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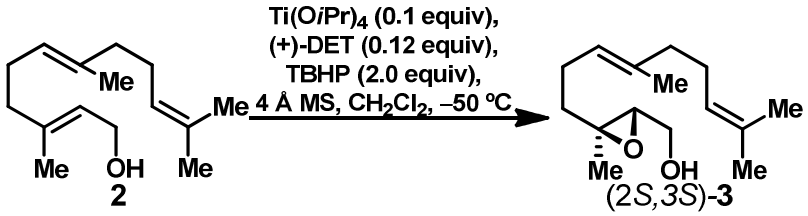
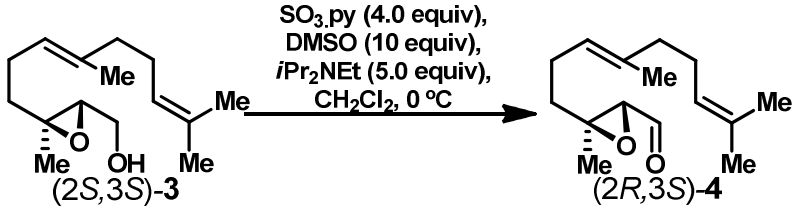
General Procedures. All reactions were performed using flame-dried round-bottomed flasks or reaction vessels. Where appropriate, reactions were carried out under an inert atmosphere of argon with dry solvents, unless otherwise stated. Dry dichloromethane (DCM), tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), toluene (PhMe), benzene (PhH), acetonitrile (MeCN) and methanol (MeOH) were obtained by passing the previously degassed solvents through activated alumina columns. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60F-254) using ultraviolet light as visualizing agent and an acidic mixture of *p*-anisaldehyde and heat as developing agents. NMR spectra were recorded on a Bruker DRX-600, DRX-500 or AMX-400 spectrometer and were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: ^{1}H NMR = 7.26, ^{13}C NMR = 77.16; pyridine-d_5: ^{1}H NMR = 7.58, ^{13}C NMR = 135.9 (middle signals); benzene-d_6: ^{1}H NMR = 7.16, ^{13}C NMR = 128.06, toluene-d_8: ^{1}H NMR = 7.00 (middle signal)). The following abbreviations or combinations thereof were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. IR spectra were recorded on a Perkin-Elmer Spectrum BX spectrometer. High resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer using ESI-TOF (electrospray ionization-time of flight). Melting points were recorded on a Fisher-Johns 12-144 melting point apparatus.



(2*S*,3*S*)-(–)-Epoxyfarnesol (3):[1]

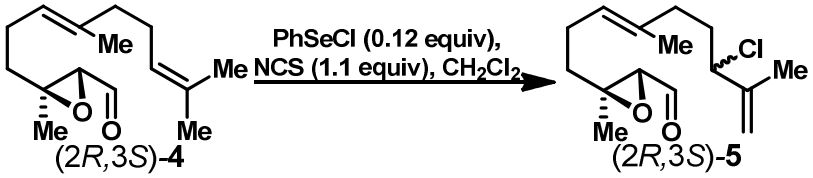
To a three-necked round-bottomed flask was added activated 4Å molecular sieves (3.50 g), dichloromethane (300 mL), (+)-diethyl tartrate (2.46 mL, 14.365 mmol, 0.12 equiv) and titanium isopropoxide (3.58 mL, 12.092 mmol, 0.10 equiv). The mixture was then cooled to –50 ºC before a 6.04*N* solution of *tert*-butyl hydroperoxide in dichloromethane (40 mL, 0.2416 mol, 2.02 equiv) was added and stirred for 30 min at the same temperature. A solution of farnesol (30 mL, 0.1197 mol, 1 equiv) in dichloromethane (300 mL) was added dropwise via an addition funnel over 45 min. The reaction mixture was allowed to stir for an additional 2 h at the same temperature before adding 20% aqueous tartaric acid (300 mL). The quenched reaction mixture was allowed to warm to room temperature and stirred for an additional 1 h, whereby the mixture would separate into two clear phases. The organic layer was separated, and the aqueous layer was further extracted with dichloromethane (2 × 200 mL). The combined organics were then dried over sodium sulfate, filtered and concentrated under reduced pressure. The pale yellow residue was then diluted with diethyl ether (~100 mL), and cooled to 0 ºC before pre-cooled 30% sodium hydroxide in brine (20 mL) was added. The mixture was allowed to stir for 1 h at the same temperature. The contents were then emptied into a separating funnel, diluted with water (50 mL), and extracted with diethyl ether (3 × 50 mL). The combined organics were dried over sodium sulfate, filtered through a pad of Celite® and concentrated under reduced pressure to afford analytically pure (2*S*,3*S*)-(–)-epoxyfarnesol (**3**) as a pale yellow oil (28.5 g, 0.1196 mol, quantitative, *ee* = 90%[2]), which was used in the subsequent step without further purification. The ^{1}H and ^{13}C NMR spectra match that reported in literature completely.



(2*R*,3*S*)-(–)-Epoxyfarnesal (4):[3]

To a solution of crude (2*S*,3*S*)-(–)-epoxyfarnesol (**3**) (29.5 g, 0.1238 mol) in dichloromethane (250 mL), was added dimethyl sulfoxide (88 mL, 1.239 mol, 10.00 equiv) and *N*,*N*-diisopropylethylamine (108 mL, 0.620 mol, 5.01 equiv) at 0 ºC. Sulfur trioxide pyridine complex (78.8 g, 0.495 mol, 4.00 equiv) was added portion-wise in 5 portions (5 min apart), and the mixture was allowed to stir at the same temperature. Upon full consumption of starting material (~30 min), the mixture was allowed to warm to room temperature before diluting with hexanes (250 mL), and then filtered through silica gel (~3 L) (20% ethyl acetate/hexanes) to remove the excess dimethyl sulfoxide and sulfur trioxide pyridine complex. The filtrate was then concentrated under reduced pressure, before diluting with ethyl acetate (250 mL). The

mixture was washed with 2*N* aqueous hydrochloric acid (4 × 100 mL), saturated sodium bicarbonate (100 mL), brine (100 mL), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure to afford analytically pure (2*R*,3*S*)-(–)-epoxyfarnesal (**4**) as an orange syrup (33.5 g, 0.1237 mol, quantitative), which was used directly without further purification. The ^{1}H and ^{13}C NMR spectra match that reported in literature completely.



Cyclization precursor 5:

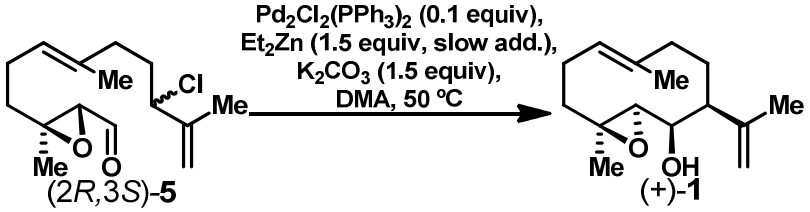
To a solution of crude (2*R*,3*S*)-(–)-epoxyfarnesal (**4**) (11.727 g, 49.620 mmol, 1 equiv) in dichloromethane (250 mL) was added phenylselenyl chloride (570.0 mg, 2.976 mmol, 6 mol %) and *N*-chlorosuccinimide (7.290 g, 54.594 mmol, 1.10 equiv). The resulting mixture was stirred for 30 min before another portion of phenylselenyl chloride (6 mol %) was added. Upon completion, the mixture was quenched by adding saturated aqueous sodium thiosulfate (250 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (250 mL). The combined organic layers were then washed with saturated aqueous sodium bicarbonate, brine and then dried over sodium sulfate, filtered through Celite® and concentrated under reduced pressure. The crude material was then purified by flash column chromatography (0–10% ethyl acetate/hexanes) to afford **5** as a yellow oil (8.515 g, 31.444 mmol, 63% over 3 steps); R_f = 0.23 (10% ethyl acetate/hexanes); $[\alpha]_D^{20}$ = +50.0º (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.45 (d, *J* = 5.0 Hz, 1 H, C**H**O), 5.12 (br t, *J* = 7.1 Hz, 1 H, C=C**H**), 4.99 (s, 1 H, **H**$_2$C=C), 4.89 (s, 1 H, **H**$_2$C=C), 4.33 (t, *J* = 7.2 Hz, 1 H, C**H**Cl), 3.18 (d, *J* = 5.0 Hz, 1 H, COC**H**), 2.13 – 2.07 (m, 3 H, C**H**$_2$ and C**H$_2$**), 2.03 – 1.98 (m, 1 H, C**H**$_2$), 1.97 – 1.84 (m, 2 H, C**H$_2$**), 1.81 (s, 3 H, C**H$_3$**), 1.75 – 1.70 (m, 1 H, C**H**$_2$), 1.62 – 1.56 (m, 1 H, C**H**$_2$), 1.60 (s, 3 H, C**H$_3$**), 1.45 (s, 3 H, C**H$_3$**); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.7 (**C**=O), 144.5 (**C**$_{quat}$=C), 135.0 (**C**$_{quat}$=C), 123.8 (**C**H=C), 114.3 (H$_2$**C**=C), 66.4 (**C**–Cl), 64.2 (**C**$_{quat}$–O), 63.6 (**C**–O), 38.3, 36.7, 34.8, 23.5 (4 × **C**H$_2$), 17.4, 17.1, 16.1 (3 × **C**H$_3$); IR (neat) ν 2942, 1721, 1448, 1384, 1236, 1107, 907, 800 cm^{-1}; HRMS (ESI-TOF) calc'd for $C_{15}H_{24}ClO_2$ [M + H$^+$] 271.1459; found 271.1462.

Table 1. Optimization table for ring closure of **5** via umpolung allylation.

#	catalyst	ligand	reductant	solvent	base	**1**[a]
1[b]	Pd_2dba_3	XPhos	Et_2Zn[c]	THF		0
2[b]	PEPPSI-IPr	none	Et_2Zn[c]	THF[d]	K_2CO_3	0
3[b]	Pd_2dba_3	PCy_3	Et_2Zn[c]	THF		0
4[b]	Pd_2dba_3	$P(^oTol)_3$	Et_2Zn[c]	THF		0
5[b]	$Pd(dppf)Cl_2$	--	Et_2Zn[c]	THF		0
6	$Pd(PPh_3)_4$[e]	--	Et_2Zn[c]	THF	--	19
7	$Pd(PPh_3)_4$[e]	--	Et_2Zn	THF	--	10-30
8	$PdCl_2(PPh_3)_2$	--	Et_2Zn	THF	K_2CO_3	13-42
9	$PdCl_2(PPh_3)_2$	--	Et_2Zn	DMF	K_2CO_3	32

10	**$PdCl_2(PPh_3)_2$**	**--**	**Et_2Zn**	**DMA**	**K_2CO_3**	**42[f]**
11	$PdCl_2(PPh_3)_2$	--	Et_2Zn	DMA	--	33
12	$PdCl_2(PPh_3)_2$	--	$Et_2Zn/ZnCl_2$[g]	DMA	K_2CO_3	34
13	$PdCl_2(PPh_3)_2$	--	Me_2Zn	DMA	K_2CO_3	0
14	$PdCl_2(PPh_3)_2$	--	Bu_2Zn	DMA	K_2CO_3	31
15	$Pd(OAc)_2$	PPh_3	Et_2Zn	DMA	K_2CO_3	15
16	$Pd(OAc)_2$	$AsPh_3$	Et_2Zn	DMA	K_2CO_3	0
17	$PdCl_2$	P^nBu_3	Et_2Zn	DMA	K_2CO_3	0

Standard conditions unless otherwise stated: cat. (10 mol %), ligand (20 mol %), K_2CO_3 (1.5 equiv), solvent (0.033 M overall), **5** (100–600 mg scale, 1.0 equiv., 0.05 M, slow addition over 1.5 h), reductant (1.5 equiv., slow addition over 1.5 h), T = 50 °C. [a] Isolated yield. [b] 10–20 mg scale of **5**, all reagents added in one pot, overall 0.01 M, 50 ºC, 3 h. [c] 4 equiv of Et_2Zn. [d] Same result with DMA as solvent. [e] cat. (20 mol %). [f] Reproduced on six occasions, 42% was obtained for gram-scale. [g] $ZnCl_2$ as additive (10 mol %).

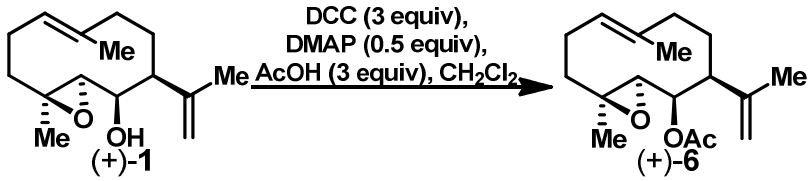


11,13-Didehydro-shiromool (+)-1:

(Bistriphenylphosphine)palladium(II) chloride (311.0 mg, 0.443 mmol, 0.10 equiv) and potassium carbonate (918.0 mg, 6.642 mmol, 1.50 equiv) were added to a flame-dried reaction flask under an argon atmosphere. To this flask was added dry *N,N*-dimethylacetamide that has been passed through activated alumina (98 mL), and the resulting mixture was stirred at 50 ºC. Quickly, the cyclization precursor **5** (1.200 g, 4.432 mmol, 1 equiv) was dissolved in *N,N*-dimethylacetamide (50 mL), and then added to the reaction flask via syringe-pump over 2 h. At the same time, a 1.5*N* solution of diethyl zinc (4.4 mL, 6.600 mmol, 1.49 equiv) in toluene was added via another syringe pump to the reaction flask over 2 h. When the syringe-pump additions were completed, the reaction was allowed to stir for another 0.5 h at the same temperature before cooling it to room temperature. Saturated aqueous sodium bicarbonate (6 mL), water (50 mL) and diethyl ether (50 mL) was added. The contents were emptied into a separating funnel and the organic phase was separated. The aqueous phase was extracted with diethyl ether (3 × 75 mL), and the combined organic layers were washed with water (3 × 75 mL), brine (75 mL), dried over sodium sulfate and concentrated under reduced pressure. The crude material was purified by flash column chromatography (0–15% ethyl acetate/hexanes) to afford (+)-**1** as a pale yellow oil (436.0 mg, 1.845 mmol, 42%); R_f = 0.22 (25% ethyl acetate/hexanes); $[\alpha]_D^{20}$ = +73.7º (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 – 5.28 (m, 1 H, C1–**H**), 4.90 (d, *J* = 13.6 Hz, 2 H, C12–**H$_2$**), 3.47 (dd, *J* = 7.9, 1.6 Hz, 1 H, C6–**H**), 2.62 (br s, 1 H, C5–**H**), 2.37 (br s, 1 H, C2–**H$_2$**), 2.22 – 2.11 (m, 2 H, C9–**H$_2$** and C2–**H$_2$**), 2.08 – 2.05 (m, 2 H, C3–**H** and C7–**H**), 1.93 – 1.86 (m, 1 H, C8–**H$_2$**), 1.81 (s, 3 H, C13–**H$_3$**), 1.81 – 1.76 (m, 1 H, C9–**H$_2$**), 1.71 (br s, 1 H, C8–**H$_2$**), 1.66 (s, 3 H, C14–**H$_3$**), 1.32 – 1.27 (m, 1 H, C3–**H$_2$**), 1.24 (s, 3 H, C15–**H$_3$**); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC) δ 111.2, 72.6, 68.2, 60.3, 22.8, 16.4; ^{13}C NMR (125 MHz, $CDCl_3$, –30 ºC) (mixture of conformers) δ 148.4 and 146.1, 138.3 and 135.0, 126.1 and 121.6, 111.4 and

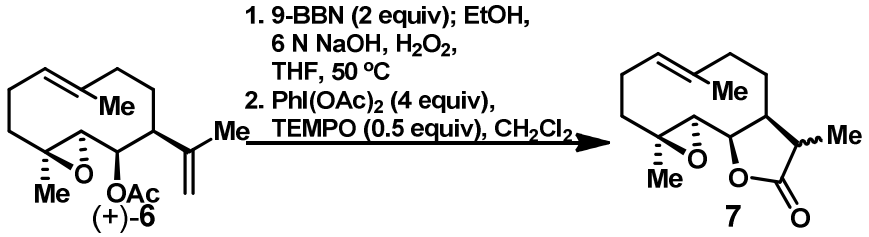
110.9, 72.0 and 71.6, 69.3 and 68.1, 61.0 and 60.9, 47.6 and 45.3, 39.6 and 38.7, 36.1 and 32.8, 27.5, 24.5 and 23.5, 23.1 and 22.9, 22.3 and 21.9, 17.0 and 16.2; IR (neat) ν 3438, 2921, 1638, 1455, 1385, 1067, 1033, 922 cm^{-1}; HRMS (ESI-TOF) calc'd for $C_{15}H_{25}O_2$ [M + H^+] 237.1849; found 237.1854.

**Compounds of this particular carbon skeleton containing the 4,5-epoxide on the 10-membered ring exists as conformers in $CDCl_3$. All the carbon signals are only visible when the NMR experiment is conducted at –30 ºC.[4]*



11,13-Didehydro-shiromool acetate (+)-6:

To the white suspension of *N,N'*-dicyclohexylcarbodiimide (780.0 mg, 3.780 mmol, 3.00 equiv), 4-dimethylaminopyridine (77.0 mg, 0.630 mmol, 0.50 equiv) and acetic acid (216 µL, 3.773 mmol, 2.99 equiv) in dichloromethane (6.3 mL), was added a solution of (+)-**1** (298.0 mg, 1.261 mmol, 1 equiv) in dichloromethane (1.0 mL) at room temperature. The reaction was allowed to go to completion by monitoring with thin layer chromatography (~1 h), before the mixture was directly purified by flash column chromatography (0–2% acetone/dichloromethane) to afford acetate (+)-**6** as a white solid (351.0 mg, 1.261 mmol, quantitative); R_f = 0.31 (2% acetone/dichloromethane); mp = 67–70 ºC; $[\alpha]_D^{20}$ = +49.2º (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.31 (br s, 1 H, C1–**H**), 4.87 (dd, *J* = 8.1, 1.7 Hz, 1 H, C6–**H**), 4.79 (d, *J* = 23.6 Hz, 2 H, C12–$\mathbf{H_2}$), 2.67 (s, 1 H, C5–**H**), 2.36 (s, 1 H, C2–H_2), 2.25 – 2.06 (m, 4 H, C2–H_2, C8/9–H_2, C7–**H** and C3–H_2), 2.04 (s, 3 H, CO$\mathbf{H_3}$), 1.95 – 1.81 (m, 3 H, C8/9–H_2 and C8/9–$\mathbf{H_2}$), 1.76 (s, 3 H, C$\mathbf{H_3}$), 1.68 (s, 3 H, C$\mathbf{H_3}$), 1.30 (s, 3 H, C$\mathbf{H_3}$), 1.30 – 1.23 (m. 1 H, C3–H_2); ^{13}C NMR (150 MHz, $CDCl_3$, 25 ºC) δ 170.1, 146.6 (br), 136.9 (br), 122.9 (br), 111.8, 74.5, 65.7, 59.9, 46.8 (br), 36.8 (br), 22.6, 21.1, 16.5; ^{13}C NMR (125 MHz, $CDCl_3$, –30 ºC) (mixture of conformers) δ 170.5, 147.0 and 144.8, 138.1 and 134.9, 126.4 and 121.8, 112.0 and 111.7, 74.5 and 73.8, 66.4 and 66.0, 60.2 and 59.9, 47.1 and 44.8, 39.5 and 38.6, 35.9 and 32.5, 28.4, 24.7 and 24.5, 22.8, 22.3 and 21.9, 21.2, 17.1, 16.4 and 16.3; IR (neat) ν 2922, 1742, 1454, 1371, 1245, 1021 cm^{-1}; HRMS (ESI-TOF) calc'd for $C_{17}H_{27}O_3$ [M + H^+] 279.1955; found 279.1957.

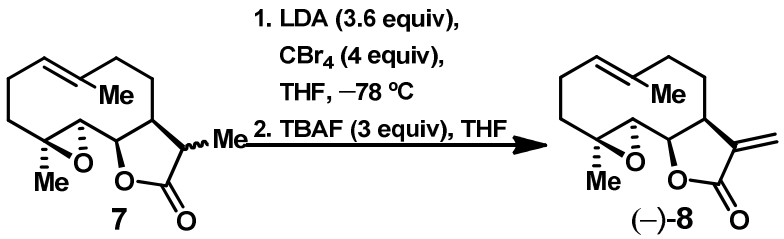


11,13-Dihydro-*epi*-parthenolide (7):[5]

To a solution of acetate (**+**)-**6** (104.0 mg, 0.374 mmol, 1 equiv) in tetrahydrofuran (3.7 mL) was added a 0.5*N* solution of 9-borabicyclo(3.3.1)nonane in tetrahydrofuran (1.5 mL, 0.750 mmol, 2.01 equiv) and stirred at room temperature for 2 h. Ethanol (1.1 mL), 6*N* aqueous sodium hydroxide (0.4 mL) and 35%

aqueous hydrogen peroxide (0.8 mL) were added sequentially before the mixture was heated to 50 ºC for 30 min. The mixture was then diluted with ethyl acetate, before quenching with saturated aqueous sodium thiosulfate (4 mL). The aqueous layer was extracted with ethyl acetate (3 × 4 mL), and the combined organic layers were washed with saturated aqueous sodium bicarbonate, brine, dried over sodium sulfate, filtered and concentrated under reduced pressure.

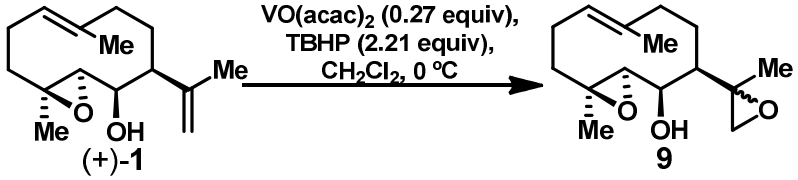
The crude material was then dissolved in dichloromethane (3.8 mL), followed by the addition of (diacetoxyiodo)benzene (482.0 mg, 1.496 mmol, 4.00 equiv) and 2,2,6,6-tetramethyl-1-piperidinyloxy (29.0 mg, 0.186 mmol, 0.50 equiv). The resulting mixture was stirred for 30 min at room temperature, before quenching with saturated aqueous sodium bicarbonate (4 mL) and saturated sodium thiosulfate (4 mL). The aqueous layer was separated and extracted with dichloromethane (3 × 4 mL). The combined organic layers were then dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude material was purified by flash column chromatography (25–33% ethyl acetate/hexanes) to afford 11,13-dihydro-*epi*-parthenolide (**7**) as a white solid (72.0 mg, 0.288 mmol, 77% over 2 steps); R_f = 0.64 (5% acetone/dichloromethane); mp = 135–137 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of diastereomers) δ 5.30 (t, *J* = 8.1 Hz, 1 H, C1–**H**), 4.20 (dd, *J* = 9.1, 5.1 Hz, 0.3 H, C6–**H** minor diastereomer), 3.98 (dd, *J* = 9.1, 4.0 Hz, 0.7 H, C6–**H** major diastereomer), 2.85 – 2.78 and 2.48 – 2.27 (2 × m, 5 H), 2.26 – 1.98 (m, 3 H), 1.74 – 1.62 (m, 4 H), 1.59 (s, 1 H), 1.34 – 1.23 (m, 7 H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC) δ 178.2, 81.8, 62.4, 62.2, 60.1, 41.3, 16.7, 16.6, 15.2, 9.8; ^{13}C NMR (125 MHz, $CDCl_3$, –30 ºC) (mixture of diastereomers and conformers) δ 179.7, 179.3 and 178.7, 137.9 and 137.7, 133.6 and 133.3, 126.5 and 125.7, 121.6, 82.1 and 81.3, 80.6 and 79.7, 62.7, 62.0 and 61.9, 61.1 and 60.7, 60.6 and 60.2, 47.6 and 45.6, 45.3 and 44.7, 42.1, 41.3 and 40.9, 40.3 and 40.0, 38.0 and 37.3, 35.4, 34.5 and 34.3, 30.4 and 28.7, 24.6 and 24.5, 22.1 and 21.8, 21.8 and 21.6, 18.3 and 16.9, 16.6 and 16.4, 15.2 and 15.1, 10.1 and 9.5; IR (neat) ν 2928, 1773, 1447, 1147, 980, 842 cm^{-1}; HRMS (ESI-TOF) calc'd for $C_{15}H_{23}O_3$ [M + H$^+$] 251.1642; found 251.1644.



7-*Epi*-parthenolide (–)-8:

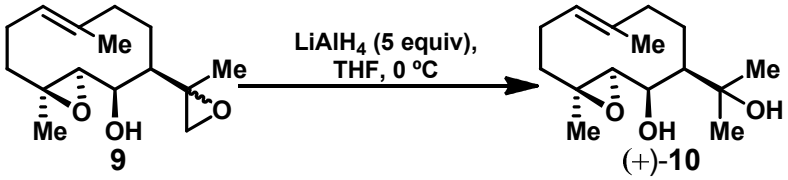
To a solution of **7** (60.0 mg, 0.240 mmol, 1 equiv), in tetrahydrofuran (2.0 mL), was added a 0.5*N* solution of lithium diisopropylamide (1.73 mL, 0.864 mmol, 3.60 equiv) in tetrahydrofuran at –78 ºC in a dropwise fashion. The resulting mixture was allowed to stir for 1 h at the same temperature. A pre-cooled solution of carbon tetrabromide (318.4 mg, 0.960 mmol, 4.00 equiv) in tetrahydrofuran (2.5 mL) was transferred to the reaction flask via cannula, giving rise to a brown mixture. After stirring for a further 0.5 h at –78 ºC, the reaction was quenched by adding saturated aqueous ammonium chloride (5 mL) and warming to room temperature. The aqueous phase was separated and then extracted with ethyl acetate (3 ×7 mL). The combined organic layers were then dried over sodium sulfate, filtered and concentrated under reduced pressure to give a black residue. The residue was diluted with hexanes, filtered through silica gel (10% ethyl acetate/hexanes), and concentrated under reduced pressure to give a pale yellow oil.

A 1.0*N* solution of tetra-*n*-butylammonium fluoride (0.36 mL, 0.360 mmol, 1.50 equiv) in tetrahydrofuran was added to the crude material in tetrahydrofuran (3 mL) at room temperature. After stirring for 0.5 h, another portion of tetra-*n*-butylammonium fluoride solution (1.50 equiv) was added. After stirring for another 0.5 h, the reaction was then quenched with saturated aqueous ammonium chloride (4 mL). The aqueous layer was extracted with ethyl acetate (3 × 5 mL), and the combined organic layers were dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude material was purified by flash column chromatography (0–2% ethyl acetate/dichloromethane) to afford 7-*epi*-parthenolide (**8**) as a white solid (35.7 mg, 0.144 mmol, 60% over 2 steps); R_f = 0.16 (20% ethyl acetate/hexanes); mp = 124–126 ºC; $[\alpha]_D^{20}$ = –27.5º (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.18 (s, 1 H, C13–**H**$_2$), 5.65 (s, 1 H, C13–**H**$_2$), 5.31 (s, 1 H, C1–**H**), 4.06 (dd, *J* = 9.6, 5.7 Hz, 1 H, C6–**H**), 2.97 – 2.90 (m, 1 H, C7–**H**), 2.81 (d, *J* = 9.6 Hz, 1 H, C5–**H**), 2.46 – 2.17 (m, 4 H, C2–**H**$_2$ and C8–**H**$_2$), 2.16 – 2.04 (m, 2 H, C3–**H**$_2$ and C9–**H**$_2$), 1.71 (s, 3 H, C**H**$_3$), 1.63 – 1.51 (m, 1 H, C3/9–**H**$_2$), 1.30 (s, 4 H, C3/9–**H**$_2$ and C**H**$_3$); ^{13}C NMR (150 MHz, $CDCl_3$, 25 ºC) δ 169.8, 143.1, 121.4, 80.0, 62.3, 60.8, 16.9; ^{13}C NMR (125 MHz, $CDCl_3$, –30 ºC) (mixture of conformers) δ 170.2, 142.6 and 142.3, 137.8 and 133.5, 126.4 and 124.8, 122.3 and 122.1, 80.0 and 79.9, 62.5 and 61.9, 61.2 and 61.1, 46.1 and 42.6, 40.7 and 37.8, 35.4 and 35.4, 33.3 and 30.8, 24.7, 22.0 and 21.8, 16.9 and 16.7; IR (neat) ν 2926, 1763, 1447, 1265, 1152, 1005 cm^{-1}; HRMS (ESI-TOF) calc'd for $C_{15}H_{21}O_3$ [M + H$^+$] 249.1485; found 249.1488.



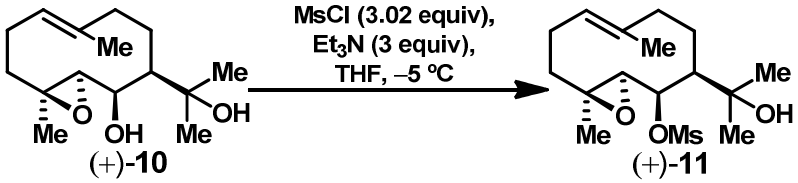
Epoxide 9:

To an ice-cooled solution of (+)-**1** (200.0 mg, 0.846 mmol, 1 equiv) in dichloromethane (20 mL) was added vanadyl acetylacetonate (61.0 mg, 0.230 mmol, 0.27 equiv), and the resulting mixture was allowed to stir for 10 min. A 5.*5N* solution of *tert*-butyl hydroperoxide in decane (0.34 mL, 1.87 mmol, 2.21 equiv) was added dropwise to the mixture and the mixture was allowed to stir at 0 ºC for 1 h. Another portion of *tert*-butyl hydroperoxide was added if the reaction was not completed by then. The reaction mixture was then quenched with saturated sodium thiosulfate (~20 mL), extracted with dichloromethane (3 × 20 mL), dried over sodium sulfate, filtered and then concentrated under reduced pressure. The crude material was purified by flash column chromatography (0–10% acetone/dichloromethane) to afford epoxide **9** as a pale yellow oil (163.9 mg, 0.649 mmol, 77%); R_f = 0.33 (10% acetone/dichloromethane); ^{1}H NMR (400 MHz, $CDCl_3$) (only major diastereomer described) δ 5.27 (br t, *J* = 7.4 Hz, 1 H, C1–**H**), 3.70 (d, *J* = 8.2 Hz, 1 H, C6–**H**), 2.80 (d, *J* = 4.8 Hz, 1 H, C12–**H**$_2$), 2.56 (d, *J* = 4.7 Hz, 2 H, C5–**H** and C12–**H**$_2$), 2.39 – 2.33 (m, 1 H, C2–**H**$_2$), 2.28 – 2.22 (m, 1 H, C9–**H**$_2$), 2.17 – 2.01 (m, 2 H, C2–**H**$_2$ and C3–**H**$_2$), 1.85 – 1.82 (m, 2 H, C8–**H**$_2$ and C9–**H**$_2$), 1.65 (s, 3 H, C**H**$_3$), 1.65 – 1.61 (m, 2 H, C8–**H**$_2$ and C7–**H**), 1.41 (s, 3 H, C**H**$_3$), 1.32 – 1.25 (m, 1 H, C3–**H**$_2$), 1.21 (s, 3 H, C**H**$_3$); ^{13}C NMR ($CDCl_3$, 150 MHz, 25 ºC) δ 71.5, 68.5, 60.7, 53.3, 45.8 (br), 36.9 (br), 22.7 (br), 21.2, 16.5; ^{13}C NMR ($CDCl_3$, 125 MHz, –30 ºC) (mixture of diastereomers; only major signals described) δ 138.1, 121.8, 69.0, 68.8, 61.5, 60.4, 53.7, 45.6, 40.0, 35.9, 21.8, 21.3, 20.6, 16.9, 16.1; IR (neat) ν 3432, 2925, 1454, 1386, 1067, 750 cm^{-1}; HRMS (ESI-TOF) calc'd for $C_{15}H_{25}O_3$ [M + H$^+$] 253.1798; found 253.1798.



Diol (+)-10:

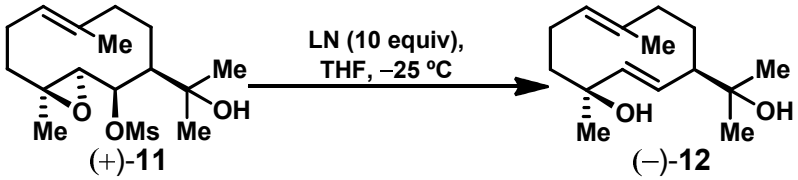
Lithium aluminum hydride (108.7 mg, 2.864 mmol, 5.00 equiv) was added to an ice-cooled solution of epoxide **9** (144.6 mg, 0.573 mmol, 1 equiv) in tetrahydrofuran (5.7 mL). The reaction was complete in 20 min as indicated by thin layer chromatography. Carefully, water (0.3 mL), 15% aqueous sodium hydroxide (0.3 mL), water (0.6 mL) and ethyl acetate (12 mL) were added sequentially in this order before allowing the mixture to stir vigorously at room temperature for 1 h. Sodium sulfate was added and the mixture was filtered through a pad of Celite® to afford diol (+)-**10**, which was used directly in the next step; R_f = 0.25 (60% ethyl acetate/ hexanes); $[\alpha]_D^{20}$ = +67.4° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24 (t, *J* = 7.6 Hz, 1 H, C1–**H**), 3.94 (d, *J* = 8.0 Hz, 1 H, C6–**H**), 3.07 (br s, 1 H, O**H**), 2.95 (br s, 1 H, O**H**), 2.64 (br s, 1 H, C5–**H**), 2.41 – 2.29 (m, 2 H, C2–$\mathbf{H}_2$ and C9–$\mathbf{H}_2$), 2.15 – 1.95 (m, 3 H, C2–$\mathbf{H}_2$, C3–$\mathbf{H}_2$ and C8–$\mathbf{H}_2$), 1.81 – 1.71 (m, 2 H, C9–$\mathbf{H}_2$ and C8–$\mathbf{H}_2$), 1.67 (s, 3 H, C14–$\mathbf{H_3}$), 1.33 (s, 3 H, C15–$\mathbf{H_3}$), 1.28 – 1.21 (m, 2 H, C3–$\mathbf{H}_2$ and C7–**H**), 1.24 (s, 3 H, C12–$\mathbf{H_3}$), 1.21 (s, 3 H, C13–$\mathbf{H_3}$); ^{13}C NMR ($CDCl_3$, 150 MHz, 25 °C) δ 137.8 (br), 122.2 (br), 73.9, 72.1, 68.3, 60.9, 47.9 (br), 36.9 (br), 29.4, 27.9, 22.8 (br), 16.3; ^{13}C NMR ($CDCl_3$, 125 MHz, –30 °C) (mixture of conformers) δ 138.7 and 134.8, 126.3 and 120.9, 73.8 and 73.6, 72.5 and 71.4, 69.2 and 68.0, 61.6, 48.1 and 44.4, 40.2 and 38.5, 36.1 and 34.7, 29.3 and 28.0, 27.2 and 25.0, 24.5 and 22.4, 21.9 and 20.7, 17.2, 16.1; IR (neat) ν 3681, 3400, 2973, 1386, 1213, 1033 cm^{-1}; HRMS (ESI-TOF) calc'd for $C_{15}H_{27}O_3$ [M + H^+] 255.1955; found 255.1956.



