66.16, 62.09, 60.01, 59.00, 54.44, 51.33, 50.33, 49.65, 45.95, 44.29, 36.16, 34.93, 32.28, 32.23, 31.92, 30.09, 29.51, 29.45, 26.97, 25.94, 25.60, 24.82, 23.66, 22.93, 21.30, 18.35, –1.43 ppm; HRMS calcd for $C_{57}H_{84}O_{12}SiNa^+$ $[M+Na^+]$ 1011.5624 found 1011.5628.

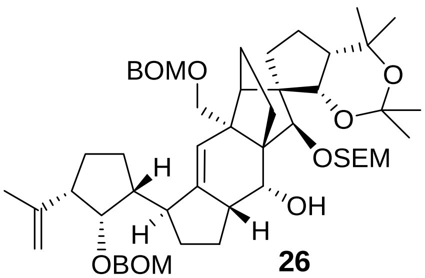
Aldehyde carbonate 25: To a stirred solution of hydroxyl carbonate **24d** (180 mg, 0.182 mmol) in CH_2Cl_2 (5 mL) at 25 °C was added $PhI(OAc)_2$ (0.293 g, 0.91 mmol) and TEMPO (28 mg, 0.182 mmol). The resulting mixture was stirred for 24 h and then quenched with saturated $NaHCO_3$ solution (10 mL). The resulting mixture was extracted with Et_2O (2 × 20 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude residue was purified by flash column chromatography (Et_2O/hexanes, 10→40 %) to furnish aldehyde carbonate **25** (175 mg, 0.178 mmol, 98 %). **25:** $R_f = 0.70$ (silica gel, Et_2O:hexanes, 1:1); $[\alpha]^{25}_{D}$ –44.76 (*c* = 2.1, $CHCl_3$); IR ν_{max} (film): 3508brs, 2953s, 2881s, 1746s, 1441w, 1374m, 1267m, 1195m, 1039s cm^{-1}; ^1H NMR:



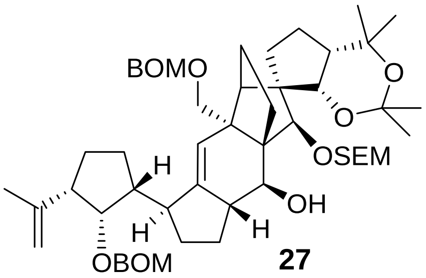
25

(C_6D_6, 500 MHz) δ = 9.95 (s, 1 H), 7.36 (m, 4 H), 7.19 (t, *J* = 7.5 Hz, 2 H), 7.17 (t, *J* = 7.5 Hz, 2 H), 7.09 – 7.05 (m, 2 H), 6.03 (s, 1 H), 5.76 (s, 1 H), 4.98 (d, *J* = 7.5 Hz, 1 H), 4.82 (s, 1 H), 4.81 (s, 1 H), 4.76 (s, 1 H), 4.68 (d, *J* = 11.5 Hz, 1 H), 4.63 (s, 1 H), 4.61 (d, *J* = 11.5 Hz, 1 H), 4.57 – 4.49 (m, 3 H), 4.46 (s, 1 H), 4.41 (d, *J* = 6.5 Hz, 1 H), 4.16 (t, *J* = 3.0 Hz, 1 H), 4.00 (d, *J* = 11.0 Hz, 1 H), 3.94 (d, *J* = 11.0 Hz, 1 H), 3.90 (m, 1 H), 3.39 (s, 3 H), 3.34 (m, 1 H), 2.90 (t, *J* = 7.5 Hz, 1 H), 2.73 (ddd, *J* = 5.0, 9.5, 14.5 Hz, 1 H), 2.61 (m, 1 H), 2.54 (m, 1 H), 2.49 (d, *J* = 3.5 Hz, 1 H), 2.43 (t, *J* = 12.5 Hz, 1 H), 2.26 (m, 2 H), 2.20 – 1.70 (m, 11 H), 1.68 (s, 3 H), 1.54 (dd, *J* = 12.6, 17.0 Hz, 1 H), 1.40 (s, 3 H), 1.40 (m, 1 H), 1.37 (s, 3 H), 1.13 (s, 3 H), 1.07 (m, 1 H), 0.98 (s, 3 H), 0.07 (s, 3 H) ppm; ^{13}C NMR: (C_6D_6, 125 MHz) δ = 199.04, 155.35, 148.19, 144.24, 138.74, 138.49, 128.73, 128.62, 128.29, 128.19, 127.80, 127.75, 125.42, 111.85, 97.42, 96.82, 95.66, 94.83, 83.32, 82.46, 77.19, 73.64, 70.99, 70.79, 69.83, 68.46, 65.80, 62.73, 56.85, 54.68, 51.32, 50.52, 49.53, 45.99, 44.18, 35.88, 34.93, 32.15, 32.02, 29.97, 29.51, 29.44, 27.48, 25.92, 24.73, 23.59, 22.97, 20.83, 19.67, 18.24, –1.26 ppm; HRMS calcd for $C_{57}H_{82}O_{12}SiNa^+$ [*M*+Na$^+$] 1009.5467 found 1009.5471.

Hydroxy olefins 26 and 27: To a stirred solution of SmI_2 (0.1 M in THF, 10.1 mL, 1.01 mmol) and HMPA (0.54 mL, 3.03 mmol) at –10 °C was added dropwise a solution of **25** (200 mg, 0.202 mmol) in THF (10 mL). The reaction mixture was warmed to 25 °C (20 min) and quenched with saturated NH_4Cl solution (20 mL). The resulting mixture was extracted with Et_2O (2 × 20 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude residue was purified by preparative TLC (EtOAc/CH_2Cl_2, 7:93, ran twice) to furnish hydroxyl olefins **26** (55 mg, 0.060 mmol, 28 %) and **27** (95 mg, 0.104 mmol, 52 %) **26:** R_f = 0.60 (silica gel, EtOAc:CH_2Cl_2, 1:9); $[\alpha]^{25}_D$ –4.33 (*c* = 0.6, $CHCl_3$); IR ν_{max} (film): 3508brs, 2928s, 2870s, 1456w, 1370m, 1251m, 1191m, 1044s cm^{-1}; ^{1}H NMR: (C_6D_6, 600 MHz) δ = 7.38 (d, *J* = 7.2 Hz, 2 H), 7.29 (d, *J* = 7.2 Hz, 2 H), 7.15 (m, 2 H), 7.08 (t, *J* = 7.2 Hz, 1 H), 7.04 (t, *J* = 7.2 Hz, 1 H), 5.87 (s, 1 H), 5.05 (d, *J* = 6.6



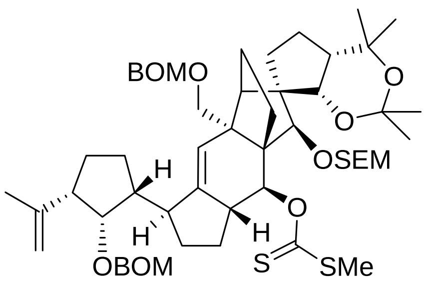
26



27

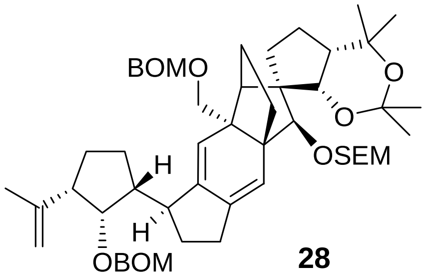
Hz, 1 H), 5.00 (s, 1 H), 4.95 (s, 1 H), 4.72 (d, *J* = 6.6 Hz, 1 H), 4.65 (d, *J* = 7.2 Hz, 1 H), 4.63 – 4.61 (m, 4 H), 4.58 (d, *J* = 12.0 Hz, 1 H), 4.55 (d, *J* = 11.4 Hz, 1 H), 4.53 (d, *J* = 12.0 Hz, 1 H), 4.41 (s, 1 H), 4.37 (t, *J* = 6.0 Hz, 1 H), 4.16 (d, *J* = 10.2 Hz, 1 H), 4.05 (t, *J* = 2.4 Hz, 1 H), 3.98 (m, 1 H), 2.85 (d, *J* = 5.4 Hz, 1 H), 2.75 (m, 1 H), 2.66 (m, 1 H), 2.39 (dt, *J* = 7.8, 11.4 Hz, 1 H), 2.24 – 2.00 (m, 7 H), 1.91 (d, *J* = 2.4 Hz, 1 H), 1.85 (s, 3 H), 1.67 (m, 2 H), 1.54 (s, 3 H), 1.52 (m, 3 H), 1.47 (s, 3 H), 1.42 (m, 3 H), 1.34 (s, 3 H), 1.17 (s, 3 H), 1.09 (m, 2 H), 0.02 (s, 3 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 145.70, 144.68, 138.93, 138.67, 128.55, 128.48, 128.29, 127.57, 123.53, 111.45, 97.36, 96.89, 94.87, 94.73, 81.67, 80.86, 73.75, 72.94, 71.22, 69.75, 69.59, 65.58, 65.33, 57.54, 55.17, 52.92, 52.63, 52.08, 50.20, 44.80, 42.90, 42.40, 37.34, 32.33, 30.19, 30.00, 29.76, 27.47, 25.55, 25.31, 24.85, 24.09, 23.78, 23.74, 22.99, 18.47, –1.42 ppm; HRMS calcd for $C_{55}H_{80}O_9SiNa^+$ [*M*+Na$^+$] 935.5464 found 935.5442. **27:** R$_f$ = 0.65 (silica gel, EtOAc:CH_2Cl_2, 1:9); $[\alpha]^{25}_D$ +6.66 (*c* = 0.6, $CHCl_3$); IR ν_{max} (film): 3508brs, 2928s, 2870s, 1456w, 1370m, 1251m, 1191m, 1044s cm^{-1}; ^{1}H NMR: (C_6D_6, 600 MHz) δ = 7.39 (d, *J* = 7.2 Hz, 2 H), 7.30 (d, *J* = 7.2 Hz, 2 H), 7.15 (m, 4 H), 7.08 (t, *J* = 7.2 Hz, 1 H), 7.04 (t, *J* = 7.2 Hz, 1 H), 5.81 (d, *J* = 1.8 Hz, 1 H), 4.97 (s, 1 H), 4.94 (d, *J* = 6.6 Hz, 1 H), 4.93 (s, 1 H), 4.76 (d, *J* = 6.6 Hz, 1 H), 4.63 – 4.59 (m, 4 H), 4.57 (d, *J* = 6.6 Hz, 1 H), 4.56 (d, *J* = 6.6 Hz, 1 H), 4.51 (d, *J* = 12.6 Hz, 1 H), 4.47 (d, *J* = 6.0 Hz, 1 H), 4.40 (s, 1 H), 4.32 (s, 1 H), 4.25 (d, *J* = 7.2 Hz, 1 H), 3.97 (m, 2 H), 3.74 (d, *J* = 9.6 Hz, 1 H), 3.66 (m, 1 H), 3.49 (d, *J* = 9.6 Hz, 1 H), 3.47 (m, 1 H), 2.79 (dt, *J* = 7.8, 11.4 Hz, 1 H), 2.59 (m, 2 H), 2.45 (m, 1 H), 2.20 – 1.90 (m, 8 H), 1.94 (d, *J* = 3.0 Hz, 1 H), 1.83 (s, 3 H), 1.80 (m, 1 H), 1.66 (m, 2 H), 1.57 (m, 1 H), 1.52 (s, 3 H), 1.48 (m, 2 H), 1.47 (s, 3 H), 1.45 – 1.33 (m, 7 H), 1.32 (s, 3 H), 1.66 (s, 3 H), 1.04 (t, *J* = 8.4 Hz, 1 H), –0.06 (s, 3 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 146.99, 144.77, 138.97, 138.58, 128.57, 128.46, 128.54, 123.62, 111.33, 98.31, 97.39, 94.87, 94.78, 94.67, 89.75, 80.84, 74.79, 73.65, 73.14, 71.20, 69.68, 69.47, 65.71, 52.49, 51.71, 49.01, 47.17, 44.75, 42.38, 37.00, 32.34, 30.27, 30.19, 30.12, 29.72, 27.41, 25.28, 24.80, 23.74, 23.44, 23.09, 20.50, 18.56, –1.48 ppm; HRMS calcd for $C_{55}H_{80}O_9SiNa^+$ [*M*+Na$^+$] 935.5464 found 935.5477.

Xanthate 27a: To a solution of alcohol **27** (70 mg, 0.077 mmol) in THF (1.5 mL) at 25 °C was added NaH (18 mg, 0.46 mmol, 60 % dispersion in mineral oil) and the reaction mixture was stirred for 20 min. The resulting mixture was cooled to 0 °C, CS_2 (37 μL, 0.61 mmol) was added, and the reaction mixture was stirred for 30 min at that temperature. MeI (57 μL, 0.92 mmol) was added at 0 °C and the mixture was warmed to 25 °C and stirred for 3 h. The reaction was quenched with saturated NH_4Cl solution (10 mL), extracted with Et_2O (2 × 20 mL), dried ($MgSO_4$), and concentrated in vacuo. The resulting xanthate could be taken on crude to the next step or purified by column chromatography (Et_2O/hexanes, 5→20 %). **27a:** $R_f = 0.40$ (silica gel, Et_2O:CH_2Cl_2, 2:8); $[\alpha]^{25}_{D}$ +50.33 (c = 0.3, $CHCl_3$); IR ν_{max} (film): 2948m, 2882m, 1647w, 1554m, 1377m, 1365m, 1229s, 1039s cm^{-1}; ^{1}H NMR: (C_6D_6, 600 MHz) δ = 7.38 (d, J = 7.2 Hz, 2 H), 7.28 (d, J = 7.2 Hz, 2 H), 7.15 (m, 2 H), 7.08 (t, J = 7.2 Hz, 1 H), 7.04 (t, J = 7.2 Hz, 1 H), 6.78 (d, J = 7.2 Hz, 1 H), 5.57 (s, 1 H), 5.00 (s, 1 H), 4.96 (s, 1 H), 4.95 (d, J = 4.2 Hz, 1 H), 4.87 (d, J = 4.2 Hz, 1 H), 4.66 (d, J = 12.0 Hz, 1 H), 4.62 (d, J = 7.2 Hz, 1 H), 4.59 – 4.55 (m, 4 H), 4.53 (d, J = 11.4 Hz, 1 H), 4.51 (d, J = 11.4 Hz, 1 H), 4.42 (s, 1 H), 4.29 (s, 1 H), 3.95 (m, 2 H), 3.80 (m, 1 H), 3.77 (d, J = 9.0 Hz, 1 H), 3.67 (d, J = 9.0 Hz, 1 H), 2.71 (m, 1 H), 2.62 – 2.54 (m, 2 H), 2.25 – 2.12 (m, 3 H), 2.06 – 2.00 (m, 2 H), 1.92 (m, 2 H), 1.86 (s, 3 H), 1.84 (m, 1 H), 1.77 (m, 1 H), 1.69 (m, 2 H), 1.66 (d, J = 2.4 Hz, 1 H), 1.64 (s, 3 H), 1.56 (s, 3 H), 1.50 – 1.38 (m, 4 H), 1.36 (s, 3 H), 1.33 (m, 2 H), 1.19 (m, 1 H), 1.16 (s, 3 H), 1.08 (m, 2 H), 0.04 (s, 9 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 146.04, 144.59, 138.85, 138.60, 128.60, 128.50, 128.29, 127.75, 127.63, 122.90, 111.47, 97.68, 97.52, 94.72, 94.68, 86.17, 84.63, 80.67, 73.63, 71.40, 71.09, 69.74, 69.57, 66.50, 58.00, 56.37, 55.47, 52.55, 51.61, 49.13, 46.55, 44.63, 41.50, 36.86, 32.14, 30.69, 30.24, 29.89, 29.79, 27.36, 25.25, 24.66, 23.97, 23.75, 22.93, 21.17, 18.88, 18.77, –1.11 ppm; HRMS calcd for $C_{57}H_{82}O_9SiS_2Na^+$ [M+Na^+] 1025.5061 found 1025.5065.



27a

Triene 28: (From **26**): To a solution of alcohol **26** (10 mg, 0.0109 mmol) in pyridine (1 mL) at 25 °C was added $POCl_3$ (61 µL, 0.65 mmol) and DBU (ca. 10 µL). The resulting mixture was heated to 60 °C for 3 h and then quenched by pouring the reaction mixture into saturated $NaHCO_3$ solution (10 mL). The resulting mixture was extracted with Et_2O (2 × 10 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude residue was purified by flash column chromatography (Et_2O/hexanes, 5→20 %) to furnish **28** (8 mg, 0.0089 mmol, 88 %). (From **27a**): A solution of xanthate **27a** (103 mg, 0.102 mmol) and $i$$Pr_2NEt$ (0.1 mL, 0.104 mmol) in 1,2-dichlorobenzene (6 mL) was heated under microwave irradiation at 185 °C for 15 min. The

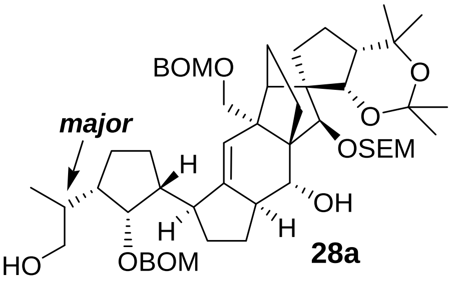


28

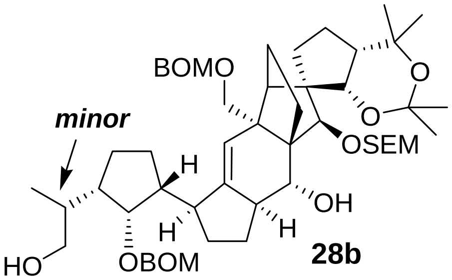
crude residue was purified directly by flash column chromatography (Et_2O/hexanes, 5→20 %) to furnish triene **28** (86 mg, 0.096 mmol, 92 % from **27**). **28:** $R_f = 0.40$ (silica gel, Et_2O:hexanes, 2:8); $[\alpha]^{25}_{D}$ +25.2 (c = 1.0, $CHCl_3$); IR ν_{max} (film): 3020w, 2941w, 2981w, 1214s, 1195m, 1041s cm^{-1}; ^{1}H NMR: (C_6D_6, 600 MHz) δ = 7.35 (d, J = 7.8 Hz, 2 H), 7.29 (d, J = 7.8 Hz, 1 H), 7.15 (m, 2 H), 7.09 (t, J = 7.8 Hz, 1 H), 7.04 (t, J = 7.8 Hz, 1 H), 6.21 (s, 1 H), 6.15 (s, 1 H), 5.11 (d, J = 7.8 Hz, 1 H), 4.95 (s, 1 H), 4.90 (s, 1 H), 4.77 (d, J = 7.8 Hz, 1 H), 4.70 – 4.59 (m, 6 H), 4.58 (d, J = 12.6 Hz, 1 H), 4.51 (d, J = 12.0 Hz, 1 H), 4.50 (d, J = 12.0 Hz, 1 H), 4.40 (s, 1 H), 4.33 (s, 1 H), 4.18 (m, 1 H), 4.08 (t, J = 3.0 Hz, 1 H), 3.85 (d, J = 9.6 Hz, 1 H), 3.81 (d, J = 9.6 Hz, 1 H), 3.54 (m, 1 H), 2.90 – 2.83 (m, 2 H), 2.36 (t, J = 6.6 Hz, 1 H), 2.21 (d, J = 2.4 Hz, 1 H), 2.16 – 1.90 (m, 6 H), 1.88 – 1.78 (m, 3 H), 1.76 (s, 3 H), 1.75 – 1.72 (m, 3 H), 1.65 (t, J = 12.0 Hz, 1 H), 1.64 – 1.58 (m, 3 H), 1.51 (s, 3 H), 1.45 (s, 3 H), 1.43 (m, 1 H), 1.37 (s, 3 H), 1.32 (m, 1 H), 1.31 (s, 3 H), 1.17 (m, 2 H), 1.14 (s, 3 H), 0.06 (s, 9 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 144.73, 144.45, 141.06, 138.87, 138.75, 128.54, 128.50, 128.29, 127.71, 127.65, 127.61, 125.54, 122.15, 111.15, 97.37, 96.84, 95.04, 94.53, 83.18, 80.49, 73.66, 71.18, 71.05, 69.73, 69.37, 64.98, 56.77, 54.75, 52.56, 50.32, 47.92, 44.61, 44.00, 36.90, 32.26, 31.73, 30.61, 30.43, 30.11, 29.71, 29.49, 28.16, 27.27, 25.41, 24.85, 23.69, 23.13, 18.51, –1.26 ppm; HRMS calcd for $C_{55}H_{78}O_8SiNa^+$ [M+Na^+] 917.5358 found 917.5357.

Diols 28a and 28b: To a solution of triene **28** (30 mg, 0.033 mmol) in THF (1.5 mL) at –10 °C was added thexylborane (0.5 M in THF, 0.34 mL, 0.168 mmol). The reaction mixture was slowly warmed to 25 °C (over 30 min), then cooled to 0 °C, and BH_3•THF (0.5 mL, 0.50 mmol, 1.0 M in THF) was added. The mixture was stirred at 25 °C for 1.5 h, and then cooled to 0 °C. A premixed solution of 30 % H_2O_2/3 N NaOH (1:1, 1.5 mL) was then added and the resulting mixture was diluted with THF (3 mL), heated to 40 °C (30 min), cooled to 25 °C, and then quenched with saturated NH_4Cl solution (5 mL). The resulting mixture was extracted with EtOAc (2 × 20 mL), washed with brine (10 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (EtOAc/hexanes, 15→20 %) to afford diols **28a** and **28b** (20 mg, 0.022 mmol, 65 %) as a 1.3:1.0 mixture of diastereoisomers. **28a:** $R_f = 0.35$ (silica gel, EtOAc:hexanes, 1:2); $[\alpha]^{25}_{D}$ +25.4 (c = 1.0, $CHCl_3$); IR ν_{max} (film):

3468brs, 2945m, 2865m, 1456w, 1374w, 1261w, 1196m, 1102m, 1044s cm^{-1}; ^{1}H NMR: (C_6D_6, 600 MHz) δ = 7.35 (d, *J* = 7.2 Hz, 2 H), 7.30 (d, *J* = 7.2 Hz, 1 H), 7.15 (m, 4 H), 7.09 (t, *J* = 7.2 Hz, 1 H), 7.04 (t, *J* = 7.2 Hz, 1 H), 6.21 (s, 1 H), 6.07 (s, 1 H), 4.95 (d, *J* = 6.6 Hz, 1 H), 4.71 – 4.63 (m, 8 H), 4.61 (s, 2 H), 4.54 (d, *J* = 12.0 Hz, 1 H), 4.49 (d, *J* = 12.0 Hz, 1 H), 4.22 (d, *J* = 10.2 Hz, 1 H), 4.08 (m, 2 H), 4.06 (d, *J* = 10.2 Hz, 1 H), 3.95 (s, 1 H), 3.85 (m, 1 H), 3.43 (dd, *J* = 3.0, 10.2 Hz, 1 H), 3.35 (m, 1 H), 3.25 (dd, *J* = 6.0, 10.2 Hz, 1 H), 2.84 (m, 1 H), 2.66 (t, *J* = 9.0 Hz, 1 H), 2.39 (dt, *J* = 7.8, 11.4 Hz, 1 H), 2.30 (m, 2 H), 2.17 (s, 1 H), 2.07 (m, 3 H), 1.89 (m, 2 H), 1.75 (m, 2 H), 1.63 (m, 6 H), 1.50 (s, 3 H), 1.45 (s, 3 H), 1.38 (m, 6 H), 1.33 (s, 3 H), 1.19 (m, 1 H), 1.16 (s, 3 H), 1.09 (d, *J* = 6.6 Hz, 3 H), 0.91 (m, 2 H), –0.041 (s, 9 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 146.03, 138.9, 138.77, 128.52, 128.29, 127.66, 125.07, 97.89, 97.32, 95.52, 95.00, 84.10, 82.86, 73.66, 72.55, 71.22, 70.0, 69.72, 69.46, 66.78, 65.69, 58.45, 55.46, 54.33, 50.61, 50.00, 49.68, 48.42, 44.57, 41.86, 37.33, 36.11, 32.36, 31.86, 31.72, 30.16, 29.75, 27.61, 26.75, 25.36, 24.90, 23.15, 21.91, 18.27, 16.90, –1.26 ppm; HRMS calcd for $C_{55}H_{82}O_{10}SiNa^{+}$ [*M*+Na^{+}] 953.5569 found 953.5566. **28b:** R$_f$ = 0.45 (silica gel, EtOAc:hexanes, 1:2); $[\alpha]^{25}_{D}$ +22.2 (*c* = 1.0, $CHCl_3$); IR ν_{max} (film): 3468brs, 2945m, 2865m, 1456w, 1374w, 1261w, 1196m, 1102m, 1044s cm^{-1}; ^{1}H NMR: (C_6D_6, 600 MHz) δ = 7.35 (d, *J* = 7.2 Hz, 2 H), 7.28 (d, *J* = 7.2 Hz, 1 H), 7.15 (m, 4 H), 7.09 (t, *J* = 7.2 Hz, 1 H), 7.04 (t, *J* = 7.2, Hz, 1 H), 6.06 (s, 1 H), 6.07 (s, 1 H), 4.95 (d, *J* = 6.6 Hz, 1 H), 4.71 – 4.67 (m, 3 H), 4.64 – 4.55 (m, 3 H), 4.62 (s, 2 H), 4.54 (d, *J* = 12.0 Hz, 1 H), 4.44 (s, 1 H), 4.40 (d, *J* = 10.2 Hz, 1 H), 4.22 (d, *J* = 10.2 Hz, 1 H), 4.13 (s, 1 H), 4.09 – 4.07 (m, 2 H), 4.06 (d, *J* = 10.2 Hz, 1 H), 3.85 (m, 1 H), 3.56 (dd, *J* = 3.0, 10.2 Hz, 1 H), 3.44 (dd, *J* = 3.0, 10.2 Hz, 1 H), 3.35 (m, 1 H), 2.84 (m, 1 H), 2.60 (t, *J* = 9.0 Hz, 1 H), 2.39 (dt, *J* = 7.8, 11.4 Hz, 1 H), 2.30 (m, 2 H), 2.17 (s, 1 H), 2.07 (m, 3 H), 1.90 (m, 1 H), 1.83 (m, 2 H), 1.75 – 1.53 (m, 6 H), 1.50 (s, 6 H), 1.45 (s, 3 H), 1.44 – 1.35 (m, 4 H), 1.33 (s, 3 H), 1.17 (s, 3 H), 1.09 (t, *J* = 8.4 Hz, 2 H), 0.89 (d, *J* = 6.6 Hz, 3 H), –0.037 (s, 9 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 146.03, 138.92, 138.42, 128.64, 128.51, 128.41, 127.73, 127.54, 125.01, 97.89, 97.32, 96.08, 94.98, 84.12, 73.65, 72.51, 71.22, 70.0, 69.75, 69.44, 68.23, 65.60, 58.45, 55.43, 54.46, 50.61, 50.43, 49.64, 48.53, 44.56, 41.84,



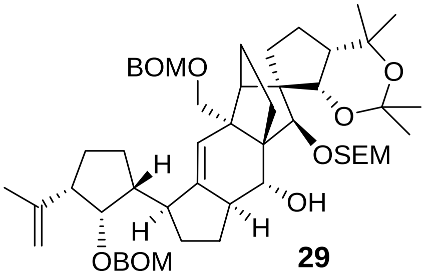
28a



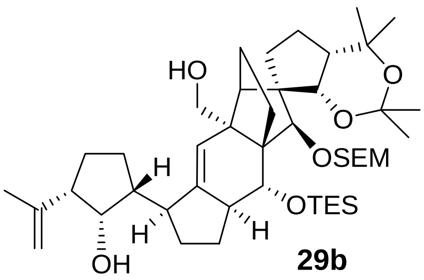
28b

37.33, 35.95, 32.36, 31.90, 31.53, 30.16, 29.75, 27.62, 26.82, 25.32, 24.90, 23.15, 21.90, 18.28, 16.05, –1.55 ppm; HRMS calcd for $C_{55}H_{82}O_{10}SiNa^+$ [*M*+Na^+] 953.5569 found 953.5566.

Diene alcohol 29: To a solution of diols **28a** and **28b** (30 mg, 0.032 mmol) in THF (1.5 mL) at 25 °C was added pyridine (31 μL, 0.387 mmol), *o*NO_2PhSeCN (15 mg, 0.064) mmol), and *n*Bu_3P (48 μl, 0.193 mmol). The reaction mixture was stirred at 25 °C for 10 min and then quenched with saturated $NaHCO_3$ solution (1 mL). The resulting mixture was extracted with Et_2O (2 x 5 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude residue was purified by flash column chromatography (EtOAc/hexanes, 15→20 %) to afford the desired selenides as a mixture of diastereoisomers. To a solution of this selenide mixture in THF (1.0 mL) at 0 °C was added a solution of 30 % H_2O_2 (0.1 mL). The reaction mixture was warmed to 25 °C and stirred for 12 h. The resulting mixture was diluted with H_2O (3 mL), extracted with Et_2O (2 x 10 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (EtOAc/hexanes, 2→6 %) to afford hydroxyl diene **29** (20 mg, 67 % for the two steps). **29:** R_f = 0.35 (silica gel, EtOAc:hexanes, 1:6); $[\alpha]^{25}_D$ +13.0 (*c* = 1.0, $CHCl_3$); IR ν_{max} (film): 3478brs, 2946m, 2881m, 1451w, 1373w, 1249w, 1193m, 1102m, 1046s cm^{-1}; ^1H NMR: (C_6D_6, 600 MHz) δ = 7.37 (d, *J* = 7.2 Hz, 2 H), 7.31 (d, *J* = 7.2 Hz, 1 H), 7.15 (m, 4 H), 7.09 (t, *J* = 7.2 Hz, 1 H), 7.04 (t, *J* = 7.2 Hz, 1 H), 6.09 (s, 1 H), 6.07 (s, 1 H), 4.96 (s, 1 H), 4.95 (s, 1 H), 4.91 (s, 1 H), 4.72 – 4.67 (m, 4 H), 4.65 – 4.62 (m, 3 H), 4.58 (d, *J* = 10.2 Hz, 1 H), 4.56 (d, *J* = 10.2 Hz, 1 H), 4.50 (d, *J* = 12.0 Hz, 1 H), 4.43 (s, 1 H), 4.23 (d, *J* = 10.2 Hz, 1 H), 4.10 – 4.05 (m, 3 H), 3.85 (m, 1 H), 3.36 (m, 1 H), 2.87 (m, 1 H), 2.82 (t, *J* = 8.4 Hz, 1 H), 2.39 (dt, *J* = 7.8, 11.4 Hz, 1 H), 2.31 (m, 2 H), 2.18 (m, 2 H), 2.08 (m, 3 H), 1.94 (m, 2 H), 1.77 (s, 3 H), 1.72 (m, 2 H), 1.69 – 1.62 (m, 2 H), 1.50 (s, 3 H), 1.48 (m, 3 H), 1.45 (s, 3 H), 1.20 (m, 1 H), 1.69 (s, 3 H), 1.09 (t, *J* = 8.4 Hz, 1 H), –0.04 (s, 9 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 146.23, 144.43, 138.92, 138.88, 128.53, 128.50, 128.29, 127.59, 124.84, 111.61, 97.88, 97.31, 95.02, 94.57, 84.08, 81.60, 73.65, 72.69, 71.22, 69.77, 69.50, 65.60, 58.42, 55.46, 54.27, 51.98, 50.60, 49.84, 49.51, 44.58, 42.22, 37.32, 32.36, 31.72, 31.43, 30.18, 29.76, 27.55, 25.60, 25.35, 24.90, 23.75, 23.15, 21.89, 18.27, –1.55 ppm; HRMS calcd for $C_{55}H_{82}O_{10}SiNa^+$ [*M*+Na^+] 935.5464 found 935.5442.



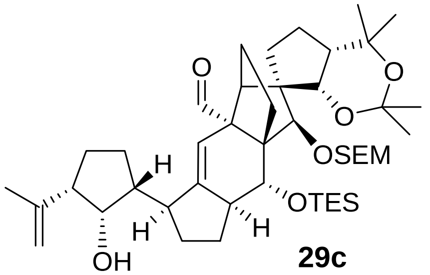
29



29b

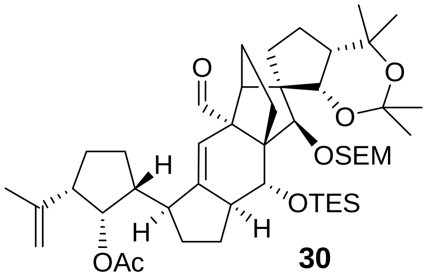
TES ether 29a and Diol 29b: To a solution of alcohol **29** (18 mg, 0.0197 mmol) in THF (1.0 mL) at –50 °C was added KHMDS (0.5 M in PhMe, 0.24 mL, 0.118 mmol, 0.5 M in toluene). The reaction mixture was stirred at –50 °C for 5 min before TESCl (14 µL, 0.079 mmol) and Et$_3$N (22 µL, 0.157 mmol) were addded. The cooling bath was removed, and the reaction mixture was stirred at 25 °C for 20 min. The resulting mixture was quenched with saturated NH$_4$Cl (4 mL) solution and extracted with Et$_2$O (2 × 10 mL). The organic layer was washed with brine (10 mL), dried (MgSO$_4$), and subjected to flash column chromatography (EtOAc/hexanes, 6 %) to furnish TES ether **29a** (19 mg, 94 %). To a solution **29a** (14 mg 0.0136mmol) in THF (1.0 mL) at –78 °C was added LiDBB (~1.0 M in THF, freshly prepared) dropwise until the reaction mixture assumed a persistent darkgreen color. The reaction mixture was allowed to warm up to –50 °C (30 min), during which time LiDBB was constantly added to maintain the solution color as darkgreen. The reaction was quenched at –50 °C with saturated NH$_4$Cl (1 mL) solution, extracted with Et$_2$O (2 × 10 mL), dried (MgSO$_4$), and concentrated in vacuo. The crude residue was dissolved in CH$_2$Cl$_2$ (5 mL) and silical gel (1.0 g) was added. The mixture was stirred at 25 °C for 30 min (to fully hydrolyze the intermediate hemiacetals), and then directly purified by flash column chromatography (EtOAc/hexanes, 5→14 %) to afford diol **29b** (9 mg, 84 %). **29b:** R$_f$ = 0.35 (silica gel, EtOAc:hexanes, 1:4); $[\alpha]^{25}_{D}$ +15.8 (*c* = 1.0, CHCl$_3$); IR ν_{max} (film): 3432brs, 2952m, 2870m, 1461w, 1373w, 1248w, 1195m, 1070s cm^{-1}; ^{1}H NMR: (C$_6$D$_6$, 600 MHz) δ = 5.78 (s, 1 H), 5.17 (d, *J* = 4.8 Hz, 1 H), 4.89 (s, 1 H), 4.84 (d, *J* = 4.8 Hz, 1 H), 4.80 (s, 1 H), 4.47 (s, 1 H), 4.44 (s, 1 H), 4.21 (s, 1 H), 4.08 (d, *J* = 11.4 Hz, 1 H), 3.97 (m, 1 H), 3.89 (s, 1 H), 3.88 (d, *J* = 11.4 Hz, 1 H), 3.82 (m, 1 H), 2.83 (dt, *J* = 7.8, 7.8 Hz, 1 H), 2.62 (t, *J* = 8.4 Hz, 1 H), 2.38 (dt, *J* = 7.8, 11.4 Hz, 1 H), 2.21 – 2.00 (m, 8 H), 1.92 (m, 2 H), 1.86 (d, *J* = 3.0 Hz, 1 H), 1.83 (m, 2 H), 1.62 (s, 3 H), 1.61 (s, 3 H), 1.57 (m, 2H), 1.49 – 1.45 (m, 4 H), 1.32 (s, 3 H), 1.20 (t, *J* = 11.4 Hz, 1 H), 1.16 (s, 3 H), 1.10 (t, *J* = 7.8 Hz, 9 H), 1.09 – 1.04 (m, 2 H), 0.80 (m, 6 H), 0.05 (s, 9 H) ppm; ^{13}C NMR: (C$_6$D$_6$, 150 MHz) δ = 146.86, 144.09, 120.89, 112.13, 98.16, 97.55, 82.05, 74.23, 73.87, 73.04, 71.17, 66.30, 65.47, 66.29, 65.47, 57.09, 56.22, 54.29, 52.56, 50.42, 49.93, 48.65, 44.52, 44.36, 37.00, 32.33, 30.32, 30.20, 29.78, 29.39, 28.82, 25.64, 24.83, 23.69, 23.37, 22.94, 22.19, 18.56, 7.54, 5.82, –1.26 ppm; HRMS calcd for $C_{45}H_{78}O_7Si_2Na^+$ [*M*+Na^+] 809.5178 found 809.5183.

Hydroxy aldehyde 29c: To a solution of diol **29b** (8 mg, 0.01 mmol) in CH_2Cl_2 (0.6 mL) at 25 °C was added $PhI(OAc)_2$ (10 mg, 0.03 mmol) and TEMPO (1.6 mg, 0.01 mmol). The reaction mixture was stirred at 25 °C for 24 h and then quenched with saturated aqueous solutions of $Na_2S_2O_3$ (1 mL) and $NaHCO_3$ solution (1 mL). The resulting mixture was extracted with Et_2O (2 × 5 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (EtOAc/hexanes, 6 %) to afford hydroxyl aldehyde **29c** (7 mg, 88 %). **29c:** R_f = 0.38 (silica gel, EtOAc:hexanes, 1:6); $[\alpha]^{25}_D$ +110.8 (*c* = 0.6, $CHCl_3$); IR ν_{max} (film): 3696brs, 2946m, 1696w, 1458w, 1370w, 1244w, 1057s cm^{-1}; ^1H NMR: (C_6D_6, 600 MHz) δ = 10.54 (s, 1 H), 5.63 (s, 1 H), 5.14 (d, *J* = 4.8 Hz, 1 H), 4.88 (d, *J* = 4.8 Hz, 1 H), 4.87 (s, 1 H), 4.76 (s, 1 H), 4.56 (s, 1 H), 4.47 (s, 1 H), 4.31 (s, 1 H), 3.99 (m, 1 H), 3.85 (s, 1 H), 3.80 (m, 1 H), 2.76 (dt, *J* = 7.8, 7.8 Hz, 1 H), 2.62 (t, *J* = 8.4 Hz, 1 H), 2.42 (dt, *J* = 7.8, 11.4 Hz, 1 H), 2.20 – 2.05 (m, 4 H), 2.04 (m, 2 H), 1.97 (m, 2 H), 1.84 (m, H), 1.72 (m, 2 H), 1.60 (s, 3 H), 1.57 (s, 3H), 1.52 (m, 2 H), 1.50 (s, 3 H), 1.49 – 1.36 (m, 5 H), 1.28 (s, 3 H), 1.20 (t, *J* = 11.4 Hz, 1 H), 1.12 (s, 3 H), 1.09 (m, 1 H), 1.06 (t, *J* = 7.8 Hz, 9 H), 0.75 (m, 6 H), 0.05 (s, 9 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 201.83, 150.53, 143.91, 115.27, 112.25, 98.00, 97.48, 81.48, 74.06, 73.21, 72.22, 71.07, 66.32, 64.30, 57.87, 56.69, 52.57, 51.49, 49.76, 48.16, 44.83, 44.38, 37.20, 32.26, 30.25, 29.72, 29.54, 28.98, 28.65, 25.58, 24.87, 23.65, 22.63, 22.30, 22.01, 18.53, 7.48, 5.84, –1.27 ppm; HRMS calcd for $C_{45}H_{76}O_7Si_2Na^+$ [*M*+Na^+] 807.5020 found 807.5031.



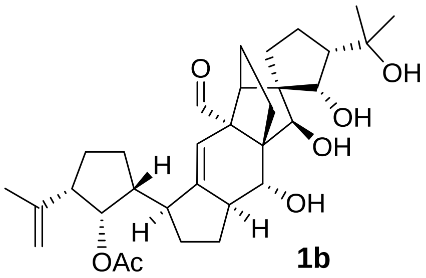
29c

Acetoxy aldehyde 30: To a solution of hydroxyl aldehyde **29c** (8 mg, 0.010 mmol) in CH_2Cl_2 (2 mL) at 25 °C was added Et_3N (75 μL, 0.68 mmol), 4-DMAP (1 crystal), and Ac_2O (50 μL, 0.045 mmol). The reaction mixture was stirred for 18 h and then quenched with saturated $NaHCO_3$ solution (10 mL). The resulting mixture was extracted with CH_2Cl_2 (2 × 5 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (EtOAc/hexanes, 5→10 %) to afford acetoxy aldehyde **30** (8 mg, 100 %). **30:** R_f



30

= 0.30 (silica gel, EtOAc:hexanes, 1:9); $[\alpha]^{25}_{D}$ +40.2 (*c* = 0.5, $CHCl_3$); IR ν_{max} (film): 2951s, 2870s, 1739s, 1701s, 1461w, 1373m, 1244m, 1074s cm^{-1}; ^{1}H NMR: (C_6D_6, 600 MHz) δ = 10.52 (s, 1 H), 5.65 (s, 1 H), 5.46 (t, *J* = 3.0 Hz, 1 H), 5.14 (d, *J* = 4.8 Hz, 1 H), 4.92 (s, 1 H), 4.88 (d, *J* = 4.8 Hz, 1 H), 4.83 (s, 1 H), 4.57 (s, 1 H), 4.46 (s, 1 H), 4.27 (s, 1 H), 3.98 (m, 1 H), 2.55 (t, *J* = 10.2 Hz, 1 H), 2.11 (d, *J* = 3.0 Hz, 1 H), 2.20 – 1.90 (m, 9 H), 1.88 (s, 3 H), 1.81 (m, 2 H), 1.73 (s, 3 H), 1.67 (m, 2 H), 1.61 (m, 2 H), 1.56 (s, 3 H), 1.51 (s, 3 H), 1.45 (m, 2 H), 1.36 (m, 4 H), 1.29 (s, 3 H), 1.12 (s, 3 H), 1.09 (m, 2 H), 1.05 (t, *J* = 7.8 Hz, 9 H), 0.75 (m, 6 H), 0.05 (s, 9 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 201.96, 169.39, 149.44, 143.61, 116.41, 111.25, 98.05, 97.50, 81.49, 77.03, 73.18, 71.06, 66.36, 64.36, 58.03, 56.72, 51.87, 51.44, 50.39, 47.10, 44.34, 44.04, 37.40, 32.26, 30.23, 30.18, 29.81, 28.91, 28.53, 26.29, 24.87, 24.09, 22.76, 22.30, 22.08, 20.69, 18.54, 7.46, 5.83, –1.27 ppm; HRMS calcd for $C_{457}H_{78}O_8Si_2Na^+$ [*M*+Na$^+$] 849.5127 found 849.5128.

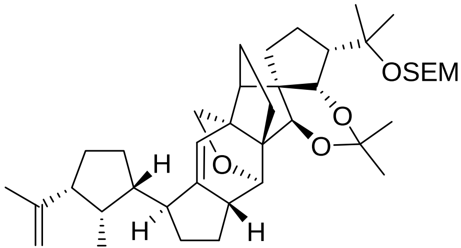


1b

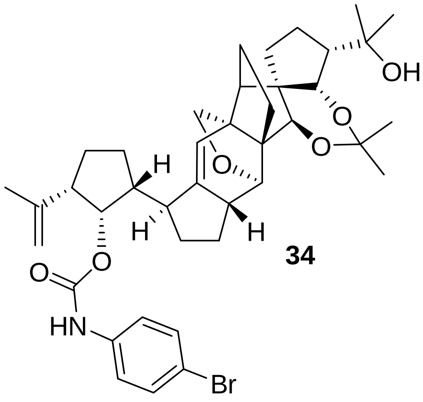
Originally assigned structure of vannusal B (1b): To a mixture of HF•py/THF (1:4, 2 mL) at 25 °C was added intermediate **30** (8 mg, 0.009 mmol, dissolved into 0.5 mL THF). The reaction mixture was stirred for 3 h at that temperature and then quenched by carefully pouring it into saturated $NaHCO_3$ solution (10 mL). The resulting mixture was extracted with CH_2Cl_2 (2 × 5 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The crude residue was then dissolved into THF/H_2O (3:1, 1.8 mL) and aqueous HCl (12 M, 50 μL) was added dropwise. The resulting mixture was stirred at 25 °C for 5 h, and then quenched by careful addition of saturated $NaHCO_3$ solution (5 mL). The resulting mixture was extracted with CH_2Cl_2 (3 × 5 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The crude residue was purified by preparative TLC (acetone/hexanes, 4:6) to furnish compound **1b** (4.1 mg, 80 %). **1b:** R_f = 0.30 (silica gel, EtOAc:hexanes, 1:9); $[\alpha]^{25}_{D}$ +9.0 (*c* = 0.5, $CHCl_3$); IR ν_{max} (film): 3393brs, 2921s, 1737s, 1686m, 1643w, 1464m, 1413m, 1373m, 1232s, 1069m, 1027m cm^{-1}; ^{1}H NMR: (CD_3OD, 600 MHz) δ = 9.52 (s, 1 H), 5.53 (s, 1 H), 5.43 (t, *J* = 3.0 Hz, 1 H), 4.80 (s, 1 H), 4.73 (s, 1 H), 4.53 (d, *J* = 2.4 Hz, 1 H), 4.40 (s, 1 H), 3.58 (d, *J* = 3.6 Hz, 1 H), 2.51 (t, *J* = 8.4 Hz, 1 H), 2.43 (dt, *J* = 6.6, 10.2 Hz, 1 H), 2.24 (d, *J* = 2.4 Hz, 1 H), 2.22 – 2.12 (m, 3 H), 2.10 (t, *J* =

9.6 Hz, 1 H), 2.02 – 1.95 (m, 3 H), 1.93 (s, 3 H) 1.87 (dt, J = 7.2, 12.0 Hz, 1 H), 1.73 (s, 3 H), 1.70 (m, 1 H), 1.63 (m, 2 H), 1.60 – 1.55 (m, 2 H), 1.50 (m, 1 H), 1.45 (t, J = 10.8 Hz, 1 H), 1.35 (s, 3 H), 1.30 (m, 2 H), 1.09 (s, 3 H), 0.92 – 0.85 (m, 2 H) ppm; ^{13}C NMR: (CD_3OD, 150 MHz) δ = 198.96, 172.20, 158.13, 144.73, 113.81, 111.56, 79.05, 78.56, 76.84, 73.34, 73.24, 69.52, 57.78, 56.63, 52.87, 52.16, 51.91, 51.02, 48.28, 45.41, 37.29, 31.48, 31.09, 30.07, 29.02, 29.00, 26.81, 25.07, 24.07, 22.14, 21.88, 20.97 ppm; HRMS calcd for $C_{32}H_{46}O_7H^+$ [M+H$^+$] 543.3316 found 543.3314.

Cyclic ether 33: To a stirred solution of alcohol **32** (15 mg, 0.0164 mmol, prepared from (–)-**2** and ($\pm$)-**31** by a similar sequence as that shown in Scheme 3) in benzene (10 mL) at 25 °C was added Ph_3P (43 mg, 0.164 mmol), $p$$NO_2$-$C_6H_4CO_2H$ (27 mg, 0.164 mmol), and DEAD (32 μL, 0.164 mmol), and the reaction mixture was heated to 60 °C for 2 h. The resulting mixture was cooled to 25 °C, concentrated in vacuo, and purified directly via preparative TLC (20 % EtOAc/hexanes) to afford **33** (7 mg, 58 %) plus recovered starting material **32** (4 mg, 30 %). **33:** R_f = 0.25 (silica gel, EtOAc:hexanes, 15:85); $[\alpha]^{25}_{D}$ –8.0 (c = 0.7, $CHCl_3$); IR ν_{max} (film): 2927s, 1531m, 1464m, 1377m, 1267m, 1093s, 1039s cm^{-1}; ^{1}H NMR: (C_6D_6, 600 MHz) δ = 7.30 (d, J = 7.2 Hz, 2 H), 7.19 – 7.16 (m, 1 H), 7.09 (m, 2 H), 5.49 (s, 1 H), 4.99 (s, 1 H), 4.94 (s, 1 H), 4.90 (d, J = 7.8 Hz, 1 H), 4.86 (d, J = 7.8 Hz, 1 H), 4.68 (d, J = 7.2 Hz, 1 H), 4.65 (d, J = 7.2 Hz, 1 H), 4.58 (d, J = 12.0 Hz, 1 H), 4.57 (d, J = 12.0 Hz, 1 H), 4.33 (d, J = 2.4 Hz, 1 H), 4.32 (s, 1 H), 4.26 (s, 1 H), 3.99 (s, 1 H), 3.85 (d, J = 7.2 Hz, 1 H), 3.83 – 3.75 (m, 2 H), 3.73 (d, J = 7.8 Hz, 1 H), 2.64 – 2.62 (m, 1 H), 2.47 (t, J = 8.4 Hz, 1 H), 2.36 – 2.32 (m, 1 H), 2.15 – 1.98 (m, 9 H), 1.88 – 1.82 (m, 1 H), 1.82 (s, 3 H), 1.78 – 1.76 (m, 3 H), 1.61 (m, 3 H), 1.50 (s, 3 H), 1.43 (s, 3 H), 1.41 (s, 3 H), 1.29 (s, 3 H), 0.96 (m, 2 H), 0.03 (s, 9 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 146.26, 144.63, 138.91, 130.59, 128.66, 124.16, 123.36, 111.46, 98.95, 94.88, 89.88, 89.30, 80.98, 79.70, 77.70, 77.52, 75.58, 74.26, 73.97, 72.97, 72.42, 69.86, 66.67, 64.93, 61.91, 54.68, 52.44, 51.38, 47.41, 46.21, 42.05, 41.09, 31.71, 30.92, 30.18, 27.50, 26.45, 25.73, 25.63, 25.34, 24.60, 24.33, 23.73 ppm; HRMS calcd for $C_{47}H_{70}O_7SiNa^+$ [M+Na$^+$] 797.4783 found 797.4762.



