Supporting Information
Catalytic, Transannular Carbonyl-Olefin Metathesis Reactions

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1. General Information

General Laboratory Procedures: All moisture-sensitive reactions were performed under nitrogen in oven- or flame-dried round bottom flasks fitted with rubber septa. Dry solvents and air- and moisture-sensitive reagents were transferred via oven-dried stainless steel needles or hypodermic needles. Flash chromatography and silica plugs were carried out using Silicycle Silia Flash® 40-63 micron (230-400 mesh) silica gel.

Materials and Instrumentation: All chemicals were purchased from Sigma Aldrich, Alfa Aesar, Acros Organics, TCI America, and Ark Pharm and were used as received unless noted otherwise. Tetrahydrofuran was dried by being passed through columns of activated alumina. Proton nuclear magnetic resonance NMR (^{1}H NMR) spectra and carbon nuclear magnetic resonance spectra (^{13}C NMR) were measured on Varian MR400, Varian vnmrs 500, Varian Inova 500, or Varian vnmrs 700 spectrometers. Chemical shifts for protons are reported in parts per million (ppm) and are referenced to the NMR solvent peak ($CDCl_3$: δ7.26; DMSO: δ2.50; C_6D_6: δ7.16). Chemical shifts for carbons are reported in parts per million and are referend to the carbon resonances of the NMR solvent ($CDCl_3$: 77.16; DMSO: δ39.52; C_6D_6: δ128.06). Data are described as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd= doublet of doublets, m = multiplet), and coupling constant in Hertz (Hz). High resolution mass spectroscopic (HRMS) data were recorded at the University of Michigan Chemistry Department's mass spectrometry facility in Ann Arbor, MI on an Agilent Q-TOF HPLC-MS with ESI high resolution mass spectrometer unless otherwise noted. Infrared (IR) spectra were measured on a Thermo-Nicolet IS-50 infrared spectrometer. IR data are represented as frequency of absorption (cm^{-1}).

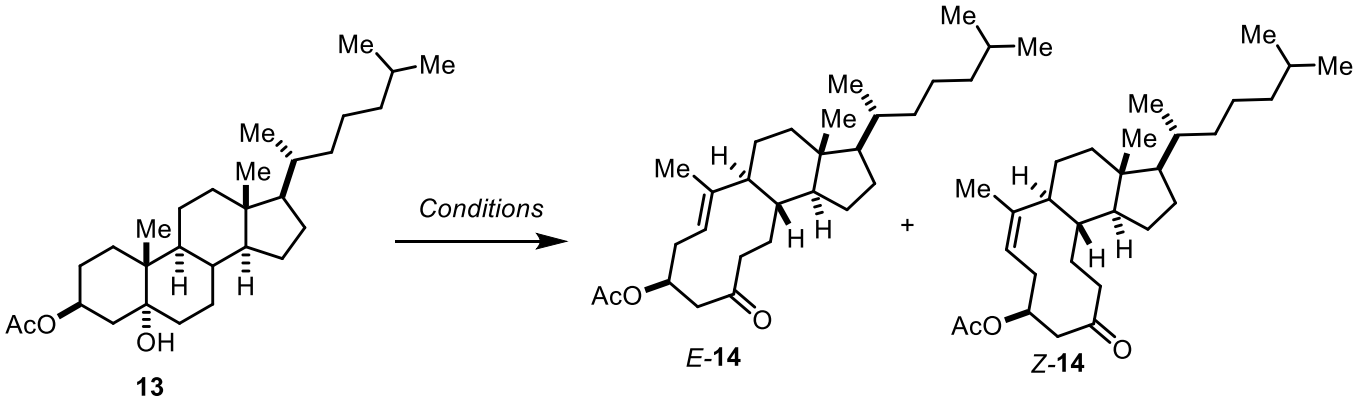
Abbreviations used:
HCl = hydrochloric acid, EtOAc = ethyl acetate, KOH = potassium hydroxide, THF = tetrahydrofuran, DCM = dichloromethane, *m*CPBA = *m*-chloroperoxybenzoic acid, TBSCl = *tert*-butyldimethylsilyl chloride, TLC = thin-layer chromatography, NH_4Cl = ammonium chloride, Na_2SO_4 = sodium sulfate, $MgSO_4$ = magnesium sulfate, DCE = dichloroethane, DMAP = (4-dimethylamino)-pyridine, PIDA = phenyliodine(III) diacetate, Et_3N = triethylamine, $LiAlH_4$ = lithium aluminum hydride, TBAF = tetrabutylammonium fluoride, TsOH = *p*-toluenesulfonic acid, TfOH = trifluoromethanesulfonic acid, TMSOK = potassium trimethylsilanoate

2. Evaluation of Reaction Conditions

a. Optimization of Ring Opening of Tertiary Alcohols

General procedure for ring opening of tertiary alcohol 13: **13**[1] (100 mg, 0.22 mmol) and PIDA (71 mg, 0.22 mmol) were dissolved in DCM (7 mL) and the solution was sparged with nitrogen for ten minutes. The flask was opened and iodine (57 mg, 0.22 mmol) was added and the septum quickly replaced. The reaction mixture was stirred under nitrogen atmosphere and irradiated with blue LEDs for 3 hours, at which time the mixture was diluted with DCM and poured into a separatory funnel containing saturated sodium bicarbonate and saturated sodium thiosulfate solutions. The layers were separated and the aqueous phase was washed with two additional portions of DCM. The combined organic layers were dried over Na_2SO_4 and concentrated by rotary evaporator before being purified by flash column chromatography eluting with hexanes/Et_2O to afford first *Z*-**14** followed *E*-**14**. The results are summarized in Table SI-1.

Table SI-1: Optimization of ring opening for cyclodecenone preparation.



entry	oxidant	solvent	light source	yield *E* (%)	yield *Z* (%)
1[a]	HgO	CCl_4	floodlamp	14-23	not measured
2[b]	PIDA	CCl_4	floodlamp	36	5
3	PIDA	cyclohexane	N/A (110°C)	9	25
4	PIDA	cyclohexane	blue LED	13	38
5	PIDA	CCl_4	blue LED	31	20
6	PIDA	benzene	blue LED	44	8
7	PIDA	DCM	blue LED	45	-[c]
8	PIDA	MeCN	blue LED	-	-
9	PIDA (1eq)	DCM	blue LED	58	9
10[d]	PIDA (1eq)	DCM	blue LED	62	3

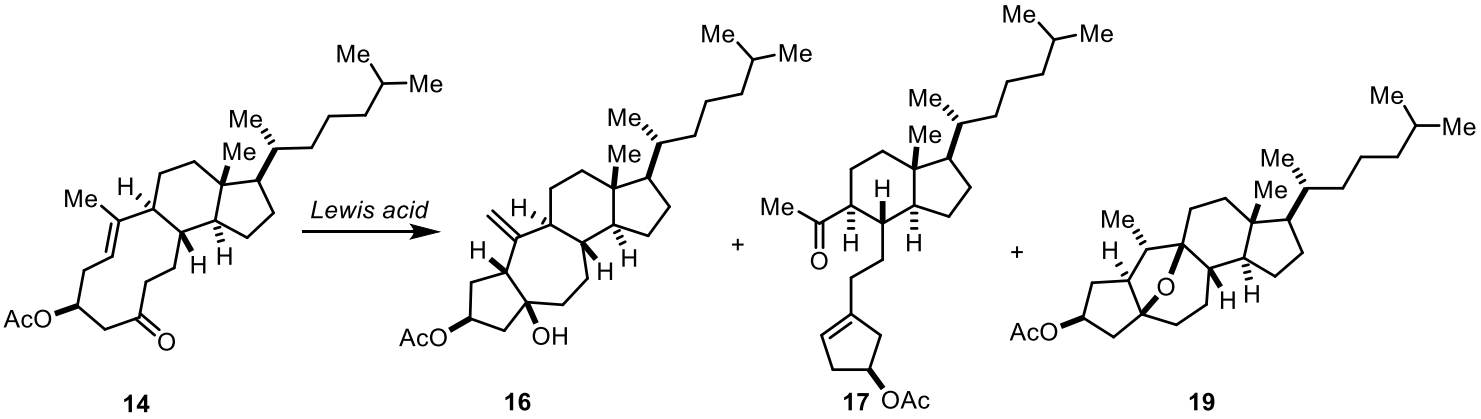
Conditions: substrate (0.22 mmol), oxidant (0.67 mmol, 3 equiv.), I_2 (0.25 mmol, 1.1 equiv.) in solvent listed (0.03 M), rt, irradiated 3 hr with light listed. [a]2.1 mmol scale, 3.1 equiv. HgO, 2.7 equiv. I_2, reaction performed in cold water chilled vessel, 1.5 hr. [b]14.8 mmol scale, 3 equiv. PIDA, 3 equiv. I_2, 0.16 M, perfomed in cold water chilled flask, 1.5 hr. [c]*Z* isomer observed by TLC but not crude NMR, was not isolated from column chromatography. [d]Reaction mixture sparged w/ N_2 before irradiation.

[1] Mihailović, M. L.; Lorenc, L.; Pavlović, V.; Kalvoda, J. *Tetrahedron* **1977**, *33*, 441.

b. Evaluation of Various Lewis and Brønsted Acids

General procedure for evaluating Lewis and Brønsted acids: **14** (50 mg, 0.11 mmol, 1 equiv.) was dissolved in DCE (2.20 mL, 0.05M) and Lewis or Bronsted acid (0.011 mmol, 0.1 equiv.) was added at room temperature and the reaction mixture was allowed to stir for 24 hours before being passed through a plug of silica gel eluting with DCM. The crude reaction mixture was purified by flash column chromatography eluting with hexanes/Et_2O to afford products **16**, **17**, and/or **19** in the yields described in Table 2. Any deviations from this procedure are described in Table SI-2.

Table SI-2: Evaluation of Lewis and Brønsted Acids.



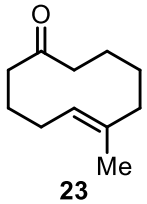
		isolated yields			
Entry	Lewis Acid	**16**	**17**	**19**	Rec. **14**
1	$Sc(OTf)_3$	15	33	20	-
2	$FeCl_3$	-	39	31	-
3	$FeCl_3$[a]	-	33	27	-
4	$FeCl_3$[b]	-	32	31	-
4	$FeCl_3$[c]	61	-	-	-
5	$AlCl_3$	-	27	27	-
6	$TiCl_4$	-	-	43	-
7	$SnCl_4$	-	22	44	-
8	$BF_3{\cdot}OEt_2$	-	30	23	-
9	$BF_3{\cdot}OEt_2$[d]	-	11	25	-
10	$GaCl_3$	-	3	-	-
11	$Y(OTf)_3$	22	-	-	18
12	Me_2AlCl	16	-	-	14
13	Me_2AlCl[e]	85	-	-	-
14	$SnCl_2{\cdot}2H_2O$	46	-	-	19
15	TfOH	-	18	16	-

Conditions: Substrate (0.11 mmol), Lewis acid listed (10 mol%), DCE (0.05M), rt, 24 hours. Deviations from standard conditions: [a]0°C. [b]80°C, 10 hours. [c]0°C, 30 minutes [d]100 mol% $BF_3{\cdot}OEt_2$, 5 hours. [e]100 mol% Me_2AlCl, 0°C, 1 hour.

3. Compound Preparation

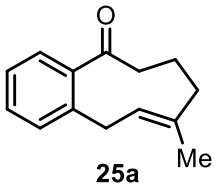
a. Preparation of Substrates

i. Non-Steroid Derived Cycloalkenones



23

(*E*)-6-methylcyclodec-5-en-1-one (23): 2-methyl-1,2-divinylcyclohexan-1-ol[2] (1.37 g, 8.26 mmol) was dissolved in THF (25 mL) and cooled on an ice bath. Freshly rinsed and dried potassium hydride (387 mg, 9.91 mmol) was added portion-wise via spatula. The reaction mixture was removed from the ice bath, equipped with a reflux condenser and heated to reflux for one hour. The reaction mixture was cooled and poured onto a saturated solution of ammonium chloride and ice. The reaction mixture was extracted with three portions of diethyl ether. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated by rotary evaporator. The crude material was purified by flash column chromatography eluting with hexanes/diethyl ether to afford 343 mg (25% yield) of the title compound[3] as a clear, slightly yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.96 (d, *J* = 7.1 Hz, 1H), 2.37 (s, 2H), 2.09 (dd, *J* = 18.0, 12.4 Hz, 7H), 1.82 (d, *J* = 16.9 Hz, 2H), 1.71 (s, 3H), 1.53 (dd, *J* = 40.3, 16.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 212.78, 134.84, 129.41, 43.69, 42.68, 40.44, 28.61, 28.56, 25.43, 22.67, 16.21. **IR** (cm^{-1}): 2924.19, 2857.74, 1701.95, 1493.97, 1355.91, 1170.16, 1096.20, 960.88, 879.62, 849.26 **HRMS**: calculated for $C_{11}H_{18}O^+$ (M^+): 166.1358 found: 166.1360.



25a

(*E*)-9-methyl-6,7,8,11-tetrahydro-5H-benzo[9]annulen-5-one (25a): 2-chloroindanone[4] (1.00 g, 6.00 mmol) was dissolved in THF (20 mL) and cooled on an ice water bath and isopropenylmagnesium bromide (0.5 M in THF, 36.0 mL, 18.0 mmol) was slowly added. The reaction mixture was stirred at 0 °C until judged complete by TLC and quenched with a saturated aqueous solution of ammonium chloride. The aqueous layer was extracted with two portions of ethyl acetate, dried over Na_2SO_4 and concentrated by rotary evaporator. The crude material taken up in THF (20 mL) and cooled on an ice bath and vinylmagnesium bromide (1.0 M in THF, 36.0 mL, 36.0 mmol) was added slowly. The reaction mixture was heated to reflux for 6 hours and cooled to 0 °C and quenched with a saturated aqueous solution of ammonium chloride, extracted into ethyl acetate, dried over Na_2SO_4 and concentrated by rotary evaporator. The crude material

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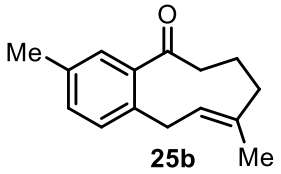
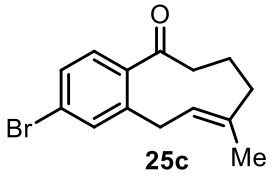
[2] Holt, D. R. *Tet. Lett.* **1981**, *22*, 2243.
[3] Clive, D. J. L.; Russel, C. G; Suri, S. C. *J. Org. Chem.* **1982**, *47*, 1632.
[4] Mei, Y.; Bentley, P. A.; Du, J. *Tet. Lett.* **2008**, *49*, 3802.

was again taken up in THF (80 mL) and cooled on an ice bath. 18-crown-6 (1.90 g, 7.20 mmol) was added as a solid followed by hexane-washed KH (282 mg, 7.20 mmol). The reaction mixture was heated to reflux for 30 minutes before cooling back to 0 °C and quenching with saturated aqueous ammonium chloride solution. The reaction mixture was extracted into ethyl acetate, dried over Na_2SO_4 and concentrated by rotary evaporator. The crude material was purified by flash chromatography eluting with hexanes/EtOAc to afford 403 mg (17% yield over 3 steps) of the title compound as an orange solid. **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 3H), 7.00 (d, *J* = 7.4 Hz, 1H), 5.38 (d, *J* = 11.0 Hz, 1H), 3.63 (dd, *J* = 14.8, 12.2 Hz, 1H), 3.11 (d, *J* = 14.7 Hz, 1H), 2.55 – 2.45 (m, 3H), 2.23 – 2.15 (m, 1H), 1.92 (dt, *J* = 10.4, 6.0 Hz, 2H), 1.54 (s, 3H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 207.60, 146.12, 141.89, 138.89, 129.75, 128.12, 126.61, 126.11, 123.84, 42.27, 39.60, 33.77, 27.89, 16.53. **IR** (cm^{-1}): 2926.12, 1675.29, 1436.99, 1420.00, 1340.10, 1232.41, 1206.85, 1174.85, 1111.38, 1049.96, 991.35, 972.98, 958.03, 913.50, 891.26, 897.44, 809.02. **HRMS**: calculated for $C_{14}H_{17}O^+$ ($[M+H]^+$): 201.1274 found: 201.1271.



25b

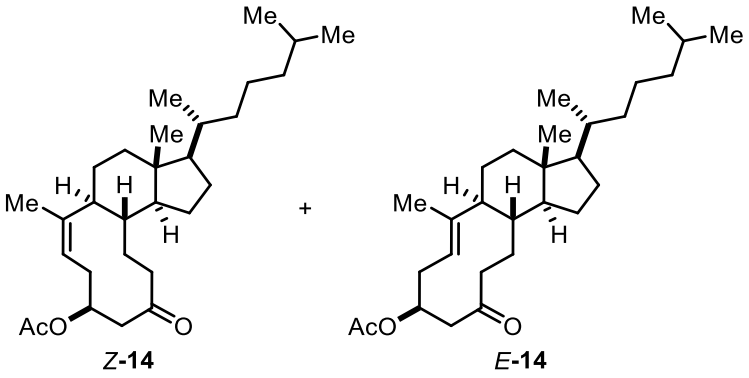
(*E*)-3,9-dimethyl-6,7,8,11-tetrahydro-5H-benzo[9]annulen-5-one (25b): Prepared by the same procedure employed to prepare compound **25a** starting from 6-methyl-indanone. **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.09 (d, *J* = 7.8 Hz, 1H), 7.06 – 7.02 (m, 1H), 6.80 (s, 1H), 5.37 (d, *J* = 10.8 Hz, 1H), 3.62 – 3.54 (m, 1H), 3.07 (d, *J* = 14.7 Hz, 1H), 2.53 – 2.43 (m, 3H), 2.30 (s, 3H), 2.18 (d, *J* = 13.0 Hz, 1H), 1.90 (dd, *J* = 9.3, 4.5 Hz, 2H), 1.53 (s, 3H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 207.90, 146.18, 141.54, 135.93, 135.88, 129.73, 128.86, 127.05, 124.59, 42.38, 39.71, 33.44, 27.90, 21.10, 16.60. **IR** (cm^{-1}): 2942.27, 2926.77, 1673.98, 1439.15, 1422.42, 1337.49, 1162.04, 1125.05, 993.61, 975.39, 909.77, 879.07, 840.99. **HRMS**: calculated for $C_{15}H_{19}O^+$ ($[M+H]^+$): 215.1430 found: 215.1413.



25c

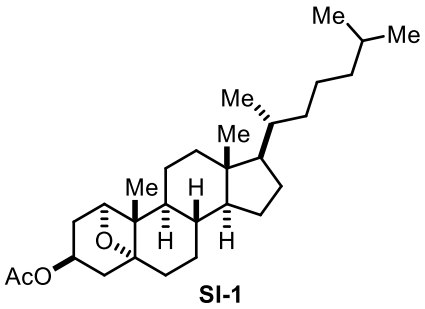
(*E*)-2-bromo-9-methyl-6,7,8,11-tetrahydro-5H-benzo[9]annulen-5-one (25c): Prepared by the same procedure employed to prepare compound **25a** starting from 5-bromo-indanone **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 5.33 (d, *J* = 12.7 Hz, 1H), 3.65 – 3.56 (m, 1H), 3.07 (d, *J* = 13.9 Hz, 1H), 2.47 (t, *J* = 9.7 Hz, 3H), 2.19 (d, *J* = 12.5 Hz, 1H), 1.95 – 1.86 (m, 2H), 1.52 (s, 3H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 206.48, 145.02, 142.76, 141.52, 132.67, 129.21, 125.94, 125.51, 121.97, 42.38, 39.63, 33.66, 27.96, 16.66. **IR** (cm^{-1}): 2925.41, 1681.09, 1581.93, 1473.62, 1417.81, 1384.32, 1339.17, 1227.56, 1081.69, 970.46, 885.53, 872.91, 859.17, 811.34. **HRMS**: calculated for $C_{14}H_{15}BrONa^+$ ($[M+Na]^+$): 301.0198 found: 301.0217.

ii. Cholesterol-Derived



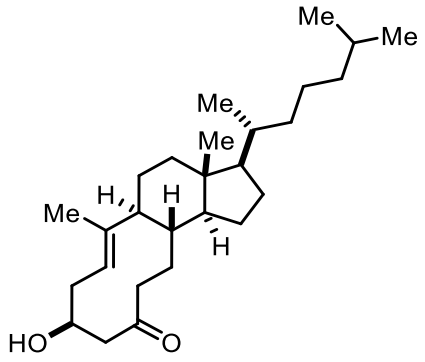
Z-**14** *E*-**14**

(3*R*,3*aR*,5a*S*,9*S*,13a*R*,13b*S*,*E*)-3a,6-dimethyl-3-(6-methylheptan-2-yl)-11-oxo-2,3,3*a*,4,5,5*a*,8,9,10,11,12,13,13*a*,13*b*-tetradecahydro-1H-cyclodeca[e]inden-9-yl acetate (14): **13**[1] (100 mg, 0.22 mmol) and PIDA (71 mg, 0.22 mmol) were dissolved in DCM (7 mL) and the solution was sparged with nitrogen for ten minutes. The flask was opened and iodine (57 mg, 0.22 mmol) was added and the septum quickly replaced. The reaction mixture was stirred under nitrogen atmosphere and irradiated with blue LEDs for 2 hours, at which time the mixture was diluted with DCM and poured into a separatory funnel containing saturated sodium bicarbonate and saturated sodium thiosulfate solutions. The layers were separated and the aqueous phase was washed with two additional portions of DCM. The combined organic layers were dried over Na_2SO_4 and concentrated by rotary evaporator before being purified by flash column chromatography eluting with hexanes/Et_2O to afford first 3 mg (3% yield) of undesired product *Z*-**14** followed by 62 mg (62% yield) of desired product *E*-**14** as a white solid. This reaction was scaled to 700 mg (1.54 mmol) scale (1.1 eq. PIDA, 1.8 eq. I_2, 37 mL DCM) and afforded 414 mg (59% yield) of *E*-**14** (any *Z*-**14** was discarded). Data for *Z*-**14**: **^{1}H NMR** (401 MHz, $CDCl_3$δ 5.46 – 5.37 (m, 1H), 5.23 (dd, *J* = 11.7, 5.0 Hz, 1H), 3.18 (dd, *J* = 16.2, 11.1 Hz, 1H), 2.65 – 2.51 (m, 1H), 2.35 (dd, *J* = 16.2, 4.8 Hz, 2H), 2.25 (dd, *J* = 12.0, 5.4 Hz, 1H), 2.13 – 1.82 (m, 8H), 1.74 – 1.48 (m, 8H), 1.41 – 0.83 (m, 22H), 0.69 (s, 3H). **IR** (cm^{-1}): 2944.09, 2862.26, 1733.14, 1679.69, 1440.08, 1372.73, 1186.01, 1028.73, 953.78, 908.74, 873.36. **HRMS**: calculated for $C_{29}H_{48}O_3^+$ ($[M+H^+]^+$): 445.3676 Found: 445.3679. **^{13}C NMR** (176 MHz, $CDCl_3$) δ 212.91, 170.44, 143.20, 119.83, 70.68, 55.91, 50.20, 42.94, 41.73, 41.06, 40.27, 39.69, 39.43, 36.54, 36.25, 35.80, 28.40, 28.19, 28.09, 27.29, 25.91, 24.16, 23.78, 22.97, 22.74, 21.49, 19.16, 18.80, 12.04. Data for *E*-**14**: **^{1}H NMR** (401 MHz, $CDCl_3$) δ 5.42 – 5.31 (m, 2H), 4.87 – 4.77 (m, 2H), 2.44 (ddd, *J* = 40.5, 26.0, 19.3 Hz, 11H), 2.09 – 0.84 (m, 70H), 0.71 (d, *J* = 10.9 Hz, 6H).**^{13}C NMR** (176 MHz, $CDCl_3$) δ 206.39, 170.00, 140.88, 123.36, 74.62, 56.44, 56.19, 54.87, 47.77, 42.86, 42.83, 39.64, 39.43, 38.26, 36.23, 35.92, 34.06, 28.16, 27.98, 27.67, 26.73, 25.50, 23.98, 22.97, 22.71, 21.40, 18.84, 13.29, 12.09. **IR** (cm^{-1}): 2945.31, 2926.35, 2865.10, 1727.69, 1700.83, 1434.60, 1419.17, 1365.78, 1236.82, 1200.37, 1118.57, 1032.10, 938.88, 907.06, 890.94. **HRMS**: calculated for $C_{29}H_{48}O_3^+$ ($[M+H^+]^+$): 445.3676 Found: 445.3674. Note: The *E*-cyclodecenone compound is not conformationally rigid in $CDCl_3$ and a minor conformer could be detected in the ^{1}H NMR (not reported above). The ^{1}H NMR spectrum was also acquired in *d*$_6$-DMSO, in which a single conformer was more preferred **^{1}H NMR** (700 MHz, DMSO) δ 5.18 (d, *J* = 11.1 Hz, 1H), 4.64 (d, *J* = 9.1 Hz, 1H), 2.55 (t, *J* = 12.5 Hz, 1H), 2.42 – 2.21 (m, 5H), 1.99 (s, 3H), 1.86 (d, *J* = 13.7 Hz, 1H), 1.72 (s, 4H), 1.55 (ddd, *J* = 29.9, 19.5, 5.7 Hz, 6H), 1.41 – 0.81 (m, 23H), 0.68 (s, 3H).



SI-1

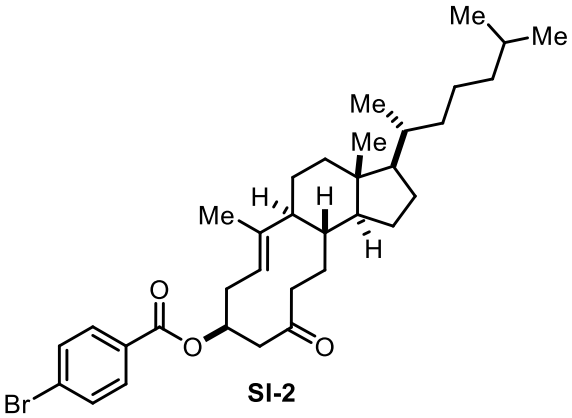
(1*S*,3*S*,5*R*,8*S*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-(6-methylheptan-2-yl)hexadecahydro-1,5-epoxycyclopenta[a]phenanthren-3-yl acetate (SI-1): 10 (250 mg, 0.56 mmol) was dissolved in 200 mL acetone and irradiated with an immersed Hanovia 450W medium-pressure UV lamp equipped with an isopropanol-cooled quartz cooling filter. When the starting material was judged consumed by TLC, the reaction mixture was concentrated and purified by flash column chromatography eluting with benzene/Et_2O to afford 28 mg (11% yield) of a clear oil. ^{1}H NMR (700 MHz, C_6D_6) δ 5.55 (ddd, *J* = 15.5, 9.7, 5.9 Hz, 1H), 3.81 (d, *J* = 5.7 Hz, 1H), 2.71 – 2.65 (m, 1H), 2.47 (dd, *J* = 14.5, 9.7 Hz, 1H), 2.03 (dd, *J* = 13.5, 4.3 Hz, 1H), 1.93 – 1.80 (m, 2H), 1.73 (d, *J* = 10.4 Hz, 3H), 1.52 (m, 11H), 1.31 – 1.08 (m, 8H), 1.07 – 0.83 (m, 13H), 0.74 (s, 3H), 0.66 (d, *J* = 8.9 Hz, 3H). ^{13}C NMR (176 MHz, C_6D_6) δ 169.64, 87.79, 82.83, 67.06, 56.55, 56.38, 47.40, 45.66, 42.80, 40.27, 39.97, 39.25, 36.67, 36.28, 34.50, 31.91, 31.45, 28.61, 28.46, 28.33, 24.73, 24.42, 23.47, 23.08, 22.82, 20.88, 19.14, 12.17, 11.83. **IR** (cm^{-1}): 2930.42, 2867.62, 1741.26, 1466.53, 1369.79, 1239.97, 1022.38 **HRMS**: calculated for $C_{29}H_{48}O_3Na^+$ ([M+Na^+]$^+$): 445.3673 found: 445.3675.



15

(3*R*,3*aR*,5*aS*,9*S*,13*aR*,13*bS*,E)-9-hydroxy-3a,6-dimethyl-3-(6-methylheptan-2-yl)-1,2,3,3*a*,4,5,5*a*,8,9,10,12,13,13*a*,13*b*-tetradecahydro-11H-cyclodeca[e]inden-11-one (15): **14** (407 mg, 0.92 mmol) was dissolved in DCM (3 mL) and KOH (1M in MeOH, 2.8 mL, 2.8 mmol) was added by syringe. The mixture was quenched with 1M aqueous HCl (1 mL), then diluted with water and DCM. The layers were separated and the aqueous layer washed with two additional portions of DCM. The combined organic layers were dried over Na_2SO_4 before being concentrated by rotary evaporator and purified by flash column chromatography eluting with hexanes/EtOAc to afford 369 mg (86% yield) of the title compound as a white solid. **^{1}H NMR** (700 MHz, DMSO) δ 4.89 (d, *J* = 5.3 Hz, 1H), 4.66 (dd, *J* = 10.5, 5.6 Hz, 1H), 4.04 (s, 1H), 2.37 (dd, *J* = 23.1, 10.0 Hz, 2H), 2.25 – 2.12 (m, 4H), 1.88 – 1.83 (m, 1H), 1.80 – 1.74 (m, 1H), 1.69 (s, 3H), 1.67 – 1.60 (m, 2H), 1.56 – 1.44 (m, 4H), 1.38 – 1.29 (m, 4H), 1.23 – 1.17 (m, 1H), 1.16 – 1.02 (m, 7H), 0.97 (dt, *J* = 17.9, 8.7 Hz, 2H), 0.88 (d, *J* = 6.4 Hz, 3H), 0.84 (dd, *J* = 6.5, 3.5

Hz, 6H), 0.67 (s, 3H).**^{13}C NMR** (176 MHz, DMSO) δ 206.91, 138.43, 124.06, 71.74, 55.75, 55.72, 54.46, 51.26, 42.16, 41.78, 38.87, 38.84, 37.42, 37.35, 35.54, 35.07, 27.32, 27.29, 27.10, 26.14, 24.83, 23.16, 22.52, 22.27, 18.44, 12.69, 11.65. **IR** (cm^{-1}): 2927.72, 2866.38, 1695.45, 1678.29, 144.52, 1383.09, 1366.17, 1273.65, 1253.95, 1168.74, 1113.34, 1086.47, 1052.40, 1026.05, 965.02, 920.39, 884.67. **HRMS**: calculated for $C_{27}H_{47}O_2^+$ ($[M+H^+]^+$): 403.3571 found: 403.3572.

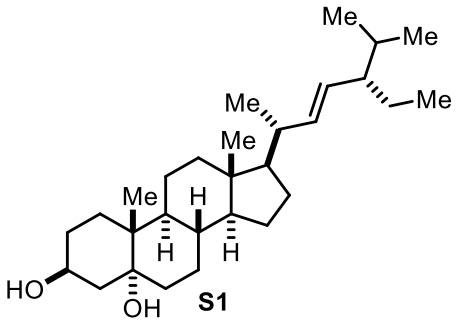


SI-2

(3*R*,3*aR*,5*aS*,9*S*,13*aR*,13*bS*,*E*)-3a,6-dimethyl-3-(6-methylheptan-2-yl)-11-oxo-2,3,3*a*,4,5,5*a*,8,9,10,11,12,13,13*a*,13*b*-tetradecahydro-1H-cyclodeca[e]inden-9-yl 4-bromobenzoate (**S-2**)[5]: **15** (25 mg, 0.062 mmol) was dissolved in DCM (0.2 mL) and pyridine (0.015 mL, 0.19 mmol), 4-bromobenzoyl chloride (16 mg, 0.075 mmol) and a spatula tip of DMAP were added. The reaction mixture was stirred at room temperature until judged complete by TLC. The reaction mixture was diluted with DCM and poured onto saturated aqueous ammonium chloride. The layers were separated and the aqueous layer was washed with two additional portions of DCM. The combined organic layers were dried over Na_2SO_4 and concentrated by rotary evaporator, then purified by flash column chromatography eluting with hexanes/EtOAc to afford 8 mg (22% yield) of product. Recrystallization by slow evaporation of diethyl ether afforded crystals that were analyzed by X-ray crystallography (see Part 5 for details). **^{1}H NMR** (700 MHz, $CDCl_3$δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 2H), 5.61 (s, 1H), 4.89 (d, *J* = 11.5 Hz, 1H), 2.70 – 2.43 (m, 5H), 2.31 – 2.25 (m, 1H), 1.93 (d, *J* = 12.1 Hz, 1H), 1.85 – 1.66 (m, 8H), 1.52 – 1.49 (m, 1H), 1.43 – 1.30 (m, 4H), 1.25 (d, *J* = 12.4 Hz, 3H), 1.13 (ddd, *J* = 28.5, 25.9, 11.5 Hz, 6H), 1.03 – 0.97 (m, 1H), 0.89 (dd, *J* = 29.8, 4.7 Hz, 9H), 0.71 (s, 3H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 206.19, 164.83, 141.13, 131.92, 131.82, 131.26, 129.48, 128.17, 123.21, 75.51, 56.45, 56.23, 54.88, 47.81, 42.91, 42.85, 39.65, 39.44, 38.30, 36.24, 35.92, 34.13, 28.17, 27.99, 27.69, 26.77, 25.52, 23.99, 22.98, 22.72, 18.85, 13.38, 12.11. **IR** (cm^{-1}): 1722.40, 1271.80, 1168.30, f1117.72, 1013.00, 974.24 **HRMS**: calculated for $C_{34}H_{49}BrO_3^+$ ($[M+H^+]^+$): 585.2938 found: 585.2937.

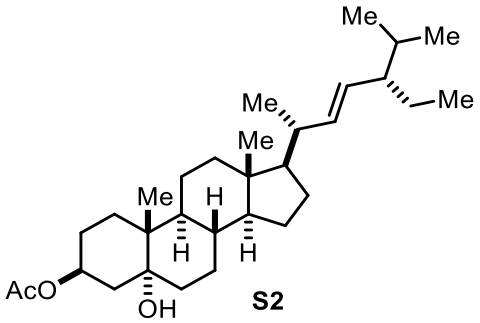
iii. Stigmasterol-Derived

[5] Mihailović, M. L.; Lorenc, L.; Popov, N.; Kalvoda, J. *Helv. Chim. Acta.* **1971**, *54*, 2281.



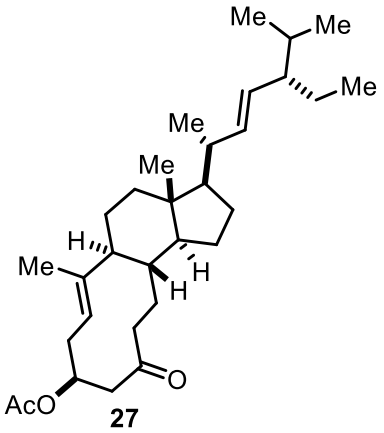
S1

(3*S*,5*R*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-17-((5*S, E*)-5-ethyl-6-methylhept-3-en-2-yl)-10,13-dimethylhexadecahydro-5H-cyclopenta[a]phenanthrene-3,5-diol (S1): Stigmasterol (3.0 g, 7.27 mmol) was dissolved in DCM (90 mL) and water (150 mL) and sodium carbonate (1.54 g, 14.5 mmol) were added. The mixture was cooled on an ice bath and *m*CPBA (~75% purity, 2.84 g, 12.4 mmol) was added as a solid. The reaction mixture was stirred at 0°C until judged complete by TLC, then quenched with a saturated aqueous solution of sodium thiosulfate. The layers were separated and the aqueous layer was washed with two additional portions of DCM. The combined organic layers were dried over Na_2SO_4, filtered through a pad of silica gel eluting with DCM, and concentrated by rotary evaporator. The crude material was then dissolved in THF (90 mL) and cooled on an ice bath. $LiAlH_4$ (552 mg, 14.5 mmol) was then added portionwise over several minutes. The reaction mixture was warmed to room temperature and then heated to reflux overnight. The mixture was again cooled on an ice bath and saturated aqueous sodium potassium tartrate was added dropwise. When gas evolution ceased, the reaction mixture was diluted with additional saturated aqueous sodium potassium tartrate and EtOAc. The mixture was stirred until the two phases began to separate. The layers were separated and the aqueous layer washed with two additional portions of EtOAc. The combined organic layers were dried over Na_2SO_4, filtered and concentrated by rotary evaporator. The crude material was purified by flash column chromatography eluting with hexanes/EtOAc to afford 1.27 g (41% yield) of the title compound as a white solid. **^{1}H NMR** (700 MHz, CDCl3) δ 5.14 (dd, *J* = 15.2, 8.7 Hz, 1H), 5.04 – 4.99 (m, 1H), 4.09 (dt, *J* = 15.9, 5.3 Hz, 1H), 2.07 – 1.77 (m, 4H), 1.74 – 1.59 (m, 4H), 1.54 – 1.38 (m, 9H), 1.32 – 0.97 (m, 18H), 0.87 – 0.75 (m, 9H), 0.69 – 0.63 (m, 3H).**^{13}C NMR** (176 MHz, $CDCl_3$) δ 138.46, 129.41, 75.50, 67.52, 56.45, 56.14, 51.38, 46.11, 44.06, 42.76, 40.68, 40.07, 38.97, 34.88, 34.56, 32.04, 31.05, 30.96, 29.09, 26.10, 25.56, 24.33, 21.50, 21.33, 21.25, 19.14, 16.41, 12.48, 12.41. **IR** (cm^{-1}): 3398.01, 2863.00, 1415.04, 1380.20, 1369.05, 1325.89, 1293.27, 1081.13, 1039.28, 969.22, 937.14, 918.88, 870.22, 823.04, 777.60, 730.76, 684.02, 665.09. **HRMS**: calculated for $C_{29}H_{50}O_2Na^+$ ($[M+Na^+]^+$): 453.3703 Found: 453.3700.



S2

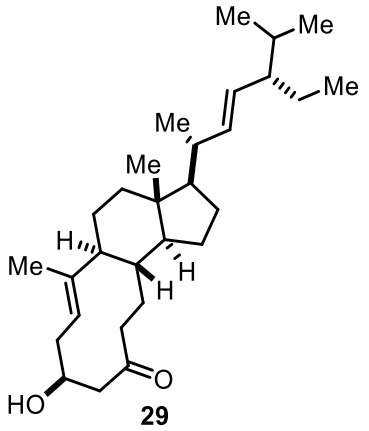
(3*S*,5*R*,8S,9*S*,10*R*,13*R*,14*S*,17*R*)-17-((5*S*,*E*)-5-ethyl-6-methylhept-3-en-2-yl)-5-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (S2): **S1** (1.26 g, 2.93 mmol) was dissolved in DCM (10 mL) and treated with DMAP (18 mg, 0.15 mmol) followed by pyridine (0.71 mL, 8.78 mmol) and acetic anhydride (0.33 mL, 3.51 mmol). The reaction mixture was stirred until judged complete by TLC and then quenched with saturated aqueous sodium bicarbonate solution and diluted with DCM. The reaction mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was washed with DCM and the combined organic layers were washed with 1M aqueous HCl and brine, then dried over Na_2SO_4, concentrated and purified by flash column chromatography eluting with hexanes/EtOAc to afford 1.21 g (88% yield) of the title compound as a white solid. **^{1}H NMR** (700 MHz, $CDCl_3$) δ 5.20 – 5.12 (m, 2H), 5.01 (dd, *J* = 15.1, 8.7 Hz, 1H), 2.02 (d, *J* = 8.1 Hz, 4H), 1.95 (d, *J* = 12.6 Hz, 1H), 1.90 – 1.85 (m, 1H), 1.73 – 1.66 (m, 4H), 1.64 – 1.06 (m, 21H), 1.05 – 0.98 (m, 7H), 0.88 – 0.75 (m, 9H), 0.67 (s, 3H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 170.75, 138.48, 129.41, 75.16, 71.00, 56.34, 56.13, 51.38, 45.80, 42.74, 40.69, 40.24, 40.01, 38.97, 34.91, 34.65, 32.04, 30.67, 29.09, 26.95, 26.06, 25.56, 24.33, 21.62, 21.42, 21.34, 21.24, 19.15, 16.26, 12.47, 12.40. **IR** (cm^{-1}): 2936.70, 2866.00, 1731.58, 1703.26, 1381.55, 1364.49, 1278.84, 1268.02, 1253.42, 1026.73, 1004.61. **HRMS**: calculated for $C_{31}H_{52}O_3Na^+$ ($[M+Na^+]^+$): 495.3809 Found: 495.3810.



27

(3*R*,3*aR*,5*aS*,9*S*,13*aR*,13*bS*,*E*)-3-((5*S*,*E*)-5-ethyl-6-methylhept-3-en-2-yl)-3*a*,6-dimethyl-11-oxo-2,3,3a,4,5,5a,8,9,10,11,12,13,13a,13b-tetradecahydro-1H-cyclodeca[e]inden-9-yl acetate (27): **S2** (500 mg, 1.06 mmol) and PIDA (375 mg, 1.16 mmol) were dissolved in DCM (33 mL) and sparged with N_2 for 10 minutes and I_2 (295 mg, 1.16 mmol) was added and the septum was quickly replaced. The reaction mixture was stirred while being irradiated with blue LED for 2 hours. The reaction mixture was poured into a separatory funnel containing saturated aqueous sodium bicarbonate and saturated aqueous sodium thiosulfate and diluted with DCM. The layers were separated and the aqueous layer was washed with an additional portion of DCM. The combined organic layers were dried over Na_2SO_4, concentrated and purified by flash column chromatography eluting with hexanes/Et_2O to afford 218 mg (44% yield) of **27** as a white solid. ^{1}H NMR (500 MHz, DMSO) δ 5.15 (dd, *J* = 15.1, 8.5 Hz, 2H), 5.02 (dd, *J* = 14.9, 8.7 Hz, 1H), 4.64 (d, *J* = 8.6 Hz, 1H), 2.54 (d, *J* = 12.3 Hz, 2H), 2.31 (ddd, *J* = 43.1, 25.2, 9.5 Hz, 5H), 2.05 – 1.93 (m, 4H), 1.84 (d, *J* = 10.1 Hz, 1H), 1.76 – 1.34 (m, 13H), 1.25 – 1.11 (m, 5H), 1.01 (dd, *J* = 29.0, 11.4 Hz, 5H), 0.85 – 0.68 (m, 11H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 206.38, 169.99, 140.84, 138.31, 129.55, 123.42, 74.62, 56.24, 56.23, 54.98, 51.37, 47.79, 42.87, 42.72, 40.65, 39.33, 38.26, 34.08, 32.04, 28.62, 27.67, 26.73, 25.57, 25.55, 21.42, 21.41, 21.25, 19.15, 13.30,

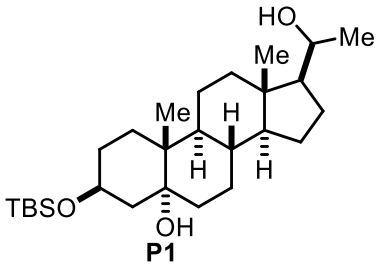
12.40, 12.31. **IR** (cm^{-1}): 2933.19, 2867.48, 1735.35, 1726.57, 1699.90, 14530.19, 1366.29, 1265.38, 1236.88, 1085.38, 1033.74, 986.82, 939.42. **HRMS**: calculated for $C_{31}H_{51}O_3^+$ ($[M+H^+]^+$): 471.3833 Found: 471.3834.



29

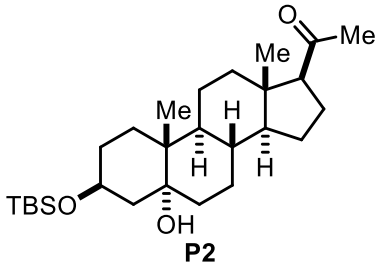
(3*R*,3*aR*,5*aS*,9*S*,13*aR*,13*bS*,*E*)-3-((5*S*,*E*)-5-ethyl-6-methylhept-3-en-2-yl)-9-hydroxy-3*a*,6-dimethyl-1,2,3,3a,4,5,5a,8,9,10,12,13,13a,13b-tetradecahydro-11H-cyclodeca[e]inden-11-one (39): **27** (60 mg, 0.13 mmol) was dissolved in DCM (0.5 mL) and a solution of KOH (1M in MeOH, 0.38 mL, 0.38 mmol) was added and the reaction mixture was allowed to stir at room temperature until judged complete by TLC. The reaction mixture was diluted with DCM and quenched with aqueous 1M HCl and poured into a separatory funnel. The layers were separated and the aqueous layer was washed with two additional portions of DCM. The combined organic layers were dried over Na_2SO_4, concentrated by rotary evaporator and purified by flash column chromatography to afford 53 mg (97% yield) of the title compound as a white solid. **^{1}H NMR** (700 MHz, DMSO) δ 5.15 (dd, *J* = 15.2, 8.6 Hz, 1H), 5.02 (dd, *J* = 15.1, 8.8 Hz, 1H), 4.89 (d, *J* = 5.3 Hz, 1H), 4.69 – 4.64 (m, 1H), 4.05 (d, *J* = 4.5 Hz, 1H), 2.37 (dd, *J* = 23.0, 10.1 Hz, 2H), 2.18 (ddd, *J* = 20.4, 19.6, 8.4 Hz, 4H), 2.02 (d, *J* = 6.7 Hz, 1H), 1.83 (d, *J* = 10.1 Hz, 2H), 1.69 (s, 2H), 1.67 – 1.59 (m, 3H), 1.56 – 1.47 (m, 4H), 1.42 – 1.30 (m, 3H), 1.23 – 1.12 (m, 5H), 1.06 – 0.96 (m, 5H), 0.82 (d, *J* = 6.2 Hz, 3H), 0.77 (dd, *J* = 9.6, 5.0 Hz, 6H), 0.69 (s, 3H). **^{13}C NMR** (176 MHz, DMSO) δ 207.16, 138.60, 137.96, 128.83, 124.08, 71.82, 55.81, 55.49, 54.60, 51.31, 50.58, 42.10, 41.83, 39.92, 38.72, 37.47, 37.36, 31.31, 28.11, 27.13, 26.21, 24.91, 24.85, 21.12, 20.93, 18.84, 12.82, 12.10, 11.92. **IR** (cm^{-1}): 2933.98, 2912.13, 2867.95, 1741.33, 1712.81, 1690.44, 1467.27, 1456.03, 1439.24, 1374.62, 1361.20, 1292.71, 1272.79, 1232.19, 1062.65, 1037.52, 1007.88, 950.17, 299.94, 918.34. **HRMS**: calculated for $C_{29}H_{49}O_2^+$ ($[M+H^+]^+$): 429.3727 Found: 437.3723.

iv. Pregnenolone-Derived



P1

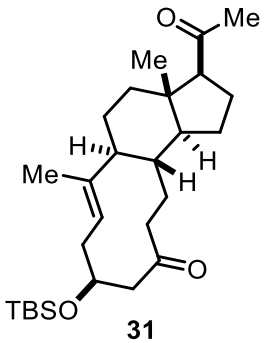
(3*S*,5*R*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-3-((*tert*-butyldimethylsilyl)oxy)-17-((S)-1-hydroxyethyl)-10,13-dimethylhexadecahydro-5H-cyclopenta[a]phenanthren-5-ol (P1): Pregnenolone (10 g, 31.6 mmol) was dissolved in DCM (200 mL) and *m*CPBA (~75% purity, 8.72 g, 37.9 mmol) was added as a solid. The reaction mixture was stirred overnight, then diluted with DCM and poured onto a mixture of saturated aqueous solutions of sodium bicarbonate and sodium thiosulfate. The layers were separated and the aqueous layer was extracted with two additional portions of DCM. The combined organic layers were dried over Na_2SO_4, filtered and concentrated by rotary evaporator. The crude material was taken up in an additional 200 mL of DCM and TBSCl (9.53 g, 63.2 mmol) was added followed by imidazole (6.45 g, 94.8 mmol). The reaction mixture was stirred at room temperature until judged complete by TLC, at which point the mixture was diluted with DCM and poured onto a solution of saturated aqueous ammonium chloride. The aqueous layer was washed with two additional portions of DCM and the combined organic layers were dried over Na_2SO_4, filtered and concentrated by rotary evaporator. The crude material was dissolved in 200 mL of THF and added by dropwise addition funnel to a suspension of $LiAlH_4$ (2.40 g, 63.2 mmol) in THF (100 mL). Upon completion of addition, the reaction mixture was heated to reflux for 24 hours. The reaction mixture was cooled on an ice bath and saturated aqueous sodium potassium tartrate was added slowly dropwise until gas evolution ceased. The mixture was then diluted with additional aqueous sodium potassium tartrate solution and ethyl acetate and stirred until the layers separated. The mixture was then poured into a separatory funnel and the layers were separated. The aqueous layer was washed with two additional portions of ethyl acetate. The combined organic layers were washed with saturated aqueous sodium chloride and dried over Na_2SO_4. After filtration and concentration under reduced pressure, the crude material was purified by flash column chromatography eluting with hexanes/EtOAc to afford 8.27 g (58% yield, 3 steps) of the title compound as a white solid. The stereochemistry of the secondary alcohol is not assigned as it is oxidized in the following step**.** **^{1}H NMR** (401 MHz, $CDCl_3$) δ 4.12 – 3.99 (m, 1H), 3.77 – 3.66 (m, 1H), 2.04 (d, *J* = 9.8 Hz, 1H), 1.78 – 1.02 (m, 26H), 0.99 (s, 3H), 0.88 (s, 9H), 0.74 (s, 3H), 0.05 (s, 6H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 75.61, 70.73, 68.15, 58.70, 55.83, 46.13, 44.67, 42.82, 40.30, 38.98, 34.75, 34.55, 31.40, 31.08, 26.15, 26.11 (3C), 25.80, 24.51, 23.79, 21.39, 18.39, 16.47, 12.79, -4.34, -4.45. **IR (cm^{-1}):** 2927.90, 2853.63, 1461.94, 1447.66, 1376.78, 1248.08, 1165.59, 1117.75, 1094.79, 1067.44, 1005.74, 693.47, 937.17, 903.93, 869.42, 836.11. **HRMS**: Calculated for $C_{27}H_{50}O_3SiNa^+$ ([M+Na$^+$]$^+$): 473.3421 Found: 473.3421.



P2

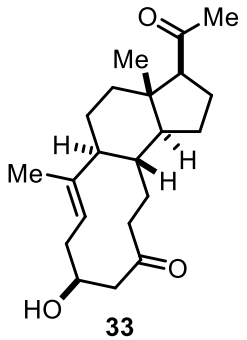
1-((3*S*,5*R*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-3-((*tert*-butyldimethylsilyl)oxy)-5-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)ethan-1-one (P2): Alcohol **P1** (3.38 g, 7.5 mmol) was suspended in DMSO (50 mL) and IBX was added as a solid. The reaction mixture was heated to 50°C and stirred until judged complete by TLC. The mixture was cooled on an ice bath and quenched with saturated aqueous sodium thiosulfate solution and diluted with ethyl acetate. After stirring until two layers were evident, the layers were separated and the aqueous layer was extracted with two additional portions of ethyl acetate. The combined

organic layers were washed with saturated sodium chloride and dried over Na_2SO_4, filtered and concentrated by rotary evaporator. The crude material was purified by flash column chromatography to afford 1.78 g (53% yield) of the desired product. **^{1}H NMR** (700 MHz, $CDCl_3$) δ 4.05 (td, *J* = 10.6, 5.5 Hz, 1H), 2.53 (t, *J* = 9.0 Hz, 1H), 2.16 (d, *J* = 11.1 Hz, 1H), 2.11 (s, 3H), 2.01 (d, *J* = 12.3 Hz, 1H), 1.76 – 1.61 (m, 5H), 1.55 – 1.38 (m, 8H), 1.35 – 1.17 (m, 6H), 1.08 (s, 2H), 0.98 (s, 3H), 0.88 (s, 9H), 0.61 (d, *J* = 13.1 Hz, 3H), 0.05 (d, *J* = 7.1 Hz, 6H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 209.75, 75.55, 68.09, 63.93, 56.57, 45.91, 44.75, 44.51, 39.28, 38.95, 34.91, 34.56, 31.68, 31.38, 31.08, 26.10 (3C), 26.03, 24.46, 22.96, 21.51, 18.38, 16.42, 13.67, -4.34, -4.45. **IR** (cm^{-1}): 2930.09, 2889.95, 2852.49, 1684.86, 1470.75, 1446.86, 1384.10, 1358.47, 1251.72, 1186.21, 1117.24, 1098.23, 1076.54, 1006.54, 851.57, 835.92. **HRMS**: Calculated for $C_{27}H_{48}O_3SiNa^+$ ([M+Na^+]$^+$): 471.3265 Found: 471.3260.



31

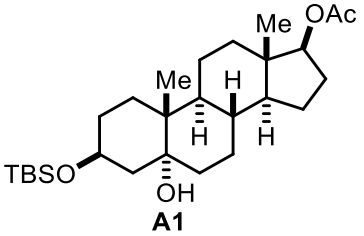
(3*S*,3*aS*,5*aS*,9*S*,13*aR*,13bS,E)-3-acetyl-9-((tert-butyldimethylsilyl)oxy)-3a,6-dimethyl-1,2,3,3a,4,5,5a,8,9,10,12,13,13a,13b-tetradecahydro-11H-cyclodeca[e]inden-11-one (31): **P2** (1.00 g, 2.23 mmol) and phenyliodine (III) diacetate (790 mg, 2.45 mmol) were dissolved in DCM and sparged with nitrogen gas for 10 minutes before the septum was quickly removed and I_2 (566 mg, 2.23 mmol) was added and the septum quickly replaced. The reaction mixture was irradiated with blue LEDs for 2 hours. The reaction mixture was poured onto saturated aqueous sodium thiosulfate and saturated aqueous sodium bicarbonate and diluted with DCM. After shaking until the purple color disappeared, the layers were separated and the aqueous layer was washed with two additional portions of DCM. The combined organic layers were dried over Na_2SO_4, filtered and concentrated by rotary evaporator before being purified by flash column chromatography eluting with hexanes/EtOAc to afford 806 mg (81% yield) of product as a white solid. **^{1}H NMR** (500 MHz, DMSO) δ 4.68 (d, *J* = 9.8 Hz, 1H), 4.24 (s, 1H), 2.59 (t, *J* = 9.2 Hz, 1H), 2.40 (dd, *J* = 29.6, 18.4 Hz, 2H), 2.20 (dd, *J* = 24.1, 14.4 Hz, 3H), 2.08 – 1.82 (m, 5H), 1.76 – 1.31 (m, 11H), 1.19 (dd, *J* = 27.1, 12.8 Hz, 4H), 0.87 (d, *J* = 9.9 Hz, 9H), 0.56 (s, 3H), 0.08 (d, *J* = 13.5 Hz, 6H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 209.66, 207.74, 139.26, 124.85, 73.85, 64.05, 56.17, 55.26, 52.15, 44.36, 42.70, 38.69, 38.62, 38.02, 31.82, 27.70, 26.70, 26.06 (3C), 25.71, 22.79, 18.36, 13.53, 13.36, -4.50, -4.66. **IR** (cm^{-1}): 2732.79, 2855.00, 1706.24, 1693.20, 1470.08, 1359.63, 1249.54, 1231.80, 1075.66 1039.85, 935.41, 899.21, 862.10. **HRMS**: Calculated for $C_{27}H_{46}O_3SiNa^+$ ([M+Na^+]$^+$): 469.3108 Found: 469.3110.