Mesylate (+)-11:

The crude material was dissolved in dichloromethane (5.7 mL) and was chilled to –5 °C using an ice/acetone bath. Triethylamine (0.12 mL, 0.860 mmol, 1.50 equiv) and methanesulfonyl chloride (67 µL, 0.866 mmol, 1.51 equiv) were added sequentially in this order and the mixture was allowed to stir for 10 min. Another portion of triethylamine and methanesulfonyl chloride was added and after a further 10 min of stirring, water (5 mL) was added to quench the mixture. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (3 × 5 mL). The organic layers were combined, dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude material was purified by flash column chromatography (0–10% acetone/dichloromethane) to afford mesylate (+)-**11** as a white foam (84.2 mg, 0.253 mmol, 44% over 2 steps); R_f = 0.48 (10% acetone/dichloromethane); $[\alpha]_D^{20}$ = +28.0° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 (br s, 1 H, C1–**H**), 4.90 (dd, *J* = 8.2, 1.4 Hz, 1 H, C6–**H**), 3.18 (s, 3 H, SC$\mathbf{H_3}$), 2.74 (br s, 1 H, C5–**H**), 2.46 – 2.38 (m, 1 H, C2–$\mathbf{H}_2$), 2.27 – 2.21 (m, 1 H, C$\mathbf{H}_2$), 2.13 – 1.99 (m, 3 H, C2–$\mathbf{H}_2$, C11–**H** and C$\mathbf{H}_2$), 1.86 (td, *J* = 12.4, 11.7, 4.8 Hz, 1 H, C$\mathbf{H}_2$), 1.71 (br s, 2 H, C$\mathbf{H_2}$), 1.66 (br s, 3 H, C15–$\mathbf{H_3}$), 1.59 (br s, 1 H, C$\mathbf{H}_2$), 1.34 (s, 3 H, C$\mathbf{H_3}$), 1.31 (s, 3 H, C$\mathbf{H_3}$), 1.29 (s, 3 H, C$\mathbf{H_3}$), 1.34 – 1.25 (m, 1 H, C7–**H**); ^{13}C NMR ($CDCl_3$, 125 MHz, 25 °C) δ 83.9, 73.1, 66.3, 61.2,

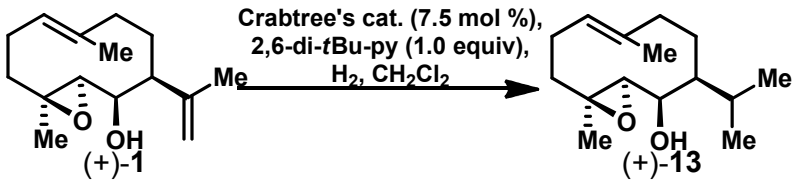
39.1, 29.0, 26.8, 16.4; ^{13}C NMR ($CDCl_3$, 125 MHz, –30 ºC) δ 138.1, 122.0, 83.7, 73.0, 65.1, 61.4, 49.8, 39.8, 38.9, 35.8, 28.7, 26.2, 22.2, 21.9, 17.2, 16.2; IR (neat) ν 3727, 2930, 2361, 2340, 1346, 1171, 912, 666 cm^{-1}; HRMS (ESI-TOF) calc'd for $C_{16}H_{28}O_5SNa$ [M + Na^+] 355.155; found 355.1557.



(+)-**11** (–)-**12**

4-Hydroxyallohedycaryol (–)-12:[6]

A pre-chilled (–60 ºC) 0.2*N* solution of freshly-prepared lithium naphthalenide in tetrahydrofuran (7.3 mL, 1.46 mmol, 5.00 equiv) was added rapidly to a solution of mesylate (+)-**11** (97.0 mg, 0.292 mmol, 1 equiv) in tetrahydrofuran (1.3 mL) at –25 ºC. After 10 min, another portion of lithium naphthalenide solution was added rapidly, and the mixture was allowed to stir for a further 10 min, before quenching with saturated sodium bicarbonate (10 mL). The organic layer was then separated, and the aqueous layer was extracted with ethyl acetate (3 × 15 mL). The organic layers were combined, dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude material was then purified by flash column chromatography (0–10% acetone/dichloromethane) to afford 4-hydroxyallohedycaryol (–)-**12** as a colorless oil (45.1 mg, 0.189 mmol, 65 %) and diol (+)-**10** as a colorless oil (17.0 mg, 0.067 mmol, 23 %); R_f = 0.45 (60% ethyl acetate/hexanes); $[\alpha]_D^{20}$ = –130.6º (*c* 1.0, $CHCl_3$); ^{1}H NMR spectrum is identical to that reported in literature; ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.6 (**C**5), 132.5 (**C**10), 129.3 (**C**6), 124.2 (**C**1), 73.4 (**C**4/11), 71.9 (**C**4/11), 58.1 (**C**7), 41.2 (**C**9), 39.7 (**C**3), 30.8 (**C**H_3), 26.8 (2 × **C**H_3), 23.8 (**C**2), 22.9 (**C**8), 16.9 (**C**14).



(+)-**1** (+)-**13**

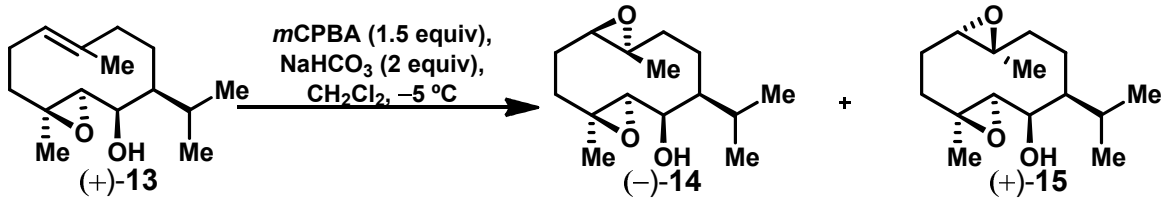
Shiromool (+)-13:[7]

A 0.1*N* solution of (+)-**1** (1 equiv) in degassed dichloromethane was cooled to –5 ºC in an ice/acetone bath, before 2,6-di-*tert*-butylpyridine (1.00 equiv) was added. To this solution was added (1,5-cyclooctadiene)(pyridine)(tricyclohexylphosphine)-iridium(I) hexafluorophosphate (5 mol %)[8] and the resulting orange solution was degassed with hydrogen gas at the same temperature immediately for 5 min. The reaction mixture was then kept under hydrogen gas (1 atm) and was allowed to warm to room temperature. After 30 min of stirring, another portion of the Crabtree's catalyst (2.5 mol %) was added and the mixture was allowed to stir for another 30 min to 1 h at the same temperature under hydrogen atmosphere. When complete, the mixture was concentrated under reduced pressure, and then the residual oil was purified by flash column chromatography (0–15% ethyl acetate/hexanes) to afford shiromool (+)-**13** as a pale yellow oil (65–84%); R_f = 0.22 (25% ethyl acetate/hexanes); $[\alpha]_D^{20}$ = +76.0º (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.26 (br t, 1 H, C1–**H**), 3.62 (dd, *J* = 7.9, 2.0 Hz, 1 H, C6–**H**), 2.62 (br s, 1 H, C5–**H**), 2.35 (br s, 1 H, C2–**H**$_2$), 2.23 – 2.23 (m, 3 H, C8/9–**H**$_2$, C2–**H**$_2$ and C3–**H**$_2$), 1.79 – 1.69 (m, 3

H, C8/9–$\mathbf{H}_2$, C8/9–$\mathbf{H}_2$ and C11–**H**), 1.65 (s, 3 H, C14–$\mathbf{H}_3$), 1.43 – 1.41 (m, 1 H, C8/9–$\mathbf{H}_2$), 1.30 – 1.25 (m, 1 H, C3–$\mathbf{H}_2$), 1.21 (s, 3 H, C15–$\mathbf{H}_3$), 1.00 – 0.92 (m, 1 H, C7–**H**), 0.99 (d, *J* = 6.7 Hz, 3 H, C12–$\mathbf{H}_3$), 0.93 (d, *J* = 6.6 Hz, 3 H, C13–$\mathbf{H}_3$); ^{13}C NMR (150 MHz, $CDCl_3$, 25 ºC) δ 71.9, 68.8, 60.8, 31.8, 21.2, 21.1, 16.5; ^{13}C NMR (125 MHz, $CDCl_3$, –30 ºC) (mixture of conformers) δ 138.5, 126.1 and 121.2, 71.2 and 70.5, 70.1 and 69.0, 61.7, 47.5 and 44.3, 40.1 and 38.8, 36.2 and 34.5, 31.6 and 31.0, 25.0 and 24.5, 22.4 and 22.0, 21.4 and 21.2, 20.9, 17.2, 16.2; IR (neat) ν 3431, 2926, 1460, 1385, 1064, 858, 824 cm^{-1}; HRMS (ESI-TOF) calc'd for $C_{15}H_{27}O_2$ [M + H^+] 239.2005; found 239.2008.

Table 2. ^{1}H and ^{13}C NMR chemical shift comparison of synthetic **13** and natural **13**.

^{1}H NMR chemical shift comparison[4]		^{13}C NMR chemical shift comparison[9]	
Synthetic **13** ($CDCl_3$)–400 MHz	Natural **13** ($CDCl_3$)–300 MHz	Synthetic **13** ($CDCl_3$)–125 MHz	Natural **13** ($CDCl_3$)–20.13 MHz
5.26 (br t)	5.29 (br t)	138.5	137.4
3.62 (dd)	3.66 (dd)	126.1 and 121.2	123.3
2.62 (br s)	2.62 (d)	71.2 and 70.5	71.8
1.65 (s)	1.68 (br s) 3H	70.1 and 69.0	68.9
1.21 (s)	1.24 (s)	61.7	60.7
0.99 (d)	1.02 (d)	47.5 and 44.3	47.1
0.93 (d	0.96 (d)	40.1 and 38.8	39.0
		36.2 and 34.5	37.4
		31.6 and 31.0	31.8
		25.0 and 24.5	26.1
		22.4 and 22.0	23.1
		21.4 and 21.2	21.1
		20.9	21.1
		17.2	18.6
		16.2	16.5



1β,10α,4β,5α-Diepoxy-7α(H)-germacran-6β-ol (–)-14 and (+)-15:[10]

To a solution of shiromool (+)-**13** (37.5 mg, 0.157 mmol, 1 equiv) in dichloromethane (1.6 mL), was added sodium bicarbonate (26.4 mg, 0.315 mmol, 2.01 equiv) and 70% *meta*-chloroperoxybenzoic acid (58.2 mg, 0.236 mmol, 1.50 equiv) respectively at –5 ºC (ice/acetone bath).After 30 min of stirring at the same temperature, the reaction was quenched by adding 1*N* aqueous sodium hydroxide (1.5 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (3 × 1.5 mL). The combined organic layers were washed with brine, dried over sodium sulfate, filtered and then concentrated under reduced pressure. The crude ^{1}H NMR spectrum indicates a *dr* = 4: 1 of **14**: **15**, and the crude material was purified by flash column chromatography (0–10% acetone/dichloromethane) to afford (–)-**14** as a white solid (24.8 mg, 0.097 mmol, 62%); R_f = 0.38 (10% acetone/dichloromethane); mp = 47–

50 ºC; $[\alpha]_D^{20}$ = –33.4º (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.69 – 3.63 (m, 1 H, C6–**H**), 3.00 (dd, *J* = 9.3, 5.8 Hz, 1 H, C1–**H**), 2.89 (d, *J* = 8.5 Hz, 1 H, C5–**H**), 2.31 – 2.25 (m, 2 H, C2–$\mathbf{H}_2$ and C9–$\mathbf{H}_2$), 2.13 (ddd, *J* = 13.1, 7.8, 1.1 Hz, 1 H, C3–$\mathbf{H}_2$), 1.93 – 1.88 (m, 1 H, C8–$\mathbf{H}_2$), 1.68 (dp, *J* = 9.5, 6.6 Hz, 1 H, C11–**H**), 1.51 (dt, *J* = 14.6, 8.8 Hz, 1 H, C2–$\mathbf{H}_2$), 1.47 – 1.42 (m, 1 H, C8–$\mathbf{H}_2$), 1.38 (s, 3 H, C$\mathbf{H_3}$), 1.33 (s, 3 H, C$\mathbf{H_3}$), 1.26 – 1.15 (m, 1 H, C3–$\mathbf{H}_2$), 1.00 (t, *J* = 13.5 Hz, 1 H, C9–$\mathbf{H}_2$), 0.94 (d, *J* = 6.6 Hz, 3 H, C12–$\mathbf{H_3}$), 0.93 (d, *J* = 6.6 Hz, 3 H, C13–$\mathbf{H_3}$), 0.88 (dq, *J* = 9.1, 3.2 Hz, 1 H, C7–**H**); ^{13}C NMR (150 MHz, $CDCl_3$) δ 70.7 (**C**6), 68.2 (**C**5), 60.1 (**C**1), 60.1 (**C**4 and 10), 49.7 (**C**7), 41.2 (**C**9), 34.6 (**C**3), 32.1 (**C**11), 24.8 (**C**2), 23.0 (**C**8), 21.0 (**C**12), 20.9 (**C**13), 16.8 (**C**14 and 15); IR (neat) ν 3441, 2947, 1456, 1388, 1065, 817 cm^{-1}; HRMS (ESI-TOF) calc'd for $C_{15}H_{27}O_3$ [M + H^+] 255.1955; found 255.1958.

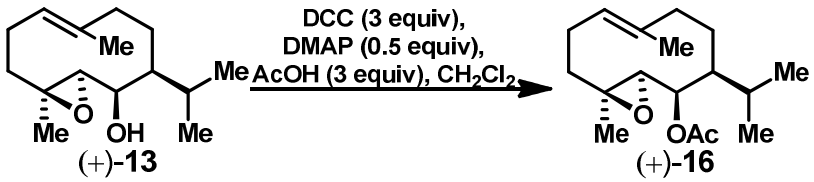
(+)-**15** as a white gum (8.8 mg, 0.035 mmol, 22%); R_f = 0.17 (10% acetone/dichloromethane); $[\alpha]_D^{20}$ = +81.7º (*c* 0.48, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (d, *J* = 6.9 Hz, 1 H, C6–**H**), 3.02 (d, *J* = 7.3 Hz, 1 H, C5–**H**), 2.95 (dd, *J* = 10.7, 1.3 Hz, 1 H, C1–**H**), 2.20 (dt, *J* = 13.6, 3.9 Hz, 1 H, C9–$\mathbf{H}_2$), 2.06 (ddd, *J* = 18.4, 12.4, 4.4 Hz, 2 H, C3–$\mathbf{H}_2$ and C8–$\mathbf{H}_2$), 1.91 (tdd, *J* = 13.7, 4.9, 1.5 Hz, 1 H, C2–$\mathbf{H}_2$), 1.76 (dt, *J* = 9.4, 6.6 Hz, 1 H, C11–**H**), 1.64 (ddd, *J* = 14.0, 5.0, 2.7 Hz, 1 H, C3–$\mathbf{H}_2$), 1.58 – 1.53 (m, 1 H, C8–$\mathbf{H}_2$), 1.52 – 1.46 (m, 1 H, C2–$\mathbf{H_2}$), 1.46 (s, 3 H, C15–$\mathbf{H_3}$), 1.37 – 1.21 (m, 2 H, C9–$\mathbf{H}_2$, C7–**H**), 1.27 (s, 3 H, C14–$\mathbf{H_3}$), 1.03 (d, *J* = 6.8 Hz, 3 H, C12–$\mathbf{H_3}$), 0.97 (d, *J* = 6.6 Hz, 3 H, C13–$\mathbf{H_3}$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 71.6 (**C**6), 68.6 (**C**5), 62.0 (**C**4), 61.6 (**C**1), 59.7 (**C**10), 44.9 (**C**7), 37.2 (**C**3), 36.8 (**C**9), 31.4 (**C**11), 25.6 (**C**2), 24.0 (**C**8), 23.3 (**C**14), 21.3 (**C**12), 21.0 (**C**13), 16.6 (**C**15); IR (neat) ν 3442, 2929, 1464, 1386, 1078, 929, 819 cm^{-1}; HRMS (ESI-TOF) calc'd for $C_{15}H_{27}O_3$ [M + H^+] 255.1955; found 255.1954.

Table 3. ^{1}H and ^{13}C NMR chemical shift comparison of synthetic **14** and natural **14**.

^{1}H NMR chemical shift comparison[10a]		^{13}C NMR chemical shift comparison[10a]	
Synthetic **14** ($CDCl_3$)–600 MHz	Natural **14** ($CDCl_3$)–200 MHz	Synthetic **14** ($CDCl_3$)–150 MHz	Natural **14** ($CDCl_3$)–50 MHz
3.69 – 3.63 (m)	3.67 (dd)	70.7	70.6
3.00 (dd)	3.00 (dd)	68.2	68.1
2.89 (d)	2.88 (d)	60.1	60.1
2.31 – 2.25 (m)	2.40 – 1.50 (m)	60.1	60.1
2.13 (ddd)		60.1	60.1
1.93 – 1.88 (m)		49.7	49.6
1.68 (dp)	1.70 (m)	41.2	41.1
1.51 (dt)		34.6	34.5
1.47 – 1.42 (m)		32.1	32.0
1.38 (s)	1.38 (s)	24.8	24.7
1.33 (s)	1.32 (s)	23.0	22.9
1.26 – 1.15 (m)		21.0	20.9
1.00 (t)	1.00 (m)	20.9	20.8
0.94 (d)	0.95 (d)	16.8	16.7
0.93 (d)	0.93(d)	16.8	16.7
0.88 (dq)			

Table 4. ^{1}H and ^{13}C NMR chemical shift comparison of synthetic **15** and natural **15**.

^{1}H NMR chemical shift comparison[10a]		^{13}C NMR chemical shift comparison[10a]	
Synthetic **15** ($CDCl_3$)–400 MHz	Natural **15** ($CDCl_3$)–200 MHz	Synthetic **15** ($CDCl_3$)–150 MHz	Natural **15** ($CDCl_3$)–50 MHz
3.70 (d)	3.70 (dd)	71.6	71.6
3.02 (d)	3.03 (d)	68.6	68.4
2.95 (dd)	2.95 (br d)	62.0	61.9
2.20 (dt)	2.40 – 1.50 (m)	61.6	61.5
2.06 (ddd)		59.7	59.6
1.91 (tdd)		44.9	44.8
1.76 (dt)	1.70 (m)	37.2	37.1
1.64 (ddd)		36.8	36.7
1.58 – 1.53 (m)		31.4	31.3
1.52 – 1.46 (m)		25.6	25.4
1.46 (s)	1.46 (s)	24.0	23.9
1.37 – 1.21 (m)		23.3	23.2
1.27 (s)	1.28 (s)	21.3	21.2
1.03 (d)	1.03 (d)	21.0	20.9
0.97 (d)	0.97 (d)	16.6	16.5



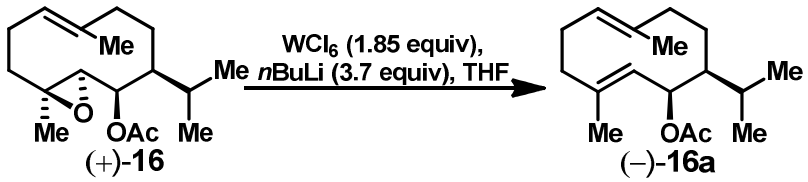
Shiromool acetate (+)-16:[9]

To the white suspension of *N,N'*-dicyclohexylcarbodiimide (656.2 mg, 3.180 mmol, 3.00 equiv), 4-dimethylaminopyridine (64.8 mg, 0.530 mmol, 0.50 equiv) and acetic acid (182 µL, 3.180 mmol, 2.96 equiv) in dichloromethane (1.8 mL), was added a solution of shiromool (+)-**13** (253.0 mg, 1.061 mmol, 1 equiv) in dichloromethane (3.5 mL) at room temperature. The reaction was allowed to go to completion by monitoring with thin layer chromatography (~1 h), before the mixture was directly purified by flash column chromatography (0–2% acetone/dichloromethane) to afford acetate (+)-**16** as a white oil (297.2 mg, 1.059 mmol, quantitative); R_f = 0.34 (2% acetone/dichloromethane); $[\alpha]_D^{20}$ = +11.5º (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.27 (br t, *J* = 8.7 Hz, 1 H, C1–**H**), 4.97 (dd, *J* = 7.9, 1.7 Hz, 1 H, C6–**H**), 2.65 (d, *J* = 7.8 Hz, 1 H, C5–**H**), 2.38 – 2.30 (m, 1 H, C2–$\mathbf{H}_2$), 2.26 – 2.12 (m, 2 H, C2–$\mathbf{H}_2$ and C8/9–$\mathbf{H}_2$), 2.10 – 2.02 (m, 1 H, C3–$\mathbf{H}_2$), 2.06 (s, 3 H, COC$\mathbf{H_3}$), 1.82 – 1.72 (m, 2 H, C8/9–$\mathbf{H}_2$ and C8/9–$\mathbf{H}_2$), 1.67 (s, 3 H, C$\mathbf{H_3}$), 1.55 – 1.48 (m, 2 H, C11–**H** and C8/9–$\mathbf{H}_2$), 1.28 – 1.20 (m, 1 H, C3–$\mathbf{H}_2$), 1.26 (s, 3 H, C$\mathbf{H_3}$), 1.13 (d, *J* = 6.1 Hz, 1 H, C7–**H**), 0.96 (d, *J* = 6.6 Hz, 3 H, C12–$\mathbf{H_3}$), 0.91 (d, *J* = 6.6 Hz, 3 H, C13–$\mathbf{H_3}$); ^{13}C NMR (150 MHz, $CDCl_3$, 25 ºC) δ 170.4, 74.3, 66.3, 59.9, 55.9, 46.3 (br), 37.1 (br), 35.0, 34.1, 31.6, 25.6, 24.8, 21.3, 20.9, 16.7; ^{13}C NMR (125 MHz, $CDCl_3$, –30 ºC) (mixture of conformers) δ 170.2, 137.6 and 134.4, 126.2 and 121.4, 74.1 and 73.3, 66.5 and 65.3, 59.7 and 59.5, 46.3 and 43.4, 39.5 and 38.3, 35.8 and 33.7, 31.1 and 30.5, 25.1 and 24.2, 22.0 and 21.7, 21.0, 20.7, 20.4, 16.8, 16.2 and 16.1; IR (neat)

ν 2928, 1738, 1369, 1231, 1018 cm^{-1}; HRMS (ESI-TOF) calc'd for $C_{17}H_{29}O_3$ [M + H^+] 281.2111; found 281.2112.

Table 5. ^1H and ^{13}C NMR chemical shift comparison of synthetic **16** and natural **16**.

^1H NMR chemical shift comparison[9]		^{13}C NMR chemical shift comparison[9]	
Synthetic **16** ($CDCl_3$)–400 MHz	Natural **16** ($CDCl_3$)–80 MHz	Synthetic **16** ($CDCl_3$)–125 MHz	Natural **16** ($CDCl_3$)–20.13MHz
5.27 (br t)	5.27 (br t)	170.2	170.0
4.97 (dd)	4.97 (dd)	137.6 and 134.4	136.8
2.65 (d)	2.62 (d)	126.2 and 121.4	123.6
2.38 – 2.30 (m)		74.1 and 73.3	74.1
2.26 – 2.12 (m)		66.5 and 65.3	66.1
2.10 – 2.02 (m)		59.7 and 59.5	59.6
2.06 (s)	2.05 (s)	46.3 and 43.4	46.0
1.82 – 1.72 (m)		39.5 and 38.3	38.3
1.67 (s)	1.67 (br s)	35.8 and 33.7	37.2
1.55 – 1.48 (m)		31.1 and 30.5	31.4
1.28 – 1.20 (m)		25.1 and 24.2	26.6
1.26 (s)	1.25 (s)	22.0 and 21.7	23.0
1.13 (d)		21.0	21.0
0.96 (d)	0.96 (s)	20.7	20.7
0.91 (d)	0.85 (s)	20.7	20.7
		20.4	18.6
		16.8 and 16.1	16.5

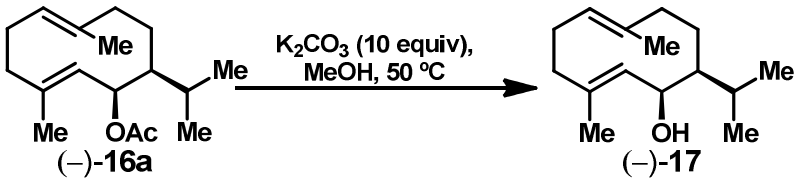


(+)-**16** (–)-**16a**

Acetate (–)-16a:

Tungsten hexachloride[11] (218.0 mg, 0.550 mmol, 1.85 equiv) was dissolved in tetrahydrofuran (1.5 mL) at –60 ºC. To this solution was added 2.25*N* *n*-butyllithium in hexanes (0.50 mL, 1.125 mmol, 3.79 equiv) in a dropwise fashion, before the mixture was allowed to warm to room temperature. After 15 min of stirring, this mixture was cooled to 0 ºC, and then a solution of (+)-**16** (83.4 mg, 0.297 mmol, 1 equiv) in tetrahydrofuran (1 mL) was added to the mixture. The mixture was then warmed to room temperature and allowed to stir for 30 min before quenching with saturated aqueous Rochelle's salt (3 mL). The mixture was stirred vigorously for 30 min until two clear phases form. The aqueous layer was then extracted with ethyl acetate (3 × 3 mL), and the combined organic layers were washed with brine, dried over sodium sulfate, filtered and concentrated under reduced pressure at 0–5 ºC. The crude material was then purified by flash column chromatography (0–10% ethyl acetate) to afford (–)-**16a** as a pale yellow oil (67.6 mg, 0.256 mmol, 86%); R_f = 0.50 (25% diethyl ether/hexanes); $[\alpha]_D^{20}$ = –25.1° (*c* 1.0, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 5.58 (d, *J* = 7.6 Hz, 1 H, C=C**H**), 4.98 – 4.87 (m, 2 H, C=C**H** and C6–**H**), 2.42 – 2.32 (m, 1 H), 2.19 – 2.07 (m, 3 H), 2.02 (s, 3 H, OC**H**$_3$), 1.96 – 1.89 (m, 1 H), 1.76 – 1.61 (m, 3 H), 1.56 (s, 3 H),

1.53 (s, 3 H), 1.47 – 1.36 (m, 1 H), 1.01 – 0.92 (m, 7 H); ^{13}C NMR (150 MHz, $CDCl_3$) (mixture of conformers) δ 171.0, 138.7 and 135.6, 134.5 and 134.2, 130.2 and 129.1, 128.2 and 121.7, 72.5 and 72.4, 50.9 and 48.3, 41.5 and 39.2, 37.2 and 35.7, 32.3 and 31.7, 30.9, 26.0, 24.6 and 24.4, 22.1 and 21.4, 21.3 and 21.0, 17.1, 16.6 and 16.5; IR (neat) ν 2924, 1736, 1367, 1238, 1021 cm^{-1}; HRMS (ESI-TOF) calc'd for $C_{17}H_{29}O_2$ [M + H$^+$] 265.2162; found 265.2158.



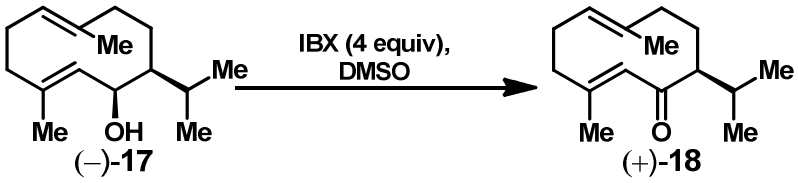
(1*E*,4*E*)-7αH-Germacra-1(10),4-dien-6β-ol (–)-17:[12]

To a solution of acetate (–)-**16a** (140.6 mg, 0.532 mmol, 1 equiv) in methanol (5.3 mL) was added potassium carbonate (735.0 mg, 5.318 mmol, 10.00 equiv). The resulting suspension was heated at 50 ºC for 2 h before quenching by adding water (5 mL) and dichloromethane (5 mL). The separated aqueous layer was extracted with dichloromethane (3 × 6 mL), and the organic layers were combined, dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude material was purified by flash column chromatography (dichloromethane) to afford (–)-**17** as a colorless oil (112.4 mg, 0.505 mmol, 95%); R_f = 0.34 (dichloromethane); $[\alpha]_D^{20}$ = –14.1º (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.00 (m, 1 H, C1–**H**), 4.93 (br s, 1 H, C5–**H**), 4.63 (br s, 1 H, C6–**H**), 2.40 – 2.01 (m, 5 H), 1.92 – 1.72 (m, 1 H), 1.63 (br s, 3 H), 1.57 (s, 2 H), 1.46 (s, 3 H), 1.37 – 1.25 (m, 2 H), 1.02 (d, *J* = 6.5 Hz, 3 H), 0.99 (s, 3 H), 0.92 – 0.74 (m, 1 H, C7–**H**); ^{13}C NMR (150 MHz, $CDCl_3$) (mixture of conformers) δ 138.8 and 135.8, 133.8 and 131.6, 133.4 and 133.0, 128.9 and 121.5, 69.0, 52.3 and 49.5, 41.5 and 39.2, 37.3 and 35.9, 32.3 and 31.9, 30.2 and 25.2, 24.7 and 24.4, 22.1 and 21.5, 21.4 and 21.3, 21.1 and 17.1, 16.5; IR (neat) ν 3373, 2920, 1663, 1446, 1383, 1041, 846 cm^{-1}; HRMS (ESI-TOF) calc'd for $C_{15}H_{26}ONa$ [M + Na$^+$] 245.1876; found 245.1877.

Table 6. ^{1}H and ^{13}C NMR chemical shift comparison of synthetic **17** and natural **17**.

^{1}H NMR chemical shift comparison[4]		^{13}C NMR chemical shift comparison[4]	
Synthetic **17** ($CDCl_3$)–600 MHz	Natural **17** ($CDCl_3$)–300 MHz	Synthetic **17** ($CDCl_3$)–150 MHz	Natural **17** ($CDCl_3$)–75 MHz
5.00 (m)	4.95 (m)	138.8 and 135.8	138.9 and 135.7
4.93 (br s)		133.8 and 131.6	133.5 and 131.4
4.63 (br s)	4.59 (br d)	133.4 and 133.0	133.3 and 133.0
2.40 – 2.01 (m)		128.9 and 121.5	128.7 and 121.3
1.92 – 1.72 (m)		69.0	68.6 and 68.6
1.63 (br s)		52.3 and 49.5	52.2 and 49.3
1.57 (s)		41.5 and 39.2	41.3 and 39.0
1.46 (s)	1.42 (br s)	37.3 and 35.9	37.2 and 35.7
1.37 – 1.25 (m)		32.3 and 31.9	32.1 and 31.7
1.02 (d)	0.99 (d)	30.2 and 25.2	30.3 and 25.2
0.99 (s)	0.97 (d)	24.7 and 24.4	24.3
0.92 – 0.74 (m)		22.1 and 21.5	22.1 and 21.5
		21.4 and 21.3	21.3 and 21.2

		21.1 and 17.1	21.0 and 17.0
		16.5	16.5 and 16.4



(–)-**17** (+)-**18**

Acoragermacrone (+)-18:[13]

To a solution of alcohol (–)-**17** (31.5 mg, 0.142 mmol, 1 equiv) in dimethyl sulfoxide (0.5 mL) was added 2-iodoxybenzoic acid[14] (159.0 mg, 0.568 mmol, 4.00 equiv). The resulting solution was allowed to stir at room temperature for 2 h, before adding water (0.5 mL) and filtering the resulting white suspension with ethyl acetate (~10 mL). The filtrate was then washed with brine (3 × 4 mL), dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude material was purified by flash column chromatography (0–10% ethyl acetate/hexanes) to afford (+)-**18** as a pale yellow oil (28.2 mg, 0.128 mmol, 90%); R_f = 0.56 (10% ethyl acetate/hexanes); $[\alpha]_D^{20}$ = +16.0º (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, C_6D_6) (mixture of conformers) δ 5.54 and 5.41 (2 × s, 1 H, C5–**H**), 4.68 – 4.60 (m, 1 H, C1–**H**), 2.31 – 2.17 (m, 1 H), 2.12 – 1.94 (m, 4 H), 1.99 (s, 3 H, C15–**H$_3$**), 1.94 – 1.85 (m, 2 H), 1.85 – 1.77 (m, 1 H), 1.66 – 1.61 (m, 1 H), 1.56 (td, *J* = 11.2, 5.9 Hz, 1 H), 1.13 (s, 3 H, C14–**H$_3$**), 1.03 and 0.89 (2 × d, *J* = 6.6 Hz, 3 H, C12/13–**H$_3$**), 0.95 and 0.79 (2 × d, *J* = 6.7 and 6.5 Hz, 3 H, C12/13–**H$_3$**); ^{13}C NMR (150 MHz, C_6D_6) δ 205.0 (**C**=O), 149.3, 140.6, 134.0 (**C**5), 125.7 (**C**1), 61.7 (**C**7), 42.4, 41.2, 31.4 (**C**11), 31.1, 26.2, 21.5 (**C**12/13), 20.9 (**C**12/13), 19.1 (**C**15), 15.2 (**C**14); IR (neat) ν 2930, 1677, 1603, 1450, 1385, 1200, 848 cm^{-1}; HRMS (ESI-TOF) calc'd for $C_{15}H_{25}O$ [M + H$^+$] 221.1900; found 221.1899.

