

Total Synthesis of (+)-Aureol

Kevin K. W. Kuan, Henry P. Pepper, Witold M. Bloch, and Jonathan H. George*

*School of Chemistry & Physics, University of Adelaide, North Terrace, Adelaide SA 5005,
Australia.*

Supporting Information

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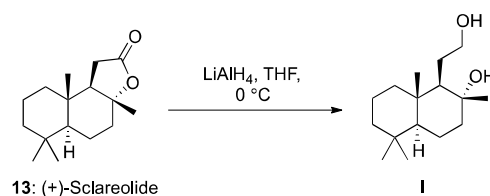
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1. General methods

All chemicals used were purchased from commercial suppliers and used as received. All organic extracts were dried over anhydrous magnesium sulfate. Thin layer chromatography was performed using Merck aluminium sheets silica gel 60 F₂₅₅. Visualisation was aided by viewing under a UV lamp and staining with CAM stain followed by heating. All R_f values were rounded to the nearest 0.05. Flash chromatography was performed using Davisil (40-63 micron) grade silica gel. Melting points were recorded on a SRS Digimelt MPA 161 melting apparatus and are uncorrected. Infrared spectra were recorded using a Perkin Elmer Spectrum BX FT-IR system spectrometer as the neat compounds. Optical rotations were obtained on a P0A1 AR21 polarimeter. ¹H and ¹³C NMR spectra were recorded using a Varian Inova-6000 spectrometer (¹H at 600 MHz, ¹³C at 150 MHz) or a Bruker AV400 spectrometer (¹H at 400 MHz, ¹³C at 100 MHz). The NMR solvent used was CDCl₃ unless otherwise specified. ¹H chemical shifts are reported in ppm on the δ -scale relative to TMS (δ 0.0) and ¹³C NMR are reported in ppm relative to chloroform (δ 77.0). Multiplicities are reported as (br) broad, (s) singlet, (d) doublet, (t) triplet, (q) quartet, (qnt) quintet, (sxt) sextet and (m) multiplet. All *J* values were rounded to the nearest 0.5 Hz. EI low resolution mass spectra were recorded on a Shimadzu GCMS-QP 5050A mass spectrometer. ESI high resolution mass spectra were recorded using an LTQ Orbitrap XL ETD (Thermo Fisher Scientific Inc., MA).

2. Experimental procedures

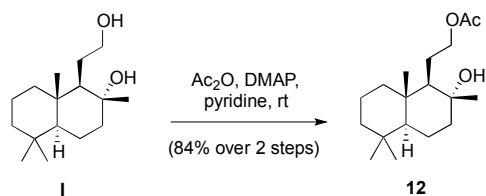
Diol I



LiAlH₄ (2.0 M in THF, 20.0 mL, 40.0 mmol) was added dropwise to a solution of (+)-sclareolide **13** (10.0 g, 40.0 mmol) in anhydrous THF (100 mL) at 0 °C. The reaction mixture was then stirred at 0 °C for 1 h. The reaction was quenched with EtOAc (10 mL), then diluted with CH₂Cl₂ (100 mL) and 1M HCl (150 mL). The mixture was extracted with CH₂Cl₂ (2 × 100 mL), washed with 1M HCl, water and brine, then dried over MgSO₄, filtered and the solvent was removed *in vacuo* to give crude diol **I** (9.76 g), which was used without further purification.

Data for **I**: R_f 0.30 (petrol ether/EtOAc, 1:1); mp 128 – 130 °C; [α]_D²⁵ (c 1.11, CHCl₃) -16.2°; IR (Diamond/ZnSe): 3230, 2918, 1460, 1441, 1389 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 3.74 (br s, 2H), 3.69 (dt, *J* = 10.0, 4.5 Hz, 1H), 3.39 – 3.33 (m, 1H), 1.83 (dt, *J* = 12.5, 3.0 Hz, 1H), 1.61 – 1.03 (overlapped m, 11H), 1.11 (s, 3H), 0.87 (m, 2H), 0.80 (s, 3H), 0.72 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 72.8, 63.9, 59.3, 56.0, 44.0, 41.9, 39.3, 38.9, 33.4, 33.2, 27.8, 24.5, 21.5, 20.4, 18.4, 15.3; HRMS (C₁₆H₃₀O₂Na, ESI): calculated 277.2138 [M+Na]⁺, found 277.2134.

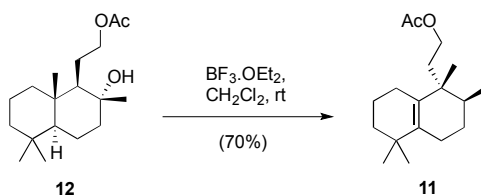
Acetate ester 12



To a solution of diol **I** (9.58 g, 37.7 mmol) in CH₂Cl₂ (80 mL) was added Ac₂O (5.33 mL, 56.4 mmol) followed by pyridine (6.07 mL, 75.3 mmol). The reaction was stirred at rt under inert atmosphere overnight, then quenched with saturated NH₄Cl solution (100 mL) and extracted with CH₂Cl₂ (2 × 100 mL). The combined organic extracts were washed with saturated NH₄Cl solution, water, and brine. The organic phase was then dried over MgSO₄, filtered and the solvent was removed *in vacuo* to give crude product, which was purified by flash column chromatography (gradient elution, petrol ether/EtOAc, 5:1 → 1:1) to give acetate ester **12** as a colourless oil (9.66 g, 87%).

Data for **12**: R_f 0.30 (petrol ether/EtOAc, 5:1); [α]_D²⁵ (c 1.76, CHCl₃) +1.1°; IR (Diamond/ZnSe): 3472, 2925, 2868, 1736, 1721, 1460, 1388, 1366 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ 4.16 – 4.08 (m, 2H), 2.05 (s, 3H), 1.89 (dt, *J* = 12.0, 3.0 Hz, 1H), 1.76 – 1.09 (overlapped m, 12H), 1.16 (s, 3H), 0.92 (d, *J* = 12.0 Hz, 2H), 0.87 (s, 3H), 0.79 (s, 6H); ¹³C NMR (150 MHz, CDCl₃): δ 171.1, 73.5, 66.6, 58.0, 56.0, 44.4, 41.9, 39.6, 38.7, 33.4, 33.3, 24.5, 23.9, 21.5, 21.1, 20.5, 18.4, 15.3; HRMS (C₁₈H₃₂O₃Na, ESI): calculated 319.2244 [M+Na]⁺, found 319.2224.

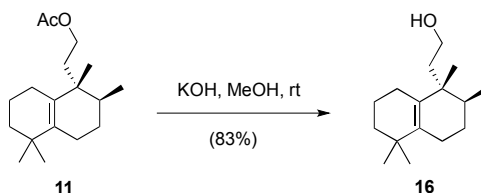
Acetate ester **11**



To a solution of acetate ester **12** (12.2 g, 41.0 mmol) in CH_2Cl_2 (140 mL) at rt was added $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (20.2 mL, 163 mmol). The reaction was stirred at rt for 12 h, then diluted with H_2O (100 mL) and CH_2Cl_2 (100 mL). The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (3×50 mL). The organic layers were combined, dried over MgSO_4 , filtered and concentrated *in vacuo*. The crude material was purified by flash column chromatography (gradient elution, petrol ether/EtOAc, 100:0 \rightarrow 10:1) to give acetate ester **11** as a colourless oil (7.76 g, 70%).

Data for **11**: R_f 0.70 (petrol ether/EtOAc, 5:1); $[\alpha]_D^{25}$ (c 1.36, CHCl_3) -75.2° ; IR (Diamond/ZnSe): 2924, 1741, 1458, 1364, 1231 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3): δ 4.06 – 4.01 (m, 1H), 3.87 – 3.83 (m, 1H), 2.06 – 1.27 (overlapped m, 13H), 2.02 (s, 3H), 0.97 (s, 3H), 0.95 (s, 3H), 0.88 (d, $J = 7.0$ Hz, 3H), 0.84 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 171.4, 137.5, 131.9, 62.3, 40.0, 39.9, 34.6, 34.6, 34.5, 29.2, 27.8, 27.3, 26.0, 25.2, 21.3, 21.2, 20.1, 16.3; HRMS ($\text{C}_{18}\text{H}_{30}\text{O}_2\text{Na}$, ESI): calculated 301.2138 $[\text{M}+\text{Na}]^+$, found 301.2139.

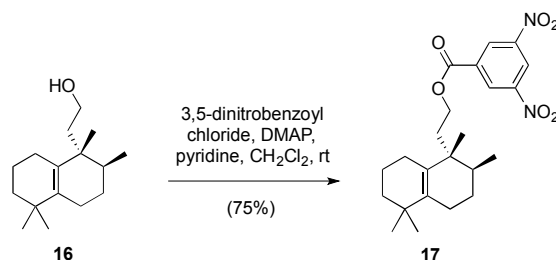
Alcohol **16**



A 10% solution of KOH (21.9 g, 391 mmol) in MeOH (220 mL) was added to a flask containing ester **11** (7.74 g, 27.8 mmol). The reaction was stirred at rt for 30 min, then diluted with aqueous NH_4Cl and Et_2O . The organic layer was separated, the aqueous phase extracted with Et_2O , washed with brine, dried over MgSO_4 , filtered and concentrated *in vacuo*. The crude alcohol was purified by flash column chromatography (gradient elution, petrol ether/EtOAc, 5:1 \rightarrow 3:1) to give alcohol **16** as a white solid (5.48 g, 83%).

Data for **16**: R_f 0.35 (petrol ether/EtOAc, 5:1); mp $46 - 48^\circ\text{C}$; $[\alpha]_D^{25}$ (c 1.21, CHCl_3) -101.6° ; IR (Diamond/ZnSe): 3308, 2923, 1458, 1359, 1015 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3): δ 3.63 – 3.59 (m, 1H), 3.51 – 3.47 (m, 1H), 2.04 – 1.30 (m, 14H), 0.98 (s, 3H), 0.95 (s, 3H), 0.88 (d, $J = 7.0$ Hz, 3H), 0.84 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 137.1, 132.6, 60.1, 39.9, 38.9, 34.6, 34.5, 29.1, 27.7, 27.2, 26.1, 25.1, 21.2, 19.9, 16.3; HRMS ($\text{C}_{16}\text{H}_{28}\text{O}$, EI): calculated 236.2140 $[\text{M}]^+$, found 236.2141.

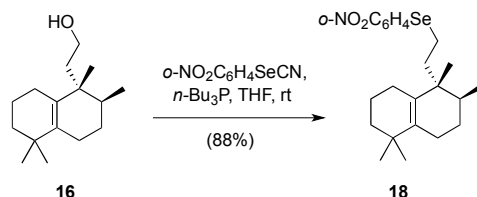
3,5-Dinitrobenzoate 17



To a solution of alcohol **16** (400 mg, 1.69 mmol) in anhydrous CH_2Cl_2 (5 mL) under N_2 at rt was added 3,5-dinitrobenzoyl chloride (733 mg, 3.38 mmol), DMAP (21 mg, 0.17 mmol) and pyridine (0.27 mL, 3.38 mmol). The reaction mixture was stirred at rt for 18 h, then diluted with CH_2Cl_2 (50 mL) and washed with 1 M HCl solution (2×30 mL). The organic phase was then dried over MgSO_4 , filtered and concentrated *in vacuo* to give a yellow solid. Purification by flash chromatography on silica gel (gradient elution, petrol ether/ CH_2Cl_2 , 10:1 \rightarrow 1:1) gave **17** (545 mg, 75%) as a white solid. Recrystallisation of a sample of **17** from EtOH gave colourless crystals that were suitable for X-ray crystallographic analysis.

