

Enantioselective Synthesis of the ABC Ring Motif of Norzoanthamine Based on Asymmetric Robinson Annulation Reactions

Thong X. Nguyen, Marianna Dakanali, Lynn Trzoss, Emmanuel A. Theodorakis*

Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0358, USA

**etheodor@ucsd.edu*

Supporting Information

Table of Contents

	<i>page</i>
1. General Techniques	1-2
2. Experimental Procedures	2-16
3. Crystallographic data	17-33
4. NMR Spectra	34-73

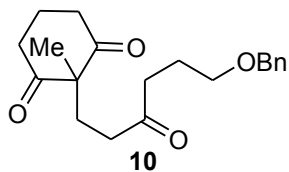
General Techniques

All reagents were commercially obtained (Aldrich, Acros) at highest commercial quality and used without further purification except where noted. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated by rotary evaporation below 45 °C at approximately 20 mmHg. All non-aqueous reactions were carried out under anhydrous conditions using flame-dried glassware within an argon atmosphere in dry, freshly distilled solvents, unless otherwise noted. Tetrahydrofuran (THF), diethyl ether (Et₂O), dichloromethane (CH₂Cl₂), toluene (PhCH₃) and benzene (PhH) were purified by passage through a bed of activated alumina.¹ *N,N*-diisopropylethylamine (DIPEA) and triethylamine (TEA) were distilled from calcium hydride prior to use.² Dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) were distilled from calcium hydride under reduced pressure (20 mmHg) and stored over 4Å molecular sieves until needed. Yields refer to chromatographically and spectroscopically (¹H NMR, ¹³C NMR) homogeneous materials, 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 the visualizing agent and 10% ethanolic phosphomolybdic acid (PMA) or *p*-anisaldehyde solution and heat as developing agents. E. Merck silica gel (60, particle size 0.040-0.063 mm) was used for flash chromatography. Preparative thin-layer chromatography separations were carried out on 0.25 or 0.50 mm E. Merck silica gel plates (60F-254). NMR spectra were recorded on Varian Mercury 300, 400 and/or Jeol Unity 500 MHz instruments and calibrated using the residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad, dd = doublet of doublet, dt = doublet of triplet. Optical rotations were recorded on a Jasco P-1010 polarimeter and values are reported as follows: [α]_Tλ (c: g/100ml, solvent). High resolution mass spectra (HRMS) were recorded on a VG 7070 HS or on a VG ZAB-ZSE mass spectrometers. X-ray data were recorded on a Bruker SMART APEX 3kW Sealed Tube X-ray diffraction system.

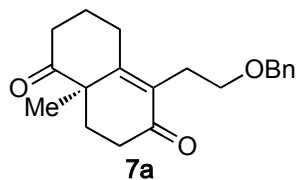
¹ Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.

² Perrin, D. D.; Armarego, W. L. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, **1988**.

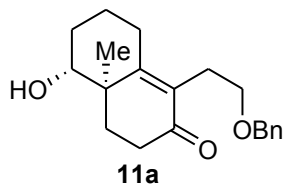
Experimental Procedures



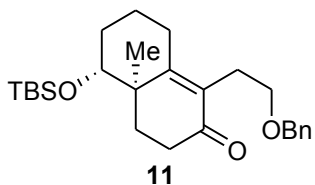
Triketone 10: To a solution of 2-methylcyclohexane-1,3-dione (**8**) (21.8 g, 173 mmol) in ethyl acetate (500 mL) was added Et₃N (31.3 mL, 224 mmol, 1.30 equiv) followed by enone **9a** (37.0 g, 181 mmol, 1.05 equiv) at 25 °C. The reaction was then warmed up to 70 °C and stirred at that temperature overnight. After evaporation of ethyl acetate under reduced pressure, the residue was purified by flash chromatography (silica, 30% EtOAc in hex.) to give triketone **10** (47.0 g, 142 mmol, 82%) as yellow oil. R_f (50% EtOAc in hex.) = 0.25; ¹H NMR (400 MHz, CDCl₃) δ: 7.37-7.27 (5H, m), 4.46 (2H, s), 3.46 (2H, t, J = 6.1 Hz), 2.73-2.56 (4H, m), 2.48 (2H, t, J = 7.2 Hz), 2.31 (2H, t, J = 7.2 Hz), 2.07-1.98 (3H, m), 1.92-1.81 (3H, m), 1.22 (3H, s); ¹³C NMR (100MHz, CDCl₃) δ: 210.0, 209.3, 138.3, 128.3, 127.6, 127.5, 72.8, 69.2, 64.4, 39.5, 37.7, 37.3, 29.8, 23.8, 19.5, 17.6; HRMS calcd. for C₂₀H₂₆O₄Na (M+Na⁺) 353.1723, found 353.1724.



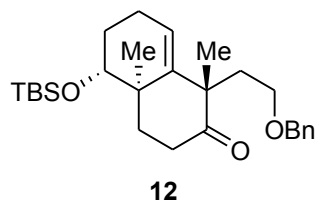
Enone 7a: To a solution triketone **10** (47.0 g, 142 mmol) in dry DMF (800 mL) was added D-Phe (23.5 g, 142 mmol, 1.0 equiv) followed by R-CSA (16.5 g, 71.1 mmol, 0.50 equiv) at 25 °C. The reaction was stirred at that temperature for 30 days before quenched with water (500 mL) and extracted with ether (3 x 500 mL). The combined organic extracts were washed with brine, dried over Na₂SO₄, concentrated under reduced pressure and purified by flash chromatography (silica, 20% EtOAc in hex.) to give enone **7a** (33.5 g, 107 mmol, 75%, 85% ee) as yellow oil. R_f (50% EtOAc in hex.) = 0.30; $[\alpha]_D^{25} = -83.8^\circ$ (c 4.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ: 7.34-7.24 (5H, m), 4.45 (2H, s), 3.49-3.37 (2H, m), 2.99 (1H, td, J = 15.1, 4.3 Hz), 2.74-2.59 (3H, m), 2.51-2.36 (4H, m), 2.15-2.00 (3H, m), 1.68-1.60 (1H, m), 1.41 (3H, s); ¹³C NMR (100MHz, CDCl₃) δ: 211.9, 197.2, 160.7, 138.3, 131.7, 128.2, 127.4, 127.4, 72.7, 69.1, 51.0, 37.1, 33.4, 29.4, 27.1, 26.2, 23.4, 21.9; HRMS calcd. for C₂₀H₂₄O₃Na (M+Na⁺) 335.1618, found 335.1621.



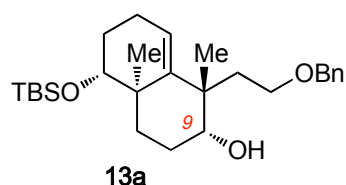
Silyl Ether 11: To a stirred solution of enone **7a** (33.5 g, 107 mmol) in dry EtOH (300 mL) at -78 °C was added NaBH₄ (1.02 g, 26.8 mmol, 0.25 equiv) portionwise. The reaction was stirred at that temperature for 1 h and was quenched with glacial acetic acid (5 mL). After evaporation of EtOH under reduced pressure, the residue was extracted with ethyl acetate (3 x 200 mL). The combined organic extracts were washed with brine, dried over Na₂SO₄, concentrated under reduced pressure and purified by flash chromatography (silica, 40% EtOAc in hex.) to give alcohol **11a** (23.6 g, 75.0 mmol, 70%) as yellow oil. $[\alpha]_D^{25} = -87.6^\circ$ (*c* 4.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ: 7.35-7.24 (5H, m), 4.47 (2H, s), 3.43-3.33 (3H, m), 2.74 (1H, m), 2.67 (2H, m), 2.44-2.40 (2H, m), 2.17-2.61 (2H, m), 1.90-1.77 (3H, m), 1.72-1.57 (2H, m), 1.34-1.21 (1H, m), 1.18 (3H, s); ¹³C NMR (100MHz, CDCl₃) δ: 198.4, 163.0, 138.5, 131.0, 128.3, 127.5, 127.4, 78.3, 72.7, 69.4, 42.0, 33.5, 33.5, 30.0, 27.2, 26.1, 23.1, 15.8; HRMS calcd. for C₂₀H₂₆O₃Na (M+Na⁺) 337.1774, found 337.1775.



A solution of the alcohol **11a** (23.6 g, 75.0 mmol) in dry DMF (150 mL) was treated with ammonium nitrate (18.1 g 225 mmol, 3.0 equiv) and TBSCl (22.6 g, 150 mmol, 2.0 equiv) at 0 °C. The mixture was warmed to 25 °C and stirred overnight, and then quenched with sat aq NH₄Cl (60 mL). The reaction mixture was extracted with ethyl acetate (3 x 150 mL). The combined organic extracts were washed with brine, dried over Na₂SO₄, concentrated under reduced pressure and purified by flash chromatography (silica, 5% EtOAc in hex.) to give silyl ether **11** (30.5 g, 71.0 mmol, 95%) as yellow oil. *R_f* (5% EtOAc in hex.) = 0.20; $[\alpha]_D^{25} = -64.8^\circ$ (*c* 4.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ: 7.34-7.24 (5H, m), 4.48 (2H, s), 3.43-3.32 (3H, m), 2.73-2.65 (3H, m), 2.41-2.37 (2H, m), 2.09-2.00 (2H, m), 1.83-1.80 (1H, m), 1.71-1.63 (3H, m), 1.28-1.20 (1H, m), 1.14 (3H, s), 0.89 (9H, s), 0.04 (3H, s), 0.03 (3H, s); ¹³C NMR (100MHz, CDCl₃) δ: 198.7, 163.6, 138.6, 130.7, 128.2, 127.5, 127.4, 78.9, 72.7, 69.4, 42.6, 33.9, 33.7, 30.4, 27.2, 26.1, 25.8, 22.9, 18.0, 16.1, -3.9, -4.9; HRMS calcd. for C₂₆H₄₀O₃Si (M⁺) 428.2741, found 428.2746.

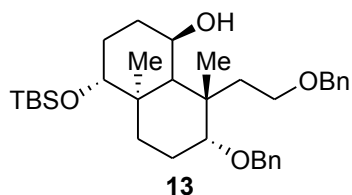


Ketone 12: To a solution enone **11** (3.00 g, 7.00 mmol) in dry benzene (25 mL) potassium *tert*-butoxide (785 mg, 7.00 mmol, 1.0 equiv) was added at 25 °C. The reaction was then warmed up to 60 °C for 30 min and allowed to cool to 25 °C. MeI (1.30 mL, 21.0 mmol, 3.0 equiv) was then added and the reaction was stirred for 15 min before it was quenched with sat aq NH₄Cl (30 mL). The aqueous layer was extracted with ethyl acetate (3 x 15 mL). The combined organic extracts were washed with brine, dried over Na₂SO₄, concentrated under reduced pressure and purified by flash chromatography (silica, 20% EtOAc in hex.) to give ketone **12** (2.20 g, 4.90 mmol, 70%) as yellow oil. R_f (5% EtOAc in hex.) = 0.22; $[\alpha]_D^{25} = -5.5^\circ$ (c 1.8, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ : 7.34-7.24 (5H, m), 5.50 (1H, t, $J = 3.6$ Hz), 4.47 (1H, d, $J = 11.7$ Hz), 4.40 (1H, d, $J = 11.7$ Hz), 3.48 (1H, dd, $J = 11.3, 4.5$ Hz), 3.43-3.37 (1H, m), 3.31-3.25 (1H, m), 2.50-2.45 (2H, m), 2.41-2.34 (1H, m), 2.17-2.13 (2H, m), 2.08-2.02 (1H, m), 1.82-1.75 (1H, m), 1.72-1.59 (3H, m), 1.23 (3H, s), 0.90 (9H, s), 0.86 (3H, s), 0.07 (3H, s), 0.05 (3H, s); ¹³C NMR (100MHz, CDCl₃) δ : 214.3, 145.2, 138.6, 128.2, 127.5, 127.3, 120.8, 76.6, 72.7, 67.2, 51.1, 39.3, 38.1, 33.9, 31.4, 29.5, 26.5, 25.8, 24.6, 18.0, 17.7, -3.9, -4.9; HRMS calcd. for C₂₇H₄₂O₃SiNa (M+Na⁺) 465.2795, found 465.2798.

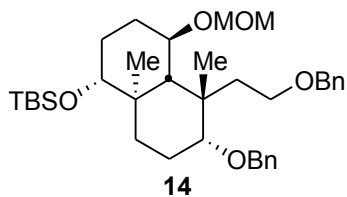


Alcohol 13: To a solution of ketone **12** (26.0 g, 58.7 mmol) in MeOH (300 mL) NaBH₄ (2.20 g 56.7 mmol, 1.0 equiv) was added at 0 °C. The reaction was stirred at that temperature for 30 min before quenched with sat aq NH₄Cl (200 mL). MeOH was then removed under reduced pressure. The reaction mixture was then extracted with ethyl acetate (3 x 100 mL). The combined organic extracts were washed with brine, dried over Na₂SO₄, concentrated under reduced pressure and purified by flash chromatography (silica, 30% EtOAc in hex.) to give C9 alcohol **13a** (24.1 g, 54.0 mmol, 92%) as yellow oil. ¹H NMR (400 MHz, CDCl₃) δ : 7.36-7.26 (5H, m), 5.40 (1H, t, $J = 3.7$ Hz), 4.49 (2H s), 3.50-3.38 (2H, m), 3.32 (1H, dd, $J = 11.9, 3.7$ Hz), 3.20-3.14 (1H, m), 2.39 (1H, m), 2.13-1.96 (3H, m), 1.89-1.50 (6H, m), 1.18 (3H, s), 1.10-1.02 (1H, m), 1.07 (3H, s), 0.89 (9H, s), 0.04 (3H, s), 0.02 (3H, s); ¹³C NMR (100MHz, CDCl₃) δ : 145.9, 138.2, 128.4, 127.7, 127.6, 121.5, 78.7, 78.3, 73.0, 67.7, 44.1, 39.4,

36.1, 33.4, 27.0, 26.6, 25.9, 25.0, 23.6, 19.3, 18.0, -4.0, -4.8; HRMS calcd. for C₂₇H₄₄O₃SiNa (M+Na⁺) 467.2952, found 467.2954.

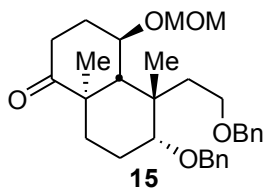


To a solution of alcohol **13a** (24.1 g, 54.0 mmol) in DMF (200 mL) NaH (5.17 g, 135 mmol, 60% w/w, 2.5 equiv) was added at 25 °C. The reaction was then heated at 60 °C for 30 minutes. Upon cooling to 25 °C, benzyl chloride (15.7 mL, 135 mmol, 2.5 equiv) was added dropwise, followed by NaI (200 mg, catalyst). The reaction was stirred overnight at 25 °C and quenched with sat aq NH₄Cl (200mL). The reaction mixture was then extracted with ethyl acetate (3 x 150 mL). The combined organic extracts were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure to give the crude product as yellow oil. To the crude benzyl ether (4.81 g, 9.00 mmol) in THF (20 mL), BH₃·THF (27.0 mL, 27 mmol, 1M in THF, 3.0 equiv) was added at 0 °C. The reaction was then left at that temperature for 3 days. Upon completion, a solution of 3N NaOH-30% w/w H₂O₂ (20 mL, 1:1) was added dropwise at 0 °C. The mixture was allowed to warm to 25 °C slowly and stirred at the same temperature for 5 h. Sat aq NH₄Cl (50 mL) was then added and extracted with ethyl acetate (3 x 50 mL). The reaction was repeated 5 additional times in 4.81 g batches. The combined organic extracts were washed with brine and dried over Na₂SO₄, concentrated under reduced pressure and purified by flash chromatography (silica, 20% EtOAc in hex.) to give alcohol **13** (15.7 g, 32.4 mmol, 60% over 2 steps) as white oil. R_f (20% EtOAc in hex.) = 0.25; [α]_D²⁵ = - 30.3° (c 4.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ: 7.43-7.29 (10H, m), 4.72 (1H, d, J = 11.7 Hz), 4.60 (1H, m), 4.53 (2H, m), 4.42 (1H, d, J = 11.7 Hz), 4.02 (1H, dt, J = 10.3, 3.7 Hz), 3.76 (1H, m), 3.66 (2H, m), 3.14 (1H, dd, J = 10.5, 5.1 Hz), 2.91 (1H, dd, J = 11.7, 3.7 Hz), 2.04-1.84 (5H, m), 1.65-1.49 (3H, m), 1.45 (3H, s), 1.24 (2H, t, J = 8Hz), 1.01 (1H, m), 0.97 (3H, s), 0.94 (9H, s), 0.08 (6H, br. s); ¹³C NMR (100MHz, CDCl₃) δ: 139.2, 137.7, 128.3, 128.1, 127.9, 127.6, 127.6, 127.0, 88.2, 79.9, 73.0, 71.3, 68.5, 58.3, 40.6, 40.4, 36.5, 34.2, 29.8, 29.3, 26.5, 25.8, 22.0, 17.9, 13.4, -4.1, -4.9; HRMS calcd. for C₃₄H₅₂O₄SiNa (M+Na⁺) 575.3527, found 575.3519.



MOM Ether 14: To a solution alcohol **13** (15.0 g, 27.1 mmol) in dry DCM (100 mL) was added DIPEA (33.2 mL, 190 mmol, 7.0 equiv) followed by MOMCl (10.3 mL, 136 mmol, 5.0 equiv) and stirred for 15 h. The reaction was then diluted with water (300 mL)

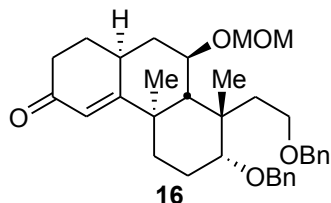
and extracted with ethyl acetate (2 x 200 mL). The combined organic extracts were dried over Na_2SO_4 , concentrated under reduced pressure and purified by flash chromatography (silica, 10% EtOAc in hex.) to give alcohol **14** (15.9 g, 26.6 mmol, 98%) as yellow oil. R_f (10% EtOAc in hex.) = 0.30; $[\alpha]_D^{25} = -23.3^\circ$ (c 3.9, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.34-7.24 (10H, m), 4.65 (3H, m), 4.48 (1H, d, $J = 12.0$ Hz), 4.40 (1H, d, $J = 12.0$ Hz), 4.34 (1H, d, $J = 11.7$ Hz), 3.91-3.85 (1H, m), 3.79 (1H, dt, $J = 4.2, 10.7$ Hz), 3.53-3.47 (1H, m), 3.34 (3H, s), 3.07 (1H, dd, $J = 4.8, 10.7$ Hz), 2.87 (1H, dd, $J = 3.5, 11.7$ Hz), 2.16-2.05 (2H, m), 1.86-1.82 (2H, m), 1.73-1.45 (5H, m), 1.37-1.30 (1H, m), 1.27 (3H, s), 1.09 (1H, m), 0.92 (3H, s), 0.86 (9H, s), 0.01 (6H, s); $^{13}\text{C NMR}$ (100MHz, CDCl_3) δ : 139.3, 138.9, 128.2, 128.1, 127.6, 127.2, 127.1, 127.0, 96.2, 88.6, 80.0, 76.5, 72.8, 71.7, 69.4, 57.7, 55.9, 41.0, 40.8, 36.9, 32.0, 31.0, 29.5, 26.3, 25.8, 21.9, 18.0, 14.0, -4.0, -4.8; HRMS calcd. for $\text{C}_{36}\text{H}_{56}\text{O}_5\text{SiNa}$ ($\text{M}+\text{Na}^+$) 619.3789, found 619.3783.



Ketone 15: To a solution **14** (15.9 g, 26.6 mmol) in THF (20 mL), TBAF (80 mL, 80.0 mmol, 1M in THF, 3.0 equiv) was added and heated to 130 °C using microwave irradiation for 60 min. The reaction was diluted with water (300 mL) and extracted with ethyl acetate (2 x 200 mL).

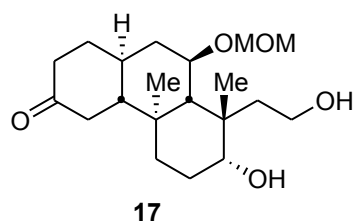
the combined organic extracts were dried over Na_2SO_4 , concentrated under reduced pressure to provide the crude alcohol. The crude product was diluted with DCM (200 mL) and cooled to 0 °C whereupon DMP (34.5 g, 80.0 mmol, 3.0 equiv) was added and stirred for 2 h. Sat aq sodium thiosulfate (200 mL) was added and stirred for 1 h. The mixture was diluted with sat aq sodium bicarbonate (200 mL) and extracted with ethyl acetate (3 x 200 mL). The combined organic extracts were washed with brine (300 mL), dried over Na_2SO_4 , concentrated under reduced pressure and purified by flash chromatography (silica, 10% EtOAc in hex.) to give ketone **15** (12.3 g, 25.7 mmol, 97% over 2 steps) as yellow oil. R_f (20% EtOAc in hex.) = 0.20; $[\alpha]_D^{25} = -36.2^\circ$ (c 2.8, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.32-7.26 (10H, m), 4.69 (2H, s), 4.64 (1H, d, $J = 11.7$ Hz), 4.49 (1H, d, $J = 11.7$ Hz), 4.43 (1H, d, $J = 11.7$ Hz), 4.36 (1H, d, $J = 11.7$ Hz),

4.15-4.11 (1H, m), 3.89-3.83 (1H, m), 3.57-3.51 (1H, m), 3.37 (3H, s), 2.90 (1H, dd, $J = 3.9$, 11.5 Hz), 2.50-2.42 (2H, m), 2.28-2.20 (1H, m), 2.14-2.08 (1H, m), 1.99-1.92 (2H, m), 1.80-1.72 (3H, m), 1.48-1.41 (2H, m), 1.19 (3H, s), 1.18 (3H, s); ^{13}C NMR (100MHz, CDCl_3) δ : 214.9, 139.0, 138.7, 129.5, 128.3, 128.2, 127.7, 127.5, 127.3, 96.4, 87.3, 75.1, 73.1, 71.7, 69.1, 56.1, 55.5, 46.8, 42.3, 33.7, 32.5, 31.9, 28.4, 24.4, 21.8, 20.8; HRMS calcd. for $\text{C}_{30}\text{H}_{40}\text{O}_5\text{Na}$ ($\text{M}+\text{Na}^+$) 503.2773, found 503.2776.

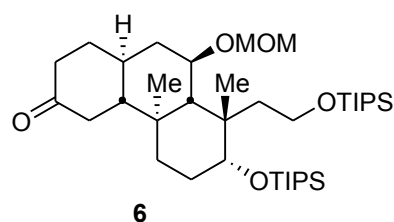


Cyclohexenone 16: To a solution ketone **7** (10.0 g, 20.8 mmol) in ethyl formate (200 mL) at 0 °C, NaH (1.66 g, 41.6 mmol, 60% w/w, 2.0 equiv) was added followed by MeOH (0.84 mL, 20.8 mmol, 1.0 equiv). The reaction was stirred for 30 min at 25 °C and then it was quenched with sat aq NH_4Cl (200 mL). The reaction mixture was then extracted with ethyl acetate (3 x 200 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure to provide the crude formylated product. The crude product was dissolved in DCM (200 mL) and then TEA (11.6 mL, 83.0 mmol, 4.0 equiv) was added followed by methyl vinyl ketone (5.15 mL, 62.4 mmol, 3.0 equiv) and the mixture was stirred for 4 h at 25 °C. The reaction mixture was concentrated under reduced pressure to provide the crude triketone. The crude triketone was dissolved in *tert*-butanol (100 mL). Potassium *tert*-butoxide (31.2 mL, 31.2 mmol, 1M in *tert*-butanol, 1.5 equiv) was added and stirred for 30 min at 25 °C. The reaction mixture was quenched with sat aq NH_4Cl (200 mL) and extracted with ethyl acetate (3 x 200 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 , concentrated under reduced pressure and purified by flash chromatography (silica, 10% EtOAc in hex.) to give cyclohexenone **16** (8.31 g, 15.6 mmol, 75% over 3 steps) as yellow oil. R_f (30% EtOAc in hex.) = 0.21; $[\alpha]_D^{25} = -29.7^\circ$ (c 4.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ : 7.34-7.27 (10H, m), 5.83 (1H, s), 4.70 (2H, s), 4.66 (1H, d, $J = 11.7$ Hz), 4.48 (1H, d, $J = 11.9$ Hz), 4.41 (1H, d, $J = 11.9$ Hz), 4.37 (1H, d, $J = 11.7$ Hz), 4.10-4.04 (1H, m), 3.91-3.85 (1H, m), 3.54-3.49 (1H, m), 3.37 (3H, s), 2.89 (1H, dd, $J = 4.0$, 11.6 Hz), 2.71-2.63 (1H, m), 2.46-2.37 (2H, m), 2.30-2.20 (1H, m), 2.15-2.06 (2H, m), 2.01-1.97 (1H, m), 1.80-1.70 (3H, m), 1.67-1.61 (2H, m), 1.54-1.50 (1H, m), 1.35-1.33 (1H, m), 1.28 (3H, s), 1.17 (3H, s); ^{13}C NMR (100MHz, CDCl_3) δ : 200.8, 173.3, 139.0, 138.7, 128.2, 128.1, 127.7, 127.3,

127.2, 120.3, 96.4, 87.6, 75.6, 72.9, 71.8, 69.2, 57.8, 56.0, 41.7, 41.5, 41.2, 36.2, 35.2, 33.1, 31.1, 29.6, 26.2, 22.9, 21.9, 14.1; HRMS calcd. for C₃₃H₄₅O₅ (M+H⁺) 533.3262, found 533.3260.

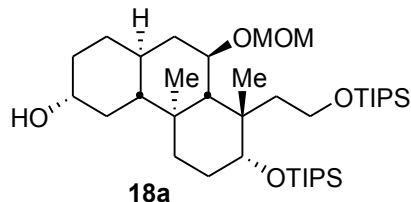


Diol 17: Liquid ammonia (150 mL) was collected in a round bottom flask mounted with a cold finger at -78 °C. Cyclohexenone **16** (5.00 g, 9.39 mmol) in THF (20 mL) and ethanol (1.10 mL, 18.8 mmol, 2.0 equiv) was added to the ammonia. Lithium wire was slowly added until a dark blue reaction mixture persisted. The reaction was stirred at reduced temperature for 4 h. The reaction was quenched with sat aq NH₄Cl (5 mL) whereupon the dark blue color faded and warmed to rt over the course of 1 h to allow for the evaporation of liquid ammonia. The reaction mixture was diluted with water (200 mL) and extracted with ethyl acetate (5 x 150 mL). The combined organic extracts were washed with brine and dried over Na₂SO₄, concentrated under reduced and purified by flash chromatography (silica, EtOAc) to give diol **17** (2.43 g, 6.85 mmol, 73%) as yellow oil. *R*_f (EtOAc) = 0.15; [α]_D²⁵ = -20.7° (*c* 4.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ: 4.71 (1H, d, *J* = 6.9 Hz), 4.59 (1H, d, *J* = 6.9 Hz), 3.84 (1H, dt, *J* = 4.2, 10.7 Hz), 3.74-3.60 (4H, m), 3.35 (3H, s), 3.17 (1H, dd, *J* = 4.0, 11.7 Hz), 2.34-2.27 (3H, m), 2.03-1.92 (3H, m), 1.72-1.54 (6H, m), 1.37 (3H, s), 1.25-1.04 (5H, m), 0.93 (3H, s); ¹³C NMR (100MHz, CDCl₃) δ: 212.6, 95.8, 78.2, 75.9, 62.4, 59.9, 58.8, 56.1, 54.8, 42.3, 41.1, 40.8, 38.9, 37.4, 34.5, 33.3, 32.6, 26.5, 25.9, 15.5; HRMS calcd. for C₂₀H₃₄O₅Na (M+Na⁺) 377.2298, found 377.2296.

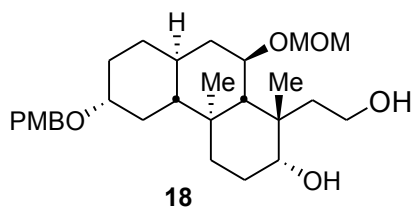


Ketone 6: To a solution of diol **17** (3.33 g, 9.39 mmol) in DCM (50 mL) at 0 °C, DIPEA (8.20 mL, 46.9 mmol, 5.0 equiv) and TIPSOTf (10.2 mL, 37.5 mmol, 4.0 equiv) were added and stirred for 2 h at rt. The reaction mixture was quenched with sat aq NaHCO₃ (100 mL) and extracted with ethyl acetate (2 x 200 mL). The combined organic extracts were washed with brine and dried over Na₂SO₄, concentrated under reduced pressure to provide the crude silyl ether. The crude product was dissolved in DCM (100 mL) and cooled to 0 °C whereupon TFA (1.09 mL, 14.1 mmol, 1.5

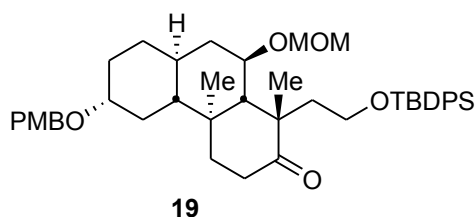
equiv) was slowly added and stirred at that temperature for 30 min. The reaction mixture was cautiously quenched with sat aq NaHCO₃ (100 mL) and extracted with ethyl acetate (2 x 200 mL). The combined organic extracts were washed with brine, dried over Na₂SO₄, concentrated under reduced pressure and purified by flash chromatography (silica, 5% EtOAc in hex.) to give ketone **6** (3.63 g, 5.44 mmol, 80% over 2 steps) as yellow oil. R_f (20% EtOAc in hex.) = 0.30; [α]_D²⁵ = - 10.8° (c 4.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ: 4.73 (s, 2H), 4.07-4.00 (1H, m), 3.92-3.86 (1H, m), 3.71-3.65 (1H, m), 3.40 (3H, s), 3.29 (1H, dd, *J* = 3.8, 11.7 Hz), 2.36-2.27 (3H, m), 2.10-1.96 (3H, m), 1.76-1.69 (2H, m), 1.63-1.51 (6H, m), 1.32 (3H, s), 1.14-1.11 (3H, m), 1.07-1.04 (43H, m), 0.97 (3H, s); ¹³C NMR (100MHz, CDCl₃) δ: 212.5, 96.6, 81.6, 76.8, 62.1, 60.4, 55.1, 42.4, 41.7, 41.0, 40.9, 38.5, 37.6, 35.0, 34.6, 33.5, 27.0, 26.8, 18.4, 18.3, 18.1, 15.9, 13.0, 12.1; HRMS calcd. for C₃₈H₇₄O₅Si₂Na (M+Na⁺) 689.4967, found 689.4966.



