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I. General Information

A. Instrumentation and Methods (Kunming Institute of Botany)

Optical rotations were measured with a Jasco P-1020 polarimeter. UV spectra were obtained using a Shimadzu UV-2401 PC spectrophotometer. IR spectra were obtained with a Bruker FT-IR Tensor 27 spectrometer using KBr pellets. 1D and 2D NMR spectra in $CDCl_3$ were recorded on an AVANCE III 500 MHz spectrometer. HREIMS were recorded on an Agilent 1290 UPLC/6540 Q-TOF mass spectrometer. ECD spectra were recorded on an Applied Photophysics spectropolarimeter. Column chromatography (CC) was performed on silica gel (200–300 mesh, Qingdao Marine Chemical Ltd., Qingdao, China) and Sephadex LH-20 (Pharmacia Biotech). Semi-preparative HPLC were performed on an Agilent 1260 instrument with a ZORBAX SBC18 column (9.4 × 250 mm, 5 μm). TLC (GF_{254}, Qingdao Haiyang Chemical Co., Ltd. Qingdao, China or RP-18 F_{254}, Merck, Darmstadt, Germany) was used to check fractions, and spots were detected by UV light (254 nm) which was followed by dipping in 10% H_2SO_4 in EtOH and heating at 110 °C. Theoretical calculations of ECD spectra for compounds **1**–**3** were performed with the Gaussian 09 program package. 3D structures of compounds were first established according to the ROESY spectra (see sections II-C and II-D). Conformational analyses were performed using the CONFLEX 8A program with an energy cutoff of 1.0 kcal/mol. Conformers with relative energies of less than 1.0 kcal/mol were first optimized using DFT calculations at the B3LYP/6-31+G(d) level of theory in the gas phase. ECD computations of compounds **1**–**3** were performed with DFT calculations at the B3LYP/6-311++G(2d,p) level of theory, and ECD spectra were produced using a SpecDis 1.6 software.

B. Instrumentation and Methods (Boston University)

^{1}H NMR spectra were recorded at ambient temperature using a Varian 400 MHz or 500 MHz spectrometer with $CDCl_3$ (Cambridge Isotope Laboratories, Inc.) as the solvent unless otherwise stated. ^{13}C NMR spectra were recorded at 100 or 125 MHz at ambient temperature with $CDCl_3$ as the solvent unless otherwise stated. Chemical shifts are reported in parts per million relative to $CDCl_3$ (^{1}H, δ 7.26; ^{13}C, δ 77.16). Data for ^{1}H NMR are reported as follows: chemical shift, integration, multiplicity (br = broad, ovrlp = overlapping, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constants. All ^{13}C NMR spectra were recorded with complete

proton decoupling. Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR spectrophotometer. High-resolution mass spectra were obtained at the Boston University Chemical Instrumentation Center (CIC) using a Waters Q-TOF mass spectrometer. Melting points were recorded on a Mel-temp apparatus (Laboratory Devices) and are uncorrected. Optical rotations were measured with a Rudolph Autopol II polarimeter (ambient temperature, 589 nm polarimeter cell). ECD spectra were recorded on an Applied Photophysics CS/2 Chirascan. Analytical liquid chromatography was performed using a Waters ACQUITY UPLC® system equipped with PDA, ELS, and SQ detectors. Analytical thin layer chromatography (TLC) was performed using 0.25 mm silica gel 60-F plates (Silicycle, Inc.). Flash chromatography was performed using 200-400 mesh silica gel (Sorbent Technologies, Inc.). Preparative TLC was conducted with glass-backed 250 μm or 1000 μm silica gel 60-F plates (Silicycle, Inc.). Preparative HPLC was conducted using a PLC 2020 Personal Purification System (Gilson, Inc.). Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise stated. All other reactions were carried out in oven-dried glassware under an argon/nitrogen atmosphere unless otherwise noted. White LED lights (LE 16.4ft Waterproof Flexible LED Light Strip, 300 Units SMD 2835 LED, 6000K Daylight White) were purchased from Lighting Ever via Amazon Electric Commerce Company. The Scilligence ELN Reaction Planner (Scilligence Corp.) was used for experimental procedure planning.

C. Reagents and Solvents

HPLC grade methylene chloride, tetrahydrofuran, benzene, and toluene were purchased from Fisher and VWR and were purified and dried by passing through a PURE SOLV® solvent purification system (Innovative Technology, Inc.). Reagents were purchased from Strem, Sigma-Aldrich (now Millipore-Sigma), Acros, TCI America, Indofine, and Alfa Aesar and were used as received without further purification.

II. Isolation and Structure Elucidation (Kunming Institute of Botany & Southwest Forestry University)

A. Plant Material

Twigs and leaves of *Rhodomyrtus tomentosa* were collected from the Hainan province of China in October 2015, and were authenticated by Dr. Sheng-Zhuo Huang (Institute of Tropical Bioscience and Biotechnology, Chinese Academy of Tropical Agricultural Sciences). A voucher specimen was deposited at the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences.

B. Extraction and Isolation

The air-dried twigs and leaves of *Rhodomyrtus tomentosa* (30 kg) were powdered and extracted with 50 L of petroleum ether (PE) at room temparature (48 h × 3) to give a crude extract. The PE extract (2110 g) was subjected to silica gel column chromatography (CC) eluted with PE–EtOAc (50:1→1:1, v/v) to obtain six fractions (A–F). Fr. E (12.3 g) was chromatographed on silica gel CC (PE–Me_2CO, 100:1→10:1, v/v) to yield five fractions (E1–E5). Fr. E2 (300 mg) which were applied to a Sephadex LH-20 column ($CHCl_3$−MeOH, 1:1, v/v), followed by semi-preparative HPLC using CH_3CN–H_2O (85:15, v/v) as the mobile phase, to afford compounds **5** (7.6 mg), **6** (3.5 mg), and **7** (3.8 mg). Similarly, Fr. E4 (1.2 g) was purified on a Sephadex LH-20 column ($CHCl_3$−MeOH, 50:50, v/v) and preparative HPLC (CH_3CN−H_2O, 80:20, v/v), to yield compounds **8** (3.3 mg), **9** (2.4 mg), **10** (35.2 mg), and **11** (4.1 mg).

C. Structure Elucidation of 5–7:

Rhodomyrtusial A (5): Colorless gum; $[\alpha]_D^{17}$ +72.6 (*c* 0.10 mg/mL, MeOH); UV (MeOH) λ_{max} (log ε) 203 (3.84), 268 (4.04) nm; ECD (MeOH) λ_{max} nm ($\Delta\varepsilon$) 235 (–0.86), 274 (+8.81), 306 (–2.72) nm; IR (KBr) ν_{max} 3440, 2965, 1722, 1660, 1617, 1465, 1184 cm^{-1}; ^1H (500 MHz) and ^{13}C NMR (125 MHz) data, see Table S1; (+)-HREIMS *m/z* 469.3303 $[M + H]^+$ (calcd for $C_{30}H_{45}O_4$, 469.3312).

Rhodomyrtusial B (6): Colorless gum; $[\alpha]_D^{17}$ –82.8 (*c* 0.10 mg/mL, MeOH); UV (MeOH) λ_{max} (log ε) 203 (3.84), 268 (4.04) nm; ECD (MeOH) λ_{max} nm ($\Delta\varepsilon$) 228 (+0.53), 272 (–8.97), 304 (+4.67) nm; IR (KBr) ν_{max} 3442, 2958, 1723, 1662, 1618, 1466, 1182 cm^{-1}; ^1H (500 MHz) and

^{13}C NMR (125 MHz) data, see Table S1; (+)-HREIMS *m/z* 491.3139 $[M + Na]^+$ (calcd for $C_{30}H_{44}O_4Na$, 491.3137).

Rhodomyrtusial C (7): Colorless gum; $[\alpha]_D^{24}$ –53.8 (*c* 0.10 mg/mL, MeOH); UV (MeOH) λ_{max} (log ε) 203 (3.82), 268 (4.01) nm; ECD (MeOH) λ_{max} nm ($\Delta\varepsilon$) 267 (–19.57), 302 (+5.17) nm; IR (KBr) ν_{max} 3441, 2959, 1721, 1663, 1620, 1465, 1181 cm^{-1}; ^{1}H (500 MHz) and ^{13}C NMR (125 MHz) data, see Table S1; (+)-HREIMS *m/z* 469.3323 $[M + H]^+$ (calcd for $C_{30}H_{45}O_4$, 469.3312).

Table S1. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data for **5**–**7** in $CDCl_3$

	5		**6**		**7**	
no.	δ_C, type	δ_H (*J* in Hz)	δ_C, type	δ_H (*J* in Hz)	δ_C, type	δ_H (*J* in Hz)
1	175.7, C		176.0, C		177.4, C	
2	45.4, C		45.4, C		45.5, C	
3	213.6, C		213.3, C		213.4, C	
4	55.3, C		55.7, C		55.6, C	
5	193.3, C		193.6, C		194.4, C	
6	115.9, C		115.8, C		112.1, C	
7	52.7, CH	3.16, d (8.3)	52.2, CH	3.18, d (9.9)	48.6, CH	3.64, d (9.5)
8	127.3, C		125.8, C		127.1, C	
9	35.8, CH	1.94, sept (6.8)	37.1, CH	1.87, sept (6.8)	35.2, CH	2.11, sept. (6.8)
10	16.6, CH_3	0.99 d (6.8)	16.3, CH_3	1.07, d (6.8)	16.3, CH	0.96, d (6.8)
11	16.7, CH_3	0.93, d (6.8)	16.8, CH_3	0.90, d (6.8)	16.4, CH_3	0.92, d (6.8)
12	23.6, CH_3	1.40, s	23.6, CH_3	1.43, s	24.3, CH_3	1.39, s
13	24.8, CH_3	1.40, s	25.2, CH_3	1.47, s	23.9, CH_3	1.43, s
14	23.9, CH_3	1.33, s	23.8, CH_3	1.33, s	23.0, CH_3	1.33, s
15	25.1, CH_3	1.35, s	24.8, CH_3	1.34, s	26.2, CH_3	1.40, s
1′	57.7, CH	1.53, m	53.5, CH	1.50, td (9.7, 1.5)	59.9, CH	1.48, m
2′a	22.8, CH_2	1.65, m	22.9, CH_2	1.50, m	23.4, CH_2	1.57, m
2′b		1.32, m		1.35, m		1.34, m
3′a	41.4, CH_2	2.40, m	39.9, CH_2	2.35, dd (15.5, 9.2)	44.5, CH_2	1.97, dd (13.9, 9.5)
3′b		1.67, m		1.45, m		1.44, m
4′	89.7, C		88.5, C		88.6, C	
5′	50.1, CH	1.97, m	51.3, CH	2.16, dt (9.9, 3.5)	45.0, CH	2.05 m,
6′a	29.8, CH_2	1.88, m	29.1, CH_2	2.05, m	29.6, CH_2	1.25 2H, m
6′b		1.73, m		1.71, m		
7′a	35.2, CH_2	2.43, m	33.1, CH_2	2.18, m	36.9, CH_2	2.61, m
7′b		1.87, m		2.04, m		2.09, m
8′	152.6, C		154.2, C		152.3, C	
9′	42.7, CH	2.33, q (9.0)	43.4, CH	2.61, q (8.6)	42.3, CH	2.40, q (9.0)
10′a	36.1, CH_2	1.68, t (10.6)	40.3, CH_2	1.88, t (7.5)	36.2, CH_2	1.79, t (10.5)
10′b		1.55, dd (10.6, 7.8)		1.49, m		1.59, dd (10.5, 7.8)
11′	33.7, C		33.3, C		34.4, C	
12′	30.1, CH_3	0.94, s	29.5, CH_3	0.94, s	29.8, CH_3	0.99, s
13′	22.2, CH_3	0.90, s	22.6, CH_3	0.89, s	21.9, CH_3	0.97, s
14′	22.5, CH_3	1.17, s	23.2, CH_3	1.13, s	21.9, CH_3	1.11, s
15′a	110.9, CH_2	4.89, s	110.6, CH_2	4.73, brs	110.9, CH_2	5.02, 2H brs
15′b		4.78, s		4.47, brs		

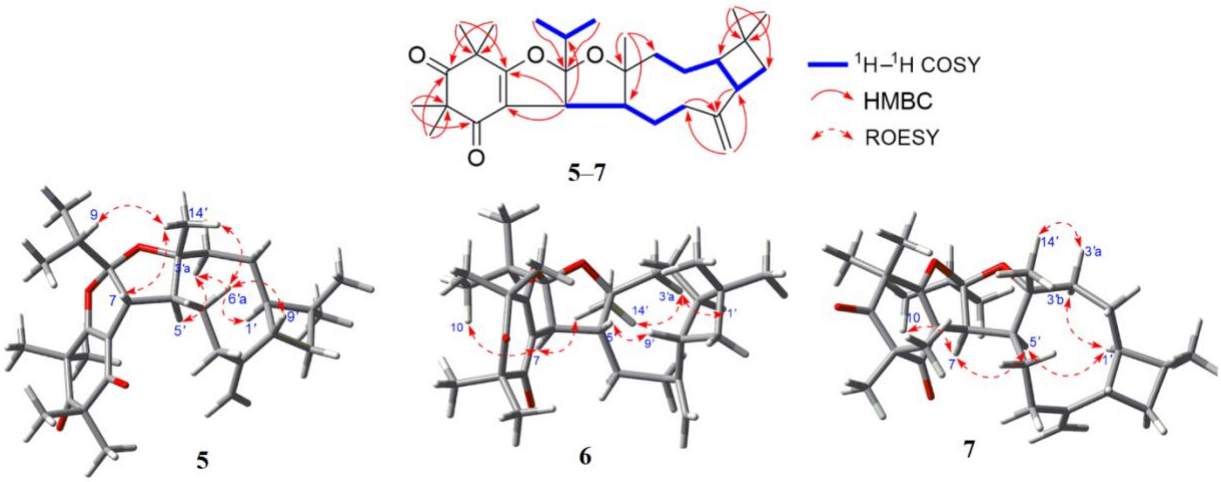


Figure S1. Key 2D NMR (HMBC, ^{1}H–^{1}H COSY, and ROESY) correlations for **5–7.**

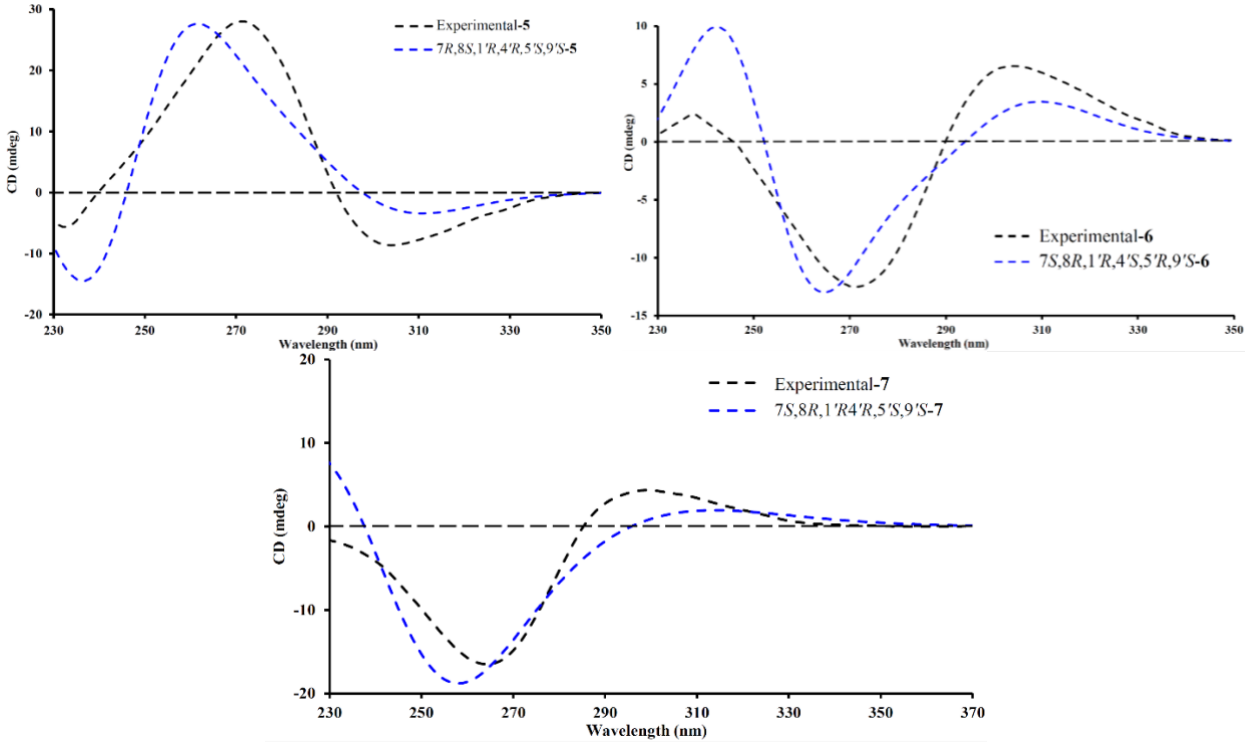


Figure S2. Calculated and experimental ECD data of **5–7**.

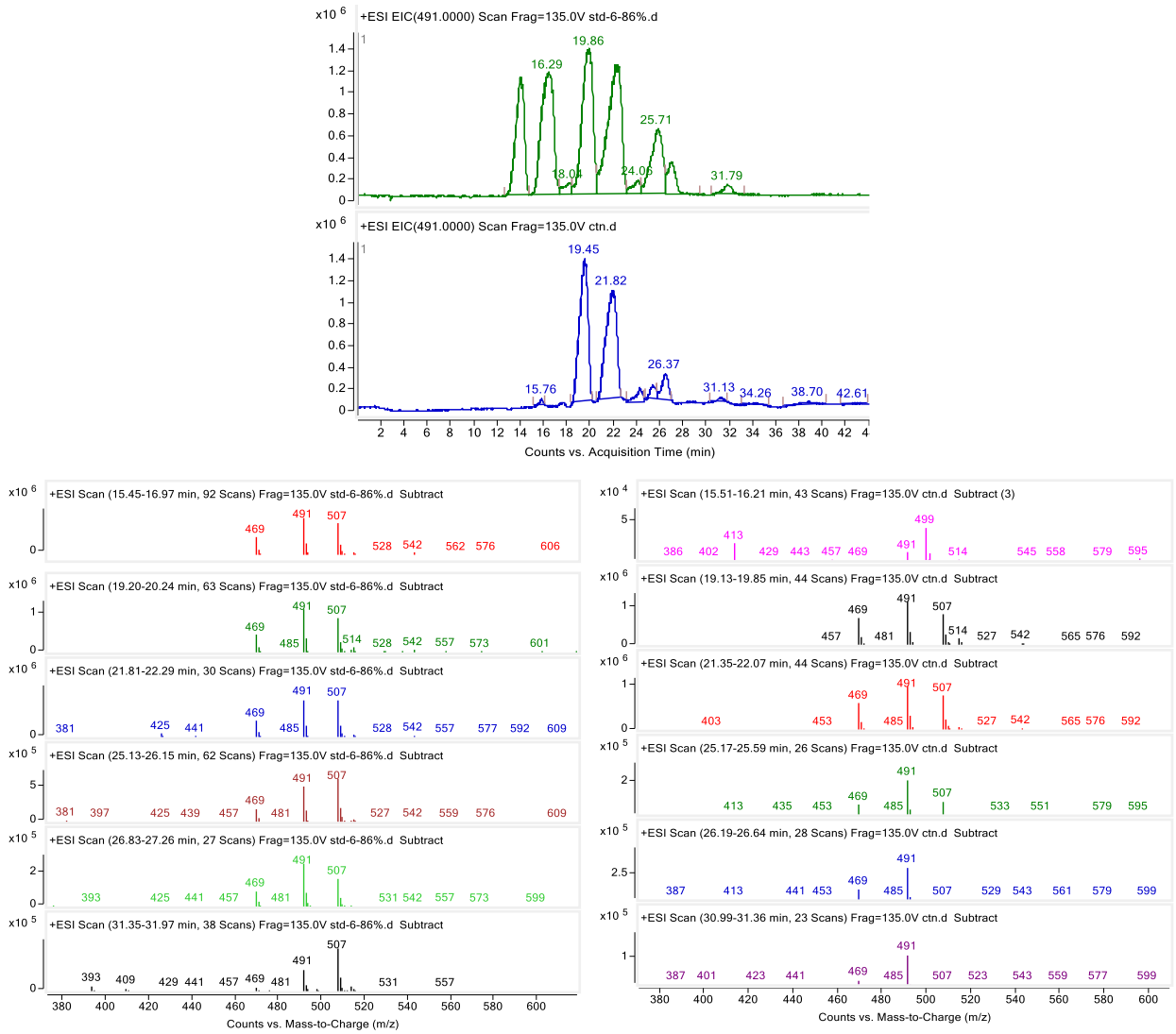


Figure S3. The LC-MS chromatography of the crude extract and meroterpenoids **5**–**11**.

