Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Enantioselective Total Synthesis of Atisane Diterpenoids: (+)-Sapinsigin H, (+)-Agallochaol C, and (+)-16α, 17-dihydroxy-atisan-3-one

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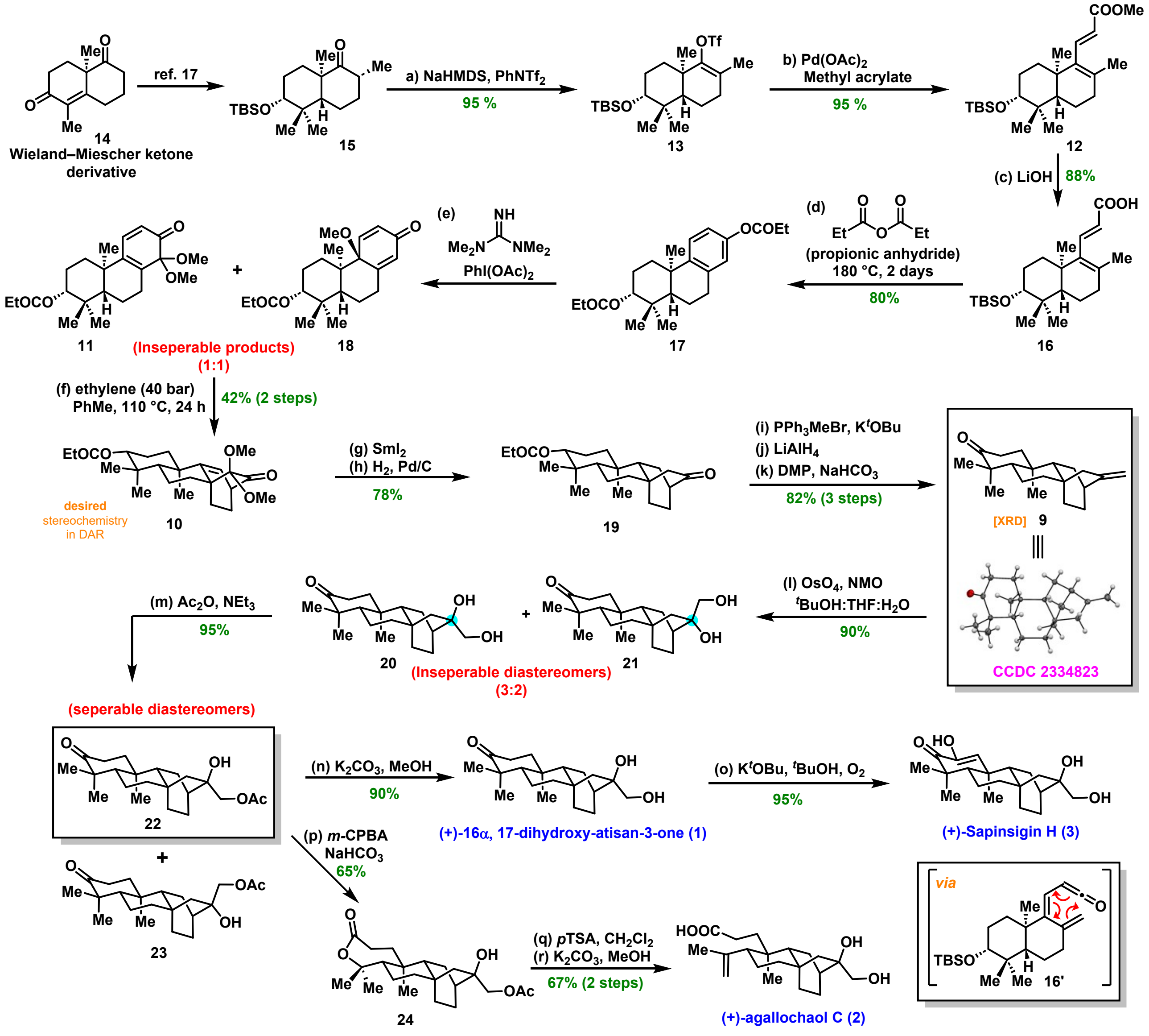
General Information

General Aspects: All reactions were carried out under nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise mentioned. All the chemicals were purchased commercially, and used without further purification. Anhydrous THF and diethyl ether were distilled from sodium benzophenone, and dichloromethane was distilled from calcium hydride. Yields refer to chromatographically pure compounds, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel plates (60F-254) using UV light as a visualizing agent and an p-anisaldehyde or ninhydrine stain, and heat as developing agents. Merck silica gel (particle size 100-200 and 230-400 mesh) was used for flash column chromatography. Neat compounds were used for record IR spectra. NMR spectra were recorded on either a Bruker Avance 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz), Bruker Avance 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz), or JEOL DELTA (ECX) 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz). Mass spectrometric data were obtained using Agilent-Premier-APCI-MS instruments and IR data recorded from PerkinElmer, FT-IR spectrometer. Optical rotations were measured using a Polarimeter (AUTOPOL II) at 20 °C.

The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of a doublet of a doublet, dt = doublet of a triplet, td = triplet of a doublet, m = multiplet, br = broad.

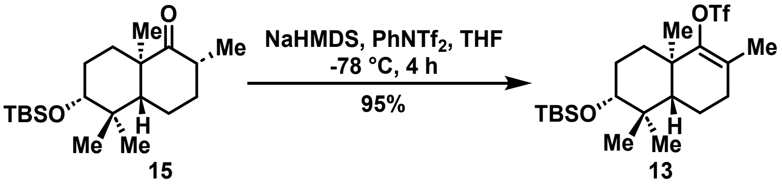
Total Synthesis of (+)-16α, 17-dihydroxy-atisan-3-one, (+)-sapinsigin H and (+)-agallochaol C[a]



[a]Yields of material isolated by silica gel chromatography.

Experimental Procedures:

Synthesis of triflate 13:



Ketone **15** (14.76 mmol, 5 g, 1.0 equiv) was dissolved in dry THF (150 ml) under nitrogen. The resulting mixture was cooled to -78 °C and a 1.9 M solution of NaHMDS (16.24 mmol, 8.5 ml, 1.1 equiv) in THF was added dropwise. The resulting yellow solution was stirred at –78 °C for 2 h. Then $PhNTf_2$ (16.24 mmol, 5.8 g, 1.1 equiv) dissolved in 30 ml THF was added at –78 °C and the reaction mixture was allowed to slowly warm to rt overnight. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl solution (100 ml) and the aqueous phase was extracted with Et_2O (3 × 100 ml). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated. The residual red oil was purified by column chromatography on silica gel to give triflate **13** (6.5 g, 95%) as a colorless oil.

$\mathbf{R_f}$ = 0.5 (2% EtOAc in hexanes)

$\mathbf{[\alpha]_D}^{23}$ = +21.5 (*c* = 0.5, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.23 – 3.14 (m, 1H), 2.17 (m, *J* = 24.4 Hz, 2H), 1.79 (dt, *J* = 13.1, 3.4 Hz, 1H), 1.70 (s, 3H), 1.62-1.54 (m, 2H), 1.54-1.44 (m, 2H), 1.41 – 1.31 (m, 1H), 1.22-1.19 (m, 1H), 1.13 (s, 3H), 0.92 (s, 3H), 0.88 (s, 9H), 0.78 (s, 3H), 0.03 (d, *J* = 4.2 Hz, 6H).

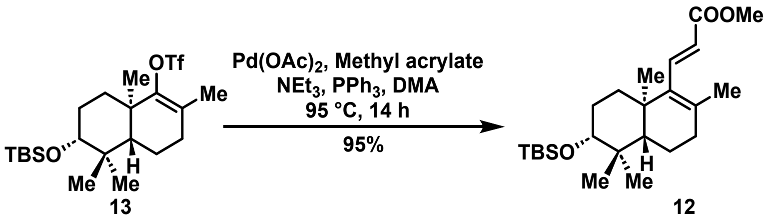
^{13}C NMR (100 MHz, $CDCl_3$) δ151.69, 124.46, 118.81 (q, *J* = 320 Hz), 78.86, 51.87, 39.32, 39.22, 33.03, 32.23, 28.51, 27.51, 25.93, 18.92, 18.28, 18.15, 17.45, 16.01, -3.76, -4.94.

^{19}F NMR (373 MHz, $CDCl_3$) δ -73.06 (s).

HRMS (EI) calculated for $C_{21}H_{37}F_3NaO_4SSi$ $[M+Na]^+$: *m/z* 493.2032, found: 493.2036

IR: 3427, 2955, 2930, 2857, 1706, 1401, 1209, 1140, 885, 607 cm^{-1}.

Synthesis of ester 12 using Heck reaction:



Triflate **13** (28.4 mmol, 13.38 g, 1.0 equiv), methyl acrylate (0.284 mol, 25.7 ml, 10.0 equiv), Et_3N (0.284 mol, 39.6 ml, 10.0 equiv), PPh_3 (2.84 mmol, 0.74 g, 0.1 equiv) and DMA (60 ml) were added to a Schlenk flask. The resulting solution was degassed by three cycles of freeze/pump/thaw technique before $Pd(OAc)_2$ (2.84 mmol, 0.638 g, 10 mol %) was added. The flask was sealed and the reaction mixture was stirred at 95 °C overnight. The resulting suspension was diluted with EtOAc and filtered through cotton. The filtrate was extracted with aqueous 1 M HCl and H_2O, dried over anhydrous Na_2SO_4 and concentrated. The residual yellow oil was purified by column chromatography on silica gel to give ester **12** (10.9 g, 95%) as a light-yellow oil.

R_f = 0.5 (5% EtOAc in hexanes)

$[\alpha]_D^{23}$ = +17.6 (*c* = 0.4, $CHCl_3$)

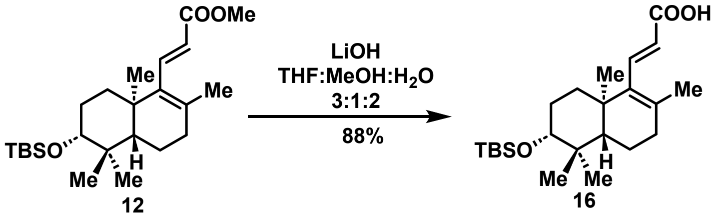
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 16.0 Hz, 1H), 5.71 (d, *J* = 16.0 Hz, 1H), 3.73 (s, 3H), 3.17 (dd, *J* = 11.1, 4.8 Hz, 1H), 1.66 (s, 3H), 1.60-1.45 (m, 5H), 1.25 – 1.06 (m, 4H), 1.03 (s, 3H), 0.90 (s, 3H), 0.86 (s, 9H), 0.76 (s, 3H), 0.00 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.48, 144.69, 139.04, 132.38, 122.57, 79.20, 51.50, 50.45, 39.62, 37.78, 36.36, 34.24, 28.46, 28.07, 25.97, 21.24, 20.43, 18.62, 18.18, 15.94, -3.73, -4.90.

HRMS (EI) calculated for $C_{24}H_{42}NaO_3Si$ $[M+Na]^+$: *m/z* 429.6718, found: 429.6719.

IR: 3440, 2949, 2932, 2855, 1723, 1633, 1306, 1256, 1105, 884 cm^{-1}.

Saponification to acid 16:



Solid LiOH (15.5 mmol, 6.5 g, 6.0 equiv) was added to a solution of ester **12** (25.8 mmol, 10.5 g, 1.0 equiv) in THF/MeOH/H_2O (v/v/v, 3:1:2; 60.0 ml), and the resultant suspension was stirred at room temperature for 12 h. The reaction mixture was diluted with 1 M HCl and acidified to pH=0. The aqueous phase was then extracted using CH_2Cl_2, and the combined organic phases were dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel to give dienoic acid **16** (0.293 g, 88%) as a white solid.

R_f = 0.5 (30% EtOAc in hexanes)

$[\alpha]_D^{23}$ = +16 (*c* = 0.1, $CHCl_3$)

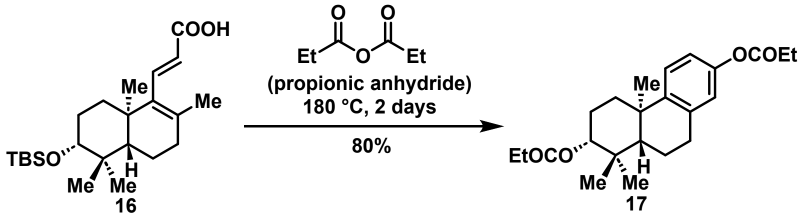
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 16.0 Hz, 1H), 5.74 (d, *J* = 16.0 Hz, 1H), 3.18 (m, 1H), 2.13 (bs, 2H), 1.71-1.68 (m, 2H), 1.69 (s, 3H), 1.62-1.44 (m, 3H), 1.24 (d, 2H), 1.11 (d, 1H), 1.05 (s, 3H), 0.91 (s, 3H), 0.87 (s, 9H), 0.76 (s, 3H), 0.01 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.53, 147.01, 138.94, 133.63, 122.02, 79.15, 50.44, 39.63, 37.83, 36.34, 34.39, 28.47, 28.07, 25.98, 21.33, 20.49, 18.59, 18.18, 15.95, -3.73, -4.89.

HRMS (EI) calculated for $C_{23}H_{41}O_3Si$ $[M+H]^+$: *m/z* 393.2825, found: 393.2806.

IR: 2938, 1697, 1643, 1355, 1240, 1047, 1001, 892, 881 cm^{-1}.

Benzannulation reaction to phenyl propionate 17:



Dienoic acid **16** (9.93 mmol, 3.9 g, 1.0 equiv) was dissolved in propionic anhydride (80 ml) and then sealed in a Schlenk flask and heated to 180 °C for 2 days. The resulting yellow suspension was concentrated and purified by column chromatography on silica gel to give tricyclic compound **17** (2.9 g, 80%) as a yellow oil.

R_f = 0.5 (15% EtOAc in hexanes)

$[\alpha]_D$ ^{23} = +14.5 (*c* = 0.45, $CHCl_3$)

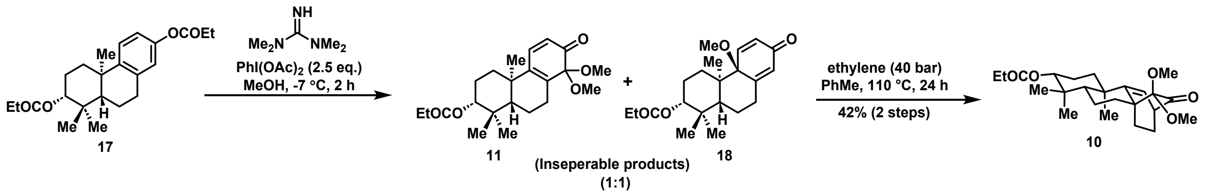
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.6 Hz, 1H), 6.81 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.74 (d, *J* = 2.5 Hz, 1H), 4.55 (dd, *J* = 11.5, 4.7 Hz, 1H), 2.96-2.79 (m, 2H), 2.54 (q, *J* = 7.6 Hz, 2H), 2.34 (q, *J* = 7.6 Hz, 2H), 2.28 (dt, *J* = 13.2, 3.4 Hz, 1H), 1.89-1.79 (m, 2H), 1.79-1.72 (m, 2H), 1.63-1.58 (m, 2H), 1.39 (dd, *J* = 12.2, 2.3 Hz, 1H), 1.23 (t, *J* = 7.6 Hz, 3H), 1.19 (s, 3H), 1.15 (t, *J* = 7.5 Hz, 3H), 0.96 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.28, 173.23, 148.39, 146.56, 136.50, 125.61, 121.30, 118.92, 80.26, 77.41, 77.09, 76.77, 49.83, 38.06, 37.41, 36.66, 30.54, 28.21, 28.12, 27.84, 25.03, 24.41, 18.65, 16.61, 9.40, 9.18.

HRMS (EI) calculated for $C_{23}H_{32}NaO_4$ $[M+Na]^+$: *m/z* 395.2198, found: 395.2190.

IR: 2971, 2945, 2880, 1760, 1731, 1493, 1193, 1156, 809 cm^{-1}.

Synthesis of compound 10 using DAR:



To a solution of **17** (2.63 mmol, 979 mg, 1.0 equiv) in MeOH (130 ml) at –7 °C was added 1,1,3,3-tetramethylguanidine (2.76 mmol, 0.347 ml, 1.05 equiv) and the resulting solution was stirred for 2 h at –7 °C. Then $PhI(OAc)_2$ (6.31 mmol, 2.03 g, 2.4 equiv) was added at –7 °C and the reaction mixture was stirred for 2 h. The resulting yellow reaction mixture was quenched by addition of solid $NaHCO_3$ at –7 °C and filtered through a plug of celite, thoroughly washing the filter cake with EtOAc (200 ml).

The filtrate was concentrated and the residual yellow oil was purified by column chromatography on silica gel to give inseperable compound **11** and **18** (826 mg) as a yellow oil.

R$_f$ = 0.30 (5% EtOAc in hexanes)

A solution of the inseperable compound **11** and **18** (826 mg) in toluene (15 ml) was sealed in a Parr high-pressure bomb and pressurized ethylene to 30 bar. The reaction mixture was heated to 110 °C (pressure raised to 40 bar) and held at this temperature for 24 h and then concentrated in vacuo. The resulting yellow residue was purified by column chromatography on silica gel to give cycloadduct **10** (446 mg, 42% from **17**) and **18** (346 mg, 38%) as a yellow oil.

R$_f$ = 0.7 (5% EtOAc in hexanes)

$[\alpha]_D$ ^{23} = +24.3 (*c* = 0.37, CHCl$_3$)

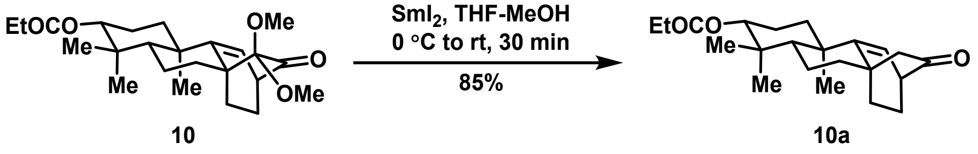
^{1}H NMR (400 MHz, CDCl$_3$) δ 5.72 (d, *J* = 6.8 Hz, 1H), 4.48 (dd, *J* = 11.5, 4.6 Hz, 1H), 3.40 (s, 3H), 3.39 (s, 3H), 3.03 (m, 1H), 2.30 (qd, *J* = 7.6, 1.2 Hz, 2H), 2.25-2.19 (m, 1H), 1.91-1.86 (m, 2H), 1.83-1.78 (m, 1H), 1.74-1.69 (m, 3H), 1.67-1.64 (m, 1H), 1.58-1.45 (m, 4H), 1.39-1.35 (m, 1H), 1.13 (t, *J* = 7.6 Hz, 3H), 1.10 (s, 3H), 0.92 (s, 3H), 0.86 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 203.83, 174.34, 160.80, 115.31, 96.23, 80.54, 56.09, 52.15, 48.23, 48.18, 46.86, 38.10, 38.10 36.42, 31.04, 28.14, 27.99, 26.53, 24.42, 24.04, 22.69, 18.47, 16.55, 9.43.

HRMS (EI) calculated for $C_{24}H_{36}NaO_5$ $[M+Na]^+$: *m/z* 427.2460, found: 427.2459.

IR: 3444, 2925, 2854, 1731, 1462, 1100, 1151, 1075, 773 cm^{-1}.

Synthesis of ketone 16:



To a solution of **10** (1.1 mmol, 446 mg, 1 equiv) in THF (5 ml) and MeOH (1 ml) was added freshly prepared SmI$_2$ until there was no disappearance of the blue color at room temperature. After 30 minutes, the resulting mixture was quenched with saturated aqueous NaHCO$_3$ (10 ml) and diluted with EtOAc (10 ml). The layers were separated, and the aqueous phase was extracted with EtOAc (15 ml × 3). The combined organic extracts were dried over anhydrous Na$_2$SO$_4$, filtered and concentrated to give the residue, which was purified by flash chromatography on silica gel to give **10a** (322 mg, 85%).

R$_f$ = 0.4 (10% EtOAc in hexanes)

$[\alpha]_D$ ^{23} = +62.0 (*c* = 0.73, CHCl$_3$)

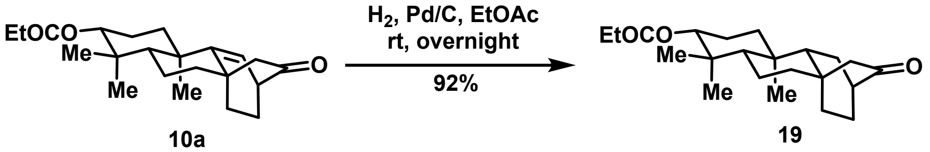
^{1}H NMR (400 MHz, CDCl$_3$) δ 5.69 (d, *J* = 6.7 Hz, 1H), 4.42 (dd, *J* = 11.1, 4.7 Hz, 1H), 3.08 (m, 1H), 2.30 (q, *J* = 7.4 Hz, 2H), 2.02-1.96 (m, 2H), 1.81 – 1.63 (m, 8H), 1.61-1.49 (m, 4H), 1.32 – 1.23 (m, 1H), 1.12 (t, *J* = 7.6, 1.0 Hz, 3H), 1.11 (s, 3H), 0.96 (s, 3H), 0.80 (s, 3H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 213.18, 174.17, 160.70, 115.61, 80.36, 49.19, 46.97, 46.65, 39.79, 38.77, 37.80, 35.96, 33.70, 30.41, 28.08, 27.33, 23.78, 22.93, 22.76, 17.70, 15.93, 9.38.

HRMS (EI) calculated for $C_{22}H_{33}O_3$ $[M+H]^+$: *m/z* 345.2430, found: 345.2423

IR: 2936, 2879, 1760, 1723, 1373, 1088, 826 cm^{-1}.

Synthesis of 19 using hydrogenation:



Compound **10a** (0.934 mmol, 322 mg) was dissolved in anhydrous EtOAc (8 ml) and the 10% Pd/C was added. The reaction mixture was stirred at rt for overnight under an H_2 balloon. After filtration through the celite pad, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to provide **19** (297 mg, 92%).

R_f = 0.5 (10% EtOAc in hexanes)

$[\alpha]_D$ ^{23} = +37.8 (*c* = 0.4, $CHCl_3$)

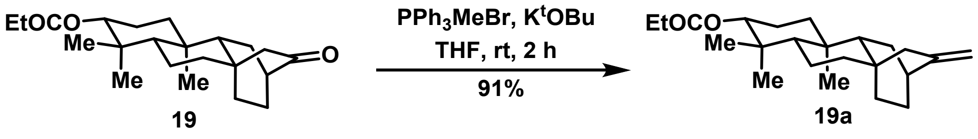
^1H NMR (400 MHz, $CDCl_3$) δ 4.48 (dd, *J* = 10.3, 6.0 Hz, 1H), 2.34-2.28 (m, 3H), 2.06-2.01 (m, 1H), 1.87-1.71 (m, 4H), 1.65-1.52 (m, 8H), 1.31-1.24 (m, 3H), 1.13 (t, *J* = 7.6 Hz, 3H), 1.03 (s, 3H), 0.87 (s, 3H), 0.86 (s, 3H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 217.42, 174.27, 80.43, 60.45, 56.02, 55.31, 51.80, 43.10, 38.60, 37.84, 37.42, 37.32, 36.11, 28.11, 27.63, 25.27, 23.80, 23.20, 18.28, 16.70, 14.08, 9.38.

HRMS (EI) calculated for $C_{22}H_{35}O_3$ $[M+H]^+$: *m/z* 347.2586, found: 347.2581

IR: 3444, 2924, 2851, 1729, 1643, 1462, 1191, 1034, 980, 652 cm^{-1}.

Synthesis of 19a using wittig olefination:



To a suspension of Ph_3PCH_3Br (0.865 mmol, 309 mg, 3 equiv) in THF (10 ml) was added KO^tBu (65 mg, 0.57 mmol, 2 equiv) at 0 °C. After 30 minutes, a solution of **19** (0.288 mmol, 100 mg, 1 equiv) in THF (5 ml) was added dropwise and the mixture was warmed to room temperature. The reaction mixture was stirred at this temperature for 2 h then quenched with sat. NH_4Cl aqueous (10 ml). The aqueous layer was extracted with EtOAc (10 ml ×3) and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to provide **19a** (90.2 mg, 91%).

R_f = 0.8 (10% EtOAc in hexanes)

$[\alpha]_D$ ^{23} = +2.4 (*c* = 1.0, $CHCl_3$)

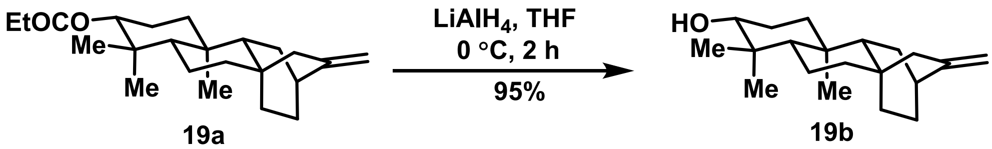
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.70 (d, *J* = 2 Hz, 1H), 4.54 (d, *J* = 2 Hz, 1H), 4.48-4.44 (m, 1H), 2.29 (q, *J* = 7.6 Hz, 2H), 2.19 (m, 1H), 2.01-2.00 (m, 1H), 1.88-1.84 (m, 2H), 1.61-1.50 (m, 6H), 1.44 – 1.34 (m, 4H), 1.29-1.20 (m, 4H), 1.11 (t, *J* = 7.5 Hz, 3H), 1.02-0.97 (m, 1H), 0.96 (s, 3H), 0.84 (s, 3H), 0.83 (s, 3H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 174.35, 152.71, 104.68, 80.81, 55.46, 52.62, 48.12, 39.33, 37.85, 37.43, 37.31, 36.45, 33.38, 28.66, 28.58, 28.15, 28.15, 27.33, 23.33, 18.45, 16.74, 14.08, 9.42.

HRMS (EI) calculated for $C_{23}H_{36}NaO_2$ $[M+Na]^+$: *m/z* 367.2613, found: 367.2607

IR: 2937, 2858, 1722, 1446, 1468, 1345, 1206, 1077, 871 cm^{-1}.

Synthesis of hydroxy compound 19b:



To a solution of the ester **19a** (0.261 mmol, 90.2 mg, 1 equiv) in THF (10 ml) was added LAH (9.9 mg, 0.261 mmol, 1 equiv) at 0 °C. The resulting mixture was then stirred at rt for 1 h. After completion of the reaction (TLC monitoring) the excess LAH was quenched with ice water. After stirring for 10 min at room temperature the whole mixture was extracted with EtOAc (3 x 10 ml). The combined organic extracts were washed with $NaHCO_3$, brine and dried (Na_2SO_4). Solvent was removed in vacuo and purification was done by flash chromatography on silica gel to yield **19b** (71.5 mg, 95%) as a clear, colorless oil.