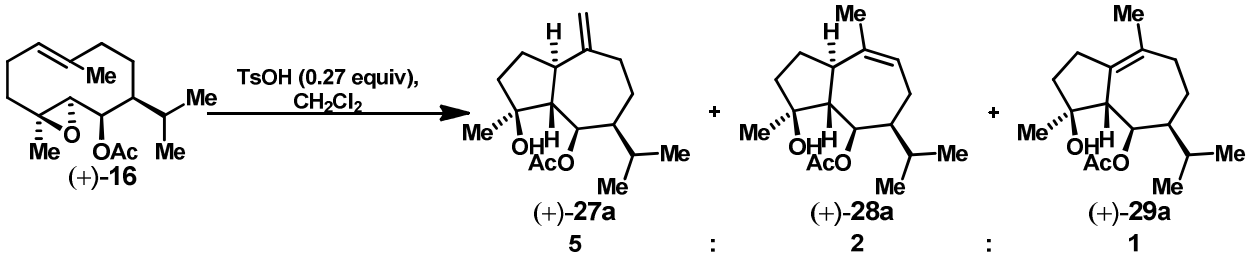
Table 7. ^{1}H NMR chemical shift comparison of synthetic **18** and existing data in literature.

Synthetic **18** ($CDCl_3$)–500 MHz	Reported ^{1}H NMR data[15] ($CDCl_3$)–400 MHz
5.67 and 5.64	5.64
4.89 (dd)	4.89
2.44 (dt)	2.44
2.39 (d)	
2.28 – 2.10 (m)	
2.01 (s)	2.01
1.98 – 1.73 (m)	
1.22 (s)	1.22
0.97 (d) (major conformer)	0.97
0.91 (d) (major conformer)	0.91

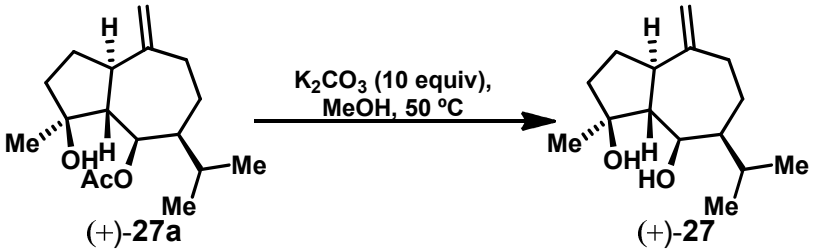
Note: No ^{13}C NMR data was found in our literature search. As we have observed with compound **17, it was expected that the ^{13}C NMR spectrum of **18** to display signs of conformers in solution. However, the ^{13}C NMR spectrum obtained only showed 15 C signals, while the ^{1}H NMR spectrum had extra signals (e.g. see spectrum in C_6D_6, δ 5.54 vs 5.41 ppm). To prove that these extra signals are as a result of **18** existing as a mixture of conformers in solution, we conducted a ^{1}H NMR experiment using toluene-d_8 both at room temperature and at 80 ºC. As expected, the*

signals (e.g. δ 5.48 and 5.35 ppm) converged to one single signal (δ 5.43 ppm) upon heating. An additional evidence of this phenomenon is the fact that the relative integrals of the specified signals change when different NMR solvents were employed. (See Pages S-65 to 69).

Acid-induced transannular cyclization of shiromool acetate (+)-16:



To a solution of shiromool acetate (+)-**16** (43.7 mg, 0.156 mmol, 1 equiv) in dichloromethane (15.6 mL) was added *p*-toluenesulfonic acid (pre-dried by azeotroping with benzene, 7.2 mg, 0.042 mmol, 27 mol %). The reaction mixture was quenched after 40 min by adding saturated aqueous sodium bicarbonate (15 mL), and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 10 mL) and the combined extracts were dried over sodium sulfate, filtered and concentrated under reduced pressure. The ^{1}H NMR spectrum of the crude material indicated a ratio of 5: 2: 1 ratio of (+)-**27a**, (+)-**28a** and (+)-**29a** respectively. The crude material was purified by flash column chromatography (0–10% ethyl acetate/dichloromethane) to afford a 6: 1 mixture (+)-**27a** and (+)-**29a** as a pale yellow oil (22.3 mg, 0.080 mmol, 51%) and (+)-**28a** as a pale yellow oil (8.3 mg, 0.030 mmol, 19%); (+)-**27a**: $[\alpha]_D^{20}$ = +1.9º (*c* 1.0, $CHCl_3$); ^{1}H and ^{13}C NMR spectra match that reported in literature completely[9]; (+)-**28a**: $[\alpha]_D^{20}$ = +9.7º (*c* 0.6, $CHCl_3$); ^{1}H and ^{13}C NMR spectra match that reported in literature completely[9]; (+)-**29a**: $[\alpha]_D^{20}$ = +37.1º (*c* 0.24, $CHCl_3$); ^{1}H and ^{13}C NMR spectra match that reported in literature completely.[9]



Teucladiol (+)-27:[16]

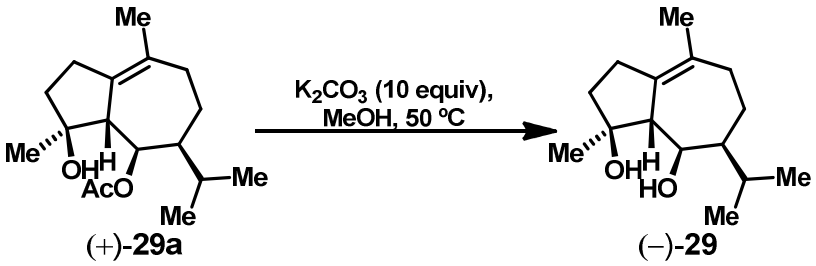
To a solution of acetate (+)-**27a** (13.9 mg, 0.050 mmol, 1 equiv) in methanol (0.5 mL) was added potassium carbonate (68.5 mg, 0.496 mmol, 10.00 equiv). The resulting suspension was heated to 50 ºC for 1 h. The mixture was then quenched by adding water (0.5 mL) and dichloromethane (1 mL), and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 1 mL), and the combined organic layers were dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude material was then purified by flash column chromatography (0–30% ethyl acetate/hexanes) to afford teucladiol (+)-**27** as a pale yellow oil (11.9 mg, 0.050 mmol, quantitative); R_f = 0.15 (10% ethyl acetate/dichloromethane); $[\alpha]_D^{20}$ = +4.0º (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.73 (d, *J* = 17.1

Hz, 2 H, C14–**H$_2$**), 4.07 (d, *J* = 9.6 Hz, 1 H, C6–**H**), 2.54 (dt, *J* = 13.2, 6.0 Hz, 1 H, C9–**H$_2$**), 2.48 (s, 1 H, O**H**), 2.29 (dt, *J* = 11.3, 7.9 Hz, 1 H, C1–**H**), 2.12 (dt, *J* = 14.4, 7.3 Hz, 1 H, C9–**H$_2$**), 2.07 (s, 1 H, O**H**), 1.87 (dd, *J* = 11.6, 9.4 Hz, 1 H, C5–**H**), 1.86 – 1.81 (m, 1 H, C3–**H$_2$**), 1.80 – 1.60 (m, 5 H, C3–**H$_2$**, C2–**H$_2$**, C8–**H$_2$** and C11–**H**), 1.58 – 1.53 (m, 1 H, C8–**H$_2$**), 1.30 (s, 3 H, C15–**H**), 1.23 (dddd, *J* = 10.3, 8.6, 3.8, 1.8 Hz, 1 H, C7–**H**), 1.01 (d, *J* = 6.6 Hz, 3 H, C12–**H**), 0.95 (d, *J* = 6.6 Hz, 3 H, C13–**H**); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.6 (**C**10), 108.2 (**C**14), 80.9 (**C**4), 72.7 (**C**6), 59.6 (**C**5), 48.6 (**C**7), 42.8 (**C**1), 40.6 (**C**3), 35.7 (**C**9), 29.0 (**C**11), 27.4 (**C**2), 24.1 (**C**15), 23.3 (**C**8), 21.7 (**C**12/13); IR (neat) ν 3387, 2956, 1638, 1461, 1382, 1260, 1018, 882, 755 cm^{-1}; HRMS (ESI-TOF) calc'd for $C_{15}H_{26}O_2Na$ [M + Na^+] 261.1825; found 261.1818.

The relative stereochemistry was verified by NOESY experiment.

Table 8. ^{1}H and ^{13}C NMR chemical shift comparison of synthetic **27** and natural **27**.

^{1}H NMR chemical shift comparison[17]		^{13}C NMR chemical shift comparison[17]	
Synthetic **27** (pyridine-d_5)–600 MHz	Natural **27** (pyridine-d_5)–500 MHz	Synthetic **27** (pyridine-d_5)–150 MHz	Natural **27** (pyridine-d_5)–125 MHz
4.87 (s) and 4.81 (s)	4.88 (s) and 4.82 (s)	154.2	153.9
4.33 (dd)	4.34 (dd)	107.8	107.5
2.62 (dt) and 2.17 (dt)	2.63 (ddd) and 2.18 (ddd)	80.7	80.4
2.37 (dt)	2.38 (ddd)	72.5	72.2
2.28 (dd)	2.27 (dd)	61.0	60.6
2.10 (m) and 1.78 (ddd)	2.10 (ddd) and 1.79 (m)	49.5	49.2
2.00 (dq)	2.01 (m)	43.5	43.2
1.90 (ttd) and 1.61 (dt)	*ca.* 1.91 and 1.63 (ddd)	41.6	41.4
1.90 (ttd) and 1.71 (dq)	*ca.* 1.89 and 1.72 (m)	37.2	36.8
1.51 (s)	1.51 (s)	30.2	29.9
1.39 (dq)	1.41 (dddd)	27.7	27.5
1.19 (d)	1.20 (d)	24.6	24.3
1.04 (d)	1.06 (d)	24.4	24.1
		22.3	22.0
		22.0	21.7

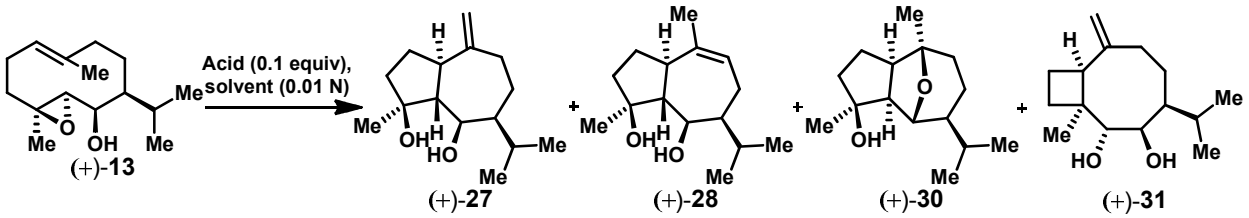


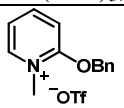
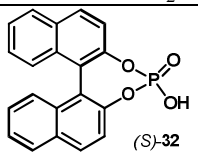
Compound (–)-29:[9]

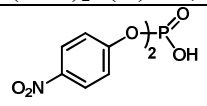
To a solution of acetate (+)-**29a** (2.4 mg, 0.009 mmol, 1 equiv) in methanol (0.1 mL) was added potassium carbonate (11.8 mg, 0.085 mmol, 10.00 equiv). The suspension was heated at 50 ºC for 1 h, before quenching by adding water (0.1 mL) and dichloromethane (0.2 mL). The separated aqueous layer was extracted with dichloromethane (3 × 0.2 mL) and the combined organic extracts were dried over

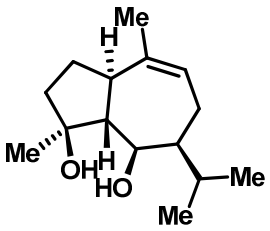
sodium sulfate, filtered and concentrated under reduced pressure. The crude material was purified by preparative thin layer chromatography (20% ethyl acetate/dichloromethane) to afford (+)-**29** as a white paste (2.0 mg, 0.008 mmol, 96%); $[\alpha]_D^{20}$ = –8.0º (*c* 0.2, $CHCl_3$); ^1H and ^{13}C NMR spectra match that reported in literature completely.[9]

Table 9. Acid-induced transannular cyclization of shiromool (+)-13:



#	Conditions	Product Distribution (based on crude ^1H NMR)				Comment
		27	**28**	**30**	**31**	
1	TsOH, CH_2Cl_2, rt, 15 min	1	3	-	-	
2	TsOH, CH_2Cl_2, 50 ºC, 1 h	-	-	-	-	Decomp.
3	TsOH, CH_2Cl_2, –78 ºC, 1 h, 0 ºC, 5 min	1	3	3.6	-	Incomplete
4	DL-CSA, CH_2Cl_2, –78 ºC, 1 h, 0 ºC, 5 min	1	2	3		Incomplete
5	TFA, CH_2Cl_2, –78 ºC, 1 h, 0 ºC, 5 min	-	-	-	-	15% conv to **28**
6	Al_2O_3 acid, CH_2Cl_2, –78 ºC, 1 h, 0 ºC, 5 min	-	-	-	-	SM rec.
7	Montmorillonite K10, CH_2Cl_2, –78 ºC, 1 h, 0 ºC, 5 min	-	-	-	-	SM rec.
8	CH_3SO_3H, CH_2Cl_2, –78 ºC, 1 h, 0 ºC, 5 min	1	3	3	-	
9	TfOH, CH_2Cl_2, –78 ºC, 1 h, 0 ºC, 5 min	1	10	-	-	2.5 (**29**)
10	$ClSO_3H$, CH_2Cl_2, –78 ºC, 1 h, 0 ºC, 5 min	-	5	-	-	3 (**29**)
11	$Sc(OTf)_3$, CH_2Cl_2, –78 ºC, 1 h, 0 ºC, 5 min	1	12	5	-	
12	$Sc(OTf)_3$ (1 eq.), CH_2Cl_2, 0 ºC, 10 min	1	>20	-	-	
13	$Bi(OTf)_3$, CH_2Cl_2, –78 ºC, 2 h, 0 ºC, 10 min	1	14	4	-	
14	$Cu(OTf)_2$, CH_2Cl_2, –78 ºC to rt	-	-	-	-	SM rec.
15	$Dy(OTf)_3$, CH_2Cl_2, –78 ºC to rt	-	-	-	-	SM rec.
16	$Yb(OTf)_3$, CH_2Cl_2, –78 ºC to rt	-	-	-	-	SM rec.
17	 CH_2Cl_2, –78 ºC to rt	-	-	-	-	SM rec.
18	 *(S)*-**32** CH_2Cl_2, –78 ºC, 1 h, 0 ºC, 5 min	-	-	-	-	SM rec.
19	*(S)*-**S1** (1 eq.), CH_2Cl_2, –78 ºC, o/n	-	-	-	-	SM rec.
20	*(S)*-**S1**, CH_2Cl_2, rt, 1 h	1	2	6.5	-	Similar result with *(R)*-**S1**
21	*(S)*-**S1**, PhH, rt, 2 h	1	2	7	-	Incomplete
22	*(S)*-**S1**, MeCN, rt, 2 h	-	-	-	-	Decomp.
23	*(S)*-**S1** (1 eq.), CH_2Cl_2, 0 ºC, 0.5 h	1	2	6	-	

24	$(PhO)_2P(O)OH$, CH_2Cl_2, rt, 1 h	1	2.65	6	-	
25	 CH_2Cl_2, rt, 1 h	1	3.6	6.6	-	
26	$(BnO)_2P(O)OH$ (1 eq.), CH_2Cl_2, rt, 1 h	1	2.6	-	5	1 (**29**)



(+)-**28**

4β,6β-Dihydroxy-1α,5β(H)-guai-9-ene (+)-28 (Table 9: entry 12):[18]

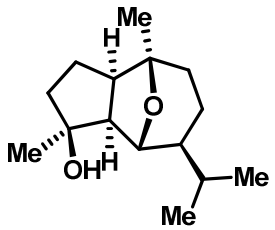
To a solution of shiromool (+)-**13** (30.0 mg, 0.126 mmol, 1 equiv) in dichloromethane (15 mL), was added scandium(III) triflate (61.9 mg, 0.126 mmol, 1.00 equiv) at 0 ºC. The resulting mixture was allowed to stir at the same temperature for 10 min, before quenching with saturated aqueous sodium bicarbonate (15 mL). The aqueous layer was then separated and extracted with dichloromethane (3 × 10 mL), the combined organic layers were dried over sodium sulfate, filtered and then concentrated under reduced pressure. The ^{1}H NMR spectrum of the crude material indicated a >20: 1 ratio of (+)-**28** and (+)-**27** respectively. The crude material was purified by flash column chromatography (0–10% acetone/dichloromethane) to afford (+)-**28** as a light yellow solid (20.0 mg, 0.084 mmol, 67%); R_f = 0.26 (10% acetone/dichloromethane); mp = 63–66 ºC; $[\alpha]_D^{20}$ = +12.5º (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.50 (d, *J* = 8.9 Hz, 1 H, C9–**H**), 4.14 (dd, *J* = 9.5, 4.1 Hz, 1 H, C6–**H**), 2.48 (br s, 1 H, O**H**), 2.36 – 2.12 (m, 3 H, O**H**, C1–**H** and C8–$\mathbf{H}_2$), 2.09 (dd, *J* = 12.0, 9.5 Hz, 1 H, C5 –**H**), 1.86 – 1.61 (m, 6 H, C8–$\mathbf{H}_2$, C11–**H**, C2–$\mathbf{H_2}$ and C3–$\mathbf{H_2}$), 1.67 (s, 3 H, C14–$\mathbf{H_3}$), 1.32 (s, 3 H, C15–$\mathbf{H_3}$), 1.29 – 1.23 (m, 1 H, C7–**H**), 1.02 (d, *J* = 6.6 Hz, 3 H, C12–$\mathbf{H_3}$), 0.95 (d, *J* = 6.6 Hz, 3 H, C13–$\mathbf{H_3}$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.4 (**C**10), 126.3 (**C**9), 81.3 (**C**4), 72.6 (**C**6), 57.6 (**C**5), 50.7 (**C**7), 42.5 (**C**1), 40.1 (**C**3), 28.6 (**C**11), 26.7 (**C**2), 24.5 (**C**8), 24.3 (**C**15), 23.3 (**C**14), 21.6 (**C**12), 21.5 (**C**13); IR (neat) ν 3403, 2957, 1453, 1377, 1152, 969 cm^{-1}; HRMS (ESI-TOF) calc'd for $C_{15}H_{26}O_2Na$ [M + Na^+] 261.1825; found 261.1825.

The relative stereochemistry was verified by NOESY experiment.

Table 10. ^{1}H and ^{13}C NMR chemical shift comparison of synthetic **28** and natural **28**.

^{1}H NMR chemical shift comparison[17]		^{13}C NMR chemical shift comparison[17]	
Synthetic **28** (pyridine-d_5)–400 MHz	Natural **28** (pyridine-d_5)–500 MHz	Synthetic **28** (pyridine-d_5)–150 MHz	Natural **28** (pyridine-d_5)–125 MHz
5.59 (br d)	5.58 (br d)	140.1	139.8
4.38 (dd)	4.37 (dd)	127.1	126.7
2.60 (br t) and 1.92 (dd)	2.59 (m) and 1.91 (dd)	80.9	80.6
2.50 (dd)	2.47 (dd)	72.6	72.3
2.37 (m)	2.37 (m)	58.7	58.3

2.01 (m) and *ca.* 1.73	*ca.* 2.01 and *ca.* 1.73	51.3	51.0
1.99 (m)	*ca.* 1.98	43.1	42.8
1.81 – 1.76 (m)	*ca.* 1.80 and *ca.* 1.76	41.2	40.8
1.71 (s)	1.70 (s)	29.7	29.3
1.54 (s)	1.52 (s)	27.5	27.2
1.46 (dt)	1.46 (ddd)	25.4	25.1
1.22 (d)	1.21 (d)	24.9	24.5
1.06 (d)	1.06 (d)	23.7	23.3
		22.2	21.8
		22.0	21.6



(+)-**30**

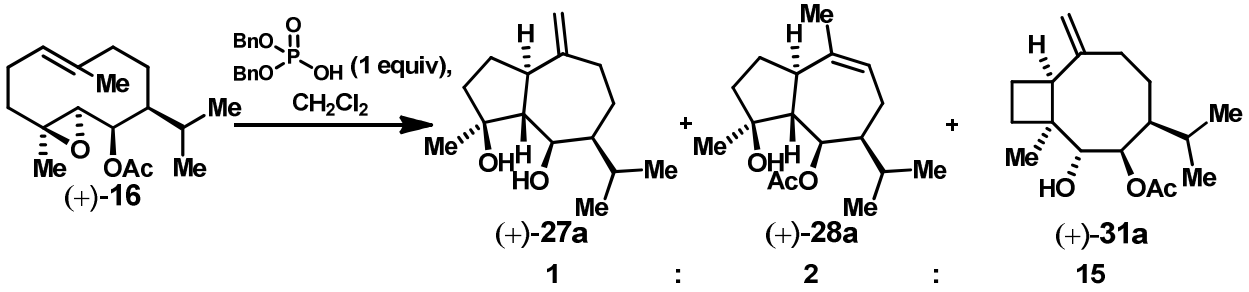
Chrysothol (+)-30 (Table 9: entry 20):[17, 19]

To a solution of shiromool (+)-**13** (54.0 mg, 0.227 mmol, 1 equiv) in dichloromethane (20 mL) was added (*S*)-(+)-1,1'-binaphthalene-2,2'-diyl hydrogen phosphate (**32**) (15.8 mg, 0.045 mmol, 0.20 equiv). The resulting mixture was allowed to stir at room temperature for 1 h, before quenching with saturated aqueous sodium bicarbonate (15 mL). The aqueous layer was then separated and extracted with dichloromethane (3 × 10 mL), and the combined organic layers were dried over sodium sulfate, filtered and concentrated under reduced pressure. The ^{1}H NMR spectrum of the crude material indicated a 2: 5: 11 ratio of (+)-**27**, (+)-**28** and (+)-**30**. The crude material was then purified by flash column chromatography (0–10% acetone/dichloromethane) to afford a 1: 3 mixture of (+)-**27** and (+)-**28** as a pale yellow oil (17.4 mg, 0.073 mmol, 32%) and (+)-**30** as a pale yellow oil (26.2 mg, 0.110 mmol, 49%); R_f = 0.15 (10% acetone/dichloromethane); $[\alpha]_D^{20}$ = +16.5º (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.01 (s, 1 H, C6–**H**), 2.34 – 2.32 (m, 2 H, C5–**H** and C1–**H**), 2.19 – 2.07 (m, 2 H, C9–**H$_2$**), 1.82 – 1.68 (m, 3 H, C3–**H**$_2$, C2–**H**$_2$ and C11–**H**), 1.59 – 1.51 (m, 2 H, C2–**H**$_2$ and C8–**H$_2$**), 1.43 (s, 3 H, C14–**H$_3$**), 1.41 – 1.37 (m, 2 H, C3–**H**$_2$ and C7–**H**), 1.19 (s, 3 H, C15–**H$_3$**), 0.95 (d, *J* = 1.9 Hz, 3 H, C12–**H$_3$**), 0.93 (d, *J* = 1.9 Hz, 3 H, C13–**H$_3$**); ^{13}C NMR (150 MHz, $CDCl_3$) δ 76.1 (**C**6), 74.6 and 74.5 (**C**4/10), 68.2 (**C**1), 53.4 (**C**5), 48.3 (**C**9), 38.7 (**C**7), 37.6 (**C**3), 32.8 (**C**11), 25.9 (**C**14), 24.0 (**C**8), 22.1 (**C**15), 21.2 (**C**12), 20.4 (**C**13), 20.3 (**C**2); IR (neat) ν 3398, 2957, 1469, 1371, 1246, 1165, 943 cm^{-1}; HRMS (ESI-TOF) calc'd for $C_{15}H_{27}O_2$ [M + H$^+$] 239.2005; found 239.2007.

The relative stereochemistry was verified by NOESY experiment.

Table 11. ^{1}H and ^{13}C NMR chemical shift comparison of synthetic **30** and natural **30**.

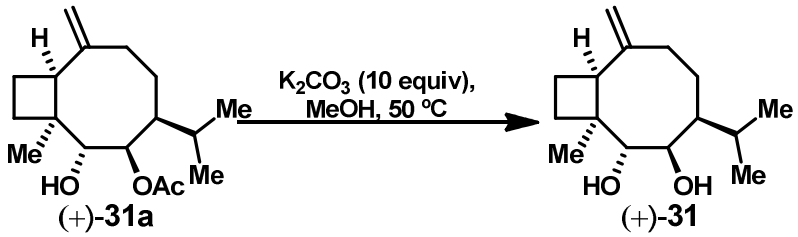
^{1}H NMR chemical shift comparison[17]		^{13}C NMR chemical shift comparison[17]	
Synthetic **30** (pyridine-d_5)–400 MHz	Natural **30** (pyridine-d_5)–500 MHz	Synthetic **30** (pyridine-d_5)–150 MHz	Natural **30** (pyridine-d_5)–125 MHz
4.18 (d)	4.17 (d)	76.5	76.3
2.78 (dd)	2.79 (dd)	74.6	74.3
2.51 (dd) and 2.15 (dt)	2.51 (dd) and 2.17 (ddd)	73.4	73.3
2.36 (ddd)	2.38 (ddd)	69.2	69.1
1.83 (dd) and 1.56 (m)	1.85 (dddd) and *ca.* 1.55	53.4	53.3
1.74 (m) and 1.39 (ddd)	1.75 (ddd) and 1.40 (ddd)	48.9	48.8
1.67 (m)	1.67 (dqq)	38.9	38.7
1.61 (s)	1.62 (s)	38.0	37.9
ca. 1.61 and 1.48	*ca.* 1.61 and *ca.* 1.49	33.5	33.3
1.48	*ca.* 1.49	26.8	26.6
1.23 (s)	1.25 (s)	24.7	24.5
0.90 (d)	0.91 (d)	22.6	22.4
0.88 (d)	0.90 (d)	21.4	21.2
		20.9	20.7
		20.7	20.4



Compound (+)-31a:

To a solution of shiromool acetate (+)-**16a** (36.5 mg, 0.130 mmol, 1 equiv) in dichloromethane (13 mL) was added dibenzyl phosphate (36.2 mg, 0.130 mmol, 1.00 equiv). The reaction mixture was quenched after 30 min by adding saturated aqueous sodium bicarbonate (10 mL) and the separated aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over sodium sulfate, filtered and concentrated under reduced pressure. The ^{1}H NMR spectrum of the crude material indicates a ratio of 15: 2: 1 of (+)-**31a**, (+)-**28a** and (+)-**27a** respectively. The crude material was purified by flash column chromatography (0–10% ethyl acetate/dichloromethane) to afford pure (+)-**31a** as a white solid (25.4 mg, 0.091 mmol, 70%); R_f = 0.50 (10% ethyl acetate/dichloromethane); mp = 82–86 ºC; $[\alpha]_D^{20}$ = +79.0º (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08 – 5.04 (m, 3 H, C14–**H$_2$** and C6–**H**), 3.67 (d, *J* = 9.2 Hz, 1 H, C5–**H**), 2.52 (ddd, *J* = 11.7, 5.1, 2.4 Hz, 1 H, C9–**H**$_2$), 2.43 (d, *J* = 8.6 Hz, 1 H, C1–**H**), 2.35 – 2.19 (m, 1 H, C2–**H**$_2$), 2.14 – 2.06 (m, 1 H, C3–**H**$_2$). 2.08 (s, 3 H, OC**H$_3$**), 1.93 – 1.83 (m, 1 H, C2–**H**$_2$), 1.77 (td, *J* = 7.3 Hz, C9–**H**$_2$), 1.72 – 1.54 (m, 3 H, C8–**H$_2$** and C3–**H**$_2$), 1.47 (h, *J* = 6.9 Hz, C11–**H**), 1.33 (s, 3 H, C15–**H$_3$**), 1.08 (t, *J* = 7.3 Hz, 1 H, C7–**H**), 0.96 (d, *J* = 6.7 Hz, 3 H, C12–**H$_3$**), 0.91 (d, *J* = 6.7 Hz, 3 H, C13–**H$_3$**); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.8 (**C**=O), 150.1 (**C**10), 111.6 (**C**14),

77.3 (**C**5/6), 77.1 (**C**5/6), 49.8 (**C**1), 45.0 (**C**7), 43.6 (**C**4), 41.3 (**C**9), 31.7 (**C**11), 30.2 (**C**3), 28.3 (**C**8), 21.4 (O**C**H_3), 21.0 (**C**2 and **C**H_3), 20.7 (**C**H_3), 20.0 (**C**H_3); IR (neat) ν 3483, 2960, 1738, 1372, 1249, 1025, 894 cm^{-1}; HRMS (ESI-TOF) calc'd for $C_{17}H_{29}O_3$ [M + H^+] 281.2111; found 281.2113.



(+)-**31a** (+)-**31**

Compound (+)-31:

To a solution of acetate (+)-**31a** (13.2 mg, 0.047 mmol, 1 equiv) in methanol (0.5 mL) was added potassium carbonate (65.0 mg, 0.470 mmol, 10.0 equiv). The resulting suspension was heated to 50 ºC for 1 h before the reaction was quenched with water (0.5 mL) and dichloromethane (1 mL). The aqueous layer was extracted with dichloromethane (3 × 1 mL) and the combined extracts were dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude material was purified by flash column chromatography (0–10% acetone/dichloromethane) to afford (+)-**31** as a colorless oil (8.7 mg, 0.036 mmol, 78%); R_f = 0.23 (10% acetone/dichloromethane); $[\alpha]_D^{20}$ = +68.8 º (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.02 (d, *J* = 16.0 Hz, 2 H, C14–**H**$_2$), 3.65 (d, *J* = 9.1 Hz, 1 H, C5–**H**), 3.52 (d, *J* = 7.6 Hz, 1 H, C6–**H**), 2.55 – 2.48 (m, 1 H, C9–**H**$_2$), 2.39 (dd, *J* = 8.5, 2.8 Hz, 1 H, C1–**H**), 2.36 – 2.18 (m, 1 H, C2–**H**$_2$), 2.02 (q, *J* = 10.3 Hz, 1 H, C3–**H**$_2$), 1.88 (ddt, *J* = 11.2, 8.8, 2.2 Hz, 1 H, C2–**H**$_2$), 1.75 (td, *J* = 12.8, 3.5 Hz, 1 H, C9–**H**$_2$), 1.58 (dddd, *J* = 24.6, 11.2, 6.3, 2.4 Hz, 3 H, C11–**H**, C3–**H**$_2$ and C8–**H**$_2$), 1.47 (dt, *J* = 14.7, 4.3 Hz, 1 H, C8–**H**$_2$), 1.26 (s, 3 H, C15–**H**$_3$), 0.97 (d, *J* = 6.5 Hz, 6 H, C12/13–**H**$_3$), 0.93 – 0.84 (m, 1 H, C7–**H**); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.5 (**C**10), 111.3 (**C**14), 78.6 (**C**5), 73.2 (**C**6), 49.9 (**C**1), 45.9 (**C**7), 41.8 (**C**9), 31.8 (**C**11), 30.0 (**C**8), 27.6 (**C**3), 21.5, 21.0 (**C**4 and 2), 20.9 (**C**12 and 13), 20.2 (**C**15); IR (neat) ν 3352, 2959, 1631, 1469, 1384, 1001, 893, 756 cm^{-1}; HRMS (ESI-TOF) calc'd for $C_{15}H_{27}O_2$ [M + H^+] 239.2005; found 239.2004.