Diol 18: To a solution ketone **6** (2.00 g, 3.00 mmol) in dry THF (10 mL) and EtOH (10 mL) at -78 °C, sodium borohydride (227 mg, 6.00 mmol, 2.0 equiv) was added and stirred for 3 hour at that temperature. Sat aq NH₄Cl (100 mL) was cautiously added to the mixture and it was allowed to warm to room temperature and extracted with ethyl acetate (3 x 200 mL). The combined organic extracts were dried over Na₂SO₄, concentrated under reduced pressure and purified by flash chromatography (silica, 10% EtOAc in hex.) to give alcohol **18a** (1.40 g, 2.10 mmol, 70%) as yellow oil. R_f (20% EtOAc in hex.) = 0.15; [α]_D²⁵ = - 9.81° (c 4.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ: 4.71 (1H, d, *J* = 6.8 Hz), 4.68 (1H, d, *J* = 6.8 Hz), 4.06-3.99 (1H, m), 3.81 (1H, dt, *J* = 4.1, 10.6 Hz), 3.69-3.63 (1H, m), 3.54-3.49 (1H, m), 3.38 (3H, s), 3.28 (1H, dd, *J* = 3.5, 11.7 Hz), 2.23-2.18 (1H, m), 2.09-2.01 (1H, m), 1.91-1.89 (2H, m), 1.80-1.53 (7H, m), 1.30 (3H, s), 1.00-1.09 (48H, m), 0.90 (3H, s); ¹³C NMR (100MHz, CDCl₃) δ: 96.4, 81.8, 77.0, 71.4, 62.1, 60.8, 55.9, 53.0, 42.4, 42.3, 38.2, 37.9, 35.3, 34.9, 34.8, 34.6, 32.2, 27.2, 26.8, 18.4, 18.3, 18.1 (2x), 16.3, 13.0, 12.0; HRMS calcd. for C₃₈H₇₆O₅Si₂Na (M+Na⁺) 691.5123, found 691.5125.

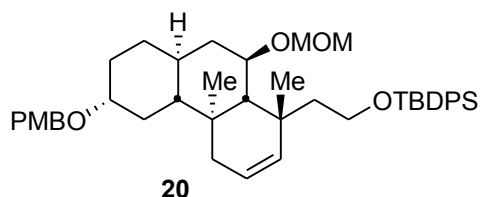


To the alcohol **18a** (2.03 g, 3.03 mmol) in DMF (15 mL), sodium hydride (364 mg, 9.10 mmol, 3.0 equiv) was added and the reaction was heated to 60 °C for 30 min. The mixture was cooled to room temperature and 4-methoxybenzyl chloride (2.07 mL, 15.2 mmol, 5.0 equiv) was added and it was stirred for 15 h. The reaction was quenched slowly with sat aq NH₄Cl (100 mL) and extracted with ethyl acetate (3 x 200 mL). The combined organic extracts were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure to provide the crude benzyl ether. The crude product was dissolved in THF (3 mL), TBAF (9.10 mL, 9.10 mmol, 1M in THF, 3.0 equiv) and the reaction was heated to 130 °C using microwave irradiation for 60 min. The mixture was diluted with water (300 mL) and extracted with ethyl acetate (3 x 200 mL). The combined organic extracts were washed with brine, dried over Na₂SO₄, concentrated under reduced pressure and purified by flash chromatography (silica, EtOAc) to give diol **18** (868 mg, 1.82 mmol, 60% over 2 steps) as yellow oil. R_f (EtOAc) = 0.51; $[\alpha]_D^{25} = -15.9^\circ$ (*c* 4.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ : 7.25 (2H, d, *J* = 8.6 Hz), 6.86 (2H, d, *J* = 8.6 Hz), 4.70 (1H, d, *J* = 6.9 Hz), 4.56 (1H, d, *J* = 6.9 Hz), 4.49 (1H, d, *J* = 11.4 Hz), 4.44 (1H, d, *J* = 11.4 Hz), 3.79 (3H, s), 3.78-3.61 (5H, m), 3.34 (3H, s), 3.29-3.22 (1H, m), 3.17 (1H, dd, *J* = 4.0, 11.8 Hz), 2.16 (1H, dt, *J* = 4.0, 12.4 Hz), 2.07-1.92 (3H, m), 1.75-1.57 (5H, m), 1.37 (3H, s), 1.27-0.91 (7H, m), 0.87 (3H, s), 0.73-0.67 (1H, m); ¹³C NMR (100MHz, CDCl₃) δ : 159.0, 130.9, 129.1, 113.7, 95.7, 78.6, 77.9, 76.2, 69.5, 60.5, 59.1, 56.1, 55.2, 53.0, 42.4, 41.8, 38.6, 37.9, 35.1, 32.6, 32.1, 31.8, 31.5, 26.9, 26.0, 16.0; HRMS calcd. for C₂₈H₄₄O₆Na (M+Na⁺) 499.3036, found 499.3038.



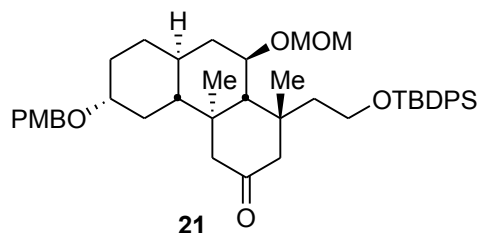
Ketone 19: To diol **18** (1.00 g, 2.10 mmol) in DCM (20 mL), DIPEA (1.47 mL, 8.39 mmol, 4.0 equiv) and TBDPSCl (1.08 mL, 4.20 mmol, 2.0 equiv) were added at 0 °C. After 2 h, the reaction was diluted with water (100 mL) and extracted with ethyl acetate (3 x 100 mL). The combined organic extracts were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure to provide the crude silylated product. The crude product was dissolved in DCM (20 mL) and cooled to 0 °C whereupon DMP (2.67 g, 6.29 mmol, 3.0 equiv) was added. After 2 h, sat aq sodium thiosulfate

(100 mL) was added and stirred for 1 hour at rt. The reaction was diluted with sat aq sodium bicarbonate (100 mL) and extracted with ethyl acetate (3 x 100 mL). The combined organic extracts were washed with brine, dried over Na₂SO₄, concentrated under reduced pressure and purified by flash chromatography (silica, 10% EtOAc in hex.) to give ketone **19** (1.35 g, 1.89 mmol, 86% over 2 steps) as yellow oil. R_f (20% EtOAc in hex.) = 0.23; [α]_D²⁵ = - 4.1° (c 4.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ: 7.67-7.64 (4H, m), 7.42-7.36 (6H, m), 7.26 (2H, m), 6.87 (2H, d, *J* = 7.6 Hz), 4.68 (1H, d, *J* = 6.6 Hz), 4.59 (1H, d, *J* = 6.6 Hz), 4.51 (1H, d, *J* = 11.2 Hz), 4.45 (1H, d, *J* = 11.2 Hz), 3.85-3.75 (1H, m), 3.79 (3H, s), 3.71-3.66 (1H, m), 3.62-3.58 (1H, m), 3.36 (3H, s), 3.31-3.26 (1H, m), 2.51 (1H, dt, *J* = 5.6, 13.8 Hz), 2.27-2.23 (2H, m), 2.18-1.84 (6H, m), 1.77-1.73 (1H, m), 1.48-1.46 (1H, m), 1.39-1.19 (7H, m), 1.04 (9H, s), 1.00 (3H, s), 1.00-0.93 (1H, m), 0.78-0.72 (1H, m); ¹³C NMR (100MHz, CDCl₃) δ: 159.0, 135.5, 135.5, 133.7, 130.9, 129.5, 129.1, 127.5, 113.7, 95.9, 77.6, 77.2, 75.6, 69.6, 61.2, 60.7, 56.1, 55.2, 52.2, 50.1, 41.6, 38.2, 38.1, 36.4, 34.9, 32.0, 31.8, 31.6, 26.8, 24.7, 19.0, 15.7; HRMS calcd. for C₄₄H₆₁O₆Si (M+H⁺) 713.4232, found 713.4228.



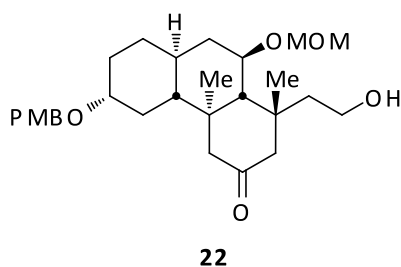
Alkene 20: To ketone **19** (3.50 g, 4.91 mmol) in dry THF (25 mL) at -78 °C, NaHMDS (24.5 mL, 24.5 mmol, 1M in THF, 5.0 equiv) was added. After 1 h, PhNTf₂ (3.51 g, 9.82 mmol, 2.0 equiv) was added and stirred for 1 h at that temperature. The reaction was warmed to room temperature, quenched with sat aq NH₄Cl (100 mL) and extracted with ethyl acetate (3 x 200 mL). The combined organic extracts were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure to provide the crude vinyl triflate. The crude product was dissolved in DMF (10 mL). Pd(OAc)₂ (110 mg, 0.491 mmol, 0.10 equiv) was added, followed by Ph₃P (258 mg, 0.982 mmol, 0.20 equiv), DIPEA (3.43 mL, 19.6 mmol, 4.0 equiv) and formic acid (0.86 mL, 19.6 mmol, 4.0 equiv). The mixture was heated to 75 °C for 60 min. The black mixture was diluted with water (300 mL) and extracted with ethyl acetate (3 x 200 mL). The combined organic extracts were washed with brine, dried over Na₂SO₄, concentrated under reduced pressure and purified by flash chromatography (silica, 5% EtOAc in hex.) to give alkene **20** (3.08 g, 4.42 mmol, 90% over 2 steps) as yellow oil. R_f (10% EtOAc in hex.) = 0.52; [α]_D²⁵ = - 16.7° (c 4.0, CHCl₃); ¹H NMR

(400 MHz, CDCl₃) δ : 7.69-7.67 (4H, m), 7.42-7.36 (6H, m), 7.27 (2H, d, J = 8.2 Hz), 6.88 (2H, d, J = 8.2 Hz), 5.41-5.39 (2H, m), 4.72 (1H, d, J = 6.8 Hz), 4.66 (1H, d, J = 6.8 Hz), 4.49 (1H, d, J = 11.3 Hz), 4.47 (1H, d, J = 11.3 Hz), 3.86-3.82 (2H, m), 3.80 (3H, s), 3.71-3.64 (1H, m), 3.40 (3H, s), 3.30 (1H, m), 2.26-2.23 (1H, m), 2.09-1.91 (4H, m), 1.79-1.72 (2H, m), 1.65-1.61 (1H, m), 1.40-1.30 (6H, m), 1.18 (3H, s), 1.08-1.02 (1H, m), 1.05 (9H, s), 0.79 (3H, s); ¹³C NMR (100MHz, CDCl₃) δ : 159.0, 136.6, 135.5, 134.0, 131.0, 129.5, 129.1, 129.1, 127.5, 125.3, 124.3, 120.6, 113.7, 96.2, 78.0, 76.9, 69.5, 61.2, 56.9, 56.1, 55.2, 51.7, 41.4, 39.2, 37.4, 36.9, 36.7, 34.2, 32.3, 31.7, 31.7, 31.6, 26.8, 19.1, 18.1, 14.9; HRMS calcd. for C₄₄H₆₀O₅SiNa (M+Na⁺) 719.4102, found 719.4107.

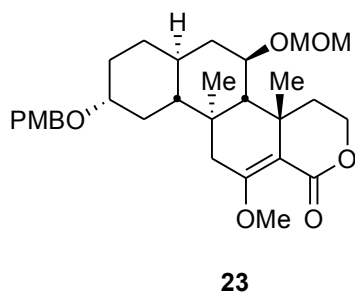


Ketone 21: To alkene **20** (3.42 g, 4.91 mmol) in dry THF (25 mL), BH₃·THF (10.0 mL, 10.0 mmol, 2.0 equiv) was added and heated to reflux. After 15 h, a solution of 3N NaOH-30% w/w H₂O₂ (20 mL, 1:1) was added at 0 °C and the reaction was warmed to room temperature. After 60 min, the mixture was diluted with water (100 mL) and extracted with ethyl acetate (3 x 200 mL). The combined organic extracts were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure to provide the crude alcohol. The crude product was dissolved in DCM (20 mL). DMP (4.17 g, 9.82 mmol, 3.0 equiv) was added at 0 °C and stirred for 2 h at room temperature. Sat aq sodium thiosulfate (100 mL) was added and stirred for an additional 60 min. The mixture was diluted with sat aq sodium bicarbonate (100 mL) and extracted with ethyl acetate (3 x 200 mL). The combined organic extracts were washed with brine, dried over Na₂SO₄, concentrated under reduced pressure and purified by flash chromatography (silica, 10% EtOAc in hex.) to give ketone **21** (1.19 g, 1.67 mmol, 34% over 2 steps) as a yellow oil and its isomeric ketone **19** (595 mg, 0.835 mmol, 17% over 2 steps) as yellow oil. R_f (20% EtOAc in hex.) = 0.18; [α]_D²⁵ = - 21.0° (c 4.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ : 7.67-7.65 (4H, m), 7.43-7.37 (6H, m), 7.25 (2H, d, J = 9.2 Hz), 6.87 (2H, d, J = 9.2 Hz), 4.67 (1H, d, J = 6.8 Hz), 4.60 (1H, d, J = 6.8 Hz), 4.48 (1H, d, J = 11.2 Hz), 4.45 (1H, d, J = 11.2 Hz), 3.80 (3H, s), 3.77-3.69 (3H, m), 3.36 (3H, s), 3.31-3.22 (1H, m), 2.58 (1H, d, J = 13.6 Hz), 2.33 (1H, d, J = 15.6 Hz), 2.28-2.24 (1H, m), 2.08-1.97 (3H, m), 1.93-1.84 (3H, m), 1.78-

1.74 (1H, m), 1.36 (1H, d, $J = 10.4$ Hz), 1.29-1.21 (3H, m), 1.16 (3H, s), 1.04 (9H, s), 1.09-0.98 (3H, m), 0.95 (3H, s); ^{13}C NMR (100MHz, CDCl_3) δ : 212.0, 159.0, 135.5, 133.7, 130.8, 129.6, 129.1, 127.6, 127.6, 113.8, 96.1, 77.4, 76.2, 69.6, 60.7, 58.7, 56.1, 55.3, 53.9, 53.1, 52.5, 42.2, 41.3, 40.1, 38.0, 34.0, 32.0, 31.7, 31.5, 26.8, 19.0, 16.9; HRMS calcd. for $\text{C}_{44}\text{H}_{61}\text{O}_6\text{Si}$ ($\text{M}+\text{H}^+$) 713.4232, found 713.4231.

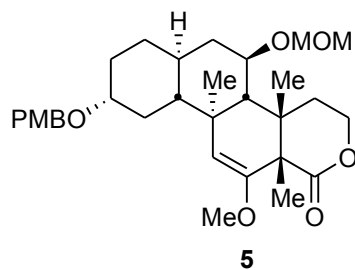


Alcohol 22: To ketone **21** (300 mg, 0.42 mmol) in THF (5.00 mL), TBAF (1.26 mL, 1.26 mmol, 1M in THF, 3.0 equiv) was added. After 4 h, the reaction was diluted with water (50 mL) and extracted with ethyl acetate (3 x 50 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 , concentrated under reduced pressure and purified by flash chromatography (silica, EtOAc) to give alcohol **22** (150 mg, 0.316 mmol, 75%) as yellow oil. R_f (EtOAc) = 0.40; $[\alpha]_D^{25} = -31.2^\circ$ (c 4.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ : 7.23 (2H, d, $J = 8.4$ Hz), 6.86 (2H, d, $J = 8.4$ Hz), 4.74 (1H, d, $J = 6.4$ Hz), 4.66 (1H, d, $J = 6.4$ Hz), 4.48 (1H, d, $J = 11.4$ Hz), 4.44 (1H, d, $J = 11.4$ Hz), 3.85-3.77 (1H, m), 3.79 (3H, s), 3.75-3.70 (2H, m), 3.38 (3H, s), 3.29-3.24 (1H, m), 2.59 (1H, d, $J = 13.6$ Hz), 2.36-2.25 (2H, m), 2.17-2.14 (1H, m), 1.93-1.74 (5H, m), 1.48 (1H, d, $J = 10.4$ Hz), 1.31-1.17 (2H, m), 1.25 (3H, s), 1.06-0.90 (3H, m), 0.99 (3H, s); ^{13}C NMR (100MHz, CDCl_3) δ : 212.1, 159.0, 130.8, 129.1, 113.8, 95.9, 77.4, 76.0, 69.6, 59.4, 59.1, 56.2, 55.2, 53.8, 53.1, 53.0, 43.0, 41.3, 41.1, 37.8, 34.2, 32.1, 31.9, 31.7, 31.5, 16.8; HRMS calcd. for $\text{C}_{28}\text{H}_{43}\text{O}_6$ ($\text{M}+\text{H}^+$) 475.3024, found 475.3052.



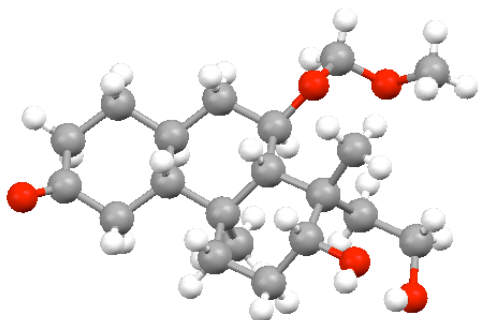
Lactone 23: To alcohol **22** (78 mg, 0.164 mmol) in THF (2.00 mL) and DMPU (2.00 mL), $t\text{BuOLi}$ (0.82 mL, 0.822 mmol, 5.0 equiv) and dimethyl carbonate (0.14 mL, 1.64 mmol, 10.0 equiv) were added and heated to 70°C for 60 min. The reaction was cooled to room temperature whereupon iodomethane (0.21 mL, 3.29 mmol, 20.0 equiv) was added. After 4 h, the reaction was diluted with water (50 mL) extracted with ethyl acetate (3 x 50 mL). The combined organic

extracts were washed with brine, dried over Na₂SO₄, concentrated under reduced pressure and purified by flash chromatography (silica, 30% EtOAc in hex.) to give lactone **23** (66 mg, 0.128 mmol, 78%) as yellow oil. R_f (50% EtOAc in hex.) = 0.25; $[\alpha]_D^{25} = -11.9^\circ$ (c 3.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ : 7.26 (2H, d, $J = 8.4$ Hz), 6.86 (2H, d, $J = 8.4$ Hz), 4.73 (1H, d, $J = 6.8$ Hz), 4.63 (1H, d, $J = 6.8$ Hz), 4.55 (1H, d, $J = 11.2$ Hz), 4.43 (1H, d, $J = 11.2$ Hz), 4.29-4.24 (1H, m), 4.13-4.06 (1H, m), 3.79 (3H, s), 3.72-3.66 (1H, m), 3.68 (3H, s), 3.37 (3H, s), 3.37-3.20 (1H, m), 2.64 (1H, d, $J = 9.2$ Hz), 2.37 (1H, d, $J = 16.4$ Hz), 2.28-2.25 (1H, m), 2.15-2.11 (1H, m), 2.08-2.03 (1H, m), 1.98-1.92 (1H, m), 1.88 (1H, d, $J = 16.4$ Hz), 1.79-1.75 (1H, m), 1.43-1.40 (1H, m), 1.37 (3H, s), 1.30-1.18 (3H, m), 1.12-0.97 (3H, m), 0.85 (3H, s); ¹³C NMR (100MHz, CDCl₃) δ : 167.9, 159.1, 157.8, 130.8, 129.2, 113.8, 111.9, 96.0, 77.7, 76.7, 69.9, 64.8, 56.1, 56.0, 55.2, 51.2, 40.8, 39.2, 38.4, 36.9, 34.9, 34.6, 32.1, 31.9, 31.5, 30.7, 14.4; HRMS calcd. for C₃₀H₄₃O₇ (M+H⁺) 515.3009, found 515.3007.



Lactone 5: To lactone **23** (58 mg, 0.113 mmol) in THF (2.00 mL) and DMPU (2.00 mL), LiHMDS (0.45 mL, 0.45 mmol, 4.0 equiv) was added at -10 °C. After 60 min, iodomethane (0.44 mL, 7.08 mmol, 15.0 equiv) was added and the reaction was allowed to stir at that temperature for an additional 30 min and then it was warmed to room temperature. After 4 h, the reaction mixture was diluted with water (50 mL) and extracted with diethyl ether (3 x 50 mL). The combined organic extracts were washed with brine, dried over Na₂SO₄, concentrated under reduced pressure and purified by flash chromatography (silica, 30% EtOAc in hex.) to give lactone **5** (45 mg, 0.090 mmol, 80%) as white solid. R_f (50% EtOAc in hex.) = 0.30; $[\alpha]_D^{25} = -16.3^\circ$ (c 4.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ : 7.26 (2H, d, $J = 8.6$ Hz), 6.86 (2H, d, $J = 8.6$ Hz), 4.69 (1H, d, $J = 6.8$ Hz), 4.67 (1H, s), 4.60 (1H, d, $J = 6.8$ Hz), 4.55 (1H, d, $J = 11.2$ Hz), 4.43 (1H, d, $J = 11.2$ Hz), 4.13 (1H, ddd, $J = 2.4, 5.5, 11.3$ Hz), 3.97 (1H, dt, $J = 4.4, 11.3$ Hz), 3.79 (3H, s), 3.52 (3H, s), 3.38 (3H, s), 3.38-3.30 (2H, m), 2.40-2.36 (1H, m), 2.28-2.24 (1H, m), 2.16-2.09 (2H, m), 1.79-1.75 (1H, m), 1.71-1.65 (2H, m), 1.42-1.35 (1H, m), 1.38 (3H, s), 1.27-1.21 (1H, m), 1.21 (3H, s), 1.15-1.06 (2H, m), 1.00-0.89 (2H, m), 0.95 (3H, s); ¹³C NMR (100MHz, CDCl₃) δ : 174.3, 159.1, 153.1, 130.9, 129.2, 113.8, 101.1, 95.7, 77.8, 75.0, 69.9, 65.4, 56.1, 55.2, 54.9,

53.2, 52.5, 51.6, 42.1, 39.7, 39.2, 35.9, 33.1, 32.5, 32.0, 31.8, 31.6, 20.9, 17.8; HRMS calcd. for $C_{31}H_{45}O_7$ ($M+H^+$) 529.3160, found 529.3163.



Crystal data and structure refinement for **17**.

Table 1. Crystal data and structure refinement for **17**.

Identification code	LT-292	
Empirical formula	C ₂₀ H ₃₄ O ₅	
Formula weight	354.47	
Temperature	90(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.1066(2) Å	α = 90°.
	b = 14.0190(5) Å	β = 90°.
	c = 16.5882(6) Å	γ = 90°.
Volume	1885.19(11) Å ³	
Z	4	
Density (calculated)	1.249 Mg/m ³	
Absorption coefficient	0.709 mm ⁻¹	
F(000)	776	
Crystal size	0.25 x 0.18 x 0.11 mm ³	
Theta range for data collection	4.13 to 65.27°.	
Index ranges	-9 ≤ h ≤ 8, -15 ≤ k ≤ 16, -18 ≤ l ≤ 19	
Reflections collected	10718	
Independent reflections	3087 [R(int) = 0.0335]	
Completeness to theta = 60.00°	99.8 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9261 and 0.8427	

Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3087 / 0 / 231
Goodness-of-fit on F ²	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0309, wR2 = 0.0755
R indices (all data)	R1 = 0.0335, wR2 = 0.0775
Absolute structure parameter	0.02(17)
Largest diff. peak and hole	0.142 and -0.147 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **17**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	-847(1)	1639(1)	9656(1)	25(1)
O(2)	-2581(1)	-440(1)	7103(1)	20(1)
O(3)	5280(2)	1679(1)	5393(1)	40(1)
O(4)	-3515(1)	2642(1)	9354(1)	28(1)
O(5)	-5417(1)	-183(1)	7000(1)	30(1)
C(1)	-1461(2)	990(1)	8322(1)	18(1)
C(2)	-156(2)	1467(1)	8871(1)	21(1)
C(3)	588(2)	2365(1)	8529(1)	23(1)
C(4)	1497(2)	2135(1)	7749(1)	22(1)
C(5)	380(2)	1686(1)	7107(1)	19(1)
C(6)	-601(2)	815(1)	7480(1)	17(1)
C(7)	-1696(2)	387(1)	6813(1)	18(1)
C(8)	-635(2)	55(1)	6106(1)	23(1)
C(9)	502(2)	808(1)	5754(1)	23(1)
C(10)	1502(2)	1274(1)	6430(1)	21(1)
C(11)	2761(2)	1997(1)	6085(1)	27(1)
C(12)	3788(2)	1588(1)	5415(1)	30(1)
C(13)	2832(2)	1084(1)	4765(1)	34(1)
C(14)	1645(2)	353(1)	5128(1)	31(1)
C(15)	-1856(2)	25(1)	8732(1)	22(1)
C(16)	-3074(2)	1560(1)	8205(1)	20(1)

C(17)	-4109(2)	1815(1)	8939(1)	23(1)
C(18)	-724(2)	2479(1)	6759(1)	22(1)
C(19)	-4028(2)	-632(1)	6666(1)	25(1)
C(20)	-6016(2)	-647(2)	7701(1)	36(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for **17**.