R_f = 0.5 (20% EtOAc in hexanes)

$[\alpha]_D$ ^{23} = +31.3 (*c* = 0.5, $CHCl_3$)

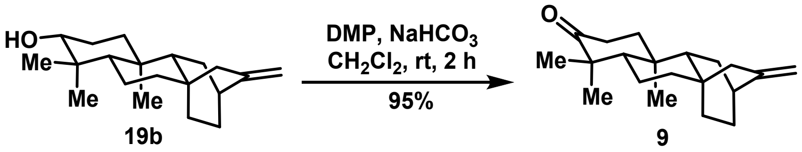
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.70 (dd, *J* = 4.2, 2.0 Hz, 1H), 4.54 (dd, *J* = 4.2, 2.0 Hz, 1H), 3.21 – 3.16 (m, 1H), 2.20 (m, 1H), 2.03 (d, *J* = 16.6 Hz, 1H), 1.88-1.84 (m, 2H), 1.59-1.53 (m, 8H), 1.42-1.34 (m, 4H), 1.12 – 1.07 (m, 2H), 0.96 (s, 3H), 0.94 (s, 3H), 0.77 (s, 3H), 0.73-0.71 (m, 1H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 152.85, 104.58, 79.25, 55.40, 52.74, 48.18, 39.47, 38.83, 37.68, 37.53, 36.50, 33.37, 28.66, 28.60, 28.18, 27.33, 26.97, 18.57, 15.56, 14.02.

HRMS (EI) calculated for $C_{20}H_{33}O$ $[M+H]^+$: *m/z* 289.2531, found: 289.2539.

IR: 3316, 2929, 2864, 1646, 1442, 1364, 1024, 872, 747 cm^{-1}.

Synthesis of 9 using DMP oxidation:



To a solution of **19b** (0.247 mmol, 71.5 mg, 1 equiv) in CH_2Cl_2 (10 ml) was added $NaHCO_3$ (1.982 mmol, 166.5 mg, 8 equiv) and Dess-Martin periodinane (0.297 mmol, 126.1 mg, 1.2 equiv) at room temperature. The reaction mixture was stirred at this temperature for 1 h then quenched with saturated aqueous Na_2SO_3 (5 ml) and diluted with CH_2Cl_2 (5 ml). The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (10 ml × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated to afford crude product, which was purified by flash chromatography on silica gel to give **9** (67.2 mg, 95%) as clear oil. This oil fully crystallized in RB within 12 hours.

R_f = 0.5 (10% EtOAc in hexanes)

$[\alpha]_D$ ^{23} = +21.5 (*c* = 2.6, $CHCl_3$)

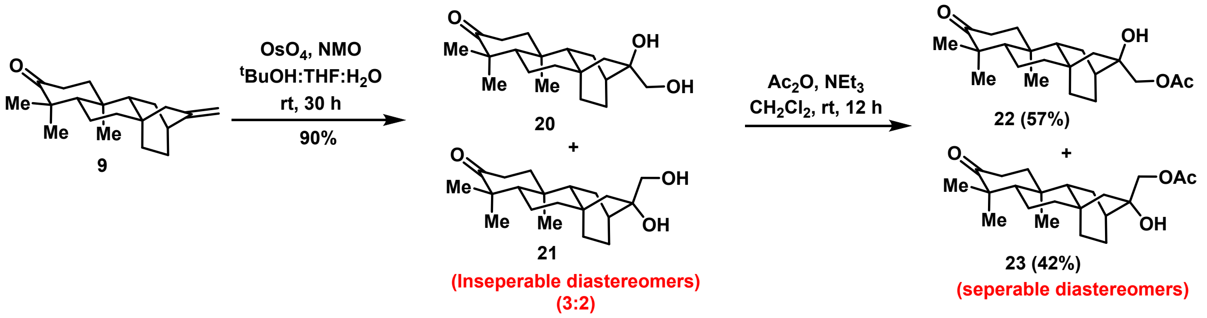
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.69 (d, *J* = 2.1 Hz, 1H), 4.53 (d, *J* = 1.9 Hz, 1H), 2.58-2.49 (m, 1H), 2.30-2.24 (m, 1H), 2.22-2.20 (m, 1H), 2.03 (d, *J* = 16.7 Hz, 1H), 1.93-1.83 (m, 2H), 1.80-1.74 (m, 1H), 1.64 – 1.50 (m, 3H), 1.46-1.37 (m, 4H), 1.32-1.22 (m, 3H), 1.17-1.12 (m, 2H), 1.08 (s, 3H), 1.03 (s, 3H), 1.00 (s, 3H), 0.98-0.97 (m, 1H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 217.28, 152.15, 105.00, 55.74, 51.89, 48.00, 47.69, 38.79, 38.17, 37.27, 36.36, 34.11, 33.35, 28.50, 28.50, 27.21, 26.20, 21.68, 19.73, 13.51.

HRMS (EI) calculated for $C_{20}H_{31}O$ $[M+H]^+$: *m/z* 287.2375, found: 287.2369

IR: 3438, 2971, 2933, 2864, 1703, 1644, 1446, 1110, 873 cm^{-1}.

Synthesis of 22 and 23:



To a solution of **9** (0.516 mmol, 147.8 mg, 1 equiv) in THF/*t*-BuOH/H_2O (1/1/0.2 ml) was added NMO (1.032 mmol, 138.2 mg, 2 equiv) and OsO_4 (0.062 mmol, 15.76 mg, 0.63 ml, 2.5% wt in *t*-BuOH, 0.20 equiv) at room temperature. The reaction mixture was stirred at this temperature for 30 h then quenched with saturated aqueous $Na_2S_2O_3$ (5 ml) and diluted with EtOAc (10 ml). The layers were separated and the aqueous phase was extracted with EtOAc (10 ml × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated to give the crude product, which was purified by flash chromatography on silica gel to give **20** and **21** as an inseparable mixture (148.8 mg, 90%)

To a solution of **20** and **21** (0.46 mmol, 148.8 mg) in CH_2Cl_2 (15 ml) was added Et_3N (2.32 mmol, 0.32 ml, 5 equiv) and Ac_2O (1.3 mmol, 0.13 ml, 3 equiv) at room temperature. The reaction mixture was stirred at this temperature for 24 hours, then quenched with saturated aqueous $NaHCO_3$ (10 ml) and diluted with CH_2Cl_2 (10 ml). The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (10 ml × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated to afford crude product, which was purified by flash chromatography on silica gel to provide **22** (95 mg, 57%) and **23** (70 mg, 42%).

22:

R_f = 0.5 (40% EtOAc in hexanes)

$[\alpha]_D{}^{23}$ = +37.0 (c = 0.2, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.08 (d, J = 11.3 Hz, 1H), 3.93 (d, J = 11.4 Hz, 1H), 2.60-2.51 (m, 1H), 2.35-2.28 (m, 1H), 2.08 (s, 3H), 2.05-1.99 (m, 2H), 1.91-1.79 (m, 2H), 1.76-1.75 (m, 1H), 1.60-1.55 (m, 2H), 1.50-1.39 (m, 4H), 1.37-1.27 (m, 2H), 1.24-2.13 (m, 4H), 1.09 (s, 3H), 1.06 (s, 3H), 1.02 (s, 3H), 0.85-0.77 (m, 1H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 217.34, 171.22, 72.81, 70.31, 55.67, 52.24, 50.65, 47.68, 38.68, 38.01, 37.23, 34.09, 32.83, 32.74, 27.12, 26.27, 23.26, 22.92, 21.68, 20.97, 19.68, 13.56.

HRMS (EI) calculated for $C_{22}H_{34}NaO_4$ $[M+Na]^+$: m/z 385.2355, found: 385.2345

IR: 2932, 2853, 1737, 1575,1410, 1320, 1381, 1260, 801 cm^{-1}.

23:

R_f = 0.4 (40% EtOAc in hexanes)

$[\alpha]_D{}^{23}$ = +19.0 (c = 0.5, $CHCl_3$)

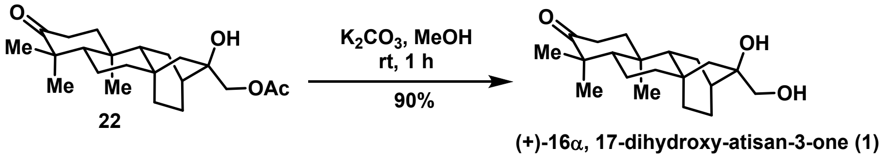
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10 (d, J = 11.3 Hz, 1H), 3.93 (d, J = 11.4 Hz, 1H), 2.60-2.53 (m, 1H), 2.35-2.28 (m, 1H), 2.10 (s, 3H), 2.15-1.99 (m, 1H), 1.90-186 (m, 1H), 1.83-1.72 (m, 2H), 1.60-1.57 (m, 1H), 1.53-1.39 (m, 4H), 1.39-1.23 (m, 5H), 1.21-1.09 (m, 2H), 1.11 (s, 3H), 1.06 (s, 3H), 1.04 (s, 3H), 0.98-0.94 (m, 1H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 217.3, 171.3, 73.0, 70.4, 55.8, 52.2, 50.8, 47.8, 38.8, 38.2, 37.2, 34.1, 32.7, 32.6, 27.5, 26.3, 24.7, 21.8, 21.7, 21.1, 19.5, 13.6.

HRMS (EI) calculated for $C_{22}H_{35}O_4$ $[M+H]^+$: m/z 363.2535, found: 363.2528

IR: 2939, 2871, 1736, 1690, 1398, 1244, 1086, 1032, 984, 882, 821, 596 cm^{-1}.

Synthesis of (+)-16α, 17-dihydroxy-atisan-3-one:



To a solution of **22** (0.068 mmol, 25 mg) in MeOH (5 ml) was added K_2CO_3 (0.13 mmol, 18.7 mg, 2 equiv) at room temperature. The reaction mixture was stirred at this temperature for one hour then quenched with saturated aqueous NH_4Cl (10 ml). MeOH was removed under reduced pressure and the aqueous layer was extracted with EtOAc (10 ml × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated to afford crude product, which was purified by flash chromatography on silica gel to provide (+)-16α, 17-dihydroxy-atisan-3-one (**1**) (19.6 mg, 90%).

R_f = 0.40 (70% EtOAc in hexanes)

$[\alpha]_D$ ^{23} = +32.0 (*c* = 0.05, $CHCl_3$)

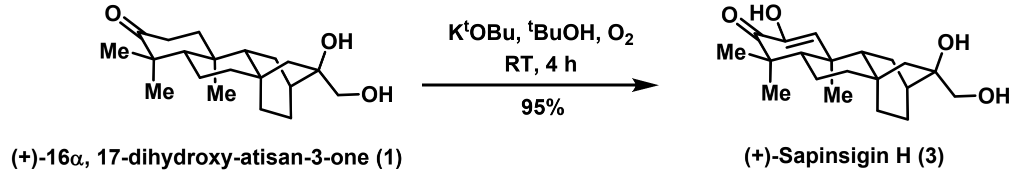
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.56 (d, *J* = 11.0 Hz, 1H), 3.42 (d, *J* = 11.0 Hz, 1H), 2.56 (ddd, *J* = 16.1, 12.3, 6.9 Hz, 1H), 2.32 (ddd, *J* = 16.0, 6.1, 3.3 Hz, 1H), 2.02 – 1.94 (m, 1H), 1.92 – 1.74 (m, 3H), 1.66 – 1.54 (m, 1H), 1.50 – 1.37 (m, 4H), 1.34 – 1.26 (m, 2H), 1.26 – 1.15 (m, 4H), 1.13-1.10 (m, 1H), 1.10 (s, 3H), 1.06 (s, 3H), 1.03 (s, 3H), 0.84-0.76 (m, 1H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 217.50, 74.23, 69.18, 55.82, 52.68, 51.05, 47.79, 38.90, 38.16, 37.37, 34.21, 33.07, 32.32, 27.33, 26.36, 23.37, 23.13, 21.78, 19.81, 13.65.

HRMS (EI) calculated for $C_{20}H_{33}O_3$ $[M+H]^+$: *m/z* 321.2430, found: 321.2415.

IR: 3435, 3924, 2852, 1693, 1650, 1461, 1262, 1080, 1041, 909, 719 cm^{-1}.

Synthesis of (+)-Sapinsigin H:



A 10 ml round-bottom flask was charged with ketone **1** (0.017 mmol, 5.6 mg) and *t*-BuOH (2 ml). This solution was then treated with KO^{t}Bu (0.12 mmol, 13.7 mg, 7.0 equiv) at room temperature. The flask was vented and back-filled with oxygen (balloon) and the mixture was vigorously stirred under an atmosphere of oxygen. The reaction was quenched by addition of saturated aqueous solution of NH_4Cl (10 ml). The pH of the mixture was adjusted to ~7 by addition of 1M HCl, and the aqueous layer was extracted with EtOAc (4 x 10 ml). The combined organic layers were dried over Na_2SO_4, filtered and concentrated to afford crude product, which was purified by flash chromatography on silica gel to provide (+)-Sapinsigin H (**3**) (5.4 mg, 95%).

R_f = 0.40 (70% EtOAc in hexanes)

$[\alpha]_D$ ^{23} = +61.0 (*c* = 0.08, $CHCl_3$)

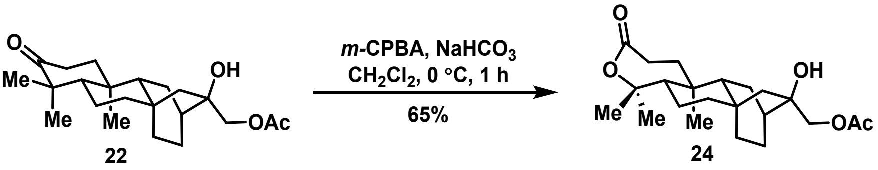
^{1}H NMR (400 MHz, CDCl$_3$) δ 6.24 (s, 1H), 5.96 (s, 1H), 3.59 (d, *J* = 11.0 Hz, 1H), 3.45 (d, *J* = 11.0 Hz, 1H), 2.18 (m, 1H), 1.89-1.88 (bs, 2H), 1.68-1.61 (m, 3H), 1.52-1.49 (m, 2H), 1.48 – 1.46 (m, 2H), 1.39 – 1.35 (m, 1H), 1.29 (s, 3H), 1.25-1.23 (m, 2H), 1.22 (s, 3H), 1.17 (m, 1H), 1.12 (s, 3H), 0.88 – 0.82 (m, 1H).

^{13}C NMR (400 MHz, CDCl$_3$) δ 201.15, 143.70, 127.85, 74.10, 68.97, 54.14, 52.58, 47.34, 44.08, 38.97, 38.88, 33.49, 32.12, 27.80, 27.04, 23.23, 23.18, 21.86, 18.93, 18.49.

HRMS (EI) calculated for $C_{20}H_{31}O_4$ $[M+H]^+$: *m/z* 335.2222, found: 335.2206.

IR: 3439, 2957, 2872, 1694, 1643, 1400, 1386, 1262, 1172, 1044, 686 cm^{-1}.

Baeyer–Villiger oxidation to 24:



To a solution of **22** (0.071 mmol, 26 mg) in CH$_2$Cl$_2$ (5 ml) was added NaHCO$_3$ (0.35 mmol, 30 mg, 5 equiv) and *m*-CPBA (0.1 mmol, 60%, 12 mg, 1.5 equiv) at room temperature. The reaction mixture was stirred at this temperature for 3 h then quenched with saturated aqueous Na$_2$S$_2$O$_3$ (10 ml). The aqueous layer was extracted by CH$_2$Cl$_2$ (10 ml × 4) and the combined organic layers were then dried over anhydrous Na$_2$SO$_4$, filtered and concentrated to give the residue, which was purified by flash chromatography on silica gel to give **24** (17.4 mg, 65%).

R$_f$ = 0.3 (40% EtOAc in hexanes)

[α]$_D$ ^{23} = +37.0 (*c* = 0.6, CHCl$_3$)

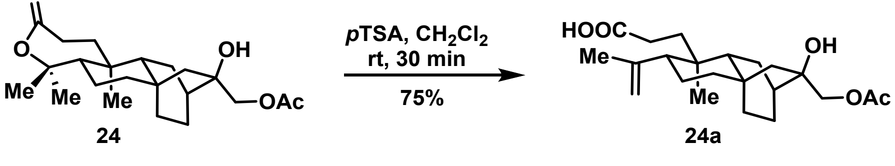
^{1}H NMR (400 MHz, CDCl$_3$) δ 4.08 (d, *J* = 11.4 Hz, 1H), 3.93 (d, *J* = 11.4 Hz, 1H), 2.61 (dd, *J* = 7.4, 3.5 Hz, 2H), 2.08 (s, 3H), 2.06 – 2.00 (m, 1H), 1.89 – 1.80 (m, 1H), 1.79 – 1.74 (m, 1H), 1.72 – 1.64 (m, 1H), 1.61-1.54 (d, 3H), 1.50-1.44 (m, 4H), 1.43 (s, 3H), 1.41 (s, 3H), 1.41-1.33 (m, 3H), 1.25-1.16 (m, 4H), 1.14 (s, 3H), 0.87-1.76 (m, 1H).

^{13}C NMR (400 MHz, CDCl$_3$) δ 175.65, 171.23, 86.51, 72.59, 70.20, 56.16, 52.12, 50.52, 40.63, 38.62, 35.78, 33.30, 32.90, 32.86, 31.72, 26.91, 25.14, 23.52, 23.13, 22.62, 20.97, 14.93.

HRMS (EI) calculated for $C_{22}H_{34}NaO_5$ $[M+Na]^+$: *m/z* 401.2304, found: 401.2293

IR: 2980, 2939, 1720, 1680, 1510, 1480, 1356, 1211, 996, 756, 692 cm^{-1}.

Synthesis of acid 24a:



Compound **24** (0.045 mmol, 17.4 mg) in CH_2Cl_2 (10 ml) was added 30 mg of *p*-toluenesulfonic acid. The mixture was stirred at room temperature for 6–8 h. The mixture was diluted with water and extracted with CH_2Cl_2. The organic layer was washed with 5% sodium bicarbonate solution, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel to give **24a** (12.7 mg, 75%).

R_f = 0.5 (50% EtOAc in hexanes)

$[\alpha]_D$ ^{23} = +26.0 (*c* = 0.37, $CHCl_3$)

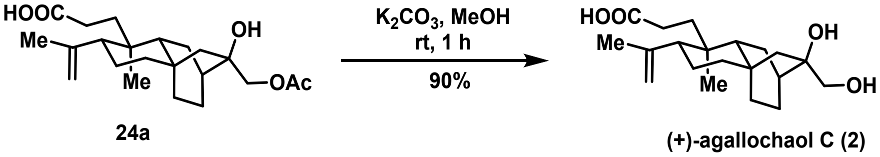
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.85 (s, 1H), 4.66 (s, 1H), 4.09 (d, *J* = 11.4 Hz, 1H), 3.93 (d, *J* = 11.4 Hz, 1H), 2.34 (ddd, *J* = 33.7, 16.6, 8.3 Hz, 3H), 2.08 (s, 3H), 1.99 – 1.83 (m, 4H), 1.78 – 1.74 (m, 1H), 1.73 (s, 3H), 1.55-1.49 (m, 3H), 1.10-1.30 (m, 3H), 1.20-1.11 (m, 4H), 0.95 (s, 3H), 0.85-0.76 (m, 1H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 177.81, 171.22, 147.34, 113.61, 73.26, 70.15, 52.10, 50.88, 42.77, 39.68, 38.04, 33.22, 32.93, 32.74, 28.08, 26.98, 24.64, 23.58, 23.18, 22.82, 20.95, 17.80.

HRMS (EI) calculated for $C_{22}H_{34}NaO_5$ $[M+Na]^+$: *m/z* 401.2304, found: 401.2292

IR: 3560, 3000, 1713, 1637, 1398, 1219, 758, 667, 596 cm^{-1}.

Synthesis of (+)-agallochaol C:



To a solution of **24a** (0.01 mmol, 4 mg) in MeOH (1.5 ml) was added K_2CO_3 (0.02 mmol, 2.9 mg, 2 equiv) at room temperature. The reaction mixture was stirred at this temperature for one hour then quenched with saturated aqueous NH_4Cl (10 ml). MeOH was removed under reduced pressure and the aqueous layer was extracted with EtOAc (10 ml × 4). The combined organic layers were dried over Na_2SO_4, filtered and concentrated to afford crude product, which was purified by flash chromatography on silica gel (10% CH_2Cl_2/MeOH) to provide (+)-agallochaol C (**2**) (3 mg, 90%).

R_f = 0.5 (30% MeOH in CH_2Cl_2)

$[\alpha]_D$ ^{23} = +27.0 (*c* = 0.25, $CHCl_3$)

^{1}H NMR (400 MHz, CD_3OD) δ 4.85 (s, 1H), 4.70 (s, 1H), 3.49 (d, *J* = 11.4 Hz, 1H), 3.35 (d, *J* = 11.4 Hz, 1H), 2.39 – 2.29 (m, 1H), 2.27-2.22 (m, 1H), 2.03-1.97 (m, 2H), 1.96-1.92 (m, 1H), 1.85-1.80 (m, 2H), 1.76 (s, 3H), 1.68-1.62 (m, 2H), 1.53-1.49 (m, 1H), 1.49-1.42 (m, 2H), 1.30-1.27 (m, 2H), 1.25-1.18 (m, 2H), 1.14 (d, *J* = 13.9 Hz, 1H), 1.06 (dd, J = 13.9, 2.8 Hz, 1H), 0.99 (s, 3H), 0.86-0.80 (m, 1H).

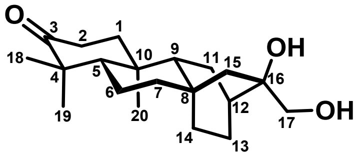
^{13}C NMR (400 MHz, CD_3OD) δ 177.91, 149.50, 114.31, 75.48, 70.10, 53.89, 52.65, 44.69, 41.23, 39.98, 35.64, 34.45, 33.71, 30.51, 28.64, 26.43, 24.66, 24.56, 24.50, 18.90.

HRMS (EI) calculated for $C_{20}H_{32}NaO_4$ $[M+Na]^+$: *m/z* 359.2198, found: 359.2188

IR: 3559, 3418, 2930, 1703, 1638, 1445, 1261, 1220, 890, 749 cm^{-1}.

^{1}H and ^{13}C NMR comparison

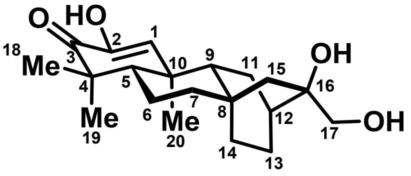
1. Comparison of NMR data for natural ***ent*-16α, 17-dihydroxy-atisan-3-one** with our synthetic **(+)-16α, 17-dihydroxy-atisan-3-one**.