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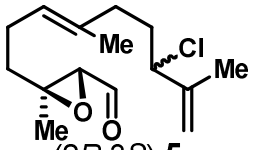
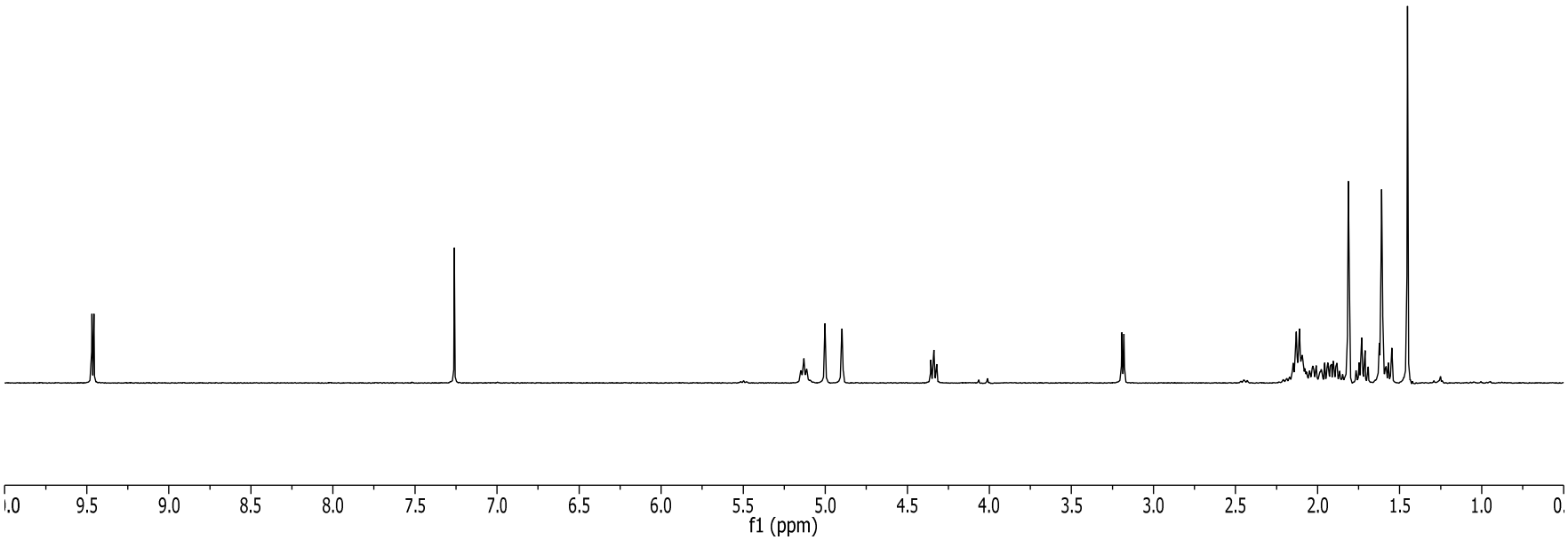
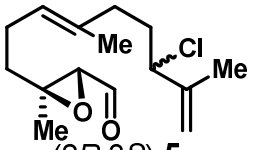


(2*R*,3*S*)-**5**

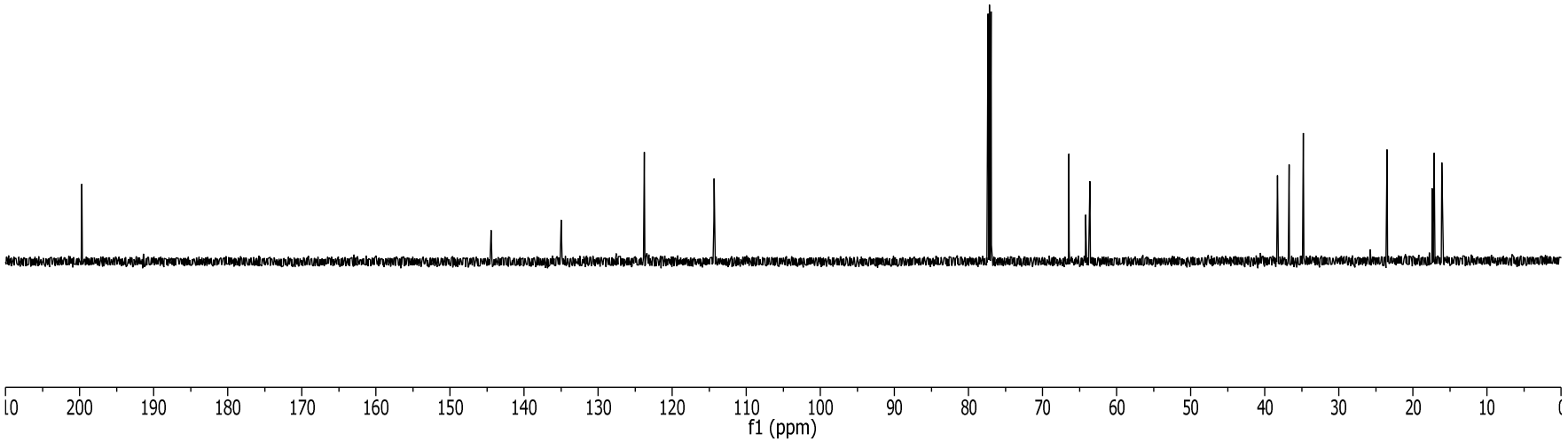
^{1}H NMR (600 MHz, $CDCl_3$)

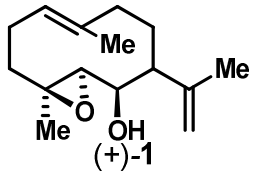




(2*R*,3*S*)-**5**

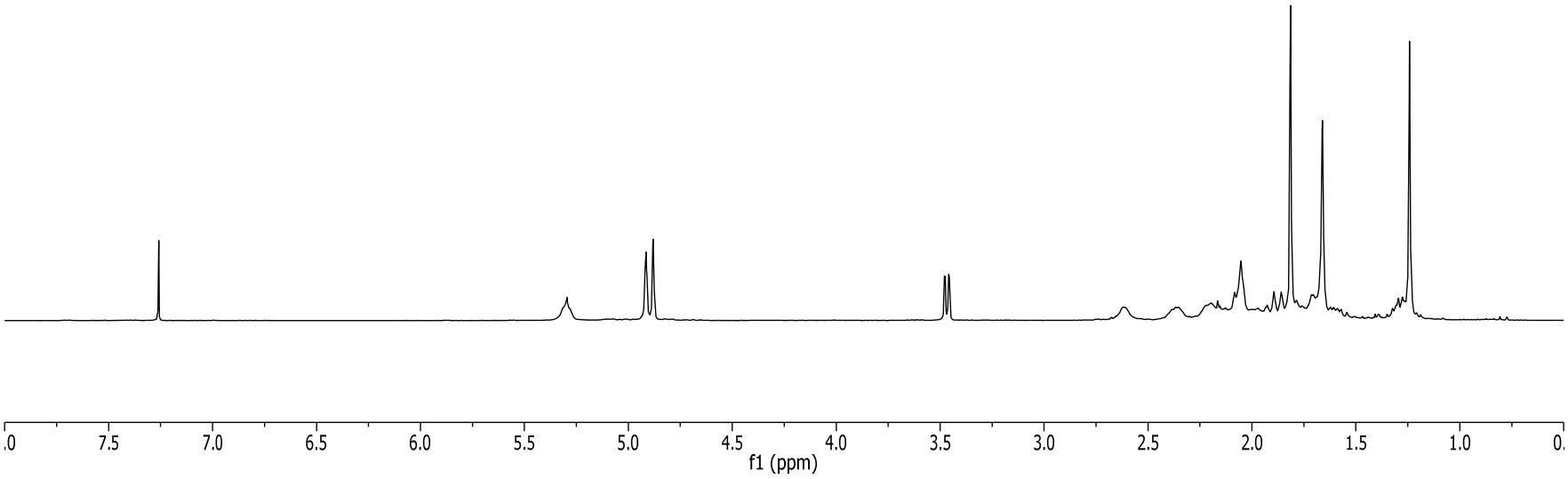
^{13}C NMR (150 MHz, $CDCl_3$)

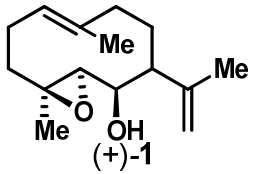




(+)-1

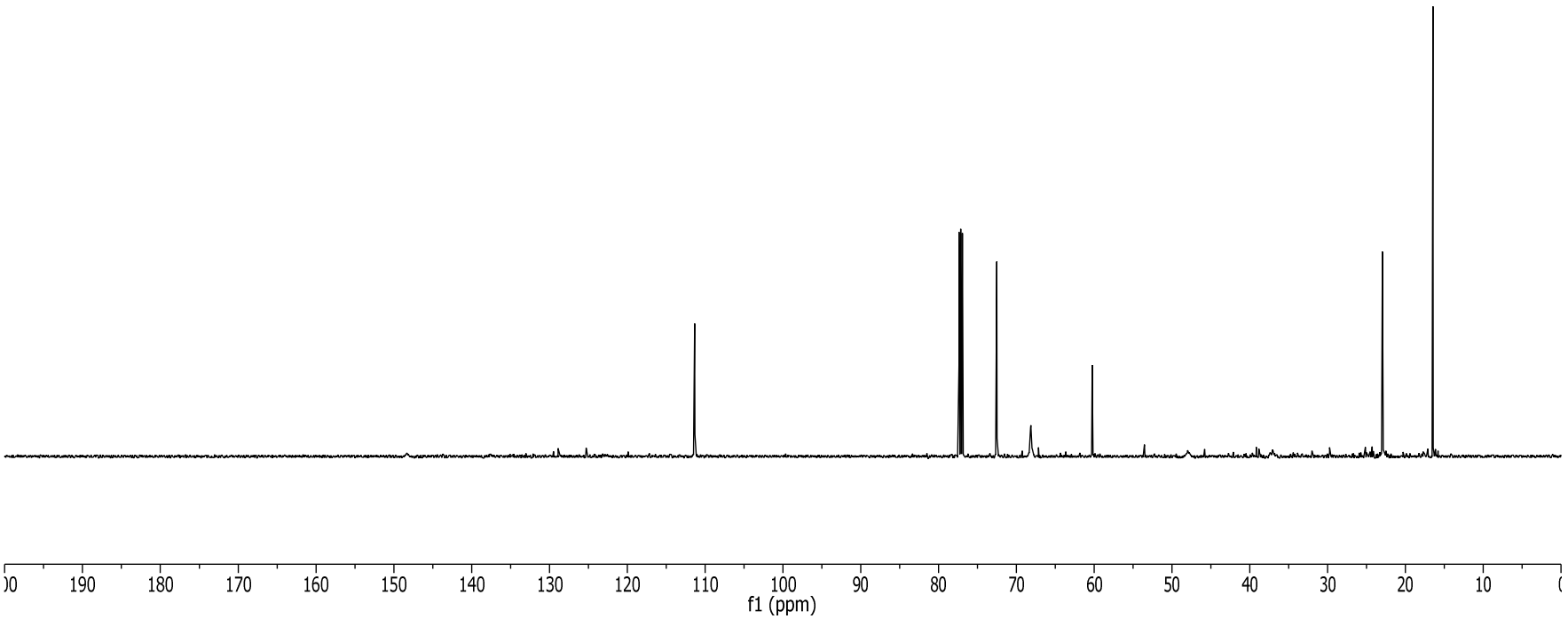
^{1}H NMR (400 MHz, $CDCl_3$)

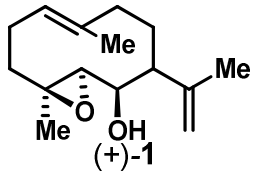




(+)-1

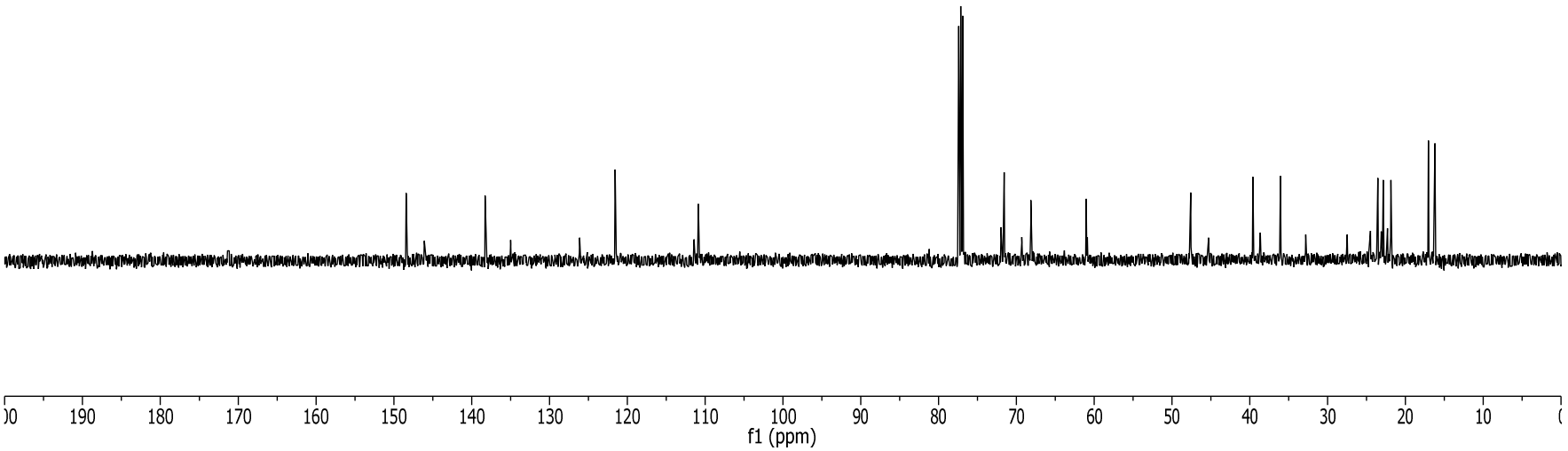
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C)

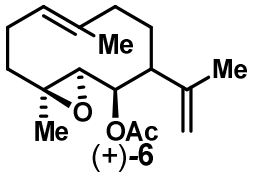




(+)-**1**

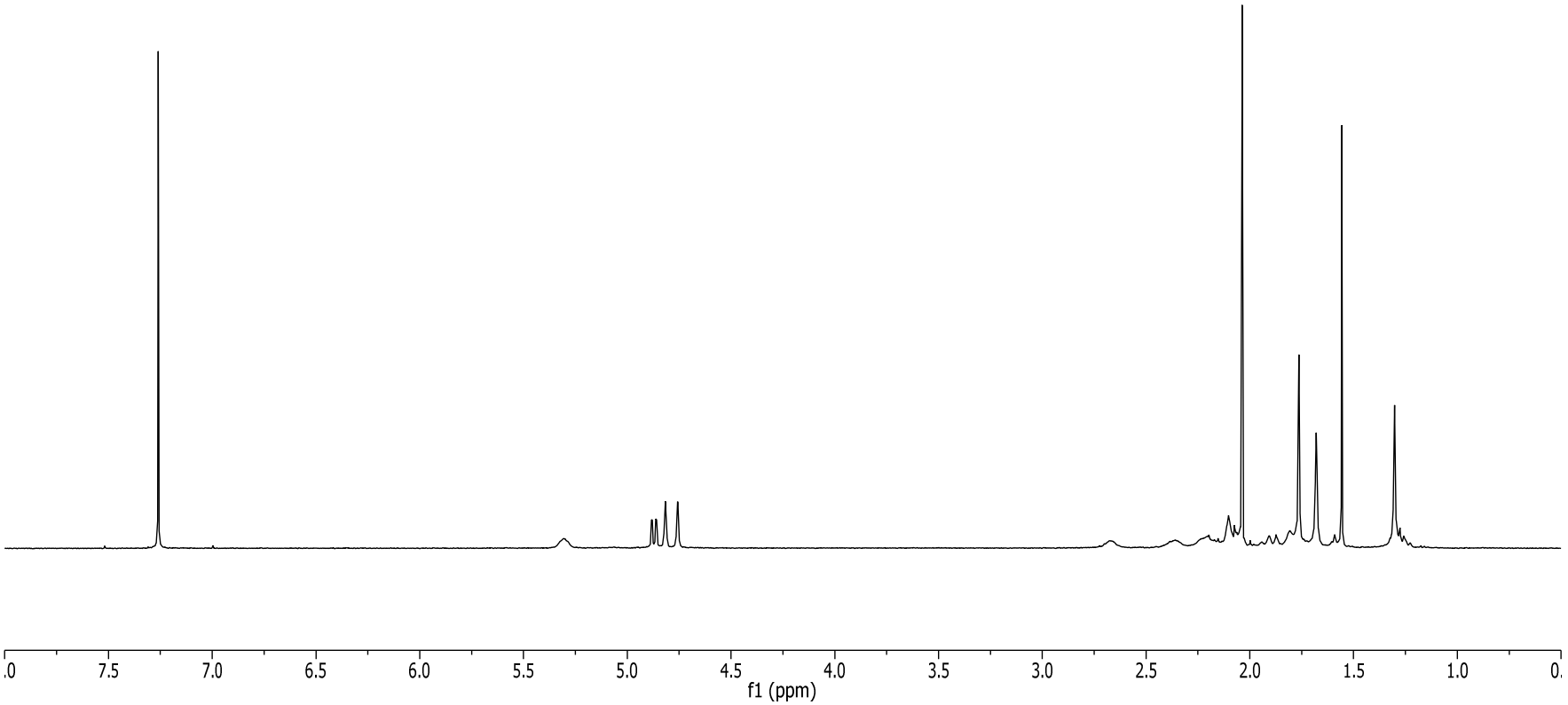
^{13}C NMR (125 MHz, $CDCl_3$, –30 ºC)

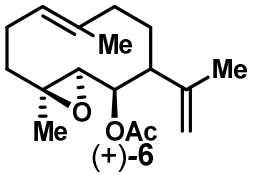




(+)-6

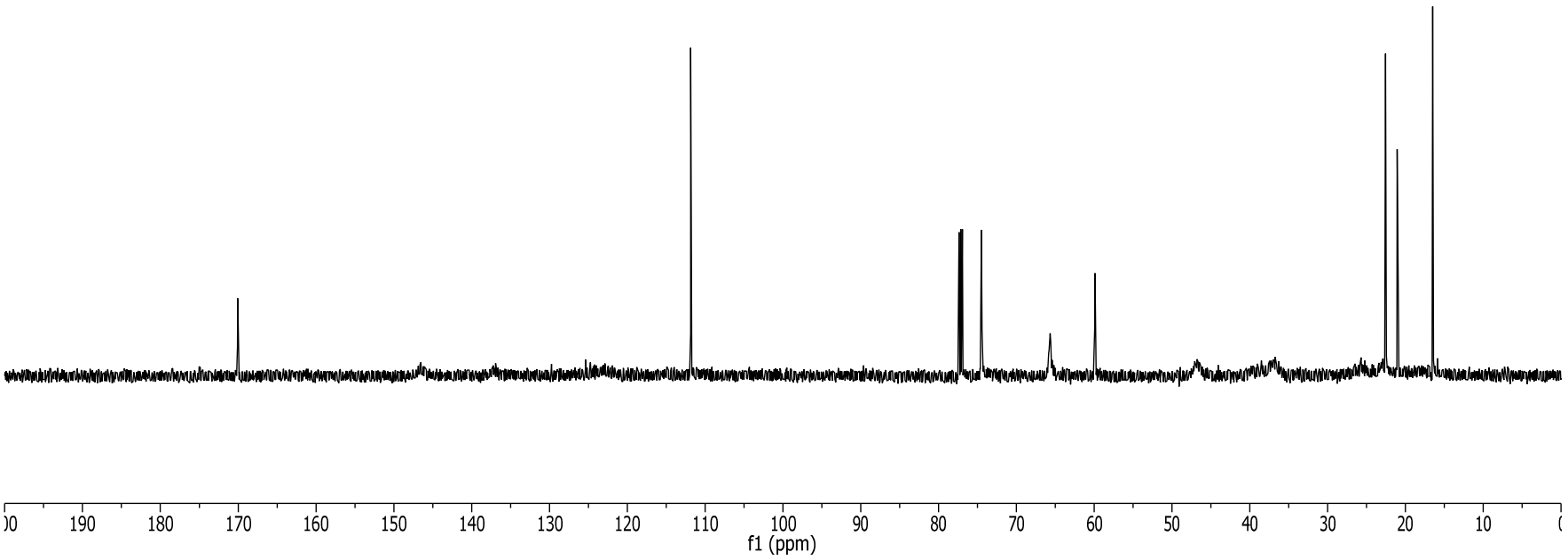
^{1}H NMR (400 MHz, $CDCl_3$)

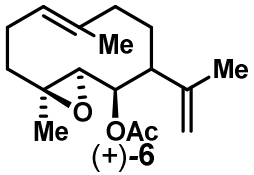




(+)-6

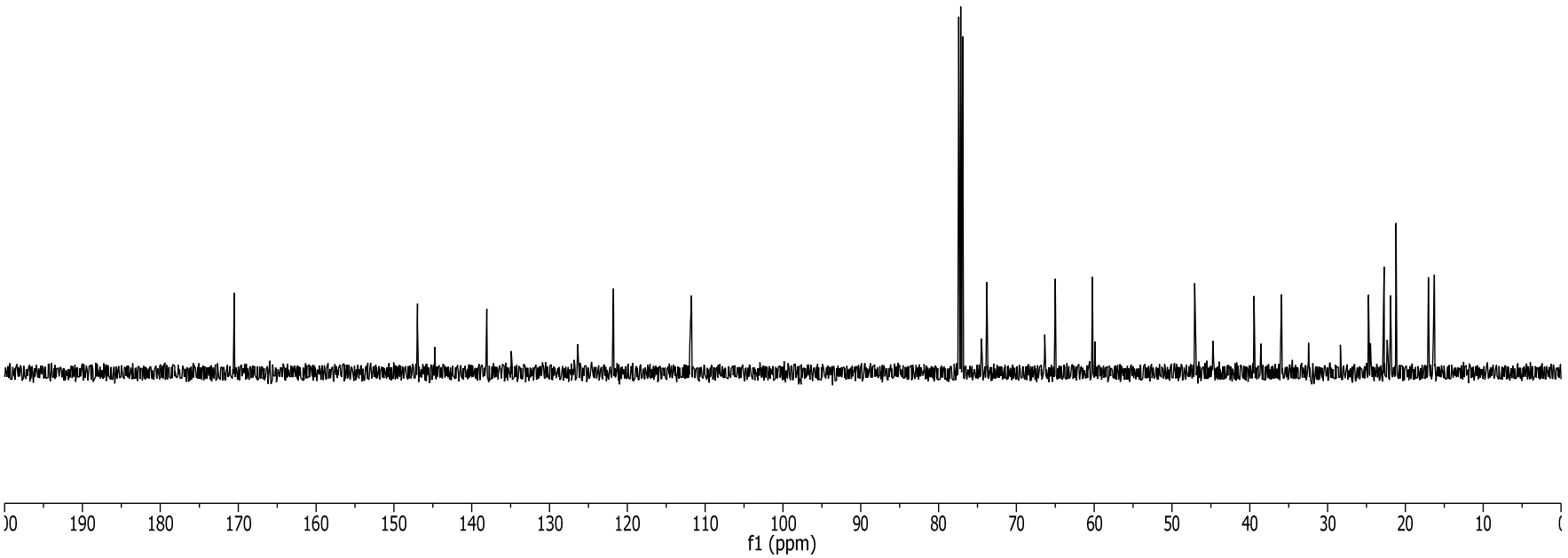
^{13}C NMR (150 MHz, $CDCl_3$, 25 °C)

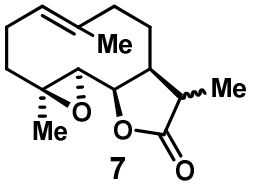




(+)-6

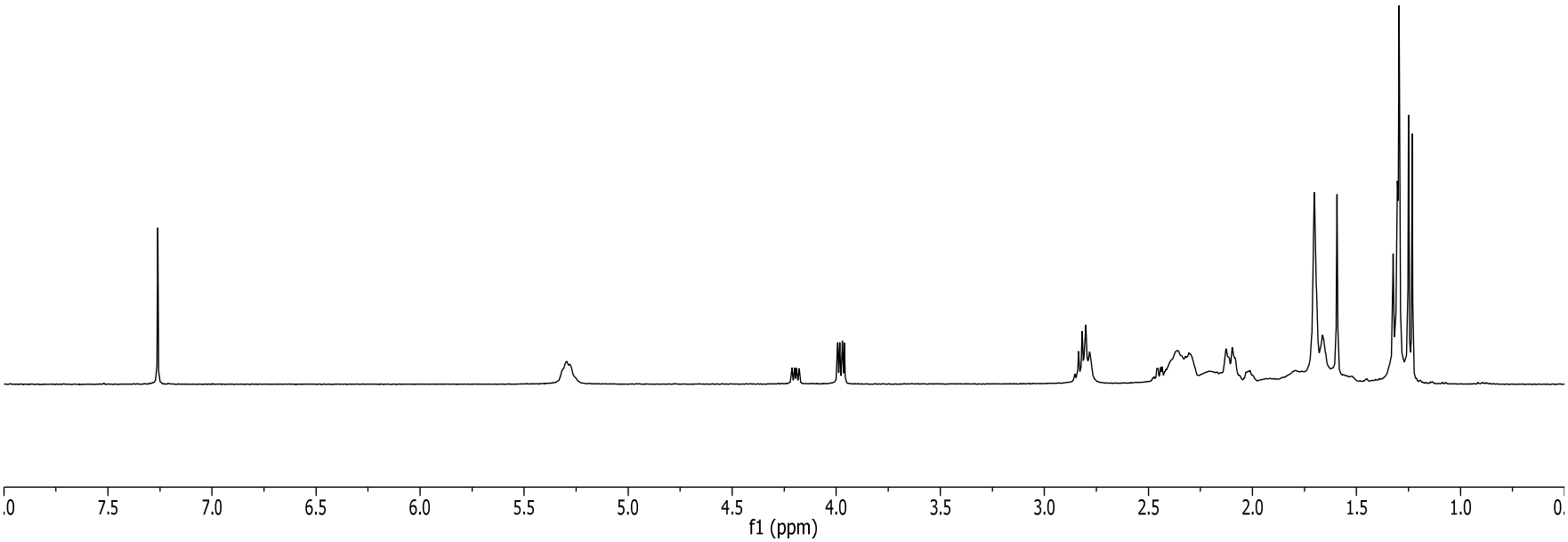
^{13}C NMR (125 MHz, $CDCl_3$, –30 °C)

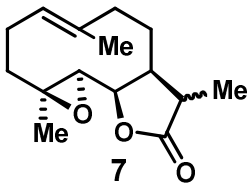




7

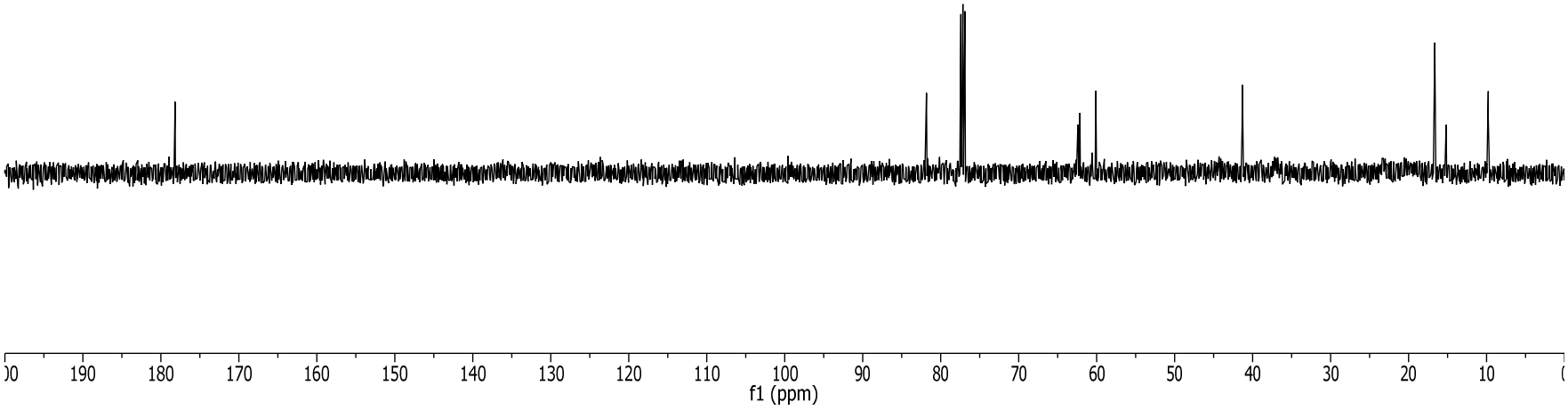
^{1}H NMR (400 MHz, $CDCl_3$)

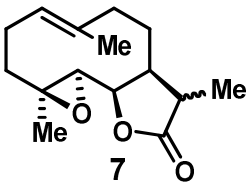




7

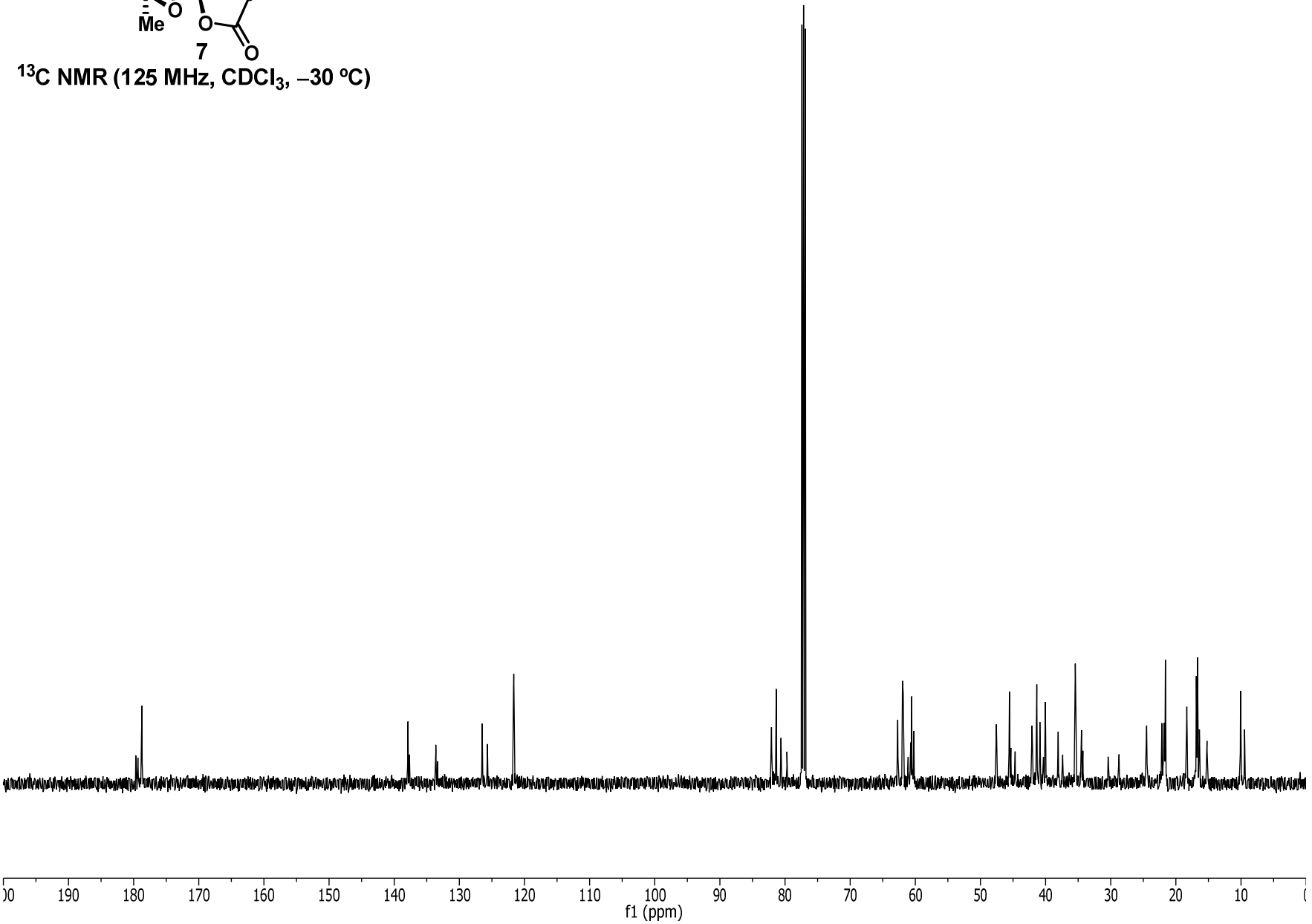
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C)

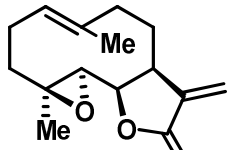




7

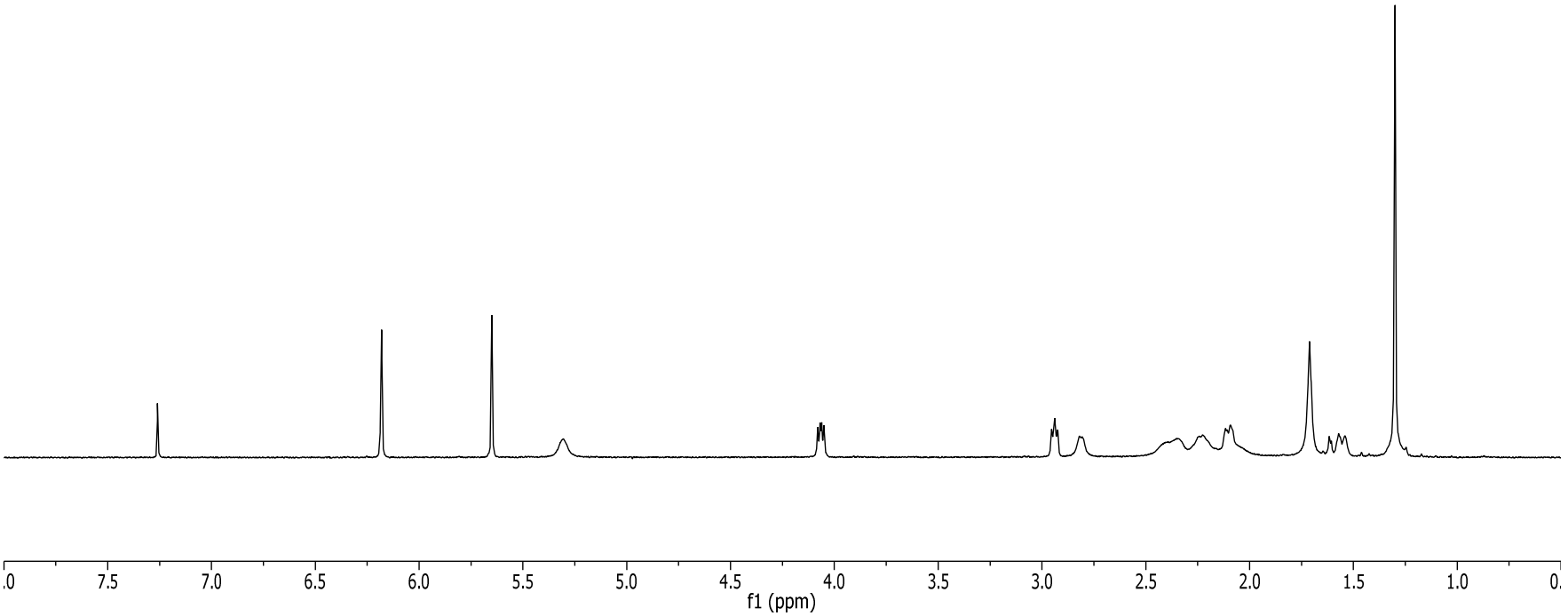
^{13}C NMR (125 MHz, $CDCl_3$, –30 °C)

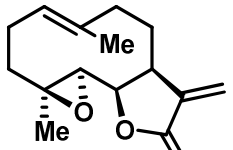




(–)-8

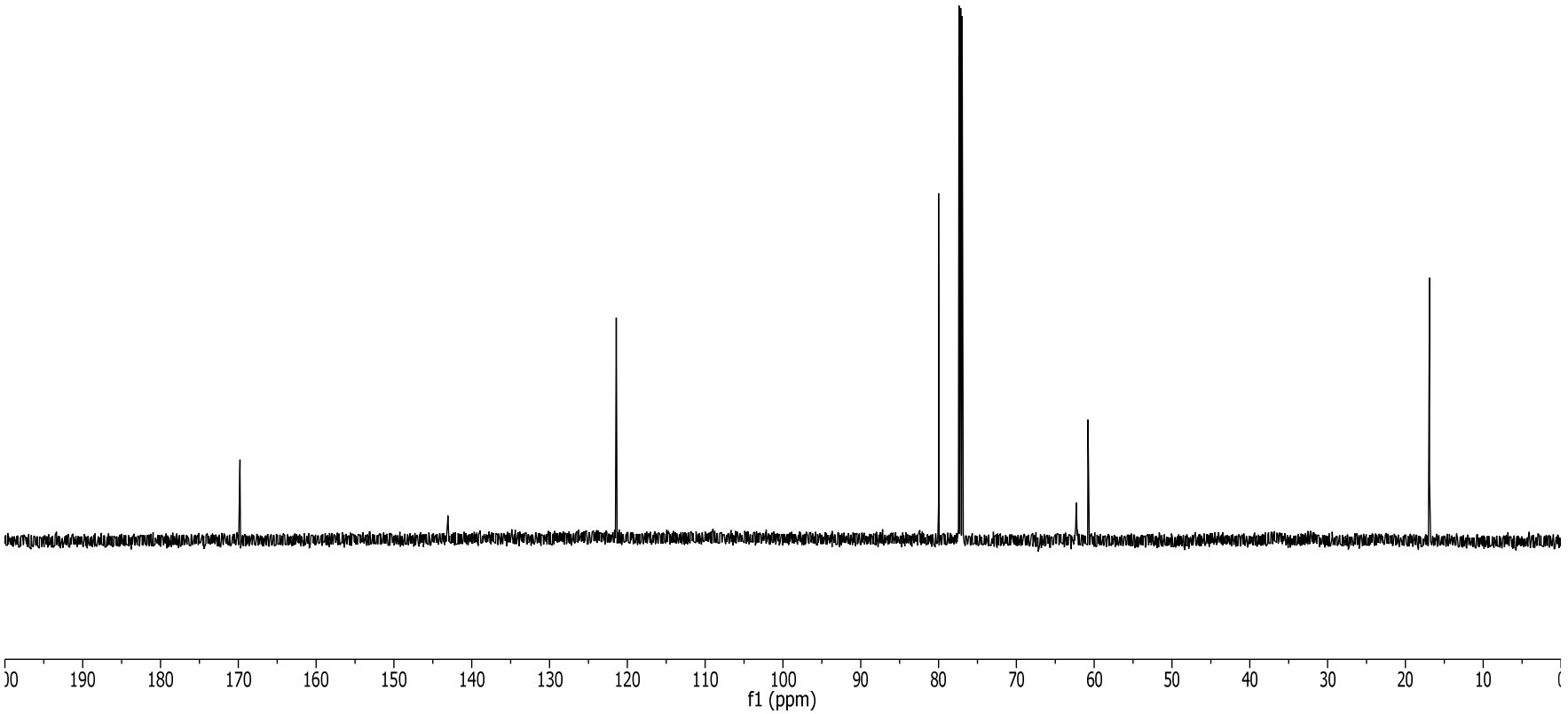
^{1}H NMR (500 MHz, $CDCl_3$)