O(1)-C(2)	1.4378(19)	C(7)-C(8)	1.527(2)
O(1)-H(10)	0.8400	C(7)-H(7)	1.0000
O(2)-C(19)	1.4049(19)	C(8)-C(9)	1.519(2)
O(2)-C(7)	1.4453(19)	C(8)-H(8B)	0.9900
O(3)-C(12)	1.217(2)	C(8)-H(8A)	0.9900
O(4)-C(17)	1.432(2)	C(9)-C(10)	1.530(2)
O(4)-H(4O)	0.8400	C(9)-C(14)	1.532(2)
O(5)-C(19)	1.404(2)	C(9)-H(9)	1.0000
O(5)-C(20)	1.418(2)	C(10)-C(11)	1.548(2)
C(1)-C(16)	1.544(2)	C(10)-H(10)	1.0000
C(1)-C(15)	1.546(2)	C(11)-C(12)	1.502(2)
C(1)-C(2)	1.548(2)	C(11)-H(11A)	0.9900
C(1)-C(6)	1.580(2)	C(11)-H(11B)	0.9900
C(2)-C(3)	1.507(2)	C(12)-C(13)	1.505(3)
C(2)-H(2)	1.0000	C(13)-C(14)	1.529(2)
C(3)-C(4)	1.523(2)	C(13)-H(13B)	0.9900
C(3)-H(3B)	0.9900	C(13)-H(13A)	0.9900
C(3)-H(3A)	0.9900	C(14)-H(14B)	0.9900
C(4)-C(5)	1.535(2)	C(14)-H(14A)	0.9900
C(4)-H(4B)	0.9900	C(15)-H(15A)	0.9800
C(4)-H(4A)	0.9900	C(15)-H(15C)	0.9800
C(5)-C(18)	1.540(2)	C(15)-H(15B)	0.9800
C(5)-C(10)	1.556(2)	C(16)-C(17)	1.521(2)
C(5)-C(6)	1.583(2)	C(16)-H(16B)	0.9900
C(6)-C(7)	1.541(2)	C(16)-H(16A)	0.9900
C(6)-H(6)	1.0000	C(17)-H(17A)	0.9900

C(17)-H(17B)	0.9900	C(5)-C(4)-H(4A)	109.0
C(18)-H(18B)	0.9800	H(4B)-C(4)-H(4A)	107.8
C(18)-H(18C)	0.9800	C(4)-C(5)-C(18)	107.88(13)
C(18)-H(18A)	0.9800	C(4)-C(5)-C(10)	107.95(12)
C(19)-H(19B)	0.9900	C(18)-C(5)-C(10)	109.70(13)
C(19)-H(19A)	0.9900	C(4)-C(5)-C(6)	109.95(12)
C(20)-H(20B)	0.9800	C(18)-C(5)-C(6)	114.33(12)
C(20)-H(20A)	0.9800	C(10)-C(5)-C(6)	106.87(12)
C(20)-H(20C)	0.9800	C(7)-C(6)-C(1)	116.17(12)
		C(7)-C(6)-C(5)	107.97(12)
C(2)-O(1)-H(10)	109.5	C(1)-C(6)-C(5)	116.61(12)
C(19)-O(2)-C(7)	113.33(12)	C(7)-C(6)-H(6)	104.9
C(17)-O(4)-H(4O)	109.5	C(1)-C(6)-H(6)	104.9
C(19)-O(5)-C(20)	113.13(14)	C(5)-C(6)-H(6)	104.9
C(16)-C(1)-C(15)	109.41(13)	O(2)-C(7)-C(8)	106.89(12)
C(16)-C(1)-C(2)	115.41(13)	O(2)-C(7)-C(6)	111.08(12)
C(15)-C(1)-C(2)	105.15(13)	C(8)-C(7)-C(6)	110.21(12)
C(16)-C(1)-C(6)	110.02(12)	O(2)-C(7)-H(7)	109.5
C(15)-C(1)-C(6)	110.10(12)	C(8)-C(7)-H(7)	109.5
C(2)-C(1)-C(6)	106.58(12)	C(6)-C(7)-H(7)	109.5
O(1)-C(2)-C(3)	110.97(13)	C(9)-C(8)-C(7)	115.21(13)
O(1)-C(2)-C(1)	109.82(13)	C(9)-C(8)-H(8B)	108.5
C(3)-C(2)-C(1)	114.37(13)	C(7)-C(8)-H(8B)	108.5
O(1)-C(2)-H(2)	107.1	C(9)-C(8)-H(8A)	108.5
C(3)-C(2)-H(2)	107.1	C(7)-C(8)-H(8A)	108.5
C(1)-C(2)-H(2)	107.1	H(8B)-C(8)-H(8A)	107.5
C(2)-C(3)-C(4)	109.69(13)	C(8)-C(9)-C(10)	109.63(13)
C(2)-C(3)-H(3B)	109.7	C(8)-C(9)-C(14)	109.77(13)
C(4)-C(3)-H(3B)	109.7	C(10)-C(9)-C(14)	110.75(13)
C(2)-C(3)-H(3A)	109.7	C(8)-C(9)-H(9)	108.9
C(4)-C(3)-H(3A)	109.7	C(10)-C(9)-H(9)	108.9
H(3B)-C(3)-H(3A)	108.2	C(14)-C(9)-H(9)	108.9
C(3)-C(4)-C(5)	113.00(13)	C(9)-C(10)-C(11)	110.96(13)
C(3)-C(4)-H(4B)	109.0	C(9)-C(10)-C(5)	112.16(12)
C(5)-C(4)-H(4B)	109.0	C(11)-C(10)-C(5)	114.18(13)
C(3)-C(4)-H(4A)	109.0	C(9)-C(10)-H(10)	106.3

C(11)-C(10)-H(10)	106.3	C(17)-C(16)-H(16B)	107.5
C(5)-C(10)-H(10)	106.3	C(1)-C(16)-H(16B)	107.5
C(12)-C(11)-C(10)	112.89(14)	C(17)-C(16)-H(16A)	107.5
C(12)-C(11)-H(11A)	109.0	C(1)-C(16)-H(16A)	107.5
C(10)-C(11)-H(11A)	109.0	H(16B)-C(16)-H(16A)	107.0
C(12)-C(11)-H(11B)	109.0	O(4)-C(17)-C(16)	112.96(13)
C(10)-C(11)-H(11B)	109.0	O(4)-C(17)-H(17A)	109.0
H(11A)-C(11)-H(11B)	107.8	C(16)-C(17)-H(17A)	109.0
O(3)-C(12)-C(11)	122.24(18)	O(4)-C(17)-H(17B)	109.0
O(3)-C(12)-C(13)	122.67(17)	C(16)-C(17)-H(17B)	109.0
C(11)-C(12)-C(13)	115.07(15)	H(17A)-C(17)-H(17B)	107.8
C(12)-C(13)-C(14)	110.89(15)	C(5)-C(18)-H(18B)	109.5
C(12)-C(13)-H(13B)	109.5	C(5)-C(18)-H(18C)	109.5
C(14)-C(13)-H(13B)	109.5	H(18B)-C(18)-H(18C)	109.5
C(12)-C(13)-H(13A)	109.5	C(5)-C(18)-H(18A)	109.5
C(14)-C(13)-H(13A)	109.5	H(18B)-C(18)-H(18A)	109.5
H(13B)-C(13)-H(13A)	108.0	H(18C)-C(18)-H(18A)	109.5
C(13)-C(14)-C(9)	111.58(15)	O(5)-C(19)-O(2)	112.33(13)
C(13)-C(14)-H(14B)	109.3	O(5)-C(19)-H(19B)	109.1
C(9)-C(14)-H(14B)	109.3	O(2)-C(19)-H(19B)	109.1
C(13)-C(14)-H(14A)	109.3	O(5)-C(19)-H(19A)	109.1
C(9)-C(14)-H(14A)	109.3	O(2)-C(19)-H(19A)	109.1
H(14B)-C(14)-H(14A)	108.0	H(19B)-C(19)-H(19A)	107.9
C(1)-C(15)-H(15A)	109.5	O(5)-C(20)-H(20B)	109.5
C(1)-C(15)-H(15C)	109.5	O(5)-C(20)-H(20A)	109.5
H(15A)-C(15)-H(15C)	109.5	H(20B)-C(20)-H(20A)	109.5
C(1)-C(15)-H(15B)	109.5	O(5)-C(20)-H(20C)	109.5
H(15A)-C(15)-H(15B)	109.5	H(20B)-C(20)-H(20C)	109.5
H(15C)-C(15)-H(15B)	109.5	H(20A)-C(20)-H(20C)	109.5
C(17)-C(16)-C(1)	119.20(13)		

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **17**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
O(1)	23(1)	33(1)	18(1)	-5(1)	-3(1)	-4(1)
O(2)	18(1)	19(1)	24(1)	-1(1)	-2(1)	-4(1)
O(3)	27(1)	46(1)	48(1)	0(1)	13(1)	-4(1)
O(4)	23(1)	33(1)	26(1)	-11(1)	1(1)	2(1)
O(5)	20(1)	31(1)	38(1)	4(1)	-1(1)	3(1)
C(1)	18(1)	18(1)	19(1)	-2(1)	-2(1)	0(1)
C(2)	21(1)	24(1)	18(1)	-3(1)	-2(1)	1(1)
C(3)	24(1)	23(1)	23(1)	-5(1)	-3(1)	-6(1)
C(4)	22(1)	21(1)	25(1)	-2(1)	1(1)	-5(1)
C(5)	20(1)	18(1)	20(1)	0(1)	1(1)	-1(1)
C(6)	17(1)	16(1)	18(1)	0(1)	-2(1)	2(1)
C(7)	18(1)	16(1)	21(1)	0(1)	-1(1)	-2(1)
C(8)	25(1)	21(1)	22(1)	-5(1)	1(1)	-2(1)
C(9)	25(1)	23(1)	22(1)	-2(1)	3(1)	0(1)
C(10)	21(1)	20(1)	21(1)	0(1)	2(1)	1(1)
C(11)	23(1)	27(1)	31(1)	-2(1)	5(1)	-4(1)
C(12)	29(1)	26(1)	35(1)	5(1)	11(1)	0(1)
C(13)	38(1)	35(1)	30(1)	-5(1)	14(1)	-6(1)
C(14)	35(1)	28(1)	29(1)	-7(1)	8(1)	-6(1)
C(15)	22(1)	21(1)	22(1)	2(1)	1(1)	0(1)
C(16)	19(1)	21(1)	20(1)	-3(1)	-2(1)	0(1)
C(17)	18(1)	28(1)	24(1)	-3(1)	0(1)	0(1)
C(18)	24(1)	17(1)	25(1)	1(1)	2(1)	1(1)
C(19)	20(1)	26(1)	28(1)	-5(1)	-3(1)	-4(1)
C(20)	21(1)	43(1)	42(1)	-1(1)	4(1)	-4(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **17**.

	x	y	z	U(eq)
H(1O)	-95	1808	9974	37
H(4O)	-2603	2518	9570	42
H(2)	763	999	8942	25
H(3B)	1364	2646	8923	28
H(3A)	-294	2837	8421	28
H(4B)	2414	1691	7870	27
H(4A)	1983	2729	7531	27
H(6)	257	318	7588	20
H(7)	-2501	878	6622	22
H(8B)	45	-491	6287	27
H(8A)	-1373	-178	5674	27
H(9)	-182	1308	5483	28
H(10)	2164	752	6684	25
H(11A)	2160	2562	5881	33
H(11B)	3499	2212	6524	33
H(13B)	3608	758	4395	41
H(13A)	2200	1557	4447	41
H(14B)	2288	-165	5386	37
H(14A)	973	66	4692	37
H(15A)	-2878	-235	8506	33
H(15C)	-1992	123	9313	33
H(15B)	-949	-422	8636	33
H(16B)	-2787	2162	7927	24
H(16A)	-3785	1191	7833	24
H(17A)	-5260	1930	8765	28
H(17B)	-4114	1268	9316	28
H(18B)	-89	2861	6373	33
H(18C)	-1114	2890	7197	33
H(18A)	-1673	2192	6484	33
H(19B)	-3884	-411	6103	30

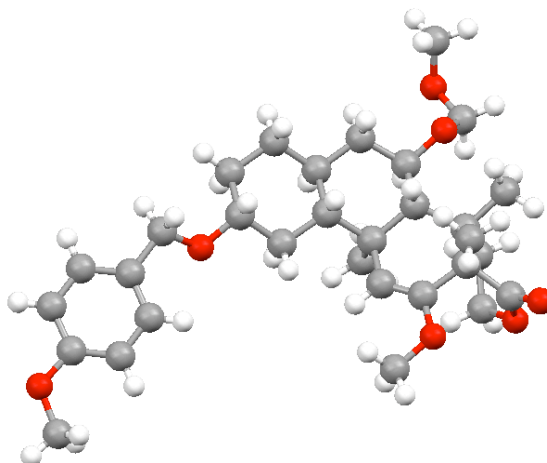
H(19A)	-4216	-1329	6653	30
H(20B)	-5208	-583	8137	53
H(20A)	-6193	-1325	7584	53
H(20C)	-7062	-355	7866	53

Table 6. Hydrogen bonds for **17** [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
O(4)-H(4O)...O(1)	0.84	1.89	2.6289(17)	146.2
O(1)-H(1O)...O(4)#1	0.84	1.86	2.6989(16)	172.0

Symmetry transformations used to generate equivalent atoms:

#1 $x+1/2, -y+1/2, -z+2$



Crystal data and structure refinement for **5**.

Table 1. Crystal data and structure refinement for **5**.

Identification code	LT-301	
Empirical formula	C ₃₁ H ₄₄ O ₇	
Formula weight	528.66	
Temperature	90(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.7566(4) Å	α = 105.563(3)°.
	b = 10.4984(5) Å	β = 93.299(3)°.
	c = 17.4472(8) Å	γ = 92.512(3)°.
Volume	1363.80(11) Å ³	
Z	2	
Density (calculated)	1.287 Mg/m ³	
Absorption coefficient	0.725 mm ⁻¹	
F(000)	572	
Crystal size	0.25 x 0.23 x 0.18 mm ³	
Crystal color, habit	Colorless Rod	
Theta range for data collection	4.38 to 64.89°.	
Index ranges	-9 ≤ h ≤ 8, -11 ≤ k ≤ 12, -20 ≤ l ≤ 20	
Reflections collected	10242	
Independent reflections	4350 [R(int) = 0.0367]	

Completeness to theta = 60.00°	98.5 %
Absorption correction	Multi-scan
Max. and min. transmission	0.8806 and 0.8395
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4350 / 0 / 349
Goodness-of-fit on F ²	1.021
Final R indices [I>2sigma(I)]	R1 = 0.0424, wR2 = 0.1039
R indices (all data)	R1 = 0.0479, wR2 = 0.1081
Largest diff. peak and hole	0.282 and -0.195 e.Å ⁻³

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for **5**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	12856(2)	9416(1)	5097(1)	32(1)
O(2)	14459(2)	8129(1)	5599(1)	37(1)
O(3)	10673(2)	6816(1)	5028(1)	24(1)
O(4)	5899(1)	2922(1)	1582(1)	22(1)
O(5)	14792(1)	7062(1)	1913(1)	20(1)
O(6)	14959(2)	7909(1)	803(1)	24(1)
O(7)	-1185(2)	395(1)	2240(1)	28(1)
C(1)	13530(2)	8239(2)	5050(1)	28(1)
C(2)	13037(2)	7122(2)	4288(1)	22(1)
C(3)	11121(2)	6753(2)	4264(1)	20(1)
C(4)	10082(2)	6360(2)	3611(1)	18(1)
C(5)	10570(2)	6399(2)	2792(1)	18(1)
C(6)	10029(2)	5054(2)	2167(1)	17(1)
C(7)	8128(2)	4564(2)	2149(1)	20(1)
C(8)	7701(2)	3242(2)	1542(1)	21(1)
C(9)	8136(2)	3298(2)	712(1)	23(1)
C(10)	10031(2)	3761(2)	724(1)	24(1)
C(11)	10473(2)	5099(2)	1330(1)	20(1)
C(12)	12361(2)	5564(2)	1319(1)	21(1)

C(13)	12970(2)	6817(2)	1967(1)	19(1)
C(14)	12579(2)	6628(2)	2788(1)	17(1)
C(15)	13483(2)	7628(2)	3547(1)	18(1)
C(16)	12953(2)	9072(2)	3669(1)	23(1)
C(17)	11919(2)	9572(2)	4387(1)	28(1)
C(18)	14003(2)	5908(2)	4357(1)	29(1)
C(19)	9515(2)	7500(2)	2586(1)	20(1)
C(20)	15472(2)	7671(2)	3541(1)	24(1)
C(21)	8928(2)	6429(2)	5106(1)	26(1)
C(22)	15221(2)	8162(2)	1635(1)	21(1)
C(23)	16150(2)	7023(2)	402(1)	32(1)
C(24)	5365(2)	1574(2)	1222(1)	24(1)
C(25)	3624(2)	1295(2)	1504(1)	22(1)
C(26)	3268(2)	1817(2)	2292(1)	28(1)
C(27)	1680(2)	1537(2)	2561(1)	28(1)
C(28)	428(2)	718(2)	2042(1)	23(1)
C(29)	772(2)	178(2)	1250(1)	26(1)
C(30)	2353(2)	475(2)	988(1)	25(1)
C(31)	-1682(3)	1063(2)	3016(1)	34(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for **5**.

O(1)-C(1)	1.348(2)	O(7)-C(28)	1.369(2)
O(1)-C(17)	1.452(2)	O(7)-C(31)	1.430(2)
O(2)-C(1)	1.199(2)	C(1)-C(2)	1.534(2)
O(3)-C(3)	1.381(2)	C(2)-C(3)	1.515(2)
O(3)-C(21)	1.421(2)	C(2)-C(18)	1.535(2)
O(4)-C(24)	1.418(2)	C(2)-C(15)	1.574(2)
O(4)-C(8)	1.4328(19)	C(3)-C(4)	1.316(2)
O(5)-C(22)	1.4020(19)	C(4)-C(5)	1.510(2)
O(5)-C(13)	1.4381(19)	C(4)-H(4)	0.9500
O(6)-C(22)	1.406(2)	C(5)-C(19)	1.552(2)
O(6)-C(23)	1.417(2)	C(5)-C(6)	1.559(2)

C(5)-C(14)	1.566(2)	C(19)-H(19C)	0.9800
C(6)-C(11)	1.532(2)	C(20)-H(20A)	0.9800
C(6)-C(7)	1.536(2)	C(20)-H(20B)	0.9800
C(6)-H(6)	1.0000	C(20)-H(20C)	0.9800
C(7)-C(8)	1.513(2)	C(21)-H(21A)	0.9800
C(7)-H(7A)	0.9900	C(21)-H(21B)	0.9800
C(7)-H(7B)	0.9900	C(21)-H(21C)	0.9800
C(8)-C(9)	1.520(2)	C(22)-H(22A)	0.9900
C(8)-H(8)	1.0000	C(22)-H(22B)	0.9900
C(9)-C(10)	1.525(2)	C(23)-H(23A)	0.9800
C(9)-H(9A)	0.9900	C(23)-H(23B)	0.9800
C(9)-H(9B)	0.9900	C(23)-H(23C)	0.9800
C(10)-C(11)	1.526(2)	C(24)-C(25)	1.506(2)
C(10)-H(10A)	0.9900	C(24)-H(24A)	0.9900
C(10)-H(10B)	0.9900	C(24)-H(24B)	0.9900
C(11)-C(12)	1.526(2)	C(25)-C(26)	1.386(3)
C(11)-H(11)	1.0000	C(25)-C(30)	1.390(2)
C(12)-C(13)	1.522(2)	C(26)-C(27)	1.390(3)
C(12)-H(12A)	0.9900	C(26)-H(26)	0.9500
C(12)-H(12B)	0.9900	C(27)-C(28)	1.382(3)
C(13)-C(14)	1.543(2)	C(27)-H(27)	0.9500
C(13)-H(13)	1.0000	C(28)-C(29)	1.392(3)
C(14)-C(15)	1.559(2)	C(29)-C(30)	1.385(3)
C(14)-H(14)	1.0000	C(29)-H(29)	0.9500
C(15)-C(20)	1.542(2)	C(30)-H(30)	0.9500
C(15)-C(16)	1.550(2)	C(31)-H(31A)	0.9800
C(16)-C(17)	1.512(2)	C(31)-H(31B)	0.9800
C(16)-H(16A)	0.9900	C(31)-H(31C)	0.9800
C(16)-H(16B)	0.9900		
C(17)-H(17A)	0.9900	C(1)-O(1)-C(17)	117.30(13)
C(17)-H(17B)	0.9900	C(3)-O(3)-C(21)	116.43(13)
C(18)-H(18A)	0.9800	C(24)-O(4)-C(8)	114.39(12)
C(18)-H(18B)	0.9800	C(22)-O(5)-C(13)	114.66(12)
C(18)-H(18C)	0.9800	C(22)-O(6)-C(23)	111.65(13)
C(19)-H(19A)	0.9800	C(28)-O(7)-C(31)	117.63(14)
C(19)-H(19B)	0.9800	O(2)-C(1)-O(1)	118.55(17)

O(2)-C(1)-C(2)	124.54(18)	C(7)-C(8)-H(8)	108.9
O(1)-C(1)-C(2)	116.91(15)	C(9)-C(8)-H(8)	108.9
C(3)-C(2)-C(1)	108.27(14)	C(8)-C(9)-C(10)	110.08(14)
C(3)-C(2)-C(18)	107.11(14)	C(8)-C(9)-H(9A)	109.6
C(1)-C(2)-C(18)	107.51(14)	C(10)-C(9)-H(9A)	109.6
C(3)-C(2)-C(15)	111.23(13)	C(8)-C(9)-H(9B)	109.6
C(1)-C(2)-C(15)	108.66(14)	C(10)-C(9)-H(9B)	109.6
C(18)-C(2)-C(15)	113.86(14)	H(9A)-C(9)-H(9B)	108.2
C(4)-C(3)-O(3)	125.78(15)	C(9)-C(10)-C(11)	112.06(14)
C(4)-C(3)-C(2)	124.97(15)	C(9)-C(10)-H(10A)	109.2
O(3)-C(3)-C(2)	109.14(13)	C(11)-C(10)-H(10A)	109.2
C(3)-C(4)-C(5)	124.57(15)	C(9)-C(10)-H(10B)	109.2
C(3)-C(4)-H(4)	117.7	C(11)-C(10)-H(10B)	109.2
C(5)-C(4)-H(4)	117.7	H(10A)-C(10)-H(10B)	107.9
C(4)-C(5)-C(19)	105.40(13)	C(12)-C(11)-C(10)	111.40(13)
C(4)-C(5)-C(6)	110.53(13)	C(12)-C(11)-C(6)	111.63(13)
C(19)-C(5)-C(6)	108.91(13)	C(10)-C(11)-C(6)	110.97(13)
C(4)-C(5)-C(14)	110.39(13)	C(12)-C(11)-H(11)	107.5
C(19)-C(5)-C(14)	114.50(13)	C(10)-C(11)-H(11)	107.5
C(6)-C(5)-C(14)	107.13(12)	C(6)-C(11)-H(11)	107.5
C(11)-C(6)-C(7)	109.91(13)	C(13)-C(12)-C(11)	114.98(13)
C(11)-C(6)-C(5)	110.85(13)	C(13)-C(12)-H(12A)	108.5
C(7)-C(6)-C(5)	115.29(13)	C(11)-C(12)-H(12A)	108.5
C(11)-C(6)-H(6)	106.8	C(13)-C(12)-H(12B)	108.5
C(7)-C(6)-H(6)	106.8	C(11)-C(12)-H(12B)	108.5
C(5)-C(6)-H(6)	106.8	H(12A)-C(12)-H(12B)	107.5
C(8)-C(7)-C(6)	112.51(13)	O(5)-C(13)-C(12)	108.02(13)
C(8)-C(7)-H(7A)	109.1	O(5)-C(13)-C(14)	111.73(13)
C(6)-C(7)-H(7A)	109.1	C(12)-C(13)-C(14)	109.20(13)
C(8)-C(7)-H(7B)	109.1	O(5)-C(13)-H(13)	109.3
C(6)-C(7)-H(7B)	109.1	C(12)-C(13)-H(13)	109.3
H(7A)-C(7)-H(7B)	107.8	C(14)-C(13)-H(13)	109.3
O(4)-C(8)-C(7)	106.40(13)	C(13)-C(14)-C(15)	117.94(13)
O(4)-C(8)-C(9)	112.47(13)	C(13)-C(14)-C(5)	107.70(12)
C(7)-C(8)-C(9)	111.19(13)	C(15)-C(14)-C(5)	115.58(13)
O(4)-C(8)-H(8)	108.9	C(13)-C(14)-H(14)	104.7

C(15)-C(14)-H(14)	104.7	H(20A)-C(20)-H(20C)	109.5
C(5)-C(14)-H(14)	104.7	H(20B)-C(20)-H(20C)	109.5
C(20)-C(15)-C(16)	106.72(13)	O(3)-C(21)-H(21A)	109.5
C(20)-C(15)-C(14)	112.32(13)	O(3)-C(21)-H(21B)	109.5
C(16)-C(15)-C(14)	113.99(13)	H(21A)-C(21)-H(21B)	109.5
C(20)-C(15)-C(2)	105.91(13)	O(3)-C(21)-H(21C)	109.5
C(16)-C(15)-C(2)	110.00(13)	H(21A)-C(21)-H(21C)	109.5
C(14)-C(15)-C(2)	107.61(13)	H(21B)-C(21)-H(21C)	109.5
C(17)-C(16)-C(15)	114.07(14)	O(5)-C(22)-O(6)	113.31(14)
C(17)-C(16)-H(16A)	108.7	O(5)-C(22)-H(22A)	108.9
C(15)-C(16)-H(16A)	108.7	O(6)-C(22)-H(22A)	108.9
C(17)-C(16)-H(16B)	108.7	O(5)-C(22)-H(22B)	108.9
C(15)-C(16)-H(16B)	108.7	O(6)-C(22)-H(22B)	108.9
H(16A)-C(16)-H(16B)	107.6	H(22A)-C(22)-H(22B)	107.7
O(1)-C(17)-C(16)	109.88(15)	O(6)-C(23)-H(23A)	109.5
O(1)-C(17)-H(17A)	109.7	O(6)-C(23)-H(23B)	109.5
C(16)-C(17)-H(17A)	109.7	H(23A)-C(23)-H(23B)	109.5
O(1)-C(17)-H(17B)	109.7	O(6)-C(23)-H(23C)	109.5
C(16)-C(17)-H(17B)	109.7	H(23A)-C(23)-H(23C)	109.5
H(17A)-C(17)-H(17B)	108.2	H(23B)-C(23)-H(23C)	109.5
C(2)-C(18)-H(18A)	109.5	O(4)-C(24)-C(25)	108.47(13)
C(2)-C(18)-H(18B)	109.5	O(4)-C(24)-H(24A)	110.0
H(18A)-C(18)-H(18B)	109.5	C(25)-C(24)-H(24A)	110.0
C(2)-C(18)-H(18C)	109.5	O(4)-C(24)-H(24B)	110.0
H(18A)-C(18)-H(18C)	109.5	C(25)-C(24)-H(24B)	110.0
H(18B)-C(18)-H(18C)	109.5	H(24A)-C(24)-H(24B)	108.4
C(5)-C(19)-H(19A)	109.5	C(26)-C(25)-C(30)	118.19(16)
C(5)-C(19)-H(19B)	109.5	C(26)-C(25)-C(24)	120.75(15)
H(19A)-C(19)-H(19B)	109.5	C(30)-C(25)-C(24)	121.03(16)
C(5)-C(19)-H(19C)	109.5	C(25)-C(26)-C(27)	121.12(17)
H(19A)-C(19)-H(19C)	109.5	C(25)-C(26)-H(26)	119.4
H(19B)-C(19)-H(19C)	109.5	C(27)-C(26)-H(26)	119.4
C(15)-C(20)-H(20A)	109.5	C(28)-C(27)-C(26)	120.10(17)
C(15)-C(20)-H(20B)	109.5	C(28)-C(27)-H(27)	119.9
H(20A)-C(20)-H(20B)	109.5	C(26)-C(27)-H(27)	119.9
C(15)-C(20)-H(20C)	109.5	O(7)-C(28)-C(27)	124.91(16)

O(7)-C(28)-C(29)	115.64(15)	C(25)-C(30)-H(30)	119.4
C(27)-C(28)-C(29)	119.44(16)	O(7)-C(31)-H(31A)	109.5
C(30)-C(29)-C(28)	119.86(16)	O(7)-C(31)-H(31B)	109.5
C(30)-C(29)-H(29)	120.1	H(31A)-C(31)-H(31B)	109.5
C(28)-C(29)-H(29)	120.1	O(7)-C(31)-H(31C)	109.5
C(29)-C(30)-C(25)	121.27(16)	H(31A)-C(31)-H(31C)	109.5
C(29)-C(30)-H(30)	119.4	H(31B)-C(31)-H(31C)	109.5

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

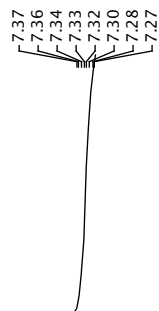
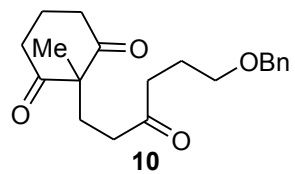
	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
O(1)	36(1)	30(1)	25(1)	2(1)	3(1)	-8(1)
O(2)	34(1)	48(1)	29(1)	14(1)	-8(1)	-18(1)
O(3)	22(1)	30(1)	21(1)	8(1)	3(1)	-6(1)
O(4)	17(1)	18(1)	30(1)	2(1)	3(1)	-2(1)
O(5)	14(1)	21(1)	28(1)	11(1)	4(1)	0(1)
O(6)	22(1)	29(1)	23(1)	8(1)	6(1)	6(1)
O(7)	23(1)	25(1)	37(1)	10(1)	7(1)	-1(1)
C(1)	23(1)	33(1)	26(1)	8(1)	2(1)	-12(1)
C(2)	19(1)	24(1)	24(1)	8(1)	0(1)	-2(1)
C(3)	21(1)	20(1)	21(1)	6(1)	4(1)	-1(1)
C(4)	14(1)	18(1)	23(1)	5(1)	4(1)	-1(1)
C(5)	15(1)	17(1)	23(1)	4(1)	3(1)	0(1)
C(6)	15(1)	15(1)	21(1)	5(1)	3(1)	2(1)
C(7)	18(1)	20(1)	21(1)	4(1)	4(1)	-1(1)
C(8)	16(1)	19(1)	27(1)	6(1)	2(1)	-1(1)
C(9)	22(1)	21(1)	23(1)	1(1)	3(1)	-2(1)
C(10)	24(1)	23(1)	22(1)	2(1)	6(1)	-1(1)
C(11)	18(1)	19(1)	21(1)	4(1)	4(1)	0(1)
C(12)	20(1)	22(1)	22(1)	6(1)	7(1)	1(1)
C(13)	13(1)	21(1)	26(1)	7(1)	4(1)	1(1)