(+)-16α,17-dihydroxy-atisan-3-one (1)

	Natural ***ent*-16α, 17-dihydroxy-atisan-3-one**		**Synthetic** **(+)-16α, 17-dihydroxy-atisan-3-one**			
	400 MHz, CDCl$_3$ δ_H , ppm, *J* in *Hz*	100 MHz δ_C , ppm	400 MHz, CDCl$_3$ δ_H , ppm, *J* in *Hz*	400 MHz δ_C , ppm	Δ δ_H ppm	Δ δ_C ppm
1	Ha: 1.85, m Hb: 1.38, m	38.0	Ha: 1.92-1.74, m Hb: 1.50-1.37, m	38.1	- -	0.1
2	Ha: 2.58, ddd, 16.0, 12.3, 6.9 Hb: 2.33, ddd, 16.0, 6.0, 3.2	34.0	Ha: 2.55, ddd, 16.1, 12.3, 6.9 Hb: 2.32, ddd, 16.0, 6.1, 3.3	34.2	- 0.03 - 0.01	0.2
3		217.5		217.5		0
4		47.6		47.7		0.1
5	1.30, m	55.6	1.26-1.34, m	55.8	-	0.2
6	Ha: 1.45, m Hb: 1.45, m	19.6	Ha: 1.50-137, m Hb: 1.50-137, m	19.8	- -	0.2
7	Ha: 1.42, m Hb: 1.18, m	38.7	Ha: 1.50-137, m Hb: 1.26-1.15, m	38.9	- -	0.2
8		32.8		33.0		0.2
9	1.32, m	50.8	Ha: 1.34-1.26, m	51.0	-	0.2
10		37.2		37.3		0.1
11	Ha: 2.03, m Hb: 1.24, m	22.9	Ha: 2.02-1.94, m Hb: 1.26-1.15, m	23.1	- -	0.2
12	1.82, m	32.1	Ha: 1.92-1.74, m	32.3	-	0.2
13	Ha: 1.63, m Hb: 1.50, m	23.2	Ha: 1.66-154, m Hb: 1.50-1.37, m	23.3	- -	0.1
14	Ha: 1.87, m Hb: 0.82, m	27.2	Ha: 1.92-1.74, m Hb: 0.84-0.76, m	27.3	- -	0.1
15	Ha: 1.24, m Hb: 1.10, m	52.4	Ha: 1.26-1.15, m Hb: 1.13-1.10, m	52.6	- -	0.2
16		74.1		74.2		0.1
17	Ha: 3.57, d, 10.9 Hb: 3.43, d, 10.9	68.9	Ha: 3.56, d, 11.0 Hb: 3.42, d, 11.0	69.1	- 0.01 - 0.01	0.2
18	1.07, s	26.1	1.06, s	26.3	- 0.01	0.2
19	1.04, s	21.6	1.03, s	21.7	- 0.01	0.1
20	1.11, s	13.4	1.10, s	13.6	- 0.01	0.2

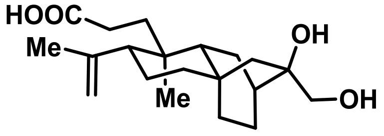
2. Comparison of NMR data for natural **Sapinsigin H** with our synthetic **(+)-Sapinsigin H.**



sapinsigin H (3)

	Natural sapinsigin H		Synthetic sapinsigin H			
	800 MHz, $CDCl_3$ δ_H , ppm, J in Hz	800 MHz δ_C , ppm	400 MHz, $CDCl_3$ δ_H , ppm, J in Hz	400 MHz δ_C , ppm	Δ δ_H ppm	Δ δ_C ppm
1	6.24, s	127.7	6.24, s	127.8	0	0.1
2		143.6		143.7		0.1
3		201.0		201.1		0.1
4		44.0		44.0		0
5	1.68, dd, 11.5, 2.6	54.1	1.68-1.61, unresolved	54.1	-	0
6	Ha: 1.52, m Hb: 1.48, m	18.8	Ha: 1.52-1.49, m Hb: 1.48-1.46, m	18.9	- -	0.1
7	Ha: 1.47, m Hb: 1.24, m	38.8	Ha: 1.48-1.46, m Hb: 1.26-1.15, m	38.8	- -	0
8		33.4		33.4		0
9	1.62, overlap	47.3	Ha: 1.68-1.61, unresolved	47.3	-	0
10		38.9		38.9		0
11	Ha: 2.19, m Hb: 1.51, m	23.1	Ha: 2.18, m Hb: 1.52-1.49, m	23.1	- -	0
12	1.89, m	32.1	1.89-1.88, bs	32.1	-	0
13	Ha: 1.63, m Hb: 1.38, m	23.2	Ha: 1.68.1.61, m Hb: 1.39-1.35, m	23.2	- -	0
14	Ha: 1.88, m Hb: 0.85, m	27.7	Ha: 1.89-1.88, bs Hb: 0.88-82, m	27.8	- -	0.1
15	Ha: 1.25, overlap Hb: 1.16, overlap	52.5	Ha: 1.25-1.23, m Hb: 1.17, m	52.5	- -	0
16		73.9		74.1		0.2
17	Ha: 3.59, dd, 10.9, 4.3 Hb: 3.45, dd, 10.9, 4.3	68.9	Ha: 3.59, d, 11.0 Hb: 3.45, d, 11.0	68.9	0 0	0
18	1.22, s	26.9	1.22, s	27.0	0	0.1
19	1.12, s	21.8	1.12, s	21.8	0	0
20	1.29, s	18.4	1.29, s	18.4	0	0

3. Comparison of NMR data for natural **Agallochaol C** with our synthetic **(+)-Agallochaol C.**

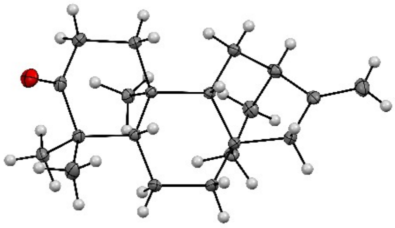


(+)-agallochaol C

	Natural agallochaol C		**Synthetic agallochaol C**			
	400 MHz, CD$_3$OD δ_H, ppm, J in Hz	100 MHz δc, ppm	400 MHz, CD$_3$OD δ_H, ppm, J in Hz	400 MHz δc, ppm	$\Delta\ \delta_H$ ppm	$\Delta\ \delta_C$ ppm
1	Ha: 1.52-1.48, m Hb: 1.63, m	35.5	Ha: 1.53-1.49, m Hb: 1.68-1.62, m	35.6	- -	0.1
2	Ha: 2.27-2.24, m Hb: 2.34, m	30.1	Ha: 2.27-2.22, m Hb: 2.39-2.29, m	30.5	- -	0.4
3		179.0		179.9		0.9
4		149.5		149.5		0
5	2.02-1.98, m	52.6	2.03-1.97, m	52.6	-	0
6	Ha: 1.83-1.80, m Hb: 1.30-1.27, m	26.4	Ha: 1.85-1.80, m Hb: 1.30-1.27, m	26.4	- -	0
7	NOT GIVEN Hb: 1.24-1.20, m	40.0	Ha: 1.30-1.27, m Hb: 1.25-1.18, m	39.9	- -	- 0.1
8		34.5		34.4		- 0.1
9	1.47-1.44, m	44.7	Ha: 1.49-1.42, m	44.6	-	- 0.1
10		41.2		41.2		0
11	Ha: 2.02-1.98, m Hb: 1.24-1.20, m	24.5	Ha: 2.03-1.97, m Hb: 1.25-1.18, m	24.5	- -	0
12	1.83-1.80, m	33.7	Ha: 1.85-1.80, m	33.7	-	0
13	Ha: 1.67-1.64, m Hb: 1.47-1.44, m	24.7	Ha: 1.68-162, m Hb: 1.49-1.42, m	24.6	- -	- 0.1
14	Ha: 1.96-1.92, m Hb: 0.85-0.82, m	28.7	Ha: 1.96-1.92, m Hb: 0.86-0.80, m	28.6	- -	- 0.1
15	Ha: 1.06, dd, 13.7, 2.7 Hb: 1.16, d, 13.7	53.9	Ha: 1.06, dd, 13.9, 2.8 Hb: 1.14, d, 13.9	53.8	- -	- 0.1
16		75.5		75.4		- 0.1
17	Ha: 3.35, d, 11.4 Hb: 3.49, d, 11.4	70.1	Ha: 3.35, d, 11.4 Hb: 3.49, d, 11..4	70.1	0 0	0
18	1.76, s	24.6	1.76, s	24.5	0	- 0.1
19	Ha: 4.86, bs Hb: 4.92, bs	114.4	Ha: 4.85, s Hb: 4.70, s	114.3	- 0.01 - 0.22	- 0.1
20	0.99, s	18.9	0.99, s	18.9	0	0

Crystallographic Data for Single Crystal X-Ray Structure of Compound 9

Table 1 Crystal data and structure refinement for 10auga_o_0m.



Identification code	10auga_o_0m
Empirical formula	$C_{20}H_{30}O$
Formula weight	286.461
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	6.0028(2)
b/Å	11.2789(3)
c/Å	13.1074(4)
α/°	64.982(1)
β/°	80.954(1)
γ/°	87.690(1)
Volume/$Å^3$	793.83(4)
Z	2
$\rho_{calc}g/cm^3$	1.198
μ/mm^{-1}	0.071
F(000)	316.2
Crystal size/mm^3	0.21 × 0.18 × 0.16
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.98 to 56.8
Index ranges	$-8 \leq h \leq 8$, $-15 \leq k \leq 15$, $-17 \leq l \leq 17$
Reflections collected	17410
Independent reflections	3957 [$R_{int} = 0.0301$, $R_{sigma} = 0.0242$]
Data/restraints/parameters	3957/0/201
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	$R_1 = 0.0390$, $wR_2 = 0.1013$
Final R indexes [all data]	$R_1 = 0.0424$, $wR_2 = 0.1040$
Largest diff. peak/hole / e $Å^{-3}$	0.38/-0.20

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 10auga_o_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O1	7194.7(14)	3983.4(8)	6087.6(7)	25.60(19)
C9	6205.7(15)	8115.5(8)	7311.4(7)	10.73(17)
C3	7619.7(16)	4941.1(9)	6234.3(8)	15.27(19)
C8	6928.6(15)	8081.3(9)	8408.6(7)	12.22(18)
C1	6386.9(16)	7264.9(9)	5824.0(8)	13.48(18)
C6	8624.8(16)	5859.0(9)	8711.9(8)	14.90(19)
C16	4802.5(16)	10132.9(9)	8122.3(8)	15.76(19)
C4	8563.0(16)	4797.3(9)	7306.0(8)	13.74(18)
C11	5846.9(16)	9558.8(9)	6484.7(8)	14.20(18)
C5	7635.4(15)	5881.8(9)	7691.7(7)	11.65(17)
C10	7643.9(15)	7301.2(8)	6747.5(7)	10.79(17)
C2	7350.0(17)	6302.2(10)	5335.2(8)	16.26(19)
C12	6335.9(16)	10503.6(9)	7001.3(8)	15.71(19)
C15	5008.1(16)	8707.1(9)	8926.1(8)	15.09(19)
C20	10029.4(15)	7902.1(9)	6189.5(8)	14.62(18)
C13	8794.3(17)	10334.2(9)	7230.7(9)	18.0(2)
C7	7203.3(17)	6666.9(9)	9249.7(8)	15.09(19)
C14	9060.5(16)	8941.7(9)	8157.2(8)	15.45(19)
C17	3441.3(19)	10958.7(11)	8379.6(10)	22.8(2)
C19	11162.4(17)	4823.0(10)	7001.8(9)	18.3(2)
C18	7822(2)	3445.7(9)	8260.9(9)	21.5(2)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for 10auga_o_0m. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	34.1(4)	20.3(4)	29.4(4)	0.2(3)	-10.1(3)	-15.4(3)
C9	10.5(4)	10.8(4)	10.8(4)	0.4(3)	-1.8(3)	-4.5(3)
C3	13.4(4)	17.6(4)	16.7(4)	0.7(3)	-0.4(3)	-9.8(4)
C8	13.9(4)	12.3(4)	11.4(4)	1.5(3)	-3.1(3)	-5.6(3)
C1	14.8(4)	14.9(4)	12.1(4)	2.3(3)	-3.9(3)	-6.5(3)
C6	18.8(4)	13.7(4)	12.4(4)	4.1(3)	-5.2(3)	-5.1(3)
C16	16.8(4)	15.5(4)	19.0(4)	1.9(3)	-6.9(4)	-9.8(4)
C4	16.0(4)	12.2(4)	13.7(4)	1.4(3)	-1.8(3)	-6.3(3)
C11	16.2(4)	12.7(4)	13.7(4)	2.0(3)	-4.3(3)	-5.0(3)
C5	12.8(4)	10.7(4)	11.2(4)	0.6(3)	-1.4(3)	-4.6(3)
C10	10.7(4)	11.4(4)	10.2(4)	0.3(3)	-1.4(3)	-4.5(3)
C2	18.7(5)	19.1(5)	13.7(4)	2.1(4)	-3.5(3)	-9.3(4)
C12	18.2(5)	11.5(4)	17.9(4)	1.5(3)	-5.2(4)	-5.9(3)
C15	16.5(4)	16.3(4)	14.7(4)	2.4(3)	-2.8(3)	-8.8(4)
C20	12.2(4)	15.0(4)	15.0(4)	-0.8(3)	0.5(3)	-5.6(3)
C13	16.5(4)	14.7(4)	23.5(5)	-1.9(3)	-3.5(4)	-8.5(4)
C7	20.5(5)	14.2(4)	10.9(4)	2.9(3)	-4.1(3)	-5.2(3)
C14	14.2(4)	16.6(4)	18.7(4)	1.0(3)	-6.0(3)	-9.4(4)
C17	22.8(5)	22.0(5)	29.8(6)	5.4(4)	-7.0(4)	-16.2(5)
C19	16.3(5)	20.7(5)	20.8(5)	5.7(4)	-4.3(4)	-11.6(4)
C18	32.3(6)	12.0(4)	18.4(5)	0.4(4)	-0.5(4)	-5.9(4)

Table 4 Bond Lengths for 10auga_o_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C3	1.2174(12)	C6	C7	1.5320(13)
C9	C8	1.5511(12)	C16	C12	1.5057(14)
C9	C11	1.5568(12)	C16	C15	1.5176(13)
C9	C10	1.5636(12)	C16	C17	1.3291(14)
C3	C4	1.5396(13)	C4	C5	1.5626(12)
C3	C2	1.5105(13)	C4	C19	1.5469(13)
C8	C15	1.5430(12)	C4	C18	1.5344(13)
C8	C7	1.5284(12)	C11	C12	1.5422(13)
C8	C14	1.5443(13)	C5	C10	1.5548(12)
C1	C10	1.5388(12)	C10	C20	1.5409(12)
C1	C2	1.5313(12)	C12	C13	1.5404(13)
C6	C5	1.5365(12)	C13	C14	1.5475(13)

Table 5 Bond Angles for 10auga_o_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	C9	C8	109.36(7)	C18	C4	C5	109.37(7)
C10	C9	C8	116.23(7)	C18	C4	C19	107.83(8)
C10	C9	C11	114.92(7)	C12	C11	C9	110.80(7)
C4	C3	O1	120.97(9)	C4	C5	C6	113.57(7)
C2	C3	O1	120.50(9)	C10	C5	C6	110.86(7)
C2	C3	C4	118.45(8)	C10	C5	C4	117.05(7)
C15	C8	C9	106.16(7)	C1	C10	C9	107.26(7)
C7	C8	C9	110.10(7)	C5	C10	C9	106.34(7)
C7	C8	C15	109.84(7)	C5	C10	C1	107.71(7)
C14	C8	C9	112.63(7)	C20	C10	C9	112.74(7)
C14	C8	C15	105.74(7)	C20	C10	C1	108.85(7)
C14	C8	C7	112.10(8)	C20	C10	C5	113.65(7)
C2	C1	C10	113.74(7)	C1	C2	C3	113.66(7)
C7	C6	C5	110.62(7)	C11	C12	C16	108.77(8)
C15	C16	C12	111.97(8)	C13	C12	C16	108.32(8)
C17	C16	C12	124.00(9)	C13	C12	C11	108.31(8)
C17	C16	C15	124.03(10)	C16	C15	C8	110.21(8)
C5	C4	C3	110.49(7)	C14	C13	C12	109.56(8)
C19	C4	C3	106.16(7)	C6	C7	C8	113.58(7)
C19	C4	C5	114.44(8)	C13	C14	C8	110.61(7)
C18	C4	C3	108.33(8)				

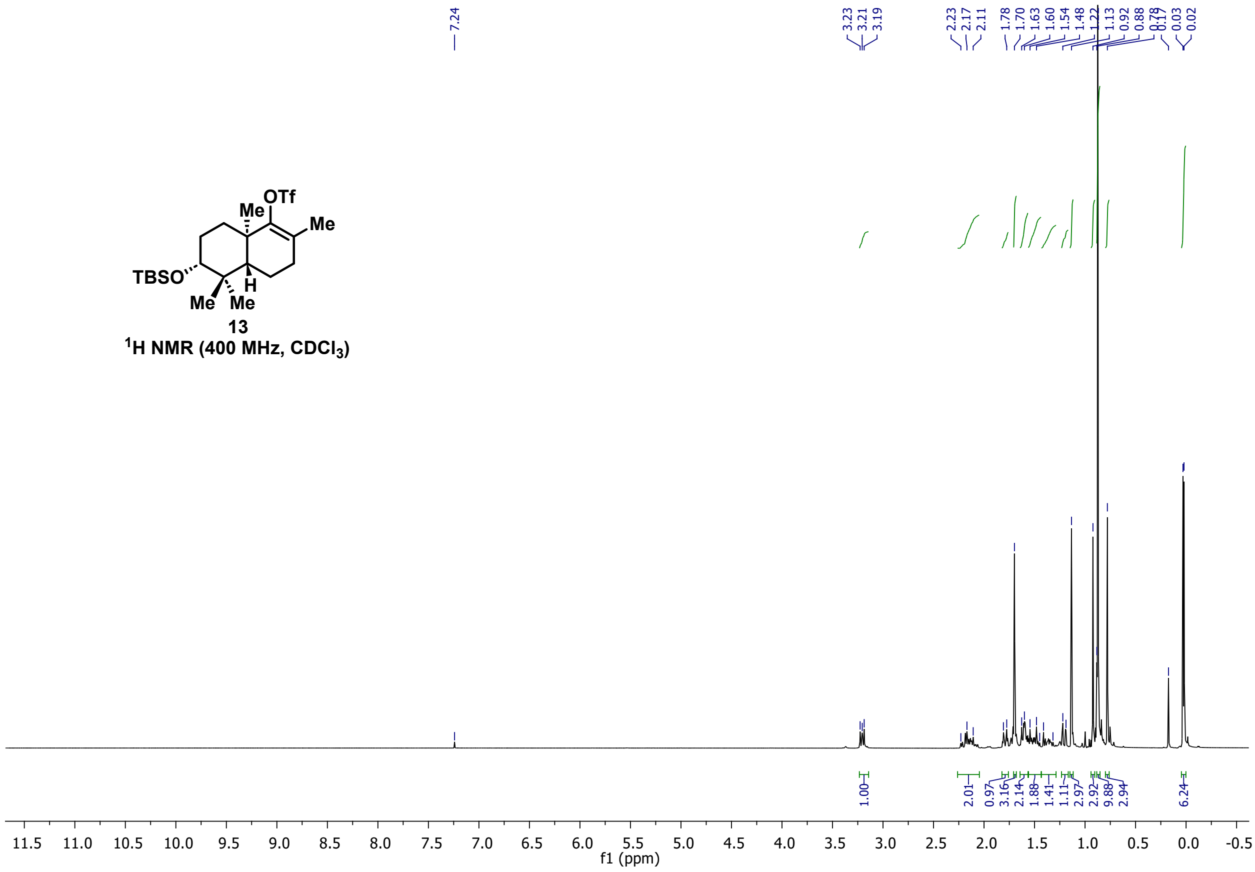
Table 6 Torsion Angles for 10auga_o_0m.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
O1	C3	C4	C5	-145.28(10)	C3	C2	C1	C10	51.24(9)
O1	C3	C4	C19	90.10(10)	C8	C15	C16	C12	6.11(8)
O1	C3	C4	C18	-25.49(11)	C8	C15	C16	C17	-173.50(8)
O1	C3	C2	C1	141.04(9)	C8	C7	C6	C5	-55.90(8)
C9	C8	C15	C16	-63.91(7)	C8	C14	C13	C12	10.02(8)
C9	C8	C7	C6	48.69(8)	C1	C10	C5	C6	-173.57(7)
C9	C8	C14	C13	50.55(8)	C1	C10	C5	C4	53.98(8)
C9	C11	C12	C16	-58.35(8)	C6	C5	C4	C19	-56.43(8)
C9	C11	C12	C13	59.17(8)	C6	C5	C4	C18	64.65(9)
C9	C10	C1	C2	-169.63(7)	C6	C5	C10	C20	65.76(8)
C9	C10	C5	C6	-58.85(7)	C16	C12	C13	C14	52.63(8)
C9	C10	C5	C4	168.69(6)	C4	C5	C10	C20	-66.69(8)
C3	C4	C5	C6	-176.18(7)	C11	C12	C13	C14	-65.18(8)
C3	C4	C5	C10	-44.96(8)					

Table 7 Hydrogen Atom Coordinates (Å×10^{4}) and Isotropic Displacement Parameters (Å^{2}×10^{3}) for 10auga_o_0m.

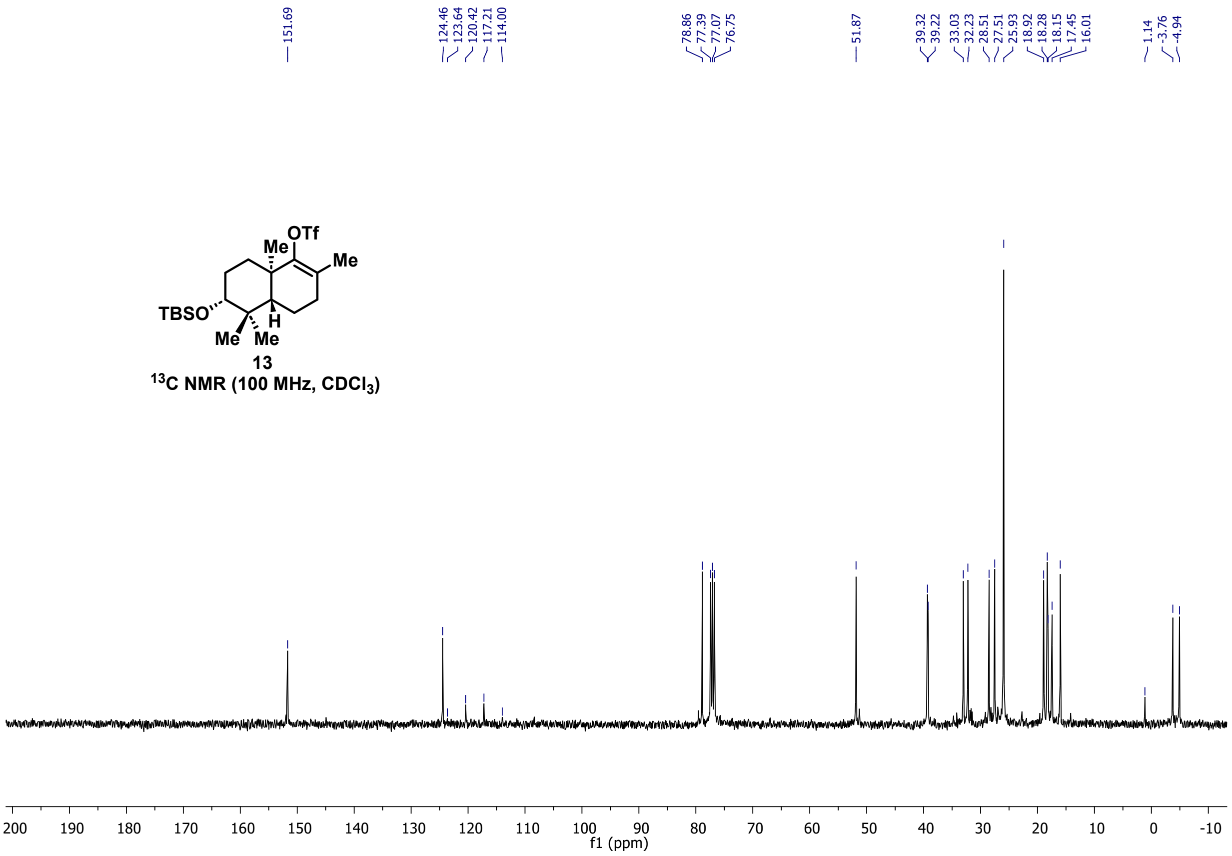
Atom	*x*	*y*	*z*	U(eq)
H9	4697.3(15)	7697.2(8)	7556.6(7)	12.9(2)
H1a	4813.8(16)	7027.9(9)	6146.0(8)	16.2(2)
H1b	6445.9(16)	8135.5(9)	5207.7(8)	16.2(2)
H6a	8661.8(16)	4962.4(9)	9276.3(8)	17.9(2)
H6b	10160.8(16)	6212.8(9)	8460.8(8)	17.9(2)
H11a	6841.1(16)	9780.9(9)	5766.5(8)	17.0(2)
H11b	4303.2(16)	9652.1(9)	6333.9(8)	17.0(2)
H5	6034.8(15)	5642.4(9)	7983.6(7)	14.0(2)
H2a	8810.4(17)	6638.3(10)	4877.8(8)	19.5(2)
H2b	6360.6(17)	6251.1(10)	4836.0(8)	19.5(2)
H12	6100.7(16)	11410.0(9)	6479.2(8)	18.9(2)
H15a	3595.7(16)	8236.6(9)	9061.9(8)	18.1(2)
H15b	5316.6(16)	8646.3(9)	9650.9(8)	18.1(2)
H20a	9959(2)	8839.2(9)	5843(6)	21.9(3)
H20b	11000(4)	7640(6)	6759.7(14)	21.9(3)
H20c	10615(5)	7602(6)	5618(5)	21.9(3)
H13a	9803.9(17)	10466.2(9)	6534.3(9)	21.6(2)
H13b	9188.6(17)	10980.8(9)	7483.5(9)	21.6(2)
H7a	7904.3(17)	6669.6(9)	9867.0(8)	18.1(2)
H7b	5720.5(17)	6248.4(9)	9574.1(8)	18.1(2)
H14a	9311.4(16)	8995.6(9)	8849.8(8)	18.5(2)
H14b	10362.9(16)	8544.7(9)	7901.0(8)	18.5(2)
H19a	11617.3(19)	4049(4)	6901(7)	27.4(3)
H19b	11643(2)	5583(4)	6309(4)	27.4(3)
H19c	11839.9(17)	4853(8)	7607(3)	27.4(3)
H18a	6221(3)	3422(3)	8497(5)	32.3(3)
H18b	8197(14)	2785.8(12)	7986(2)	32.3(3)
H18c	8583(11)	3284(4)	8897(3)	32.3(3)
H17a	2450(30)	10663(14)	9128(13)	29(4)
H17b	3410(30)	11857(16)	7837(13)	35(4)

NMR Spectra



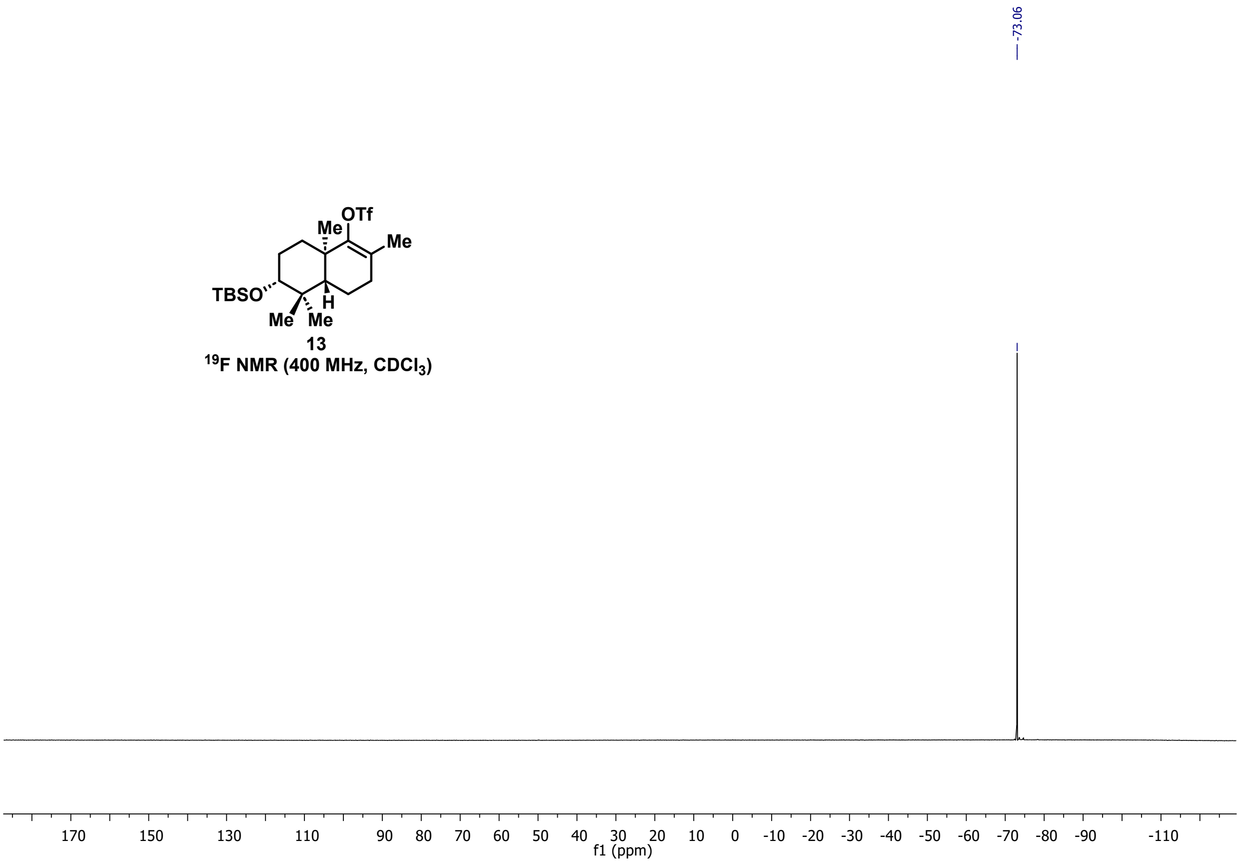
13

^{1}H NMR (400 MHz, CDCl$_3$)