33



34

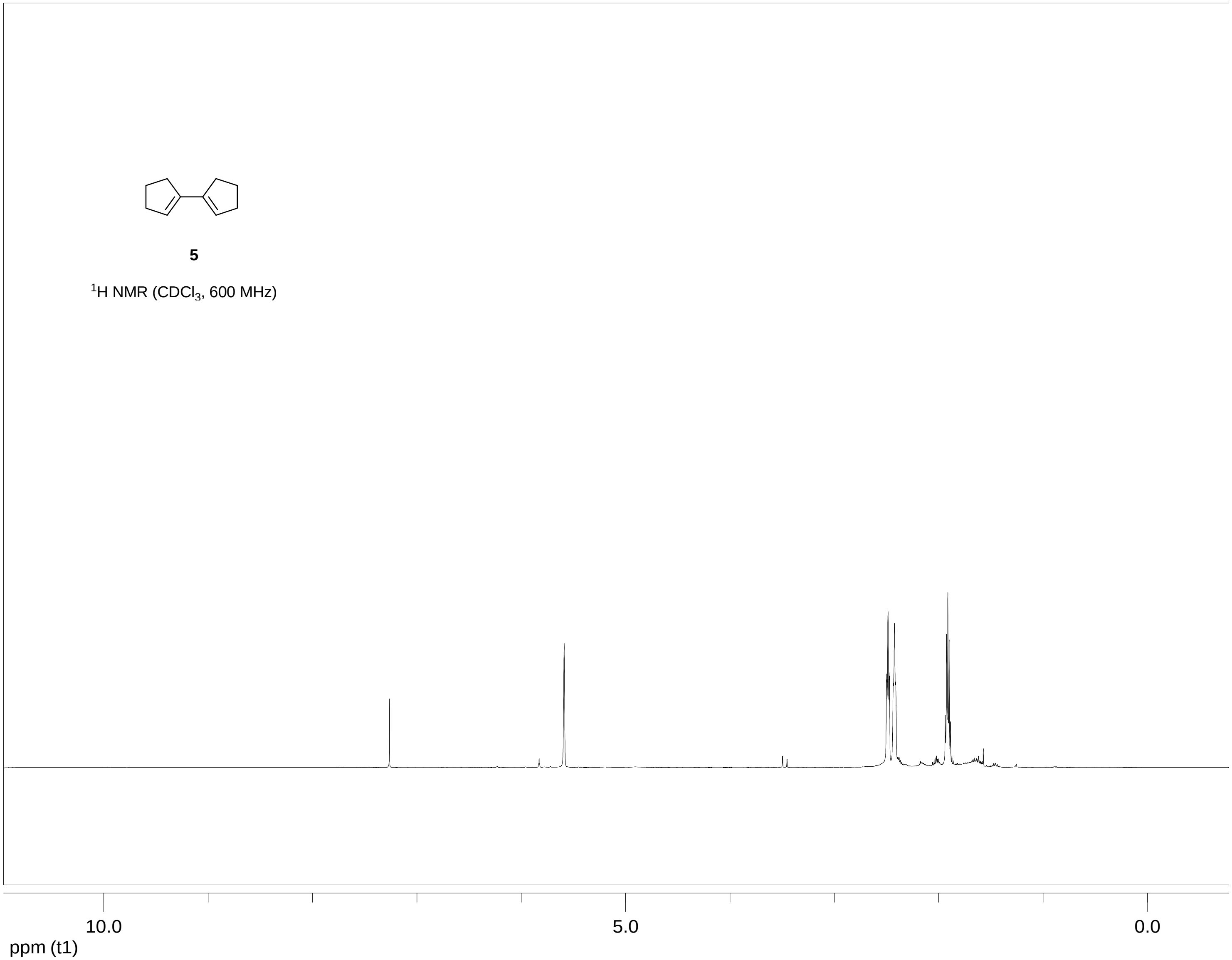
***P*-phenylcarbamate 34**: To a solution of BOM ether **33** (29 mg 0.037 mmol) in THF (2.0 mL) at –78 °C was added LiDBB (~1.0 M in THF, freshly prepared) dropwise until the reaction mixture developed a persistent dark green color. The reaction mixture was warmed to –50 °C and stirred at that temperature for 30 min. During this period, LiDBB was constantly added to maintain the reaction color as dark green. The reaction was quenched at –50 °C with saturated NH_4Cl solution (1 mL), and extracted with Et_2O (2 x 10 mL). The combined organic extracts were dried ($MgSO_4$), concentrated in vacuo, and the crude residue was purified by flash column chromatography (9→14 % EtOAc/hexanes) to afford the corresponding secondary alcohol **33a** (22 mg, 90 %). To a solution of the so-formed alcohol in THF (1.5 mL) at 25 °C was added HF•py (0.75 mL, 70 % HF in pyridine). The reaction mixture was stirred for 30 min at that temperature, and then quenched with saturated $NaHCO_3$ solution (10 mL). The resulting mixture was extracted with Et_2O (2 × 10 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude residue was purified by flash column chromatography (25 % EtOAc/hexanes) to furnish the corresponding diol (16 mg, 93 %). To a solution of this diol (15 mg, 0.029 mmmol) in CH_2Cl_2 (1.0 mL) at 25 °C was added Et_3N (12 μL, 0.085 mmol), 4-bromophenyl isocyanate (17 mg, 0.085 mmol), and 4-DMAP (3.5 mg, 0.029 mmol). The reaction mixture was heated at 40 °C for 12 h, quenched with saturated $NaHCO_3$ solution (3 mL), and then extracted with Et_2O (2 × 10 mL). The combined organic layers were washed with brine (3 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude residue was taken up in saturated K_2CO_3/MeOH solution (1.0 mL) and stirred for 1 h. The reaction mixture was quenched with saturated NH_4Cl solution (5 mL) and extracted with EtOAc (2 x 10 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), concentrated in vacuo, and subjected to flash column chromatography to afford the desired carbamate (**34)** (17 mg, 84 %). Recrystallization from EtOAc/hexanes gave **34** as colorless crystals, mp 180 – 182 °C. **34:** $R_f = 0.25$ (silica gel, EtOAc:hexanes, 15:85); $[\alpha]^{25}_D$ –8.0 (c = 0.7, $CHCl_3$); IR ν_{max} (film): 3513brs, 3281brs, 2965s, 2243w, 1730s, 1648w, 1593m, 1531s, 1397s, 1212s, 1084m cm^{-1}; ^1H NMR: (C_6D_6, 600 MHz) δ = 7.11 (d, J = 9.0 Hz, 1 H), 6.91 (brs, 1 H), 6.17 (s, 1 H), 5.54 (brs, 1 H), 5.50 (s, 1 H), 4.95 (s, 1 H), 4.93 (s, 1 H), 4.38 (d, J = 3.6 Hz, 1 H), 4.25 (d, J = 1.8 Hz, 1 H), 4.21 (s, 1 H), 3.83 (d, J = 7.8 Hz, 1 H), 3.72 (d, J = 7.8

Hz, 1 H), 3.52 (s, 1 H), 2.48 – 2.38 (m, 3 H), 2.31 – 2.25 (m, 2 H), 2.16 – 2.02 (m, 2 H), 2.02 – 1.93 (m, 2 H), 1.91 (s, 3 H), 1.87 (t, *J* = 6.6 Hz, 2 H), 1.79 – 1.68 (m, 4 H), 1.66 (m 1 H), 1.58 (dt, *J* = 6.6, 11.4 Hz, 2 H), 1.50 (brs, 2 H), 1.45 (s, 3 H), 1.44 (m, 2 H), 1.33 (ddd, *J* = 3.6, 6.6, 9.6 Hz, 1 H), 1.28 (s, 6 H), 1.11 (s, 3 H) ppm; ^{13}C NMR: (C_6D_6, 150 MHz) δ = 152.73, 146.43, 143.74, 137.71, 131.99, 128.53, 124.19, 120.22, 120.21, 115.74, 111.232, 99.57, 79.15, 77.64, 74.06, 73.89, 70.75, 66.37, 62.14, 55.00, 51.53, 50.85, 50.13, 46.26, 42.41, 40.60, 31.71, 30.76, 30.46, 29.32, 28.19, 2639, 26.00, 25.93, 24.14, 23.68, 23.00, 17.45, ppm; HRMS calcd for $C_{40}H_{52}O_6BrNNa^+$ [M+Na$^+$] 744.2870 found 744.2844.

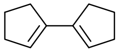
II) References

[1] K. C. Nicolaou, M. P. Jennings, P. Dagneau, *Chem. Commun*. **2002**, 2480–2481.

II) ^{1}H and ^{13}C NMR Spectra

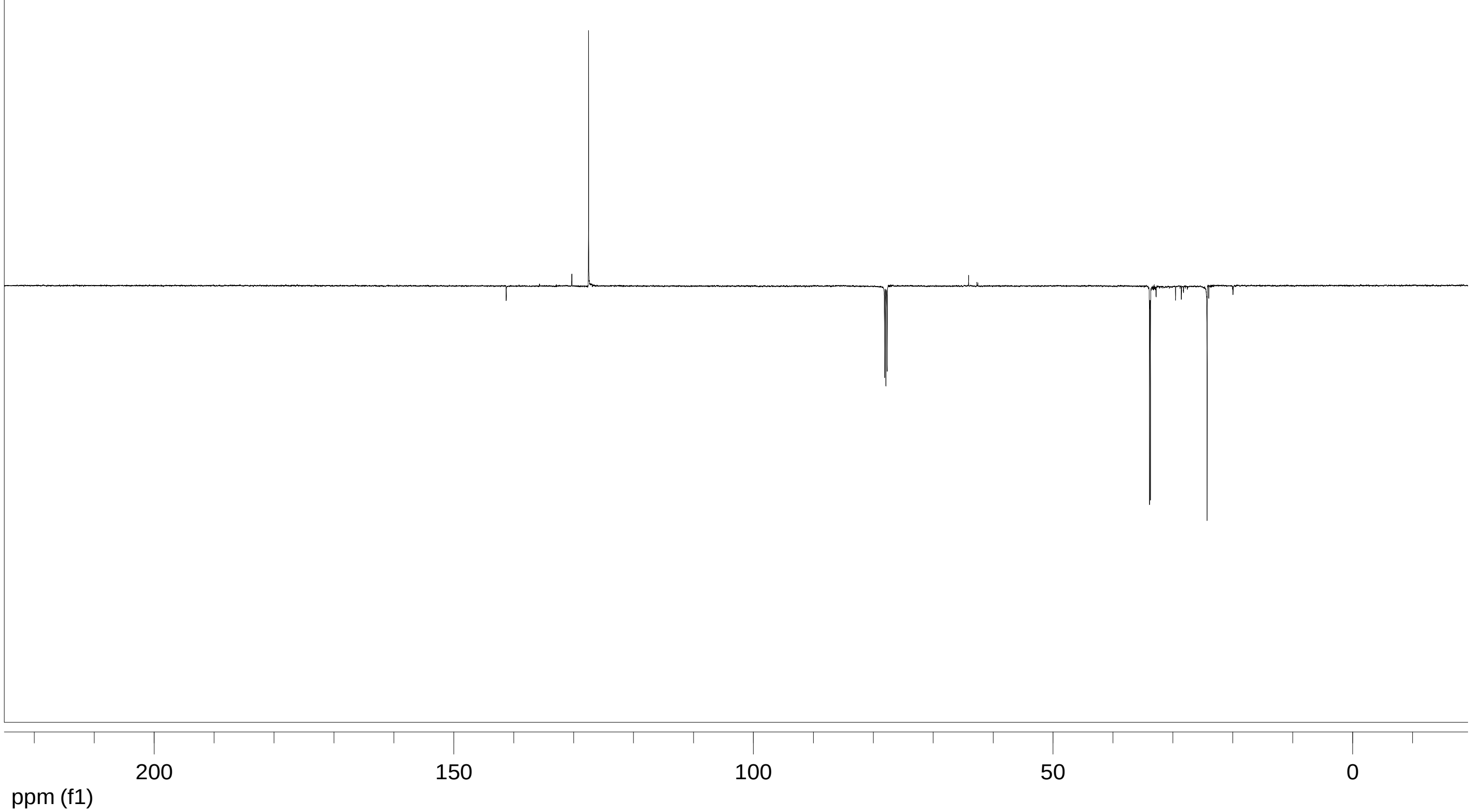

5

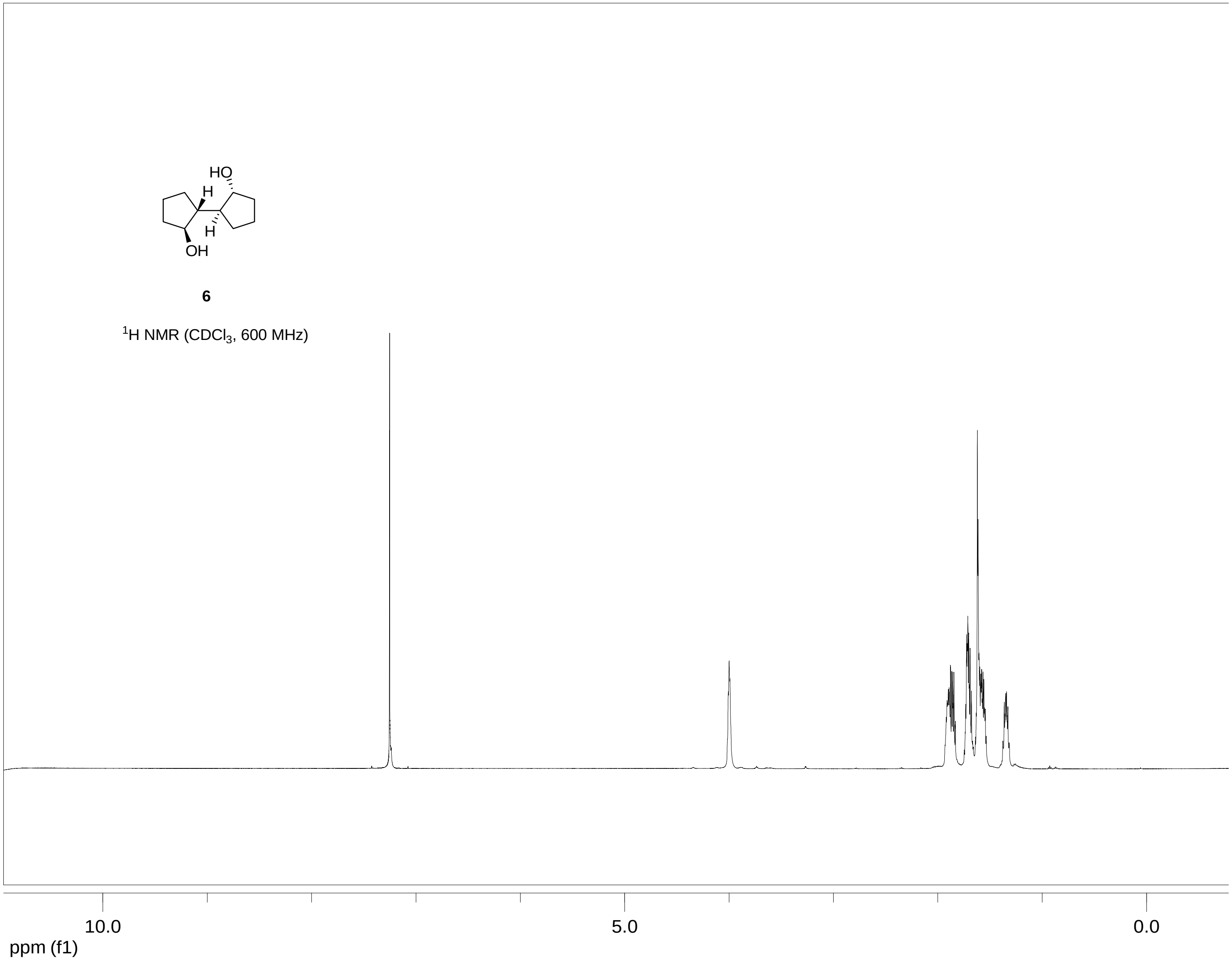
^{1}H NMR ($CDCl_3$, 600 MHz)

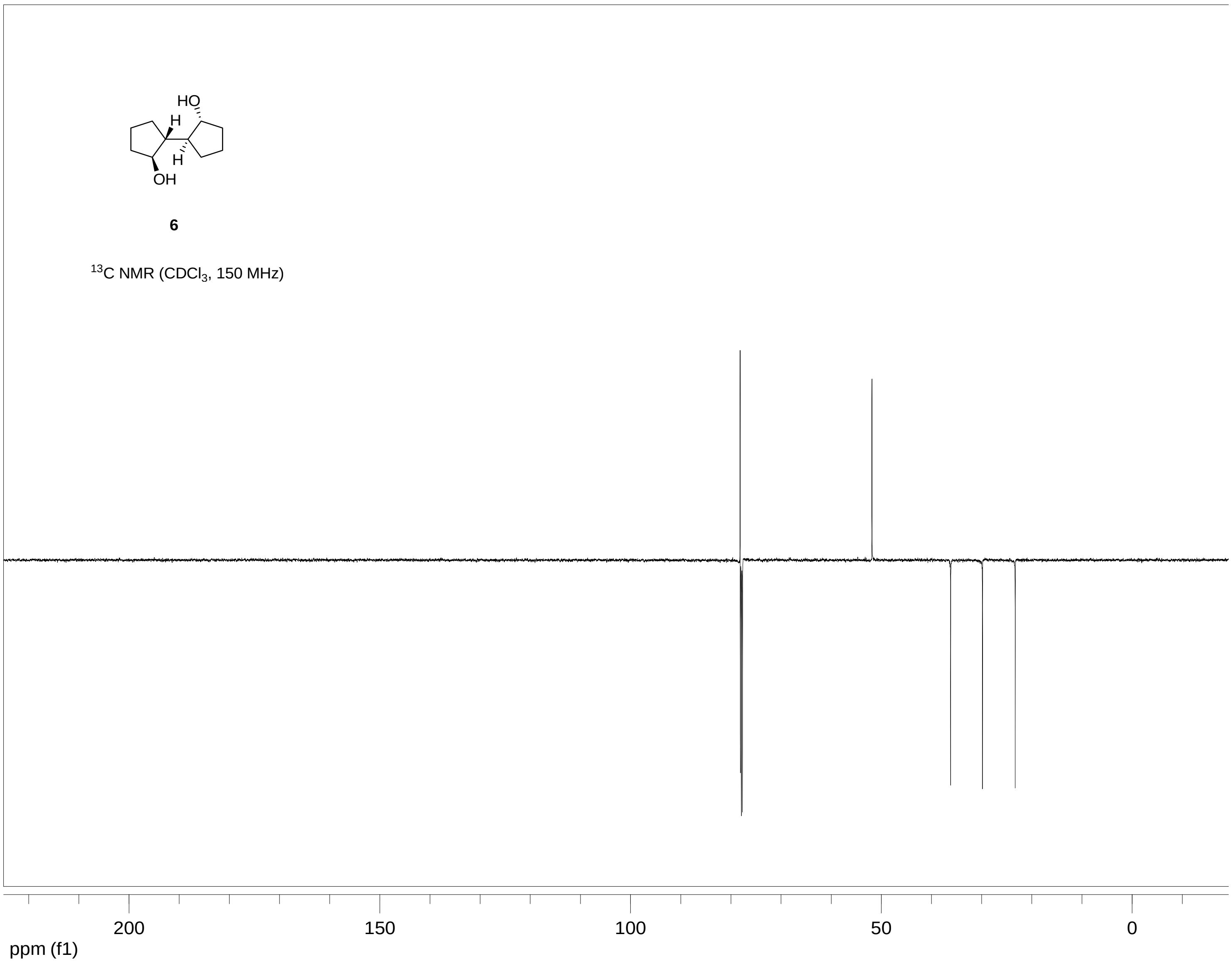


5

^{13}C NMR ($CDCl_3$, 150 MHz)

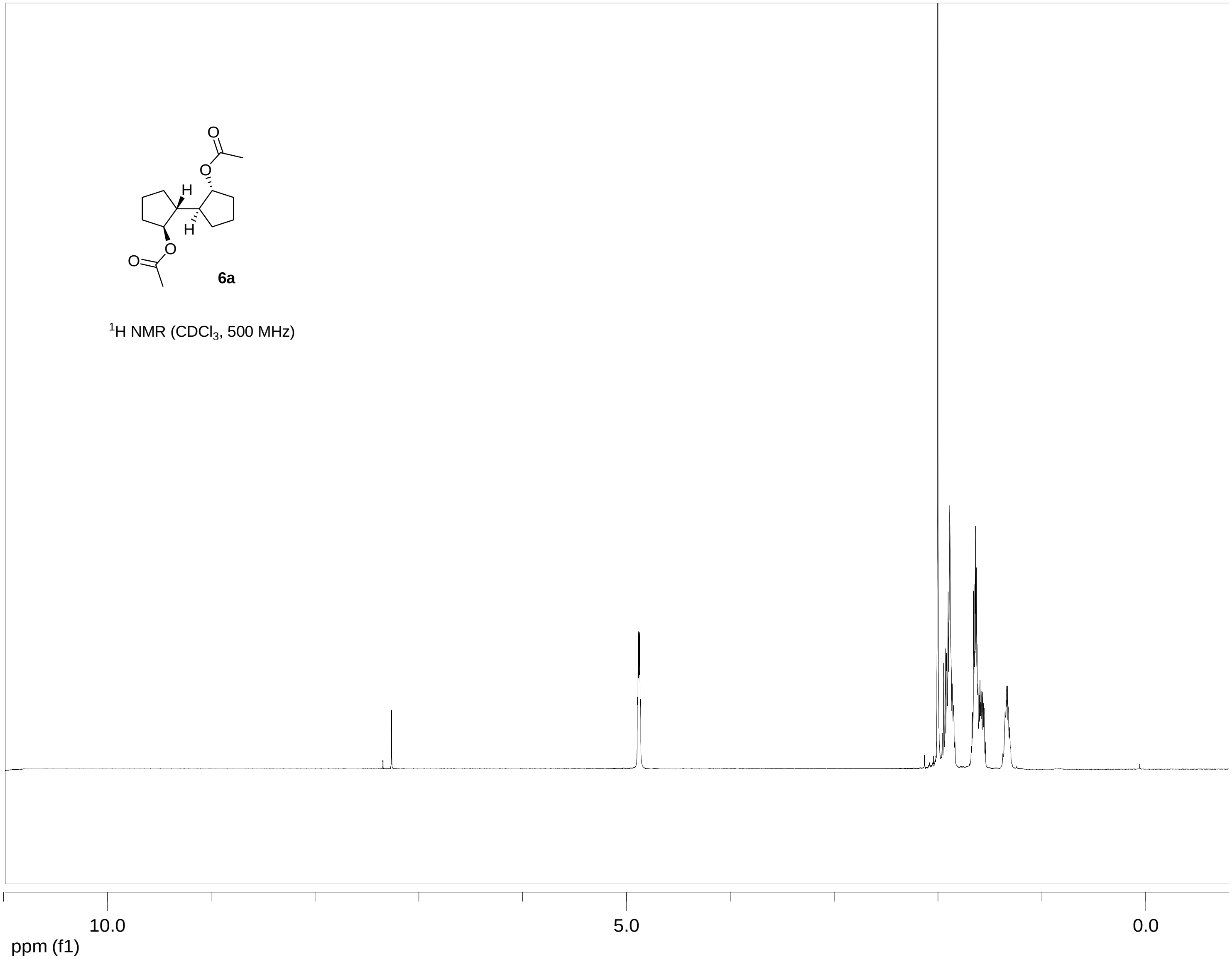


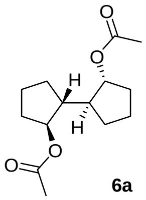

HO
H
H
OH
6
^{1}H NMR (CDCl$_3$, 600 MHz)
10.0
5.0
0.0
ppm (f1)



6

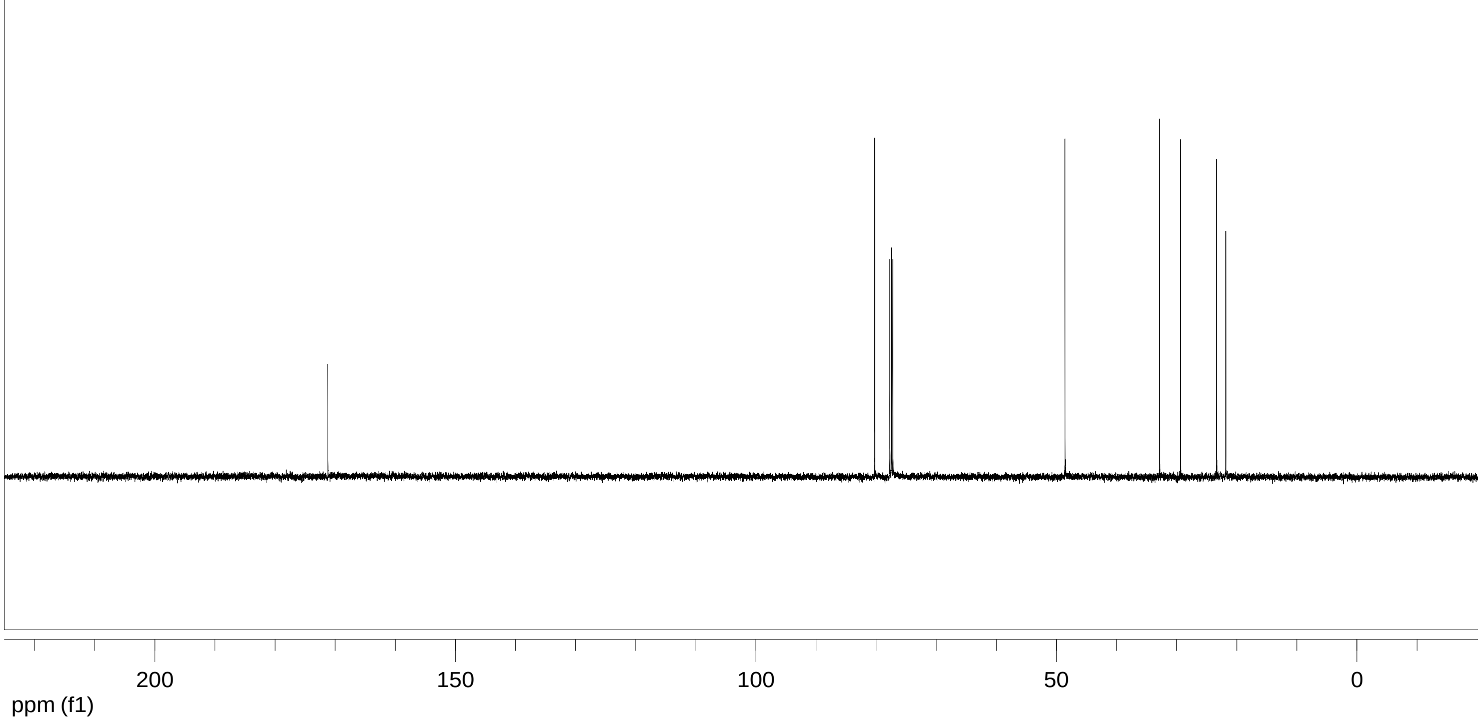
^{13}C NMR (CDCl$_3$, 150 MHz)

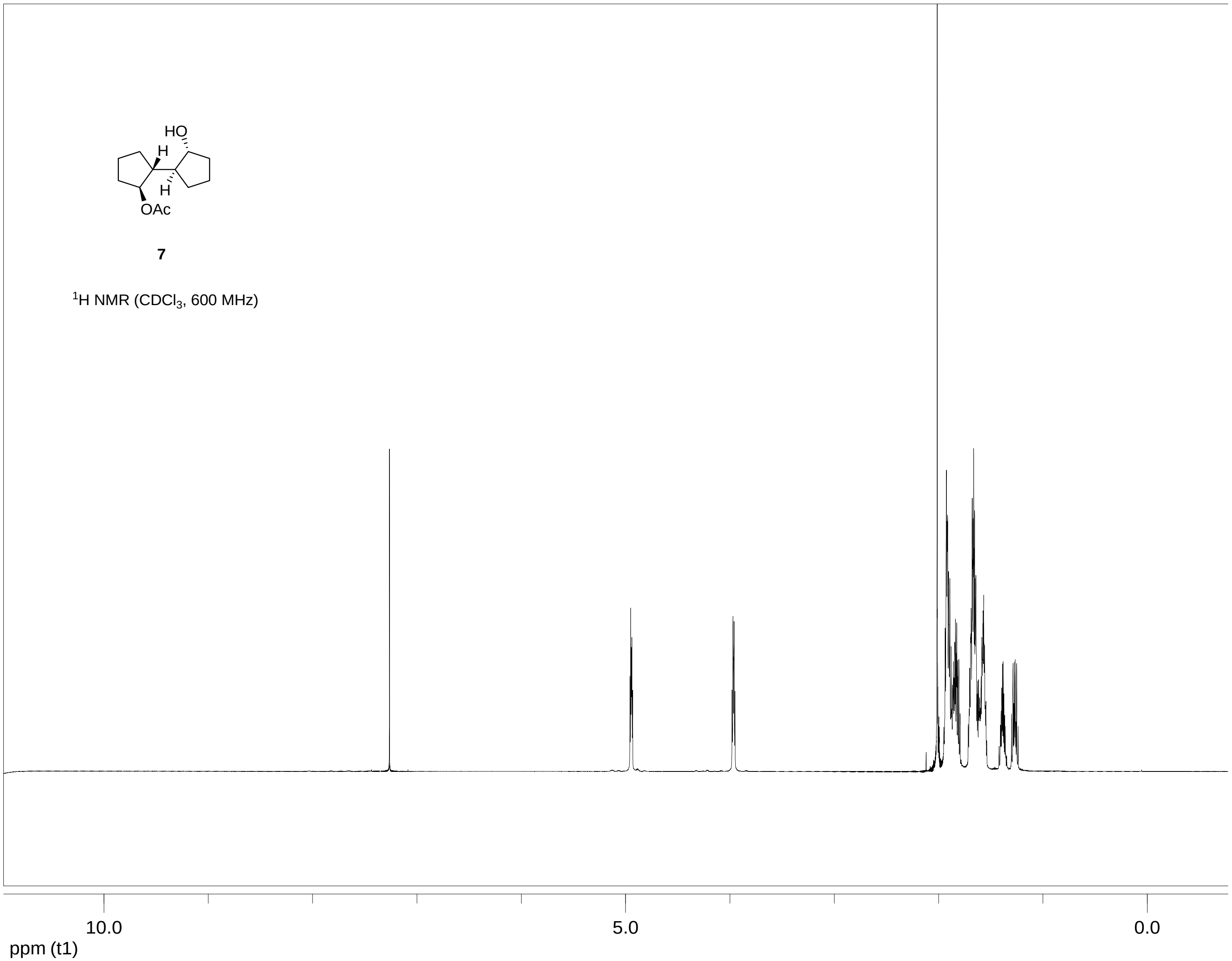

O
O
H
H
O
O
6a
^{1}H NMR (CDCl$_3$, 500 MHz)
10.0
5.0
0.0
ppm (f1)



6a

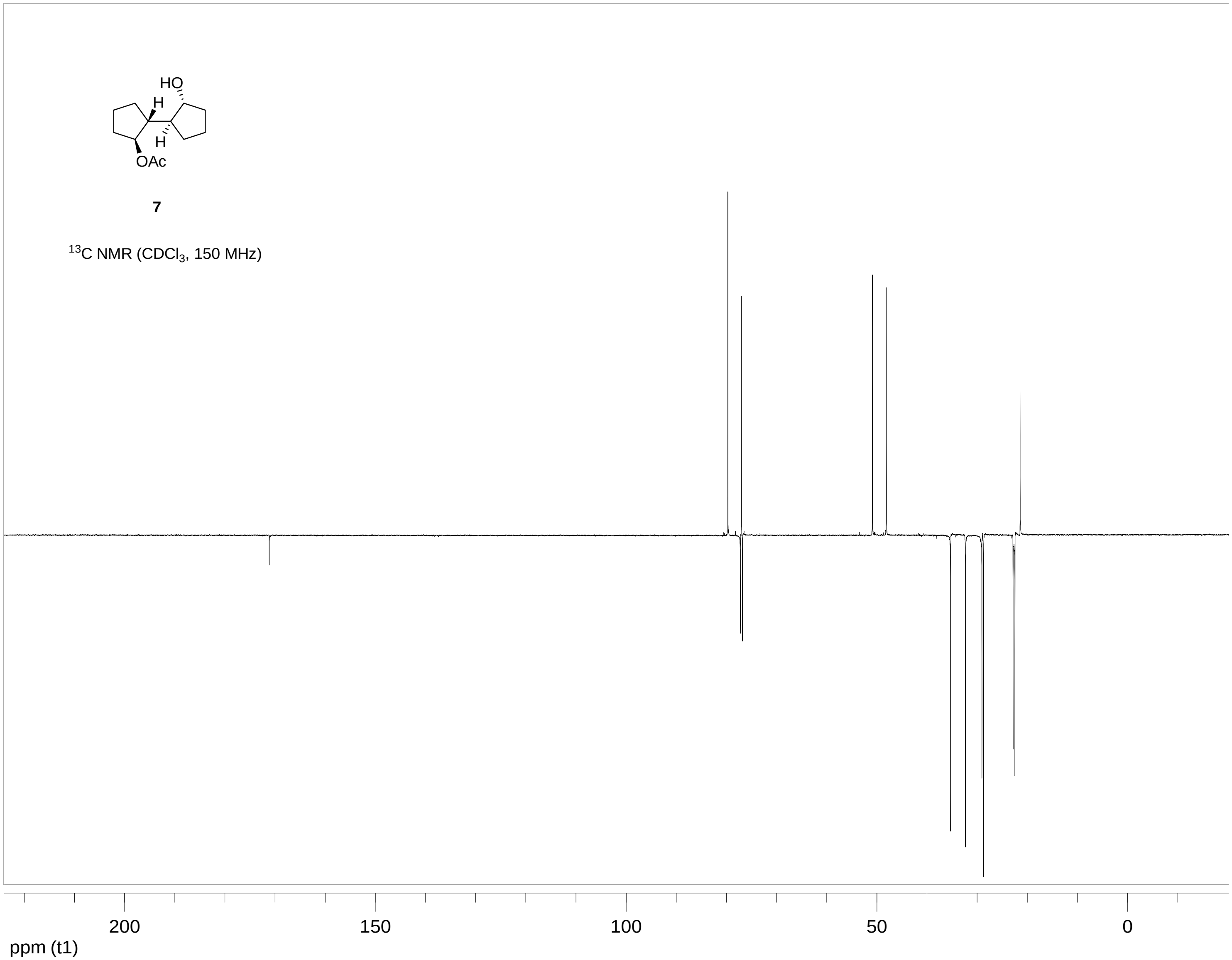
^{13}C NMR (CDCl$_3$, 125 MHz)





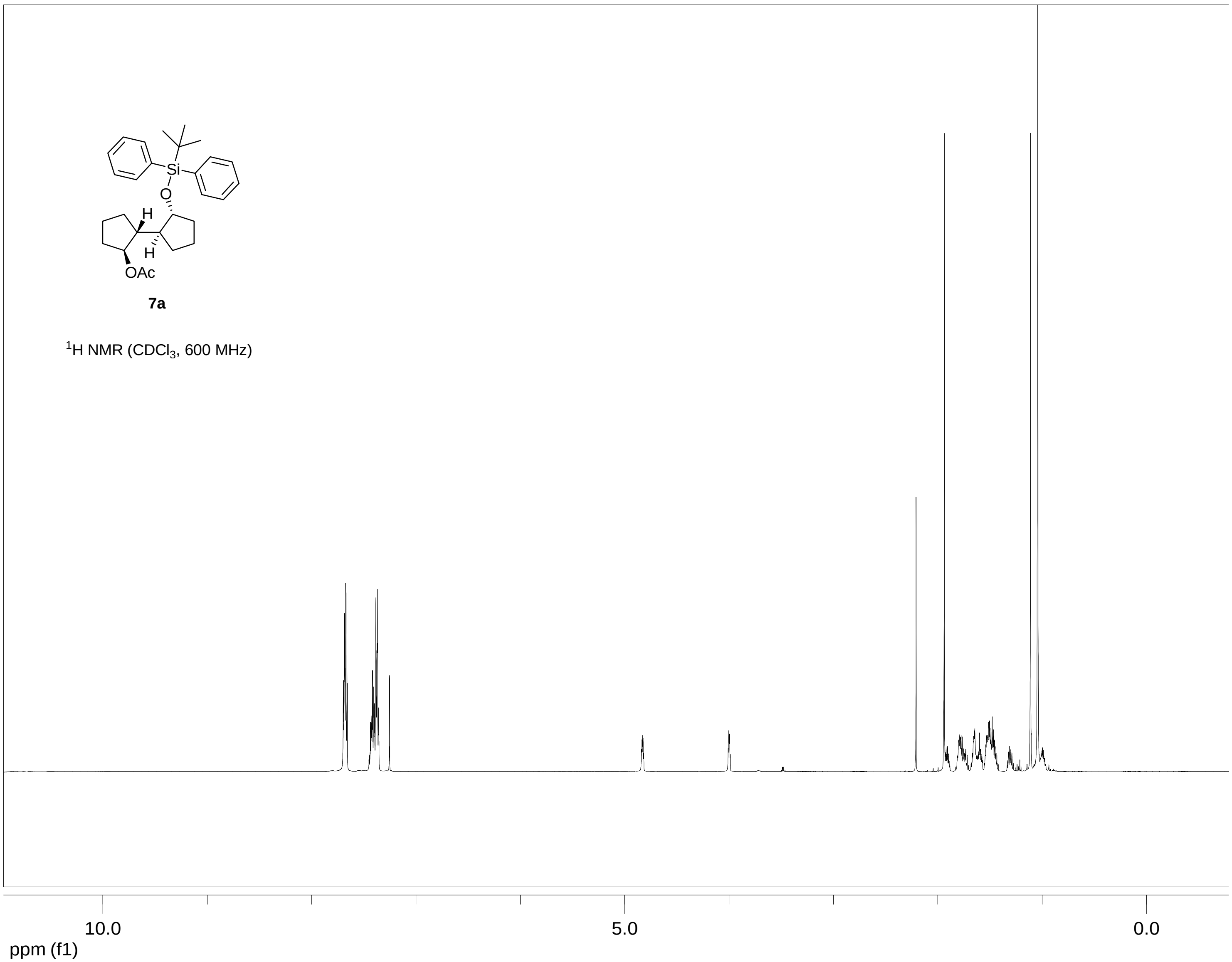
7

^{1}H NMR (CDCl$_3$, 600 MHz)



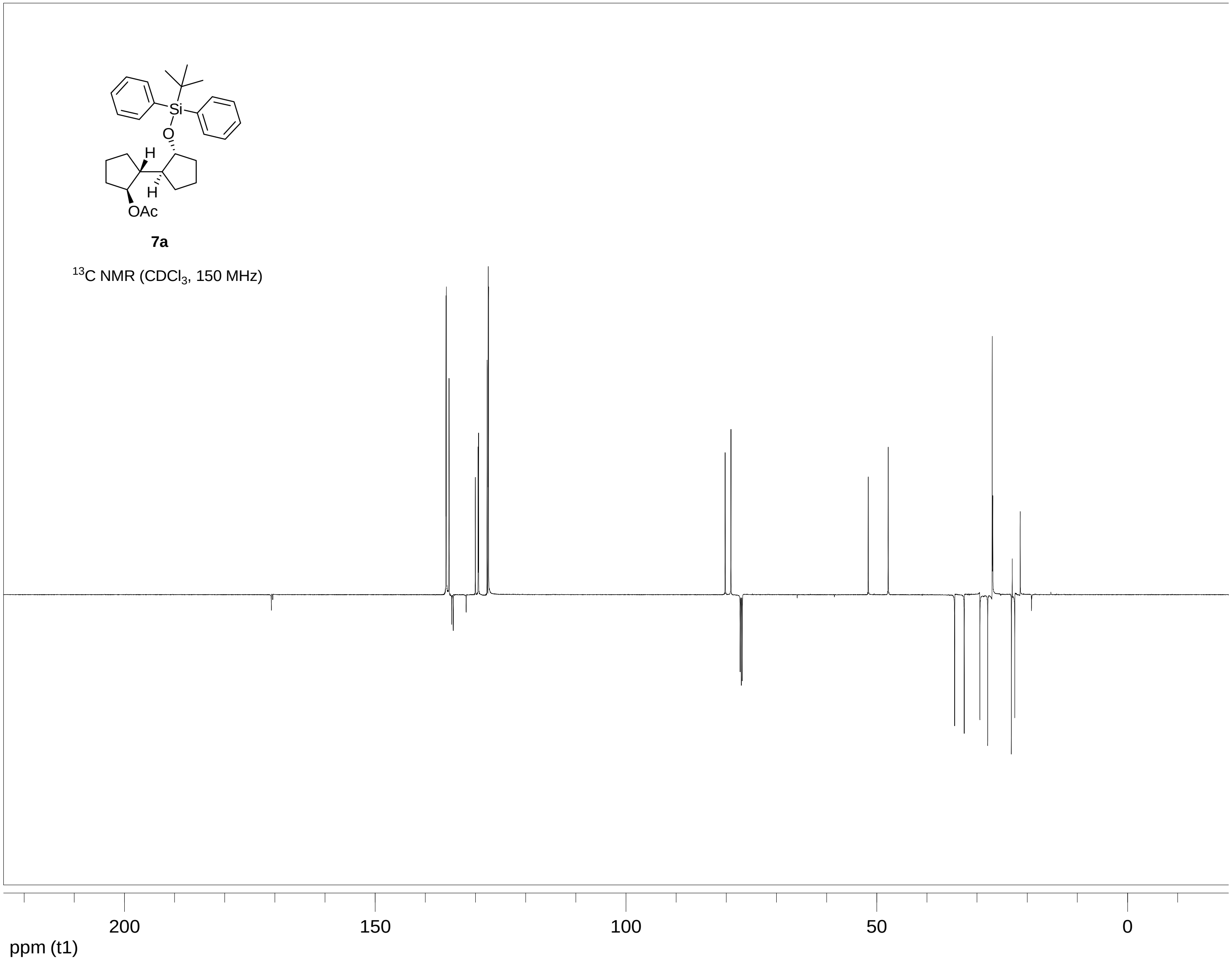
7

^{13}C NMR (CDCl$_3$, 150 MHz)



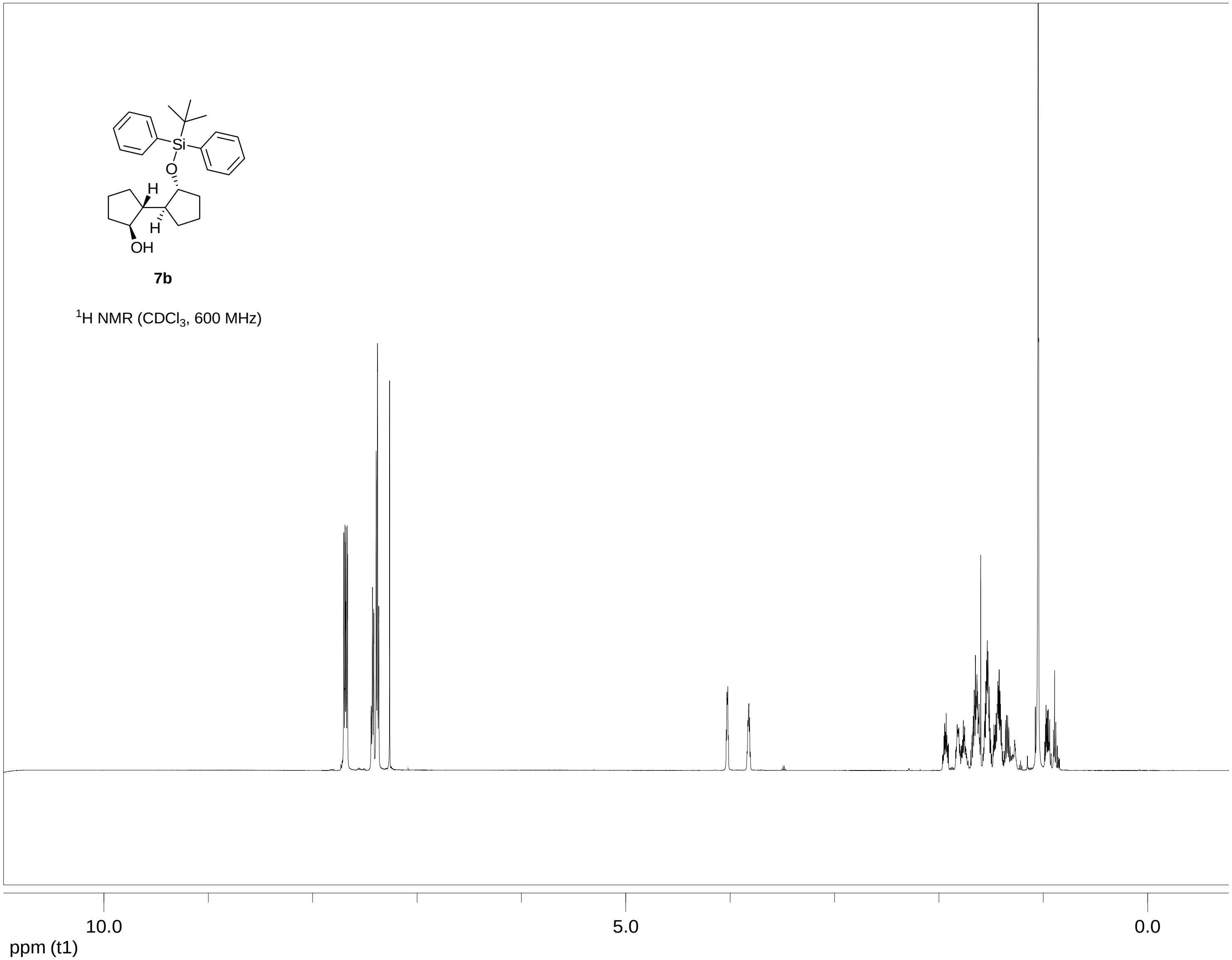
7a

^{1}H NMR ($CDCl_3$, 600 MHz)



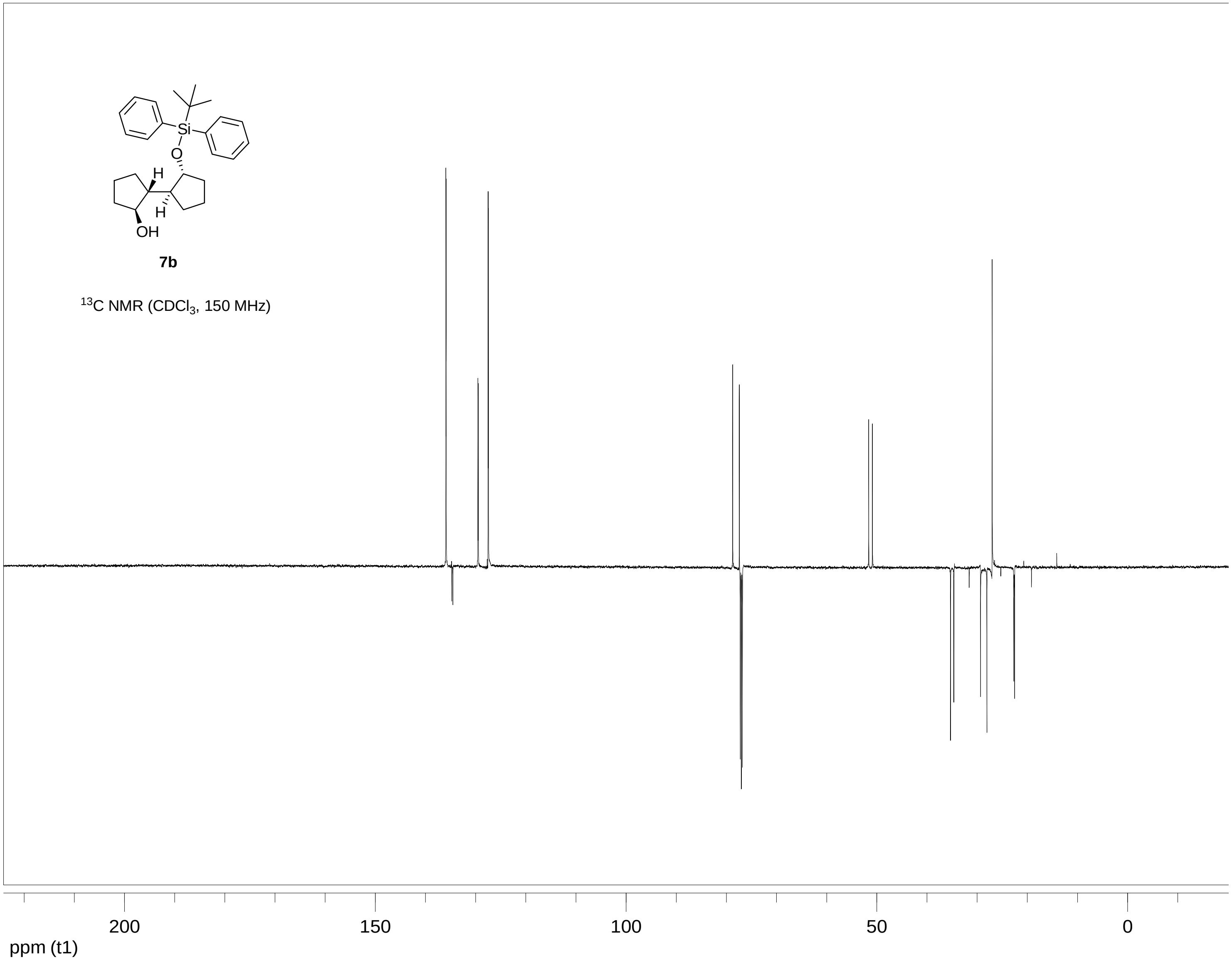
7a

^{13}C NMR ($CDCl_3$, 150 MHz)

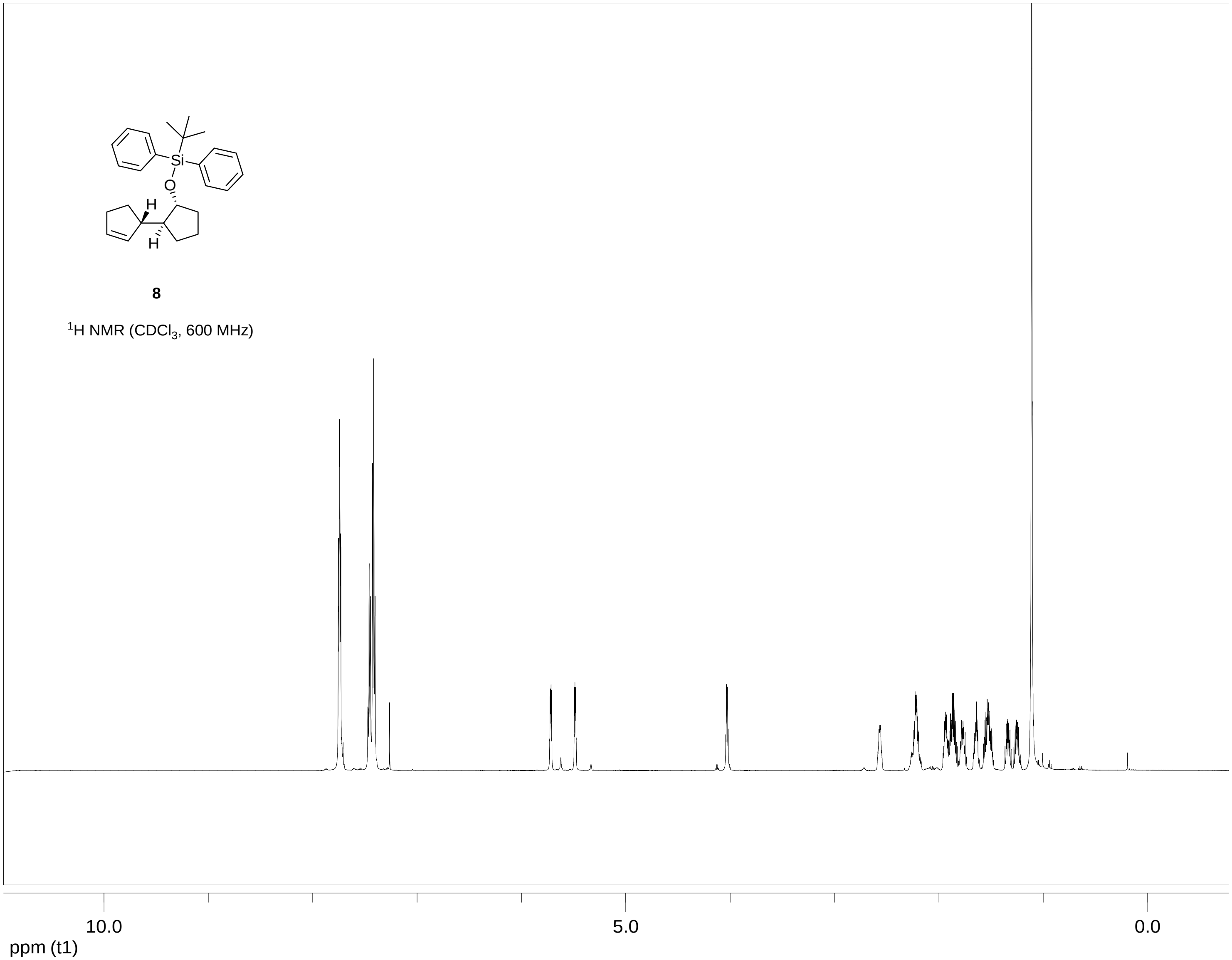


7b

^1H NMR ($CDCl_3$, 600 MHz)