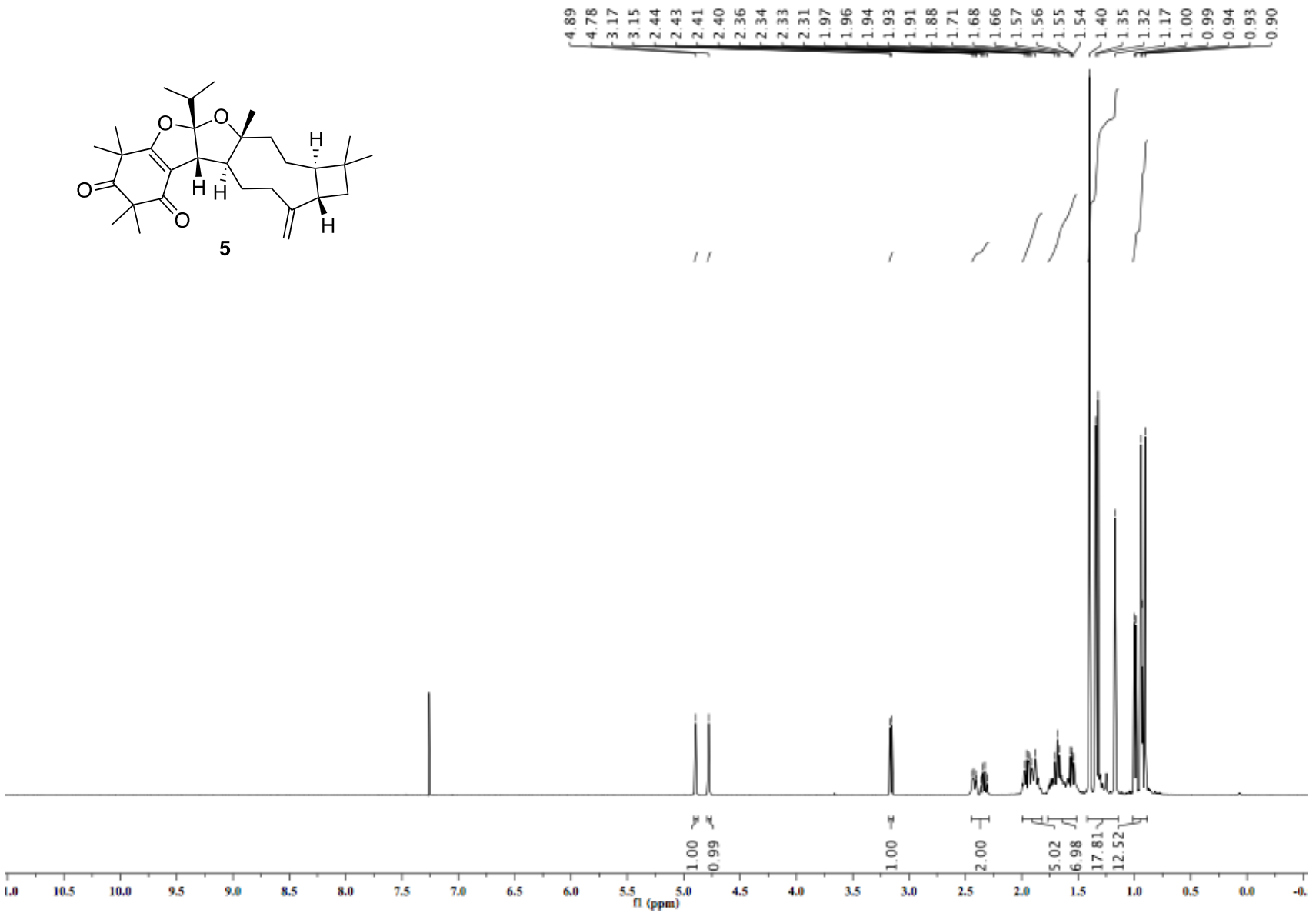


Figure S4. ^{1}H NMR spectrum for compound **5**

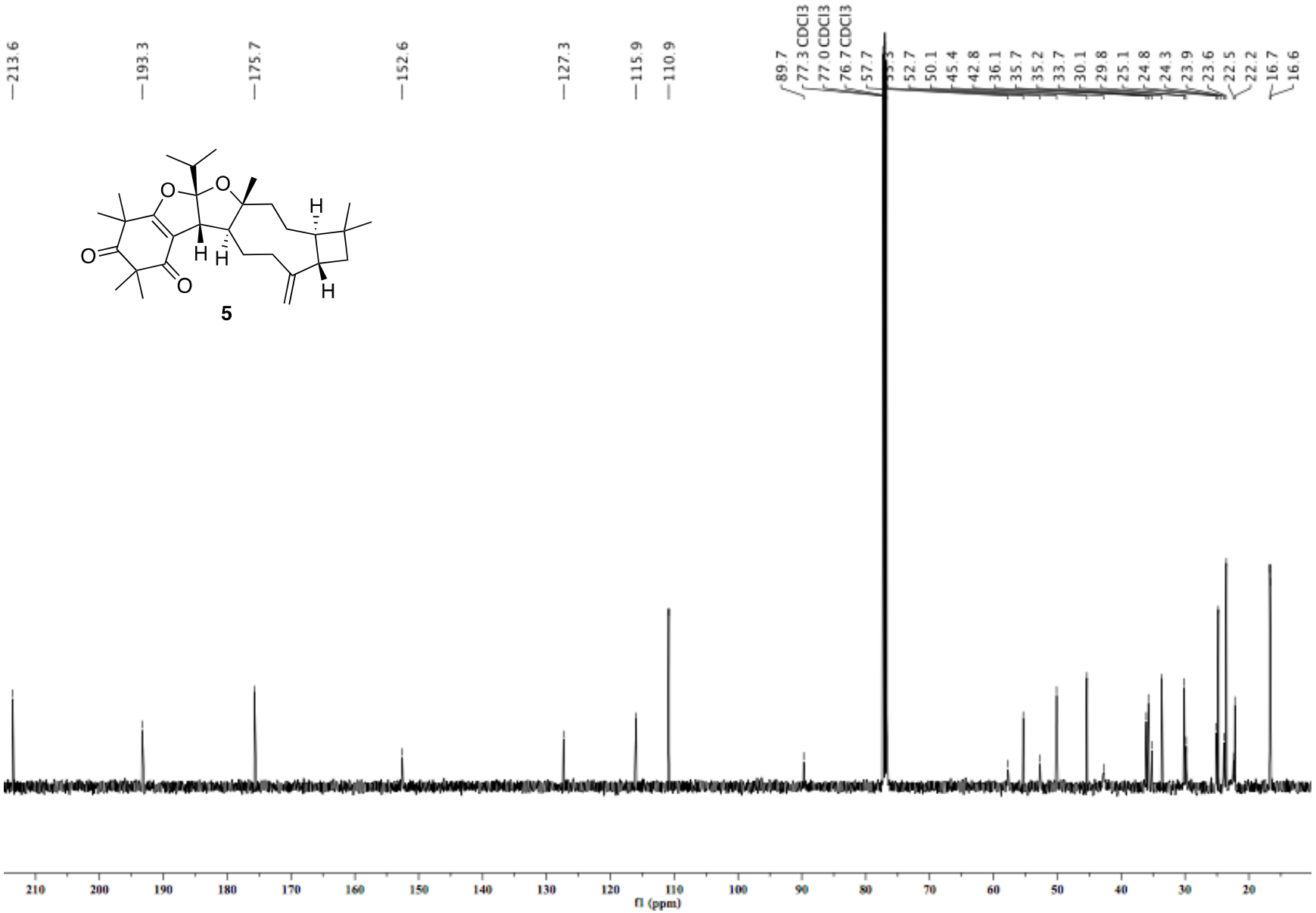


Figure S5. ^{13}C NMR spectrum for compound **5**

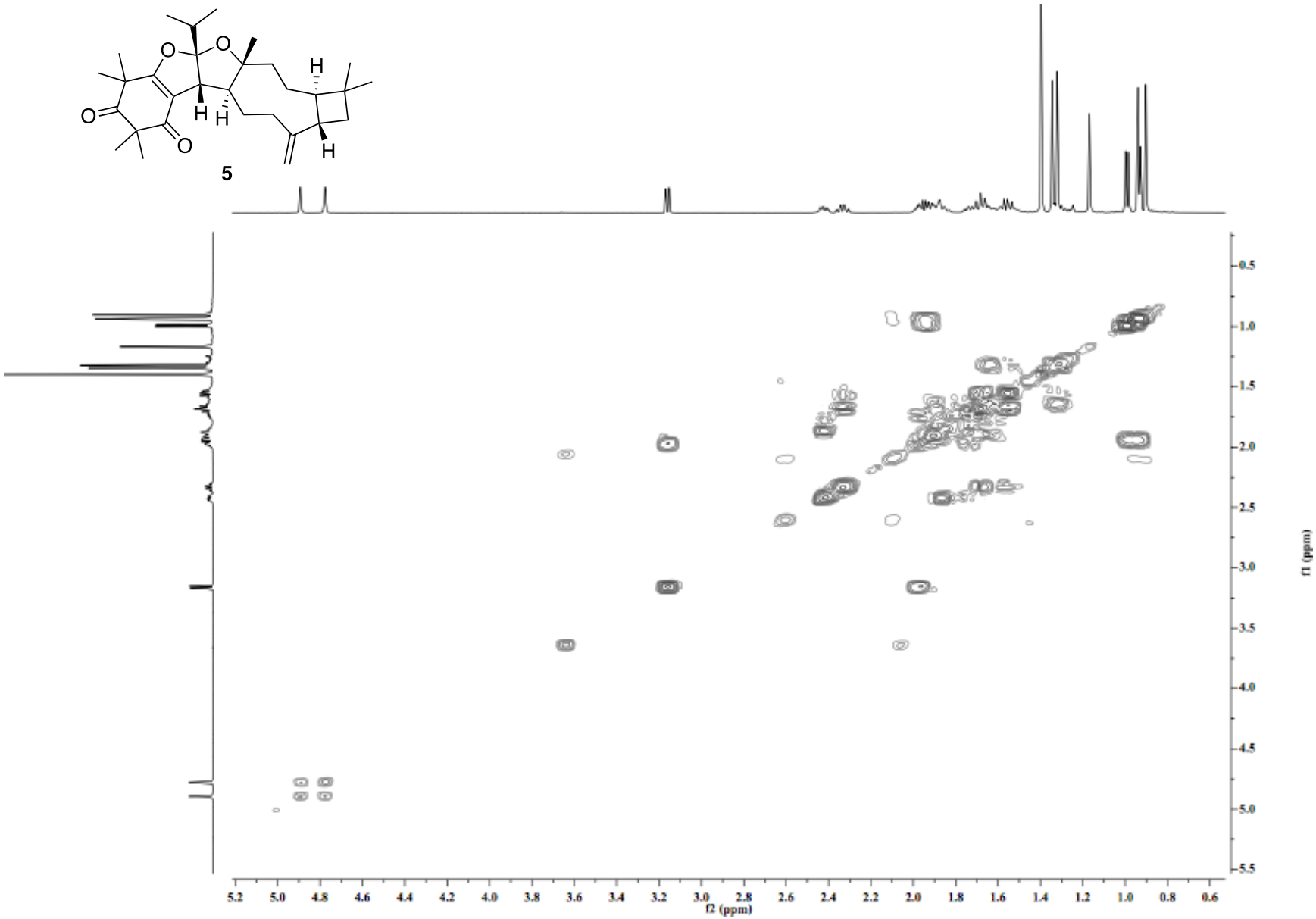


Figure S6. ^{1}H–^{1}H COSY spectrum for compound **5**

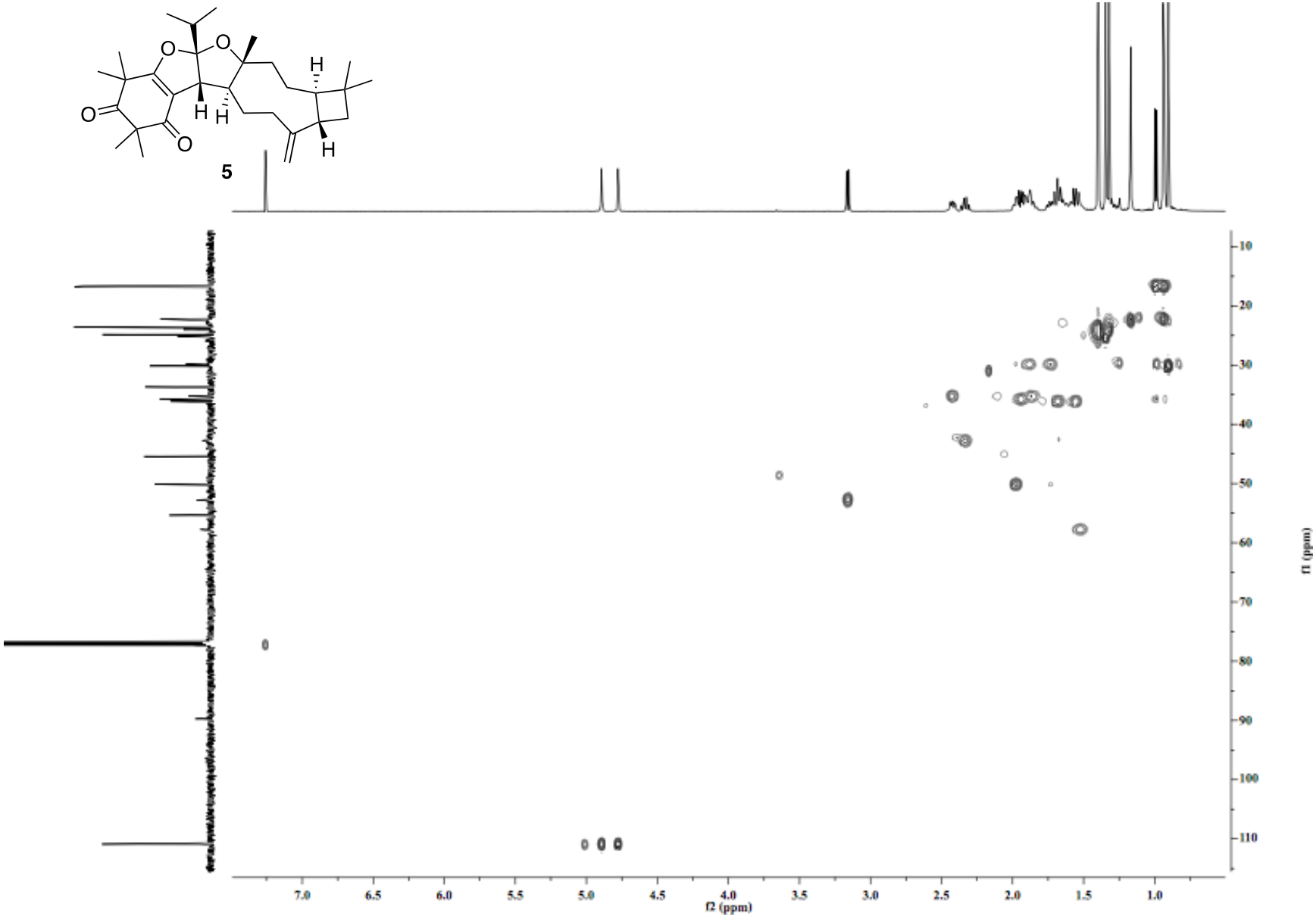


Figure S7. HSQC spectrum for compound **5**

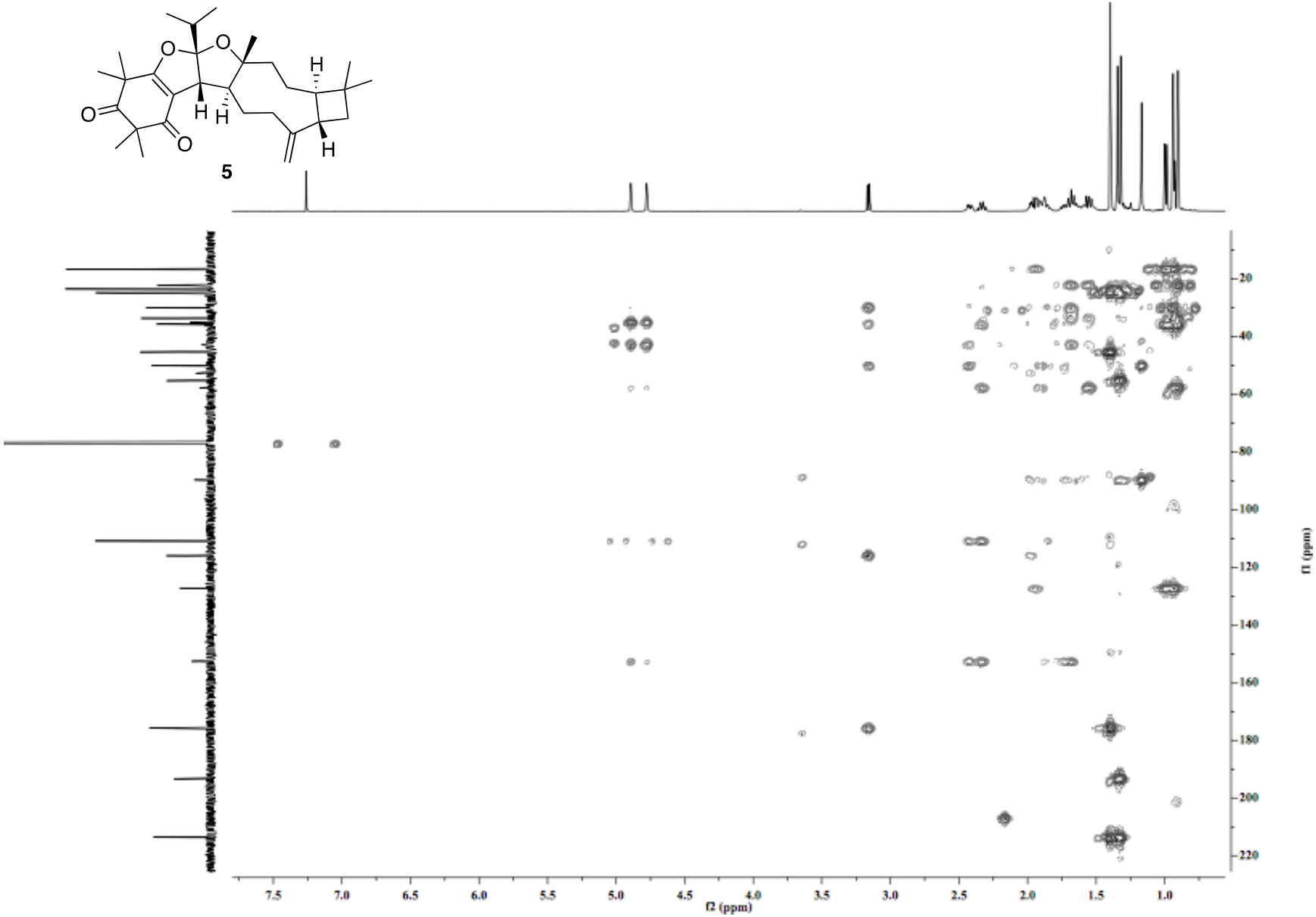


Figure S8. HMBC spectrum for compound **5**

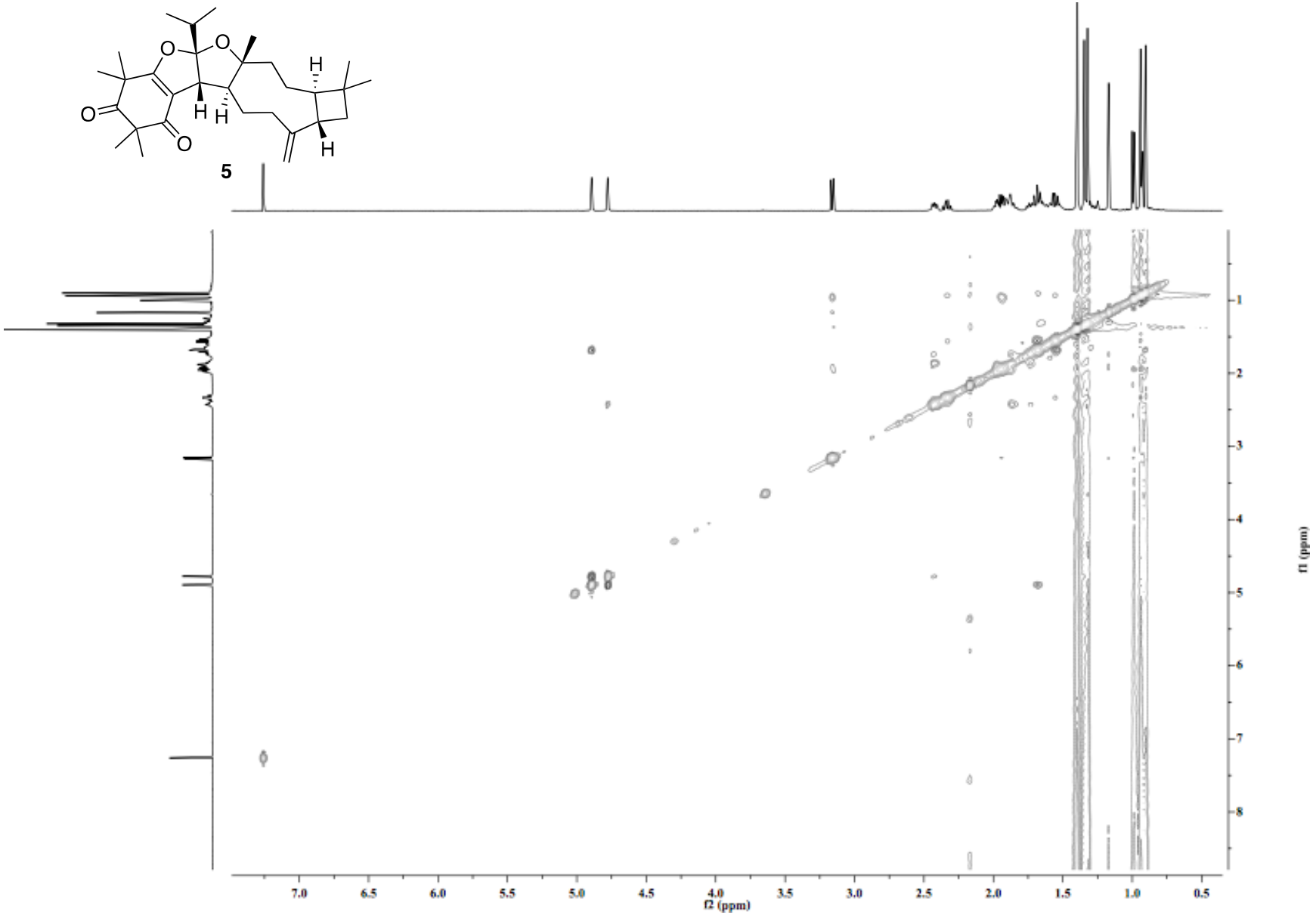
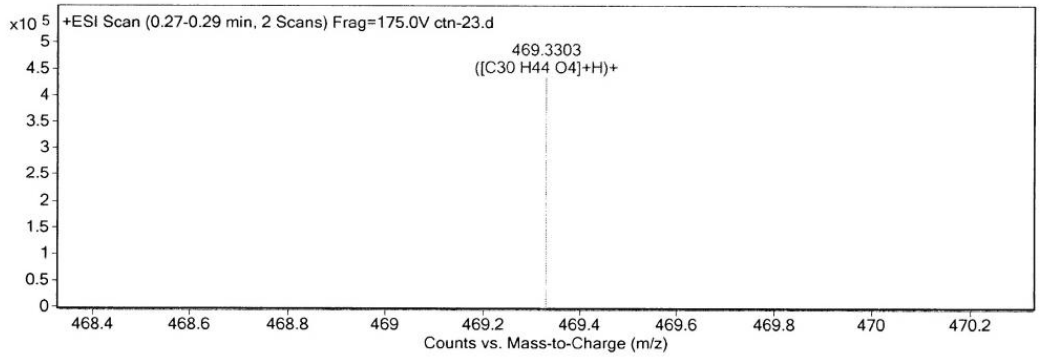


Figure S9. ROESY spectrum for compound **5**

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
149.0233	1	60259.85		
245.0776	1	25539.38		
399.2866	1	33007.16		
469.3303	1	434941.5	C30 H44 O4	(M+H)+
470.333	1	123757.77	C30 H44 O4	(M+H)+
491.3115	1	122116.58		
492.3139	1	36542.68		
507.2851	1	93923.07		
508.2882	1	27889.08		
959.6308	1	29043.36		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	40

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C30 H44 O4	468.3240	469.3312	469.3303	1.2	2.5	9.0000