C(14)	14(1)	15(1)	22(1)	6(1)	4(1)	1(1)
C(15)	15(1)	18(1)	22(1)	5(1)	3(1)	-1(1)
C(16)	23(1)	17(1)	27(1)	4(1)	2(1)	-4(1)
C(17)	31(1)	20(1)	30(1)	2(1)	5(1)	-1(1)
C(18)	20(1)	35(1)	38(1)	20(1)	-1(1)	0(1)
C(19)	18(1)	18(1)	24(1)	4(1)	3(1)	2(1)
C(20)	18(1)	26(1)	28(1)	8(1)	1(1)	-3(1)
C(21)	22(1)	30(1)	25(1)	6(1)	6(1)	-6(1)
C(22)	21(1)	21(1)	24(1)	8(1)	4(1)	-1(1)
C(23)	28(1)	39(1)	31(1)	7(1)	11(1)	10(1)
C(24)	21(1)	18(1)	31(1)	4(1)	2(1)	-2(1)
C(25)	21(1)	16(1)	30(1)	7(1)	1(1)	2(1)
C(26)	26(1)	27(1)	28(1)	4(1)	-1(1)	-4(1)
C(27)	30(1)	28(1)	26(1)	6(1)	5(1)	-2(1)
C(28)	21(1)	18(1)	34(1)	12(1)	3(1)	1(1)
C(29)	20(1)	21(1)	34(1)	4(1)	-1(1)	-1(1)
C(30)	25(1)	20(1)	28(1)	2(1)	3(1)	2(1)
C(31)	33(1)	35(1)	38(1)	12(1)	13(1)	1(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **5**.

	x	y	z	U(eq)
H(4)	8945	6027	3658	22
H(6)	10747	4373	2311	20
H(7A)	7879	4482	2685	24
H(7B)	7375	5228	2023	24
H(8)	8389	2556	1698	25
H(9A)	7389	3917	532	28
H(9B)	7915	2409	333	28
H(10A)	10283	3830	186	29
H(10B)	10772	3093	855	29

H(11)	9739	5760	1173	24
H(12A)	13100	4844	1373	26
H(12B)	12533	5722	793	26
H(13)	12338	7580	1876	23
H(14)	13043	5755	2790	20
H(16A)	14012	9661	3727	27
H(16B)	12260	9128	3186	27
H(17A)	11712	10519	4454	34
H(17B)	10783	9069	4304	34
H(18A)	13612	5615	4809	44
H(18B)	15249	6143	4440	44
H(18C)	13764	5191	3865	44
H(19A)	8282	7214	2510	30
H(19B)	9899	7667	2094	30
H(19C)	9697	8315	3023	30
H(20A)	15848	8227	3204	36
H(20B)	15843	6771	3329	36
H(20C)	15988	8042	4086	36
H(21A)	8161	7056	4960	39
H(21B)	8785	6425	5660	39
H(21C)	8635	5539	4753	39
H(22A)	16451	8451	1798	26
H(22B)	14513	8900	1892	26
H(23A)	15936	6873	-175	48
H(23B)	16005	6179	537	48
H(23C)	17333	7405	567	48
H(24A)	6218	994	1375	29
H(24B)	5286	1394	634	29
H(26)	4123	2375	2655	34
H(27)	1455	1910	3103	34
H(29)	-75	-394	890	31
H(30)	2572	112	445	30
H(31A)	-927	833	3422	52
H(31B)	-2884	791	3068	52
H(31C)	-1574	2022	3088	52



4.46

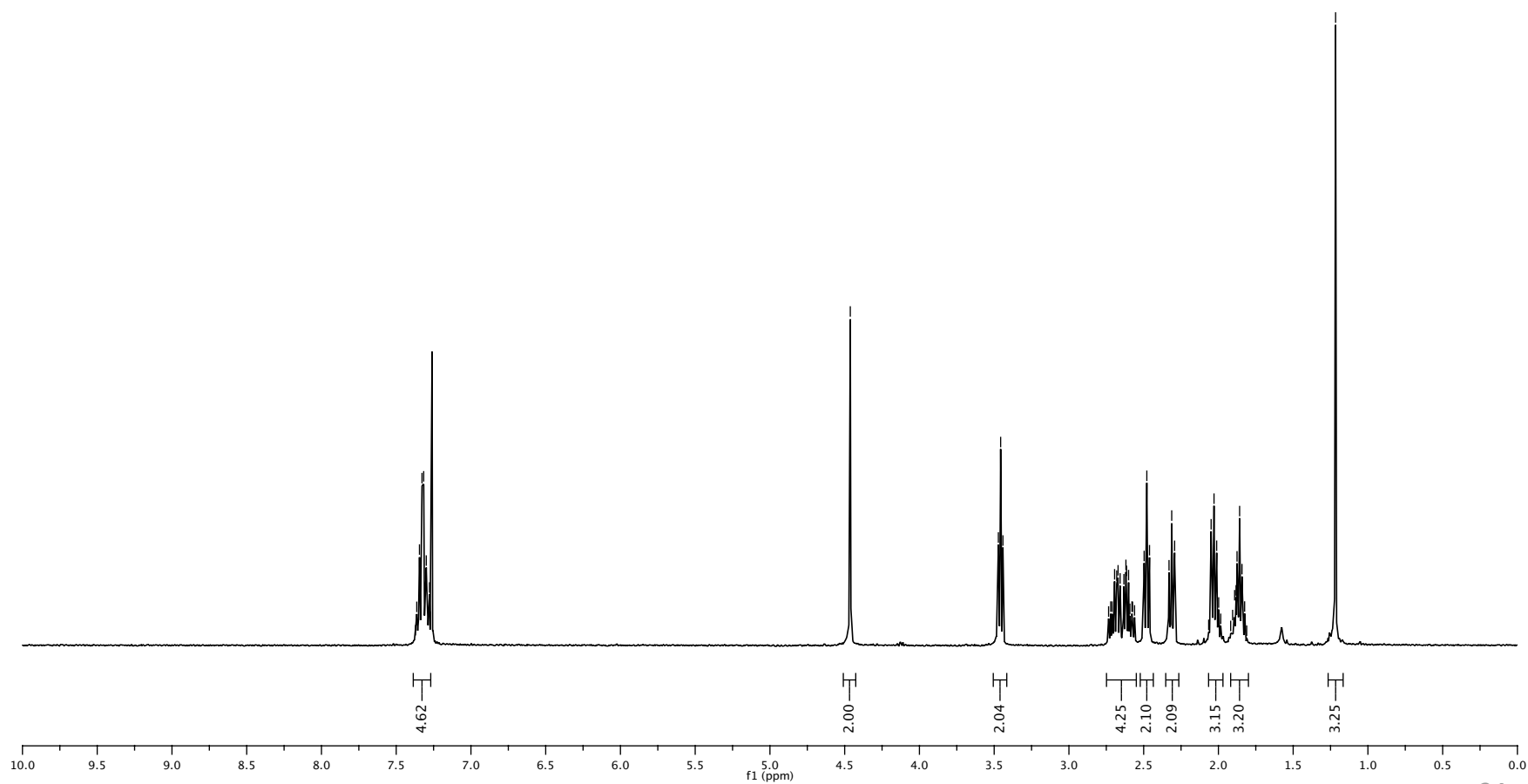
3.47
3.46
3.44

2.71
2.67
2.62
2.59
2.56
2.46

2.31
2.09
2.00

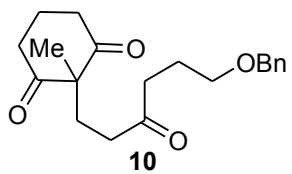
1.92
1.89
1.88
1.84
1.81

1.22



$^1\text{H NMR}$ (400 MHz, CDCl_3)

210.0
209.3

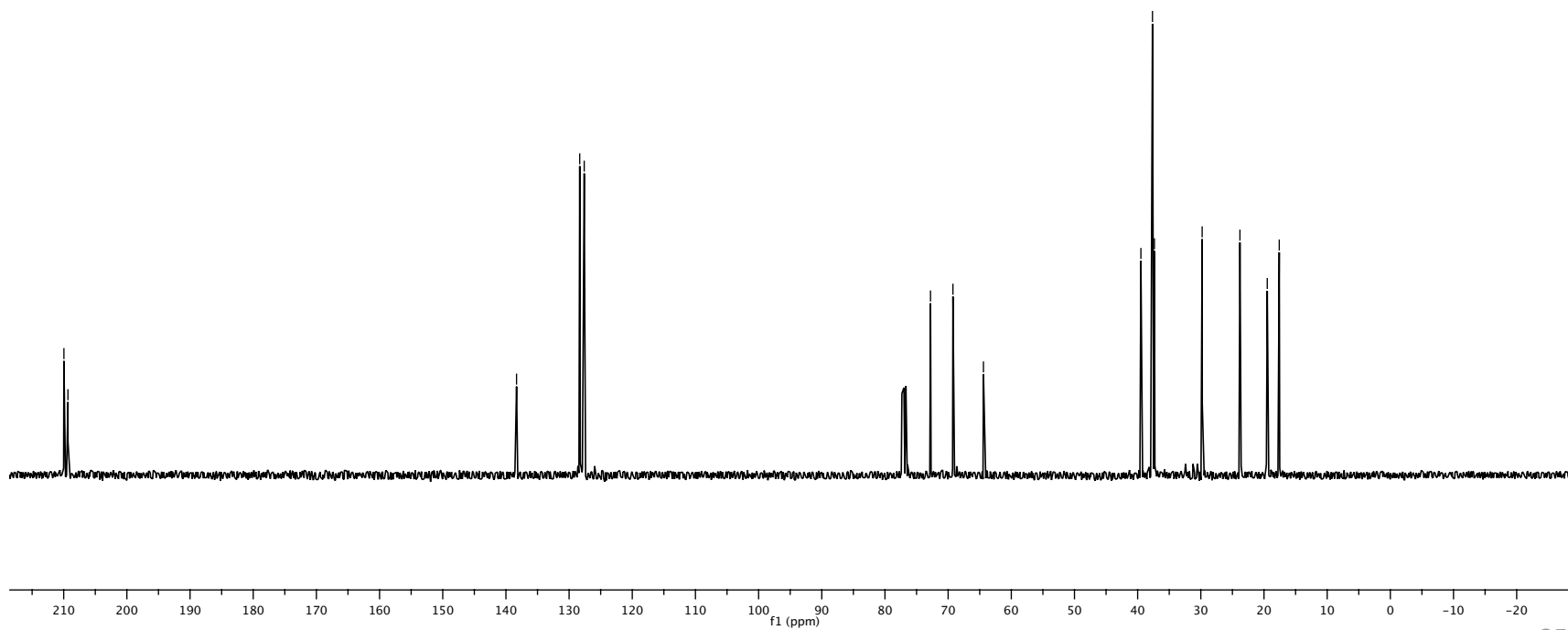


138.3

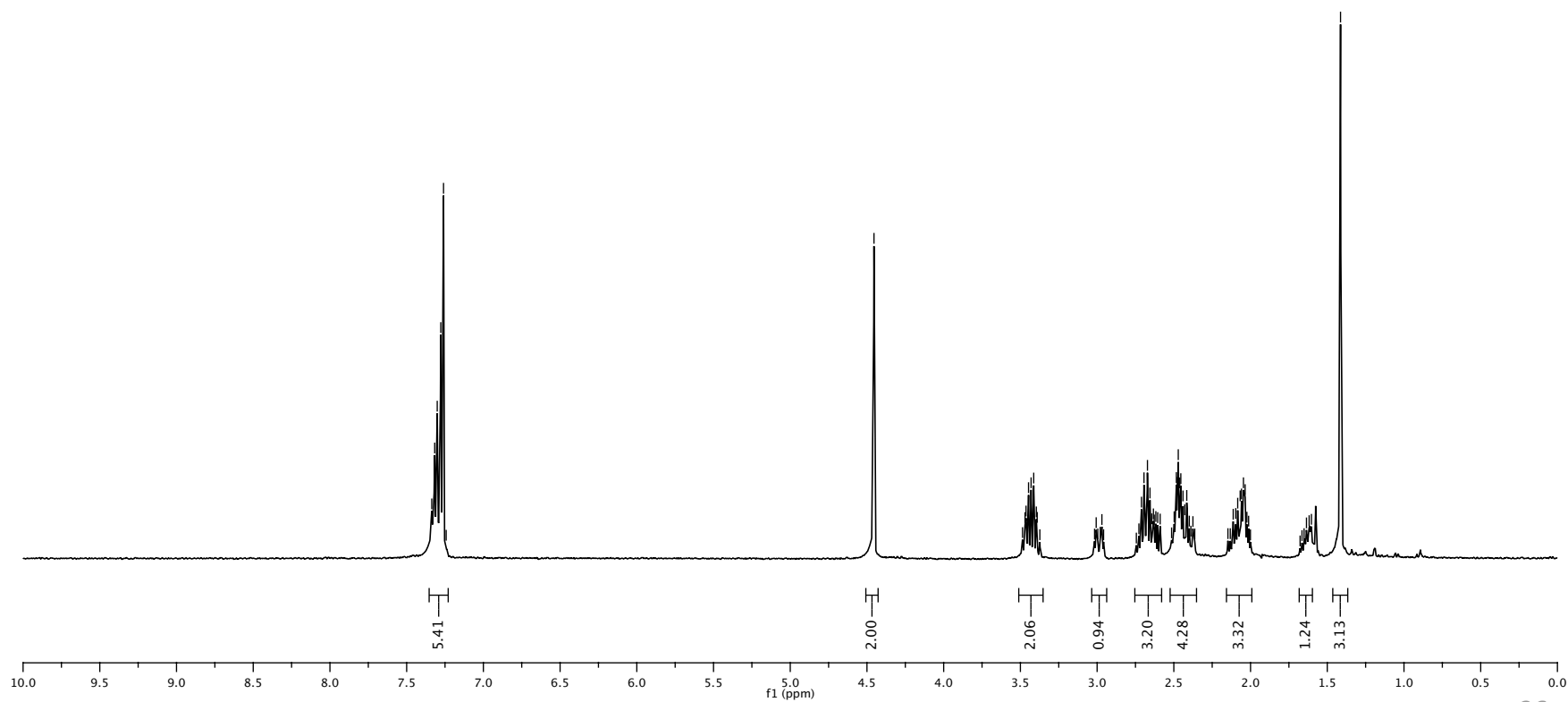
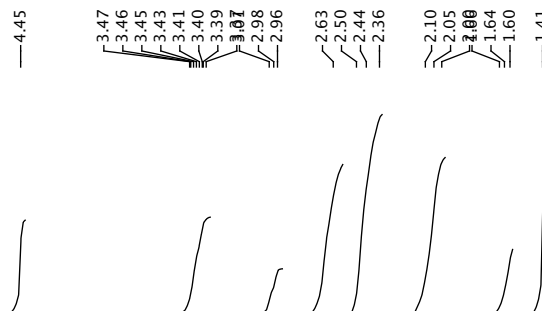
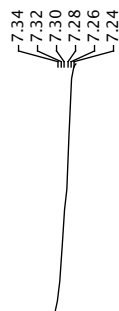
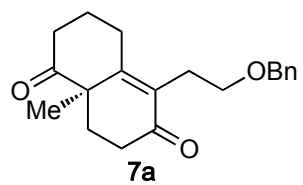
128.3
127.6
127.5

72.8
69.2
64.4

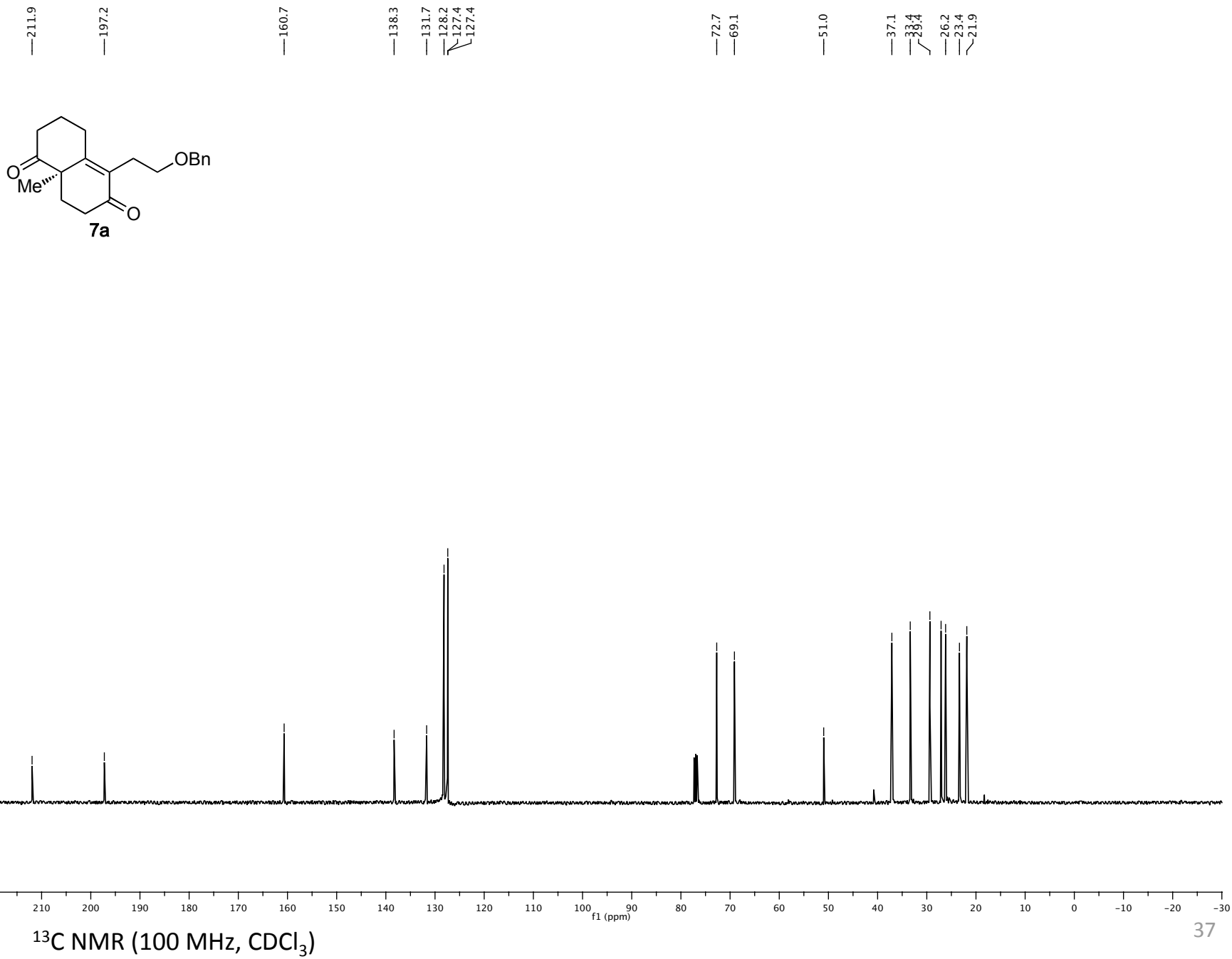
39.5
37.7
37.3
29.8
23.8
19.5
17.6

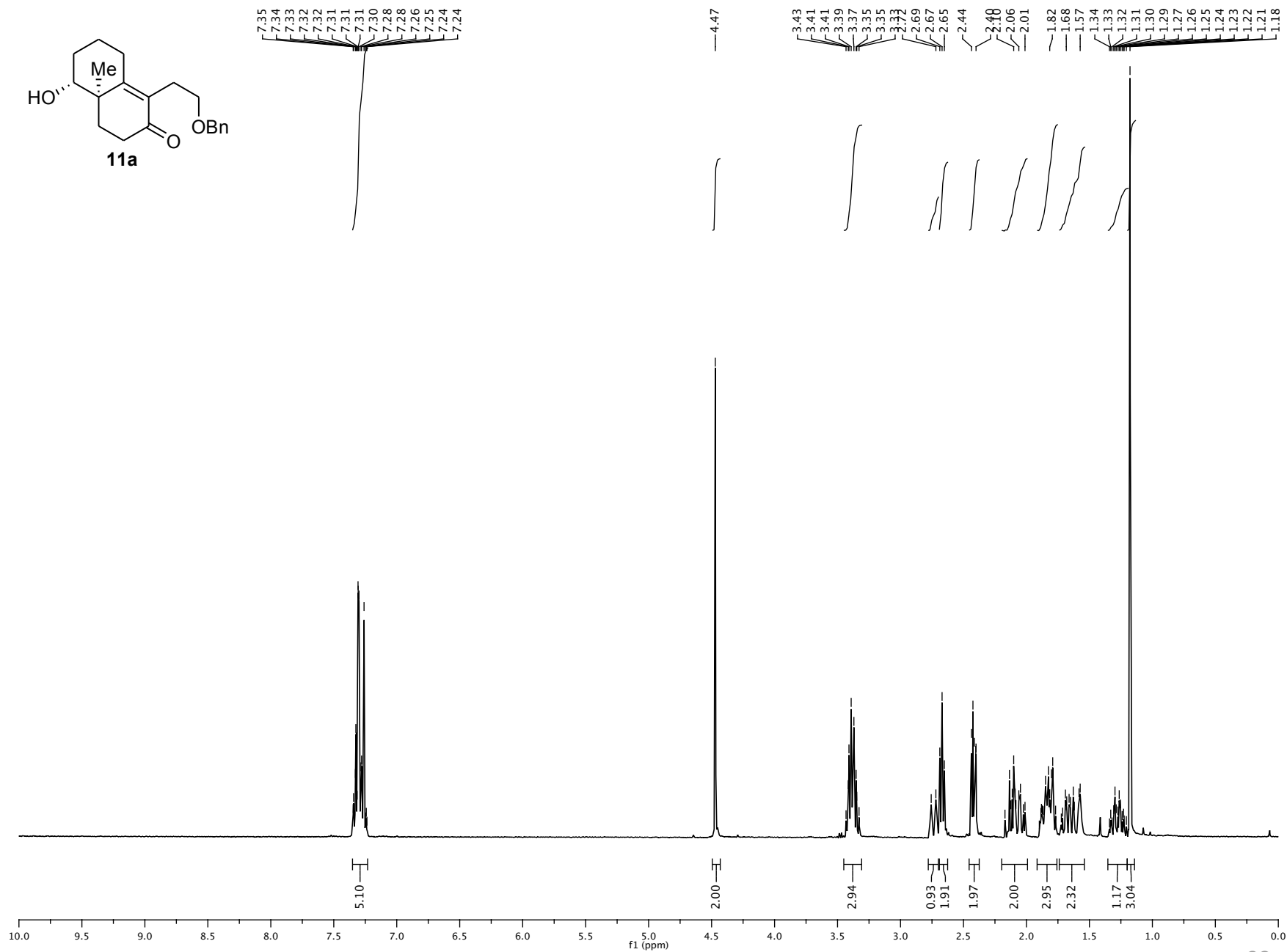
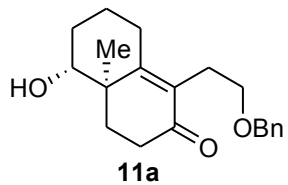


^{13}C NMR (100 MHz, CDCl_3)

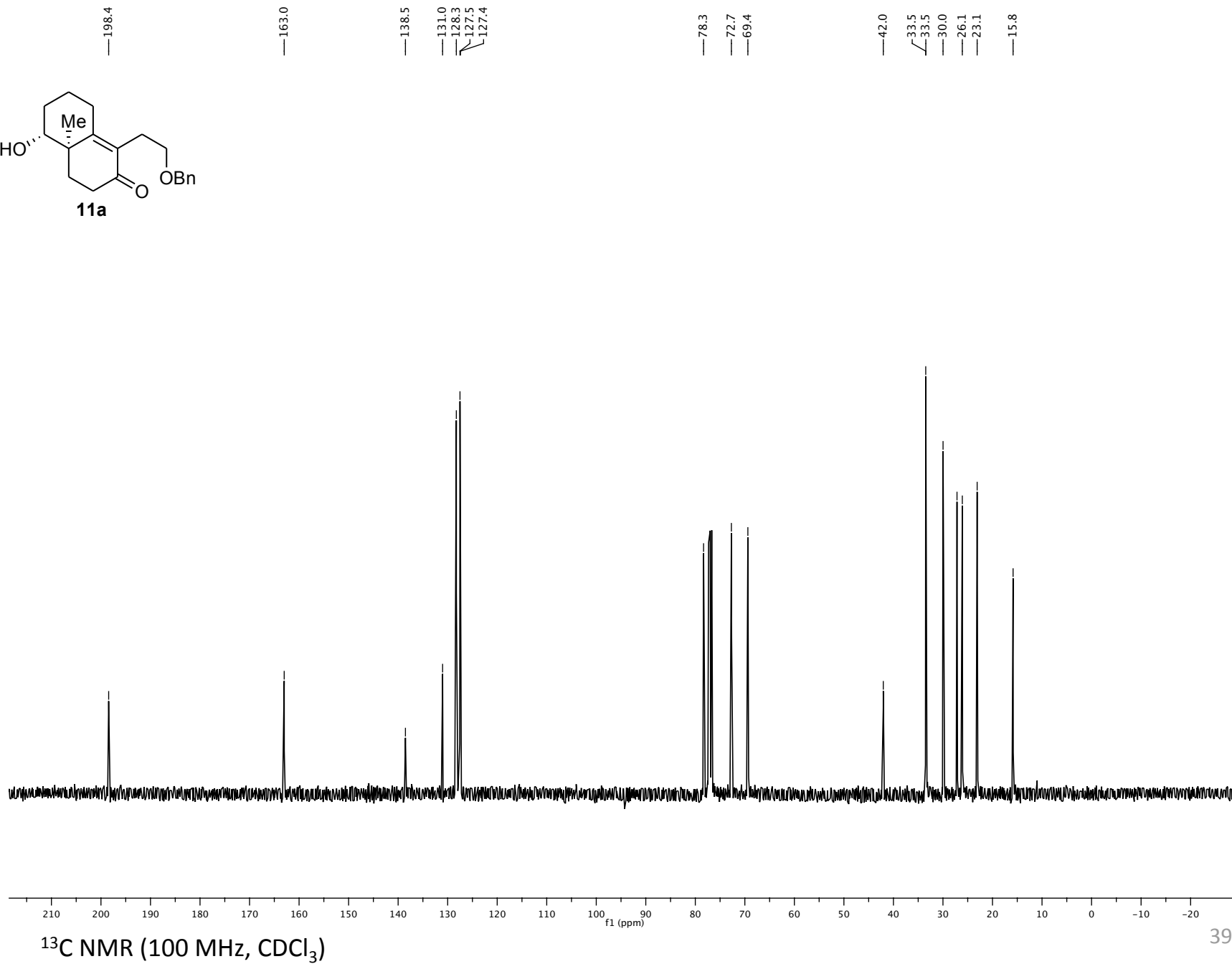
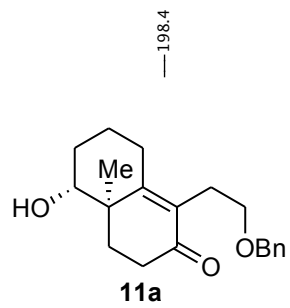


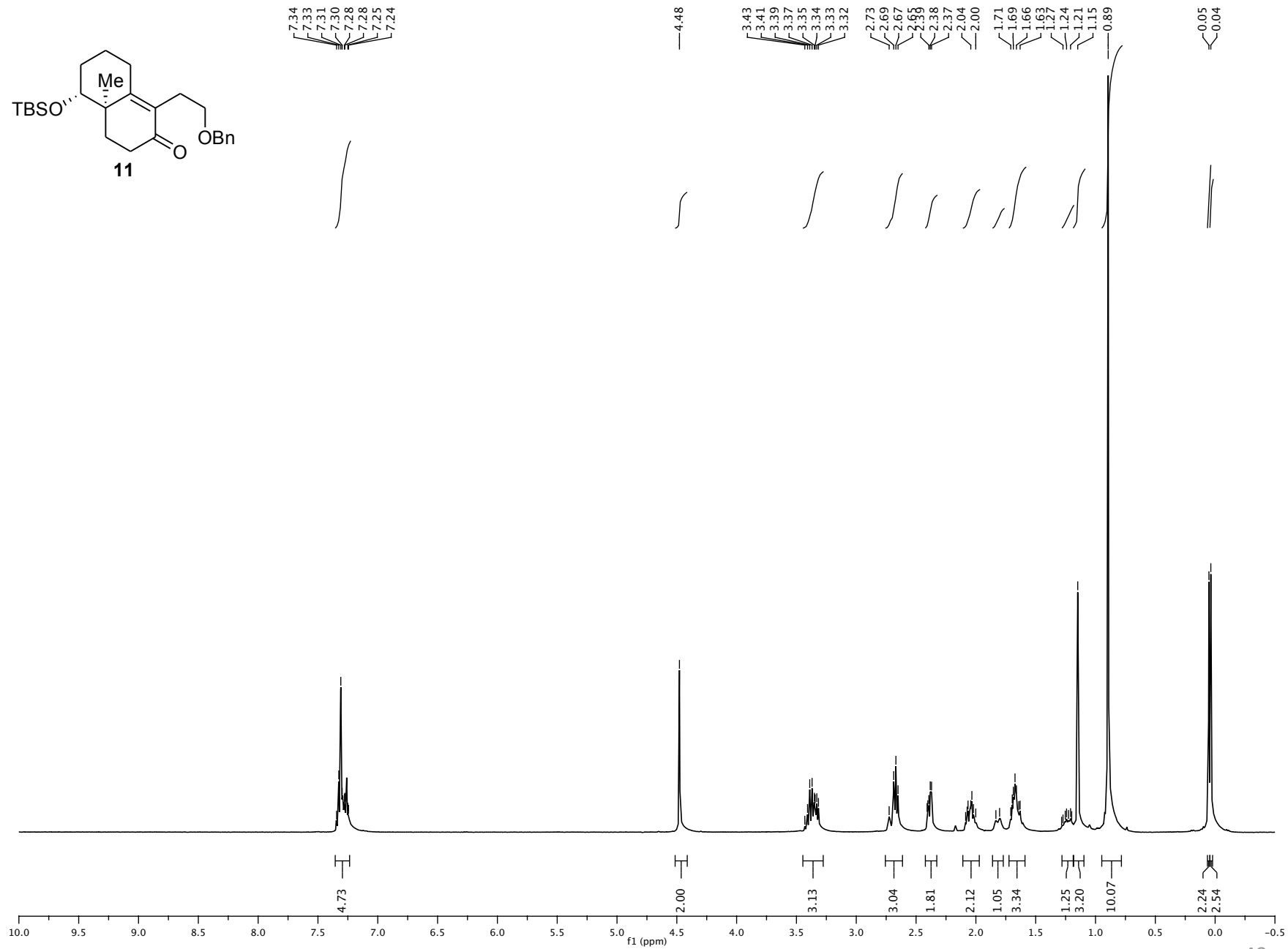
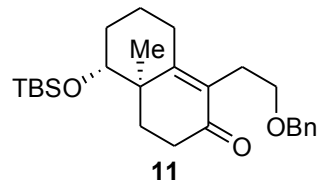
^1H NMR (400 MHz, CDCl_3)