Data for **17**: R_f 0.45 (petrol ether/EtOAc, 10:1); IR (Diamond/ ZnSe): 2877, 1720, 1543, 1461, 1346, 1282, 1169 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.21 (t, $J = 2.0$ Hz, 1H), 9.14 (d, $J = 2.0$ Hz, 2H), 4.42 – 4.35 (m, 1H), 4.30 – 4.24 (m, 1H), 2.09– 1.83 (m, 6H), 1.69 – 1.32 (m, 7H), 0.99 (s, 3H), 0.96 (s, 3H), 0.95 (d, $J = 7.0$ Hz, 3H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): 162.6, 148.6, 138.1, 134.2, 131.2, 129.4, 122.2, 64.8, 40.1, 39.7, 34.7, 34.5, 34.3, 29.1, 27.6, 27.0, 26.0, 25.1, 21.0, 19.9, 16.2. HRMS ($\text{C}_{23}\text{H}_{31}\text{N}_2\text{O}_6$, ESI): calculated 431.2177 $[\text{M}+\text{H}]^+$, found 431.2189.

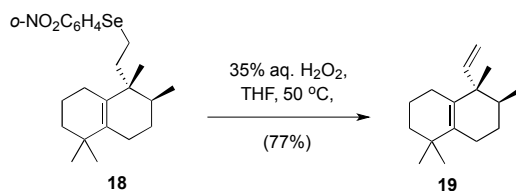
Aryl selenide 18



To a solution of alcohol **16** (1.30 g, 5.52 mmol) in anhydrous THF (25 mL) was added 2-nitrophenylselenocyanate (1.88 g, 8.29 mmol) and Me_3P (1.0 M in THF, 11.2 mL, 11.2 mmol) under N_2 atmosphere. The reaction mixture was left to stir at rt for 1 h, then quenched with saturated NH_4Cl solution (50 mL). The mixture was extracted with Et_2O (3×50 mL). The organic phases were combined, washed with brine, dried over MgSO_4 , filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (gradient elution, petrol ether/EtOAc, 100:0 \rightarrow 10:1) to give aryl selenide **18** as a bright yellow oil (2.29 g, 88%).

Data for **18**: R_f 0.55 (petrol ether/EtOAc, 10:1); $[\alpha]_D^{25}$ (c 1.42, CHCl_3) -31.1° ; IR (Diamond/ ZnSe): 2923, 1738, 1590, 1511, 1452, 1330, 728 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.19 (d, $J = 8.0$ Hz, 1H), 7.44 – 7.41 (m, 2H), 7.24 – 7.19 (m, 1H), 2.80 – 2.73 (m, 1H), 2.52 – 2.45 (m, 1H), 1.95 – 1.93 (m, 3H), 1.73 – 1.25 (m, 10H), 0.91 (s, 6H), 0.81 (d, $J = 7.0$ Hz, 3H), 0.78 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 145.7, 137.2, 133.3, 132.5, 130.4, 128.1, 125.4, 124.2, 40.9, 38.8, 33.5, 33.2, 32.8, 28.2, 26.6, 26.0, 24.9, 24.0, 20.5, 19.9, 18.8, 15.3; HRMS ($\text{C}_{22}\text{H}_{32}\text{NO}_2\text{Se}$, EI): calculated 421.1521 $[\text{M}+\text{H}]^+$, found 421.1510.

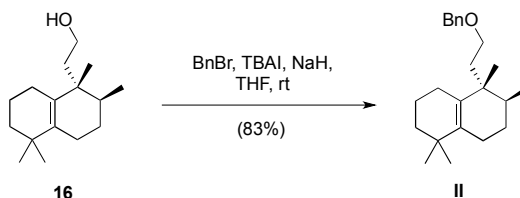
Alkene 19



To a solution of aryl selenide **18** (2.23 g, 5.31 mmol) in THF (34 mL) was added 30% H₂O₂ (1.09 mL, 10.6 mmol). The reaction mixture was left to stir at rt for 15 min, then heated to 50 °C for 45 min. The reaction mixture was quenched with Na₂S₂O₃ (50 mL) and extracted with Et₂O (3 × 50 mL). The organic phases were combined, washed with brine, dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (neat petrol) to give alkene **19** as a colourless oil (900 mg, 77%).

Data for **19**: R_f 0.80 (neat petrol); [α]_D²⁵ (c 1.52, CHCl₃) +54.1°; IR (Diamond/ZnSe): 2923, 1631, 1459, 1360 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 5.55 (dd, *J* = 17.5, 10.5 Hz, 1H), 5.03 (dd, *J* = 10.5, 1.5 Hz, 1H), 4.88 (dd, *J* = 17.5, 1.5 Hz, 1H), 2.08 – 1.92 (m, 2H), 1.84 – 1.78 (m, 2H), 1.65 – 1.27 (m, 7H), 1.00 (s, 3H), 0.99 (s, 3H), 0.95 (s, 3H), 0.81 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 147.9, 135.5, 131.2, 112.3, 45.0, 39.9, 37.0, 34.3, 28.6, 28.2, 27.5, 26.5, 24.0, 20.0, 17.4, 15.9; HRMS (C₁₆H₂₆, EI): calculated 218.2034 [M⁺], found 218.2037.

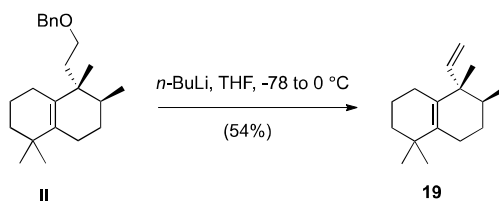
Benzyl ether II



To a cooled solution of alcohol **16** (270 mg, 1.14 mmol) in anhydrous THF (3 mL) at 0 °C was added NaH (60% in dispersion oil, 60 mg, 1.37 mmol) and TBAI (4.2 mg, 0.01 mmol). The reaction was allowed to stir for 15 min, followed by the addition of BnBr (230 mg, 1.37 mmol). The reaction was allowed to warm to rt and stirred overnight, then quenched with MeOH (1 mL). The mixture was extracted with Et₂O (3 × 50 mL). The organic phase were combined, dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (gradient elution, petrol ether/EtOAc, 100:1 → 10:1) to give benzyl ether **II** as a colourless oil (310 mg, 83%).

Data for **II**: R_f 0.20 (petrol ether/EtOAc, 50:1); IR (Diamond/ZnSe): 2926, 2871, 1496, 1454, 1310 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ 7.38 – 7.22 (m, 5H), 4.51 – 4.42 (m, 2H), 3.46 – 3.37 (m, 1H), 3.30 – 3.22 (dt, *J* = 9.0, 5.0 Hz, 1H), 2.05 – 1.67 (m, 6H), 1.61 – 1.32 (m, 7H), 0.96 (s, 3H), 0.91 (s, 3H), 0.86 (d, *J* = 7.0 Hz, 3H), 0.82 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 138.7, 136.8, 132.3, 128.3, 127.6, 127.4, 72.9, 67.4, 39.88, 39.86, 35.6, 34.6, 34.4, 29.1, 27.7, 27.2, 25.9, 25.1, 21.0, 19.9, 16.3; HRMS (C₂₃H₃₅O, ESI): calculated 327.2682 [M+H]⁺, found 327.2685.

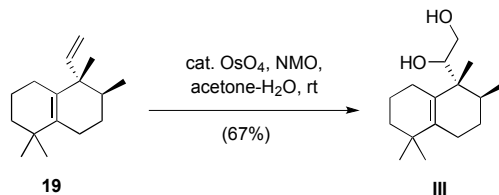
Alkene 19



To a solution of benzyl ether **II** (1.61 g, 4.92 mmol) in anhydrous THF (50 mL) was at $-78\text{ }^{\circ}\text{C}$ was added $n\text{-BuLi}$ (2.5 M in hexane, 9.86 mL, 24.7 mmol) dropwise under N_2 atmosphere. The reaction was allowed to stir at $-78\text{ }^{\circ}\text{C}$ for 30 min, then warmed to $0\text{ }^{\circ}\text{C}$ and quenched with saturated NH_4Cl solution (10 mL). The reaction mixture was extracted with Et_2O (3×50 mL). The organic phase were combined, washed with brine, dried over MgSO_4 , filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (neat petrol) to give alkene **19** as a colourless oil (580 mg, 54%).

Data for **19**: R_f 0.80 (neat petrol); $[\alpha]_D^{25}$ (c 1.52, CHCl_3) $+54.1^{\circ}$; IR (Diamond/ ZnSe): 2923, 1631, 1459, 1360 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 5.55 (dd, $J = 17.5, 10.5\text{ Hz}$, 1H), 5.03 (dd, $J = 10.5, 2.0\text{ Hz}$, 1H), 4.88 (dd, $J = 17.5, 2.0\text{ Hz}$, 1H), 2.08 – 1.92 (m, 2H), 1.84 – 1.78 (m, 2H), 1.65 – 1.27 (m, 7H), 1.00 (s, 3H), 0.99 (s, 3H), 0.95 (s, 3H), 0.81 (d, $J = 7.0\text{ Hz}$, 3H); ^{13}C NMR (100MHz, CDCl_3): δ 147.9, 135.5, 131.2, 112.3, 45.0, 39.9, 37.0, 34.3, 28.6, 28.2, 27.5, 26.5, 24.0, 20.0, 17.4, 15.9; HRMS ($\text{C}_{16}\text{H}_{26}$, EI): calculated 218.2034 $[\text{M}^+]$, found 218.2037.

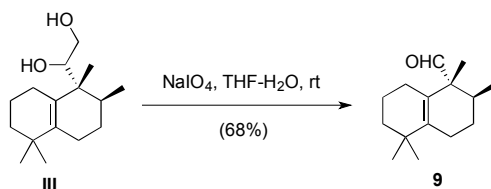
Diol III



To a solution of alkene **19** (302 mg, 1.38 mmol) in acetone- H_2O (9:1, 10 mL) at rt was added NMO (324 mg, 2.77 mmol) and OsO_4 (18 mg, 0.07 mmol). The reaction mixture was then stirred at rt for 36 h. The mixture was then diluted with Et_2O (50 mL) and H_2O (50 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O (2×50 mL). The combined organics were washed with water and brine, dried over MgSO_4 and concentrated *in vacuo*. The resultant residue was then purified by flash chromatography on silica gel (gradient elution, petrol ether/ EtOAc , 5: 1 \rightarrow 2:1) to give diol **III** as a colourless oil (232 mg, 67%).

Data for **III**: R_f 0.35 (petrol ether/ EtOAc , 2:1); $[\alpha]_D^{25}$ (c 1.01, CHCl_3) -0.9° ; IR (Diamond/ ZnSe): 3387, 2924, 1459, 1016, 1059 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 3.60 (s, 3H), 2.10 – 1.83 (m, 6H), 1.66 – 1.62 (m, 2H), 1.57 – 1.48 (m, 2H), 1.40 – 1.37 (m, 2H), 1.25 – 1.19 (m, 1H), 0.96 (s, 3H), 0.94 (s, 3H), 0.88 (s, 3H), 0.77 (d, $J = 7.0\text{ Hz}$, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 141.2, 128.5, 77.9, 63.9, 44.4, 39.7, 34.9, 32.5, 29.0, 28.5, 26.9, 26.1, 22.0, 19.9, 19.6, 17.5; HRMS ($\text{C}_{16}\text{H}_{28}\text{O}_2\text{Na}$, ESI): calculated 275.1982 $[\text{M}+\text{Na}]^+$, found 275.1980.

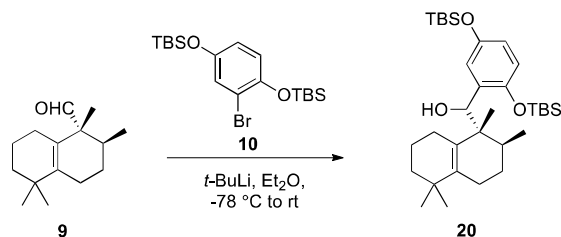
Aldehyde **9**



To a solution of diol **III** (670 mg, 2.66 mmol) in THF-H₂O (2:1, 100 mL) was added NaIO₄ (1.37 g, 6.39 mmol). The reaction mixture was stirred at rt for 30 min. H₂O (50 mL) and Et₂O (50 mL) were then added and the organic layer was separated, dried over MgSO₄, filtered and concentrated *in vacuo*. The residue was then purified by flash chromatography on silica gel (petrol ether/EtOAc, 10:1) to give aldehyde **9** (400 mg, 68%) as a colourless solid.