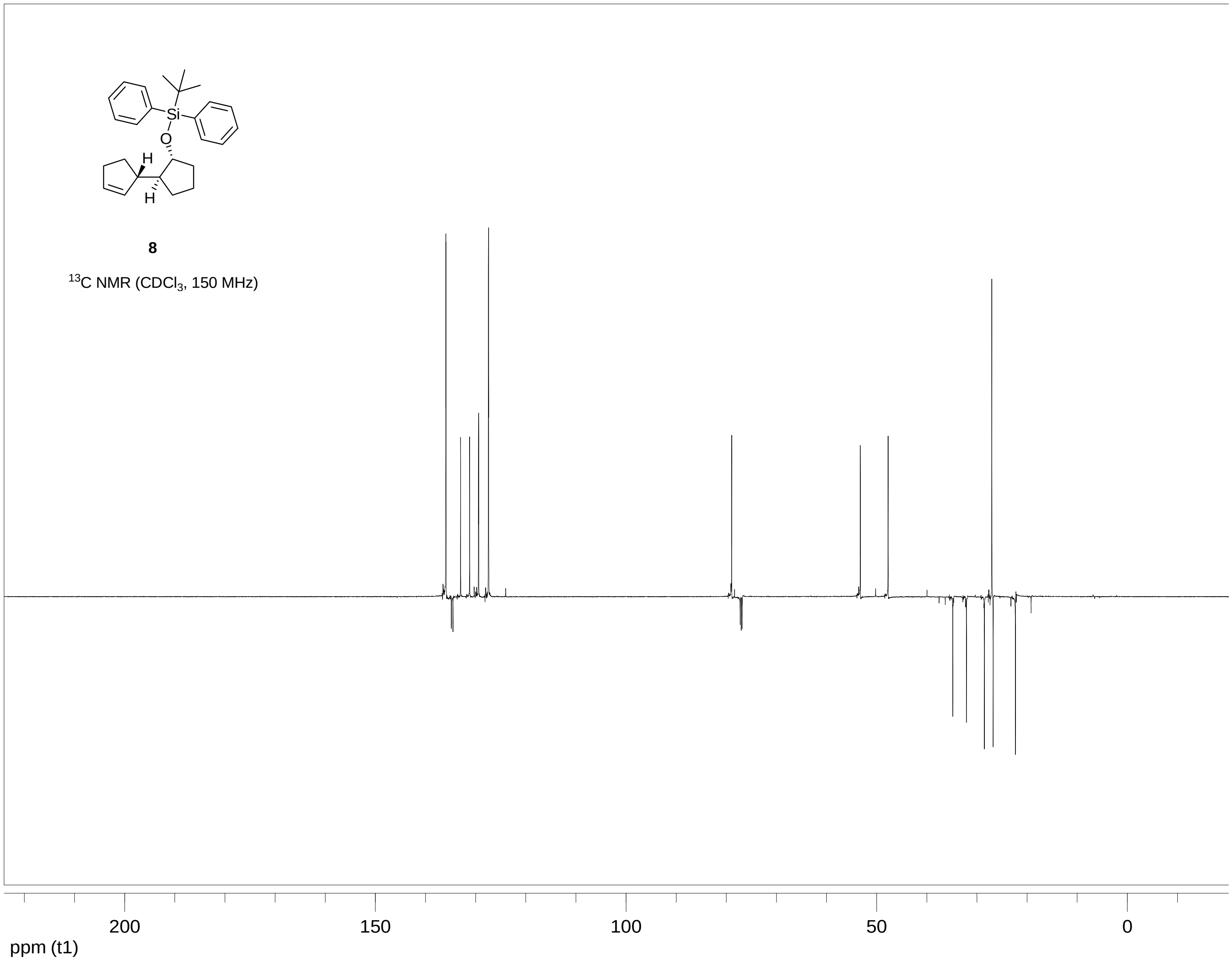

7b

^{13}C NMR (CDCl$_3$, 150 MHz)



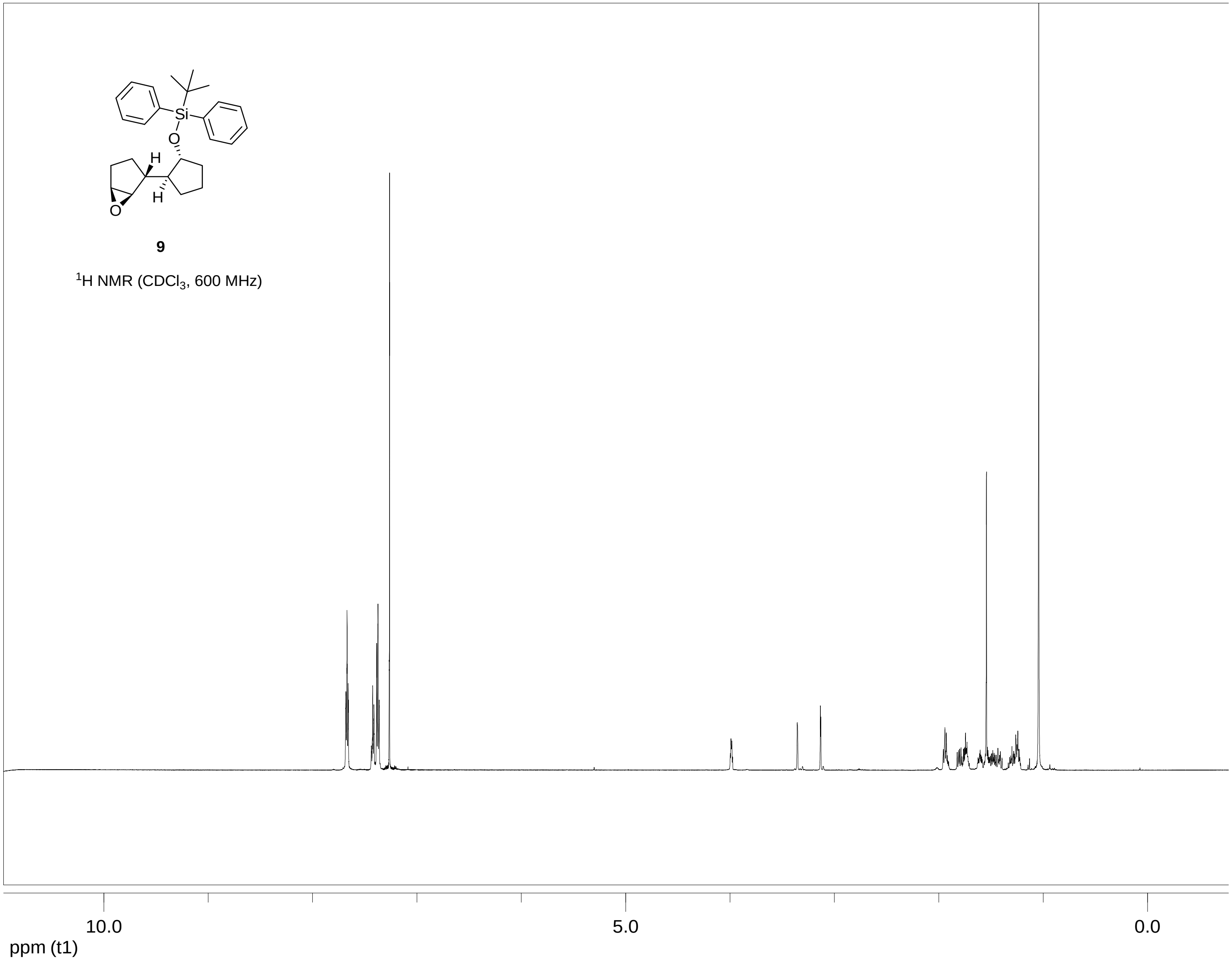
8

^{1}H NMR (CDCl$_3$, 600 MHz)



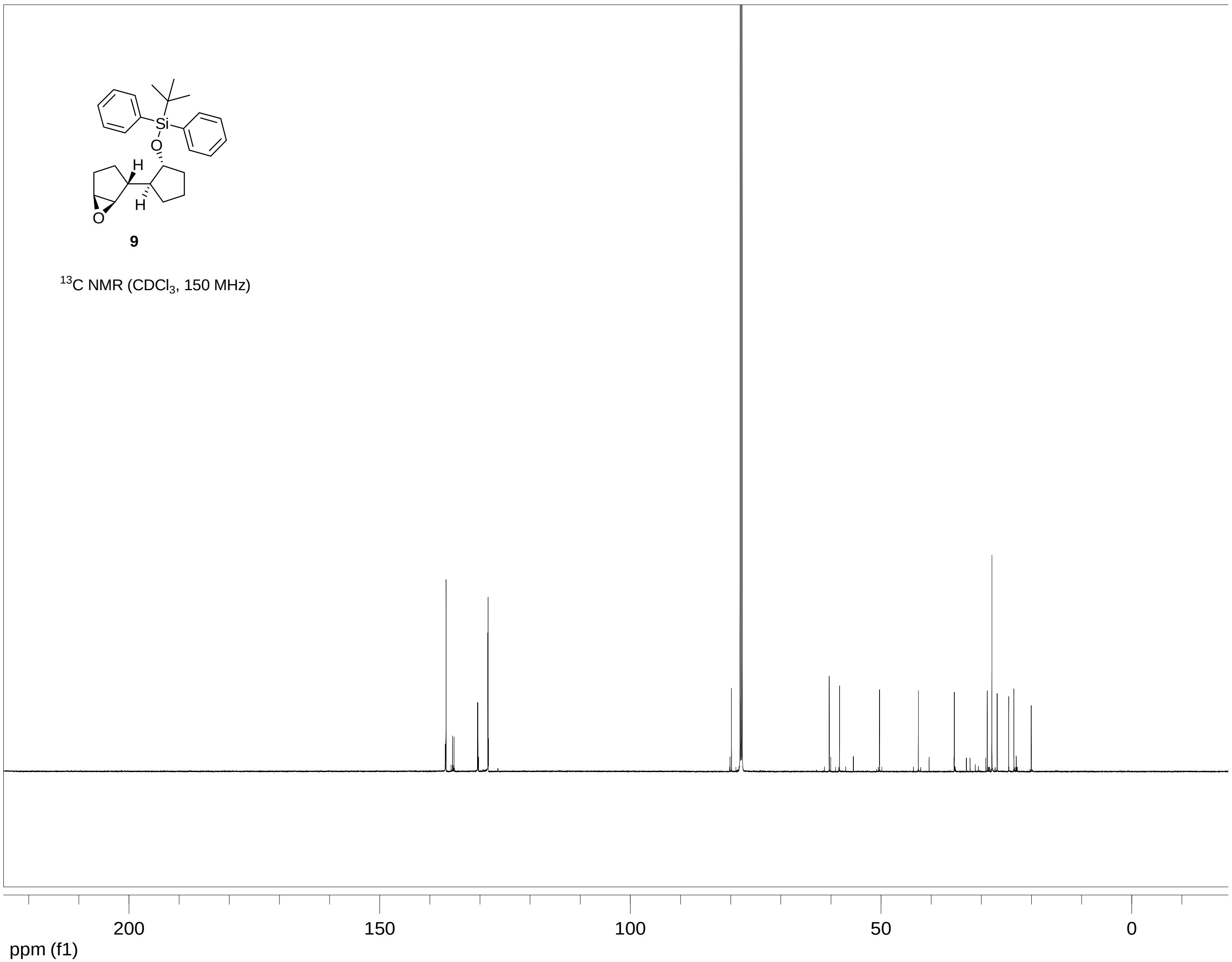
8

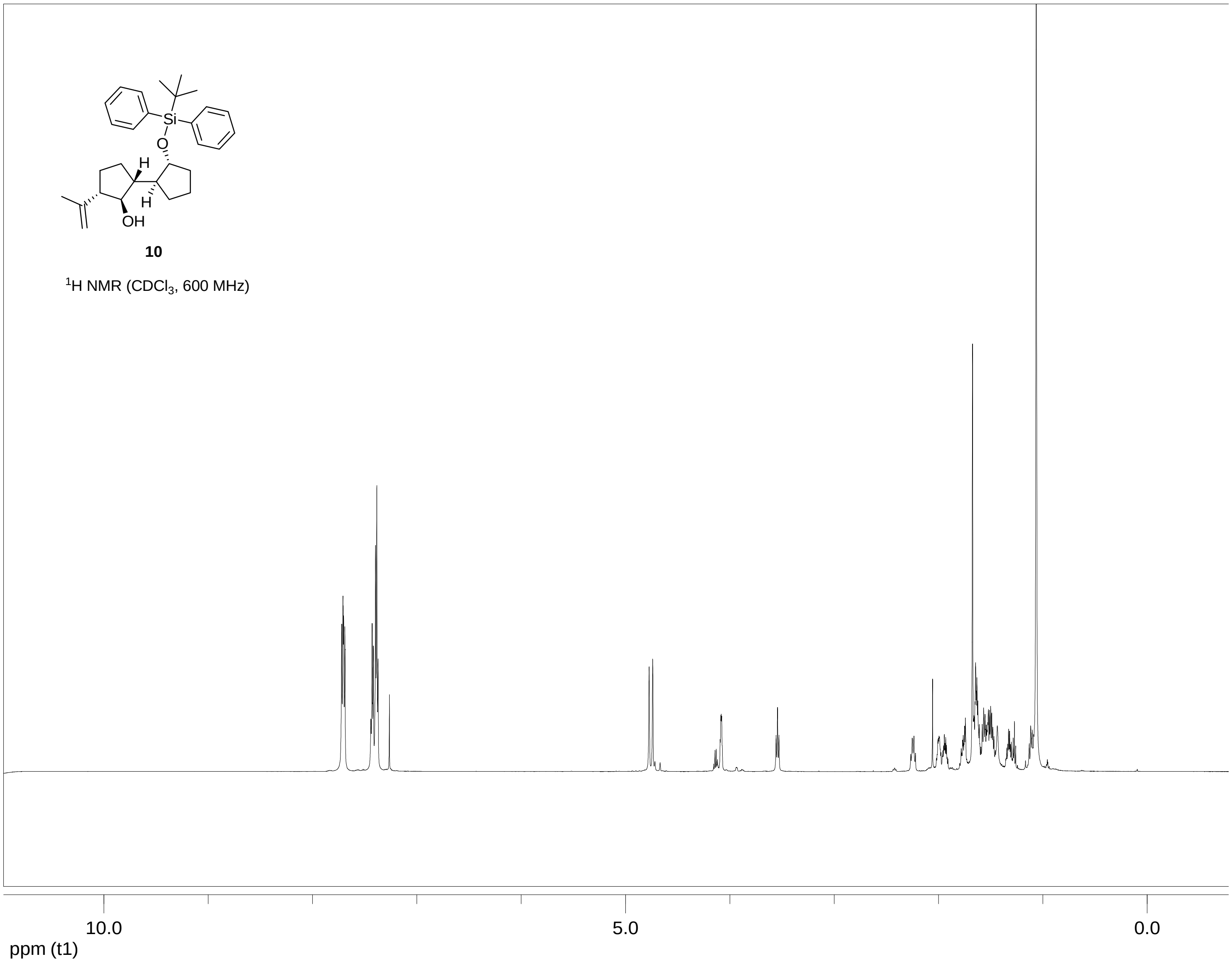
^{13}C NMR ($CDCl_3$, 150 MHz)



9

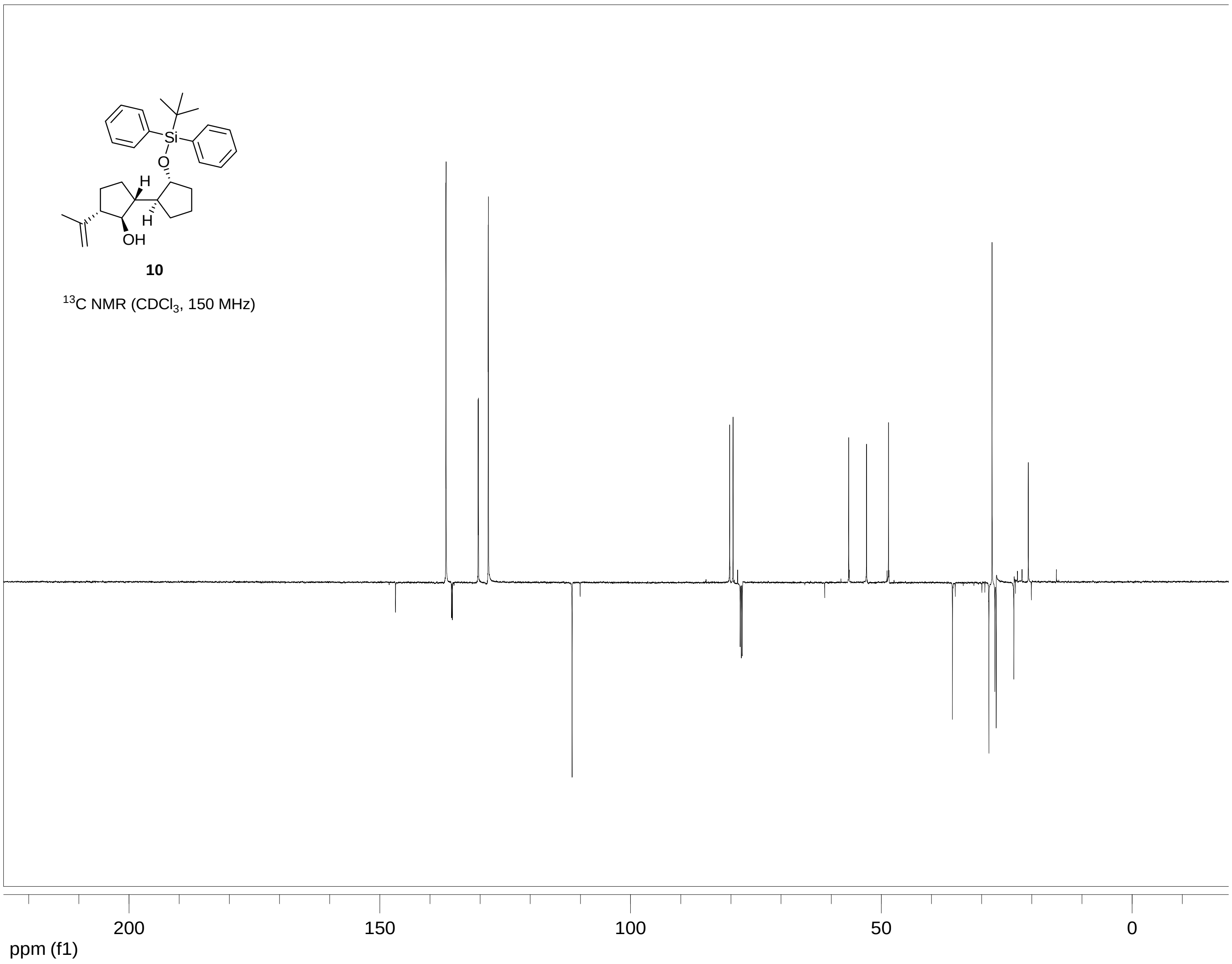
^{1}H NMR (CDCl$_3$, 600 MHz)


Si
O
H
H
O
9
^{13}C NMR (CDCl$_3$, 150 MHz)
200
150
100
50
0
ppm (f1)



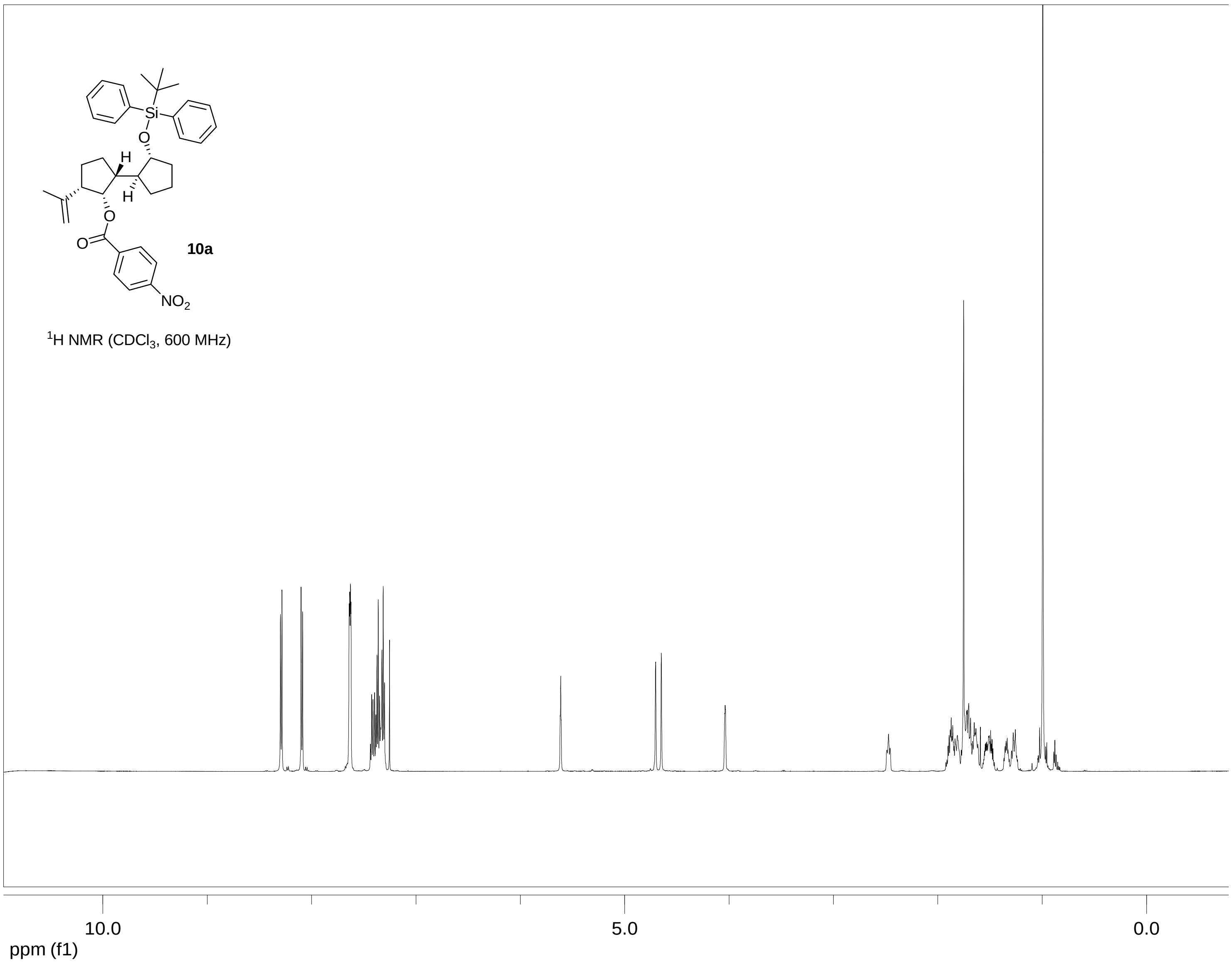
10

^{1}H NMR (CDCl$_3$, 600 MHz)



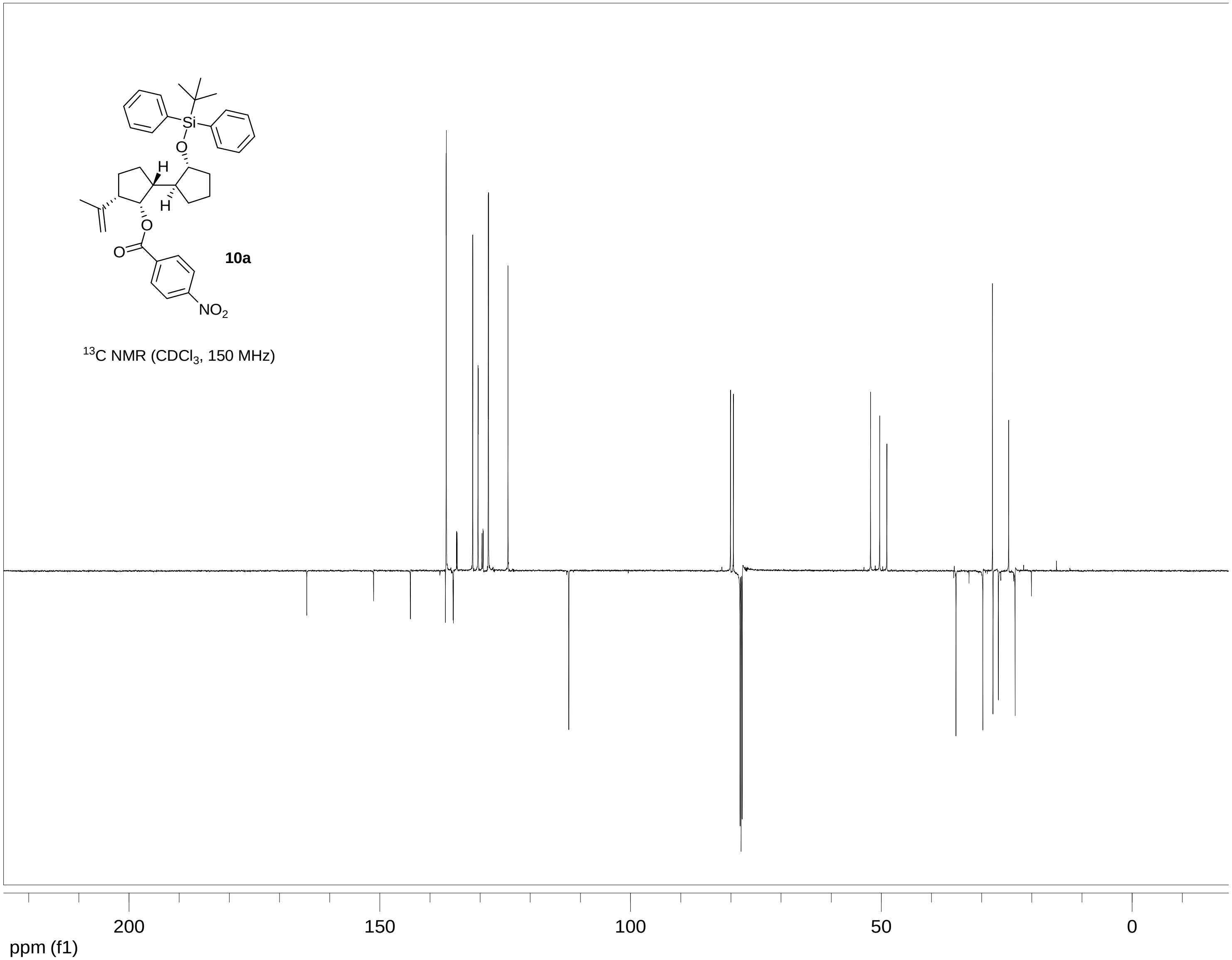
10

^{13}C NMR (CDCl$_3$, 150 MHz)



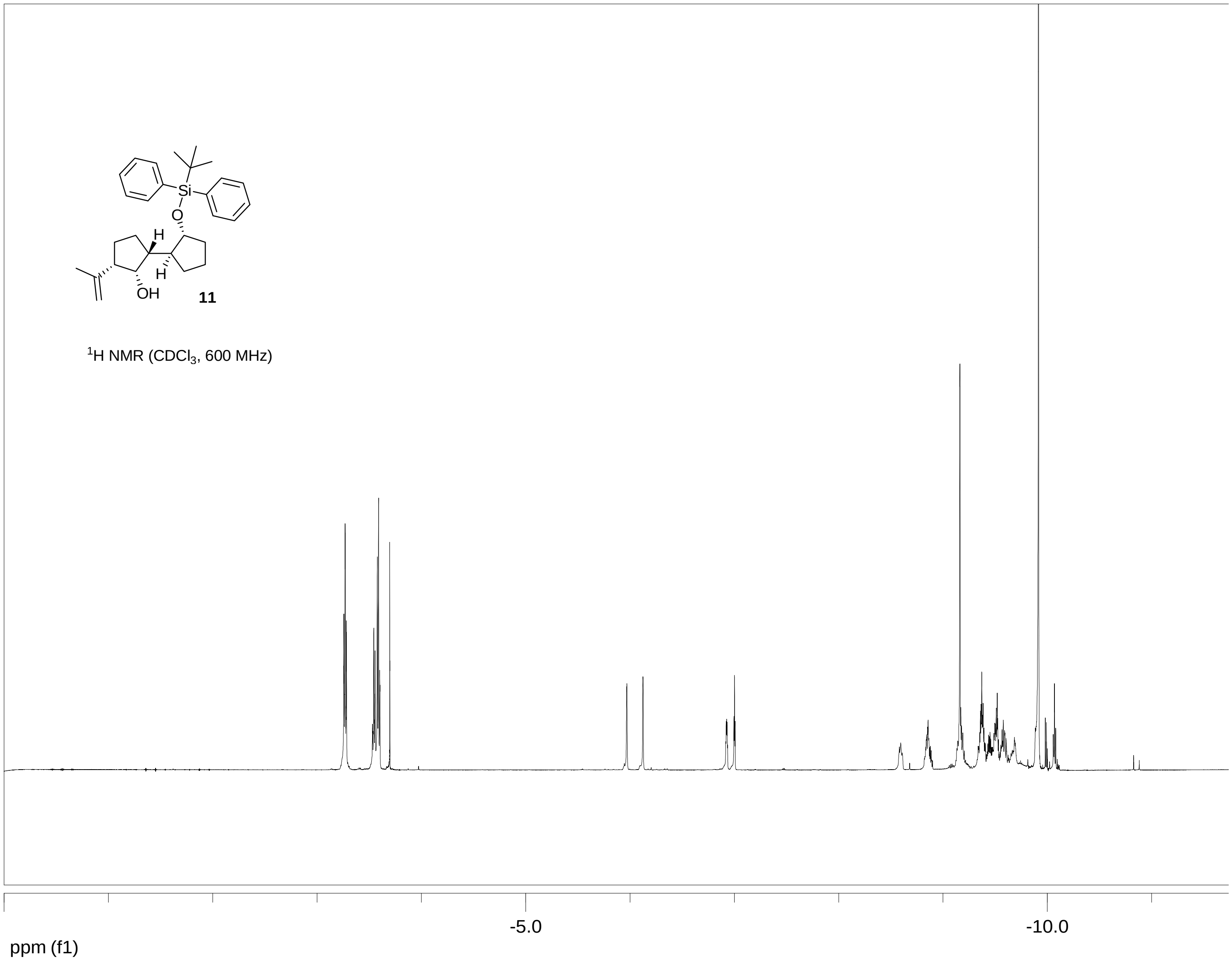
10a

^{1}H NMR ($CDCl_3$, 600 MHz)



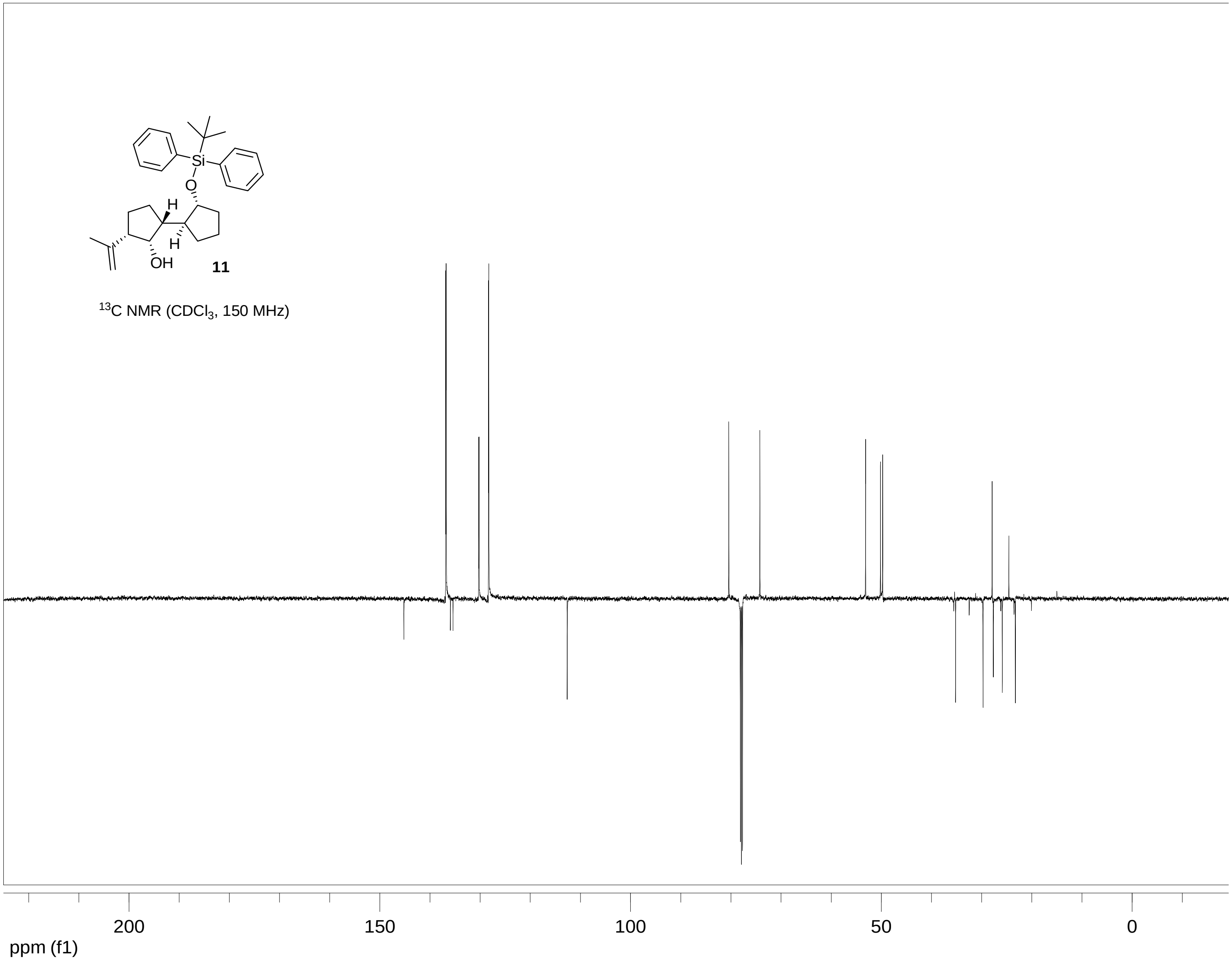
10a

^{13}C NMR (CDCl$_3$, 150 MHz)



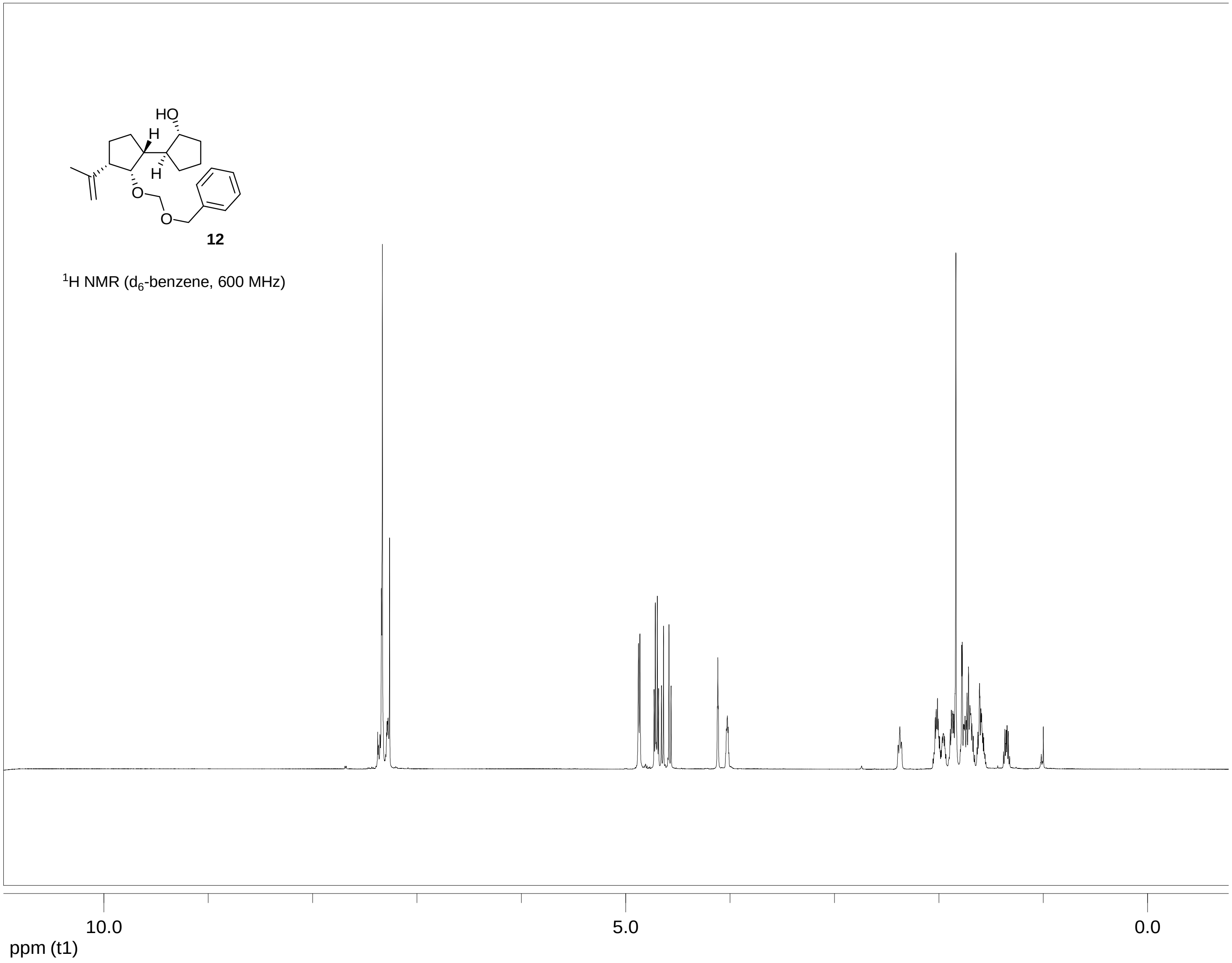
11

^{1}H NMR ($CDCl_3$, 600 MHz)



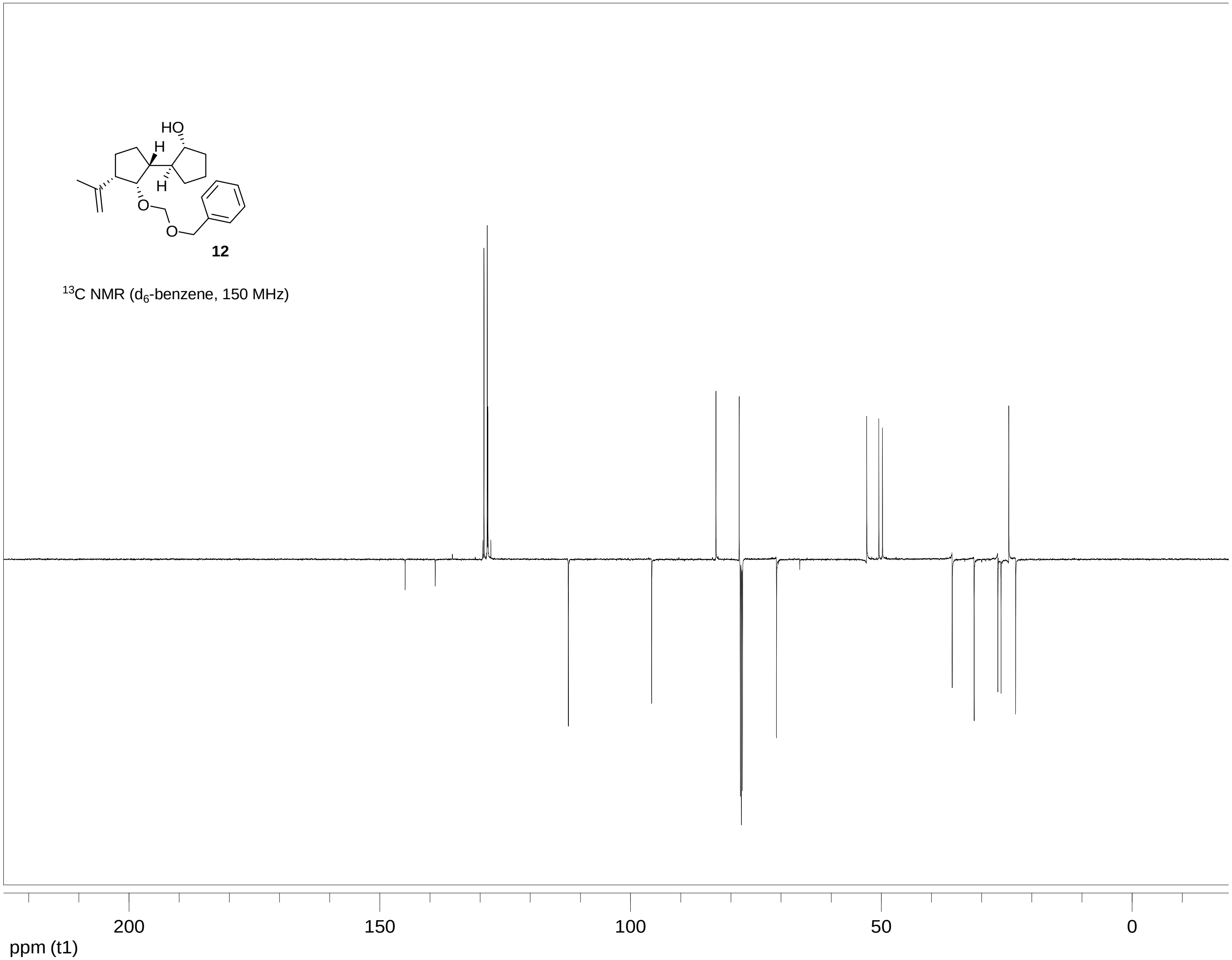
11

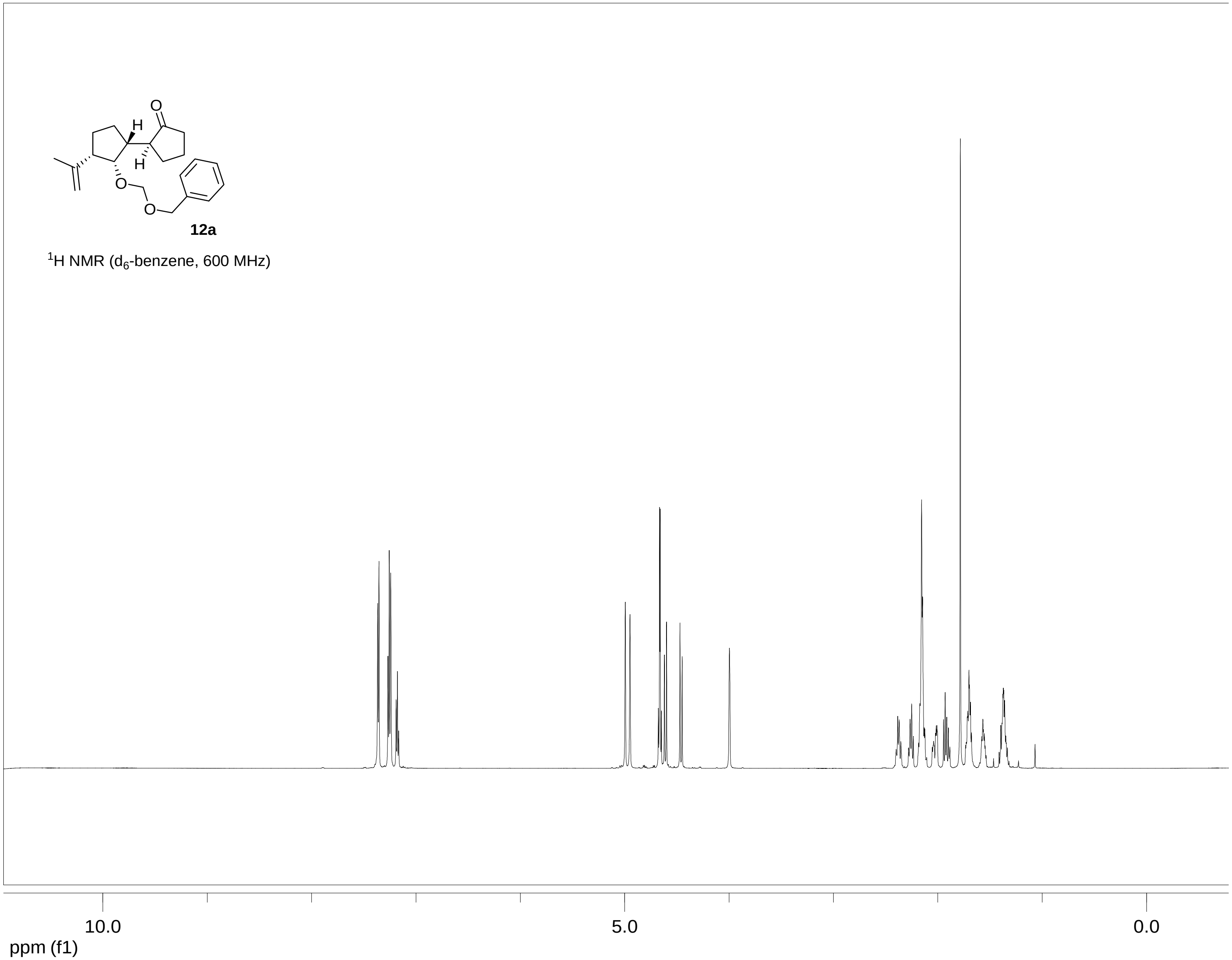
^{13}C NMR (CDCl$_3$, 150 MHz)

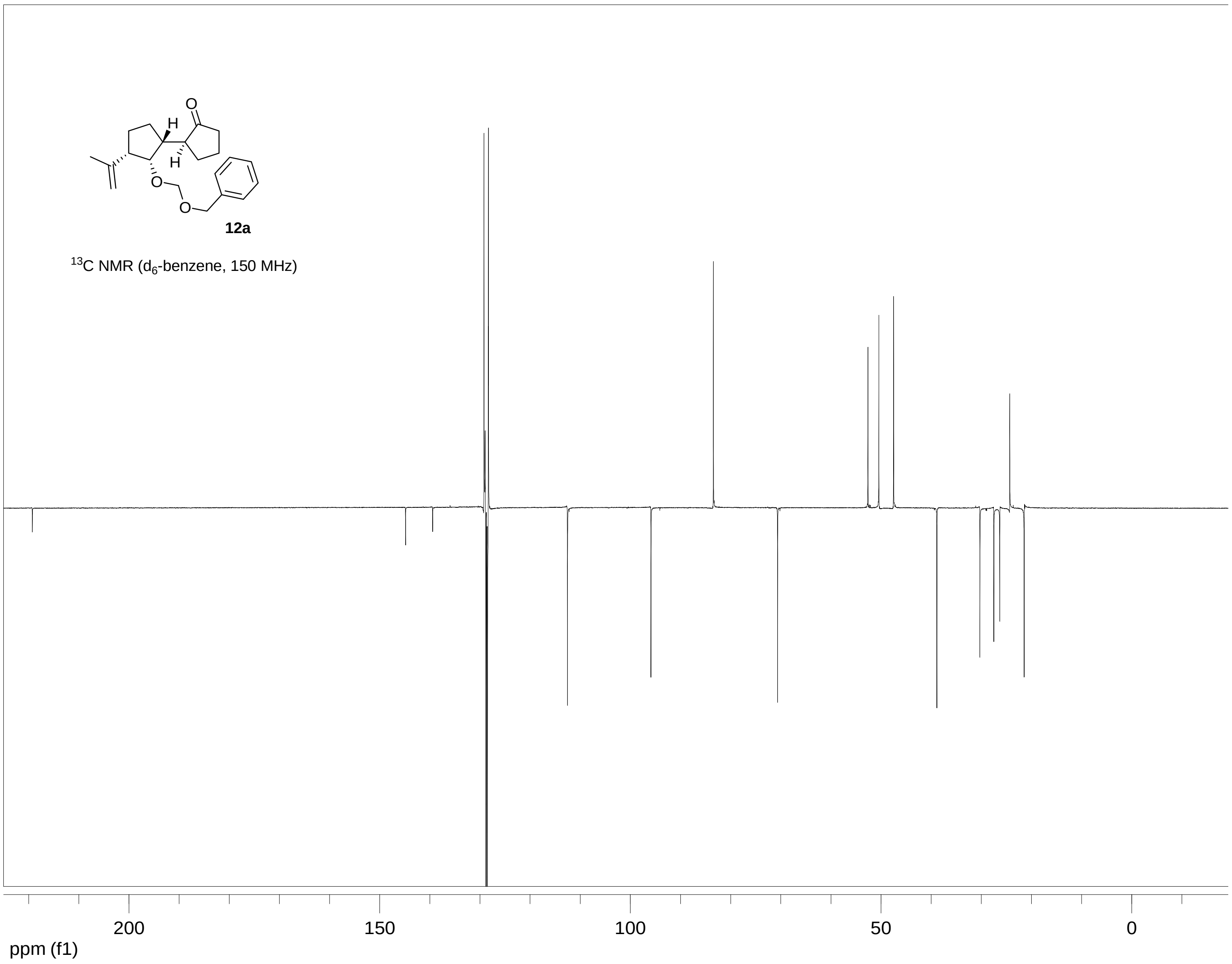

12
^{1}H NMR (d_6-benzene, 600 MHz)
10.0
5.0
0.0
ppm (t1)

12

^{13}C NMR (d_6-benzene, 150 MHz)