Figure S10. HRESIMS spectrum for compound **5**

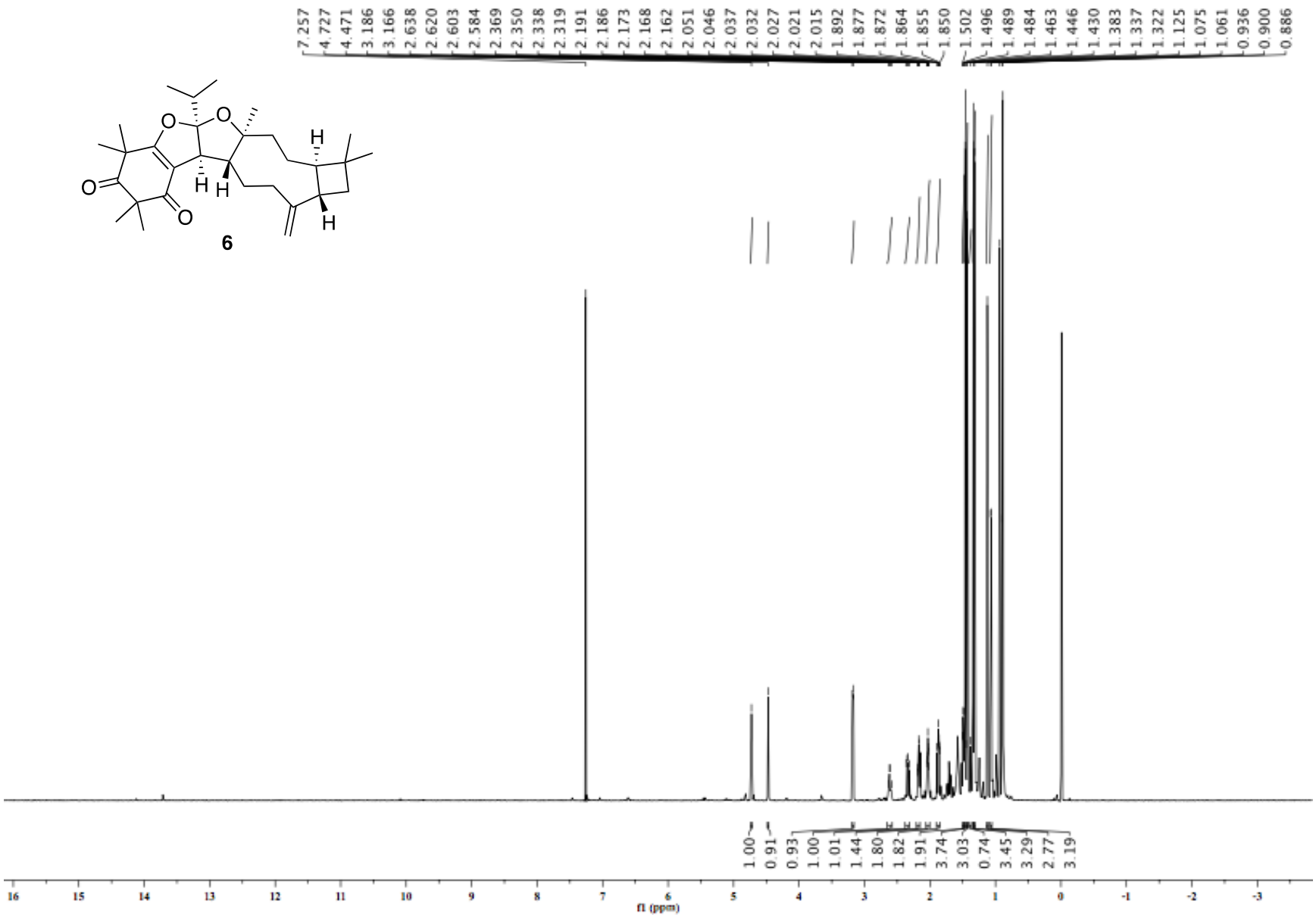


Figure S11. ^{1}H NMR spectrum for compound **6**

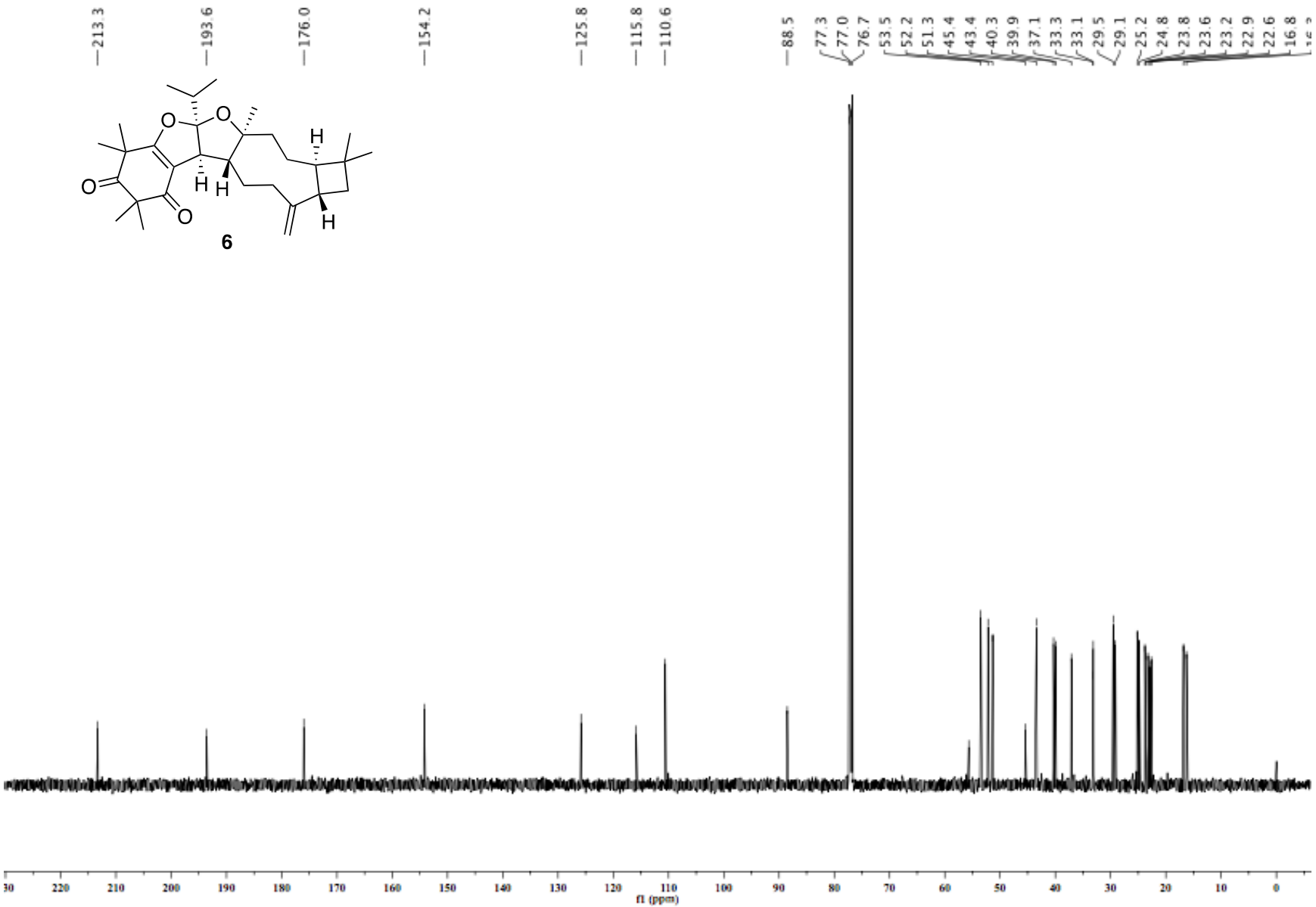


Figure S12. ^{13}C NMR spectrum for compound **6**

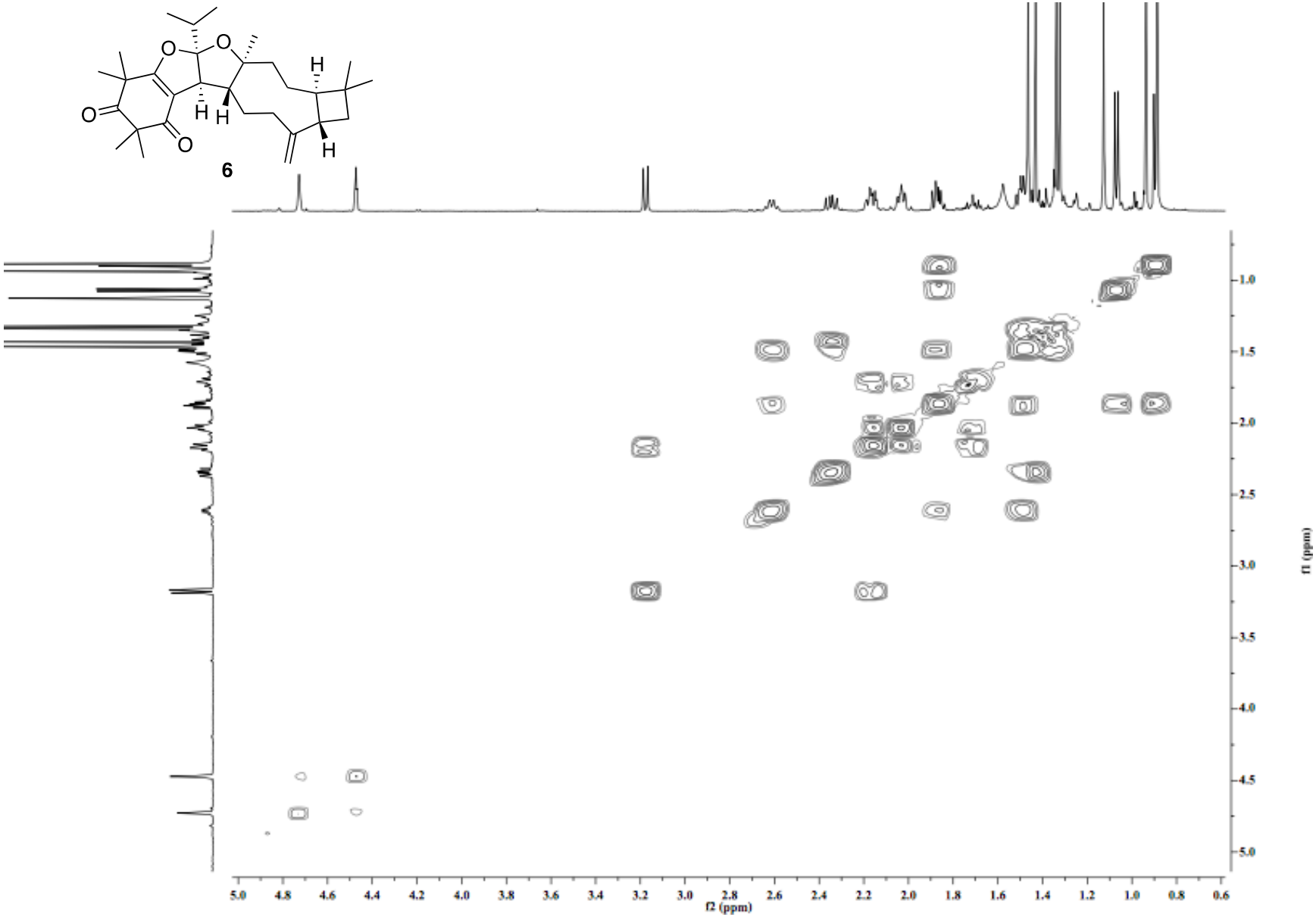


Figure S13. ^{1}H–^{1}H COSY spectrum for compound **6**

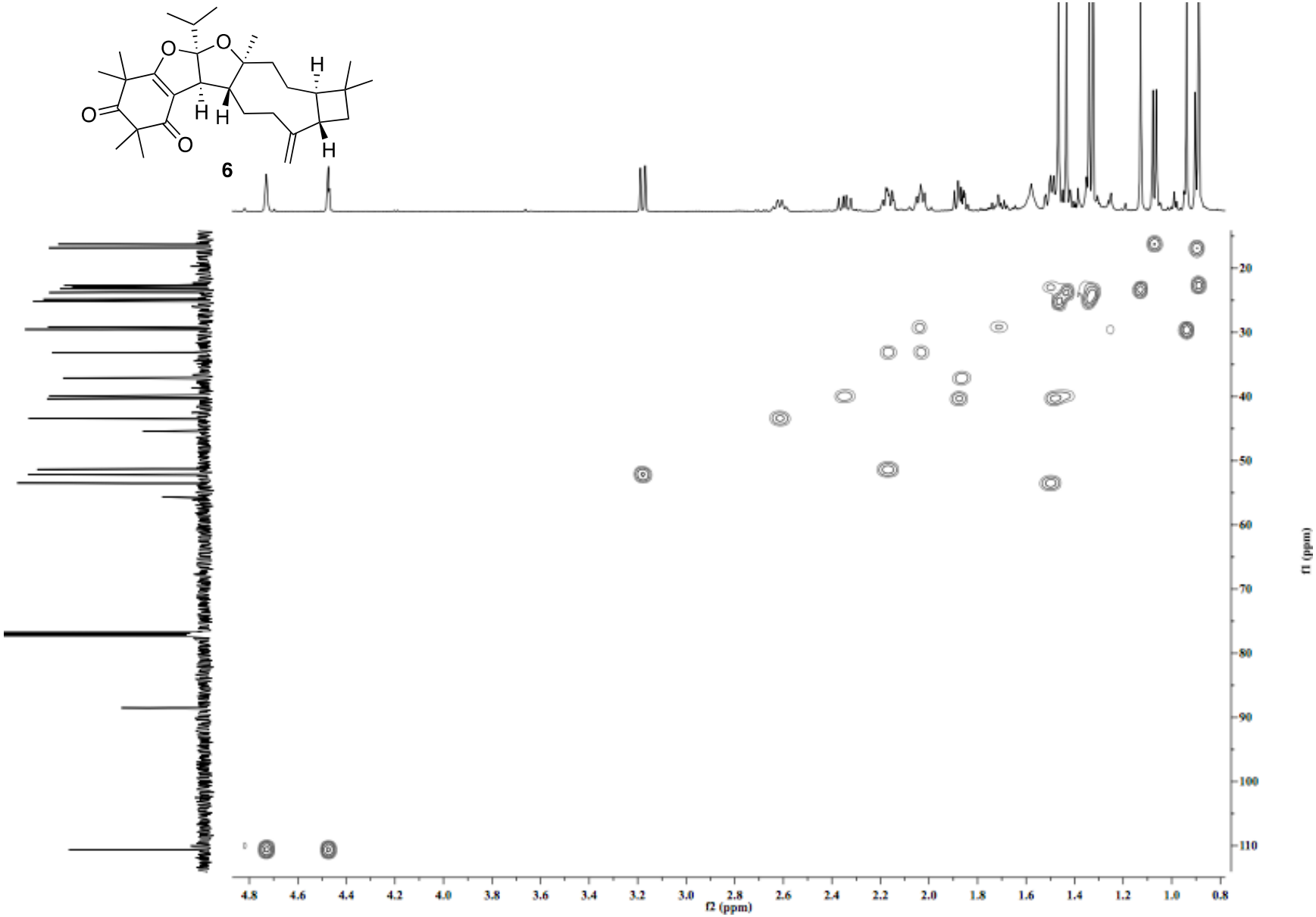


Figure S14. HSQC spectrum for compound **6**

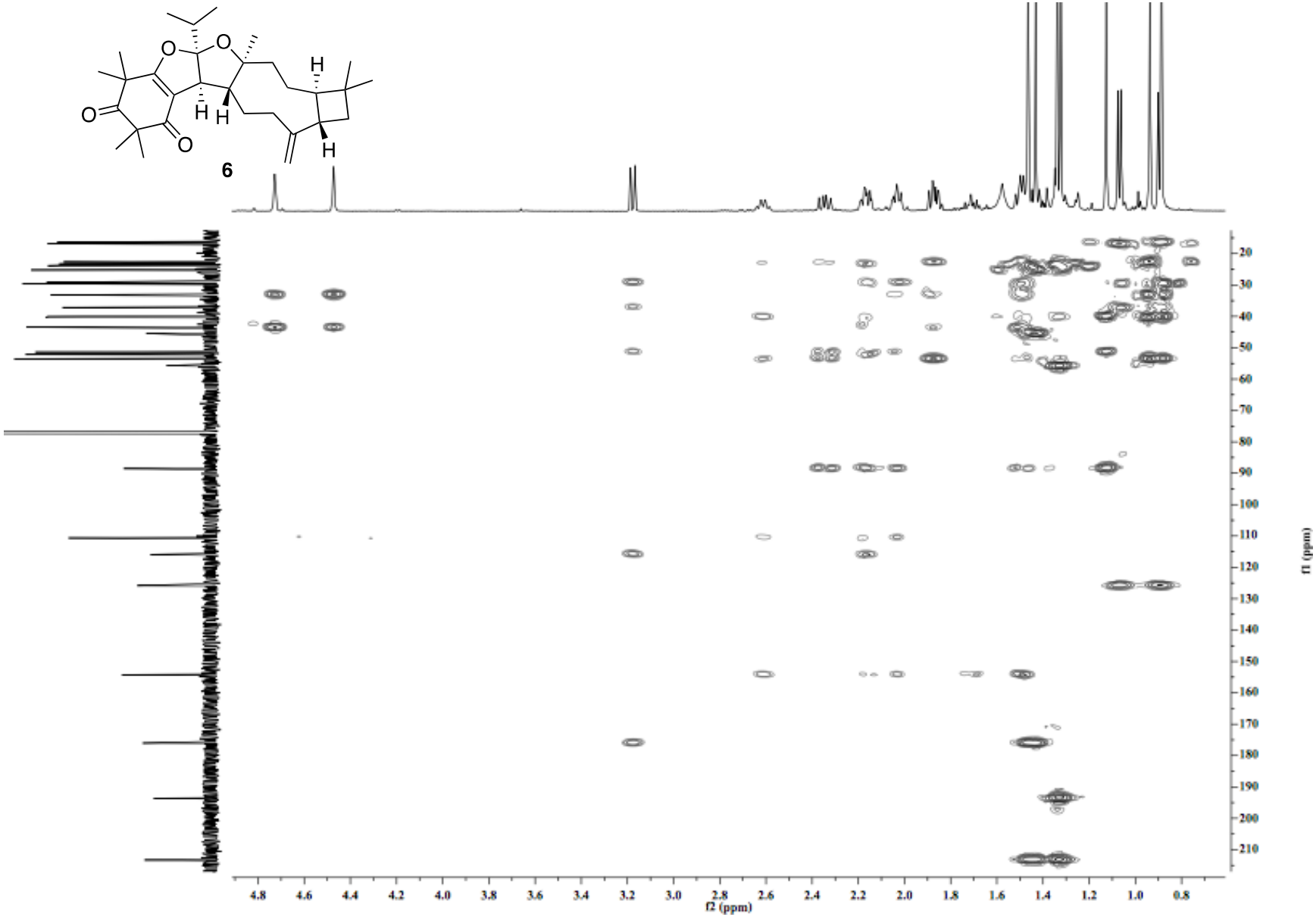


Figure S15. HMBC spectrum for compound **6**

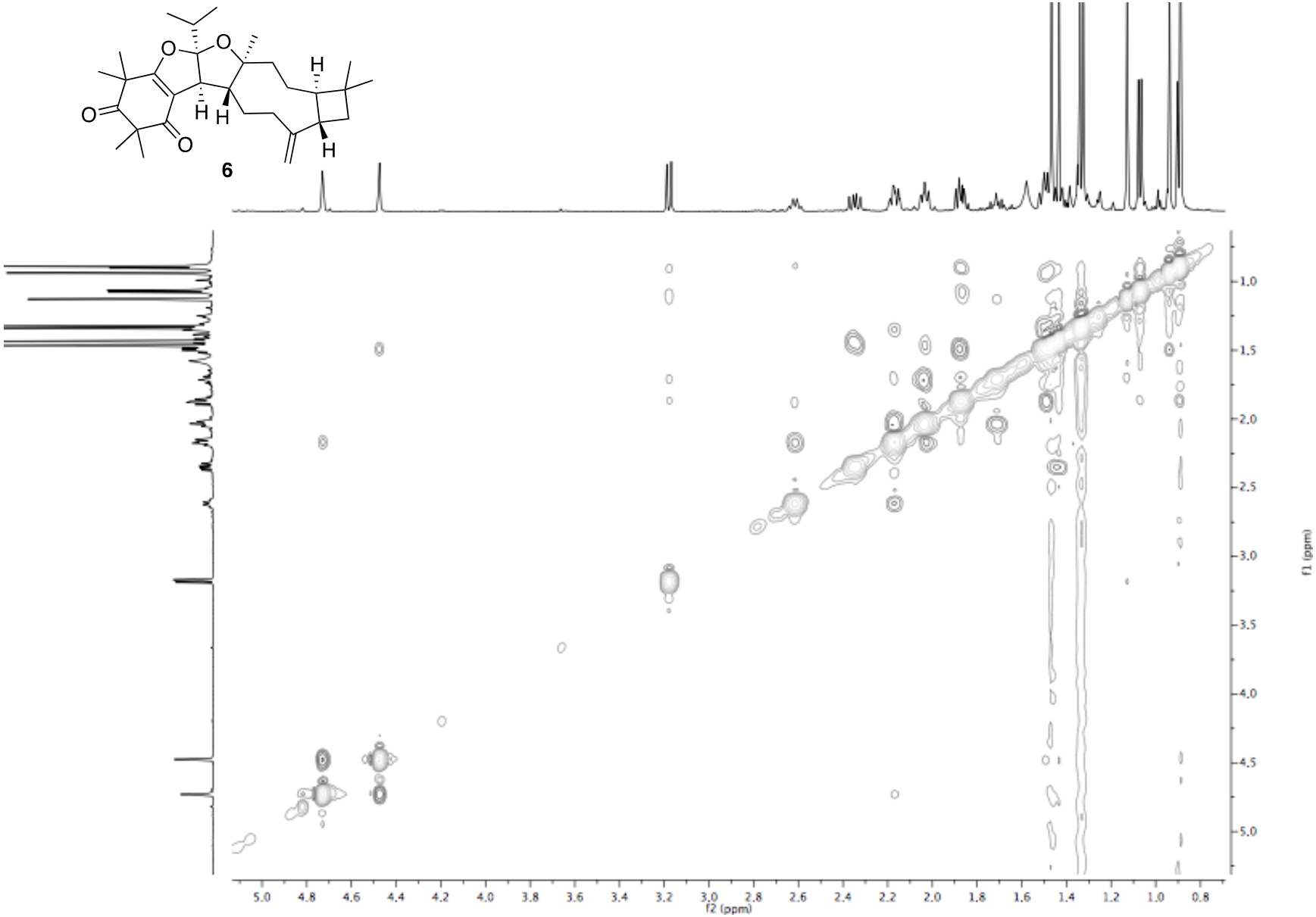
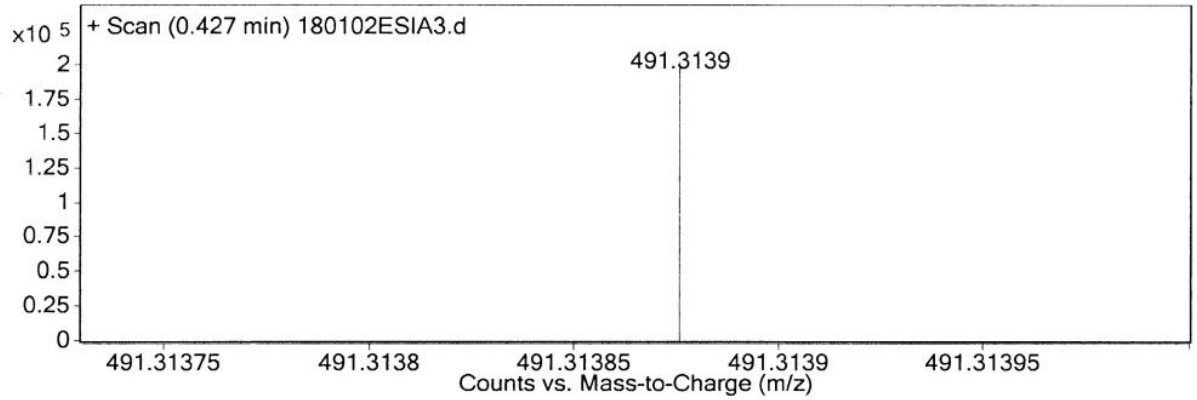


Figure S16. ROESY spectrum for compound **6**

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
200	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
102.1283	1	87604.33		
121.0509	1	71678.75		
469.3315	1	89952.31		
491.3139	1	202277.25	C30 H44 Na O4	M+
507.2874	1	81885.45		
959.6384	1	899677.75		
960.6418	1	581375.19		
961.6433	1	197150.05		
975.6121	1	247011.41		
976.6152	1	154723.25		

Formula Calculator Element Limits

Element	Min	Max
C	0	200
H	0	400
O	0	10
Na	1	1

Formula Calculator Results

Formula	CalculatedMass	Mz	Diff.(mDa)	Diff. (ppm)	DBE
C30 H44 Na O4	491.3137	491.3139	-0.2	0.3	8.5