Data for **9**: R_f 0.80 (petrol ether/EtOAc, 5:1); mp 37 – 39 °C; [α]_D²⁵ (c 1.80, CHCl₃) +92.4°; IR (Diamond/ZnSe): 2927, 1722, 1458 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 9.17 (s, 1H), 2.04 – 2.00 (m, 2H), 1.90 – 1.85 (m, 1H), 1.82 – 1.75 (m, 1H), 1.61 – 1.27 (m, 7H), 0.95 (s, 3H), 0.93 (s, 6H), 0.69 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 205.5, 138.9, 125.5, 54.5, 38.5, 33.4, 30.8, 27.7, 26.8, 26.8, 25.2, 23.8, 18.6, 15.2, 11.9; HRMS (C₁₅H₂₄O, EI): calculated 220.1827 [M⁺], found 220.1835.

Benzylic alcohol **20**

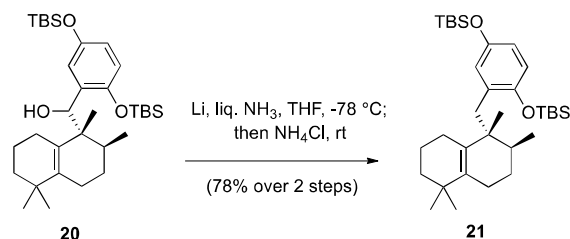


To a solution of **10**¹ (820 mg, 1.95 mmol) in anhydrous Et₂O (6 mL) under N₂ atmosphere at -78 °C was added *t*-BuLi (1.7M in pentene, 1.10 mL, 1.87 mmol) dropwise. The reaction was stirred at -78 °C for 30 min and a solution of aldehyde **9** (210 mg, 0.93 mmol) in anhydrous Et₂O (6 mL) was added dropwise. The resultant mixture was stirred at -78 °C for 30 min, then allowed to warm to rt. The mixture was quenched with saturated NH₄Cl solution (50 mL) and extracted with Et₂O (3 × 50 mL). The organic phases were combined, dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (gradient elution, petrol ether/EtOAc, 100:1 → 50:1 → 20:1) to give **20** (520 mg) as a mixture of diastereomers with some inseparable impurities. The crude material was then used directly in the next step without further purification.

Partial data for **20**: R_f 0.60 (petrol ether/EtOAc, 20:1); IR (Diamond/ZnSe): 3508, 2956, 2929, 1253, 911, 837, 778 cm⁻¹.

¹ Willis, J. P.; Gogins, K. A. Z.; Miller, L. L. *J. Org. Chem.* **1981**, *46*, 3215.

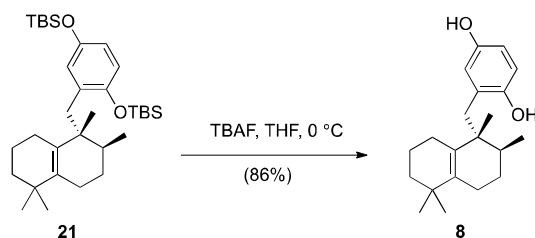
TBS-protected hydroquinone **21**



To a stirred mixture of liquid NH_3 (35 mL) and anhydrous THF (18 mL) at $-78\text{ }^\circ\text{C}$ was added Li (65 mg, 9.29 mmol). The mixture was stirred for 15 min, followed by dropwise addition of **20** (520 mg, crude from previous step) in THF (10 mL). The reaction stirred at $-78\text{ }^\circ\text{C}$ for 15 min, then quenched with solid NH_4Cl (2.00 g) and the NH_3 was allowed to evaporate over 2 h by warming to rt. The resultant mixture was diluted with H_2O (100 mL) and extracted with Et_2O ($3 \times 50\text{ mL}$). The organic phases were combined, dried over MgSO_4 , filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (petrol ether/ EtOAc , 50:1) to give **21** as a colourless oil (390 mg, 78% over two steps).

Data for **21**: R_f 0.80 (petrol ether/ EtOAc , 50:1); $[\alpha]_D^{25}$ (c 1.89, CHCl_3) -3.1° ; IR (Diamond/ ZnSe): 2927, 1489, 1211, 918, 837, 777 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3): δ 6.76 (d, $J = 3.0\text{ Hz}$, 1H), 6.60 (d, $J = 9.0\text{ Hz}$, 1H), 6.48 (dd, $J = 9.0, 3.0\text{ Hz}$, 1H), 2.87 (d, $J = 15.5\text{ Hz}$, 1H), 2.55 (d, $J = 15.5\text{ Hz}$, 1H), 2.09 – 1.92 (m, 5H), 1.71 – 1.55 (m, 5H), 1.47 – 1.45 (m, 2H), 1.38 – 1.32 (m, 2H), 1.03 (s, 3H), 1.00 (s, 9H), 0.99 (s, 3H), 0.96 (s, 9H), 0.92 (s, 3H), 0.75 (d, $J = 7.0\text{ Hz}$, 3H), 0.17 (d, $J = 10.5\text{ Hz}$, 6H), 0.14 (s, 6H); ^{13}C NMR (150 MHz, CDCl_3): δ 148.9, 148.3, 135.8, 133.0, 131.6, 122.0, 118.6, 116.9, 41.6, 39.8, 35.0, 34.4, 33.5, 28.5, 28.1, 27.1, 26.5, 26.03, 25.95, 25.8, 24.0, 22.4, 20.1, 18.3, 18.1, 16.2, -4.1 , -4.2 , -4.38 , -4.40 ; HRMS ($\text{C}_{33}\text{H}_{58}\text{O}_2\text{Si}_2\text{Na}$, ESI): calculated 565.3868 $[\text{M}+\text{Na}]^+$, found 565.3862.

Hydroquinone **8**

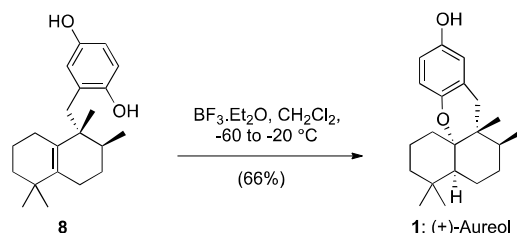


To a solution of **21** (190 mg, 0.34 mmol) in anhydrous THF (4 mL) under N_2 was added TBAF (1 M in THF, 0.80 mL, 0.80 mmol) at $0\text{ }^\circ\text{C}$. The reaction was stirred at $0\text{ }^\circ\text{C}$ for 20 min, then quenched with water (30 mL) and extracted with Et_2O ($3 \times 20\text{ mL}$). The organic phases were combined, dried over MgSO_4 , filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (gradient elution, petrol ether/ EtOAc , 10:1 \rightarrow 4:1 \rightarrow 2:1) to give **8** as a white solid (93 mg, 86%).

Data for **8**: R_f 0.35 (petrol ether/ EtOAc , 4:1); mp $134 - 135\text{ }^\circ\text{C}$; $[\alpha]_D^{25}$ (c 0.99, CHCl_3) $+40.6^\circ$; IR (Diamond/ ZnSe): 3367, 2925, 2870, 1499, 1454, 1196, 908 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3): δ 6.67 (d, $J = 8.5\text{ Hz}$, 1H), 6.65 (d, $J = 3.0\text{ Hz}$, 1H), 6.55 (dd, $J = 8.5, 3.0\text{ Hz}$, 1H), 4.87 (s, 1H), 4.31 (s, 1H), 2.93 (d, $J = 14.5\text{ Hz}$, 1H), 2.50 (d, $J = 14.5\text{ Hz}$, 1H), 2.13 – 2.08 (m, 1H), 2.00 – 1.95 (m, 1H), 1.91 – 1.86 (m, 2H), 1.76 – 1.73 (m, 1H), 1.66 – 1.63 (m, 1H), 1.59 – 1.39 (m, 5H), 1.05 (s, 3H), 1.00 (s, 3H), 0.98 (s, 3H), 0.84 (d, $J = 7.0\text{ Hz}$, 3H); ^{13}C NMR

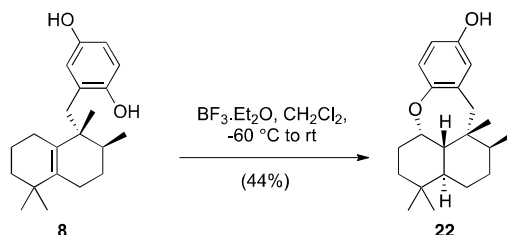
(150 MHz, CDCl₃): δ 148.9, 148.7, 137.8, 132.7, 127.7, 118.4, 116.5, 113.7, 41.7, 40.5, 39.6, 35.7, 34.6, 28.5, 28.1, 27.1, 26.2, 22.4, 22.3, 19.7, 15.8; HRMS (C₂₁H₃₀O₂, EI): calculated 315.2319 [M+H]⁺, found 315.2310.

(+)-Aureol **1**



To a solution of hydroquinone **8** (79 mg, 0.25 mmol) in anhydrous CH₂Cl₂ (25 mL) at -60 °C was added BF₃·Et₂O (0.14 mL, 1.13 mmol). The reaction mixture was stirred for 3 h at -60 °C, and then warmed to -20 °C and quenched with saturated NH₄Cl solution. The mixture was then extracted with CH₂Cl₂ (3 x 20 mL). The organic phases were combined, dried over MgSO₄, filtered and concentrated *in vacuo*. The crude material was purified by flash column chromatography (petrol ether/EtOAc, 4:1) to give (+)-aureol **1** as a white solid (52 mg, 66%). Data for **1**: R_f 0.50 (petrol ether/EtOAc, 4:1); mp 143 – 144 °C [lit. mp 144 – 145 °C]; [α]_D²⁵ (c 0.84, CHCl₃) +52.3°; IR (Diamond/ZnSe): 3298, 2935, 2870, 1495, 1450, 952 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ 6.60 (d, *J* = 9.0 Hz, 1H), 6.56 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.49 (d, *J* = 3.0 Hz, 1H), 4.31 (br s, 1H), 3.37 (d, *J* = 17.0 Hz, 1H), 2.11 – 1.99 (m, 2H), 1.97 (d, *J* = 17.0 Hz, 1H), 1.84 – 1.76 (m, 2H), 1.71 – 1.64 (m, 2H), 1.60 – 1.52 (m, 1H), 1.49 – 1.33 (m, 5H), 1.11 (d, *J* = 7.5 Hz, 3H), 1.06 (s, 3H), 0.92 (s, 3H), 0.78 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 148.3, 145.8, 122.2, 117.3, 115.1, 114.0, 82.4, 44.0, 39.3, 38.1, 37.4, 33.9, 33.8, 31.9, 29.8, 29.3, 27.9, 22.2, 20.2, 18.4, 17.3; HRMS (C₂₁H₃₀O₂, EI): calculated 315.2319 [M+H]⁺, found 315.2312.

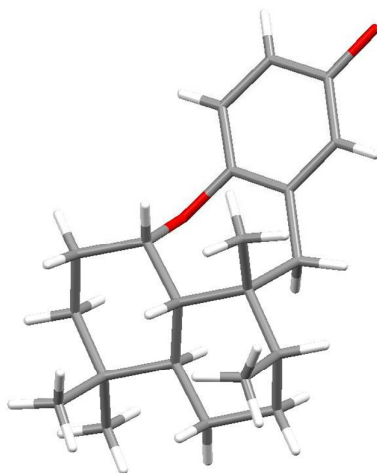
Cyclic ether **22**



To a solution of hydroquinone **8** (61 mg, 0.19 mmol) in anhydrous CH₂Cl₂ (20 mL) at -60 °C was added BF₃·Et₂O (0.10 mL, 0.81 mmol). The reaction was stirred for 3 h at -60 °C, and then warmed to rt for 10 min. The reaction mixture was quenched with saturated NH₄Cl solution (30 mL) and extracted with CH₂Cl₂ (3 x 20 mL). The organic phases were combined, dried over MgSO₄, filtered and concentrated *in vacuo*. The crude material was purified by flash column chromatography (petrol ether/EtOAc, 4:1) to give ether **22** as a white solid (27 mg, 44%).