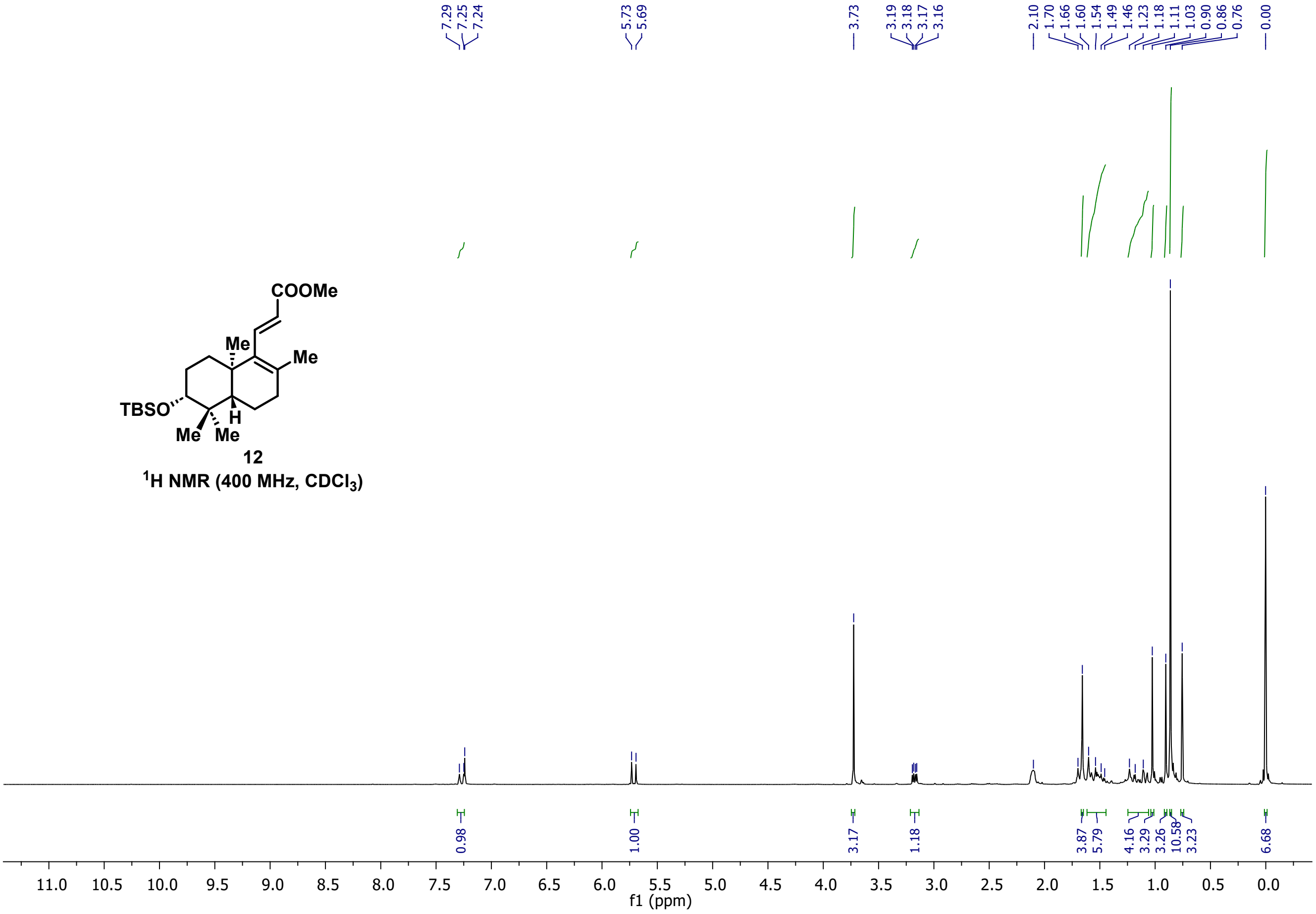
13

^{13}C NMR (100 MHz, CDCl$_3$)



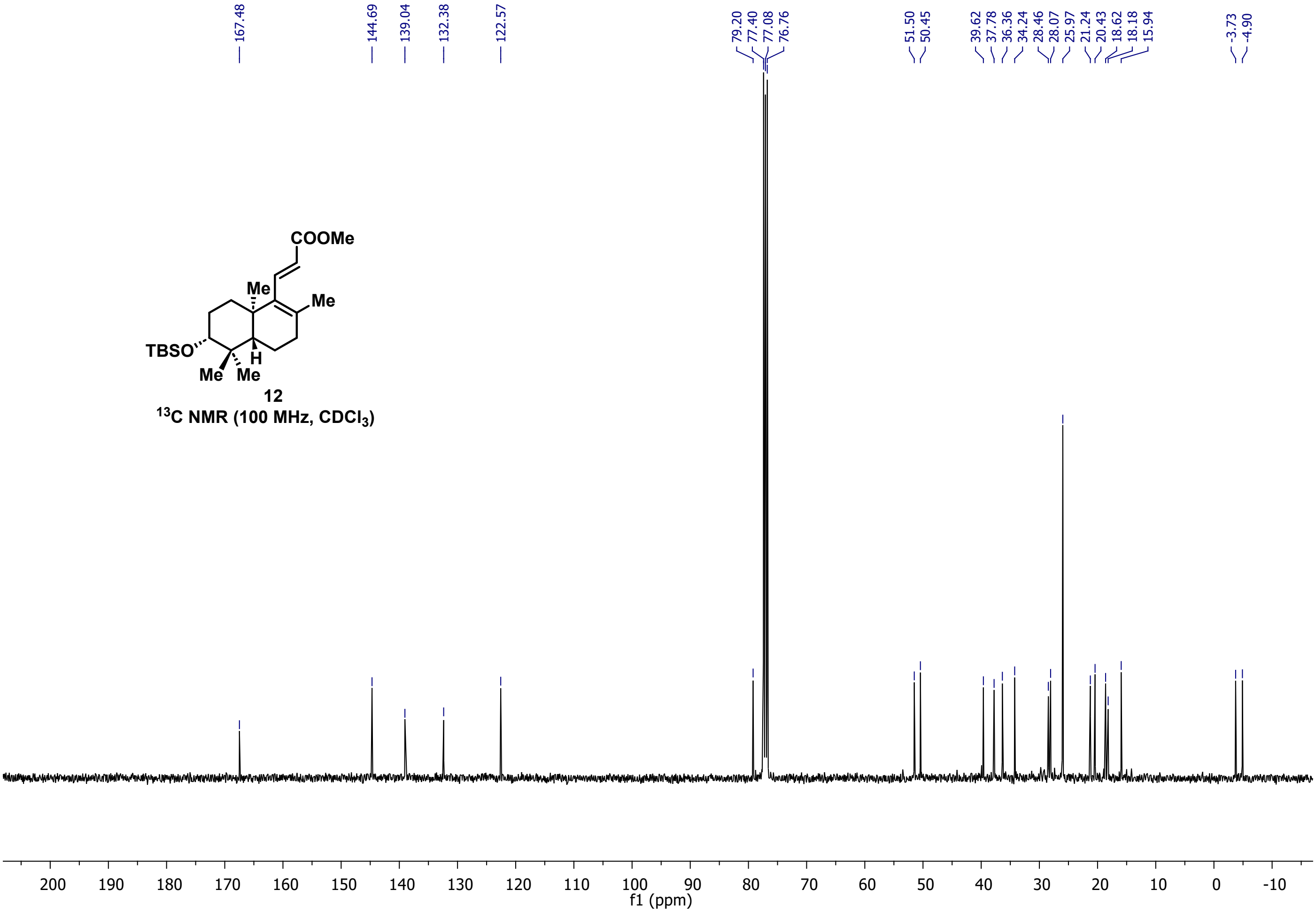
13

^{19}F NMR (400 MHz, CDCl$_3$)



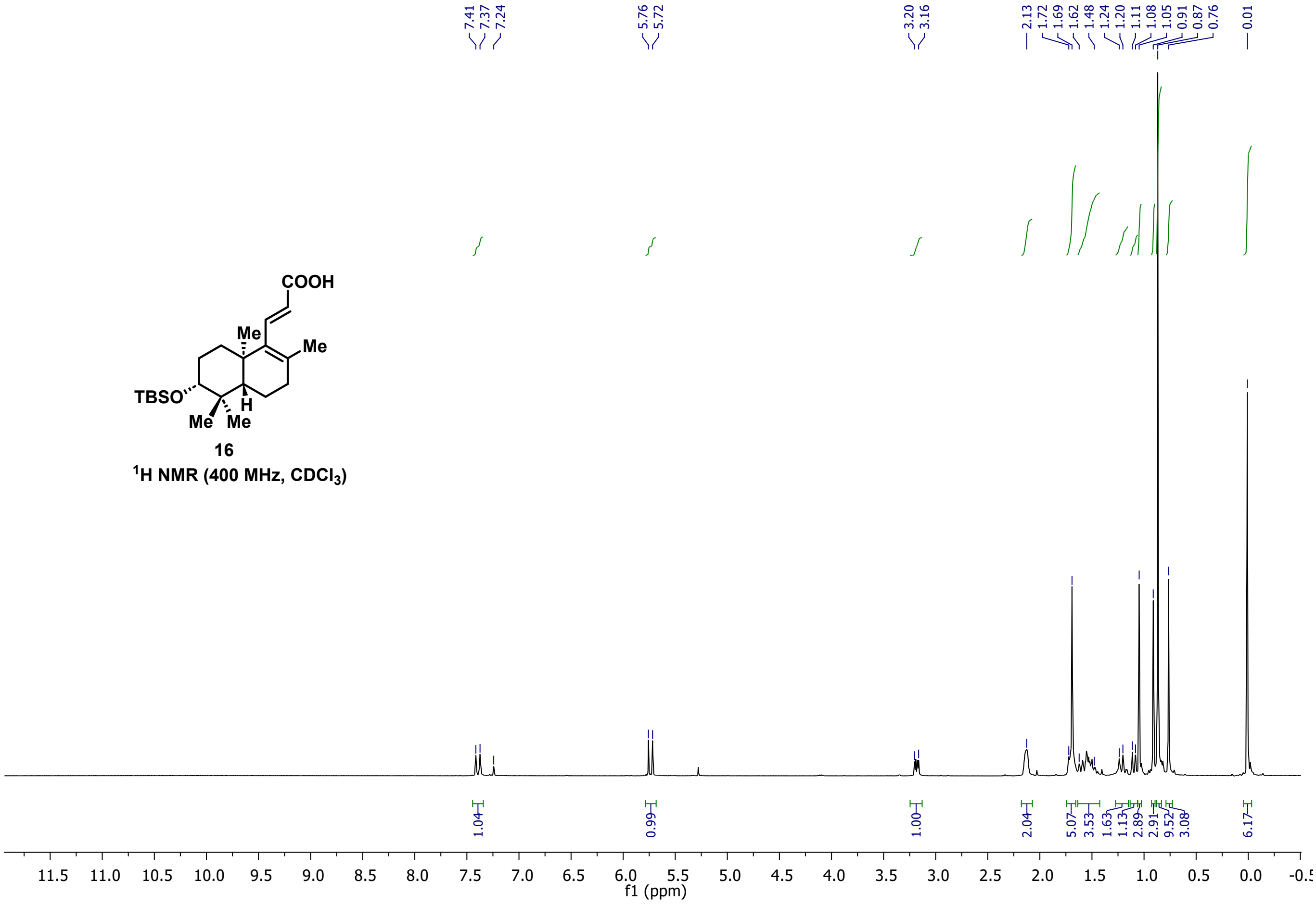
12

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



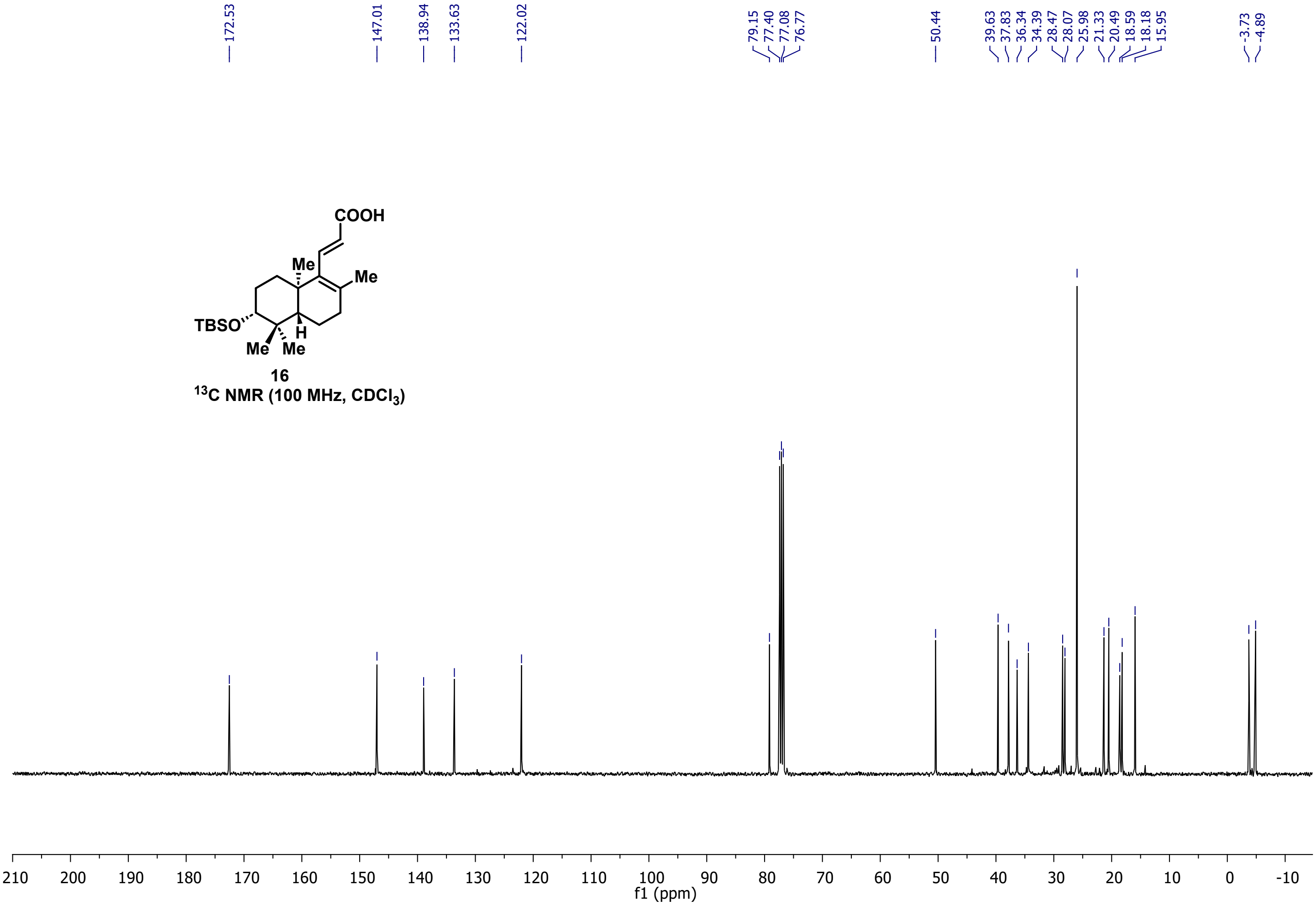
12

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



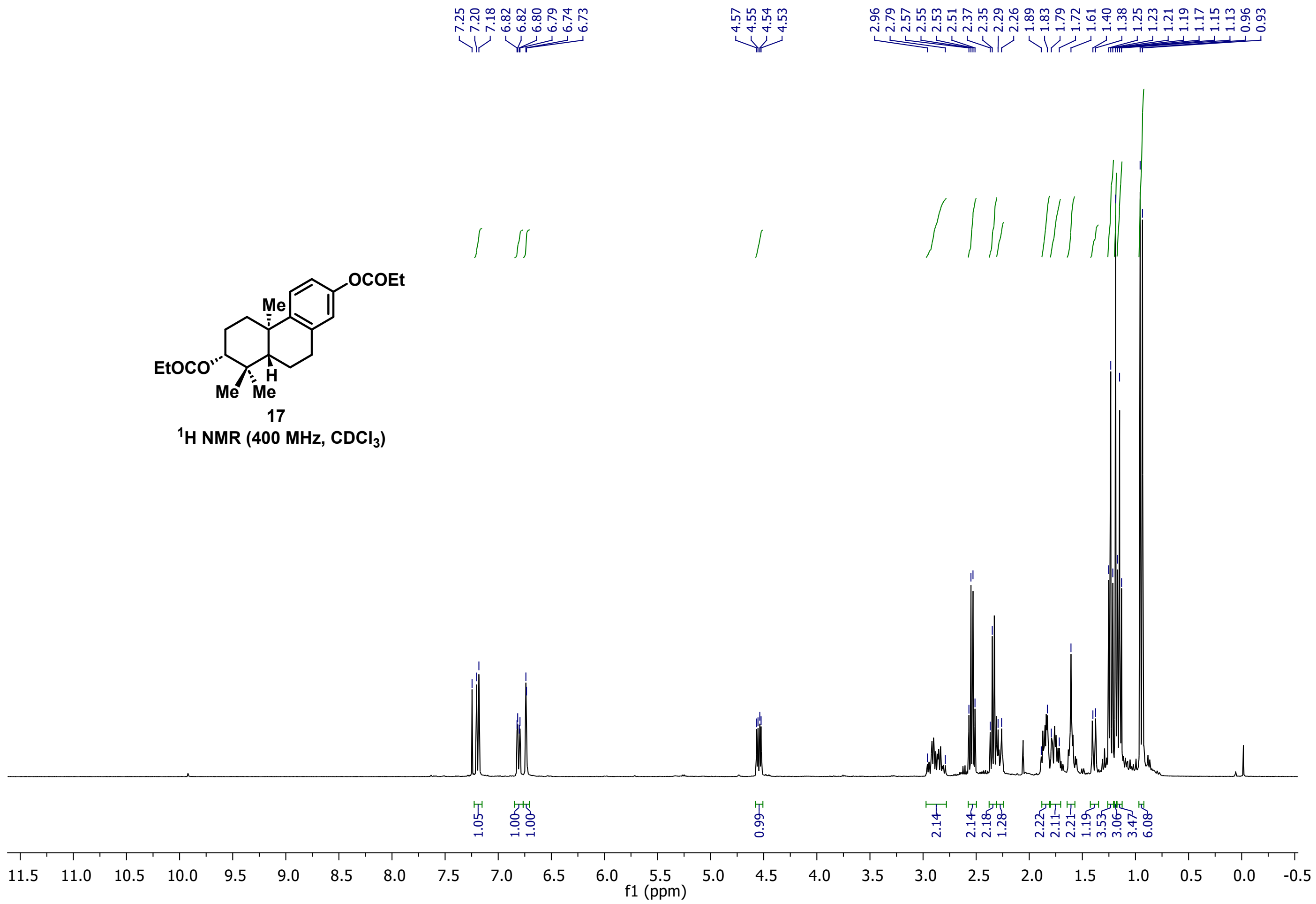
16

^{1}H NMR (400 MHz, CDCl$_3$)



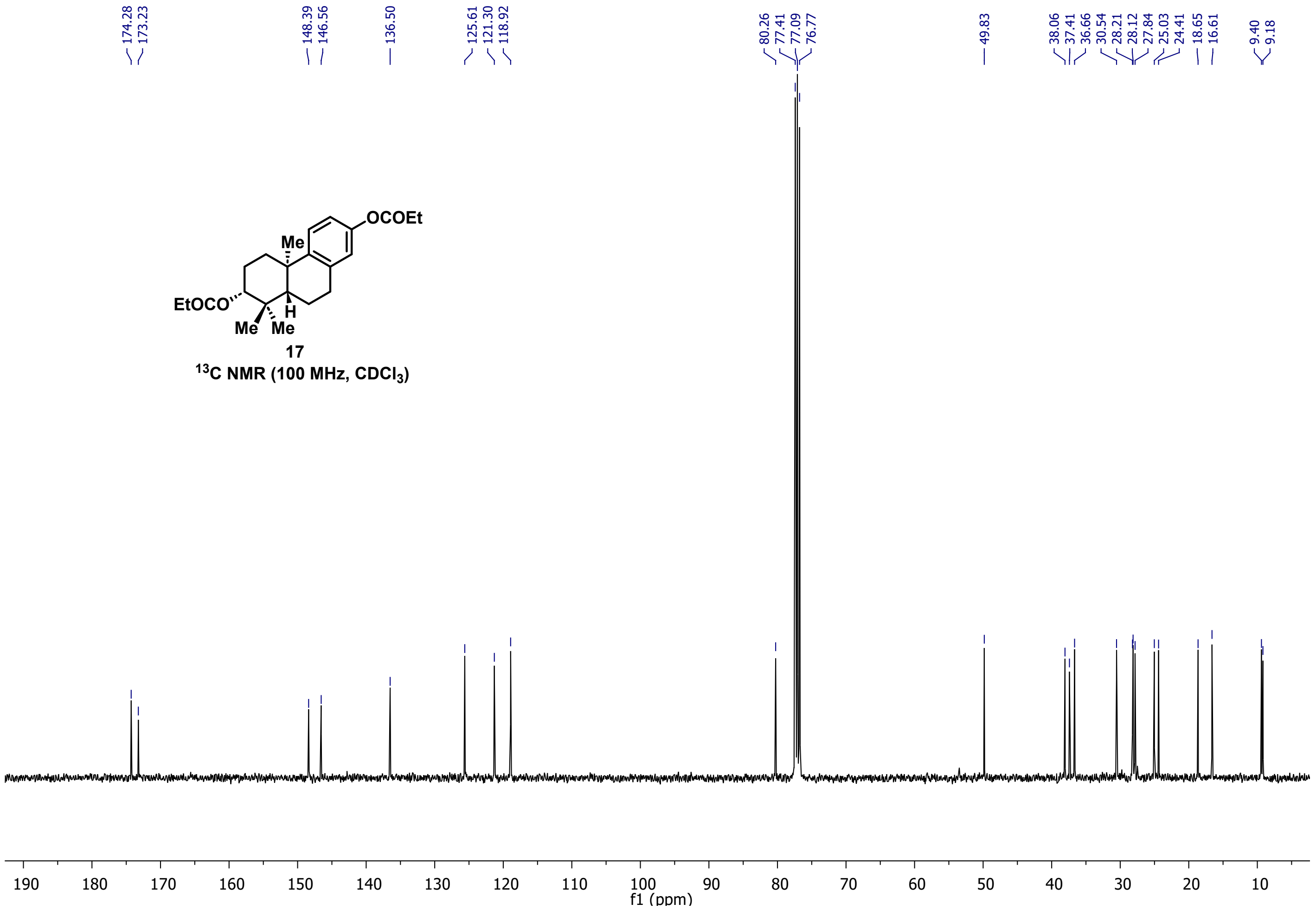
16

^{13}C NMR (100 MHz, CDCl$_3$)