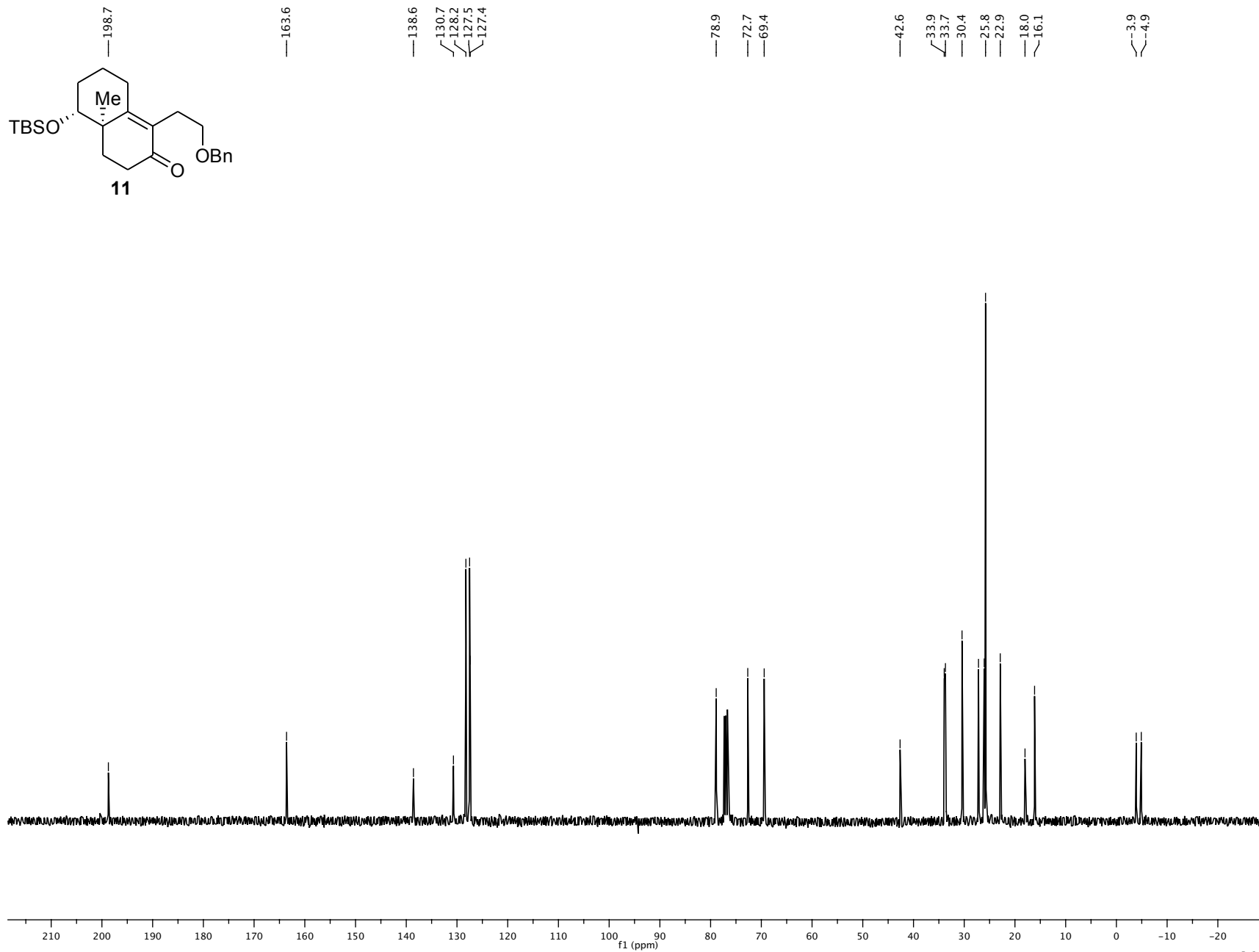
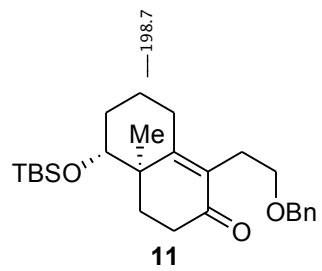


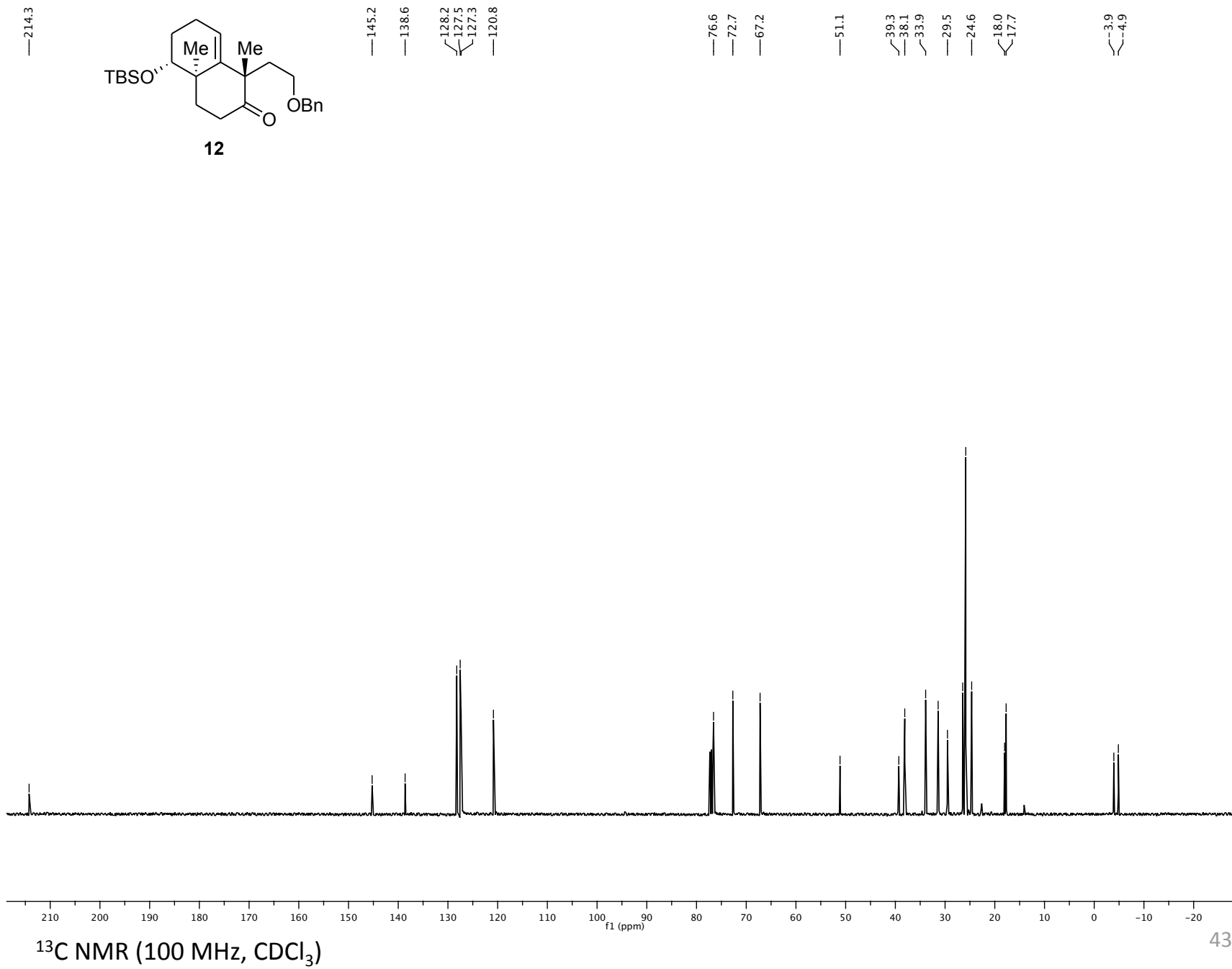
¹H NMR (400 MHz, CDCl₃)

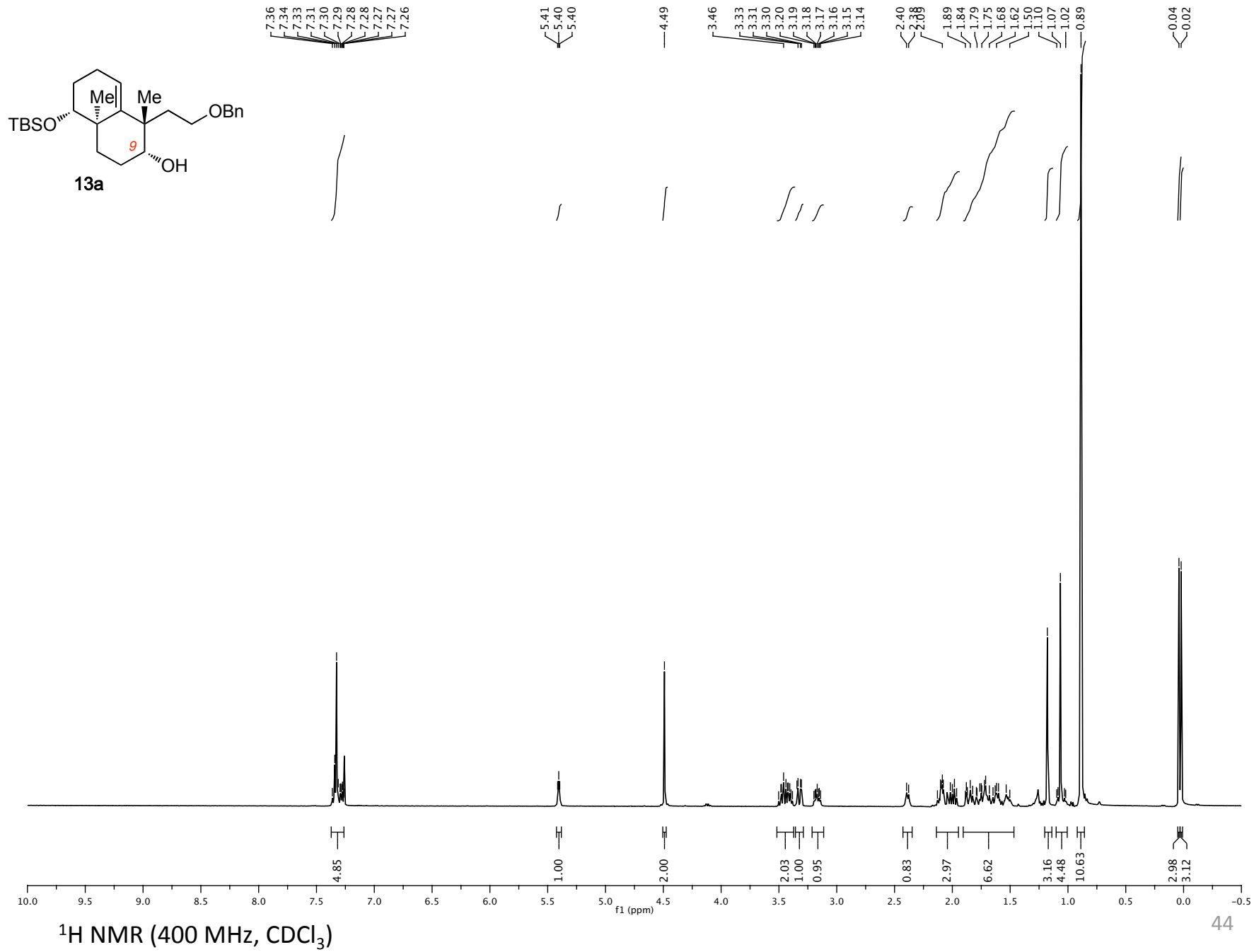


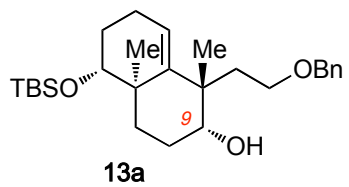


¹H NMR (400 MHz, CDCl₃)







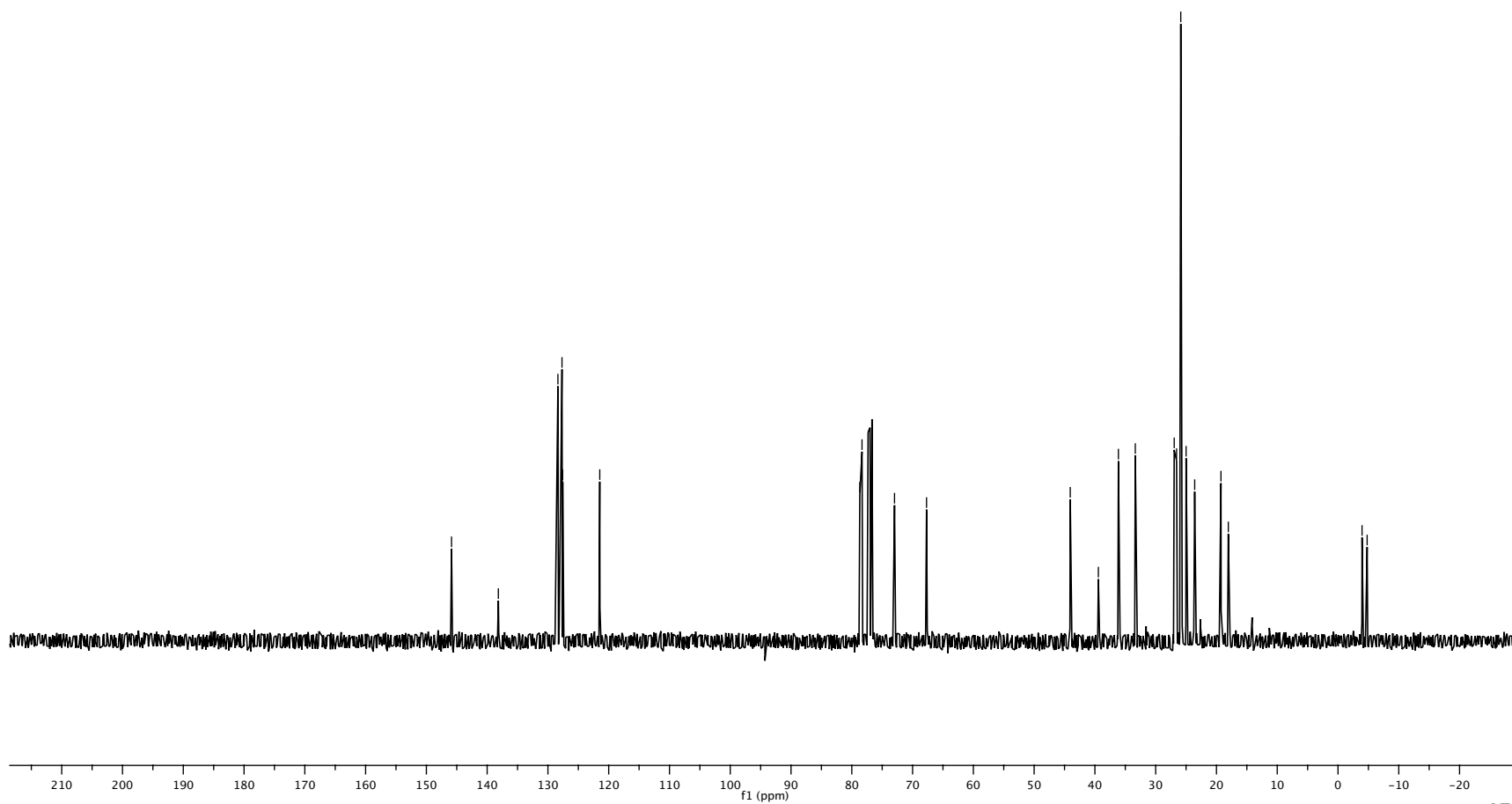


—145.9
—138.2
128.4
127.7
127.6
—121.5

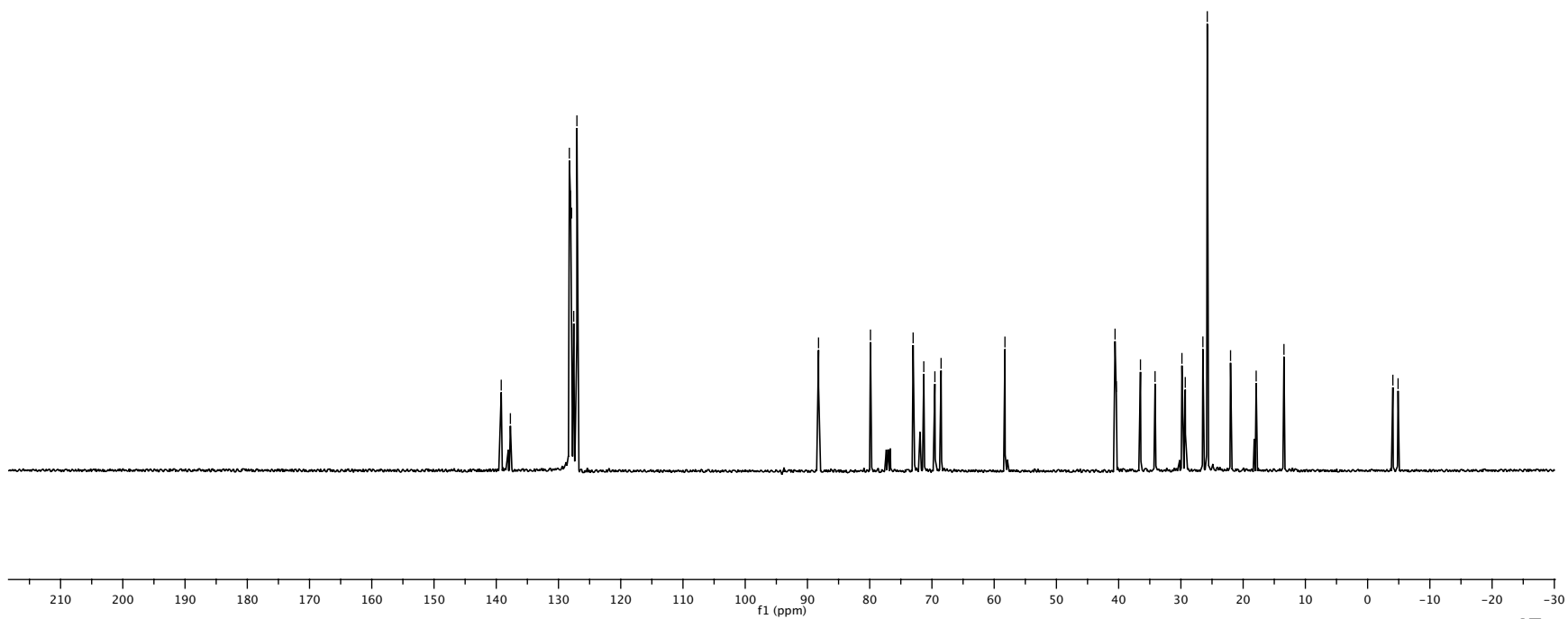
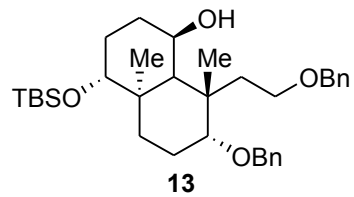
78.7
78.3
—73.0
—67.7

—44.1
—39.4
—36.1
—33.4
25.9
25.0
—23.6
—19.3
—18.0

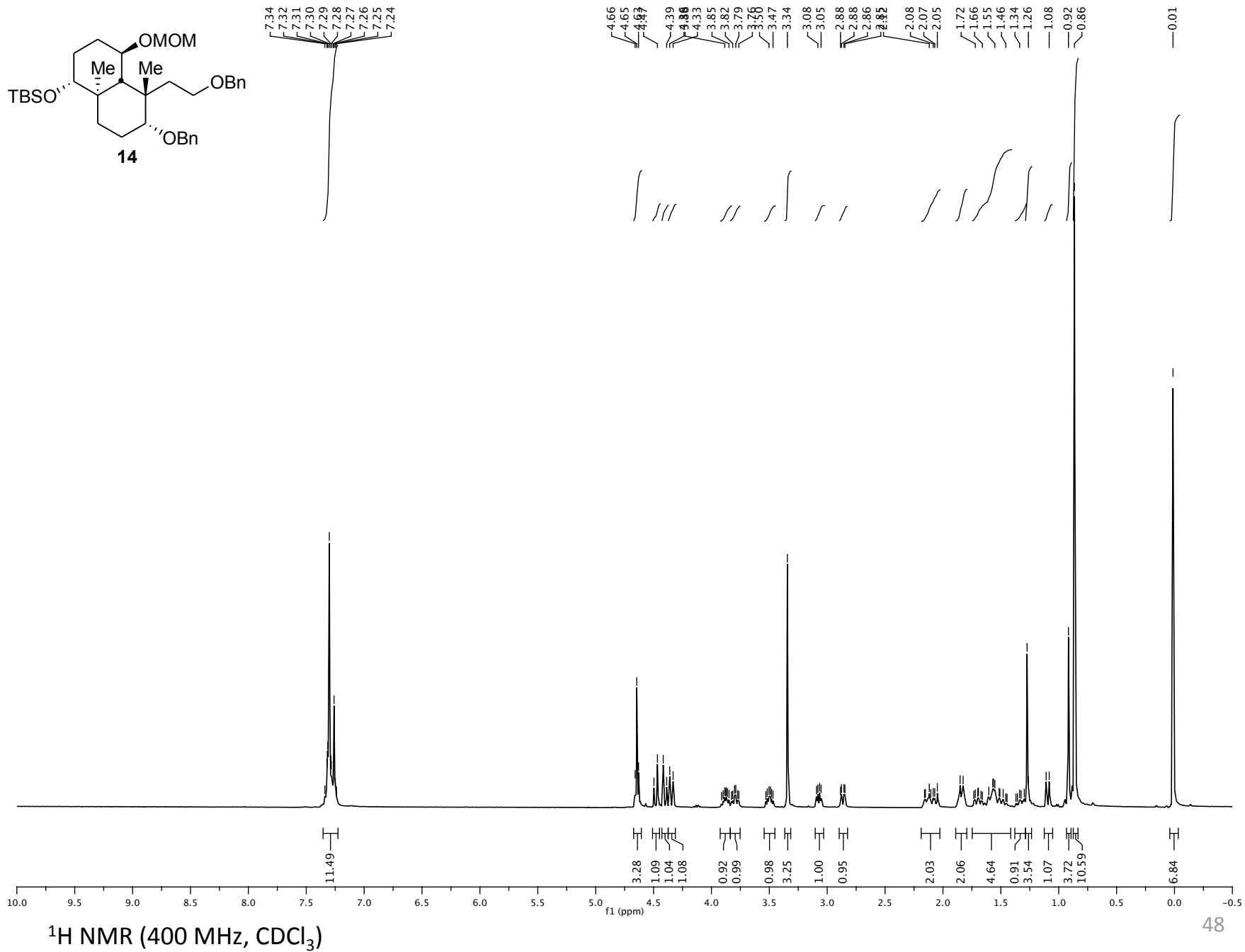
—4.0
—4.8

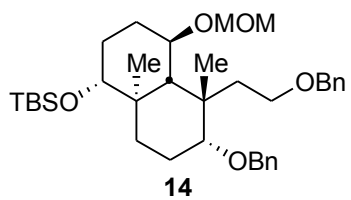


^{13}C NMR (100 MHz, CDCl_3)

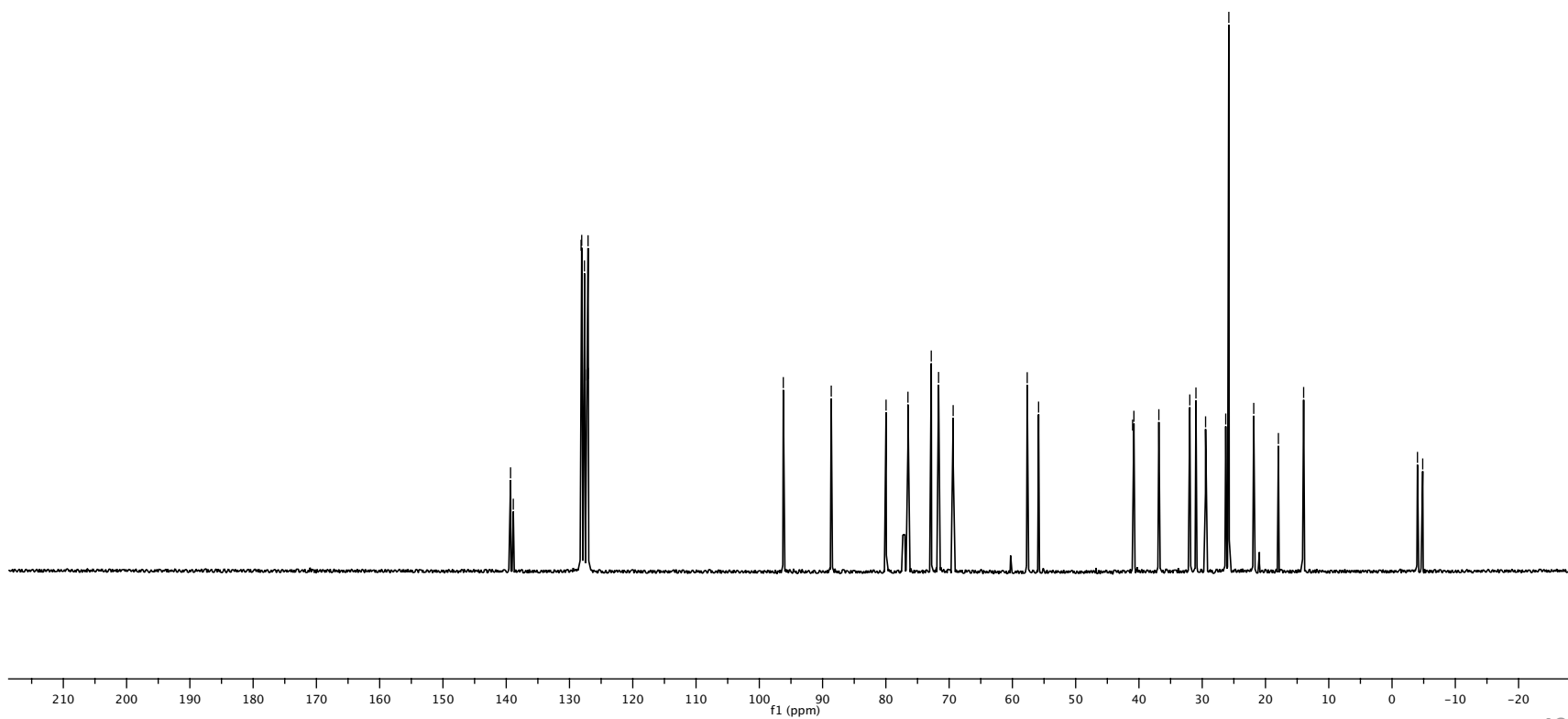


^{13}C NMR (100 MHz, CDCl_3)