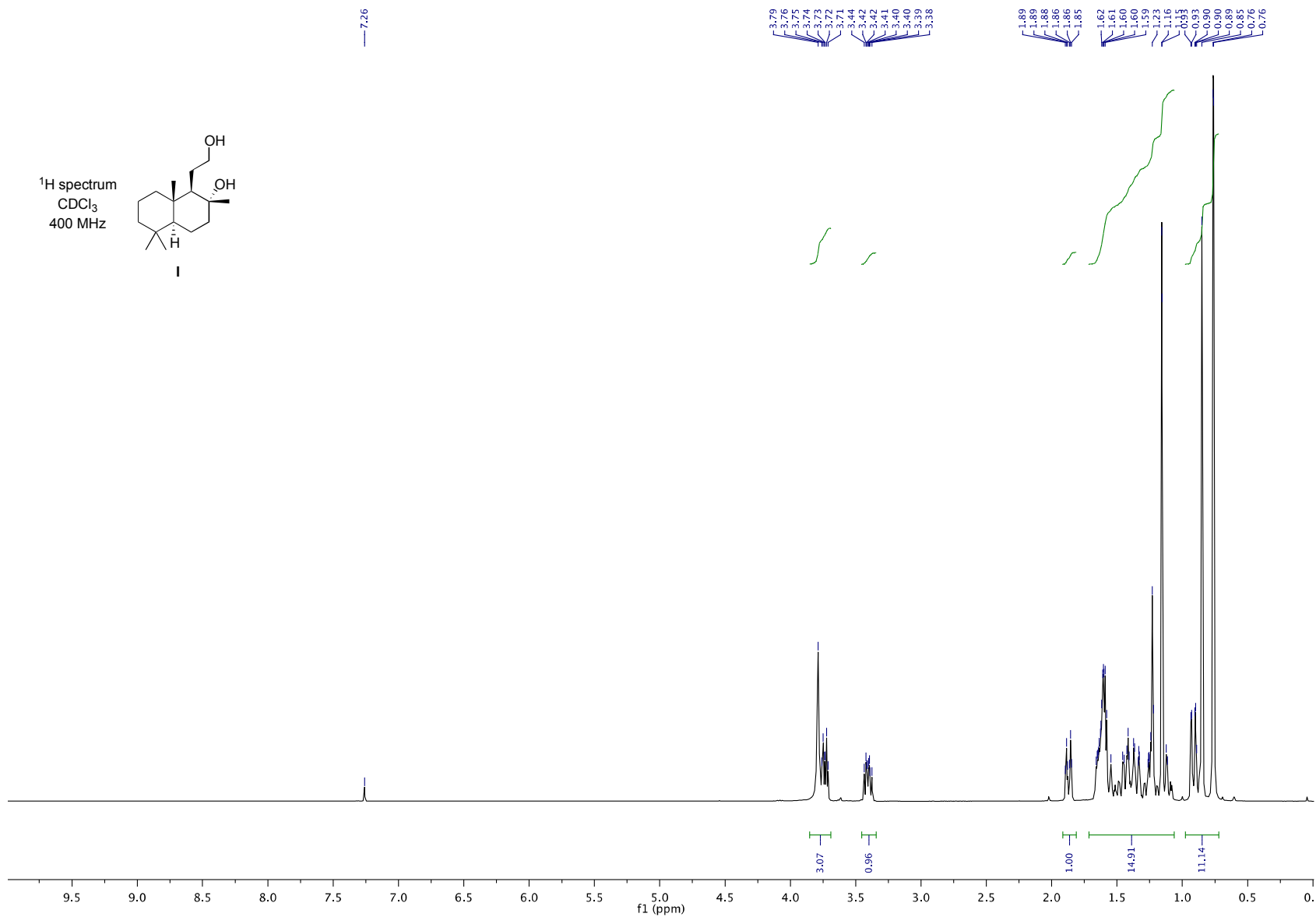
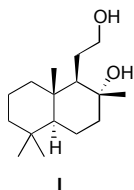
Data for **22**: R_f 0.50 (petrol ether/EtOAc, 4:1); mp 189 – 191 °C; [α]_D²⁵ (c 0.66, CHCl₃) -3.0°; IR (Diamond/ZnSe): 3390, 2942, 2909, 2869, 1606, 1501, 1449, 1368 cm⁻¹; ¹H NMR (600

MHz, CDCl₃): δ 6.77 (d, J = 8.5 Hz, 1H), 6.52 (dd, J = 8.5, 3.0 Hz, 1H), 6.48 (d, J = 3.0 Hz, 1H), 4.37 (s, 1H), 3.88 (br s, 1H), 3.81 (d, J = 14.0 Hz, 1H), 2.03 (dt, J = 12.0, 4.0 Hz, 1H), 1.95 – 1.89 (m, 2H), 1.84 (dt, J = 14.0, 4.0 Hz, 1H), 1.79 (d, J = 14.0 Hz, 1H), 1.63 – 1.57 (m, 2H), 1.53 – 1.51 (m, 1H), 1.49 (d, J = 12.0 Hz, 1H), 1.38 – 1.33 (m, 1H), 1.30 (dd, J = 13.0, 4.0 Hz, 1H), 1.19 (dt, J = 10.0, 3.0 Hz, 1H), 0.97 (s, 3H), 0.95 (overlapped d, 3H), 0.89 (s, 3H), 0.72 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 153.1, 151.0, 136.1, 121.3, 117.6, 113.1, 76.3, 43.2, 42.8, 41.9, 39.1, 35.9, 35.8, 33.3, 30.5, 30.0, 27.8, 24.4, 19.7, 19.6, 15.2.

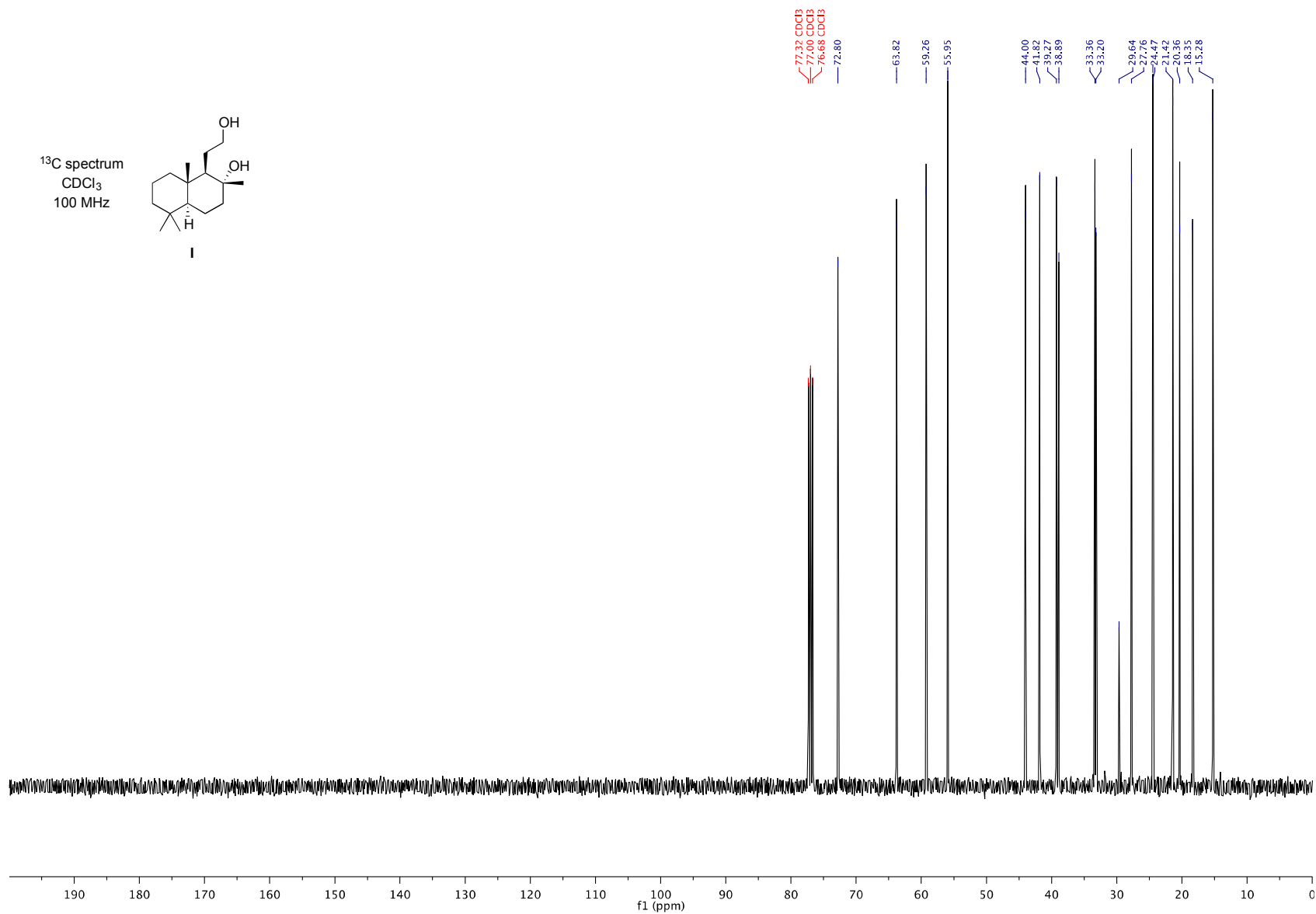
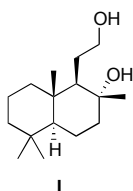