33

(3*S*,3*aS*,5*aS*,9*S*,13*aR*,13*bS*,*E*)-3-acetyl-9-hydroxy-3a,6-dimethyl-1,2,3,3*a*,4,5,5*a*,8,9,10,12,13,13*a*,13*b*-tetradecahydro-11H-cyclodeca[e]inden-11-one (33): **31** (720 mg, 1.61 mmol) was dissolved in THF (16 mL) and cooled on an ice bath. TBAF (1M in THF, 3.22 mL, 3.22 mmol) was added slowly via syringe and the reaction mixture was warmed to room temperature and stirred overnight. The reaction mixture was concentrated and directly purified by silica gel column chromatography to afford 462 mg (86% yield) of the desired product as a white solid. **^{1}H NMR** (700 MHz, DMSO) δ 4.91 (d, *J* = 15.2 Hz, 1H), 4.73 – 4.61 (m, 1H), 4.05 (s, 1H), 2.58 (dd, *J* = 21.9, 13.1 Hz, 1H), 2.37 (t, *J* = 12.4 Hz, 2H), 2.31 – 2.11 (m, 4H), 2.05 (s, 3H), 1.99 (dd, *J* = 21.0, 10.4 Hz, 1H), 1.89 (d, *J* = 11.2 Hz, 1H), 1.77 – 1.33 (m, 11H), 1.25 – 1.09 (m, 3H), 0.56 (s, 3H). **^{13}C NMR** (176 MHz, DMSO) δ 208.57, 207.24, 138.41, 124.31, 71.85, 62.76, 55.66, 54.48, 51.33, 43.49, 41.80, 37.55, 37.50, 37.31, 31.28, 27.13, 26.26, 25.05, 21.98, 13.05, 12.86 **IR** (cm^{-1}): 2934.46, 2854.53, 1692.91, 1677.88, 1427.72, 1381.84, 1354.73, 1249.84, 1102.68, 1036.37, 887.23, 863.22, 833.32, 799.36, 774.64, 636.80 **HRMS**: Calculated for $C_{21}H_{32}O_3Na^+$ ($[M+Na^+]^+$): 355.2244 Found: 355.2247.

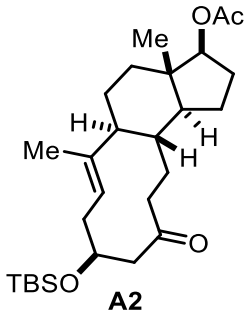
v. Androsterone-Derived (from Pregnenolone-Derived Intermediate)



A1

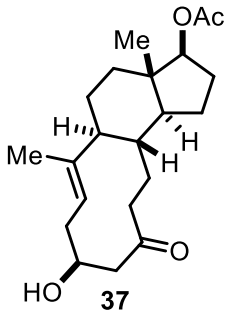
(3*S*,5*R*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-3-((*tert*-butyldimethylsilyl)oxy)-5-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl acetate (A1): 1-((3S,5R,8S,9S,10R,13S,14S,17S)-3-((tert-butyldimethylsilyl)oxy)-5-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)ethan-1-one (500 mg, 1.11 mmol) was dissolved in DCM (10 mL) and treated with *m*CPBA (1.03 g, 4.46 mmol) and allowed to stir at room temperature for 48 hours, at which point an additional portion of *m*CPBA (1.03 g, 4.46 mmol) was added and the reaction mixture was stirred for an additional 48 hours. The reaction was then poured onto a saturated solution of sodium thiosulfate and sodium bicarbonate and diluted with DCM. The layers were separated and the aqueous layer was washed with DCM. The combined organic layers were dried over Na_2SO_4 and concentrated by rotary evaporator before being purified by flash column chromatography to afford 200 mg (39% yield) of the title compound as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.59 (t, *J* = 8.5 Hz, 1H), 4.05 (td, *J* = 10.4, 5.1 Hz, 1H), 2.21 – 2.10 (m, 1H), 2.03 (s, 3H), 1.76 – 1.07 (m, 21H), 0.99 (s, 3H), 0.88 (s, 9H), 0.76 (d, *J* = 10.9 Hz, 3H), 0.05 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.35, 82.95,

75.54, 68.09, 50.65, 46.03, 44.73, 42.91, 39.02, 37.13, 34.72, 34.49, 31.38, 31.09, 27.72, 26.11 (3C), 25.66, 23.60, 21.34, 20.97, 18.39, 16.44, 12.34, -4.35, -4.45. **IR** (cm^{-1}): 2932.40, 2854.78, 1722.44, 1369.33, 1246.02, 1094.91, 1062.42, 1037.95, 1022.18, 1006.57, 871.14, 832.18. **HRMS**: Calculated for $C_{27}H_{48}O_4SiNa^+$ ($[M+Na^+]^+$): 487.3214 Found: 487.3214.



A2

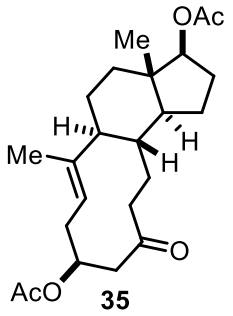
(3*S*,3*aS*,5*aS*,9*S*,13*aR*,13*bS*,*E*)-9-((*tert*-butyldimethylsilyl)oxy)-3a,6-dimethyl-11-oxo-2,3,3a,4,5,5a,8,9,10,11,12,13,13a,13b-tetradecahydro-1H-cyclodeca[e]inden-3-yl acetate (A2): **A1** (95 mg, 0.20 mmol) and phenyliodine(III) diacetate (200 mg, 0.43 mmol) were dissolved in DCM (6.5 mL) and sparged with N_2 for 10 minutes before I_2 (67 mg, 1.3 mmol) was added and the septum quickly replaced. The reaction mixture was irradiated with blue LEDs for 2 hours, at which time it was poured onto a mixture of saturated aqueous sodium thiosulfate and saturated aqueous sodium bicarbonate and diluted with DCM. The layers were separated and the aqueous layer was washed with two additional portions of DCM. The combined organic layers were dried over Na_2SO_4 and concentrated by rotary evaporator before purification by flash column chromatography eluting with hexanes/EtOAc to afford 140 mg (70% yield) of the title compound as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.85 – 4.76 (m, 1H), 4.59 (t, *J* = 8.5 Hz, 1H), 4.42 – 4.32 (m, 1H), 2.51 – 2.12 (m, 7H), 2.03 (s, 3H), 1.79 – 1.70 (m, 4H), 1.69 – 1.56 (m, 5H), 1.47 (ddd, *J* = 21.8, 14.6, 6.2 Hz, 2H), 1.36 – 1.22 (m, 2H), 1.18 (t, *J* = 12.1 Hz, 1H), 1.08 (td, *J* = 11.5, 7.4 Hz, 1H), 0.89 (s, 9H), 0.82 (s, 3H), 0.09 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.64, 171.24, 139.22, 124.69, 82.89, 73.79, 56.27, 52.11, 49.31, 42.77, 42.58, 38.63, 37.78, 36.45, 27.28, 27.17, 26.19, 26.00 (3C), 24.64, 21.31, 18.29, 13.33, 12.15, -4.56, -4.73. **IR** (cm-1): 2947.65, 2926.38, 2856.28, 1734.59, 1699.19, 1357.96, 1240.14, 1080.69, 1058.69, 1025.87, 936.20, 898.72, 832.69. HRMS: Calculated for $C_{27}H_{46}O_4Si^+$ ($[M+Na^+]^+$): 485.3058 Found: 485.3060.



37

(3*S*,3*aS*,5*aS*,9*S*,13*aR*,13*bS*,*E*)-9-hydroxy-3a,6-dimethyl-11-oxo-2,3,3a,4,5,5a,8,9,10,11,12,13,13a,13b-tetradecahydro-1H-cyclodeca[e]inden-3-yl acetate (37): **A2** (140 mg, 0.30 mmol) was dissolved in THF (3 mL) and cooled on an ice bath. A solution of TBAF (1M in THF, 0.61 mL, 0.61 mmol) was added slowly and the reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was directly

concentrated by rotary evaporator and purified by flash column chromatography eluting with hexanes/EtOAc to afford 98 mg (93% yield) of the title product as a white solid. **^{1}H NMR** (700 MHz, DMSO) δ 4.92 (s, 1H), 4.67 (s, 1H), 4.52 (t, *J* = 8.3 Hz, 1H), 4.05 (s, 1H), 2.37 (t, *J* = 10.8 Hz, 2H), 2.19 (ddd, *J* = 31.1, 21.0, 11.0 Hz, 4H), 2.03 (d, *J* = 4.6 Hz, 1H), 1.98 (s, 3H), 1.69 (s, 4H), 1.64 – 1.36 (m, 7H), 1.27 (dd, *J* = 10.8, 5.6 Hz, 2H), 1.14 (dd, *J* = 21.9, 12.5 Hz, 2H), 1.09 – 0.93 (m, 2H), 0.78 (s, 3H). **^{13}C NMR** (176 MHz, DMSO) δ 207.28, 170.28, 138.38, 124.27, 81.94, 71.84, 55.75, 51.33, 48.62, 42.22, 41.74, 37.51, 37.12, 35.84, 26.77, 26.69, 25.76, 24.04, 20.88, 12.89, 11.90. **IR** (cm^{-1}): 2925.60, 2857.16, 1374.43, 1712.46, 1699.16, 1441.59, 1357.31, 1243.09, 1199.06, 1081.14, 1056.02, 950.20, 935.80. **HRMS**: Calculated for $C_{21}H_{32}O_4Na^+$ $[M+Na^+]^+$: 371.2193 Found 371.2197



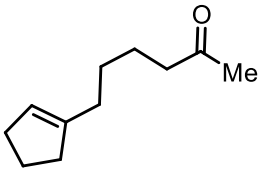
35

(3*S*,3a*S*,5a*S*,9*S*,13a*R*,13b*S*,*E*)-3a,6-dimethyl-11-oxo-2,3,3a,4,5,5a,8,9,10,11,12,13,13a,13b-tetradecahydro-1H-cyclodeca[e]indene-3,9-diyl diacetate (35): **37** (88 mg, 0.25 mmol) was dissolved in DCM (1 mL) and treated with acetic anhydride (36 μL, 0.379 mmol) and pyridine (0.10 mL, 1.26 mmol) as well as a spatula tip of DMAP. The reaction was stirred until judged complete by TLC and quenched with saturated aqueous sodium bicarbonate and diluted with DCM. The layers were separated and the aqueous layer was extracted with two additional portions of DCM. The combined organic layers were then washed successively with 1M HCl and brine, then dried over Na_2SO_4 and concentrated by rotary evaporator. The crude product was purified by flash column chromatography eluting with hexanes/EtOAc to afford 60 mg (61% yield) of the title compound as an off white, powdery solid. **^{1}H NMR** (700 MHz, DMSO) δ 5.18 – 5.11 (m, 1H), 4.70 – 4.62 (m, 1H), 4.52 (t, *J* = 8.5 Hz, 1H), 2.57 (dd, *J* = 22.8, 10.0 Hz, 1H), 2.42 – 2.22 (m, 4H), 2.06 – 1.96 (m, 7H), 1.75 – 1.40 (m, 11H), 1.35 – 1.23 (m, 2H), 1.23 – 1.11 (m, 2H), 1.07 (td, *J* = 11.6, 7.4 Hz, 1H), 0.83 – 0.75 (m, 3H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 206.14, 171.21, 169.95, 140.18, 123.84, 82.84, 74.51, 56.13, 49.24, 47.75, 42.75, 42.64, 37.97, 36.38, 34.06, 27.26, 27.10, 26.24, 24.63, 21.37, 21.29, 13.29, 12.14 **IR** (cm^{-1}): 1731.47, 1699.70, 1372.08, 1237.94, 1089.74, 1025.77, 939.78, 880.21. **HRMS**: Calculated for $C_{23}H_{34}O_5Na^+$ $[M+Na^+]^+$: 413.2298 Found: 413.2302.

b. Lewis Acid Reactions

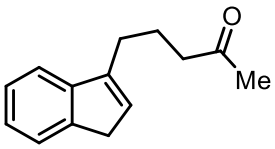
i. $FeCl_3$-Catalyzed Carbonyl-Olefin Metathesis

General procedure A for $FeCl_3$-catalyzed carbonyl-olefin metathesis: Cyclodecenone substrate (1 equiv.) was dissolved in DCE (0.05M) and $FeCl_3$ (0.1 equiv.) was added and the reaction mixture was stirred at room temperature until judged complete by TLC or for 24 hours. The crude reaction mixture was filtered through a plug of silica gel eluting with DCM to afford the crude products, which were purified by flash column chromatography.



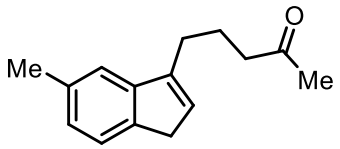
24

6-(cyclopent-1-en-1-yl)hexan-2-one (24): **23** (39 mg, 0.24 mmol) was subjected to the general metathesis procedure with $FeCl_3$ (3.8 mg) at room temperature for 1 hour to afford 42% yield by NMR vs. dimethyl terephthalate as an internal standard. An analytical sample was obtained by flash column chromatography eluting with hexanes/diethyl ether. **^{1}H NMR** (401 MHz, $CDCl_3$) δ 5.32 (s, 1H), 2.43 (t, *J* = 7.3 Hz, 2H), 2.28 (dd, *J* = 9.9, 4.6 Hz, 2H), 2.20 (d, *J* = 6.8 Hz, 2H), 2.13 (s, 3H), 2.07 (t, *J* = 7.0 Hz, 2H), 1.89 – 1.78 (m, 2H), 1.58 (dd, *J* = 15.2, 7.6 Hz, 2H), 1.48 – 1.38 (m, 2H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 209.52, 144.56, 123.68, 43.88, 35.20, 32.62, 31.10, 30.10, 27.48, 23.87, 23.63. **IR** (cm^{-1}): 2930.45, 2849.67, 1709.14, 1408.14, 1358.15, 1162.14, 1030.83, 970.30.



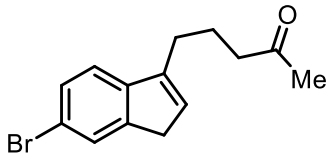
26a

5-(1H-inden-3-yl)pentan-2-one (26): Prepared by subjecting **25a** (50 mg, 0.25 mmol) to general procedure A. The crude product was purified by flash column chromatography eluting with hexanes/EtOAc to afford 32 mg (64% yield) of the title compound. **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.20 (td, *J* = 7.4, 0.9 Hz, 1H), 6.22 (s, 1H), 3.33 (d, *J* = 1.8 Hz, 2H), 2.57 (ddd, *J* = 7.6, 3.4, 1.6 Hz, 2H), 2.53 (t, *J* = 7.3 Hz, 2H), 2.14 (s, 3H), 2.01 – 1.95 (m, 2H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 209.01, 145.35, 144.61, 143.76, 128.44, 126.17, 124.72, 123.90, 119.11, 43.37, 37.87, 30.16, 27.13, 22.08. **IR** (cm^{-1}): 2884.40, 1711.72, 1456.48, 1398.19, 1354.93, 1156.18. **HRMS**: calculated for $C_{14}H_{17}O$ ($[M+H^+]^+$): 201.1274 Found: 201.1273.



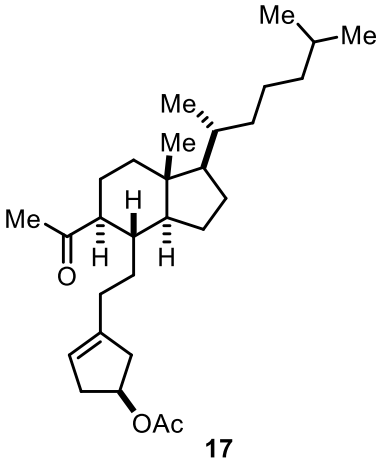
26b

5-(5-methyl-1H-inden-3-yl)pentan-2-one(26b): Prepared by subjecting **25b** (50 mg, 0.23 mmol) to general procedure A. The crude product was purified by flash column chromatography eluting with hexanes/EtOAc to afford 26.5 mg (53% yield) of the title compound as a yellow-white solid. **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.5 Hz, 1H), 7.18 (s, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.20 (s, 1H), 3.29 (s, 2H), 2.54 (ddd, *J* = 17.1, 11.8, 4.4 Hz, 4H), 2.41 (s, 3H), 2.14 (s, 3H), 2.03 – 1.94 (m, 2H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 209.08, 145.66, 143.71, 141.75, 135.83, 128.81, 125.61, 123.65, 119.93, 43.47, 37.55, 30.21, 27.21, 22.20, 21.77. **IR** (cm^{-1}): 1715.41, 1405.49, 1365.80, 1348.44, 1239.05, 1152.39, 963.39, 870.40, 813.51. **HRMS**: calculated for $C_{15}H_{19}O^+$ ($[M+H]^+$): 215.1430 found: 215.1419.



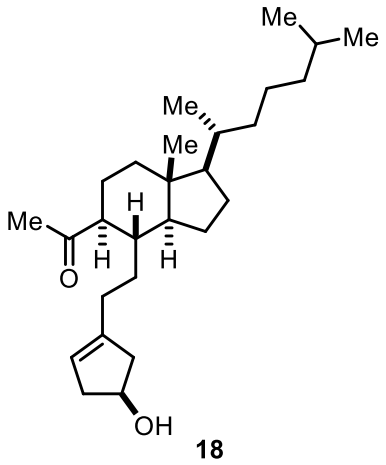
26c

5-(6-bromo-1H-inden-3-yl)pentan-2-one (26c): Prepared by subjecting **25c** (30 mg, 0.11 mmol) to general procedure A. The crude product was purified by flash column chromatography eluting with hexanes/EtOAc to afford 12 mg (40% yield) of the title compound as a yellow solid. **^{1}H NMR** (401 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.42 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 6.20 (s, 1H), 3.31 (s, 2H), 2.52 (dd, *J* = 9.0, 5.4 Hz, 4H), 2.17 (s, 1H), 2.14 (s, 3H), 1.95 (dt, *J* = 14.7, 7.4 Hz, 2H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 208.58, 146.49, 144.15, 143.23, 129.06, 128.59, 127.00, 120.17, 118.75, 43.07, 37.61, 30.00, 26.89, 21.85. **IR** (cm^{-1}):2934.09, 1715.22, 1405.45, 1365.31, 1348.32, 1239.49, 1182.05, 1152.84, 963.33, 870.45, 812.59. **HRMS**: calculated for $C_{14}H_{15}BrONa^+$ ($[M+Na]^+$): 301.0198 found: 301.0165.



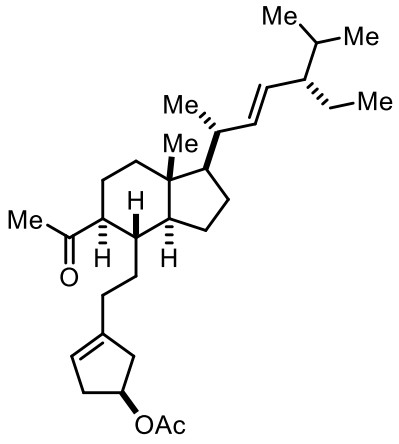
17

(1*S*)-3-(2-((1*R*,3*aS*,4*S*,5*S*,7a*R*)-5-acetyl-7a-methyl-1-(6-methylheptan-2-yl)octahydro-1H-inden-4-yl)ethyl)cyclopent-3-en-1-yl acetate (17): Prepared by subjecting substrate **14** (50 mg, 0.11 mmol) to general procedure A. The crude product was purified by silica gel column chromatography eluting with hexanes/Et_2O to afford 16 mg (31% yield) of furan **19** followed by 20 mg (39% yield) of the title compound **17**. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.35 – 5.27 (m, 1H), 5.24 (s, 1H), 2.67 (ddd, *J* = 24.1, 17.3, 6.1 Hz, 2H), 2.35 – 2.19 (m, 3H), 2.15 (s, 3H), 2.06 – 1.96 (m, 5H), 1.88 – 1.78 (m, 2H), 1.72 – 1.47 (m, 5H), 1.43 – 1.24 (m, 6H), 1.21 – 1.06 (m, 7H), 1.04 – 0.96 (m, 1H), 0.94 – 0.79 (m, 9H), 0.73 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 213.56, 171.28, 142.71, 120.47, 74.83, 56.80, 56.29, 53.03, 43.03, 42.37, 39.79, 39.70, 39.53, 36.71, 36.33, 35.91, 30.17, 29.30, 28.24, 28.06, 26.96, 26.42, 24.86, 23.99, 23.04, 22.78, 21.60, 18.92, 12.03. **IR** (cm^{-1}): 2929.48, 2866.74, 1736.06, 1707.86, 1364.74, 1026.23, 608.43. **HRMS**: calculated for $C_{29}H_{48}O_3$ ($[M+H^+]^+$): 445.3676 Found: 445.3675.



18

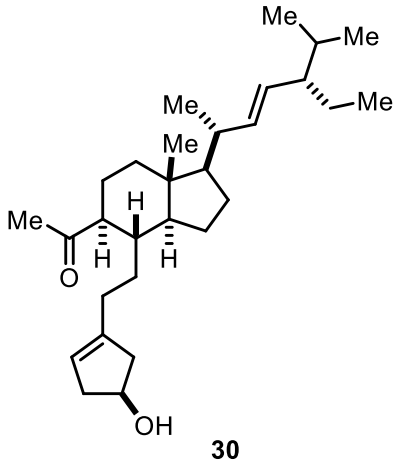
1-((1R,3aS,4S,5S,7aR)-4-(2-((S)-4-hydroxycyclopent-1-en-1-yl)ethyl)-7a-methyl-1-(6-methylheptan-2-yl)octahydro-1H-inden-5-yl)ethan-1-one (18): Prepared by subjecting substrate **15** (39 mg, 0.096 mmol) to general procedure A. The crude product was purified by silica gel column chromatography eluting with hexanes/EtOAc to afford 29 mg (75% yield) of the title compound as a clear oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.24 (s, 1H), 4.46 (s, 1H), 2.68 – 2.51 (m, 2H), 2.34 – 2.20 (m, 2), 2.16 (d, *J* = 12.7 Hz, 4H), 2.06 – 1.90 (m, 3H), 1.83 (dd, *J* = 10.2, 5.6 Hz, 2H), 1.73 – 1.58 (m, 3H), 1.51 (dd, *J* = 13.1, 6.5 Hz, 2H), 1.44 – 1.23 (m, 6H), 1.23 – 1.06 (m, 7H), 1.03 – 0.97 (m, 1H), 0.94 – 0.82 (m, 9H), 0.71 (d, *J* = 14.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 213.61, 142.68, 120.42, 72.28, 56.73, 56.23, 52.98, 45.52, 42.97, 39.64, 39.47, 36.65, 36.27, 35.85, 30.24, 29.21, 28.18, 28.00, 27.06, 26.35, 24.81, 23.93, 22.97, 22.71, 18.86, 11.97. **IR** (cm^{-1}): 2928.98, 2866.97, 1702.43, 1456.60, 1365.03, 1045.50, 955.33, 907.63, 839.04, 730.18. **HRMS**: Calculated for $C_{27}H_{47}O_2^+$ ($[M+H^+]^+$): 403.3571 Found: 403.3577.



28

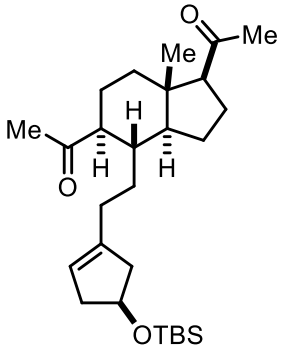
(1*S*)-3-(2-((1*R*,3*aS*,4*S*,5*S*,7*aR*)-5-acetyl-1-((5*S*,*E*)-5-ethyl-6-methylhept-3-en-2-yl)-7a-methyloctahydro-1H-inden-4-yl)ethyl)cyclopent-3-en-1-yl acetate (28): Prepared by subjecting substrate **27** (30 mg, 0.0064 mmol) to general procedure A. The crude product was purified by silica gel column chromatography eluting with hexanes/EtOAc to afford 8 mg (26% yield) of the title compound as a white solid. **^{1}H** NMR (700 MHz, $CDCl_3$) δ 5.30 (s, 1H), 5.23 (s, 1H), 5.14 (dd, *J* = 15.1, 8.7 Hz, 1H), 5.02 (dd, *J* = 15.0, 8.6 Hz, 1H), 2.70 (dd, *J* = 17.1, 6.0 Hz, 1H), 2.62 (dd, *J* = 17.2, 6.7 Hz, 1H), 2.27 (ddd, *J* = 44.5, 36.0, 17.8 Hz, 3H), 2.16 (d, *J* = 16.6

Hz, 3H), 2.08 – 1.93 (m, 7H), 1.82 (s, 1H), 1.75 – 1.65 (m, 2H), 1.63 – 1.50 (m, 5H), 1.45 – 1.32 (m, 3H), 1.29 – 1.24 (m, 1H), 1.22 – 1.11 (m, 5H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.84 (d, *J* = 6.0 Hz, 3H), 0.80 (dd, *J* = 10.9, 6.5 Hz, 5H), 0.77 – 0.71 (m, 3H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 213.45, 171.20, 142.61, 138.13, 129.72, 120.42, 74.76, 56.74, 56.04, 53.10, 51.40, 42.84, 42.28, 40.56, 39.71, 39.35, 36.62, 32.02, 30.12, 29.26, 28.70, 26.90, 26.32, 25.56, 24.88, 21.53, 21.34, 21.26, 19.12, 12.41, 12.15. **IR** (cm^{-1}): 2931.45, 2871.15, 1734.96, 1724.26, 1456.59, 1436.44, 1375.31, 1362.16, 1239.16, 1034.49, 1021.04, 969.19, 954.71, 944.93, 924.28, 906.74, 877.40. **HRMS**: Calculated for $C_{31}H_{50}O_3Na^+$ ($[M+Na^+]^+$): 493.3652 Found: 493.3659.



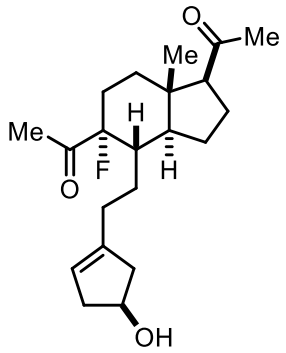
30

1-((1*R*,3*aS*,4*S*,5*S*,7*aR*)-1-((5*S*,*E*)-5-ethyl-6-methylhept-3-en-2-yl)-4-(2-((*S*)-4-hydroxycyclopent-1-en-1-yl)ethyl)-7a-methyloctahydro-1H-inden-5-yl)ethan-1-one (30): Prepared by subjecting substrate **29** (26 mg, 0.061 mmol) to general procedure A at room temperature for 3 hours. The crude product was purified by silica gel column chromatography eluting with hexanes/EtOAc to afford 13 mg (51% yield) of the title compound as a clear oil. **^{1}H NMR** (700 MHz, $CDCl_3$) δ 5.23 (s, 1H), 5.14 (dd, *J* = 14.7, 8.8 Hz, 1H), 5.05 – 4.99 (m, 1H), 4.46 (s, 1H), 2.62 (d, *J* = 16.5 Hz, 1H), 2.55 (d, *J* = 16.6 Hz, 1H), 2.33 – 2.21 (m, 2H), 2.14 (d, *J* = 8.7 Hz, 4H), 2.08 – 1.92 (m, 4H), 1.80 (d, *J* = 26.9 Hz, 1H), 1.63 (ddd, *J* = 63.2, 33.2, 15.4 Hz, 7H), 1.46 – 1.10 (m, 10H), 1.01 (d, *J* = 5.8 Hz, 3H), 0.86 – 0.72 (m, 11H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 213.60, 142.63, 138.14, 129.69, 120.44, 72.25, 56.70, 56.02, 53.08, 51.38, 45.46, 42.93, 42.82, 40.56, 39.34, 36.61, 32.01, 30.23, 29.24, 28.69, 27.04, 26.31, 25.55, 24.88, 21.34, 21.25, 19.11, 12.41, 12.15. **IR** (cm^{-1}): 2952.76, 2927.85, 2876.55, 1704.07, 1366.32, 1047.42, 838.80, 735.80. **HRMS**: Calculated for $C_{29}H_{49}O_2^+$ ($[M+H^+]^+$): 429.3727 Found: 429.3732.



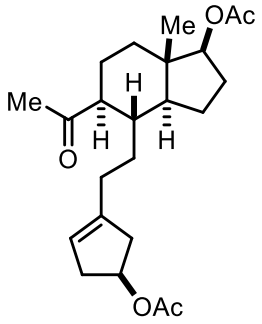
32

1,1'-((1*S*,3*aS*,4*S*,5*S*,7*aS*)-4-(2-((*S*)-4-((tert-butyldimethylsilyl)oxy)cyclopent-1-en-1-yl)ethyl)-7*a*-methyloctahydro-1H-indene-1,5-diyl)bis(ethan-1-one) (32): The reaction of **31** (30 mg, 0.067 mmol) was performed according general procedure A for 15 minutes and purification by flash column chromatography eluting with hexanes/EtOAc provided 21 mg (69% yield) of **32** as a clear wax followed by 4 mg (16% yield; see below for data) of **34**. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.19 (s, 1H), 4.53 – 4.45 (m, 1H), 2.53 (dd, *J* = 19.3, 10.0 Hz, 2H), 2.44 (dd, *J* = 15.6, 7.2 Hz, 1H), 2.32 (td, *J* = 12.0, 4.3 Hz, 1H), 2.25 – 2.14 (m, 5H), 2.12 (s, 4H), 2.05 (d, *J* = 12.4 Hz, 1H), 1.95 (s, 2H), 1.86 – 1.56 (m, 4H), 1.47 – 1.24 (m, 5H), 0.87 (d, *J* = 13.2 Hz, 9H), 0.69 (s, 3), 0.03 (d, *J* = 19.9 Hz, 6H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 212.79, 209.26, 142.14, 120.80, 72.94, 63.59, 56.49, 53.35, 45.30, 44.37, 42.78, 38.52, 36.73, 31.63, 30.19, 29.39, 27.43, 26.18, 26.12 (3C), 25.06, 22.84, 18.43, 13.34, -4.54, -4.56. **IR** (cm^{-1}): 2927.63, 2854.57, 1703.86, 1471.65, 1358.87, 1254.71, 1099.43, 1072.25, 908.89, 835.54 **HRMS**: Calculated for $C_{27}H_{46}O_3SiNa^+$ $[M+Na^+]^+$: 469.3108 Found: 469.3111.



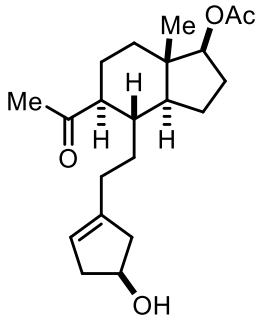
34

1,1'-((1*S*,3*aS*,4*S*,5*R*,7*aS*)-5-fluoro-4-(2-((*S*)-4-hydroxycyclopent-1-en-1-yl)ethyl)-7*a*-methyloctahydro-1H-indene-1,5-diyl)bis(ethan-1-one) (34): The reaction of **33** (31 mg, 0.093 mmol) was performed according to general procedure A at room temperature for 3 hours and purified by flash column chromatography eluting with hexanes/EtOAc to provide 26 mg of **34** (84%). **^{1}H NMR** (700 MHz, $CDCl_3$) δ 5.26 (s, 1H), 4.49 (d, *J* = 5.8 Hz, 1H), 2.70 – 2.61 (m, 1H), 2.56 (dt, *J* = 18.5, 7.6 Hz, 2H), 2.34 (td, *J* = 12.0, 4.3 Hz, 1H), 2.27 (d, *J* = 16.8 Hz, 1H), 2.23 – 1.95 (m, 10H), 1.89 – 1.82 (m, 1H), 1.82 – 1.65 (m, 3H), 1.64 – 1.55 (m, 3H), 1.49 – 1.24 (m, 5H), 0.70 (s, 3H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 212.71, 209.13, 142.16, 120.49, 72.02, 63.37, 56.31, 53.17, 45.28, 44.20, 42.77, 38.31, 36.47, 31.48, 30.13, 29.22, 27.08, 25.99, 24.90, 22.64, 13.16. Two signals coincidentally overlap; all 27 can be seen in the C_6D_6 spectrum: **^{13}C NMR** (176 MHz, C_6D_6) δ 210.86, 142.81, 120.88, 72.02, 56.53, 56.45, 53.20, 45.61, 43.21, 43.08, 39.95, 39.68, 36.77, 36.65, 36.11, 30.62, 28.90, 28.47, 28.25, 27.52, 26.39, 25.03, 24.38, 23.06, 22.81, 19.03, 11.95. **IR** (cm^{-1}): 2923.67, 1699.09, 1421.99, 1354.59, 1231.48, 1174.89, 1046.29, 949.37, 918.72, 838.74, 729.40, 646.38. **HRMS**: Calculated for $C_{21}H_{33}O_3^+$ $[M+H^+]^+$: 333.2424 Found: 333.2431.



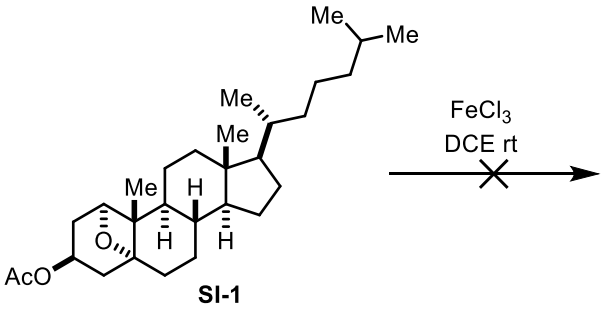
36

(*S*)-3-(2-((1*S*,3*aS*,4*S*,5*S*,7*aS*)-1-acetoxy-5-acetyl-7*a*-methyloctahydro-1H-inden-4-yl)ethyl)cyclopent-3-en-1-yl acetate (36): The reaction of **35** (18.7 mg, 0.048 mmol) was performed according to general procedure A at room temperature for 24 hours and purified by flash column chromatography eluting with hexanes/EtOAc to provide 9 mg of **36** (46%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.31 (s, 1H), 5.25 (s, 1H), 4.62 (t, *J* = 8.3 Hz, 1H), 2.76 – 2.58 (m, 2H), 2.38 – 2.13 (m, 6H), 2.01 (dd, *J* = 17.2, 10.2 Hz, 7H), 1.88 (t, *J* = 11.0 Hz, 1H), 1.74 (dd, *J* = 34.5, 17.2 Hz, 3H), 1.61 – 1.47 (m, 4H), 1.47 – 1.28 (m, 3H), 1.28 – 1.14 (m, 2H), 0.83 (d, *J* = 15.1 Hz, 3H**). ^{13}C NMR** (126 MHz, $CDCl_3$) δ 212.74, 171.30, 171.17, 142.30, 120.67, 82.51, 74.71, 56.54, 47.73, 43.05, 42.27, 39.71, 36.56, 36.46, 29.91, 29.70, 27.29, 27.22, 25.89, 24.25, 21.50, 21.29, 12.03. **IR** (cm^{-1}): 1729.56, 1707.54, 1732.33, 1023.31, 733.29. **HRMS**: Calculated for $C_{23}H_{34}O_5Na^+$ $[M+H^+]^+$: 413.2298 Found:413.2300.



38

(1*S*,3*aS*,4*S*,5*S*,7*aS*)-5-acetyl-4-(2-((*S*)-4-hydroxycyclopent-1-en-1-yl)ethyl)-7*a*-methyloctahydro-1H-inden-1-yl acetate (38): The reaction of **37** (20 mg, 0.057 mmol) was performed according to general procedure A at room temperature for 3 hours and purified by flash column chromatography eluting with hexanes/EtOAc to provide 9 mg of **38** (44%). **^{1}H NMR** (700 MHz, $CDCl_3$**)** δ 5.25 (s, 1H), 4.62 (t, *J* = 8.3 Hz,12H), 4.48 (s, 1H), 2.64 (d, *J* = 16.4 Hz, 1H), 2.55 (d, *J* = 14.6 Hz, 1H), 2.34 – 2.21 (m, 2H), 2.15 (d, *J* = 16.5 Hz, 4H), 2.02 (d, *J* = 35.6 Hz, 5H), 1.89 (s, 1H), 1.81 – 1.66 (m, 3H), 1.61 – 1.47 (m, 4H), 1.47 – 1.31 (m, 3H), 1.21 (d, *J* = 12.1 Hz,24H), 0.84 (d, *J* = 20.2 Hz, 3H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 212.92, 171.33, 142.33, 120.66, 82.52, 72.20, 56.48, 47.69, 45.45, 43.03, 42.94, 36.53, 36.42, 30.01, 29.70, 27.34, 27.28, 25.88, 24.25, 21.31, 12.03. **IR** (cm^{-1}): 2922.74, 1731.67, 1706.10, 1452.62, 1359.87, 1044.89, 1021.12, 959.55, 916.03, 839.28. **HRMS**: Calculated for $C_{21}H_{33}O_4^+$ $[M+H^+]^+$: 349.2373 Found: 349.2377.

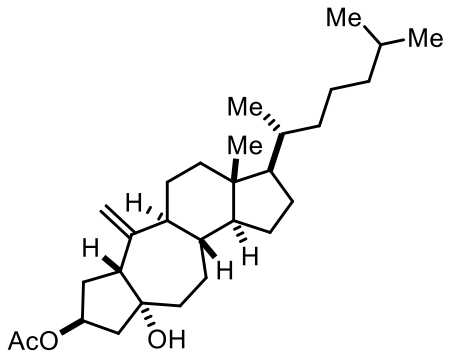


SI-1

Note: subjecting the isolated oxetane **SI-1** to the optimized conditions for FeCl3-catalyzed carbonyl-olefin metathesis afforded only a complex mixture.

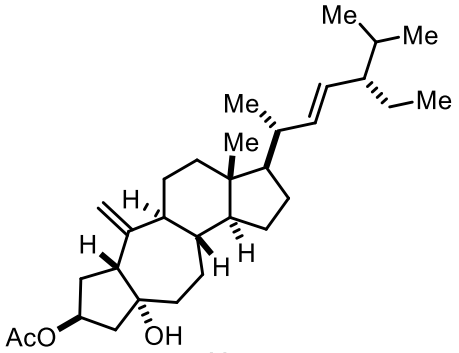
ii. Me_2AlCl-Mediated Carbonyl-Ene Reaction

General procedure B for Me_2AlCl-mediated carbonyl-ene reaction: Cyclodecenone substrate (1 equiv.) was dissolved in DCE (0.05M) and cooled to 0°C on an ice bath. Me_2AlCl (1M in hexanes, 1 equiv.) was added and the reaction mixture was stirred at this temperature for 1 hour. The reaction mixture was diluted with DCM, quenched with aqueous 1M HCl and extracted with two additional portions of DCM. The combined organic layers were dried over Na_2SO_4 and concentrated by rotary evaporator before purification by flash column chromatography.



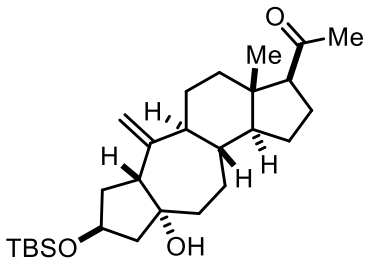
16

(3*R*,3*aR*,5*aS*,6*aR*,8*S*,9*aR*,11*aR*,11*bS*)-9a-hydroxy-3a-methyl-6-methylene-3-(6-methylheptan-2-yl)hexadecahydro-1H-indeno[5,4-f]azulen-8-yl acetate (16): The reaction of **14** (50 mg, 0.11 mmol) was performed according to general procedure B and purified by flash column chromatography eluting with hexanes/EtOAc to afford 42 mg (85% yield) of **16** as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.25 – 5.19 (m, 1H), 5.14 (s, 1H), 5.00 (s, 1H), 2.99 (dd, *J* = 12.7, 6.4 Hz, 1H), 2.52 (dd, *J* = 15.0, 7.4 Hz, 1H), 2.31 (td, *J* = 13.4, 6.7 Hz, 1H), 2.13 (s, 1H), 2.08 – 1.78 (m, 7H), 1.76 – 1.60 (m, 4H), 1.54 – 1.08 (m, 16H), 1.03 – 0.82 (m, 11H), 0.73 (s, 3H**). ^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.92, 151.24, 114.21, 78.46, 74.45, 56.63, 55.24, 55.13, 48.90, 47.90, 43.23, 42.81, 40.82, 40.57, 39.66, 36.24, 35.92, 35.52, 33.36, 28.16, 28.15, 26.09, 24.64, 23.98, 22.97, 22.71, 21.58, 18.76, 12.51. **IR** (cm^{-1}): 2931.29, 2864.17, 11726.61, 1690.03, 1466.46, 1375.83, 1362.19, 1289.27, 1199.76, 1052.85, 1026.63, 1012.80, 968.70, 894.1. **HRMS**: calculated for $C_{29}H_{49}O_3^+$ $[M+H^+]^+$: 445.3676 Found: 445.3682.



41

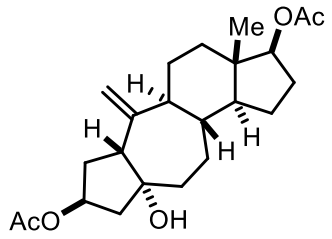
(3*R*,3*aR*,5*aS*,6*aR*,8*S*,9*aR*,11*aR*,11*bS*)-3-((5*S*,*E*)-5-ethyl-6-methylhept-3-en-2-yl)-9*a*-hydroxy-3*a*-methyl-6-methylenehexadecahydro-1H-indeno[5,4-f]azulen-8-yl acetate (41): The reaction of **27** (25 mg, 0.053 mmol) was performed according to general procedure B and purified by flash column chromatography eluting with hexanes/EtOAc to afford 19 mg (76% yield) of the title compound as white solid. **^{1}H NMR** (700 MHz, $CDCl_3$) δ 5.22 (s, 1H), 5.18 – 5.09 (m, 2H), 5.02 (dd, *J* = 16.1, 9.7 Hz, 2H), 2.99 (dd, *J* = 12.4, 6.2 Hz, 1H), 2.52 (dd, *J* = 14.8, 7.3 Hz, 1H), 2.31 (td, *J* = 13.4, 7.0 Hz, 1H), 2.14 (s, 1H), 2.10 – 1.87 (m, 7H), 1.67 (ddd, *J* = 47.5, 25.2, 14.9 Hz, 5H), 1.57 – 1.36 (m, 7H), 1.37 – 1.05 (m, 7H), 0.97 (dd, *J* = 52.1, 7.9 Hz, 4H), 0.88 – 0.67 (m, 11H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 170.93, 151.17, 138.26, 129.56, 114.25, 78.45, 74.43, 56.39, 55.32, 55.13, 51.37, 48.87, 47.88, 43.10, 42.79, 40.77, 40.63, 40.40, 35.51, 33.31, 32.02, 28.78, 26.06, 25.54, 24.68, 21.59, 21.31, 21.25, 19.14, 12.69, 12.41. **IR** (cm^{-1}): 2929.22, 2871.42, 1735.48, 1724.56, 1456.61, 1375.56, 1362.03, 1239.47, 1035.08, 1021.20, 969.50, 954.80, 924.47, 907.01, 877.71. **HRMS**: Calculated for $C_{31}H_{50}O_3Na^+$ $[M+Na^+]^+$: 493.3652 Found: 493.3666.



42

1-((3*S*,3*aS*,5*aS*,6*aR*,8*S*,9*aR*,11*aR*,11*bS*)-8-((tert-butyldimethylsilyl)oxy)-9*a*-hydroxy-3*a*-methyl-6-methylenehexadecahydro-1H-indeno[5,4-f]azulen-3-yl)ethan-1-one (42): The reaction of **31** (30 mg, 0.067 mmol) was performed according to general procedure B and purified by flash column chromatography to eluting with hexanes/EtOAc to afford 22 mg (73% yield) of the title compound as a white solid. **^{1}H NMR** (700 MHz, $CDCl_3$) δ 5.14 (s, 1H), 5.01 (s, 1H), 4.40 (d, *J* = 5.9 Hz, 1H), 3.12 (dd, *J* = 12.2, 6.9 Hz, 1H), 2.56 (t, *J* = 9.3 Hz, 1H), 2.36 (dd, *J* = 14.2, 6.8 Hz, 1H), 2.22 – 2.14 (m, 2H), 2.11 (d, *J* = 5.7 Hz, 3H), 2.02 – 1.93 (m, 3H), 1.80 – 1.75 (m, 1H), 1.70 – 1.63 (m, 3H), 1.61 – 1.51 (m, 4H), 1.46 (ddt, *J* = 17.2, 10.4, 4.9 Hz, 3H), 1.38 – 1.32 (m, 1H), 1.31 – 1.25 (m, 1H), 1.02 – 0.95 (m, 1H), 0.88 (s, 9H), 0.68 (s, 3H), 0.04 (s, 6H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 209.52, 151.66, 113.93, 71.34, 64.08, 55.56, 55.13, 52.50, 47.44, 44.65, 42.88, 40.75, 39.57, 38.83, 33.07, 31.61, 26.16, 26.08 (3C), 26.00, 24.79, 22.79, 18.33, 13.77, -4.54, -4.56. **IR** (cm^{-1}): 295.72, 2853.16, 1696.88, 1356.62, 1249.83, 1227.18,

1199.23, 1051.18, 966.68, 832.98, 877.97 **HRMS**: Calculated for $C_{27}H_{46}O_3Na^+[M^+Na^+]^+$: 469.3108 Found: 469.3160.

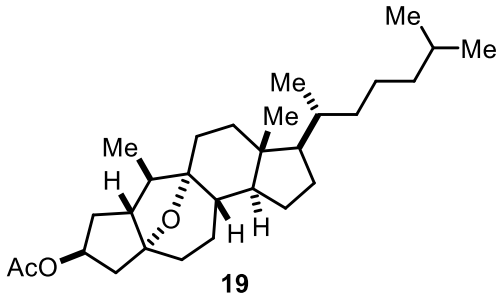


43

(3*S*,3*aS*,5*aS*,6*aR*,8*S*,9*aR*,11*aR*,11*bS*)-9*a*-hydroxy-3*a*-methyl-6-methylenehexadecahydro-1H-indeno[5,4-f]azulene-3,8-diyl diacetate (43): The reaction of **35** (20 mg, 0.051 mmol) was performed according to general procedure B and purified by flash column chromatography to eluting with hexanes/EtOAc to afford 12 mg (59% yield) of the title compound as a white solid. **^{1}H NMR** (700 MHz, $CDCl_3$) δ 5.23 (s, 1H), 5.16 (s, 1H), 5.02 (s, 1H), 4.63 (t, *J* = 8.4 Hz, 1H), 2.97 (dd, *J* = 12.6, 6.3 Hz, 1H), 2.54 (dd, *J* = 14.9, 7.4 Hz, 1H), 2.32 (td, *J* = 13.4, 7.1 Hz, 1H), 2.24 – 2.10 (m, 2H), 2.03 (dd, *J* = 18.2, 10.1 Hz, 7H), 1.95 (t, *J* = 9.8 Hz, 1H), 1.67 (ddd, *J* = 39.2, 29.1, 15.0 Hz, 5H), 1.54 – 1.43 (m, 5H), 1.34 (dt, *J* = 24.8, 9.3 Hz, 2H), 1.26 – 1.21 (m, 1H), 1.00 – 0.92 (m, 1H), 0.91 – 0.81 (m, 3H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 171.26, 170.89, 150.55, 114.68, 82.71, 78.39, 74.37, 54.99, 49.56, 48.86, 47.92, 43.24, 42.68, 40.54, 37.34, 35.52, 32.72, 27.44, 25.46, 23.89, 21.58, 21.33, 12.53. **IR** (cm^{-1}): 2932.01, 1728.02, 1374.31, 1358.76, 1233.81, 1200.43, 1098.29, 1075.01, 1039.84, 1018.48, 980.48, 969.19, 908.95, 868.63, 827.89. **HRMS**: Calculated for $C_{23}H_{34}O_5Na^+[M+Na^+]^+$: 413.2298 Found: 413.2318.

iii. $TiCl_4$-Catalyzed Tetrahydrofuran Formation

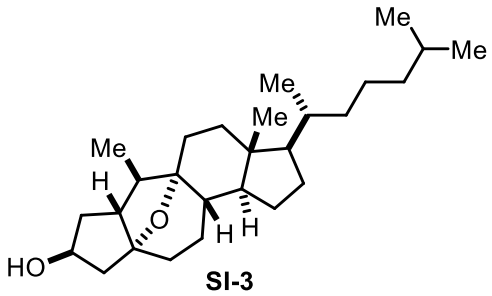
General procedure C for $TiCl_4$-catalyzed tetrahydrofuran formation: Cyclodecenone substrate (1 equiv.) was dissolved in DCE (0.05M) and a freshly prepared solution of $TiCl_4$ (1M in toluene, 0.1 equiv.) was added and the reaction mixture was stirred at room temperature for 24 hours.



19

(3*R*,3*aR*,5*aS*,6*R*,6*aR*,8*S*,9*aR*,11*aS*,11*bS*)-3*a*,6-dimethyl-3-(6-methylheptan-2-yl)tetradecahydro-6H-5*a*,9*a*-epoxyindeno[5,4-f]azulen-8-yl acetate (19): Compound **12** (50 mg; 0.11 mmol) was subjected to general procedure C and purified by flash column chromatography eluting with hexanes/EtOAc to afford 22 mg (43% yield) of the title compound. Unambiguous structural determination was achieved by X-ray crystallographic analysis of the deacetylated product **SI-3** (see below). **^{1}H NMR** (700 MHz, $CDCl_3$) δ 5.33 – 5.26 (m, 1H), 2.18 (dd, *J* = 13.8, 5.6 Hz, 1H), 2.10 (d, *J* = 9.1 Hz, 1H), 2.00 (s, 2H), 1.97 – 1.89 (m, 2H), 1.89 – 1.42 (m, 13H), 1.39 – 1.19 (m, 9H), 1.16 – 1.07 (m, 3H), 1.01 (dd, *J* = 20.0, 8.5 Hz, 4H), 0.91 – 0.82 (m, 9H), 0.63 (s, 3H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 170.81, 90.03, 86.47, 77.57, 56.11,

53.47, 51.70, 46.78, 43.42, 42.17, 39.73, 39.69, 36.59, 36.22, 35.82, 33.43, 32.74, 30.56, 28.19, 28.16, 24.50, 23.80, 22.96, 22.73, 21.83, 21.46, 18.77, 13.33, 10.76. **IR** (cm^{-1}): 2933.08, 2912.57, 2866.52, 1741.12, 1467.21, 1456.21, 1439.22, 1374.42, 1360.66, 1232.22, 1062.64, 1037.56, 1007.71, 950.33, 930.14. **HRMS**: Calculated for $C_{29}H_{49}O_3^+[M+H^+]^+$: 445.3676 Found: 445.3672.



SI-3

(3*R*,3*aR*,5*aS*,6*R*,6*aR*,8*S*,9*aR*,11*aS*,11*bS*)-3*a*,6-dimethyl-3-(6-methylheptan-2-yl)tetradecahydro-6H-5*a*,9*a*-epoxyindeno[5,4-f]azulen-8-ol (SI-3): Furan **19** (120 mg, 0.27 mmol; combined material from various reactions) was dissolved in THF (7 mL) and treated with a solution of TMSOK (87 mg, 0.68 mmol) in THF (5 mL) and stirred at room temperature overnight before being concentrated and purified by flash column chromatography on silica gel to afford 28 mg (26% yield) of the title compound as a white solid suitable for X-ray crystallography (See section 5 below). **^{1}H NMR** (700 MHz, $CDCl_3$) δ 4.54 – 4.49 (m, 1H), 2.13 (dt, *J* = 13.8, 7.1 Hz, 2H), 1.95 (td, *J* = 12.5, 7.6 Hz, 1H), 1.89 – 1.79 (m, 3H), 1.77 – 1.59 (m, 5H), 1.50 (dddd, *J* = 31.3, 20.0, 13.7, 6.9 Hz, 7H), 1.39 – 1.28 (m, 4H), 1.28 – 1.19 (m, 4H), 1.17 – 1.06 (m, 3H), 1.06 – 0.96 (m, 5H), 0.91 – 0.84 (m, 8H), 0.63 (s, 3H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 90.35, 85.84, 74.33, 56.18, 53.87, 51.44, 46.83, 46.56, 42.63, 42.18, 39.69, 36.67, 36.22, 35.82, 33.50, 32.79, 30.62, 28.18, 28.16, 24.52, 23.82, 22.96, 22.73, 21.83, 18.78, 13.38, 10.75. **IR** (cm^{-1}): 2927.99, 2867.75, 1465.26, 1435.98, 1065.41, 1042.92, 1004.09, 952.50, 930.28, 919.27, 870.46. **HRMS**: Calculated for $C_{27}H_{47}O_2^+$ $[M+H^+]^+$: 425.3390 Found:425.3365.

4. Computational Investigation of Mechanism

All quantum chemical calculations utilized density functional theory (DFT) as implemented in the Q-Chem 4.3 quantum chemistry package.[6]The unrestricted B97-D density functional[7] with singlet spin was used in combination with the 6-31G* basis set[8] to acquire gas phase geometries for the intermediates discussed. The reaction discovery tools developed by the Zimmerman group, specifically the Growing String Method (GSM)[9]were used to probe potential reaction paths and determine the exact transition state and minimum energy reaction path for each proposed elementary step. By optimizing the reaction path, GSM provides verification that the saddle point connects the reactant to product geometries through a single transition state. Frequency calculations were performed on all structures at the same level of theory to confirm that optimizations led to stable minima (intermediates) or transition states. Stable intermediates were characterized by all real frequencies, and transition states were identified by a single imaginary frequency. The ωB97X-D3[10] density functional and the triple-zeta, polarized 6-311G* basis set[8] were used to calculate energies with the SMD solvent model[11] using 1,2-dichloroethane as the implicit solvent, in the ORCA software package.[12] Thermodynamic corrections were applied to the solvated energies at a temperature of 353.15 K. For these corrections, low frequencies ($<50 cm^{-1}$) were set to 50 cm^{-1}. Energies are either reported as solvent-phase enthalpies (H) or solvent-phase Gibbs free energies (G).