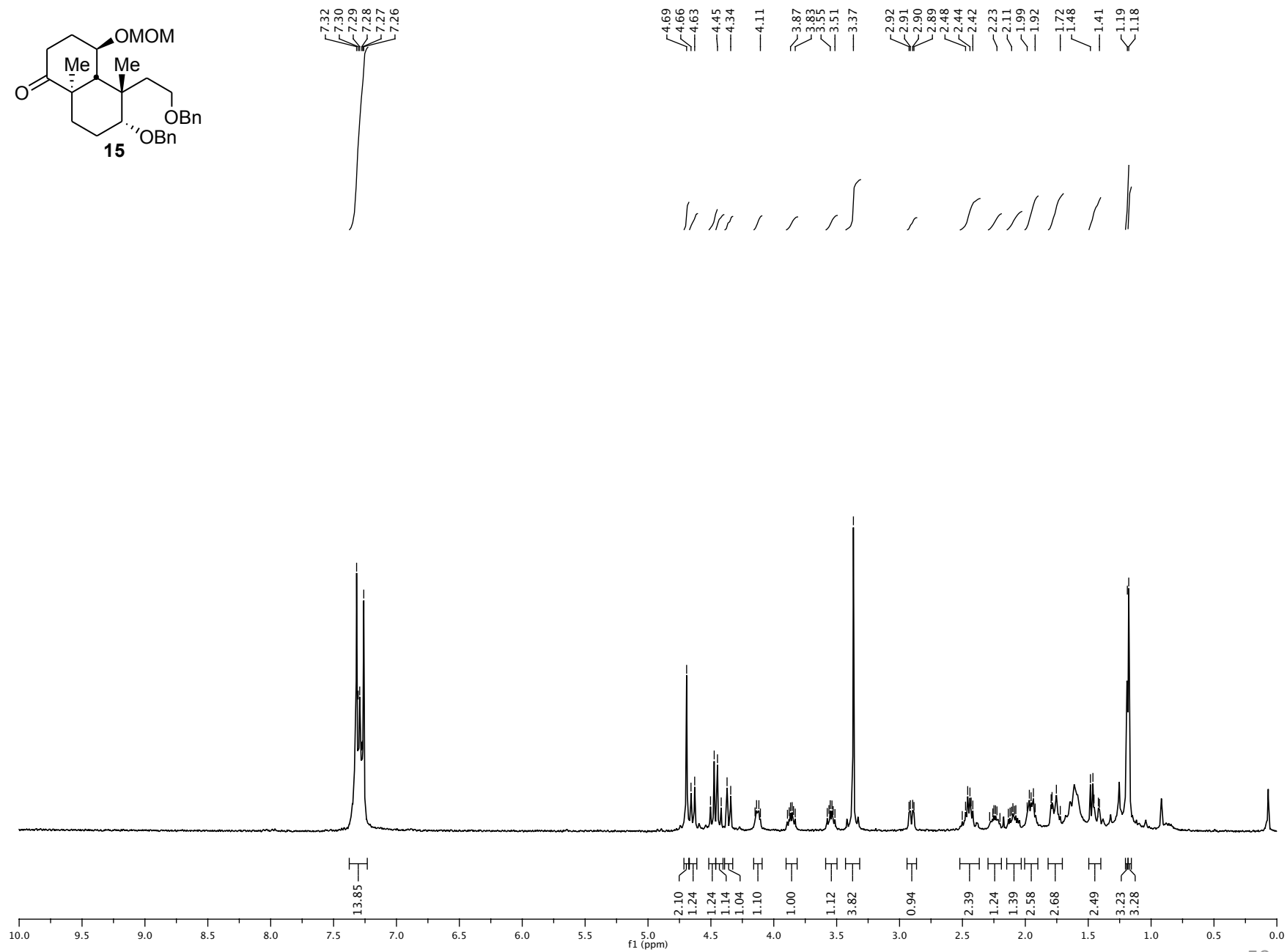
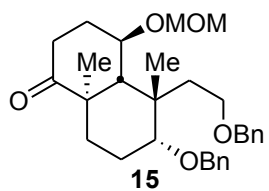


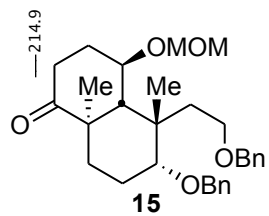


139.3
138.9
128.2
128.1
127.6
127.2
127.1
127.0
96.2
88.6
80.0
76.5
72.8
71.7
69.4
57.7
55.9
41.0
40.8
36.9
29.5
25.8
21.9
18.0
14.0
4.0
-4.8



¹³C NMR (100 MHz, CDCl₃)





δ 139.0
 δ 138.7
 δ 129.5
 δ 128.3
 δ 128.2
 δ 127.7
 δ 127.5
 δ 127.3

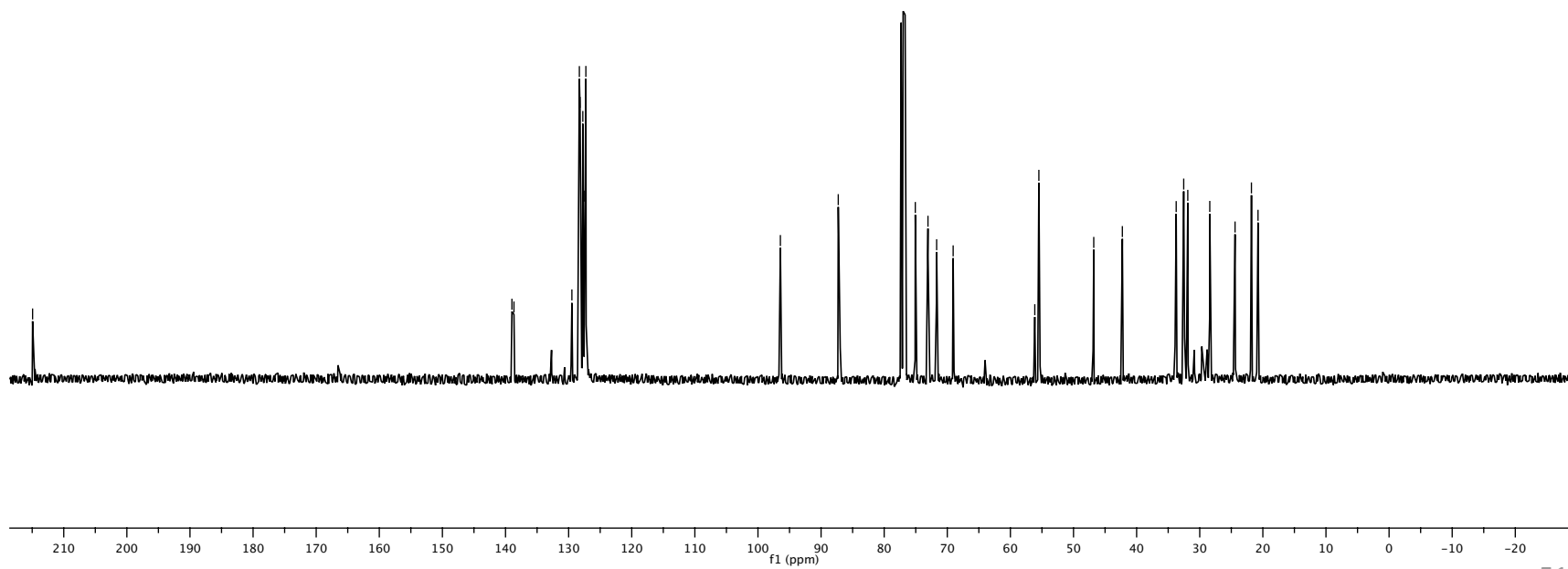
 δ 96.4
 δ 87.3

 δ 75.1
 δ 73.1
 δ 71.7
 δ 69.1

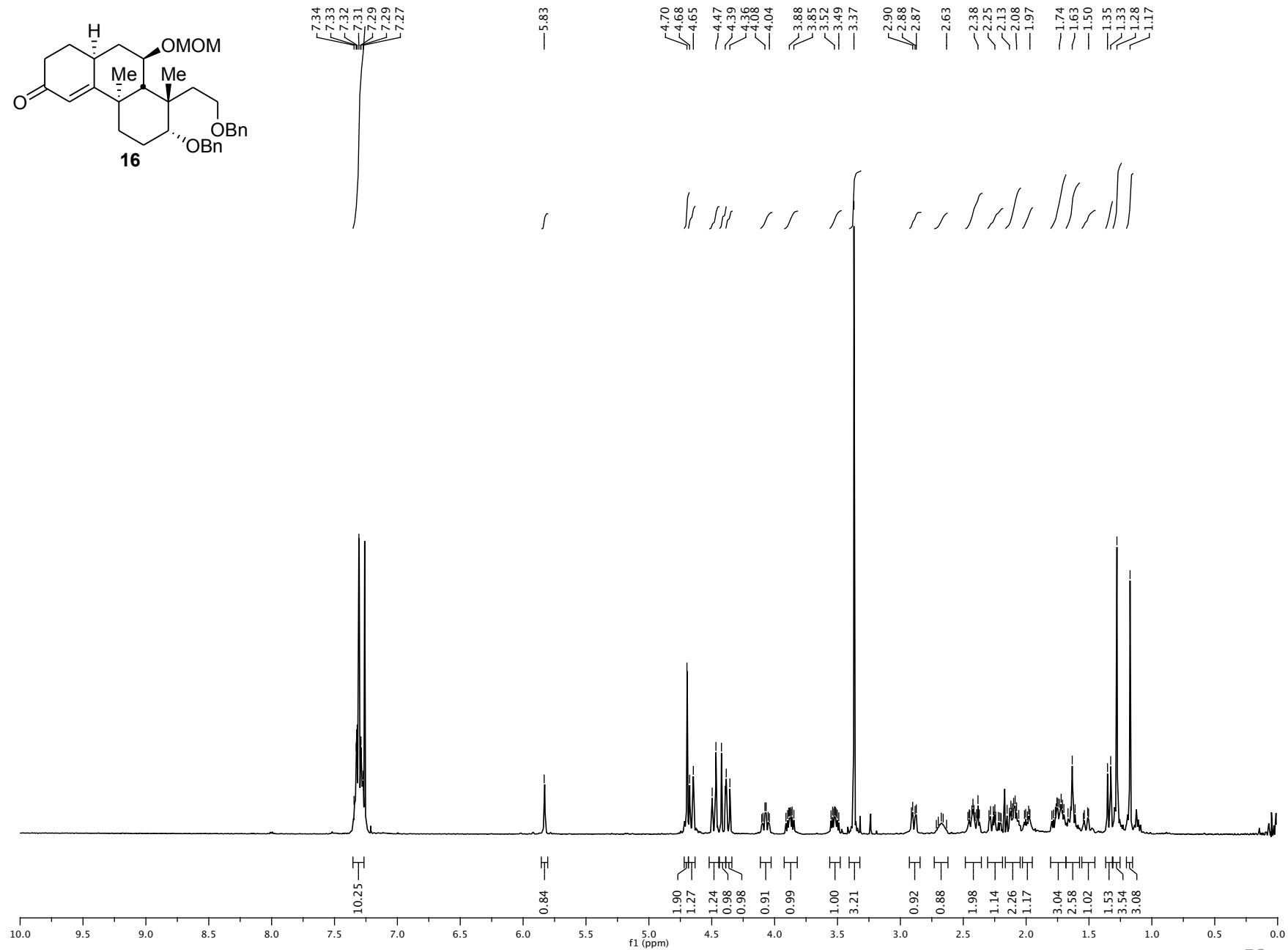
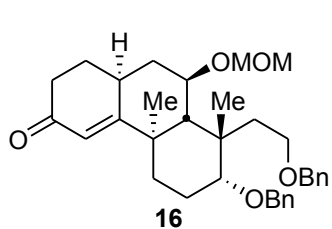
 δ 56.1
 δ 55.5

 δ 46.8
 δ 42.3

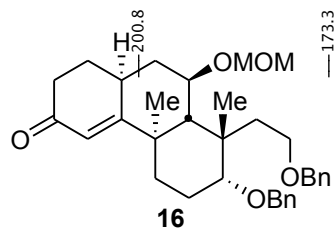
 δ 33.7
 δ 32.5
 δ 31.9
 δ 28.4
 δ 24.4
 δ 21.8
 δ 20.8



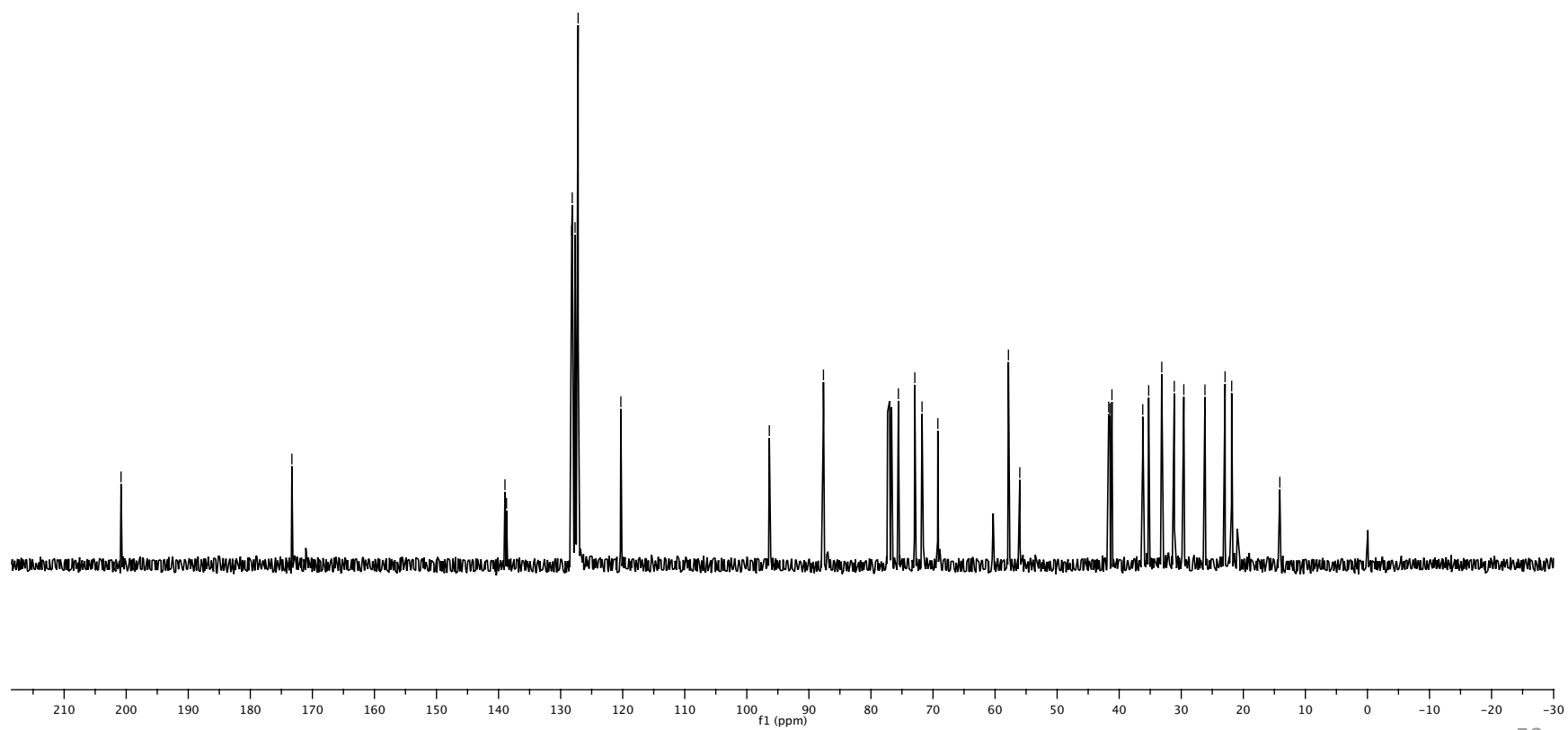
^{13}C NMR (100 MHz, CDCl_3)



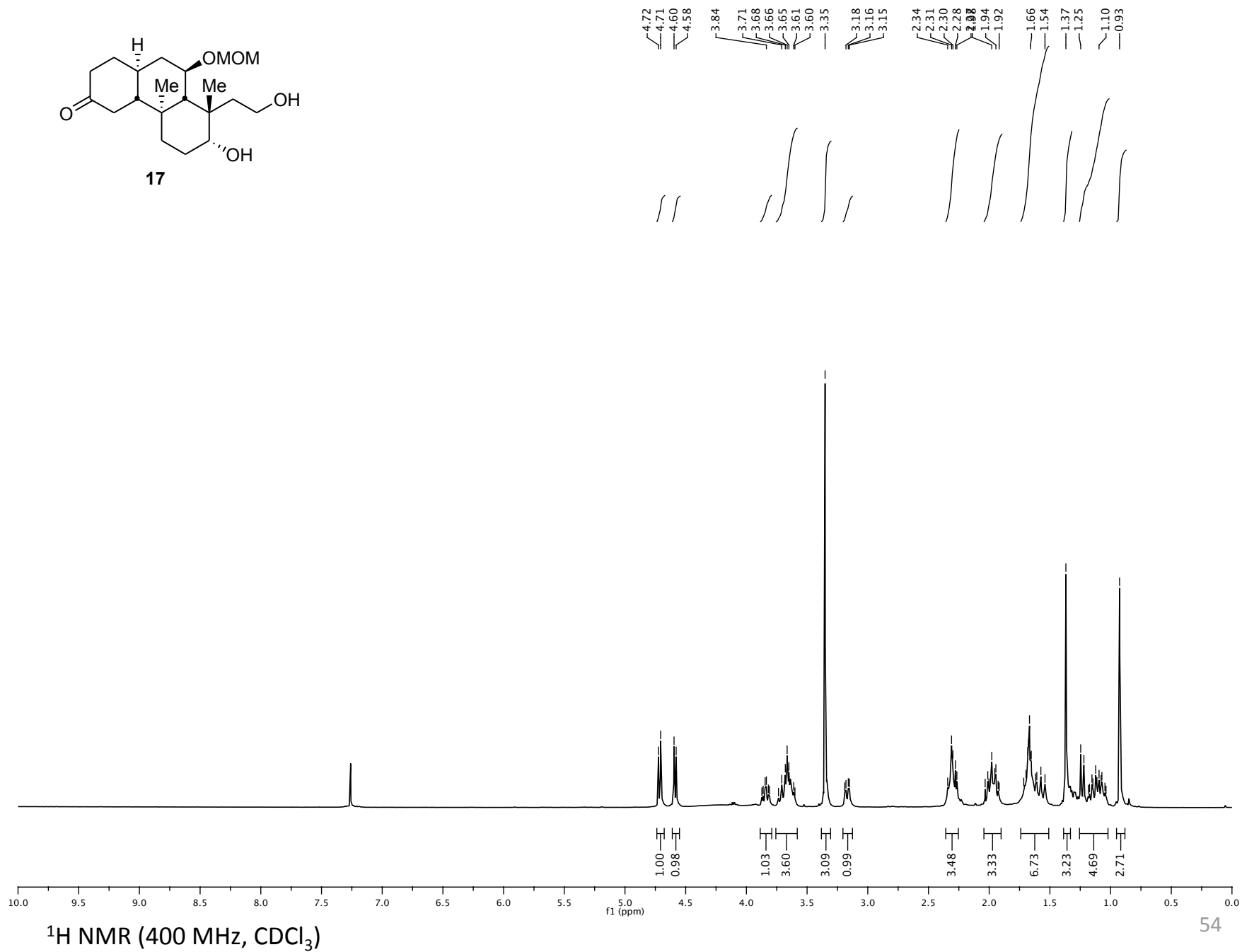
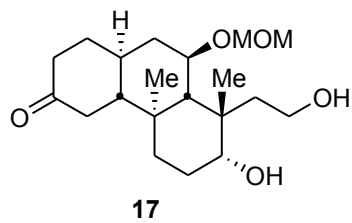
¹H NMR (400 MHz, CDCl₃)



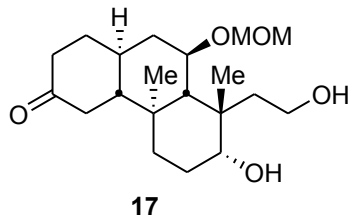
δ 139.0
 δ 138.7
 δ 128.1
 δ 127.7
 δ 127.3
 δ 127.2
 δ 120.3
 δ 96.4
 δ 87.6
 δ 75.6
 δ 72.9
 δ 71.8
 δ 69.2
 δ 57.8
 δ 56.0
 δ 41.7
 δ 41.5
 δ 41.2
 δ 33.1
 δ 31.1
 δ 29.6
 δ 26.2
 δ 22.9
 δ 21.9
 δ 14.1



^{13}C NMR (100 MHz, CDCl_3)



—212.6



—95.8

—78.2
—75.9

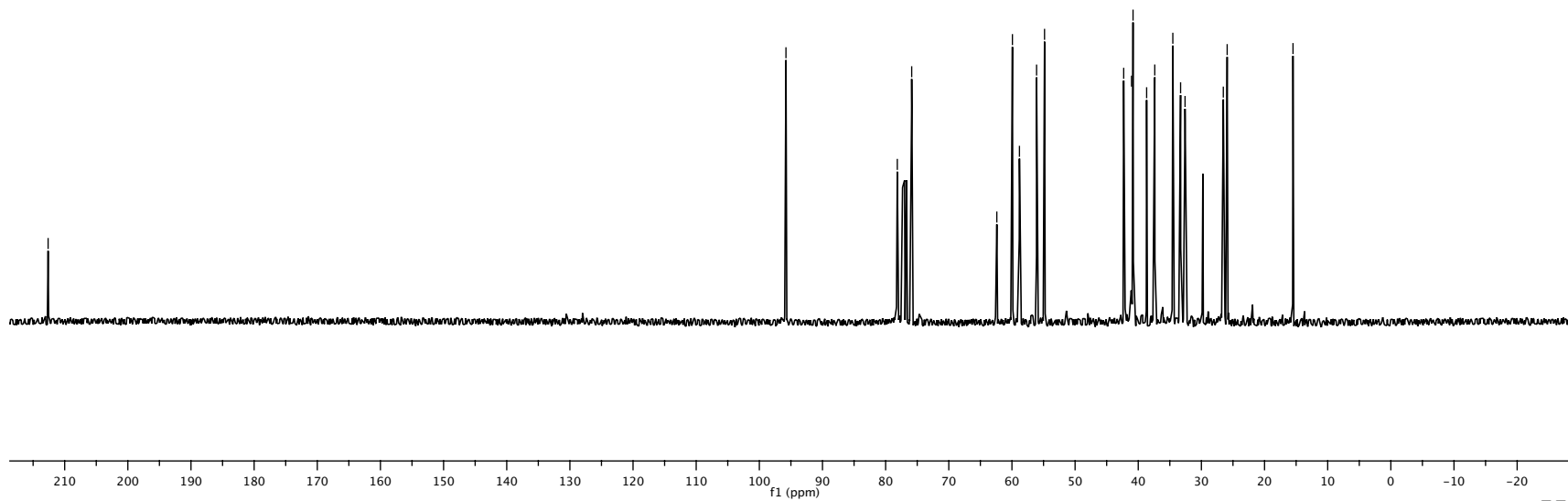
—62.4
—59.9
—58.8
—56.1
—54.8

—42.3
—41.1
—40.8
—38.7
—37.4

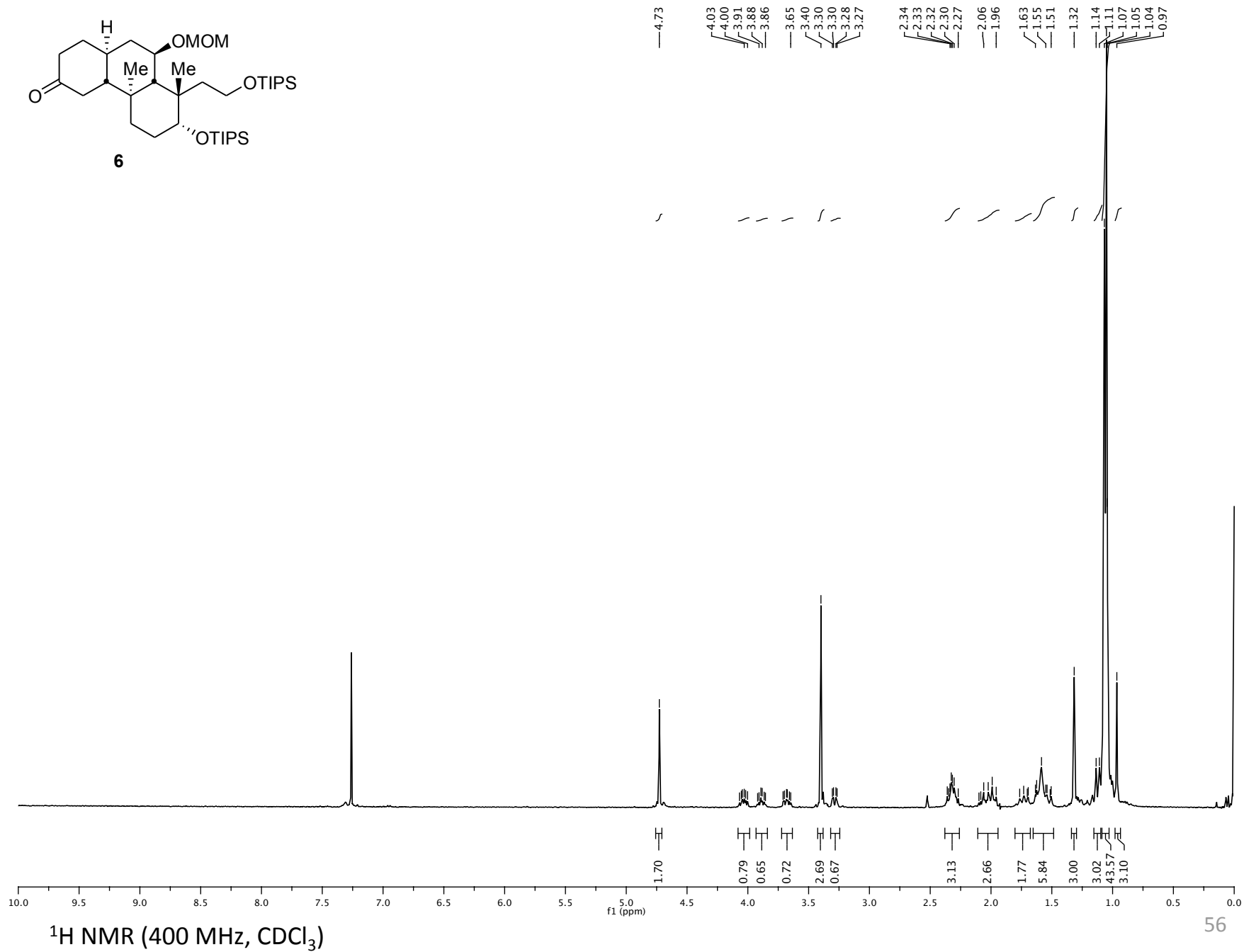
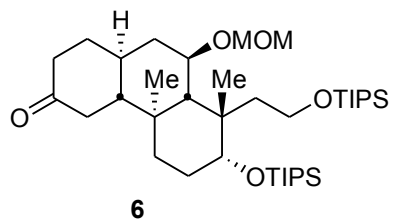
—32.6

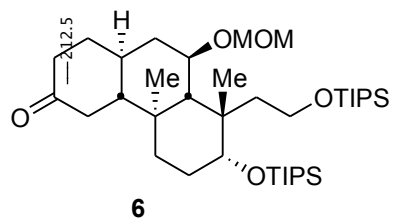
—26.5
—25.9

—15.5

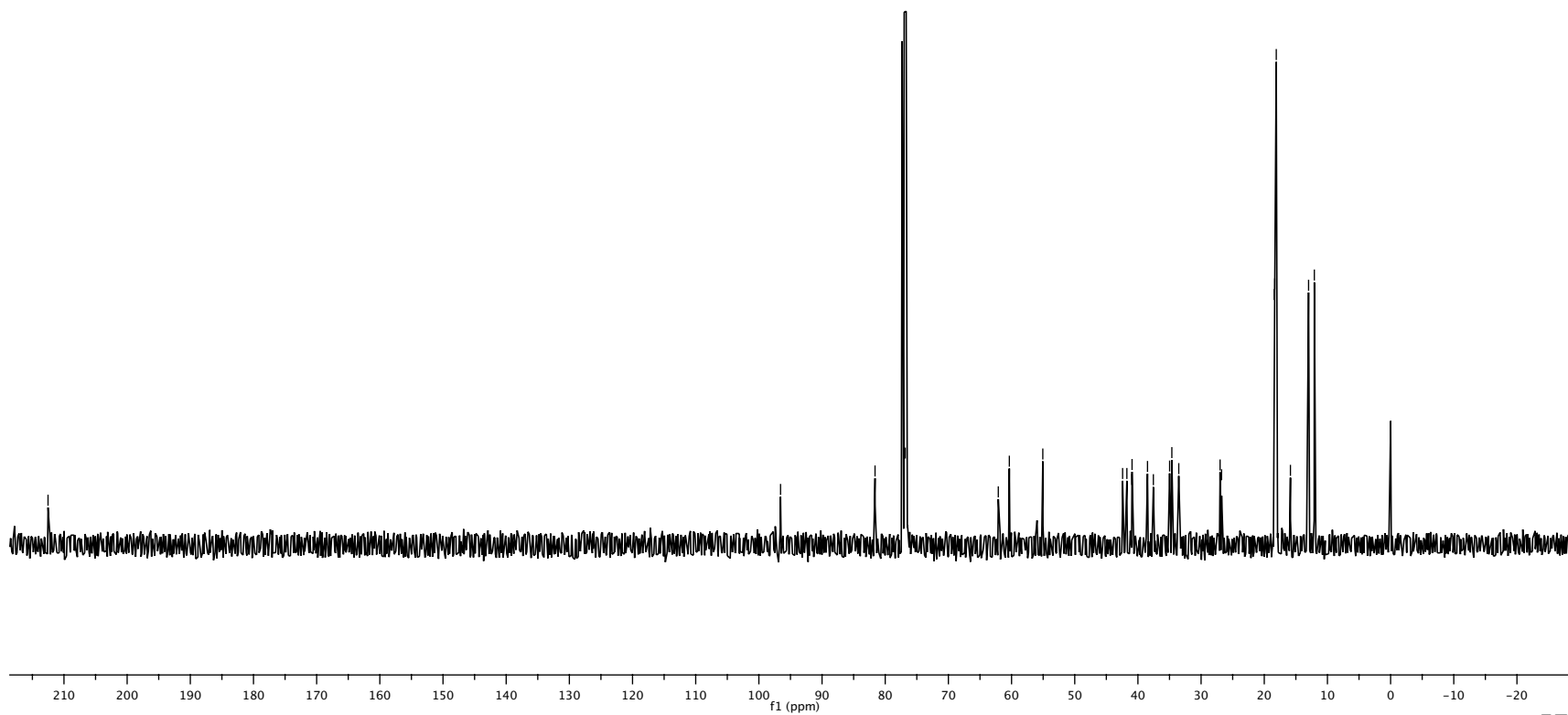


¹³C NMR (100 MHz, CDCl₃)