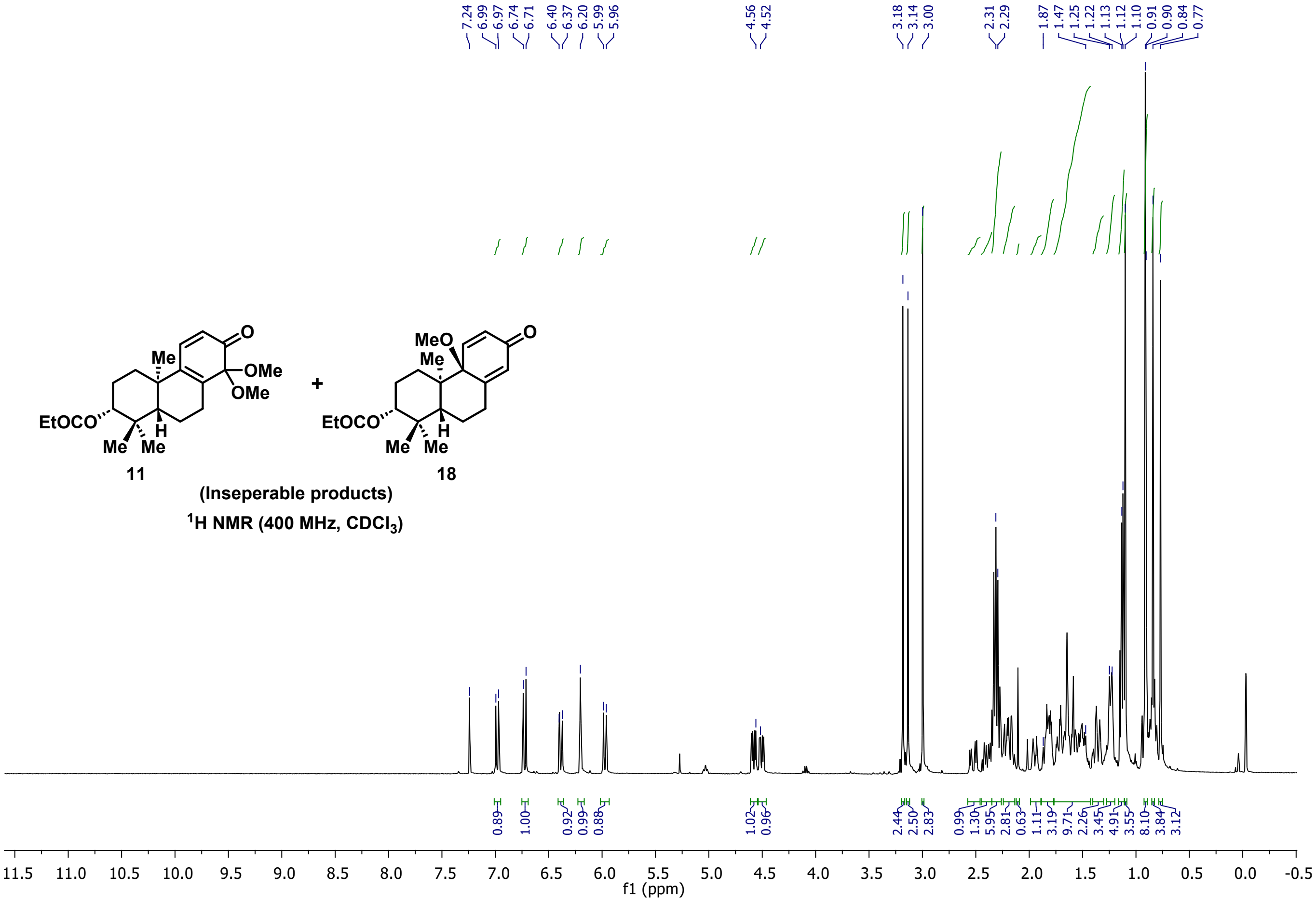
17

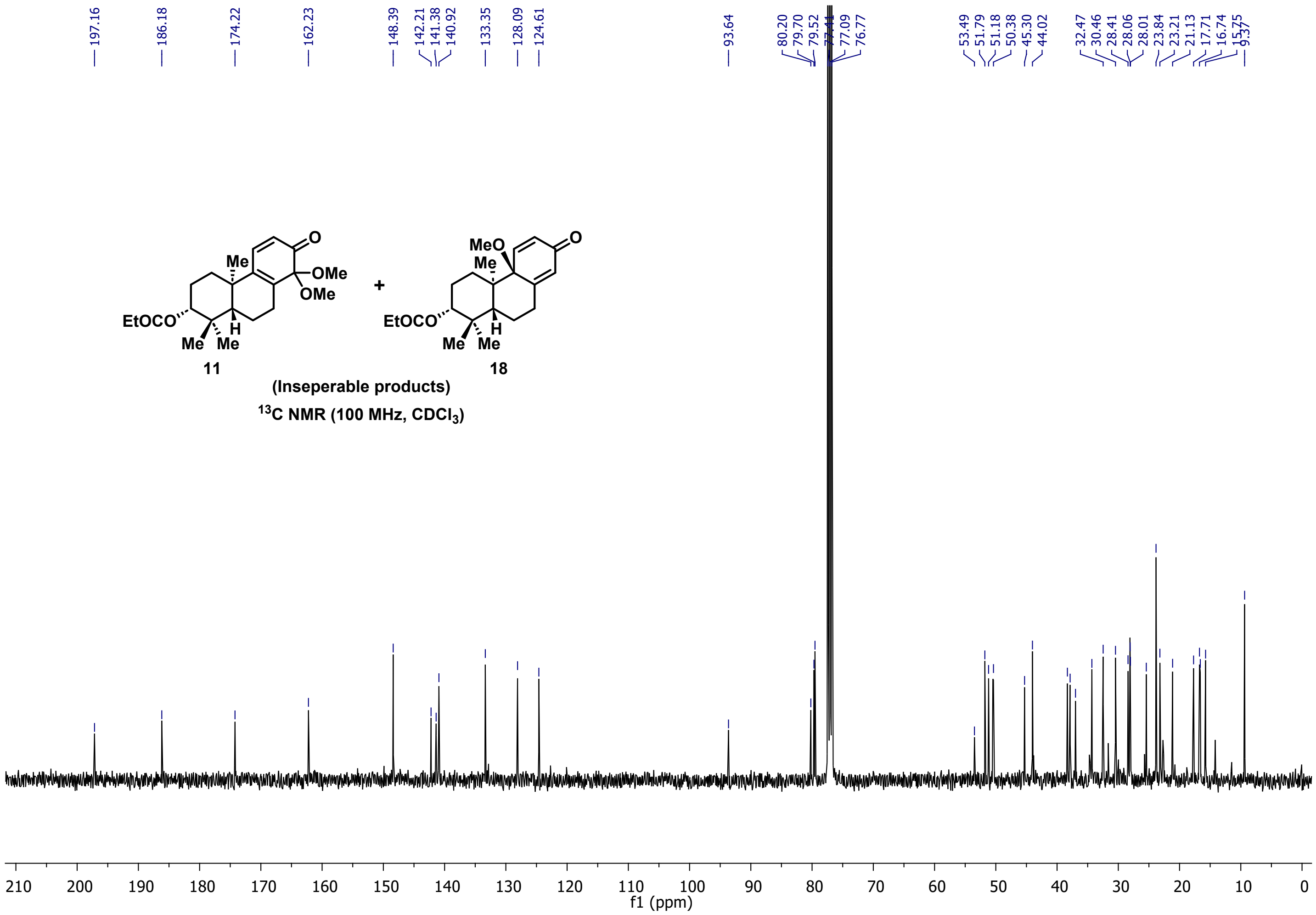
^{1}H NMR (400 MHz, $CDCl_3$)



17

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


7.24
6.99
6.97
6.74
6.71
6.40
6.37
6.20
5.99
5.96
4.56
4.52
3.18
3.14
3.00
2.31
2.29
1.87
1.47
1.25
1.22
1.13
1.12
1.10
0.91
0.90
0.84
0.77
Me
O
OMe
OMe
EtOCO
H
Me
Me
11
+
MeO
Me
O
EtOCO
H
Me
Me
18
(Inseperable products)
^{1}H NMR (400 MHz, CDCl$_3$)
0.89
1.00
0.92
0.99
0.88
1.02
0.96
2.44
2.50
2.83
0.99
1.30
5.95
2.81
0.63
1.11
3.19
9.71
2.26
3.45
4.91
3.55
8.10
3.84
3.12
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

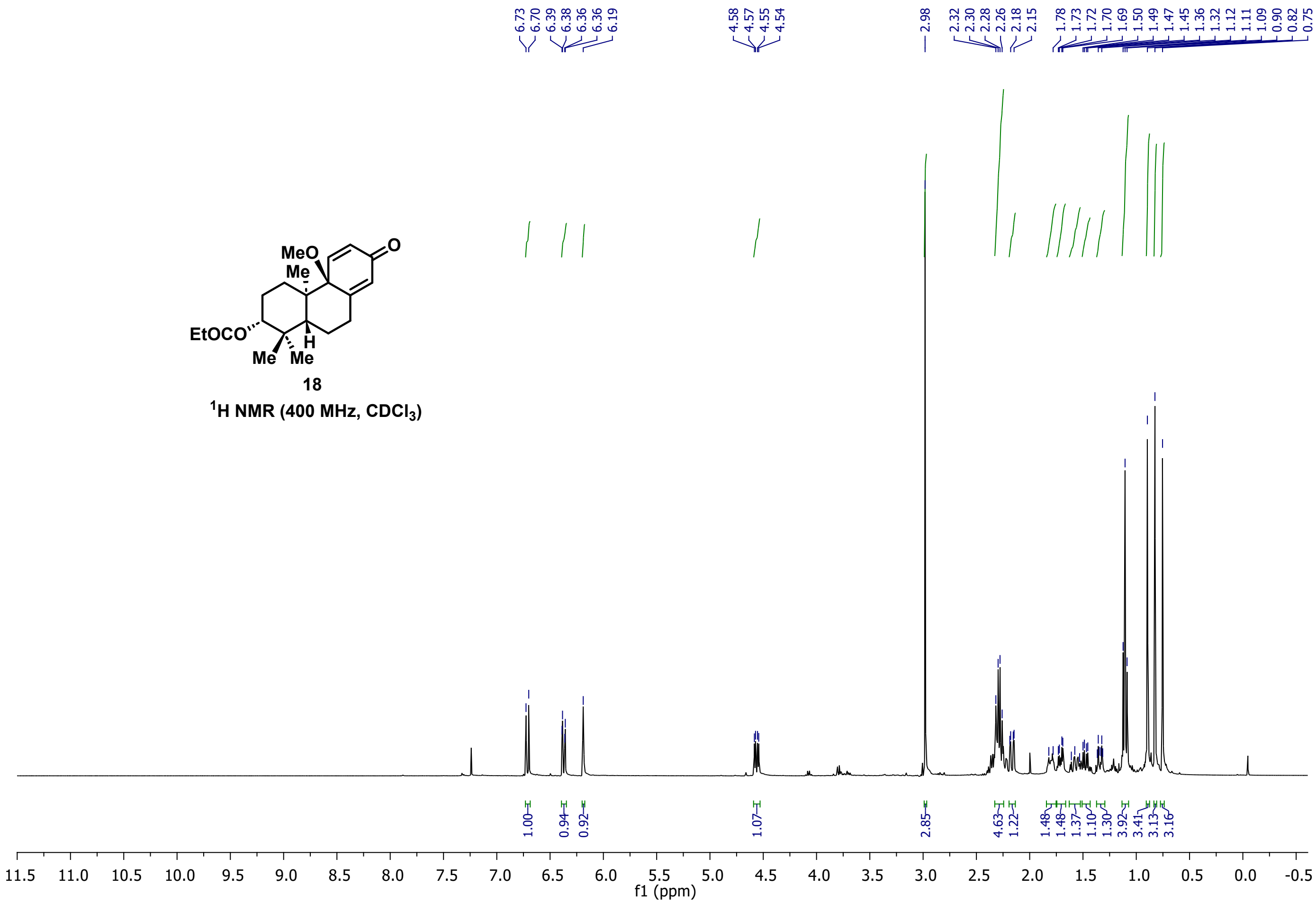


11

18

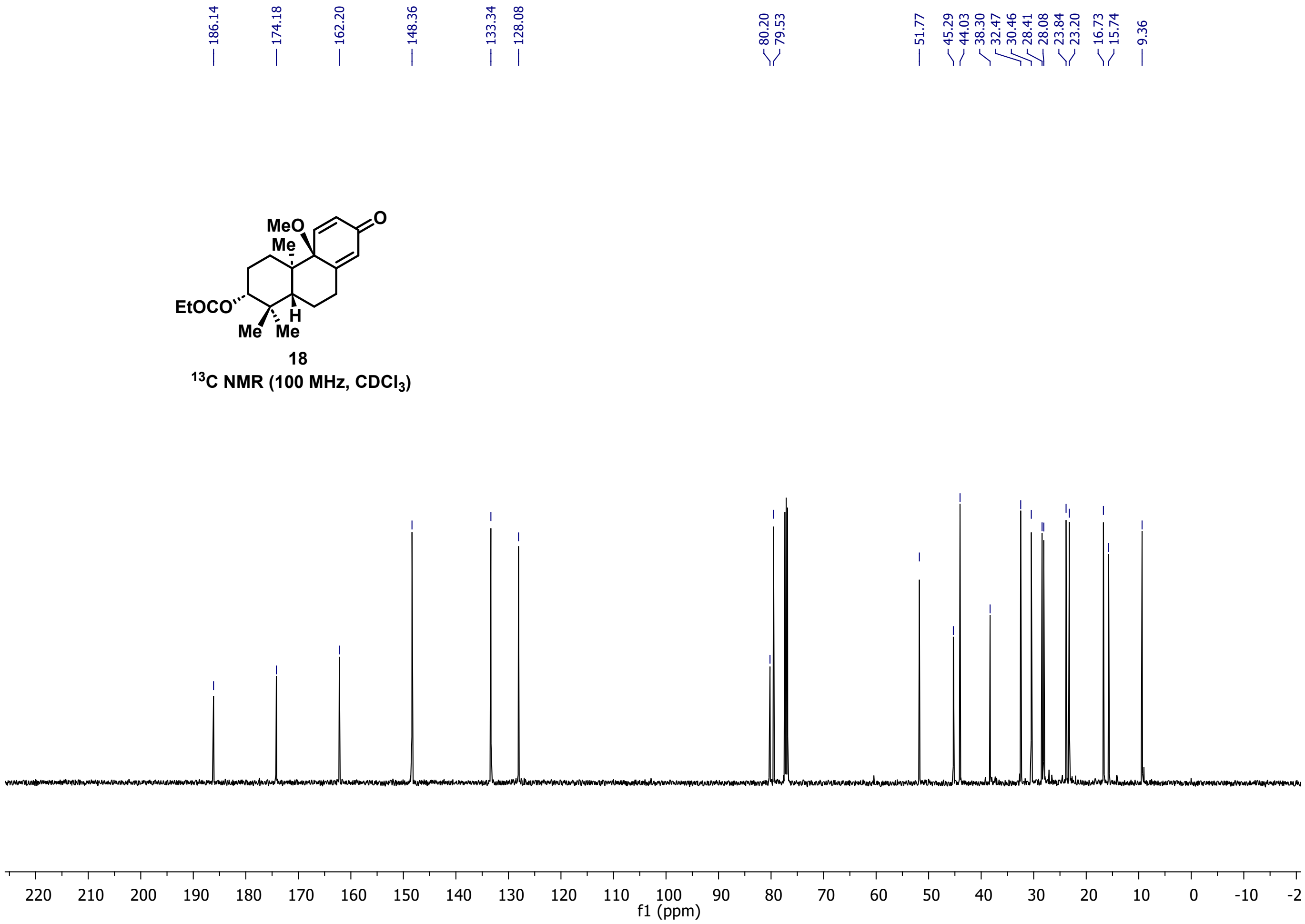
(Inseperable products)

^{13}C NMR (100 MHz, CDCl$_3$)



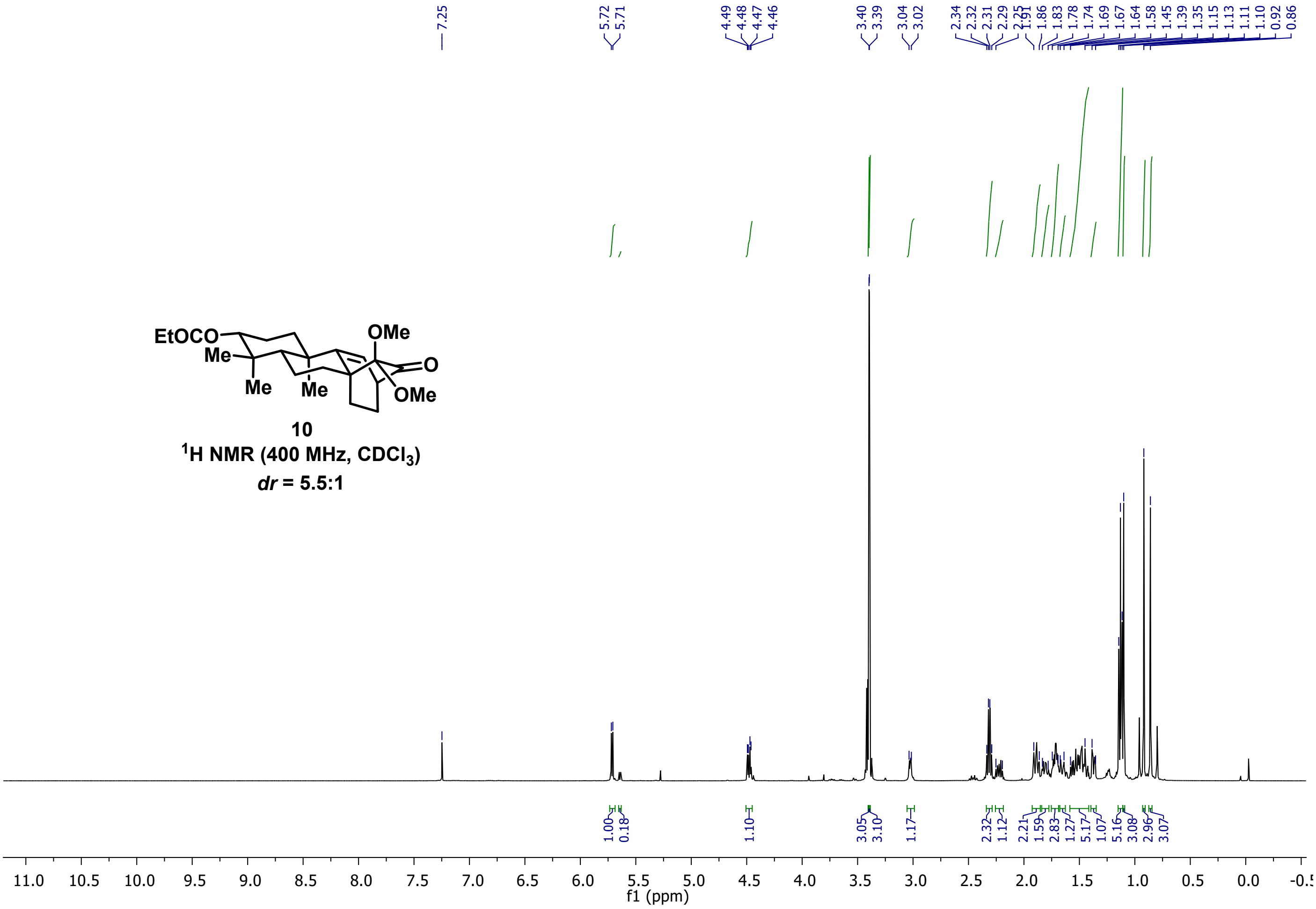
18

^{1}H NMR (400 MHz, CDCl$_3$)



18

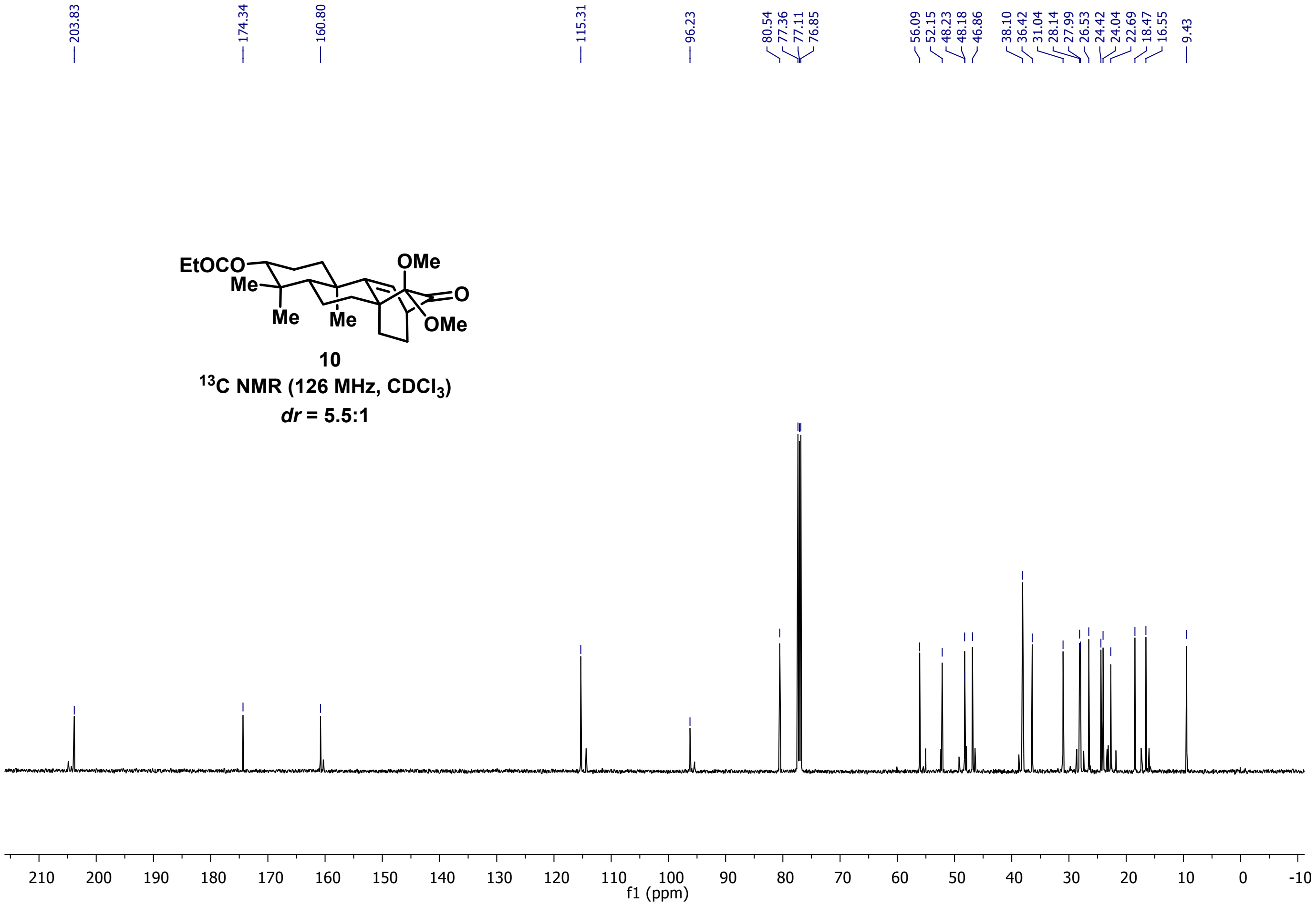
^{13}C NMR (100 MHz, CDCl$_3$)



10

^{1}H NMR (400 MHz, CDCl$_3$)

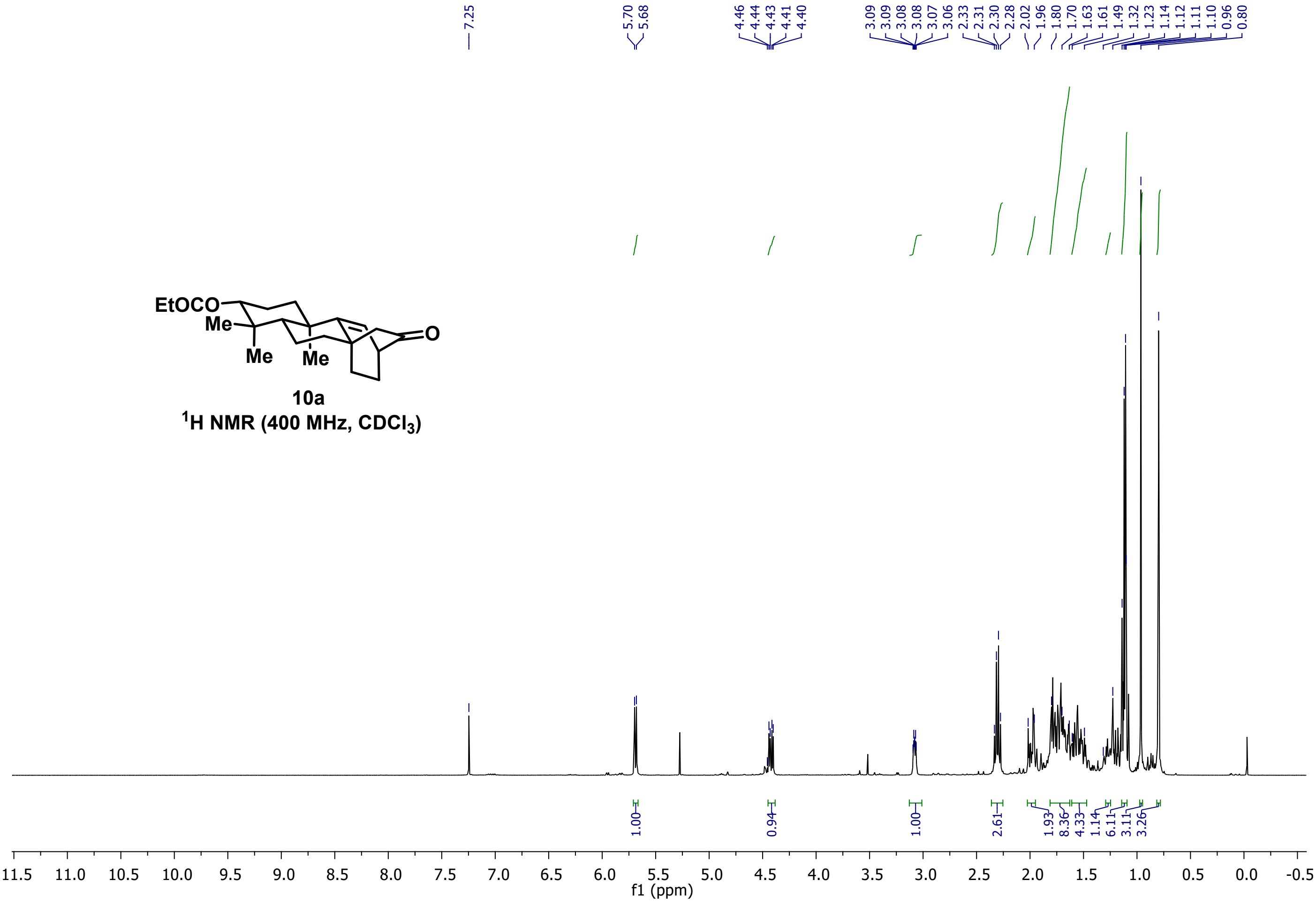
dr = 5.5:1



10

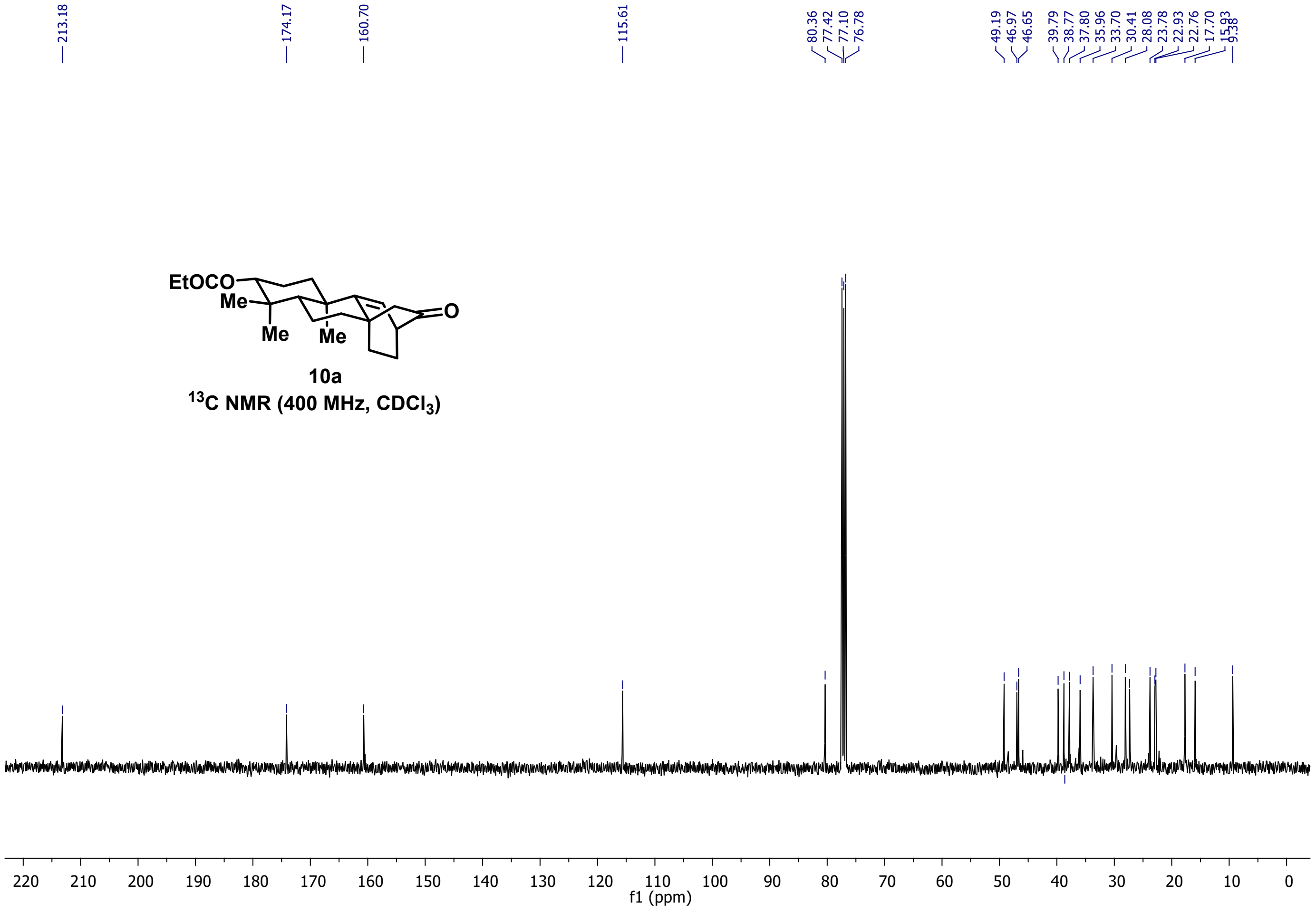
^{13}C NMR (126 MHz, CDCl$_3$)