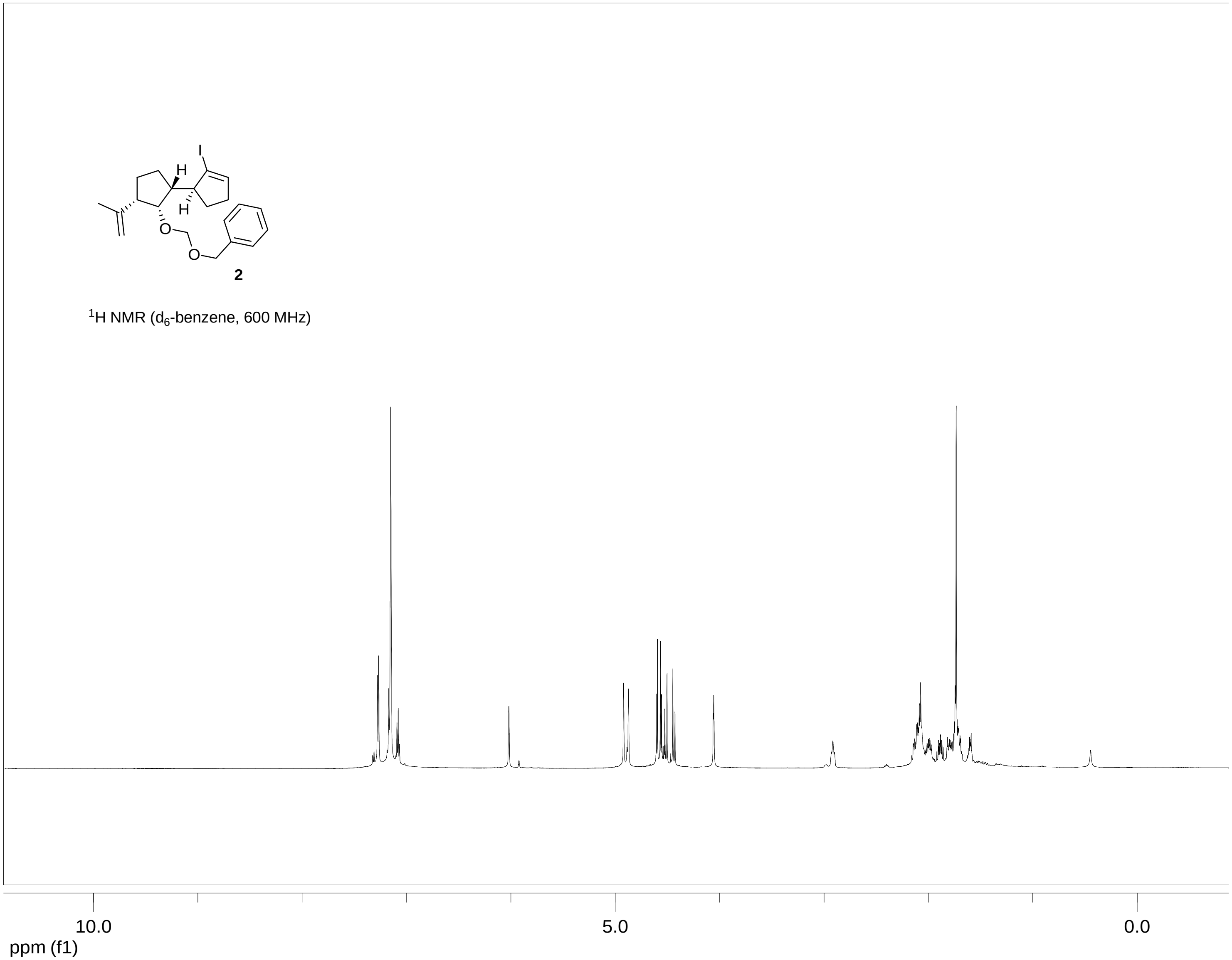



12a
^{1}H NMR (d_6-benzene, 600 MHz)
10.0
5.0
0.0
ppm (f1)



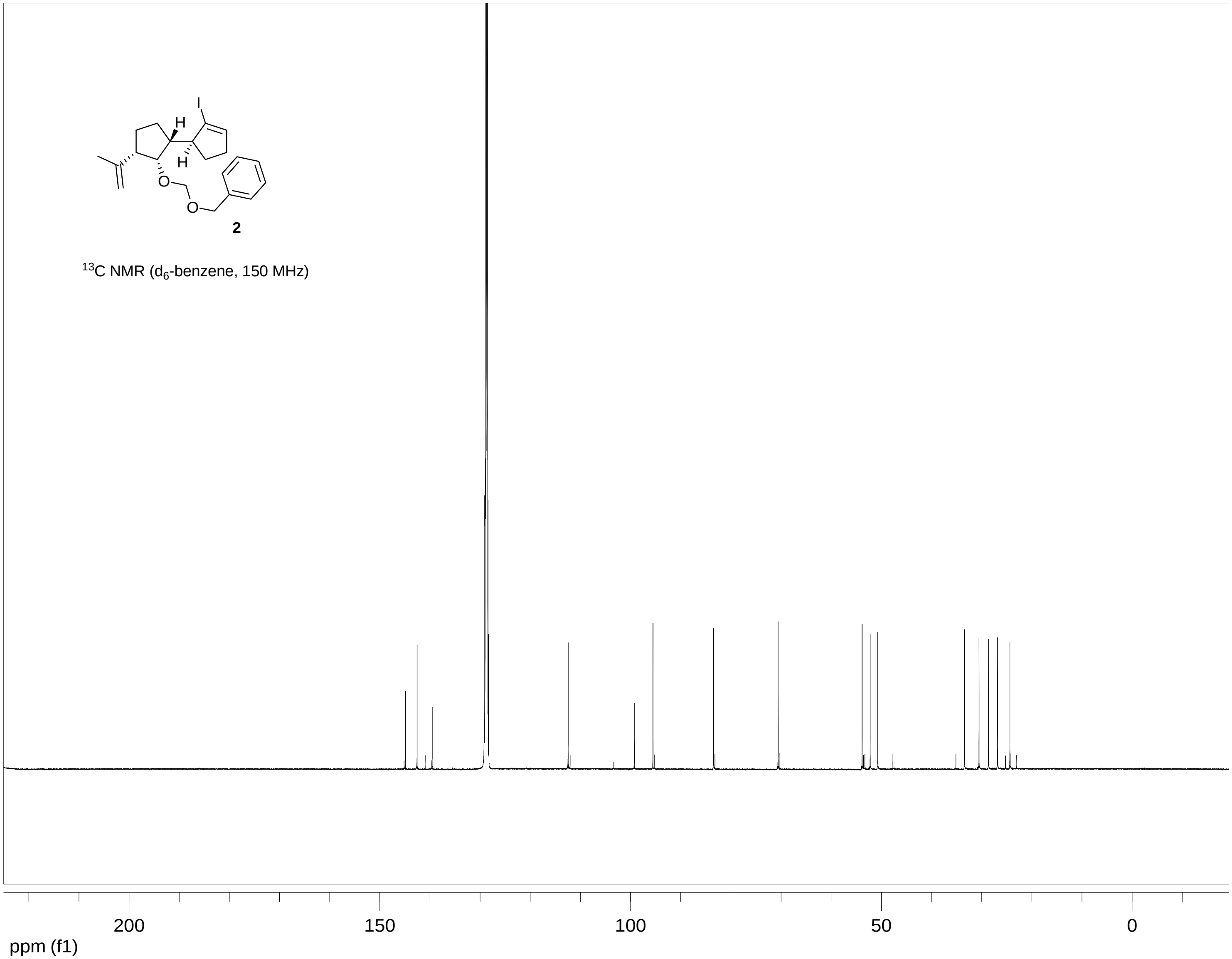
12a

^{13}C NMR (d_6-benzene, 150 MHz)



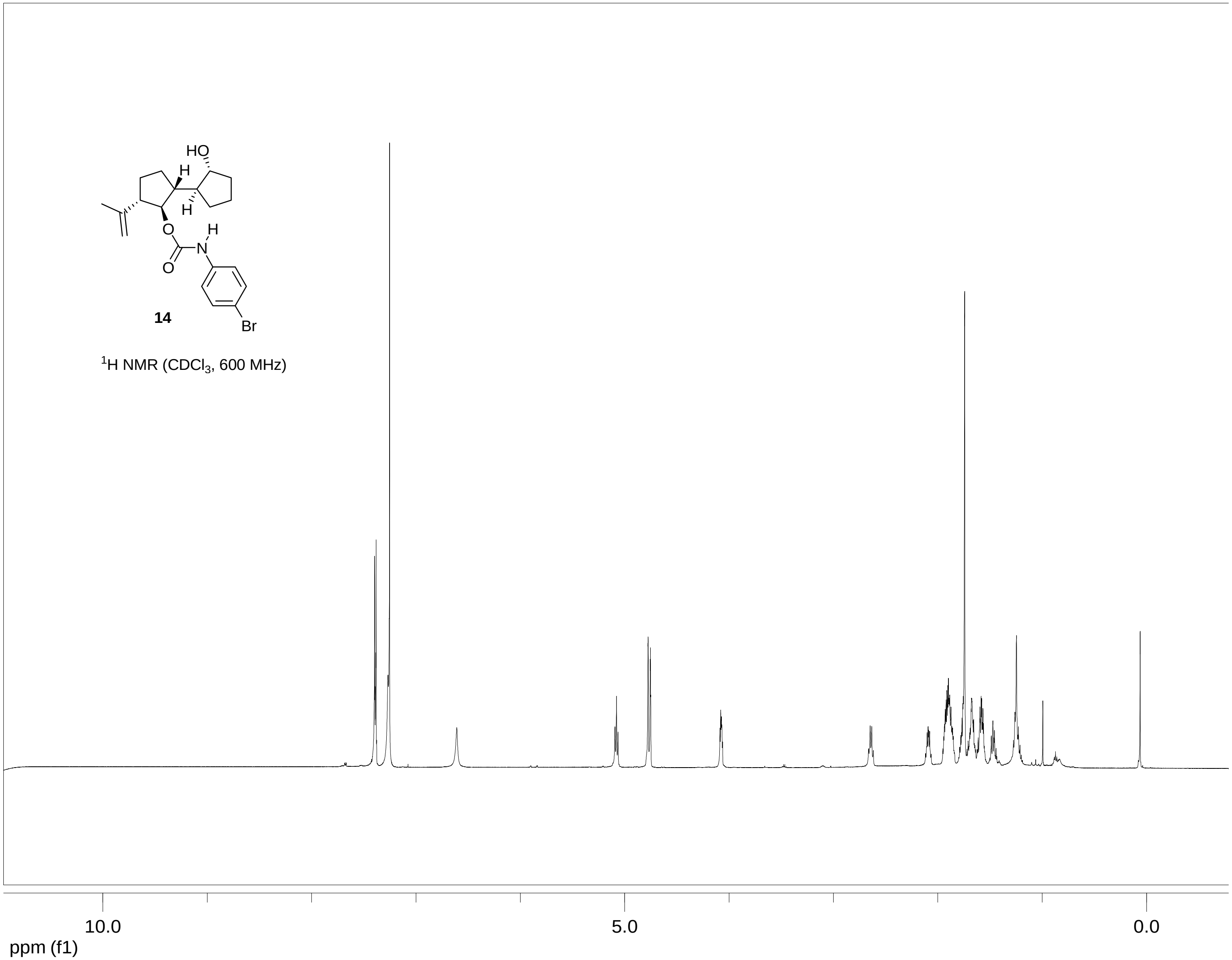
2

^{1}H NMR (d_6-benzene, 600 MHz)



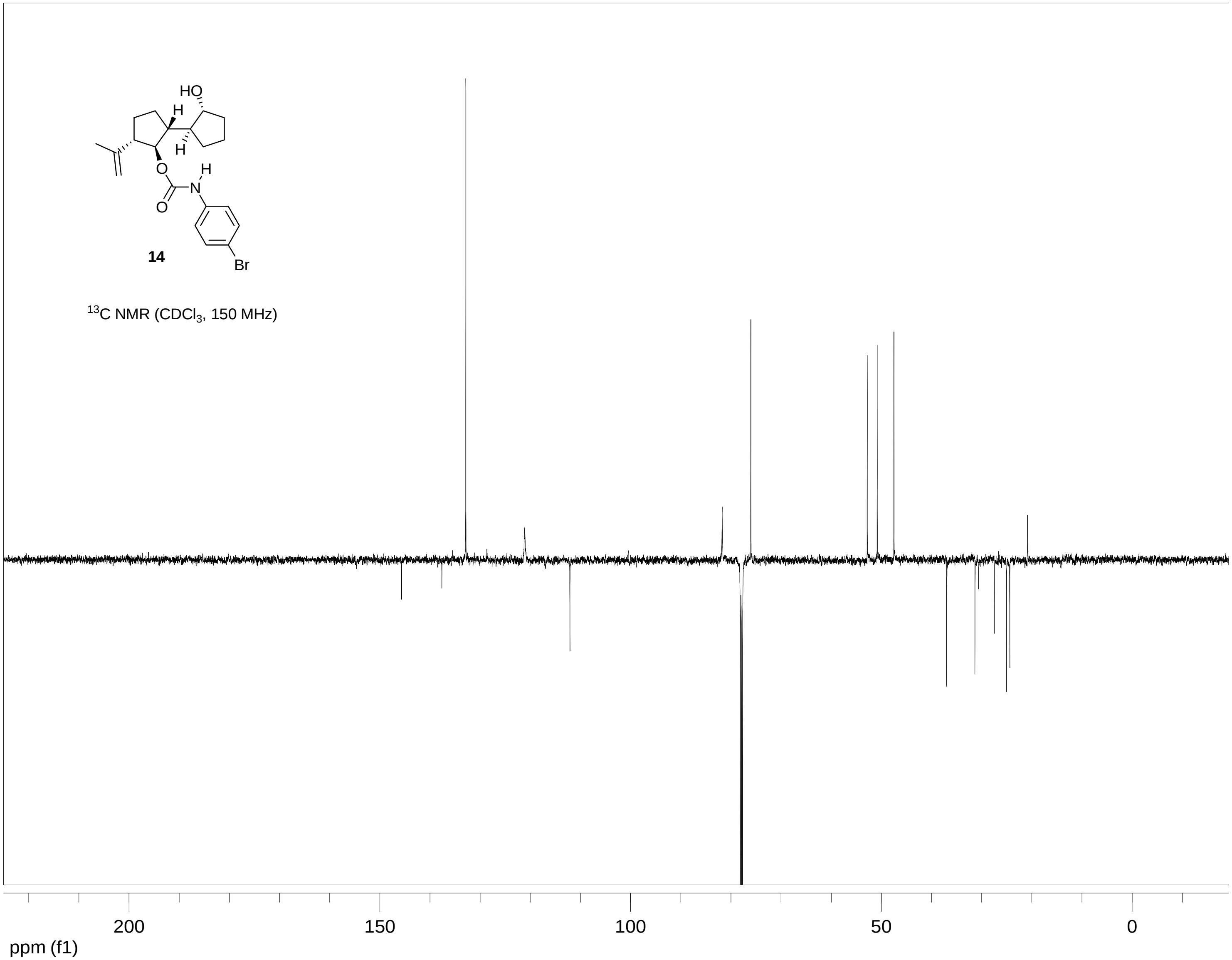
2

^{13}C NMR (d$_6$-benzene, 150 MHz)



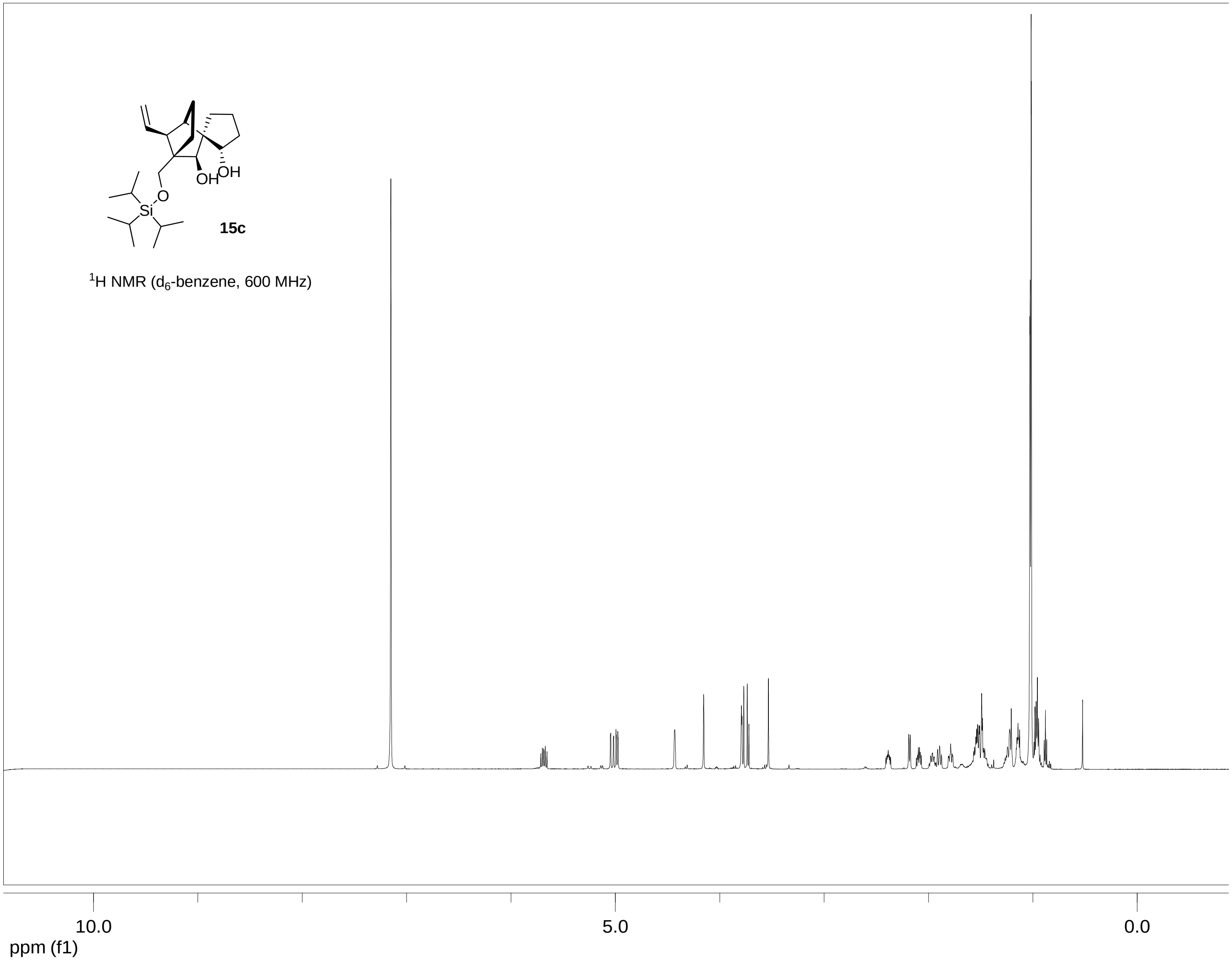
14

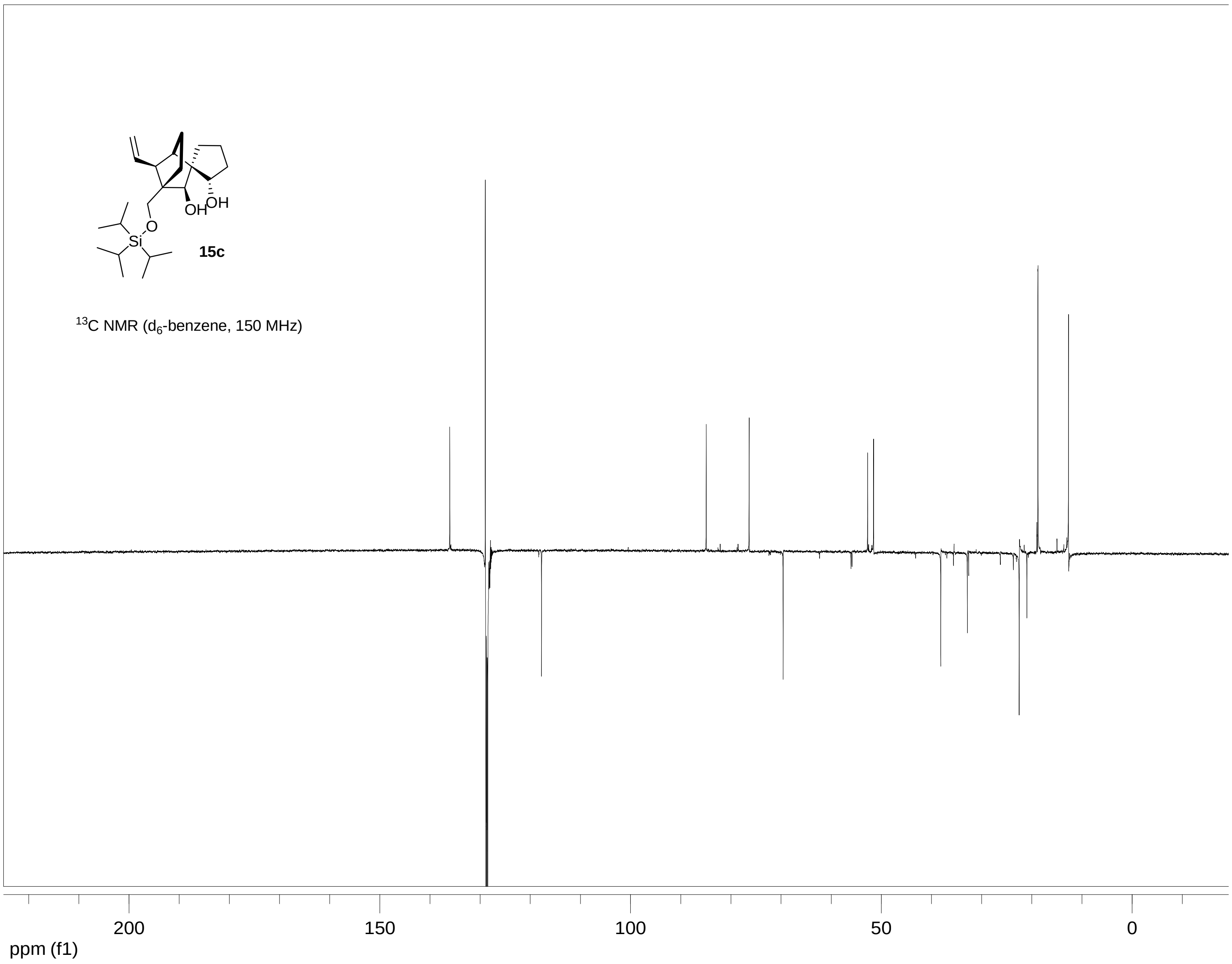
^{1}H NMR ($CDCl_3$, 600 MHz)



14

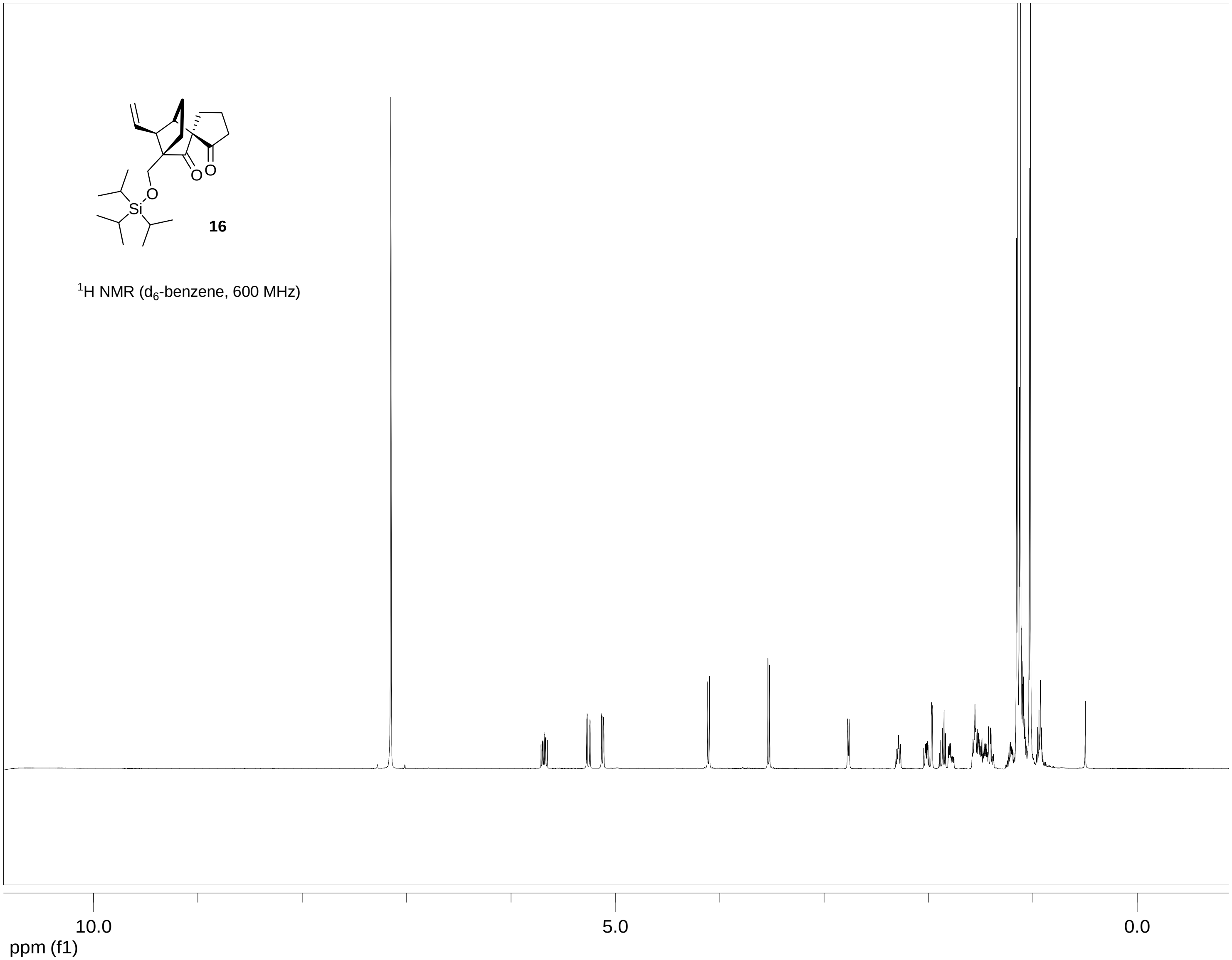
^{13}C NMR (CDCl$_3$, 150 MHz)


OH
OH
O
Si
15c
^{1}H NMR (d$_6$-benzene, 600 MHz)
10.0
5.0
0.0
ppm (f1)



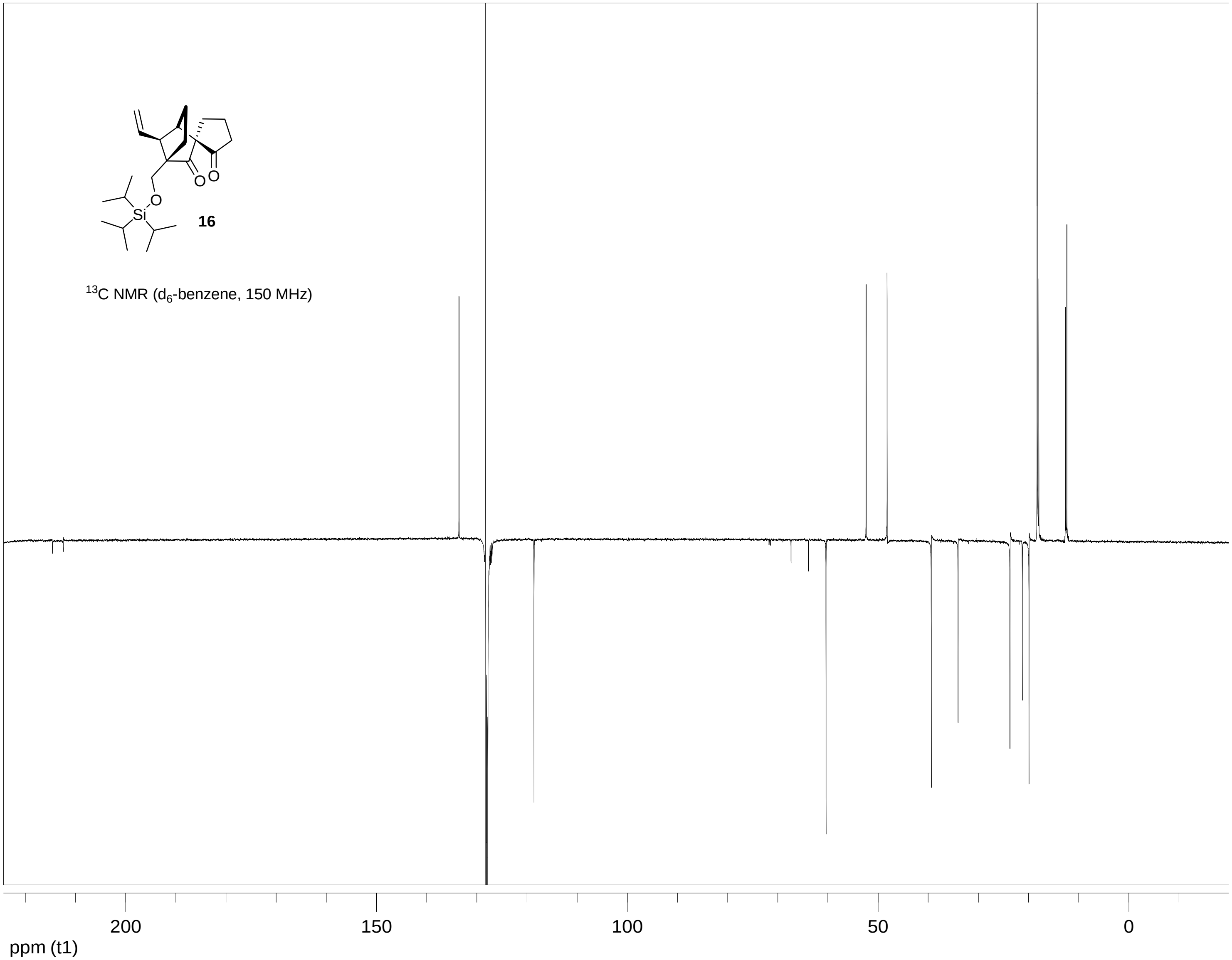
15c

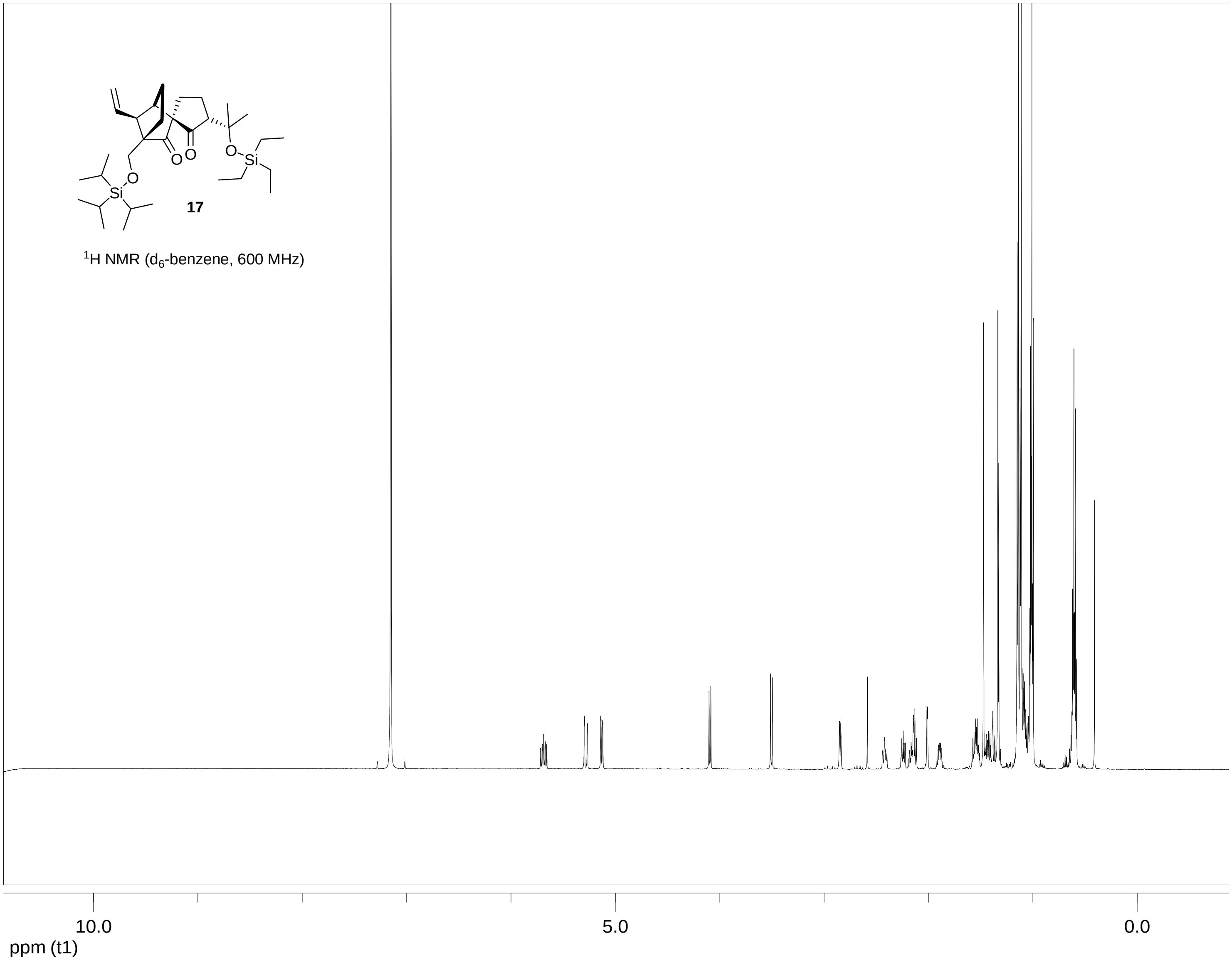
^{13}C NMR (d_6-benzene, 150 MHz)



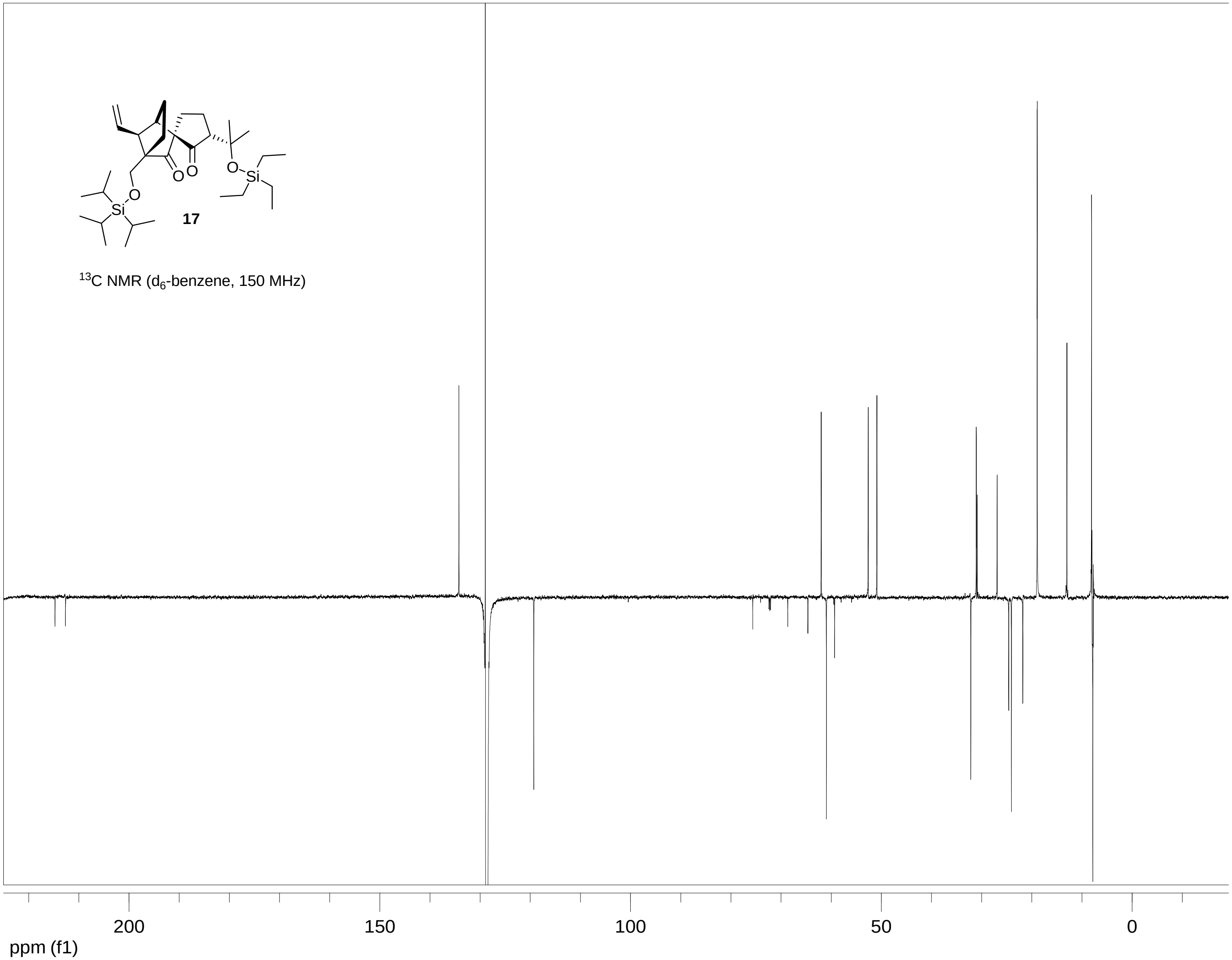
16

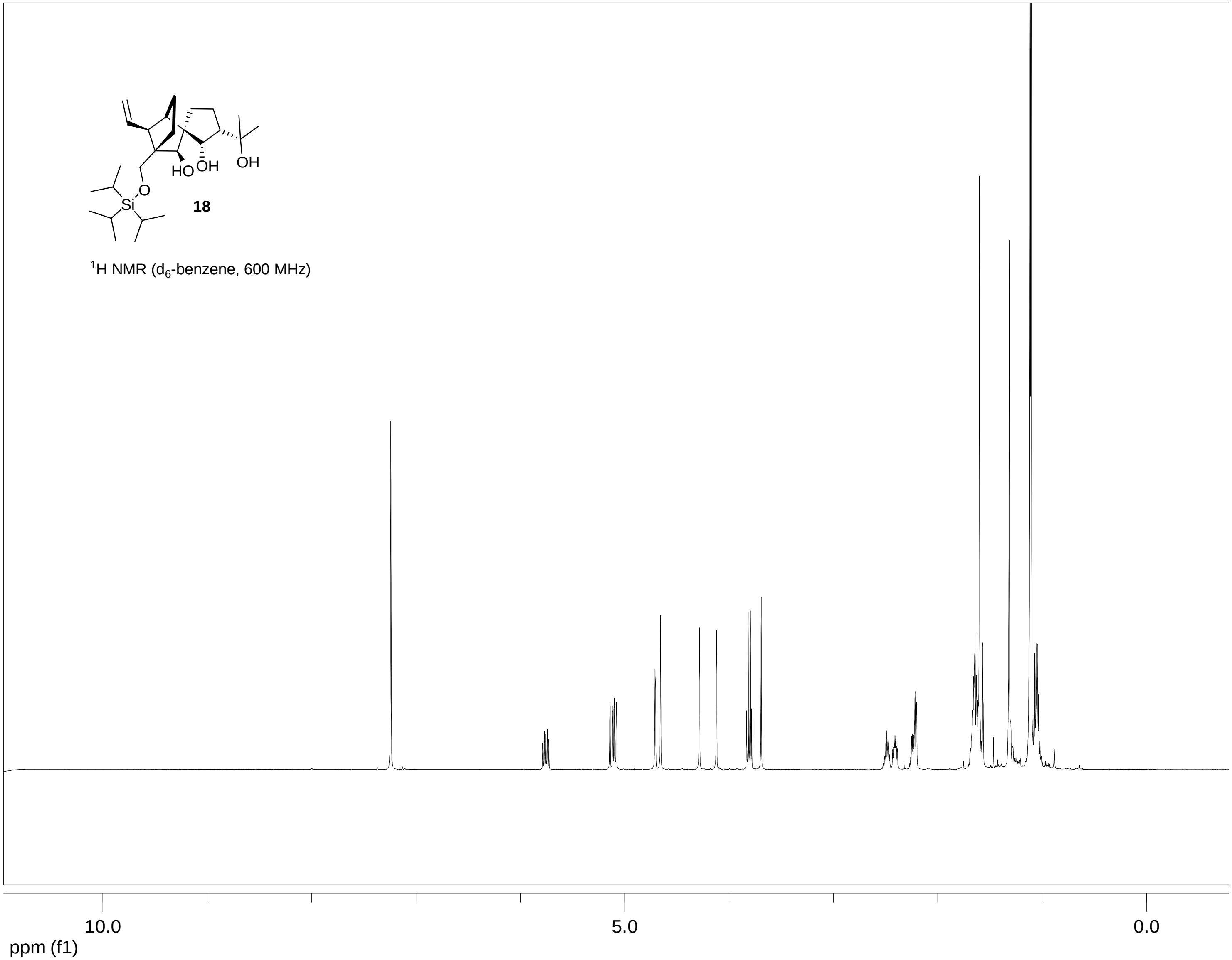
^{1}H NMR (d$_6$-benzene, 600 MHz)


16
^{13}C NMR (d_6-benzene, 150 MHz)
O
O
O
Si
200
150
100
50
0
ppm (t1)


17

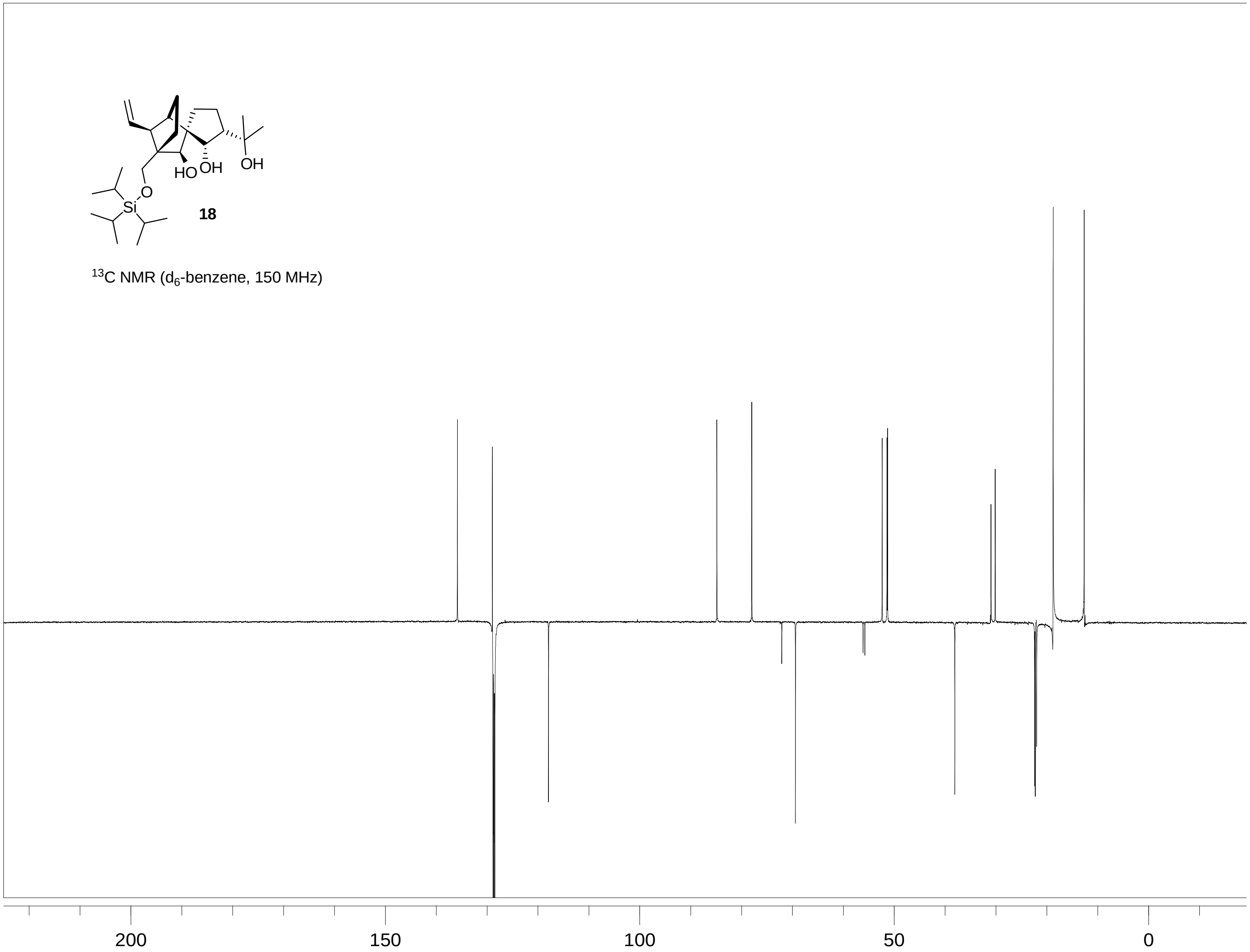
^1H NMR (d_6-benzene, 600 MHz)


O
O
O
Si
O
Si
17
^{13}C NMR (d$_6$-benzene, 150 MHz)
200
150
100
50
0
ppm (f1)



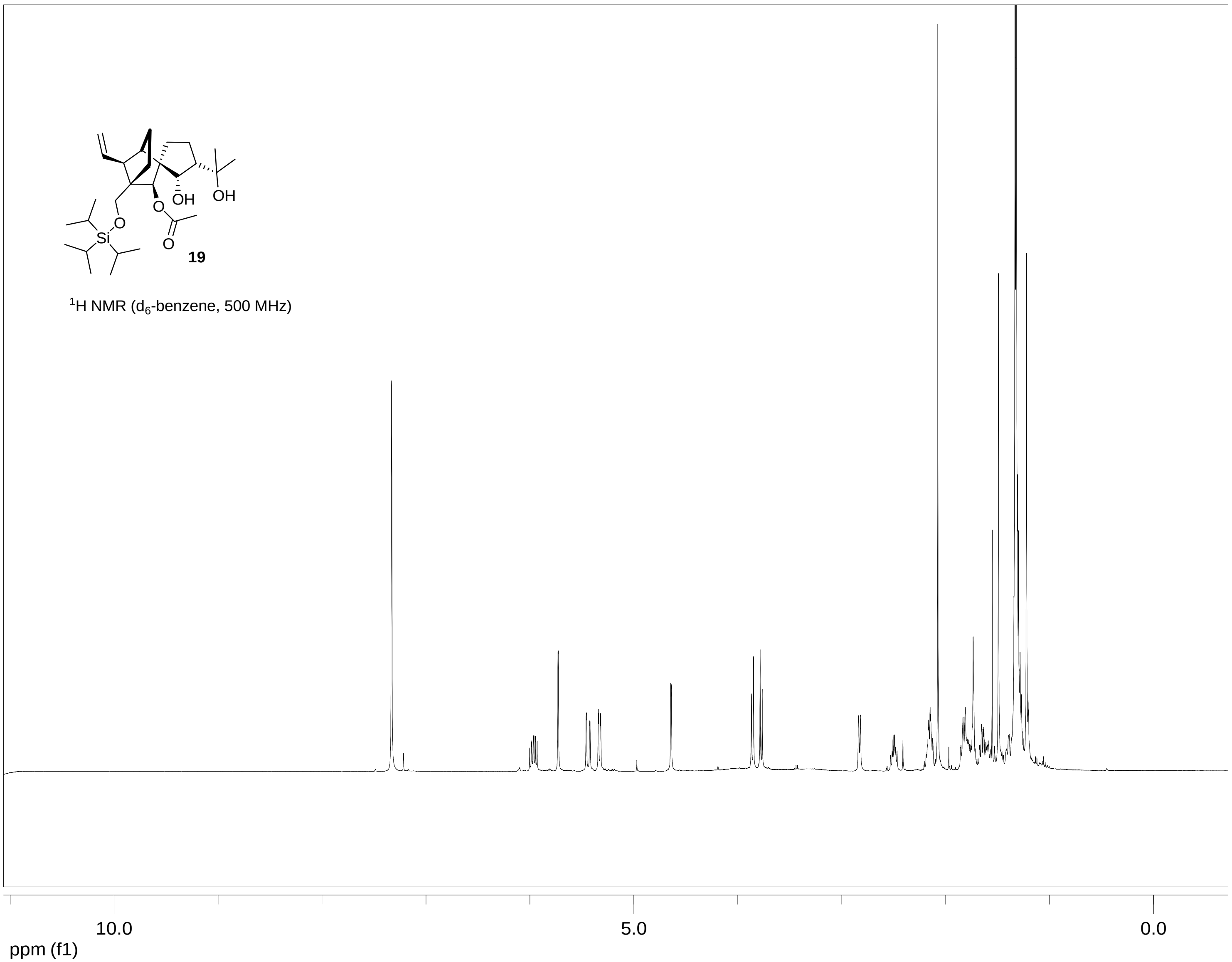
18

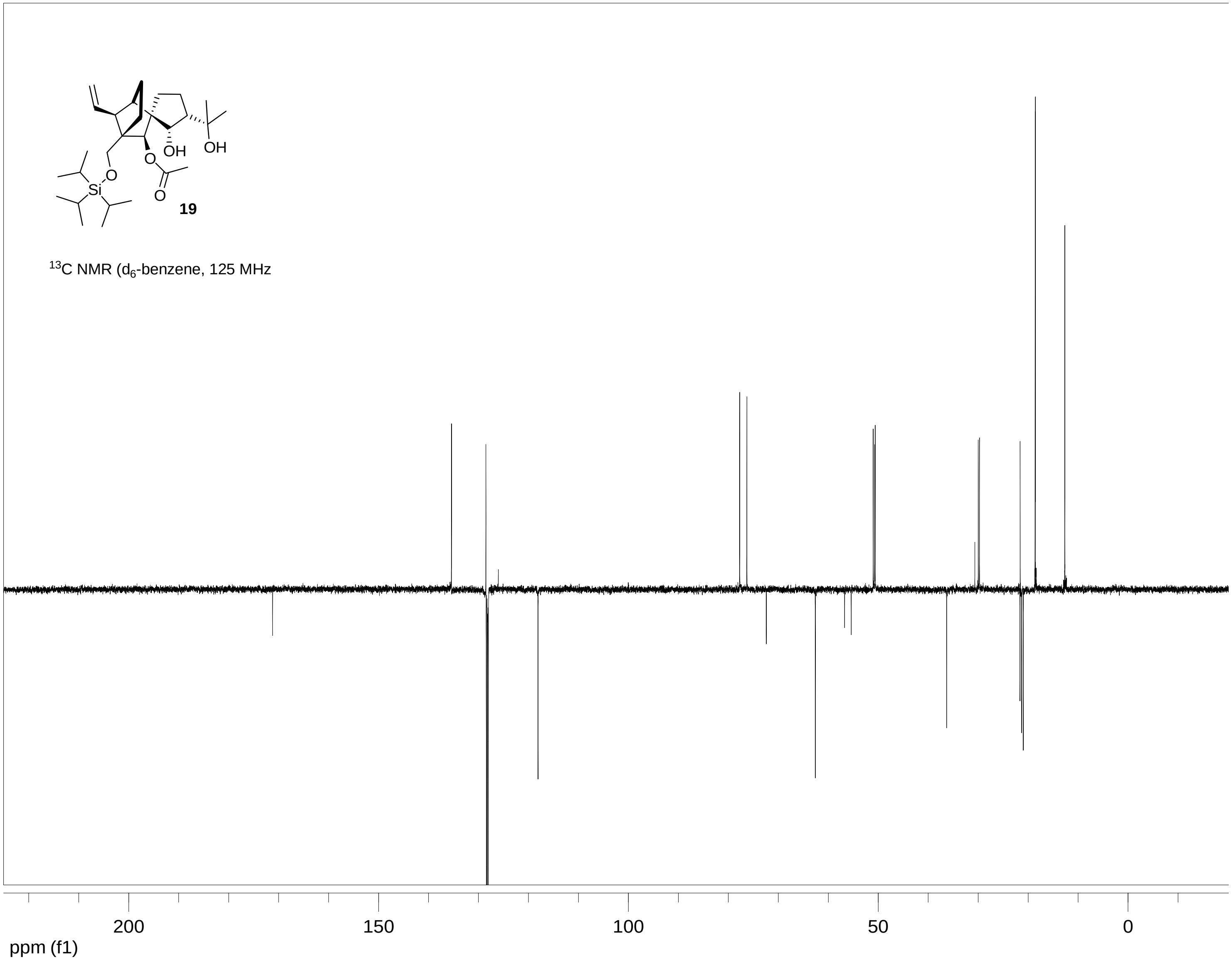
^{1}H NMR (d_6-benzene, 600 MHz)