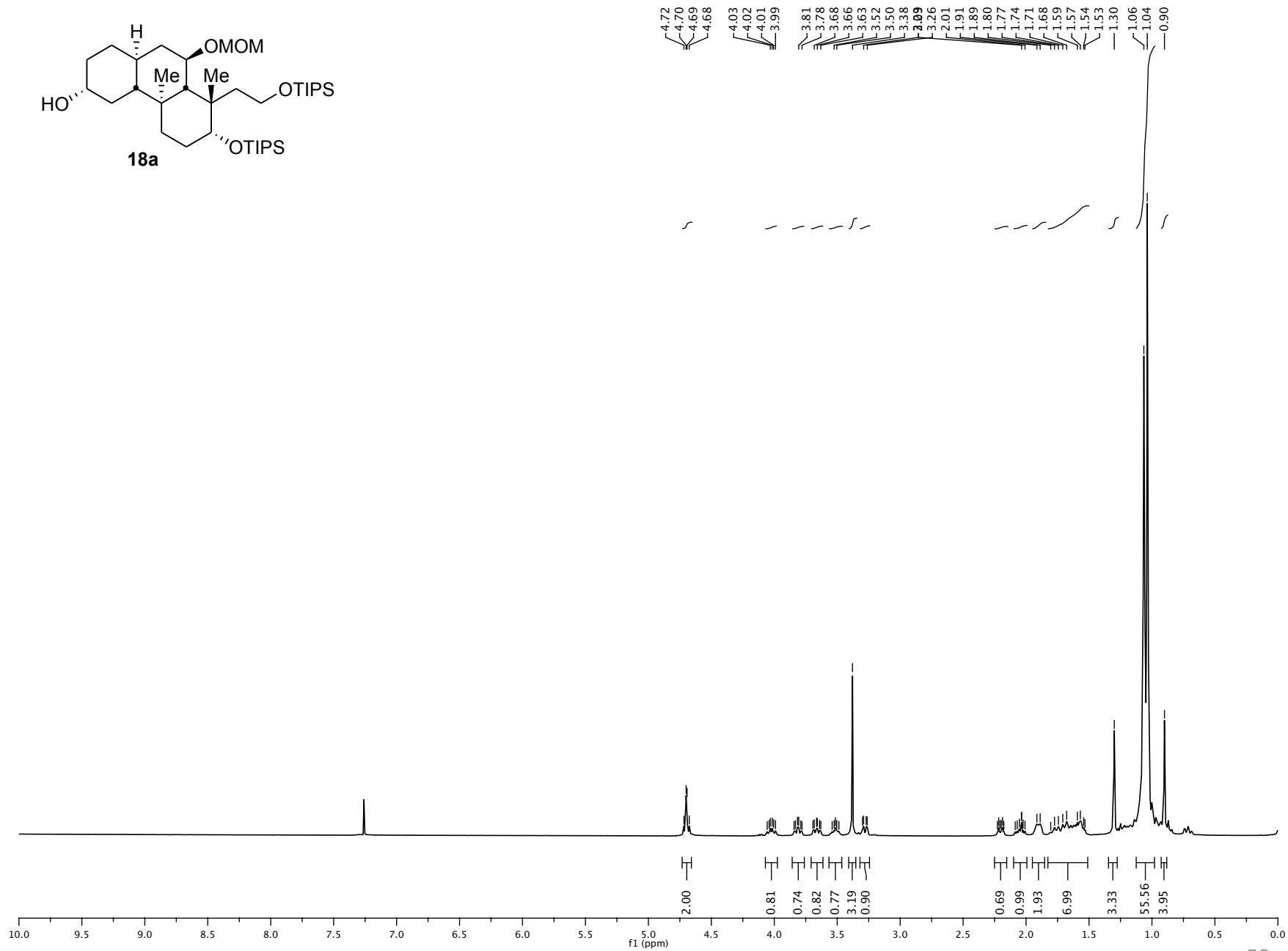
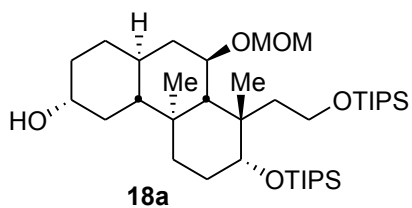


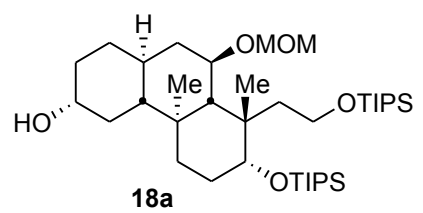


—96.6
 —81.6
 —76.8
 —62.1
 —60.4
 —55.1
 —40.9
 —38.5
 —37.6
 —35.0
 —34.6
 —33.5
 —27.0
 —26.8
 —18.3
 —18.1
 —15.9
 —13.0
 —12.1

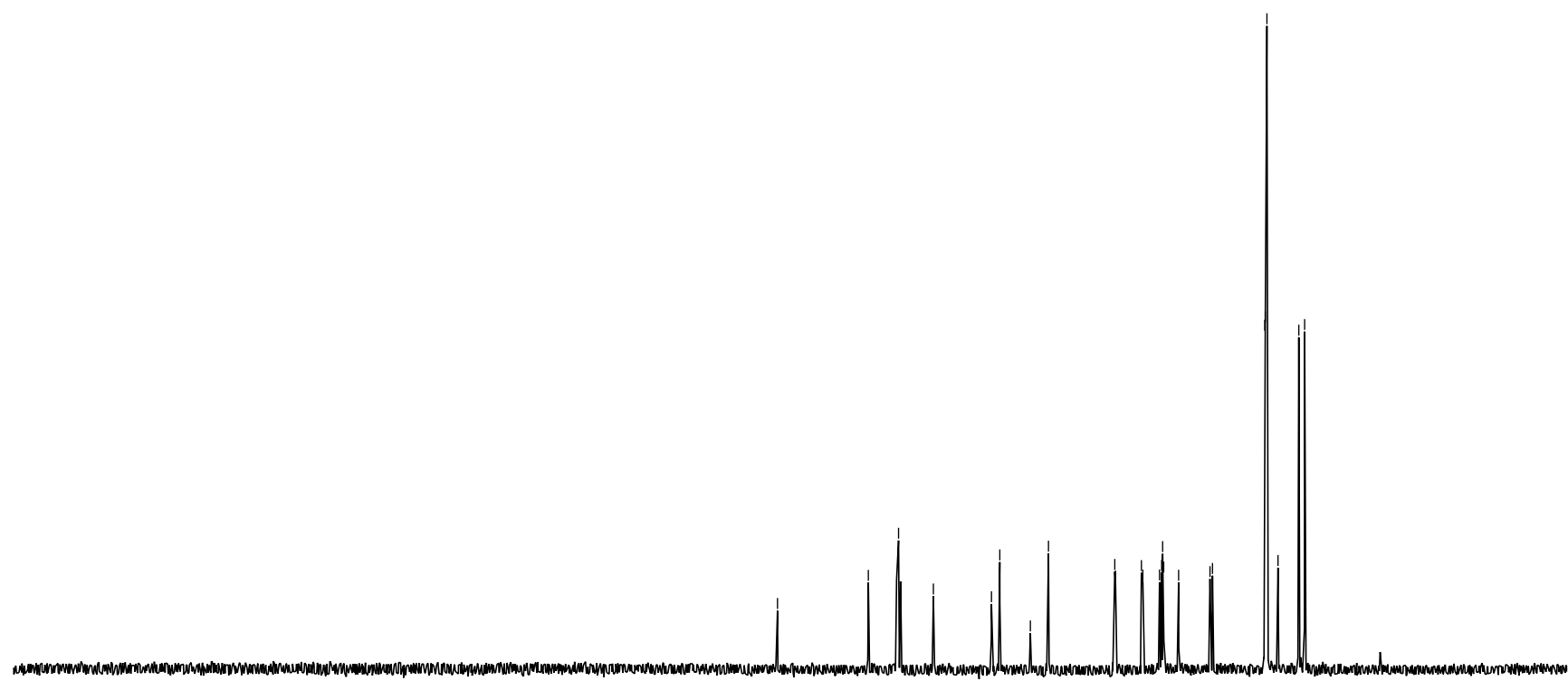


^{13}C NMR (100 MHz, CDCl_3)

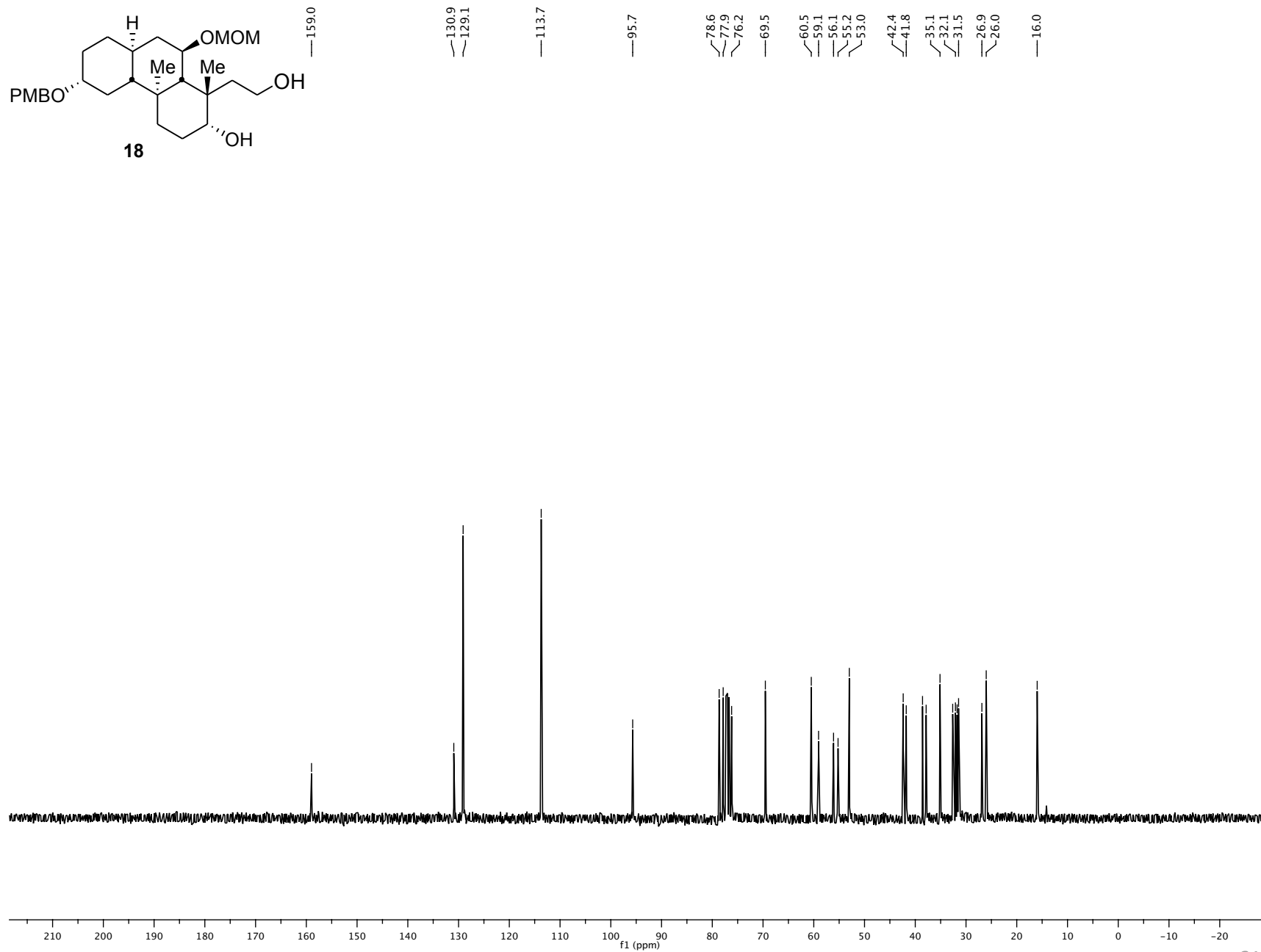
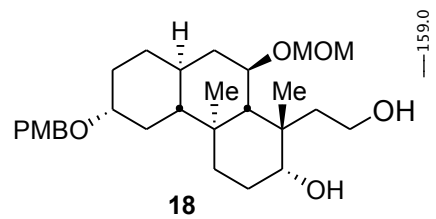


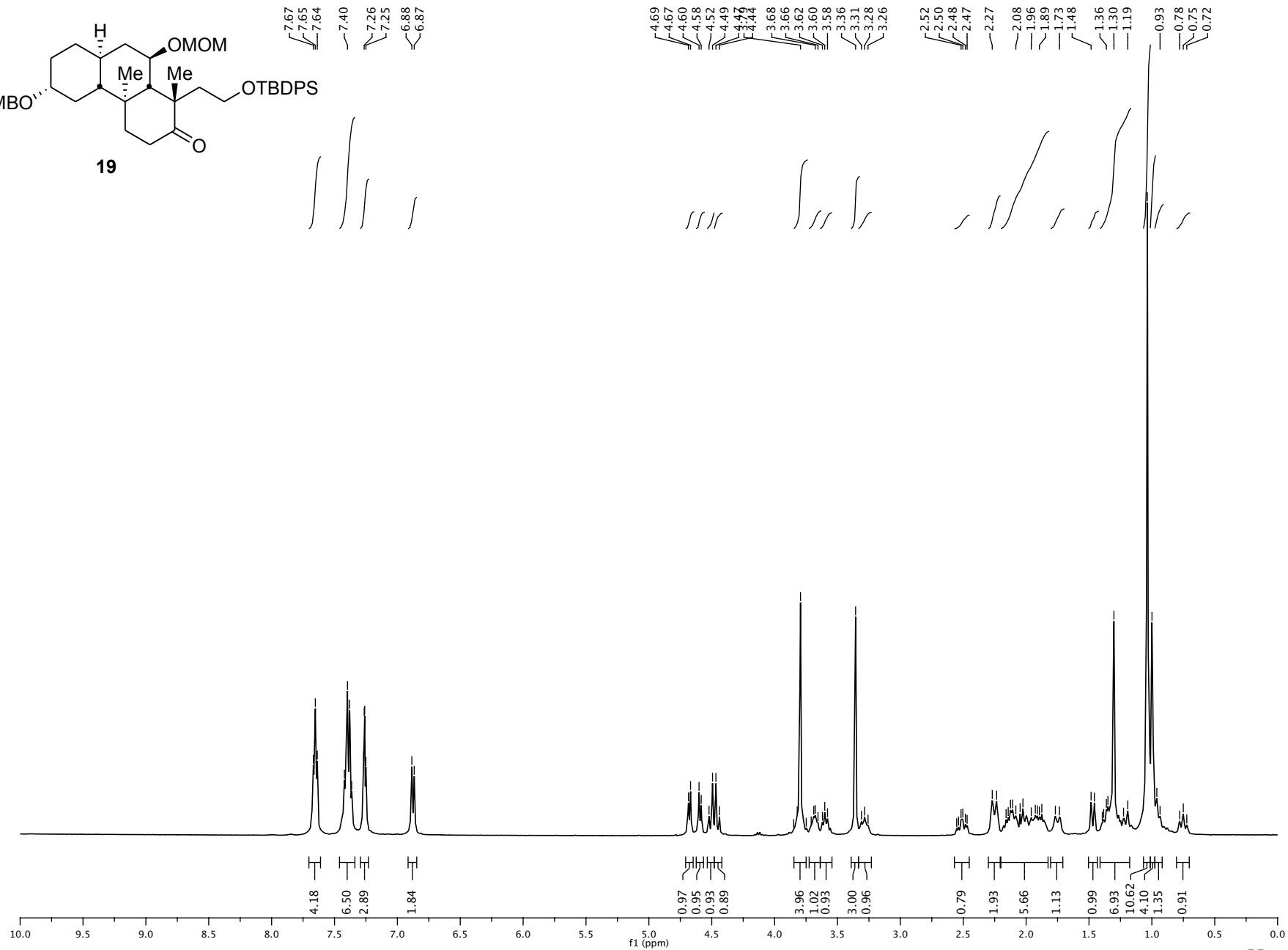
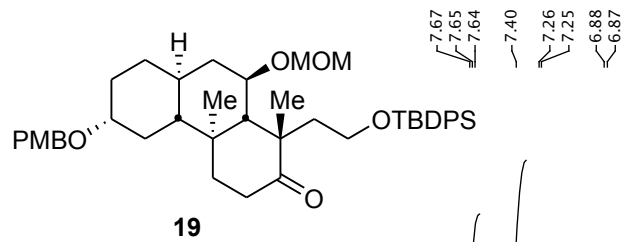


- 96.4
- 81.8
- 77.0
- 71.4
- 62.1
- 60.8
- 55.9
- 53.0
- 42.4
- 36.2
- 34.8
- 32.2
- 27.2
- 26.8
- 18.3
- 18.1
- 16.3
- 13.0
- 12.0

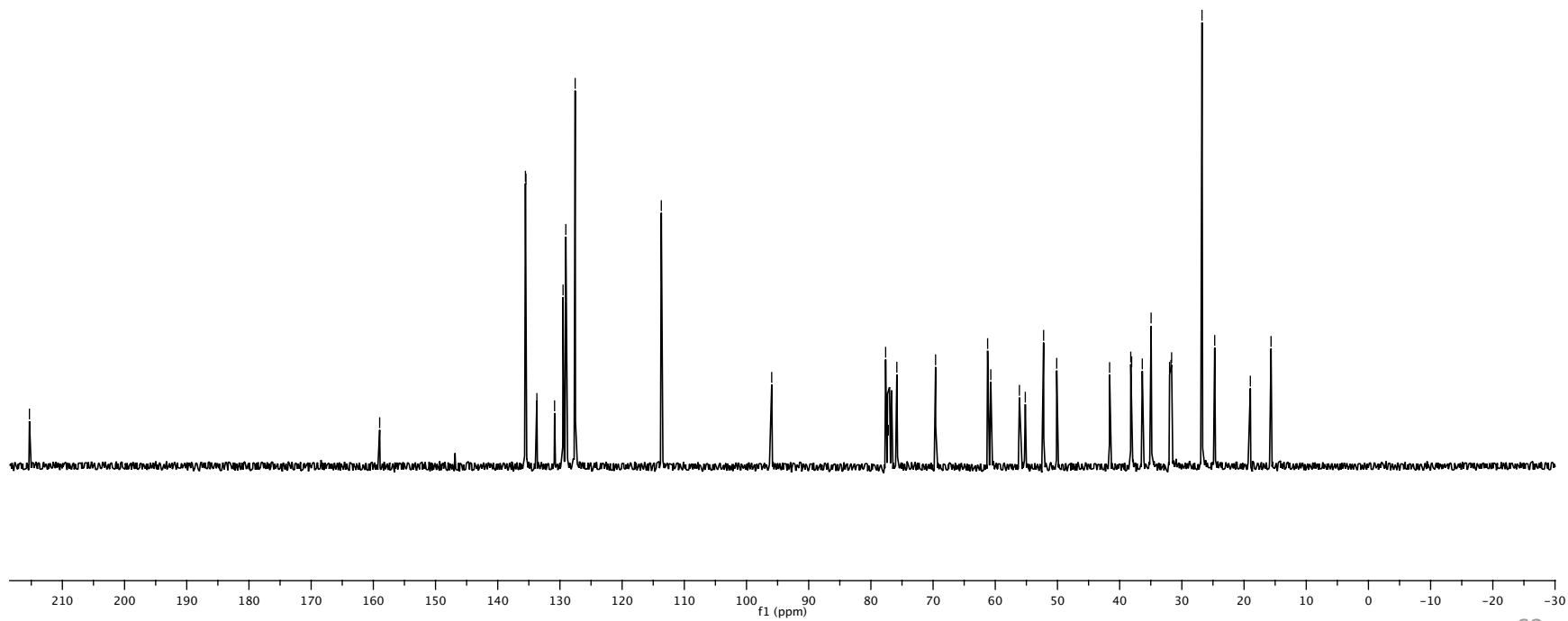
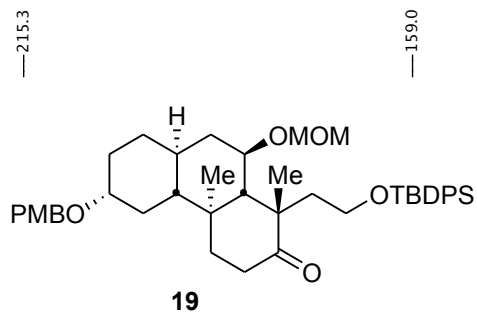


¹³C NMR (100 MHz, CDCl₃)

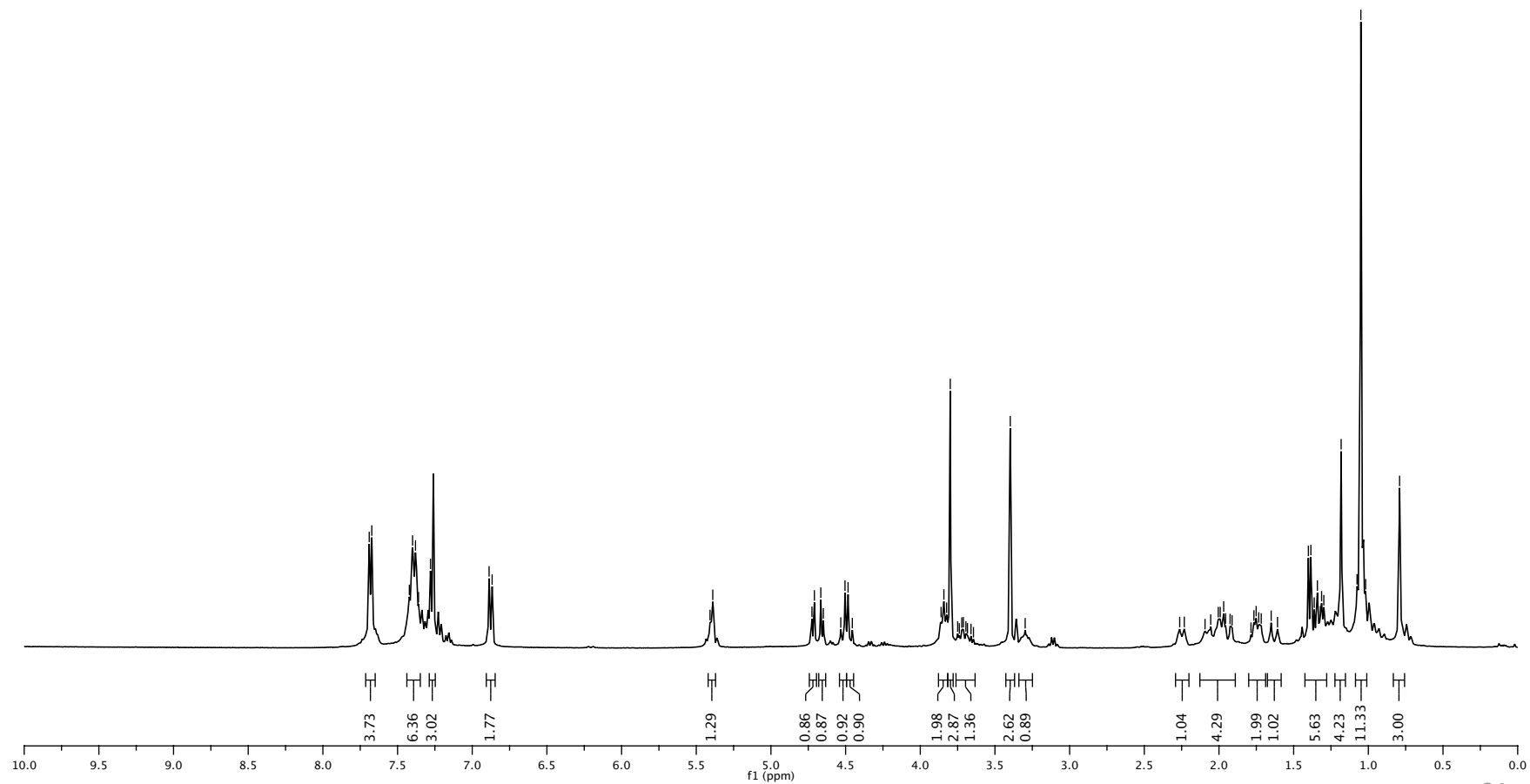
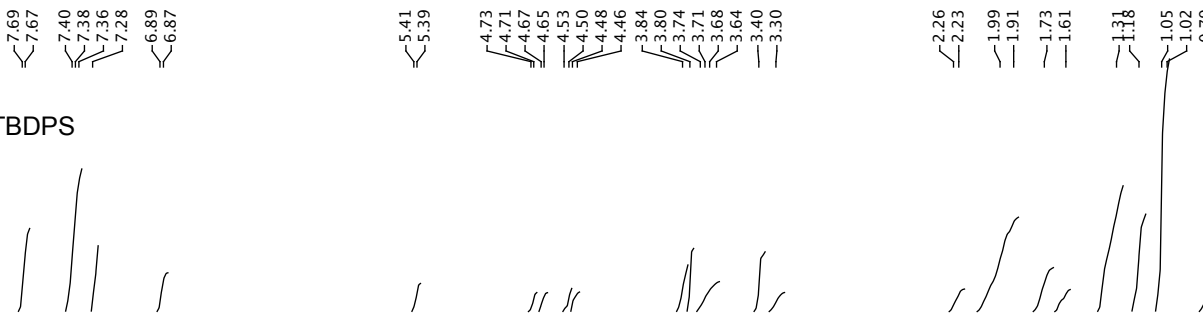
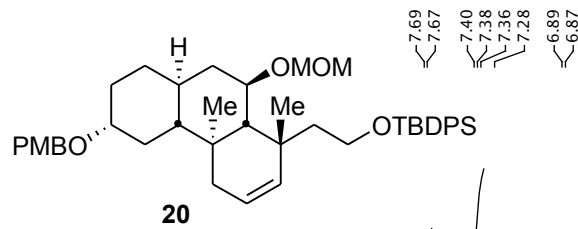




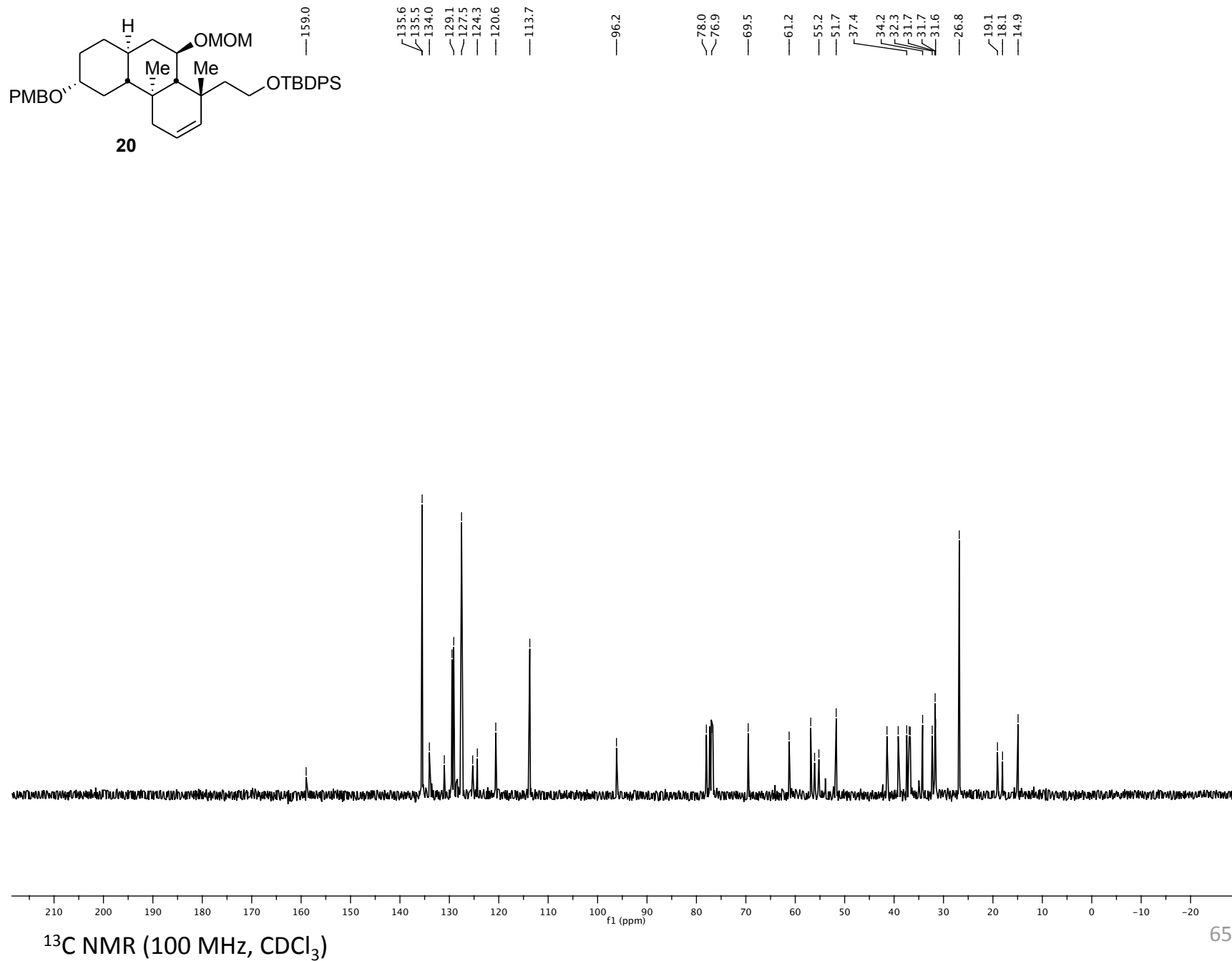
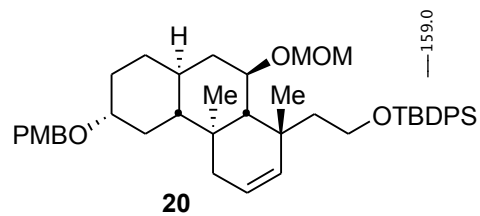
¹H NMR (400 MHz, CDCl₃)