dr = 5.5:1



10a

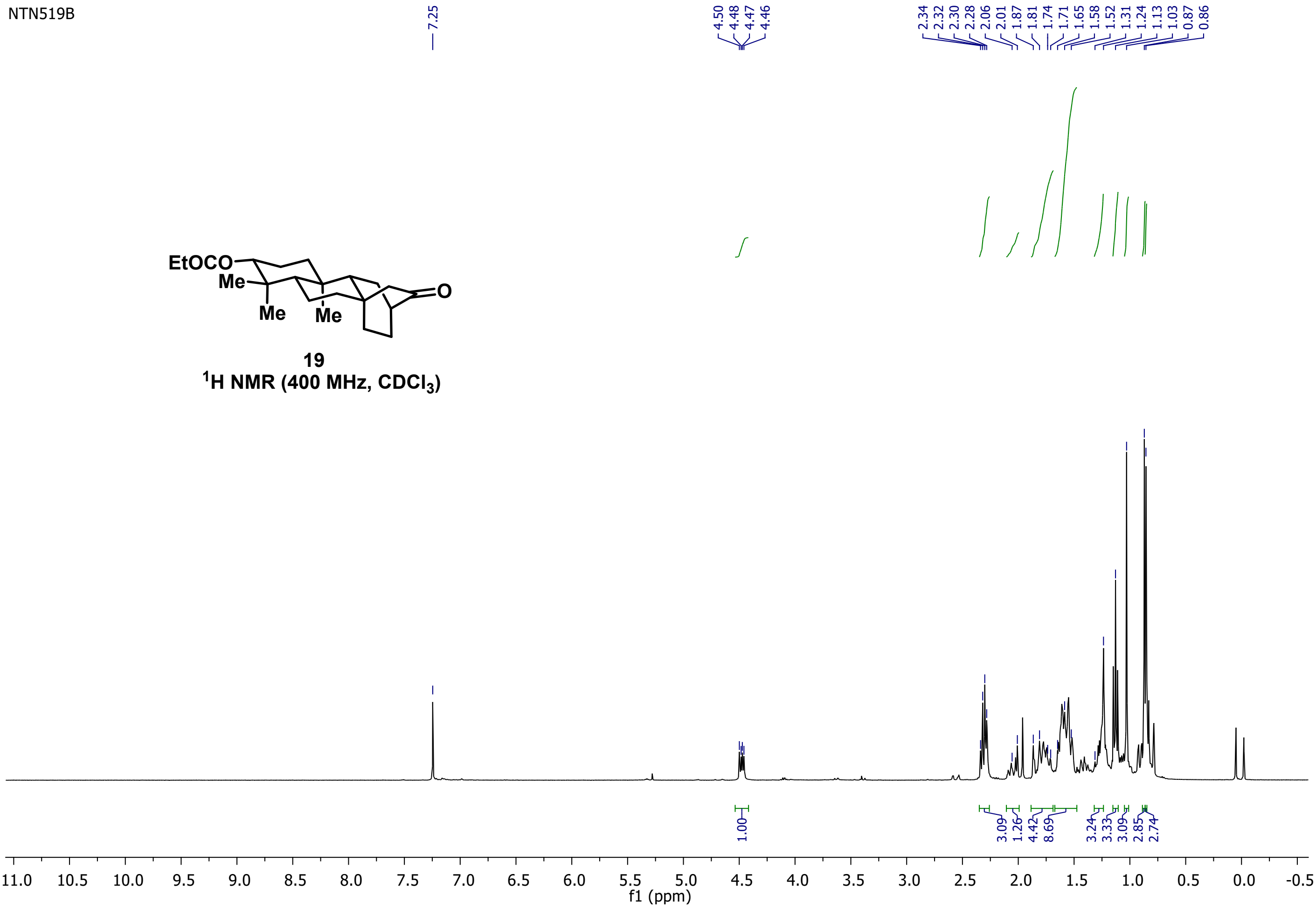
^{1}H NMR (400 MHz, CDCl$_3$)



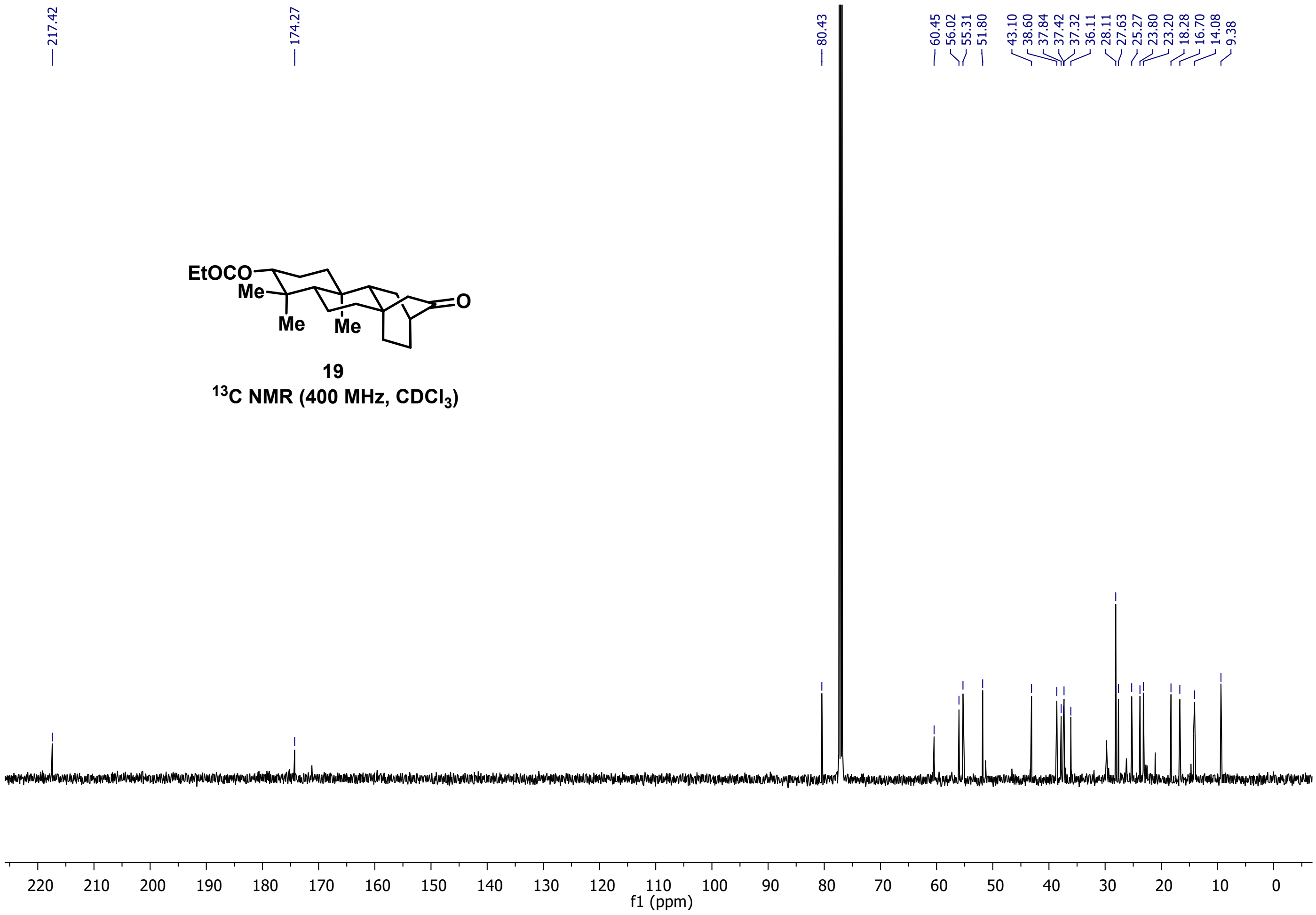
10a

^{13}C NMR (400 MHz, CDCl$_3$)

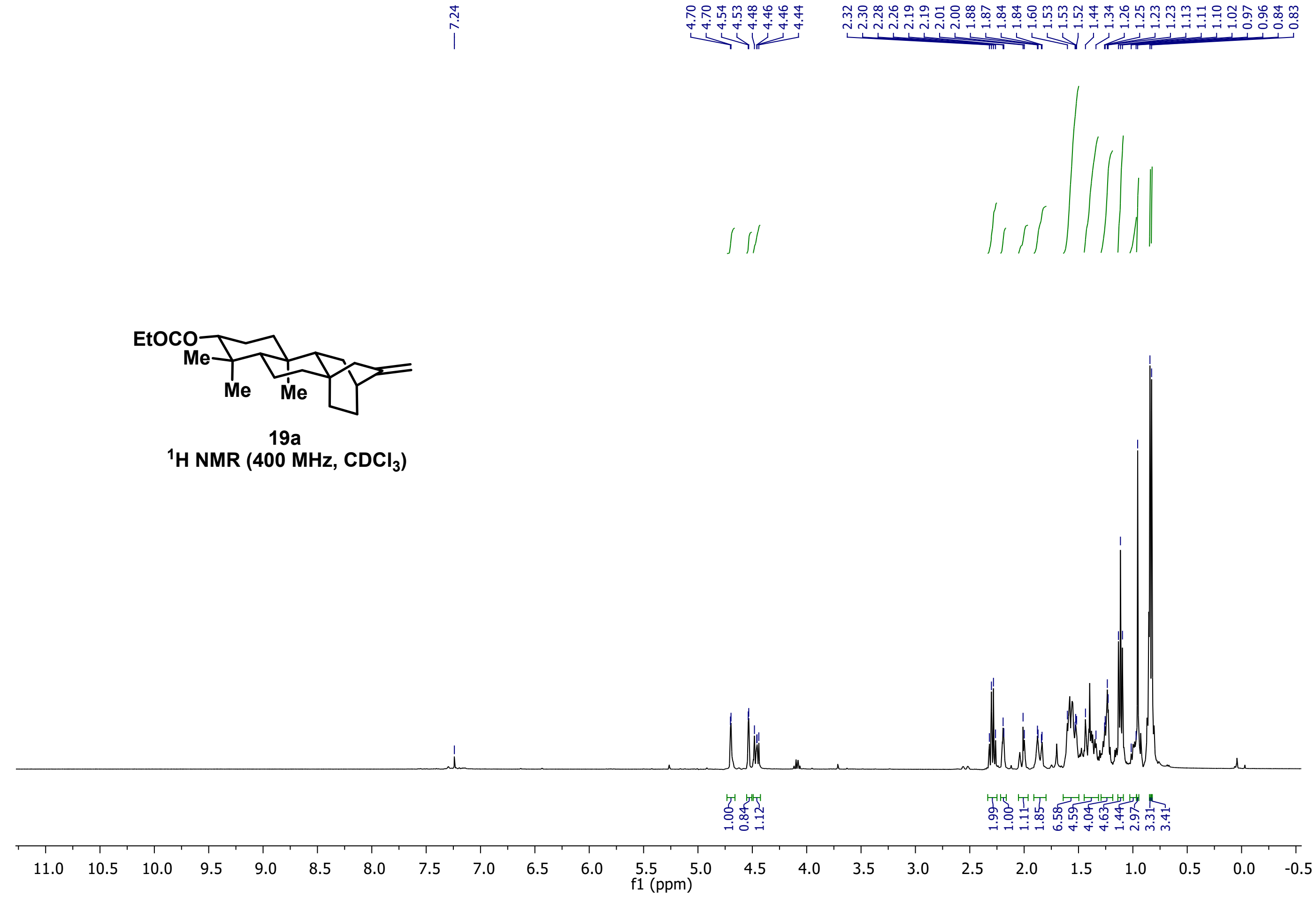
NTN519B



19
^{1}H NMR (400 MHz, CDCl$_3$)

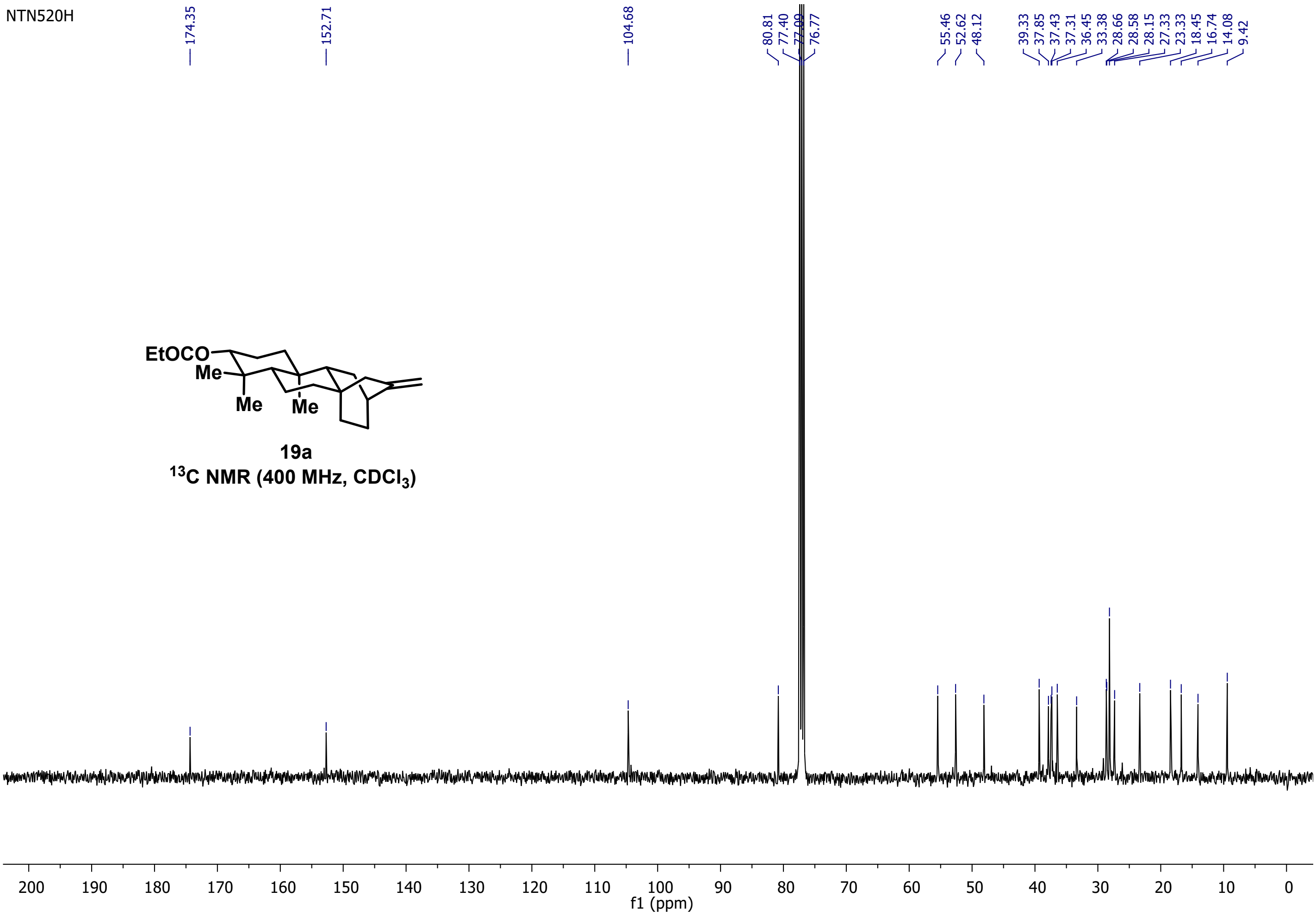


19
^{13}C NMR (400 MHz, CDCl$_3$)



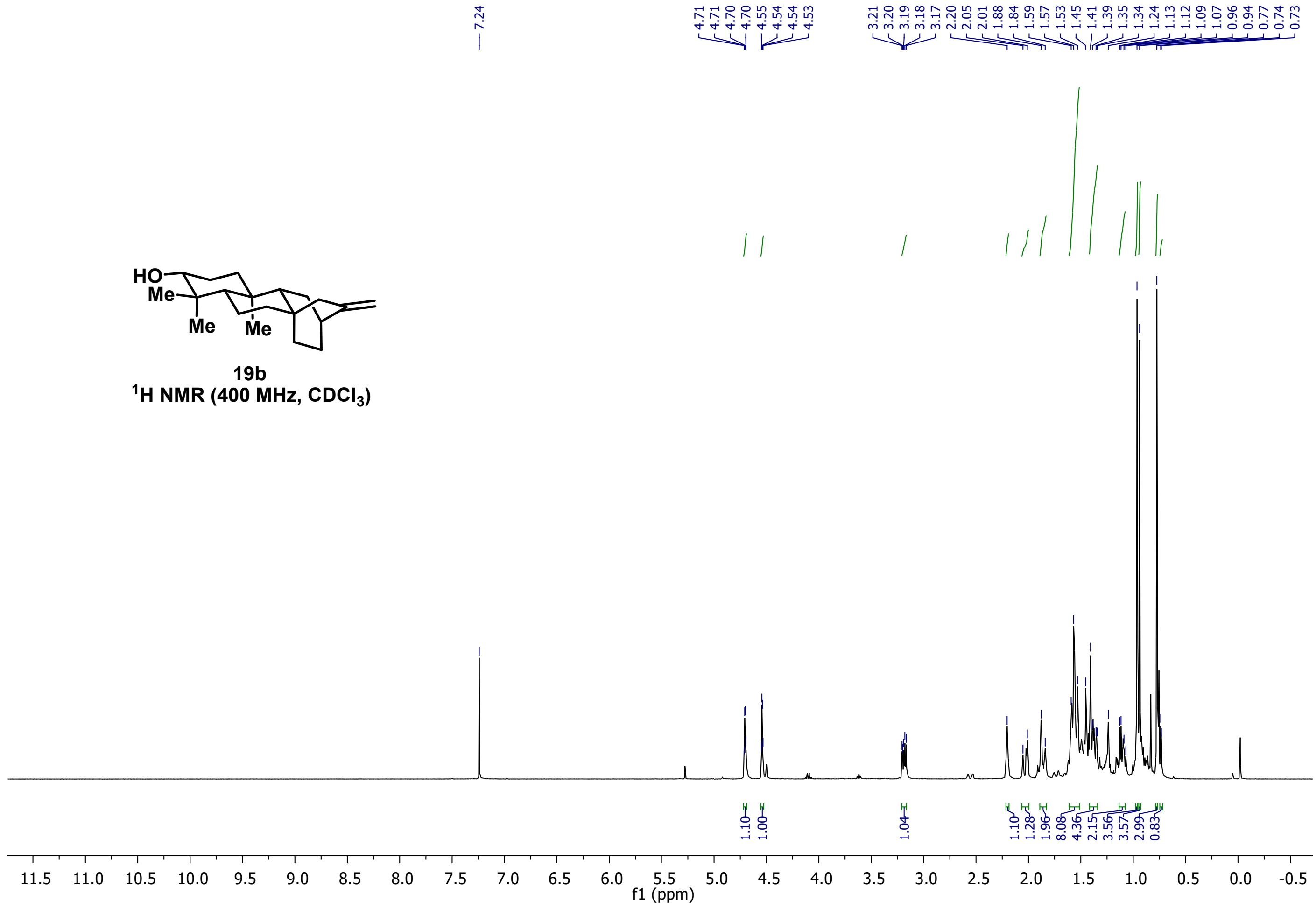
19a

^{1}H NMR (400 MHz, CDCl$_3$)



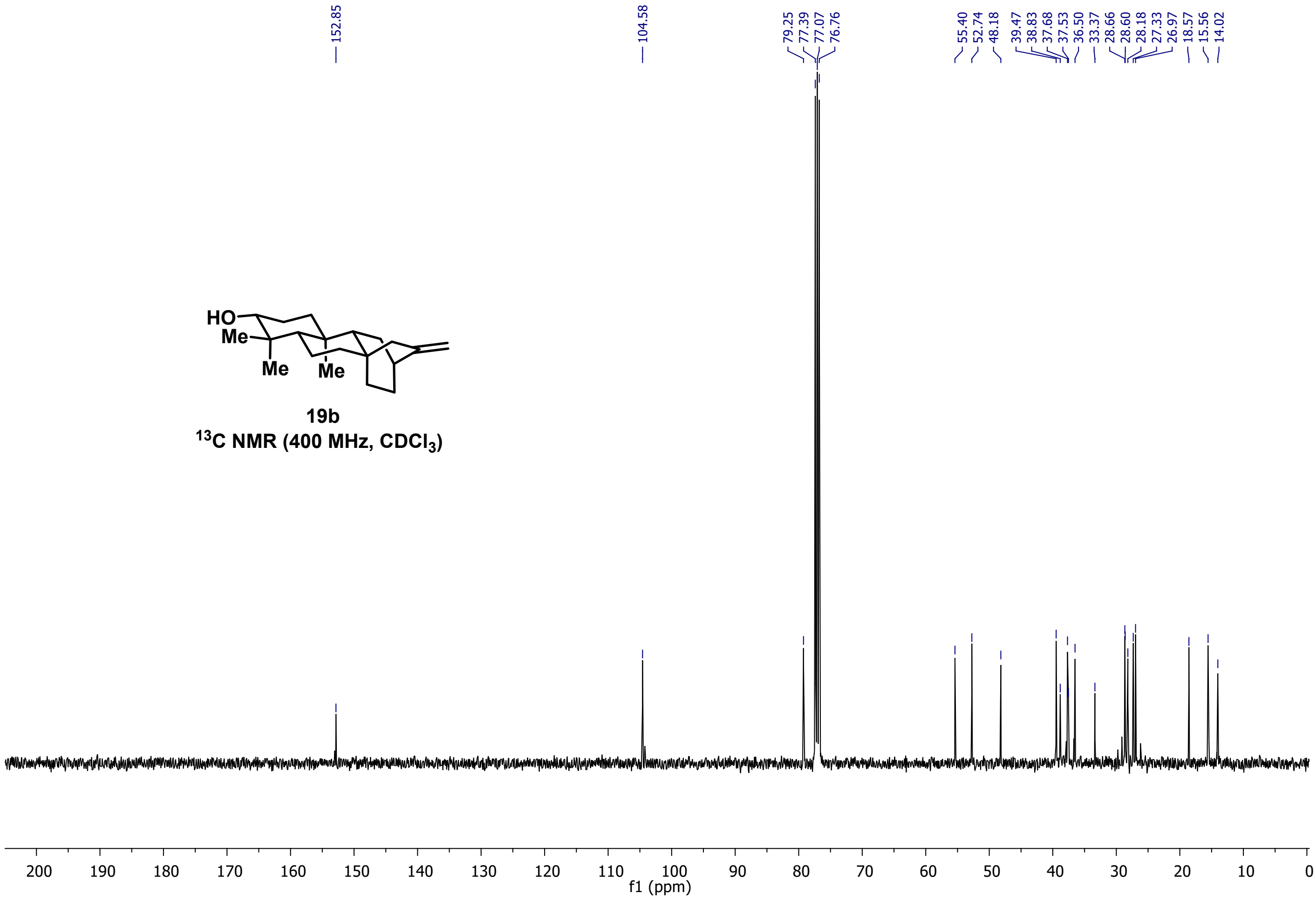
19a

^{13}C NMR (400 MHz, CDCl$_3$)