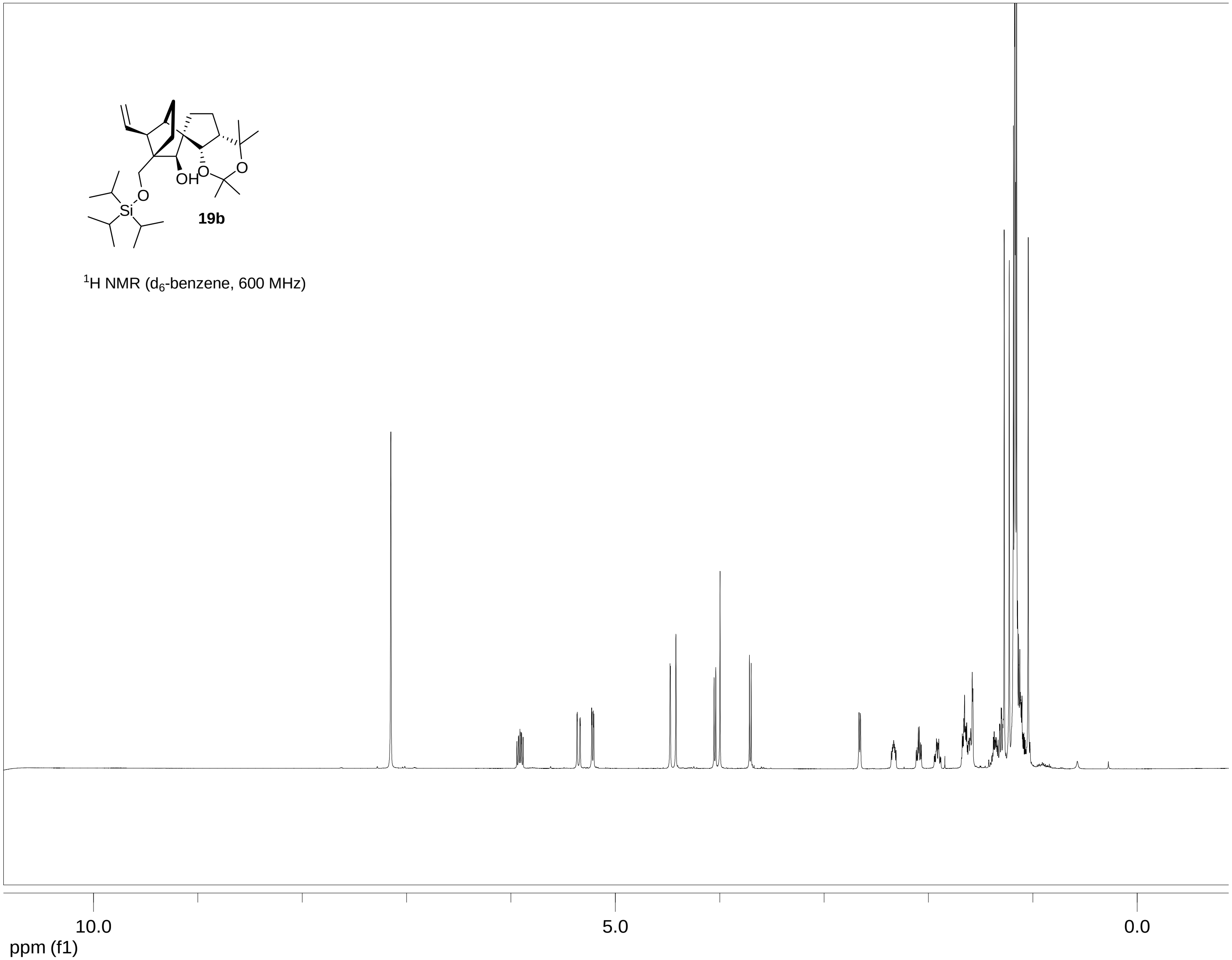


18

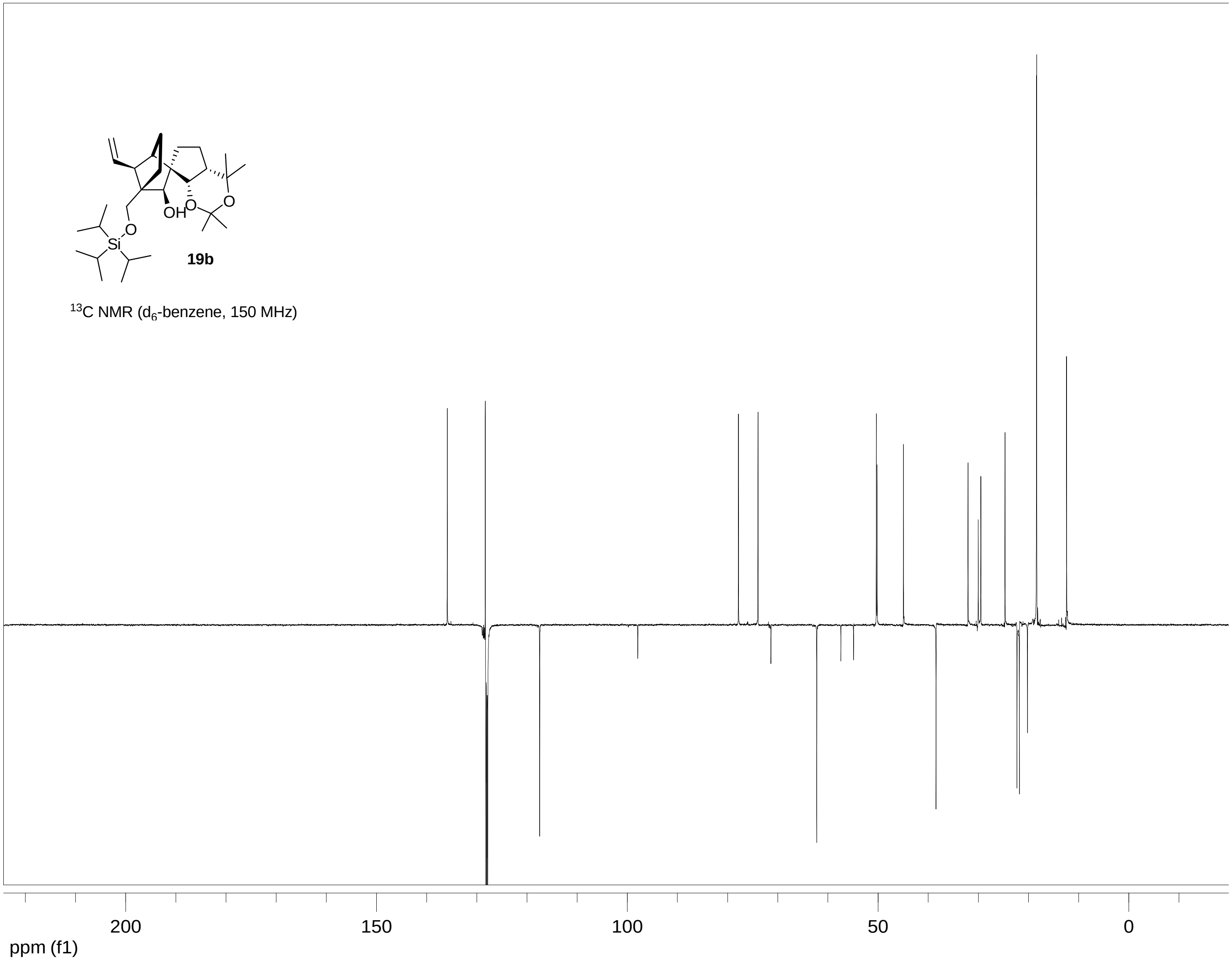
^{13}C NMR (d_6-benzene, 150 MHz)


OH
OH
O
O
O
Si
19
^{1}H NMR (d$_6$-benzene, 500 MHz)
10.0
5.0
0.0
ppm (f1)


19
^{13}C NMR (d$_6$-benzene, 125 MHz
OH
OH
O
O
O
Si
200
150
100
50
0
ppm (f1)

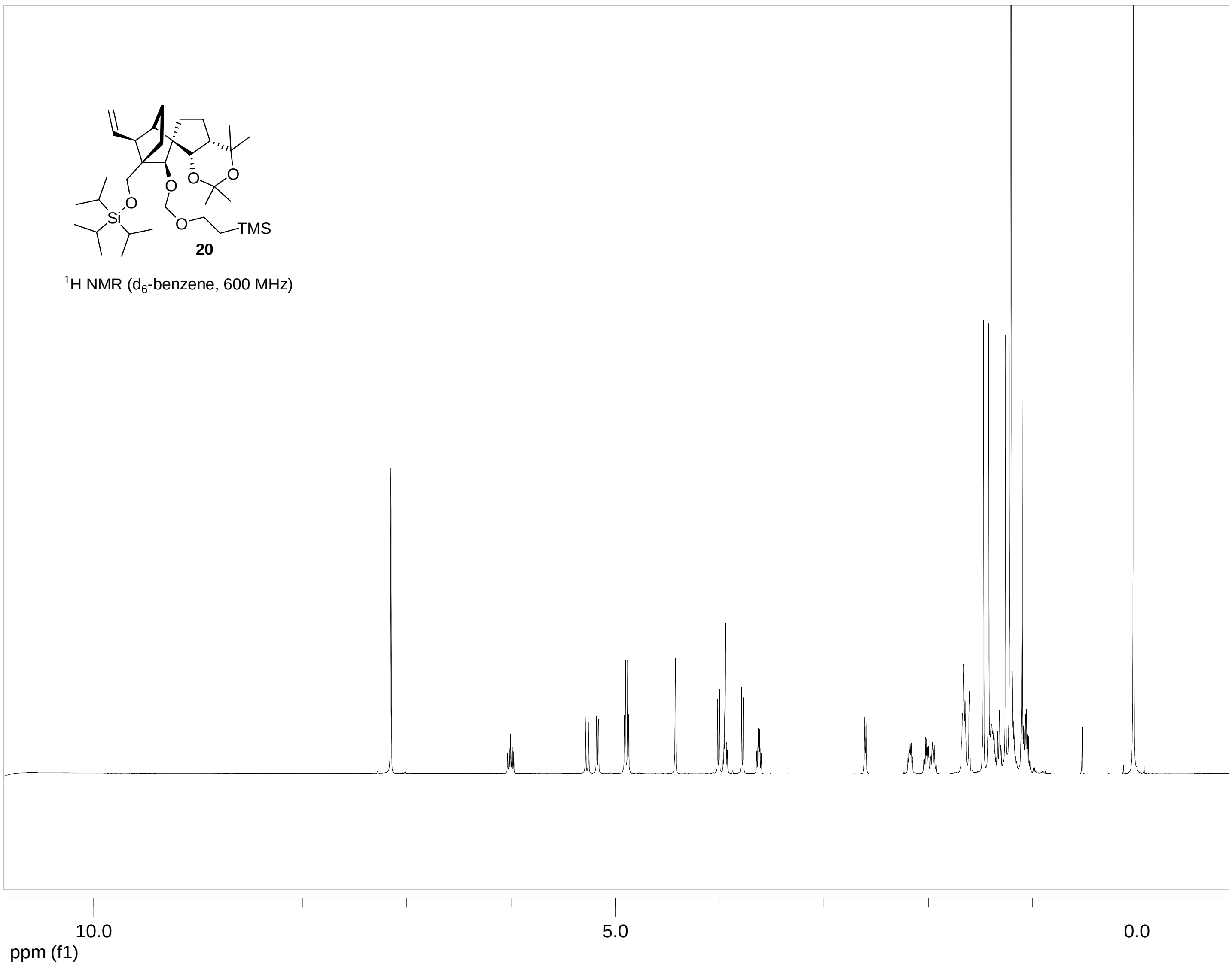

19b

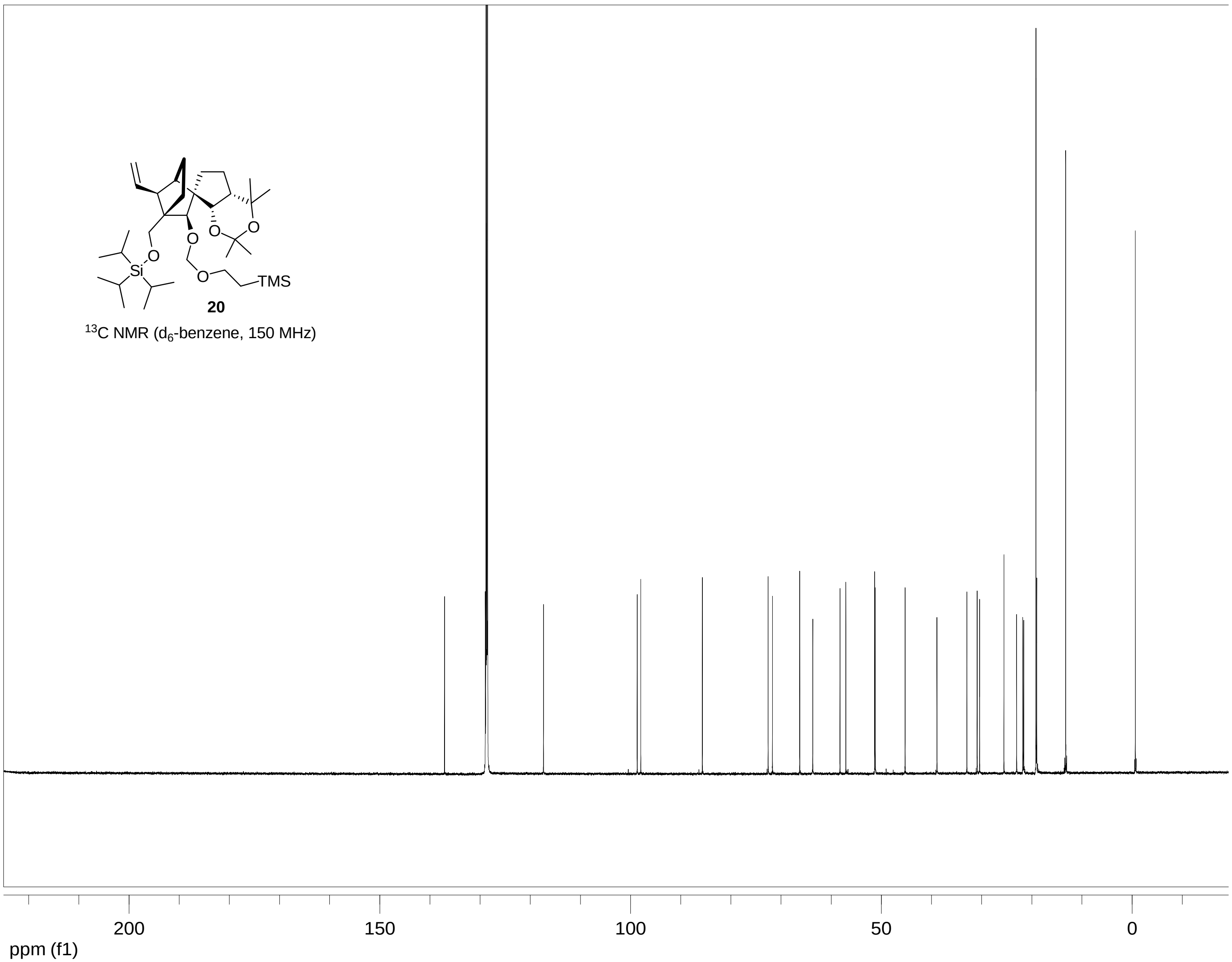
^{1}H NMR (d$_6$-benzene, 600 MHz)

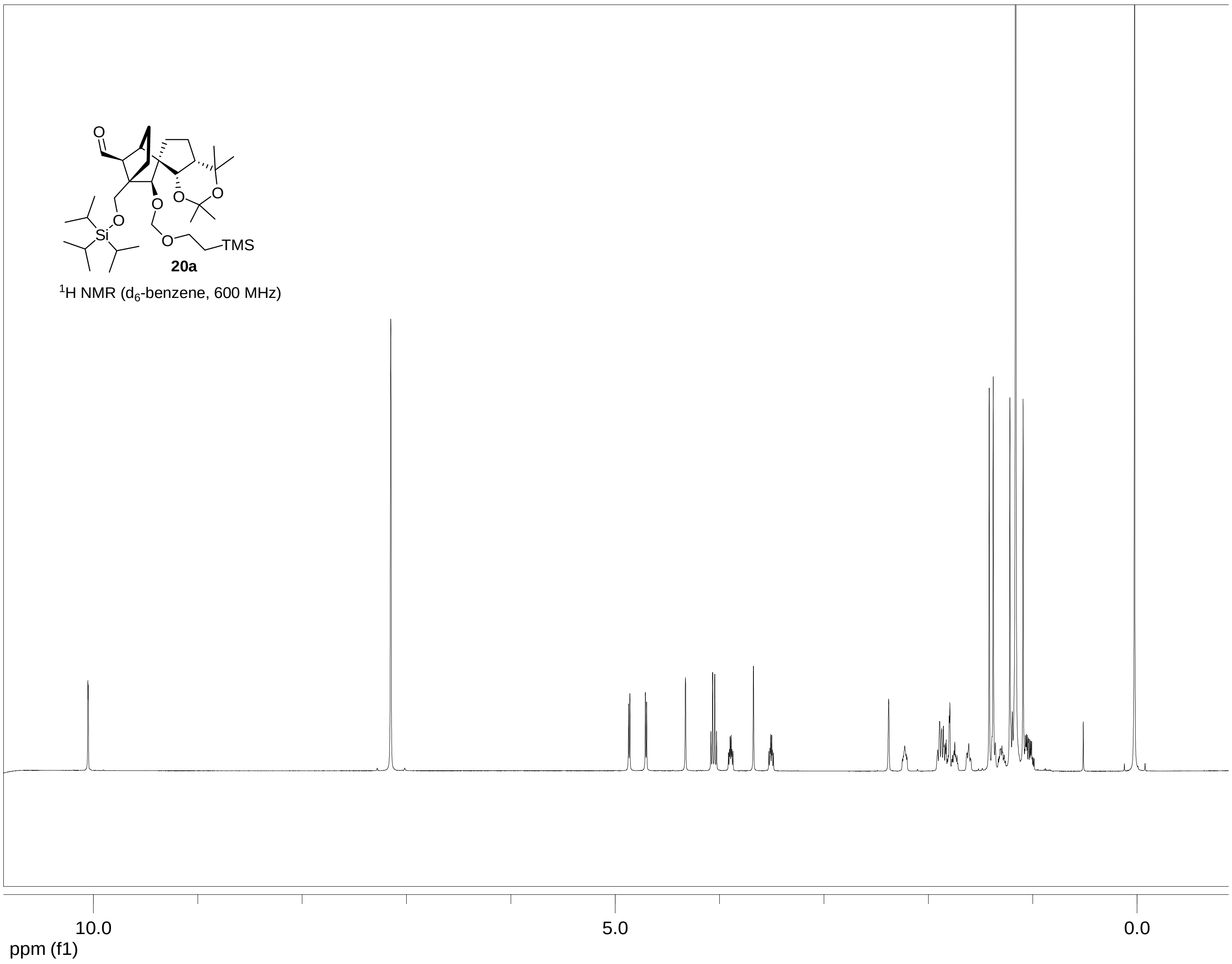


19b

^{13}C NMR (d_6-benzene, 150 MHz)

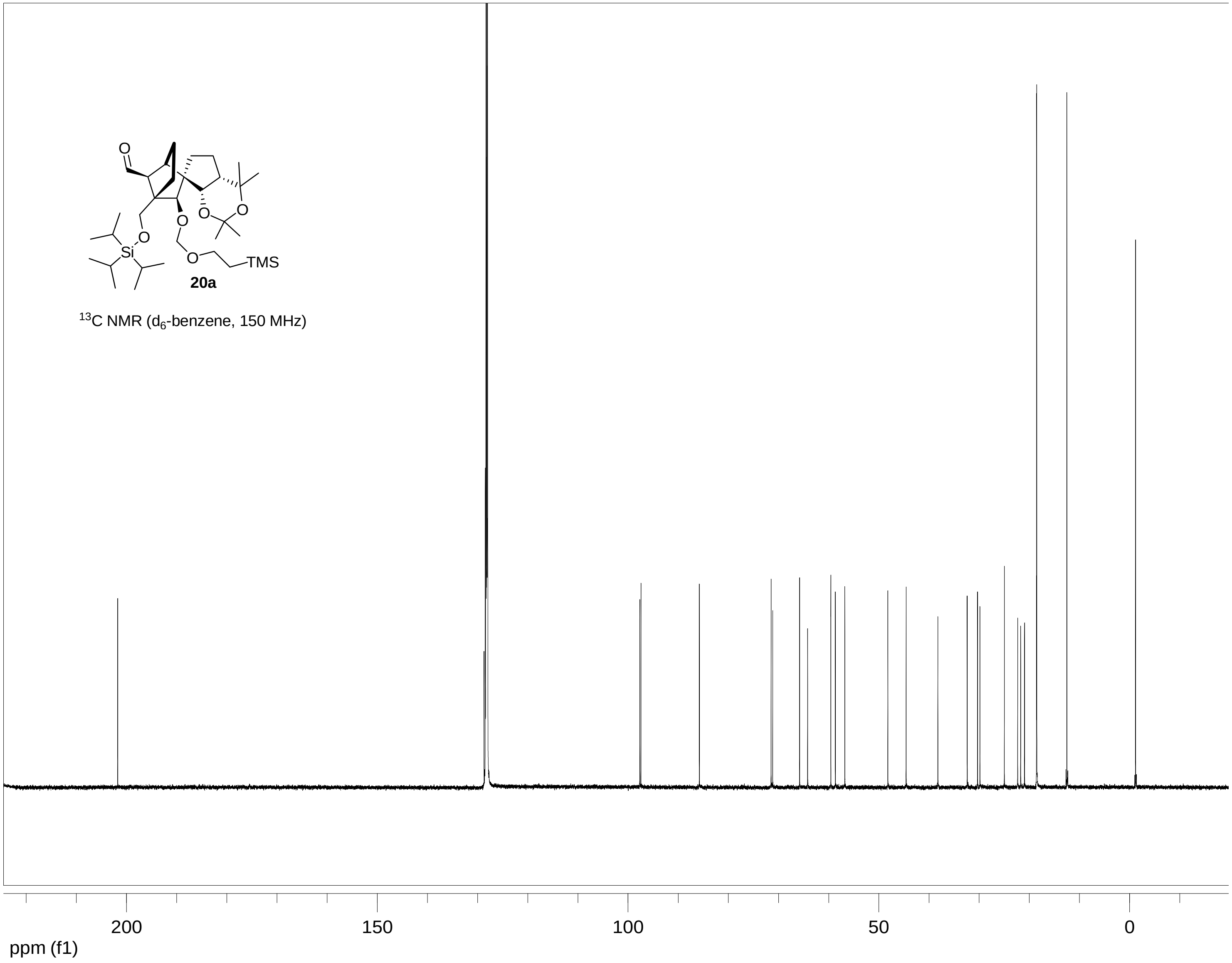

TMS
Si
O
20
^{1}H NMR (d$_6$-benzene, 600 MHz)
10.0
5.0
0.0
ppm (f1)


O
Si
O
O
O
O
O
TMS
20
^{13}C NMR (d$_6$-benzene, 150 MHz)
200
150
100
50
0
ppm (f1)

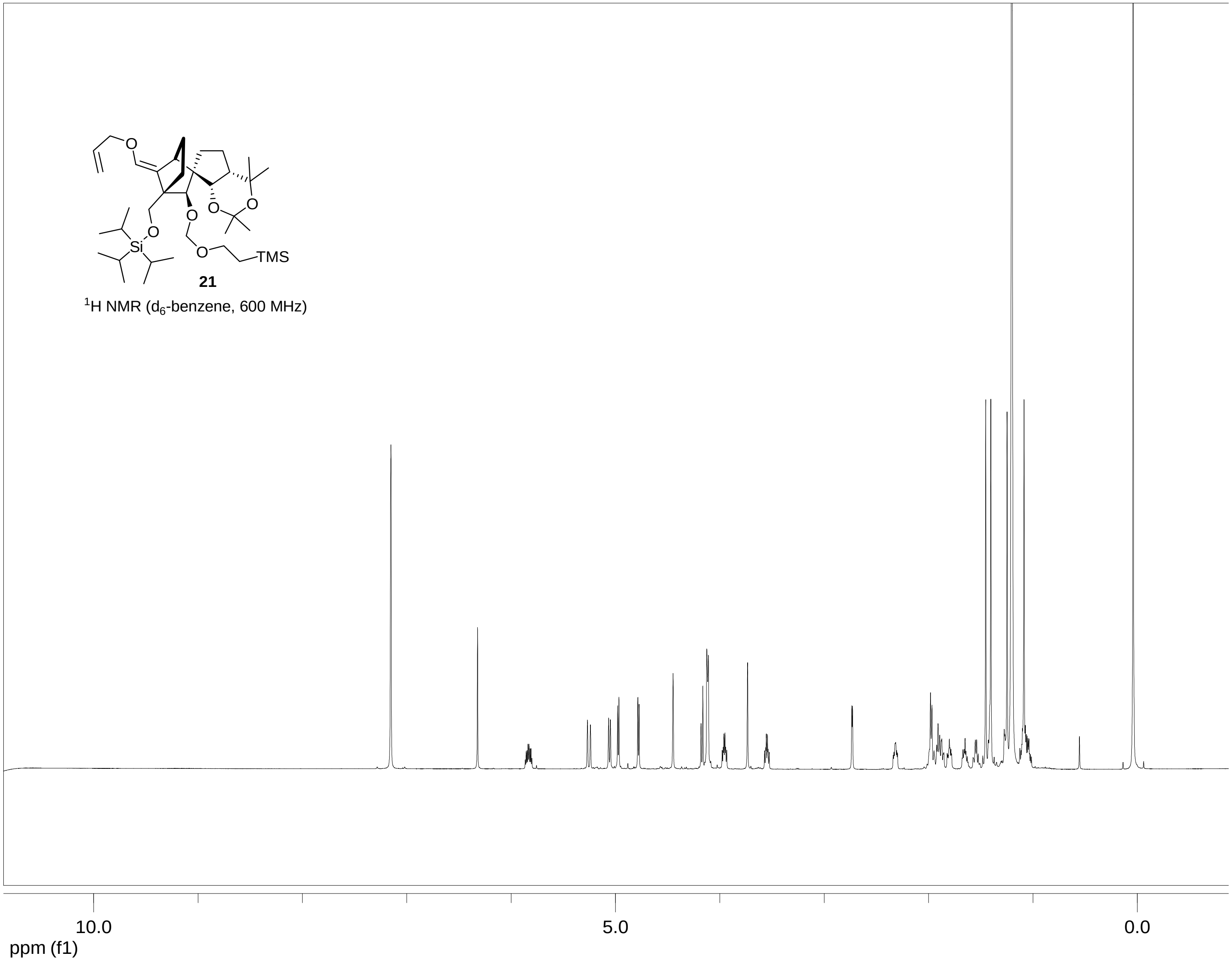


20a

^{1}H NMR (d_6-benzene, 600 MHz)

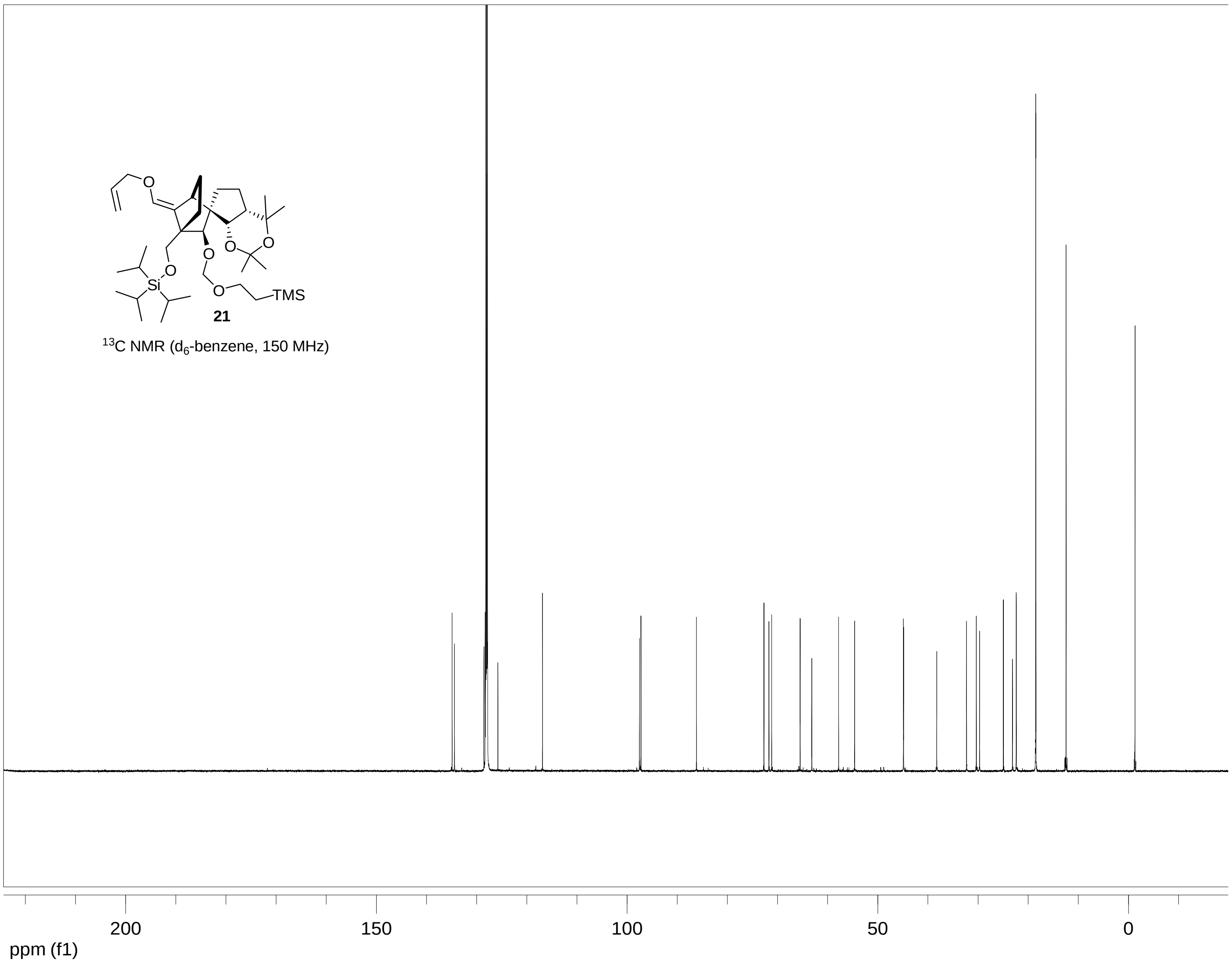


^{13}C NMR (d$_6$-benzene, 150 MHz)



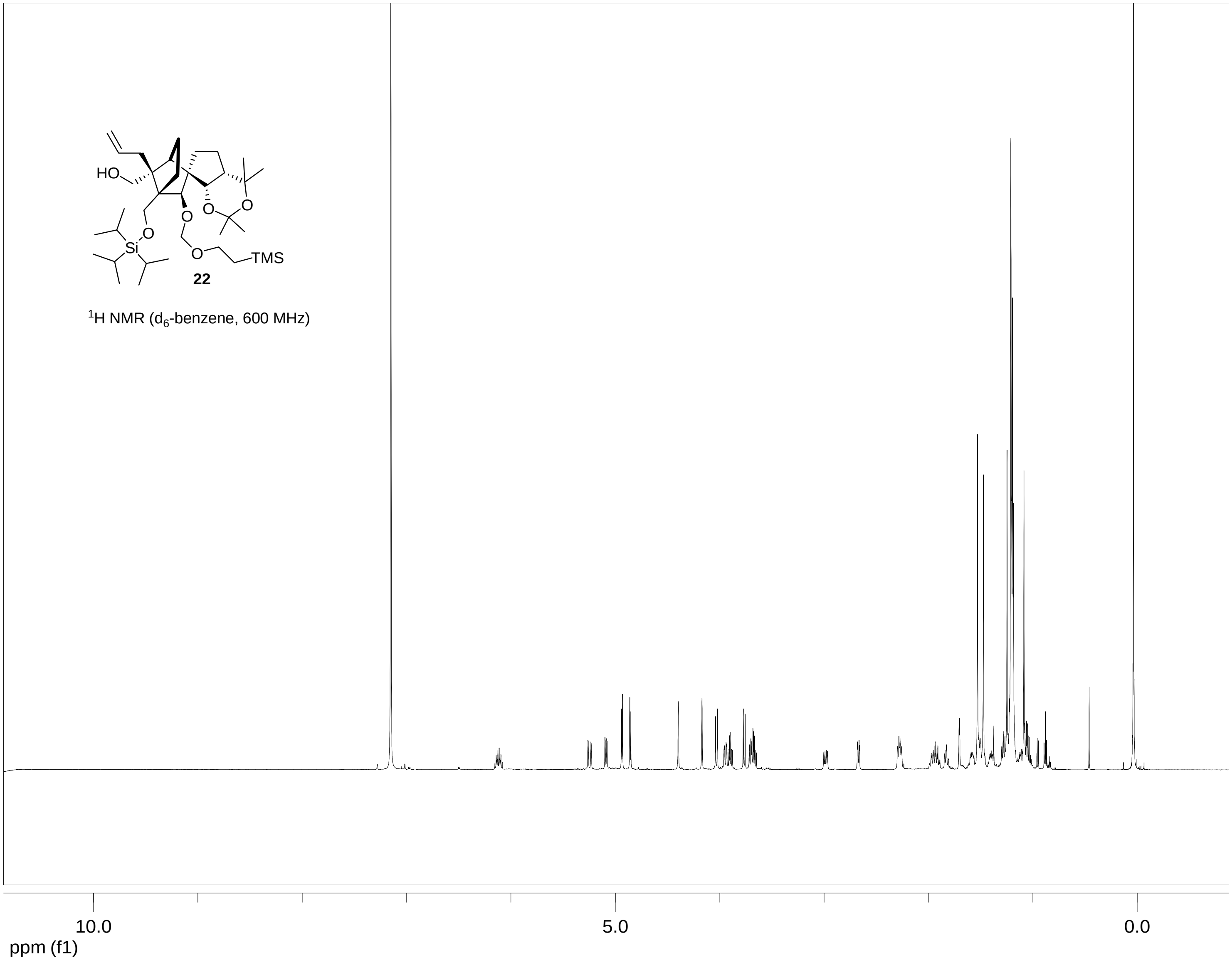
21

^{1}H NMR (d$_6$-benzene, 600 MHz)



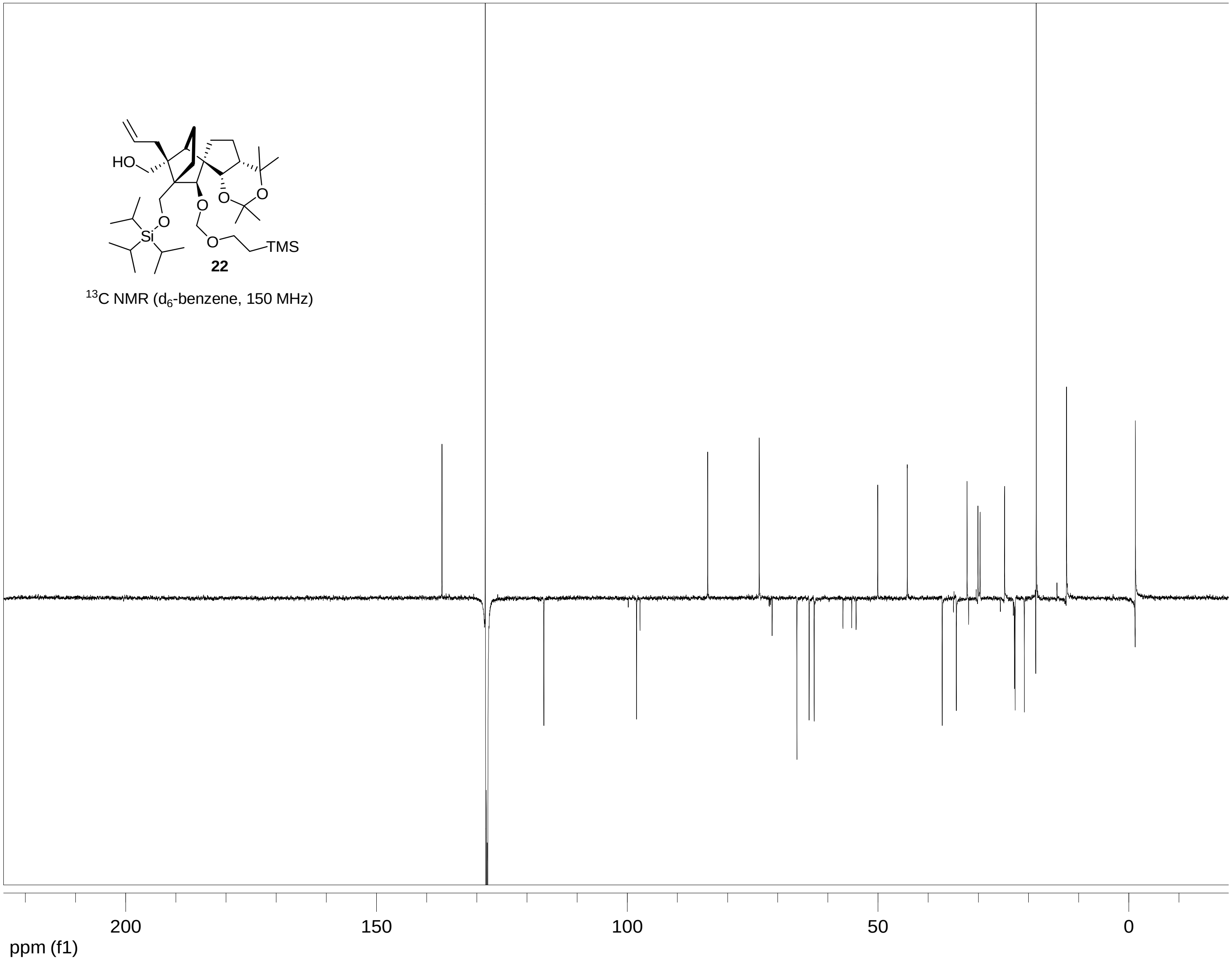
21

^{13}C NMR (d_6-benzene, 150 MHz)



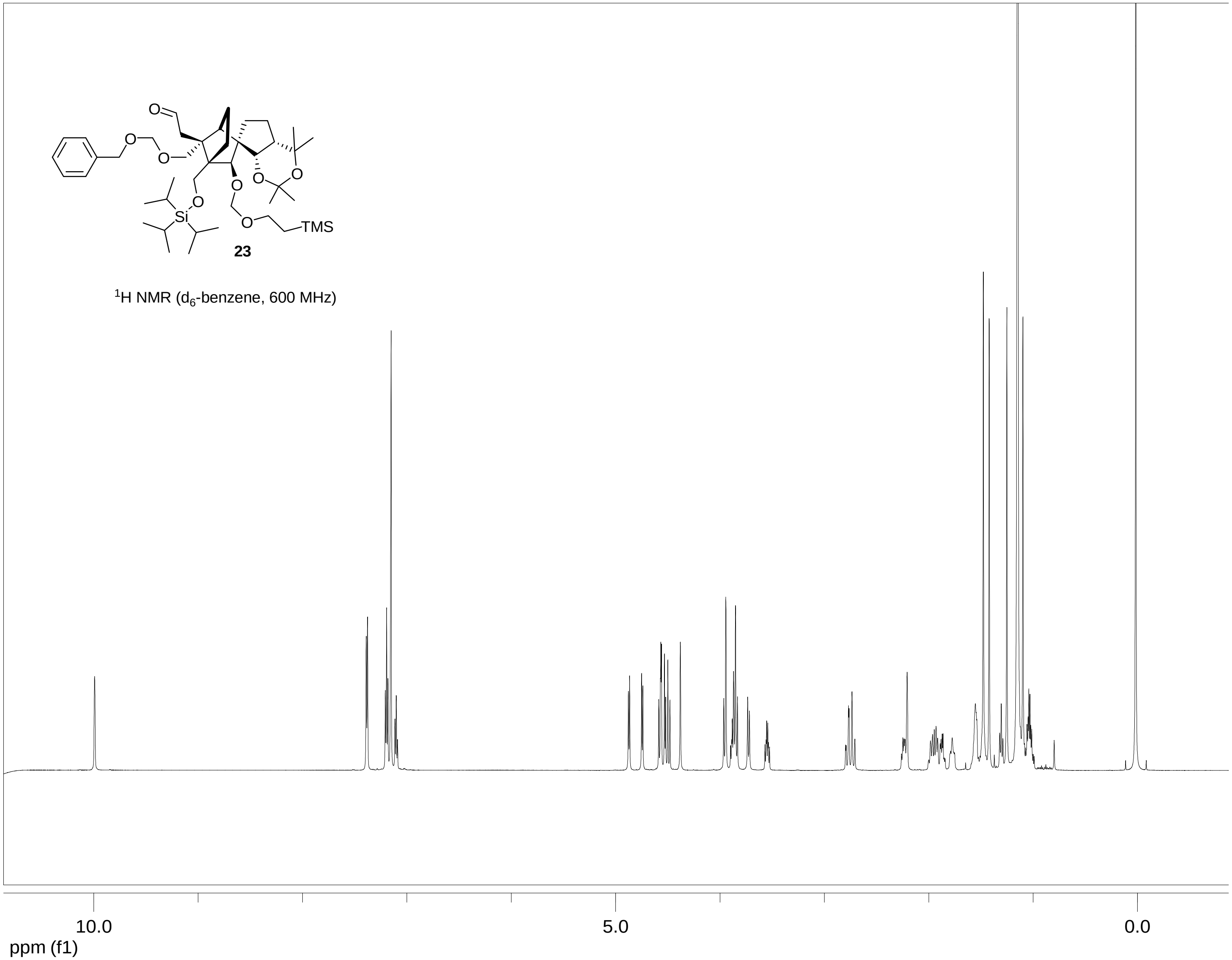
22

^{1}H NMR (d_6-benzene, 600 MHz)

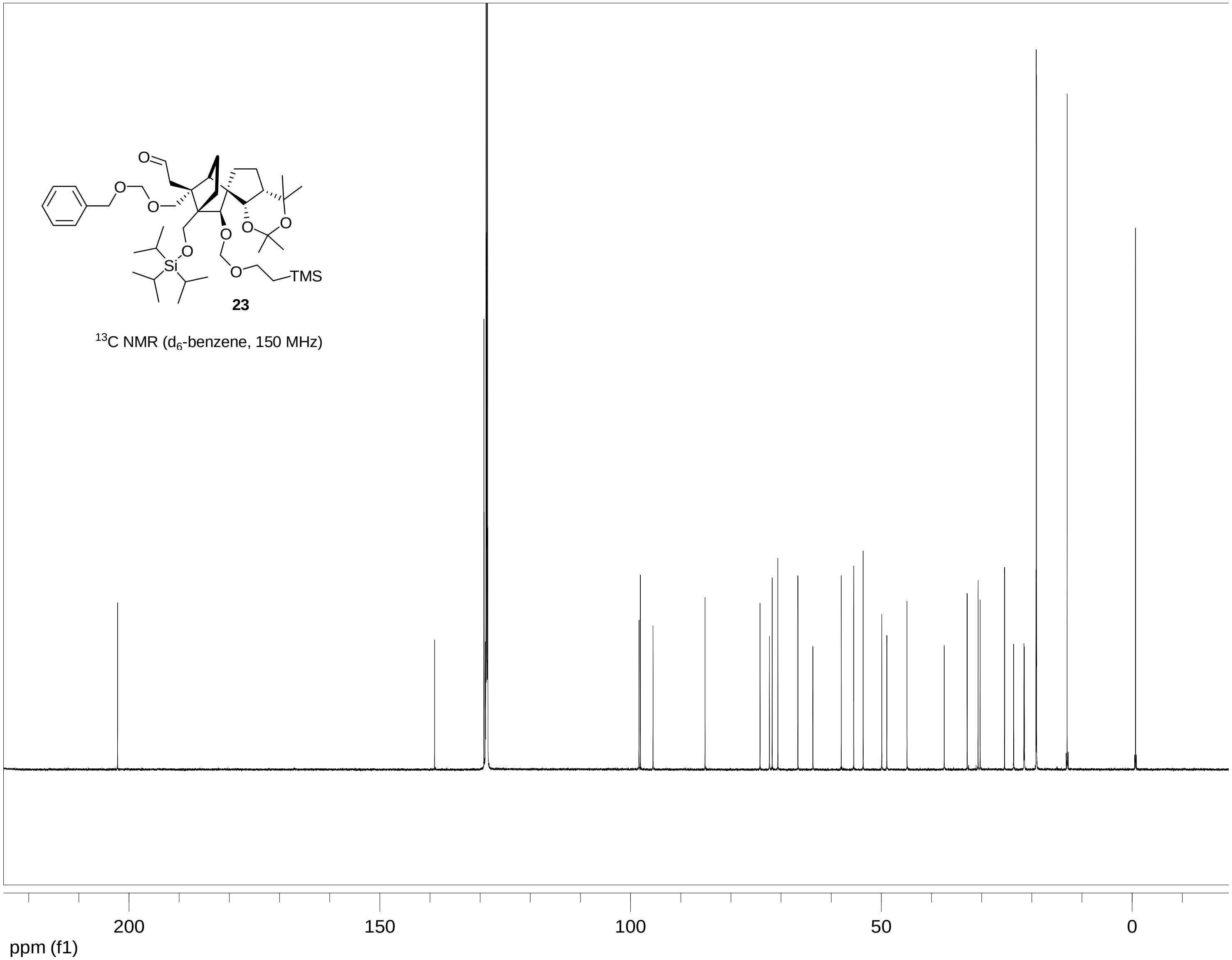


22

^{13}C NMR (d$_6$-benzene, 150 MHz)

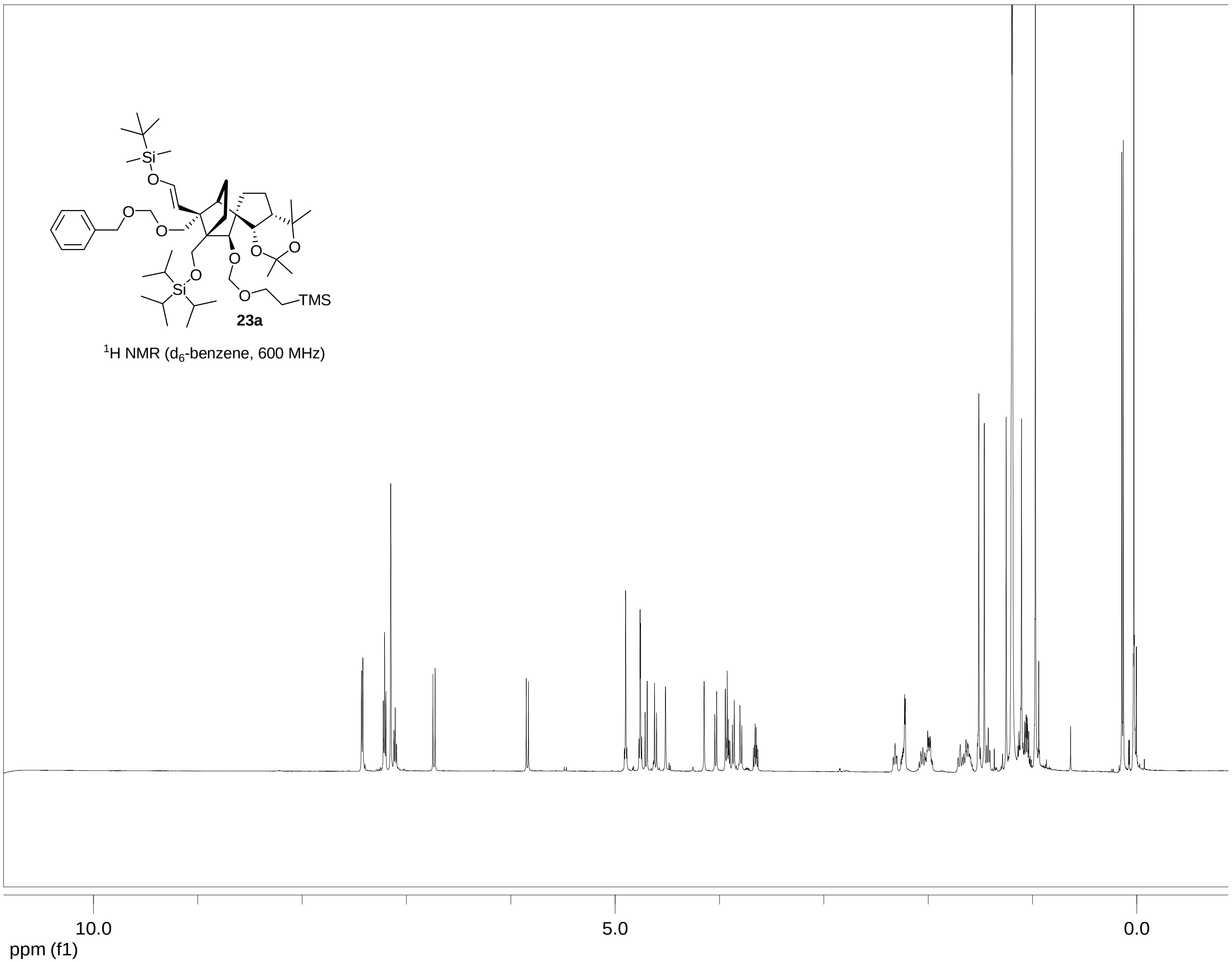

23

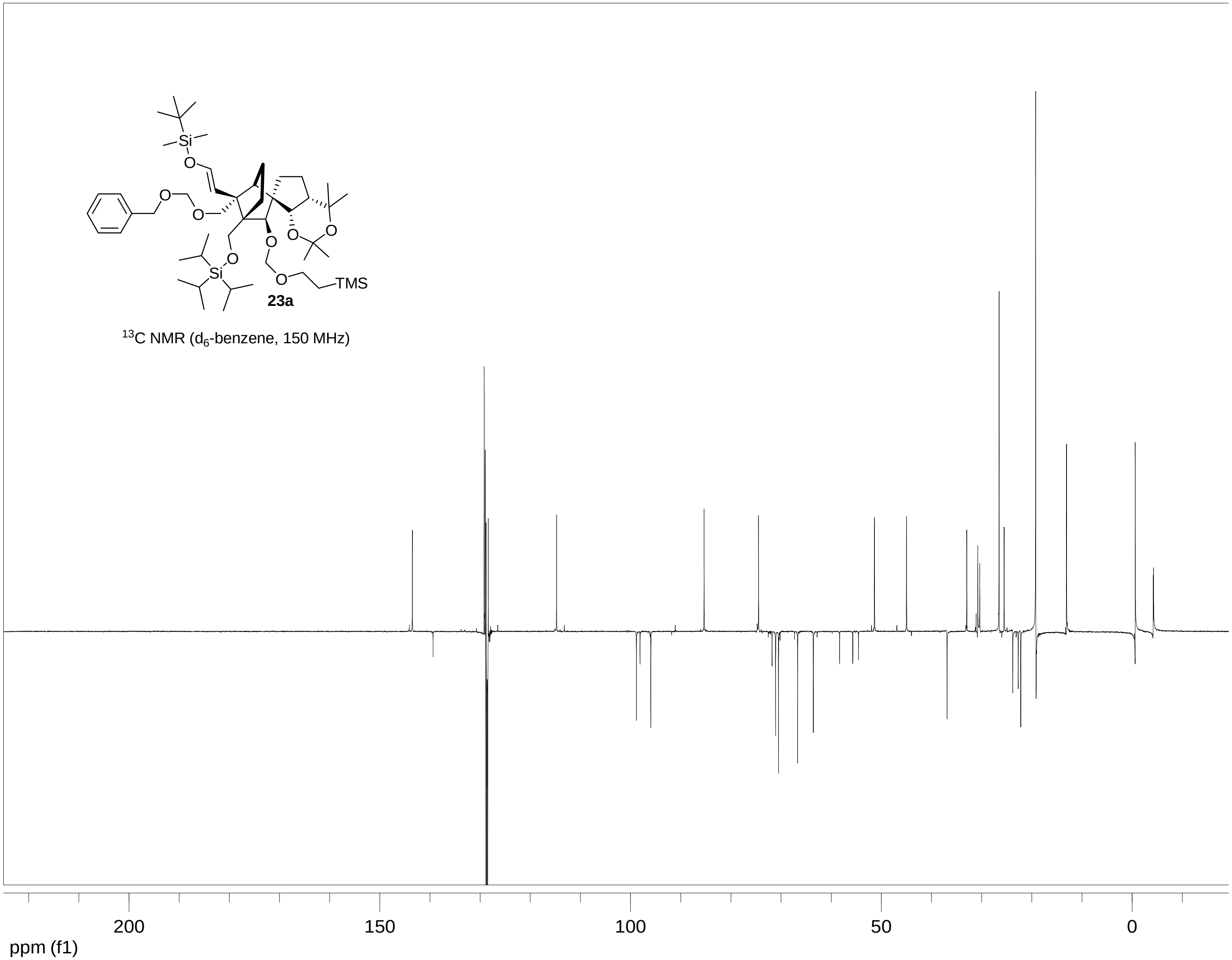
^{1}H NMR (d$_6$-benzene, 600 MHz)