Figure S17. HRESIMS spectrum for compound **6**

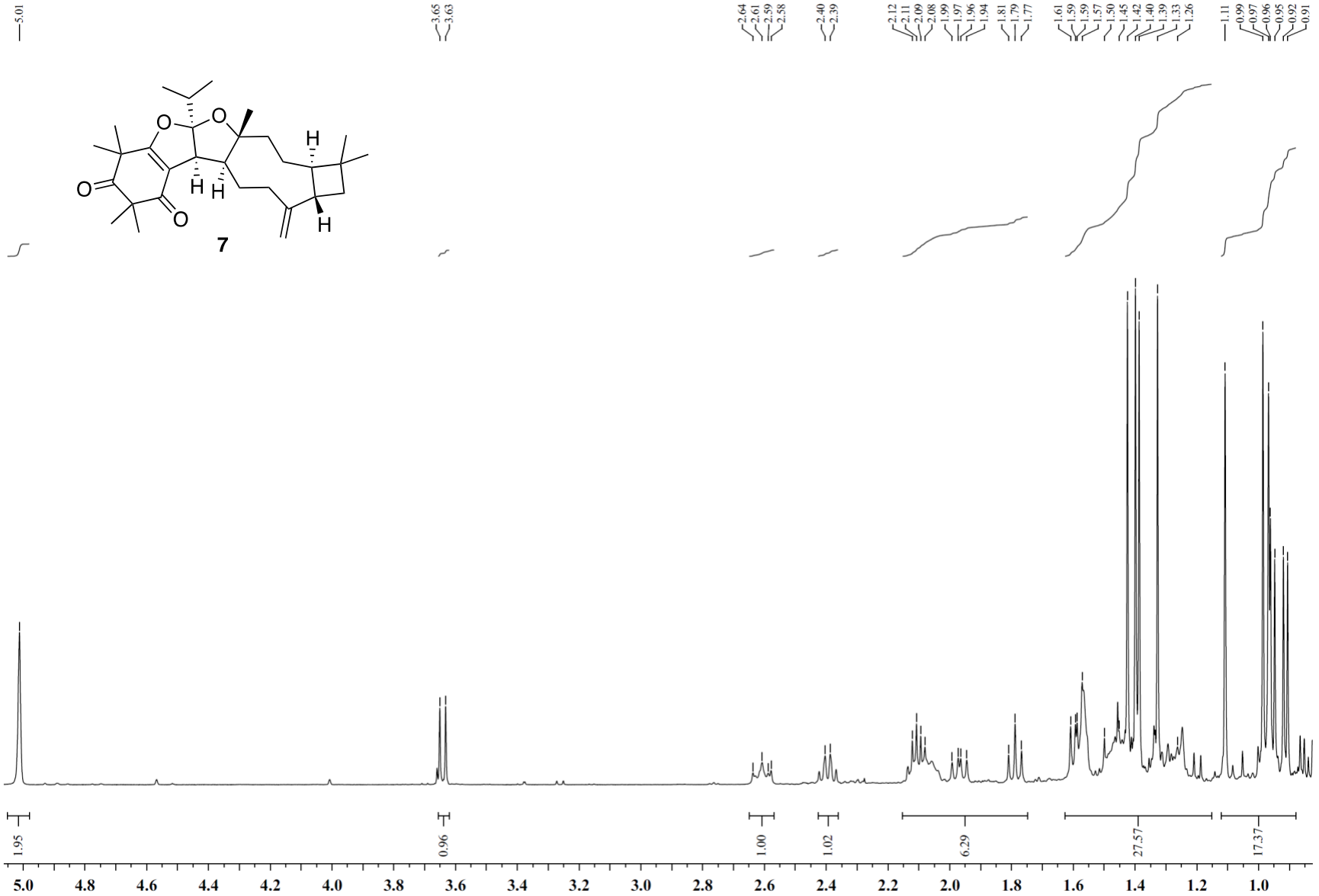


Figure S18. ^{1}H NMR spectrum for compound **7**

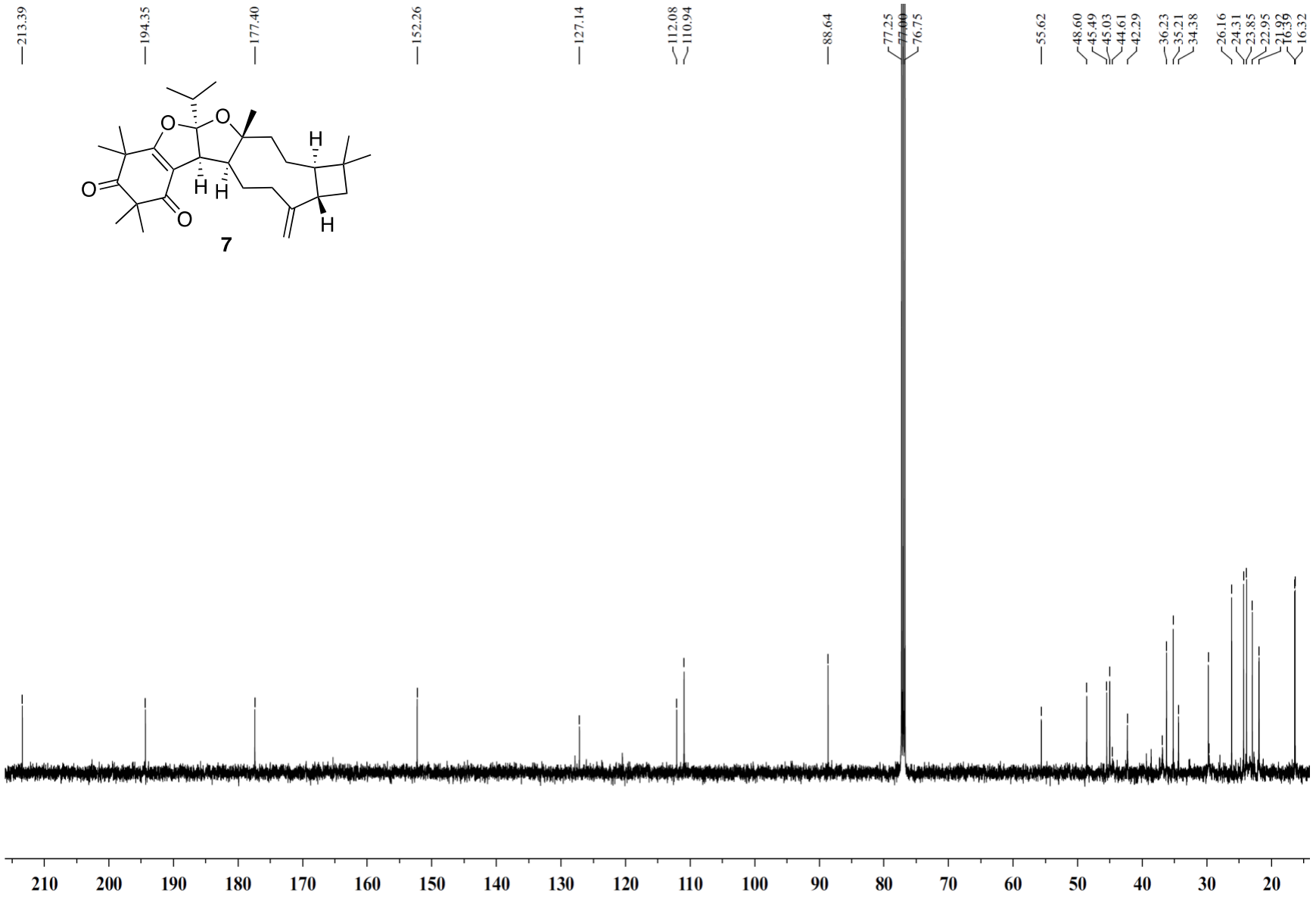


Figure S19. ^{13}C NMR spectrum for compound **7**

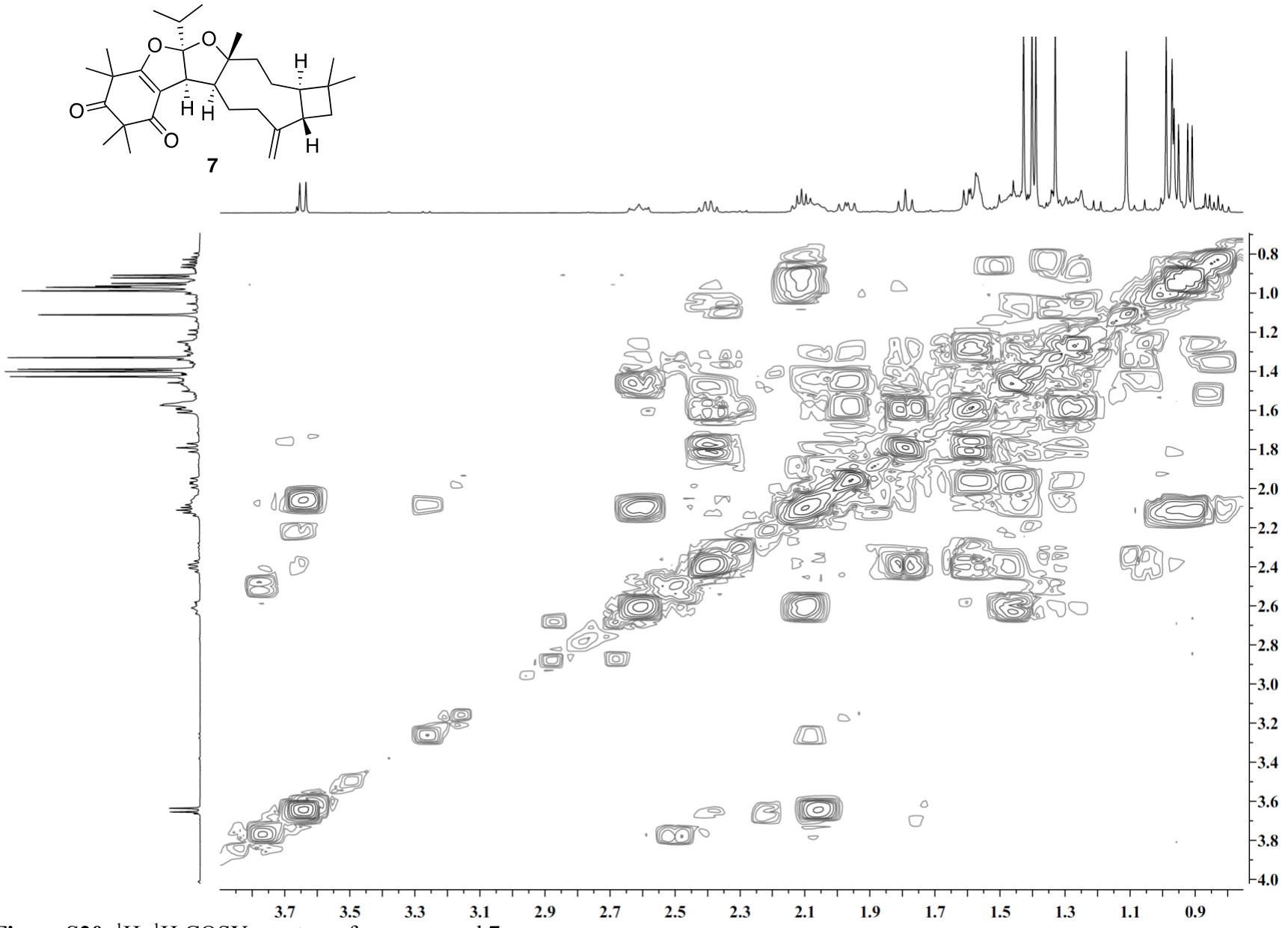


Figure S20. ^{1}H–^{1}H COSY spectrum for compound **7**

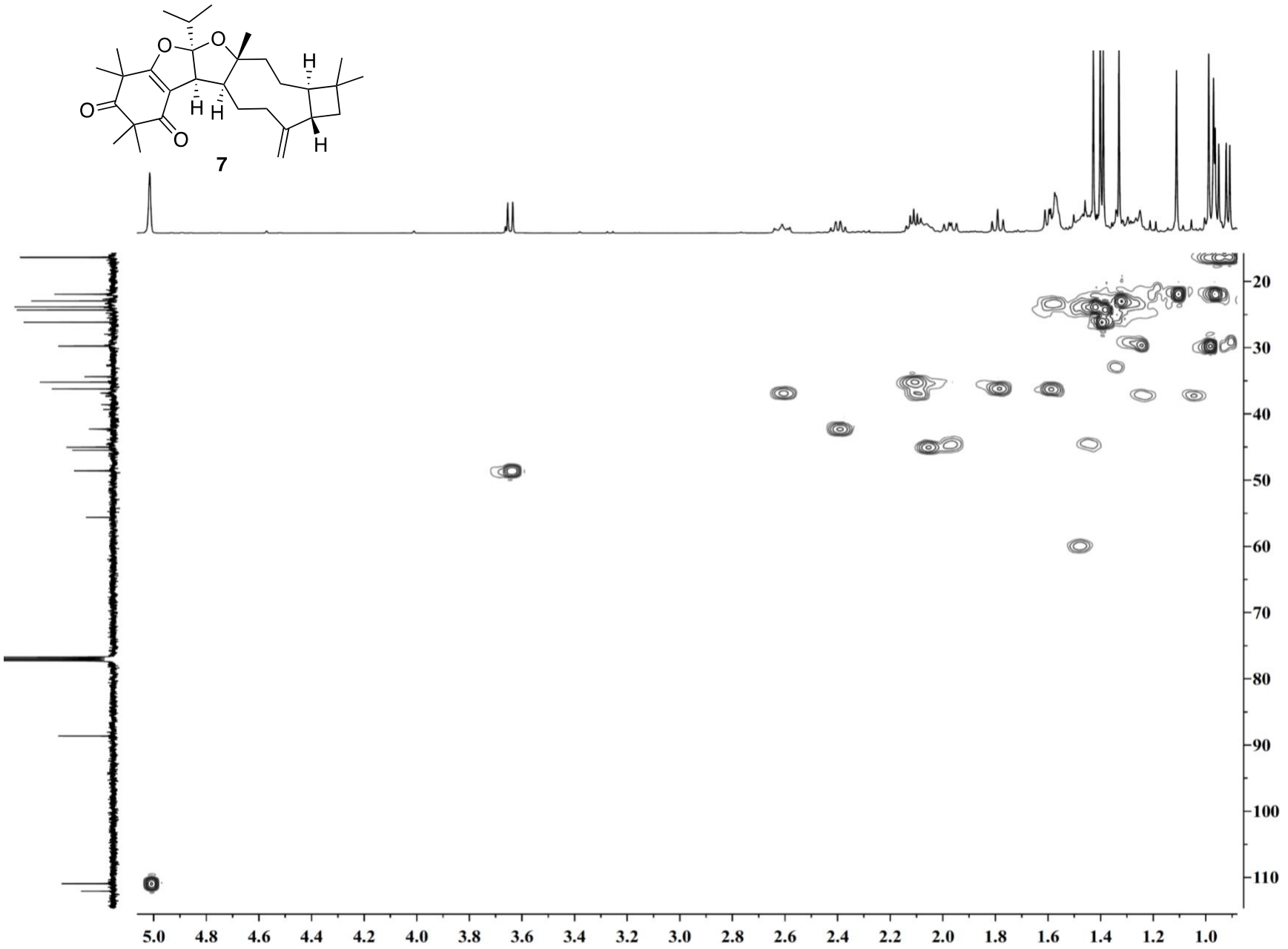


Figure S21. HSQC spectrum for compound **7**

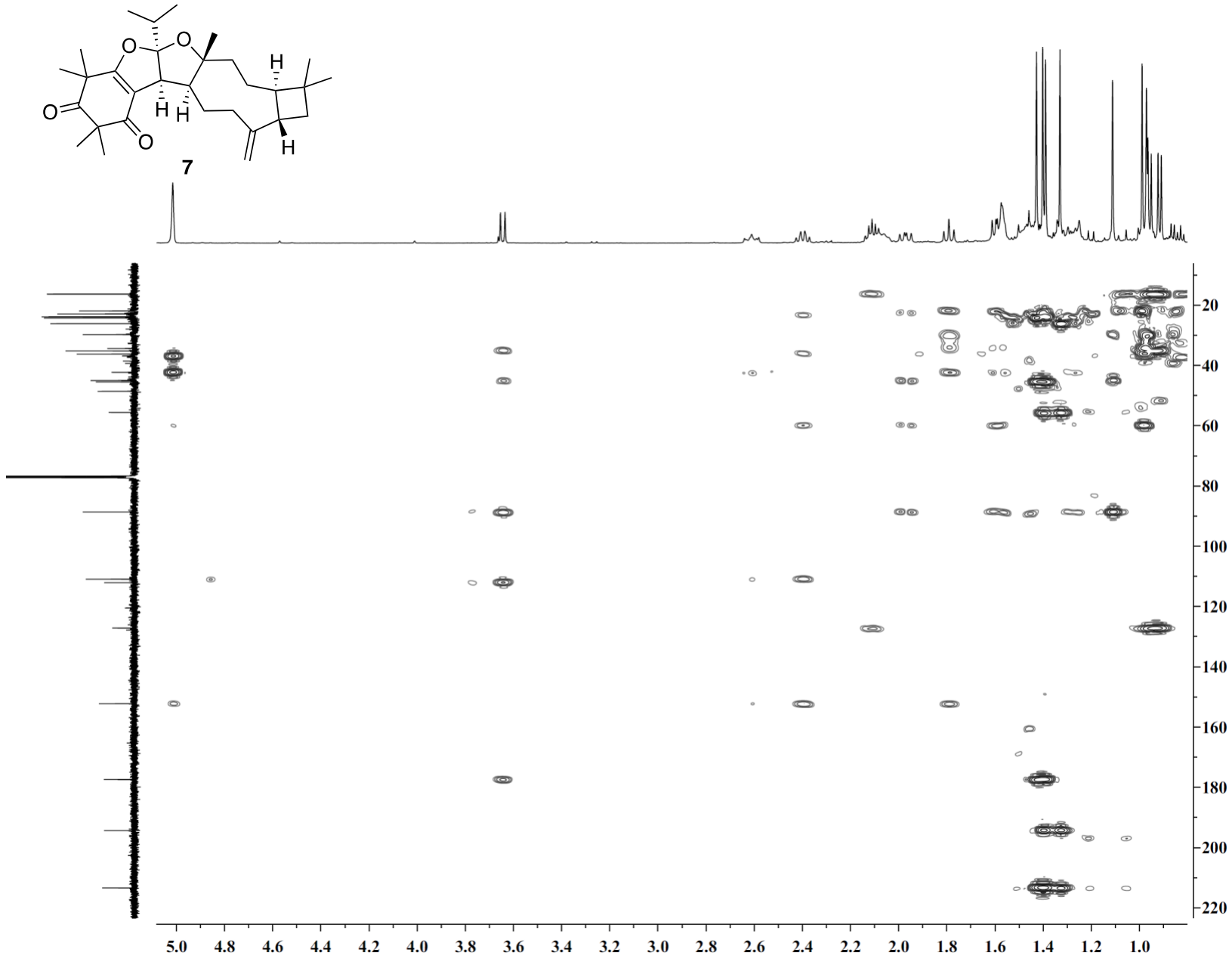


Figure S22. HMBC spectrum for compound **7**

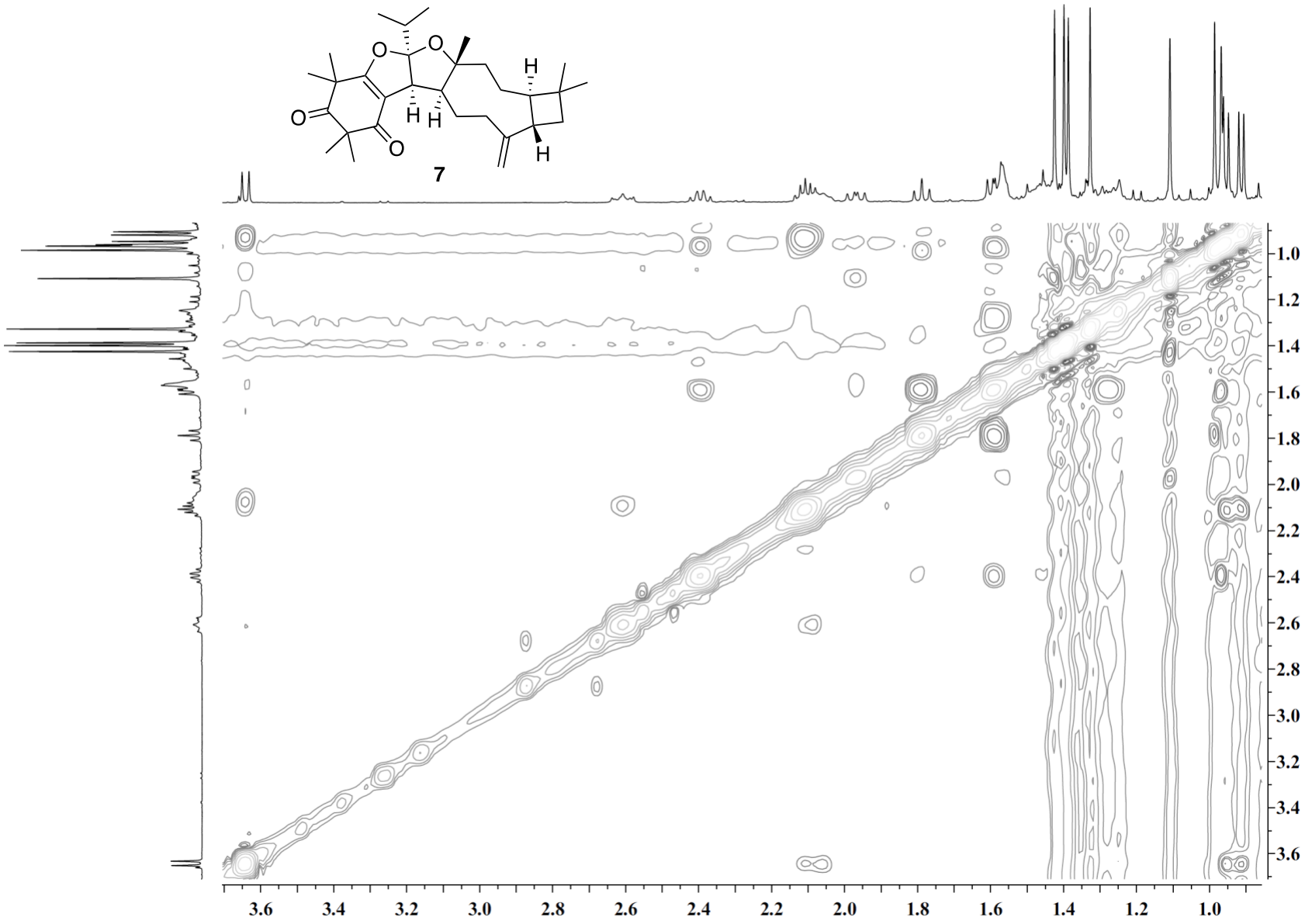
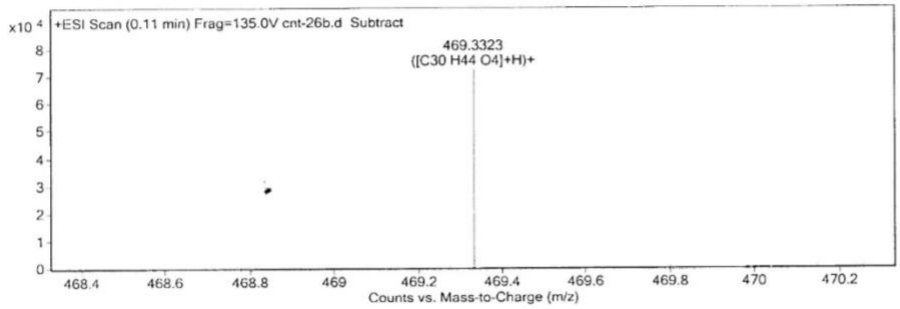


Figure S23. ROESY spectrum for compound **7**

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
295.1708	2	14835.04		
315.6835	2	13785.81		
393.2983	1	30957.53		
409.2722	1	15771.9		
469.3323	1	72573.16	C30 H44 O4	(M+H)+
470.336	1	23153	C30 H44 O4	(M+H)+
491.3142	1	15670.75		
507.2881	1	21364.91		
959.6386	1	22448.85		
960.6422	1	15730.4		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C30 H44 O4	468.3240	469.3312	469.3323	-1.10	-2.34	9.0000

Figure S24. HRESIMS spectrum for compound **7**

D. Structure Elucidation of 8 and 9

Rhotomentodiones A and B (**8** and **9**) shared the same molecular formula of $C_{30}H_{44}O_4$, as determined by their HRESIMS ions at *m/z* 491.3136 $[M + Na]^+$ and 491.3135 $[M + Na]^+$ (both calcd for $C_{30}H_{44}O_4Na$, 491.3132), respectively. Extensive analysis of the 1D and 2D NMR data (Table S2 and Figure S25) of **8** and **9** indicated that all of the isolates were likely caryophyllene-based meroterpenoids similar to tomentodiones A–D,[S1] except for the presence of C-8 carbonyl groups. This assertion was further confirmed by the ^1H–^1H COSY correlations of Me-10/H-9/Me-11 and the HMBC correlations from Me-9/Me-10/H-7 to C-8. The relative configurations of **8** and **9** were subsequently assigned by their ROESY experiments as shown in Figure S18. Finally, the absolute configurations of **8** and **9** were established as 7*S*,1′*R*,4′*R*,5′*S*,9′*S* and 7*R*,1′*R*,4′*S*,5′*R*,9′*S* by electronic circular dichroism (ECD) calculations (Figures S26).

Rhotomentodione A (8): Colorless gum; $[\alpha]_D^{17}$ +171.0 (*c* 0.10 mg/mL, MeOH); UV (MeOH) λ_{max} (log ε) 203 (3.42), 265 (3.49) nm; ECD (MeOH) λ_{max} nm ($\Delta\varepsilon$) 213 (+18.57), 263 (–11.86), 304 (–8.44) nm; IR (KBr) ν_{max} 3441, 2945, 1712, 1628, 1454, 1187 cm^{-1}; ^1H (500 MHz) and ^{13}C NMR (125 MHz) data, see Table S1; (+)-HREIMS *m/z* 491.3136 $[M + Na]^+$ (calcd for $C_{30}H_{44}O_4Na$, 491.3132).

Rhotomentodione B (9): Colorless gum; $[\alpha]_D^{17}$ +146.2 (*c* 0.10 mg/mL, MeOH); UV (MeOH) λ_{max} (log ε) 203 (3.42), 265 (3.49) nm; ECD (MeOH) λ_{max} nm ($\Delta\varepsilon$) 259 (–6.25), 298 (+3.98) nm; IR (KBr) ν_{max} 3442, 2948, 1712, 1630, 1455, 1186 cm^{-1}; ^1H (500 MHz) and ^{13}C NMR (125 MHz) data, see Table S1; (+)-HREIMS *m/z* 491.3135 $[M + Na]^+$ (calcd for $C_{30}H_{44}O_4Na$, 491.3132).

Tomentodione Q (10): ECD (MeOH) λ_{max} nm ($\Delta\varepsilon$) 213 (+18.13), 252 (–10.46), 298 (–10.58) nm.

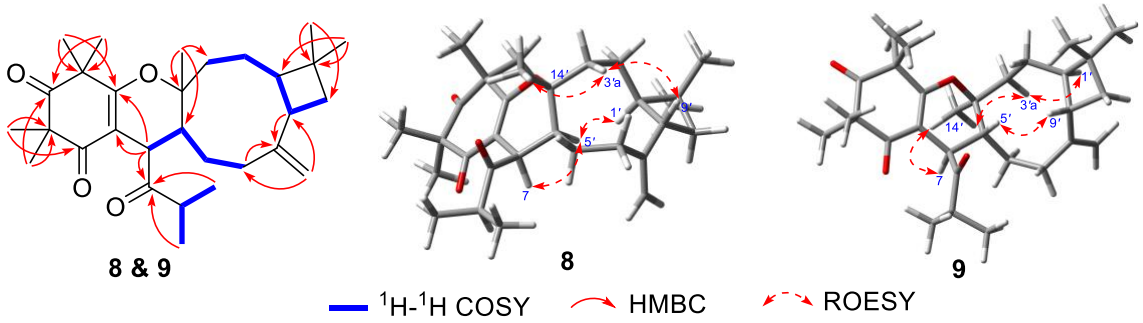


Figure S25. Key ^{1}H–^{1}H COSY, HMBC, and ROESY correlations for **8** and **9**.

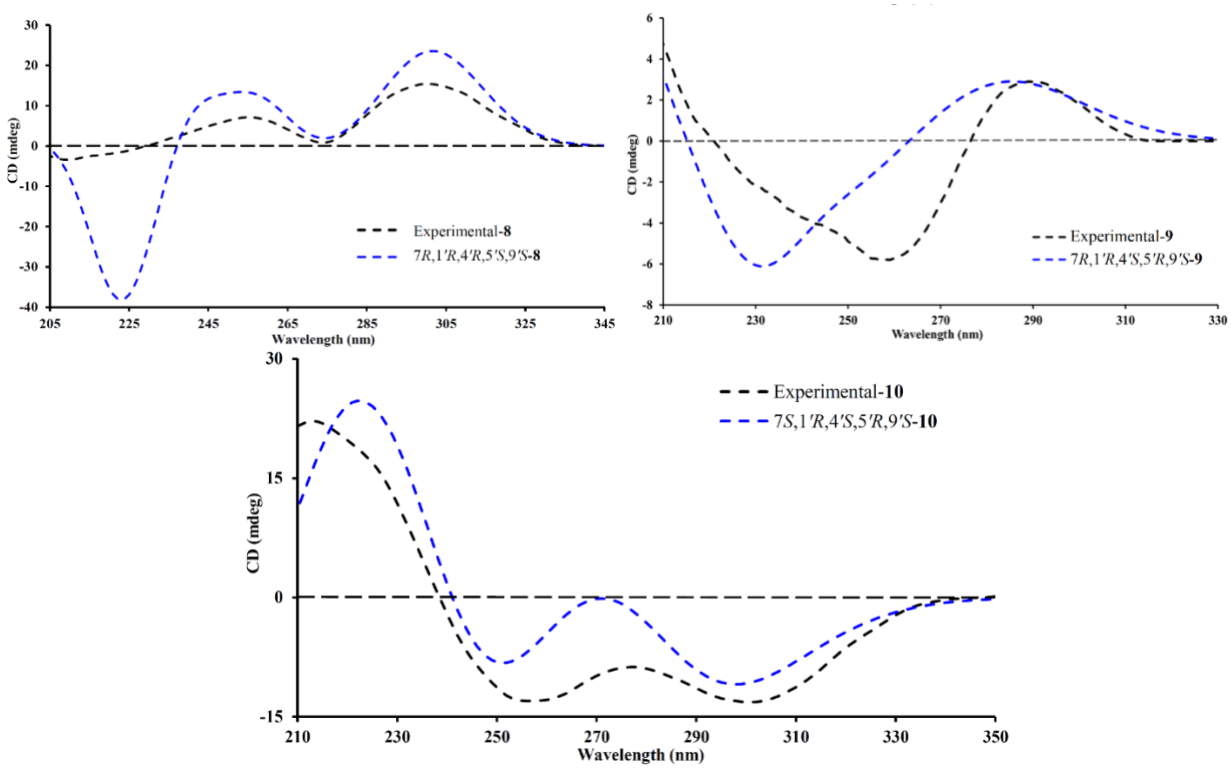


Figure S26. Calculated and experimental ECD data for **8**–**10**.