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[9] (a) Zimmerman, P.M. *J. Chem. Phys*. **2013**, *138*, 184102. (b) Zimmerman, P.M. *J. Chem. Theory Comput*. **2013**, *9*, 3043. (c) Zimmerman, P.M. *J. Comput. Chem.* **2015**, *36*, 601. (d) Jafari, M.; Zimmerman, P.M. *J. Comput. Chem.* **2017**, *38*, 645.
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[11] Marenich, A.V.; Cramer, C.J.; Truhlar, D.G. *J. Phys. Chem. B* **2009**, *113*, 6378.
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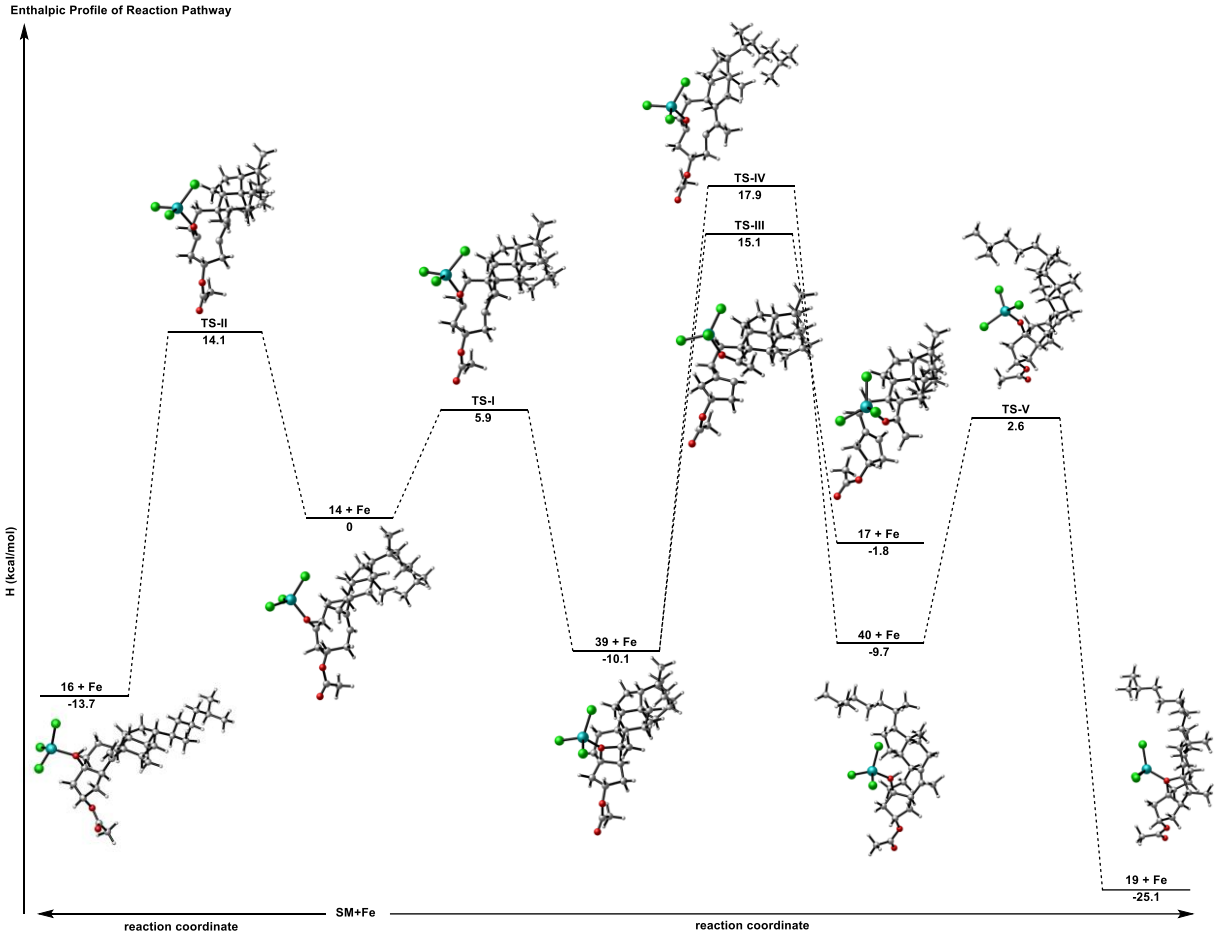
Figure SI-1: Complete reaction pathway



XYZ coordinates for all reported structures

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Structure **TS-I**

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Cl	-4.76656889	-2.59513069	0.41210644

Structure **TS-II**

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H	-3.24412032	2.64814446	-3.06081690
H	-5.15277405	0.44504258	-3.09575841
H	-5.47582017	2.06241033	-2.44057529
H	-5.93605118	-0.58717590	-0.93332175
H	-7.16242655	0.33397994	-1.79809654
H	-7.25326418	0.32400351	3.29801583
H	-7.43065879	1.97759405	3.93238093
H	-5.67227352	2.80769942	2.37536314
H	-5.04688477	1.42121872	3.28198429
H	-9.25522976	0.07531919	-0.88728395
H	-9.13501541	1.84253571	-0.84063622
H	-11.01330750	0.14766515	0.73295721
H	-10.94895667	1.90822039	0.63631556

H	-9.45238980	-0.00403539	2.47904157
C	-10.71895126	0.52722852	4.47882404
H	-12.36831670	1.74783184	2.42789525
H	-12.36241102	2.45429380	4.04466601
H	-11.05351589	3.76050663	1.59787665
H	-11.03837192	4.40797765	3.23523113
H	-13.56683346	4.44979873	3.22335595
H	-13.56246213	3.83876781	1.56138295
H	-12.31190558	6.49217236	2.46069161
H	-1.99783082	0.68924268	1.29863215
H	-3.11511138	-0.14224568	0.09833428
H	-3.31816664	-0.37689568	2.03959914
H	-7.39668198	3.61012956	1.37135792
H	-9.07747319	3.38498542	0.84645350
H	-8.71556431	3.70299501	2.55691054
H	-2.17242051	5.80765737	-3.42316247
H	-1.95360172	5.77042606	-1.66013445
H	-2.95965928	4.52859694	-2.43951815
H	-12.73202135	5.31345990	-0.35431232
H	-11.15820278	5.61953883	0.42899708
H	-12.20731753	6.98644363	-0.02338324
H	-14.93730467	5.94155216	0.94173248
H	-14.27035003	7.55690583	1.29984932
H	-14.81703497	6.49778071	2.63201023
C	-2.32898658	2.83964178	-0.33783587
H	-1.06231053	1.38981760	-1.31256794
H	-2.47965474	3.92257371	-0.40422220
H	-1.72103488	2.65761004	0.55827274
H	-4.52051989	2.85245767	-0.48162696
H	-9.78163456	0.02889641	4.77613887
H	-11.38623223	-0.23974484	4.04880543
H	-11.20156069	0.92881571	5.38495556
H	-9.78673031	2.38144606	3.94255999
Fe	-3.56871415	-2.02663902	-1.68914772
Cl	-4.73202502	-2.25543771	-3.53211802
Cl	-1.55751915	-2.88928906	-1.82045902
Cl	-4.62314893	-2.73349855	0.14174569

Structure **16 + Fe**

O	2.85306450	6.62995557	20.77324482
O	5.91988746	9.85919721	20.88379529
O	3.15129961	4.75028999	22.04302187
C	5.72665182	8.83620174	17.08210869
H	4.80904634	8.22676007	17.13923405
C	6.14120561	7.68379696	14.80409107
C	2.60088296	5.33051308	21.12552588
C	6.04984720	9.02960329	15.59174410
H	7.05883042	9.48365550	15.53405809
C	5.49879783	9.50030586	13.27334262
H	6.01715546	10.31996912	12.75617569
H	4.59868626	9.27043314	12.68069165
C	7.06204638	6.65894368	16.96542992
H	7.92229532	6.12196256	17.39516628
H	6.17069094	6.03810000	17.15969334
C	5.44145248	10.15009549	17.85120256
H	6.37761682	10.56797830	18.26205173
H	5.04617103	10.90722124	17.15865564
C	6.90198477	8.01967269	17.69588223
H	7.82310660	8.59686700	17.49659176
C	5.12049053	9.90082999	14.73086831
H	5.25964565	10.97550606	14.91765349
H	4.06583060	9.66518966	14.94746052
C	6.23375698	7.28796119	12.15333777
H	5.16175058	7.02461878	12.09560992
C	7.26683097	6.84060412	15.44274557
H	7.34530108	5.85000407	14.97418107
H	8.22848892	7.35767603	15.27426721
C	6.60122000	8.03348529	10.84504658
H	7.69830817	8.17046293	10.81195374
H	6.16346169	9.04474515	10.85901830
C	6.41986725	8.23049773	13.36653126
H	7.47429106	8.56587265	13.36135954
C	6.49110815	8.14100126	8.29703520
H	7.59201853	8.20905567	8.21164882
H	6.12376589	9.17660384	8.41788912
C	5.92512804	7.56576850	6.98154608
H	4.82602486	7.50070707	7.08804610
C	6.81675111	7.81351642	19.20050381
C	6.12891709	7.33696044	9.55730509
H	5.03209968	7.20372880	9.60241651
H	6.56449607	6.32815295	9.48517374
C	4.84432298	9.12113624	20.16430773
C	4.80873291	6.89796779	14.82021535
H	4.91338084	5.97366560	14.23342265
H	3.98864220	7.48369463	14.37889022
H	4.50739824	6.61054124	15.83766525
C	4.39759288	9.96909724	18.97222268
H	4.07534863	10.94750522	19.35908900
H	3.50433350	9.47900226	18.54811217
C	5.43800059	7.70804060	19.81648217
H	4.74276460	7.27519451	19.08163518
C	3.85038133	7.33976850	21.58067164
H	3.65207874	7.13130968	22.63843262
C	6.46436439	6.15192696	6.69111790
H	6.07512383	5.77308800	5.73189243
H	6.18169179	5.43724744	7.47956772
H	7.56639546	6.17105709	6.62634228
C	7.05054856	5.98645801	12.27431204
H	7.02409863	5.41275792	11.33568884
H	6.66421584	5.33163487	13.06779876
H	8.10481523	6.21527920	12.50333922
C	5.26567014	6.93700359	21.13972913
H	5.97612890	7.29675688	21.89951598
H	5.38209910	5.85170181	21.03795583
C	1.53190011	4.74621046	20.21759202
H	1.41407050	3.67831681	20.43678055
H	1.80232682	4.89238056	19.16071816
H	0.57647857	5.26744905	20.38750311
C	3.72858520	8.83237040	21.20300465
H	3.85528873	9.45958428	22.09469270
H	2.73821213	9.05056497	20.78213411
C	6.24112425	8.51099588	5.80758405

H	7.33284189	8.59644460	5.66890287
H	5.84304818	9.52233714	5.99317186
H	5.80837987	8.13492048	4.86603433
C	7.94006940	7.80757724	19.95295675
H	7.92641617	7.61131551	21.02655923
H	8.91960420	7.95182810	19.49070348
Fe	5.86839868	11.40635620	22.16037711
Cl	7.90363995	12.13941874	21.82157703
Cl	4.25861999	12.73693890	21.51107729
Cl	5.52844351	10.54058436	24.14332065
H	6.78898984	9.63793994	20.46297822

Structure **39 + Fe**

C	-1.68994523	2.07902772	-1.50178064
C	-2.76821994	1.65669316	-2.52625784
C	-4.01515783	1.47381624	-1.67418279
C	-4.08682052	1.06582130	0.44817201
C	-3.85688710	2.35093083	-0.38729502
C	-5.36466283	1.43968283	-2.37892559
C	-6.46758313	0.74889903	-1.55005211
C	-6.64892314	1.30976789	-0.12523119
C	-5.54735232	0.86977165	0.90315111
C	-7.99325241	0.88342108	0.48946501
C	-8.30323423	1.60378479	1.82719581
C	-7.20263001	1.24829904	2.83971273
C	-5.79082744	1.54476804	2.28066115
C	-9.30031160	1.03344147	-0.32316340
C	-10.43219670	1.03922075	0.76242756
C	-9.69690200	0.99329819	2.14433714
O	-3.87054545	0.24410362	-0.81180573
H	-6.64461089	2.41062027	-0.20473309
H	-5.66410125	-0.21875311	1.04201941
H	-7.89281688	-0.19159073	0.73184726
C	-10.42332186	1.53369067	3.42123147
C	-11.75789266	2.27977132	3.17749346
C	-11.63825234	3.71284116	2.63400723
C	-13.01508204	4.35693752	2.41194394
C	-12.96962360	5.80163998	1.86810346
C	-3.04089928	0.65880242	1.47340336
C	-8.39572415	3.13553230	1.65740757
O	-0.46799564	2.60718906	-2.05506397
O	0.75720947	3.95376489	-3.31468887
C	-0.32069104	3.75715254	-2.79596868
C	-1.44874256	4.78476257	-2.88244999
C	-12.30845946	5.86896060	0.47759335
C	-14.39007666	6.39319379	1.81175827
H	-2.50445895	0.73915687	-3.07100423
H	-2.96792436	2.44327038	-3.26795873
H	-5.25825421	0.92946748	-3.34804600
H	-5.64460753	2.48867790	-2.58227137
H	-6.26559109	-0.33174617	-1.50225370
H	-7.41164899	0.86844190	-2.10198215
H	-7.26974283	0.16923719	3.06489463
H	-7.34556683	1.79184302	3.78959507
H	-5.64025840	2.63348130	2.17965747
H	-5.04829518	1.18752298	3.00847713
H	-9.42415140	0.21947897	-1.05109537
H	-9.29904671	1.97932876	-0.88897889
H	-11.10678266	0.17775913	0.65027418
H	-11.04912684	1.94010430	0.65693129
H	-9.49079950	-0.07679312	2.32796342
C	-10.66235889	0.37674596	4.41613249
H	-12.39038553	1.67995798	2.49994121
H	-12.30378658	2.33137223	4.13642124
H	-11.07617981	3.72072399	1.69225977
H	-11.05320538	4.32455112	3.34530462
H	-13.57402007	4.34423176	3.36513807
H	-13.59366618	3.73431536	1.70322693
H	-12.36689654	6.41031689	2.56788182
H	-2.05223701	0.57578371	1.00348855
H	-3.30267054	-0.31095681	1.92245895
H	-2.98724932	1.41181456	2.27323112
H	-7.42540712	3.57960682	1.39294580
H	-9.11431159	3.40730965	0.87142704
H	-8.72698117	3.60400863	2.59577548
H	-1.28507736	5.38353162	-3.78728187
H	-1.37594879	5.45573534	-2.01075769
H	-2.45935006	4.35987792	-2.89406348
H	-12.84691501	5.21552377	-0.23109045
H	-11.25523952	5.54635863	0.50423791
H	-12.33647065	6.89652252	0.08001051
H	-15.02161214	5.80688942	1.12177057
H	-14.37548444	7.43617935	1.45450871
H	-14.86741034	6.37496216	2.80530688
C	-2.43071939	2.93999111	-0.44164086
H	-1.33660273	1.16230890	-1.01358461
H	-2.49526716	3.98872213	-0.75414411
H	-1.91519548	2.91422112	0.52892797
H	-4.62527360	3.11641516	-0.22725263
H	-9.71822036	-0.13893253	4.65671953
H	-11.35309299	-0.36797654	3.98410206
H	-11.10591166	0.74837539	5.35444092
H	-9.73913186	2.24471049	3.91845915
Fe	-3.48122912	-1.64011041	-1.21367912
Cl	-4.12024062	-1.84726815	-3.30116091
Cl	-1.31029722	-1.80924803	-0.94615310
Cl	-4.65791959	-2.77796901	0.24524336

Structure **TS-III**

C	-1.63132268	2.19573336	-1.57039201
C	-2.77227206	1.63725929	-2.45980532
C	-4.03059106	1.91674912	-1.75331533
C	-3.95682655	0.93565408	0.49424587
C	-3.77799881	2.40355052	-0.40420607
C	-5.34400037	1.65375200	-2.36851885
C	-6.28687365	0.72934222	-1.53635109
C	-6.53786574	1.25869508	-0.11296884
C	-5.45415627	0.85414352	0.94436024
C	-7.89353947	0.80246108	0.45288807
C	-8.25594433	1.53555765	1.77112288
C	-7.17442787	1.22007332	2.81459561
C	-5.75531340	1.55803754	2.29271593

C	-9.17598086	0.92884215	-0.40244367
C	-10.34080399	0.92681141	0.64828602
C	-9.64787463	0.90062416	2.05111793
O	-3.61883582	-0.08157237	-0.37288215
H	-6.56782021	2.36146046	-0.18004030
H	-5.57976602	-0.22880465	1.11231383
H	-7.78059580	-0.26699143	0.70570504
C	-10.43229657	1.42678015	3.29906567
C	-11.73374488	2.21789701	3.01426834
C	-11.54575279	3.65451473	2.50255849
C	-12.87912527	4.40264752	2.34800089
C	-12.73094113	5.87570232	1.90732009
C	-2.96945782	0.94498424	1.66673365
C	-8.37283560	3.06354619	1.58595669
O	-0.61772379	2.93926772	-2.27674730
O	0.11677277	4.57887177	-3.57450039
C	-0.83314288	4.08638812	-3.00677587
C	-2.21327025	4.74855315	-3.07390513
C	-12.05769935	5.99671324	0.52660107
C	-14.10424509	6.57154814	1.89391776
H	-2.73233594	0.53036893	-2.58204088
H	-2.78434945	2.02069539	-3.49345777
H	-5.21515637	1.25597177	-3.38427269
H	-5.85373057	2.63691583	-2.42931178
H	-5.88452756	-0.28867063	-1.52339128
H	-7.23272983	0.71322425	-2.09521558
H	-7.20949939	0.14047139	3.04325506
H	-7.36179654	1.76349294	3.75656962
H	-5.63589654	2.65040849	2.18089070
H	-5.03405805	1.23882635	3.05650354
H	-9.26707412	0.10754811	-1.12744357
H	-9.17351625	1.87221970	-0.97377884
H	-11.00167513	0.05706332	0.52078627
H	-10.96443425	1.82128565	0.52172825
H	-9.42509779	-0.16369110	2.24697082
C	-10.75574677	0.24398203	4.23924893
H	-12.36116496	1.64931338	2.30584058
H	-12.30860587	2.27219088	3.95591771
H	-11.02081428	3.65095431	1.53941613
H	-10.89456020	4.20571702	3.20585293
H	-13.42640134	4.36639090	3.30750209
H	-13.50958180	3.87408323	1.60835865
H	-12.08926804	6.38726479	2.64914413
H	-1.94391750	0.83210873	1.29222246
H	-3.19672284	0.06665750	2.29194773
H	-3.04805411	1.85055873	2.28443427
H	-7.40455907	3.52714775	1.34830292
H	-9.07437531	3.31714493	0.77943840
H	-8.73775618	3.52807816	2.51318412
H	-2.37967740	5.06223767	-4.11366908
H	-2.17473848	5.66143160	-2.45884210
H	-3.06003464	4.14152909	-2.73464782
H	-12.63210906	5.43135521	-0.22832566
H	-11.02783825	5.60517146	0.53565732
H	-12.01705272	7.04957811	0.20300626
H	-14.77566734	6.07891304	1.16947995
H	-14.01092778	7.63104933	1.60352805
H	-14.58379505	6.52580164	2.88555820
C	-2.33989243	2.96739436	-0.42190686
H	-1.06610877	1.35523509	-1.15374626
H	-2.37290261	4.04297789	-0.64280721
H	-1.81276051	2.85603845	0.53171426
H	-4.53845206	3.07522079	0.01031211
H	-9.83765664	-0.29536831	4.52402930
H	-11.42601687	-0.47288018	3.73482109
H	-11.25527560	0.59214746	5.15809339
H	-9.75697065	2.10458030	3.85252563
Fe	-3.72122527	-1.88002227	-0.75673617
Cl	-3.74815120	-1.81885172	-3.01184454
Cl	-1.92324745	-2.84579511	0.08093356
Cl	-5.60182090	-2.74185544	0.06065393

Structure **TS-IV**

C	-1.68858650	2.29830586	-1.36172030
C	-2.47016592	1.30026168	-2.23152023
C	-3.81372134	1.12173890	-1.49064770
C	-4.41638812	2.37536799	0.64201127
C	-4.00898965	2.63778720	-0.75095946
C	-5.04335605	0.87884126	-2.37194722
C	-6.28672868	0.56668955	-1.52215414
C	-6.65261435	1.48093313	-0.31285792
C	-5.56460466	1.55077723	0.84582491
C	-8.00359653	0.96440775	0.21255136
C	-8.39905688	1.42929488	1.62799475
C	-7.39369658	0.80019054	2.59687328
C	-5.97023581	1.33319572	2.33303757
C	-9.24893343	1.27440492	-0.65522918
C	-10.45815676	1.17063801	0.33689061
C	-9.82665891	0.82161229	1.72164128
O	-3.70122640	0.14427561	-0.50508725
H	-6.78997557	2.51935198	-0.66709497
H	-4.76238891	0.66107691	0.50942133
H	-7.91167844	-0.13373357	0.27736925
C	-10.62885704	1.10900182	3.03529763
C	-11.89166884	1.99134322	2.87768354
C	-11.62767379	3.49326632	2.69489137
C	-12.92194361	4.31676665	2.61196519
C	-12.69778361	5.84035745	2.51316903
C	-3.49308943	2.64474920	1.78988192
C	-8.41026840	2.96663997	1.74599488
O	-0.37853991	2.68567138	-1.81788155
O	1.11402342	3.51975871	-3.22274102
C	-0.06114959	3.40065194	-2.95175860
C	-1.15047131	4.07832498	-3.77987714
C	-11.93129878	6.22747477	1.23394620
C	-14.04315879	6.58588229	2.57507335
H	-1.96291398	0.33374773	-2.34265161
H	-2.67071897	1.70716752	-3.23288337
H	-4.84402444	0.02207840	-3.03453076
H	-5.20094078	1.76413327	-3.01199159
H	-6.18783885	-0.45244730	-1.12418911
H	-7.15990888	0.55225499	-2.19095149

H	-7.41632074	-0.29321842	2.46609724
H	-7.65403169	1.01814650	3.64637923
H	-5.87373111	2.30174289	2.84968608
H	-5.23823517	0.65939547	2.80332437
H	-9.33945573	0.57782924	-1.50103987
H	-9.17596946	2.29135224	-1.07596315
H	-11.18091889	0.40156259	0.02648372
H	-11.00139038	2.12472193	0.36671203
H	-9.65341374	-0.26895321	1.69851955
C	-11.01635533	-0.22706244	3.70554240
H	-12.49837210	1.61398348	2.03624275
H	-12.51288155	1.86591983	3.78253845
H	-11.02712271	3.66515522	1.79190874
H	-11.01807694	3.85802530	3.54214101
H	-13.54049101	4.10347313	3.50286929
H	-13.51175778	3.98553098	1.73652226
H	-12.09118599	6.14871657	3.38541270
H	-2.52186975	3.04153601	1.48003947
H	-3.33071551	1.72053302	2.36740345
H	-3.96860285	3.35844104	2.48582883
H	-7.40221373	3.38559679	1.60721367
H	-9.06065100	3.41498498	0.98223661
H	-8.77872682	3.27937624	2.73295931
H	-0.72736606	4.29733415	-4.76792160
H	-1.42095598	5.03366745	-3.30130506
H	-2.06623789	3.48606487	-3.89332363
H	-12.48392316	5.88516801	0.34151720
H	-10.92526282	5.77921154	1.20467285
H	-11.81671407	7.32161349	1.16205029
H	-14.67826883	6.30551556	1.71665830
H	-13.89311515	7.67746145	2.54258868
H	-14.59338607	6.33917831	3.49823044
C	-2.70944597	3.41115518	-1.05609032
H	-1.45780223	1.78086839	-0.41858407
H	-2.88520696	4.03356446	-1.94175148
H	-2.37862507	4.08197460	-0.25129268
H	-4.85942114	3.08897078	-1.27968866
H	-10.12851768	-0.86020997	3.86659720
H	-11.71831139	-0.78769613	3.06446309
H	-11.50488320	-0.05673425	4.67861596
H	-9.95145085	1.63648633	3.73350411
Fe	-3.69616745	-1.74601160	-0.34489722
Cl	-3.94041765	-2.62463171	-2.34898530
Cl	-1.77604470	-2.23965938	0.61176418
Cl	-5.41664363	-2.10620009	1.03478351

Structure **40 + Fe**

C	-0.94023988	-0.57714707	1.62475528
C	-0.84287192	-0.65395994	0.09906767
C	-0.51597839	0.79383300	-0.32624360
C	0.21249706	1.43282205	0.88612799
C	0.23333387	0.93074321	3.43442463
C	0.24812475	0.34240812	2.00888510
C	1.59459435	2.01864694	0.55292021
C	2.59359247	2.01557494	1.72258014
C	2.12095288	2.68450540	3.02558894
C	0.98925447	2.00584446	3.82028374
C	1.77395781	4.17550578	2.81962893
C	1.55042658	4.95980062	4.14135808
C	0.43612852	4.23765326	4.92182655
C	0.77080491	2.73157924	5.14535299
C	2.73004258	5.06705815	2.01129473
C	2.23867037	6.50632624	2.36936579
C	1.19999341	6.35374108	3.53520653
H	2.99370621	2.65800343	3.70355044
C	1.16295155	7.59239392	4.45559175
H	0.81229408	4.21965479	2.28360218
C	0.88556338	8.87524281	3.62848157
C	-0.42467332	8.85123997	2.82245566
C	-0.67633261	10.16350865	2.06328783
C	-1.82458423	10.07655710	1.03427388
O	-0.67396033	2.52247150	1.40140484
H	1.16409801	-0.24480205	1.84338274
O	0.27724020	-1.53653455	-0.19277610
O	1.50466437	-2.66295783	-1.66529250
C	0.48495969	-2.04087518	-1.45718300
C	-0.60516242	-1.81472205	-2.49900639
C	2.82413375	5.07395712	5.00860542
H	2.16541534	7.70985591	4.90590212
C	-3.15929311	9.67891203	1.69150484
C	-1.96441180	11.41138848	0.28031877
C	-0.75085159	0.23820379	4.36522776
H	-0.89422273	-1.57182966	2.08586686
H	-1.89897957	-0.10559515	1.88906777
H	-1.75993858	-1.03894516	-0.36645855
H	-1.45124064	1.32200166	-0.54736654
H	0.10294283	0.82807360	-1.23199924
H	1.45080525	3.03140711	0.14686961
H	2.02447315	1.40784595	-0.25657243
H	3.50019543	2.54508417	1.39244781
H	2.90121199	0.98019323	1.93739627
H	-0.50937501	4.31748762	4.35834298
H	0.26819487	4.69799078	5.90549499
H	-0.03646027	2.29152617	5.74149773
H	1.69176324	2.66096307	5.74959852
H	2.68452653	4.86177589	0.93162704
H	3.77175574	4.90928194	2.33541503
H	1.77843782	7.00595635	1.50478586
H	3.08032785	7.13784090	2.69534832
H	0.19863236	6.23965020	3.09122892
C	0.13739875	7.45199427	5.59934987
H	0.87363921	9.73821121	4.31818087
H	1.72204216	9.04467242	2.92983665
H	-1.27280585	8.64029454	3.49223280
H	-0.39544306	8.02538500	2.09183172
H	0.24974697	10.45670982	1.53503518
H	-0.89672893	10.97489538	2.78206139
H	-1.55601578	9.29014431	0.30438847
H	-0.25587004	-2.22360766	-3.45377276
H	-0.84749796	-0.74771977	-2.61506667
H	-1.53286835	-2.32985596	-2.20034745
H	3.25683724	4.09539696	5.26287463

H	3.60085225	5.66243230	4.49955316
H	2.58149676	5.58669978	5.95217112
H	-3.42345778	10.39825727	2.48716830
H	-3.10777815	8.67468294	2.14025786
H	-3.97452216	9.67768612	0.94948672
H	-2.22921446	12.22063959	0.98334694
H	-2.75327145	11.35692798	-0.48823463
H	-1.01792796	11.68853272	-0.21348808
H	-1.79566015	0.51059807	4.13617214
H	-0.56540354	0.45087225	5.42364054
H	-0.67521569	-0.85242933	4.23283688
Fe	-2.07318898	3.69156827	0.59622582
Cl	-3.84516982	2.41370032	0.35951657
Cl	-2.32365207	5.20837701	2.15583828
Cl	-1.21415223	4.41055813	-1.28168501
H	-0.48575973	2.59612483	2.37685864
H	-0.83731133	7.11168793	5.21561841
H	-0.01372260	8.42151822	6.10305894
H	0.47348845	6.73178310	6.35919327

Structure **17 + Fe**

C	-2.35763497	3.21329189	-1.49749761
C	-3.20070567	2.08156057	-2.16382360
C	-4.63281343	2.40599335	-1.78718884
C	-3.99266724	0.26092936	1.29255448
C	-4.71580533	3.56762930	-1.10476858
C	-5.76489237	1.47062585	-2.11664505
C	-5.81680496	0.28784266	-1.10874233
C	-6.24234399	0.75919655	0.30478835
C	-5.46154593	0.02278353	1.47042975
C	-7.73459134	0.52438332	0.57198071
C	-8.22063958	1.06479643	1.94041427
C	-7.46724486	0.31611503	3.05265224
C	-5.93874607	0.46178870	2.88652494
C	-8.76957131	1.07509651	-0.43520645
C	-10.11013346	1.09086227	0.37408223
C	-9.73203731	0.70462226	1.84263450
O	-3.23026538	-0.60309310	0.79908056
H	-6.02254263	1.83449347	0.39122044
H	-5.64510665	-1.05258546	1.34485904
H	-7.87491978	-0.57287408	0.60101812
C	-10.65919685	1.17619109	3.01675135
C	-11.73621262	2.22524126	2.64305854
C	-11.22419304	3.65872871	2.43503007
C	-12.33967050	4.62607056	2.01035036
C	-11.88563394	6.09495795	1.87282523
C	-3.39699329	1.59227655	1.66279940
C	-8.00364303	2.58766211	2.06891525
O	-1.34229418	3.78984472	-2.35227295
O	-0.63796937	4.72306593	-4.23584470
C	-1.59114989	4.43099651	-3.54412543
C	-3.01815681	4.82343383	-3.92406996
C	-10.76749608	6.25330506	0.82363398
C	-13.08621380	6.98976297	1.51347523
H	-2.88349396	1.08186014	-1.82592850
H	-3.06866497	2.07951276	-3.25951391
H	-5.63380908	1.06117164	-3.13184295
H	-6.72333214	2.01047075	-2.09178027
H	-4.82771388	-0.18964843	-1.10105407
H	-6.51454174	-0.48241601	-1.47058676
H	-7.73874613	-0.75307246	3.00241468
H	-7.76175883	0.68376071	4.05023378
H	-5.64753273	1.50786406	3.06300551
H	-5.41698729	-0.14977733	3.64039724
H	-8.82515828	0.45935531	-1.34410894
H	-8.50198084	2.09568846	-0.74901612
H	-10.83926580	0.37761096	-0.03777103
H	-10.57380509	2.08356253	0.31964526
H	-9.73969593	-0.39975224	1.86903925
C	-11.34228135	-0.05317209	3.65516770
H	-12.27134538	1.88730118	1.73898971
H	-12.49085832	2.25104069	3.44988040
H	-10.43097239	3.67503688	1.67609040
H	-10.75959637	4.01823053	3.37158487
H	-13.16561665	4.57326361	2.74273582
H	-12.75736105	4.29112962	1.04200237
H	-11.48767478	6.41932034	2.85255696
H	-2.39001695	1.69294368	1.24091840
H	-3.34228022	1.66959692	2.76147650
H	-4.05189974	2.39994636	1.30362697
H	-6.93733398	2.85466463	2.11639915
H	-8.43091641	3.12597599	1.21192388
H	-8.48761049	2.96654536	2.97970956
H	-3.07911604	4.84228326	-5.01974440
H	-3.19535085	5.84907149	-3.56033241
H	-3.80387068	4.18248476	-3.50815434
H	-11.09764611	5.84504095	-0.14788616
H	-9.84854384	5.72333668	1.12191236
H	-10.51407034	7.31594717	0.67679009
H	-13.49789633	6.69601356	0.53250892
H	-12.78905722	8.04957376	1.45456312
H	-13.89129319	6.89566185	2.26089400
C	-3.37655915	4.22888668	-0.87856839
H	-1.74570740	2.78206688	-0.69597896
H	-3.30347260	5.21886538	-1.35771044
H	-3.16084328	4.39568055	0.19177662
H	-5.65583119	4.00852993	-0.76236519
H	-10.59661687	-0.80237072	3.96835270
H	-12.01785131	-0.53350066	2.92688955
H	-11.93821556	0.23456938	4.53615874
H	-10.01765483	1.63215534	3.79214579
Fe	-3.33359929	-2.39990457	-0.09715134
Cl	-2.67070106	-1.88963241	-2.12158130
Cl	-1.91773007	-3.56403763	1.08099857
Cl	-5.35149538	-3.27055081	-0.05804294

Structure **TS-V**

C	-1.21360403	-0.23530620	1.48776781
C	-0.90894029	-0.48307452	0.00481428
C	-0.46450934	0.90262695	-0.49807626
C	0.22590883	1.58952537	0.72324629
C	-0.19624248	1.46820483	3.23223595

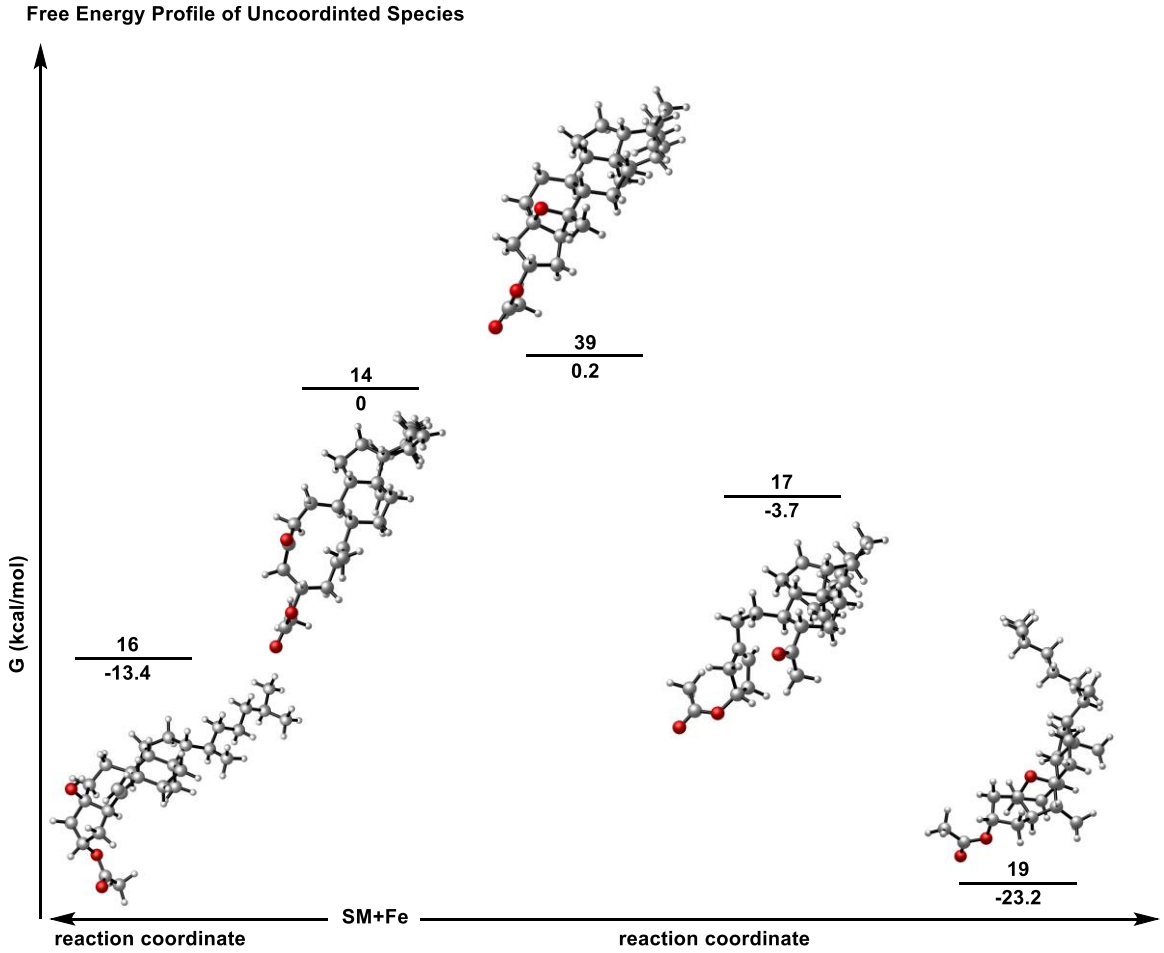
C	-0.00542853	0.60899436	1.94141257
C	1.72114627	1.89261097	0.48973971
C	2.61587471	1.85732739	1.74638995
C	2.15004196	2.58770476	3.02470629
C	0.96182528	2.10099209	3.80571425
C	1.78101580	4.11236157	2.81730340
C	1.68623757	4.91083279	4.14417201
C	0.62711799	4.24290662	5.03806047
C	0.91113597	2.69145400	5.17638466
C	2.67594126	4.96091930	1.89860458
C	2.25808200	6.41478168	2.29572114
C	1.29590441	6.29158335	3.52161090
H	3.01164471	2.58436044	3.71138511
C	1.29222680	7.55181426	4.40883795
H	0.78167466	4.13201553	2.36510258
C	0.90260002	8.79105665	3.55633168
C	-0.44943293	8.67634794	2.82823605
C	-0.83109025	9.96933523	2.08866887
C	-2.01288367	9.79519169	1.10999372
O	-0.45688180	2.78869473	1.06235371
H	0.85214645	-0.06619765	2.04711325
O	0.20167767	-1.42655182	-0.03126761
O	1.60904718	-2.69443727	-1.19343005
C	0.58341805	-2.04613358	-1.19796092
C	-0.33332910	-1.91262803	-2.40877549
C	3.02879852	5.02086220	4.89625461
H	2.32052129	7.72099738	4.77703534
C	-3.28711202	9.30784286	1.82341835
C	-2.28144913	11.10950527	0.35535442
C	-1.34713725	1.08088778	4.17733269
H	-1.34798306	-1.16488814	2.05785381
H	-2.14288457	0.35297976	1.53177842
H	-1.76909057	-0.89231519	-0.54264140
H	-1.35141301	1.48547795	-0.78134980
H	0.19880368	0.83893193	-1.37164497
H	1.78536154	2.86901436	-0.01303949
H	2.12815654	1.14166728	-0.20558691
H	3.58802165	2.30131996	1.48164002
H	2.82630227	0.80969026	2.01372700
H	-0.37439313	4.37782930	4.60780460
H	0.62193682	4.65391695	6.05609372
H	0.15312626	2.22885828	5.81638426
H	1.89502679	2.57293844	5.65545507
H	2.48481010	4.75471764	0.83794975
H	3.74249668	4.77427899	2.10012487
H	1.75433298	6.92386825	1.46510649
H	3.14186647	7.01186764	2.57150459
H	0.27227316	6.16260078	3.13872393
C	0.35962456	7.41530869	5.62885785
H	0.88947134	9.67495383	4.21877208
H	1.68960344	8.97426033	2.80582312
H	-1.24122999	8.40799675	3.54583253
H	-0.40922764	7.86008095	2.08912982
H	0.04543265	10.32813008	1.51722057
H	-1.07488327	10.76392529	2.81906247
H	-1.71964704	9.02318550	0.37554873
H	0.14647437	-2.41267049	-3.25797049
H	-0.53378634	-0.86011075	-2.65866382
H	-1.30619943	-2.39084372	-2.20737464
H	3.42998669	4.04019931	5.19834208
H	3.79080250	5.51750921	4.27973323
H	2.89517777	5.61943240	5.81001581
H	-3.57601401	10.01381697	2.62302250
H	-3.14223264	8.31547234	2.27626075
H	-4.12683841	9.23656833	1.11285757
H	-2.57660158	11.90617741	1.06097643
H	-3.09593536	10.98558321	-0.37710661
H	-1.38037258	11.44971804	-0.18210248
H	-2.22103599	0.76400627	3.59845021
H	-1.66438878	1.94001486	4.78159676
H	-1.05786914	0.25431868	4.84673699
Fe	-1.66162168	4.14506786	0.72544363
Cl	-3.29368466	3.41858564	-0.58166927
Cl	-2.42020943	4.61294138	2.78931628
Cl	-0.54560826	5.85445132	-0.15458653
H	-0.53466541	2.45405767	2.64763479
H	-0.62688288	7.02840600	5.33033374
H	0.20943590	8.39567200	6.11009693
H	0.77823914	6.73683129	6.38804073

Structure **19 + Fe**

C	-0.52370568	-1.26470976	1.81228391
C	-0.76559758	-1.17318962	0.30129762
C	-0.88601432	0.34322290	0.05739996
C	0.12594482	0.97974292	1.03521928
C	0.42648201	0.55898229	3.45133493
C	0.48426250	-0.12778825	2.07284979
C	1.35411775	1.63834256	0.41112473
C	2.34628815	2.06320648	1.51564893
C	1.67745846	2.74977373	2.73745092
C	0.33465130	2.07782412	3.14052841
C	1.42543974	4.25275597	2.56325697
C	0.95311762	4.94997323	3.87648337
C	-0.41464233	4.34620853	4.25286175
C	-0.39138802	2.80438732	4.27823160
C	2.59210953	5.12109824	2.05835533
C	2.21419061	6.56214394	2.51587267
C	0.92699139	6.43409529	3.39233041
H	2.35738191	2.62055210	3.59249473
C	0.82098159	7.55855836	4.44300856
H	0.59663891	4.37730350	1.84034226
C	0.83647426	8.95102369	3.76038214
C	-0.30470803	9.18510153	2.75509032
C	-0.33898654	10.62697938	2.22602239
C	-1.37051761	10.86091524	1.10135872
O	-0.51766475	2.04976257	1.89023969
H	1.49579444	-0.49560894	1.85842666
O	0.43743255	-1.69113303	-0.33380855
O	1.56112923	-2.20834555	-2.18068682
C	0.48362761	-1.95618477	-1.68467665
C	-0.83190060	-1.95925763	-2.45388681
C	1.95993252	4.78384905	5.03437395

H	1.72170557	7.50549828	5.08197333
C	-2.80870244	10.57073786	1.56997132
C	-1.25964035	12.29896159	0.56335062
C	1.57346588	0.17247971	4.39546757
H	-0.15840744	-2.25425639	2.12053191
H	-1.47569747	-1.05781166	2.32854853
H	-1.64703449	-1.73539979	-0.03731794
H	-1.91176647	0.65145127	0.30208314
H	-0.68829988	0.63137659	-0.98099261
H	1.02787273	2.49613653	-0.19482615
H	1.82793776	0.91204869	-0.26757090
H	3.10727752	2.73786392	1.09951585
H	2.88203467	1.16778613	1.86445196
H	-1.16287950	4.69192654	3.53187530
H	-0.75836654	4.68622615	5.24057069
H	-1.41639754	2.40487169	4.34196040
H	0.12641417	2.47474576	5.19406185
H	2.72098863	5.04287415	0.96880991
H	3.53607166	4.79230288	2.52347737
H	2.03987945	7.23320673	1.66240809
H	3.02906011	7.00586766	3.11055896
H	0.05331073	6.51512829	2.72930542
C	-0.41599841	7.42462723	5.35508554
H	0.77989248	9.71872798	4.55367667
H	1.80182885	9.10027393	3.24832777
H	-1.26825552	8.94127501	3.22876143
H	-0.19700056	8.49555647	1.90011740
H	0.66533179	10.89638243	1.84971809
H	-0.55677328	11.32000918	3.06055532
H	-1.13095777	10.16368371	0.27673613
H	-0.61178223	-2.17254144	-3.50611236
H	-1.35617051	-0.99480142	-2.37364310
H	-1.50748314	-2.73451280	-2.05669653
H	2.07632736	3.73499093	5.34728202
H	2.95216947	5.17046604	4.75659731
H	1.61264437	5.35261747	5.90971364
H	-3.06312813	11.20614227	2.43705886
H	-2.93683412	9.51832427	1.86616125
H	-3.53248466	10.78642192	0.76696738
H	-1.48602107	13.02669447	1.36215188
H	-1.97068106	12.46999907	-0.26161244
H	-0.24198564	12.50726841	0.19311808
H	1.52567130	-0.90403293	4.62102033
H	1.51210265	0.72103808	5.34829486
H	2.55324806	0.38129350	3.93994043
Fe	-1.87177945	3.33472035	1.04987313
Cl	-3.70524828	2.28929581	1.70120717
Cl	-2.14429611	5.49118143	1.39870771
Cl	-1.53839508	3.28057633	-1.13150745
H	-0.52879804	0.28644460	3.92877916
H	-1.33368492	7.28176572	4.76375676
H	-0.54171813	8.33538628	5.96433947
H	-0.32014344	6.57345170	6.04376027

Figure SI-2: Relative energies of species uncoordinated from $FeCl_3$



XYZ coordinates for structures uncoordinated to $FeCl_3$

Structure **14**

C	-1.81147049	2.19611853	-1.44318721
C	-2.78237303	1.90840493	-2.61575721
C	-3.85231203	0.88372479	-2.17868169
C	-4.02191812	1.55349370	0.76451196
C	-3.74582340	2.69736801	0.10255946
C	-5.31550597	1.31886435	-2.28217788
C	-6.28757559	0.64488962	-1.28875445
C	-6.54084790	1.40246632	0.04124007
C	-5.44324198	1.14661435	1.12311312
C	-7.88312443	0.95869030	0.65791045
C	-8.25672524	1.70936807	1.96185756
C	-7.18544416	1.41322067	3.02213652
C	-5.78450658	1.79023591	2.50316851
C	-9.17849315	1.03449945	-0.18861303
C	-10.34049448	1.04448765	0.86349178
C	-9.64097728	1.07015872	2.26316361
O	-3.52506921	-0.25001415	-1.84733693
H	-6.60042165	2.48156987	-0.18310172
H	-5.44258544	0.05008572	1.27375774
H	-7.74967238	-0.10308121	0.94512570
C	-10.41096214	1.63372694	3.50489403
C	-11.78364508	2.28452389	3.20660484
C	-11.72535436	3.70587193	2.62403212
C	-13.12434136	4.26909703	2.32988272
C	-13.12916072	5.70609084	1.76433591
C	-2.95508573	0.60353232	1.25088677
C	-8.38713494	3.23162350	1.73393961
O	-0.46767776	2.56104729	-1.88011403
O	1.06247597	3.79186693	-2.90121182
C	-0.09789650	3.69422136	-2.55572829
C	-1.10304537	4.81611571	-2.81053455
C	-12.40784775	5.78831740	0.40494449
C	-14.57498248	6.21960444	1.63284733
H	-2.19191887	1.44723749	-3.42214090
H	-3.26334974	2.81963402	-2.99911351
H	-5.61270213	1.05295470	-3.31624290
H	-5.38464863	2.41564751	-2.22146916
H	-5.92580545	-0.37470673	-1.07628410
H	-7.25408261	0.53815305	-1.80191184
H	-7.20862978	0.33183474	3.24872847
H	-7.40124565	1.95159589	3.96145146

H	-5.69504956	2.88353371	2.40342362
H	-5.01752154	1.48414967	3.23426661
H	-9.26458961	0.19354646	-0.89164111
H	-9.18957489	1.95992824	-0.78753465
H	-10.98653831	0.15916058	0.76625896
H	-10.98275428	1.92078645	0.70793796
H	-9.41045580	0.01291545	2.48893371
C	-10.58758991	0.52015539	4.56003715
H	-12.35729082	1.63016863	2.52734834
H	-12.36083400	2.33007182	4.14734044
H	-11.12501754	3.71688484	1.70610229
H	-11.20423921	4.36999030	3.33782618
H	-13.72309968	4.24170614	3.25820652
H	-13.63814122	3.60598849	1.60795030
H	-12.59267305	6.35558135	2.48104433
H	-1.95307782	1.05661478	1.26489727
H	-2.92476568	-0.28206828	0.59268534
H	-3.19404385	0.24990460	2.26811251
H	-7.43162857	3.68496058	1.43575068
H	-9.12245338	3.45000297	0.94716496
H	-8.71764042	3.73060978	2.65739051
H	-0.78263167	5.35237704	-3.71289126
H	-1.06244070	5.52017716	-1.96368516
H	-2.13894321	4.47962716	-2.92115099
H	-12.88369939	5.10260990	-0.31793037
H	-11.34417019	5.51407105	0.48512022
H	-12.46335843	6.80891401	-0.00755440
H	-15.14032379	5.58923546	0.92444496
H	-14.60144507	7.25694508	1.25993702
H	-15.09660320	6.18821193	2.60368701
C	-2.37027285	3.14140451	-0.35077522
H	-1.61573444	1.22145223	-0.98028837
H	-2.43039024	4.16957844	-0.73032039
H	-1.64450897	3.14022362	0.47967321
H	-4.58312712	3.32336590	-0.21725098
H	-9.61706089	0.06803227	4.82197839
H	-11.24007939	-0.28094496	4.17099787
H	-11.04766886	0.91600900	5.48051877
H	-9.77666409	2.41114399	3.96753706

Structure **16**

O	2.90271702	6.80028416	20.81940883
O	6.28030758	9.67963305	20.97086292
H	7.10319186	9.50133297	20.47330314
O	3.00756175	4.90290554	22.09462600
C	5.96735711	8.74447586	17.08406814
H	4.97907019	8.25915204	17.14910410
C	6.19585636	7.60606500	14.76976597
C	2.52130581	5.54080451	21.17704703
C	6.28449736	8.93278770	15.59129788
H	7.34095380	9.26047523	15.52108896
C	5.74219544	9.52205159	13.29410455
H	6.33918944	10.28530269	12.77459707
H	4.80535216	9.41060660	12.72481642
C	7.02806900	6.42581315	16.88558065
H	7.82745845	5.78186807	17.28502808
H	6.07539805	5.90475465	17.08255890
C	5.87197679	10.06648001	17.88866145
H	6.86245341	10.33747934	18.29676712
H	5.57918507	10.88788560	17.21710359
C	7.03838855	7.77171092	17.65735085
H	8.01993171	8.24124210	17.45854827
C	5.45394825	9.93285625	14.76956205
H	5.73212885	10.97693010	14.97401337
H	4.38335848	9.82741235	15.00976830
C	6.18257677	7.26387833	12.11089137
H	5.08513593	7.13313387	12.07441181
C	7.22489446	6.61961380	15.36398621
H	7.17958765	5.63855239	14.87008629
H	8.23710070	7.02553510	15.18509981
C	6.60777478	7.98859262	10.80854615
H	7.71272329	8.01917302	10.76494872
H	6.27031784	9.03723897	10.84382037
C	6.50690780	8.15102931	13.33776830
H	7.59383857	8.35748131	13.31401467
C	6.48297474	8.14572722	8.26224454
H	7.58594276	8.12851404	8.17685967
H	6.19763491	9.20582729	8.39145604
C	5.87561159	7.62687861	6.94140636
H	4.77450359	7.65331103	7.04340996
C	6.94848993	7.53043219	19.15919750
C	6.05974146	7.36071045	9.51533319
H	4.95582796	7.32650912	9.57021509
H	6.40103202	6.31811184	9.42207803
C	5.20864035	9.09104495	20.21482816
C	4.77848633	6.98821364	14.80124141
H	4.75071810	6.07803172	14.18396770
H	4.02617984	7.68583835	14.40419329
H	4.47308257	6.70776251	15.81854451
C	4.83225719	9.99540176	19.02649990
H	4.65071693	11.00425231	19.43233803
H	3.87838523	9.63560657	18.60109898
C	5.58444026	7.61026625	19.80103414
H	4.82284738	7.28303223	19.07508838
C	4.00043340	7.40074085	21.59507502
H	3.80523510	7.20469060	22.65658999
C	6.29593567	6.17461854	6.64371154
H	5.89097558	5.83995037	5.67454875
H	5.94071015	5.47892704	7.41958410
H	7.39647376	6.09955540	6.59634168
C	6.83648397	5.87056860	12.18867168
H	6.71091111	5.31945541	11.24457445
H	6.39520011	5.25622751	12.98543236
H	7.91739279	5.96280294	12.38739278
C	5.34680490	6.84141394	21.11354051
H	6.11019891	7.12116432	21.85446422
H	5.34008540	5.74968424	21.00541924
C	1.40892827	5.05671981	20.25893305
H	1.79512170	4.94978973	19.23259578
H	0.59012847	5.79146702	20.22678354
H	1.03725496	4.08878688	20.61635017
C	4.03316150	8.89905812	21.21956621

H	4.21350588	9.52134218	22.10708348
H	3.07148501	9.20116969	20.78076019
C	6.27469972	8.54825897	5.77377706
H	7.37012182	8.53987229	5.63776577
H	5.96479430	9.58916478	5.96431558
H	5.81369347	8.21596461	4.82907757
C	8.07424602	7.32010865	19.87222239
H	8.05797617	7.10331958	20.94114534
H	9.05246843	7.32541774	19.38301531

Structure **39**

C	-1.72907568	2.14439021	-1.48791391
C	-2.78793345	1.68085044	-2.51004586
C	-4.01832151	1.44035537	-1.63498345
C	-4.07915821	1.08159658	0.42998057
C	-3.90136924	2.38631895	-0.39084125
C	-5.36080533	1.36220473	-2.36675921
C	-6.44802209	0.65521581	-1.53205485
C	-6.65300353	1.25426596	-0.12526680
C	-5.53998708	0.85757743	0.90986676
C	-7.99691115	0.83028707	0.49050111
C	-8.31774975	1.56516769	1.81770669
C	-7.22171098	1.22504913	2.83905081
C	-5.81021933	1.52699552	2.28336459
C	-9.30330998	0.96613878	-0.32877796
C	-10.44165605	0.99240917	0.75033270
C	-9.71225142	0.95689597	2.13441796
O	-3.82471629	0.26396049	-0.77372098
H	-6.66647663	2.35263715	-0.23521100
H	-5.62755634	-0.23726393	1.04550060
H	-7.89382973	-0.24155026	0.74914581
C	-10.44572964	1.50440019	3.40386307
C	-11.76629773	2.27256267	3.15145754
C	-11.61734710	3.70422802	2.61241918
C	-12.97854619	4.38805540	2.41370816
C	-12.89754361	5.83883976	1.89007078
C	-3.03835139	0.74732159	1.49672201
C	-8.41126999	3.09472376	1.63014282
O	-0.49241121	2.66539407	-2.03440433
O	0.74511942	3.98343336	-3.31191327
C	-0.33827560	3.79473347	-2.79627492
C	-1.46830629	4.81646414	-2.91404933
C	-12.24493722	5.90850923	0.49577680
C	-14.30058372	6.47195149	1.85396877
H	-2.48163243	0.76914503	-3.04299901
H	-3.01520781	2.45862338	-3.25484430
H	-5.22820269	0.82301826	-3.32106850
H	-5.67826154	2.39041666	-2.61764755
H	-6.18626526	-0.40963509	-1.43590327
H	-7.39559909	0.71590304	-2.08963709
H	-7.28549430	0.14646222	3.07115319
H	-7.37731861	1.77303632	3.78516999
H	-5.66646313	2.61687820	2.18421938
H	-5.06949081	1.18023847	3.01854964
H	-9.42632706	0.14051965	-1.04399617
H	-9.29866611	1.90187503	-0.91122502
H	-11.12471209	0.13629530	0.64424334
H	-11.05046262	1.89834166	0.63493772
H	-9.50567329	-0.11183438	2.32696129
C	-10.71335757	0.34747341	4.39165124
H	-12.40489912	1.68509551	2.46869512
H	-12.31695247	2.33253721	4.10750789
H	-11.06964659	3.70122578	1.66238477
H	-11.00480863	4.29566262	3.31771796
H	-13.52870115	4.37819619	3.37229561
H	-13.58109552	3.79180774	1.70233157
H	-12.27233539	6.41956910	2.59388904
H	-2.03702291	0.71090211	1.04567867
H	-3.25385479	-0.23722025	1.94170760
H	-3.02951587	1.49912841	2.30054353
H	-7.43997709	3.53434844	1.36438237
H	-9.12611132	3.35659539	0.83731426
H	-8.74735717	3.57285395	2.56211662
H	-1.28564821	5.41492842	-3.81561524
H	-1.42547207	5.48779224	-2.04088204
H	-2.47298967	4.37983230	-2.95022590
H	-12.80515373	5.27917116	-0.21790495
H	-11.20041748	5.55857062	0.51047897
H	-12.24949208	6.94211992	0.11296920
H	-14.95461279	5.91459079	1.16095573
H	-14.25756704	7.51890492	1.51078035
H	-14.77045211	6.45391480	2.85114336
C	-2.49263181	3.01706584	-0.45593923
H	-1.38099952	1.24357089	-0.96922835
H	-2.58395883	4.05482735	-0.79885887
H	-1.97870414	3.02977086	0.51651476
H	-4.68669940	3.13921754	-0.24266272
H	-9.77844754	-0.17955630	4.64363328
H	-11.40616469	-0.38761410	3.94632827
H	-11.16633485	0.72015432	5.32532724
H	-9.75536502	2.20285126	3.91011341

Structure **17**

C	-2.55841385	3.44327830	-1.33719032
C	-3.24974636	2.16161562	-1.89782273
C	-4.73360828	2.46385691	-1.80739750
C	-3.93942419	0.32908672	1.29066570
C	-4.95785641	3.71325206	-1.35171075
C	-5.77411500	1.43150713	-2.14756429
C	-5.79154315	0.27626843	-1.10955184
C	-6.22851237	0.75403783	0.30028274
C	-5.43404966	0.02034128	1.44288686
C	-7.72619450	0.52566489	0.54226385
C	-8.22055276	1.01576016	1.92584808
C	-7.48733903	0.20816211	3.01035306
C	-5.95538041	0.35265756	2.86916234
C	-8.75060196	1.12231945	-0.44960371
C	-10.09945811	1.11991437	0.34548516
C	-9.73654622	0.68119639	1.80269257
O	-3.16342158	-0.48514397	0.80120549
H	-6.01617662	1.83260068	0.37844880

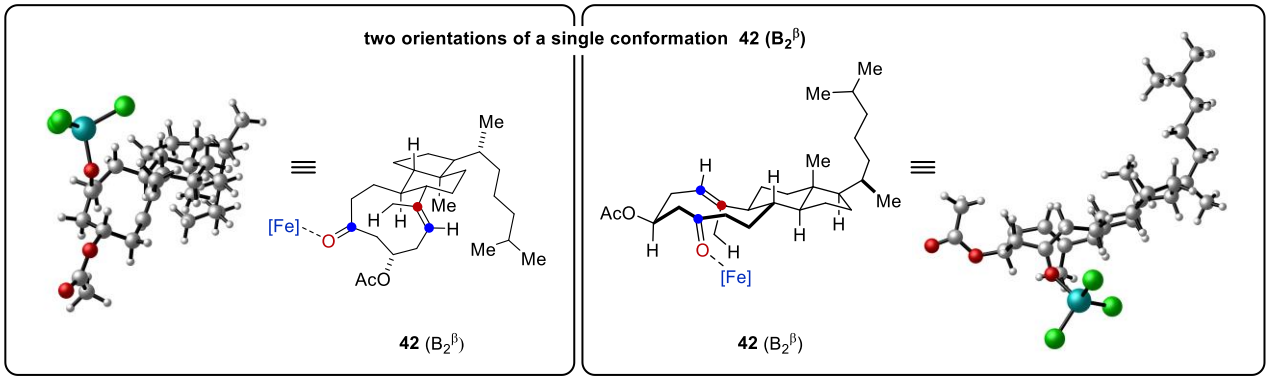
H	-5.54542566	-1.06232965	1.26680004
H	-7.87732453	-0.57186644	0.53510313
C	-10.66611779	1.12762160	2.98470408
C	-11.72055882	2.20966095	2.64363847
C	-11.17824279	3.63746937	2.47664733
C	-12.26694112	4.63636912	2.05531457
C	-11.78159315	6.09830128	1.95364730
C	-3.46110844	1.72316440	1.69809712
C	-7.97997274	2.52897635	2.11366340
O	-1.44195464	3.92525818	-2.12660205
O	-0.49083330	4.62523780	-4.00140760
C	-1.52592195	4.34612309	-3.43036756
C	-2.88362294	4.51126937	-4.11374373
C	-10.65006628	6.25619777	0.91910324
C	-12.95954188	7.02588844	1.60176627
H	-2.96766830	1.27057281	-1.31489967
H	-2.93840294	1.96324378	-2.93812607
H	-5.56404405	1.00546923	-3.14479373
H	-6.76656500	1.90518830	-2.19054469
H	-4.79006196	-0.17671813	-1.07365993
H	-6.47728729	-0.51376337	-1.45924528
H	-7.76990337	-0.85478375	2.89969621
H	-7.79876280	0.52569499	4.02092297
H	-5.67008811	1.38126574	3.13714010
H	-5.44824521	-0.30806395	3.59166412
H	-8.80408551	0.54780195	-1.38601404
H	-8.46895063	2.15267534	-0.71876203
H	-10.83078947	0.42706390	-0.09735374
H	-10.55741535	2.11667445	0.32347164
H	-9.75978384	-0.42339842	1.79450538
C	-11.37856038	-0.10947496	3.57410765
H	-12.26271351	1.91048958	1.72981343
H	-12.47519566	2.22754082	3.45097273
H	-10.37182679	3.65288737	1.73251190
H	-10.72260046	3.96682887	3.42843885
H	-13.10560435	4.58678117	2.77348483
H	-12.67630553	4.33023384	1.07379085
H	-11.38749813	6.39453324	2.94373728
H	-2.40719936	1.84007332	1.41564794
H	-3.56398591	1.86936151	2.78582369
H	-4.07355921	2.49475852	1.20428271
H	-6.91044218	2.76862979	2.19296495
H	-8.37609846	3.10330297	1.26487781
H	-8.47755103	2.88704105	3.02541439
H	-2.77402211	4.17784700	-5.15478267
H	-3.11544836	5.58866621	-4.13792580
H	-3.72259685	3.99257028	-3.63801731
H	-10.98366224	5.88843015	-0.06739648
H	-9.74993857	5.69013024	1.20724279
H	-10.36402193	7.31498589	0.80815087
H	-13.37253444	6.75716655	0.61414260
H	-12.63764394	8.07942239	1.56065747
H	-13.77080938	6.93930779	2.34359440
C	-3.69196684	4.48821452	-1.07148287
H	-2.06488784	3.20002979	-0.39033703
H	-3.58591543	5.37074807	-1.72474258
H	-3.64514438	4.86552878	-0.03520826
H	-5.95360295	4.14276755	-1.21518740
H	-10.64986245	-0.88345295	3.86607205
H	-12.05834094	-0.55077761	2.82483410
H	-11.97636574	0.15828483	4.46050125
H	-10.02155755	1.54180945	3.78153810

Structure **19**

C	-0.53139295	-1.17993665	1.78254982
C	-0.85913651	-0.93697683	0.30279740
C	-0.83595288	0.60119762	0.17061222
C	0.23542035	1.07380715	1.18042015
C	0.63187752	0.43405157	3.51908164
C	0.58590675	-0.15998183	2.08618269
C	1.48167603	1.71214712	0.55186096
C	2.51507987	2.01862722	1.65786085
C	1.86356371	2.67284418	2.90225498
C	0.50932682	1.97384982	3.26935763
C	1.57990112	4.16652549	2.68539242
C	0.98342182	4.88322232	3.92800106
C	-0.36917263	4.20994116	4.23846087
C	-0.21471864	2.68325044	4.41924404
C	2.74116101	5.07501841	2.23684574
C	2.25371740	6.51164453	2.60284101
C	0.91034196	6.34699407	3.38713635
H	2.55332834	2.55856906	3.75396432
C	0.67133627	7.49479782	4.39061854
H	0.79937292	4.22400380	1.90657099
C	0.69971358	8.87625531	3.68906181
C	-0.40502007	9.09921979	2.64218993
C	-0.39361736	10.53039357	2.08221410
C	-1.41290544	10.78493331	0.95119047
O	-0.35542820	2.02261156	2.10203238
H	1.55443686	-0.58853079	1.79396805
O	0.24413882	-1.52306085	-0.45412020
O	1.16441032	-2.07543217	-2.40157125
C	0.16827898	-1.71228165	-1.80985329
C	-1.18276578	-1.49414499	-2.48702129
C	1.91712798	4.82164818	5.15598934
H	1.51709660	7.49106418	5.10251881
C	-2.86316363	10.57464472	1.42537266
C	-1.23813290	12.20544726	0.38364012
C	1.82226615	-0.00856747	4.37942816
H	-0.25030312	-2.22515265	1.97694663
H	-1.43033248	-0.93978116	2.37441910
H	-1.80794936	-1.39606060	-0.01174971
H	-1.81372269	1.01008687	0.46830760
H	-0.62281964	0.92841471	-0.85756082
H	1.17019066	2.63456183	0.03434445
H	1.90973168	1.02643886	-0.19724135
H	3.31443837	2.67083858	1.27469999
H	2.99751320	1.07498358	1.95311254
H	-1.05744150	4.39866227	3.39775720
H	-0.83341229	4.62609422	5.14428065
H	-1.20818156	2.21741388	4.52565602
H	0.34118643	2.46490258	5.34626607

H	2.96080206	4.96741251	1.16429795
H	3.66367726	4.82069248	2.78475413
H	2.11618574	7.13970639	1.70968735
H	2.99343358	7.02592567	3.23769964
H	0.08111673	6.35601081	2.65678076
C	-0.62736066	7.33424420	5.20773200
H	0.60838915	9.65351037	4.46987500
H	1.68204701	9.02609262	3.21089597
H	-1.38643810	8.88596503	3.09451345
H	-0.28202988	8.38611187	1.80775793
H	0.62028535	10.75878039	1.70543763
H	-0.58946437	11.24458481	2.90414560
H	-1.20587673	10.06059711	0.14103429
H	-1.04876242	-1.62260340	-3.56727287
H	-1.58657885	-0.49359955	-2.27424423
H	-1.91833023	-2.22933031	-2.12038298
H	2.12163268	3.78791905	5.46973578
H	2.88145540	5.30694688	4.94234610
H	1.45628094	5.34797961	6.00649315
H	-3.09199468	11.25615036	2.26377947
H	-3.03620825	9.54271064	1.76822033
H	-3.57654329	10.78688225	0.61197692
H	-1.43742441	12.95688202	1.16735405
H	-1.93707252	12.39132777	-0.44863343
H	-0.21065098	12.36286683	0.01604438
H	1.79004956	-1.09592464	4.55482812
H	1.80530208	0.49237800	5.36186283
H	2.78170032	0.22729444	3.89475886
H	-0.29440598	0.13859199	4.04130579
H	-1.48394271	7.10094606	4.55532710
H	-0.85673351	8.26716237	5.74998199
H	-0.53946824	6.52714602	5.94885648

Possible Reactive conformations:



The above computational results suggest that conformation **14** (B_2^{β}) is the one leading to product formation (**14**, **16** and **19**) under our optimized reaction conditions for $FeCl_3$-catalyzed transannular carbonyl-olefin metathesis.