23

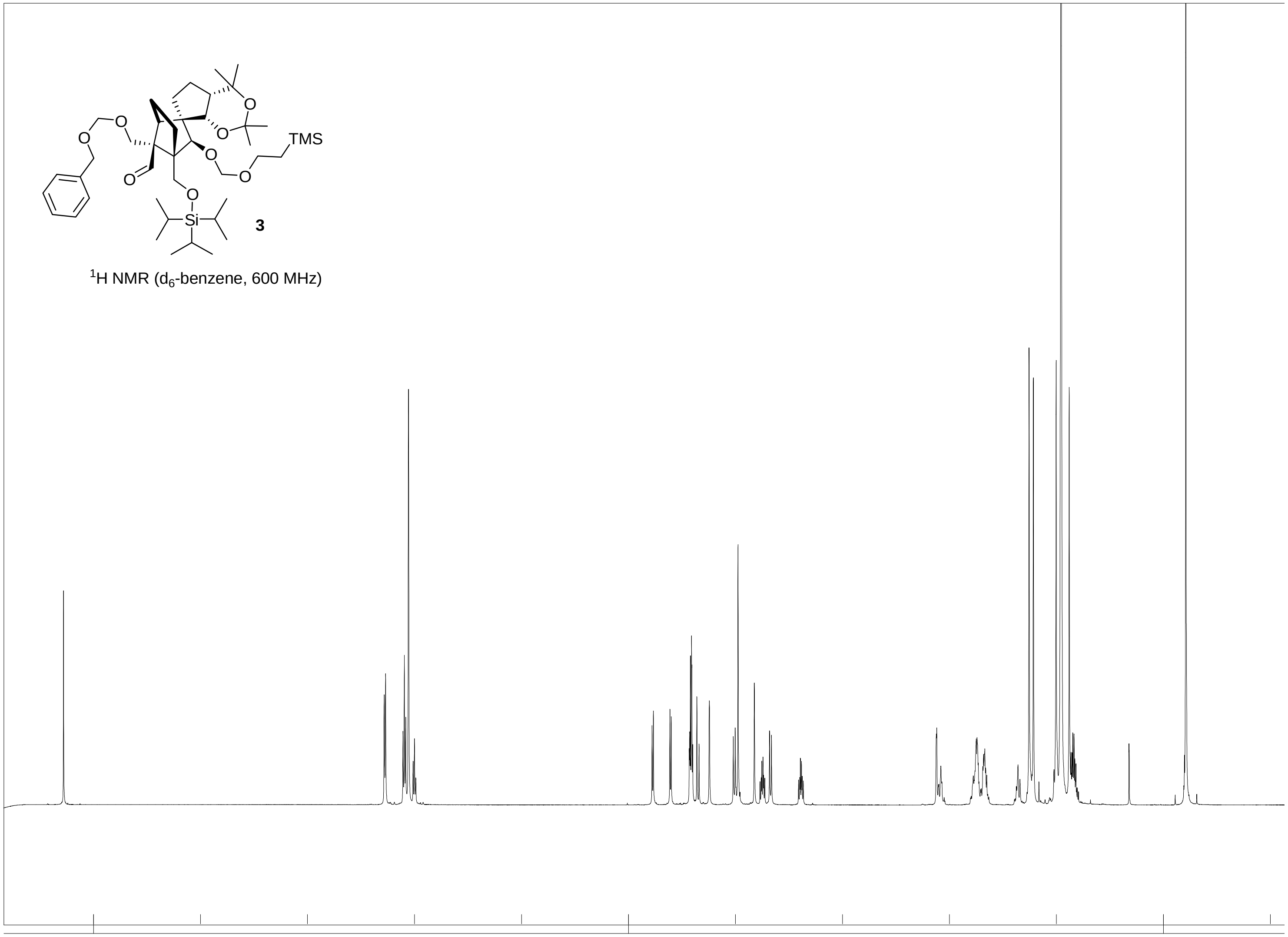
^{13}C NMR (d_6-benzene, 150 MHz)


TMS
23a
^{1}H NMR (d$_6$-benzene, 600 MHz)
10.0
5.0
0.0
ppm (f1)



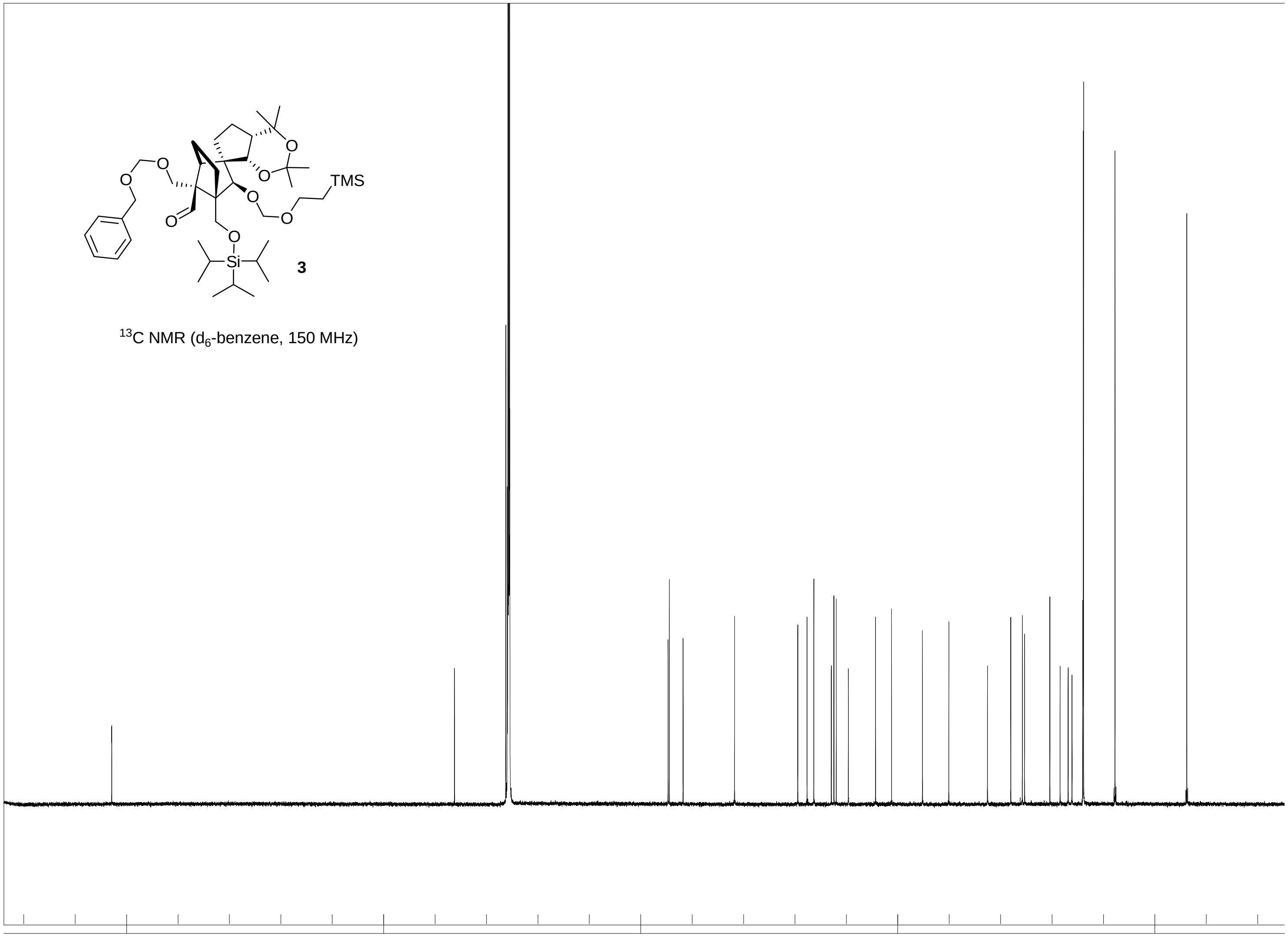
23a

^{13}C NMR (d$_6$-benzene, 150 MHz)



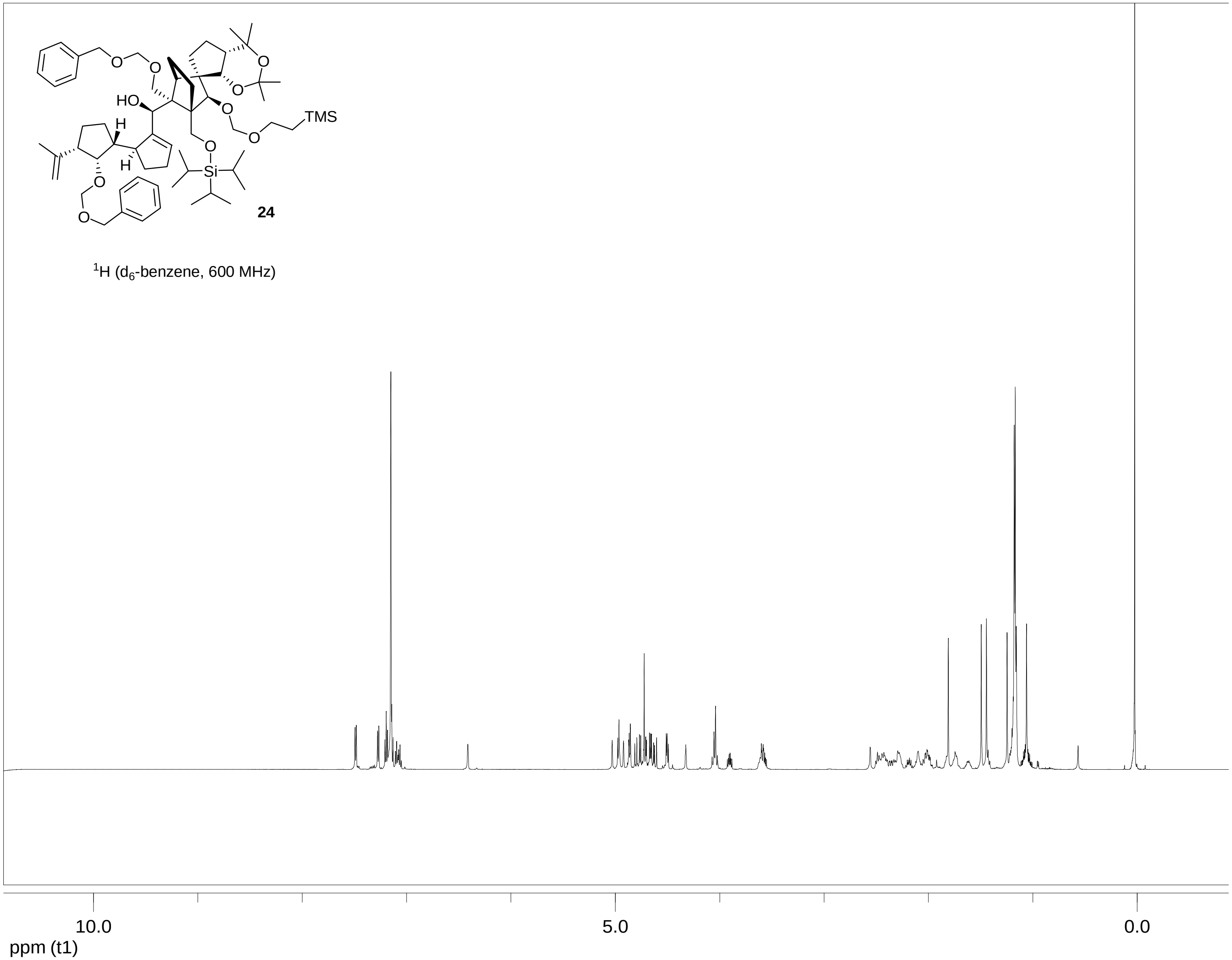
3

^{1}H NMR (d_6-benzene, 600 MHz)



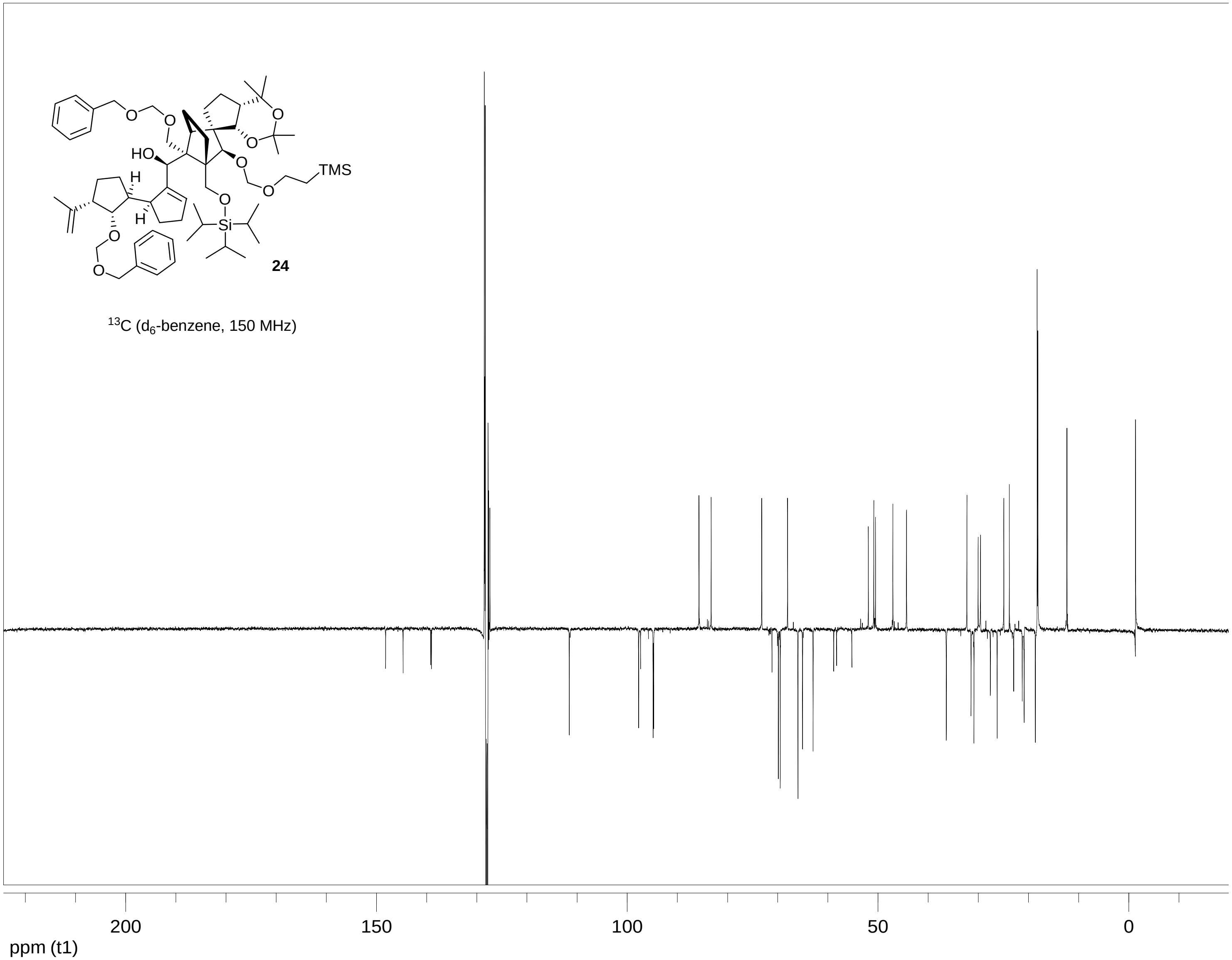
3

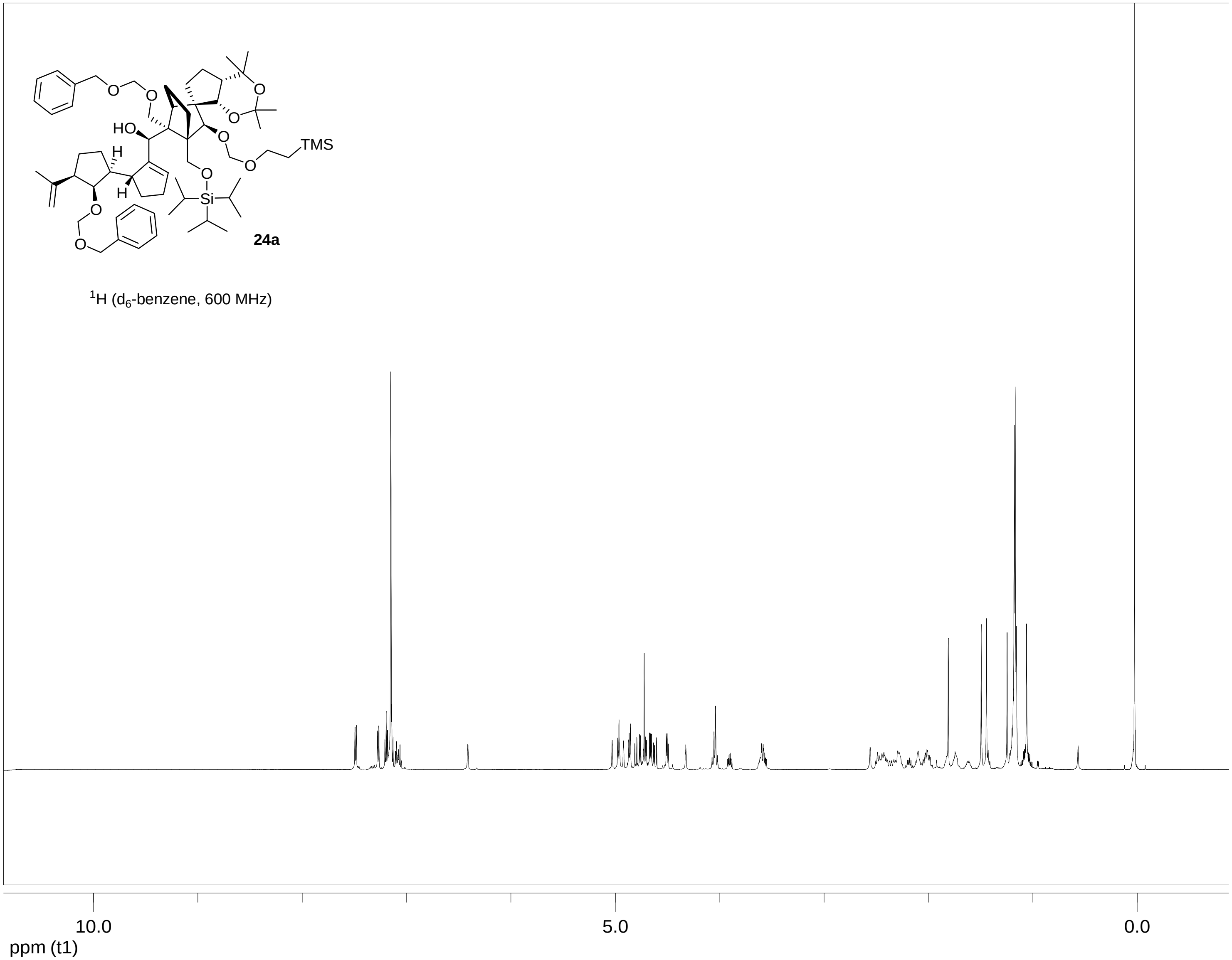
^{13}C NMR (d$_6$-benzene, 150 MHz)

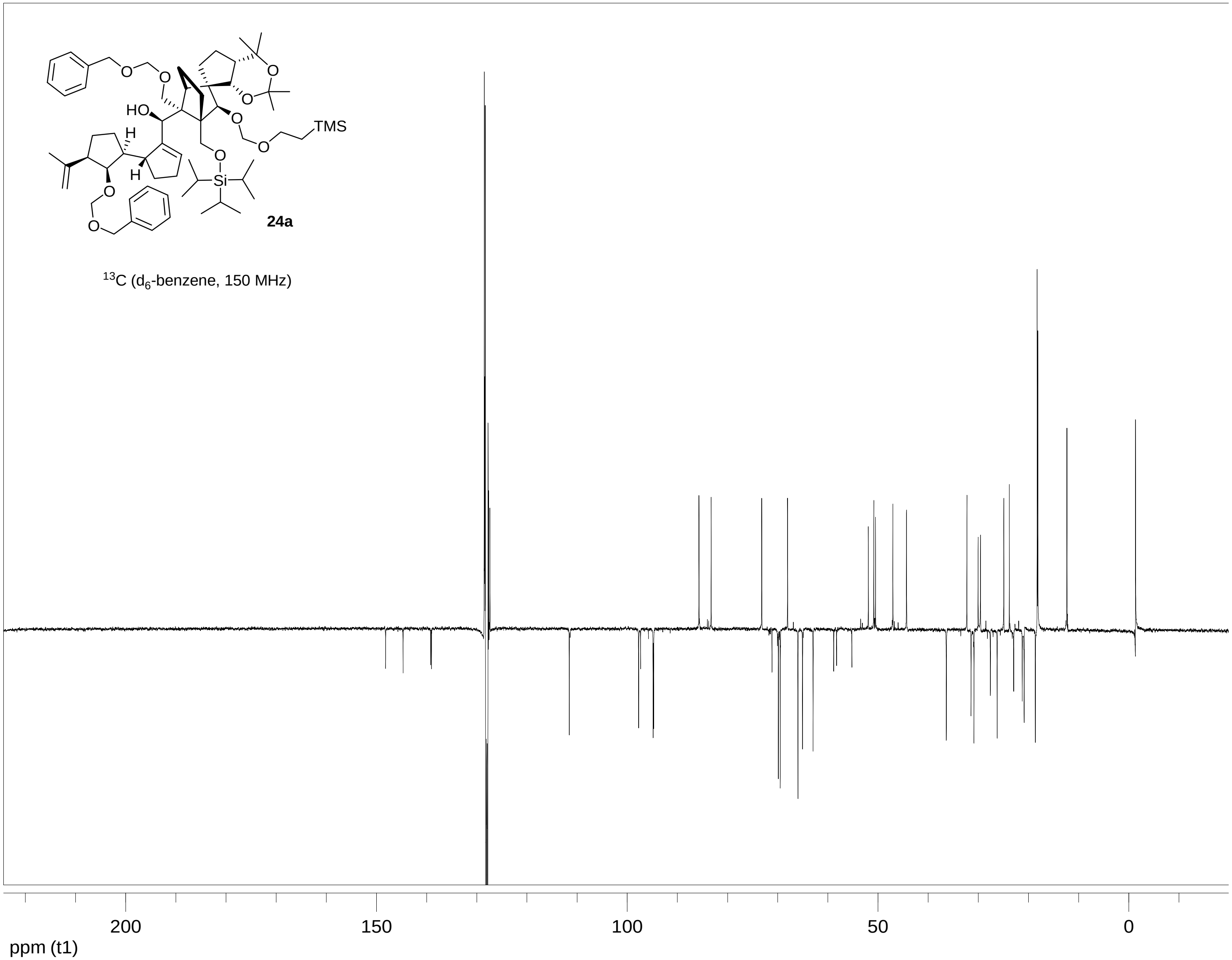


24

^{1}H (d$_6$-benzene, 600 MHz)

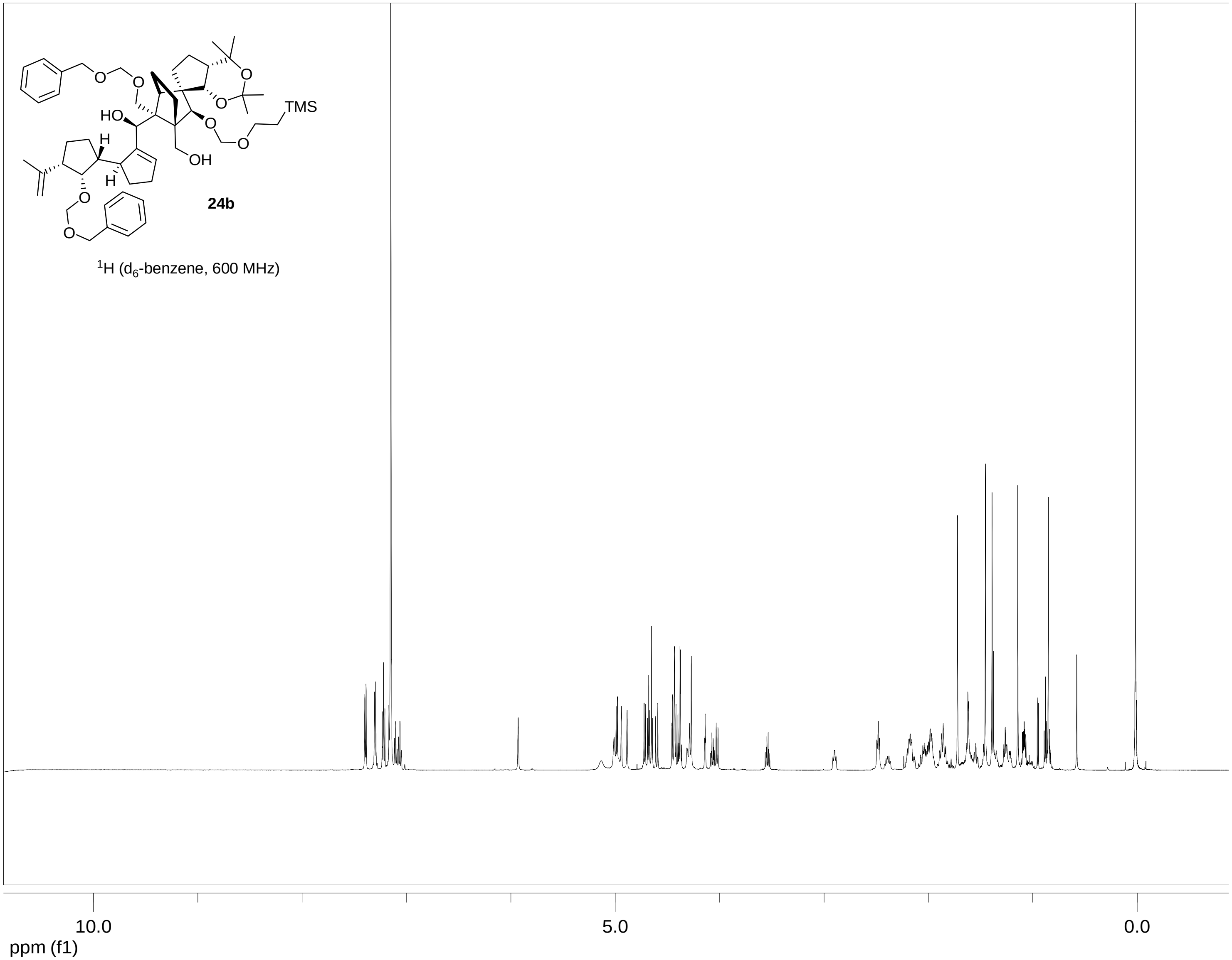

HO
H
H
O
O
O
O
O
O
O
O
Si
TMS
24
^{13}C (d$_6$-benzene, 150 MHz)
200
150
100
50
0
ppm (t1)

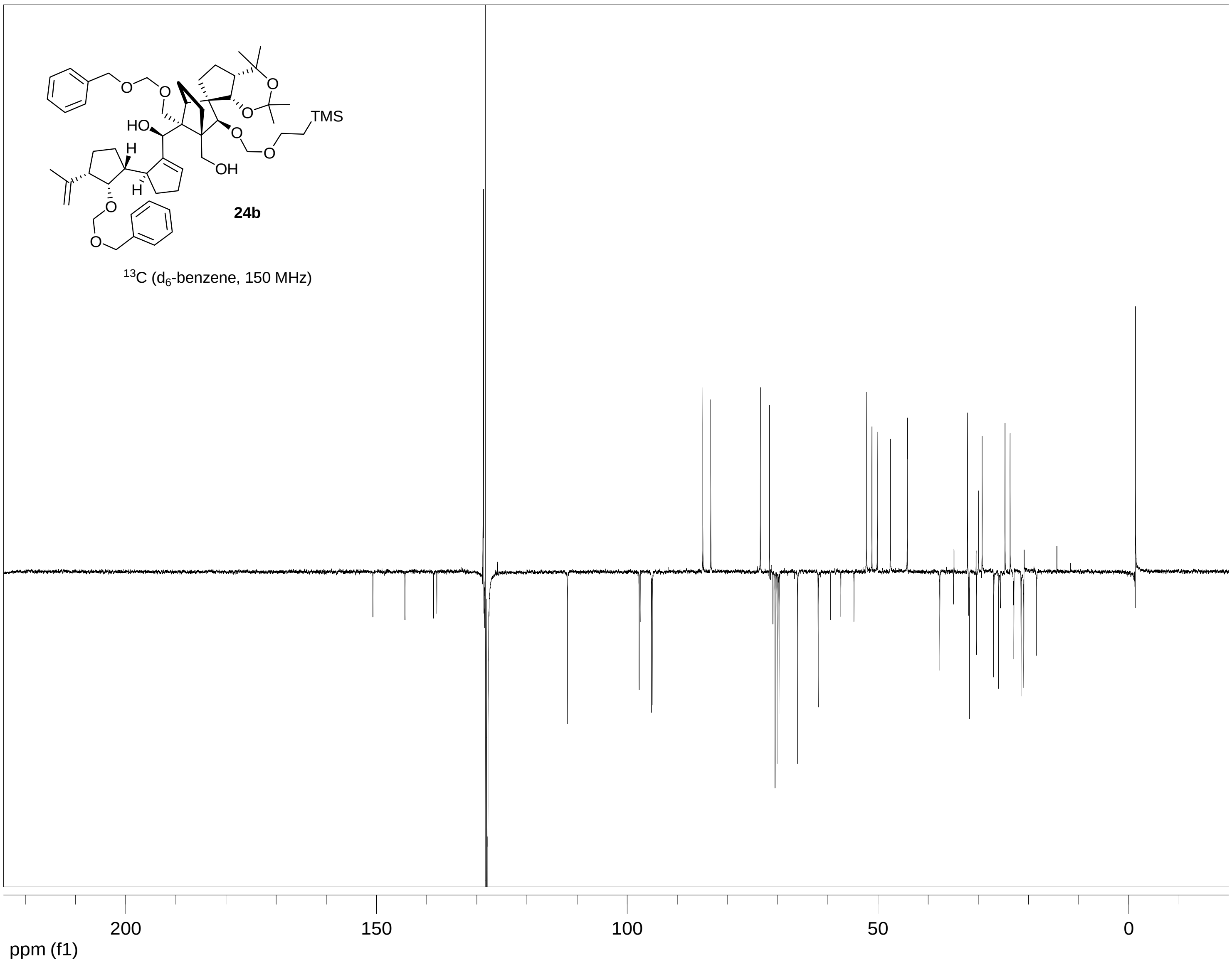

HO
H
H
O
TMS
Si
24a
^{1}H (d$_6$-benzene, 600 MHz)
10.0
5.0
0.0
ppm (t1)



24a

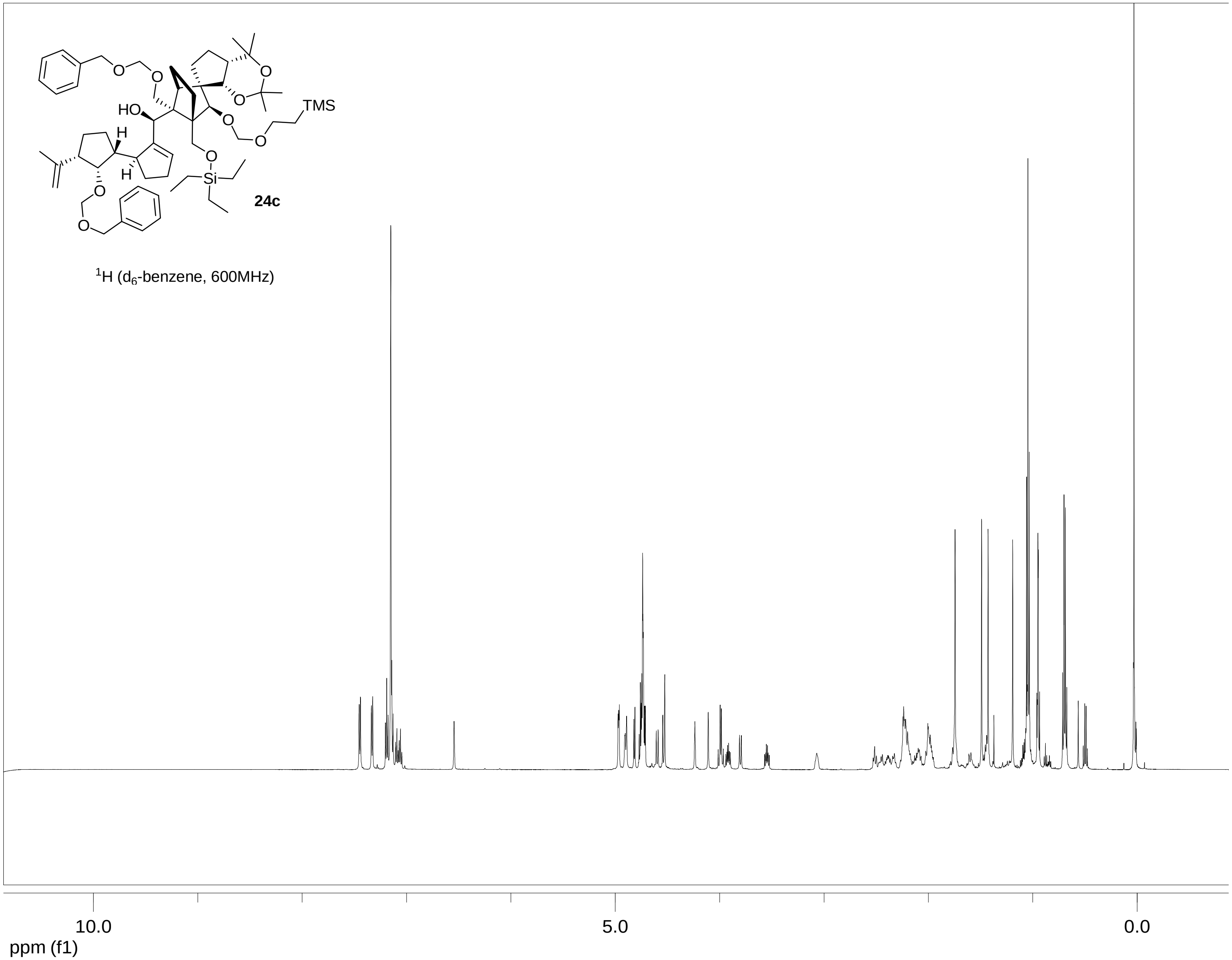
^{13}C (d$_6$-benzene, 150 MHz)


TMS
HO
OH
H
24b
^{1}H (d$_6$-benzene, 600 MHz)
10.0
5.0
0.0
ppm (f1)

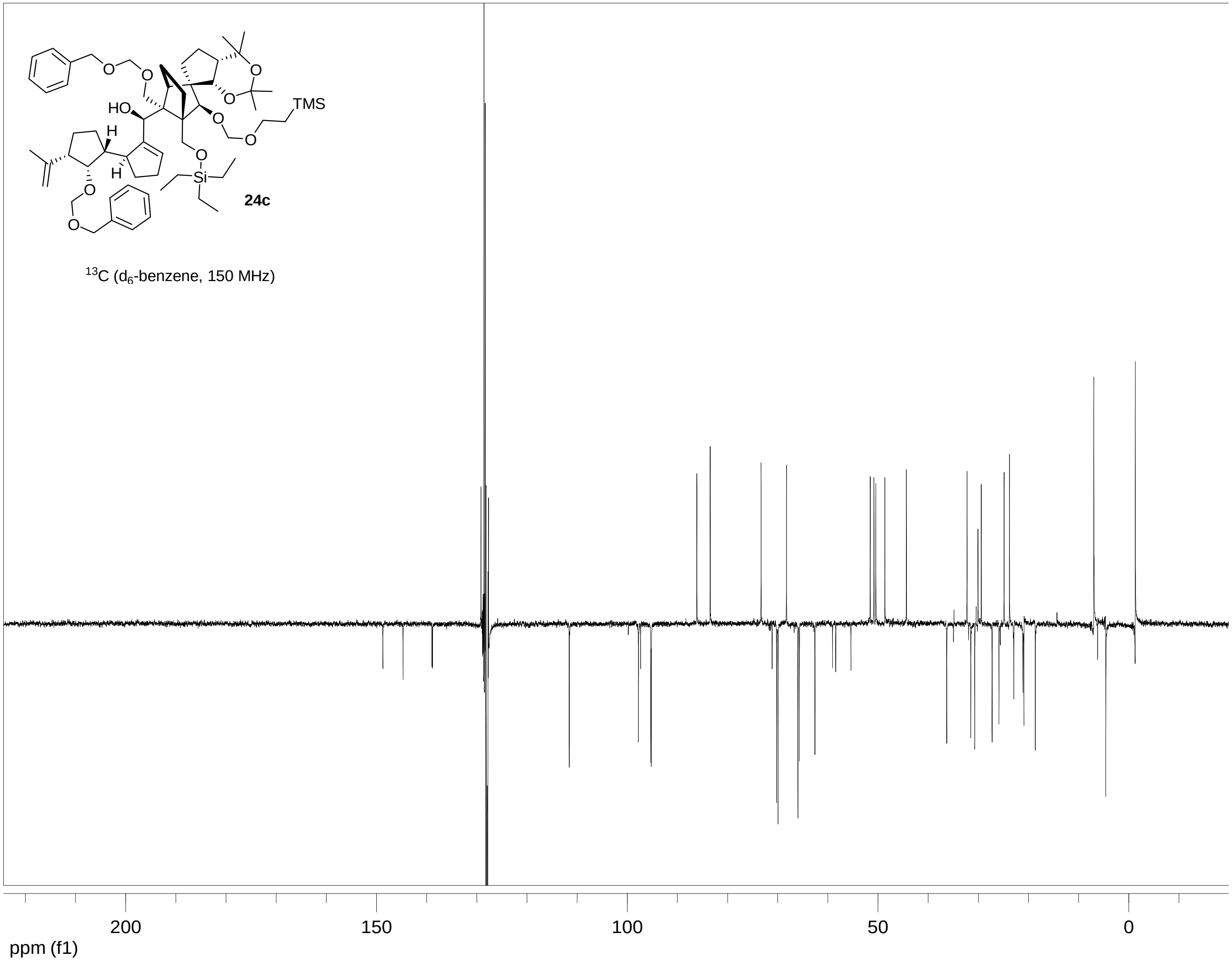


24b

^{13}C (d$_6$-benzene, 150 MHz)

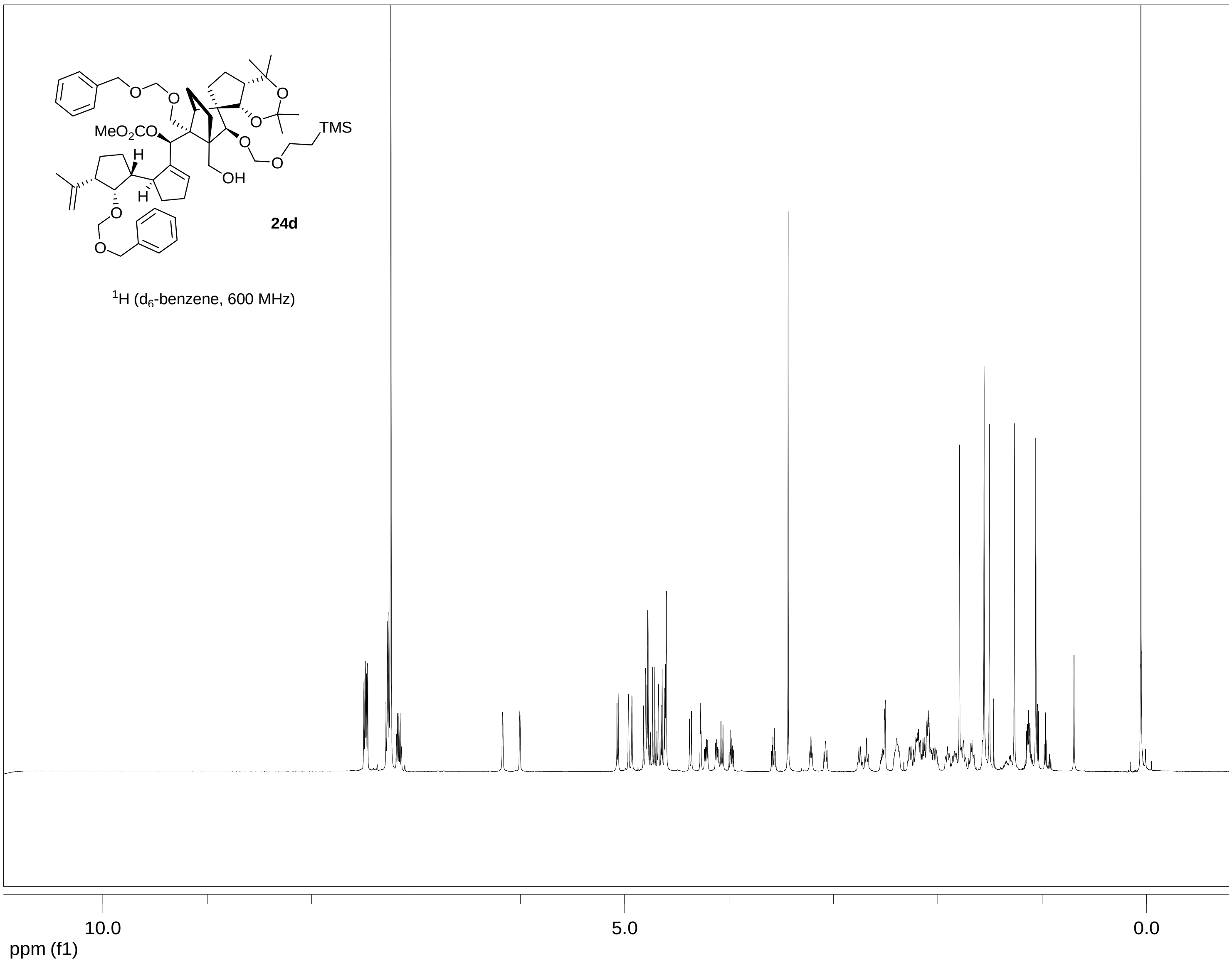


TMS
HO
H
H
O
Si
24c
^{1}H (d$_6$-benzene, 600MHz)
10.0
5.0
0.0
ppm (f1)



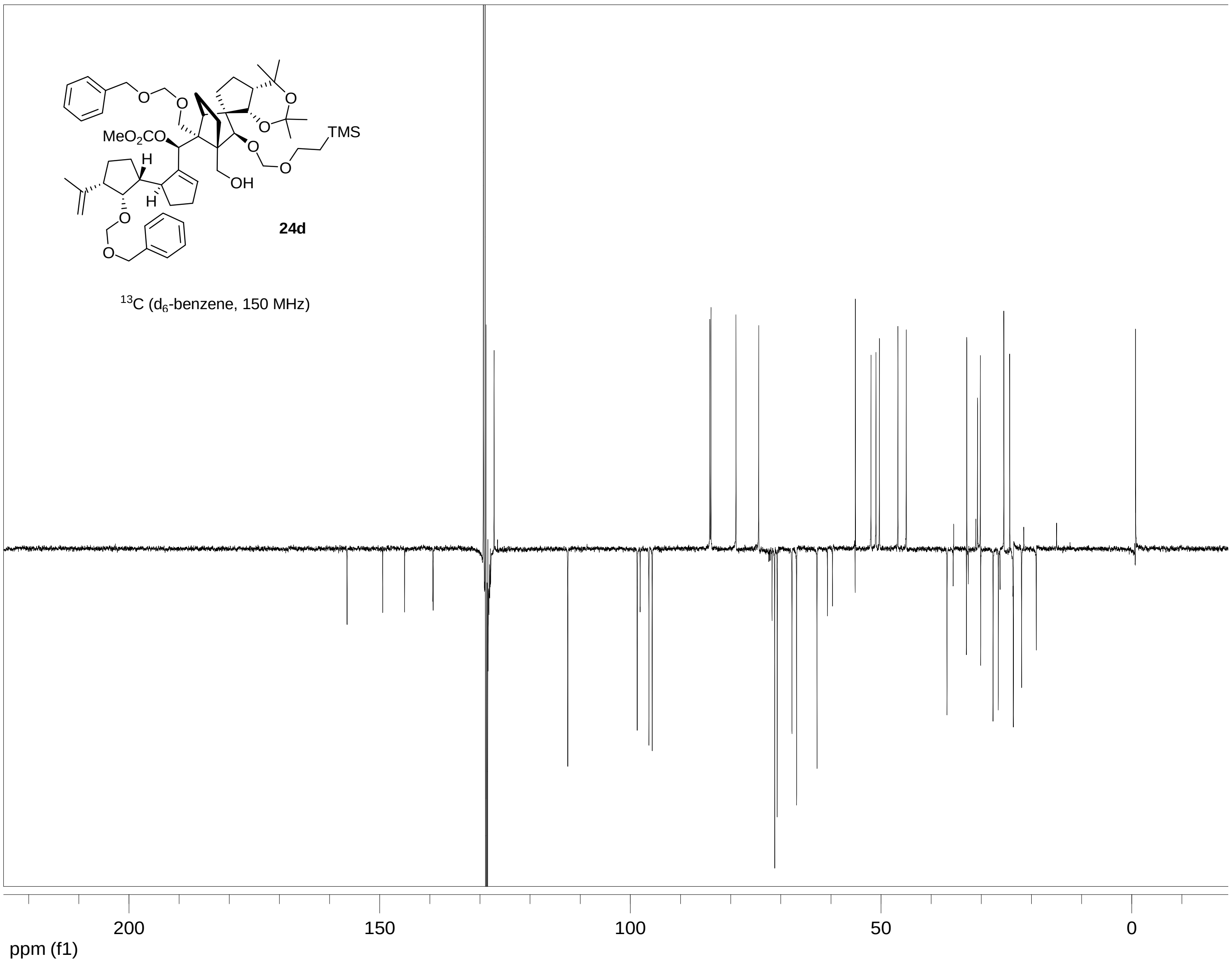
24c

^{13}C (d_6-benzene, 150 MHz)

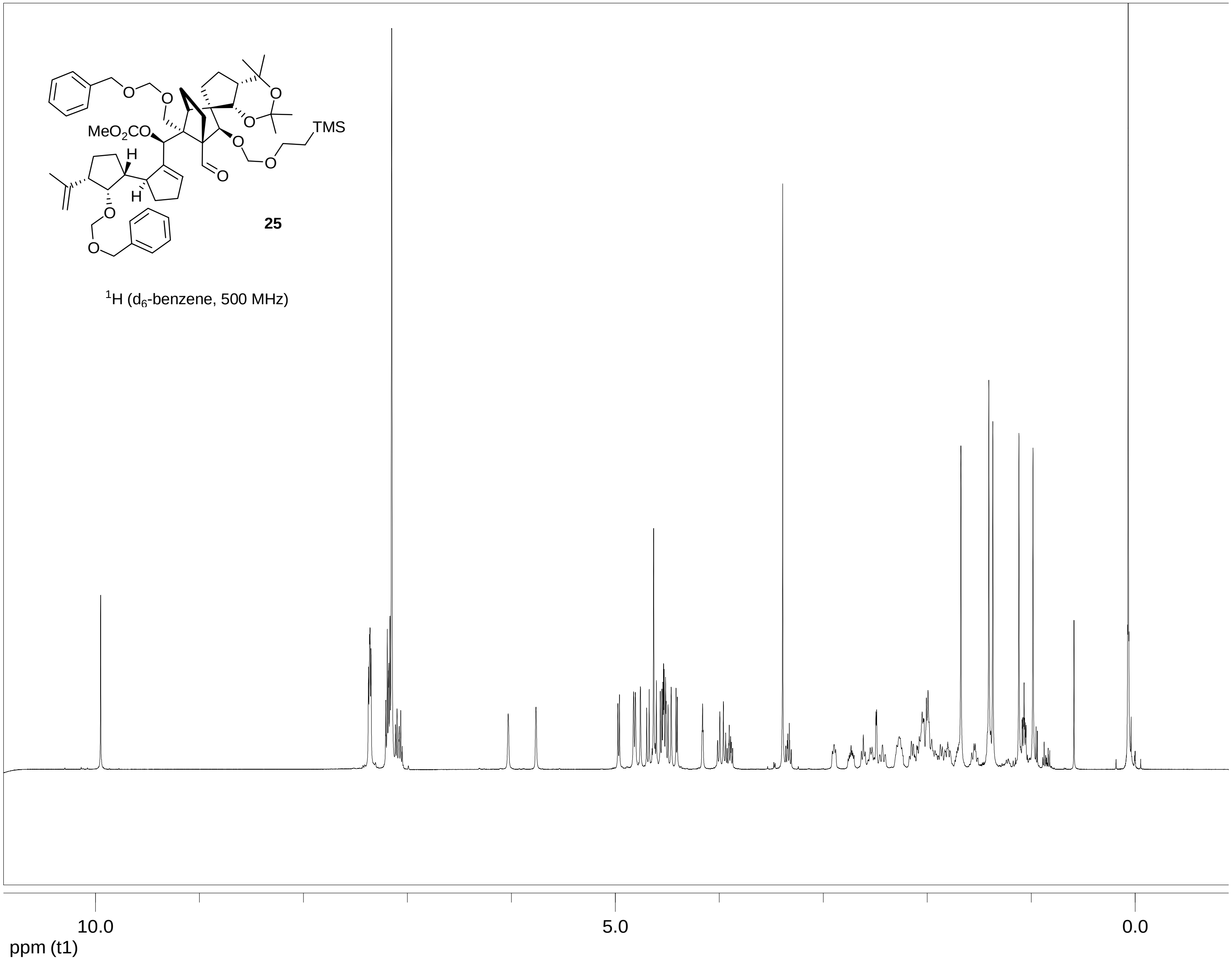


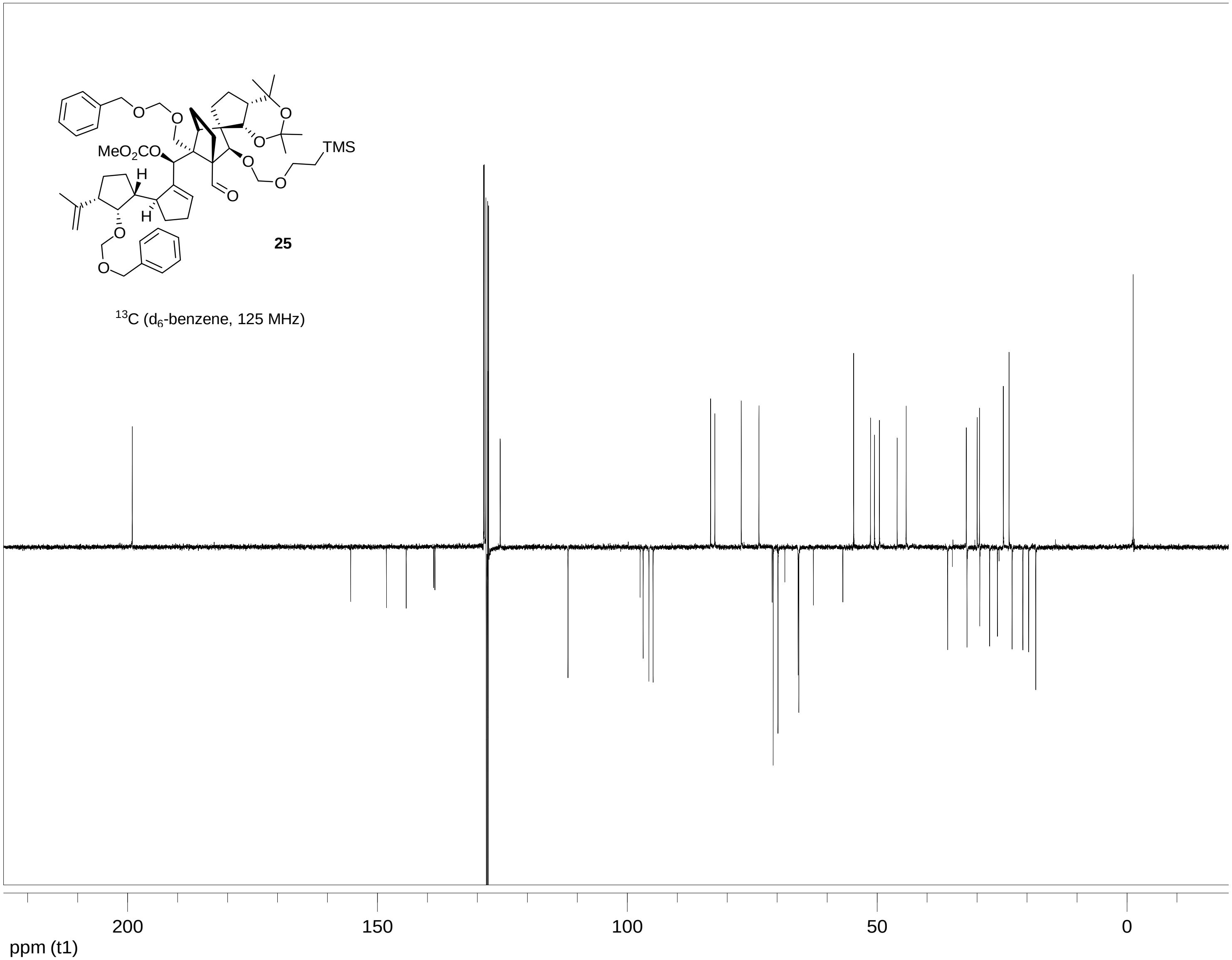
24d

^{1}H (d_6-benzene, 600 MHz)