Table S2. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data for **8** and **9** in $CDCl_3$

	8		**9**	
No.	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)
1	171.8, C		171.3, C	
2	47.8, C		47.6, C	
3	213.2, C		212.9, C	
4	55.1, C		55.1, C	
5	196.7, C		197.0, C	
6	107.5, C		109.3, C	
7	43.3, CH	4.06, d (6.6)	47.6, CH	3.40, d (10.5)
8	216.7, C		216.3, C	
9	42.7, CH	2.89, sept (6.9)	42.4, CH	2.85, sept (6.9)
10	19.9, CH_3	1.21, d (6.9)	20.1, CH_3	1.33, (6.9)
11	17.9, CH_3	1.07, d (6.9)	18.4, CH_3	1.14, d (6.9)
12	25.7, CH_3	1.43, s	24.6, CH_3	1.44, s
13	24.5, CH_3	1.36, s	25.2, CH_3	1.32, s
14	22.4, CH_3	1.31, s	23.8, CH_3	1.30, s
15	26.1, CH_3	1.31, s	24.5, CH_3	1.29, s
1′	56.8, CH	1.59, m	57.1, CH	1.56, m
2′a	23.2, CH_2	1.63, m	22.1, CH_2	1.52, m
2′b		1.40 m		1.42, m
3′a	43.7, CH_2	2.12, brdd (14.0, 10.6)	38.0, CH_2	2.10, brdd (15.5, 10.9)
3′b		1.57, m		1.77, brdd (15.5, 6.4)
4′	84.8, C		83.2, C	
5′	38.0, CH	2.08, dt (8.5, 6.9)	39.2, CH	2.22, dt (10.5, 5.2)
6′a	26.9, CH_2	1.78, m	33.0, CH_2	1.67, m
6′b		1.68, m		1.50, m
7′a	35.8, CH_2	2.51, ddd (14.3, 10.0, 4.4)	37.6, CH_2	2.32, brdd (13.3, 9.7)
7′b		2.24, m		1.84, brdd (13.3, 8.6)
8′	150.5, C		154.7, C	
9′	41.5, CH	2.43, q (8.2)	42.1, CH	2.49, q (9.1)
10′a	36.3, CH_2	1.75, t (10.6)	38.9, CH_2	1.74, dd (10.5, 8.4)
10′b		1.62, dd (10.6, 7.7)		1.61, t (10.1)
11′	34.3, CH_3		33.2, CH_3	
12′	29.8, CH_3	0.97, s	29.6, CH_3	0.99, s
13′	21.8, CH_3	0.98, s	22.1, CH_3	0.97, s
14′	21.5, CH_3	1.32, s	20.0, CH_3	1.07, s
15′a	111.5, CH_2	5.00, 2H brs	110.1, CH_2	4.78, brs
15′b		4.06, d (6.6)		4.74, brs

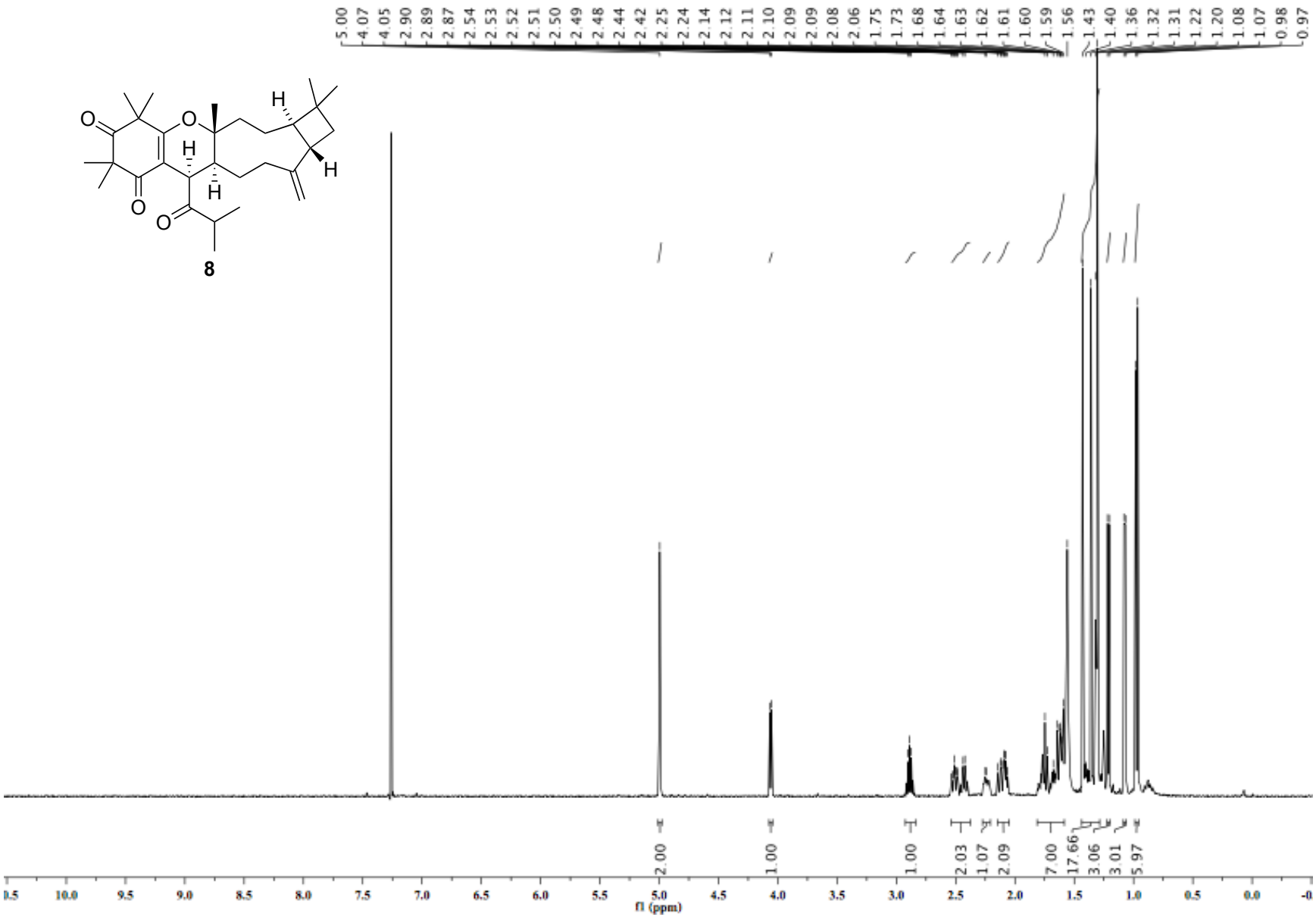


Figure S27. ^{1}H NMR spectrum for compound **8**

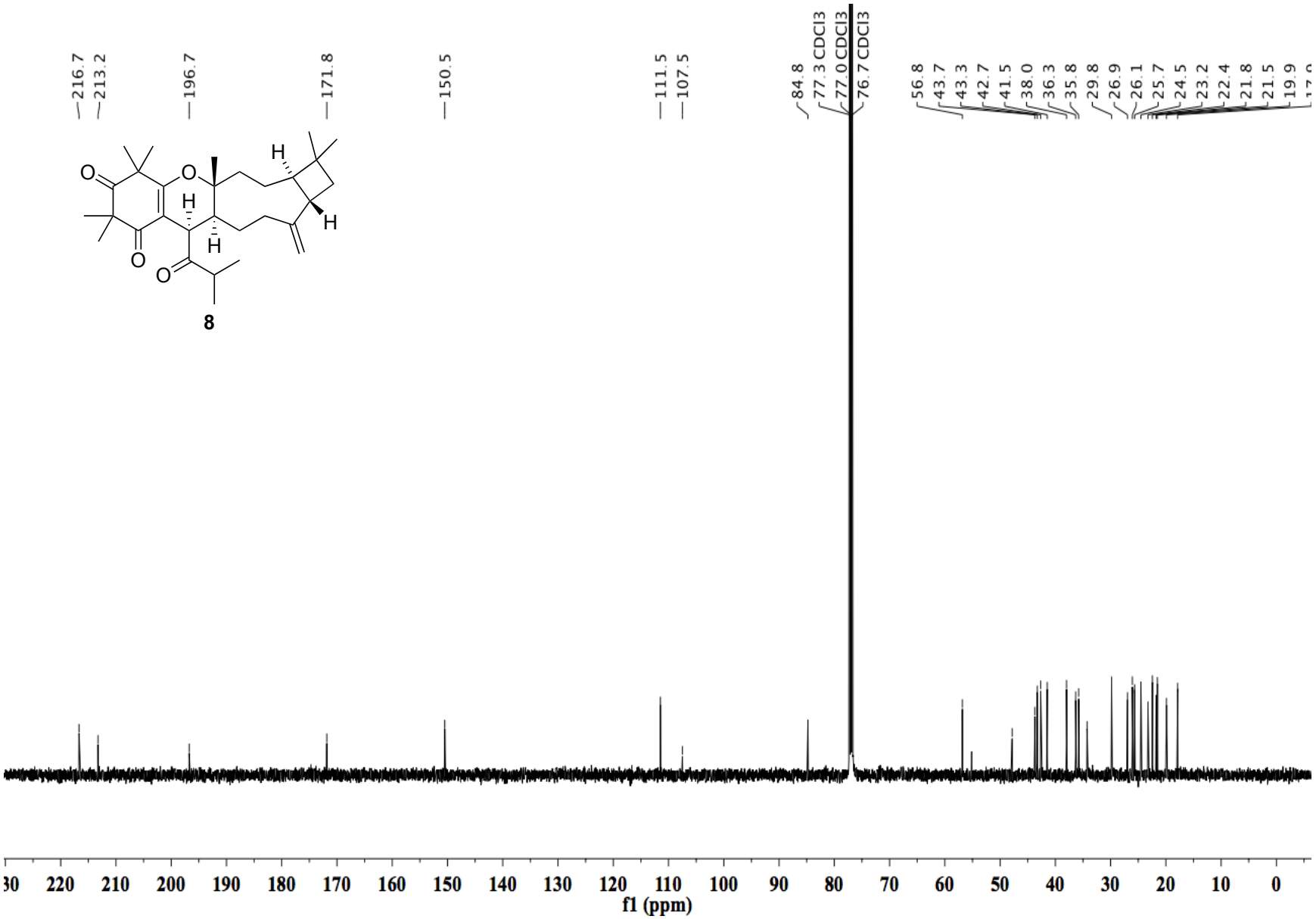


Figure S8. ^{13}C NMR spectrum for compound **8**

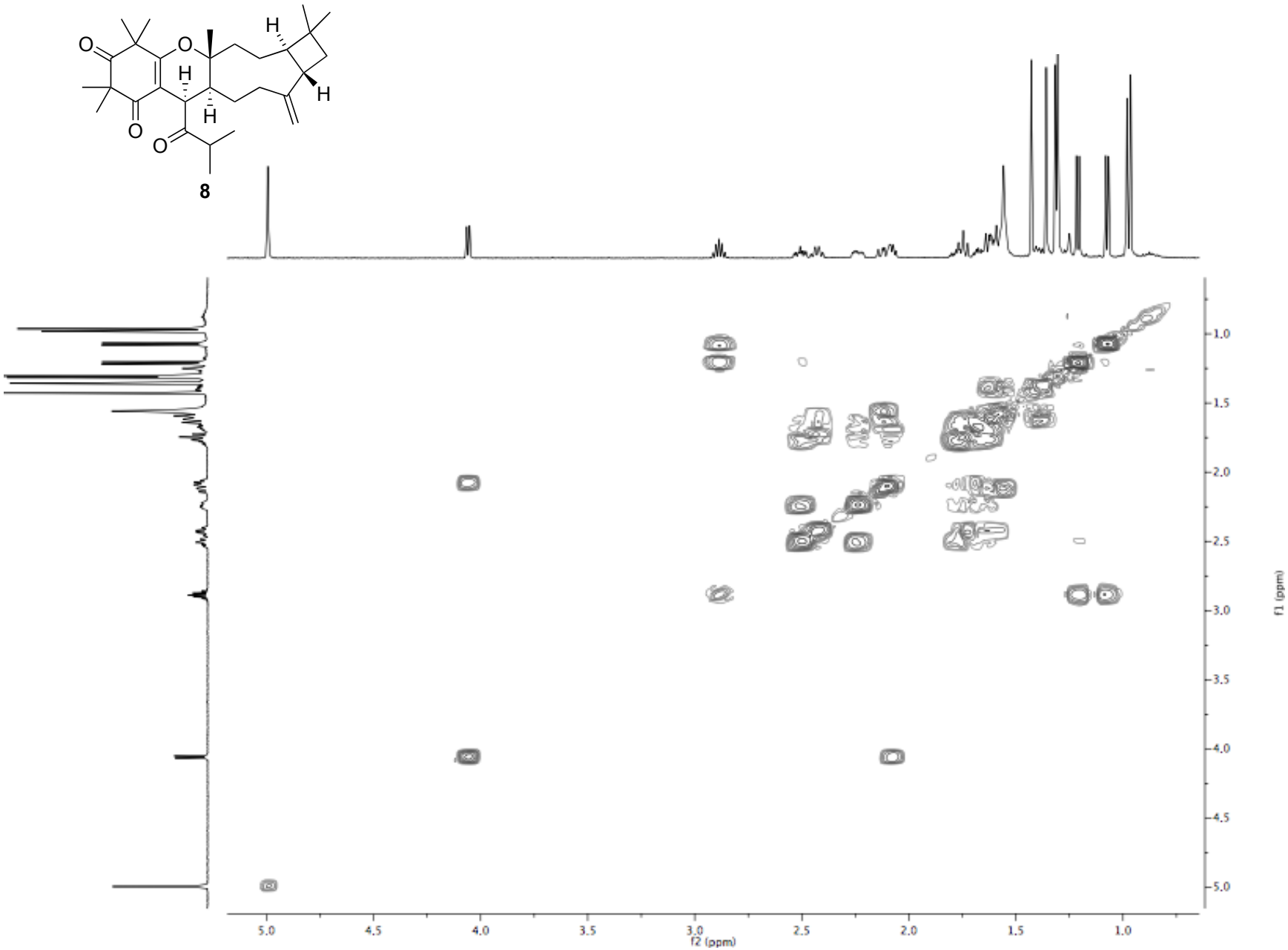


Figure S29. ^{1}H–^{1}H COSY spectrum for compound **8**

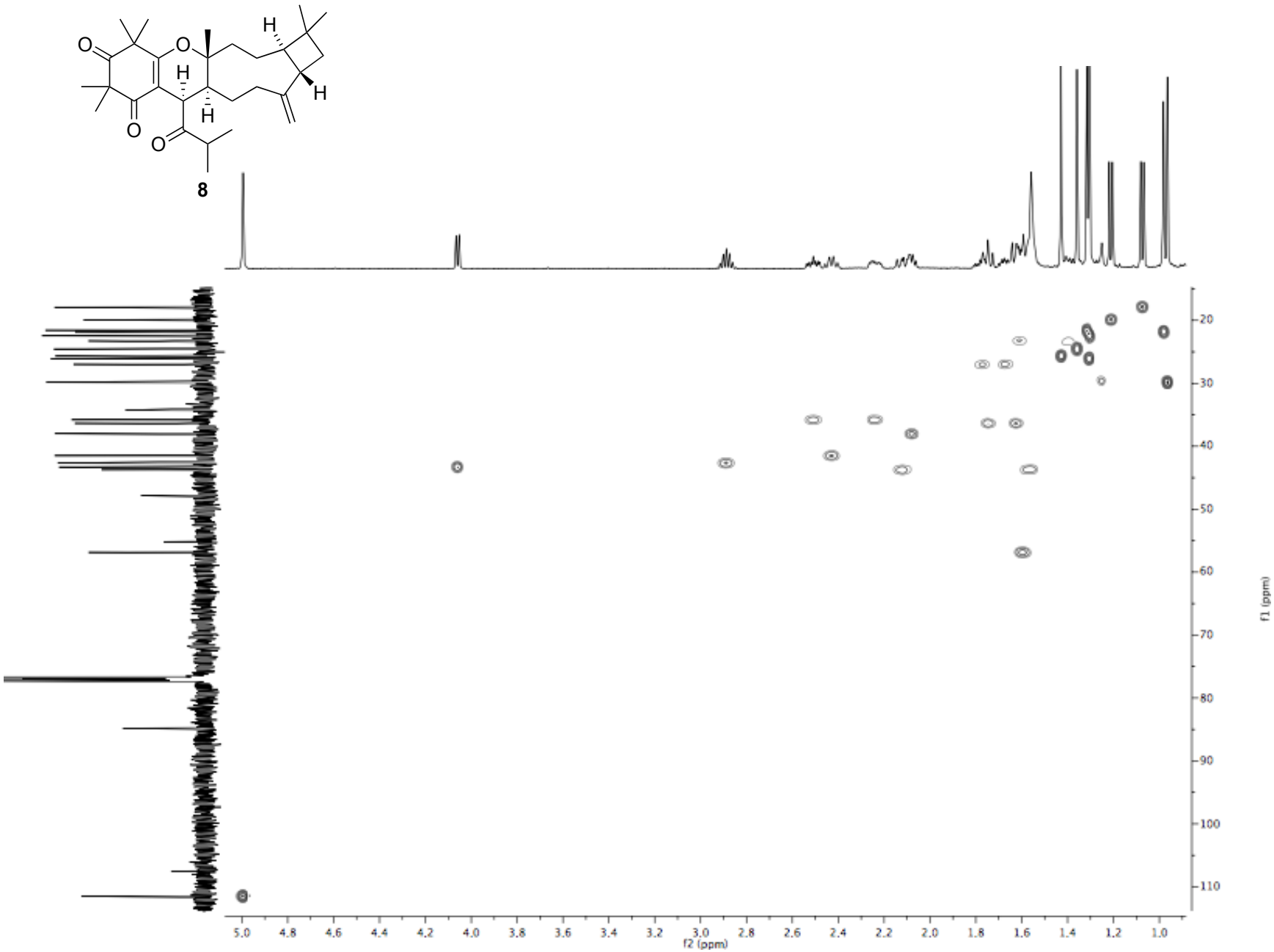


Figure S30. HSQC spectrum for compound **8**

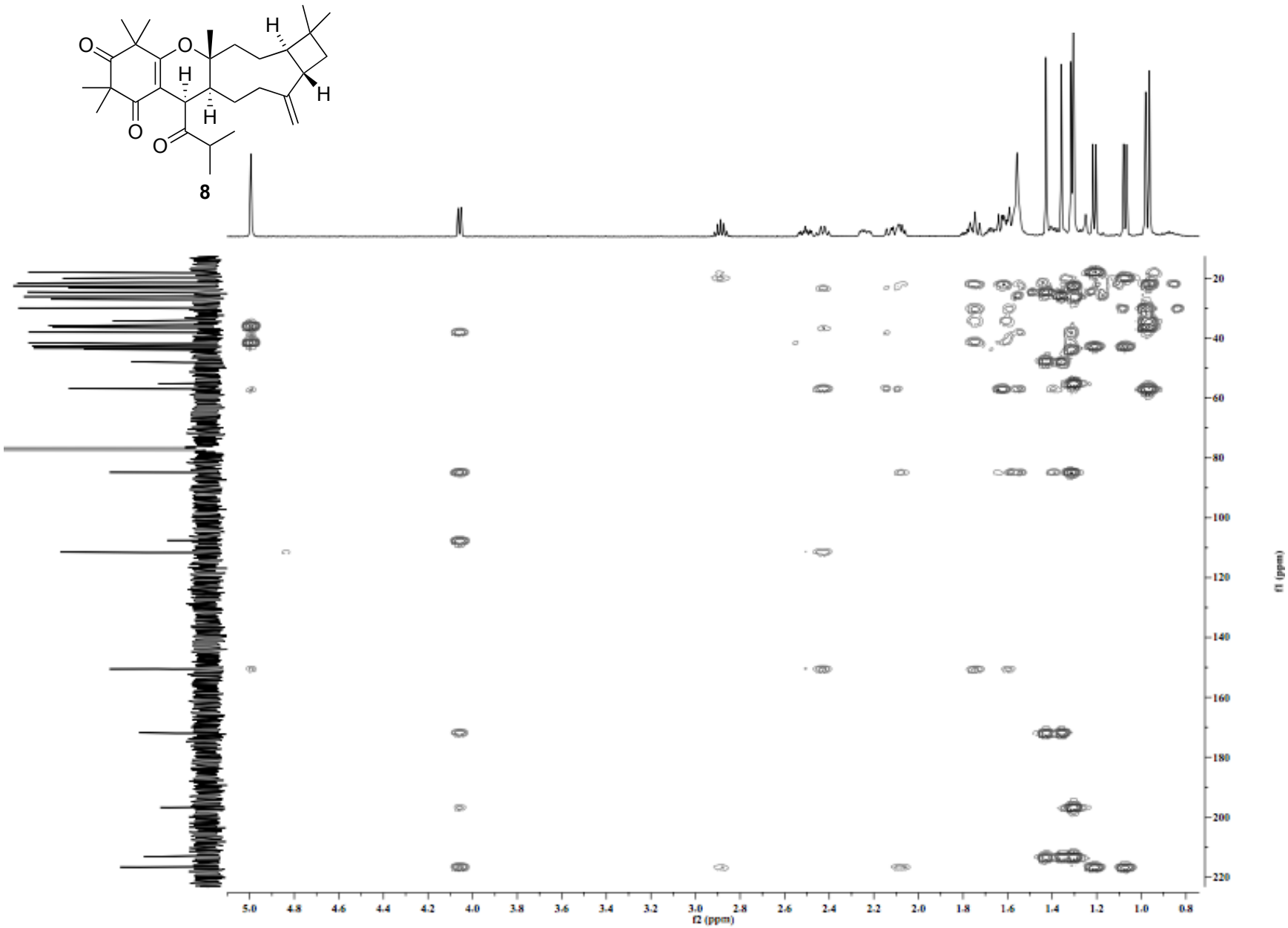


Figure S31. HMBC spectrum for compound **8**

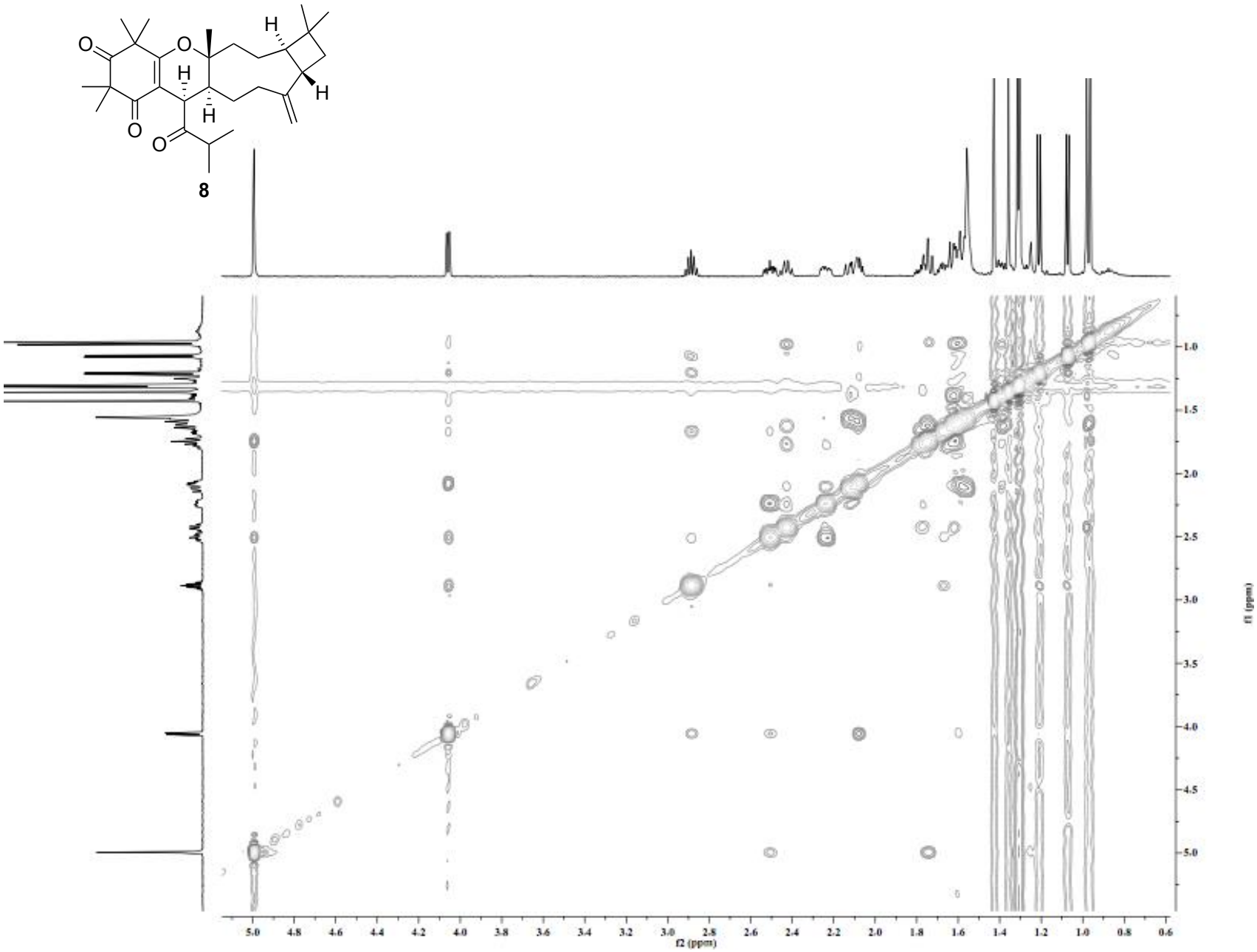
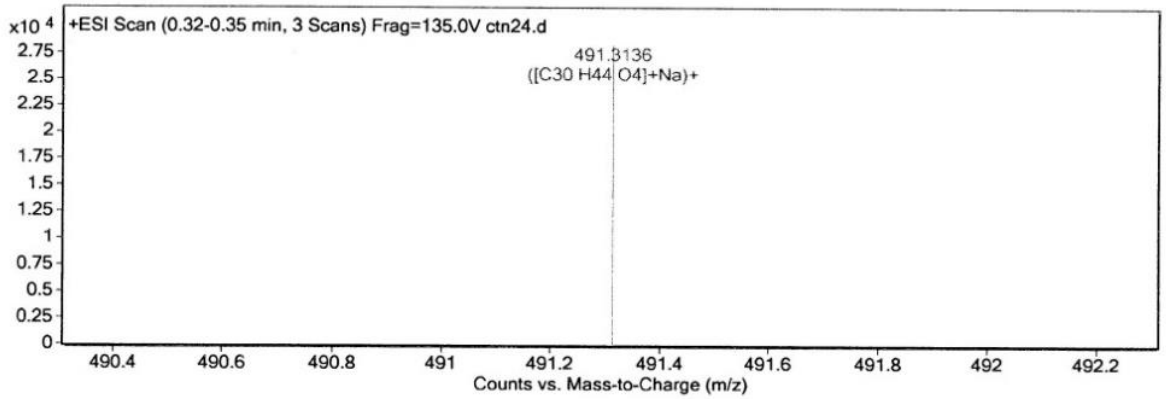