In comparison, conformation **14** (B_1^{β}) was found to lead to the preferential formation of diastereomeric product *epi*-**16** that is not observed experimentally under our optimal reaction conditions, suggesting it is not a reactive conformation for the transannular reactions discussed in this report.

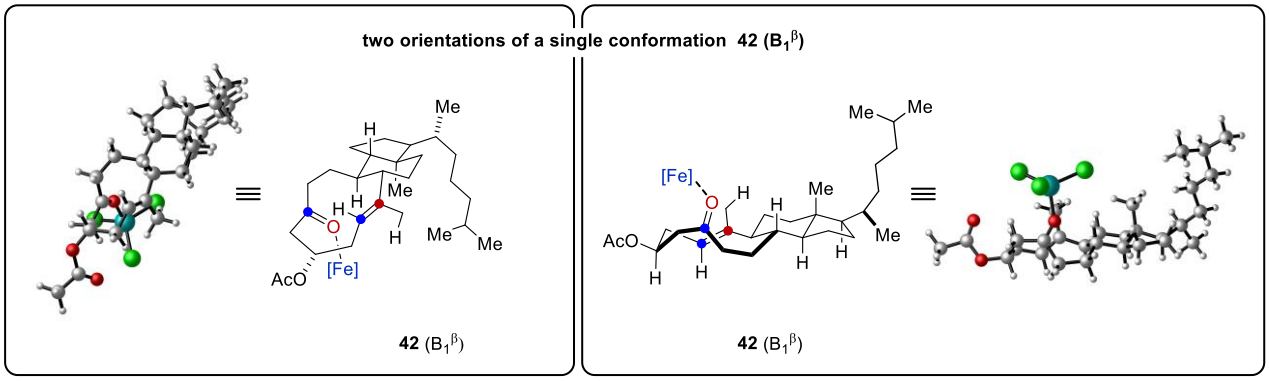
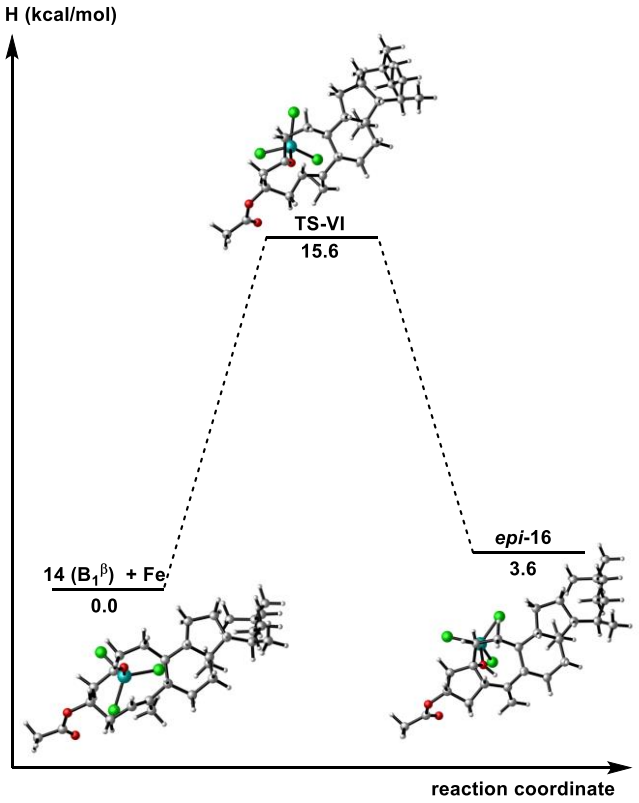


Figure SI-3: Computed Reaction pathway of **14** (B_1^{β}) + Fe



Structure **14 (B_1^{β}) + Fe**

C	-1.96198776	2.12734063	-1.82223758
C	-3.10356447	2.88960728	-2.53785776
C	-4.51656819	2.53965206	-2.12985490
C	-4.21513008	2.51826727	0.73498957
C	-3.08340397	1.87463404	0.36044720
C	-4.97513714	1.11314283	-1.96349945
C	-6.28612418	0.91379280	-1.15584829
C	-6.57293353	1.73306012	0.13399798
C	-5.42404741	1.71510030	1.20503180
C	-7.84529954	1.13697947	0.76314614
C	-8.30462990	1.84850991	2.05798554
C	-7.20822203	1.64738175	3.11604797
C	-5.86444701	2.21718488	2.61730513
C	-9.12815523	1.06582125	-0.09841060
C	-10.29460398	0.95645843	0.94012714
C	-9.61969777	1.06919141	2.34690623
O	-5.39672533	3.43368976	-2.10624383
H	-6.78253381	2.77114374	-0.15853982
H	-5.12309361	0.65616278	1.31054123
H	-7.59002069	0.09955783	1.05985340
C	-10.46800184	1.55653562	3.57054284
C	-11.89145288	2.06514350	3.23802353
C	-11.95246228	3.47887200	2.63719193
C	-13.37887374	3.88459887	2.23740876
C	-13.49978592	5.30940850	1.65571865
C	-4.34989182	4.02468914	0.73455659
C	-8.57662068	3.34982079	1.81798111
O	-0.70377155	2.31010836	-2.53317225
O	-0.58408898	4.55798102	-2.06679870
C	-0.12031907	3.55429307	-2.57217994
C	1.18501014	3.47420549	-3.34355125
C	-12.68609015	5.47316324	0.35699406
C	-14.97945110	5.65625219	1.40667595
H	-3.04387235	2.64040842	-3.61426175
H	-2.96028215	3.97283124	-2.44123502
H	-4.15246256	0.50953514	-1.56710273
H	-5.15103784	0.74685702	-2.99533934
H	-6.33058188	-0.15944562	-0.90280743
H	-7.12794716	1.10823831	-1.83479826
H	-7.10993605	0.56470151	3.31454623
H	-7.47903696	2.13223620	4.06962022
H	-5.94179600	3.31269304	2.60325608
H	-5.05631007	1.97287971	3.32645471
H	-9.10899833	0.21775646	-0.79849344
H	-9.22654230	1.98413398	-0.69965369
H	-10.83872588	0.00486254	0.84479650
H	-11.02605270	1.75564391	0.76953279
H	-9.28182378	0.04471968	2.58899340
C	-10.54928331	0.43150486	4.62526809
H	-12.38669081	1.35065822	2.55732097
H	-12.48953665	2.06541812	4.16690363
H	-11.29605791	3.54763441	1.76058929
H	-11.55343987	4.20189155	3.37202552
H	-14.03991831	3.79849618	3.11928958
H	-13.76199271	3.16420050	1.48966336
H	-13.09885709	6.01655879	2.40579353
H	-4.22316988	4.41557476	1.75769109
H	-5.35230932	4.33428904	0.40282281
H	-3.61254194	4.52452509	0.09694413
H	-7.66749528	3.89448053	1.53241120
H	-9.30038900	3.49955058	1.00573199
H	-8.98220656	3.82044373	2.72552158
H	1.63804490	4.47145942	-3.38818418
H	0.99978885	3.09639801	-4.36079356
H	1.87125749	2.76819637	-2.85062418
H	-13.02321487	4.74128119	-0.39815560
H	-11.60845836	5.32054380	0.52226460
H	-12.82212277	6.48206849	-0.06520380
H	-15.41152953	4.96914140	0.65832820
H	-15.08921561	6.68477419	1.02551161
H	-15.57043818	5.56373536	2.33309560
C	-1.87080876	2.45902244	-0.31076515
H	-2.12361212	1.04610553	-1.93550403
H	-1.78458974	3.54158104	-0.17654799
H	-0.94854014	1.99207414	0.07279560
H	-3.08507603	0.78016998	0.43079228
H	-9.54166004	0.08412361	4.90708844
H	-11.10490974	-0.43349430	4.22324533
H	-11.06629929	0.77643404	5.53578213
H	-9.92964508	2.39821340	4.04265853
Fe	-5.70672007	5.36718901	-2.42423813
Cl	-3.93313875	6.54432811	-1.91385093

Cl	-6.13919090	5.38368104	-4.57241319
Cl	-7.43941912	5.76212949	-1.13156900

Structure **TS-VI**

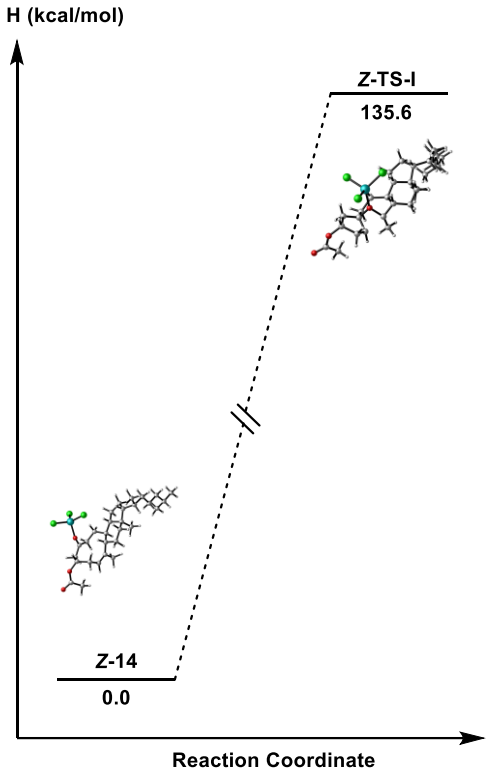
C	-1.80091994	1.96574531	-2.03856917
C	-2.90457670	2.86608297	-2.61762826
C	-4.13113492	2.70731031	-1.67581063
C	-4.13800929	2.54847314	0.83758699
C	-3.43687989	1.95453548	-0.30271494
C	-5.21427565	1.75177672	-2.18598916
C	-6.14603668	1.11120251	-1.12299960
C	-6.53564193	1.91300038	0.14794572
C	-5.41867830	1.89107263	1.29217076
C	-7.79323073	1.26272750	0.76304907
C	-8.31895194	1.95524881	2.04462774
C	-7.24108388	1.82105845	3.13093154
C	-5.91773204	2.44826577	2.65281491
C	-9.05603929	1.12269688	-0.12534607
C	-10.23622317	0.96790892	0.89123152
C	-9.59442091	1.10637338	2.30908941
O	-4.65677433	3.95931784	-1.35711781
H	-6.74707402	2.95536103	-0.12106354
H	-5.18822008	0.81590371	1.41840382
H	-7.49060571	0.24037368	1.06726773
C	-10.48842332	1.54480750	3.51902870
C	-11.92804185	1.98775593	3.16114978
C	-12.04287644	3.40205081	2.56989707
C	-13.48064184	3.75575599	2.16152394
C	-13.64732252	5.18043777	1.59038799
C	-3.84327490	3.89574575	1.13488960
C	-8.67288560	3.43694814	1.78755971
O	-0.47961923	2.17590625	-2.59821269
O	-0.28292686	4.32945664	-1.81135293
C	0.15177237	3.38286694	-2.44279719
C	1.47631546	3.35731912	-3.18492224
C	-12.82936023	5.38384472	0.29991425
C	-15.13621379	5.47770429	1.33281256
H	-3.16597936	2.60463629	-3.65307324
H	-2.57690156	3.91080008	-2.58306260
H	-4.71139701	0.93817942	-2.73507963
H	-5.81652317	2.30751981	-2.91862526
H	-5.72322067	0.14726574	-0.78782761
H	-7.07278088	0.86239325	-1.65516943
H	-7.09314977	0.74808321	3.35057102
H	-7.55472442	2.30842770	4.06913603
H	-6.07164667	3.53200021	2.57040687
H	-5.12378898	2.29658746	3.40261496
H	-8.98578561	0.26075536	-0.80426580
H	-9.18174909	2.02095405	-0.74725256
H	-10.74109753	-0.00388528	0.78537668
H	-10.99402009	1.73895850	0.70645775
H	-9.20821596	0.09948242	2.55374547
C	-10.53715246	0.40891768	4.56397875
H	-12.37511461	1.25615294	2.46543560
H	-12.54309848	1.95199919	4.07810215
H	-11.38327935	3.50381057	1.69928327
H	-11.67913899	4.13494000	3.31329768
H	-14.14520588	3.63830303	3.03706438
H	-13.83048409	3.02813363	1.40459015
H	-13.27736719	5.89434850	2.35000699
H	-4.36823773	4.40618181	1.94116325
H	-4.37696317	4.18724607	0.01740769
H	-2.82791739	4.26106077	0.95240098
H	-7.79614124	4.04529449	1.53115493
H	-9.37804316	3.53440274	0.95176326
H	-9.14001598	3.87880164	2.67958002
H	2.00540962	4.30143875	-3.01008706
H	1.29622641	3.22351153	-4.26304667
H	2.08841736	2.50764963	-2.84591212
H	-13.13439393	4.64800631	-0.46476643
H	-11.74831002	5.26719268	0.47219757
H	-12.99693217	6.39134216	-0.11400368
H	-15.53830366	4.78345324	0.57445295
H	-15.27894949	6.50553572	0.96085802
H	-15.73082393	5.35578767	2.25353094
C	-1.92789503	2.14059132	-0.51311710
H	-2.00016400	0.91445936	-2.29638040
H	-1.59135836	3.14598494	-0.24321026
H	-1.34249645	1.39712610	0.04749091
H	-3.69074992	0.89305559	-0.40630966
H	-9.52037294	0.10572158	4.86379985
H	-11.04411984	-0.47744407	4.14467266
H	-11.08735946	0.72159424	5.46653612
H	-10.00057093	2.40858058	4.00606797
Fe	-6.07661920	5.12167016	-1.92562288
Cl	-5.28866660	6.29401688	-3.60779770
Cl	-7.92183313	4.04790026	-2.50913456
Cl	-6.38749368	6.25860887	-0.04797680

Structure ***epi*-16**

C	-1.82224847	1.95031416	-2.04819790
C	-2.99981645	2.73049616	-2.67084491
C	-4.14528502	2.56526235	-1.64078038
C	-4.13130194	2.55008505	0.92187282
C	-3.46411650	1.99657284	-0.32862477
C	-5.30237791	1.68491658	-2.11726380
C	-6.14975388	1.01215334	-1.01590848
C	-6.55230645	1.84767356	0.22879648
C	-5.43506004	1.87344860	1.35183285
C	-7.81847574	1.21666028	0.84342827
C	-8.34767859	1.94207024	2.10436678
C	-7.27359487	1.82798193	3.19491546
C	-5.94337836	2.43419750	2.70807165
C	-9.07734621	1.05995969	-0.04768721
C	-10.26900228	0.95386126	0.96279573
C	-9.63287538	1.11266172	2.38055111
O	-4.68969117	3.91906592	-1.34476528
H	-6.78015619	2.87717148	-0.08426340
H	-5.18393734	0.80521508	1.51148303
H	-7.52468225	0.20073910	1.17648588
C	-10.52857146	1.58323104	3.57643924
C	-11.95808301	2.04674938	3.20410836

C	-12.04820788	3.45574368	2.59663013
C	-13.48445915	3.84104934	2.21164394
C	-13.62971329	5.27097845	1.64791098
C	-3.61490817	3.64176968	1.53353013
C	-8.68809371	3.42008446	1.81155532
O	-0.52854730	2.21589145	-2.64818972
O	-0.48835316	4.43547788	-2.04468149
C	0.01194480	3.47298668	-2.59914637
C	1.32985495	3.48501994	-3.35432039
C	-12.82395993	5.46339249	0.34823414
C	-15.11522778	5.60019611	1.41070406
H	-3.27771927	2.36966880	-3.66941456
H	-2.72941818	3.78915025	-2.74404726
H	-4.87063616	0.89221713	-2.75098393
H	-5.94687660	2.28530066	-2.77768765
H	-5.63812925	0.10065921	-0.65916661
H	-7.06371275	0.66341328	-1.51501916
H	-7.13261956	0.75899907	3.43714834
H	-7.58788043	2.33574470	4.12260481
H	-6.07385209	3.52338134	2.62025375
H	-5.15606104	2.27647684	3.46284654
H	-9.01544744	0.17494211	-0.69748311
H	-9.18921114	1.93807384	-0.70167937
H	-10.79586575	-0.00808617	0.87536965
H	-11.00826034	1.73786399	0.75646572
H	-9.25721749	0.10731405	2.64671858
C	-10.60599330	0.46242177	4.63611238
H	-12.41480667	1.31464387	2.51536746
H	-12.57800389	2.03320471	4.11852854
H	-11.40322755	3.53047056	1.71214534
H	-11.65272291	4.18808950	3.32437811
H	-14.13696400	3.73586184	3.09773004
H	-13.86236424	3.12319566	1.45901138
H	-13.23551662	5.97378626	2.40576845
H	-4.07731663	4.09651900	2.40764896
H	-4.57328575	4.11769380	-0.37896609
H	-2.68149825	4.09598689	1.19999724
H	-7.79865618	4.00302304	1.53777593
H	-9.39436404	3.50558001	0.97544624
H	-9.14332789	3.89194545	2.69447228
H	1.80817741	4.46337969	-3.22797647
H	1.14491243	3.29732545	-4.42379476
H	1.99052347	2.68430717	-2.98888443
H	-13.15565885	4.73935283	-0.41657686
H	-11.74393890	5.31968410	0.50649112
H	-12.97337748	6.47705087	-0.05774292
H	-15.54132318	4.91819603	0.65437534
H	-15.24163355	6.63264596	1.04557746
H	-15.70027345	5.48598532	2.33844093
C	-1.95385574	2.22341671	-0.53886493
H	-1.94717493	0.87280940	-2.23356759
H	-1.65974710	3.26071448	-0.34750429
H	-1.34032886	1.55286576	0.07891456
H	-3.64084717	0.90997713	-0.35579220
H	-9.59701823	0.14575010	4.94771090
H	-11.12502300	-0.42035444	4.22400852
H	-11.15781612	0.79657678	5.52993707
H	-10.02826353	2.44446866	4.05591284
Fe	-5.91063303	5.07650014	-2.43284598
Cl	-5.58136975	6.97226068	-1.39337100
Cl	-5.14993209	4.90292650	-4.47488266
Cl	-7.97111781	4.34510876	-2.22894888

Figure SI-4: Computed pathway for COM of ***Z*-14**



Structure ***Z*-14**

C	-1.78657804	1.40136288	-1.07098887
C	-2.61579641	1.47488343	-2.38570603
C	-4.00759693	0.91781212	-2.18703792
C	-4.53416396	3.57586987	-0.38630912
C	-3.18351236	3.50175932	-0.37680221
C	-5.22449259	1.63506556	-2.71278892
C	-6.52259865	1.42429571	-1.89683888
C	-6.76396670	2.29419489	-0.63543065
C	-5.47389912	2.53469226	0.21874093
C	-7.82327514	1.56938726	0.20907796
C	-8.16754486	2.26286976	1.54554682
C	-6.89522514	2.26733416	2.40684851
C	-5.74950380	3.01073689	1.68854359
C	-9.19704355	1.27268299	-0.43512544
C	-10.15456665	1.05205341	0.78454108
C	-9.28158148	1.30359275	2.05575542
O	-4.08607888	-0.20568670	-1.64213868
H	-7.17619524	3.26579038	-0.94809773
H	-4.96938092	1.55935160	0.29820493
H	-7.38337551	0.59561253	0.48187865
C	-9.97926467	1.68588518	3.40381039
C	-11.49208500	2.00038362	3.31382184
C	-11.83757384	3.39042681	2.75791279
C	-13.35241090	3.62973787	2.66311707
C	-13.74334059	5.05660091	2.22297283
C	-5.18810910	4.83717269	-0.92038893
C	-8.70077866	3.69570528	1.33232888
O	-0.36692927	1.46727869	-1.34828889
O	1.52336395	2.35513923	-2.08312712
C	0.36606654	2.55108776	-1.78118596
C	-0.27478728	3.92964966	-1.80702840
C	-13.19946546	5.39598708	0.82137916
C	-15.27299346	5.22788124	2.25989256
H	-2.11325046	0.81736327	-3.11543214
H	-2.67401019	2.49171656	-2.78880344
H	-5.38317278	1.18141793	-3.71253097
H	-4.98133534	2.69264012	-2.87451864
H	-6.55262872	0.36897200	-1.59691635
H	-7.37450972	1.55659482	-2.57821338
H	-6.60140240	1.22005976	2.59447585
H	-7.07680551	2.74057040	3.38741133
H	-5.97273448	4.08873459	1.68102853
H	-4.80764518	2.89823103	2.24867146
H	-9.15520037	0.39884432	-1.10101987
H	-9.53089719	2.13145192	-1.04179008
H	-10.57487181	0.03588338	0.79558089
H	-11.00325815	1.74640723	0.72968216
H	-8.75257000	0.35101493	2.23684025
C	-9.74405429	0.56597436	4.44143472
H	-11.99522187	1.22298908	2.71300211
H	-11.92375767	1.92804452	4.32818645
H	-11.38665477	3.52707189	1.76603625
H	-11.38307035	4.16038687	3.40880514
H	-13.81434967	3.41988038	3.64498530
H	-13.79000469	2.90473085	1.95102007
H	-13.29690124	5.76495979	2.94592146
H	-4.44851975	5.63411721	-1.08864559
H	-5.70702819	4.64514478	-1.87602394
H	-5.95625999	5.21517762	-0.22578929
H	-7.93543350	4.35226731	0.89376835
H	-9.56358653	3.70137462	0.65137436
H	-9.02060886	4.13724503	2.28794275
H	0.43104614	4.62070215	-2.28203195
H	-0.47432007	4.26745234	-0.77910019
H	-1.22762972	3.94159206	-2.35159226
H	-13.58268901	4.67377785	0.07904714
H	-12.09907328	5.36385759	0.79163198
H	-13.51928787	6.40404881	0.51006679
H	-15.75179893	4.54028024	1.54126425
H	-15.56619661	6.25637675	1.99225057
H	-15.67256114	5.00245840	3.26244684
C	-2.33189792	2.33813409	0.06650106
H	-1.87044572	0.36988498	-0.71090677
H	-1.46346195	2.68734009	0.64719963
H	-2.91226928	1.69238059	0.74059659
H	-8.66824421	0.35597463	4.55565591
H	-10.23611165	-0.36716119	4.11740665
H	-10.15256451	0.84399213	5.42681691
H	-9.48392952	2.59416760	3.79376812
Fe	-5.09572283	-1.90585524	-1.36980680
Cl	-6.53295374	-2.02572172	-3.02014730

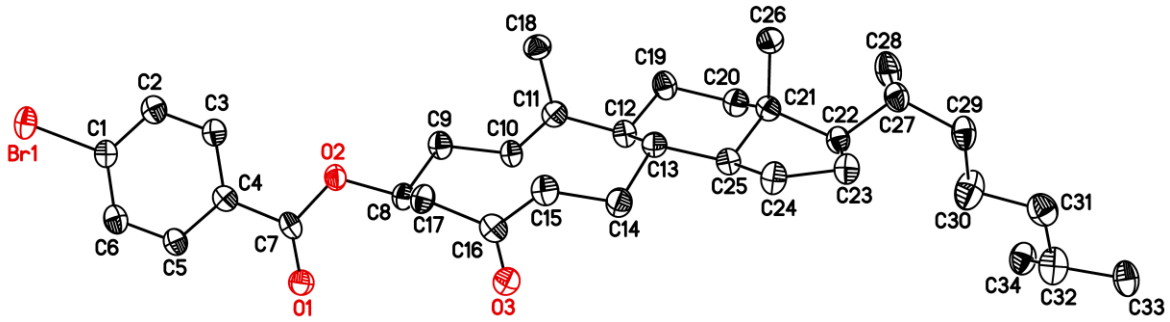
Cl	-3.52822162	-3.41624576	-1.50125001
Cl	-5.92553419	-1.72053664	0.64785421
H	-2.64779501	4.37382665	-0.75621483

Structure **Z-TS-I**

C	-1.42030038	1.03308707	-2.12642638
C	-2.87460606	1.18565591	-2.65140134
C	-3.63986180	2.09288477	-1.67497494
C	-4.25666948	2.58155393	0.44486141
C	-2.53932863	2.82219363	-0.85495885
C	-4.99789992	2.67585774	-2.23749114
C	-6.28132001	2.10754292	-1.49231736
C	-6.61011846	2.36758109	0.03236492
C	-5.48183507	2.10069945	1.20019757
C	-7.83184064	1.57984621	0.52543191
C	-8.36629364	2.12903494	1.88352472
C	-7.27140797	2.01074336	2.96584335
C	-5.94505670	2.69813332	2.53803320
C	-9.09517438	1.48170506	-0.35757854
C	-10.22346373	1.09101222	0.65754308
C	-9.57126151	1.16230603	2.08098555
O	-4.14682378	1.37919388	-0.48878765
H	-6.87069749	3.42969700	0.09935464
H	-5.42969914	1.02331989	1.38205113
H	-7.50658940	0.54448941	0.71456120
C	-10.48548819	1.41368128	3.32821393
C	-11.95090254	1.81113153	3.02552056
C	-12.15615256	3.26037198	2.55586156
C	-13.62512360	3.57108039	2.23004336
C	-13.89457548	5.03921961	1.83658502
C	-4.43103691	4.12480586	0.28151352
C	-8.83763447	3.59766038	1.78203922
O	-0.40272466	1.27192114	-3.13495548
O	0.65158274	2.42188252	-4.70644723
C	-0.16893574	2.44120368	-3.81227346
C	-0.88806493	3.72226472	-3.39754264
C	-13.12025929	5.44819557	0.56830435
C	-15.40391717	5.27099273	1.63780019
H	-3.37406570	0.21850812	-2.78452522
H	-2.87735728	1.66774517	-3.63906319
H	-5.09812874	2.34861755	-3.28323143
H	-5.01063607	3.77417054	-2.26215657
H	-6.31749096	1.02906384	-1.68987922
H	-7.14192445	2.53503115	-2.03253447
H	-7.06713576	0.94154225	3.14317516
H	-7.62022366	2.44323411	3.91837833
H	-6.07701140	3.78835678	2.47155382
H	-5.16954703	2.50902499	3.29767183
H	-8.97152150	0.74146130	-1.16068368
H	-9.31764282	2.45075150	-0.83356346
H	-10.60694923	0.07928763	0.46098228
H	-11.07358095	1.77720188	0.55843176
H	-9.10029135	0.17578153	2.23502510
C	-10.46929925	0.16467122	4.23732754
H	-12.37287155	1.11527752	2.27937027
H	-12.54499186	1.66718000	3.94538374
H	-11.53650032	3.46336121	1.67271208
H	-11.79963012	3.94881270	3.34444109
H	-14.25086274	3.31508973	3.10440153
H	-13.95953873	2.91432884	1.40461687
H	-13.55197403	5.67993698	2.67067077
H	-3.72796353	4.50934959	1.03956124
H	-4.15023870	4.58589709	-0.66576756
H	-5.42787067	4.50194747	0.54508099
H	-7.99622987	4.29490087	1.65580315
H	-9.52332734	3.74935148	0.93684437
H	-9.36856587	3.88555759	2.70023986
H	-0.68154330	4.48206308	-4.16093549
H	-0.49773756	4.07564598	-2.43064625
H	-1.97313552	3.59288693	-3.29109691
H	-13.39697633	4.79129811	-0.27510302
H	-12.03093424	5.37703507	0.71310843
H	-13.35840197	6.48567823	0.28181926
H	-15.77983027	4.64843216	0.80735033
H	-15.61604452	6.32497245	1.39380191
H	-15.97001656	5.00393679	2.54536692
C	-1.33159030	1.91551614	-0.83718817
H	-1.21613392	-0.00838906	-1.86670879
H	-0.38311550	2.46717908	-0.78206195
H	-1.37105968	1.23152601	0.02281609
H	-9.43774363	-0.10999453	4.51070399
H	-10.91911399	-0.69589780	3.71307590
H	-11.04216236	0.33934070	5.16261762
H	-10.04160868	2.24145340	3.91029051
Fe	-4.44570001	-0.64925880	-0.26765814
Cl	-5.24286661	-1.42134913	-2.18352303
Cl	-2.41073382	-1.40328052	0.13724744
Cl	-5.72001952	-1.47467383	1.33541663
H	-2.33788625	3.88545366	-0.98455465

5. X-Ray Crystallographic Data

Structure Determination of (3*R*,3*aR*,5*aS*,9*S*,13*aR*,13*bS*,*E*)-3a,6-dimethyl-3-(6-methylheptan-2-yl)-11-oxo-2,3,3*a*,4,5,5*a*,8,9,10,11,12,13,13*a*,13*b*-tetradecahydro-1H-cyclodeca[e]inden-9-yl 4-bromobenzoate (SI-2)



(CCDC 1861046)

Colorless needles of **SI-2** were grown from a diethyl ether solution of the compound at 23 deg. C. A crystal of dimensions 0.19 x 0.08 x 0.07 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (l = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in w. The exposure times were 1 sec. for the low angle images, 3 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The crystal was determined to be a two component non-merohedral twin. The twin domains are related by a 180 deg. rotation about the direct (1 0 0) axis. Reflections from both domains as well as overlaps were used as the basis for a HKLF5 reflection file for refinement. The integration of the data yielded a total of 38308 reflections to a maximum 2q value of 138.56° of which 10306 were independent and 10028 were greater than 2s(I). The final cell constants (Table 1) were based on the xyz centroids 14185 reflections above 10s(I). Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2016/6) software package, using the space group P2(1) with Z = 2 for the formula $C_{34}H_{49}O_3Br$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. The twin fraction refined to a BASF = 0.419(2). Full matrix least-squares refinement based on F^2 converged at R1 = 0.0595 and wR2 = 0.1696 [based on I > 2sigma(I)], R1 = 0.0601 and wR2 = 0.1706 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

G.M. Sheldrick (2015) "Crystal structure refinement with SHELXL", Acta Cryst., C71, 3-8 (Open Access).

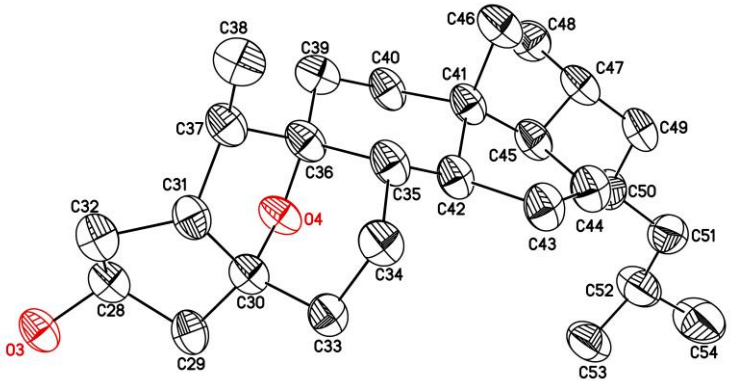
CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

Crystal data and structure refinement for **(3*R*,3*aR*,5*aS*,9*S*,13*aR*,13*bS*,*E*)-3a,6-dimethyl-3-(6-methylheptan-2-yl)-11-oxo-2,3,3*a*,4,5,5*a*,8,9,10,11,12,13,13*a*,13*b*-tetradecahydro-1H-cyclodeca[e]inden-9-yl 4-bromobenzoate (SI-2)**

Identification code	**(3*R*,3*aR*,5*aS*,9*S*,13*aR*,13*bS*,*E*)-3a,6-dimethyl-3-(6-methylheptan-2-yl)-11-oxo-2,3,3*a*,4,5,5*a*,8,9,10,11,12,13,13*a*,13*b*-tetradecahydro-1H-cyclodeca[e]inden-9-yl 4-bromobenzoate (SI-2)**
Empirical formula	C34 H49 Br O3
Formula weight	585.64
Temperature	85(2) K
Wavelength	1.54184 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 14.8070(5) A alpha = 90 deg. b = 6.83670(10) A beta = 102.062(3) deg. c = 15.3104(4) A gamma = 90 deg.
Volume	1515.67(7) A^3
Z, Calculated density	2, 1.283 Mg/m^3
Absorption coefficient	2.085 mm^-1
F(000)	624
Crystal size	0.190 x 0.080 x 0.070 mm
Theta range for data collection	2.951 to 69.260 deg.
Limiting indices	-17<=h<=17, -8<=k<=8, -18<=l<=18
Reflections collected / unique	38308 / 10296 [R(int) = 0.0766]
Completeness to theta = 67.684	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.62051
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10296 / 1 / 350
Goodness-of-fit on F^2	1.071
Final R indices [I>2sigma(I)]	R1 = 0.0595, wR2 = 0.1696
R indices (all data)	R1 = 0.0601, wR2 = 0.1706
Absolute structure parameter	-0.026(17)
Extinction coefficient	0.0060(14)
Largest diff. peak and hole	0.975 and -0.588 e.A^-3

Structure Determination of (3*R*,3*aR*,5*aS*,6*R*,6*aR*,8*S*,9*aR*,11*aS*,11*bS*)-3*a*,6-dimethyl-3-(6-methylheptan-2-yl)tetradecahydro-6H-5*a*,9*a*-epoxyindeno[5,4-f]azulen-8-ol (SI-3)



(CCDC 1861045)

Colorless needles of **SI-3** were grown from an ethyl acetate solution of the compound at 20 deg. C. A crystal of dimensions 0.06 x 0.01 x 0.01 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (l = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in w. The exposure times were 10 sec. for the low angle images, 60 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 40651 reflections to a maximum 2q value of 139.36° of which 9030 were independent and 5521 were greater than 2s(I). The final cell constants (Table 1) were based on the xyz centroids of 3749 reflections above 10s(I). Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2016/6) software package, using the space group P2(1)2(1)2(1) with Z = 8 for the formula $C_{27}H_{46}O_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0934 and wR2 = 0.2218 [based on I > 2sigma(I)], R1 = 0.1451 and wR2 = 0.2753 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

G.M. Sheldrick (2015) "Crystal structure refinement with SHELXL", Acta Cryst., C71, 3-8 (Open Access).
CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

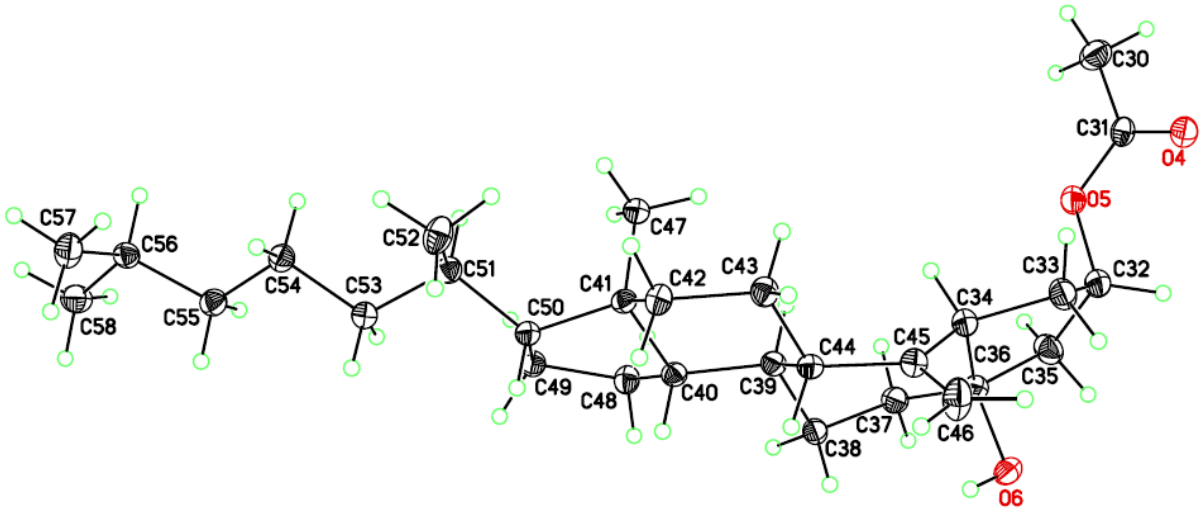
CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

Crystal data and structure refinement for **(3*R*,3*aR*,5*aS*,6*R*,6*aR*,8*S*,9*aR*,11*aS*,11*bS*)-3*a*,6-dimethyl-3-(6-methylheptan-2-yl)tetradecahydro-6H-5*a*,9*a*-epoxyindeno[5,4-f]azulen-8-ol (SI-3)**

Identification code	**(3*R*,3*aR*,5*aS*,6*R*,6*aR*,8*S*,9*aR*,11*aS*,11*bS*)-3*a*,6-dimethyl-3-(6-methylheptan-2-yl)tetradecahydro-6H-5*a*,9*a*-epoxyindeno[5,4-f]azulen-8-ol (SI-3)**
Empirical formula	C27 H46 O2
Formula weight	402.64

Temperature	85(2) K
Wavelength	1.54184 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 6.1663(4) A alpha = 90 deg.
	b = 17.4271(17) A beta = 90 deg.
	c = 45.499(4) A gamma = 90 deg.
Volume	4889.3(7) A^3
Z, Calculated density	8, 1.094 Mg/m^3
Absorption coefficient	0.502 mm^-1
F(000)	1792
Crystal size	0.060 x 0.010 x 0.010 mm
Theta range for data collection	2.715 to 69.680 deg.
Limiting indices	-7<=h<=7, -20<=k<=20, -55<=l<=54
Reflections collected / unique	40651 / 9030 [R(int) = 0.1360]
Completeness to theta = 67.684	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.44226
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9030 / 0 / 536
Goodness-of-fit on F^2	1.063
Final R indices [I>2sigma(I)]	R1 = 0.0935, wR2 = 0.2218
R indices (all data)	R1 = 0.1451, wR2 = 0.2753
Absolute structure parameter	0.3(3)
Extinction coefficient	0.0041(5)
Largest diff. peak and hole	0.421 and -0.357 e.A^-3

Structure determination of (3*R*,3*aR*,5*aS*,6*aR*,8*S*,9*aR*,11*aR*,11*bS*)-9a-hydroxy-3a-methyl-6-methylene-3-(6-methylheptan-2-yl)hexadecahydro-1H-indeno[5,4-f]azulen-8-yl acetate (16)



(CCDC 1914933)

Colorless plates of **16** were grown from an ethyl acetate solution of the compound at 23 deg. C. A crystal of dimensions 0.24 x 0.03 x 0.03 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω. The exposure times were 1 sec. for the low angle images, 5 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 80727 reflections to a maximum 2□ value of 138.62□ of which 9793 were independent and 9616 were greater than 2□(I). The final cell constants (Table 1) were based on the xyz centroids of 45003 reflections above 10□(I). Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2018/3) software package, using the space group P2(1)2(1)2(1) with Z = 8 for the formula $C_{29}H_{48}O_3$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a combination of idealized and refined positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0305 and wR2 = 0.0767 [based on I > 2sigma(I)], R1 = 0.0312 and wR2 = 0.0773 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

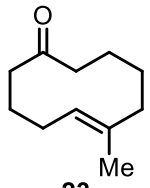
G.M. Sheldrick (2015) "Crystal structure refinement with SHELXL", Acta Cryst., C71, 3-8 (Open Access).
CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

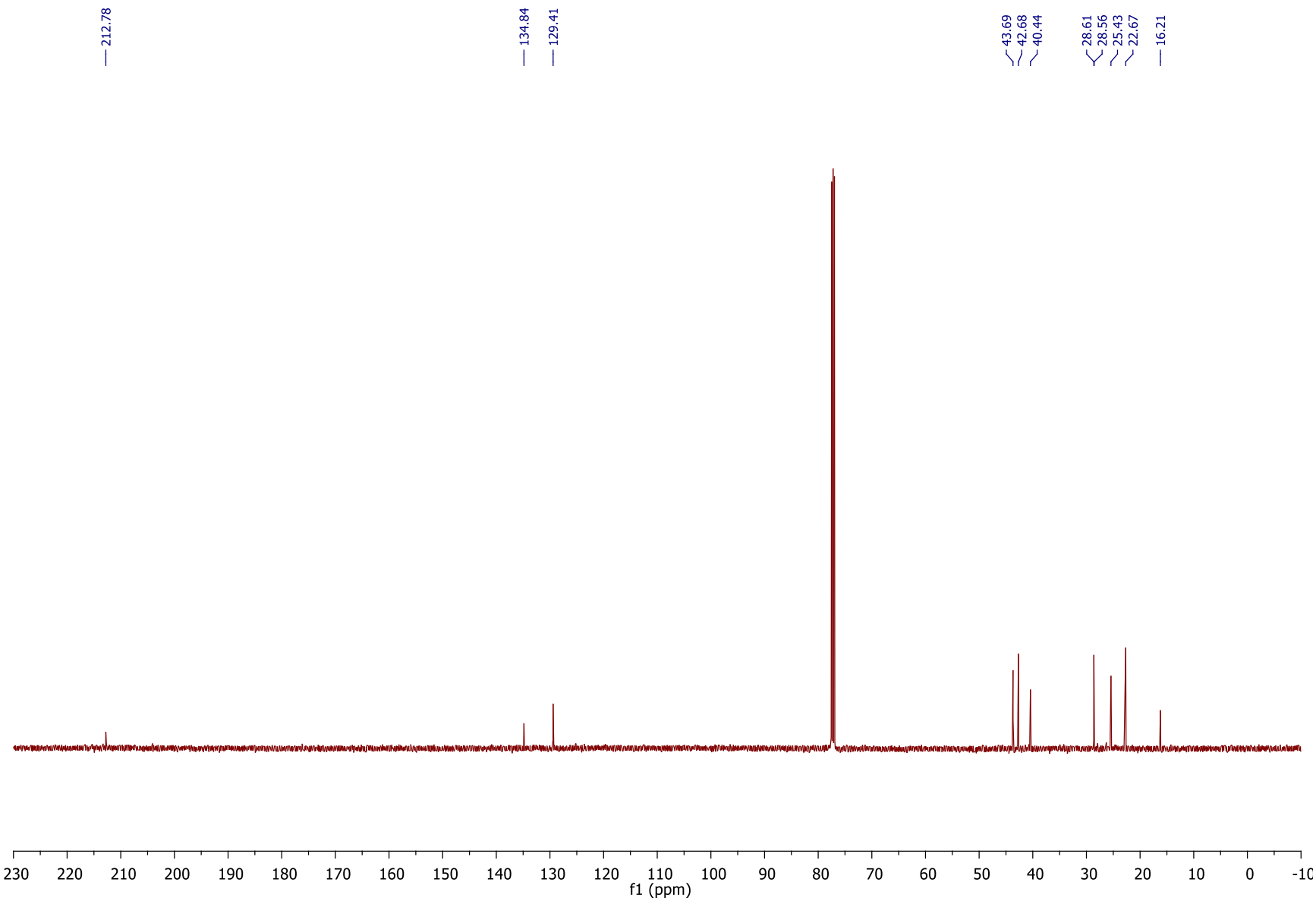
Crystal data and structure refinement for **(3*R*,3*aR*,5*aS*,6*aR*,8*S*,9*aR*,11*aR*,11*bS*)-9a-hydroxy-3a-methyl-6-methylene-3-(6-methylheptan-2-yl)hexadecahydro-1H-indeno[5,4-f]azulen-8-yl acetate (16)**

Identification code	**(3*R*,3*aR*,5*aS*,6*aR*,8*S*,9*aR*,11*aR*,11*bS*)-9a-hydroxy-3a-methyl-6-methylene-3-(6-methylheptan-2-yl)hexadecahydro-1H-indeno[5,4-f]azulen-8-yl acetate (16)**
Empirical formula	C29 H48 O3
Formula weight	444.67
Temperature	85(2) K
Wavelength	1.54184 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 10.32230(10) A alpha = 90 deg. b = 11.39260(10) A beta = 90 deg. c = 44.7577(6) A gamma = 90 deg.
Volume	5263.41(10) A^3
Z, Calculated density	8, 1.122 Mg/m^3
Absorption coefficient	0.540 mm^-1
F(000)	1968
Crystal size	0.240 x 0.030 x 0.030 mm
Theta range for data collection	3.951 to 69.307 deg.
Limiting indices	-12<=h<=12, -13<=k<=13, -51<=l<=54
Reflections collected / unique	80727 / 9793 [R(int) = 0.0502]
Completeness to theta = 67.684	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.84450
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9793 / 0 / 595
Goodness-of-fit on F^2	1.011
Final R indices [I>2sigma(I)]	R1 = 0.0305, wR2 = 0.0767
R indices (all data)	R1 = 0.0312, wR2 = 0.0773
Absolute structure parameter	-0.04(5)
Extinction coefficient	n/a
Largest diff. peak and hole	0.197 and -0.170 e.A^-3