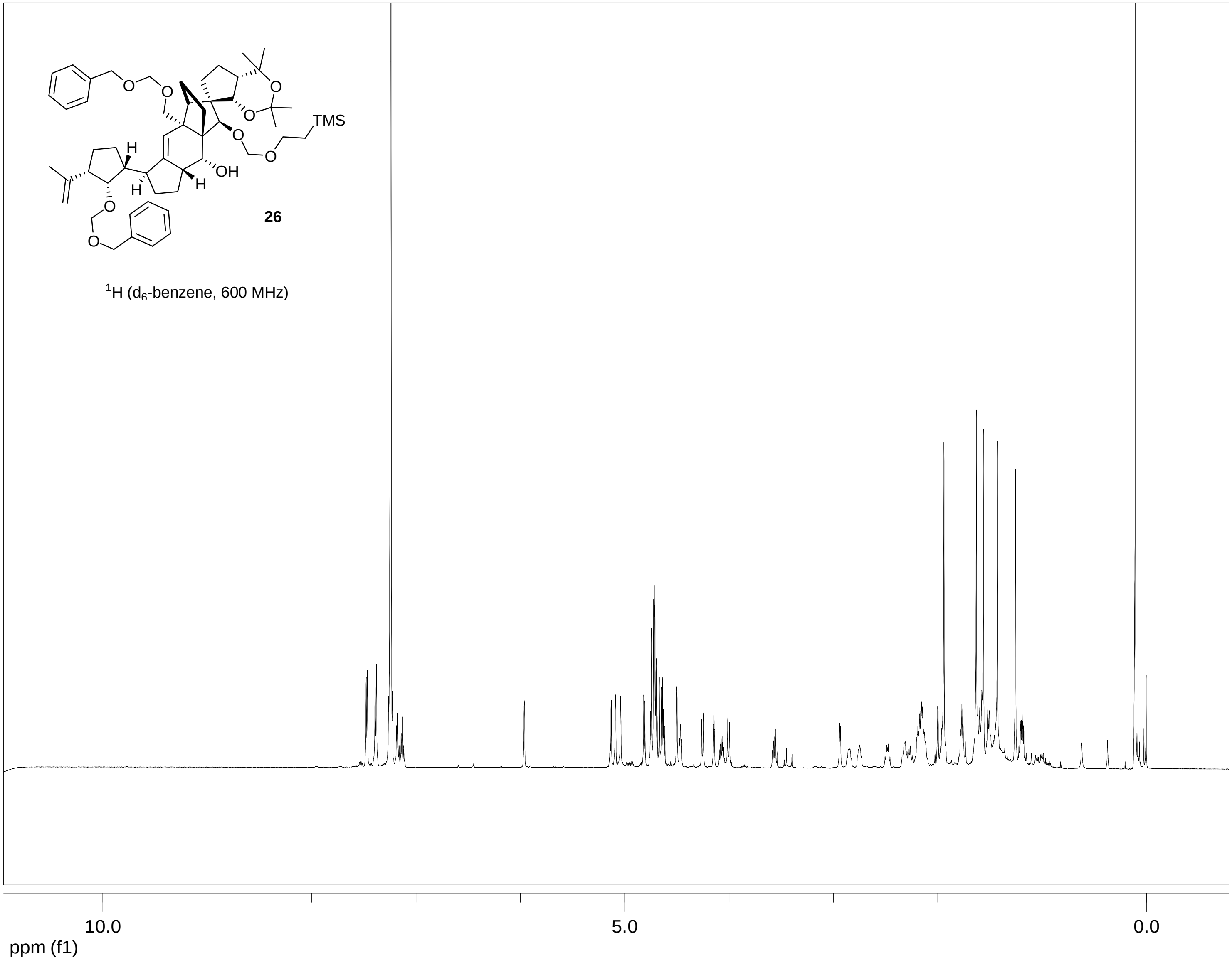
MeO$_2$CO
O
O
O
O
O
O
O
H
H
OH
TMS
24d
^{13}C (d$_6$-benzene, 150 MHz)
200
150
100
50
0
ppm (f1)


MeO$_2$CO
TMS
H
H
O
25
^{1}H (d$_6$-benzene, 500 MHz)
10.0
5.0
0.0
ppm (t1)



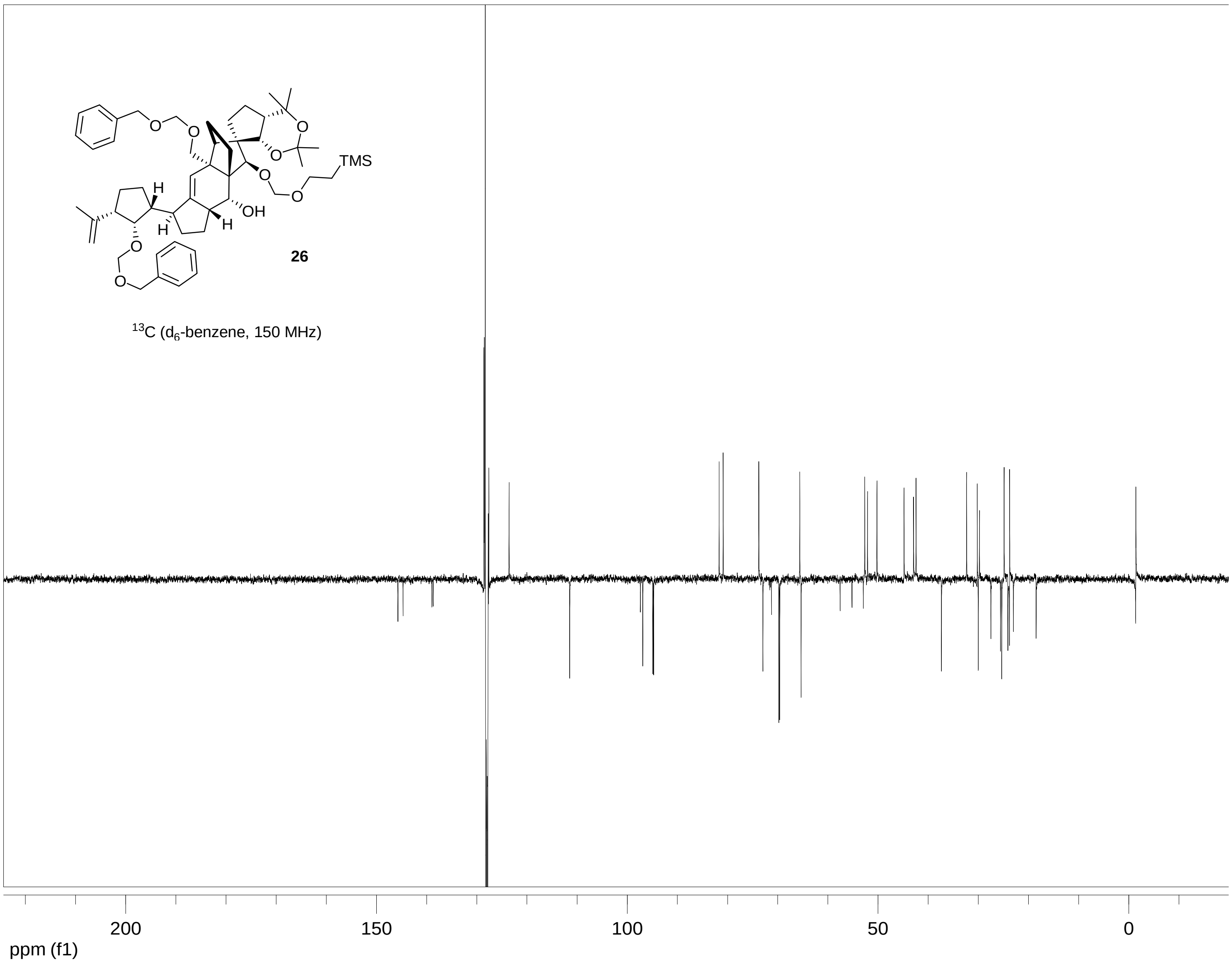
25

^{13}C (d$_6$-benzene, 125 MHz)



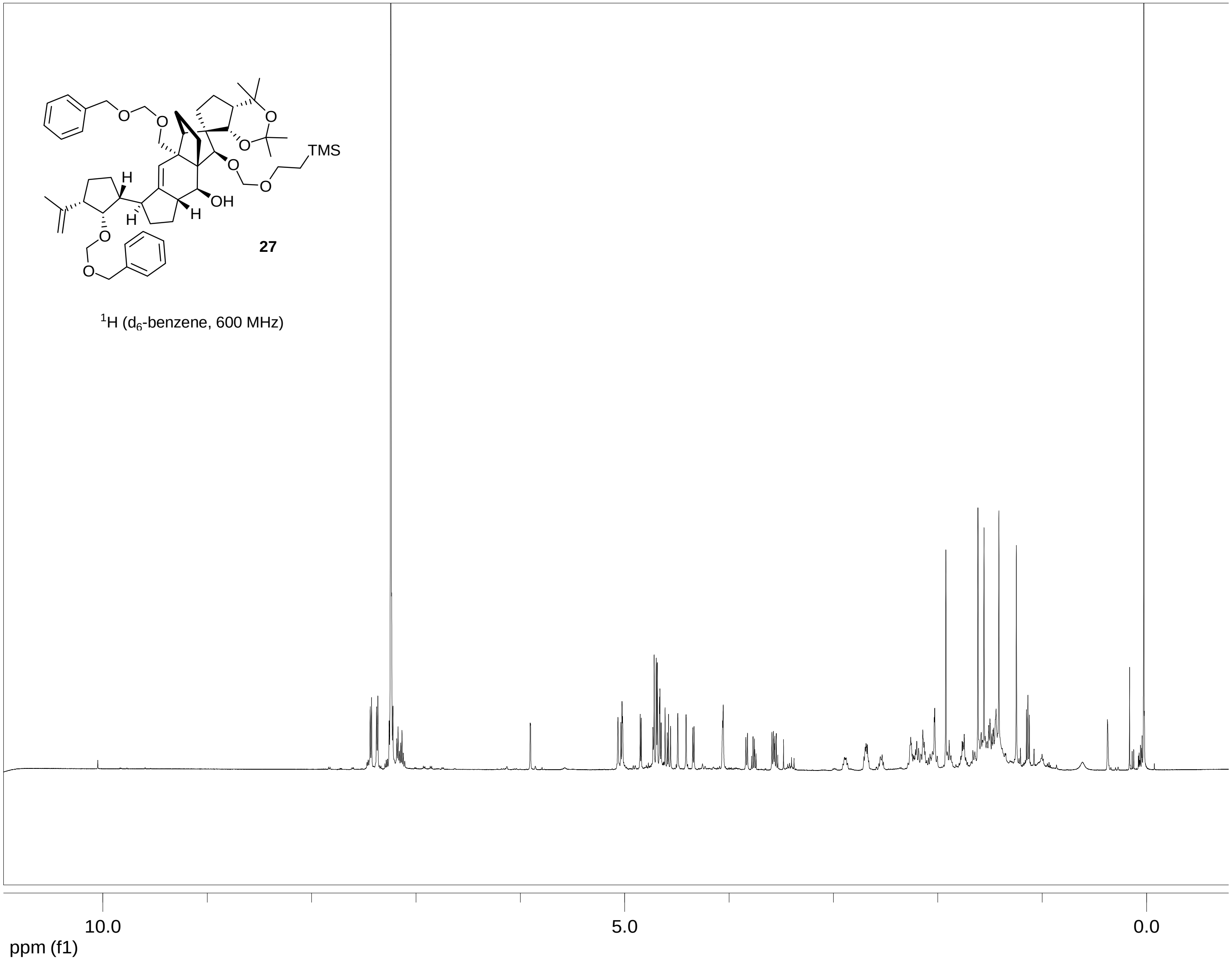
26

^{1}H (d$_6$-benzene, 600 MHz)



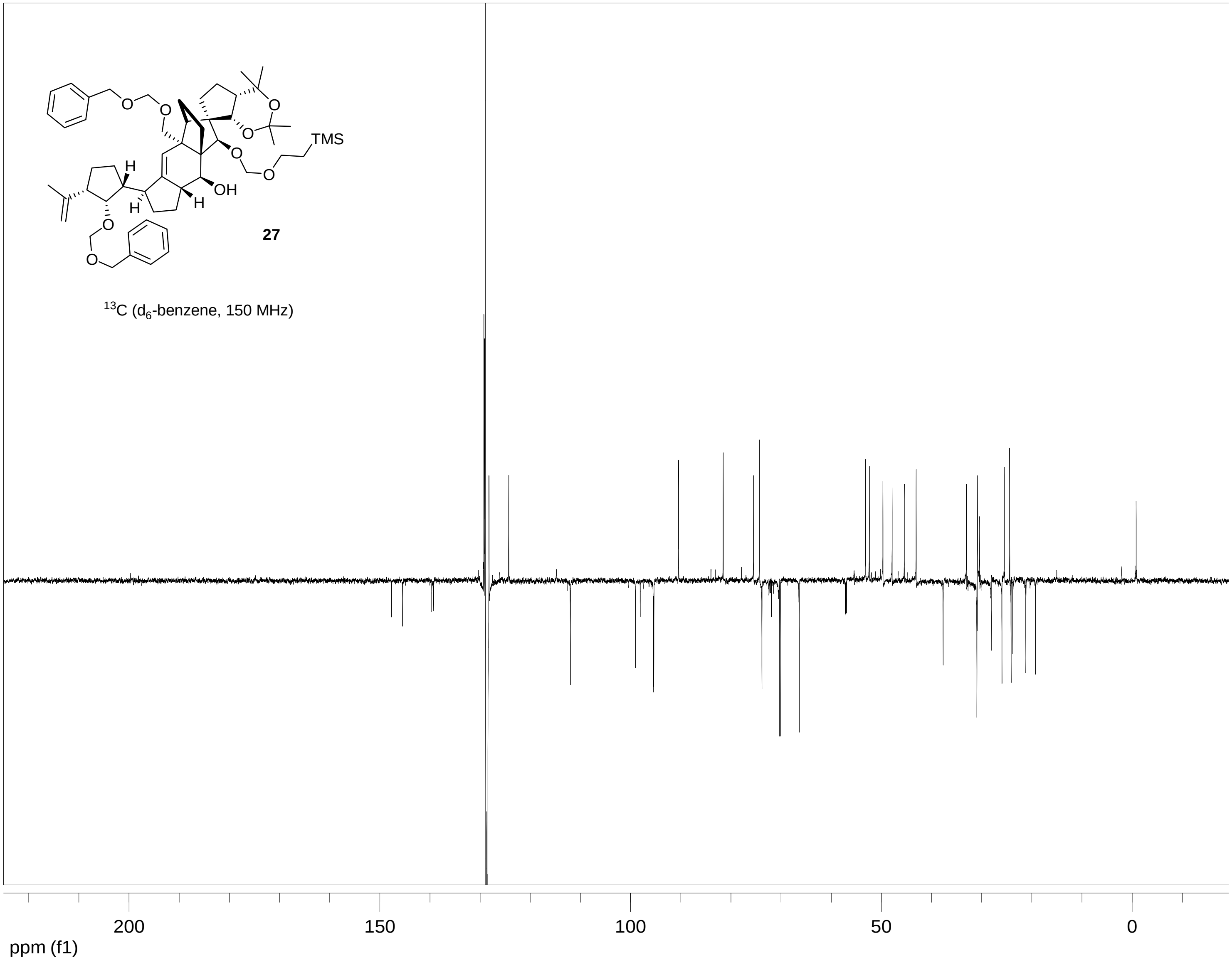
26

^{13}C (d_6-benzene, 150 MHz)



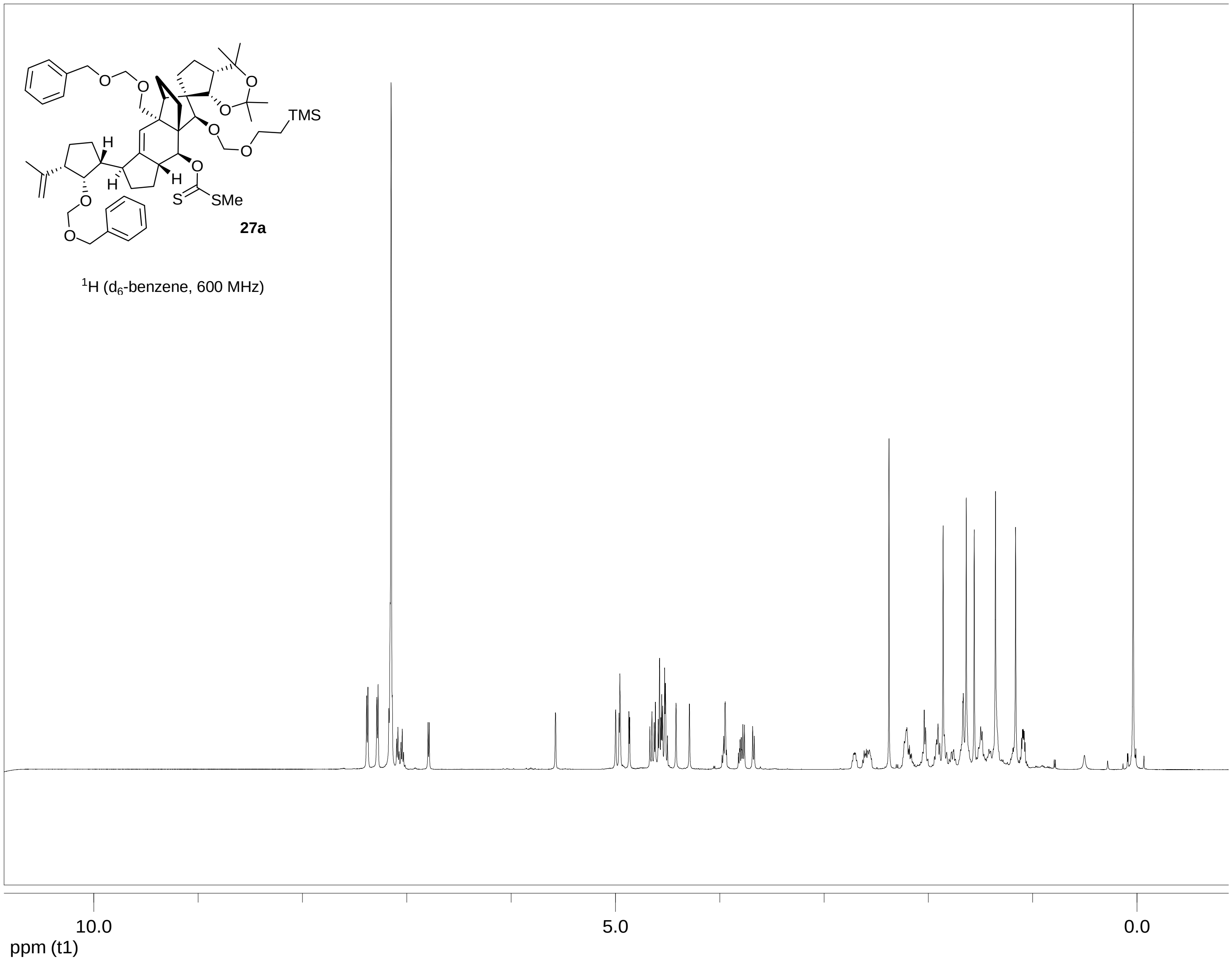
27

^{1}H (d_6-benzene, 600 MHz)

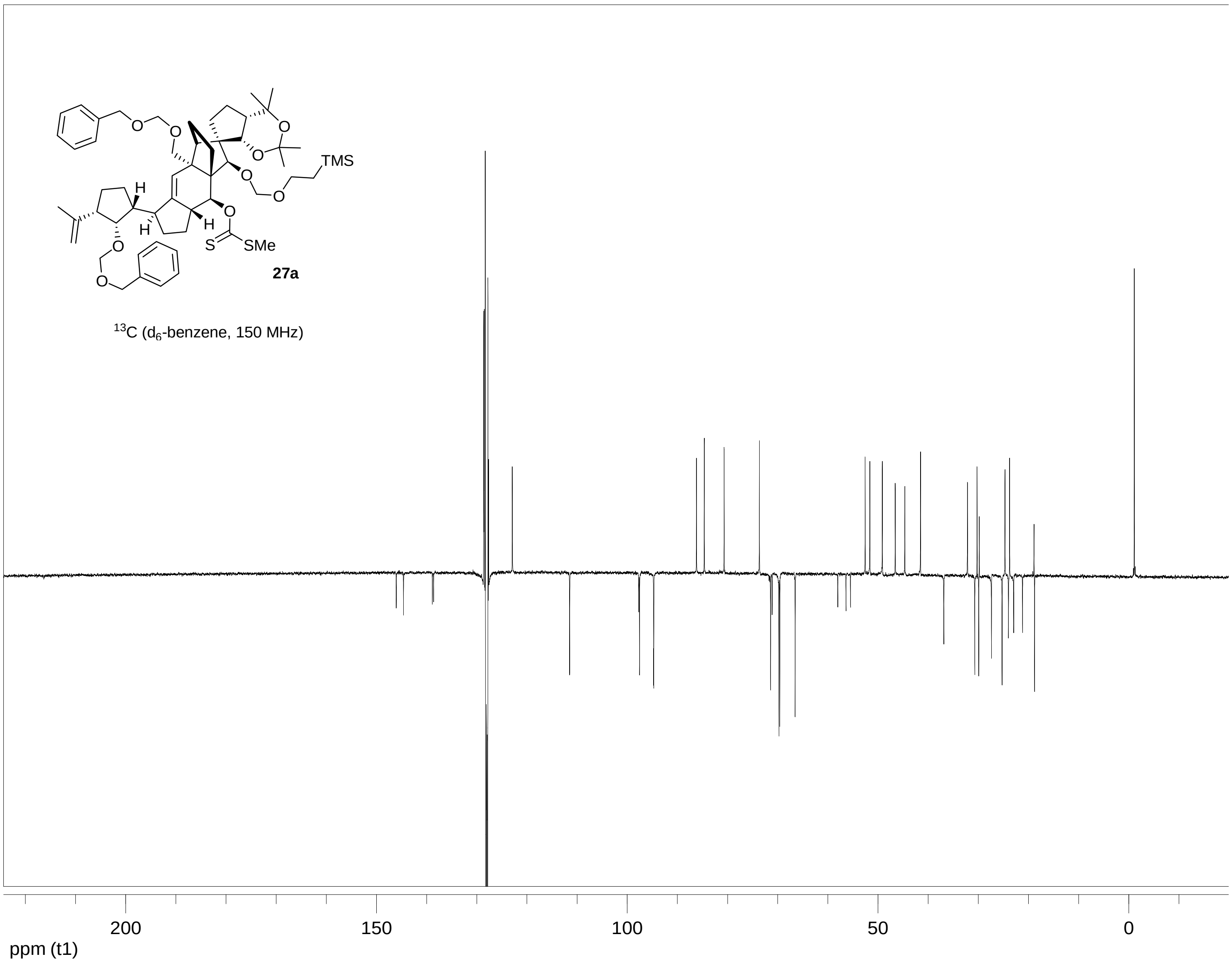


27

^{13}C (d$_6$-benzene, 150 MHz)

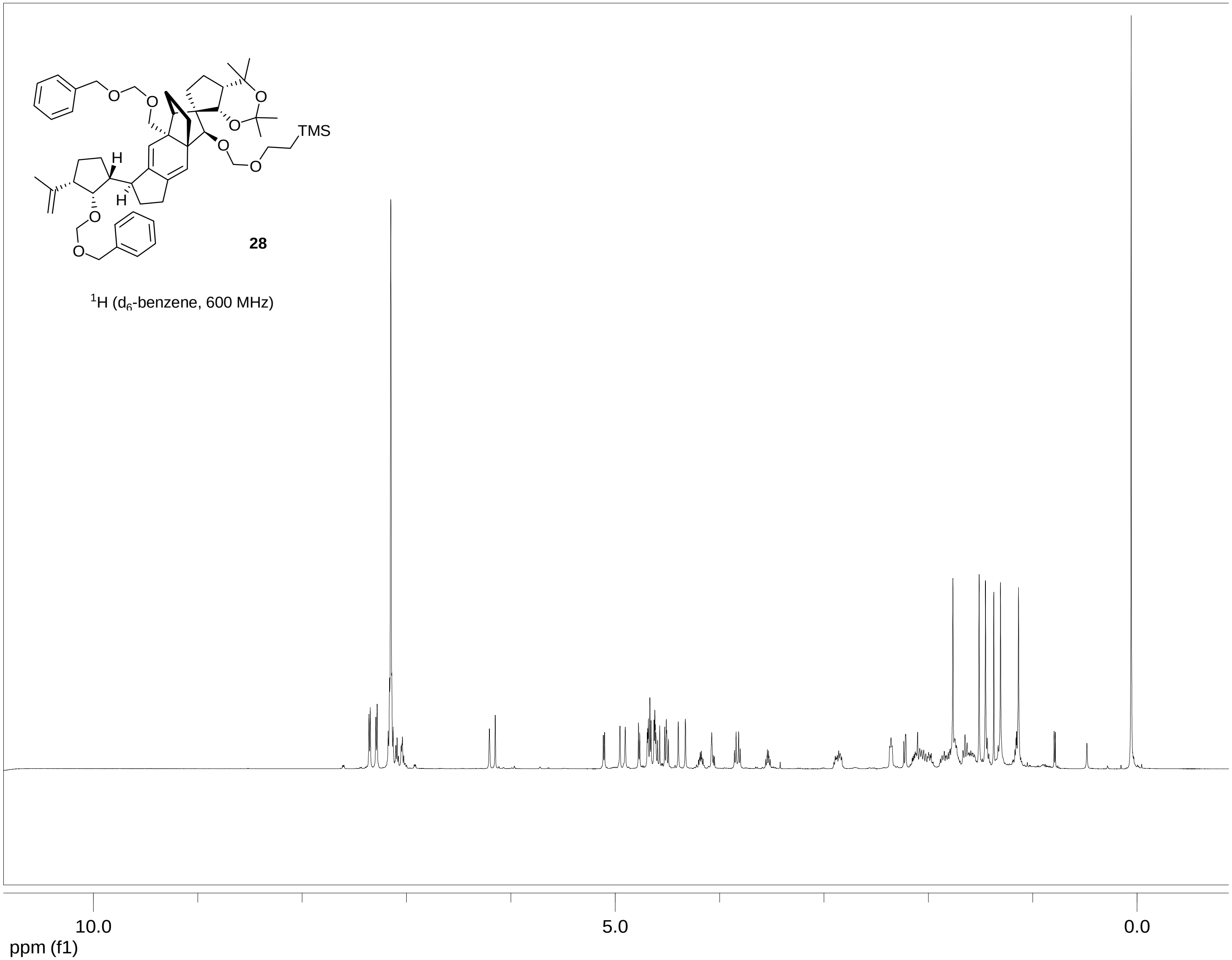


TMS
O
O
O
O
O
O
O
O
H
H
H
S
SMe
27a
¹H (d6-benzene, 600 MHz)
10.0
5.0
0.0
ppm (t1)



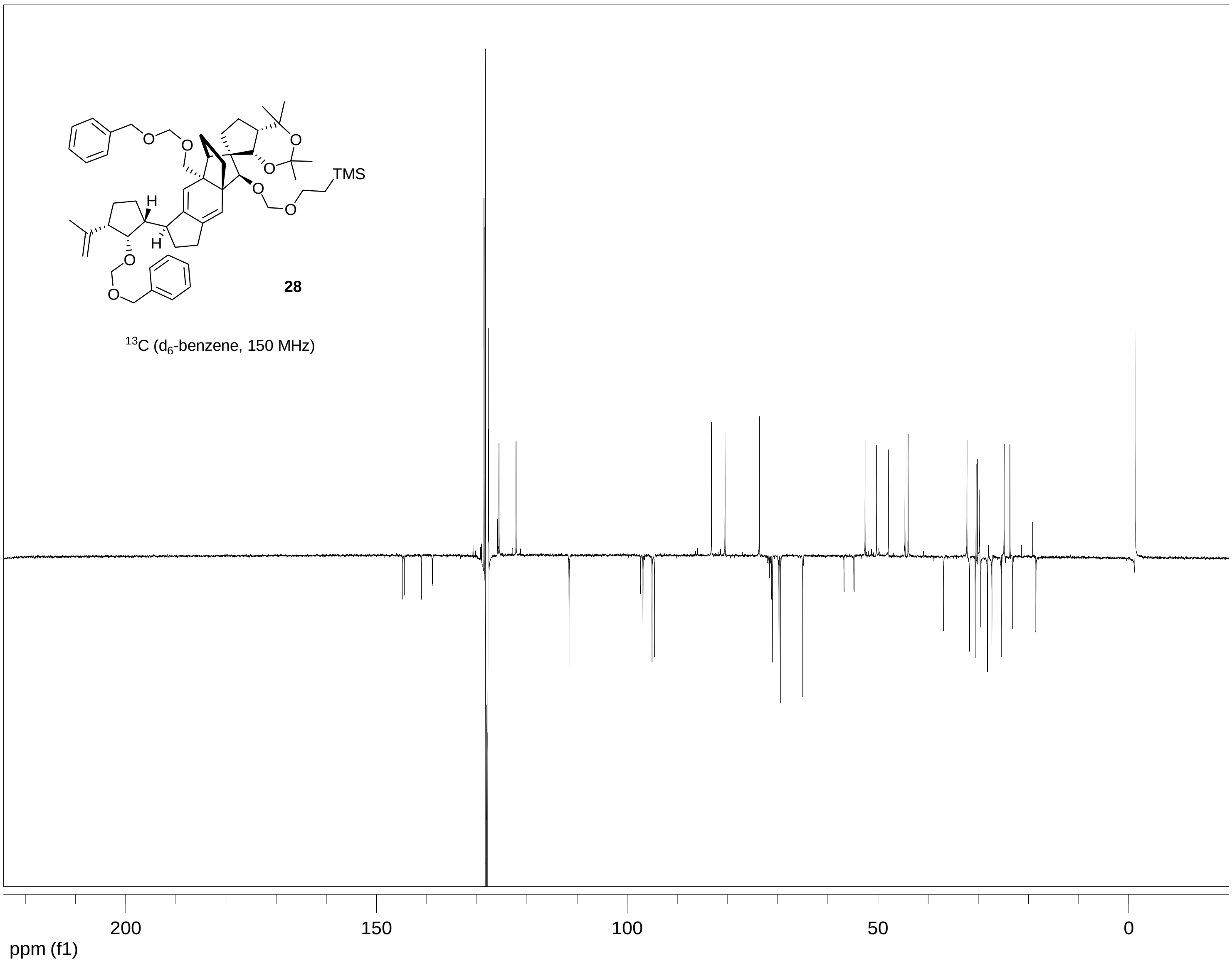
27a

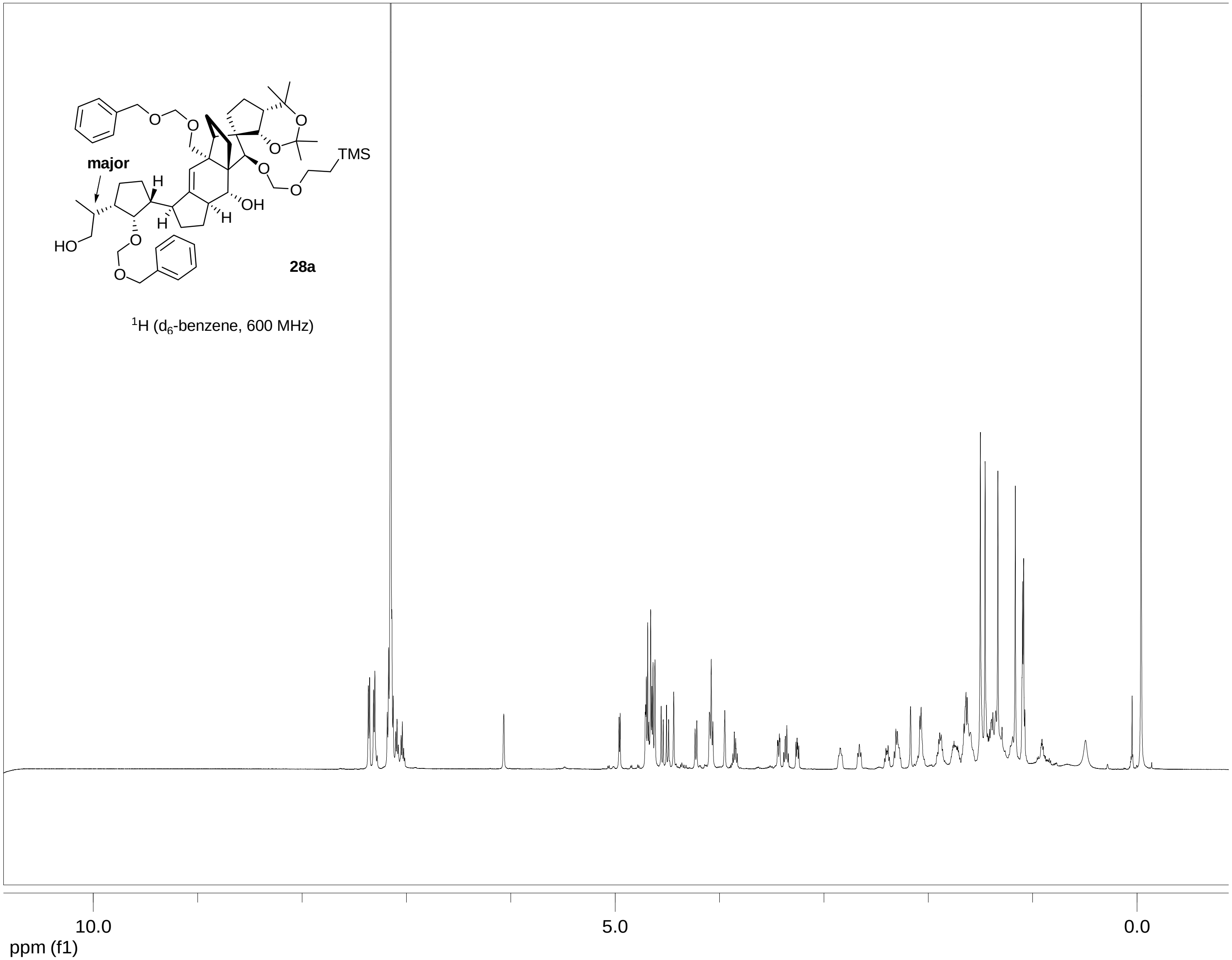
^{13}C (d$_6$-benzene, 150 MHz)



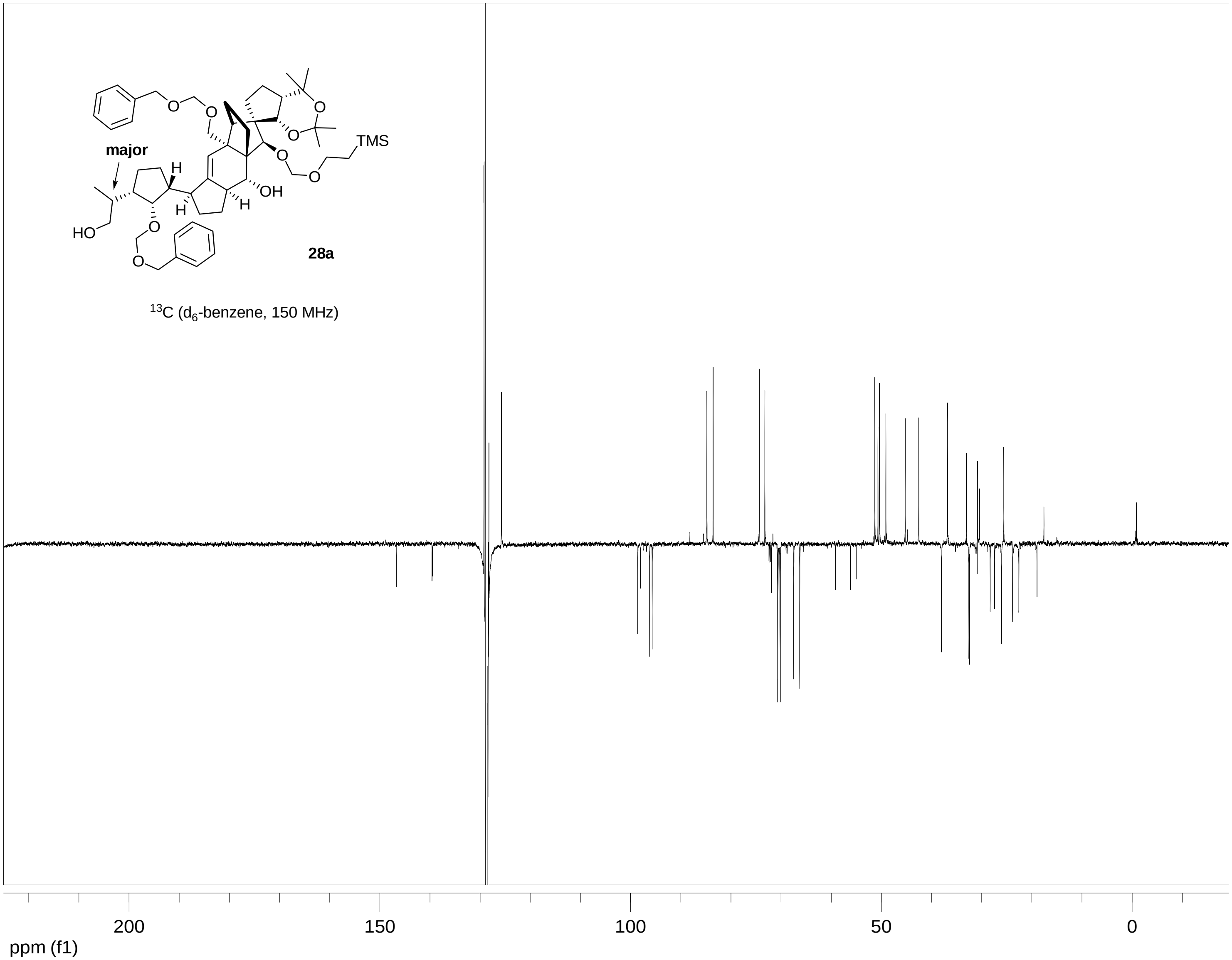
28

^{1}H (d$_6$-benzene, 600 MHz)


O
O
TMS
O
O
O
O
H
H
O
O
28
^{13}C (d_6-benzene, 150 MHz)
200
150
100
50
0
ppm (f1)

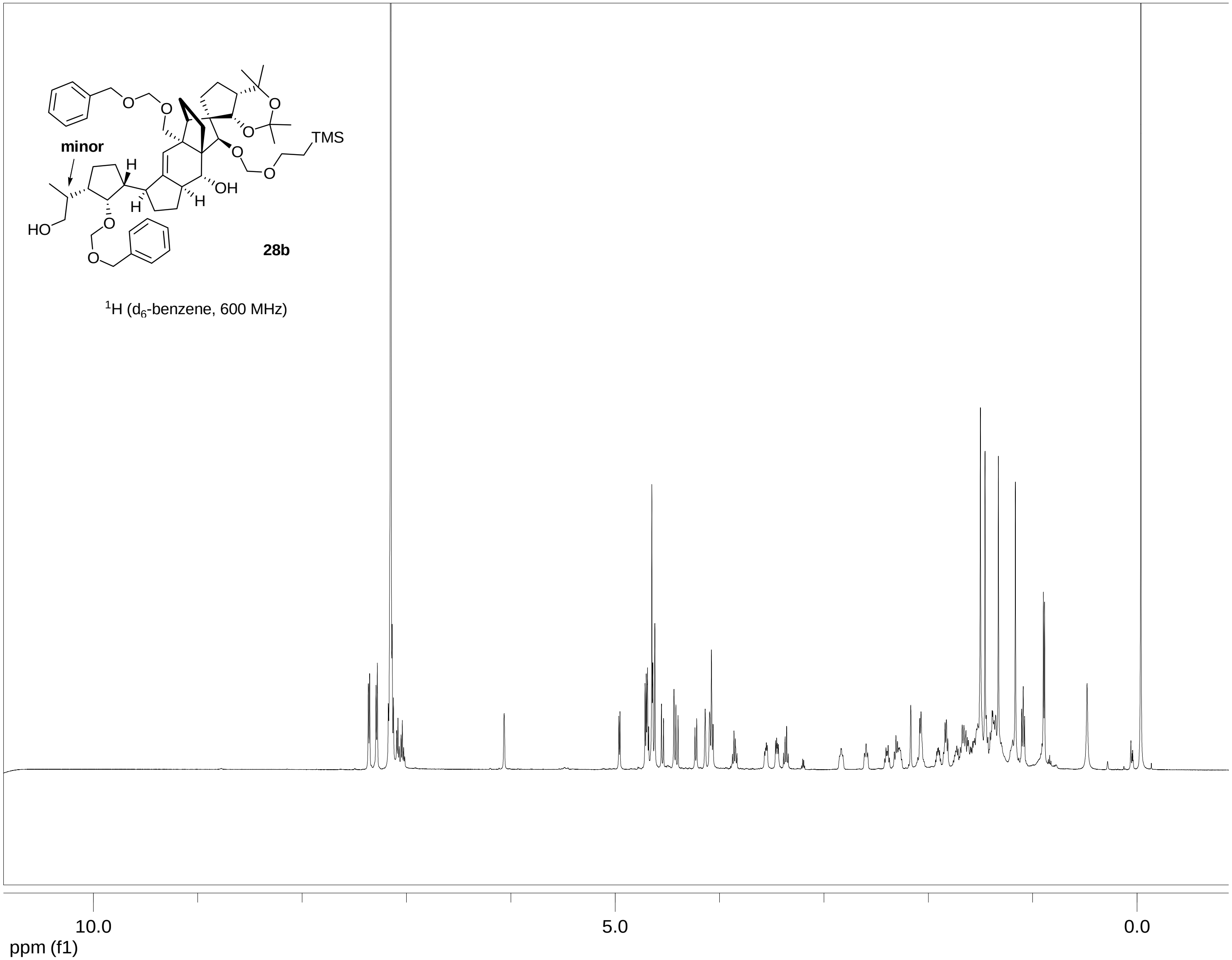


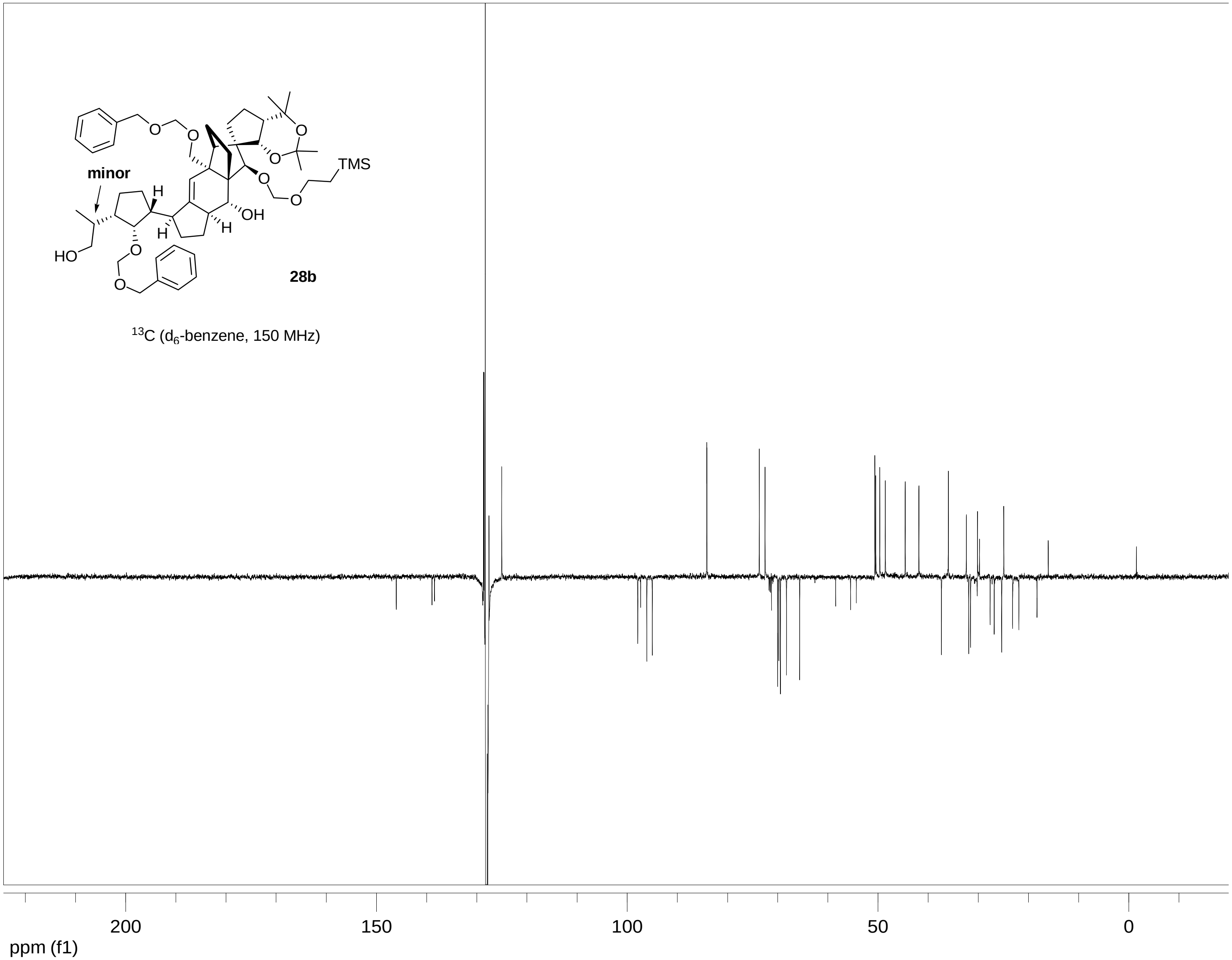
28a

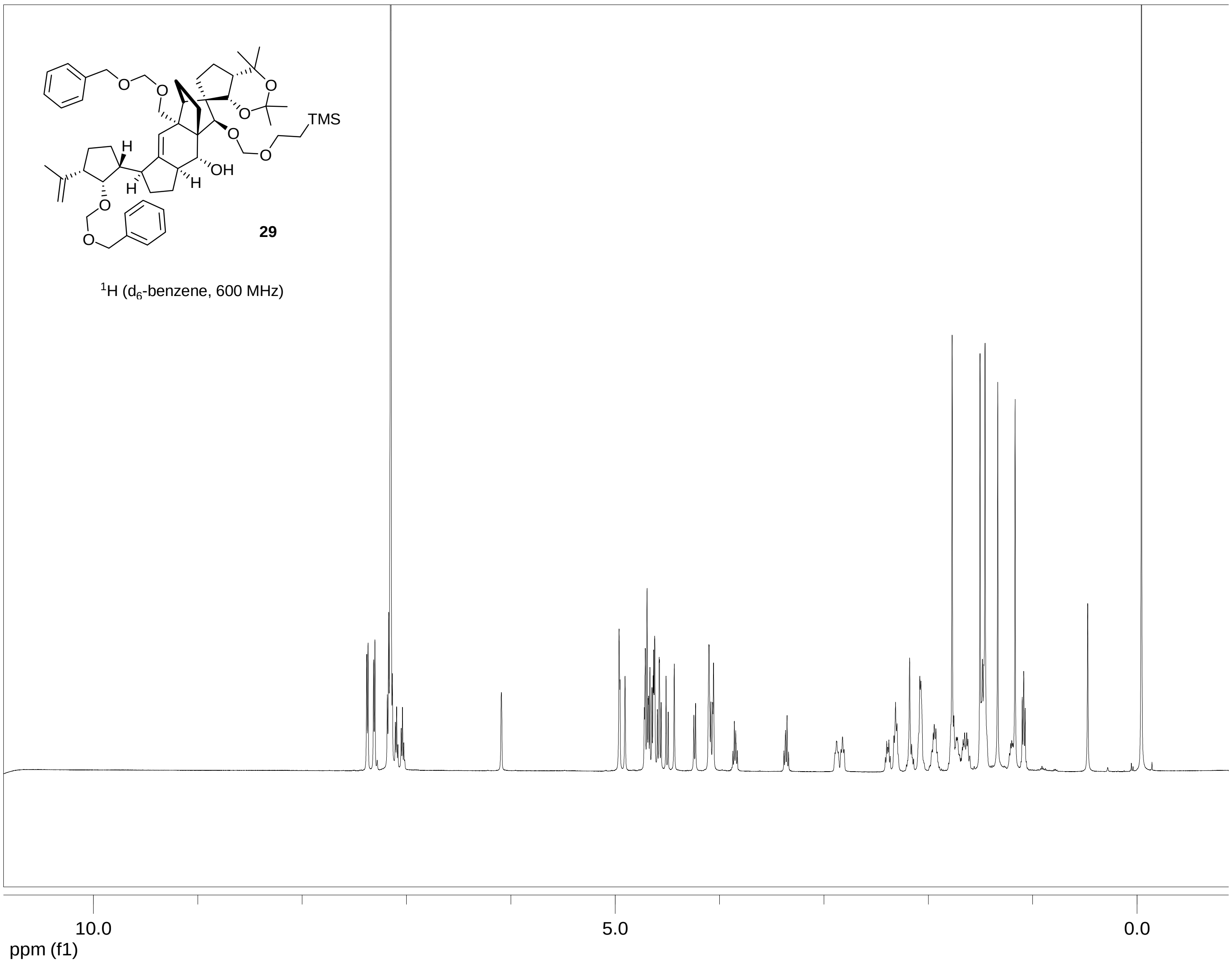


28a

^{13}C (d_6-benzene, 150 MHz)