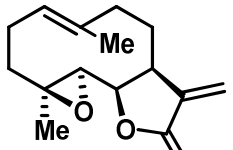




(–)-**8**

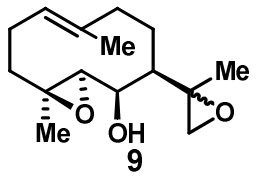
^{13}C NMR (150 MHz, $CDCl_3$, 25 °C)





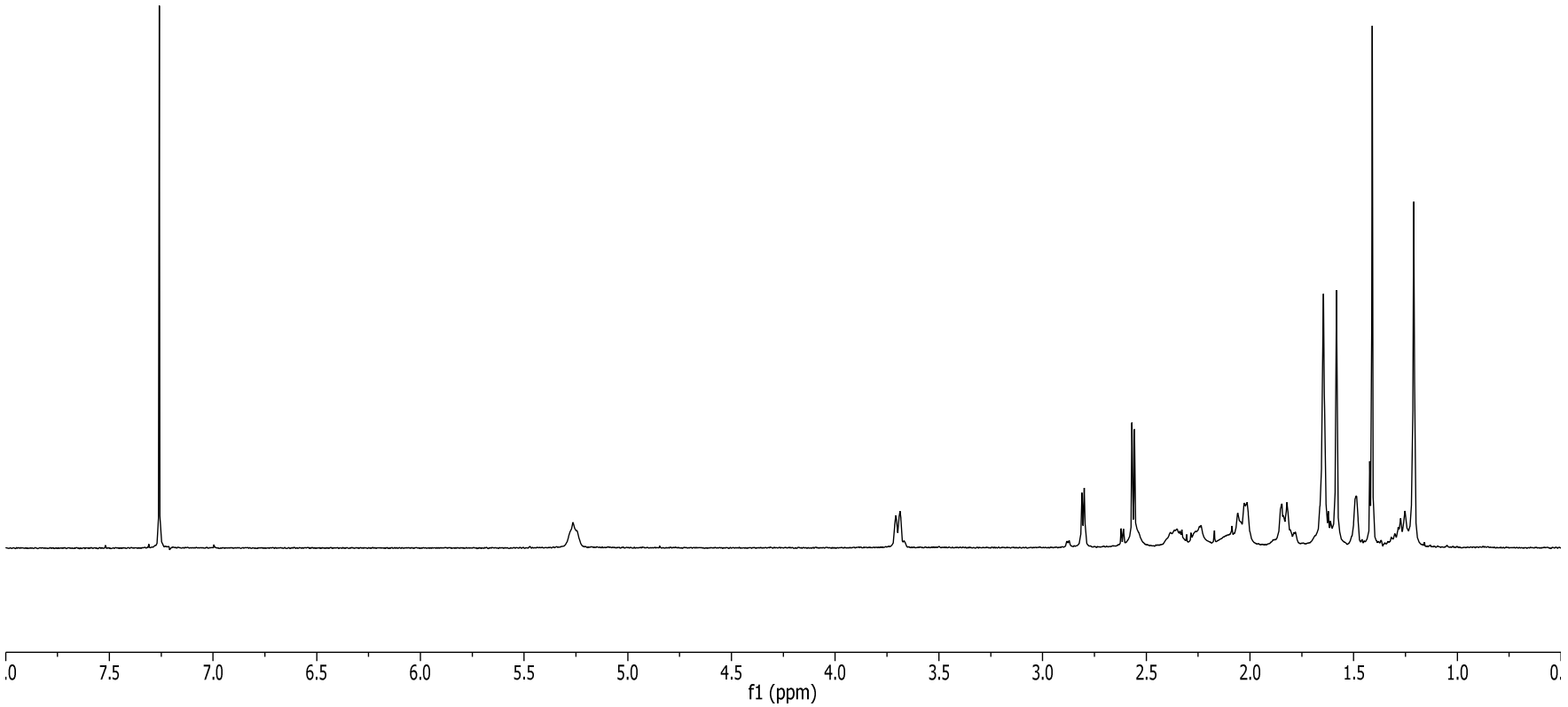
(–)-8

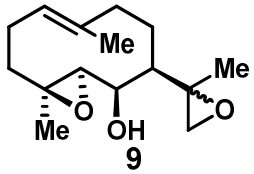
^{13}C NMR (125 MHz, $CDCl_3$, –30 °C)



9

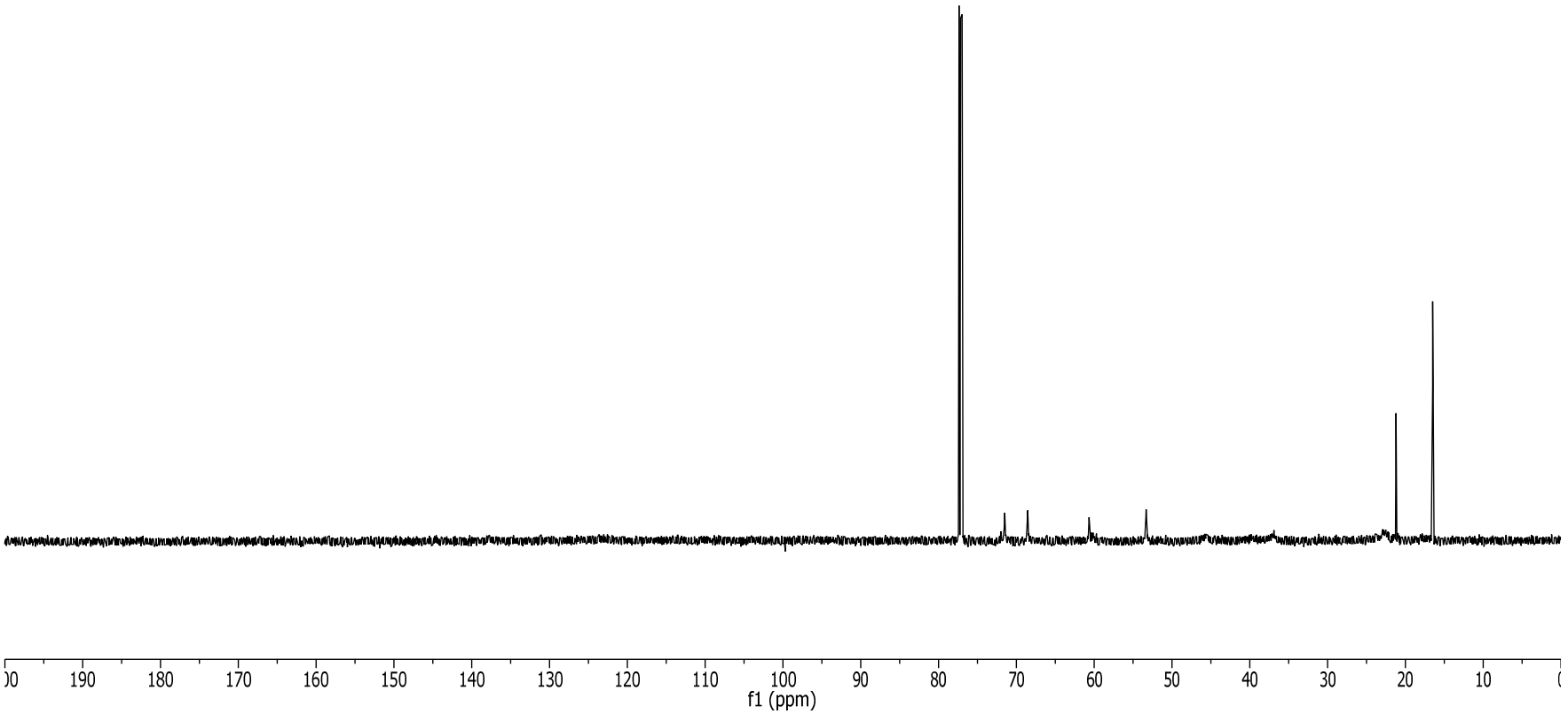
^{1}H NMR (400 MHz, $CDCl_3$)

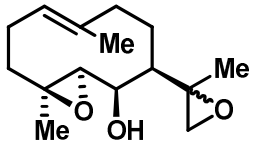




9

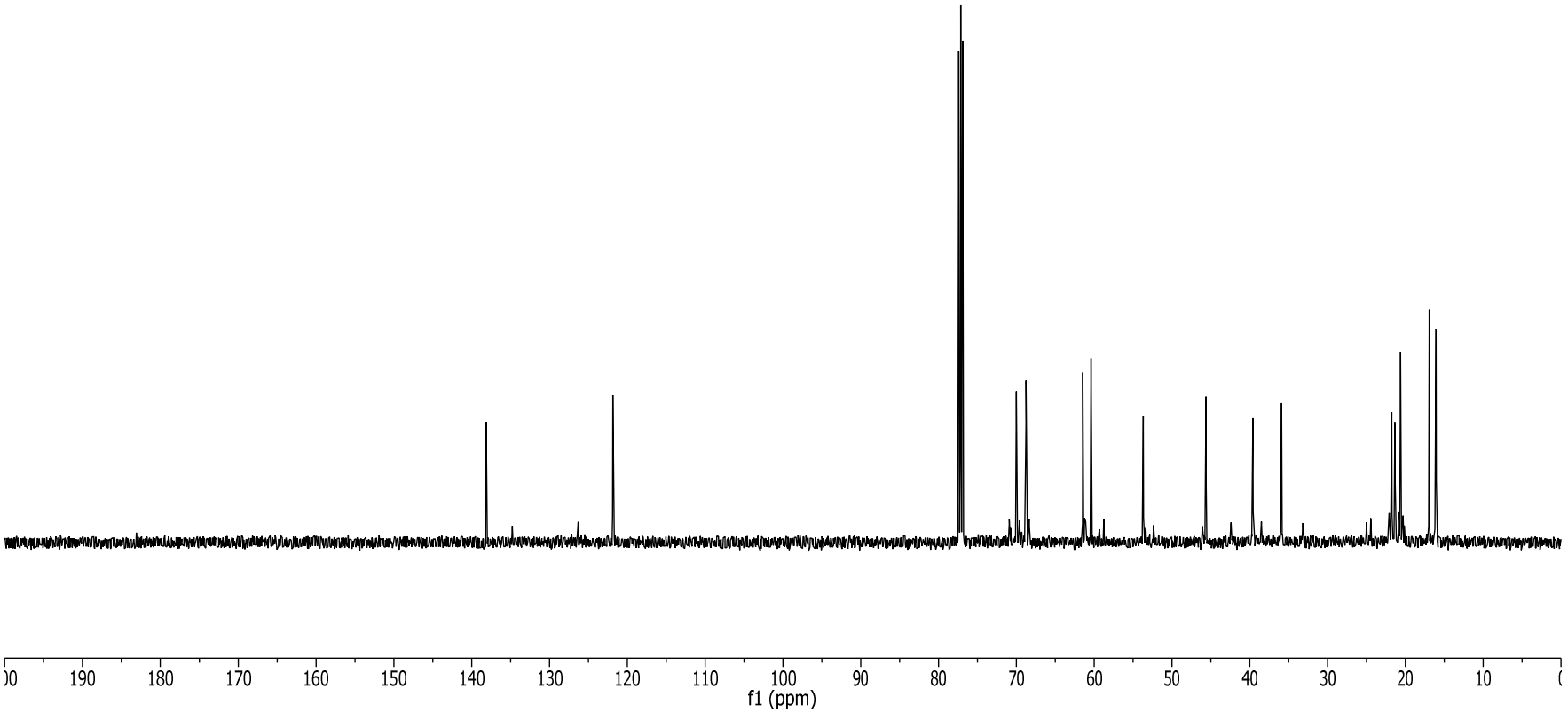
^{13}C NMR (150 MHz, $CDCl_3$, 25 °C)

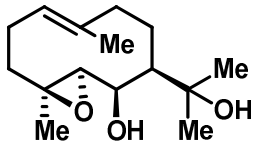




9

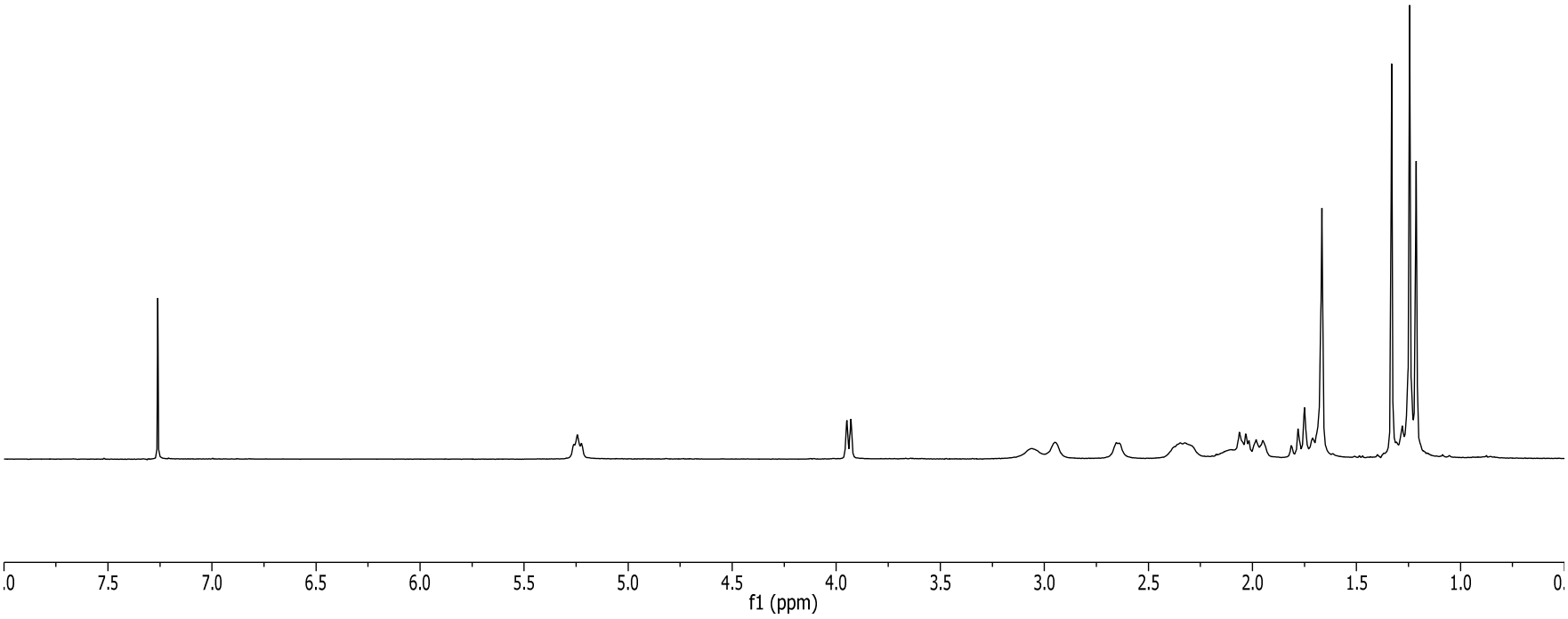
^{13}C NMR (125 MHz, $CDCl_3$, –30 °C)

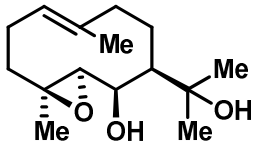




(+)-**10**

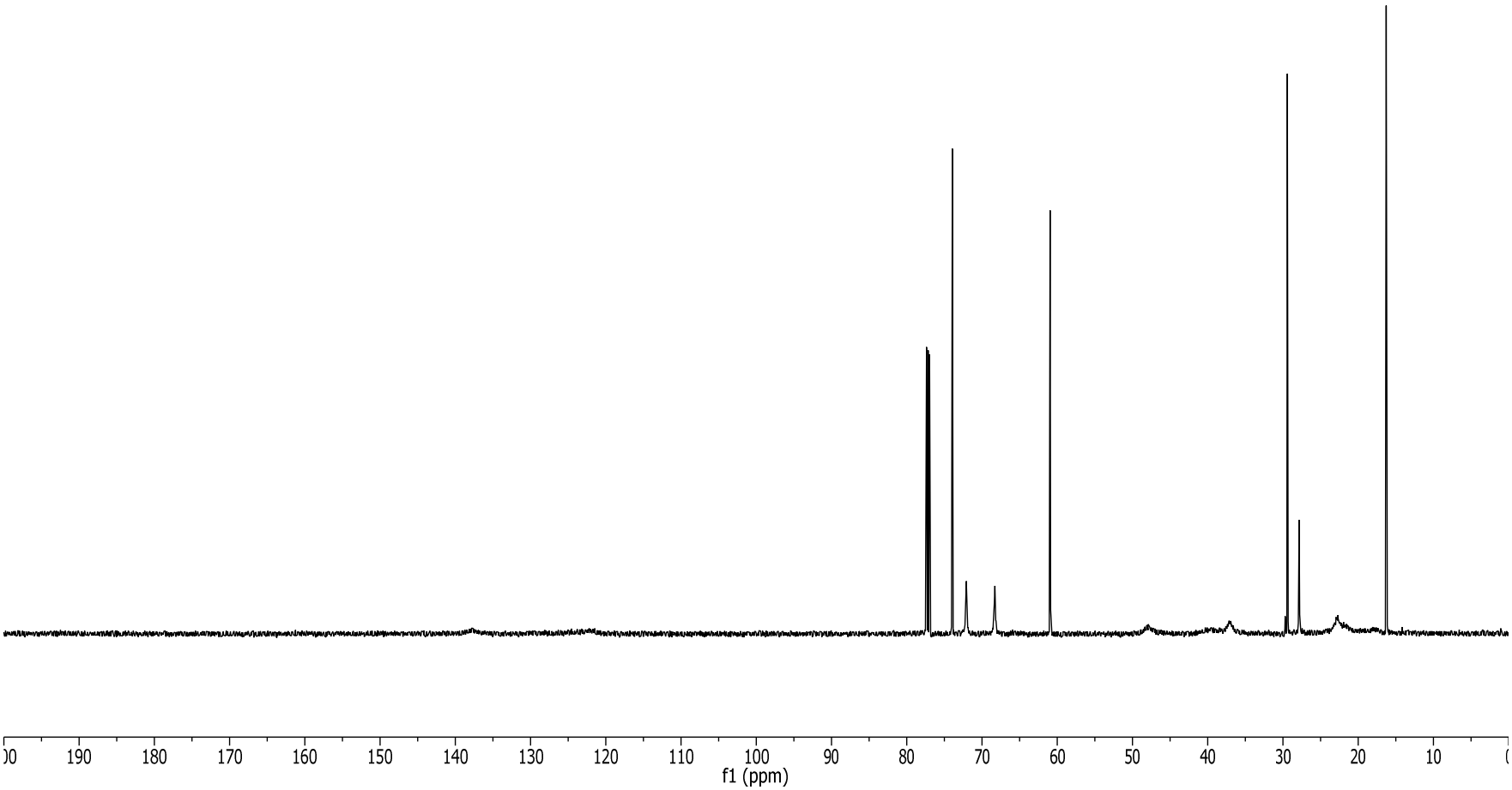
^{1}H NMR (400 MHz, $CDCl_3$)

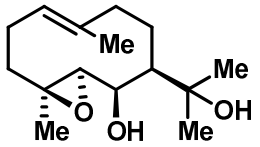




(+)-10

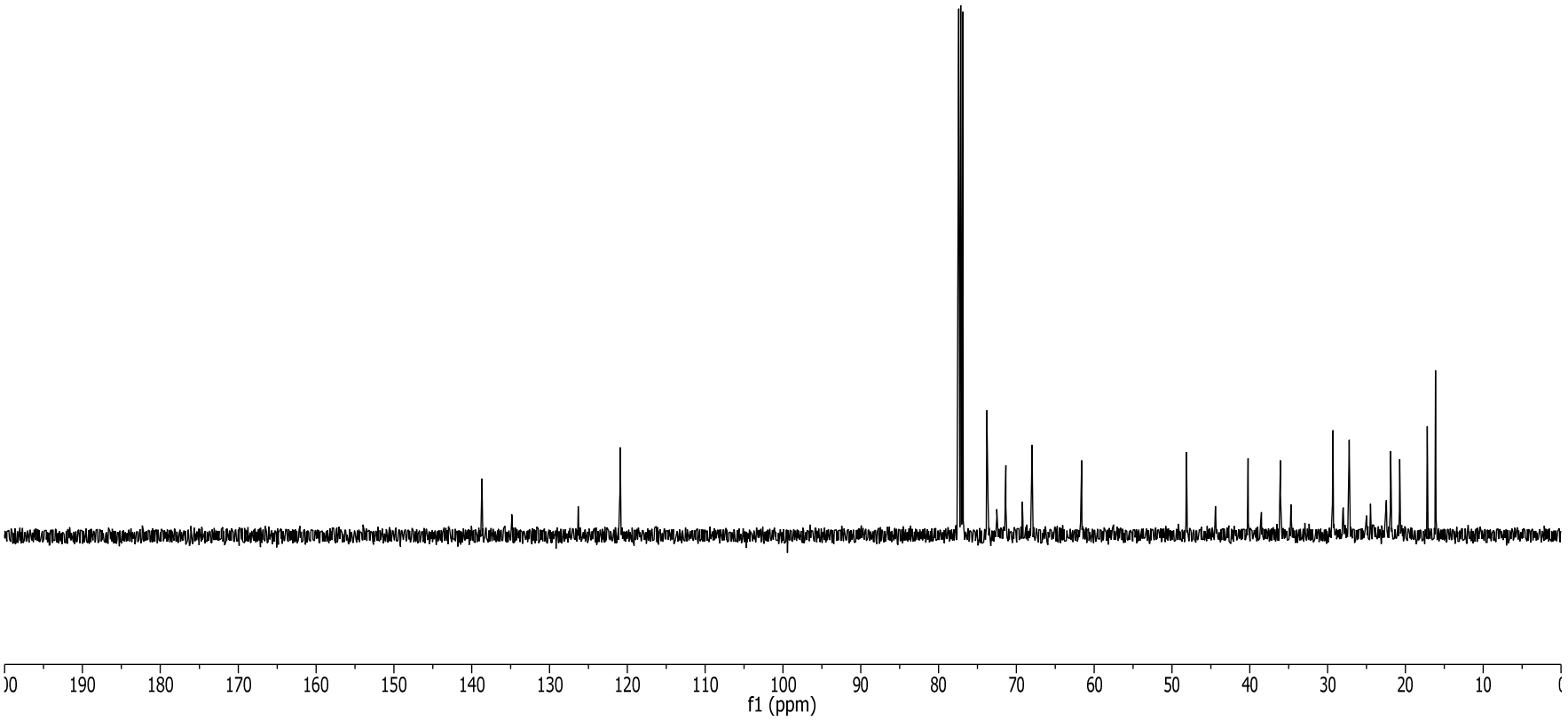
^{13}C NMR (150 MHz, $CDCl_3$, 25 °C)

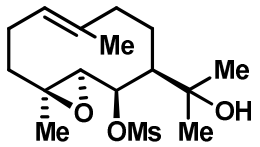




(+)-**10**

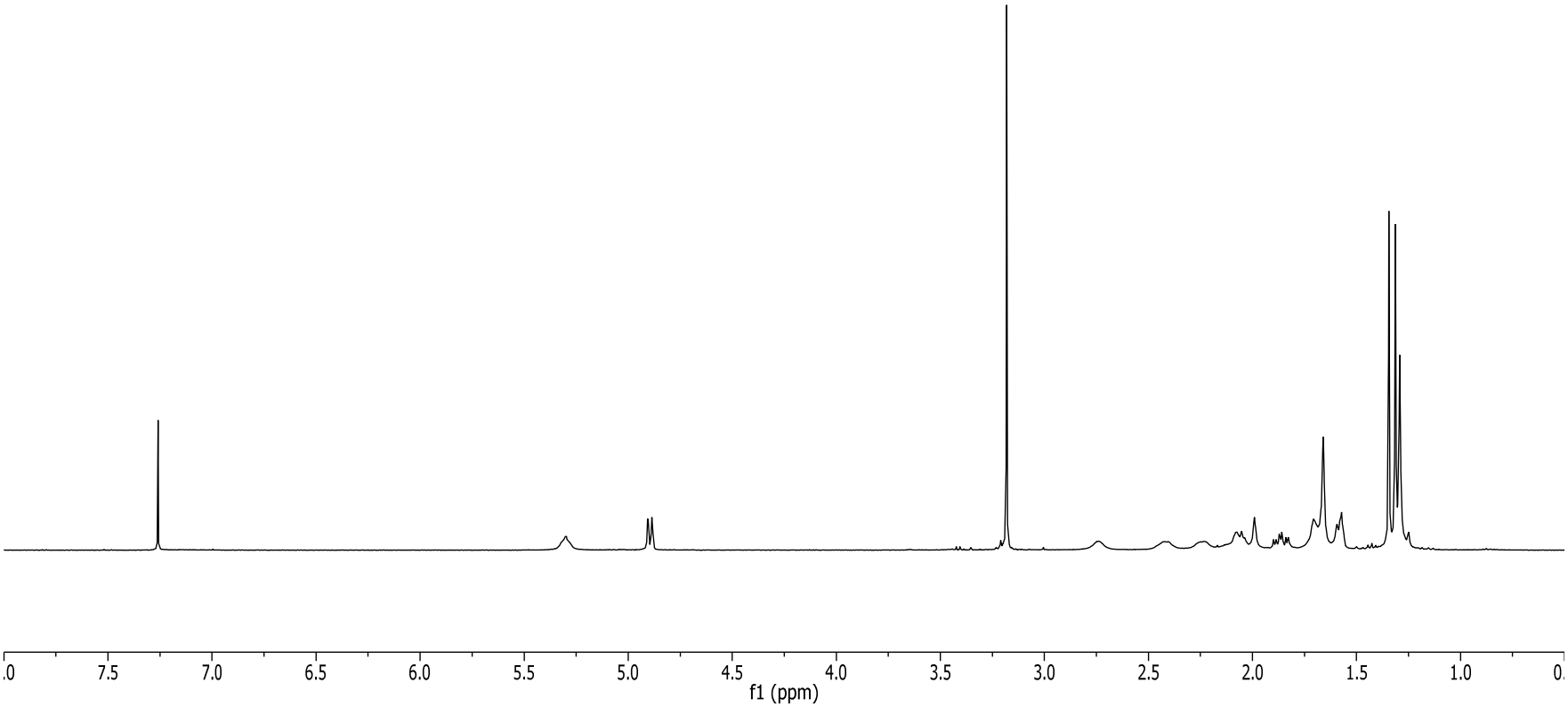
^{13}C NMR (125 MHz, $CDCl_3$, –30 °C)

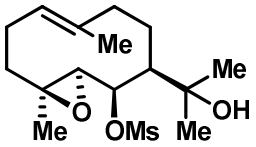




(+)-**11**

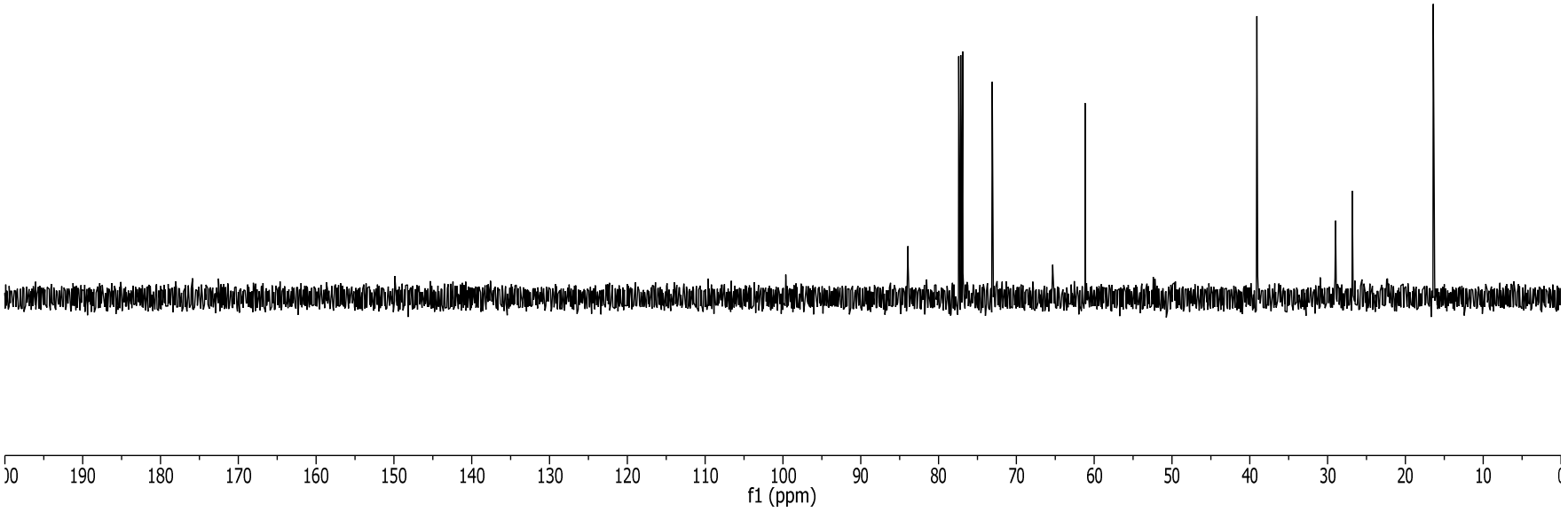
^{1}H NMR (400 MHz, $CDCl_3$)

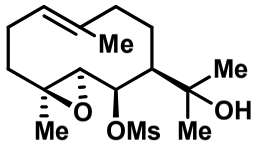




(+)-**11**

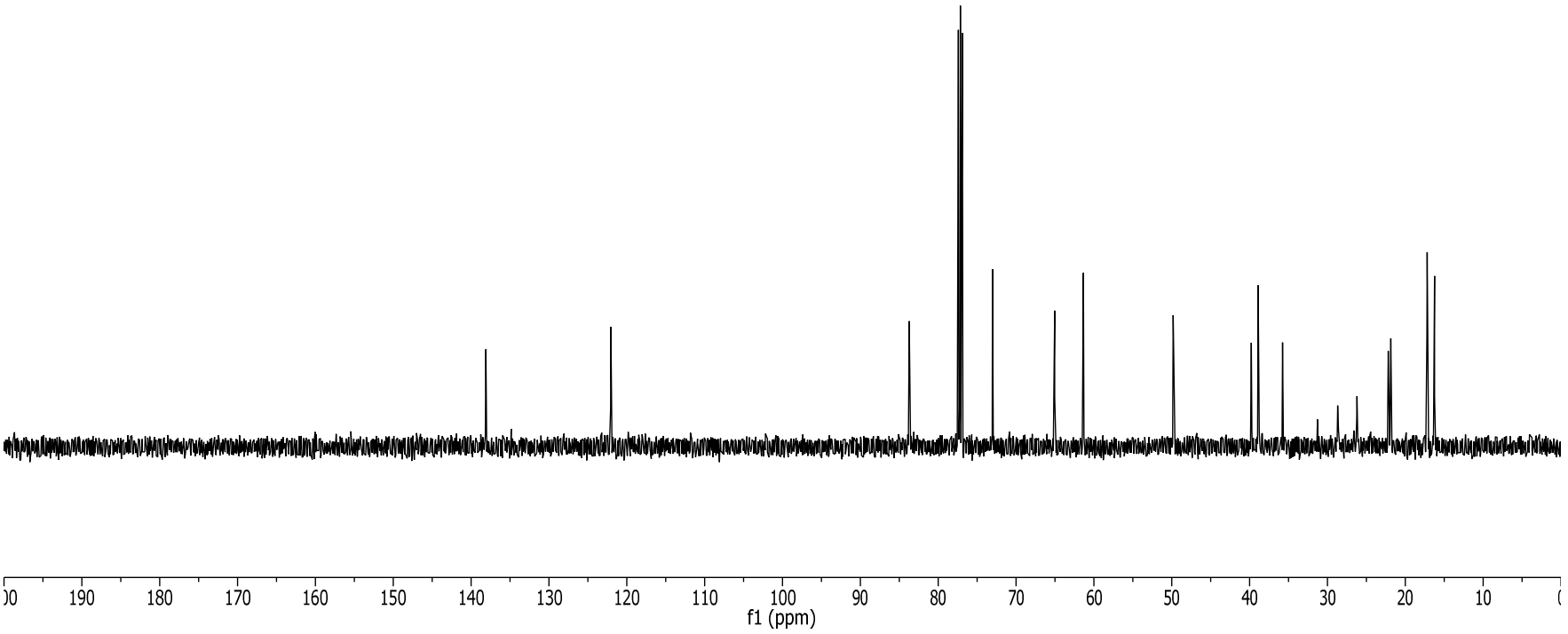
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C)