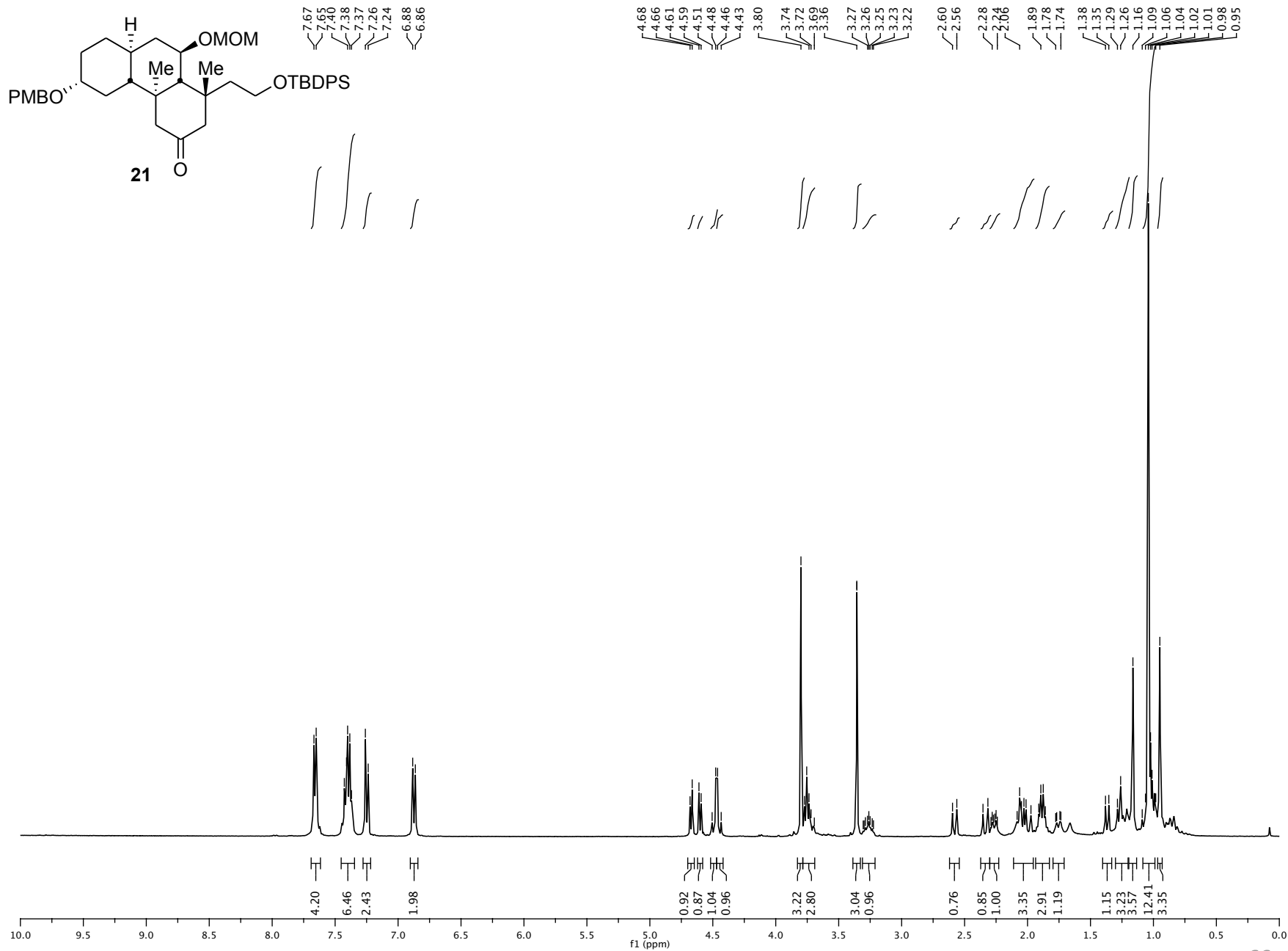
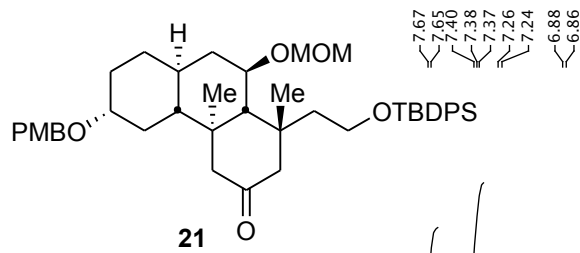


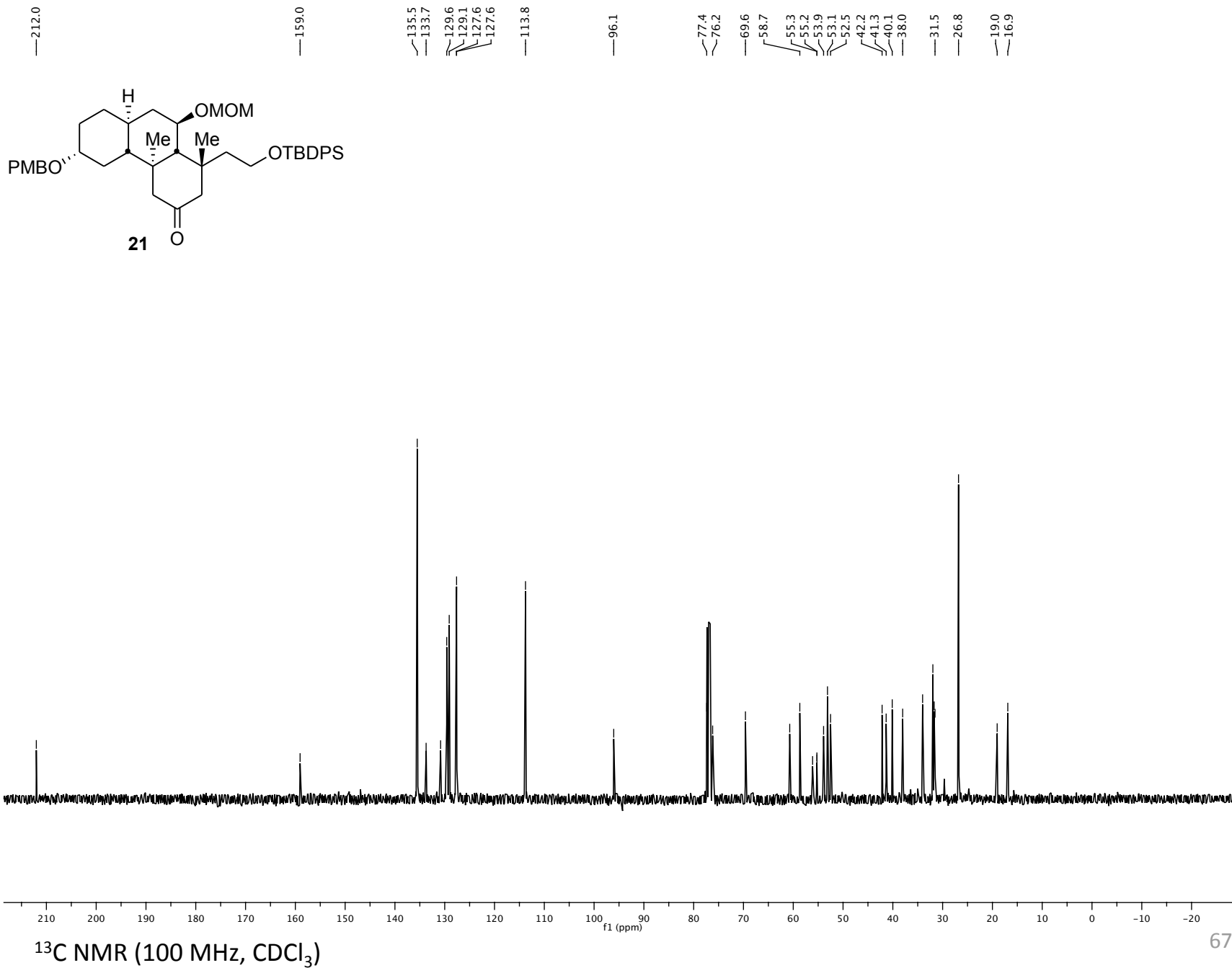
^{13}C NMR (100 MHz, CDCl_3)

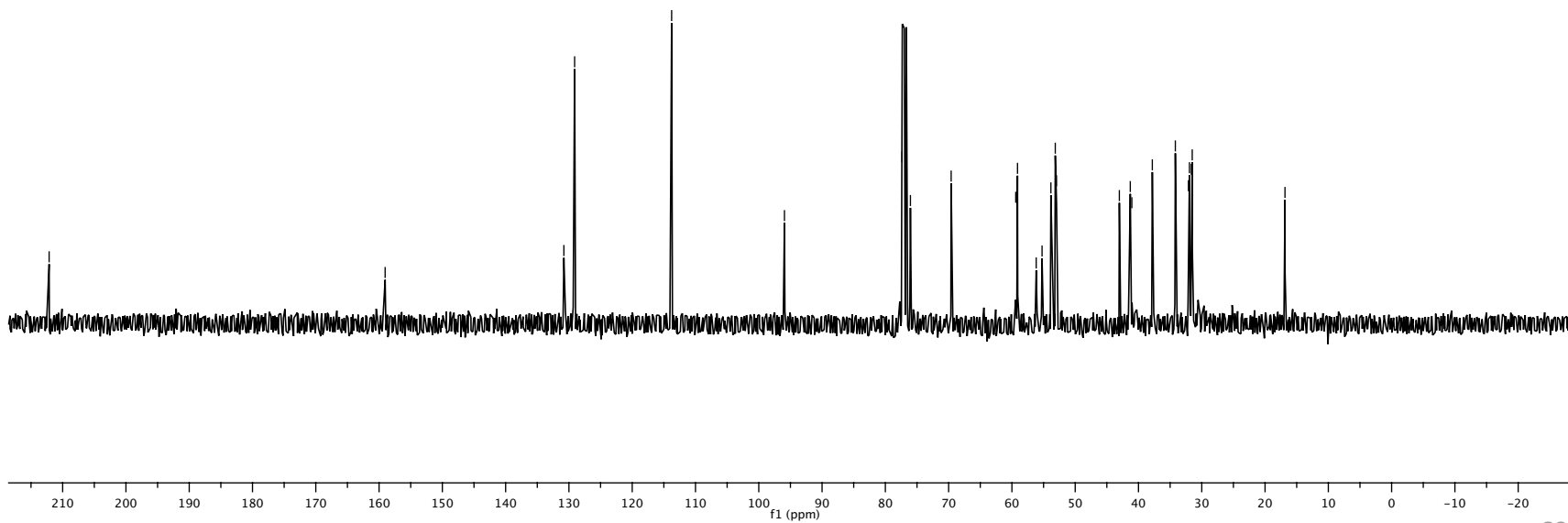
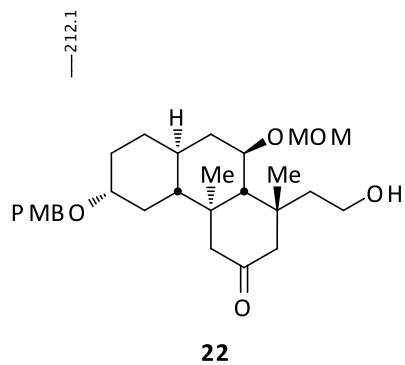


^1H NMR (400 MHz, CDCl_3)

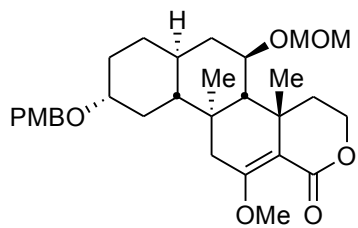




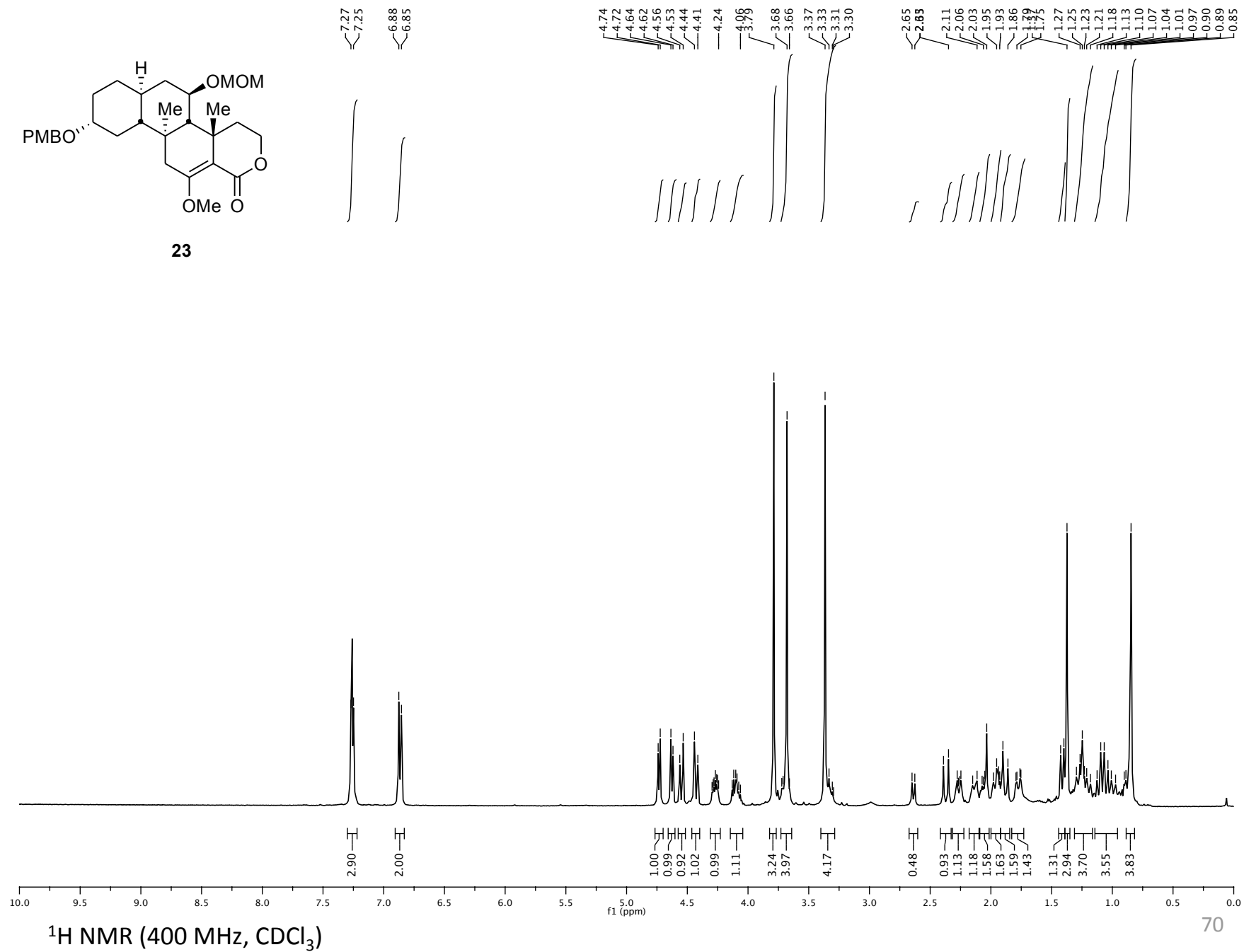


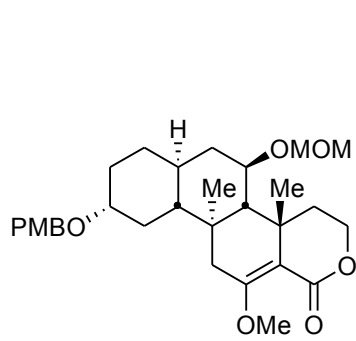


^{13}C NMR (100 MHz, CDCl_3)



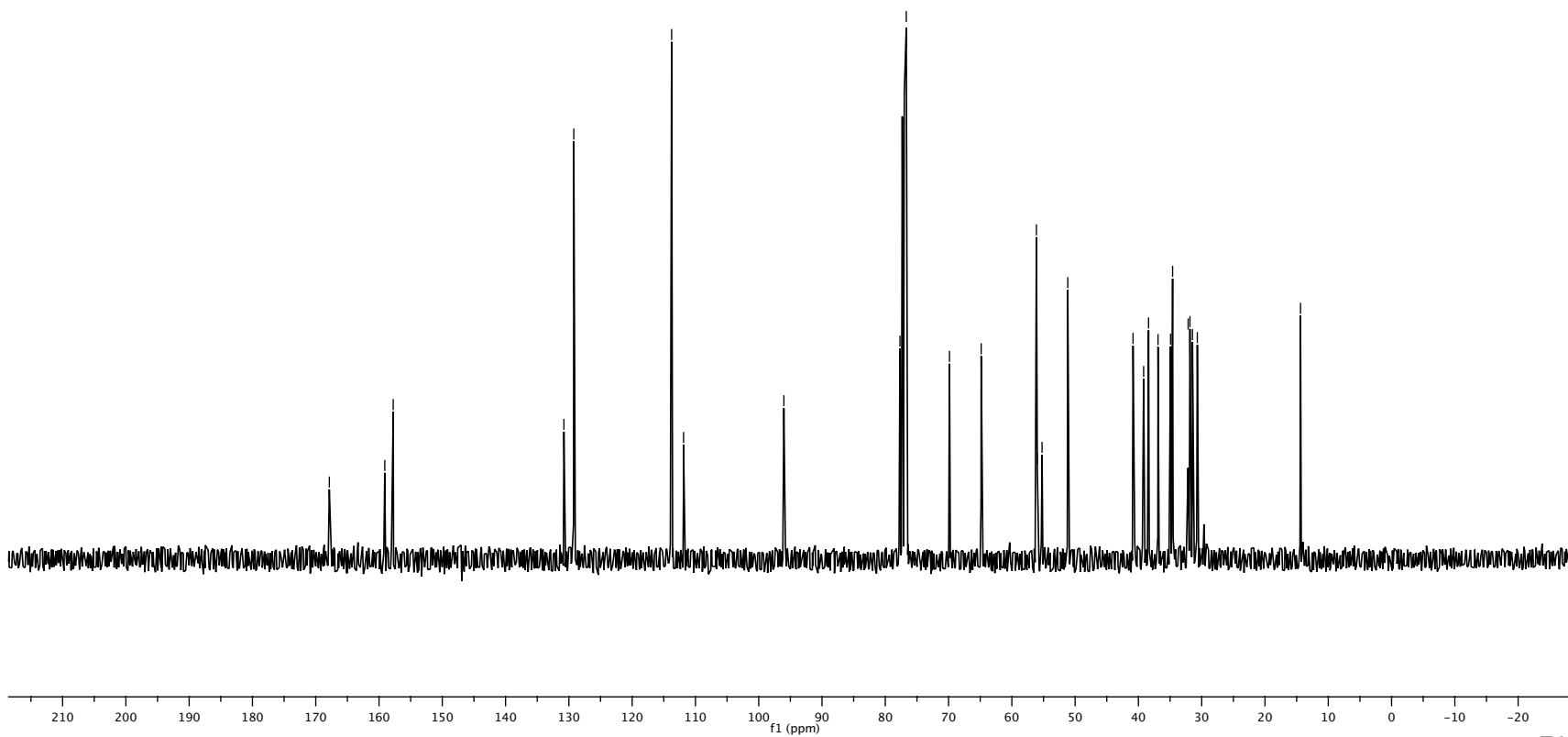
23



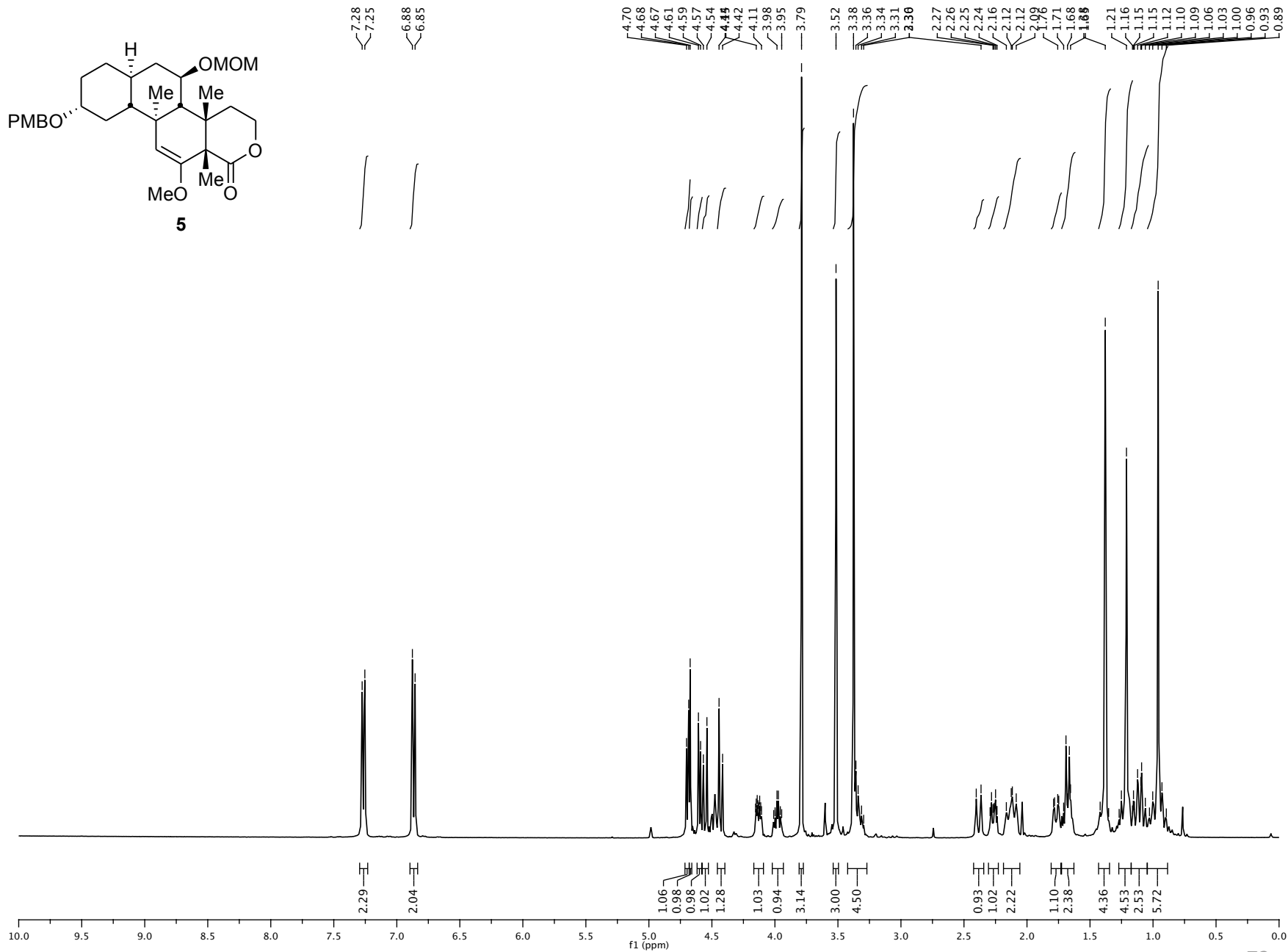
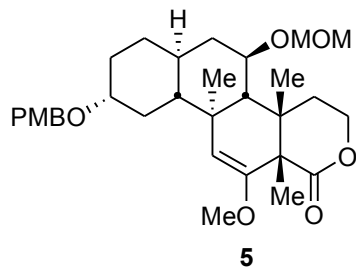


23

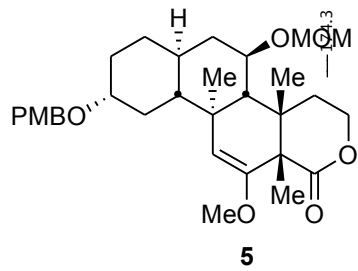
—167.9
 ~159.1
 ~157.8
 ~130.8
 ~129.2
 ~113.8
 ~111.9
 —96.0
 ~77.7
 ~76.7
 —69.9
 —64.8
 ~56.1
 ~55.2
 —51.2
 ~40.8
 ~38.4
 ~36.9
 ~34.9
 ~34.6
 ~32.1
 ~31.9
 ~31.5
 ~30.7
 —14.4



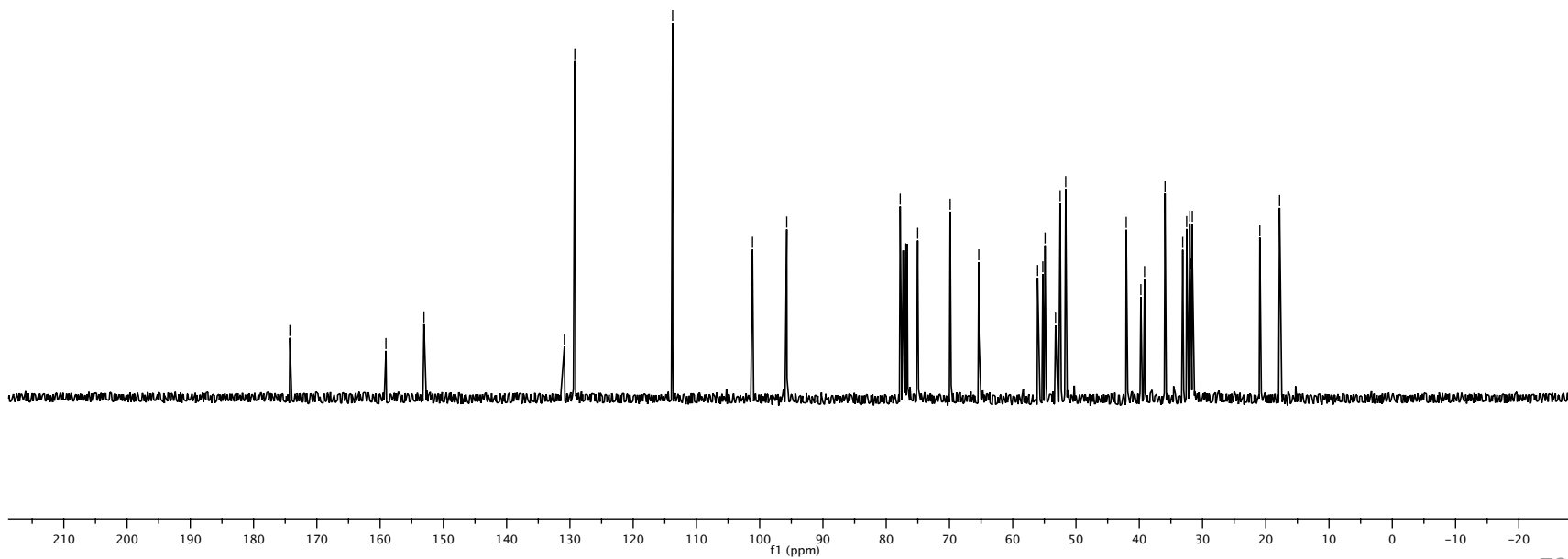
^{13}C NMR (100 MHz, CDCl_3)



^1H NMR (400 MHz, CDCl_3)



- 159.1
- 153.1
- ~ 130.9
- ~ 129.2
- 113.8
- 101.1
- 95.7
- 77.8
- 75.0
- 69.9
- 65.4
- ~ 55.2
- ~ 54.9
- ~ 53.2
- ~ 52.5
- ~ 51.6
- ~ 42.1
- ~ 39.7
- ~ 39.2
- 35.9
- ~ 32.0
- ~ 31.8
- ~ 31.6
- 20.9
- 17.8



^{13}C NMR (100 MHz, CDCl_3)