Figure S32. ROESY spectrum for compound **8**

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
121.0509	1	6664.11		
245.0784	1	9070.59		
469.3316	1	9643.45		
491.3136	1	28218.13	C30 H44 O4	(M+Na)+
492.3172	1	8922.6	C30 H44 O4	(M+Na)+
493.2945	1	4152.24		
507.288	1	21589.38		
508.2914	1	6785.18		
922.0098	1	11224.43		
959.9658	1	4590.55		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30
N	0	10

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)
C30 H44 O4	468.3240	491.3132	491.3136	-0.4	

Figure S33. HRESIMS spectrum for compound **8**

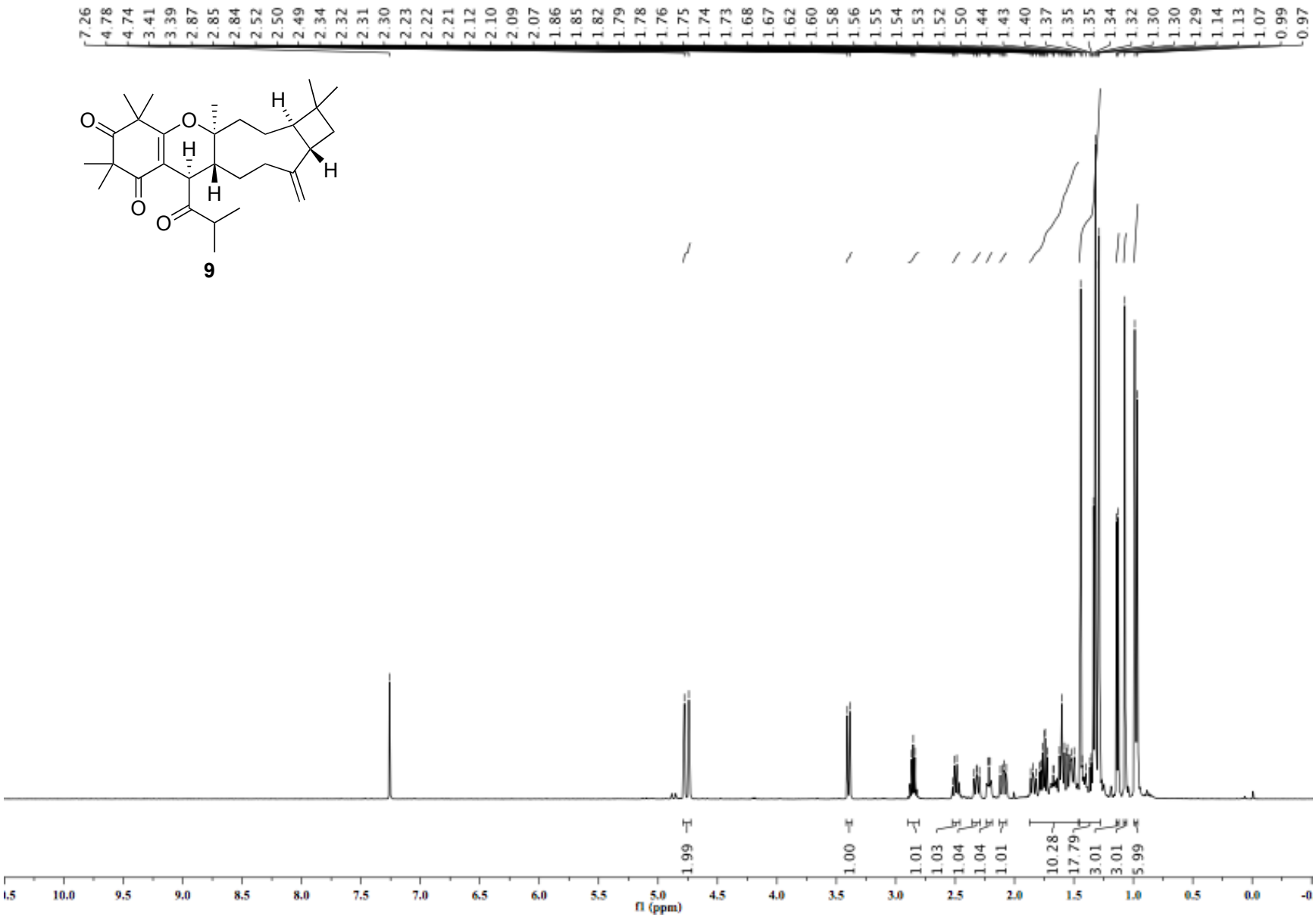


Figure S34. ^{1}H NMR spectrum for compound **9**

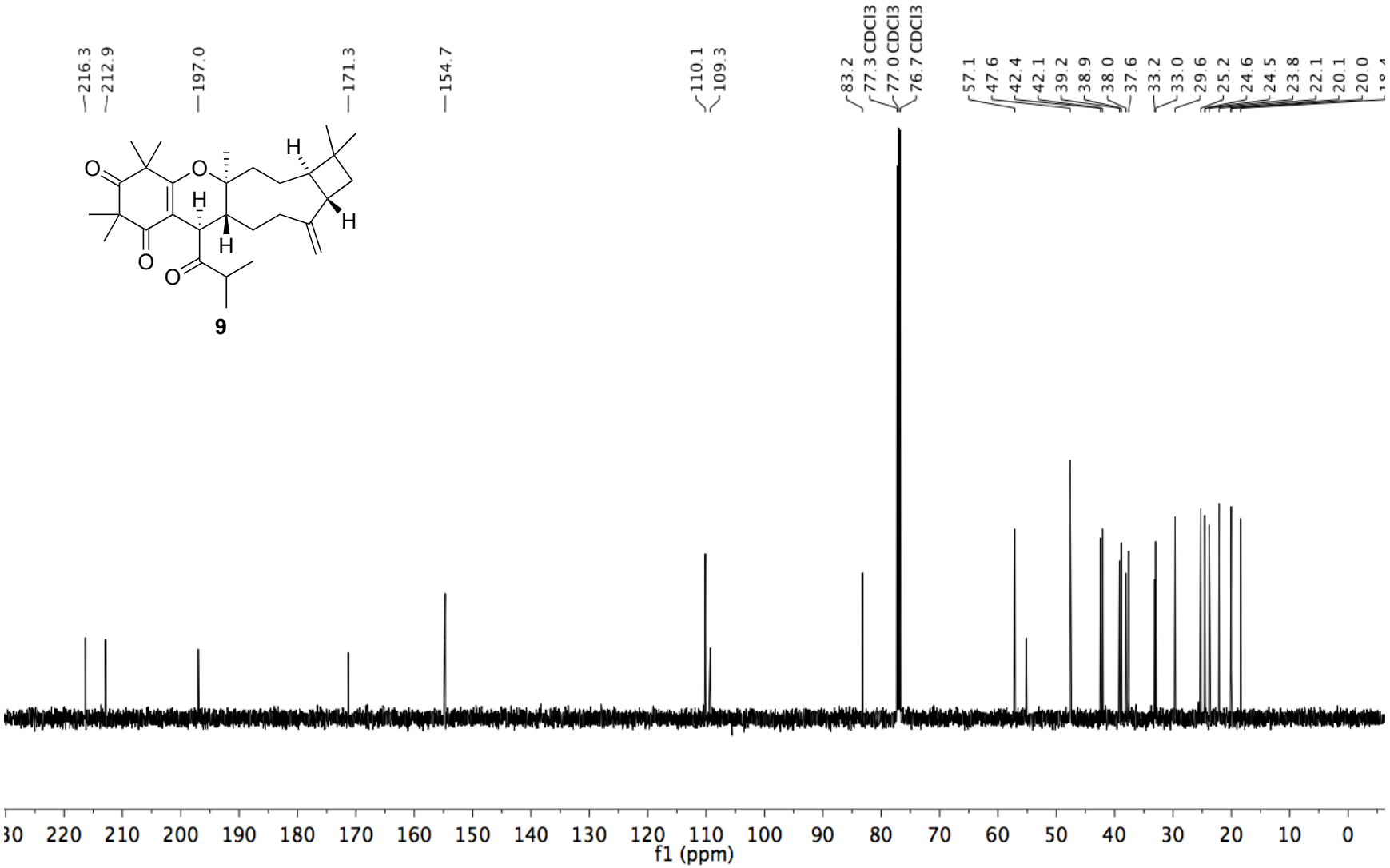


Figure S35. ^{13}C NMR spectrum for compound **9**

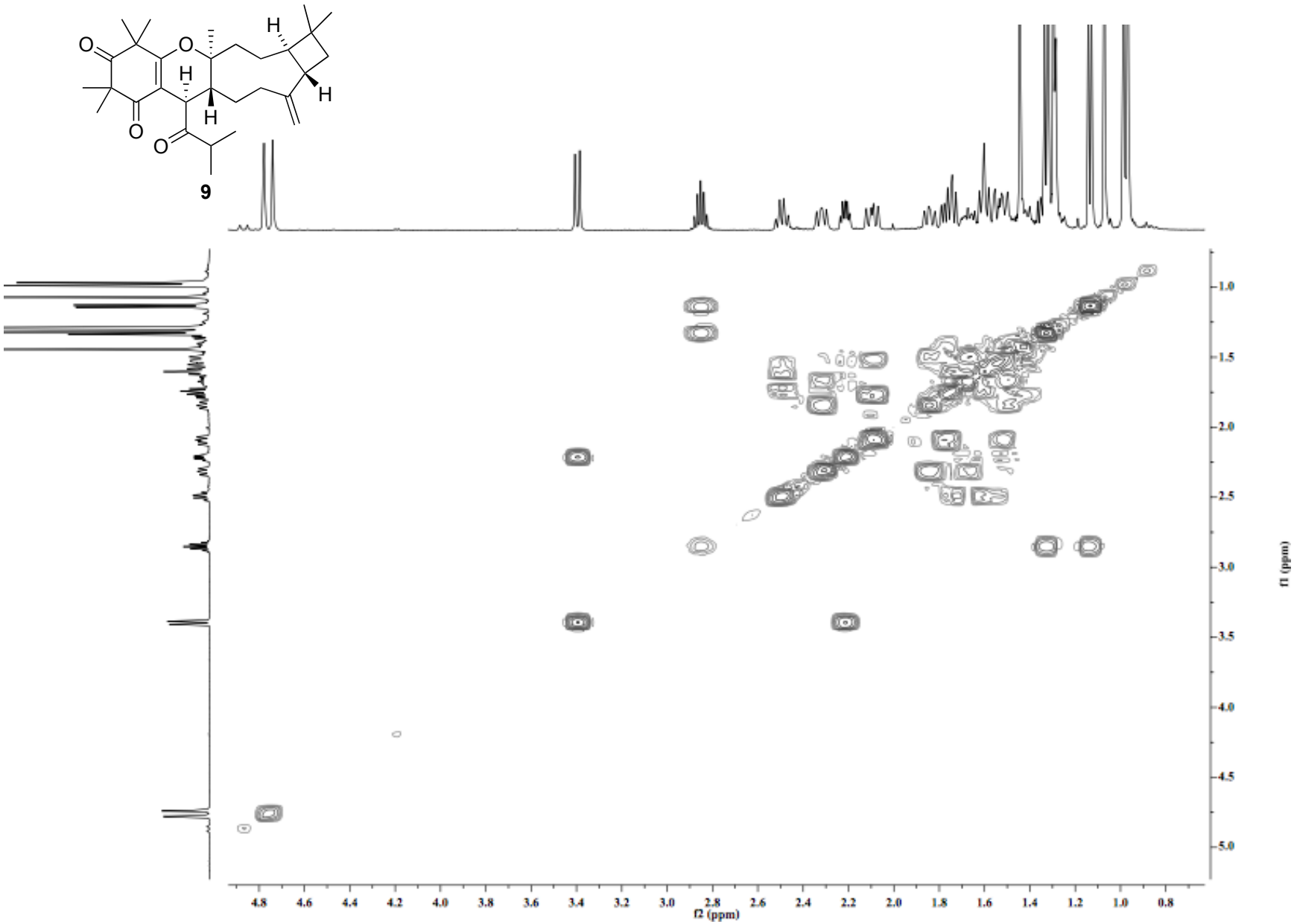


Figure S36. ^{1}H–^{1}H COSY spectrum for compound **9**

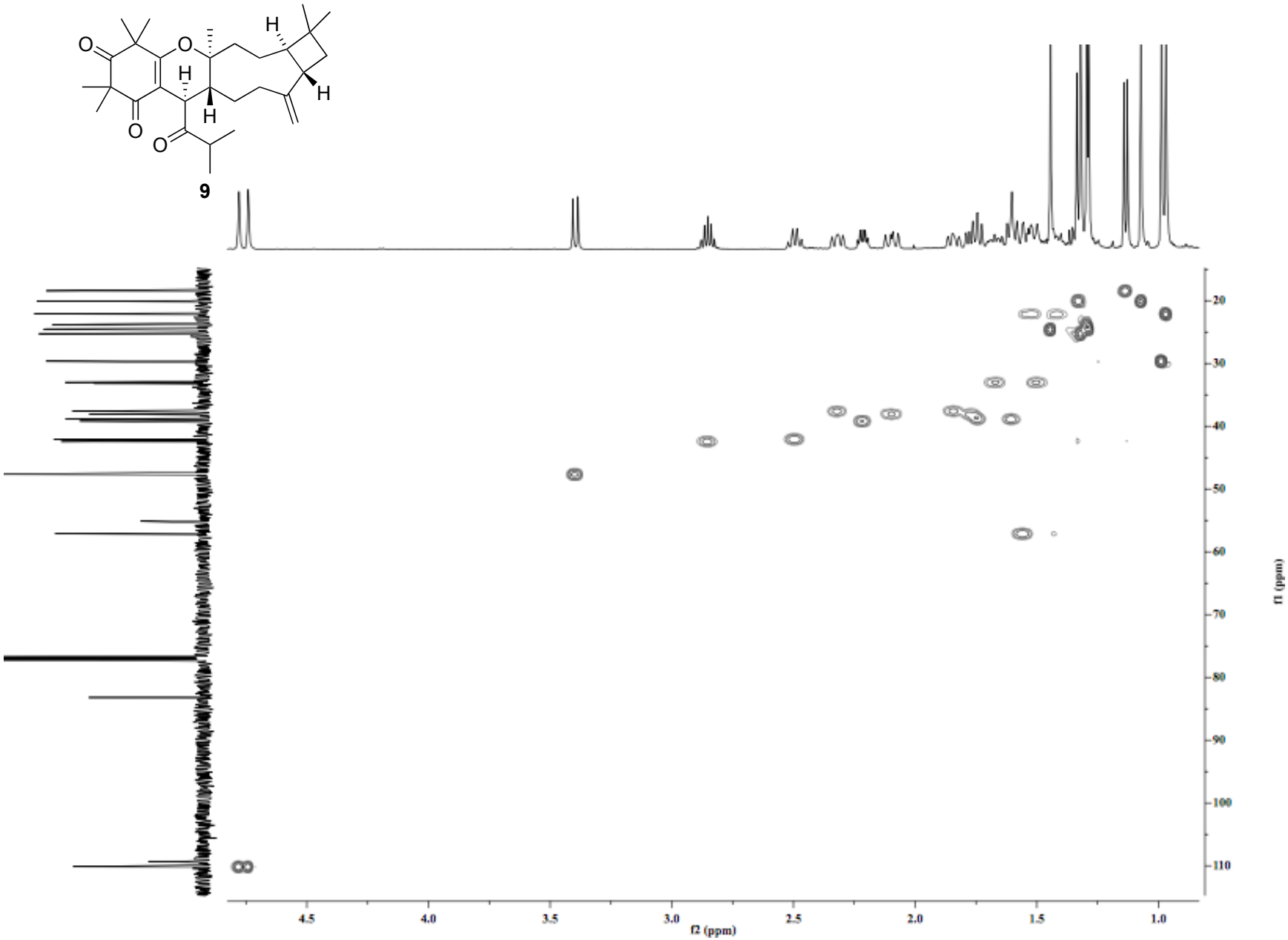


Figure S37. HSQC spectrum for compound **9**

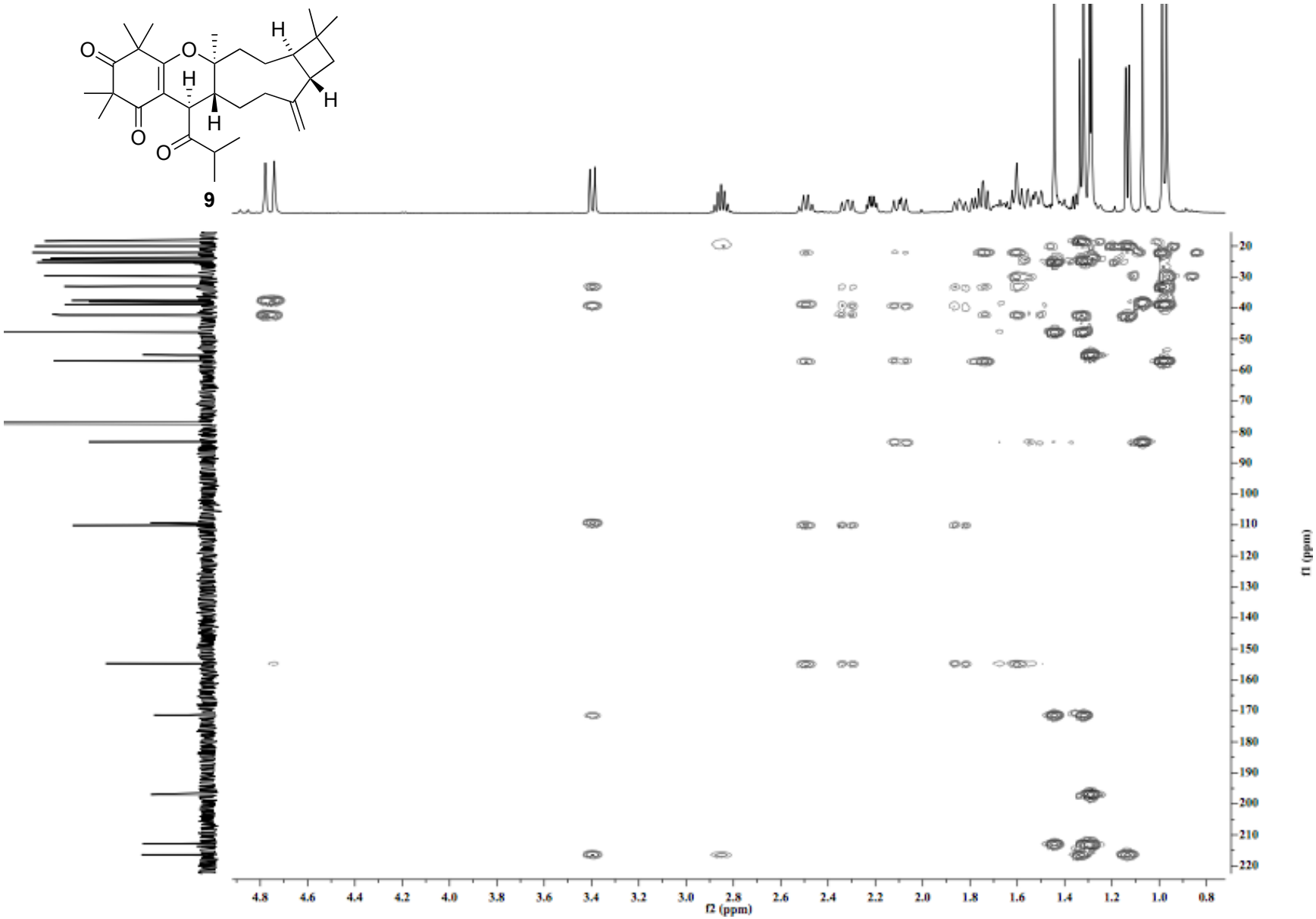


Figure S38. HMBC spectrum for compound **9**

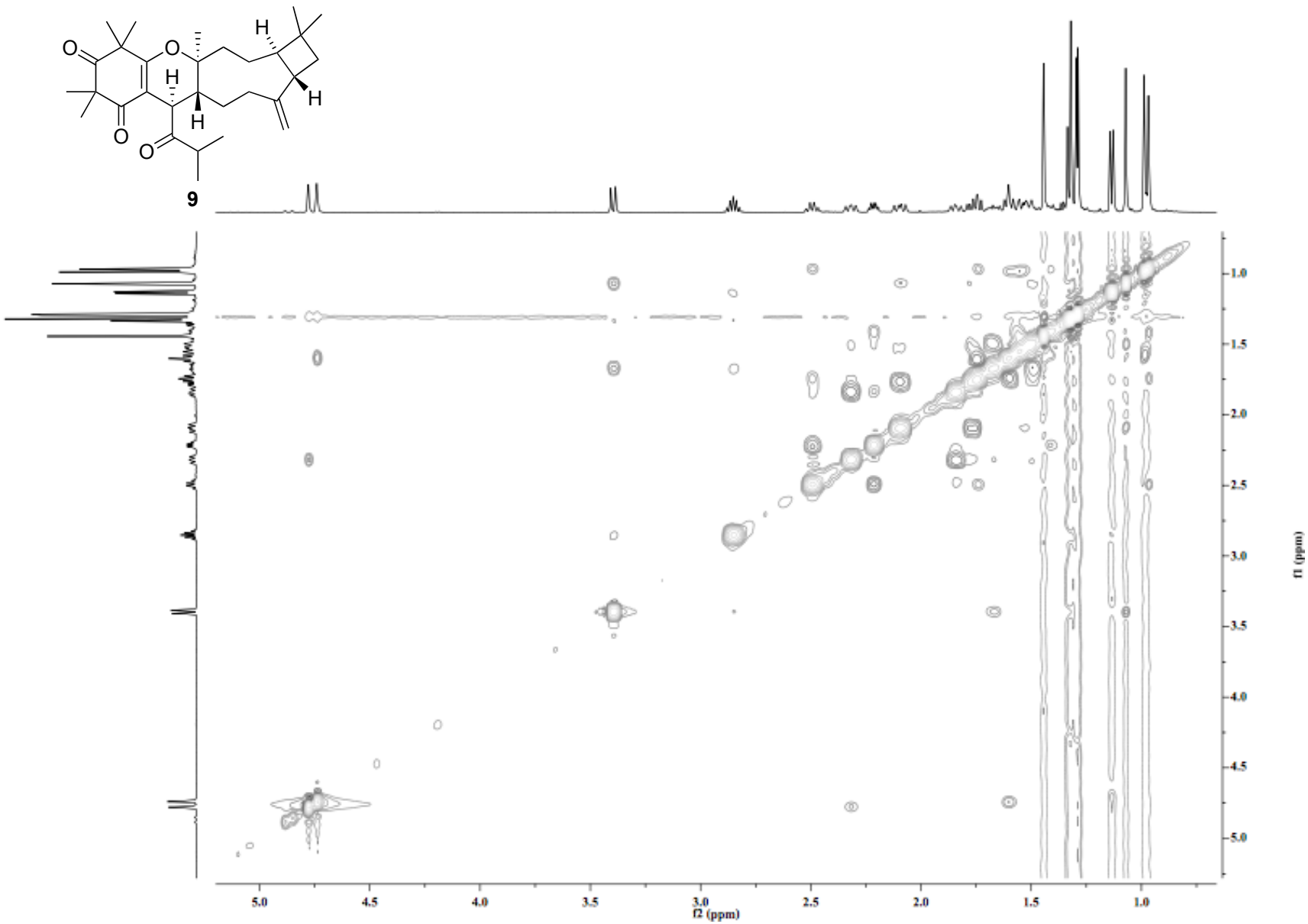
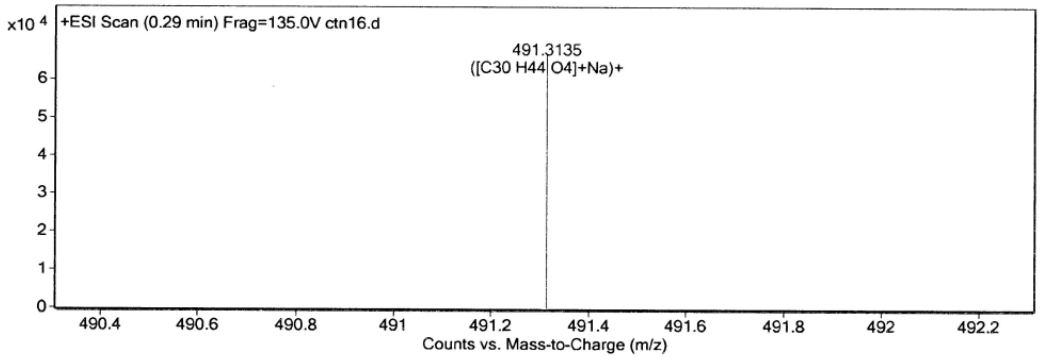