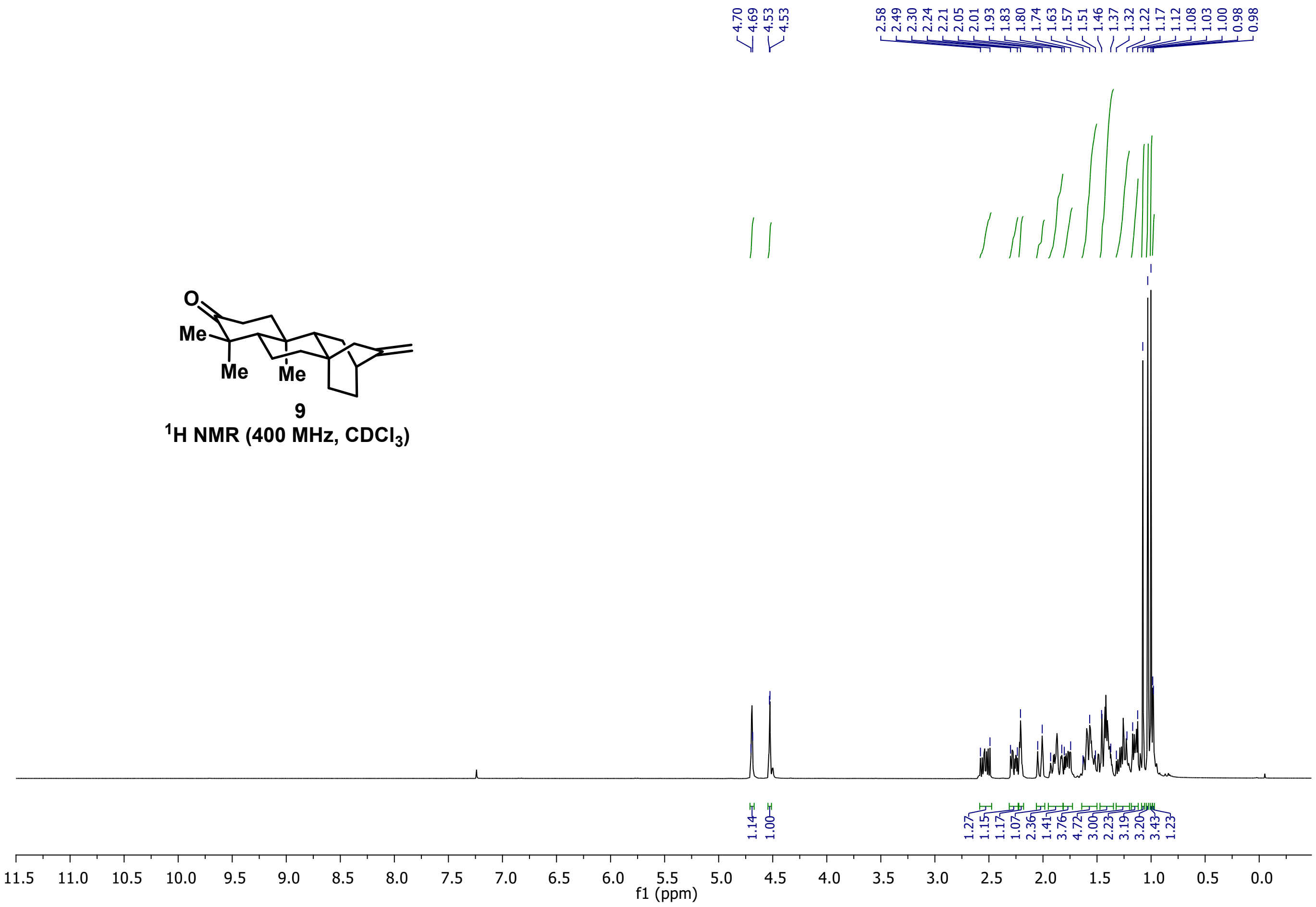
19b

^{1}H NMR (400 MHz, CDCl$_3$)



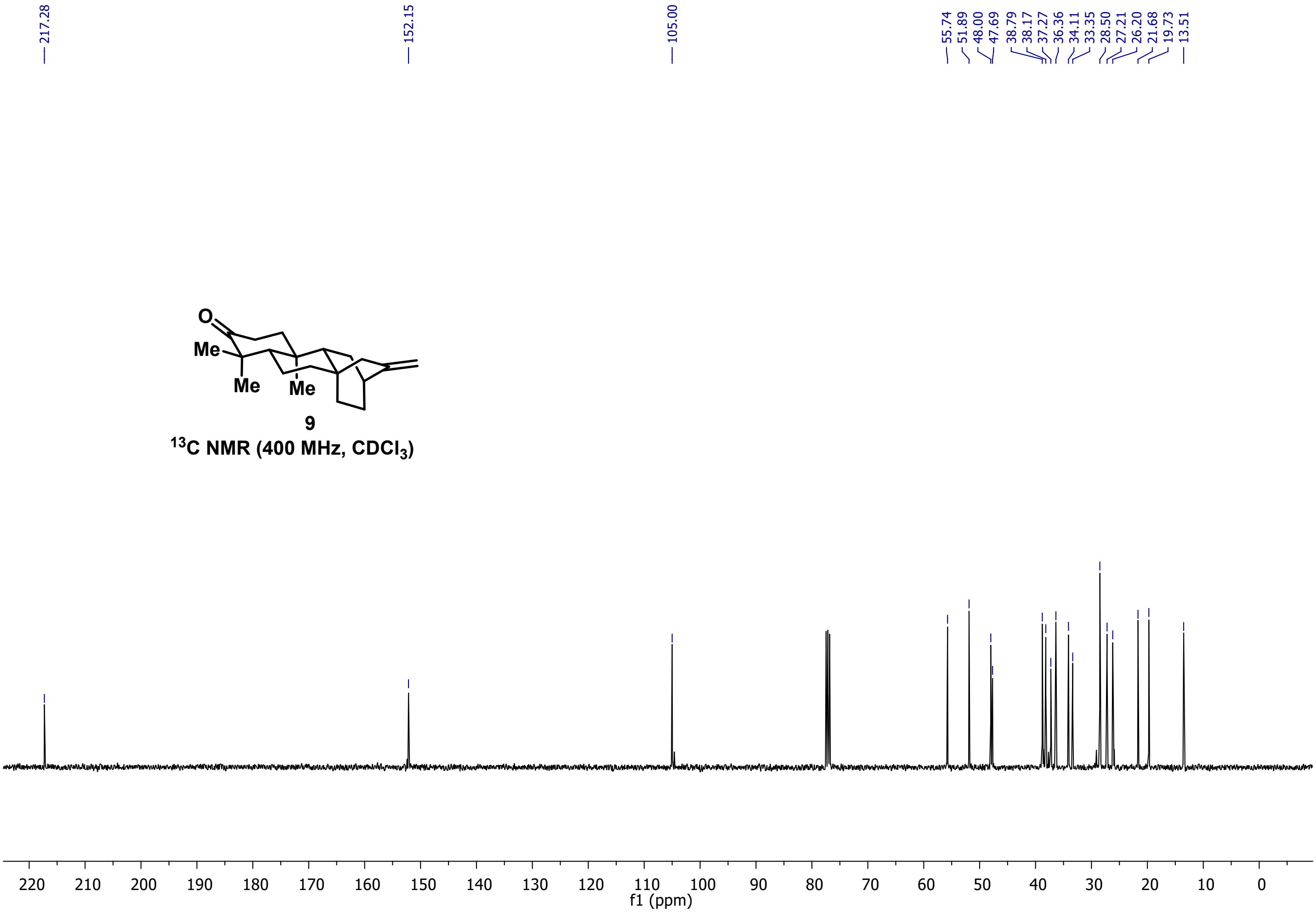
19b

^{13}C NMR (400 MHz, CDCl$_3$)



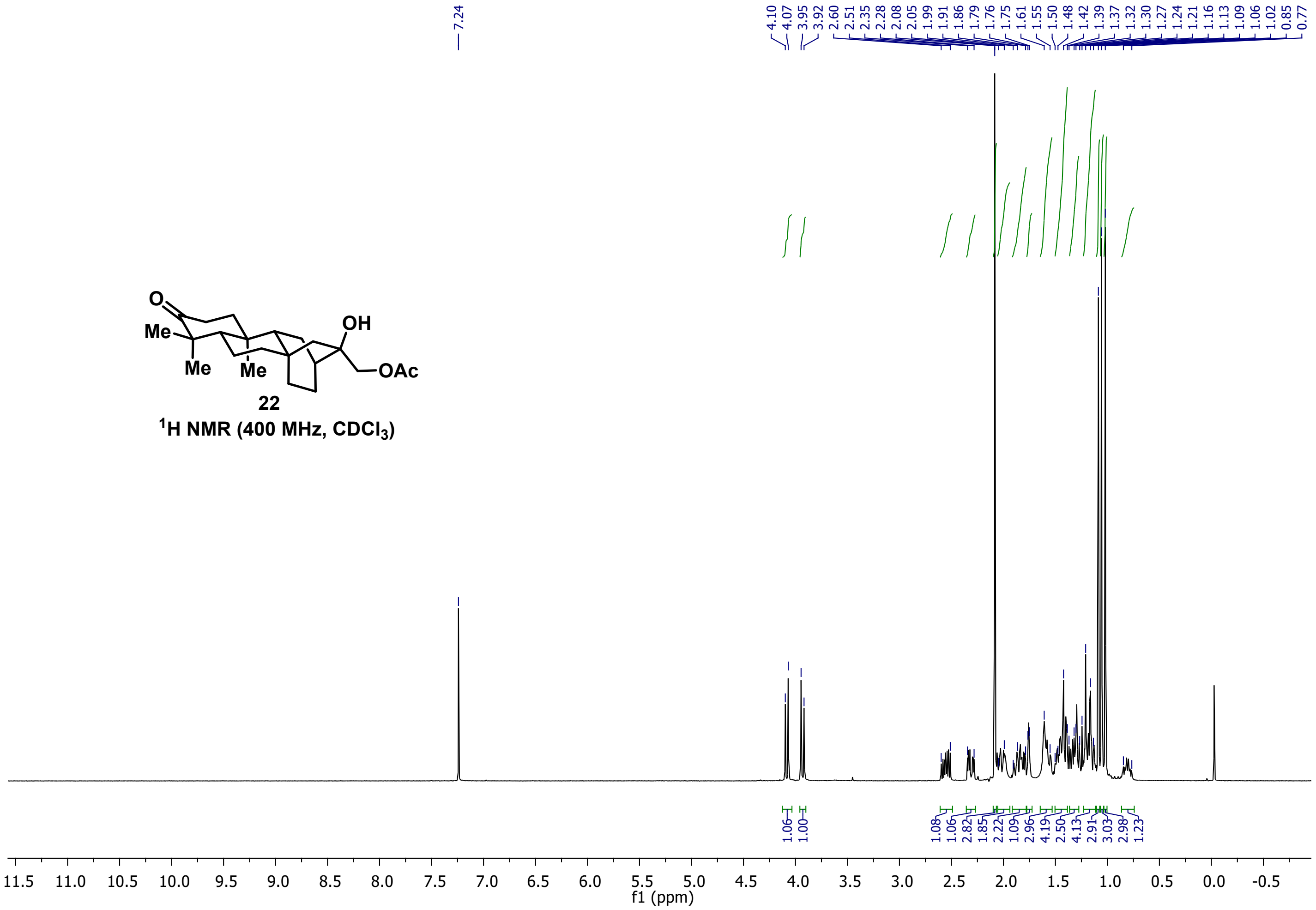
9

^{1}H NMR (400 MHz, CDCl$_3$)



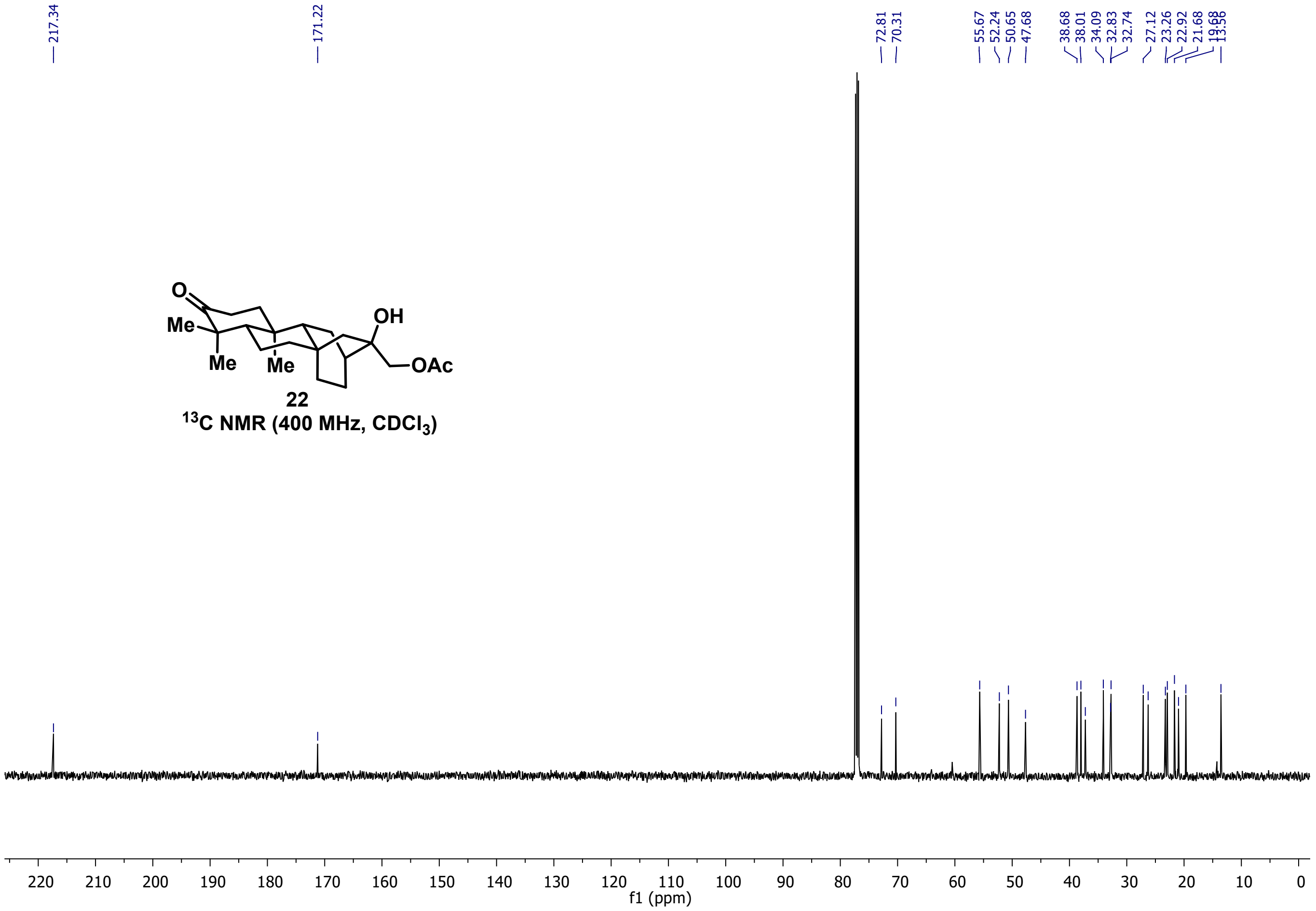
9

^{13}C NMR (400 MHz, CDCl$_3$)



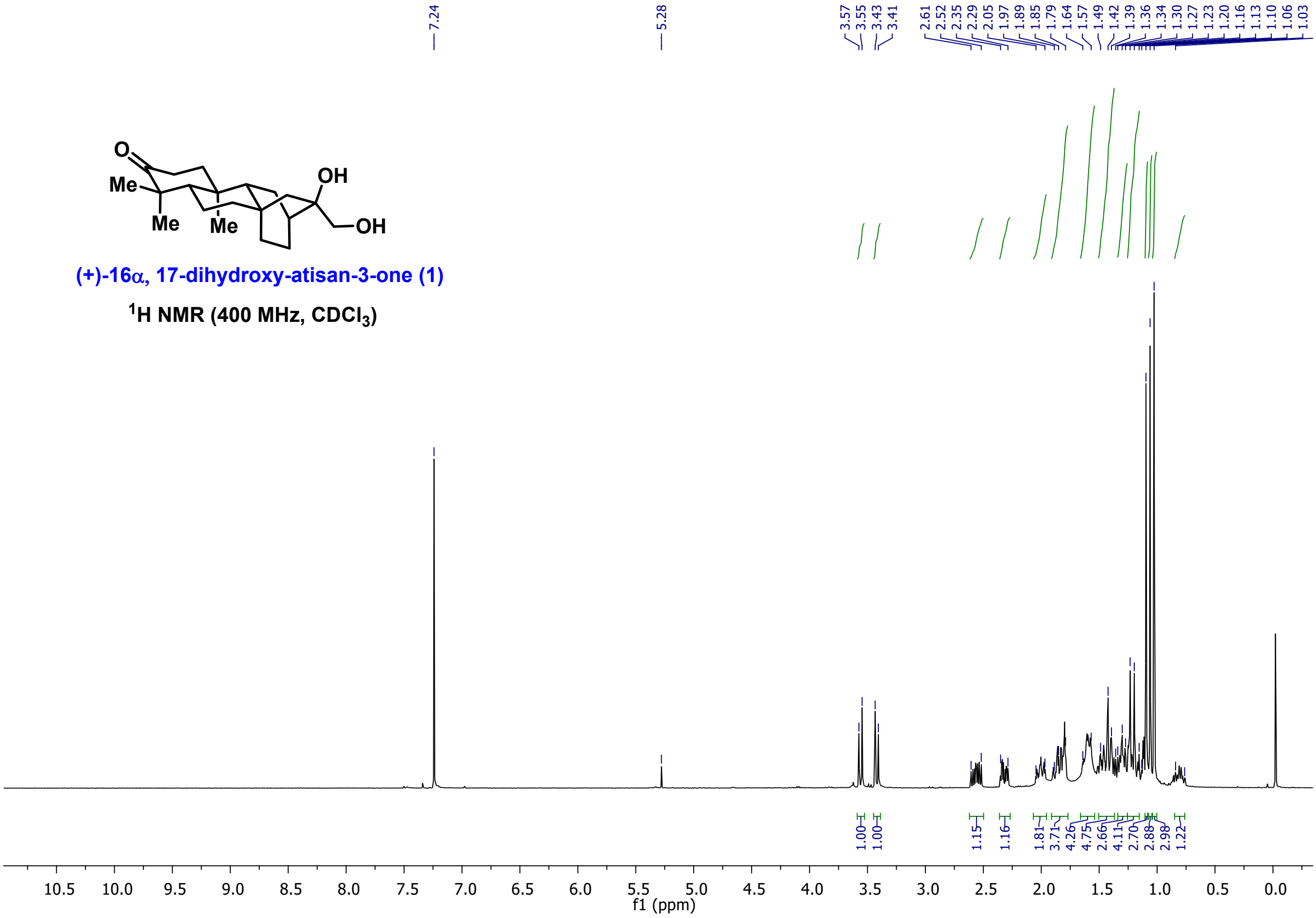
22

^{1}H NMR (400 MHz, CDCl$_3$)



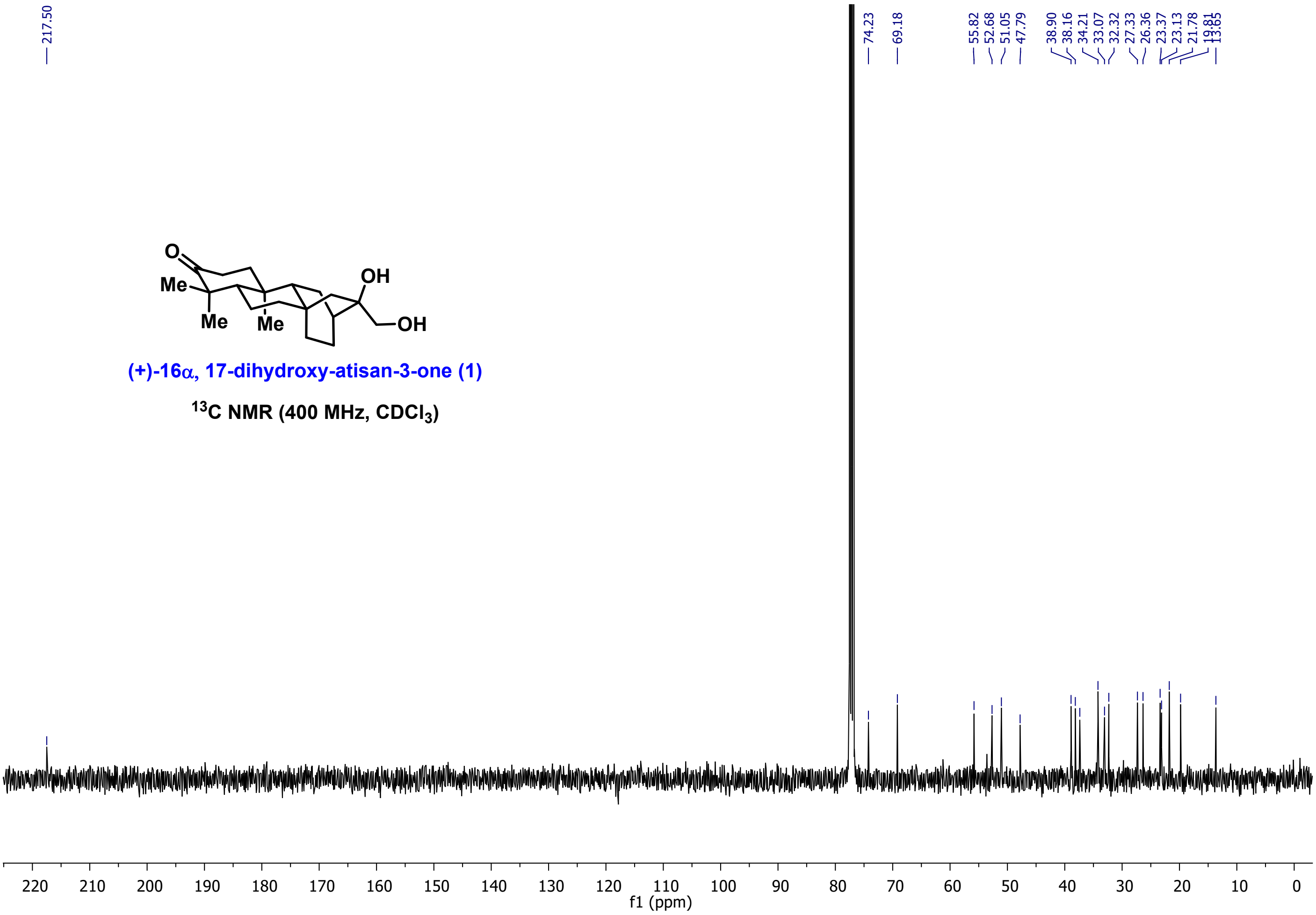
22

^{13}C NMR (400 MHz, CDCl$_3$)



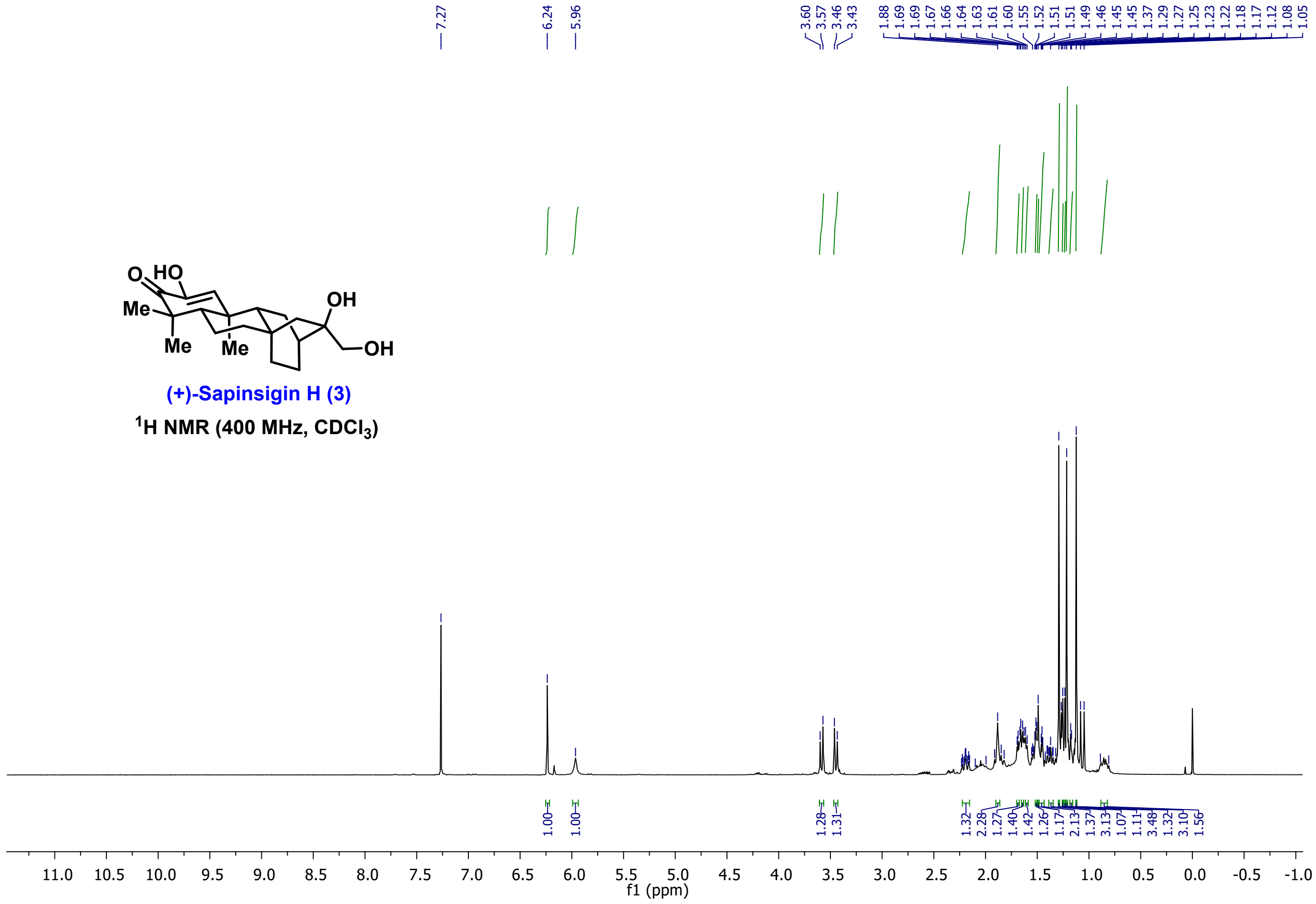
(+)-16α, 17-dihydroxy-atisan-3-one (1)