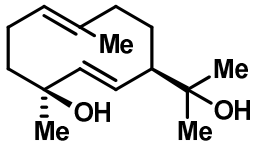




(+)-**11**

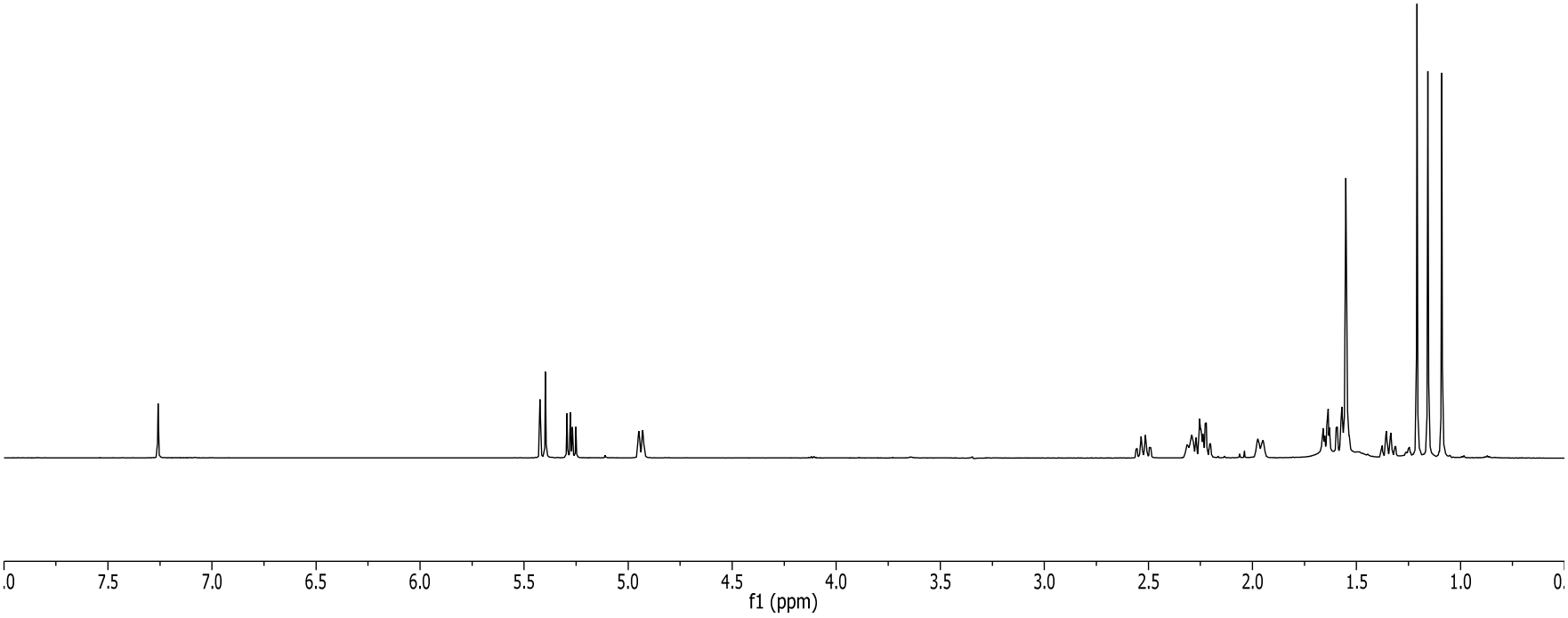
^{13}C NMR (125 MHz, $CDCl_3$, –30 ºC)

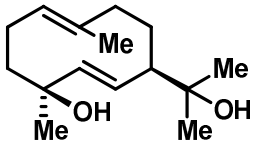




(–)-**12**

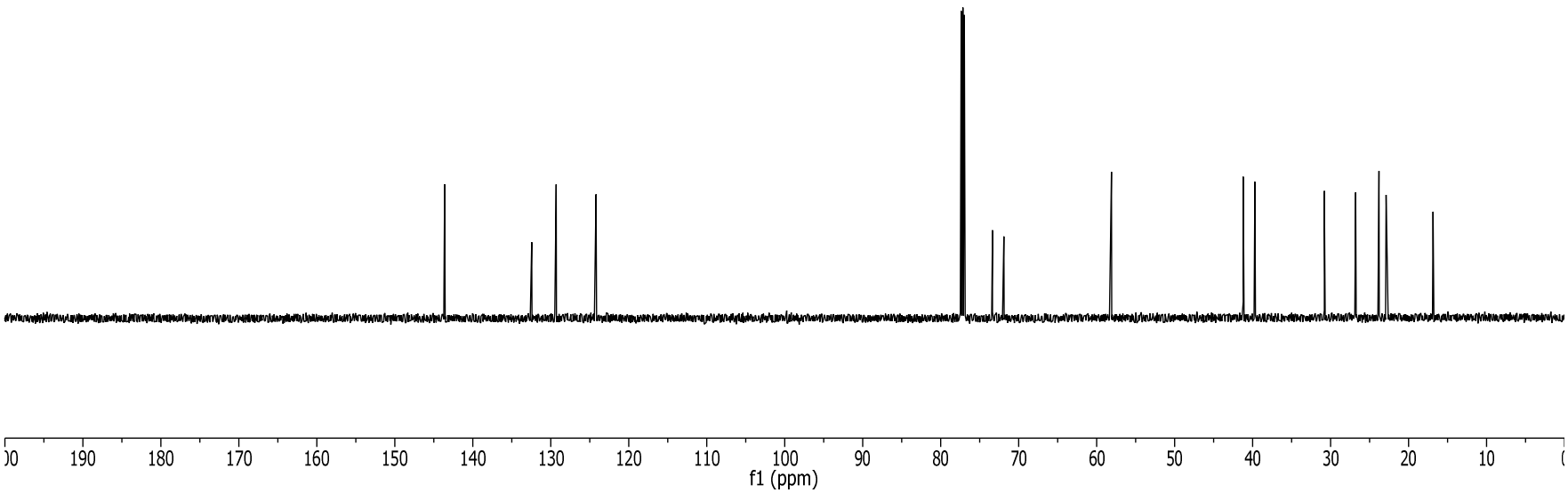
^{1}H NMR (600 MHz, $CDCl_3$)

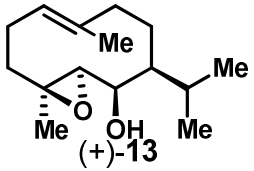




(–)-**12**

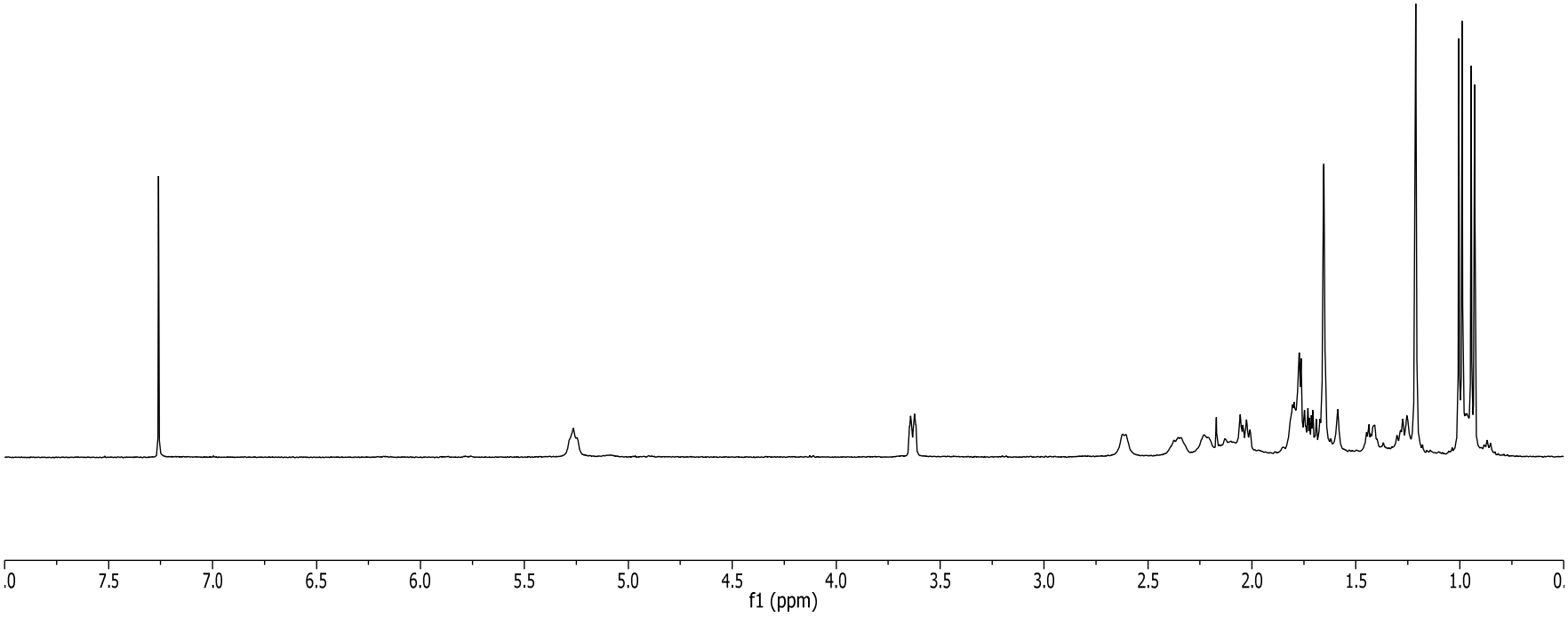
^{13}C NMR (150 MHz, $CDCl_3$)

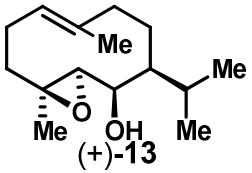




(+)-**13**

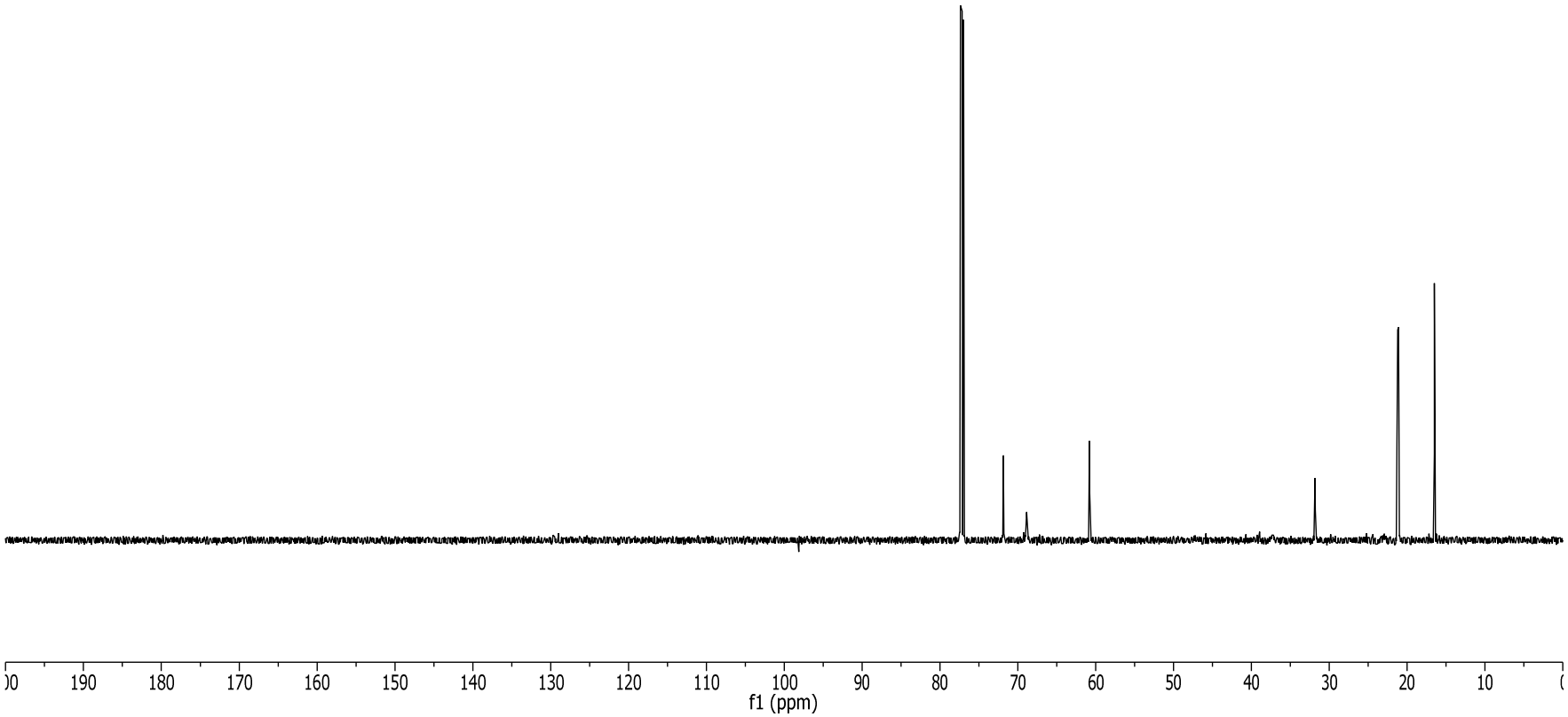
^{1}H NMR (400 MHz, $CDCl_3$)

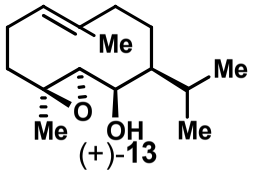




(+)-13

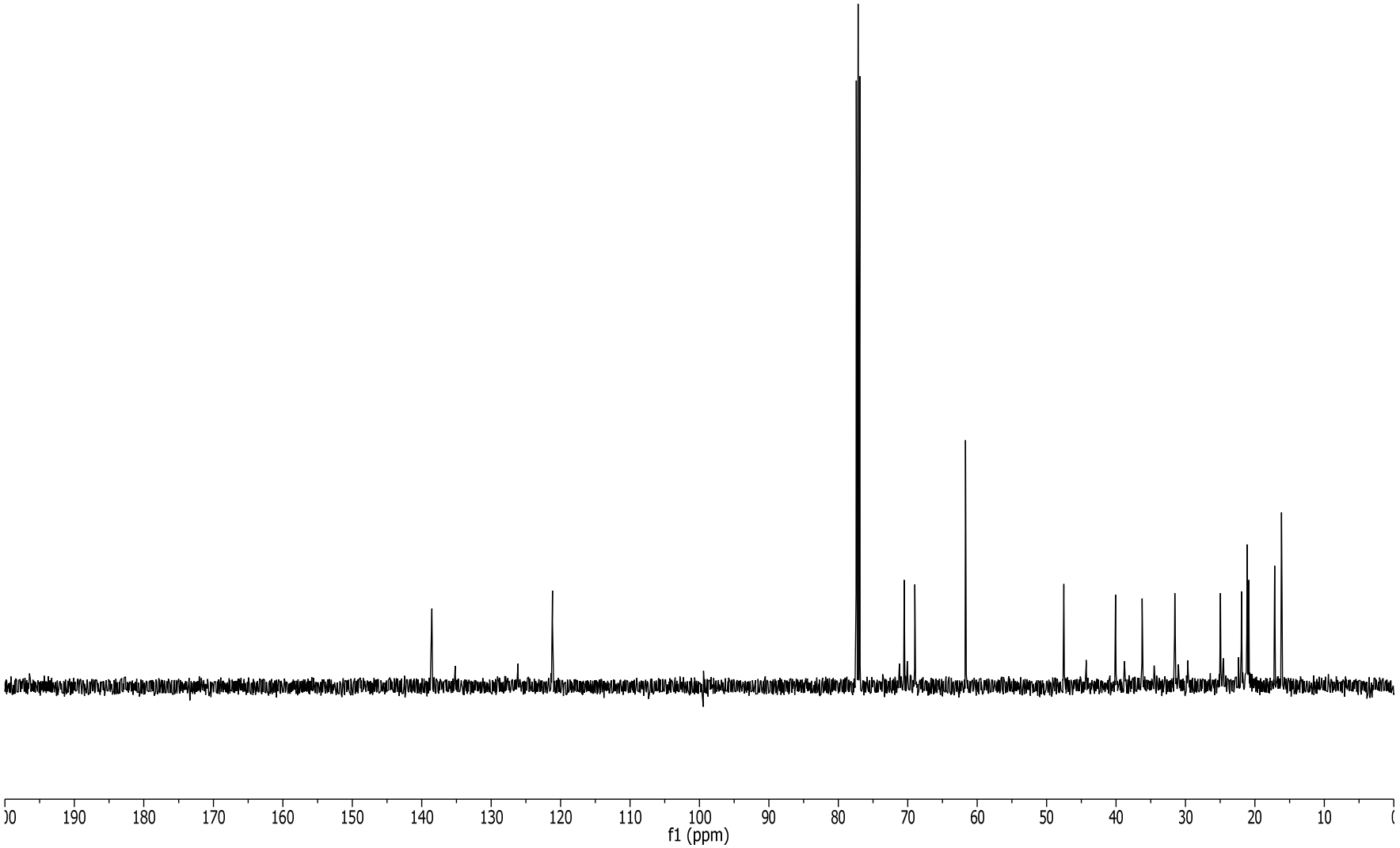
^{13}C NMR (150 MHz, $CDCl_3$, 25 °C)

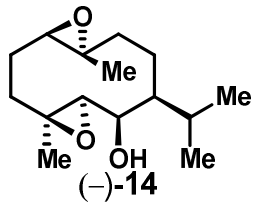




(+)-**13**

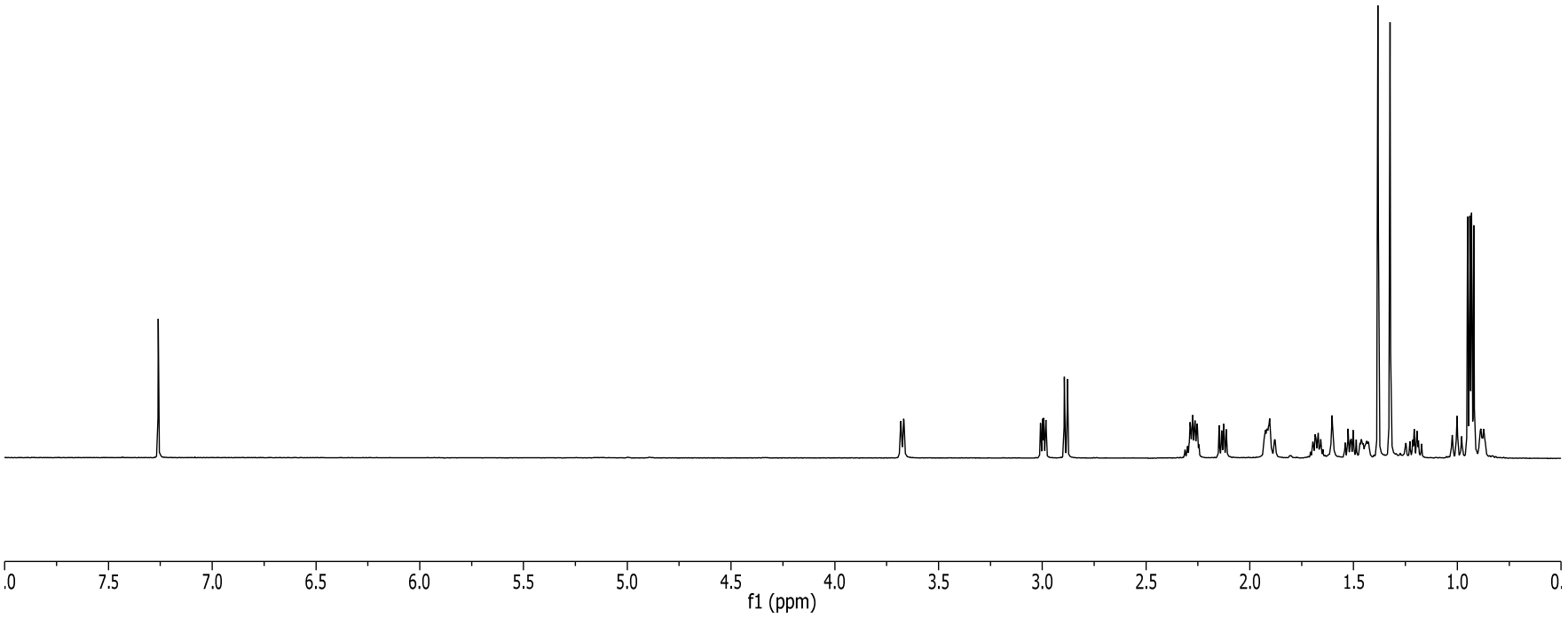
^{13}C NMR (125 MHz, $CDCl_3$, –30 °C)

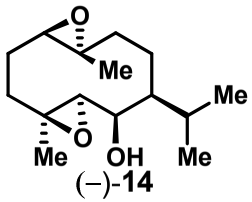




(–)-**14**

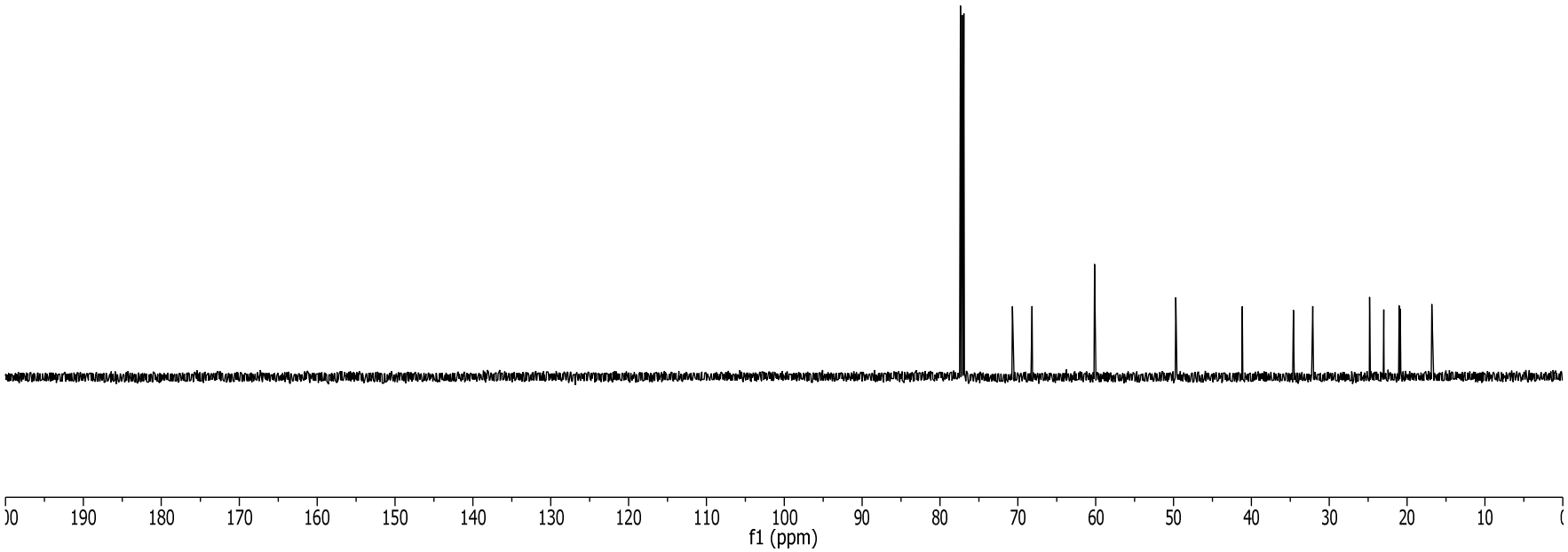
^{1}H NMR (600 MHz, $CDCl_3$)

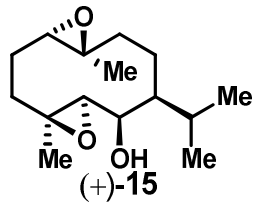




(–)-**14**

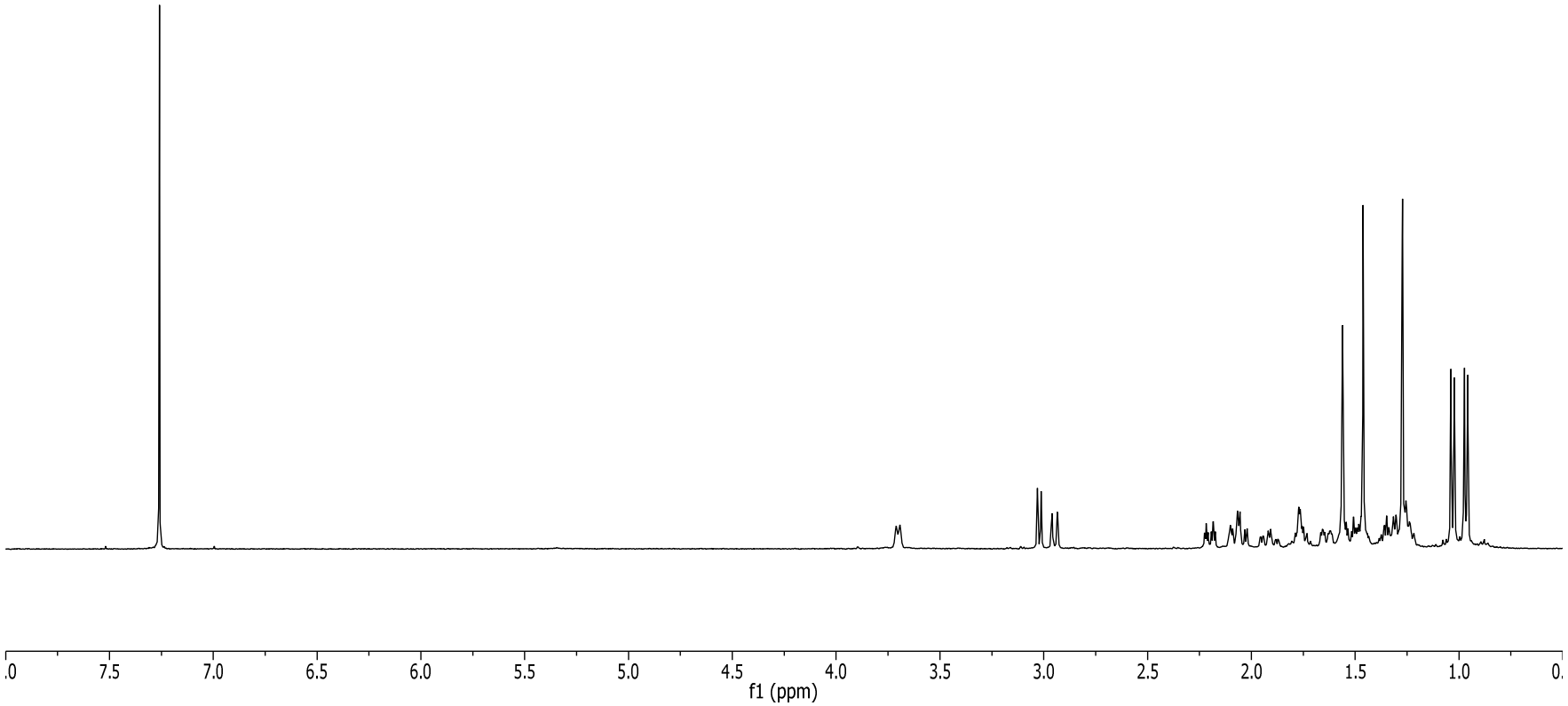
^{13}C NMR (150 MHz, $CDCl_3$)

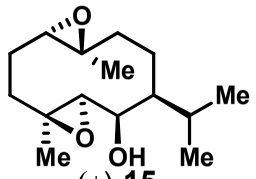




(+)-15

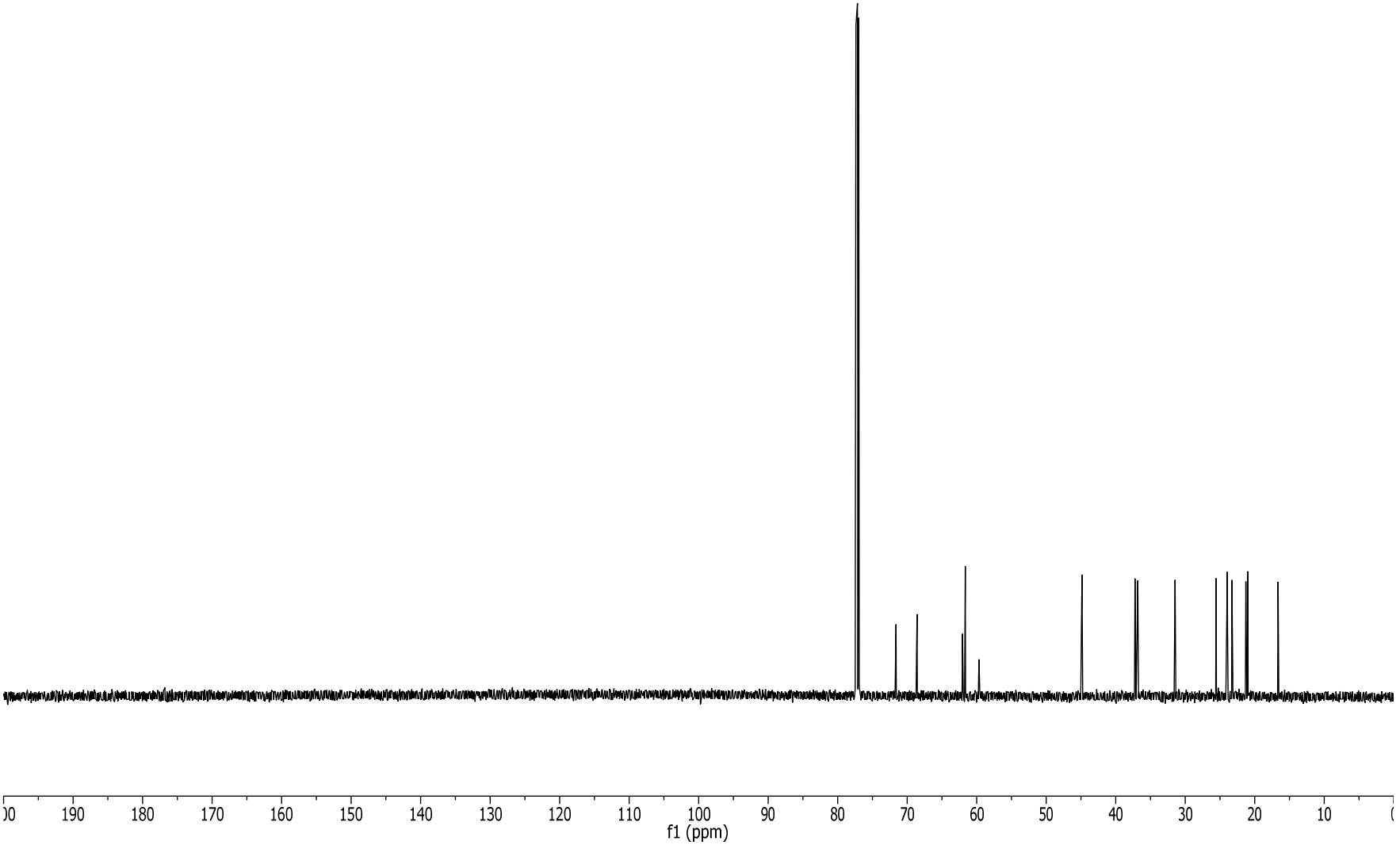
^{1}H NMR (400 MHz, $CDCl_3$)

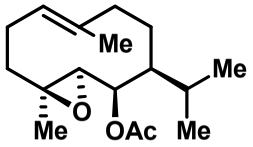




(+)-**15**

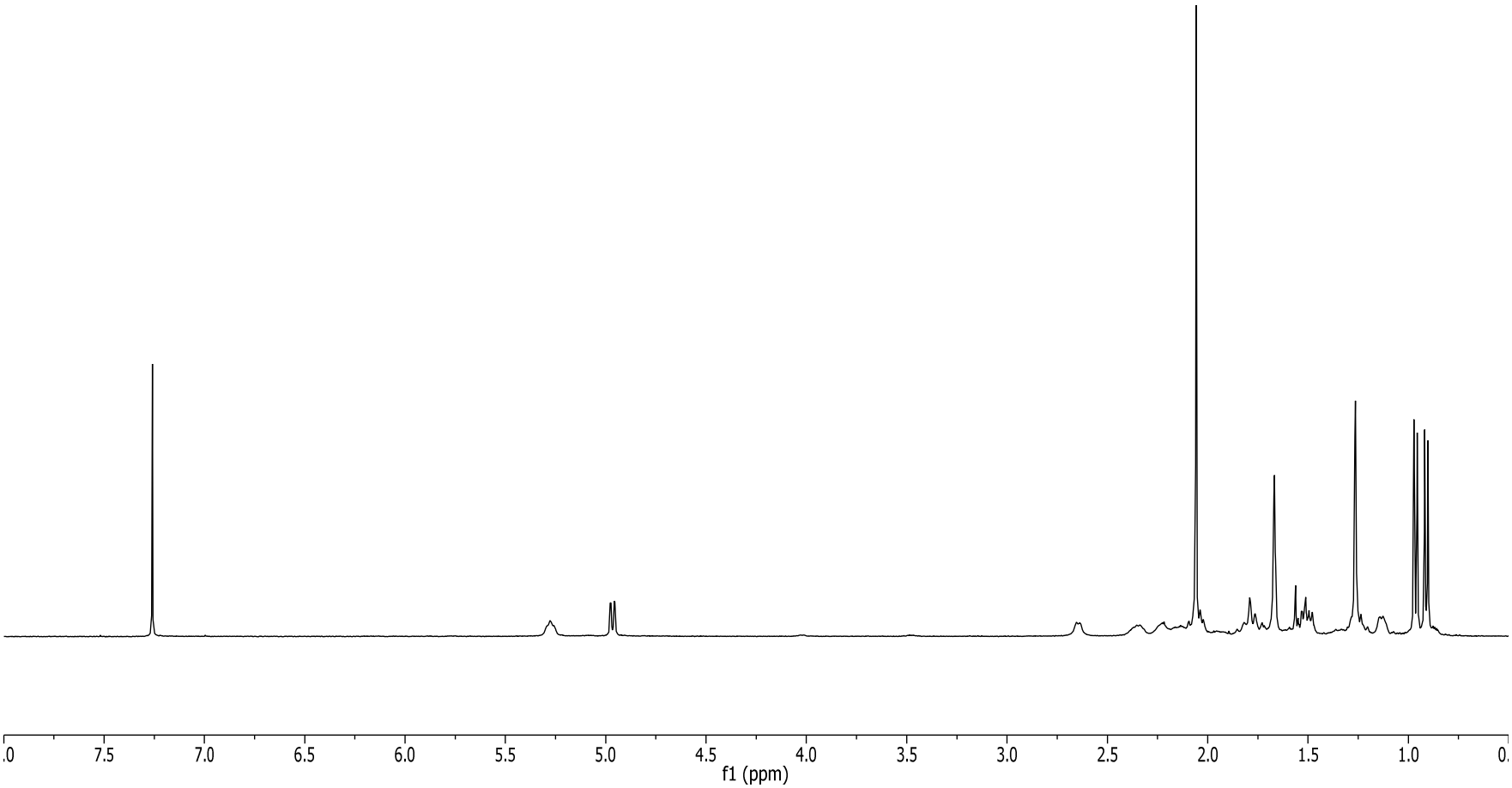
^{13}C NMR (150 MHz, $CDCl_3$)