6. ^{1}H NMR and ^{13}C NMR Spectra



23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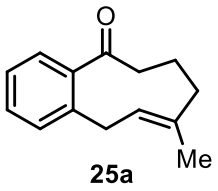
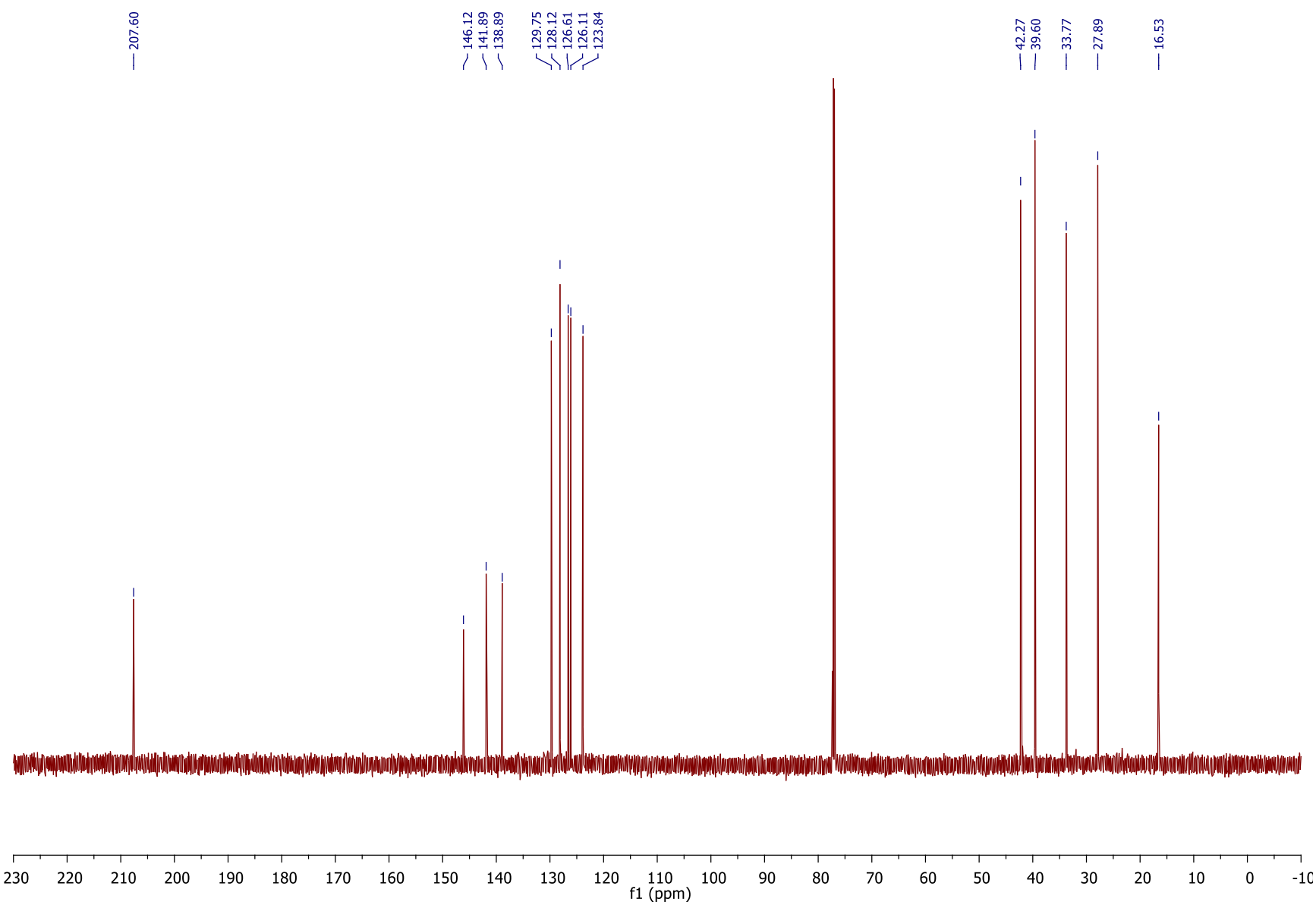
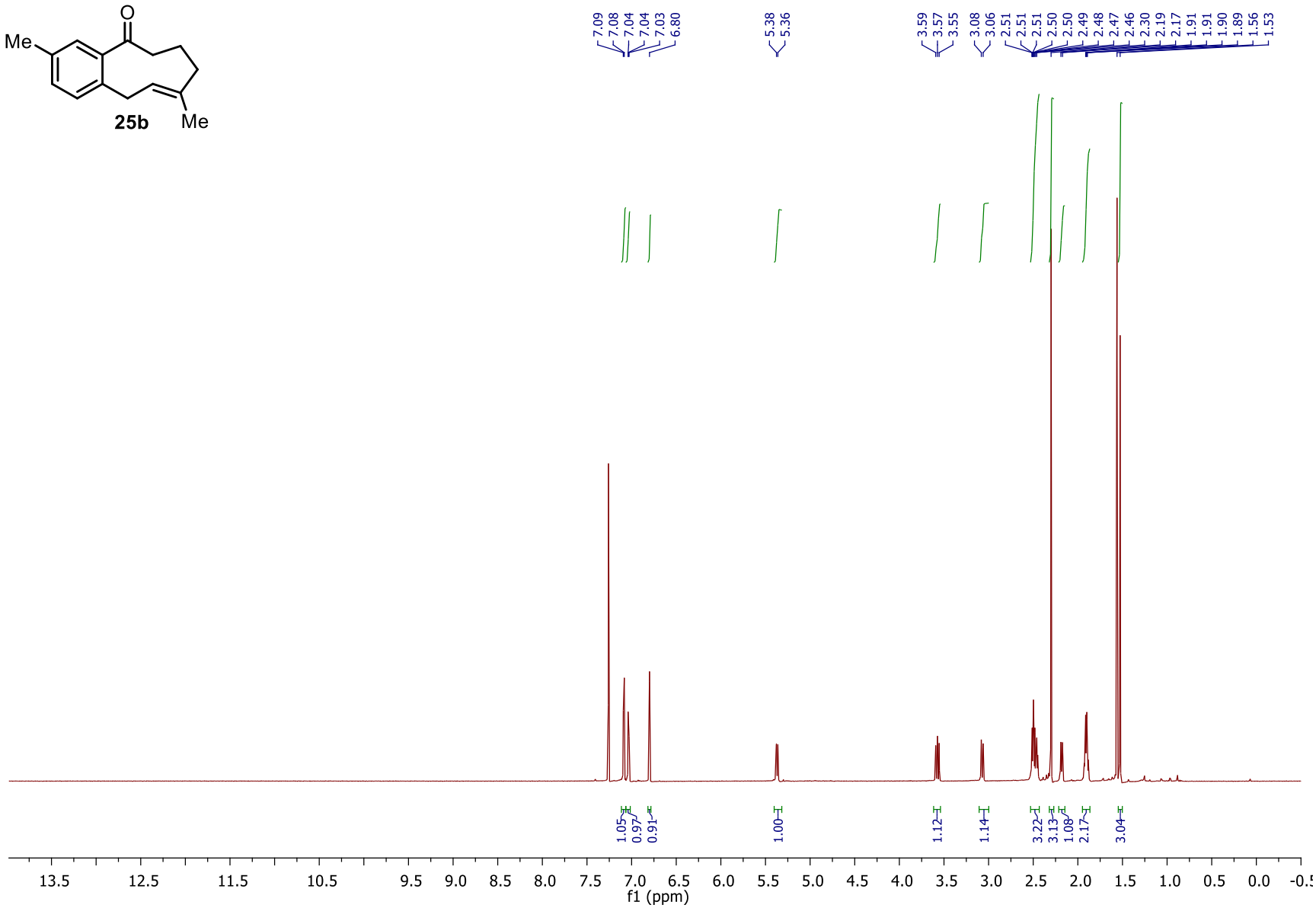
129.41
43.69
42.68
40.44
28.61
28.56
25.43
22.67
16.21
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

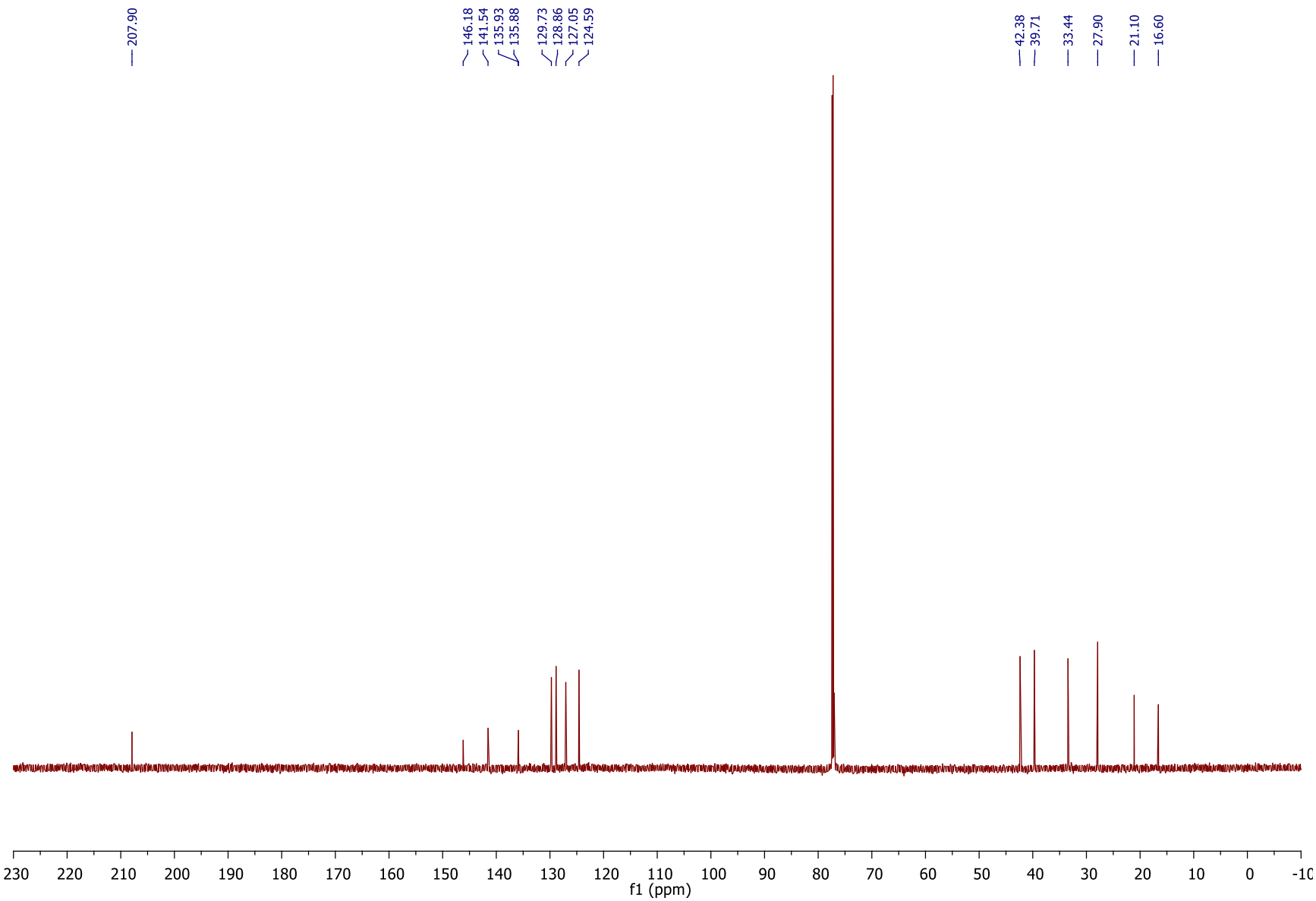

O
Me

25a

7.23
7.22
7.22
7.21
7.18
7.01
6.99
5.39
5.37
3.65
3.63
3.63
3.61
3.13
3.10
2.51
2.50
2.49
2.48
1.92
1.92
1.54
2.79
0.87
1.00
1.09
1.06
3.06
1.08
2.16
2.87
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


207.60
146.12
141.89
138.89
129.75
128.12
126.61
126.11
123.84
42.27
39.60
33.77
27.89
16.53
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
O
Me
25b
7.09
7.08
7.04
7.04
7.03
6.80
5.38
5.36
3.59
3.57
3.55
3.08
3.06
2.51
2.51
2.51
2.50
2.50
2.49
2.48
2.47
2.46
2.30
2.19
2.17
1.91
1.91
1.90
1.89
1.56
1.53
1.05
0.97
0.91
1.00
1.12
1.14
3.22
3.13
1.08
2.17
3.04
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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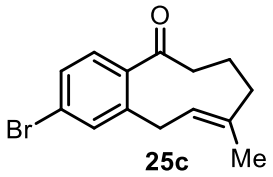
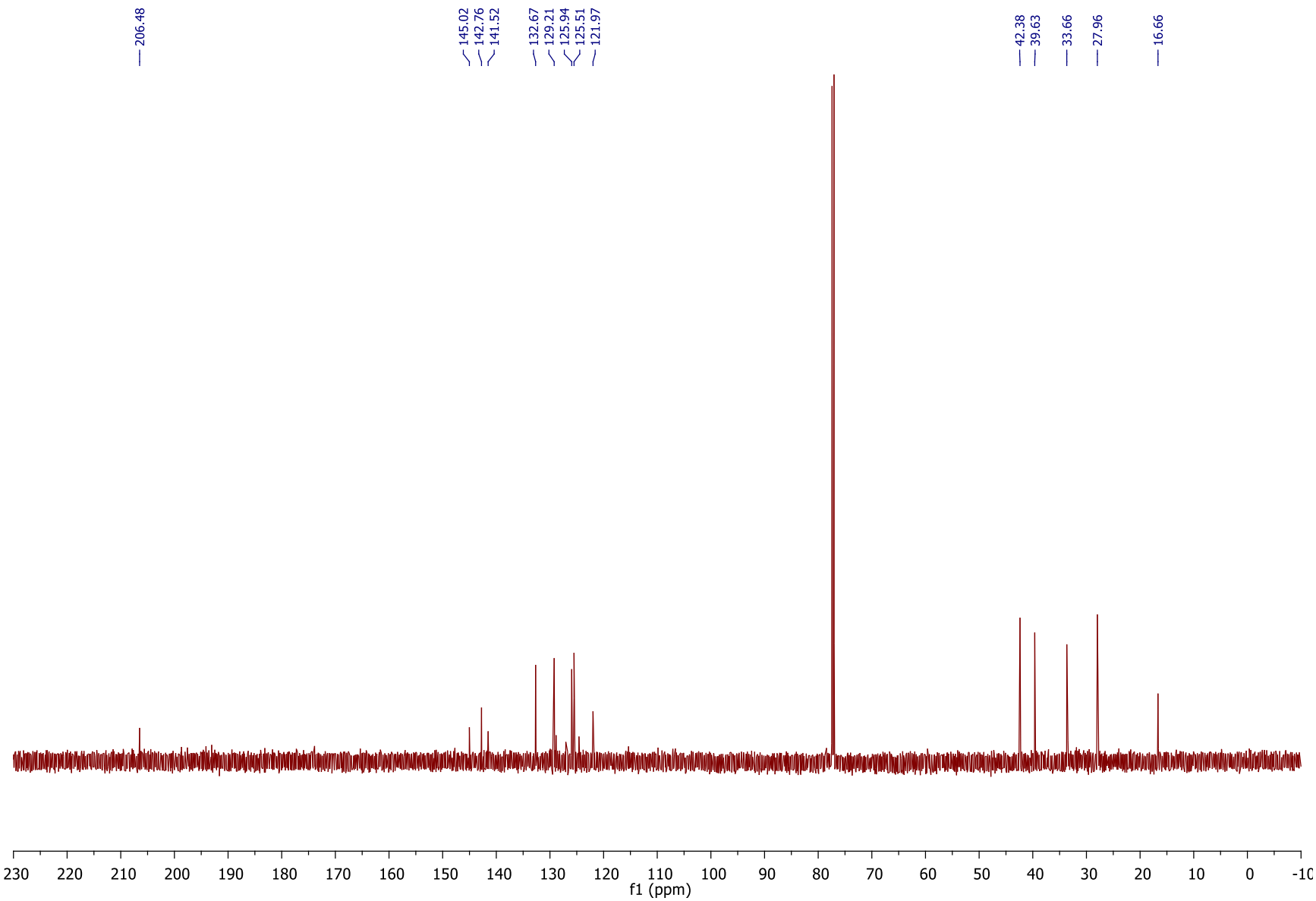
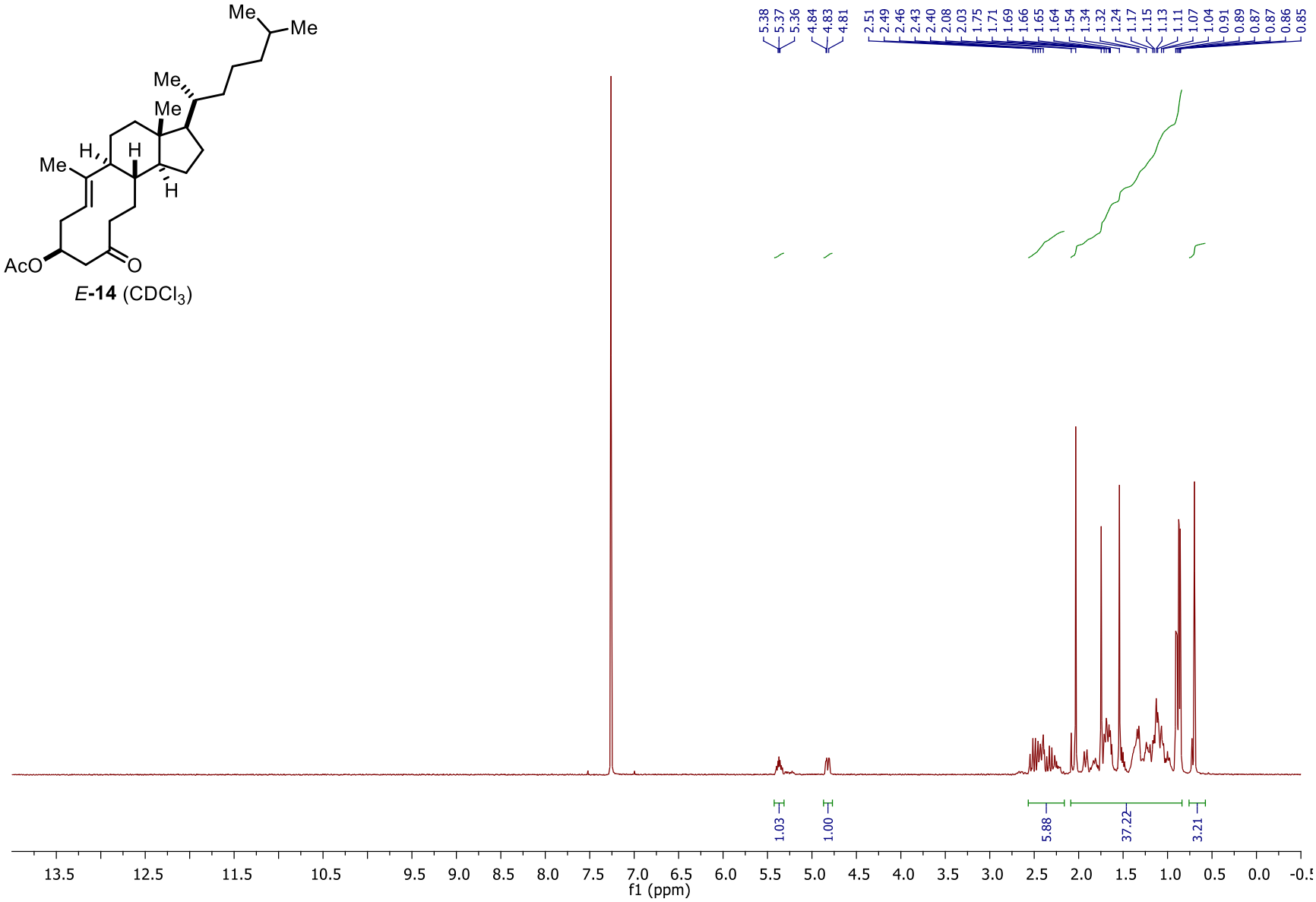
146.18
141.54
135.93
135.88
129.73
128.86
127.05
124.59
42.38
39.71
33.44
27.90
21.10
16.60
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
Br
Me

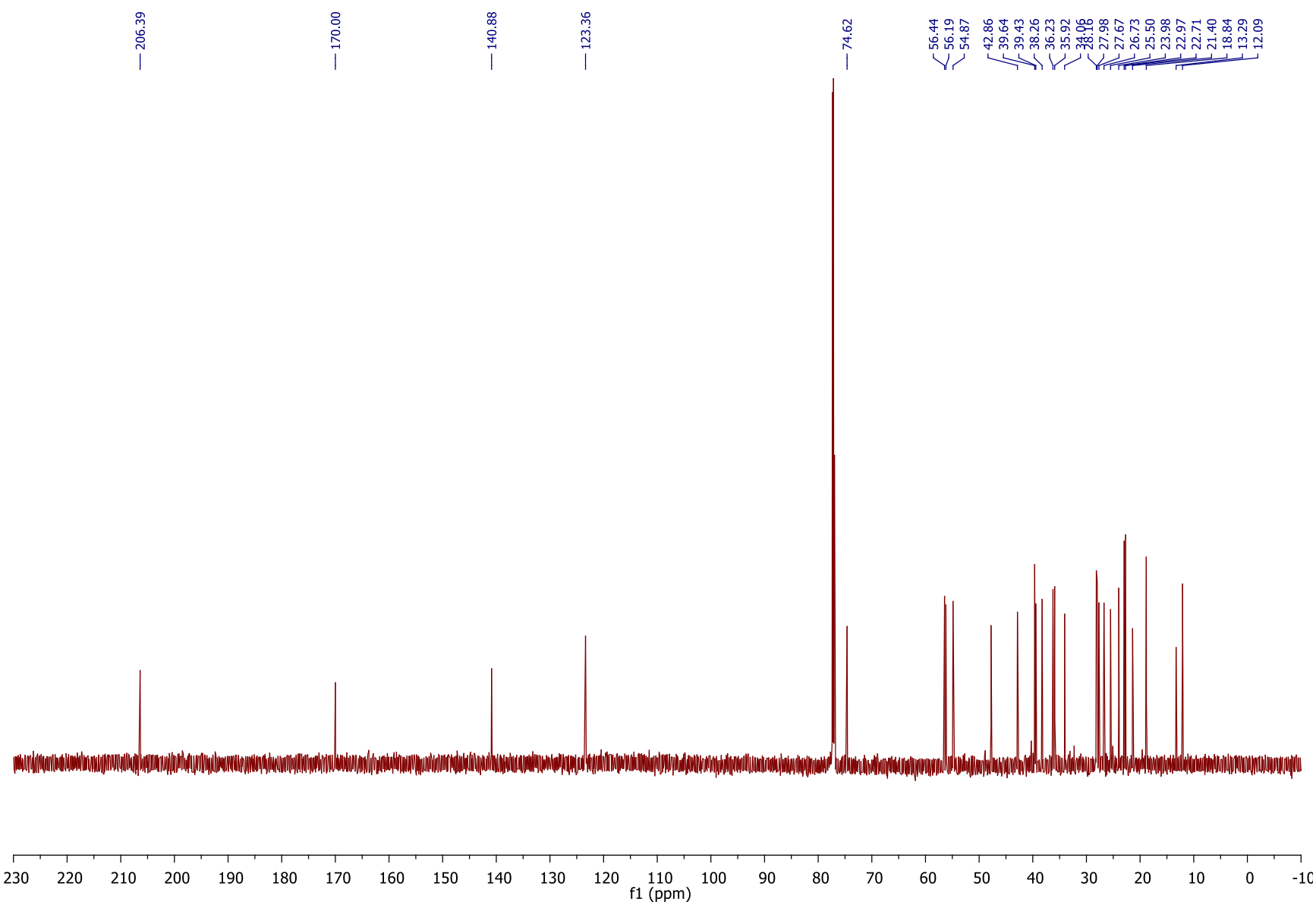
25c

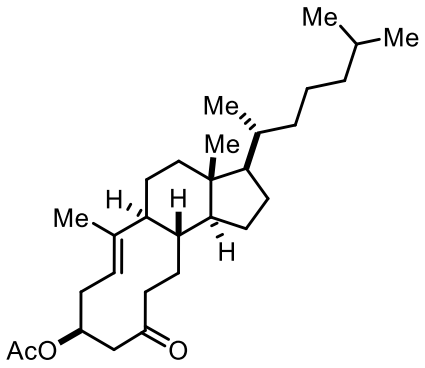
7.38
7.33
7.31
6.88
6.86
5.35
5.32
3.63
3.60
3.57
3.09
3.06
2.50
2.47
2.45
2.17
1.93
1.92
1.91
1.52
0.97
0.85
0.89
1.00
1.19
1.28
3.31
1.27
2.21
3.07
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


206.48
145.02
142.76
141.52
132.67
129.21
125.94
125.51
121.97
42.38
39.63
33.66
27.96
16.66
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
Me
Me
Me
H
H
H
Me
AcO
O
5.38
5.37
5.36
4.84
4.83
4.81
2.51
2.49
2.46
2.43
2.40
2.08
2.03
1.75
1.71
1.69
1.66
1.65
1.64
1.54
1.34
1.32
1.24
1.17
1.15
1.13
1.11
1.07
1.04
0.91
0.89
0.87
0.87
0.86
0.85
1.03
1.00
5.88
37.22
3.21
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

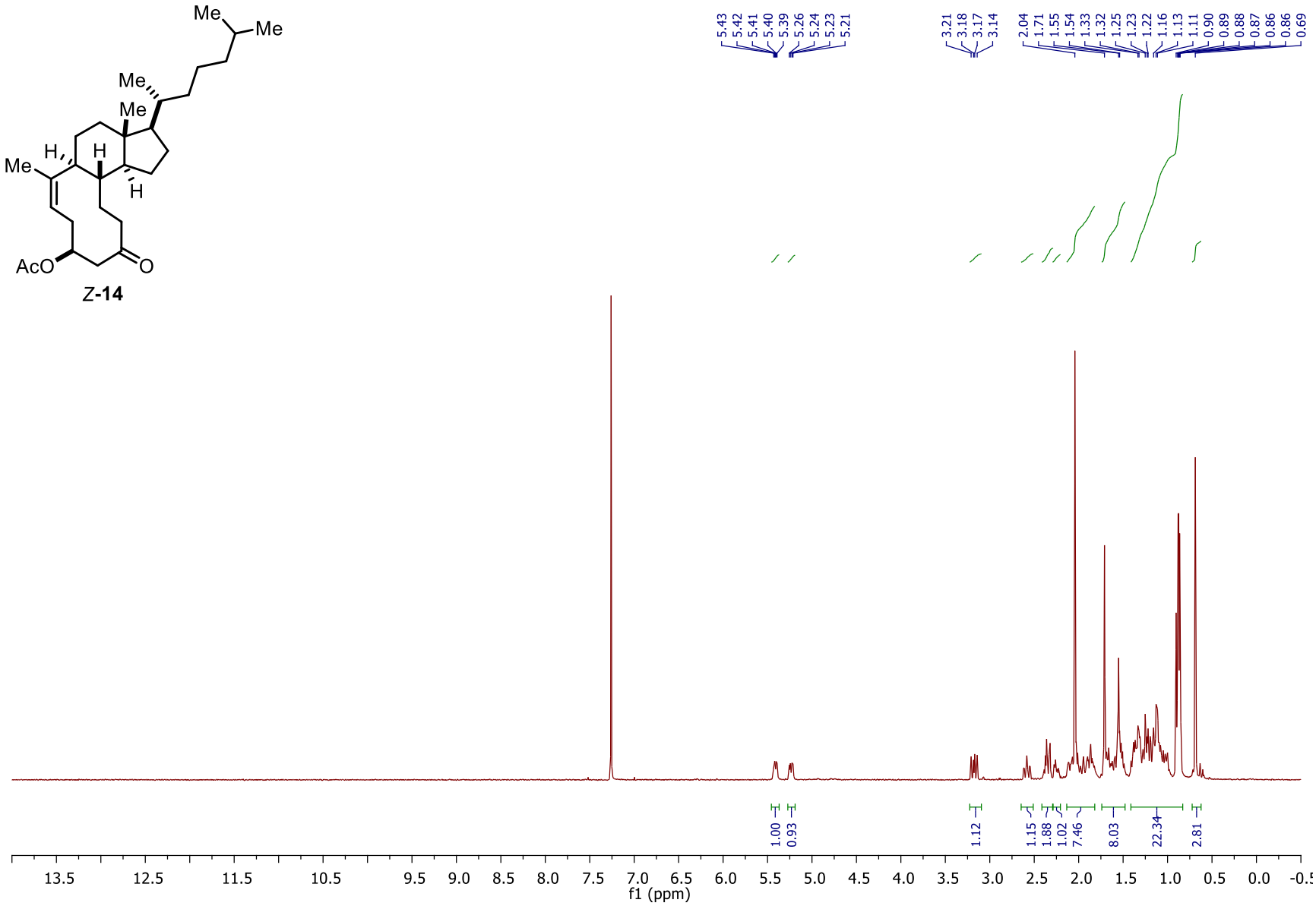
E-**14** ($CDCl_3$)

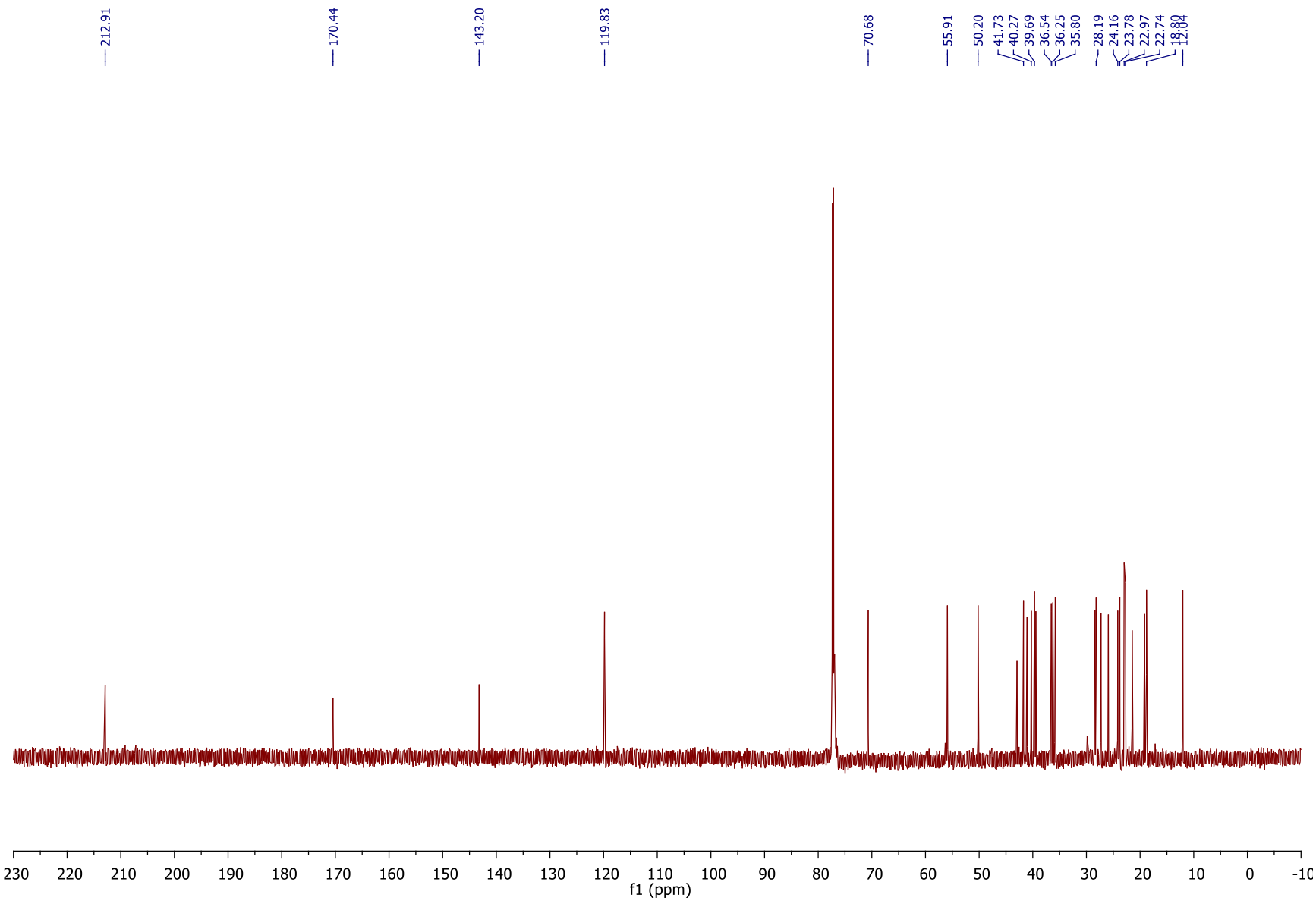

206.39
170.00
140.88
123.36
74.62
56.44
56.19
54.87
42.86
39.64
39.43
38.26
36.23
35.92
34.06
28.16
27.98
27.67
26.73
25.50
23.98
22.97
22.71
21.40
18.84
13.29
12.09
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

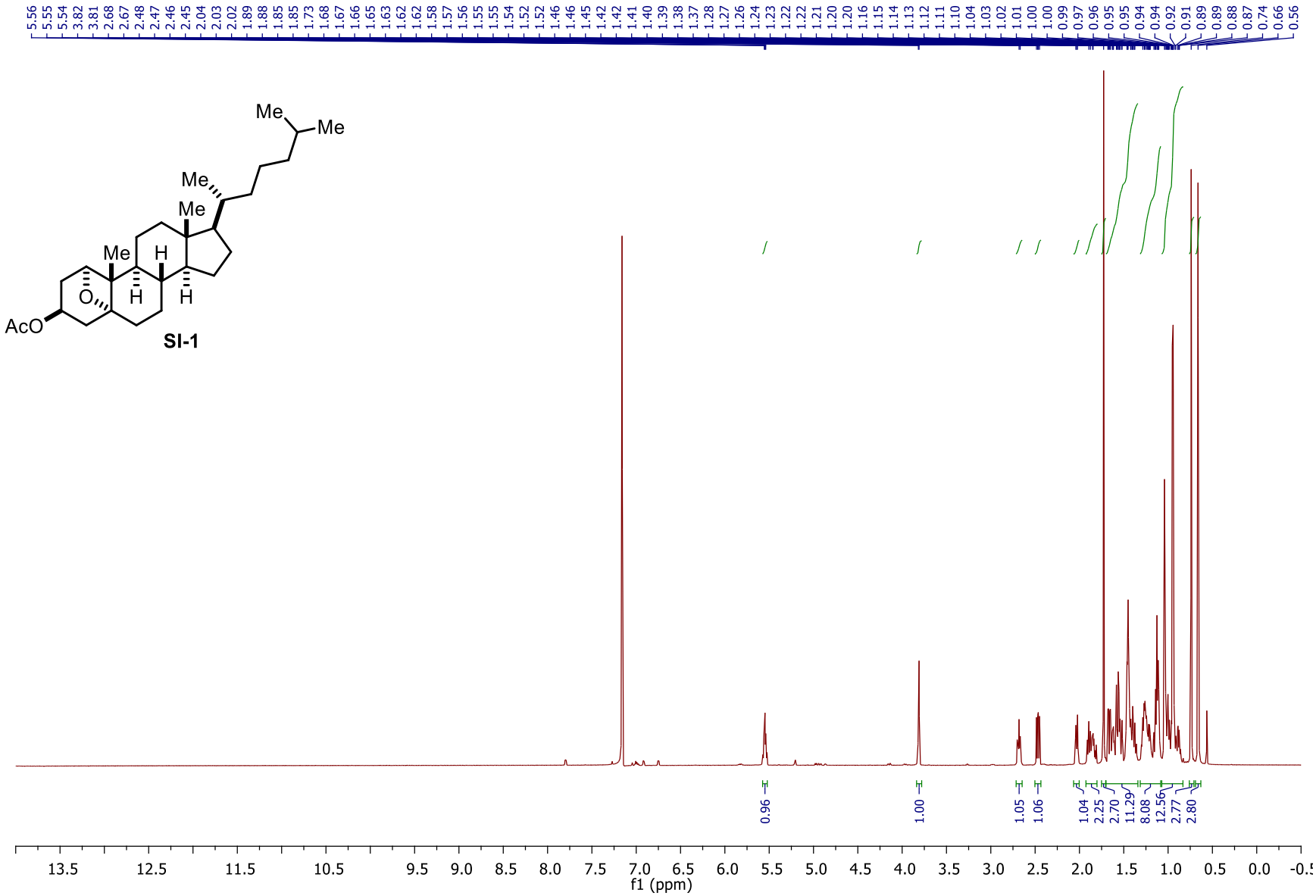

Me
Me
Me
Me
H
H
Me
H
AcO
O

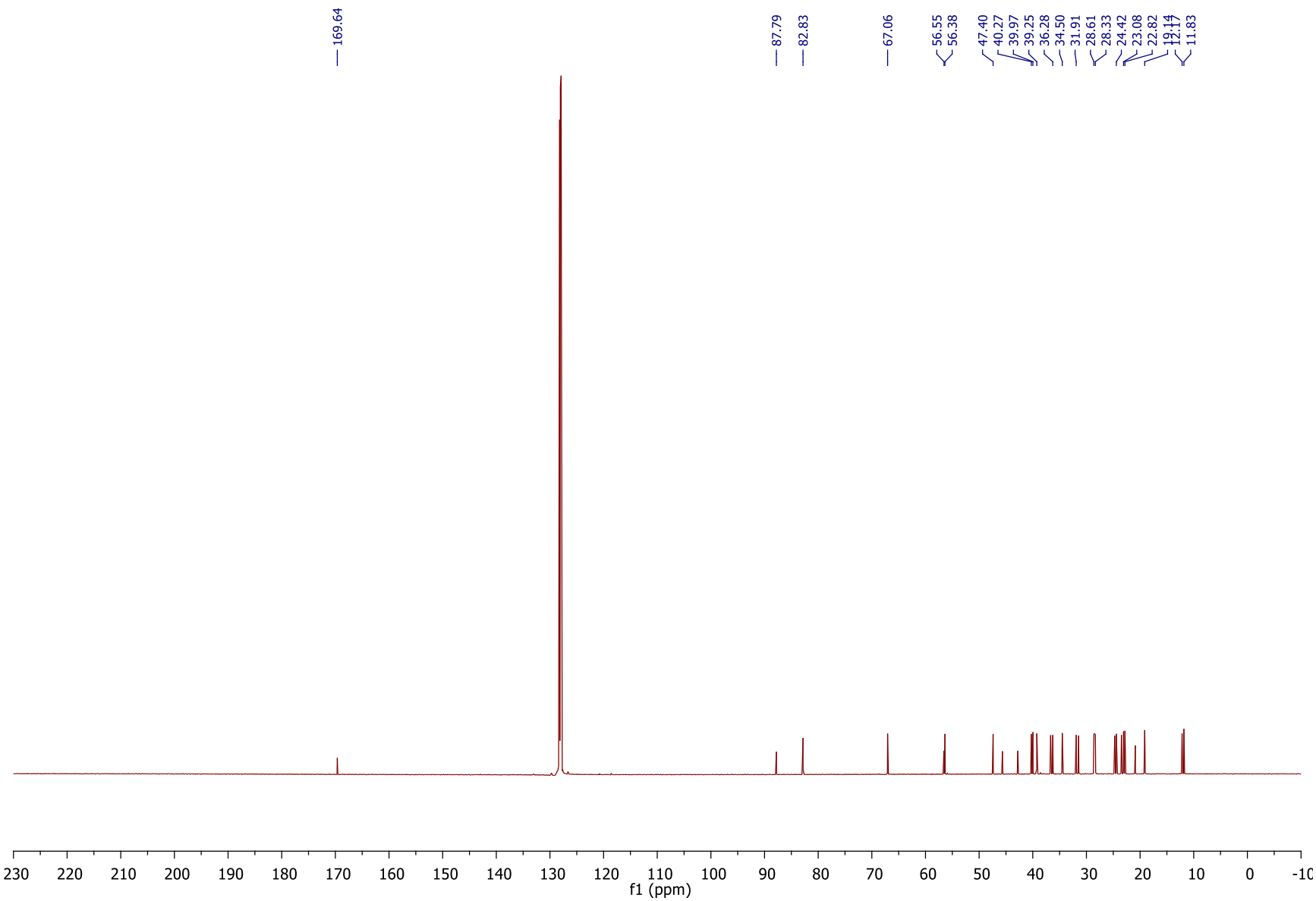
E-**14** (d_6-DMSO)

5.18
5.17
4.65
4.64
2.55
2.50
2.37
2.31
2.24
1.99
1.72
1.65
1.64
1.51
1.50
1.49
1.31
1.30
1.15
1.13
1.11
1.10
1.08
1.07
0.98
0.88
0.87
0.85
0.84
0.84
0.84
0.68
1.12
1.00
1.17
5.16
2.93
1.19
3.84
6.25
23.40
2.80
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Me
Me
Me
Me
H
H
H
Me
AcO
O
Z-14
5.43
5.42
5.41
5.40
5.39
5.26
5.24
5.23
5.21
3.21
3.18
3.17
3.14
2.04
1.71
1.55
1.54
1.33
1.32
1.25
1.23
1.22
1.16
1.13
1.11
0.90
0.89
0.88
0.87
0.86
0.86
0.69
1.00
0.93
1.12
1.15
1.88
1.02
7.46
8.03
22.34
2.81
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


212.91
170.44
143.20
119.83
70.68
55.91
50.20
41.73
40.27
39.69
36.54
36.25
35.80
28.19
24.16
23.78
22.97
22.74
18.80
12.04
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


5.56 5.55 5.54 3.82 3.81 2.68 2.67 2.48 2.47 2.46 2.45 2.04 2.03 2.02 1.89 1.88 1.85 1.85 1.73 1.68 1.67 1.66 1.65 1.63 1.62 1.62 1.58 1.57 1.56 1.55 1.55 1.54 1.52 1.52 1.46 1.46 1.45 1.42 1.42 1.41 1.40 1.39 1.38 1.37 1.28 1.27 1.26 1.24 1.23 1.22 1.22 1.21 1.20 1.20 1.16 1.15 1.14 1.13 1.12 1.11 1.10 1.04 1.03 1.02 1.01 1.00 1.00 0.99 0.97 0.96 0.95 0.95 0.94 0.94 0.92 0.91 0.89 0.89 0.88 0.87 0.74 0.66 0.56
Me
Me
Me
Me
Me
H
O
H
H
AcO
SI-1
0.96
1.00
1.05
1.06
1.04
2.25
2.70
11.29
8.08
12.56
2.77
2.80
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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67.06
56.55
56.38
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40.27
39.97
39.25
36.28
34.50
31.91
28.61
28.33
24.42
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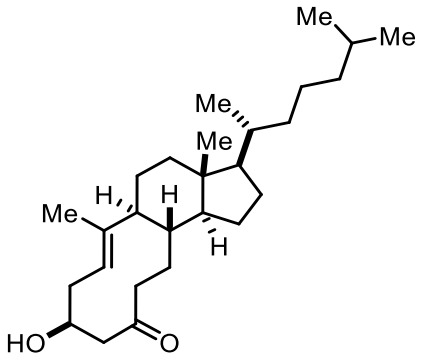
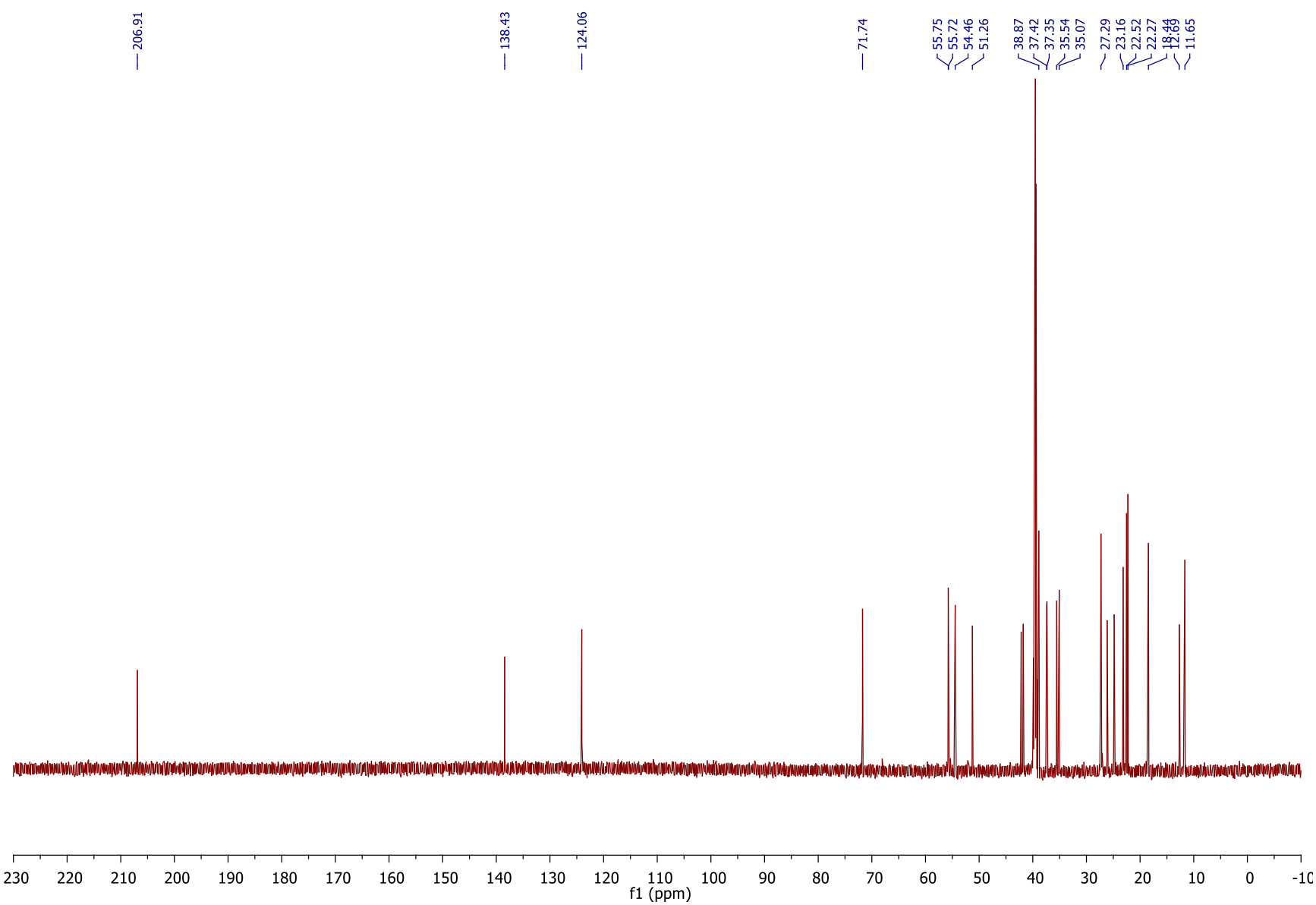
f1 (ppm)


Me
Me
Me
Me
H
H
Me
H
HO
O

15

4.90
4.89
4.67
4.67
4.66
4.65
4.04
2.38
2.36
2.15
2.15
2.14
1.69
1.63
1.52
1.50
1.35
1.31
1.30
1.14
1.12
1.11
1.09
1.08
0.97
0.88
0.87
0.85
0.85
0.84
0.84
0.67
0.96
1.01
1.18
2.41
4.23
1.17
1.32
2.54
2.20
4.22
3.99
1.35
7.29
2.24
3.02
5.90
3.00
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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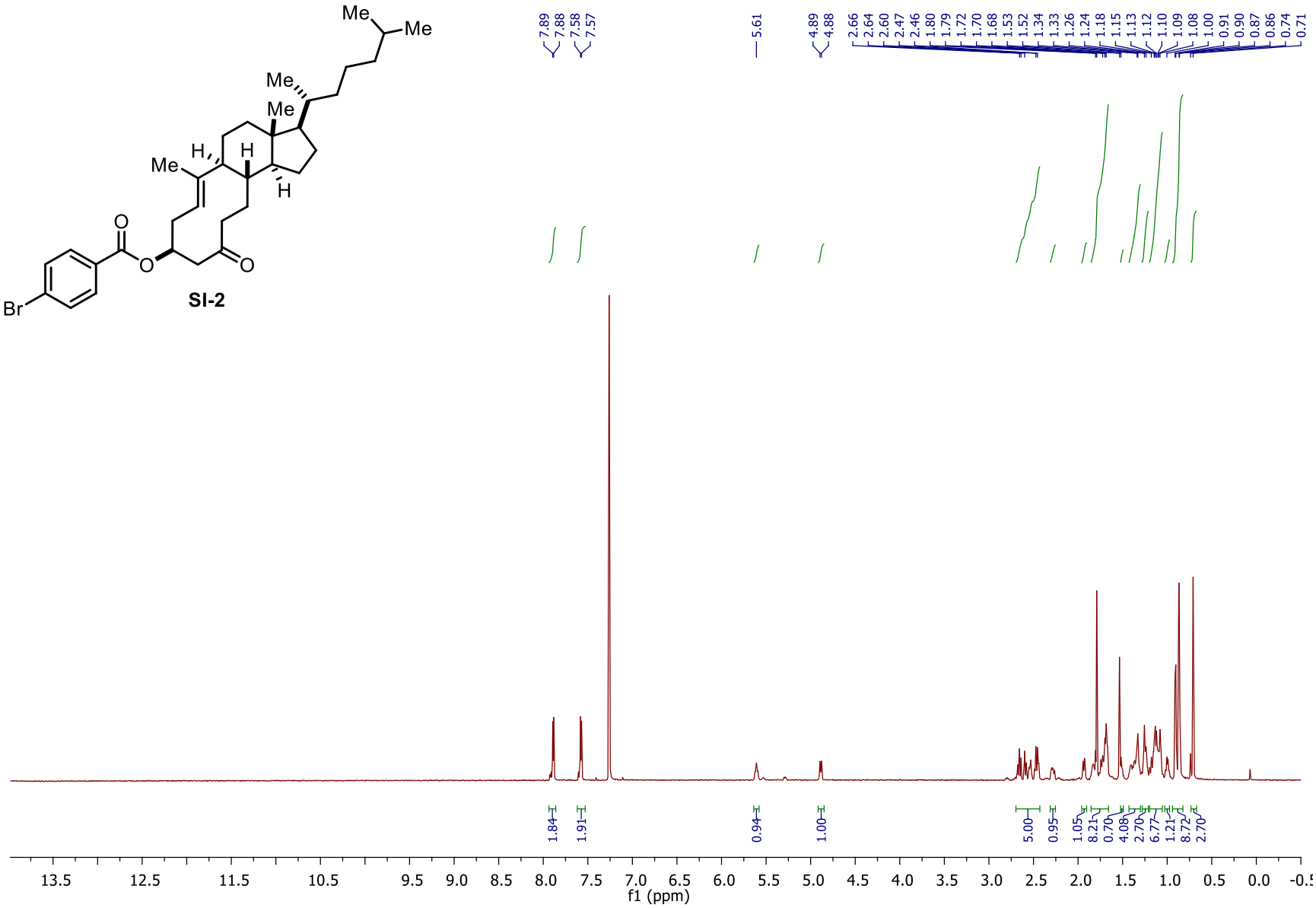
55.75
55.72
54.46
51.26
38.87
37.42
37.35
35.54
35.07
27.29
23.16
22.52
22.27
18.44
18.09
11.65
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
Me
Me
Me
H
H
H
Me
O
O
O
Br
SI-2
7.89
7.88
7.58
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5.61
4.89
4.88
2.66
2.64
2.60
2.47
2.46
1.80
1.79
1.72
1.70
1.68
1.53
1.52
1.34
1.33
1.26
1.24
1.18
1.15
1.13
1.12
1.10
1.09
1.08
1.00
0.91
0.90
0.87
0.86
0.74
0.71
1.84
1.91
0.94
1.00
5.00
0.95
1.05
8.21
0.70
4.08
2.70
6.77
1.21
8.72
2.70
13.5
12.5
11.5
10.5
9.5
9.0
8.5
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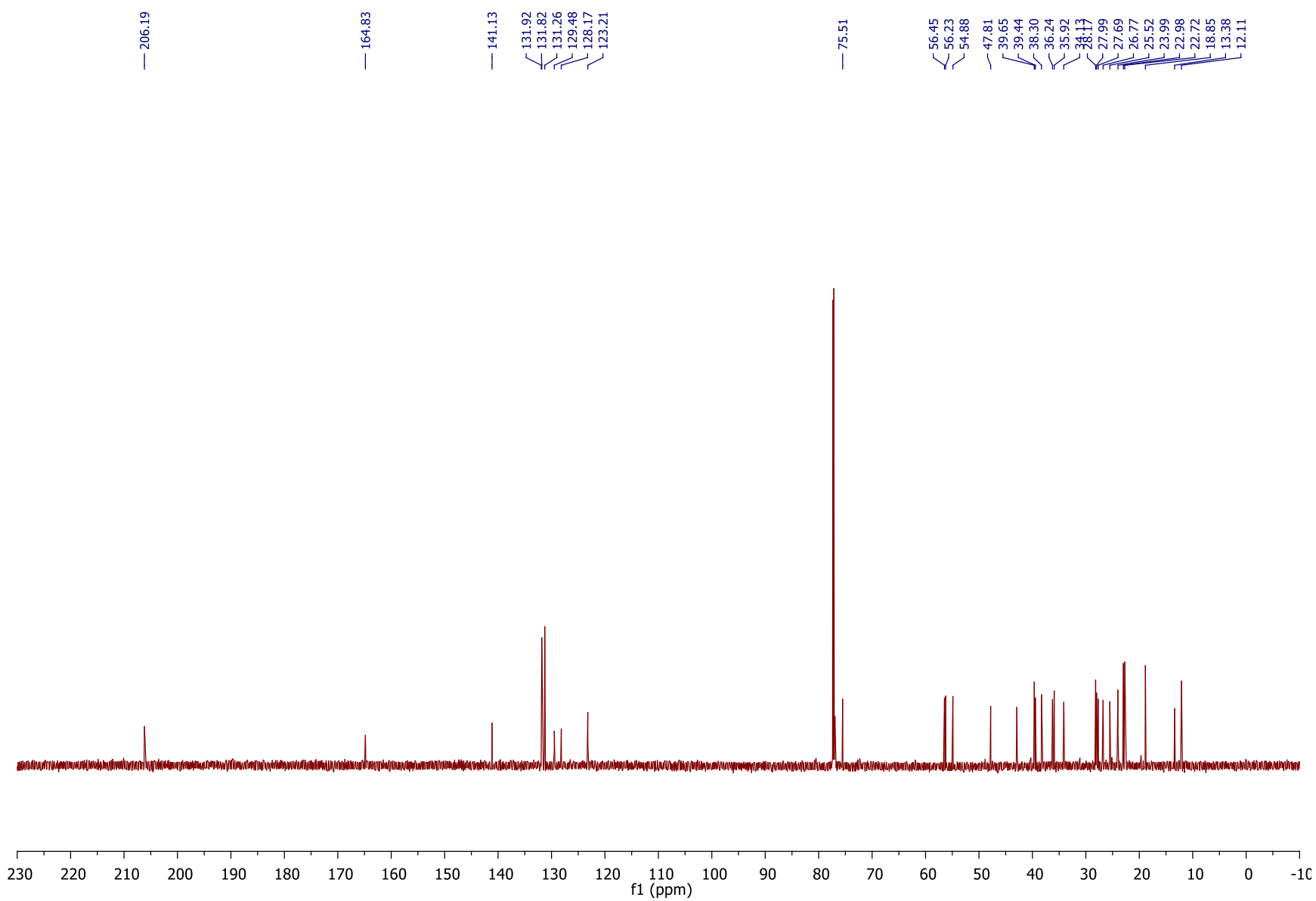
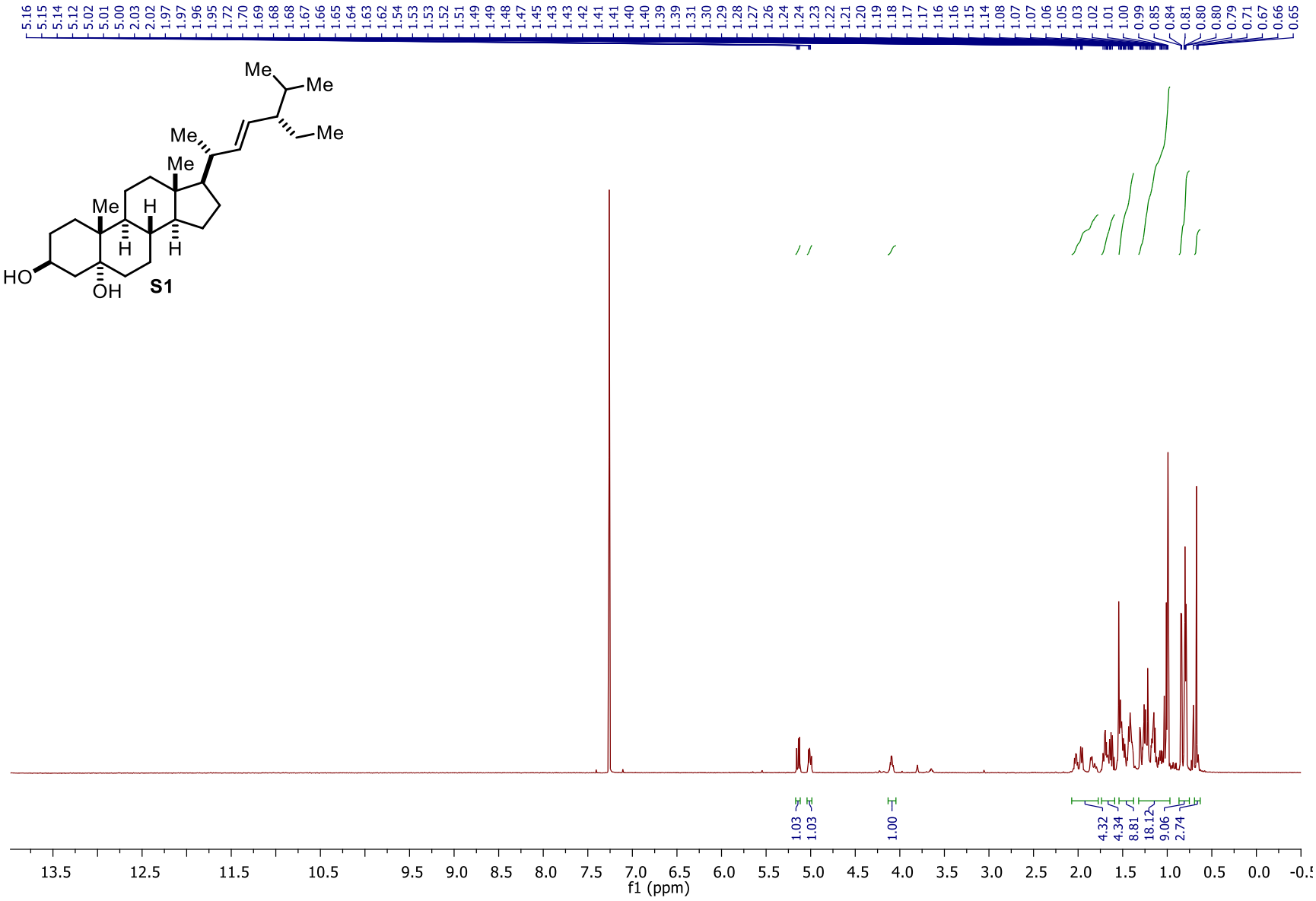
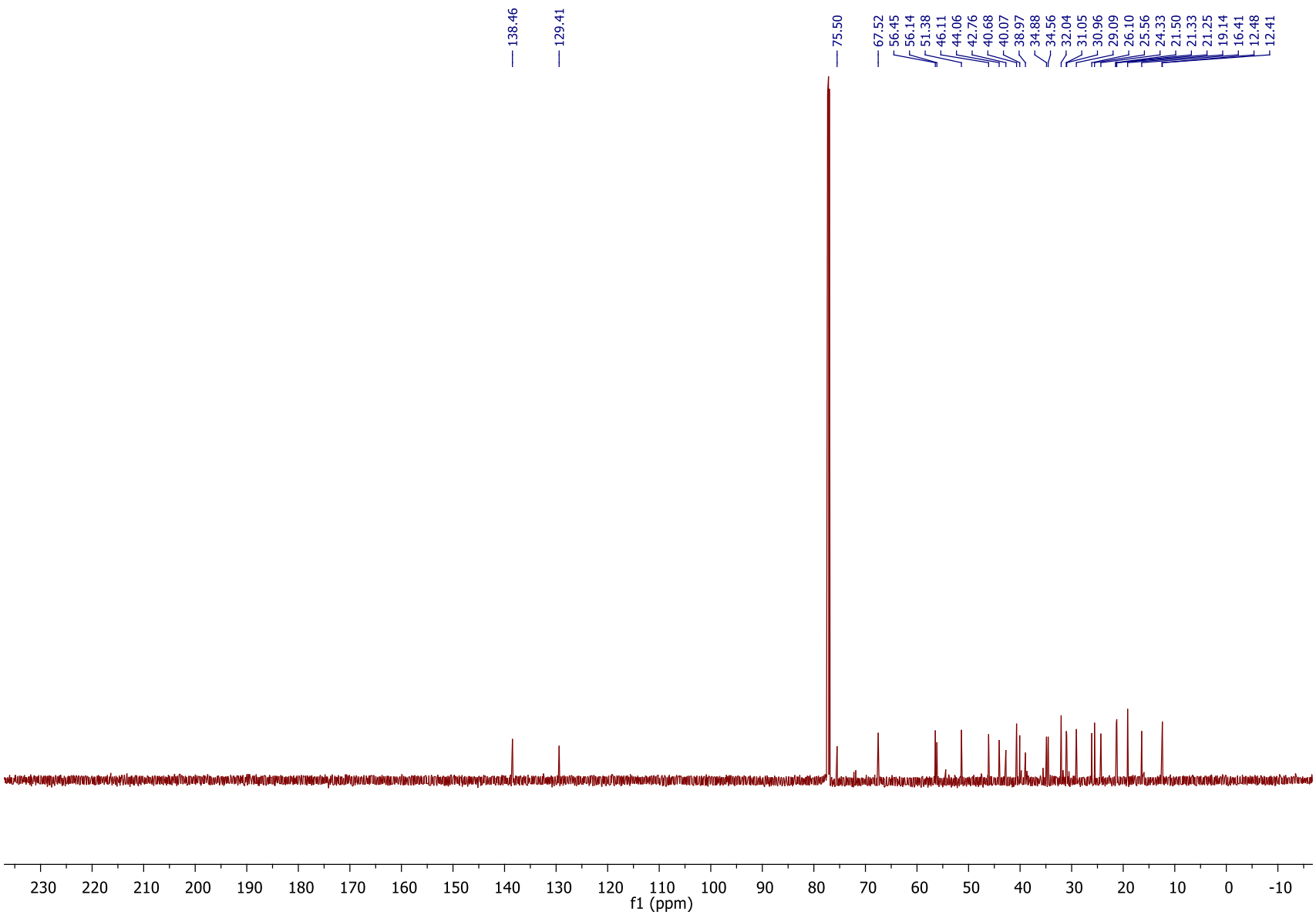
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