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



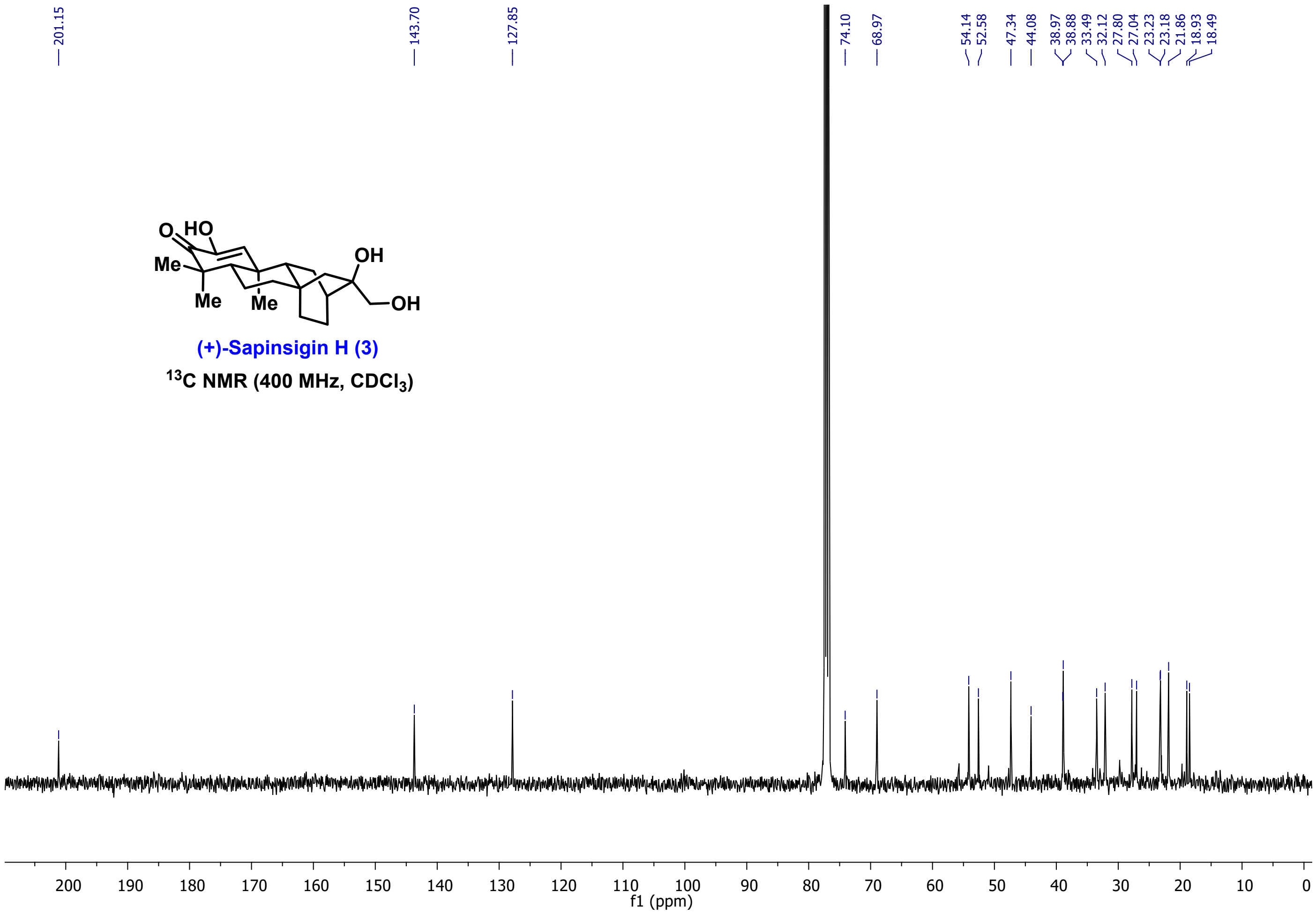
(+)-16α, 17-dihydroxy-atisan-3-one (1)

^{13}C NMR (400 MHz, $CDCl_3$)



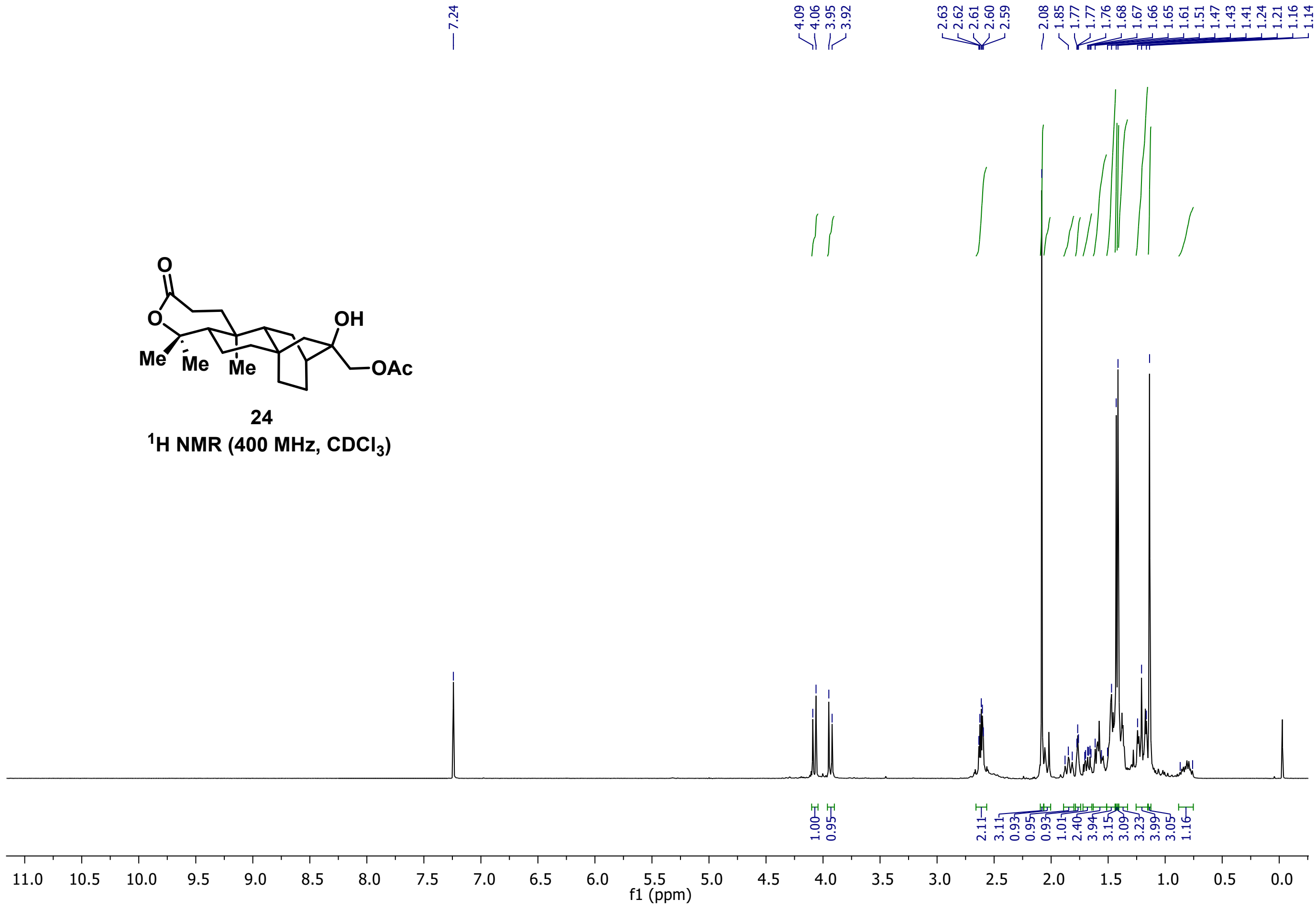
(+)-Sapinsigin H (3)

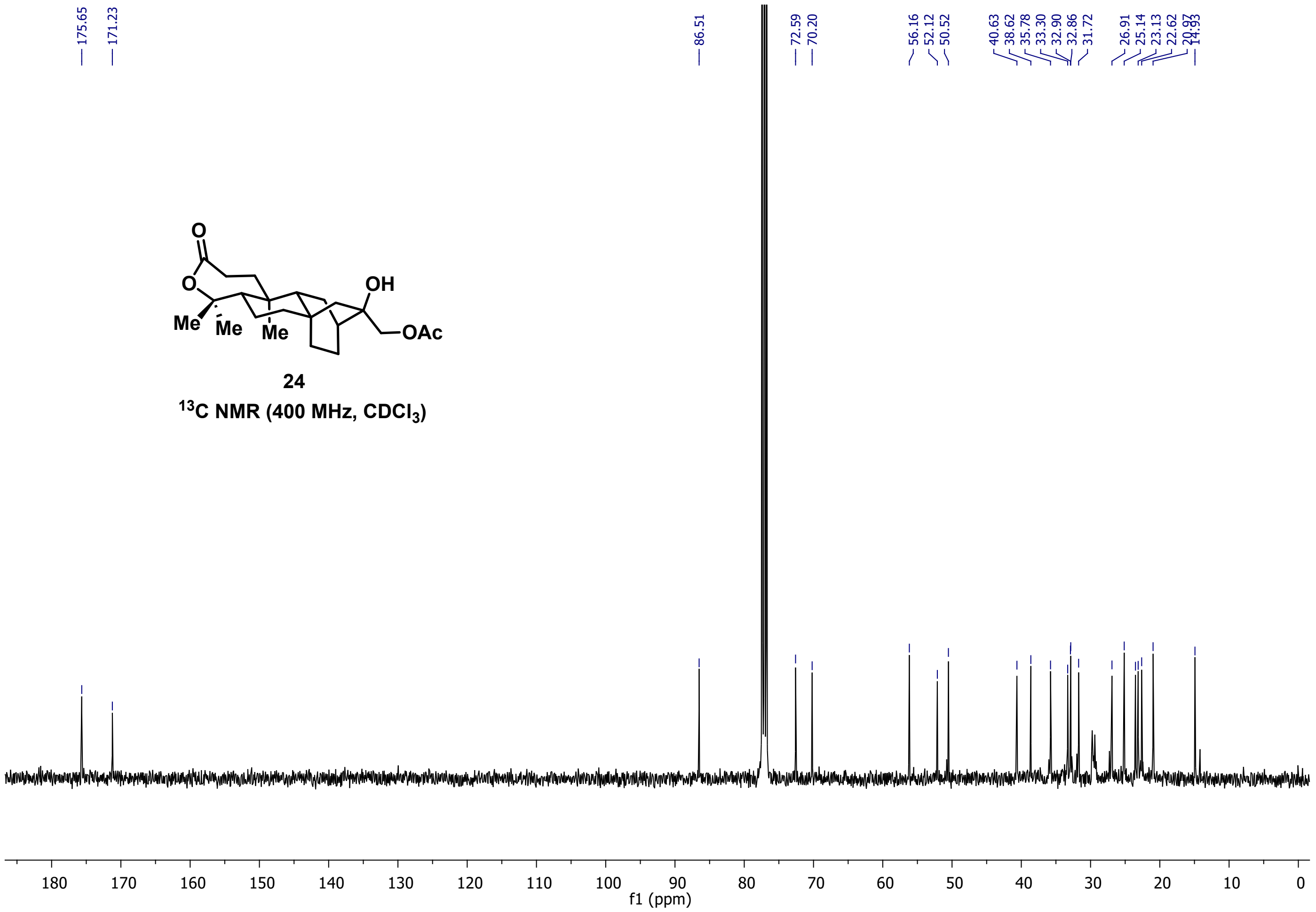
^{1}H NMR (400 MHz, CDCl$_3$)

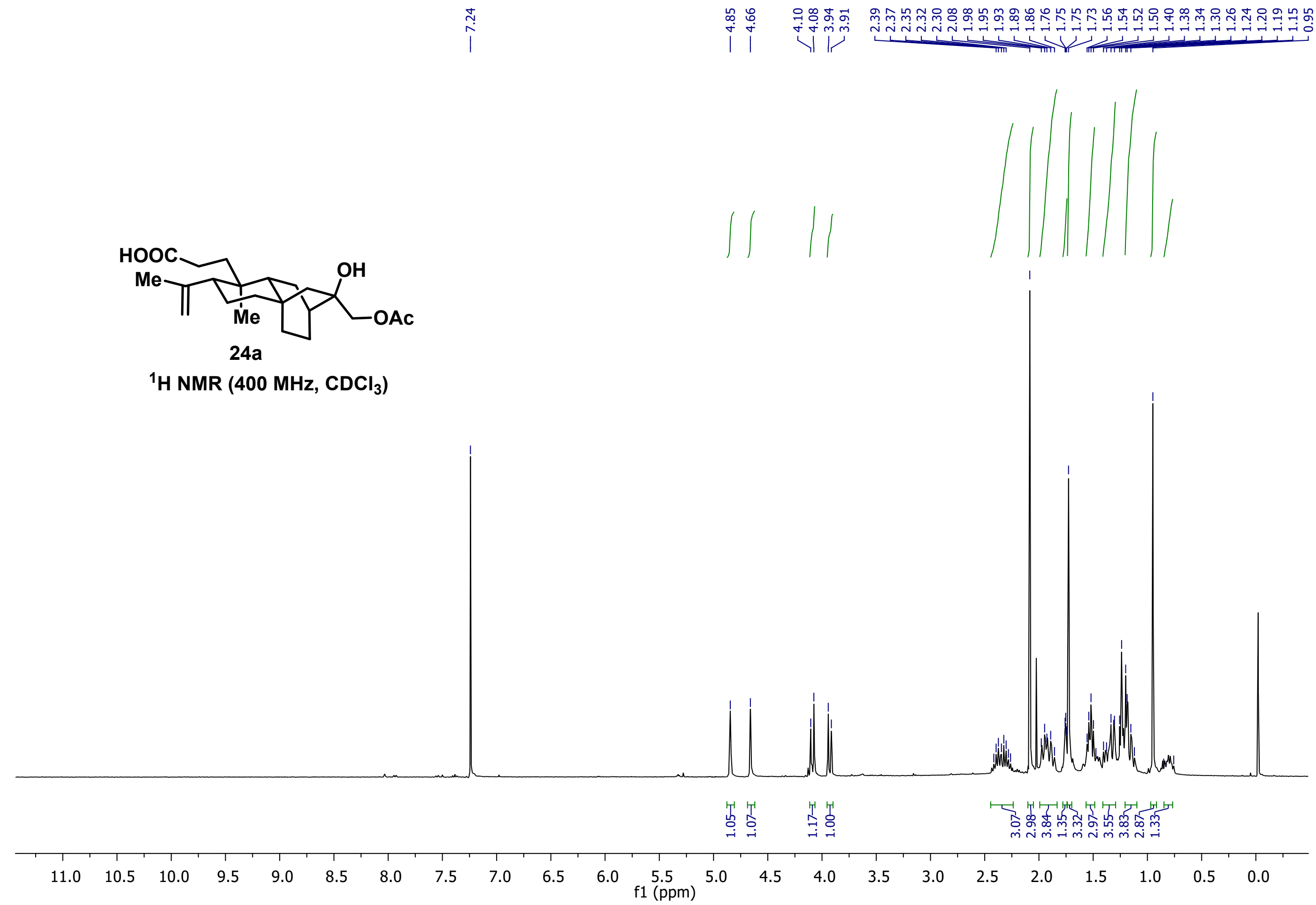


(+)-Sapinsigin H (3)

^{13}C NMR (400 MHz, CDCl$_3$)

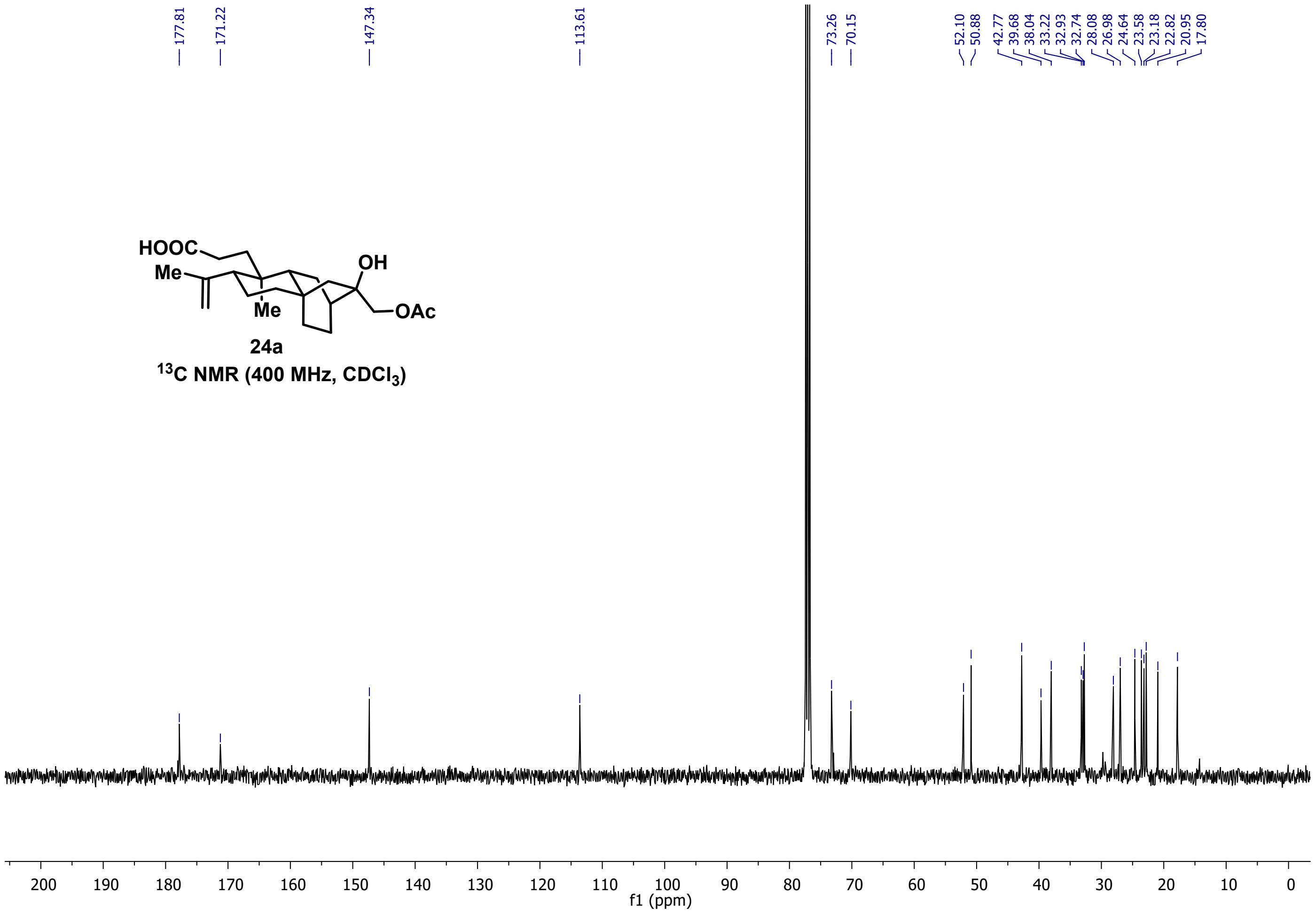

7.24
4.09
4.06
3.95
3.92
2.63
2.62
2.61
2.60
2.59
2.08
1.85
1.77
1.76
1.68
1.67
1.66
1.65
1.61
1.51
1.47
1.43
1.41
1.24
1.21
1.16
1.14
O
O
OH
Me
Me
Me
OAc
24
^{1}H NMR (400 MHz, CDCl$_3$)
1.00
0.95
2.11
3.11
0.93
0.95
0.93
1.01
2.40
3.94
3.15
3.09
3.23
3.99
3.05
1.16
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


175.65
171.23
86.51
72.59
70.20
56.16
52.12
50.52
40.63
38.62
35.78
33.30
32.90
32.86
31.72
26.91
25.14
23.13
22.62
20.97
14.93
O
O
OH
Me
Me
Me
OAc
24
^{13}C NMR (400 MHz, CDCl$_3$)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



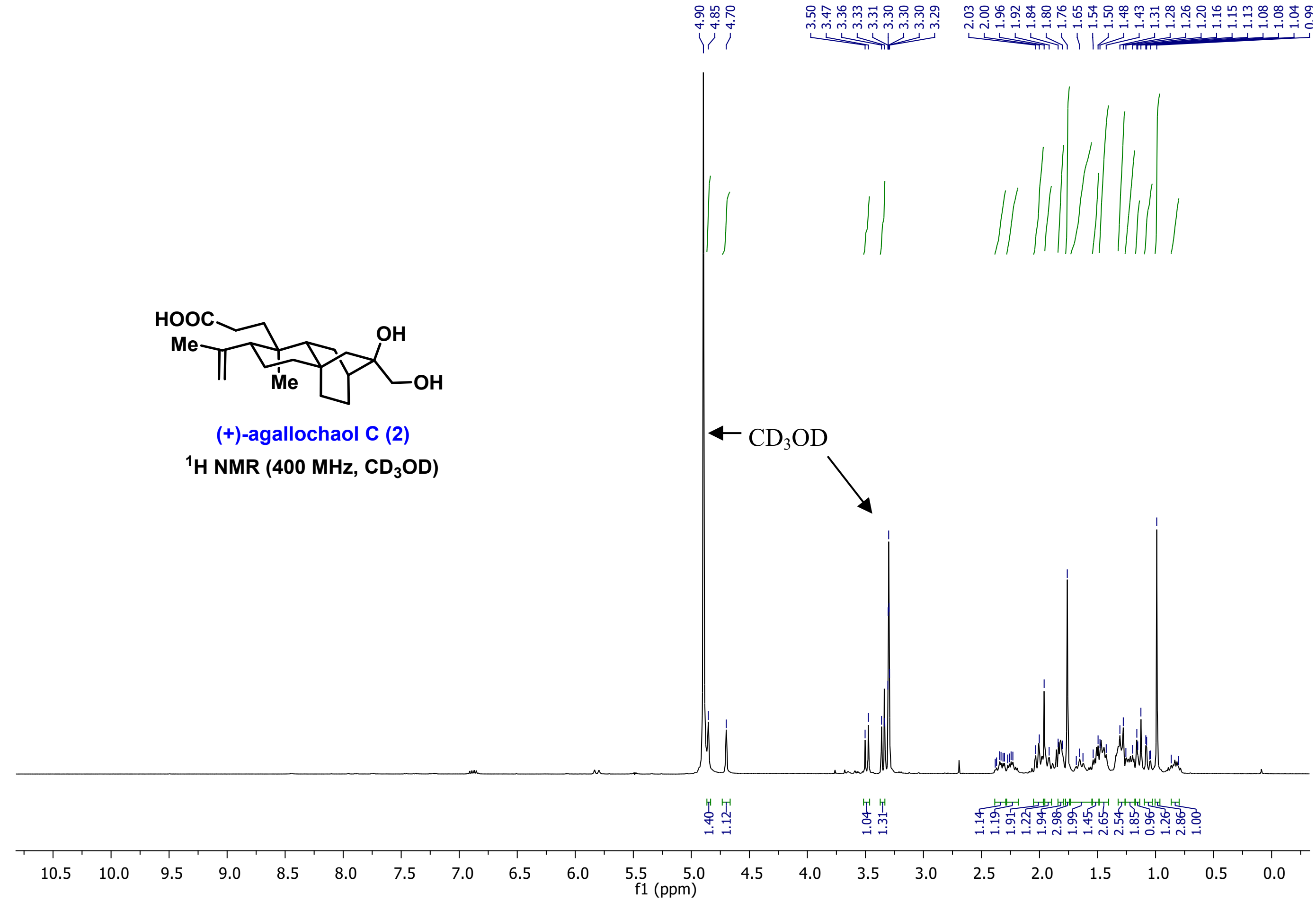
24a

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



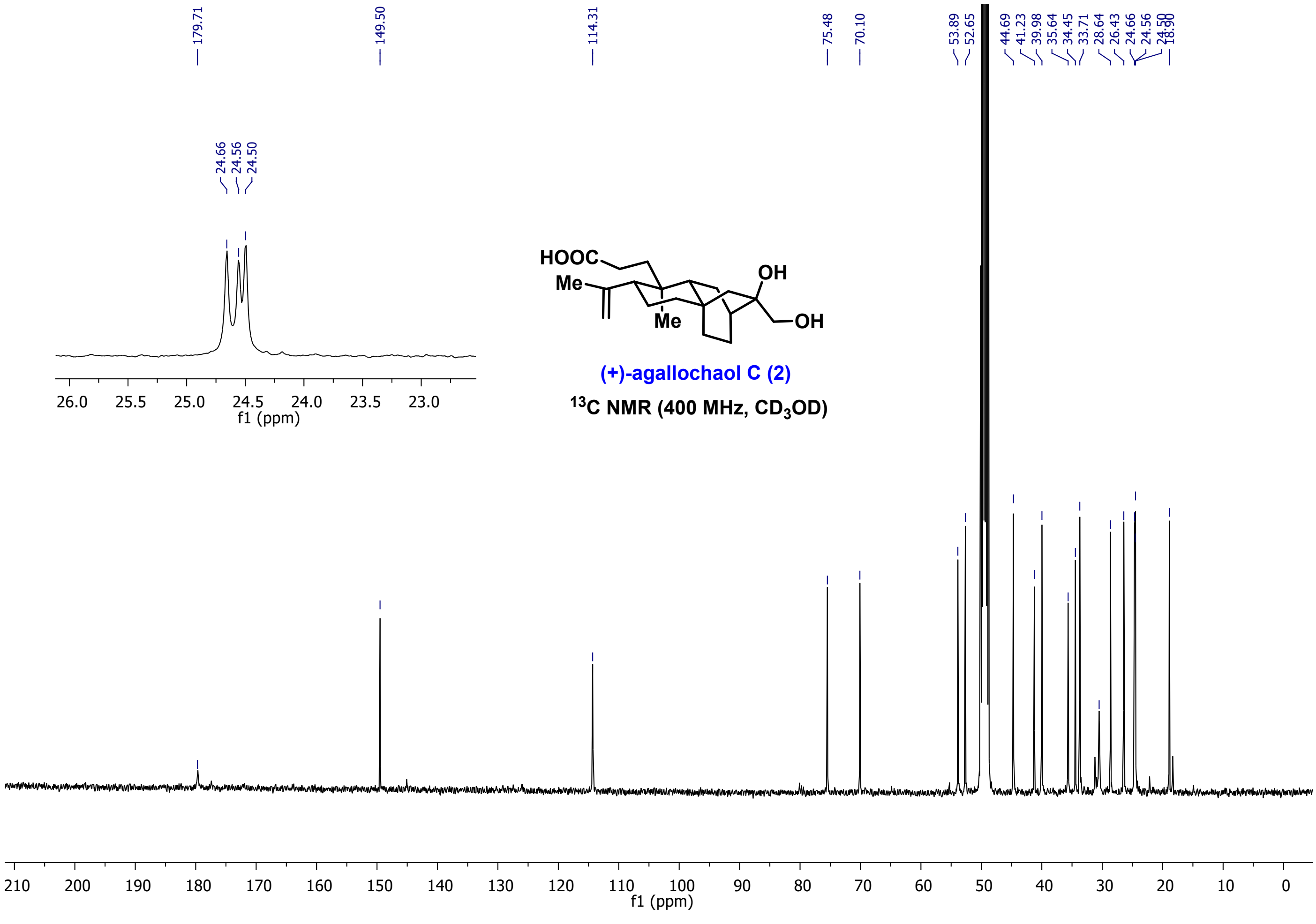
24a

^{13}C NMR (400 MHz, $CDCl_3$)



(+)-agallochaol C (2)

^{1}H NMR (400 MHz, CD$_3$OD)



(+)-agallochaol C (2)

^{13}C NMR (400 MHz, CD$_3$OD)