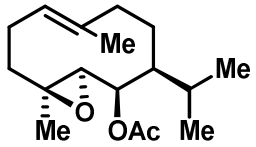




(+)-**16**

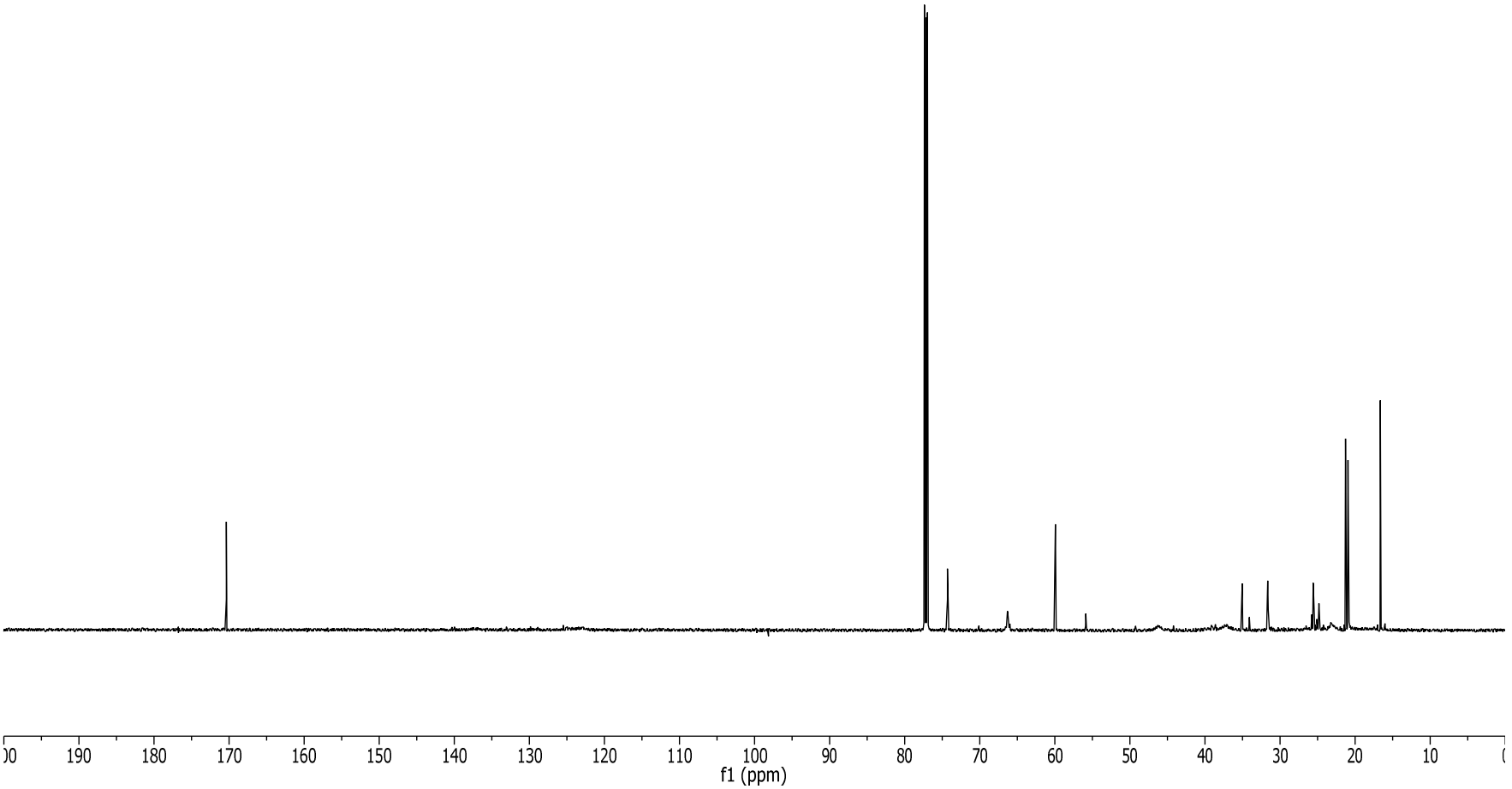
^{1}H NMR (400 MHz, $CDCl_3$)

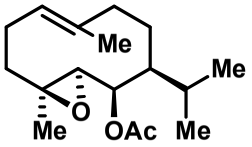




(+)-**16**

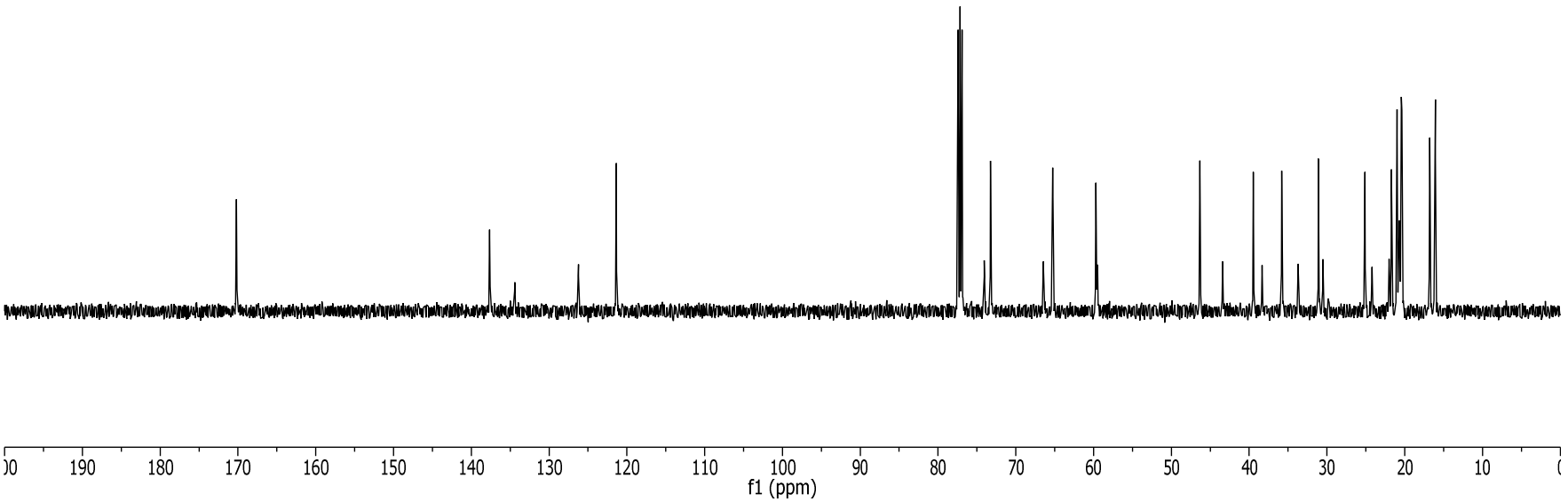
^{13}C NMR (150 MHz, $CDCl_3$, 25 °C)

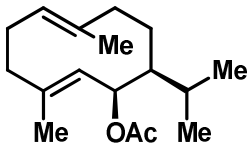




(+)-**16**

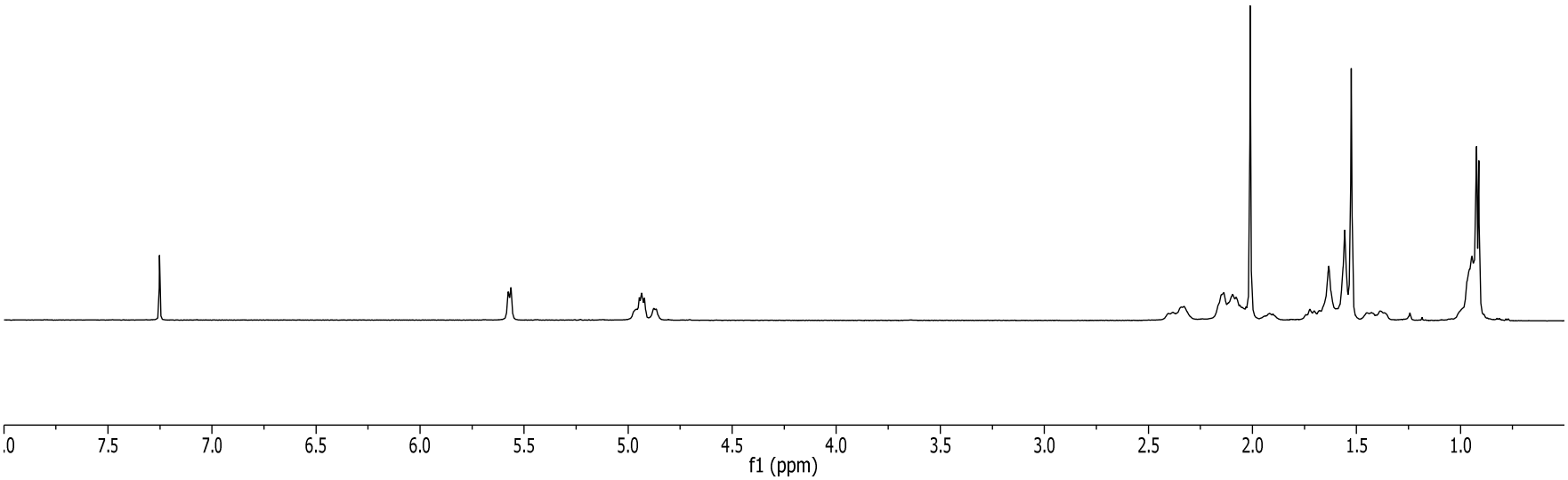
^{13}C NMR (125 MHz, $CDCl_3$, –30 °C)

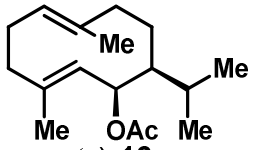




(–)-16a

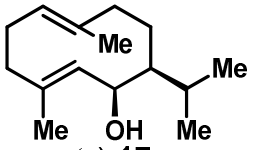
^{1}H NMR (600 MHz, $CDCl_3$)





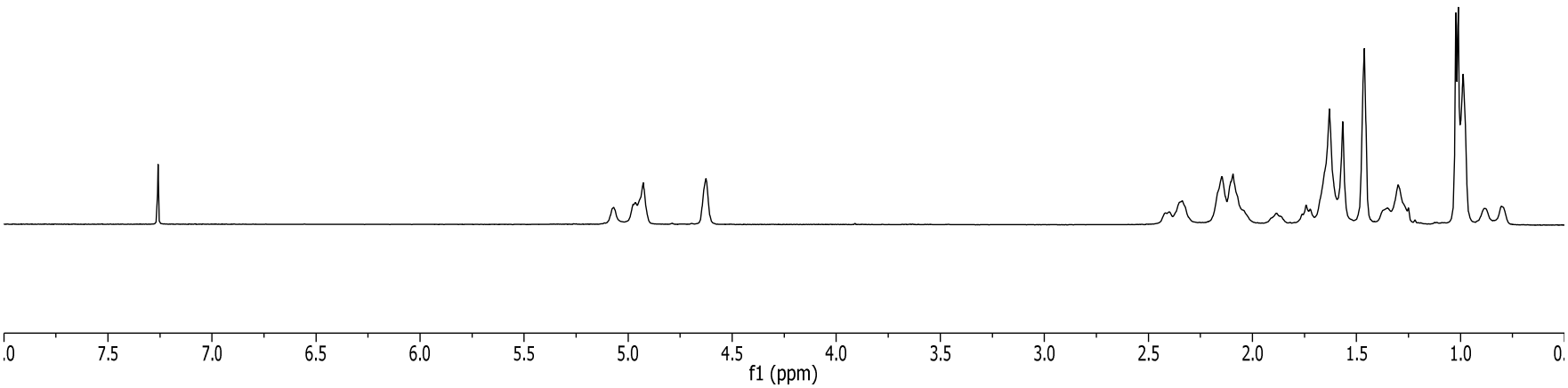
(–)-**16a**

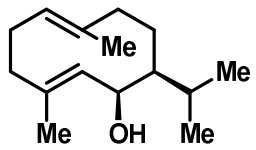
^{13}C NMR (150 MHz, $CDCl_3$)



(–)-**17**

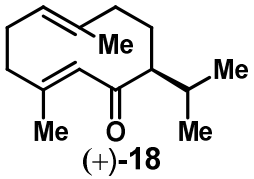
^{1}H NMR (600 MHz, $CDCl_3$)





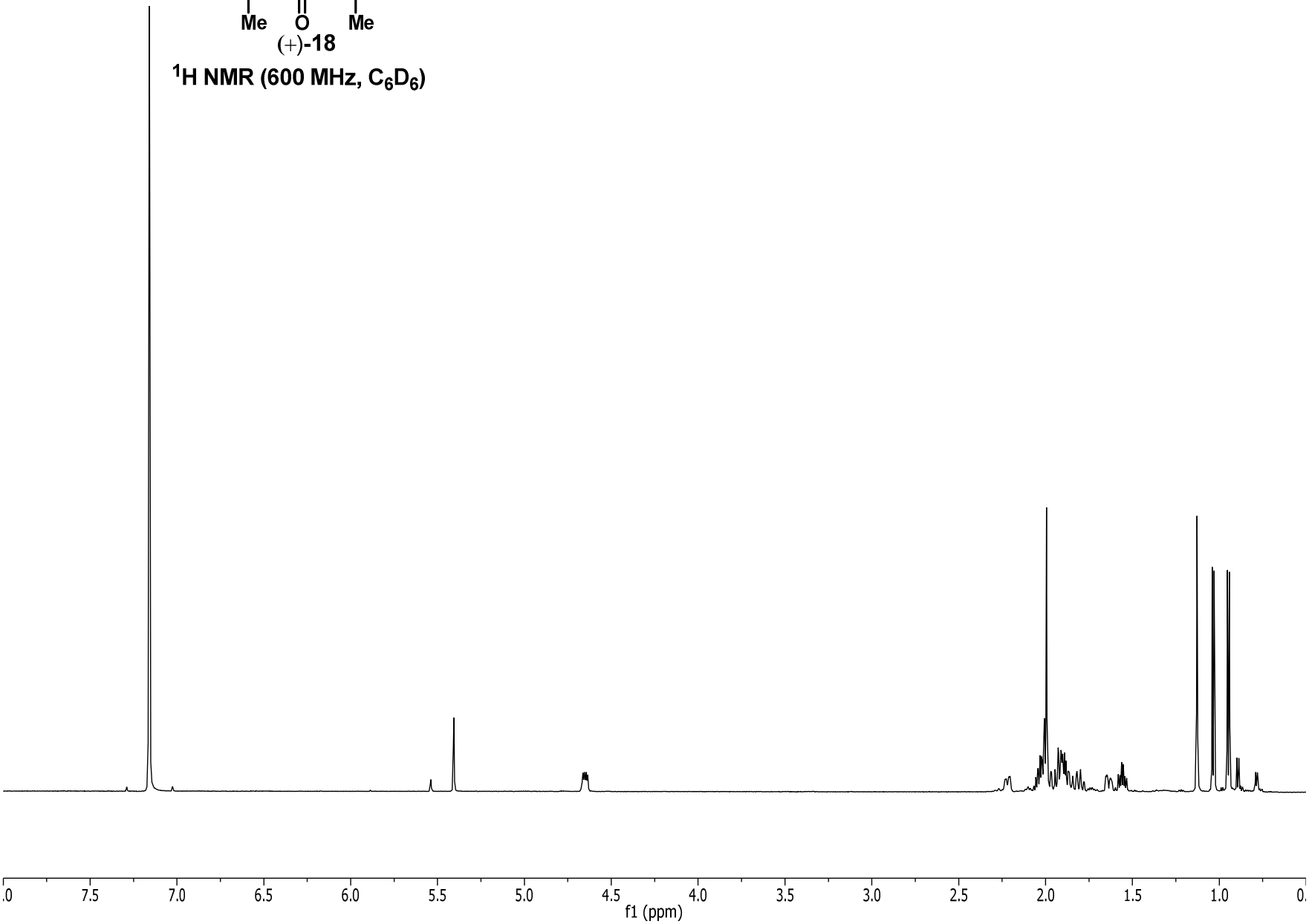
(–)-**17**

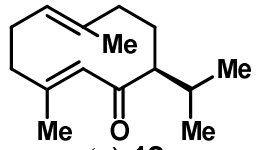
^{13}C NMR (150 MHz, $CDCl_3$)



(+)-18

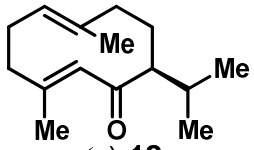
^{1}H NMR (600 MHz, C_6D_6)





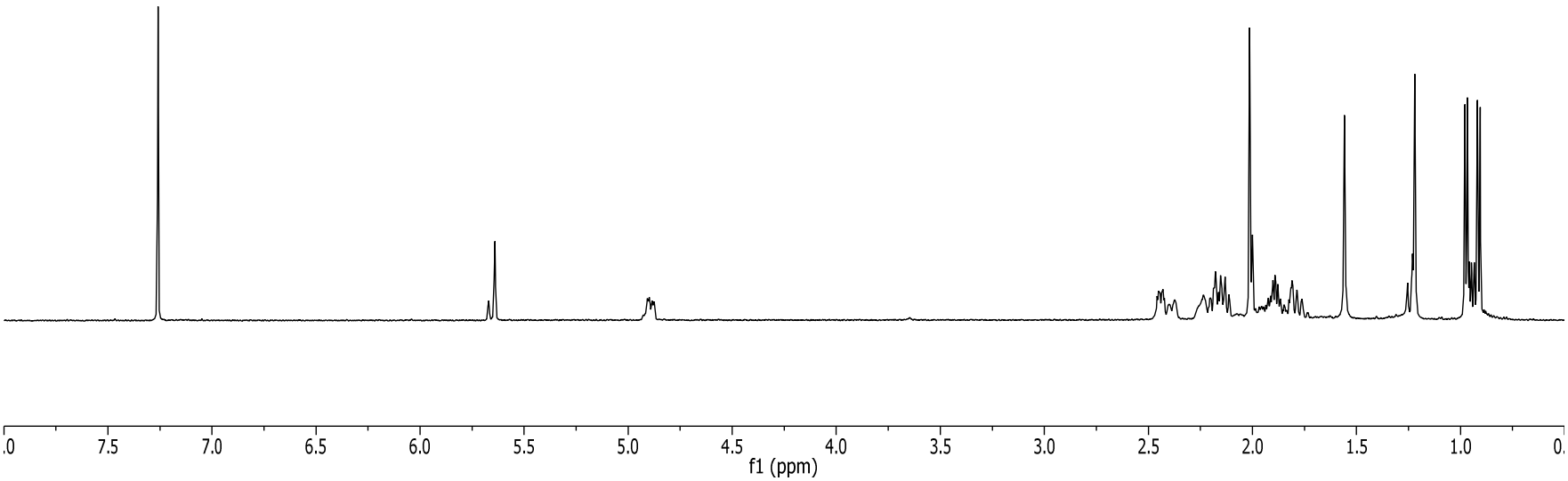
(+)-**18**

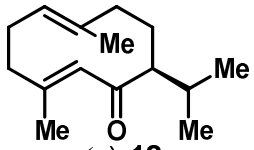
^{13}C NMR (150 MHz, C_6D_6)



(+)-**18**

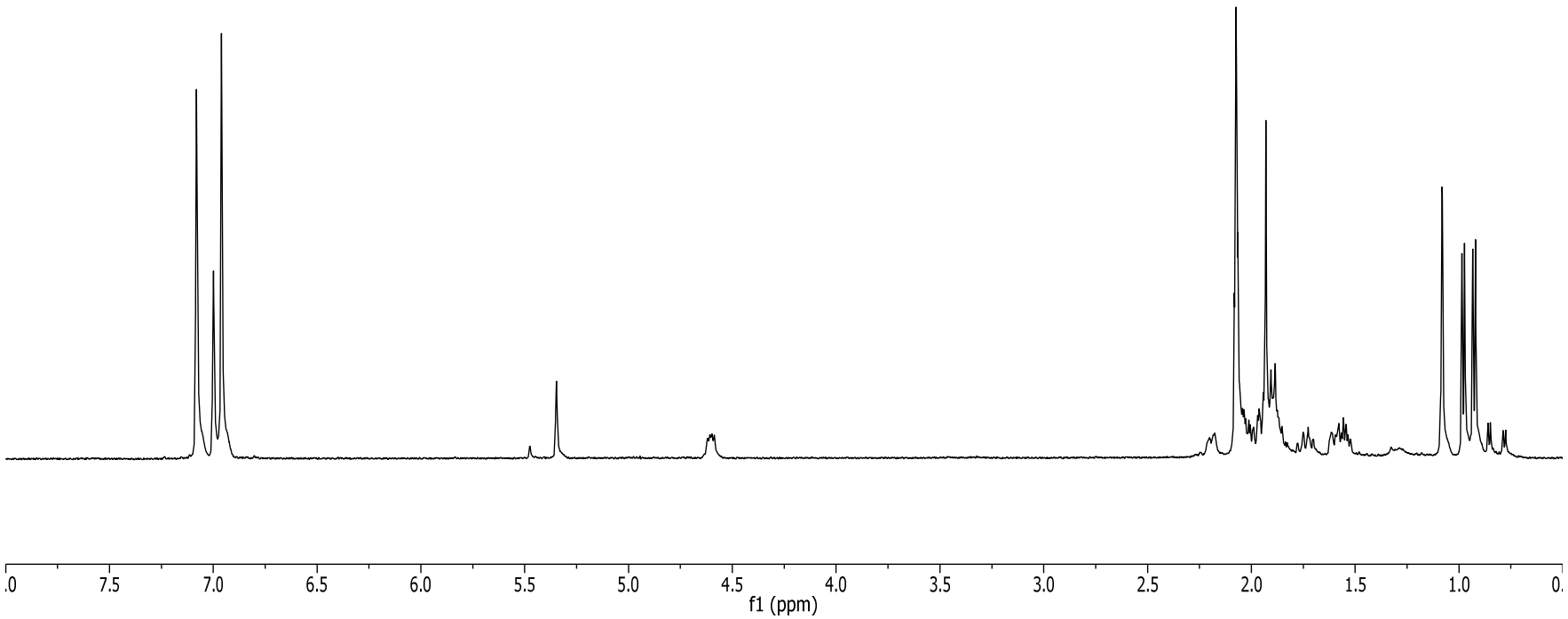
^{1}H NMR (500 MHz, $CDCl_3$)

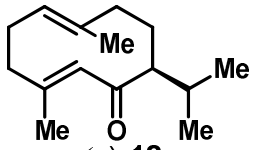




(+)-**18**

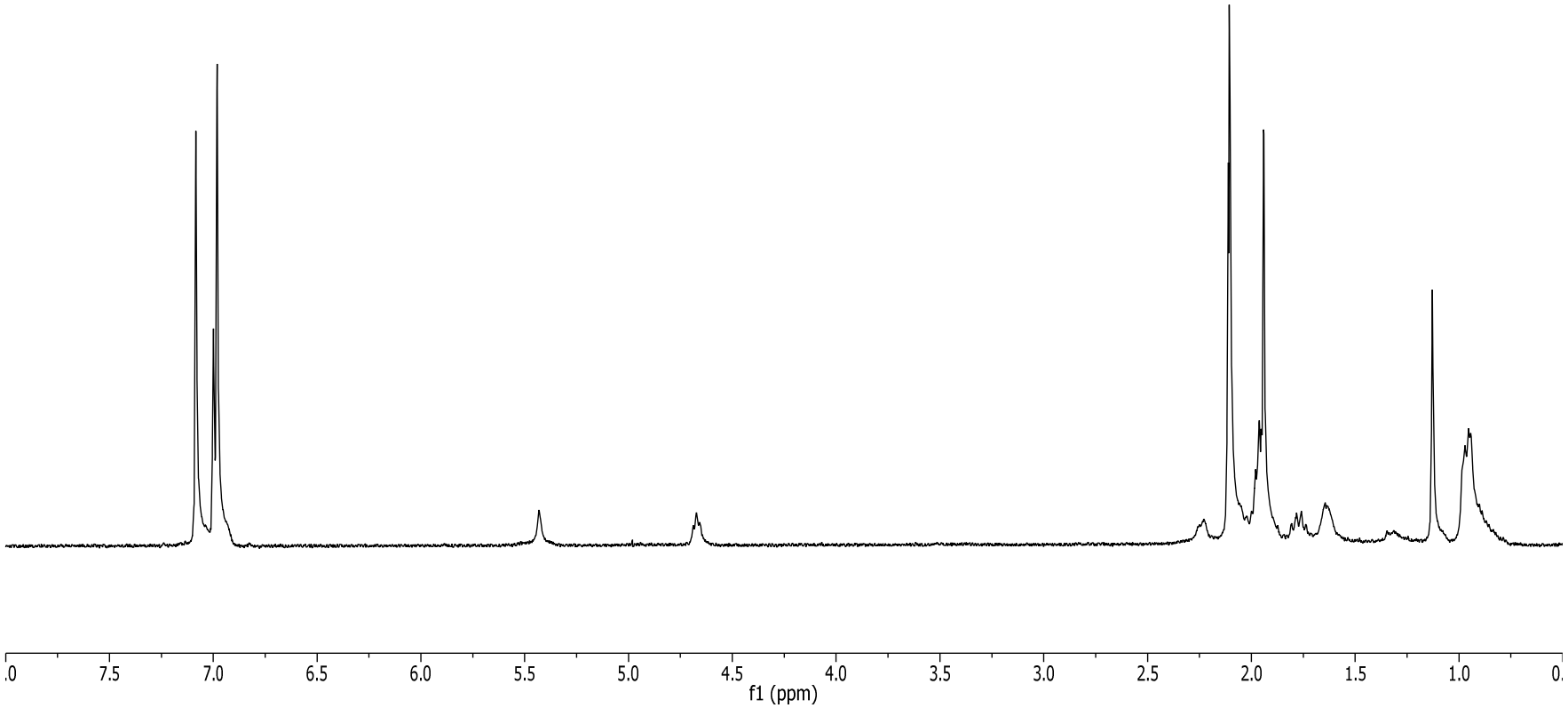
^{1}H NMR (500 MHz, Toluene-d_8, 25 °C)

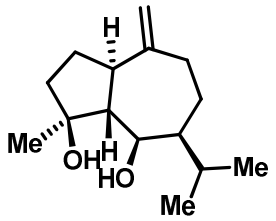




(+)-**18**

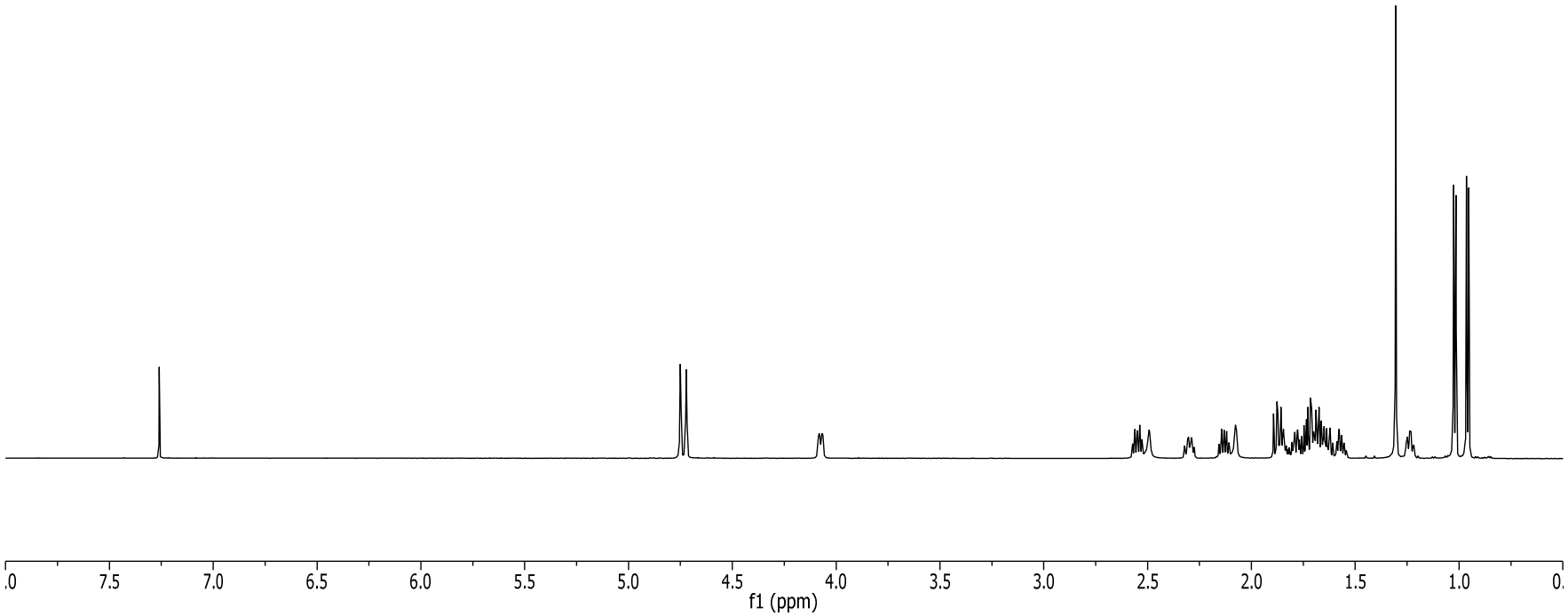
^{1}H NMR (500 MHz, Toluene-d_8, 80 °C)

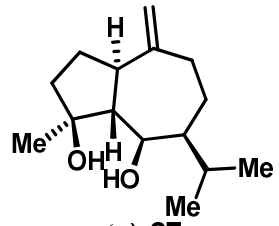




(+)-**27**

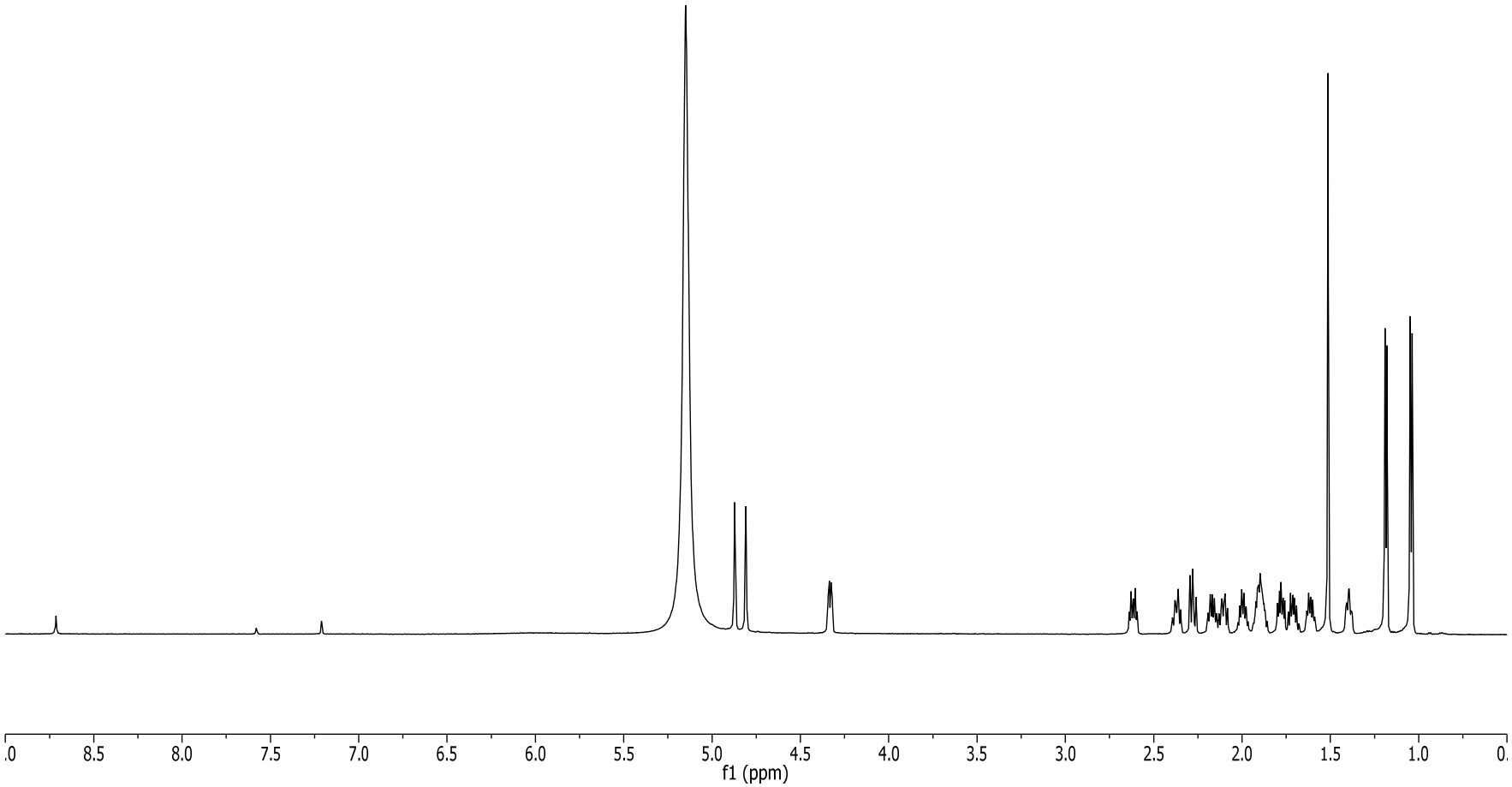
^{1}H NMR (600 MHz, $CDCl_3$)

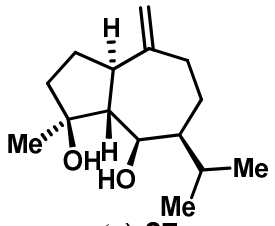




(+)-27

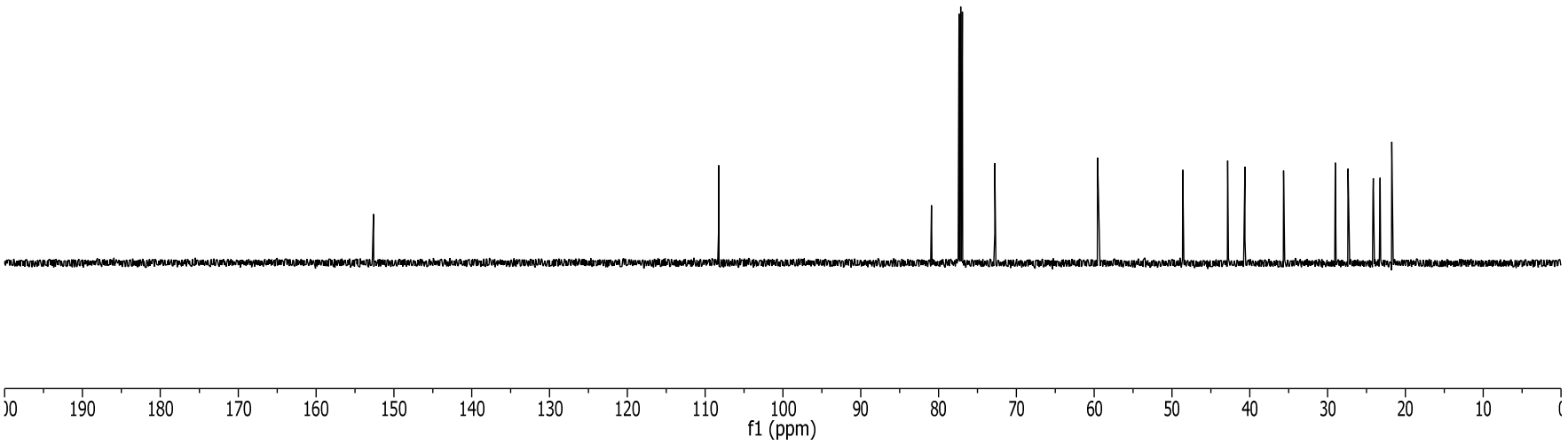
^{1}H NMR (600 MHz, pyridine-d_5)