Figure S39. ROESY spectrum for compound **9**

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
245.078	1	8317.92		
469.3312	1	21043.38		
470.3348	1	6699.11		
491.3135	1	66585.97	C30 H44 O4	(M+Na)+
492.3165	1	19507.32	C30 H44 O4	(M+Na)+
507.2874	1	51840.4		
508.2905	1	16073.62		
509.2901	1	5507.71		
922.0098	1	9236.87		
959.6372	1	7934.6		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30
N	0	10

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C30 H44 O4	468.3240	491.3132	491.3135	-0.2	-0.4	9.0000

Figure S40. HRESIMS spectrum for compound **9**

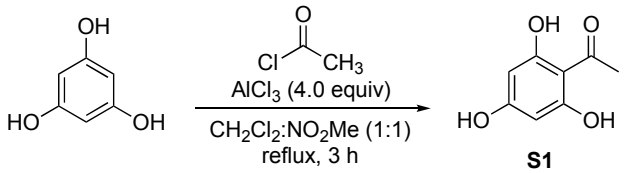
III. Bioactivity Assay (Kunming Institute of Botany)

AChE Inhibitory Assay

AChE (acetylcholinesterase) inhibitory effects of **5–11** were evaluated by the spectrophotometric method using a slight modification. Meroterpenoids were dissolved in DMSO. The reaction mixture (totally 200 μL) containing phosphate buffer (pH = 8.0), **5–11** (50 μM), and acetyl cholinesterase (0.02 U/mL) was heated for 20 min at 37°C. Then, the reaction was initiated by the addition of 40 μL of a solution containing DTNB (0.625 mM) and acetylthiocholine iodide (0.625 mM) for the AChE inhibitory activity assay. Hydrolysis of acetylthiocholine was monitored at 405 nm every 30 seconds for 1 hour. Tacrine was used as positive control with a final concentration of 0.333 μM. All experiments were performed in triplicate. Percentage inhibition was calculated as follows: inhibition (%) = (E – S)/E × 100 (E and S are the activities of the enzyme without and with **5–11**).

IV. Experimental Procedures and Compound Characterization (Boston University)

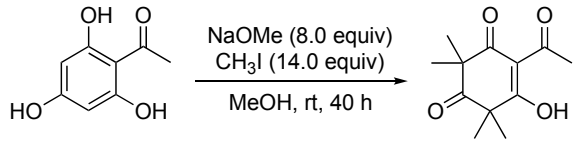
A. Reaction details and additional experiments



S1

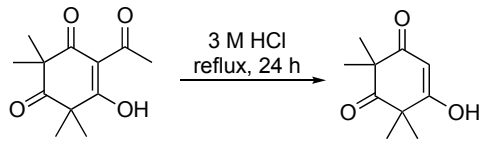
1-(2,4,6-Trihydroxyphenyl)ethan-1-one (acyl-phloroglucinol) (S1): A flame-dried, round-bottom flask was charged with anhydrous phloroglucinol (10.0 g, 79.3 mmol), nitromethane (80 mL), and CH_2Cl_2 (80 mL). The resulting suspension was cooled to 0 °C and aluminum trichloride (42.3 g, 317.2 mmol, 4.0 equiv) was added in small portions. The resulting purple, heterogeneous solution was stirred at 0 °C for 30 minutes and then acetyl chloride (5.66 mL, 6.22 g, 79.3 mmol, 1.0 equiv) was added slowly. After complete

addition of acetyl chloride, the reaction mixture was removed from the ice bath and was then heated at reflux. At 3.5 h, the reaction was cooled to room temperature and poured into crushed ice/ice water (150 mL). Excess solvent was removed under reduced pressure, followed by extraction with EtOAc (4 x 100 mL). The combined organic layers were washed with sat. NaCl (200 mL), dried (Na_2SO_4), filtered, and concentrated. The crude material was purified *via* flash column chromatography (hexane:EtOAc = 1:1) to afford acyl-phloroglucinol (**S1**) 10.3 g (77%) as a light yellow solid. ^{1}H NMR and ^{13}C NMR shifts were consistent with those reported in the literature.[S2]

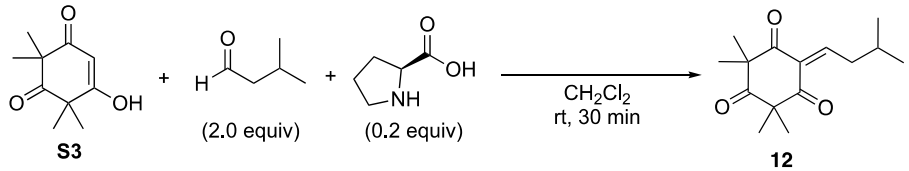


S1 **S2**

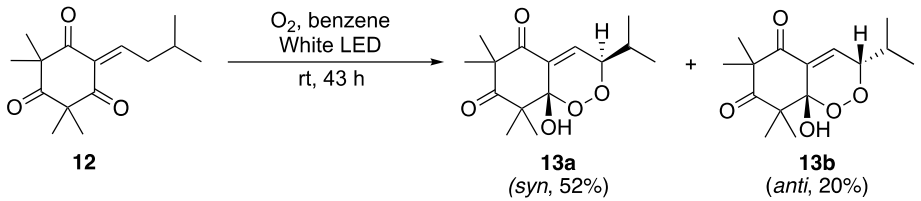
4-Acetyl-5-hydroxy-2,2,6,6-tetramethyl-cyclohex-4-ene-1,3-dione (acyl-syncarpic acid) (S2): A flame-dried, round-bottom flask was charged with anhydrous MeOH (160 mL) and a magnetic stir bar. The flask was submerged in an ice bath and sodium metal (11.27 g, 490.1 mmol, 8.0 equiv) was added in small portions. The mixture was stirred at 0 °C for 30 minutes (most sodium had dissolved) and then a solution of acylphloroglucinol (**S1**, 10.3 g, 61.3 mmol) in anhydrous MeOH (80 mL) was added in one portion. The reaction was stirred at 0 °C for an additional 30 minutes and then methyl iodide (53.4 mL, 121.7 g, 857.6 mmol, 14.0 equiv) was added dropwise. After the addition of methyl iodide, the ice bath was removed and the reaction was stirred at room temperature for 40 h, at which point it was quenched with 1M aqueous HCl (430 mL). The reaction was then extracted with CH_2Cl_2 (4 x 250 mL), dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane:EtOAc = 75:25 up to 1:1) to afford 10.7 g (77%) acyl-syncarpic acid (**S2**) as a yellow, rod-like solid. ^{1}H NMR and ^{13}C NMR shifts were consistent with those reported in the literature.[S3]



5-Hydroxy-2,2,6,6-tetramethyl-cyclohex-4-ene-1,3-dione (syncarpic acid) (S3): A flame-dried, round-bottom flask containing 4-acetyl-5-hydroxy-2,2,6,6-tetramethyl-cyclohex-4-ene-1,3-dione (**S2**, 10.7 g, 47.7 mmol) was charged with a magnetic stir bar and 3 M aqueous HCl (440 mL). The reaction was stirred vigorously at reflux for 27 h, at which point the resulting mixture was cooled to room temperature, extracted with EtOAc (4 x 500 mL), and the combined organic extracts were evaporated under a stream of nitrogen. The resulting crude orange solid was purified by flash column chromatography (hexane:EtOAc = 1:1) to afford 6.57 g (76%) of syncarpic acid (**S3**) as an orange solid. ^{1}H NMR and ^{13}C NMR data were consistent with those reported in the literature.[S3]



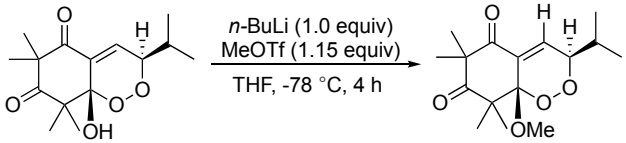
2,2,4,4-Tetramethyl-6-(3-methylbutylidene)cyclohexane-1,3,5-trione (12): A 50-mL round bottom flask was charged with a magnetic stir bar, syncarpic acid (**S3**, 757 mg, 4.2 mmol), and CH_2Cl_2 (21 mL). To the round bottom flask was added isovaleraldehyde (894.6 μL, 715.6 mg, 8.3 mmol, 2.0 equiv) followed by proline (95.7 mg, 830.9 μmol, 0.2 equiv). The reaction was stirred at room temperature for 30 minutes at which point the reaction was filtered through a plug of silica and concentrated under reduced pressure to afford 0.902 g (87%) of 2,2,4,4-tetramethyl-6-(3-methylbutylidene)cyclohexane-1,3,5-trione (**12**) as a light yellow oil. ^{1}H NMR and ^{13}C NMR shifts were consistent with those reported in the literature. [S3]



(3*R*, 8a*R*)-8a-Hydroxy-3-isopropyl-6,6,8,8-tetramethyl-8,8a-dihydrobenzo[c][1,2]dioxine-5,7(3H,6H)-dione (13a) and (3*S*, 8a*R*)-8a-hydroxy-3-isopropyl-6,6,8,8-tetramethyl-8,8a-dihydrobenzo[c][1,2]dioxine-5,7(3H,6H)-dione (13b): A flame-dried, round-bottom flask containing 2,2,4,4-tetramethyl-6-(3-methylbutylidene)cyclohexane-1,3,5-trione (**12**, 945 mg, 3.8 mmol) was charged with a magnetic stir bar, and benzene (38 mL). The flask was stoppered with a rubber septum and then oxygen was bubbled through the solution while simultaneously sonicating for 30 minutes. The reaction was then placed under a balloon of O_2 and was clamped to the middle of glass dish lined with white LED lights (see Supporting Information, page S3, Section IB, for details on the white LED lights). The reaction was then stirred at room temperature in the presence of white LED lights for 43 h, at which point ^{1}H NMR analysis indicated full consumption of starting material. The reaction was concentrated under reduced pressure and was purified by flash column chromatography (hexane:EtOAc = 90:10) to afford 554 mg (52%) of (3*R*, 8a*R*)-8a-hydroxy-3-isopropyl-6,6,8,8-tetramethyl-8,8a-dihydrobenzo[c][1,2]dioxine-5,7(3H,6H)-dione (**13a**) and 217 mg (20%) of (3*S*, 8a*R*)-8a-hydroxy-3-isopropyl-6,6,8,8-tetramethyl-8,8a-dihydrobenzo[c][1,2]dioxine-5,7(3H,6H)-dione (**13b**) both as white solids (72% combined yield).

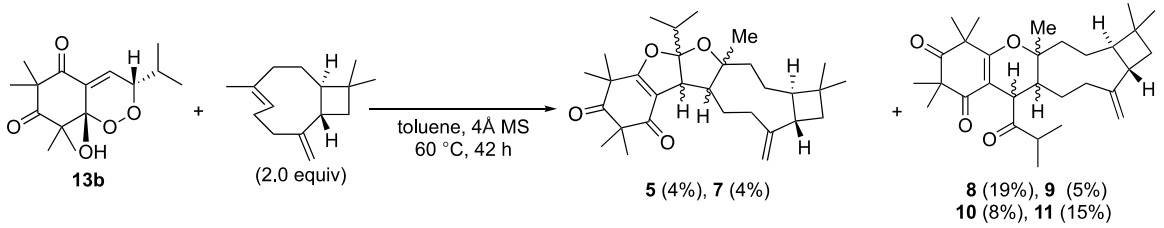
Diastereomer **13a**: White solid, m.p. = 125 – 130 °C; R_f = 0.24 (hexane:EtOAc = 9:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (d, *J* = 1.5 Hz, 1H), 4.73 (dd, *J* = 5.9, 1.5 Hz, 1H), 2.01 (pd, *J* = 6.9, 5.8 Hz, 1H), 1.38 (s, 3H), 1.36 (s, 3H), 1.31 (s, 3H), 1.05 (d, *J* = 6.8 Hz, 6H), 1.02 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ210.51, 197.74, 137.90, 134.33, 97.90, 83.47, 54.89, 51.70, 30.49, 26.60, 24.06, 20.66, 18.17, 17.89, 15.11.; IR ν_{max} (film): 3464, 2974, 2876, 1724, 1633, 1469, 1377, 1284, 1161, 1099, 1070, 1046, 995 cm^{-1} ; HRMS (ESI+): m/z calculated for $C_{15}H_{22}O_5Na$ (M + Na^+): 305.1365, found (M + Na^+): 305.1354.

Diastereomer **13b**: White solid, m.p. = 137 – 142 °C; R_f = 0.12 (hexane:EtOAc = 9:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (d, *J* = 4.1 Hz, 1H), 2.13 (dp, *J* = 8.4, 6.7 Hz, 1H), 1.38 (s, 3H), 1.37 (s, 3H), 1.32 (s, 3H), 1.14 (d, *J* = 6.7 Hz, 3H), 1.07 (d, *J* = 6.9 Hz, 3H), 1.02 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): 210.57, 197.79, 137.79, 133.08, 97.42, 84.75, 55.02, 51.58, 32.03, 26.60, 24.05, 20.95, 19.87, 19.01, 15.17; IR ν_{max} (film): 3454, 2973, 2940, 2874, 1724, 1691, 1635, 1470, 1378, 1279, 1192, 1163, 1073, 1047, 994 cm^{-1} ; HRMS (ESI+): m/z calculated for $C_{15}H_{23}O_5$ ($M + H^+$): 283.1545, found: 283.1466.



13a **18**

(3*R*,8a*R*)-3-Isopropyl-8a-methoxy-6,6,8,8-tetramethyl-8,8a-dihydrobenzo[*c*][1,2]dioxine-5,7(3*H*,6*H*)-dione (13): A solution of (3*R*, 8a*R*)-8a-hydroxy-3-isopropyl-6,6,8,8-tetramethyl-8,8a-dihydrobenzo[c][1,2]dioxine-5,7(3H,6H)-dione (21.0 mg, 74.4 μmol) (**8a**) in THF (5.3 mL) was cooled to was cooled to -78 °C (dry/ice acetone bath) and *n*-butyllithium (2.5 M, 30 μL, 1.0 equiv) was added dropwise The reaction was stirred for 15 minutes at this temperature and then methyl trifluoromethanesulfonate (14.0 mg, 85.5 μmol, 9.4 μL, 1.15 equiv) was added. The reaction was stirred -78 °C for 4 h at which point the reaction mixture was quenched with sat. aqueous NH_4Cl (5 mL), warmed to room temperature, and solvents were removed *in vacuo*. The residual aqueous layer was then, extracted with CH_2Cl_2 (3 x 5 mL). The combined organic extracts were washed with water (2 x 5 mL), brine (5 mL), and the organic layer was collected, dried (Na_2SO_4), filtered, and concentrated *in vacuo* to afford 16 mg of a crude yellow oil. The crude product was purified by preparative TLC (hex:EtOAc = 90:10) to afford 5.6 mg (25%) of a colorless gum. R_f = 0.50 (hexane:EtOAc = 9:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (d, *J* = 1.5 Hz, 1H), 4.64 (dd, *J* = 5.4, 1.5 Hz, 1H), 3.46 (s, 3H), 2.07 (pd, *J* = 7.0, 5.5 Hz, 1H), 1.34 (s, 3H), 1.31 (s, 3H), 1.28 (s, 3H), 1.06 (d, *J* = 7.0 Hz, 6H), 1.01 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 210.39, 198.67, 141.02, 131.43, 100.96, 82.83, 54.72, 54.69, 53.28, 30.67, 25.98, 24.91, 21.16, 18.23, 17.94, 15.52.; IR ν_{max} (film): 2973, 2939, 1726, 1690, 1637, 1465, 1375, 1285, 1259, 1159, 1051, 1025, 999, 988 cm^{-1}; HRMS (ESI+): m/z calculated for $C_{15}H_{21}O_4$ ($M + H^+ - MeOH$): 265.3290 found: 265.1515.



Rhodomyrtusial A (5), rhodomyrtusial C (7), rhotomentodione A (8), rhotomentodione B (9), tomentodione Q (10), tomentodione R (11): A 4-mL reaction vial containing a magnetic stir bar and 4Å molecular sieves was flame dried under vacuum and then purged with argon. The vial was then charged with (*3S*, 8a*R*)-8a-hydroxy-3-isopropyl-6,6,8,8-tetramethyl-8,8a-dihydrobenzo[c][1,2]dioxine-5,7(3H,6H)-dione (**13b**, 16 mg, 56.6 μmol), toluene (541 μL), and *trans*-caryophyllene (23.2 mg, 113.3 μmol, 26.0 μL, 2.0 equiv). The vial was capped, placed in a pre-heated heating block at 60 °C, and stirred at this temperature for 42 h at which point the vial was removed from the heating block and was cooled to room temperature. Once cooled, the reaction was filtered through a plug of celite (CH_2Cl_2 was used as the eluent) and was concentrated under reduced pressure. The crude oil obtained was first purified by pipette column (hexane:EtOAc = 90:10) and was then subjected to preparative HPLC purification (MeCN:H_2O = 90:10 over 45 minutes) to afford **5** (1.0 mg, 4%), **7** (1.0 mg, 4%), **8** (5.1 mg, 19%), **9** (1.2 mg, 5%), **10** (2.0 mg, 8%), and **11** (4.1 mg, 15%).

Rhodomyrtusial A (5): Colorless gum; $[\alpha]_D^{17}$ +16.4 (*c* 0.10 mg/mL, MeOH); ^{1}H (500 MHz) δ 4.90 (s, 1H), 4.78 (s, 1H), 3.16 (d, *J* = 8.3 Hz, 1H), 2.42 (dd, *J* = 13.5, 5.7 Hz, 1H), 2.34 (q, *J* = 9.3 Hz, 1H), 2.03 – 1.82 (m, 4H), 1.80 – 1.61 (m, 3H), 1.58 – 1.53 (m, 2H), 1.40 (s, 6H), 1.35 (s, 3H), 1.32 (s, 3H), 1.17 (s, 3H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.94 (s, 3H), 0.94 (d, *J* = 5.2 Hz, 1H), 0.91 (s, 3H); ^{13}C NMR (126 MHz) δ 213.5, 193.2, 175.6, 152.5, 127.2, 115.9, 110.8, 89.6, 57.6, 55.2, 52.7, 50.0, 45.3, 42.6, 36.0, 35.7, 35.1, 33.6, 30.0, 29.7, 25.0, 24.7, 23.9, 23.5, 22.3, 22.1, 16.6, 16.5; HRMS (ESI+): m/z calculated for $C_{30}H_{45}O_4$ ($M + H^+$): 469.3318 , found: 469.3314.

Rhodomyrtusial C (7): Colorless gum; $[\alpha]_D^{17}$ + -19.8 (*c* 0.10 mg/mL, MeOH); ^{1}H (500 MHz) δ 5.02 (s, 1H), 3.64 (d, *J* = 9.5 Hz, 1H), 2.66 – 2.57 (m, 1H), 2.45 – 2.36 (m, 1H), 2.15 – 2.03 (m, 2H), 1.97 (dd, *J* = 14.1, 9.7 Hz, 1H), 1.79 (t, *J* = 10.5 Hz, 1H), 1.60 (dd, *J* =

10.7, 7.6 Hz, 1H), 1.55 (d, J = 7.6 Hz, 1H), 1.52 – 1.44 (m, 0H), 1.43 (s, 2H), 1.40 (d, J = 5.7 Hz, 4H), 1.33 (s, 2H), 1.32 – 1.26 (m, 1H), 1.25 (s, 1H), 1.11 (s, 2H), 0.99 (s, 2H), 0.97 (s, 2H), 0.96 (d, J = 6.9 Hz, 2H), 0.92 (d, J = 6.8 Hz, 2H); ^{13}C NMR (126 MHz) δ 213.5, 194.5, 177.5, 152.4, 127.3, 112.3, 111.1, 88.8, 60.0, 55.8, 48.8, 45.7, 45.2, 42.5, 37.0, 36.4, 35.4, 34.5, 29.9, 26.3, 24.5, 24.0, 23.5, 23.1, 22.0, 16.6, 16.5; HRMS (ESI+): m/z calculated for $C_{30}H_{45}O_4$ ($M + H^+$): 469.3318, found: 469.3318.

Rhotomentodione A (8): Colorless gum; $[\alpha]_D^{17}$ +90.4 (*c* 0.10 mg/mL, MeOH); ^{1}H (500 MHz) and ^{13}C NMR (126 MHz) data, see Table S3; HRMS (ESI+): m/z calculated for $C_{30}H_{45}O_4$ ($M + H^+$): 469.318, found: 469.3334.

Rhotomentodione B (9): Colorless gum; $[\alpha]_D^{17}$ +20.5 (*c* 0.10 mg/mL, MeOH); ^{1}H (500 MHz) and ^{13}C NMR (126 MHz) data, see Table S3; HRMS (ESI+): m/z calculated for $C_{30}H_{45}O_4$ ($M + H^+$): 469.3318, found: 469.3315.

Tomentodione Q (10): Colorless gum; $[\alpha]_D^{17}$ -263.9 (*c* 0.10 mg/mL, MeOH); ^{1}H (500 MHz) and ^{13}C NMR (126 MHz) data, see Table S3; HRMS (ESI+): m/z calculated for $C_{30}H_{45}O_4$ ($M + H^+$): 469.3318, found: 469.3307.

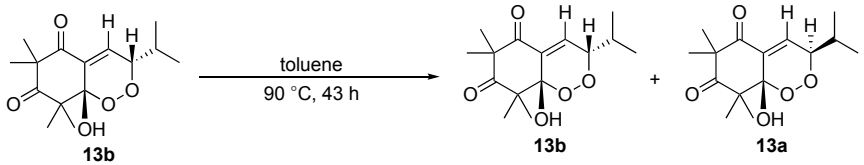
Tomentodione R (11): White, amorphous solid; $[\alpha]_D^{17}$ +4.2 (*c* 0.10 mg/mL, MeOH); ^{1}H (500 MHz) and ^{13}C NMR (126 MHz) data, see Table S3; HRMS (ESI+): m/z calculated for $C_{30}H_{44}O_4Na$ ($M + Na^+$): 305.1365, found: 305.1354.