206.19
164.83
141.13
131.92
131.82
131.26
129.48
128.17
123.21
75.51
56.45
56.23
54.88
47.81
39.65
39.44
38.30
36.24
35.92
34.13
28.17
27.99
27.69
26.77
25.52
23.99
22.98
22.72
18.85
13.38
12.11
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


5.16 5.15 5.14 5.12 5.02 5.01 5.00 2.03 2.02 1.97 1.97 1.96 1.95 1.72 1.70 1.69 1.68 1.68 1.67 1.66 1.65 1.64 1.63 1.62 1.54 1.53 1.52 1.51 1.49 1.49 1.48 1.47 1.45 1.43 1.43 1.42 1.41 1.41 1.40 1.40 1.39 1.39 1.31 1.30 1.29 1.28 1.27 1.26 1.24 1.24 1.23 1.22 1.21 1.20 1.19 1.18 1.17 1.17 1.16 1.16 1.15 1.14 1.08 1.07 1.07 1.06 1.05 1.03 1.02 1.01 1.00 0.99 0.85 0.84 0.81 0.80 0.80 0.79 0.71 0.67 0.66 0.65
Me
Me
Me
Me
Me
H
H
H
HO
OH
S1
1.03
1.03
1.00
4.32
4.34
8.81
18.12
9.06
2.74
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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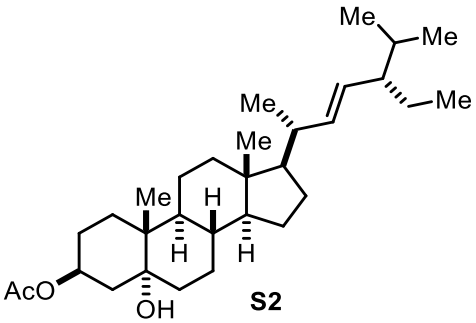
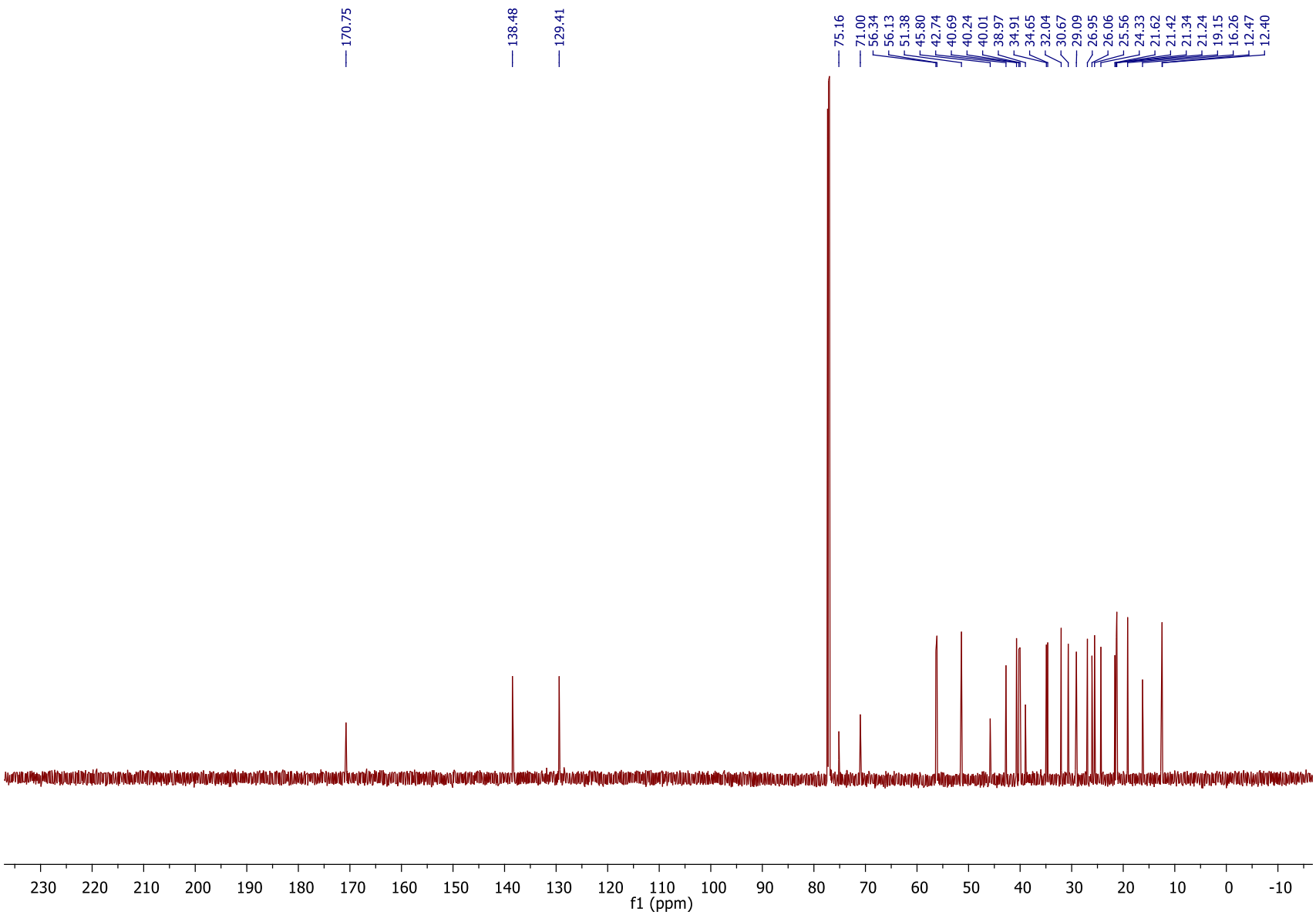
129.41
75.50
67.52
56.45
56.14
51.38
46.11
44.06
42.76
40.68
40.07
38.97
34.88
34.56
32.04
31.05
30.96
29.09
26.10
25.56
24.33
21.50
21.33
21.25
19.14
16.41
12.48
12.41
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
Me
Me
Me
Me
H
H
H
AcO
OH

S2

5.18 5.17 5.16 5.15 5.14 5.13 5.02 5.01 5.00 4.99
2.01 1.69 1.68 1.54 1.53 1.53 1.52 1.43 1.41 1.41 1.40 1.27 1.25 1.23 1.17 1.17 1.15 1.14 1.01 1.00 0.85 0.84 0.81 0.80 0.80 0.79 0.67
2.00
1.06
3.91
1.02
1.13
3.96
21.23
6.50
8.52
2.86
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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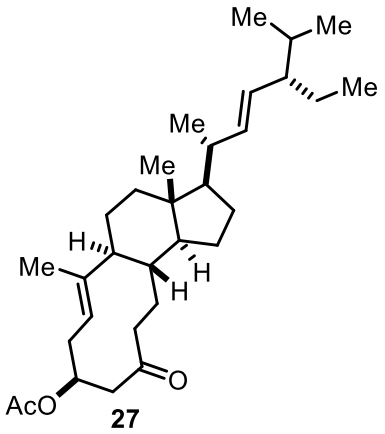
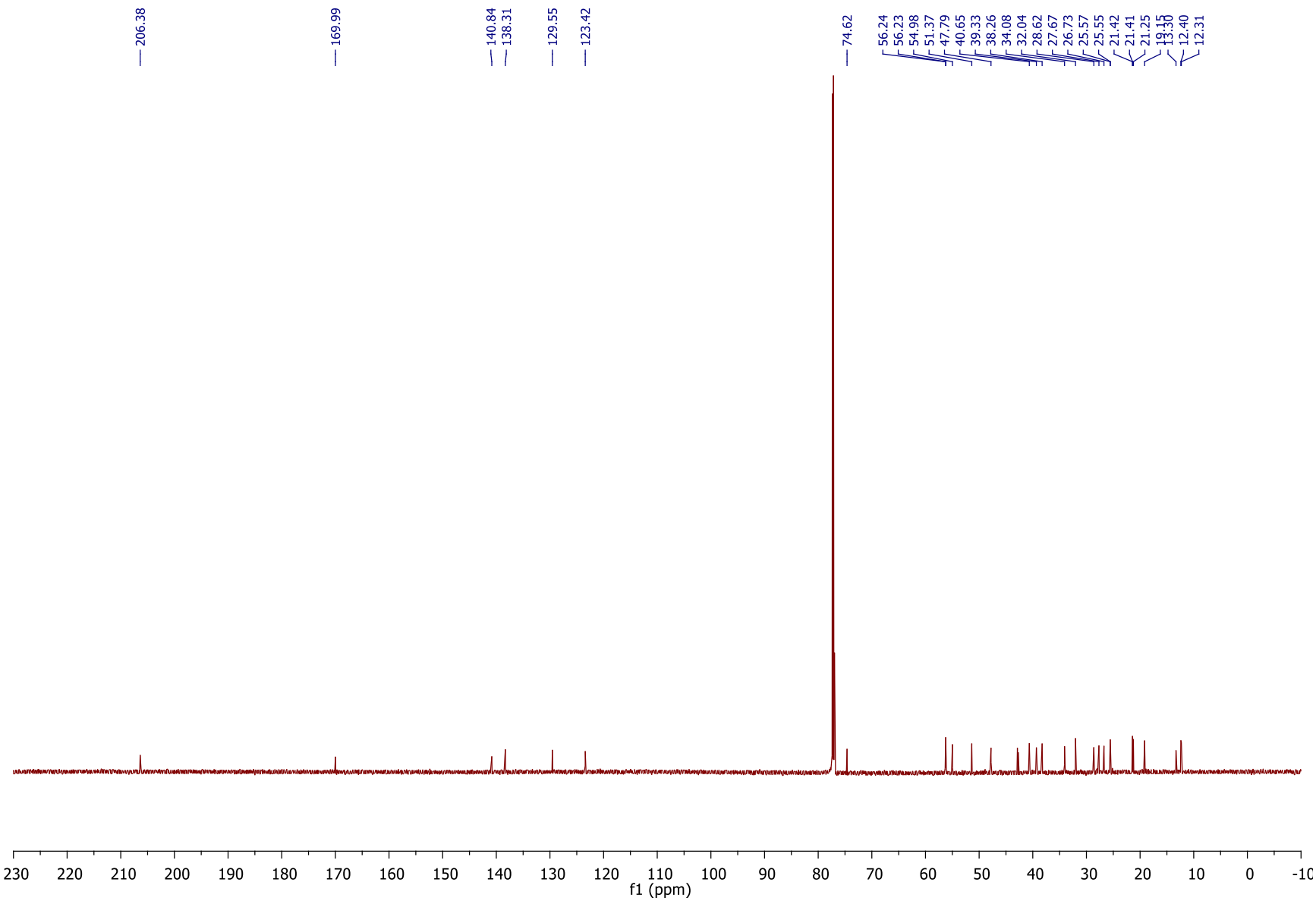
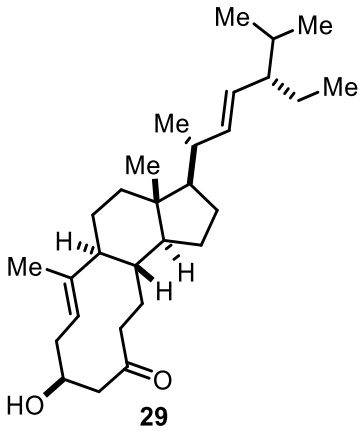
138.48
129.41
75.16
71.00
56.34
56.13
51.38
45.80
42.74
40.69
40.24
40.01
38.97
34.91
34.65
32.04
30.67
29.09
26.95
26.06
25.56
24.33
21.62
21.42
21.34
21.24
19.15
16.26
12.47
12.40
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
Me
Me
Me
Me
H
H
H
Me
O
AcO

27

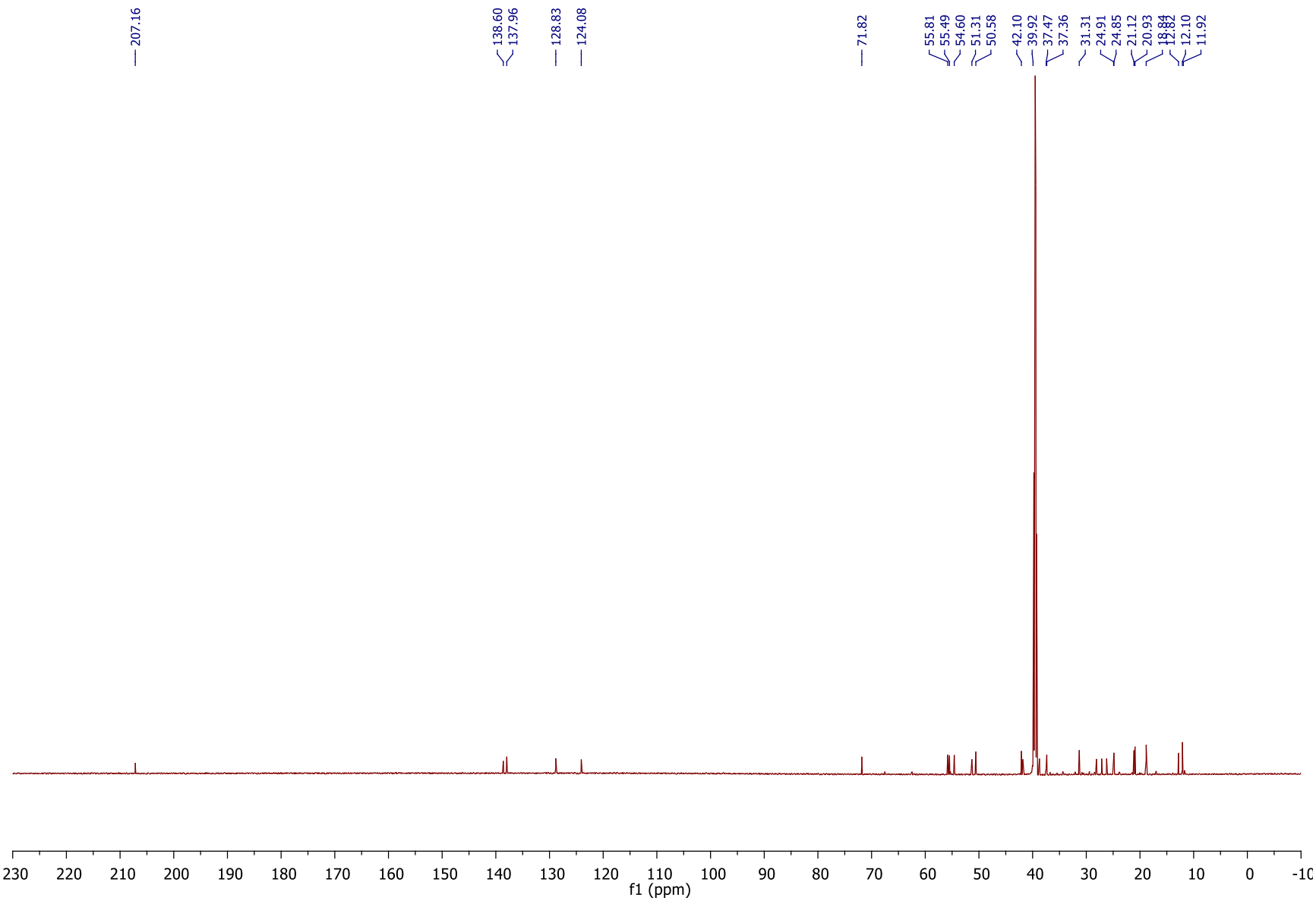
5.17
5.16
5.14
5.13
5.04
5.03
5.01
5.00
4.65
4.64
2.55
2.53
2.37
2.24
2.02
1.99
1.73
1.65
1.63
1.61
1.53
1.51
1.50
1.39
1.18
1.16
1.14
1.02
0.99
0.97
0.83
0.82
0.79
0.78
0.77
0.70
1.97
1.09
1.00
2.13
5.00
3.99
1.10
13.18
5.05
4.82
10.92
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


206.38
169.99
140.84
138.31
129.55
123.42
74.62
56.24
56.23
54.98
51.37
47.79
40.65
39.33
38.26
34.08
32.04
28.62
27.67
26.73
25.57
25.55
21.42
21.41
21.25
19.15
19.10
12.40
12.31
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

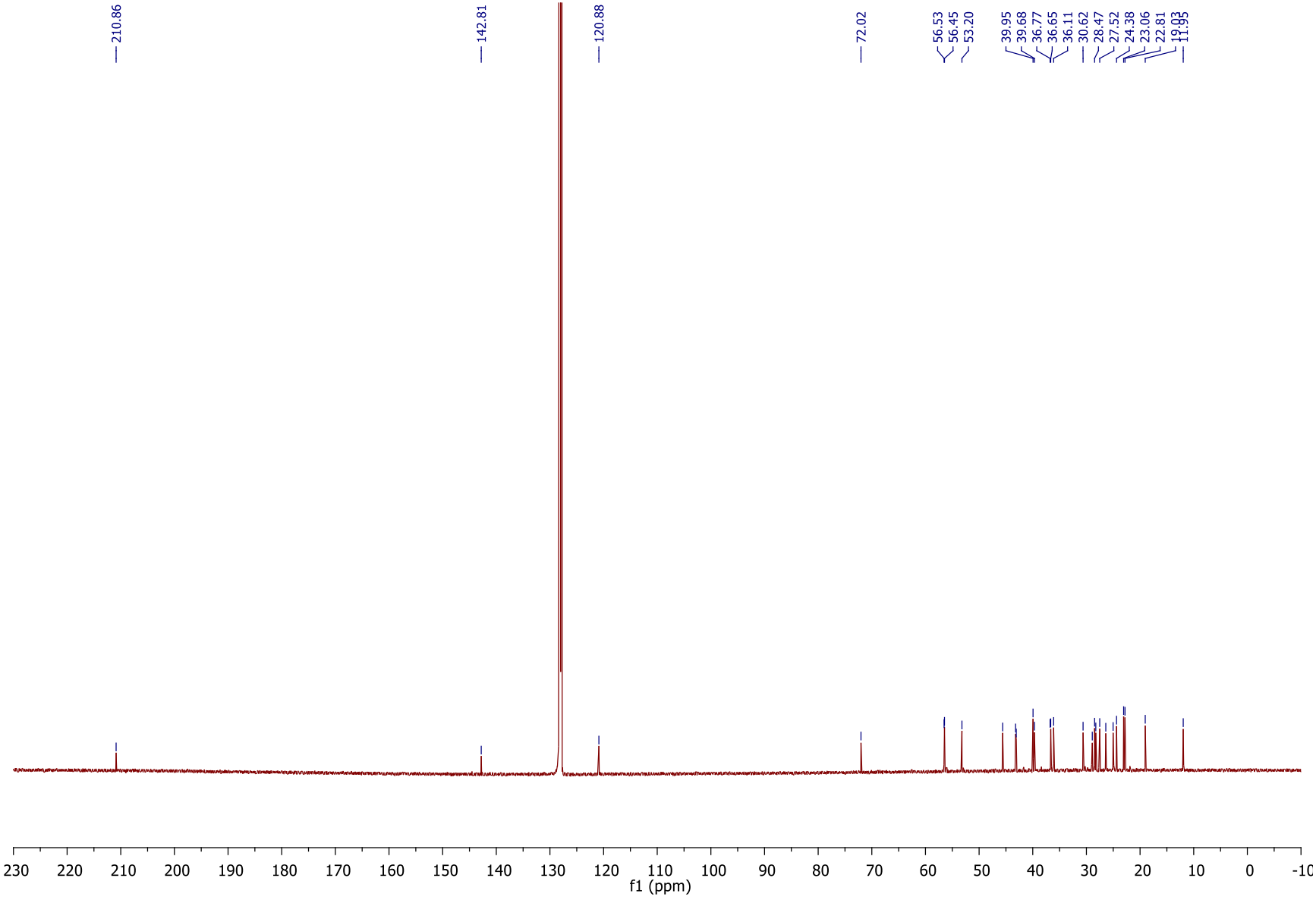

Me
Me
Me
Me
Me
H
H
H
Me
O
HO

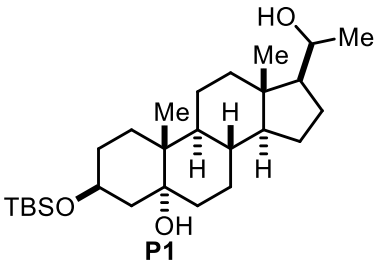
29

5.17
5.15
5.15
5.13
5.04
5.02
5.02
5.00
4.90
4.89
4.68
4.67
4.66
4.65
4.64
4.05
4.04
2.36
2.15
2.14
1.69
1.62
1.52
1.51
1.51
1.16
1.15
1.14
1.14
1.13
0.98
0.98
0.97
0.88
0.83
0.82
0.79
0.78
0.77
0.77
0.69
0.61
1.16
1.20
0.94
1.11
1.04
2.06
4.00
1.16
2.04
2.29
3.26
4.32
2.75
5.31
5.10
3.11
5.75
2.90
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


207.16
138.60
137.96
128.83
124.08
71.82
55.81
55.49
54.60
51.31
50.58
42.10
39.92
37.47
37.36
31.31
24.91
24.85
21.12
20.93
18.84
18.82
12.10
11.92
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

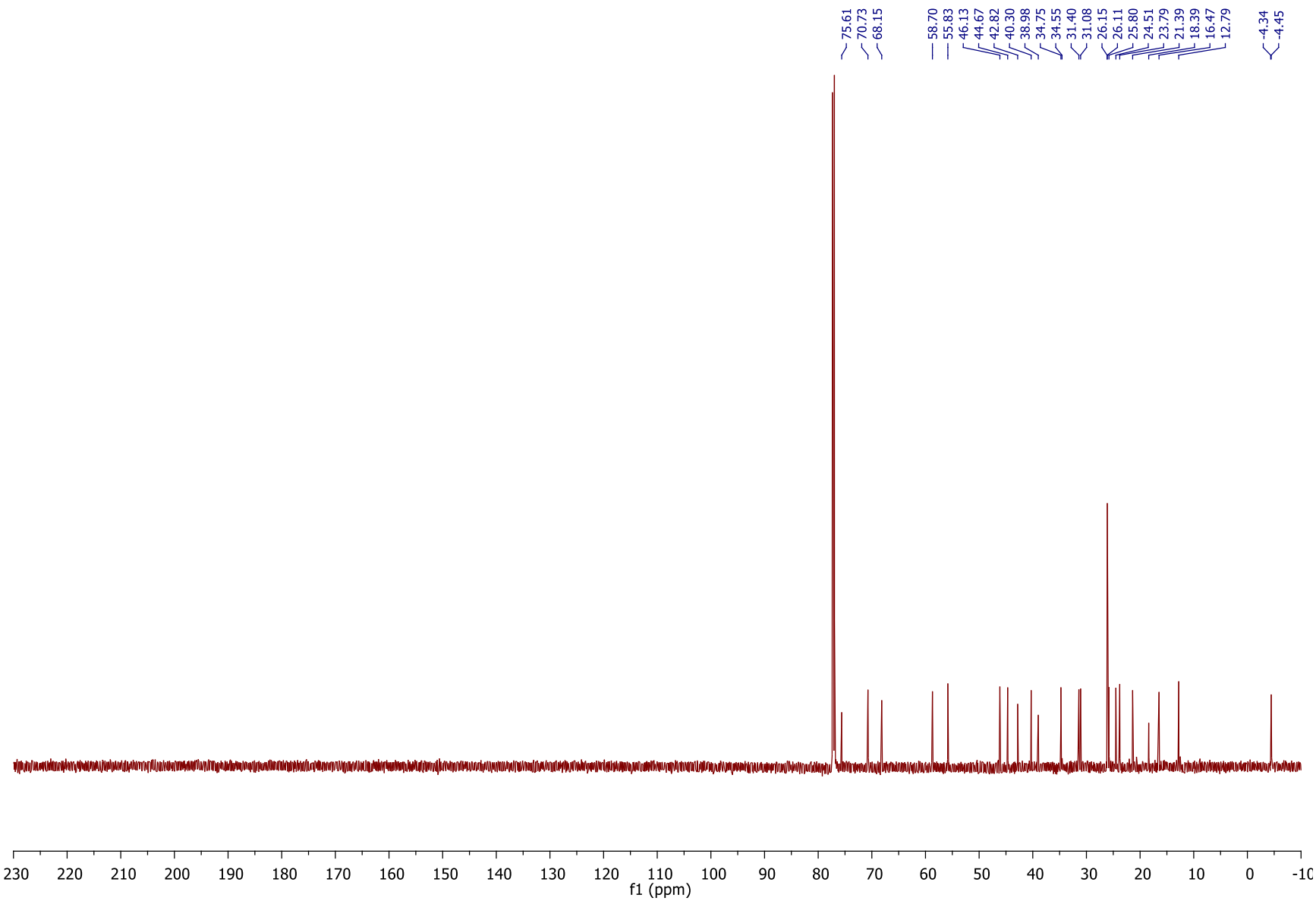
C_6D_6:

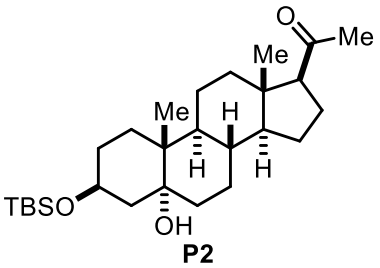

210.86
142.81
120.88
72.02
56.53
56.45
53.20
39.95
39.68
36.77
36.65
36.11
30.62
28.47
27.52
24.38
23.06
22.81
19.03
11.95
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


HO
Me
Me
Me
H
H
H
TBSO
OH

P1

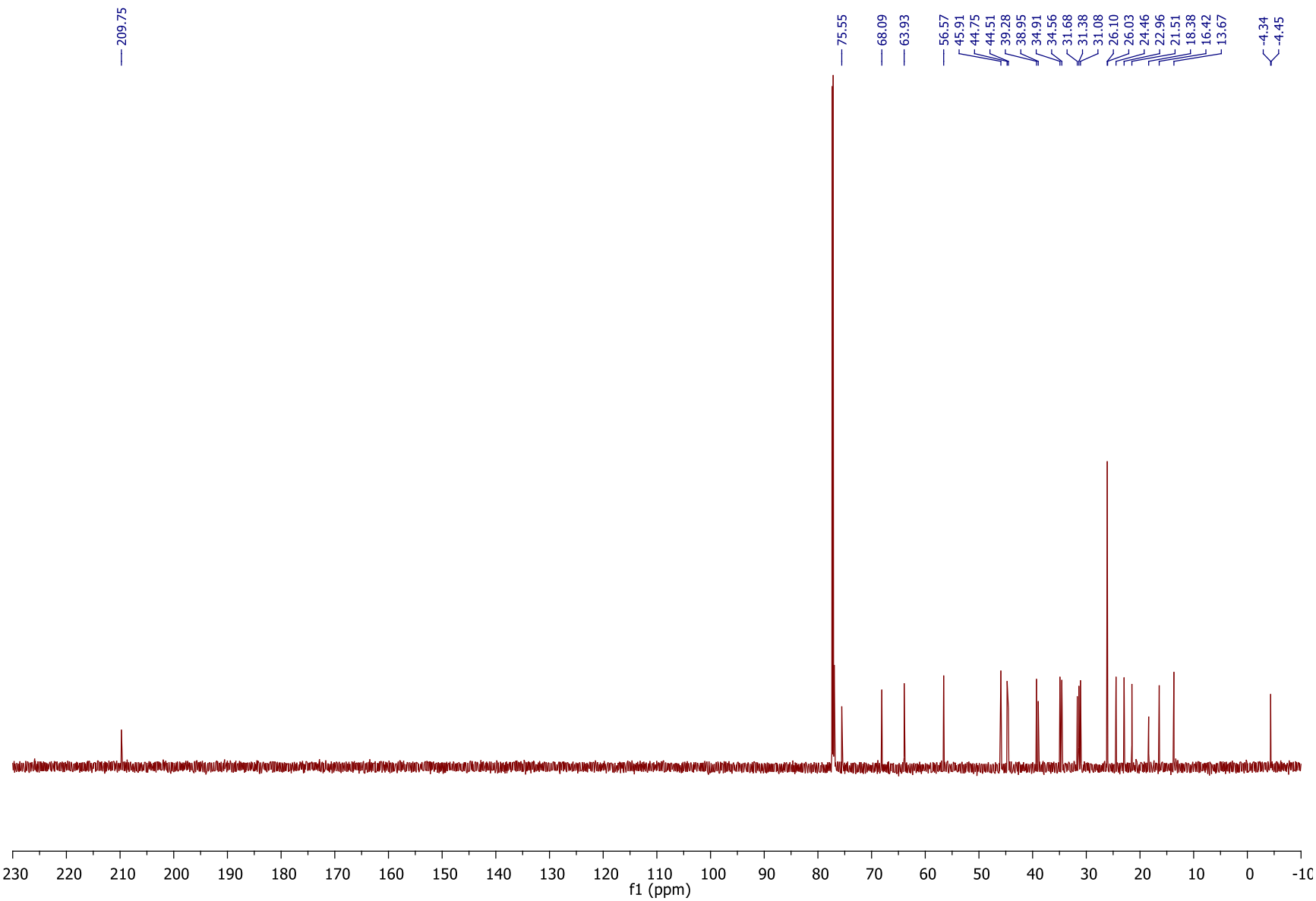
4.05
4.04
3.73
3.72
3.71
1.68
1.64
1.62
1.55
1.50
1.48
1.47
1.43
1.40
1.32
1.27
1.25
1.22
1.16
1.14
1.12
0.99
0.88
0.74
0.05
1.10
1.05
1.00
25.51
2.80
8.54
2.98
5.38
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

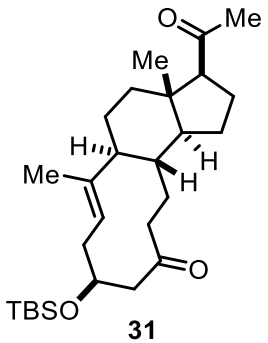

75.61
70.73
68.15
58.70
55.83
46.13
44.67
42.82
40.30
38.98
34.75
34.55
31.40
31.08
26.15
26.11
25.80
24.51
23.79
21.39
18.39
16.47
12.79
-4.34
-4.45
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
Me
Me
Me
H
H
H
TBSO
OH

P2

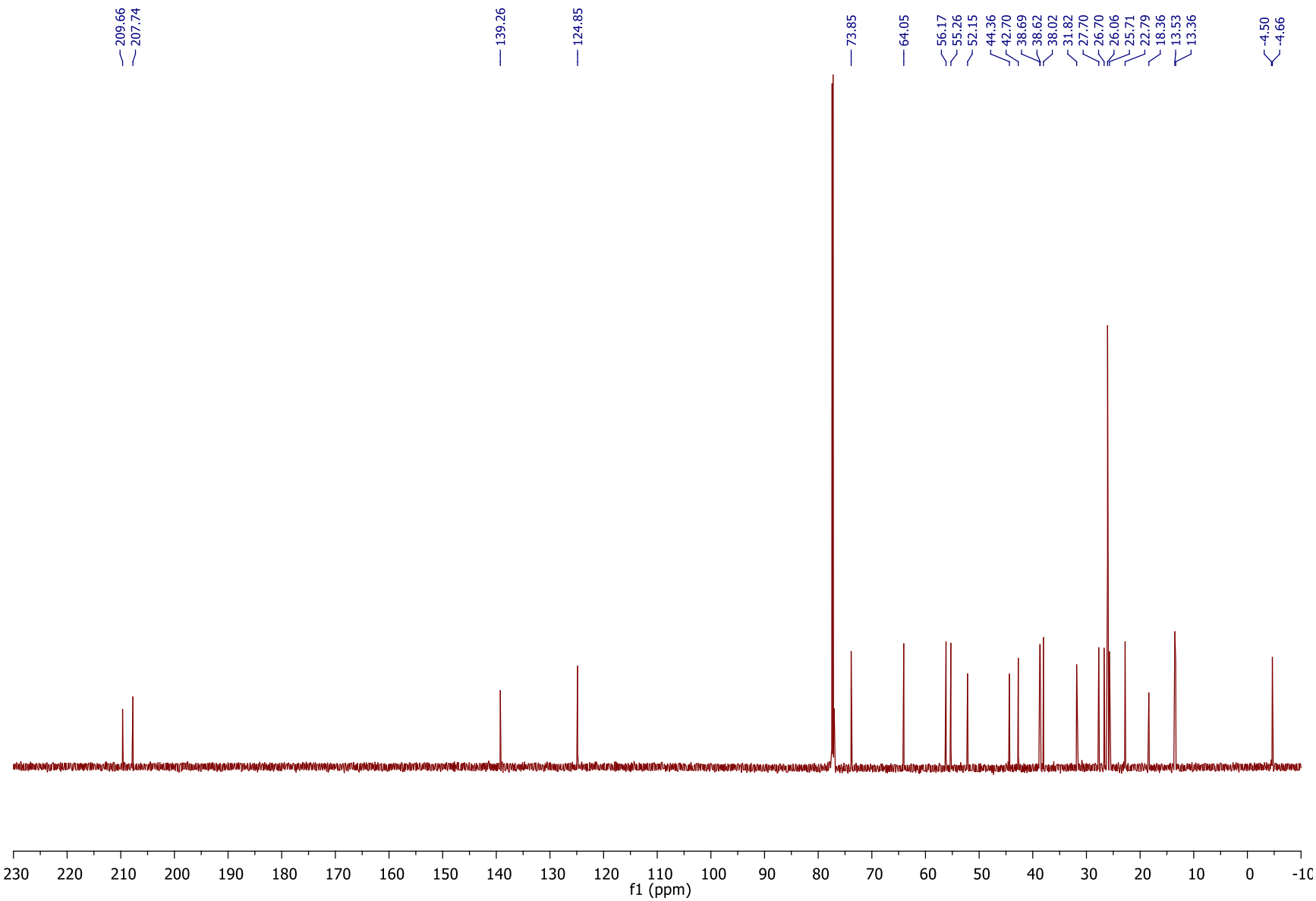
4.07
4.06
4.06
4.05
4.04
4.03
2.54
2.53
2.52
2.11
1.68
1.66
1.54
1.51
1.50
1.44
1.29
1.08
0.98
0.88
0.04
1.21
1.13
1.11
2.78
1.06
5.25
8.41
6.28
1.11
3.00
8.84
2.95
5.72
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

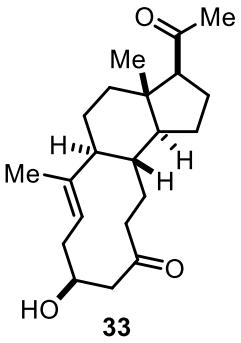

209.75
75.55
68.09
63.93
56.57
45.91
44.75
44.51
39.28
38.95
34.91
34.56
31.68
31.38
31.08
26.10
26.03
24.46
22.96
21.51
18.38
16.42
13.67
-4.34
-4.45
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
Me
Me
H
H
Me
H
O
TBSO

31

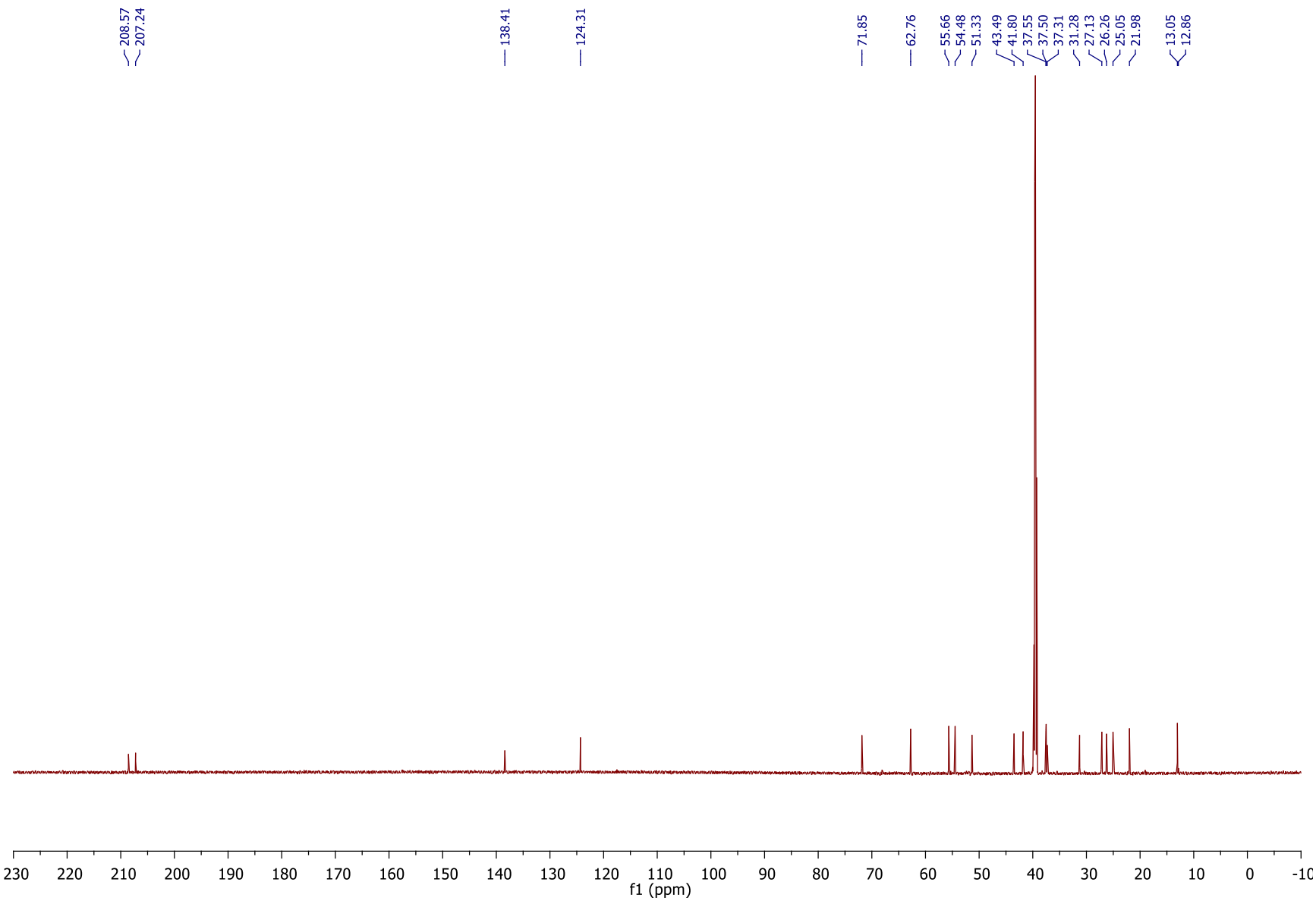
4.69
4.67
4.24
2.59
2.36
2.23
2.22
2.20
2.15
2.05
1.88
1.70
1.63
1.61
1.59
1.56
1.53
1.51
1.20
1.15
0.88
0.86
0.56
0.07
1.05
1.13
1.24
2.28
3.39
5.22
10.64
3.56
8.46
2.77
6.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

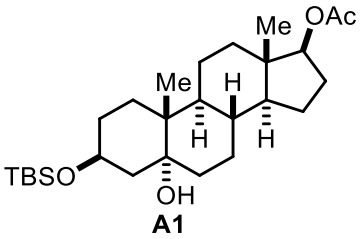

209.66
207.74
139.26
124.85
73.85
64.05
56.17
55.26
52.15
44.36
42.70
38.69
38.62
38.02
31.82
27.70
26.70
26.06
25.71
22.79
18.36
13.53
13.36
-4.50
-4.66
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
Me
Me
H
H
Me
H
O
HO

33

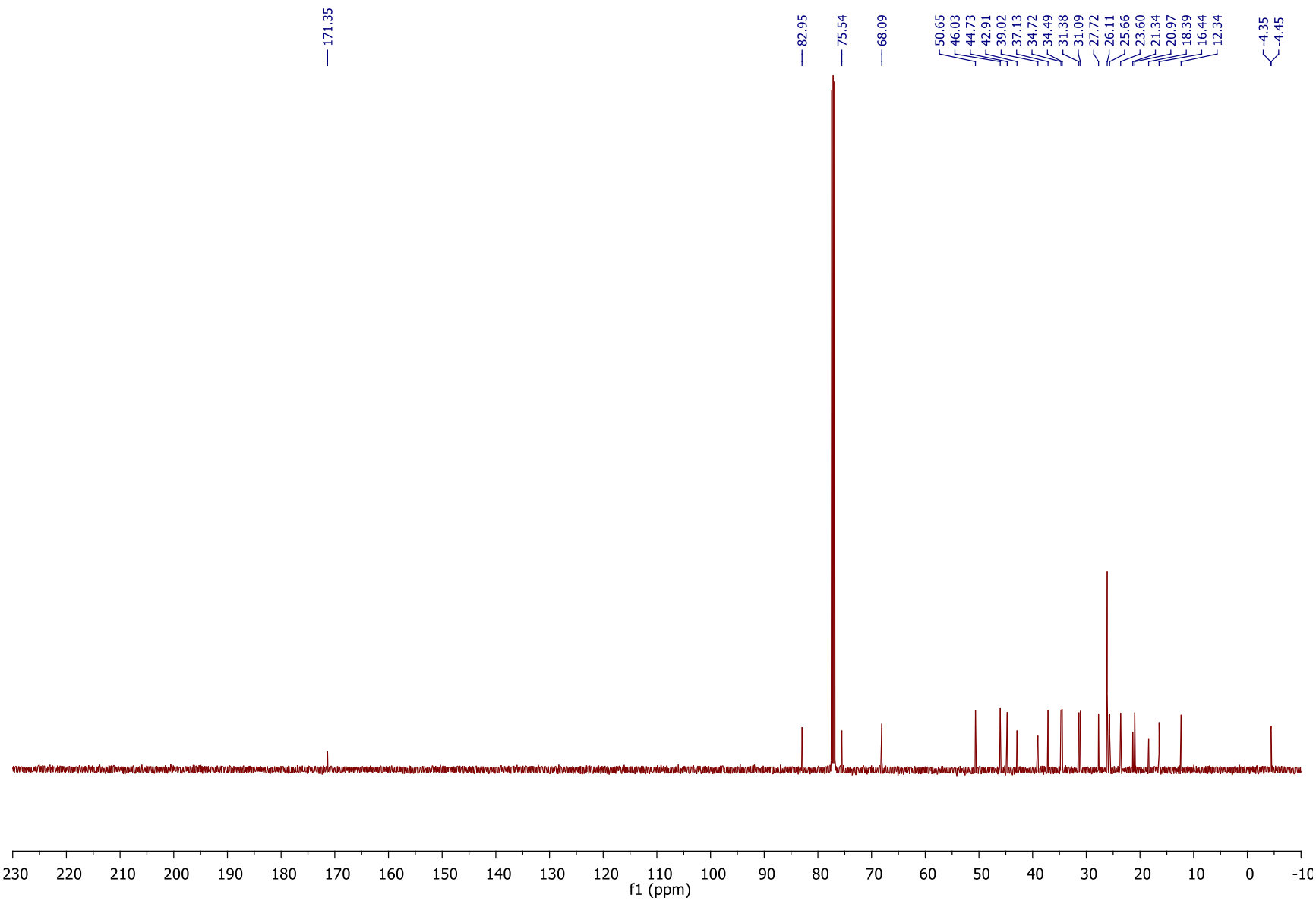
4.92
4.70
4.68
4.67
4.05
2.59
2.38
2.37
2.25
2.23
2.17
2.15
2.14
2.05
1.90
1.88
1.72
1.69
1.60
1.59
1.52
1.51
1.15
0.56
1.03
1.00
0.97
1.01
1.80
3.49
2.52
1.00
0.94
9.84
2.85
2.47
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

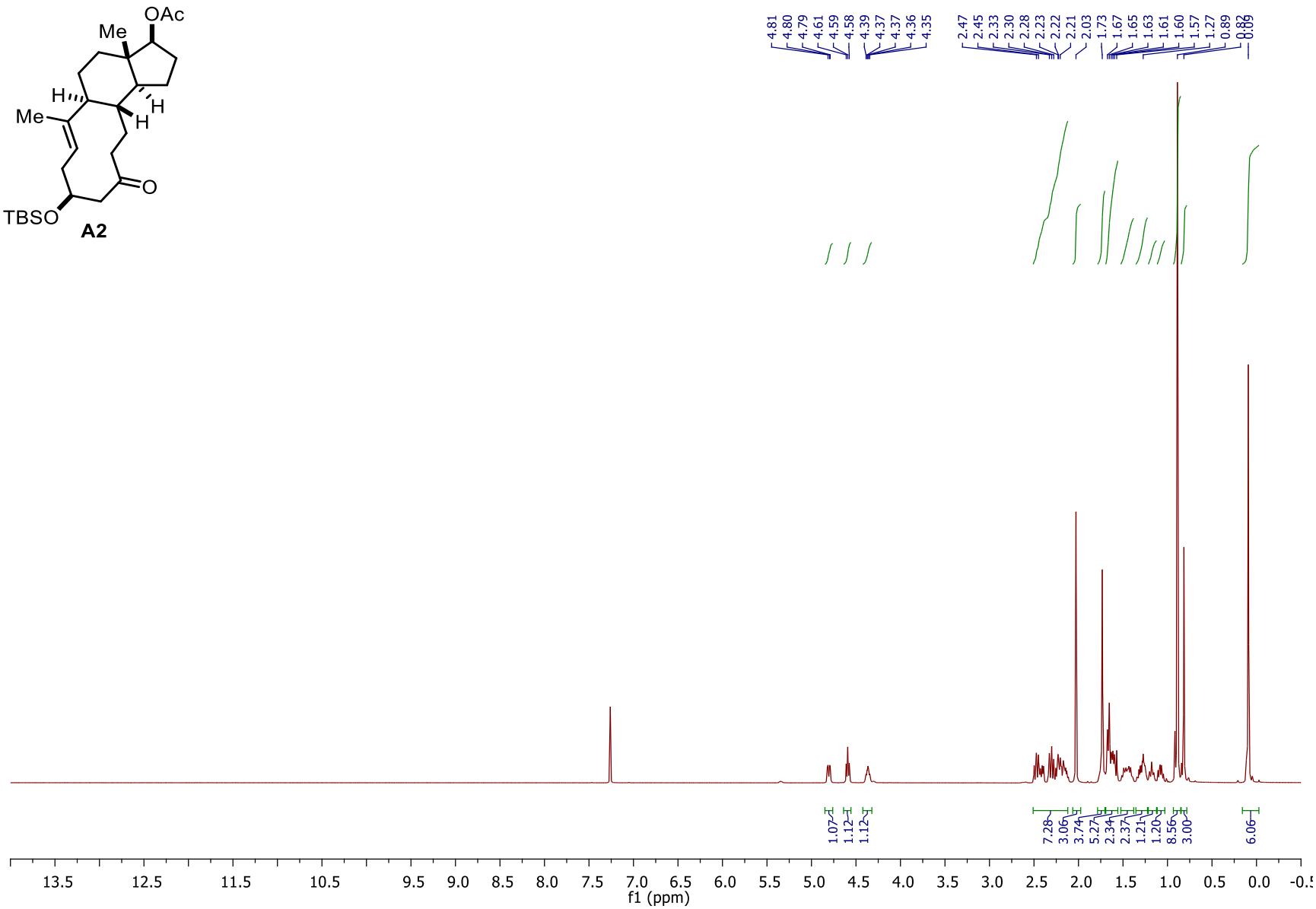

208.57
207.24
138.41
124.31
71.85
62.76
55.66
54.48
51.33
43.49
41.80
37.55
37.50
37.31
31.28
27.13
26.26
25.05
21.98
13.05
12.86
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

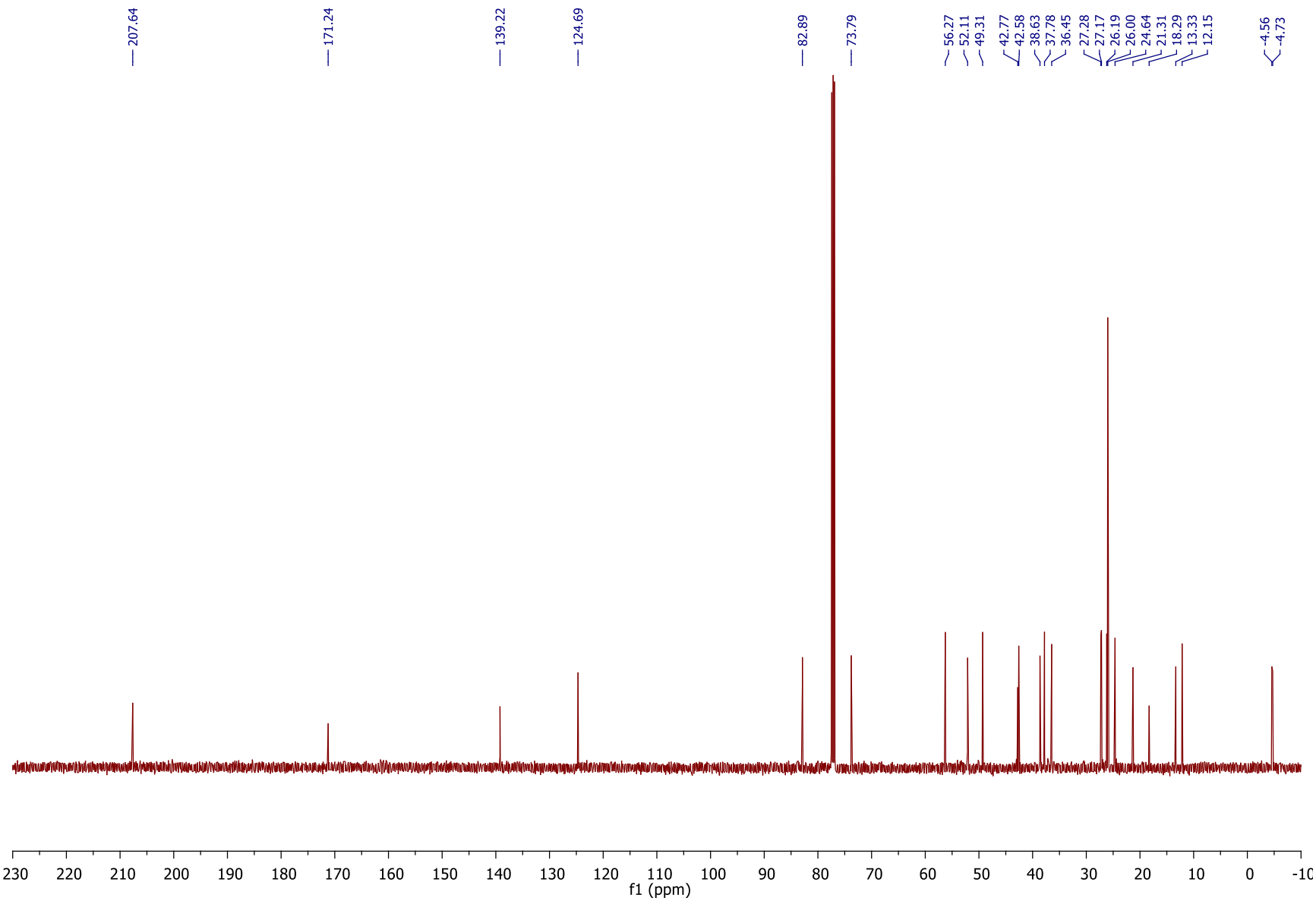

Me
OAc
Me
H
H
H
TBSO
OH

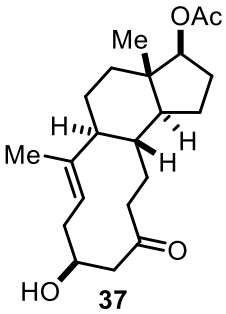
A1

4.60
4.59
4.57
4.07
4.06
4.05
4.04
4.03
2.03
1.74
1.72
1.65
1.63
1.55
1.50
1.48
1.47
1.46
1.45
1.29
1.27
1.26
1.25
1.23
0.99
0.88
0.78
0.05
1.00
1.06
1.22
2.79
21.67
2.87
8.14
2.86
5.24
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


171.35
82.95
75.54
68.09
50.65
46.03
44.73
42.91
39.02
37.13
34.72
34.49
31.38
31.09
27.72
26.11
25.66
23.60
21.34
20.97
18.39
16.44
12.34
-4.35
-4.45
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