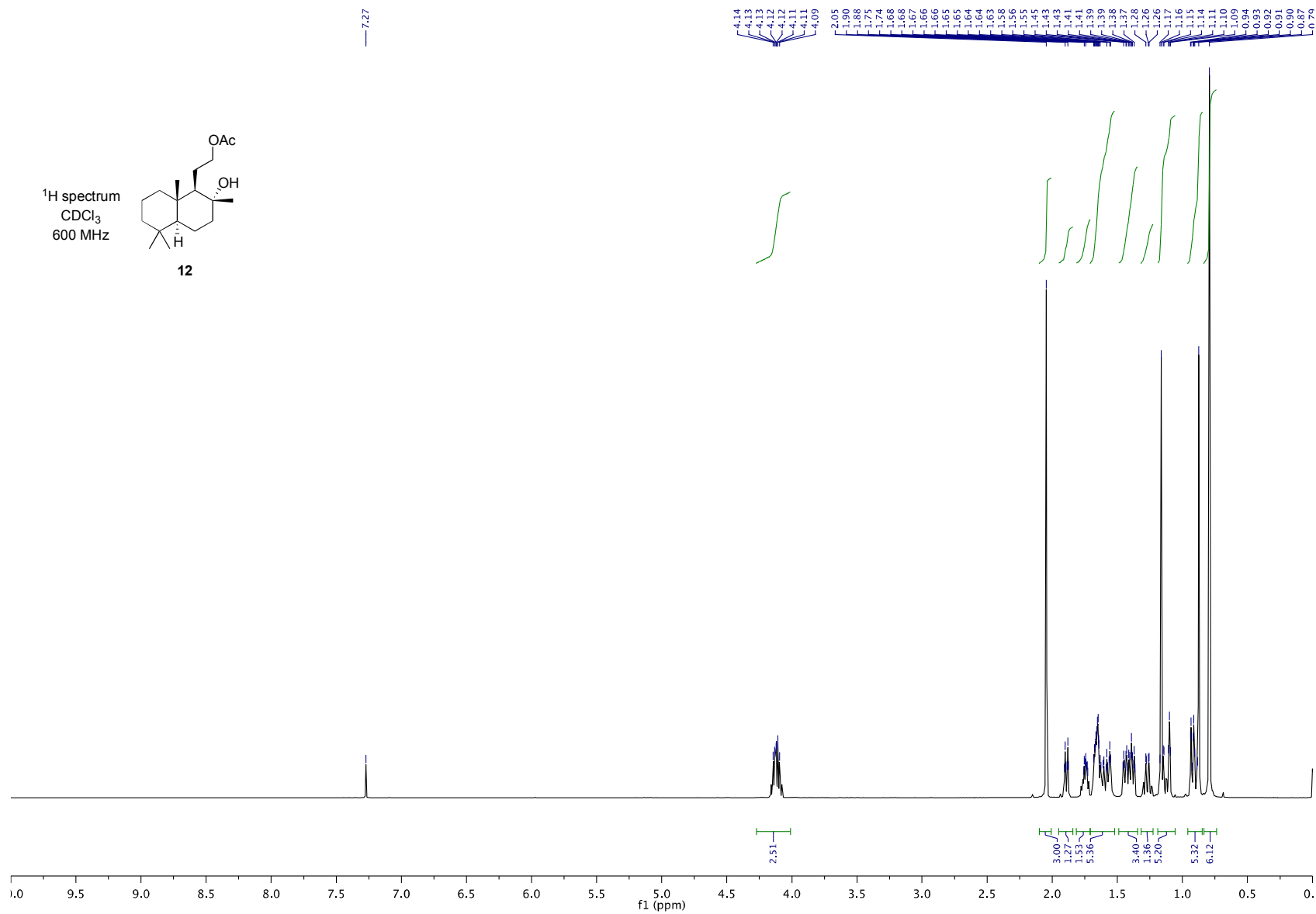
X-ray crystal structure of **22**

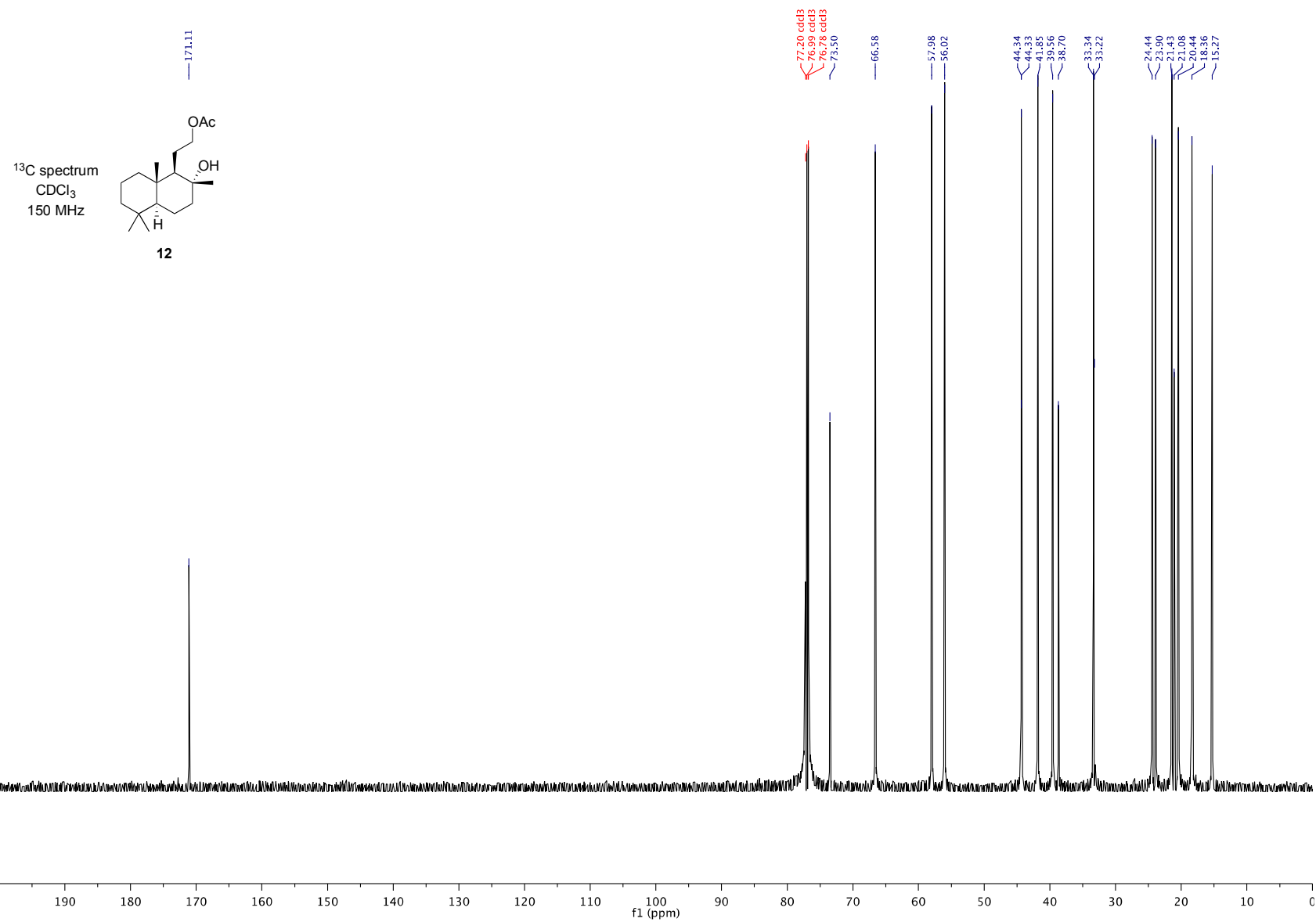
¹H spectrum
CDCl₃
400 MHz

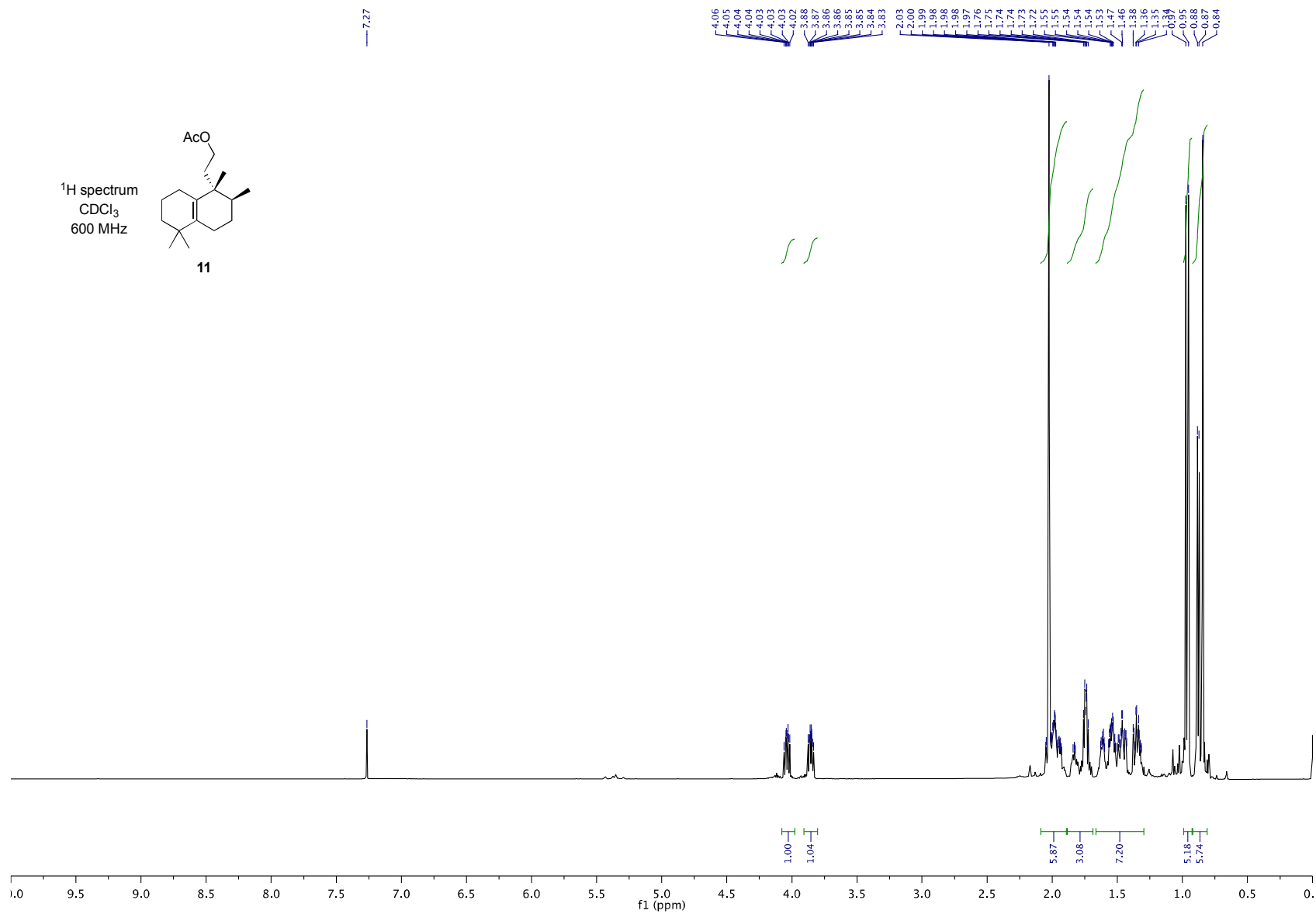