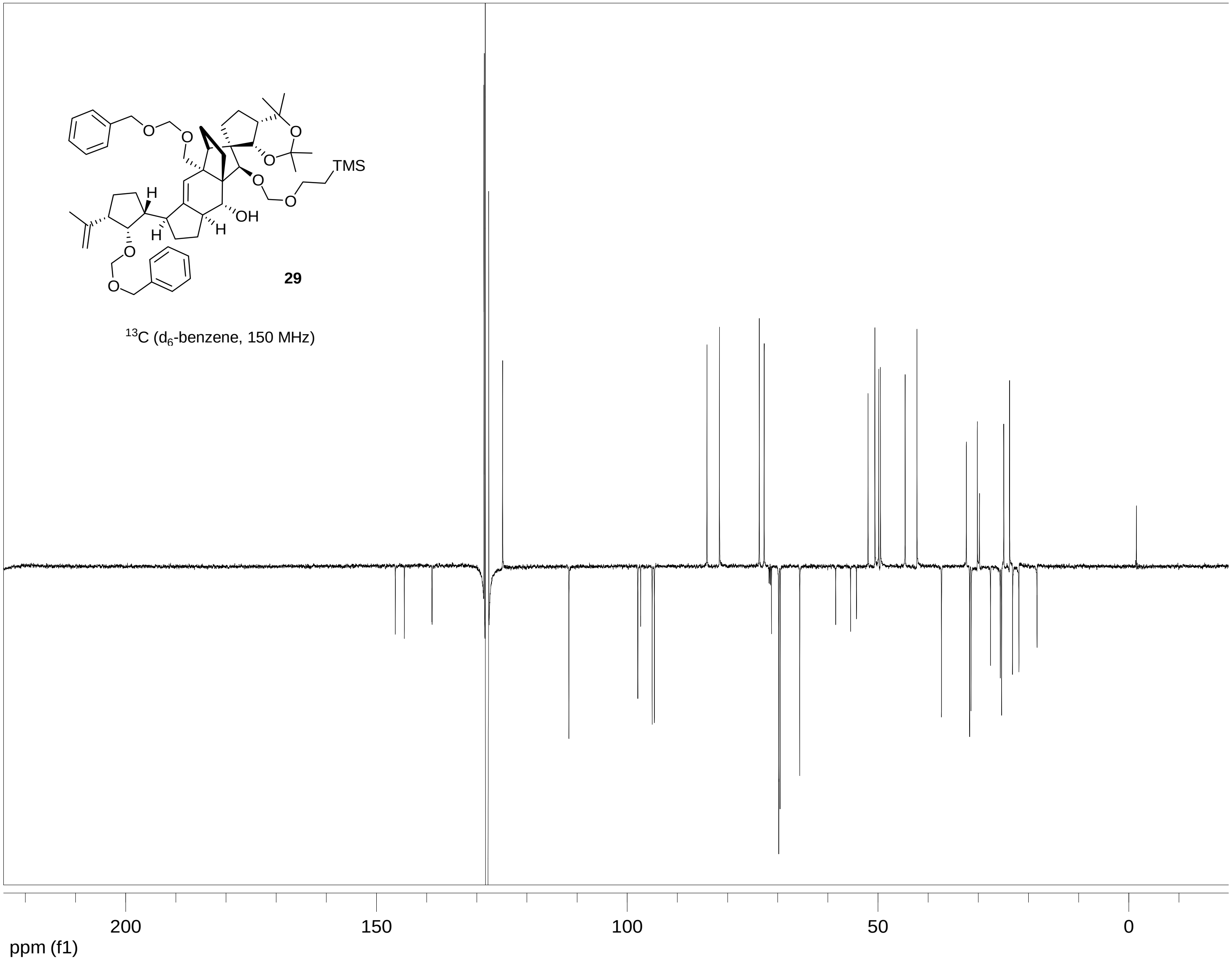

minor
HO
O
O
O
O
H
H
H
OH
O
O
O
O
O
TMS
28b
^{1}H (d$_6$-benzene, 600 MHz)
10.0
5.0
0.0
ppm (f1)

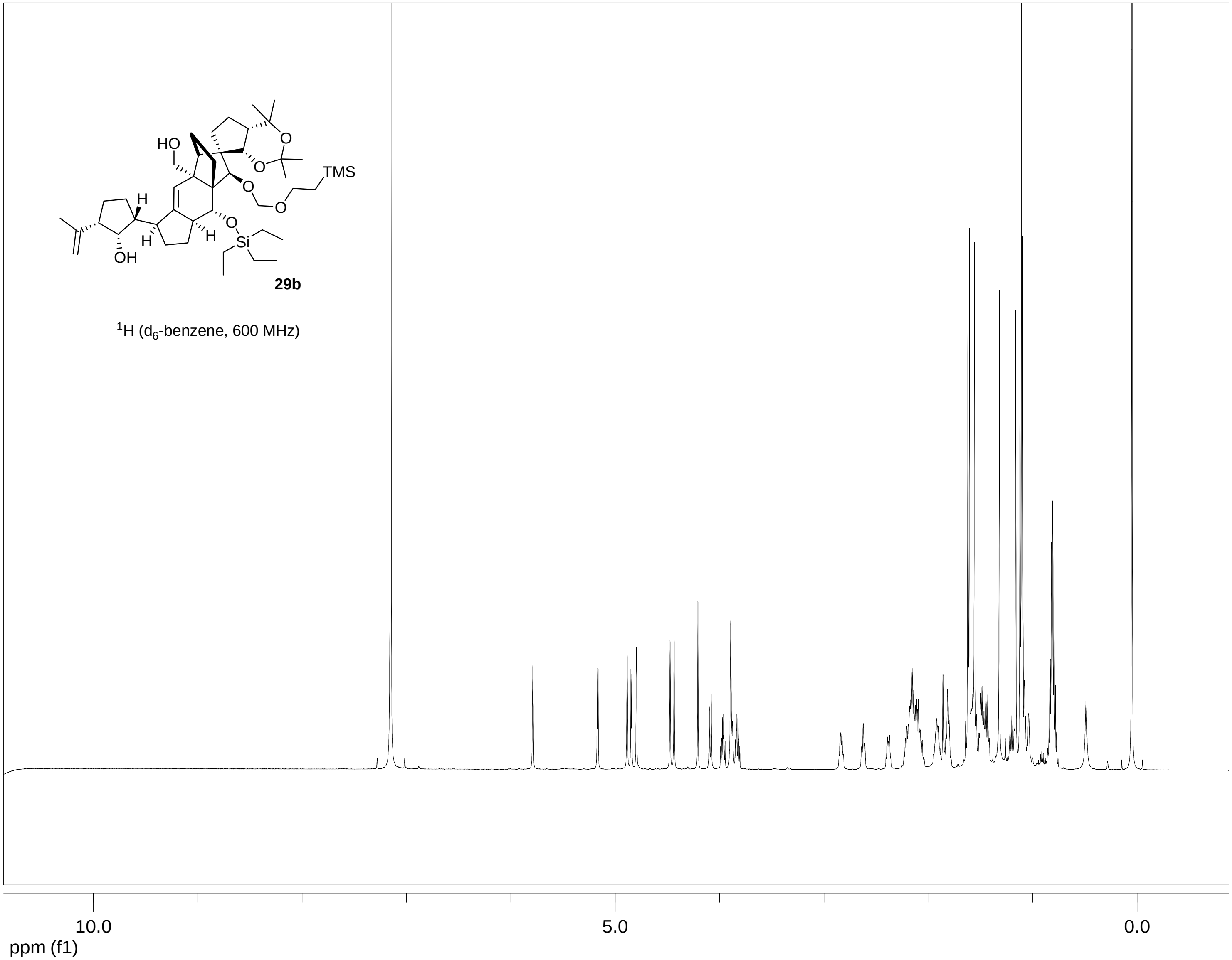

minor
HO
O
O
O
O
H
H
H
OH
O
O
O
O
TMS
28b
^{13}C (d$_6$-benzene, 150 MHz)
200
150
100
50
0
ppm (f1)



29

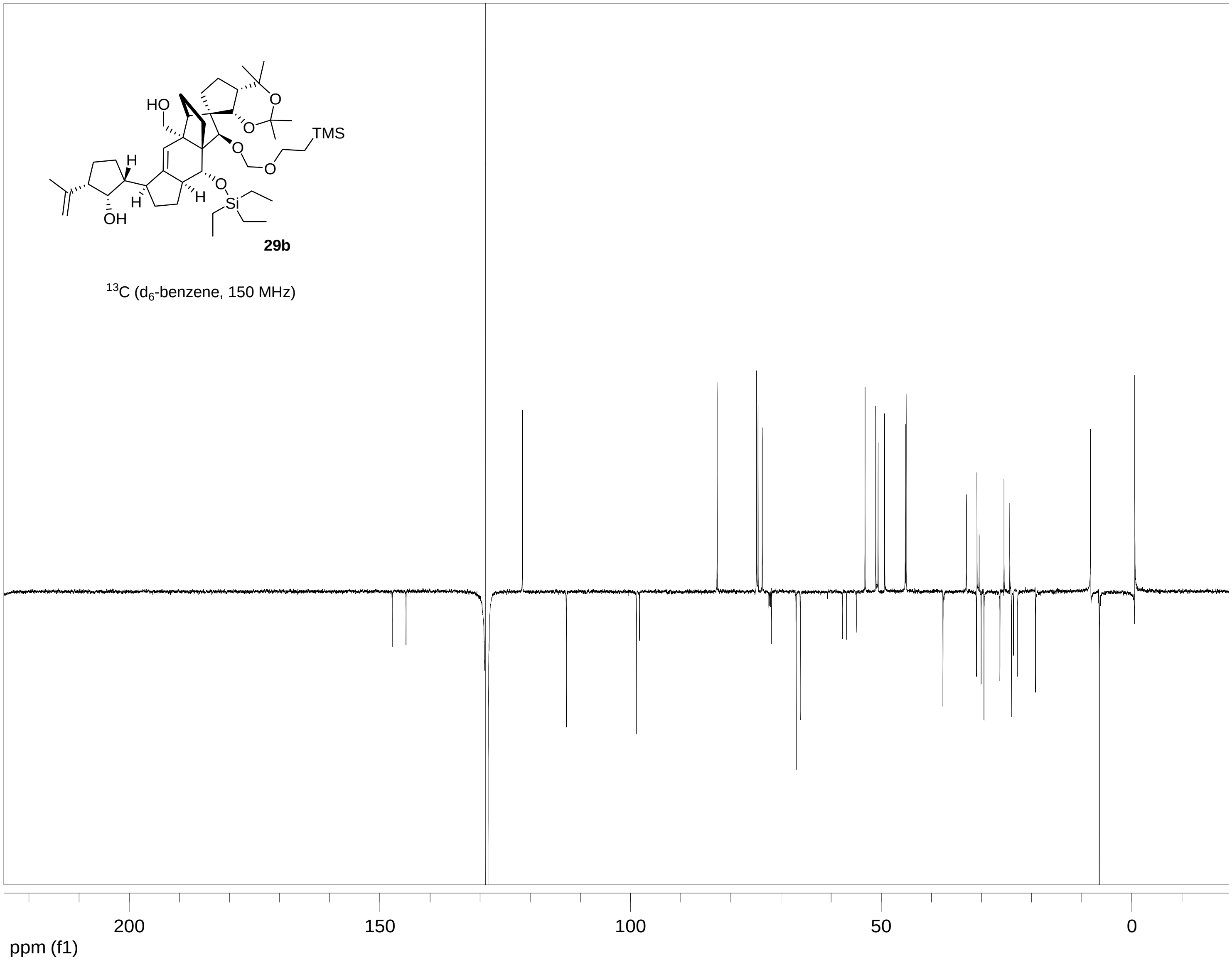
^{1}H (d$_6$-benzene, 600 MHz)


TMS
OH
H
O
29
^{13}C (d$_6$-benzene, 150 MHz)
200
150
100
50
0
ppm (f1)



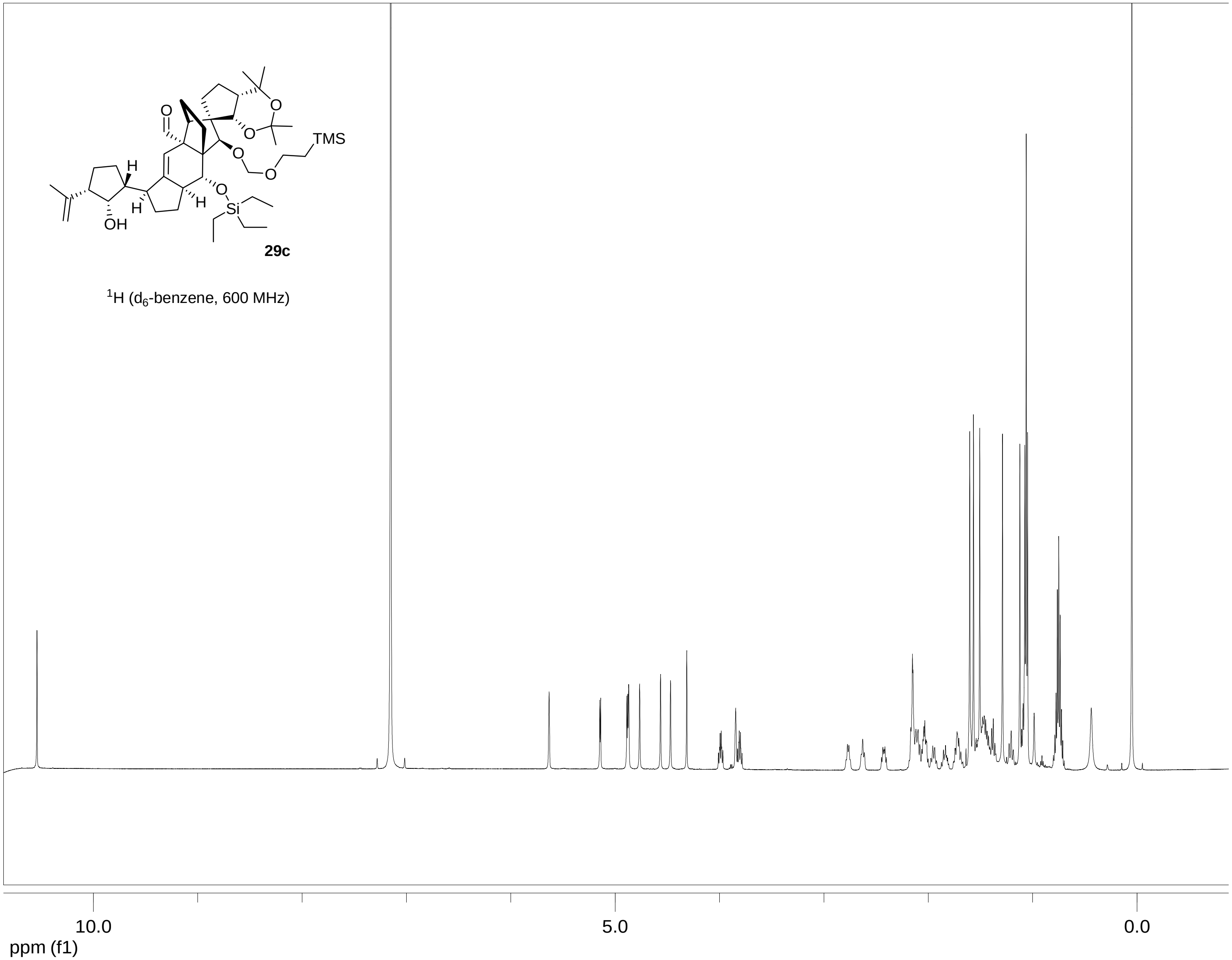
29b

^{1}H (d_6-benzene, 600 MHz)



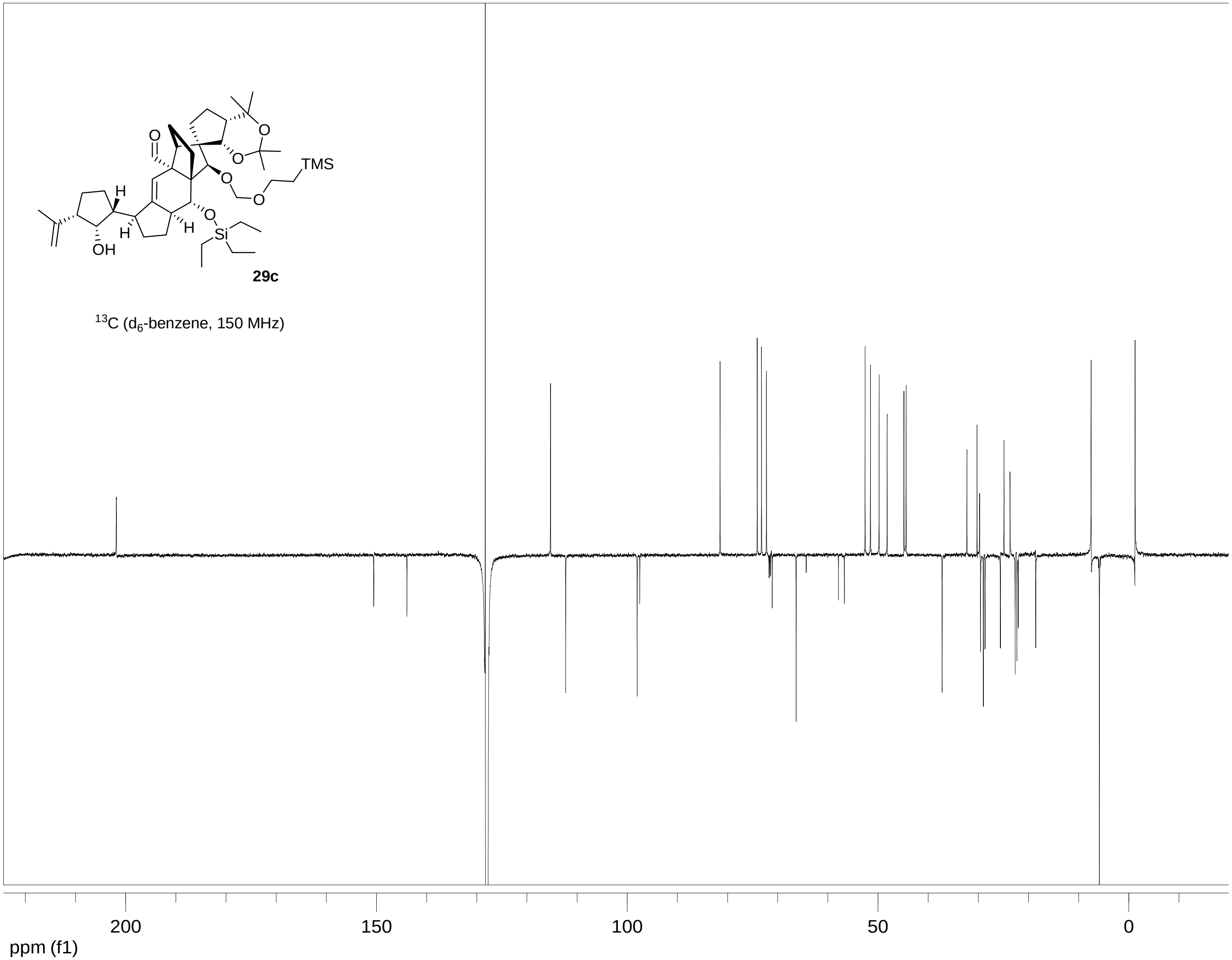
29b

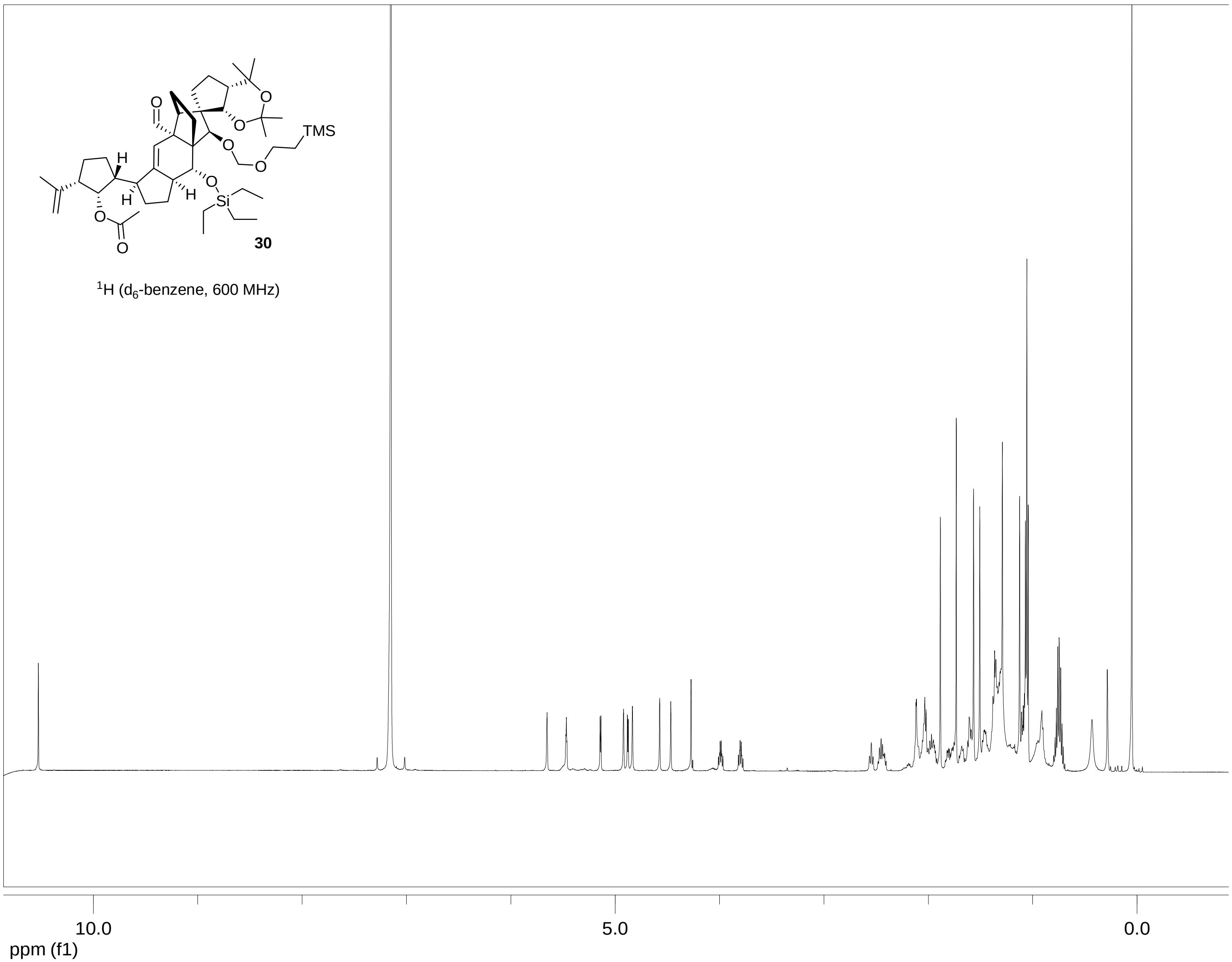
^{13}C (d_6-benzene, 150 MHz)

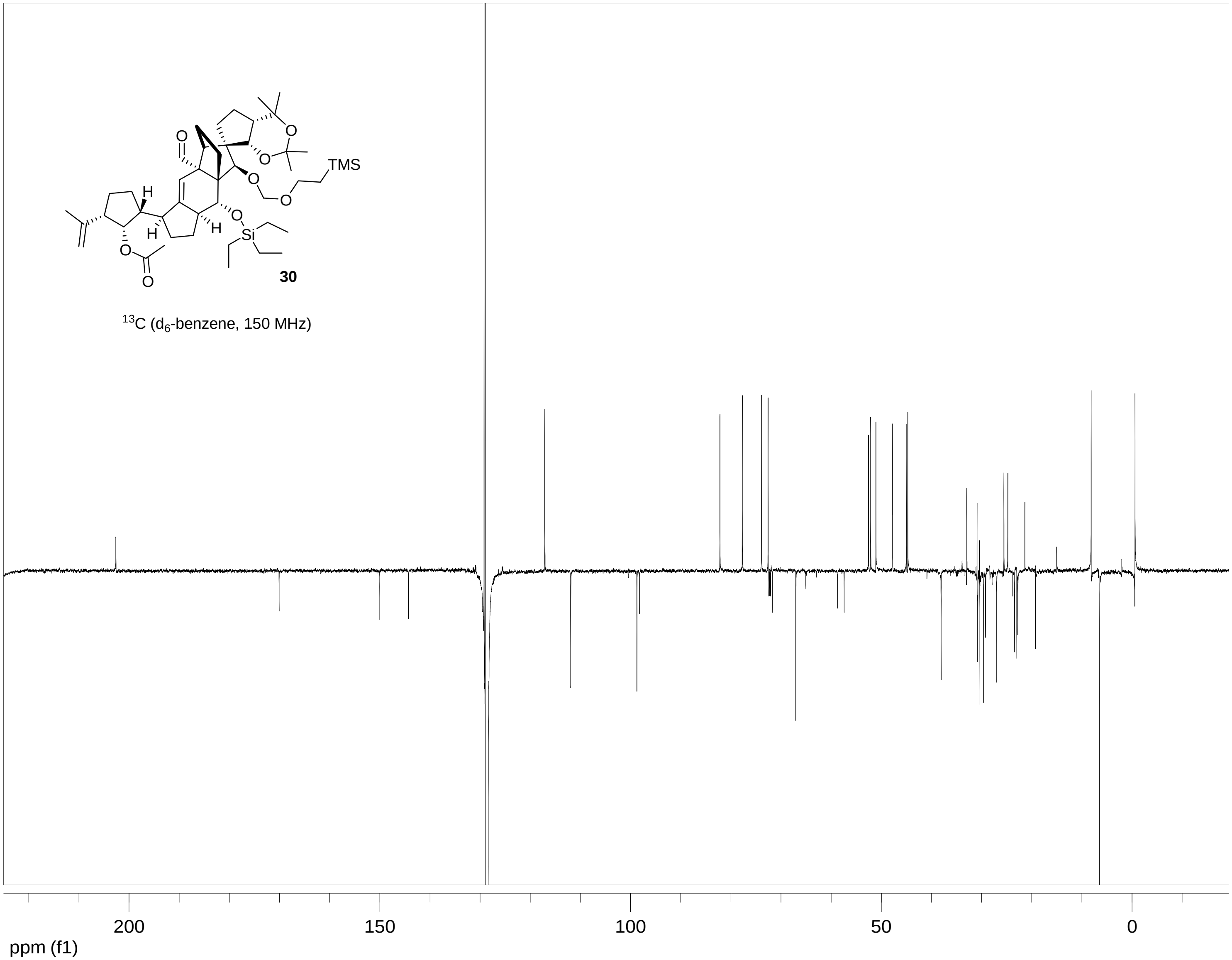


29c

^{1}H (d_6-benzene, 600 MHz)

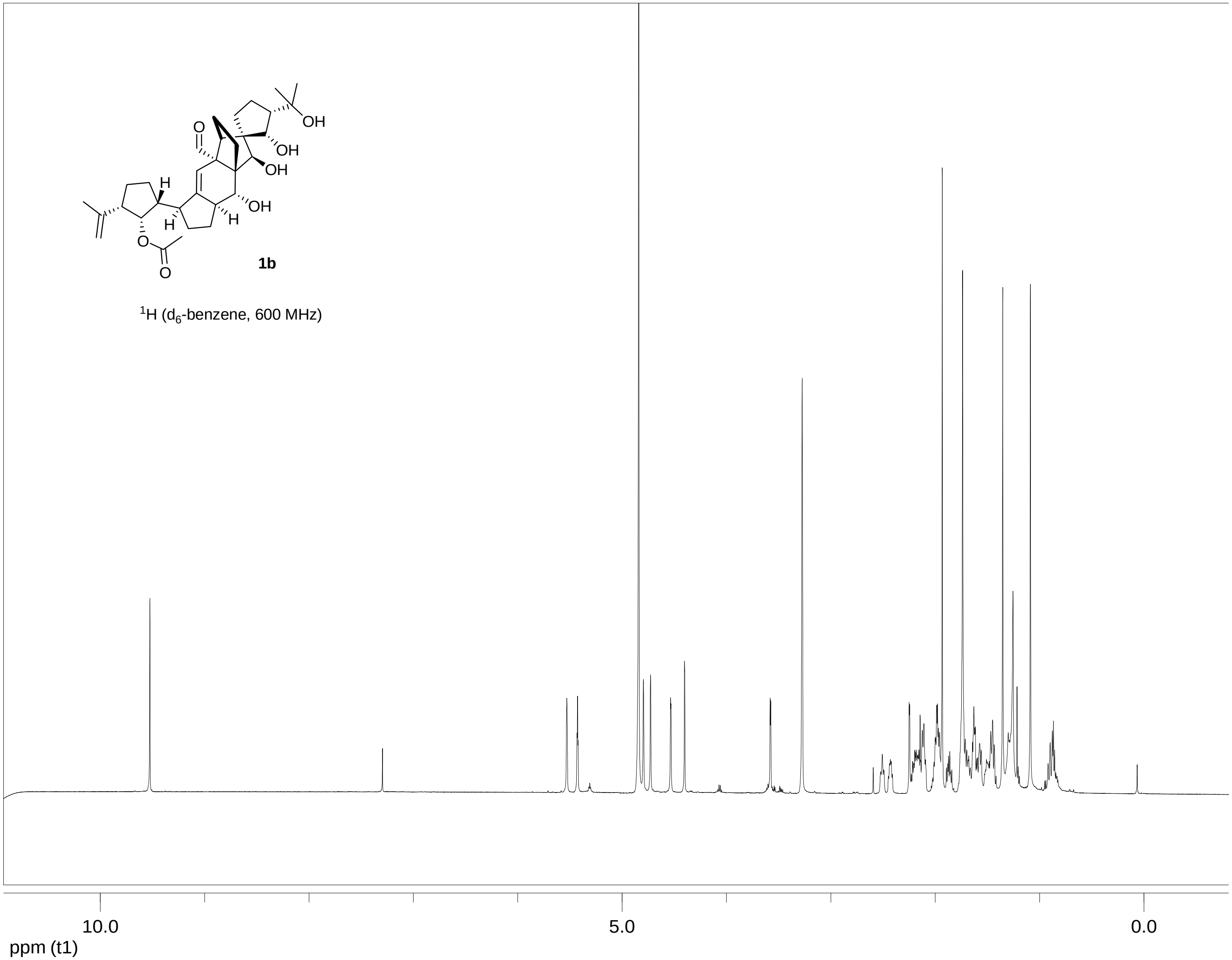

O
TMS
O
O
O
O
H
H
H
O
Si
OH
29c
^{13}C (d$_6$-benzene, 150 MHz)
200
150
100
50
0
ppm (f1)


O
O
O
TMS
O
O
H
H
H
O
Si
O
O
30
^{1}H (d$_6$-benzene, 600 MHz)
10.0
5.0
0.0
ppm (f1)



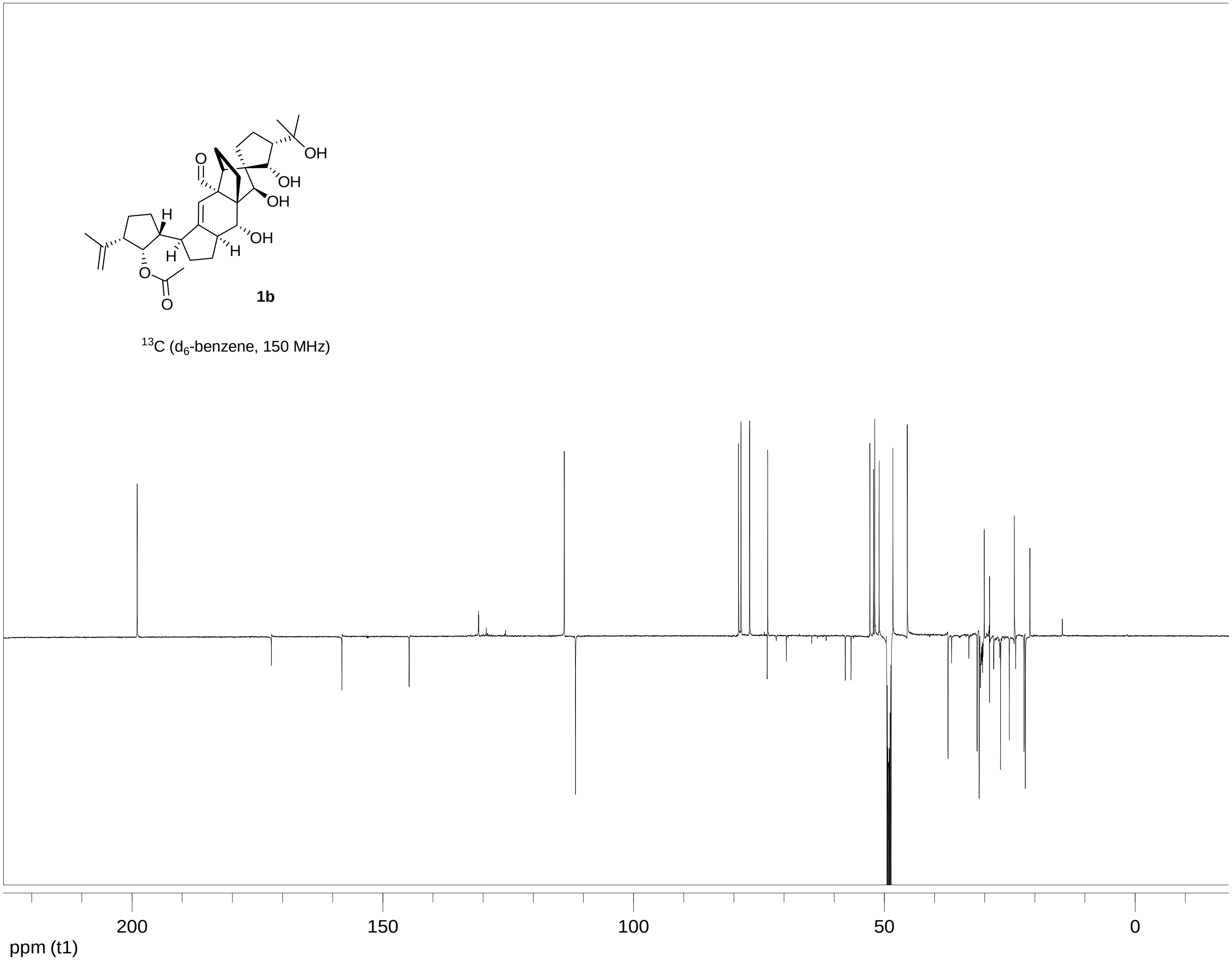
30

^{13}C (d_6-benzene, 150 MHz)



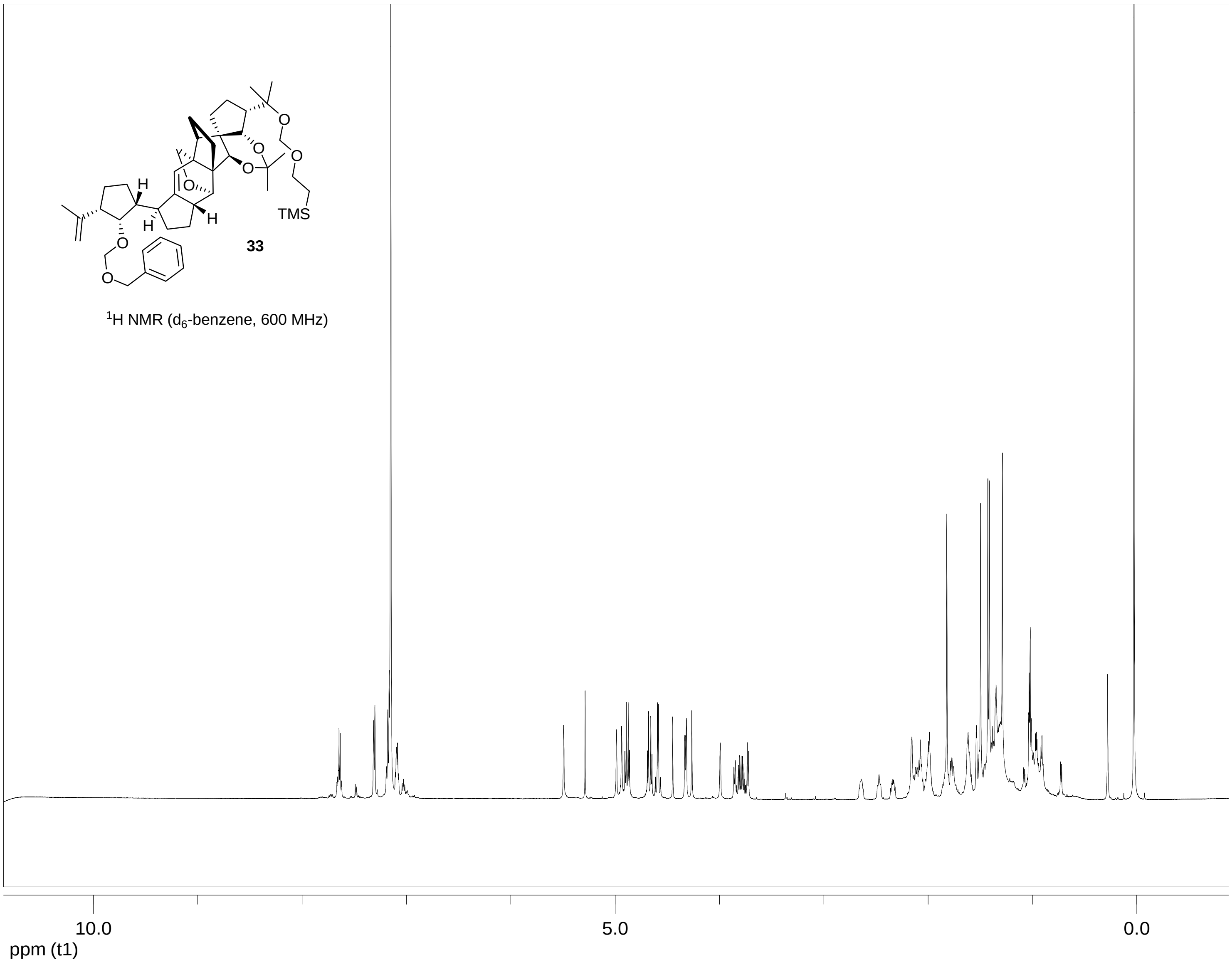
1b

^{1}H (d$_6$-benzene, 600 MHz)



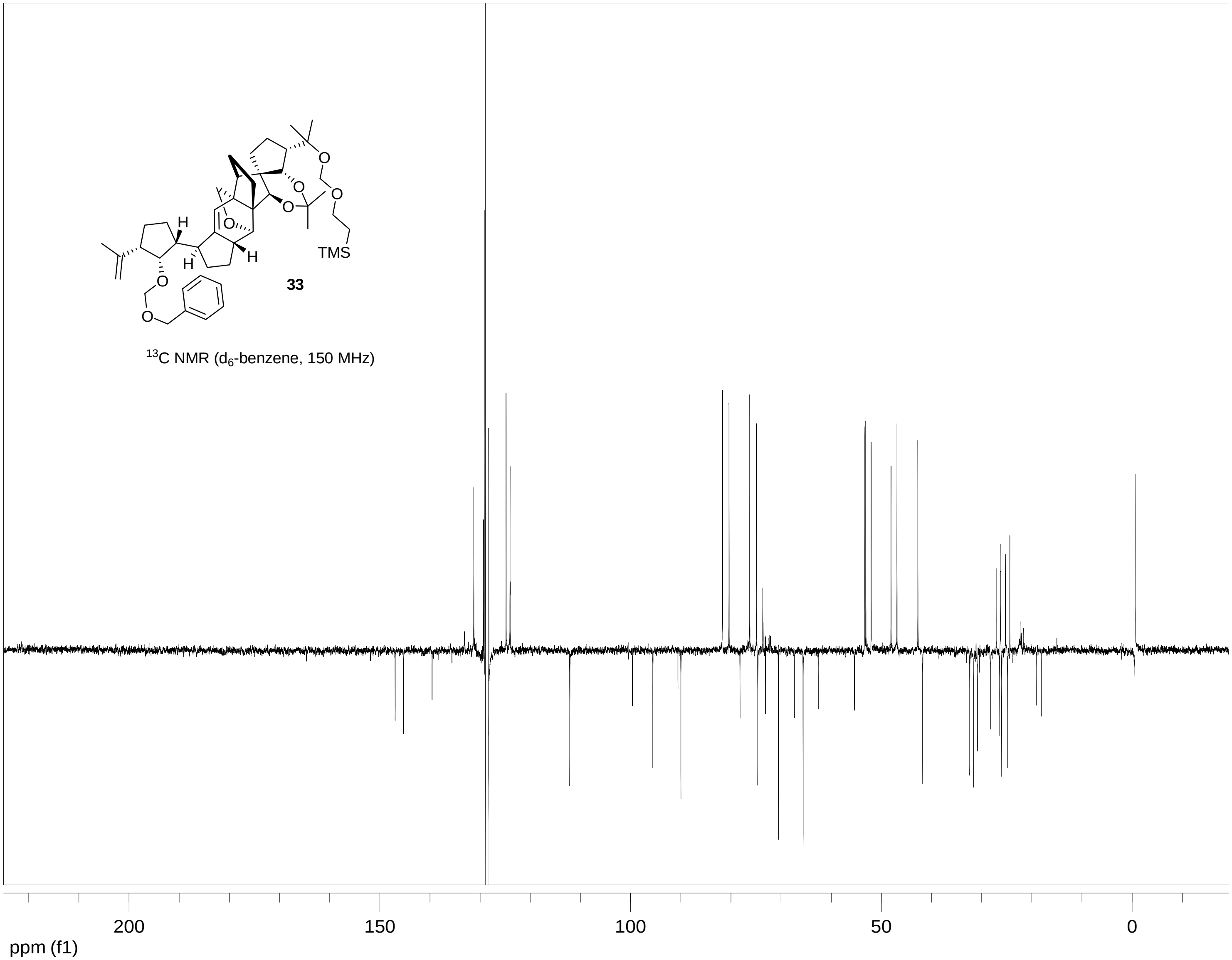
1b

^{13}C (d_6-benzene, 150 MHz)



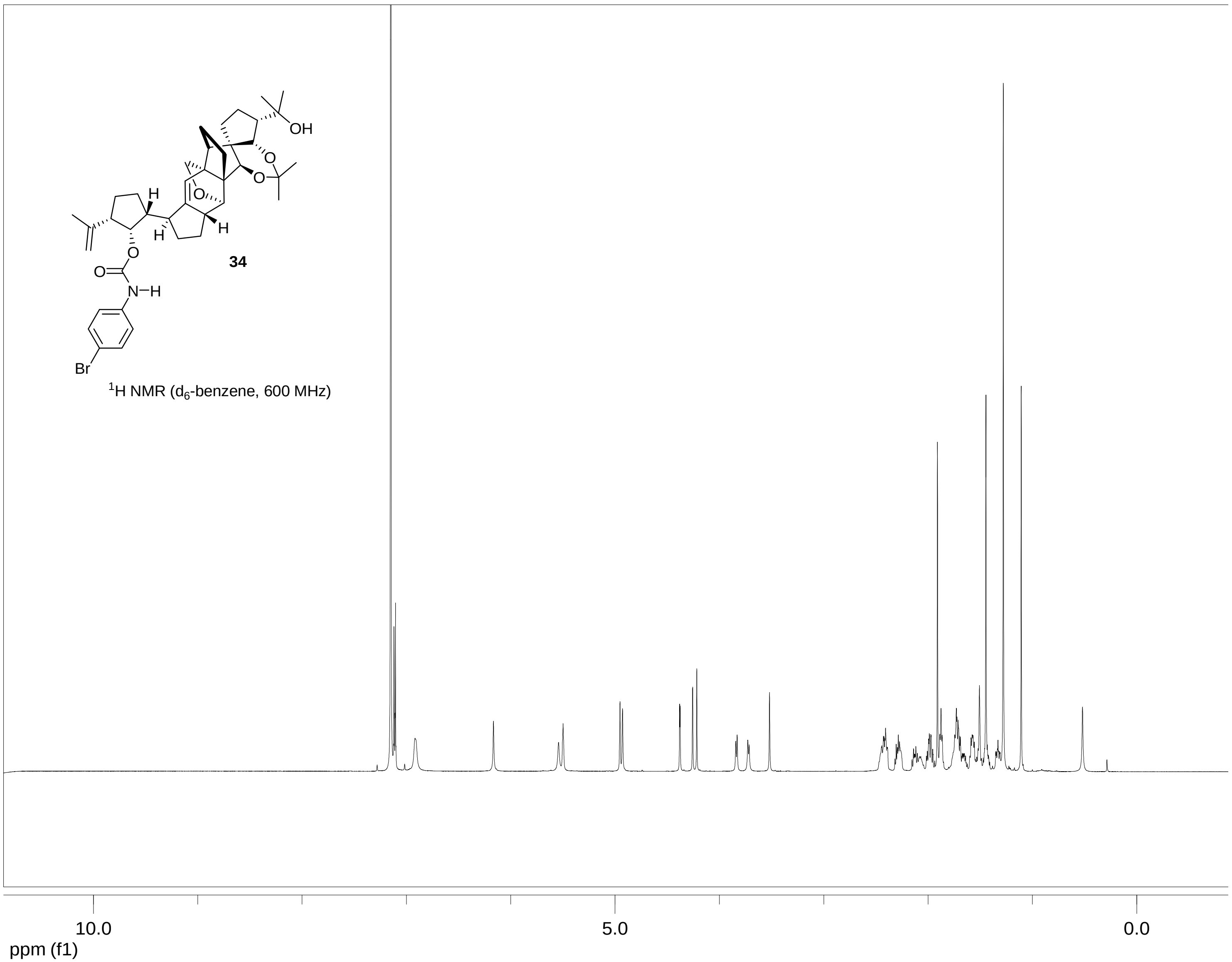
33

^{1}H NMR (d_6-benzene, 600 MHz)

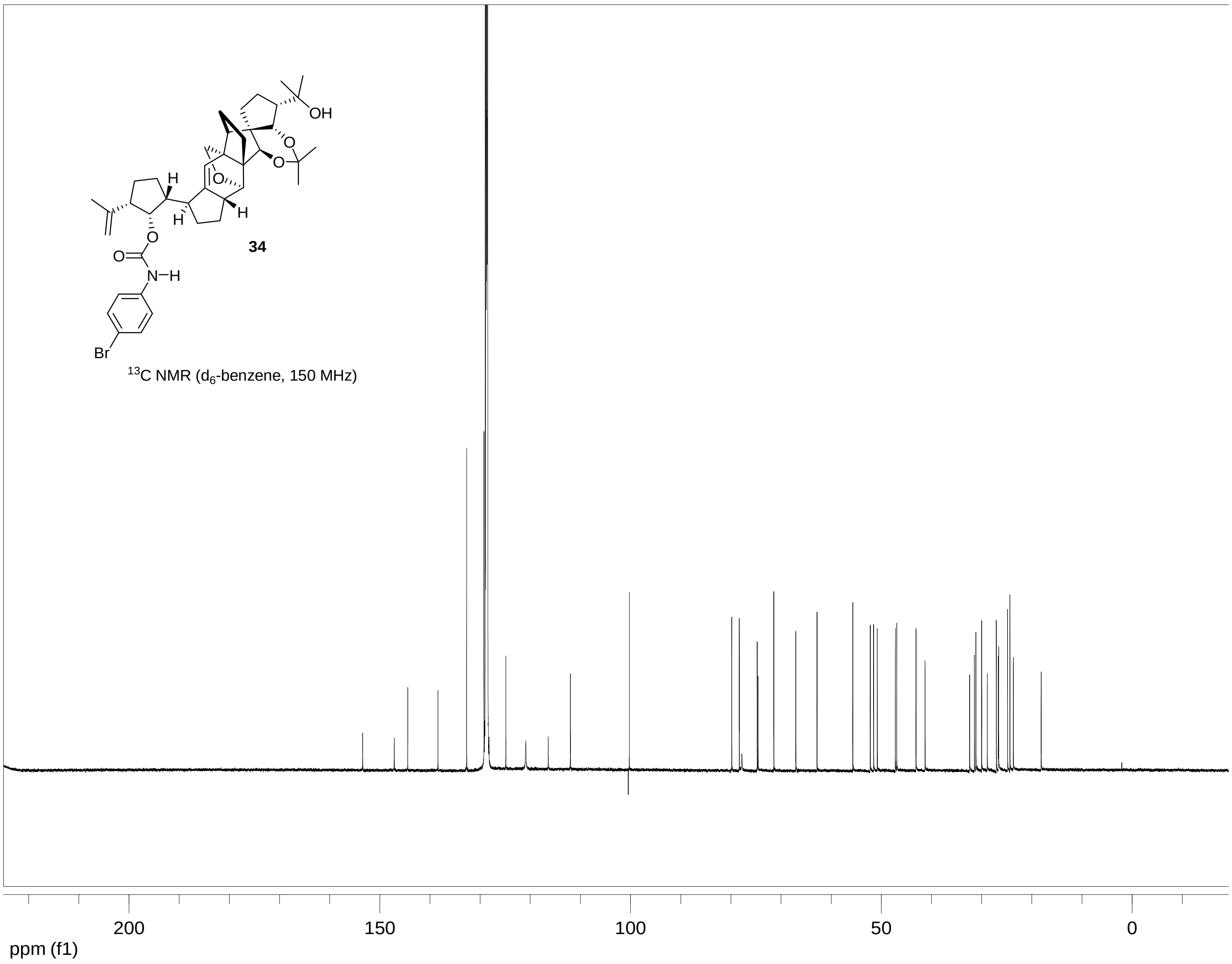


33

^{13}C NMR (d$_6$-benzene, 150 MHz)


34

^{1}H NMR (d$_6$-benzene, 600 MHz)


OH
O
O
H
O
H
H
O
O
N–H
Br
34
^{13}C NMR (d$_6$-benzene, 150 MHz)
200
150
100
50
0
ppm (f1)