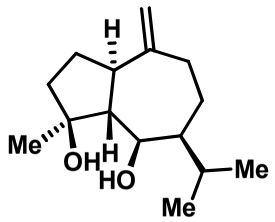




(+)-**27**

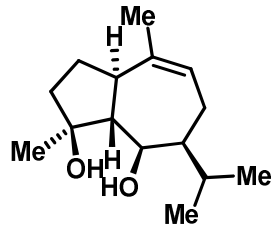
^{13}C NMR (150 MHz, $CDCl_3$)





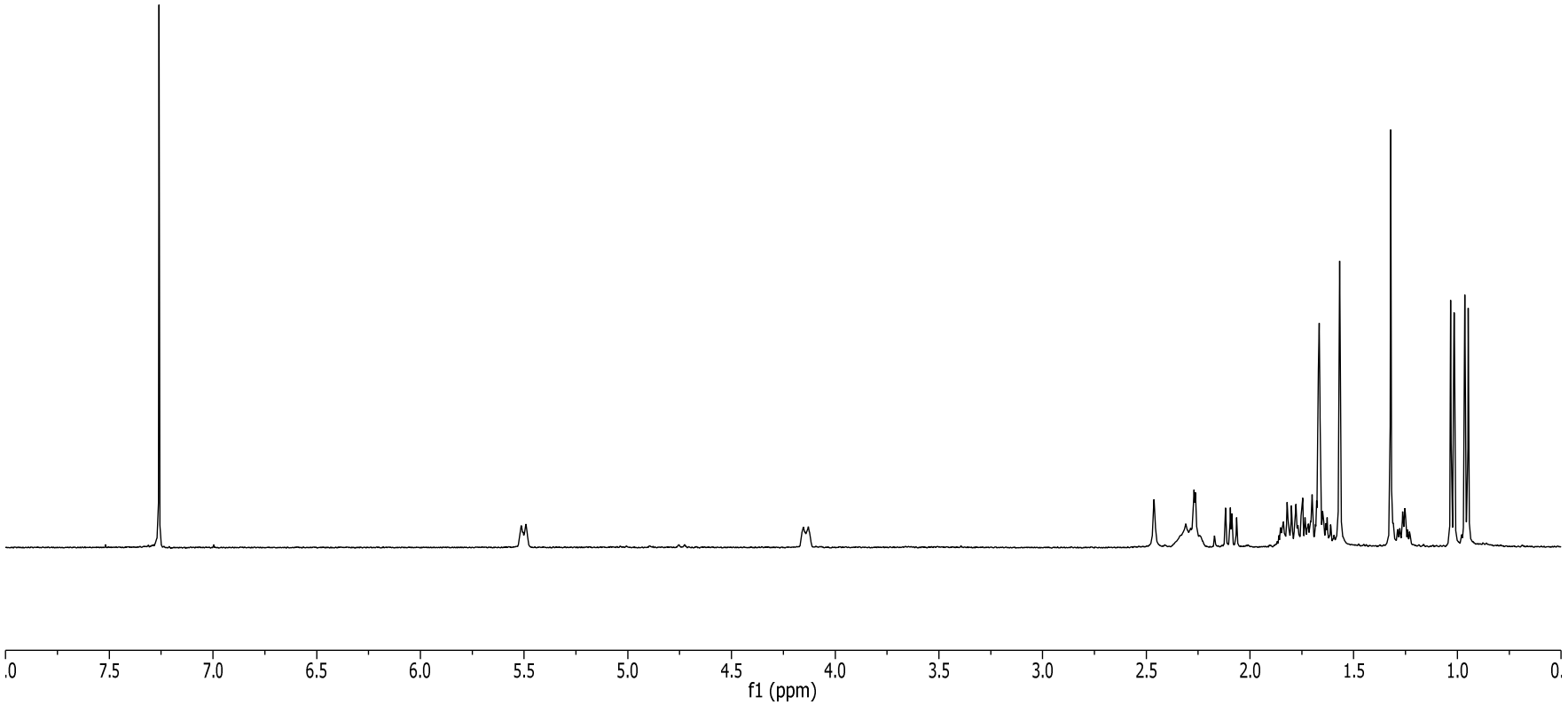
(+)-**27**

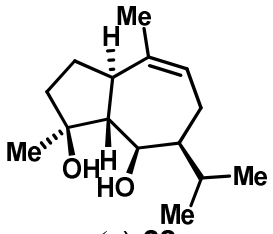
^{13}C NMR (150 MHz, pyridine-d_5)



(+)-**28**

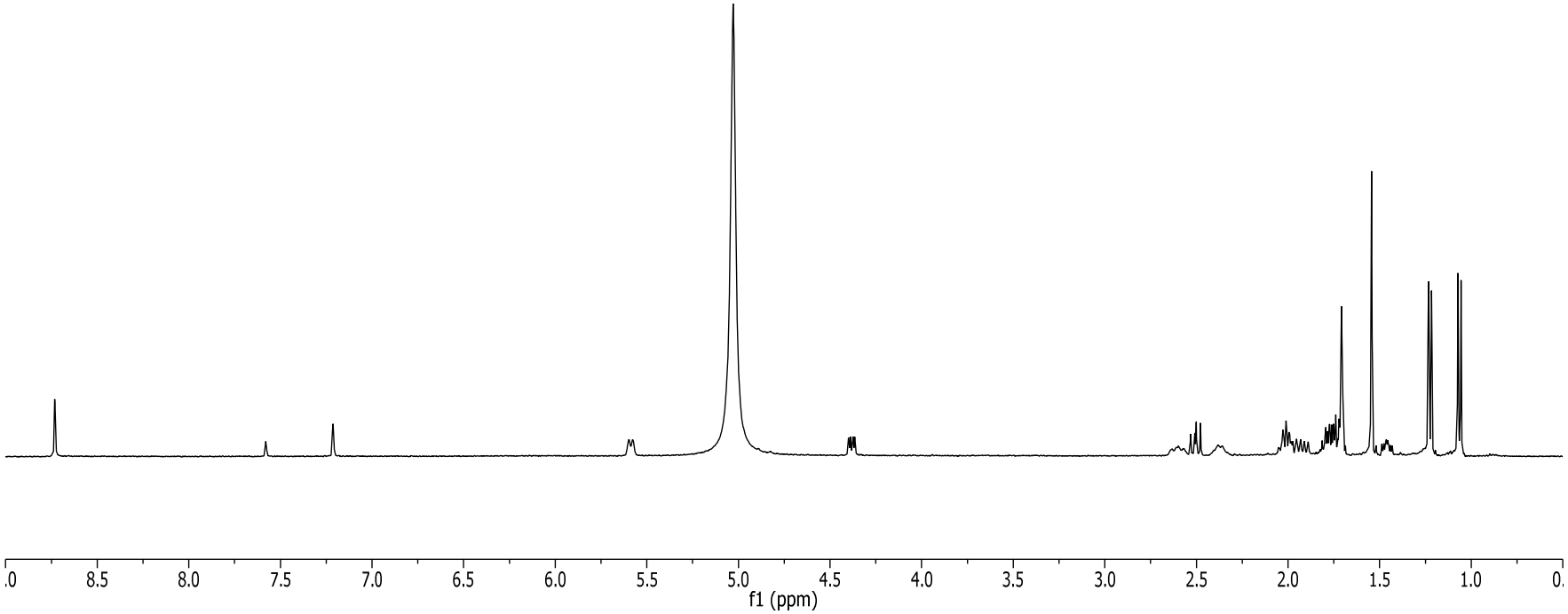
^{1}H NMR (400 MHz, $CDCl_3$)

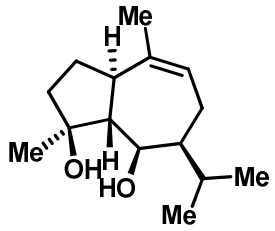




(+)-**28**

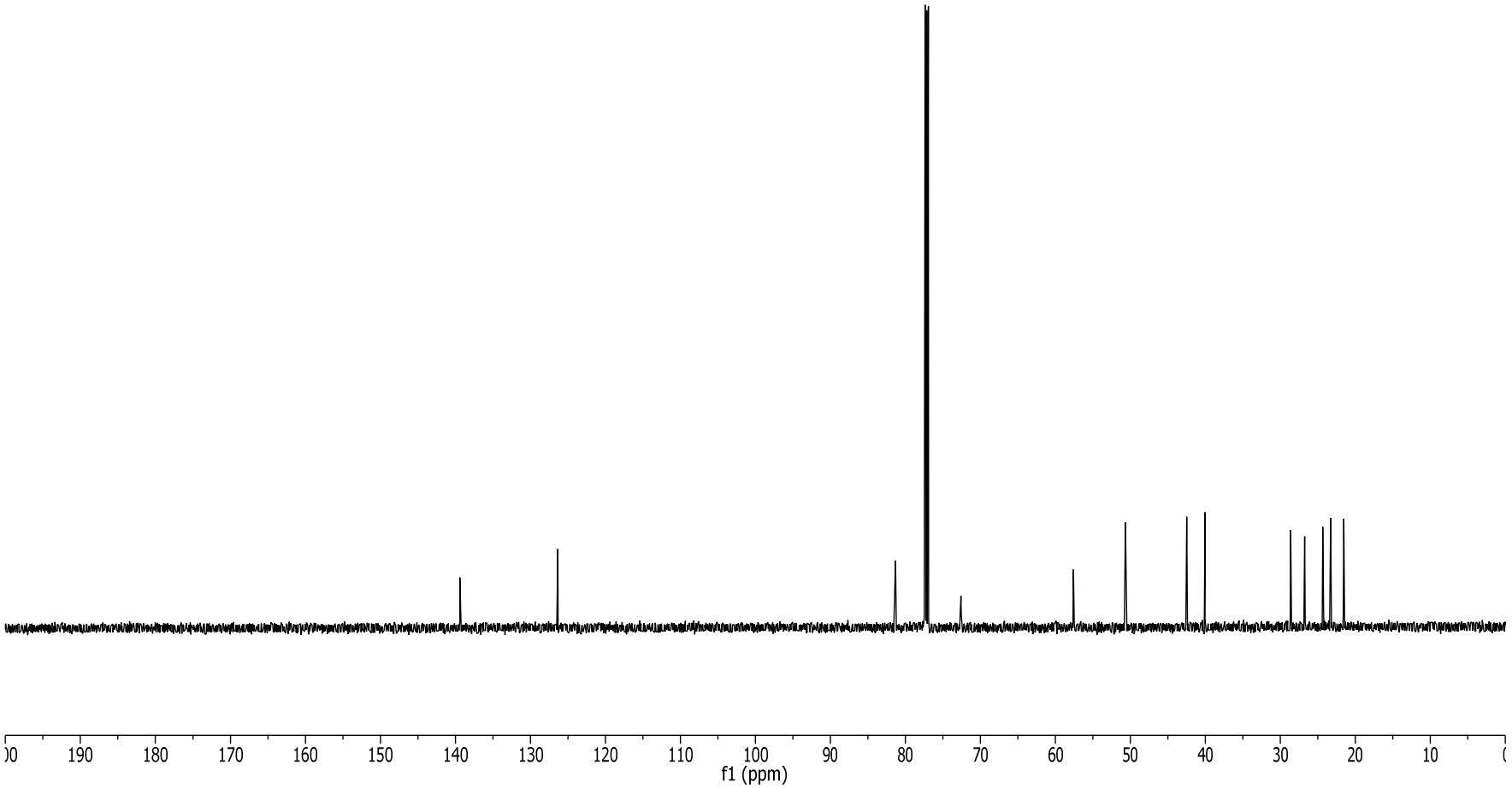
^{1}H NMR (400 MHz, pyridine-d_5)

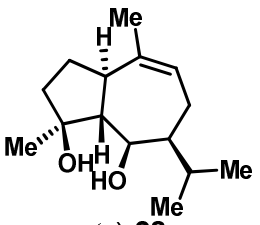




(+)-**28**

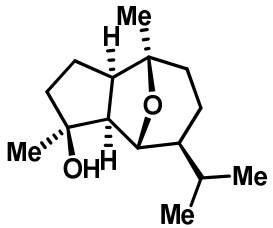
^{13}C NMR (150 MHz, $CDCl_3$)





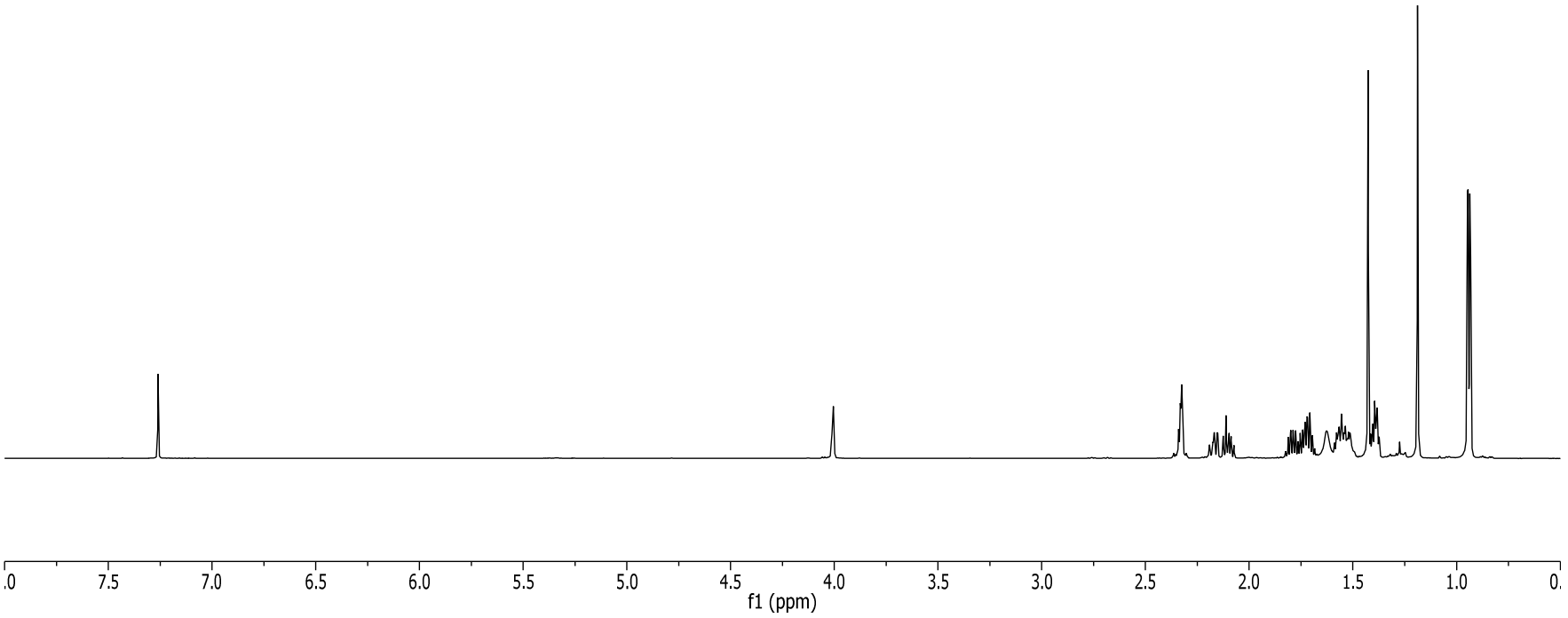
(+)-28

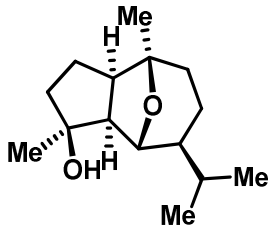
^{13}C NMR (150 MHz, pyridine-d_5)



(+)-30

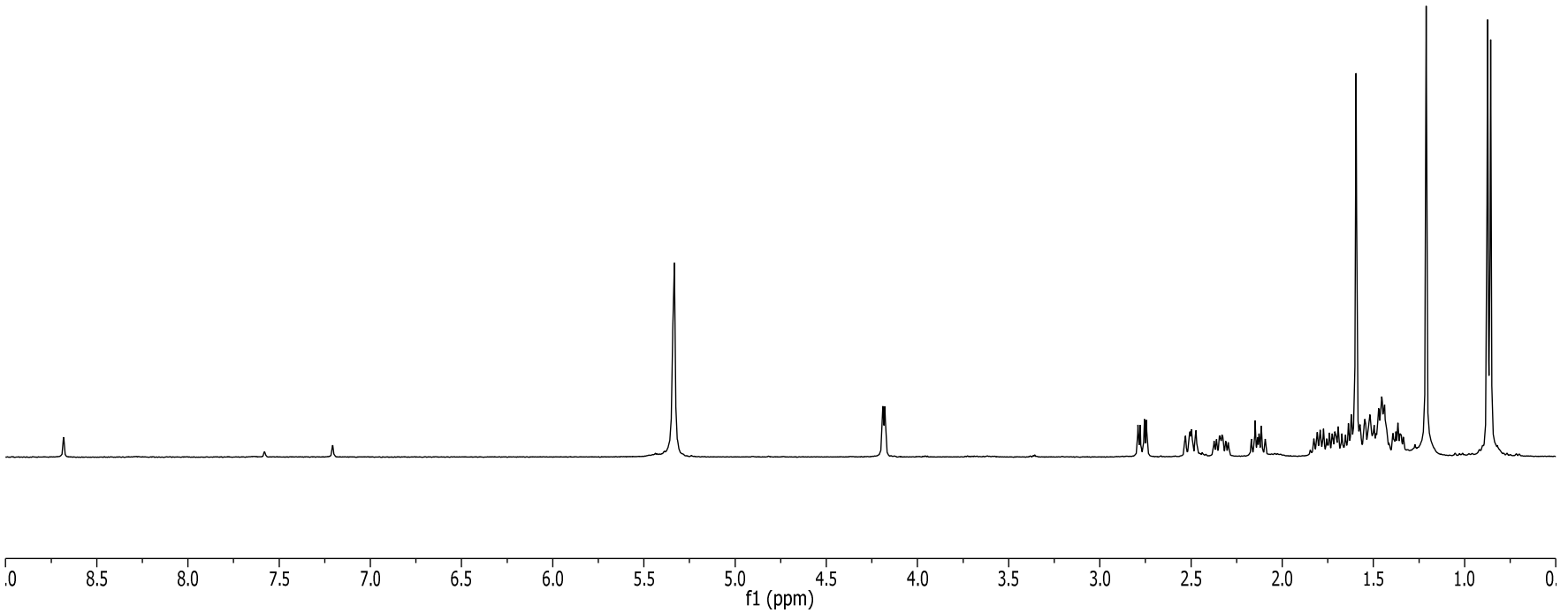
^{1}H NMR (600 MHz, $CDCl_3$)

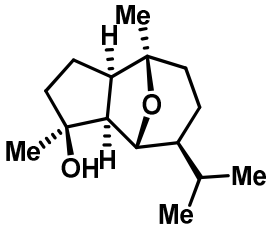




(+)-**30**

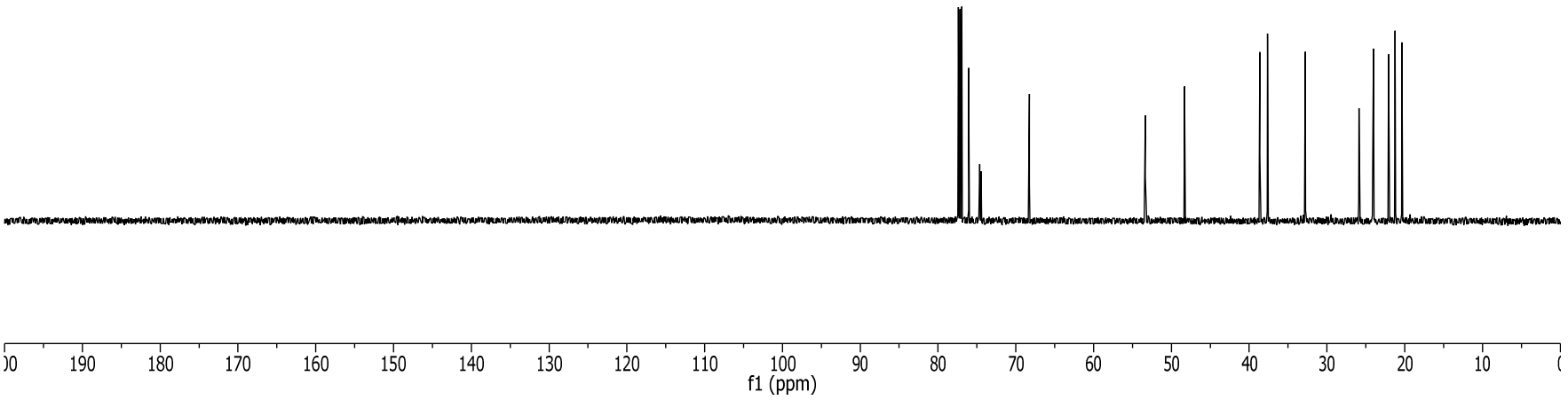
^{1}H NMR (400 MHz, pyridine-d_5)

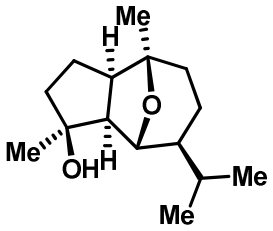




(+)-30

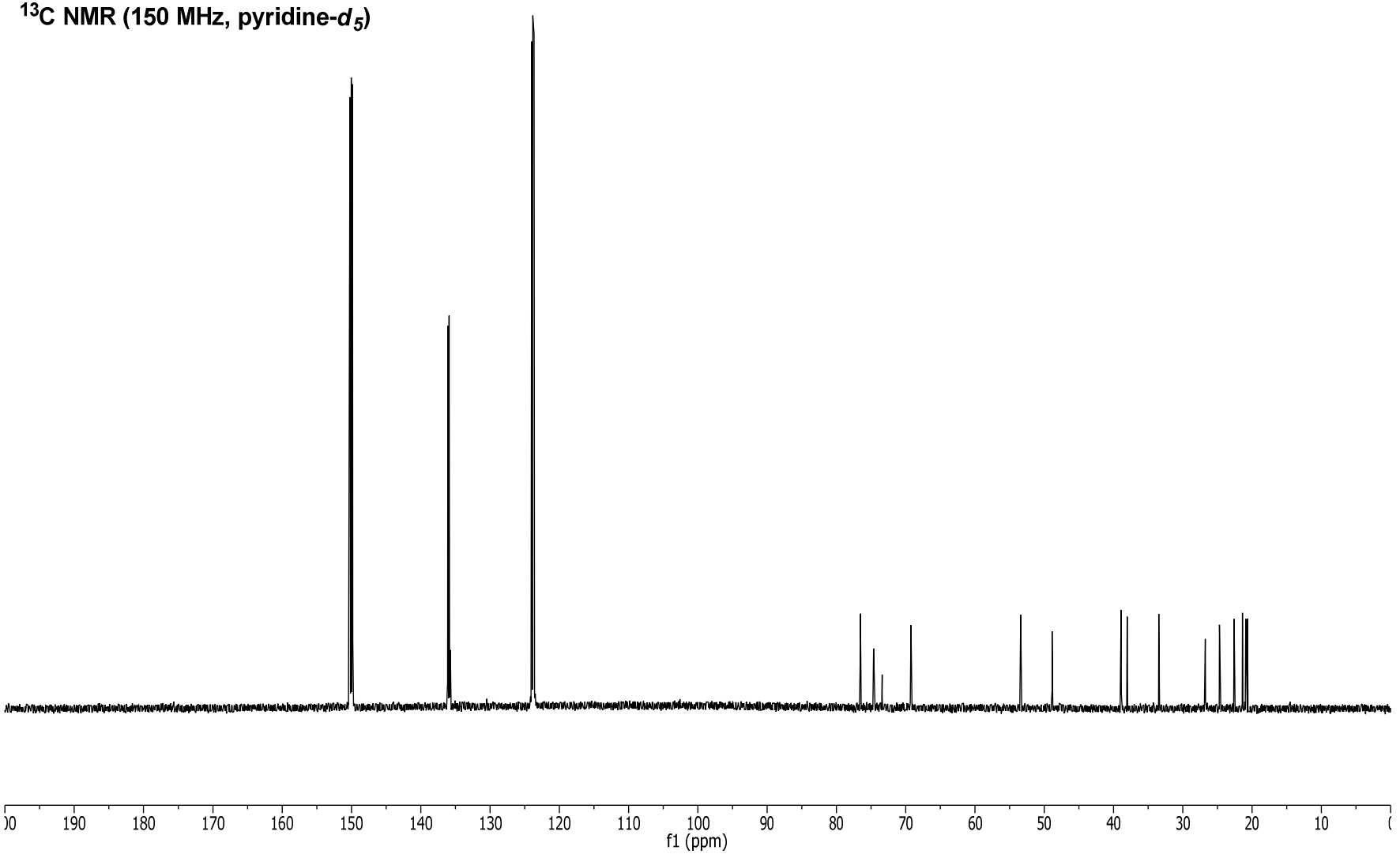
^{13}C NMR (150 MHz, $CDCl_3$)

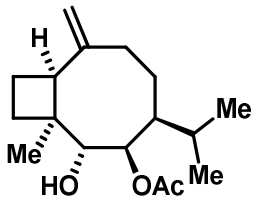




(+)-30

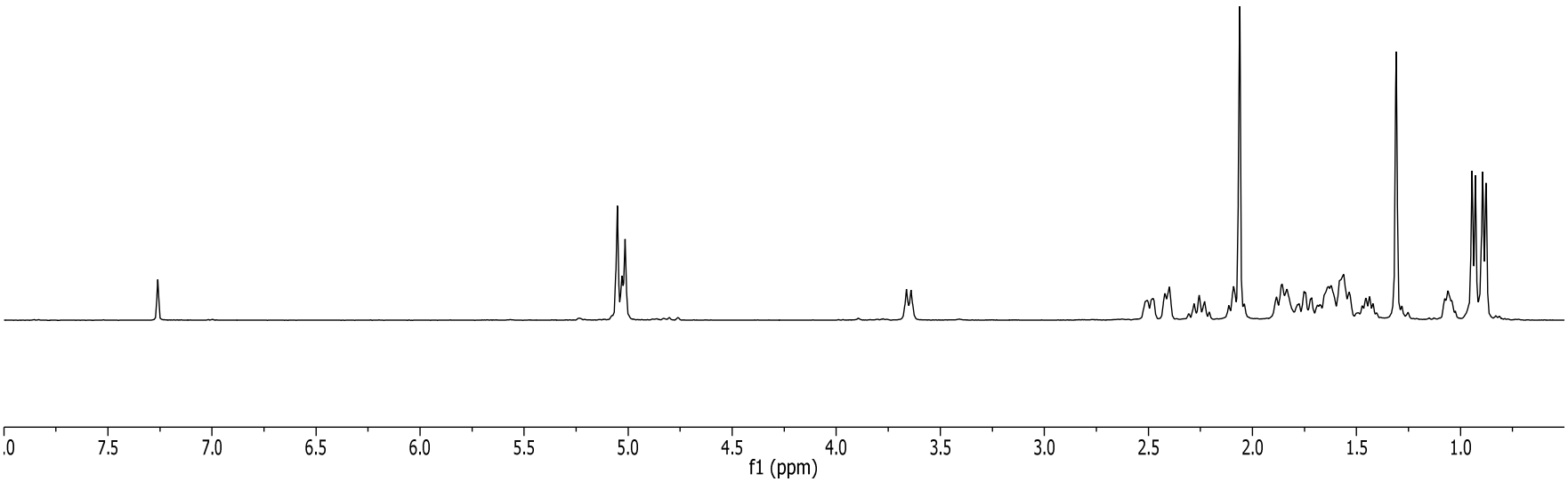
^{13}C NMR (150 MHz, pyridine-d_5)

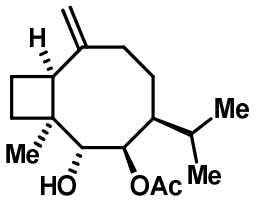




(+)-**31a**

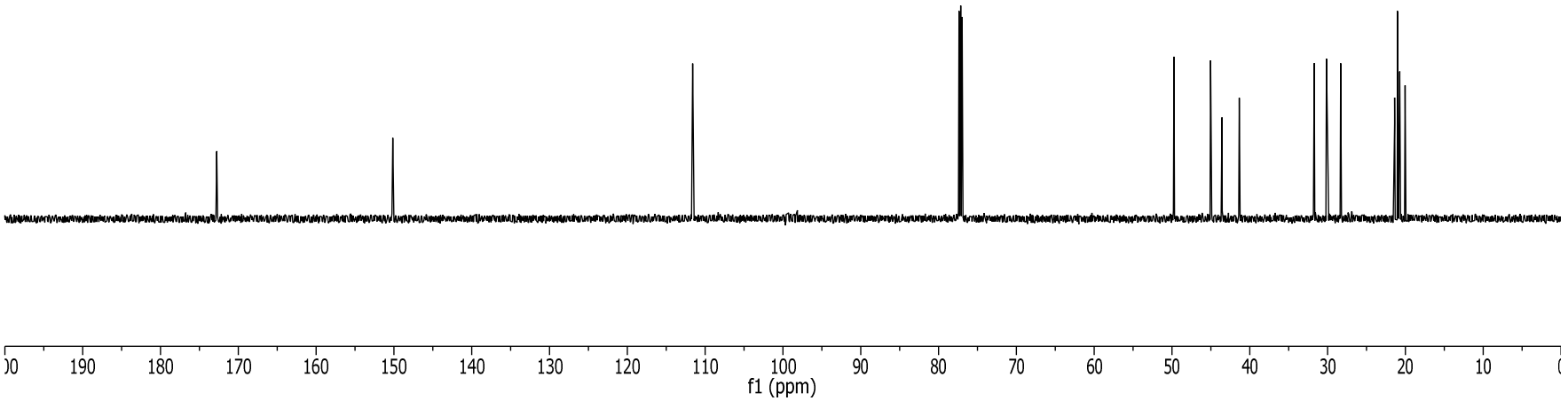
^{1}H NMR (400 MHz, $CDCl_3$)

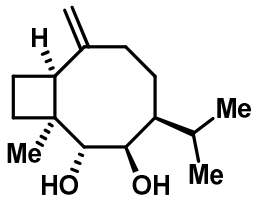




(+)-**31a**

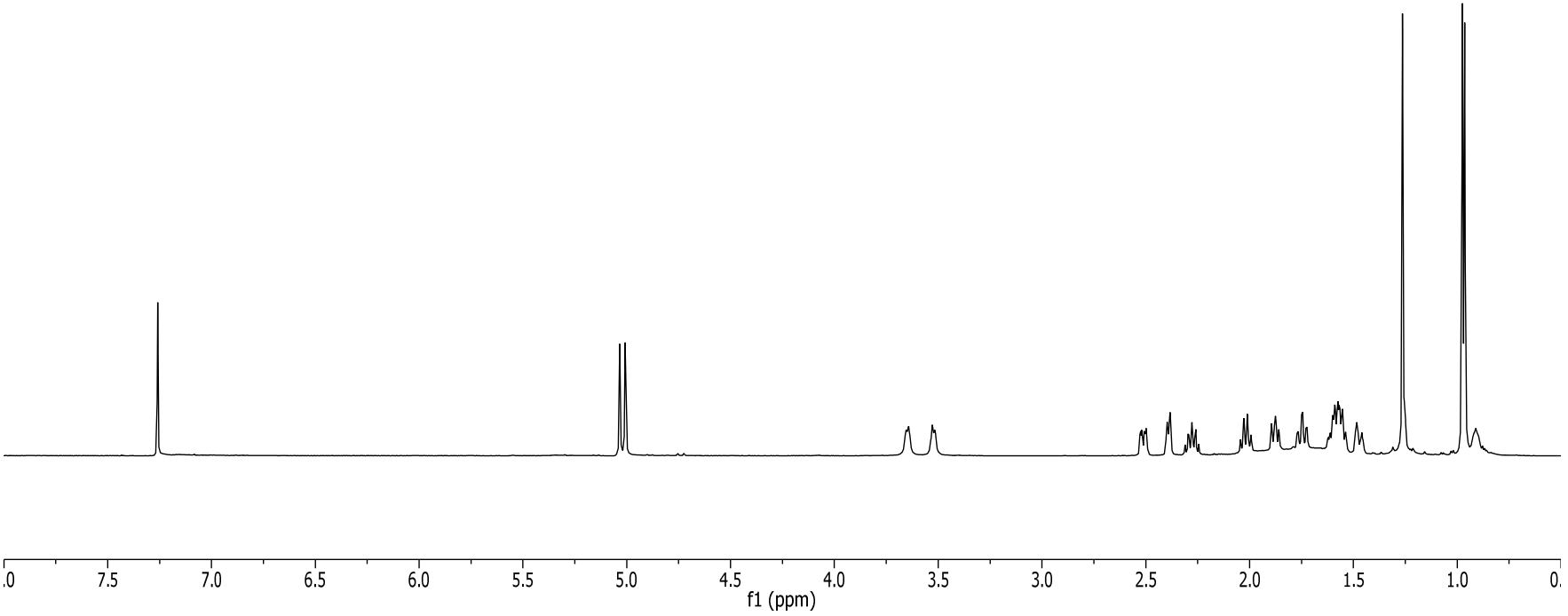
^{13}C NMR (150 MHz, $CDCl_3$)

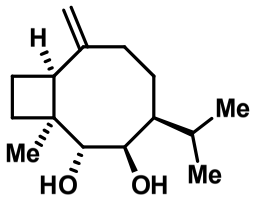




(+)-**31**

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





(+)-**31**

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