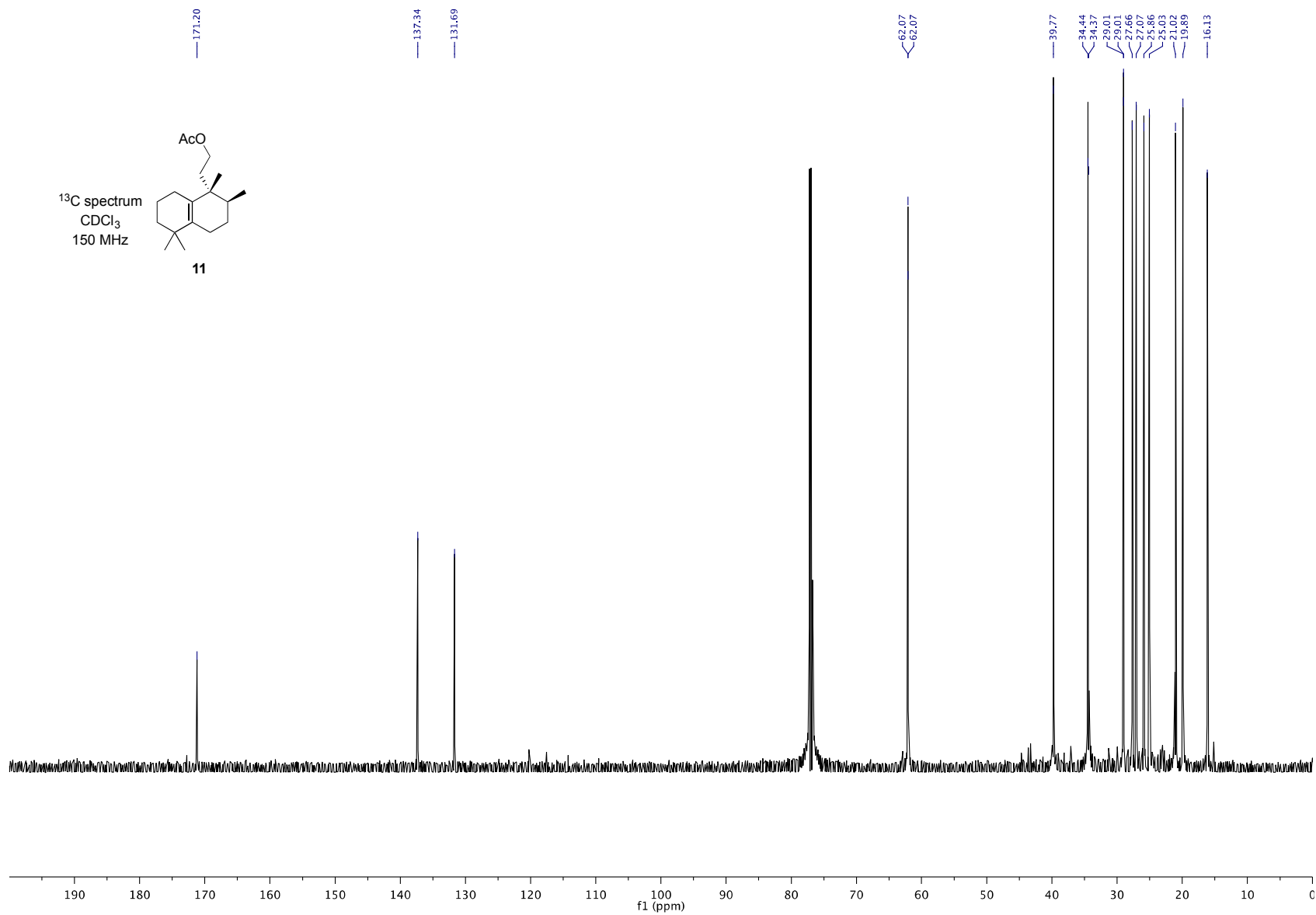
¹³C spectrum
CDCl₃
100 MHz

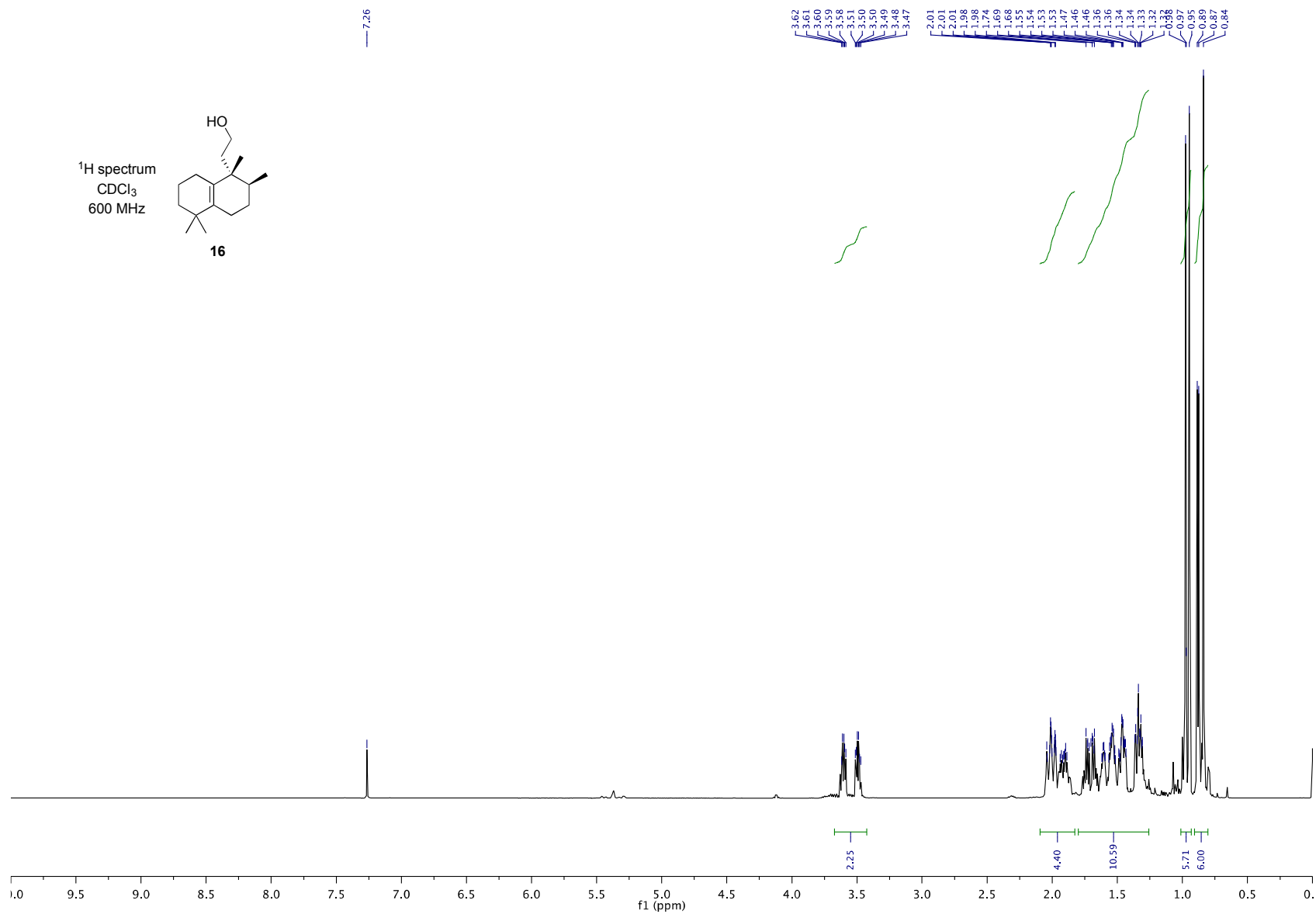


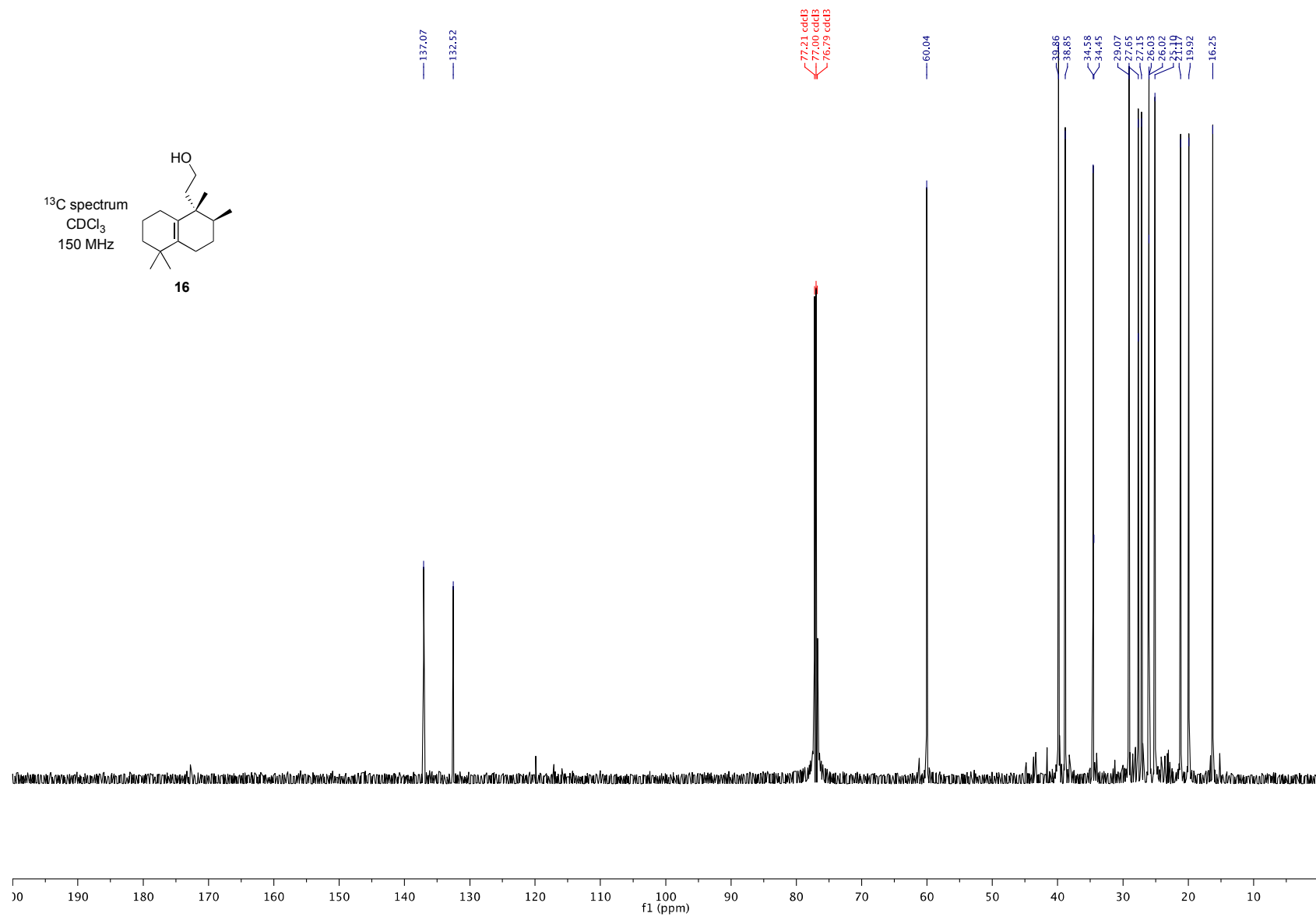


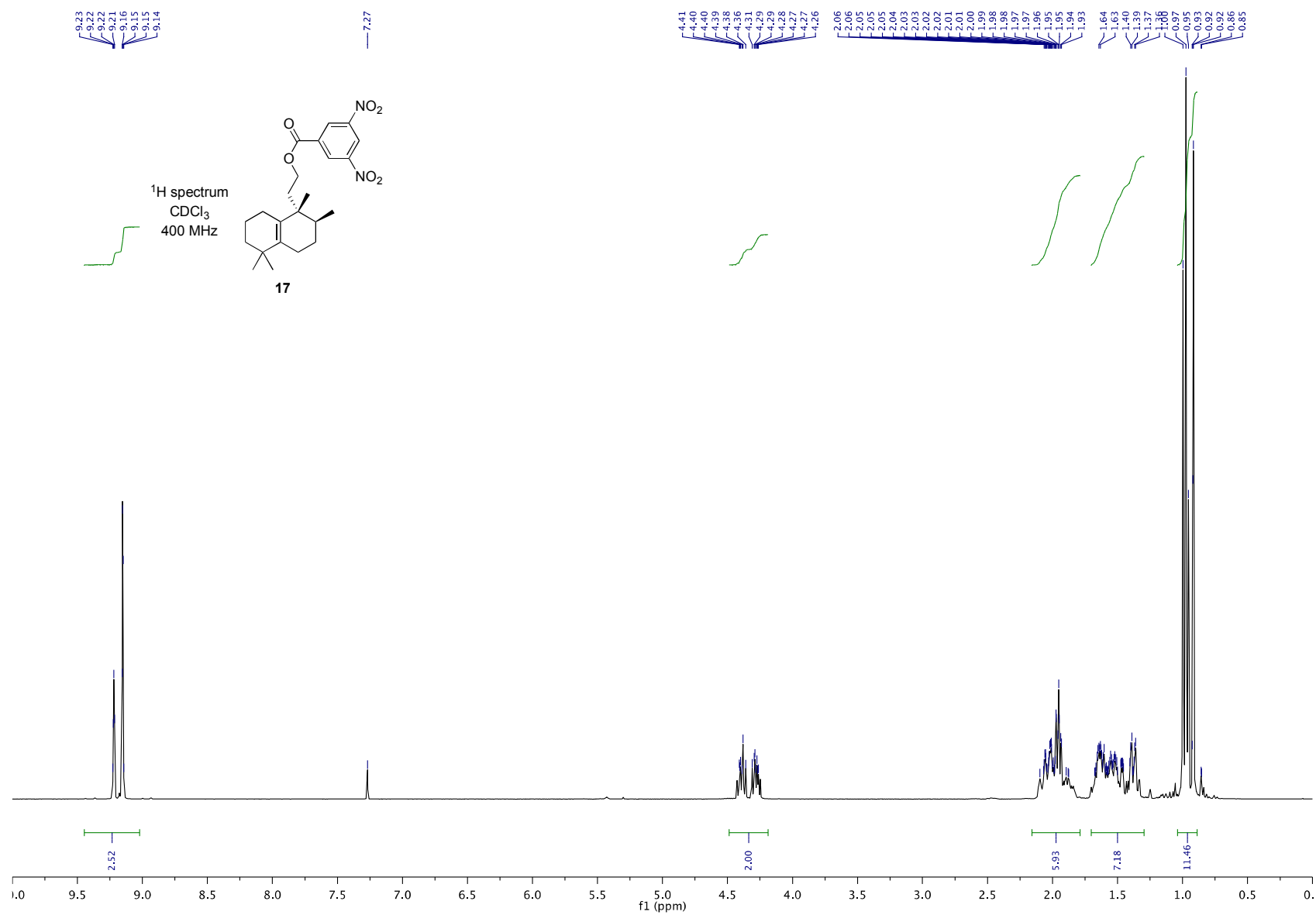