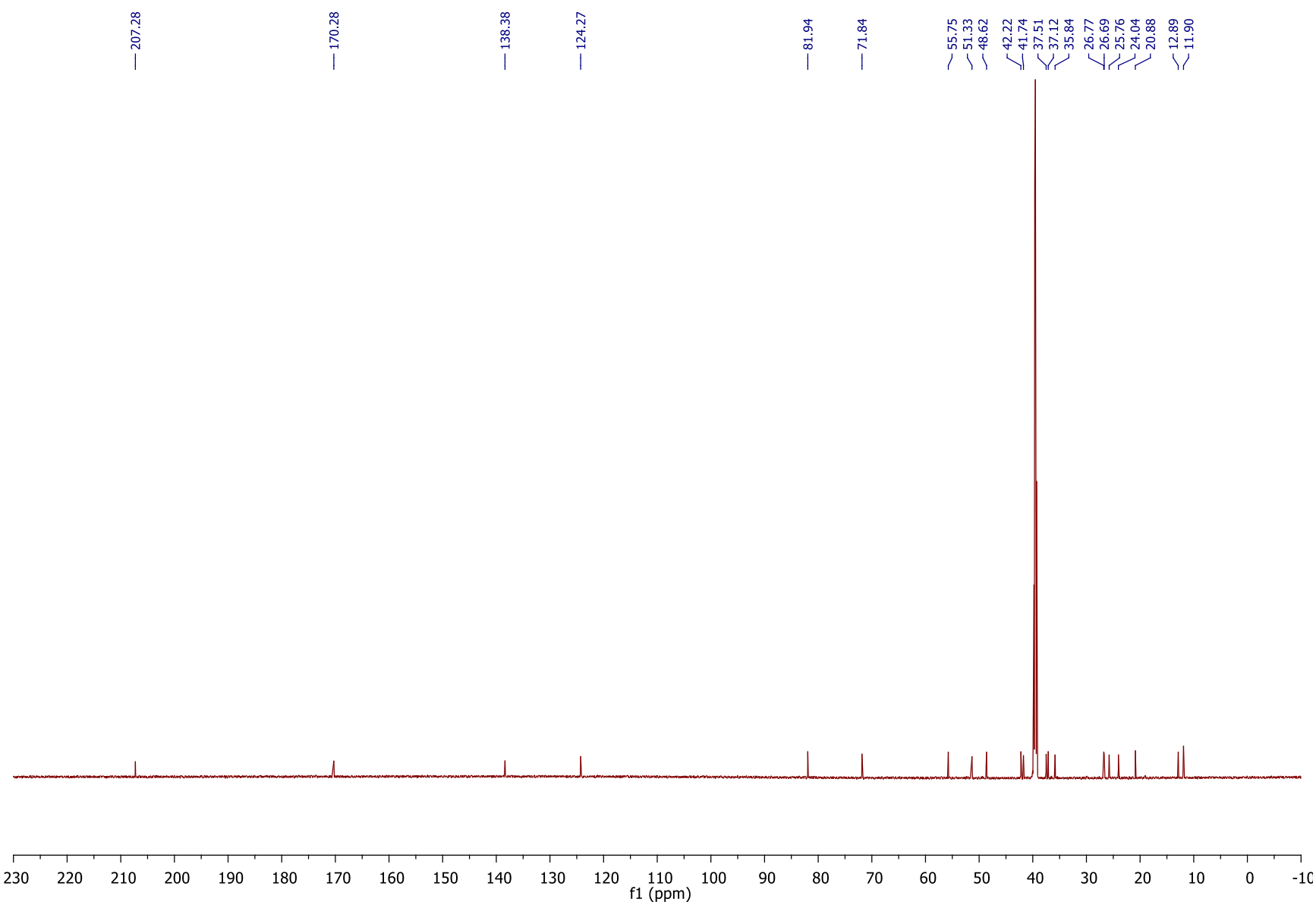

OAc
Me
H
Me
H
H
O
TBSO
A2
4.81
4.80
4.79
4.61
4.59
4.58
4.39
4.37
4.37
4.36
4.35
2.47
2.45
2.33
2.30
2.28
2.23
2.22
2.21
2.03
1.73
1.67
1.65
1.63
1.61
1.60
1.57
1.27
0.89
0.09
1.07
1.12
1.12
7.28
3.06
3.74
5.27
2.34
2.37
1.21
1.20
8.56
3.00
6.06
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

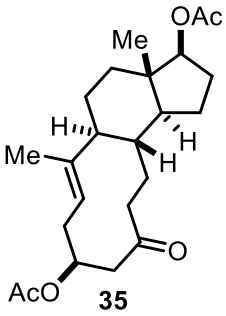

207.64
171.24
139.22
124.69
82.89
73.79
56.27
52.11
49.31
42.77
42.58
38.63
37.78
36.45
27.28
27.17
26.19
26.00
24.64
21.31
18.29
13.33
12.15
-4.56
-4.73
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OAc
Me
H
Me
H
H
O
HO

37

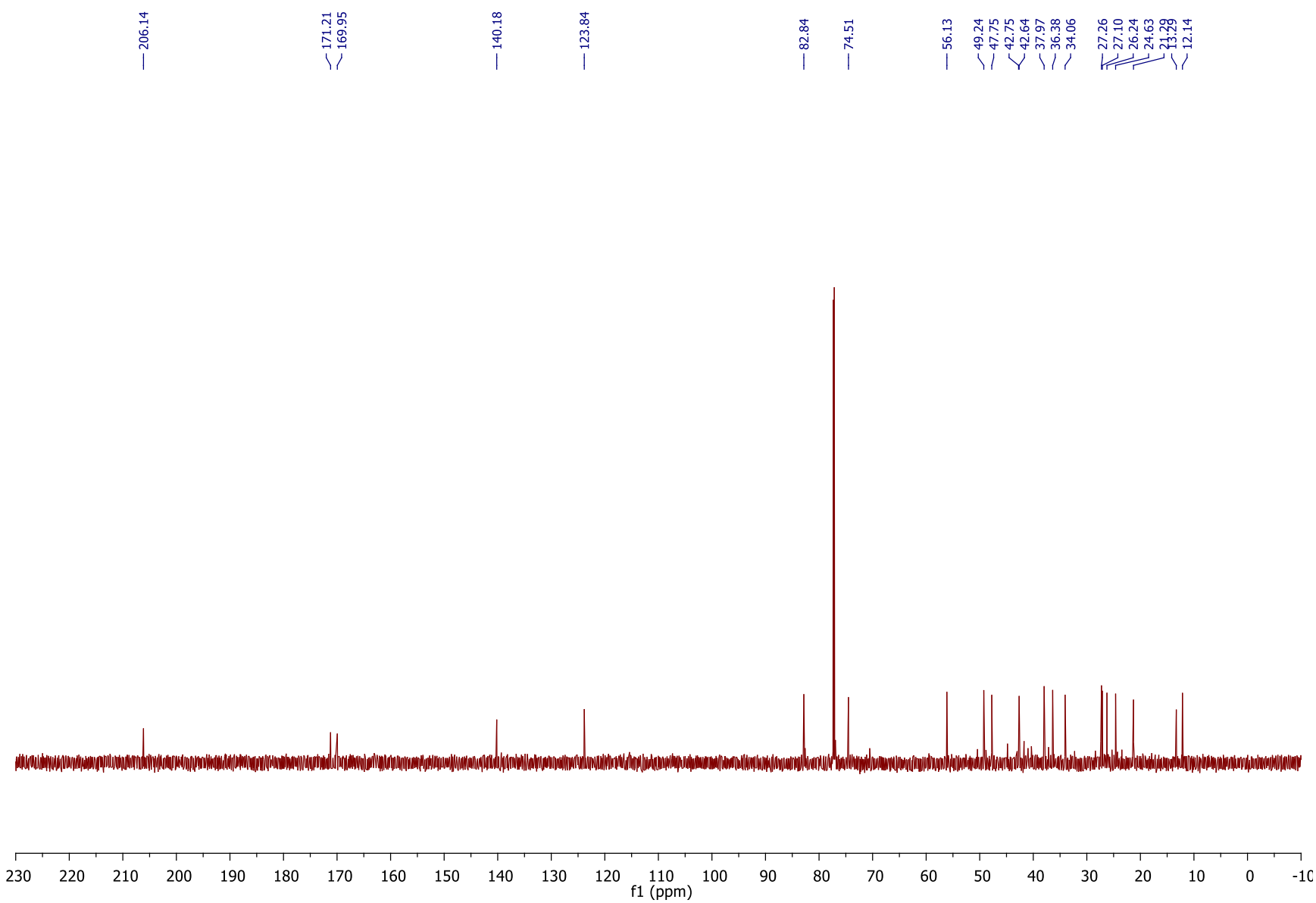
1.07
1.00
1.09
1.12
2.14
3.93
1.25
2.82
3.84
7.43
1.90
2.18
1.77
3.02
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

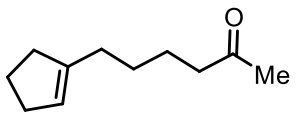

207.28
170.28
138.38
124.27
81.94
71.84
55.75
51.33
48.62
42.22
41.74
37.51
37.12
35.84
26.77
26.69
25.76
24.04
20.88
12.89
11.90
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OAc
Me
H
Me
H
H
O
AcO

35

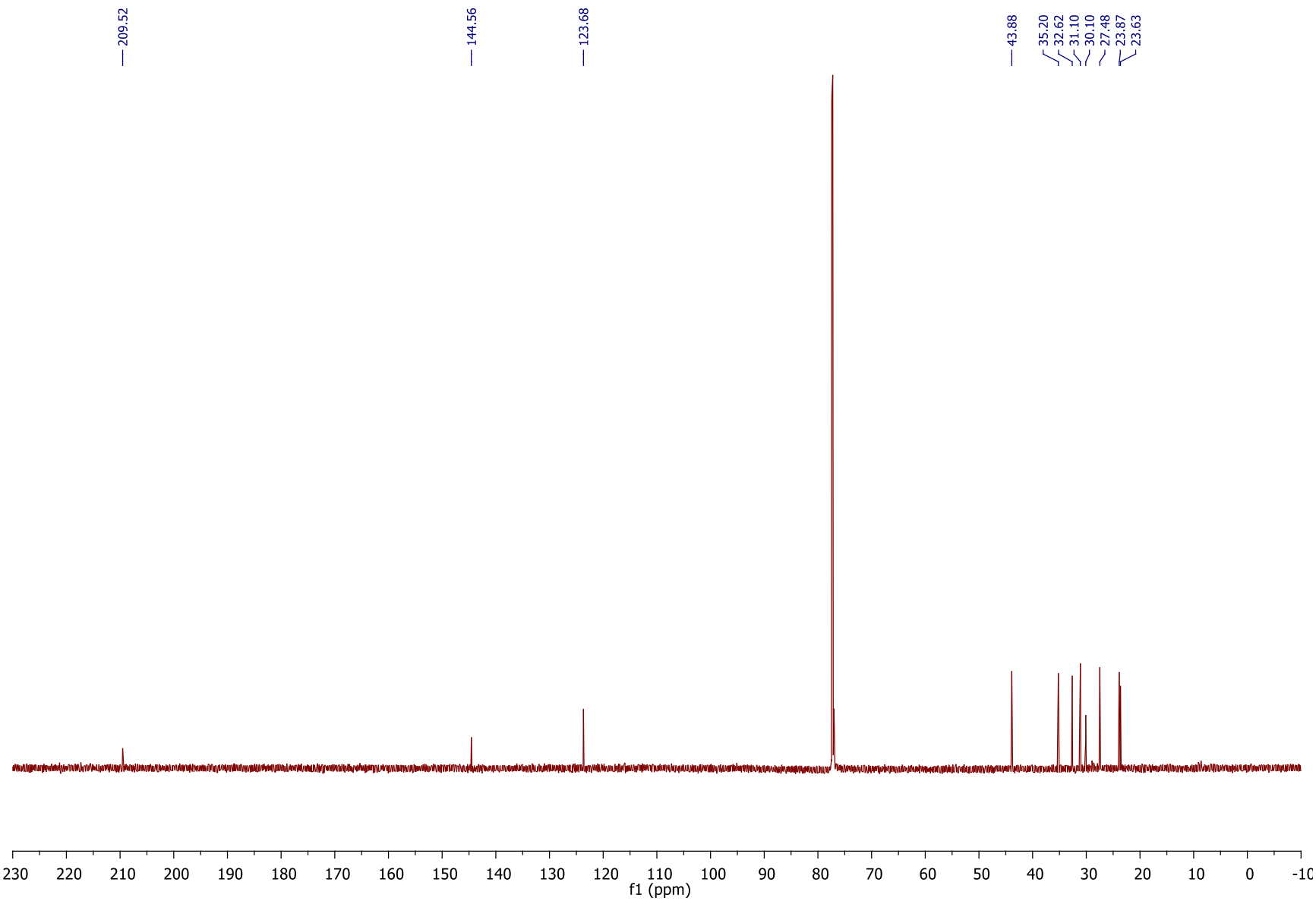
0.92
0.90
1.01
1.12
4.52
6.63
10.80
1.78
2.08
1.39
3.00
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

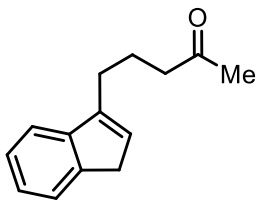

206.14
171.21
169.95
140.18
123.84
82.84
74.51
56.13
49.24
47.75
42.75
42.64
37.97
36.38
34.06
27.26
27.10
26.24
24.63
21.29
13.29
12.14
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
Me

24

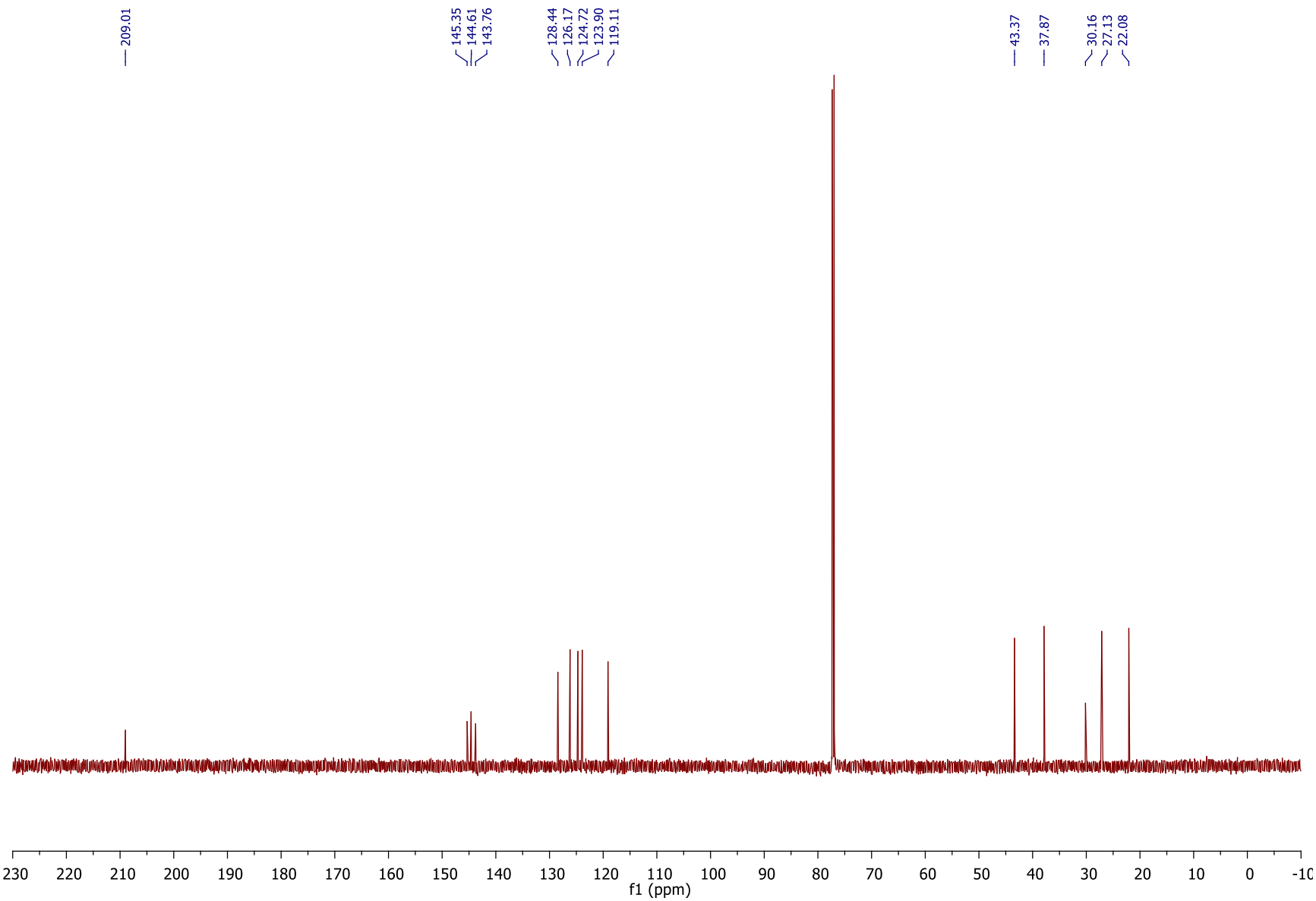
5.32
2.45
2.43
2.41
2.30
2.28
2.27
2.26
2.21
2.19
2.13
2.09
2.07
2.05
1.86
1.84
1.82
1.59
1.57
1.55
1.54
1.45
1.44
1.42
1.00
2.07
1.94
2.07
2.73
2.14
2.17
1.85
2.18
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

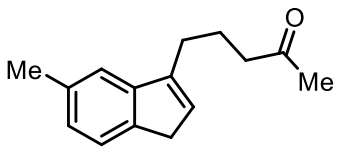

209.52
144.56
123.68
43.88
35.20
32.62
31.10
30.10
27.48
23.87
23.63
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
Me

26

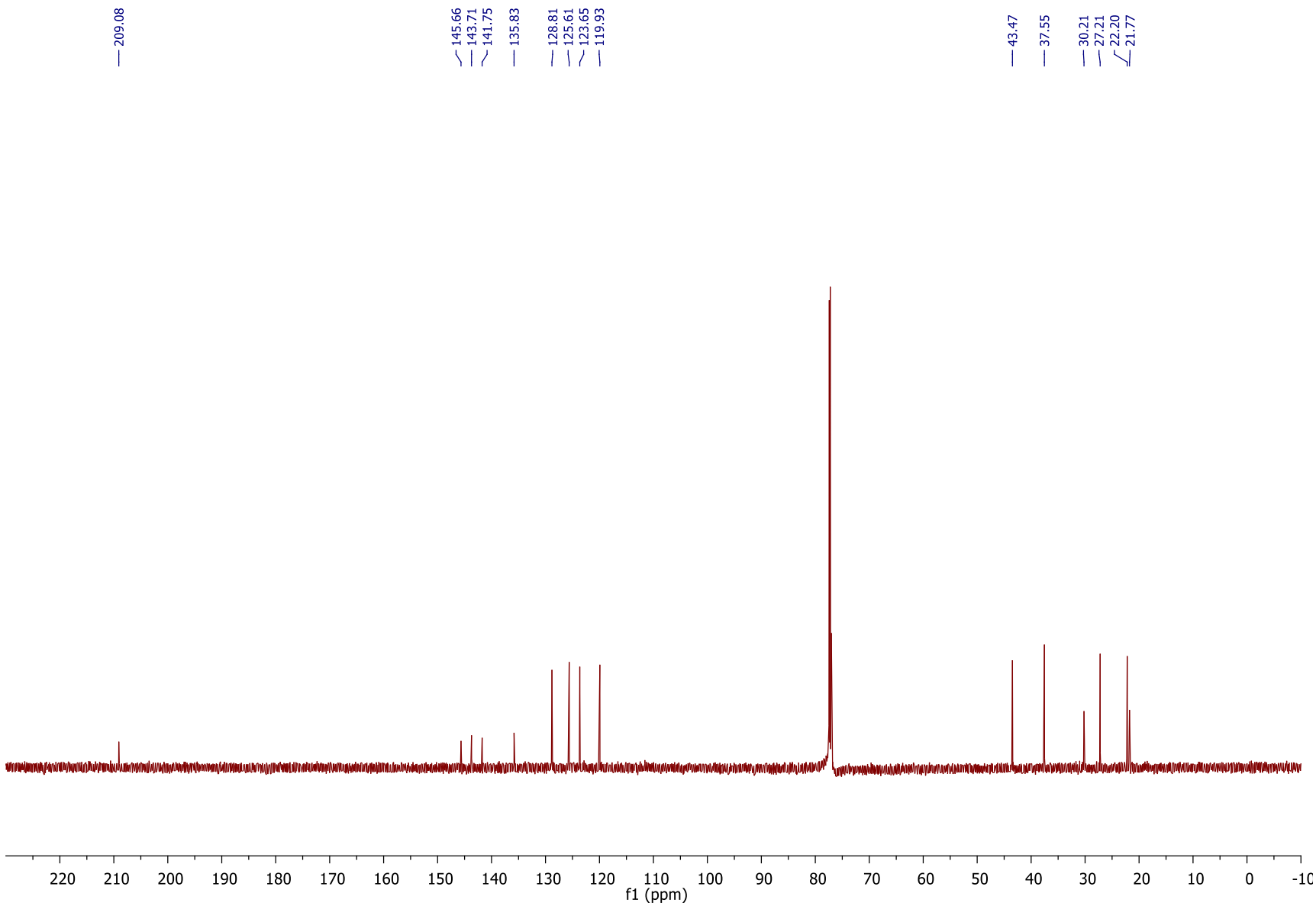
7.47
7.45
7.38
7.36
7.31
7.30
7.29
7.21
7.21
7.20
7.20
7.19
7.19
6.22
3.33
3.33
2.57
2.54
2.53
2.14
2.00
1.99
1.98
1.97
1.96
1.02
1.09
1.11
1.07
1.00
2.15
2.27
2.16
2.96
2.32
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

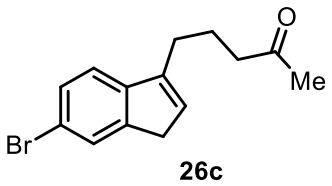

209.01
145.35
144.61
143.76
128.44
126.17
124.72
123.90
119.11
43.37
37.87
30.16
27.13
22.08
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
O
Me

26b

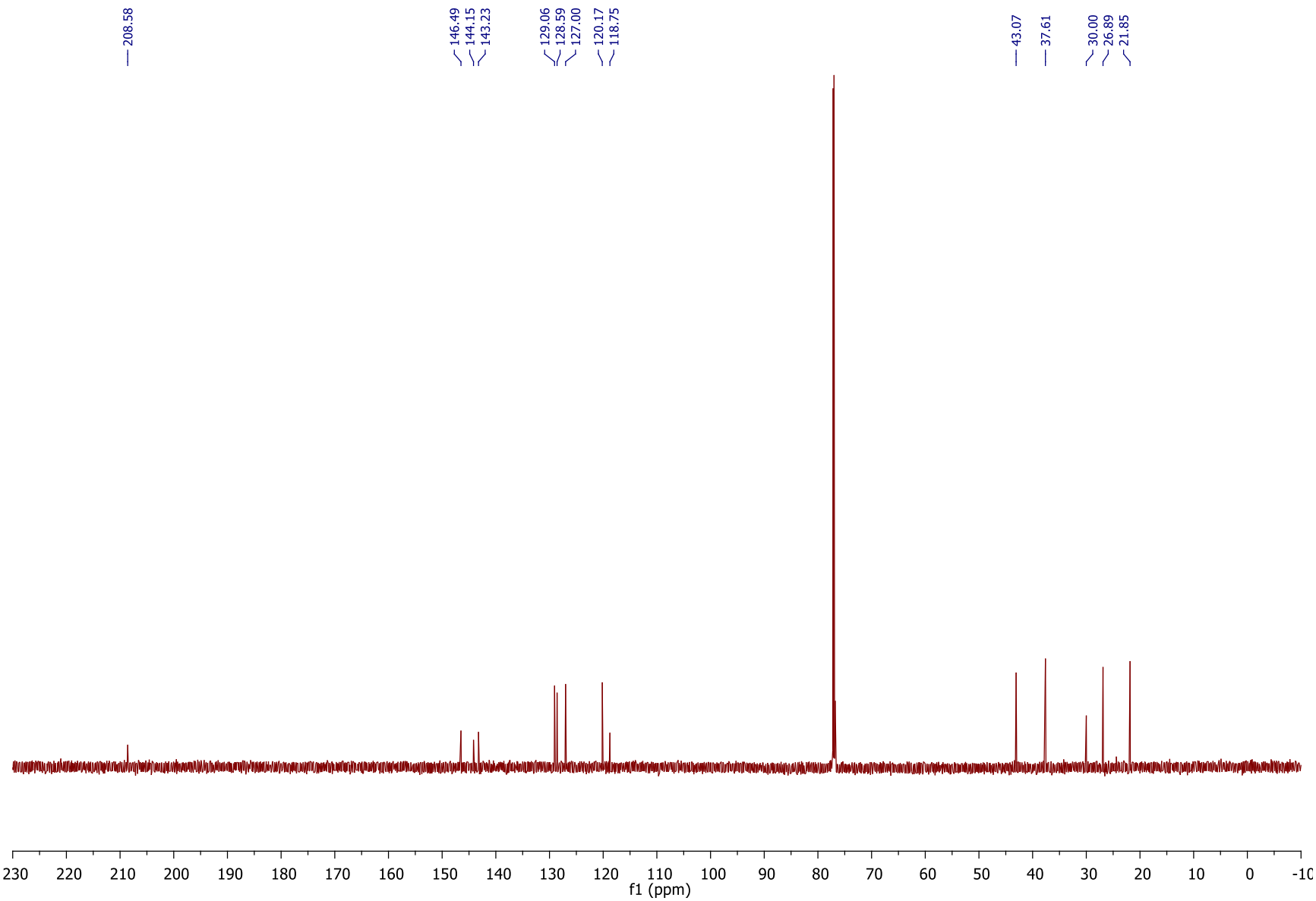
7.34
7.33
7.18
7.02
7.01
6.20
3.29
2.56
2.56
2.55
2.54
2.54
2.54
2.52
2.51
2.41
2.14
1.99
1.98
1.97
0.89
0.92
0.91
0.91
2.00
4.00
2.92
2.76
2.05
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

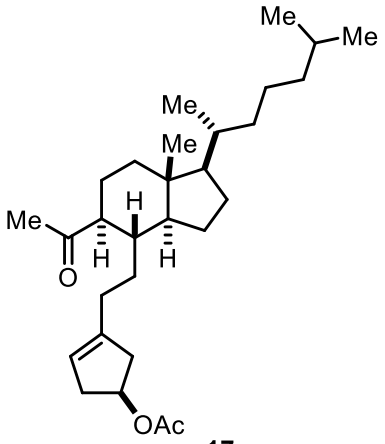

209.08
145.66
143.71
141.75
135.83
128.81
125.61
123.65
119.93
43.47
37.55
30.21
27.21
22.20
21.77
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
Me
Br

26c

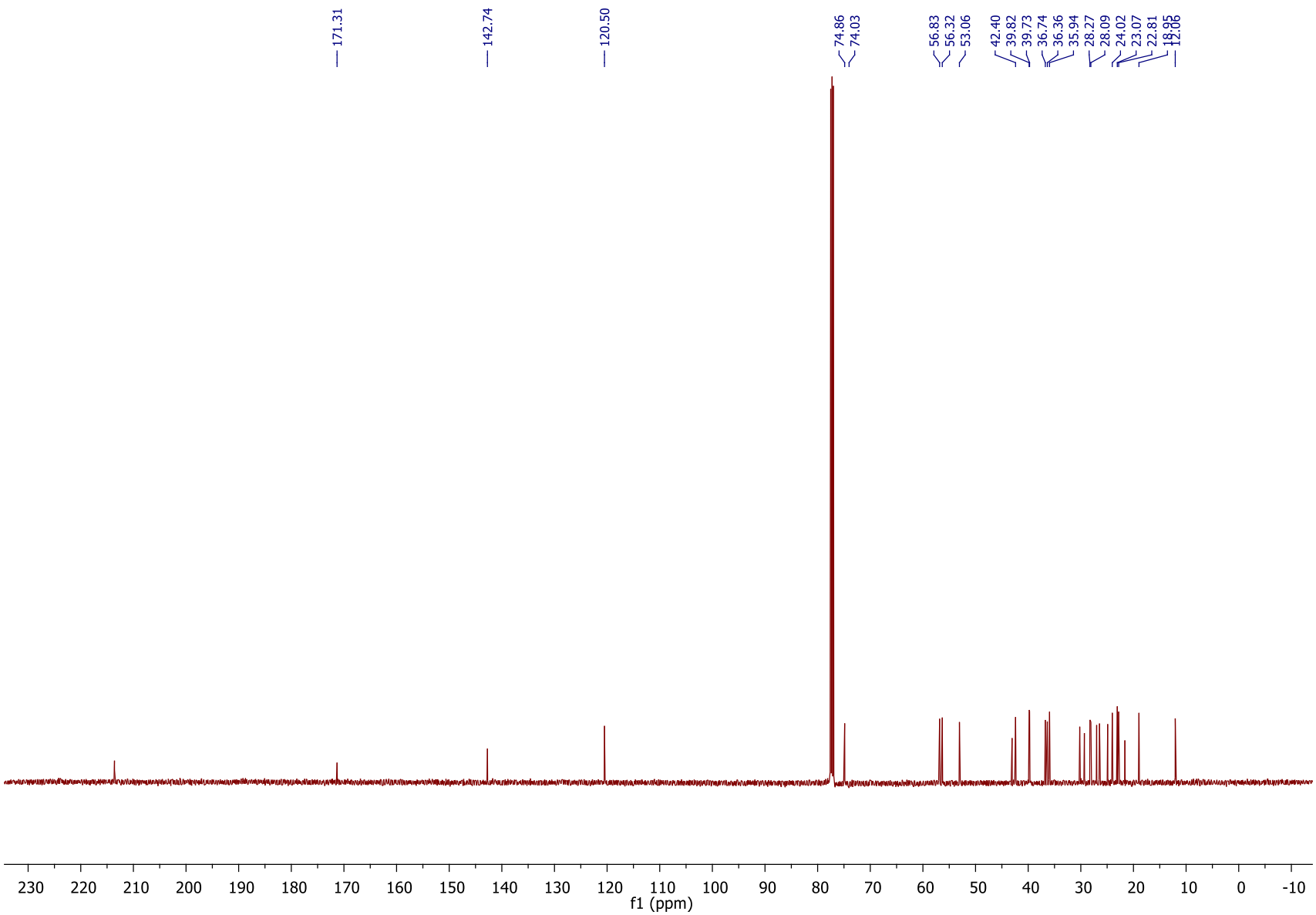
7.57
7.43
7.43
7.41
7.41
7.23
7.21
6.20
3.31
2.54
2.52
2.51
2.50
2.17
2.14
1.97
1.95
1.55
0.96
1.11
1.03
1.00
2.09
4.23
1.33
3.07
2.32
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

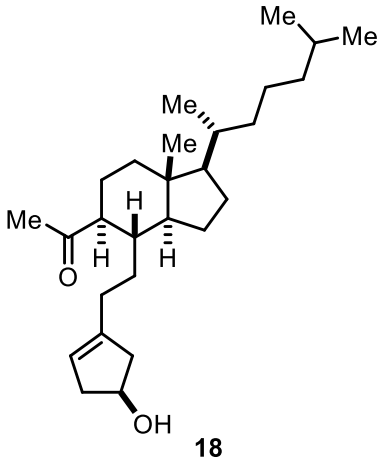

208.58
146.49
144.15
143.23
129.06
128.59
127.00
120.17
118.75
43.07
37.61
30.00
26.89
21.85
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
Me
Me
Me
H
Me
O
H
H
OAc

17

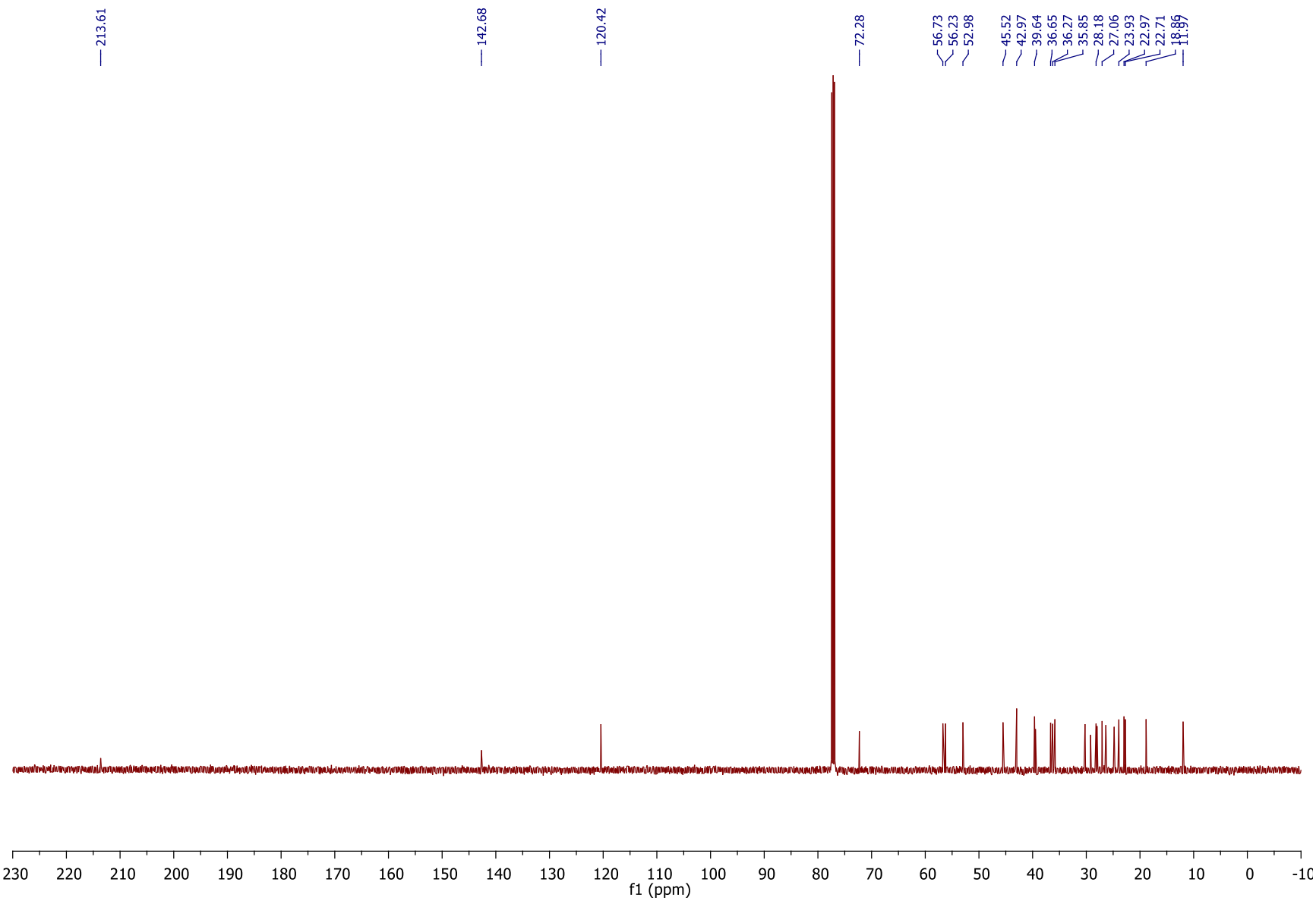
5.32
5.32
5.31
5.31
5.30
5.29
5.24
2.31
2.24
2.15
2.02
2.01
1.99
1.56
1.39
1.38
1.37
1.37
1.36
1.35
1.34
1.33
1.16
1.15
1.14
1.13
1.12
1.12
1.10
0.91
0.90
0.87
0.87
0.86
0.86
0.73
1.04
0.99
2.15
3.25
2.72
5.42
2.13
5.41
6.48
7.00
1.29
8.96
3.00
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


171.31
142.74
120.50
74.86
74.03
56.83
56.32
53.06
42.40
39.82
39.73
36.74
36.36
35.94
28.27
28.09
24.02
23.07
22.81
18.95
12.06
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

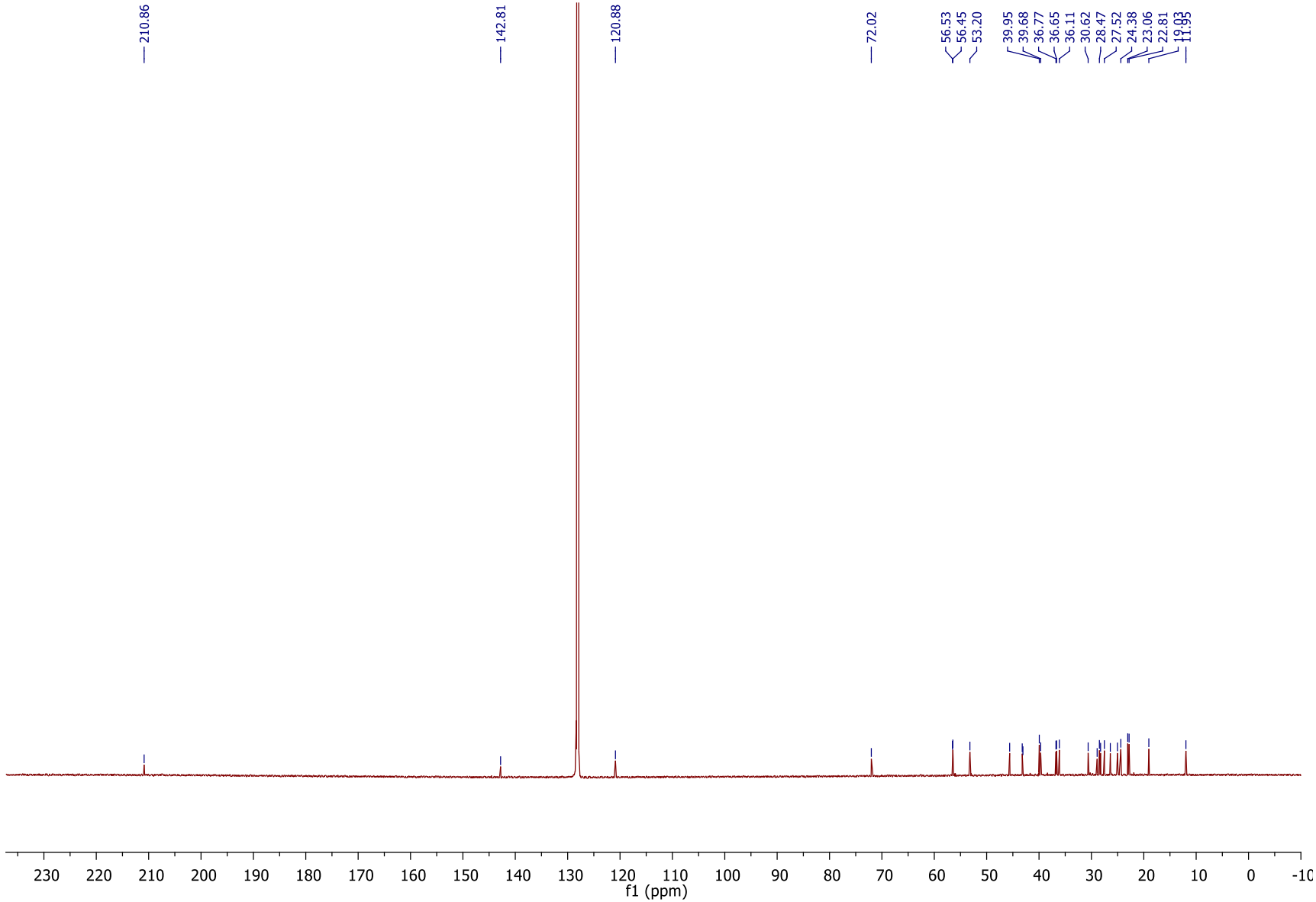

Me
Me
Me
Me
H
Me
O
H
H
OH

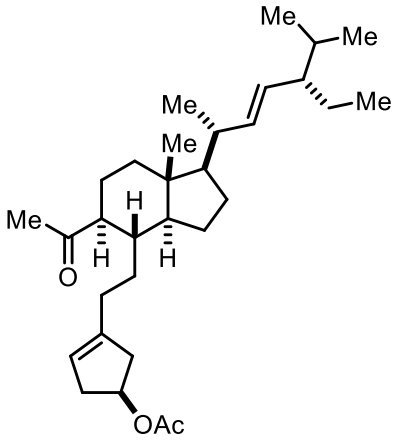
18

5.24
4.47
2.26
2.24
2.16
2.15
2.02
2.01
1.83
1.82
1.65
1.62
1.57
1.51
1.39
1.38
1.33
1.26
1.16
1.14
1.12
1.11
1.10
1.00
0.91
0.90
0.87
0.86
0.86
0.73
0.98
1.03
1.00
1.09
2.14
3.77
3.12
2.70
5.76
6.57
7.04
1.39
8.80
3.07
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


213.61
142.68
120.42
72.28
56.73
56.23
52.98
45.52
42.97
39.64
36.65
36.27
35.85
28.18
27.06
23.93
22.97
22.71
18.86
11.97
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

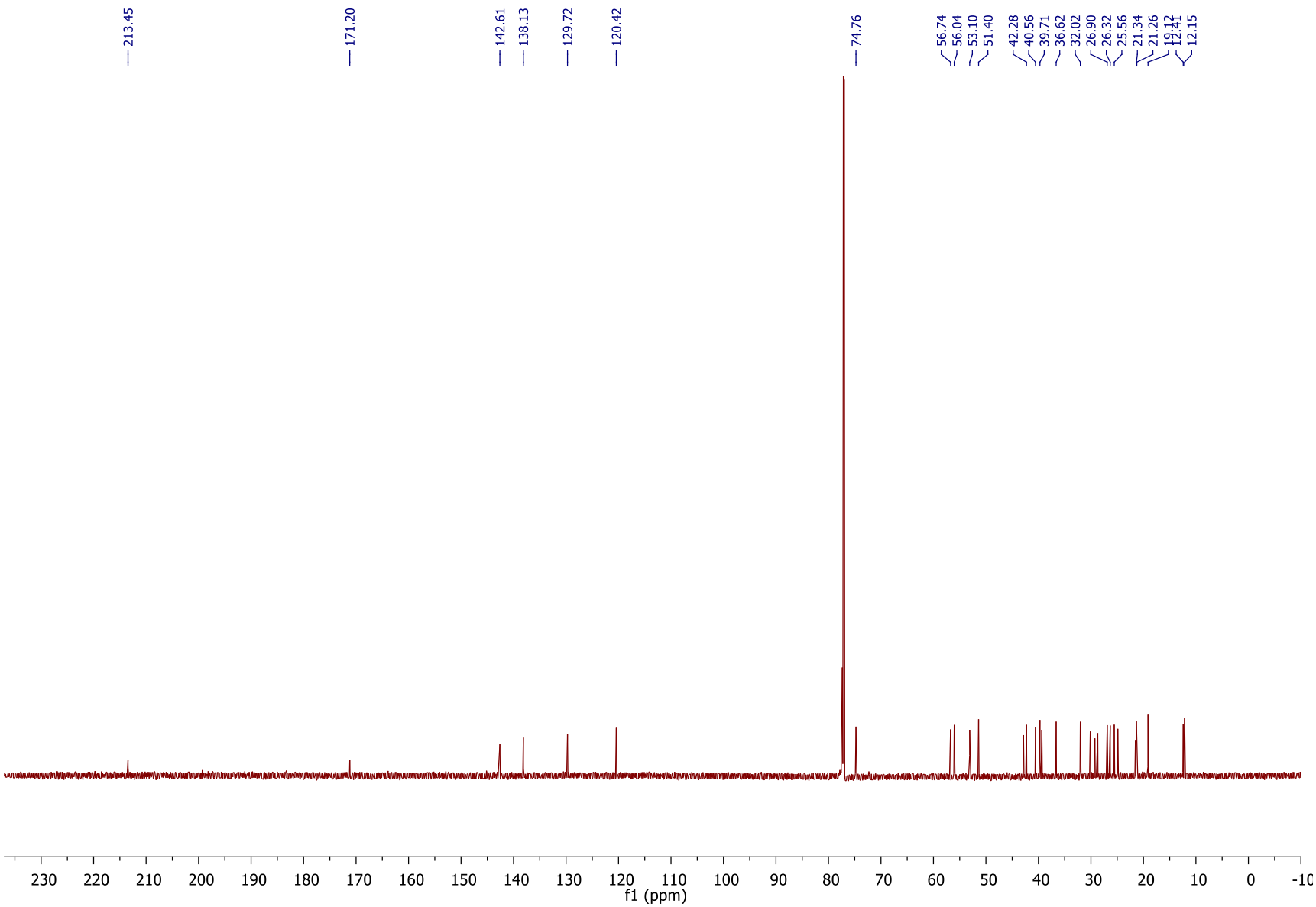
C_6D_6

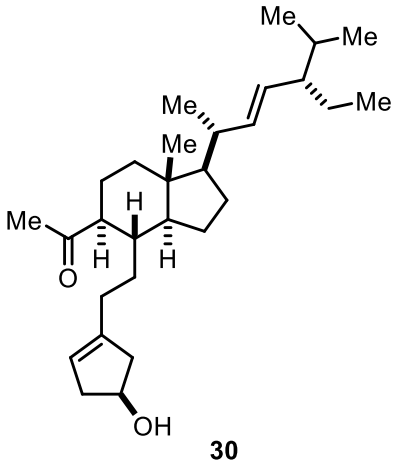

210.86
142.81
120.88
72.02
56.53
56.45
53.20
39.95
39.68
36.77
36.65
36.11
30.62
28.47
27.52
24.38
23.06
22.81
19.03
11.95
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
Me
Me
Me
Me
H
Me
O
H
H
OAc

28

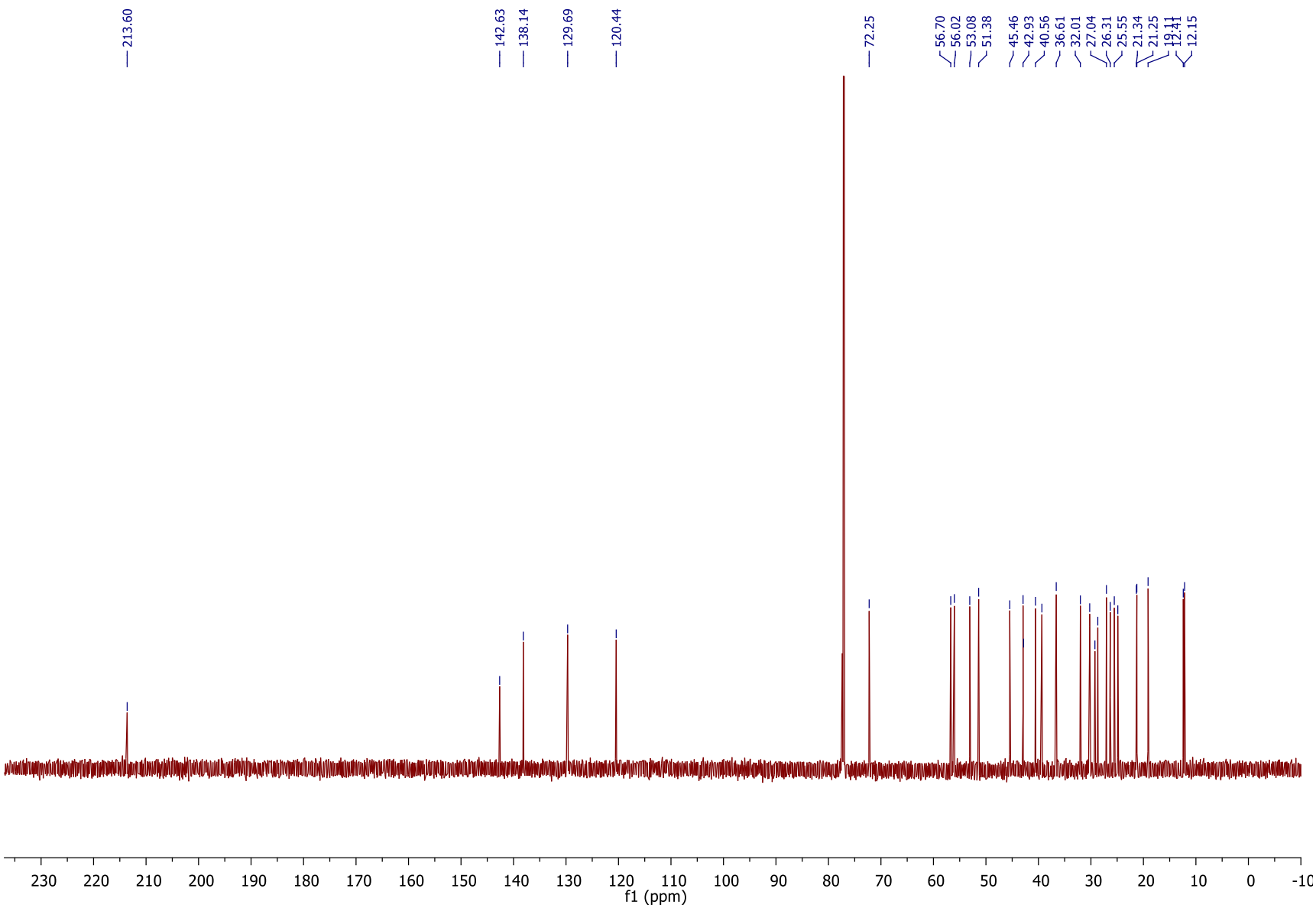
5.30
5.23
5.16
5.14
5.14
5.12
5.04
5.03
5.02
5.01
2.33
2.30
2.23
2.21
2.15
2.04
2.02
2.01
1.99
1.67
1.60
1.56
1.54
1.53
1.19
1.18
1.16
1.15
1.02
1.01
0.85
0.84
0.81
0.80
0.80
0.79
0.75
1.00
1.03
1.10
1.15
1.09
1.10
3.28
2.98
6.89
1.17
2.28
5.06
3.25
1.33
5.10
2.80
3.03
5.46
3.05
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

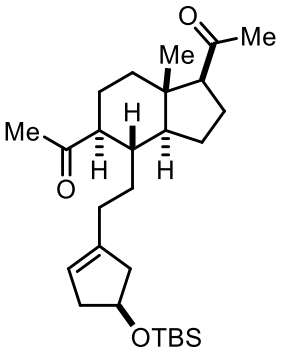

213.45
171.20
142.61
138.13
129.72
120.42
74.76
56.74
56.04
53.10
51.40
42.28
40.56
39.71
36.62
32.02
26.90
26.32
25.56
21.34
21.26
19.12
12.41
12.15
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
Me
Me
Me
Me
H
Me
H
H
O
OH

30

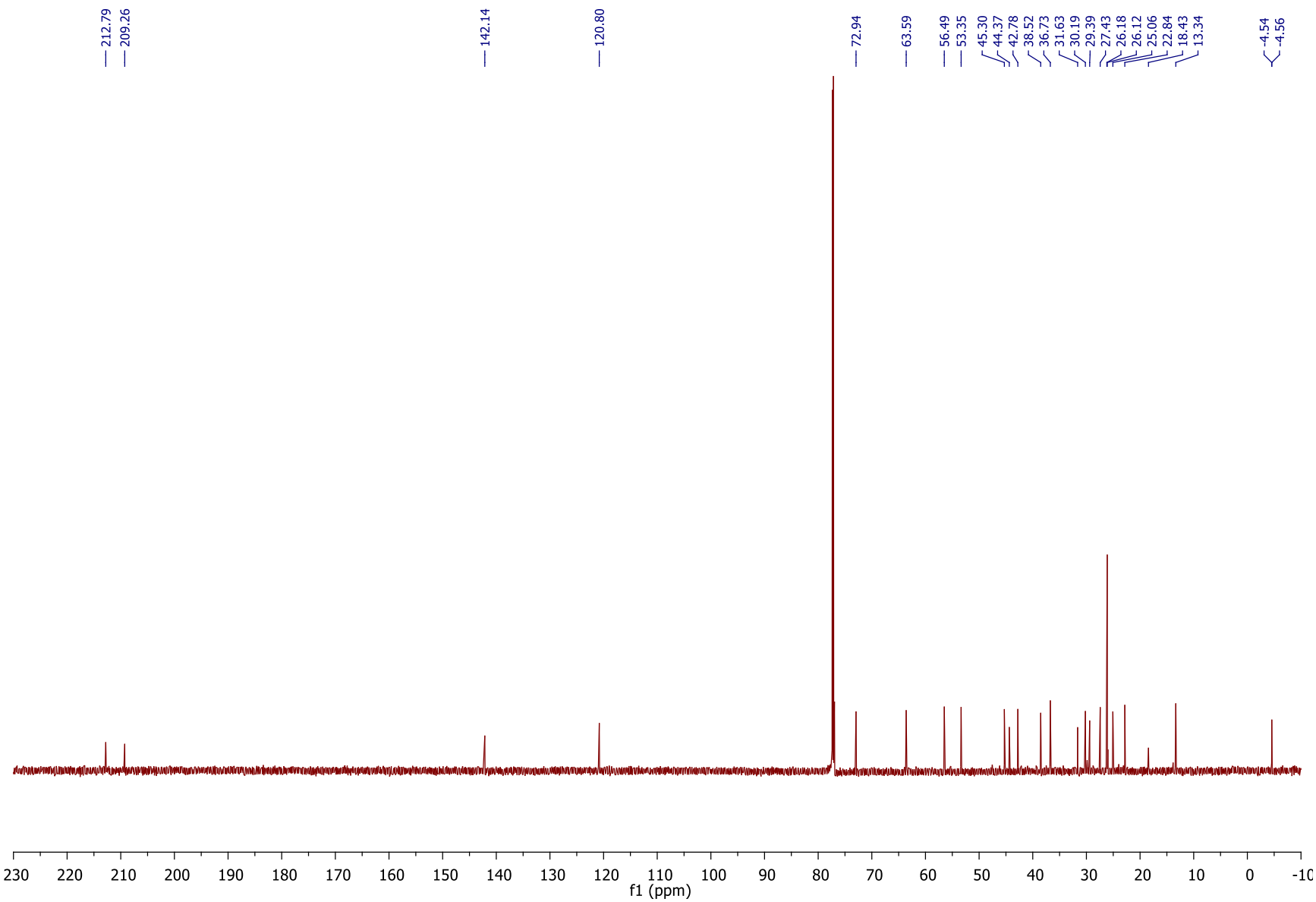
5.23
5.16
5.14
5.13
5.12
5.04
5.03
5.00
4.46
2.29
2.26
2.23
2.15
2.13
2.04
2.00
1.99
1.82
1.66
1.62
1.58
1.56
1.53
1.41
1.40
1.39
1.36
1.16
1.01
1.01
0.84
0.84
0.81
0.80
0.79
0.79
0.74
0.97
1.03
1.02
0.94
1.05
1.05
2.15
3.72
4.08
1.23
7.36
9.83
3.00
11.18
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

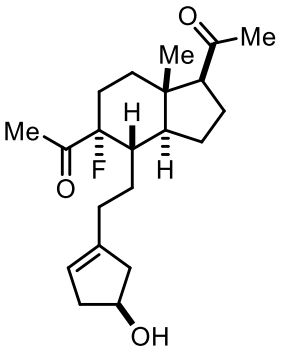

213.60
142.63
138.14
129.69
120.44
72.25
56.70
56.02
53.08
51.38
45.46
42.93
40.56
36.61
32.01
27.04
26.31
25.55
21.34
21.25
19.11
12.41
12.15
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
Me
Me
H
Me
O
H
H
OTBS