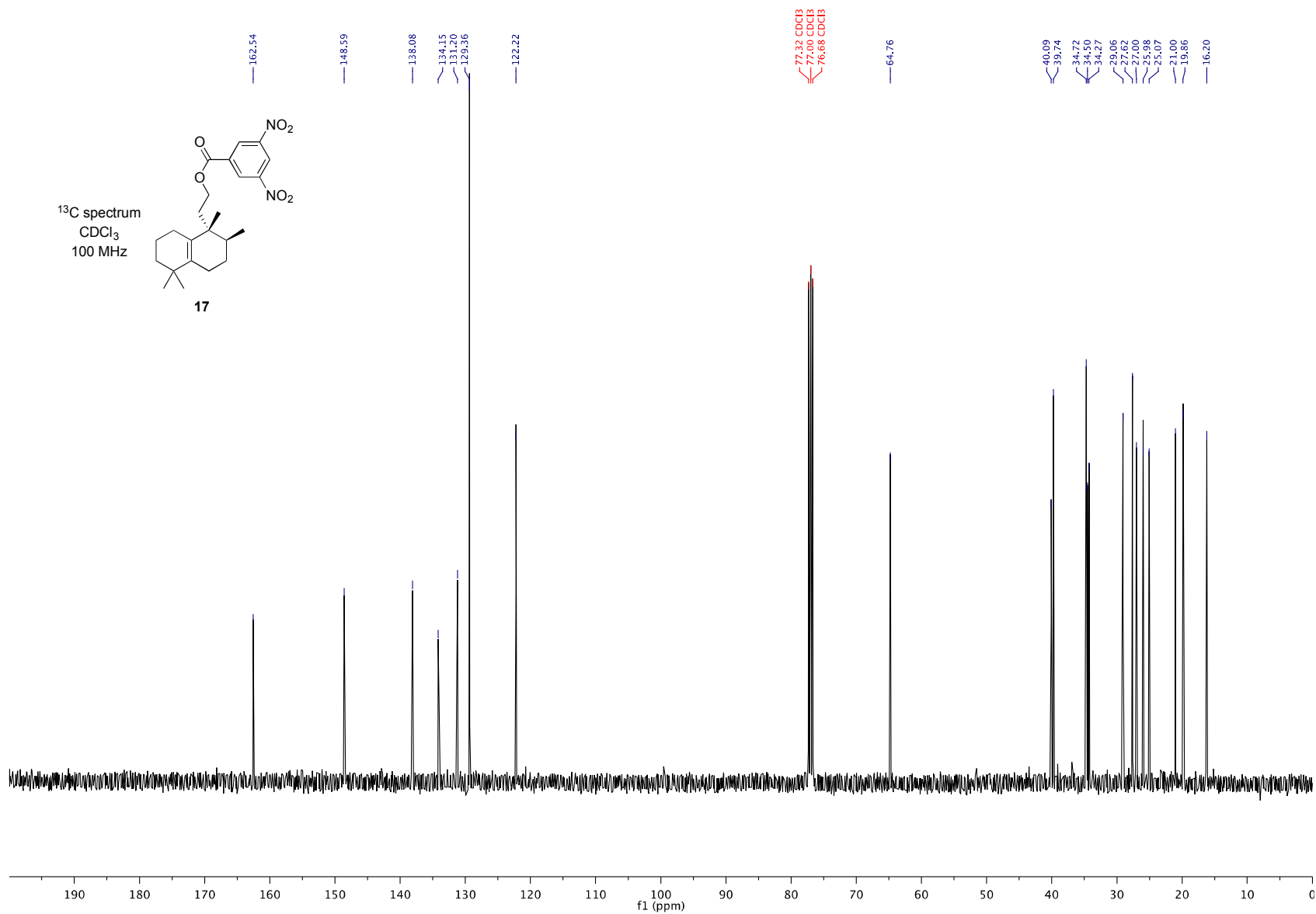


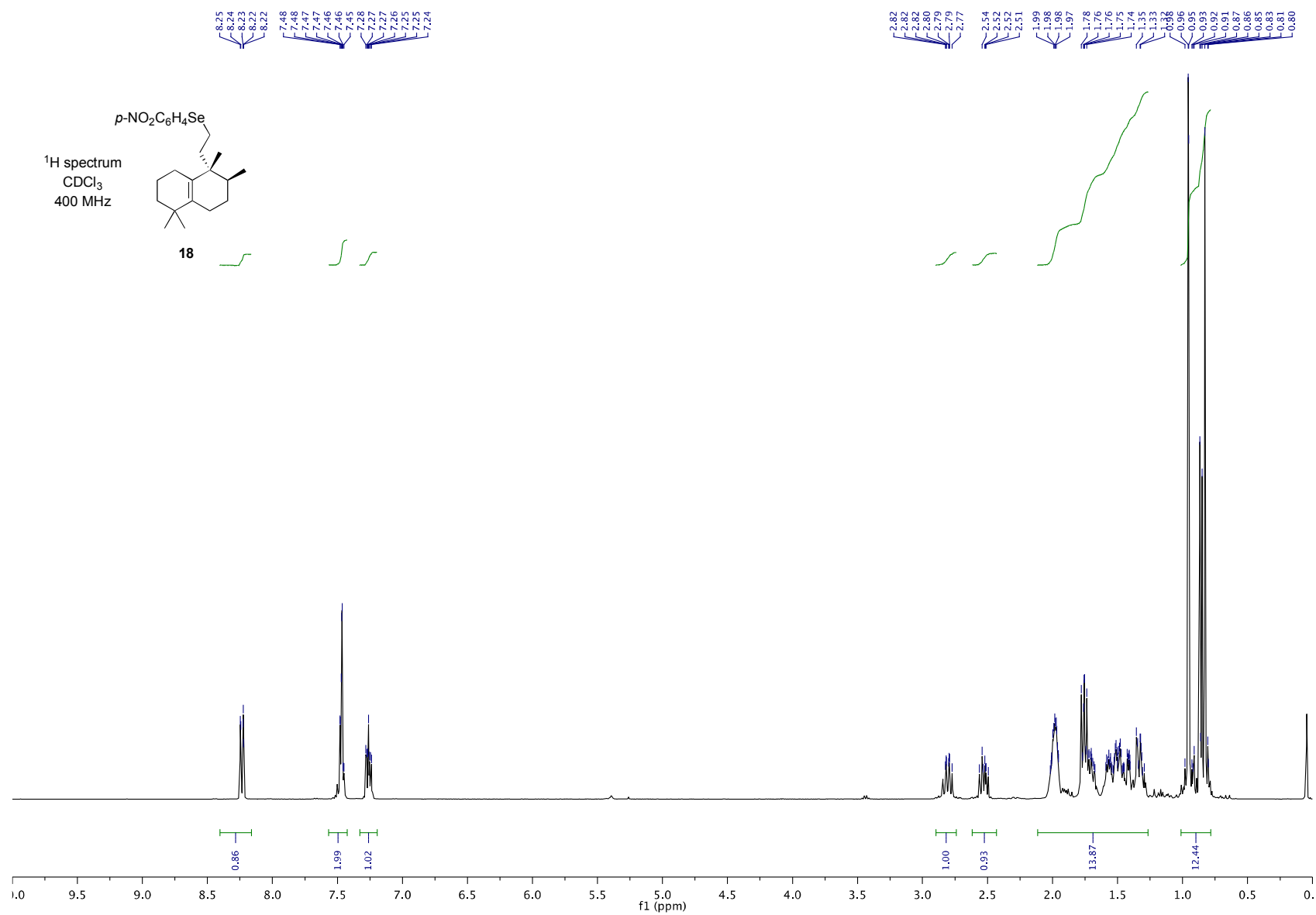


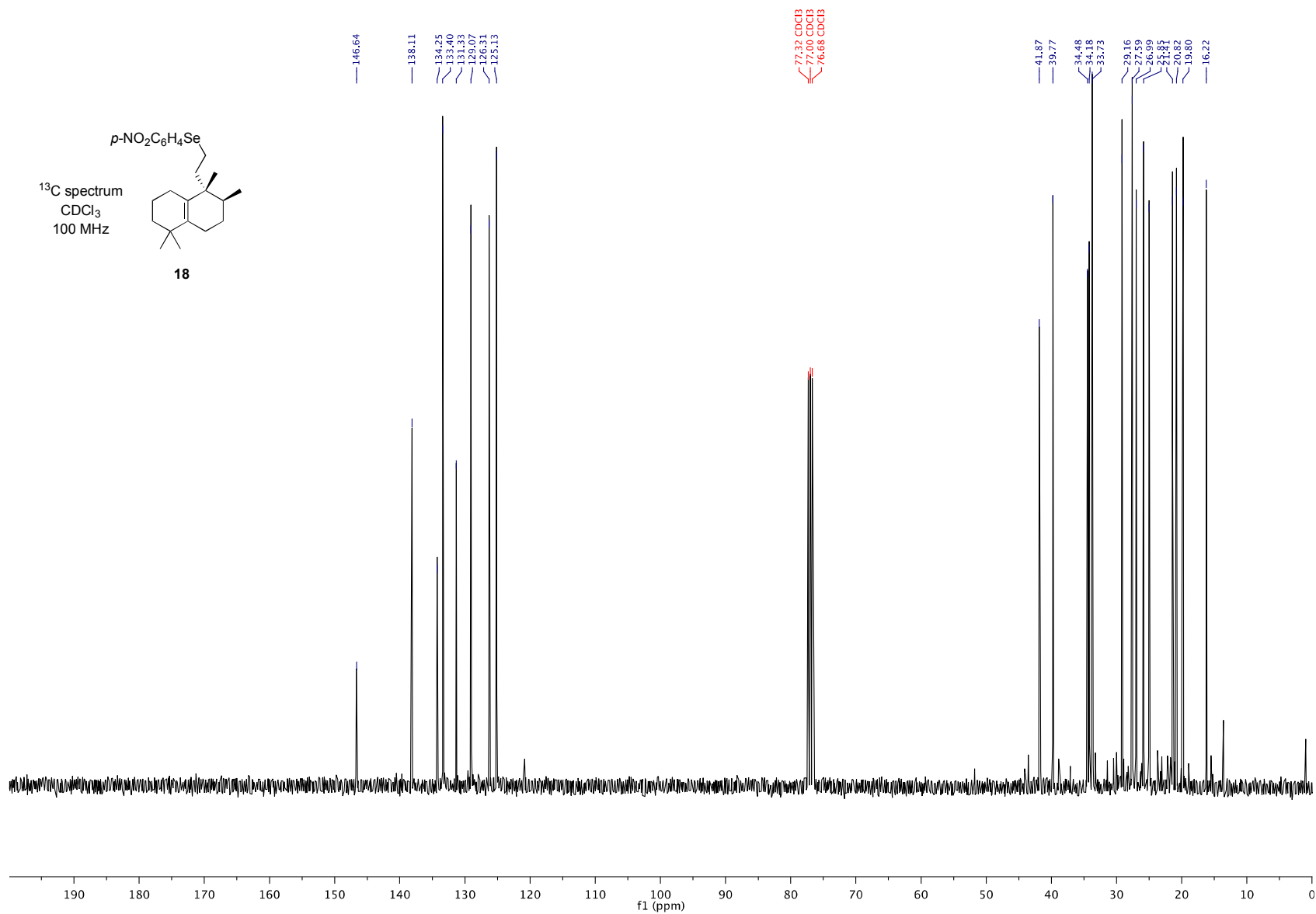




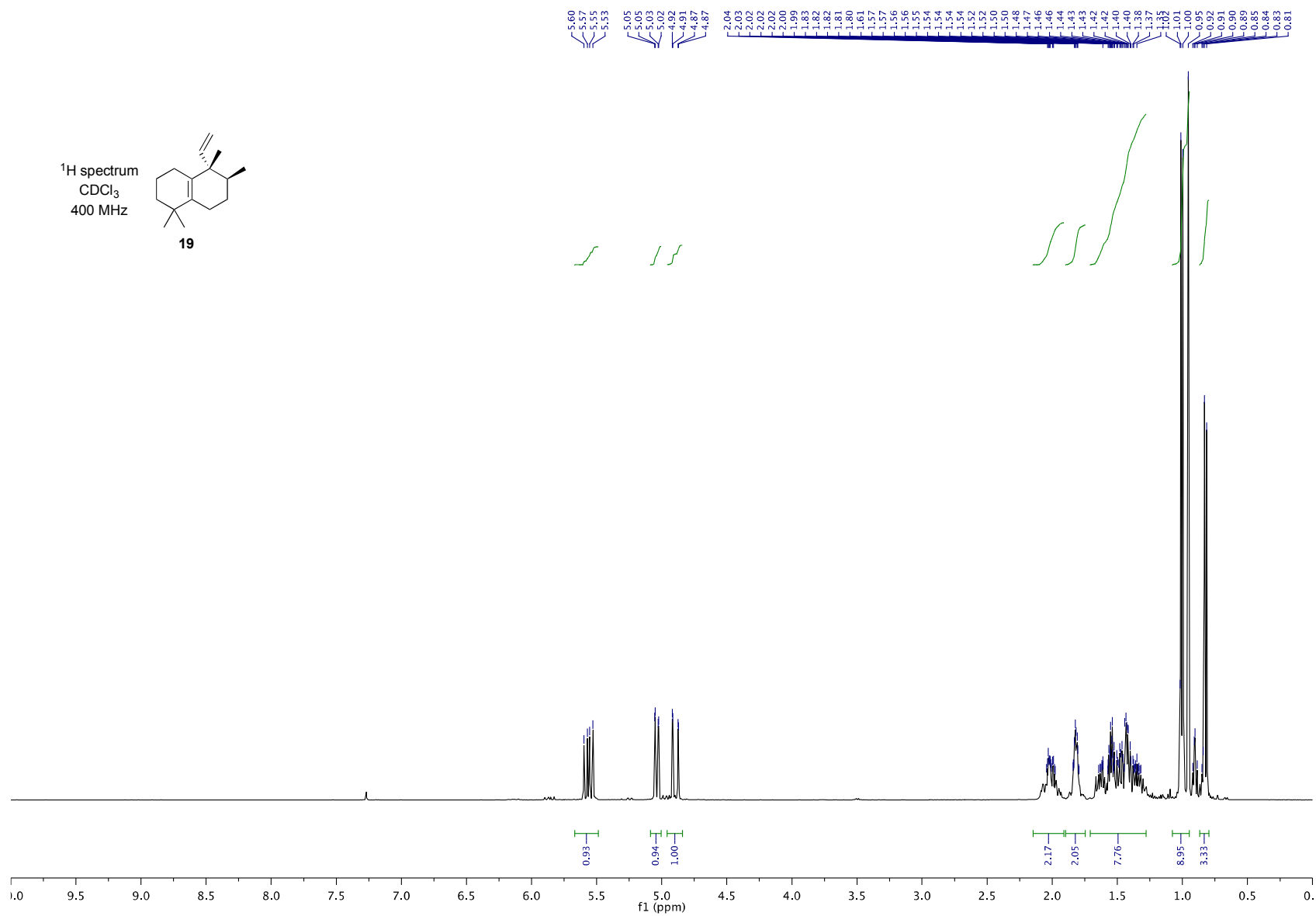
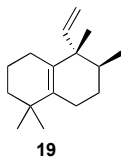


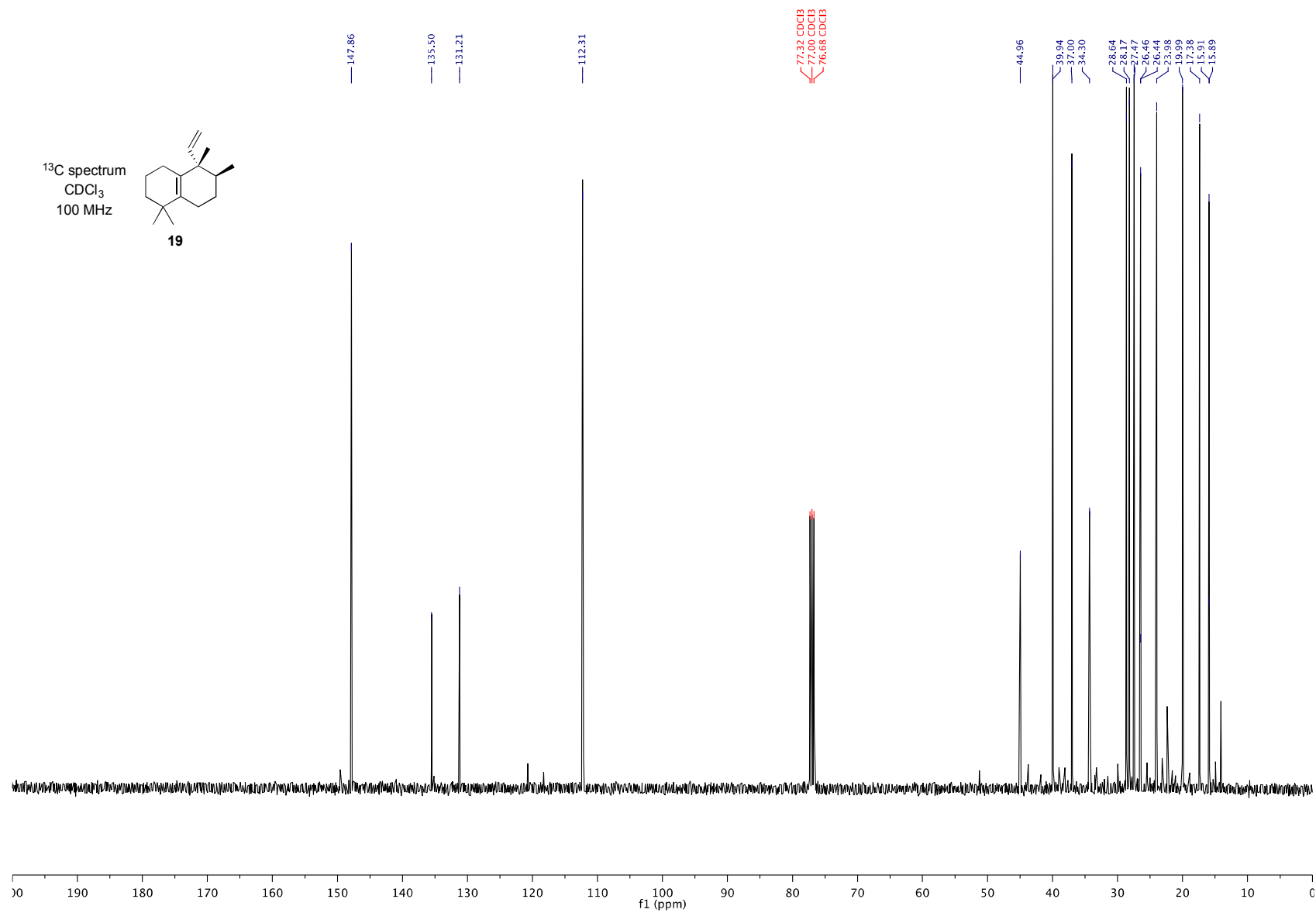


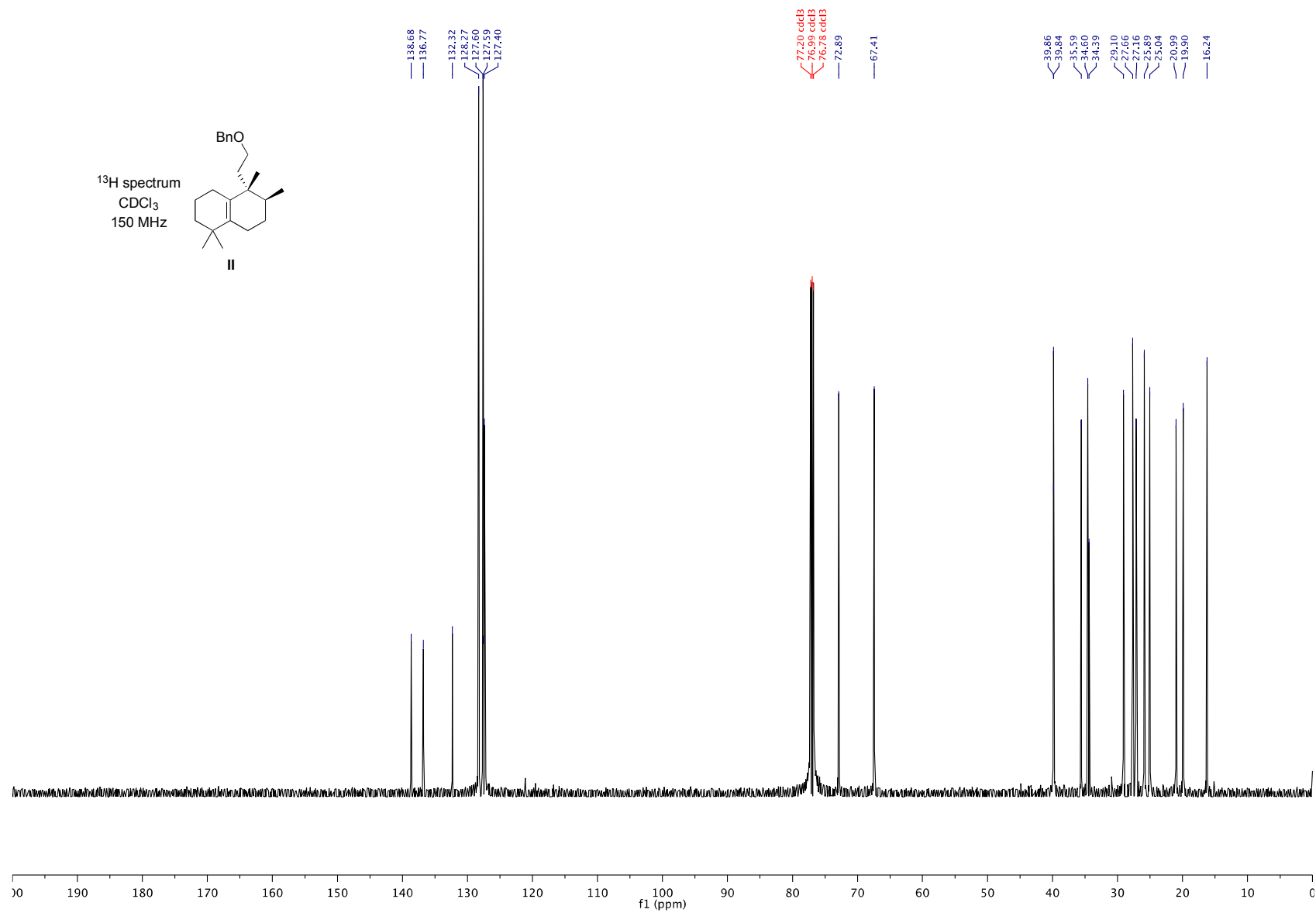




¹H spectrum
CDCl₃
400 MHz







¹H spectrum
CDCl₃
400 MHz