32

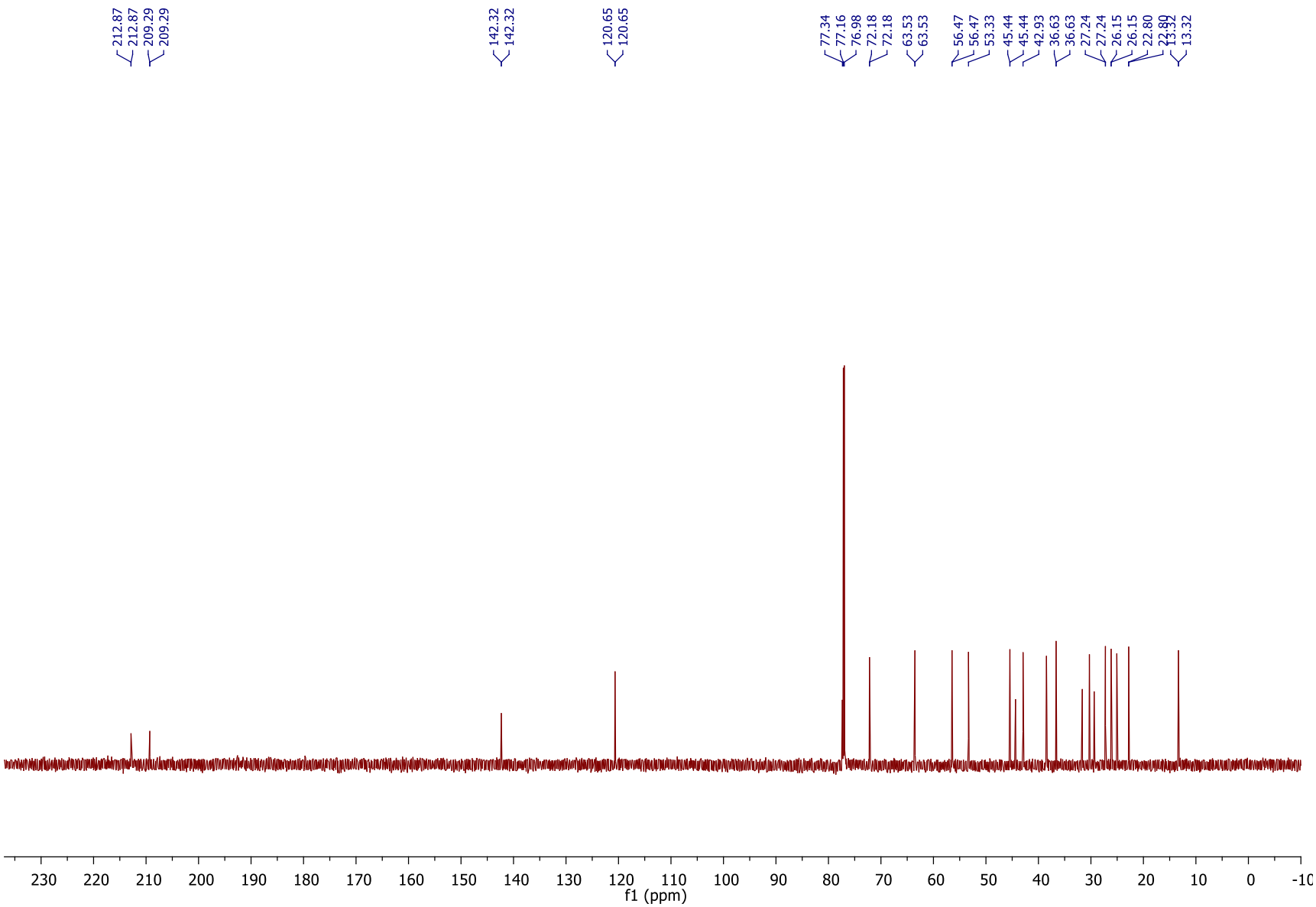
5.19
4.51
4.50
4.49
4.48
4.48
2.54
2.52
2.50
2.16
2.12
2.06
2.04
1.95
1.74
1.72
1.56
1.43
1.37
1.36
1.35
1.33
0.88
0.69
0.05
0.79
0.78
1.63
0.72
0.76
4.86
3.56
1.12
1.80
4.82
5.32
8.84
3.00
5.42
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

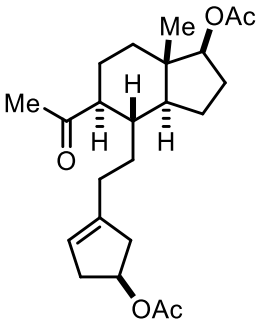

212.79
209.26
142.14
120.80
72.94
63.59
56.49
53.35
45.30
44.37
42.78
38.52
36.73
31.63
30.19
29.39
27.43
26.18
26.12
25.06
22.84
18.43
13.34
-4.54
-4.56
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
Me
Me
H
Me
F
H
O
OH

34

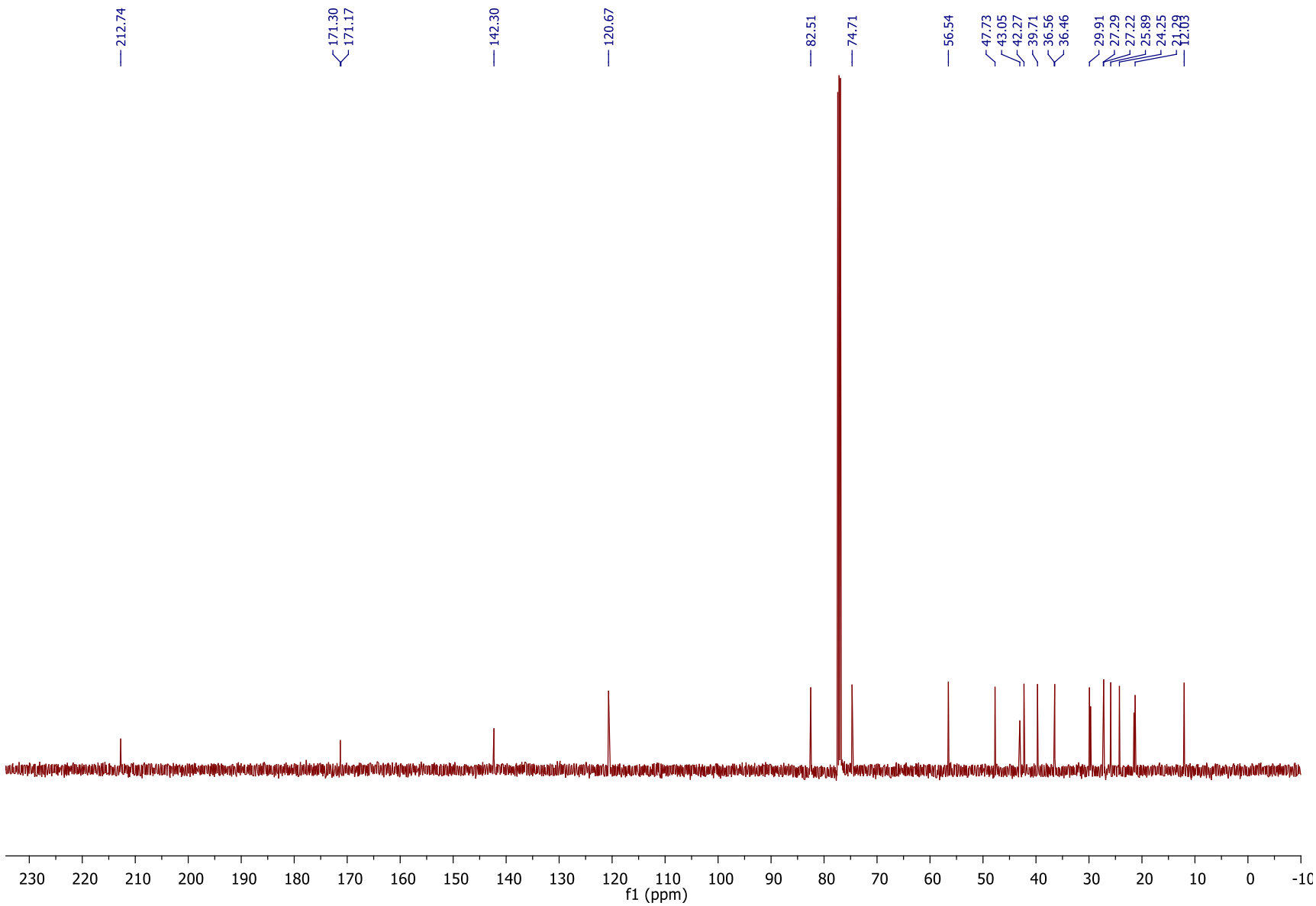
5.25
4.48
4.47
2.54
2.53
2.27
2.24
2.16
2.14
2.13
2.07
2.05
2.01
1.76
1.76
1.57
1.56
1.55
1.44
1.44
1.42
1.42
0.89
1.08
1.09
1.02
1.96
1.04
1.00
10.03
1.03
3.17
3.26
5.03
2.53
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

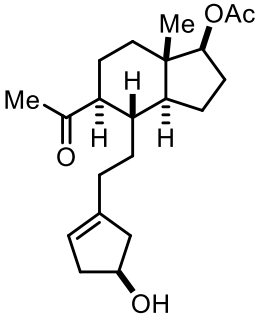

212.87
212.87
209.29
209.29
142.32
142.32
120.65
120.65
77.34
77.16
76.98
72.18
72.18
63.53
63.53
56.47
56.47
53.33
45.44
45.44
42.93
36.63
36.63
27.24
27.24
26.15
22.80
13.32
13.32
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
OAc
H
Me
O
H
H
OAc

36

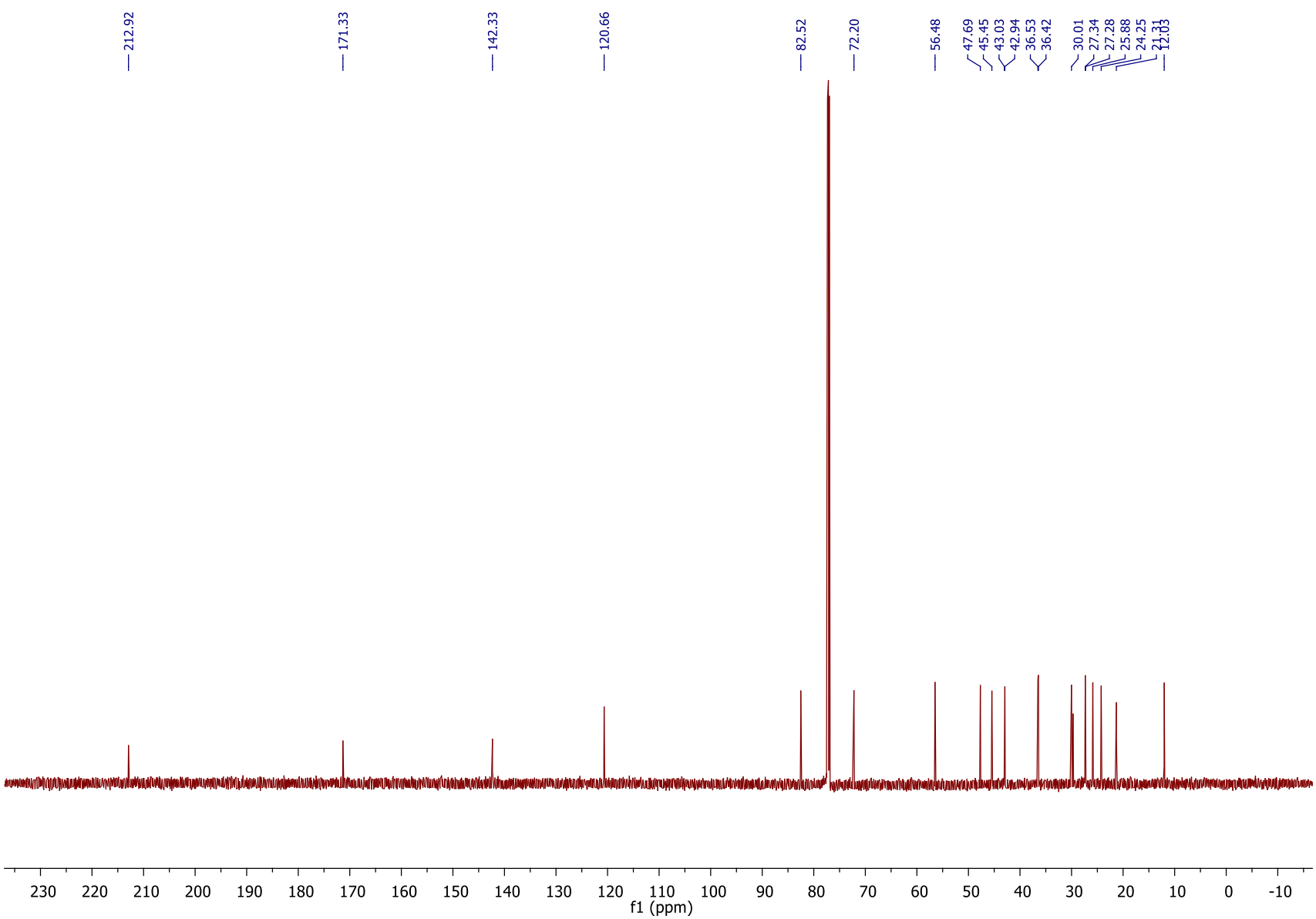
5.31
5.25
4.63
4.62
4.60
2.34
2.30
2.24
2.20
2.16
2.04
2.02
2.00
1.98
1.88
1.79
1.76
1.72
1.57
1.54
1.53
1.51
1.44
1.42
1.41
1.40
1.25
1.22
1.20
1.18
1.18
0.85
0.92
0.89
1.00
1.92
6.27
6.59
1.17
3.02
3.50
3.04
2.45
2.76
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

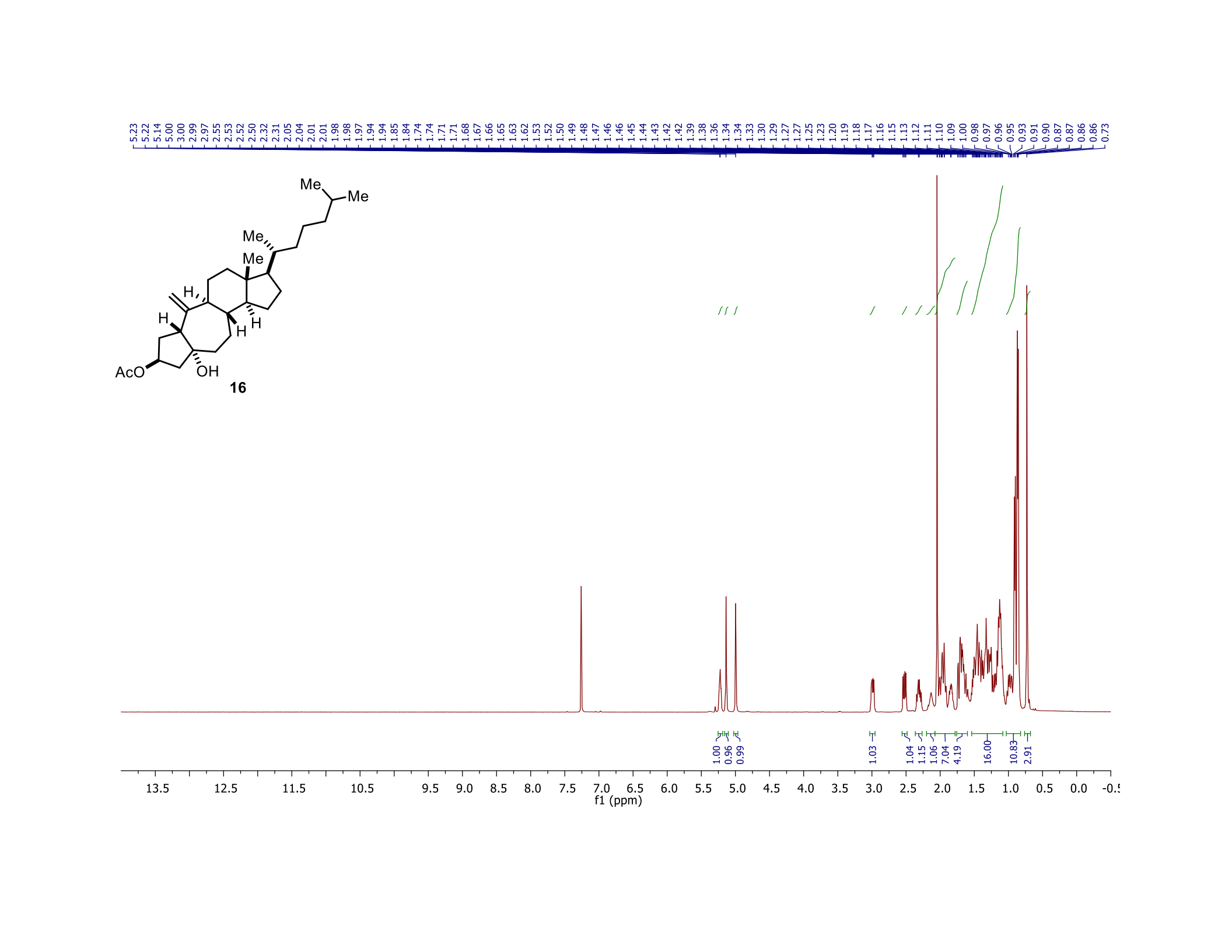

212.74
171.30
171.17
142.30
120.67
82.51
74.71
56.54
47.73
43.05
42.27
39.71
36.56
36.46
29.91
27.29
27.22
25.89
24.25
21.29
21.03
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

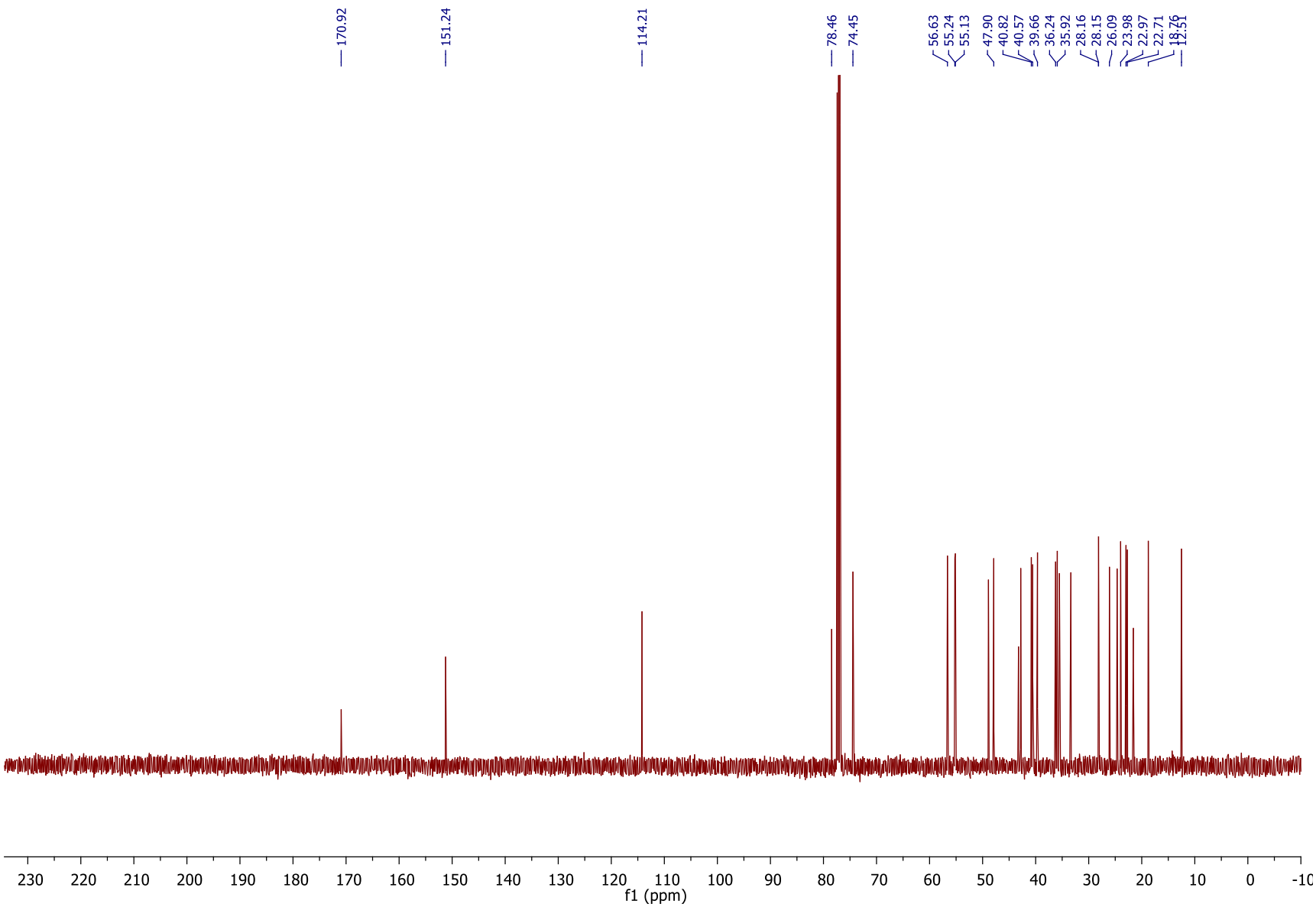

Me
OAc
H
Me
O
H
H
OH

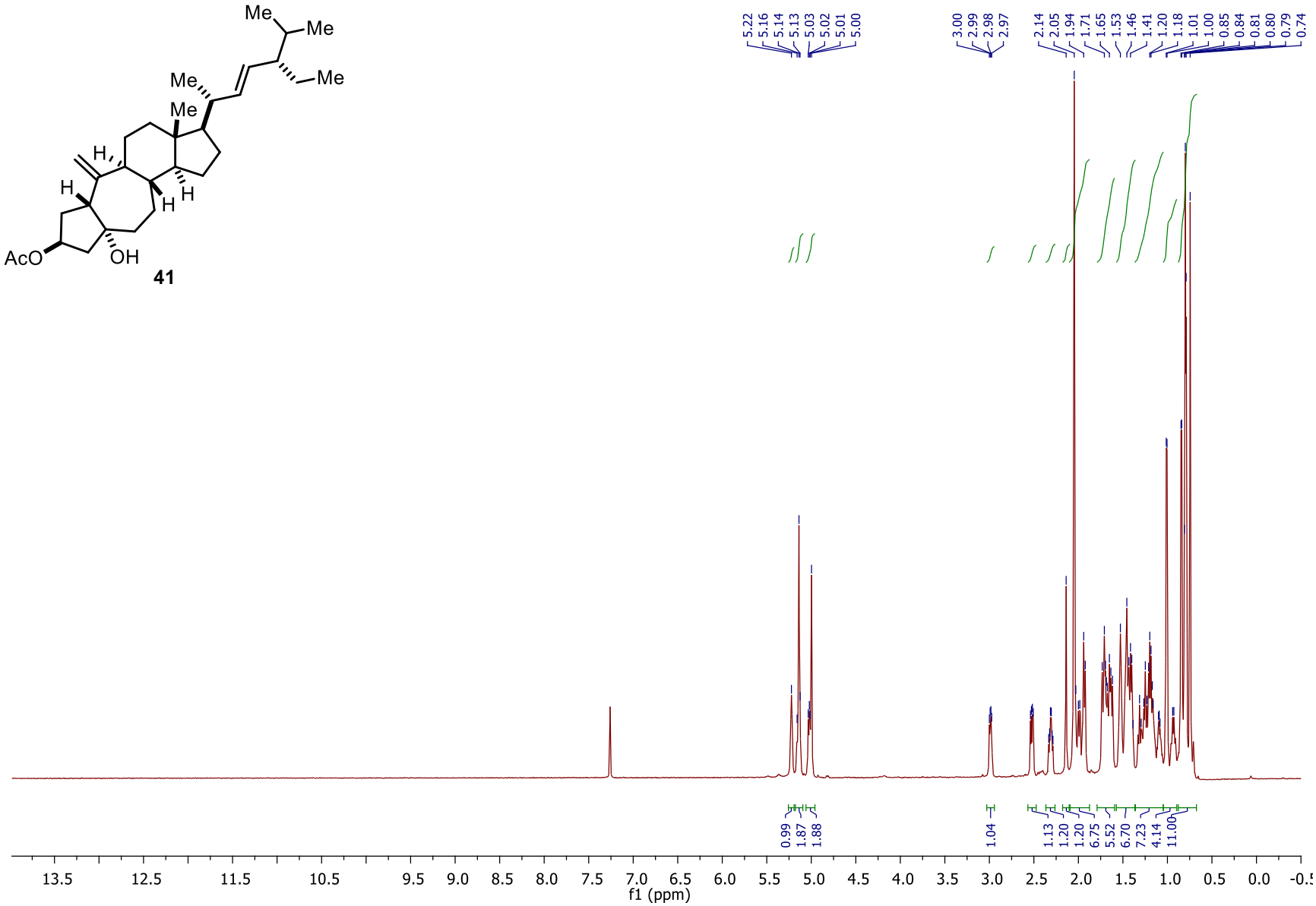
38

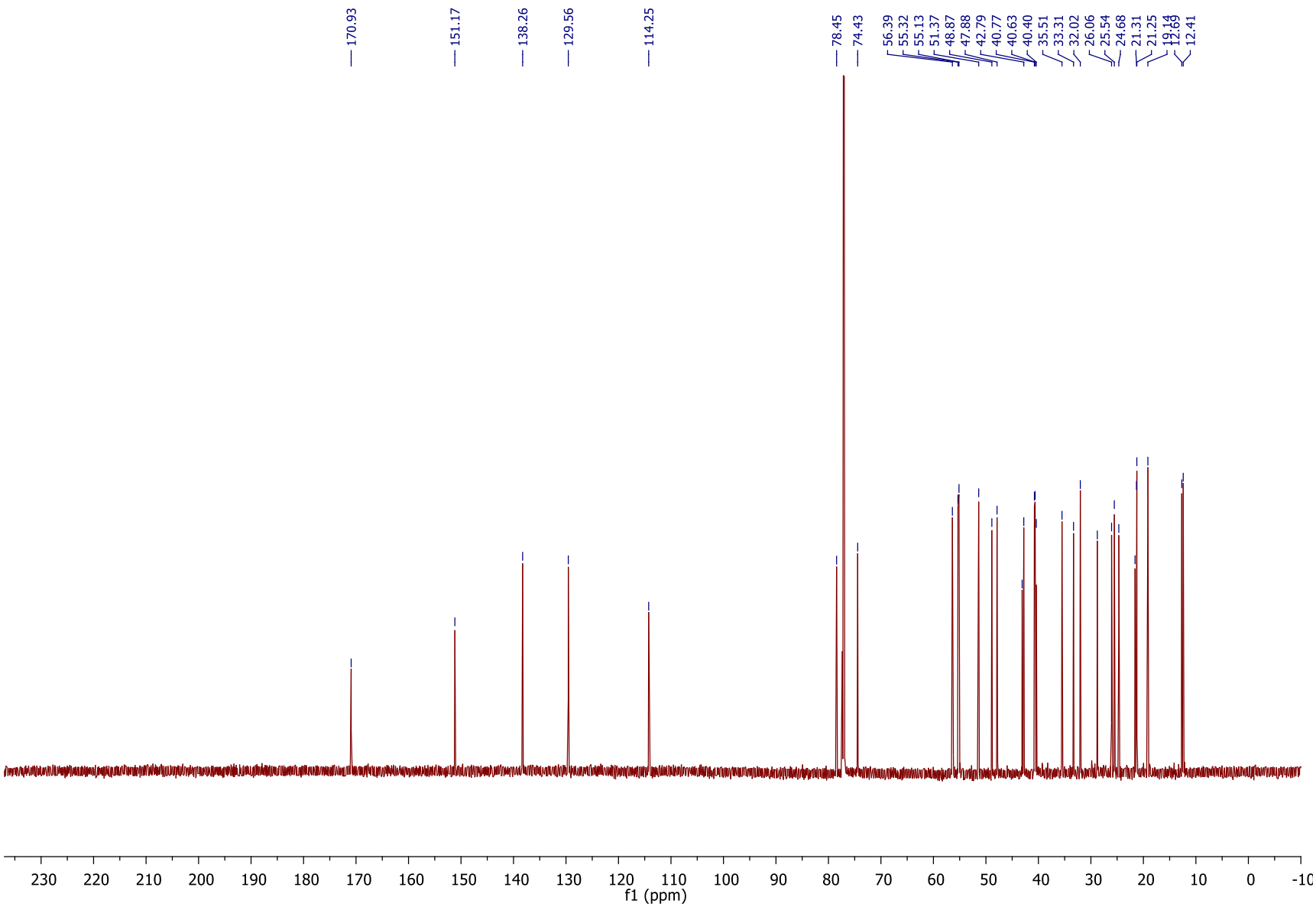
5.25
4.63
4.62
4.61
4.48
2.31
2.27
2.24
2.16
2.14
2.04
1.99
1.78
1.76
1.72
1.70
1.55
1.53
1.52
1.43
1.41
1.22
1.20
0.85
1.00
1.04
0.95
1.00
1.09
2.21
4.61
5.07
1.18
3.38
3.91
3.29
2.20
2.78
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

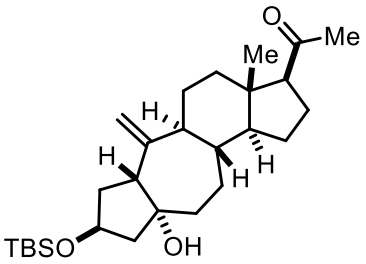

212.92
171.33
142.33
120.66
82.52
72.20
56.48
47.69
45.45
43.03
42.94
36.53
36.42
30.01
27.34
27.28
25.88
24.25
21.31
12.03
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
Me
Me
Me
H
H
H
H
AcO
OH
16
f1 (ppm)


170.92
151.24
114.21
78.46
74.45
56.63
55.24
55.13
47.90
40.82
40.57
39.66
36.24
35.92
28.16
28.15
26.09
23.98
22.97
22.71
18.76
12.51
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

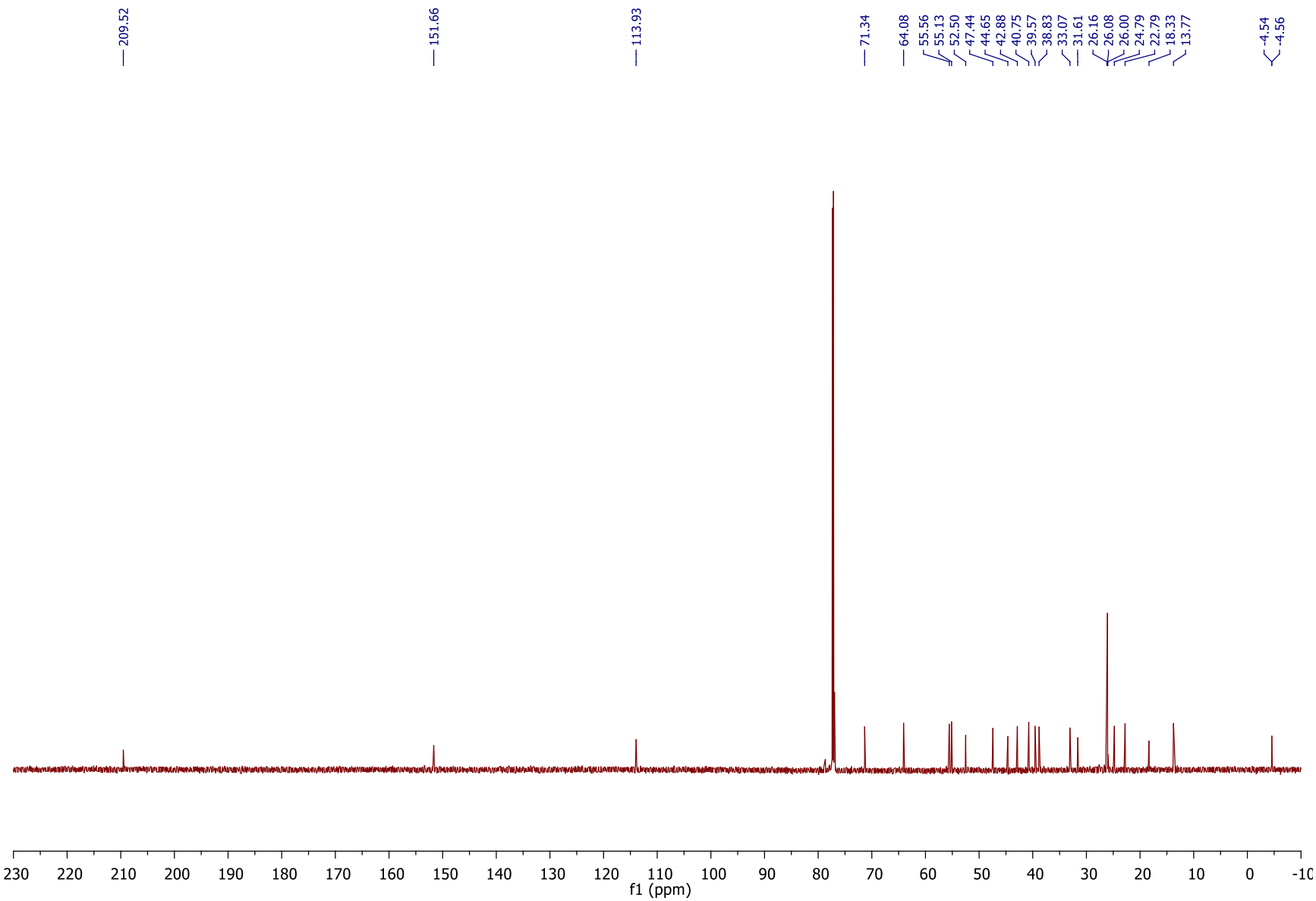

Me
Me
Me
Me
Me
H
H
H
H
AcO
OH
41
5.22
5.16
5.14
5.13
5.03
5.02
5.01
5.00
3.00
2.99
2.98
2.97
2.14
2.05
1.94
1.71
1.65
1.53
1.46
1.41
1.20
1.18
1.01
1.00
0.85
0.84
0.81
0.80
0.79
0.74
0.99
1.87
1.88
1.04
1.13
1.20
1.20
6.75
5.52
6.70
7.23
4.14
11.00
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

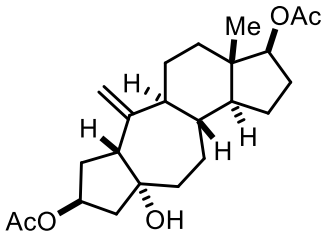

170.93
151.17
138.26
129.56
114.25
78.45
74.43
56.39
55.32
55.13
51.37
48.87
47.88
42.79
40.77
40.63
40.40
35.51
33.31
32.02
26.06
25.54
24.68
21.31
21.25
19.14
19.09
12.41
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
Me
Me
H
H
H
H
TBSO
OH

42

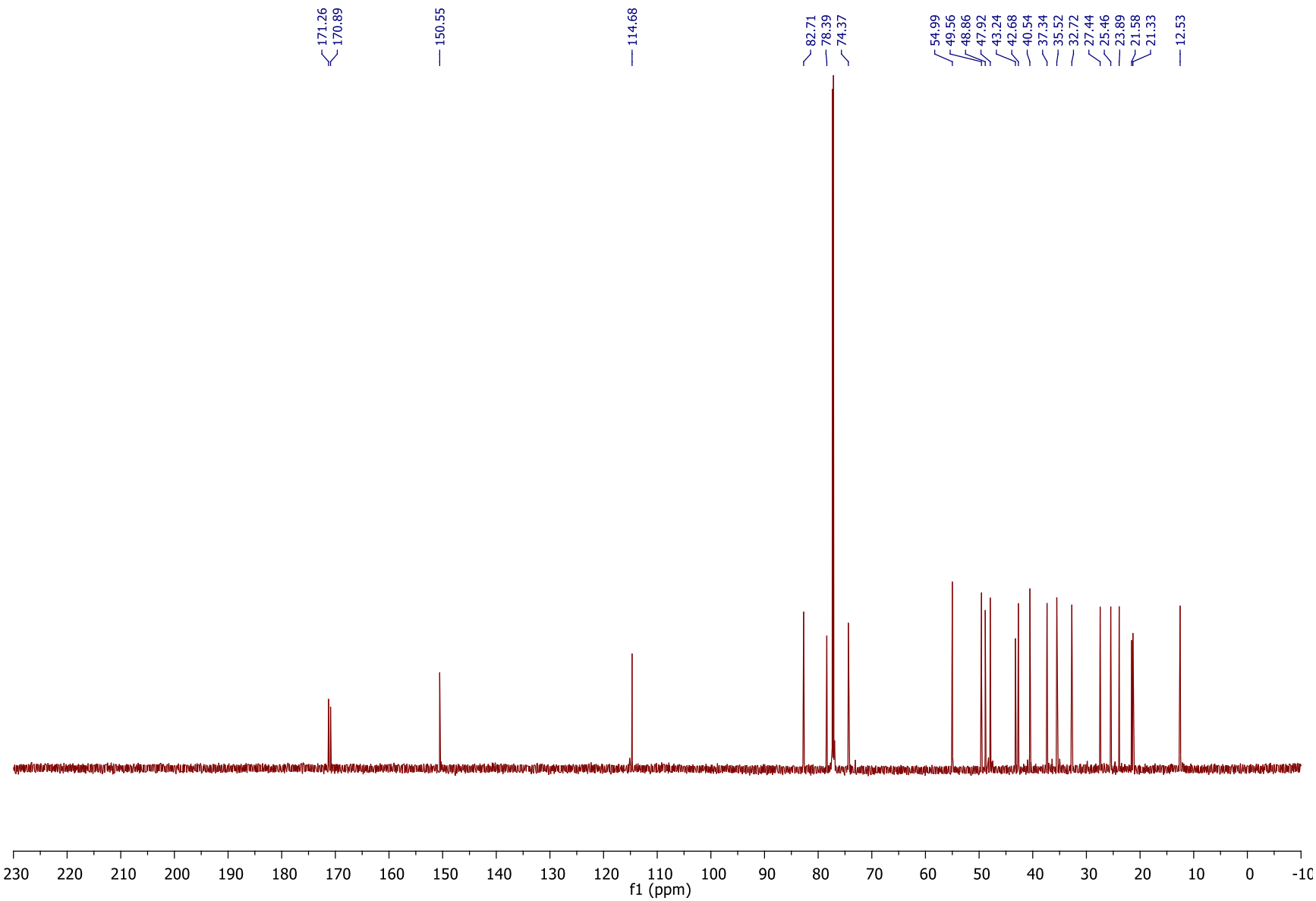
5.14
5.01
4.40
4.40
3.14
3.13
3.12
3.11
2.56
2.12
1.98
1.97
1.67
1.66
1.65
1.56
1.47
1.45
0.88
0.68
0.04
1.00
1.05
1.11
0.97
1.06
1.04
2.13
2.89
2.95
1.22
3.15
3.88
3.20
1.15
1.34
1.05
8.72
2.69
5.89
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

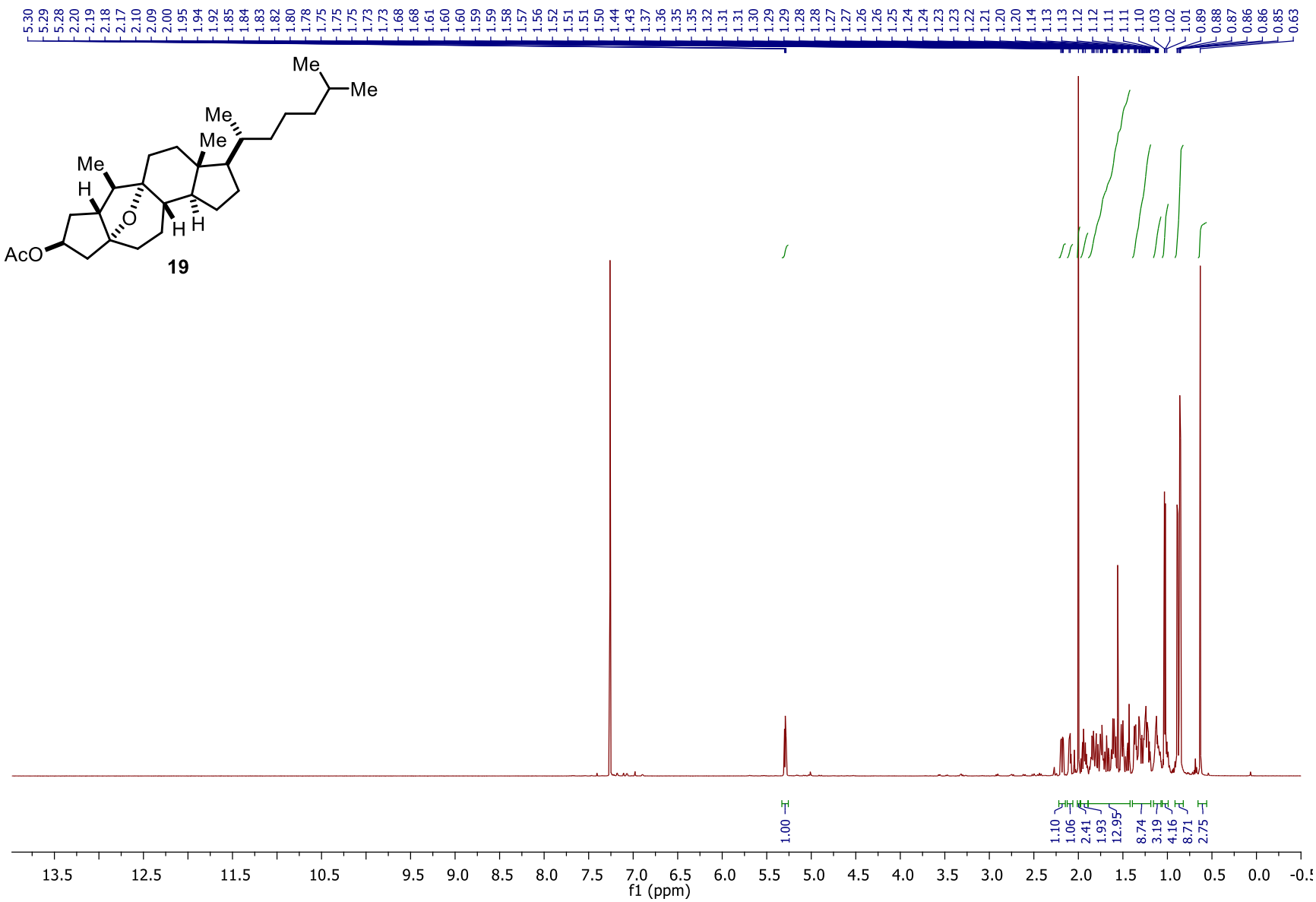

209.52
151.66
113.93
71.34
64.08
55.56
55.13
52.50
47.44
44.65
42.88
40.75
39.57
38.83
33.07
31.61
26.16
26.08
26.00
24.79
22.79
18.33
13.77
-4.54
-4.56
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

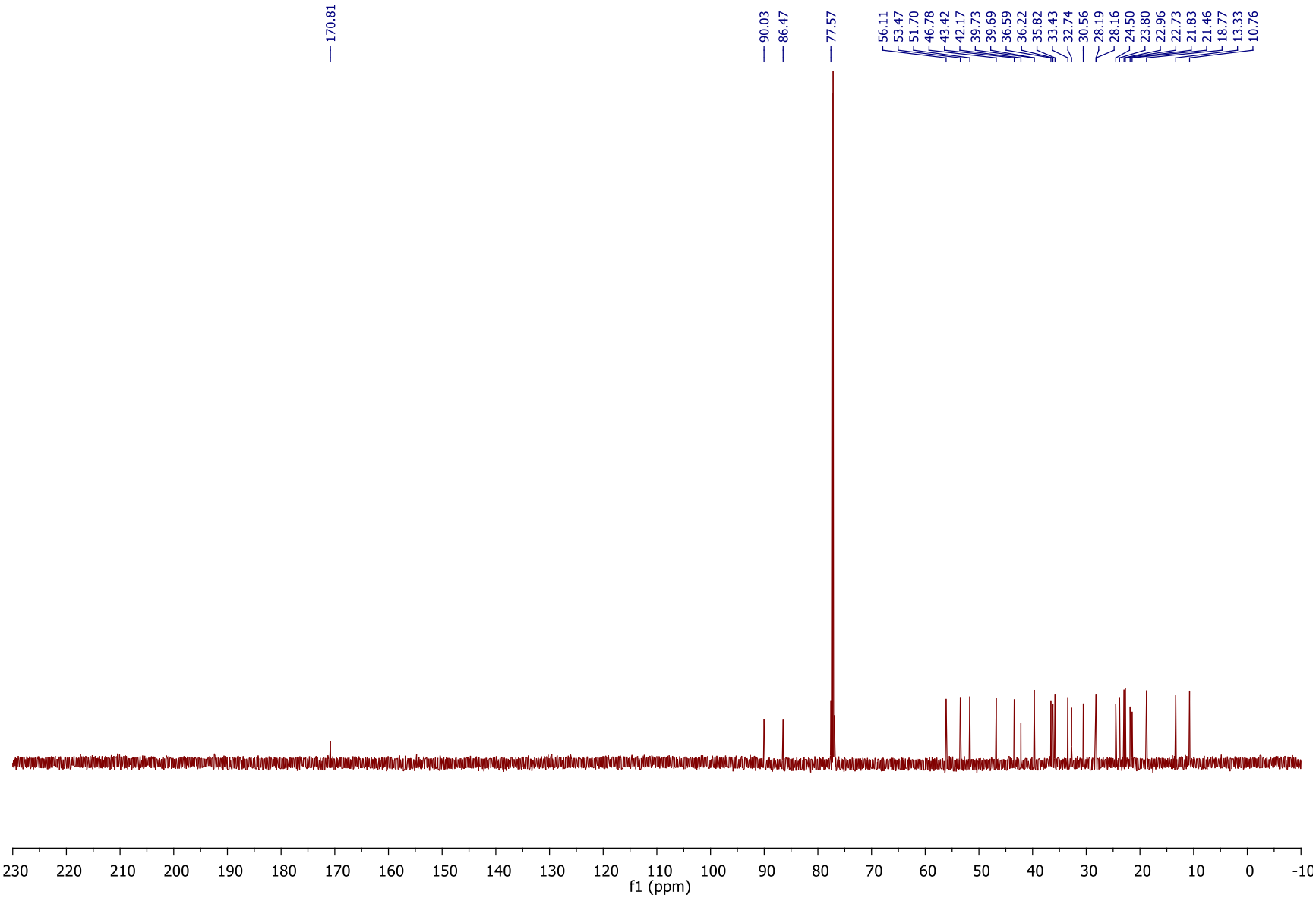

Me
OAc
H
H
H
H
AcO
OH

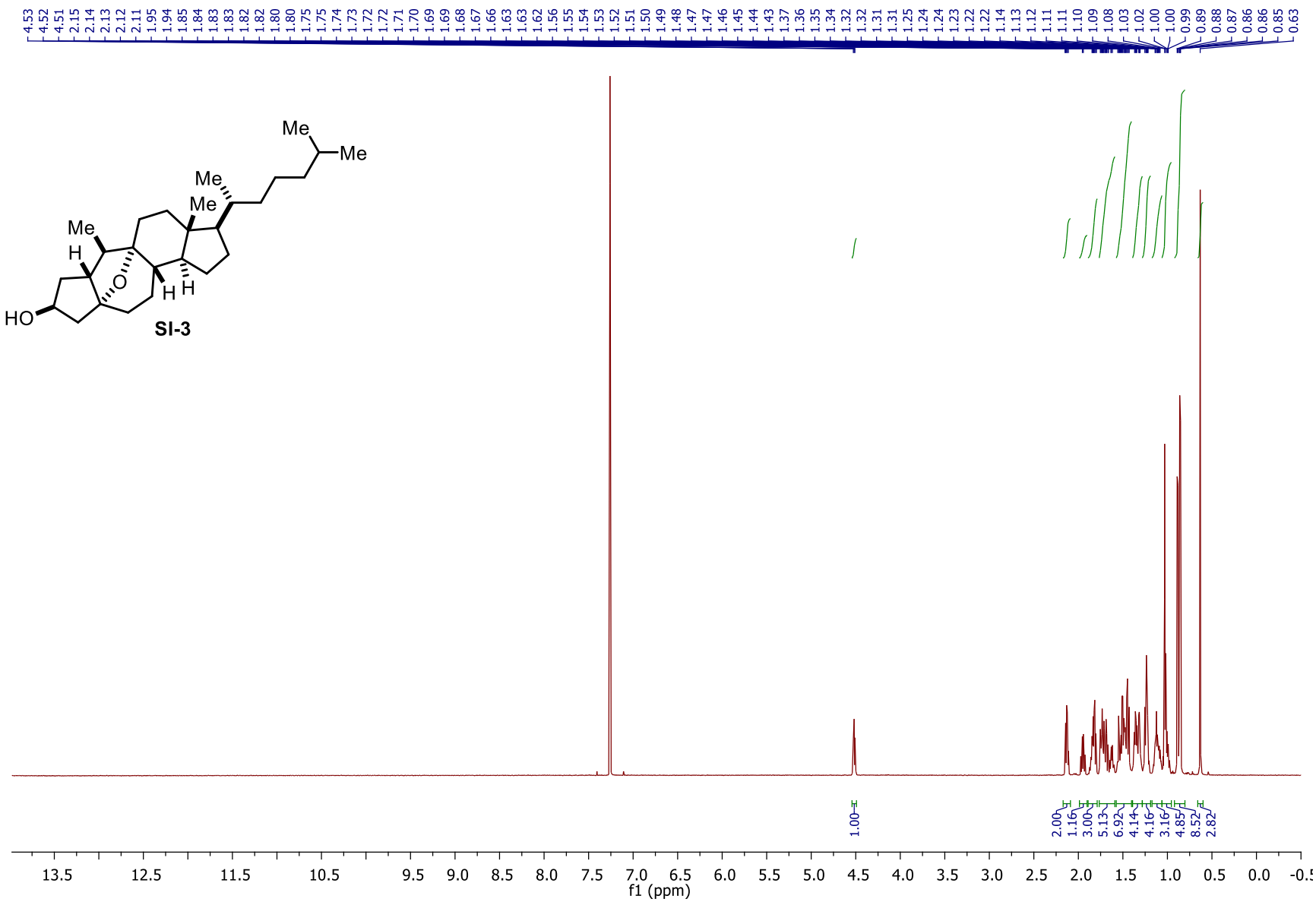
43

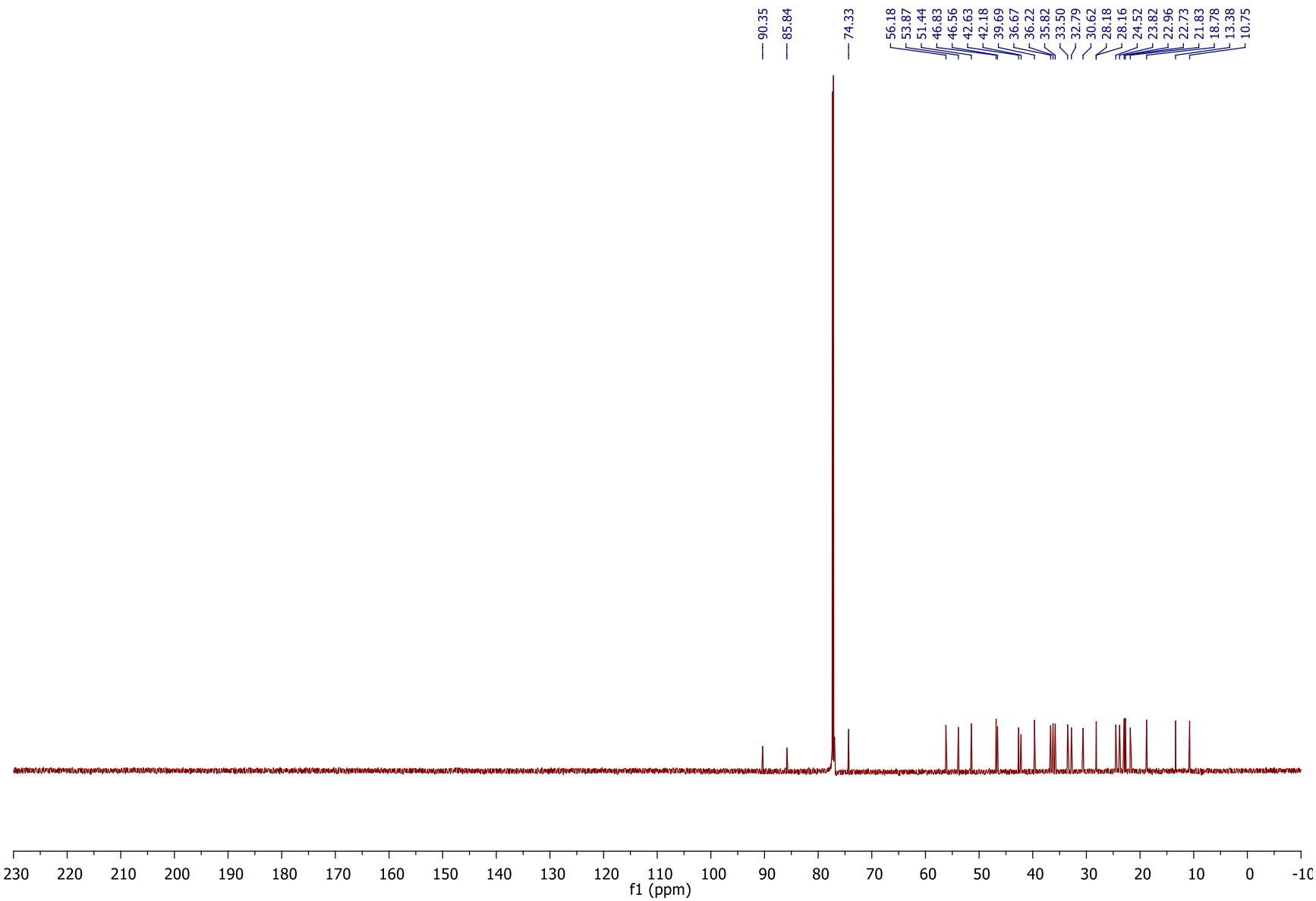
5.23
5.16
5.02
4.64
4.63
4.62
2.99
2.98
2.97
2.96
2.13
2.05
2.04
2.03
1.74
1.71
1.55
1.52
1.50
1.49
1.48
1.46
1.45
1.44
1.34
1.32
1.25
0.87
0.96
1.08
0.99
1.04
0.96
1.00
1.11
2.36
6.69
1.22
5.25
4.80
2.32
1.47
1.23
3.26
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


171.26
170.89
150.55
114.68
82.71
78.39
74.37
54.99
49.56
48.86
47.92
43.24
42.68
40.54
37.34
35.52
32.72
27.44
25.46
23.89
21.58
21.33
12.53
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


5.30 5.29 5.28 2.20 2.19 2.18 2.17 2.10 2.09 2.00 1.95 1.94 1.92 1.85 1.84 1.83 1.82 1.80 1.78 1.75 1.75 1.75 1.73 1.73 1.68 1.68 1.61 1.60 1.60 1.59 1.59 1.58 1.57 1.56 1.52 1.51 1.51 1.50 1.44 1.43 1.37 1.36 1.35 1.35 1.32 1.31 1.31 1.30 1.29 1.29 1.28 1.28 1.27 1.27 1.26 1.26 1.25 1.24 1.24 1.23 1.23 1.22 1.21 1.20 1.20 1.14 1.13 1.13 1.12 1.12 1.11 1.11 1.10 1.03 1.02 1.01 0.89 0.88 0.87 0.86 0.86 0.85 0.63
Me
Me
Me
Me
Me
H
O
H
H
AcO
19
1.00
1.10
1.06
2.41
1.93
12.95
8.74
3.19
4.16
8.71
2.75
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


170.81
90.03
86.47
77.57
56.11
53.47
51.70
46.78
43.42
42.17
39.73
39.69
36.59
36.22
35.82
33.43
32.74
30.56
28.19
28.16
24.50
23.80
22.96
22.73
21.83
21.46
18.77
13.33
10.76
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


4.53 4.52 4.51 2.15 2.14 2.13 2.12 2.11 1.95 1.94 1.85 1.84 1.83 1.83 1.82 1.82 1.80 1.80 1.75 1.74 1.73 1.72 1.72 1.71 1.70 1.69 1.69 1.68 1.67 1.66 1.63 1.63 1.62 1.56 1.55 1.54 1.53 1.52 1.51 1.50 1.49 1.48 1.47 1.47 1.46 1.45 1.44 1.43 1.37 1.36 1.35 1.34 1.32 1.32 1.31 1.31 1.25 1.24 1.24 1.23 1.22 1.22 1.14 1.13 1.12 1.11 1.11 1.10 1.09 1.08 1.03 1.02 1.00 1.00 0.99 0.89 0.88 0.87 0.86 0.86 0.85 0.63
Me
Me
Me
Me
Me
H
O
H
H
HO
SI-3
1.00
2.00 1.16 3.00 5.13 6.92 4.14 4.16 3.16 4.85 8.52 2.82
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


90.35
85.84
74.33
56.18
53.87
51.44
46.83
46.56
42.63
42.18
39.69
36.67
36.22
35.82
33.50
32.79
30.62
28.18
28.16
24.52
23.82
22.96
22.73
21.83
18.78
13.38
10.75
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)