Table S3. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data for synthetic **3**–**6** in $CDCl_3$

	rhotomentodione A (3)		**rhotomentodione B (4)**		**tomentodione Q (5)**		**tomentodione R (6)**	
No.	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
1	172.0 C		171.4 C		172.0 C		171.5 C	
2	48.0 C		47.8 C		48.2 C		47.7 C	
3	213.4 C		213.1 C		213.5 C		212.9 C	
4	55.3 C		55.3 C		55.8 C		55.1 C	
5	196.9 C		197.2 C		197.6 C		197.2 C	
6	107.7 C		109.3 C		108.2 C		108.9 C	
7	43.4 CH	4.06 d (6.6)	47.8 CH	3.40 d (10.5)	43.2 CH	4.20 d (7.3)	49.3 CH	3.24 d (10.7)
8	216.8 C		216.5 C		217.2 C		215.0 C	
9	42.8 CH	2.89 sept. (6.8)	42.6 CH	2.86 sept. (6.9)	43.2 CH	2.84 sept. (6.7)	39.5 CH	2.73 sept. (6.9)
10	20.0 CH_3	1.21 d (6.8)	20.2 CH_3	1.33 d (6.9)	20.9 CH_3	1.32 d (6.9)	20.5 CH_3	1.19 d (6.9)
11	18.0 CH_3	1.07 d (6.6)	18.6 CH_3	1.14 d (6.9)	17.9 CH_3	1.07 d (6.6)	19.6 CH_3	1.06 d (6.8)
12	25.8 CH_3	1.43 s	24.7 CH_3	1.45 s	25.8 CH_3	1.44 s	25.1 CH_3	1.43 s

13	24.7 CH_3	1.36 s	25.4 CH_3	1.32 s	25.1 CH_3	1.38 s	24.7 CH_3	1.35 s
14	21.7 CH_3	1.31 s	24.0 CH_3	1.30 s	21.7 CH_3	1.30 s	23.5 CH_3	1.27 s
15	26.2 CH_3	1.30 s	24.7 CH_3	1.29	27.4 CH_3	1.35 s	25.0 CH_3	1.31 s
1′	57.0 CH	1.59 m	57.3 CH	1.52 m	57.9 CH	1.56 m	51.7 CH	1.95 m
2′a	23.4 CH_2	1.63 m	22.3 CH_2	1.52 m	23.5 CH_2	1.49 br m	22.3 CH_2	1.77 (unresolved)
2′b		1.40 m		1.42 m		1.24 dt		1.42 (unresolved)
3′a	43.9 CH_2	2.12 br dd (14.8, 10.7)	38.2 CH_2	2.10 ddd (15.4, 10.7, 1.3)	41.0 CH_2	2.05 brdd (15.7, 9.9)	36.9 CH_2	2.15 ddd (15.6, 12.5, 3.0)
3′b		1.57 m		1.77 brdd (14.1, 7.3)		1.78 brdd (15.9, 8.3)		1.97 m
4′	84.9 C		83.4 C		84.2 C		83.0 C	
5′	38.1 CH	2.08 m	39.3 CH	2.22 dt (10.2, 5.0)	39.3 CH	2.36 td (9.0, 3.1)	38.2 CH	2.25 td (11.0, 2.7)
6′a	27.1 CH_2	1.80 m	33.2 CH_2	1.67 m	28.8 CH_2	1.67 m	31.6 CH_2	1.77 (unresolved)
6′b		1.68 m		1.50 m		1.49 br m		1.53 m
7′a	35.9 CH_2	2.51 ddd (14.2, 9.9, 4.4)	37.8 CH_2	2.32 brddd	37.2 CH_2	2.51 brdd (13.4, 8.5)	34.9 CH_2	2.35 dt (13.8, 5.2)
7′b		2.24 ddd (14.0, 7.0, 3.9)		1.85 brdd		2.27 brdd (13.8, 9.6)		2.09 td (13.1, 4.3)
8′	150.6 C		154.8 C		154.1 C		150.9 C	
9′	41.6 CH	2.43 q (9.6)	42.2 CH	2.50 q (9.4)	43.0 CH	2.58 q (9.0)	41.9 CH	2.38 ovrlp dt
10′a	36.5 CH_2	1.75 (10.5)	39.0 CH_2	1.74 d (8.4)	37.9 CH_2	1.74 d (10.0)	36.6 CH_2	1.94 m
10′b		1.62 m		1.61 t (10.3)		1.70 d (8.1)		1.63 ovrlp dd
11′	34.4 CH_3		33.3 CH_3		33.9 CH_3		33.6 CH_3	
12′	30.0 CH_3	0.96 s	29.8 CH_3	0.99 s	29.9 CH_3	0.99 s	30.2 CH_3	0.98 s
13′	22.6 CH_3	0.98 s	22.3 CH_3	0.97 s	22.7 CH_3	0.94 s	22.1 CH_3	0.98 s
14′	21.9 CH_3	1.31 s	20.2 CH_3	1.08 s	21.3 CH_3	1.15 s	21.1 CH_3	1.13 s
15′*a*	111.6 CH_2	5.00 2H s	110.3 CH_2	4.78 s	110.8 CH_2	4.87 brs	111.3 CH_2	4.84 brs
15′b				4.74 s		4.81 brs		4.76 brs

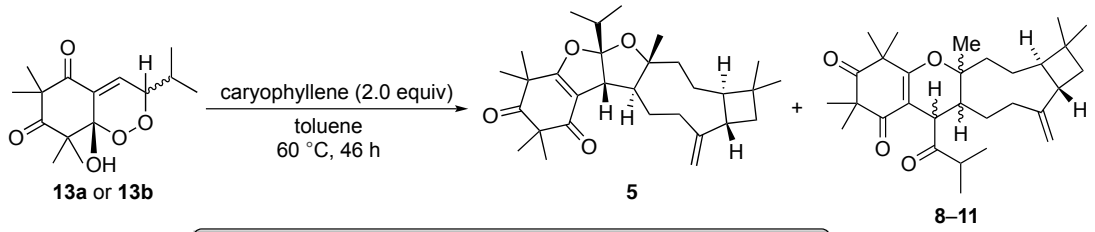
Thermal equilibration of endoperoxides 13a and 13b:



A 4-mL reaction vial containing a magnetic stir bar was flame dried under vacuum, cooled to room temperature, and was purged with argon. To the vial was added pure endoperoxide **13b** (20.0 mg, 70.8 μmol, see **Figure S62** for ^{1}H NMR of starting material) and toluene (354 μL). The reaction was heated at 90 °C for 43 h at which point the reaction was cooled to room temperature and was concentrated

under reduced pressure. ^{1}H NMR without further purification indicated a 1:1.5 ratio of **13b** : **13a** (see **Figure S63** for crude ^{1}H NMR spectrum).

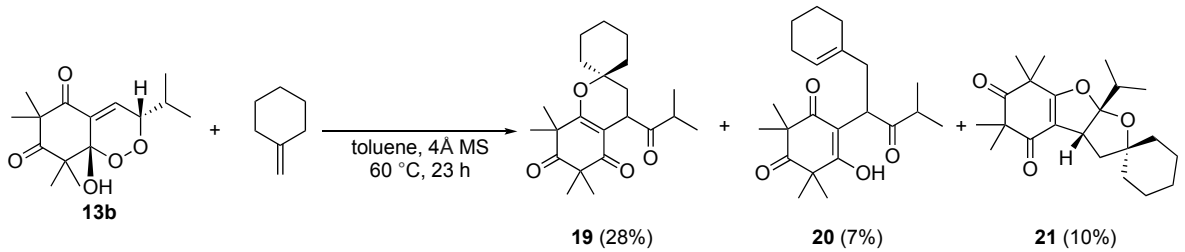
Cycloaddition product distribution for each endoperoxide starting material with or without molecular sieves present:



13a or **13b** **5** **8–11**

Entry	SM	4Å MS?	Distribution (**13a** : **13b** : **5** : **8** : **9** : **10** : **11**)
1	**13a**	No	1.00 : 0.18 : 0.00 : 0.00 : 0.00 : 0.00 : 0.00
2	**13a**	Yes	1.00 : 0.54 : 0.51 : 0.74 : 0.57 : 0.57: 0.64
3	**13b**	No	0.25 : 1.00 : 0.00 : 0.00 : 0.00 : 0.00 : 0.00
4	**13b**	Yes	1.14 : 1.00 : 2.59 : 4.06 : 3.30 : 3.64 : 3.43

A 4-mL reaction vial containing a magnetic stir bar (and 4Å molecular sieves for entries 2 and 4) was flame dried under vacuum, cooled to room temperature, and purged with argon. The vial was charged with either **13a** or **13b** (10 mg, 35.4 μmol), toluene (354 μL), and *trans*-caryophyllene (14.5 mg, 70.8 μmol, 16.0 μL, 2.0 equiv). The reaction vials were placed on a pre-heated reaction block at 60 °C and were stirred at this temperature for 46 h at which point they were removed from the heating block and cooled to room temperature. Entries 1 and 3 were concentrated directly under reduced pressure, whereas entries 2 and 4 were filtered through a plug of Celite (CH_2Cl_2 as eluent) and then concentrated. Product distributions were analyzed by ^{1}H NMR analysis. Integration of the vinyl proton on the starting endoperoxide was normalized to 1.0, and integration of the indicative doublets in products **5** and **8–11** allowed for the comparison of starting material to products.



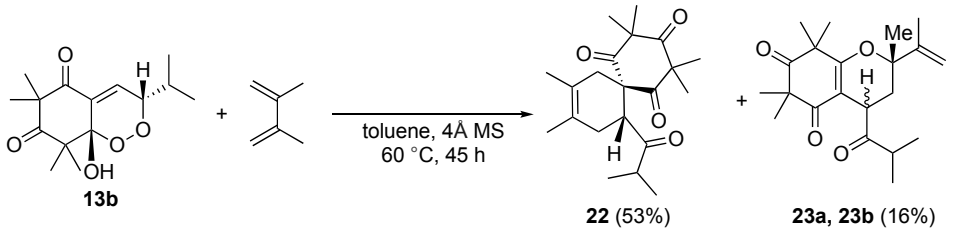
4-Isobutyryl-6,6,8,8-tetramethyl-4,8-dihydrospiro[chromene-2,1'-cyclohexane]-5,7(3*H*,6*H*)-dione (19), 4-(1-(cyclohex-1-en-1-yl)-4-methyl-3-oxopentan-2-yl)-5-hydroxy-2,2,6,6-tetramethylcyclohex-4-ene-1,3-dione (20), and (3a'*R*,8a'*S*)-8a'-isopropyl-5',5',7',7'-tetramethyl-3a',8a'-dihydro-3'*H*-spiro[cyclohexane-1,2'-furo[2,3-*b*]benzofuran]-4',6'(5'*H*,7'*H*)-dione (21): An 8-mL reaction vial containing a magnetic stir bar and 4Å molecular sieves was flame dried under vacuum and then purged with argon. The vial was then charged with (*3S*, 8a*R*)-8a-hydroxy-3-isopropyl-6,6,8,8-tetramethyl-8,8a-dihydrobenzo[c][1,2]dioxine-5,7(3H,6H)-dione (**13b**, 60 mg, 213 μmol), toluene (2.1 mL), and methylenecyclohexane (40.8 mg, 425 μmol, 51.0 μL, 2.0 equiv). The vial was capped, placed in a pre-heated heating block at 60 °C, and stirred at this temperature for 23 h at which point the vial was removed from the heating block and cooled to room temperature. Once cooled, the reaction was filtered through a plug of Celite (CH_2Cl_2 was used as the eluent) and was concentrated under reduced pressure. The crude oil obtained was first purified by preparative TLC (hexane:EtOAc = 9:1) to afford 21.6 mg (28%) of **19**, 5.6 mg (7%) of **20**, and 7.7 mg (10%) of a 6:1 mixture of **21**:**20**, respectively. This mixture was further purified by preparative HPLC (MeCN:H_2O = 90:10 over 30 minutes) to afford 0.4 mg of **20** and 3.1 mg of **21**.

Spirocycle (19): White solid, m.p. = 99 – 102 °C; R_f = 0.32 (hexane:EtOAc = 9:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.76 (dd, *J* = 10.9, 6.5 Hz, 1H), 3.02 (hept, *J* = 6.9 Hz, 1H), 1.98 (dd, *J* = 13.7, 6.5 Hz, 1H), 1.88 – 1.75 (m, 2H), 1.75 – 1.70 (m, 1H), 1.66 (dd, *J* = 13.7, 10.9 Hz, 2H), 1.56 (m, 4H), 1.47 (s, 4H), 1.39 (s, 4H), 1.34 (s, 4H), 1.30 (s, 4H), 1.22 (d, *J* = 6.8 Hz, 4H), 1.14 (d, *J* = 7.0 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 215.2, 213.2, 197.6, 171.6, 108.6, 78.1, 55.3 48.3, 41.2, 39.4, 37.2, 36.0, 33.0, 29.9, 25.9, 25.7, 25.6, 25.4,

23.0, 21.8, 18.8, 18.6; IR ν_{max} (film): 2931, 2856, 1715, 1652, 1619, 1467, 1385, 1358, 1280, 1217, 1184, 1149, 1121, 1072, 1050, 962 cm^{-1} ; HRMS (ESI+): m/z calculated for $C_{22}H_{33}O_4$ ($M + H^+$): 361.2379, found ($M + H^+$): 361.2360.

Alder-ene product (20): Colorless oil; R_f = 0.43 (hexane:EtOAc = 9:1); ^1H NMR (500 MHz, $CDCl_3$): δ 11.33 (s, 1H), 5.36 (br s, 1H), 4.85 (dd, *J* = 9.3, 7.1 Hz, 1H), 2.79 (hept, *J* = 7.0 Hz, 1H), 2.37 – 2.24 (m, 2H), 2.06 – 1.78 (m, 4H), 1.58 – 1.43 (m, 4H), 1.41 (d, *J* = 1.3 Hz, 6H), 1.30 (s, 3H), 1.29 (s, 3H), 1.13 (d, *J* = 3.2 Hz, 3H), 1.11 (d, *J* = 3.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 224.5, 213.1, 197.2, 176.8, 134.0, 125.2, 107.9, 55.0, 49.1, 42.9, 42.8, 38.4, 28.0, 25.2, 25.4, 25.3, 24.0, 22.9, 22.3, 17.4, 17.2; IR ν_{max} (film): 2975, 2932, 2874, 2858, 2837, 1716, 1680, 1645, 1608, 1469, 1379, 1358, 1314, 1209, 1195, 1048 cm^{-1} ; HRMS (ESI+): m/z calculated for $C_{22}H_{33}O_4$ ($M + H^+$): 361.2379, found ($M + H^+$): 361.2368.

Spirocycle (21): White amorphous solid; R_f = 0.43 (hexane:EtOAc = 9:1); ^1H NMR (500 MHz, $CDCl_3$): δ 3.56 (dd, *J* = 9.9, 1.5 Hz, 1H), 2.23 – 2.14 (m, 2H), 1.82 (dd, *J* = 13.2, 10.0 Hz, 1H), 1.76 – 1.48 (m, 7H), 1.46 – 1.27 (m, 3H), 1.40 (s, 3H), 1.38 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 213.6, 194.1, 176.0, 128.4, 114.2, 88.0, 55.2, 45.5, 44.6, 40.6, 39.2, 38.0, 35.2, 25.4, 25.1, 24.4, 23.9, 23.8, 23.7, 23.4, 16.7, 16.7; IR ν_{max} (film): 2976, 2935, 2859, 1717, 1637, 1472, 1408, 1332, 1190, 1107, 1086, 1068, 1040, 899, 833 cm^{-1}; HRMS (ESI+): m/z calculated for $C_{22}H_{33}O_4$ ($M + H^+$): 361.2379, found ($M + H^+$): 361.2415.



13b **22** (53%) **23a, 23b** (16%)

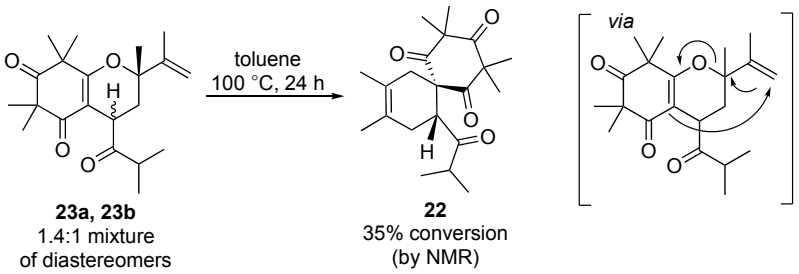
(*R*)-11-Isobutyryl-2,2,4,4,8,9-hexamethylspiro[5.5]undec-8-ene-1,3,5-trione (22) and (2*S*)-4-isobutyryl-2,6,6,8,8-pentamethyl-2-(prop-1-en-2-yl)-2,3,4,8-tetrahydro-5*H*-chromene-5,7(6*H*)-dione (23a and 23b): A 4-mL reaction vial containing a magnetic stir bar and 4Å molecular sieves was flame dried under vacuum and then purged with argon. The vial was then charged with (*3S*, 8a*R*)-8a-

hydroxy-3-isopropyl-6,6,8,8-tetramethyl-8,8a-dihydrobenzo[c][1,2]dioxine-5,7(3H,6H)-dione (**13b**, 15 mg, 53.1 μmol), toluene (519 μL), and 2,3-dimethylbutadiene (8.9 mg, 106 μmol, 12.3 μL, 2.0 equiv). The vial was capped, placed in a pre-heated heating block at 60 °C, and stirred at this temperature for 45 h at which point the vial was removed from the heating block and cooled to room temperature. Once cooled, the reaction was filtered through a plug of Celite (CH_2Cl_2 was used as the eluent) and was concentrated under reduced pressure. The crude oil obtained was purified by preparative TLC (hexane:EtOAc = 9:1) to afford 9.8 mg (53%) of **22** and 2.9 mg (16%) of a 2:1 mixture of unassigned diastereomers **23a** and **23b**.

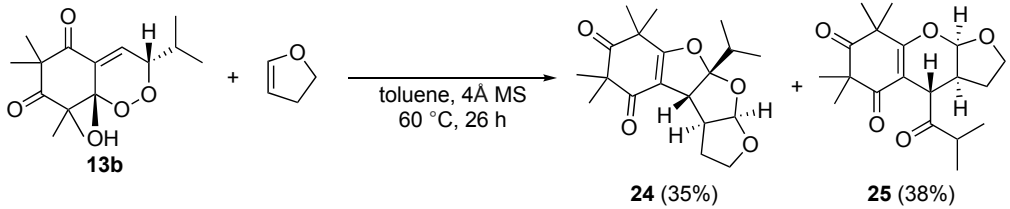
Spirocycle (22): Off white solid, m.p. = 81 – 83 °C; R_f = 0.36 (hexane:EtOAc = 9:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.63 (dd, *J* = 11.7, 7.8 Hz, 1H), 2.91 (hept, *J* = 6.9 Hz, 1H), 2.78 – 2.68 (m, 1H), 2.54 (dd, *J* = 16.9, 7.8 Hz, 1H), 2.16 – 2.01 (m, 2H), 1.67 (s, 3H), 1.54 (s, 3H), 1.51 (s, 3H), 1.49 (s, 3H), 1.41 (s, 3H), 1.35 (s, 3H), 1.17 (d, *J* = 7.1 Hz, 3H), 1.05 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 213.6, 212.8, 209.7, 207.7, 127.4, 119.1, 61.4, 56.7, 56.4, 49.0, 38.0, 37.1, 32.3, 27.0, 27.0, 25.4, 24.2, 19.8, 19.0, 18.8, 17.8; IR ν_{max} (film): 2978, 2923, 1698, 1467, 1380, 1271, 1087, 1059, 418, 403 cm^{-1}; HRMS (ESI+): m/z calculated for $C_{21}H_{31}O_4$ ($M + H^+$): 347.2222, found ($M + H^+$): 347.2200.

Dihydropyran (23a and 23b): Colorless oil; R_f = 0.32 (hexane:EtOAc = 9:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.05 (s, 1H), 4.94 (s, 2H), 4.93 (s, 0H), 4.87 (s, 1H), 3.80 (dd, *J* = 11.6, 6.2 Hz, 1H), 3.56 (dd, *J* = 11.2, 5.6 Hz, 1H), 3.10 – 2.98 (m, 2H), 2.29 (dd, *J* = 13.9, 5.5 Hz, 1H), 2.06 (dd, *J* = 13.6, 6.2 Hz, 1H), 1.85 – 1.83 (m, 3H), 1.82 – 1.78 (m, 2H), 1.72 (dd, *J* = 14.0, 11.3 Hz, 1H), 1.56 (s, 3H), 1.48 (d, *J* = 2.7 Hz, 7H), 1.46 (s, 2H), 1.39 (d, *J* = 4.1 Hz, 2H), 1.37 (s, 2H), 1.35 (d, *J* = 1.8 Hz, 5H), 1.32 (s, 6H), 1.29 (s, 2H), 1.25 (s, 2H), 1.23 (d, *J* = 6.9 Hz, 2H), 1.21 (d, *J* = 6.9 Hz, 2H), 1.15 (dd, *J* = 7.2, 5.6 Hz, 6H), 1.08 – 0.96 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 214.8, 214.7, 212., 210.52, 205.0, 197.7, 197.2, 171.5, 171.1, 147.5, 145.1, 111.8, 111.4, 109.7, 108.6, 102.0, 84.7, 82.1, 80.8, 67.7, 57.0, 55.4, 55.3, 48.2, 48.1, 41.7, 41.4, 40.0, 39.8, 34.9, 34.6, 31.0, 27.2, 26.4, 26.2, 25.8, 25.6, 25.0, 24.8, 24.6, 24.1, 22.8, 22.1, 20.4, 19.7, 18.9, 18.8, 18.8, 18.6, 18.6, 18.5; HRMS (ESI+): m/z calculated for $C_{21}H_{31}O_4$ ($M + H^+$): 347.2222, found ($M + H^+$): 347.2208.

Thermolysis of dihydropyran diastereomers 23a and 23b:



A 4-mL vial containing a 1.4:1 mixture of **23a** and **23b** (2.9 mg, 8.37 μmol, see **Figure S82** for ^{1}H NMR of starting material) was charged with a magnetic stir bar and toluene (100 μL). The vial was capped, placed in a pre-heated heating block at 100 °C, and stirred at this temperature for 24 h at which point the vial was removed from the heating block, cooled to room temperature, and concentrated under reduced pressure. Crude ^{1}H NMR analysis without further purification indicated 35% conversion of hetero-Diels Alder adducts (**23a** and **23b**) to Diels Alder adduct **22**, presumably *via* Claisen rearrangement (see **Figure S84** for crude ^{1}H NMR spectrum).



Tris-furan (24) and (3a*S*,4*S*,9a*R*)-4-isobutyryl-6,6,8,8-tetramethyl-2,3,3a,4,8,9a-hexahydro-5*H*-furo[2,3-*b*]chromene-5,7(6*H*)-dione (25): A 4-mL reaction vial containing a magnetic stir bar and 4Å molecular sieves was flame dried under vacuum and then purged with argon. The vial was then charged with (*3S*, 8a*R*)-8a-hydroxy-3-isopropyl-6,6,8,8-tetramethyl-8,8a-

dihydrobenzo[c][1,2]dioxine-5,7(3H,6H)-dione (**13b**, 10 mg, 35.4 μmol), toluene (348 μL), and dihydrofuran (5.0 mg, 70.8 μmol, 5.4 μL, 2.0 equiv). The vial was capped, placed in a pre-heated heating block at 60 °C, and was stirred at this temperature for 26 h at which point the vial was removed from the heating block and cooled to room temperature. Once cooled, the reaction was filtered through a plug of Celite (CH_2Cl_2 was used as the eluent) and was concentrated under reduced pressure. The crude oil obtained was purified by preparative TLC (hexane:EtOAc = 8:2) to afford 4.1 mg (35%) of **24** and 4.5 mg (38%) of **25**.

***Tris*-furan (24):** White amorphous solid; R_f = 0.49 (hexane:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.84 (d, *J* = 4.6 Hz, 1H), 4.11 – 3.99 (m, 2H), 3.42 (d, *J* = 1.7 Hz, 1H), 2.86 – 2.78 (m, 1H), 2.27 (ddt, *J* = 13.0, 10.3, 8.3 Hz, 1H), 2.17 (hept, *J* = 6.8 Hz, 1H), 1.86 (ddt, *J* = 12.8, 7.5, 4.9 Hz, 1H), 1.54 (s, 3H), 1.43 (s, 3H), 1.42 (s, 3H), 1.34 (s, 6H), 1.07 (d, *J* = 6.8 Hz, 3H), 1.01 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 213.0, 194.4, 176.6, 126.4, 112.9, 111.0, 68.9, 55.6, 50.1, 49.1, 45.6, 35.7, 30.9, 24.9, 24.6, 24.3, 24.2, 16.8, 16.4; IR ν_{max} (film): 2926, 2855, 1716, 1637, 1472, 1410, 1185, 1120, 1069, 1045, 922, 914, 901, 841, 793 cm^{-1}; HRMS (ESI+): m/z calculated for $C_{19}H_{27}O_5$ ($M + H^+$): 335.1858, found ($M + H^+$): 335.1868.

Dihydropyran (25): White amorphous solid; R_f = 0.54 (hexane:EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.77 (d, *J* = 4.2 Hz, 1H), 4.18 (s, 1H), 4.09 (td, *J* = 9.3, 3.2 Hz, 1H), 4.02 (app q, *J* = 8.5 Hz, 1H), 2.98 (hept, *J* = 6.9 Hz, 1H), 2.55 (ddd, *J* = 12.4, 8.5, 4.2 Hz, 1H), 2.15 (dtd, *J* = 11.6, 8.2, 3.3 Hz, 1H), 1.63 – 1.59 (m, 1H), 1.45 (s, 3H), 1.40 (s, 3H), 1.33 (s, 3H), 1.33 (s, 3H), 1.18 (d, *J* = 7.0 Hz, 3H), 1.11 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 214.0, 212.4, 198.2, 171.9, 103.7, 101.6, 68.1, 55.7, 48.3, 42.0, 40.1, 38.5, 26.9, 26.1, 25.2, 24.9, 22.8, 18.8, 18.2; IR ν_{max} (film): 2978, 2971, 2962, 2924, 2872, 2849, 1713, 1652, 1628, 1466, 1394, 1381, 1178, 1101, 1070, 1043, 1028 cm^{-1}; HRMS (ESI+): m/z calculated for $C_{19}H_{27}O_5$ ($M + H^+$): 335.1858, found ($M + H^+$): 335.1846.

B. Select NMR Spectra (Boston University)

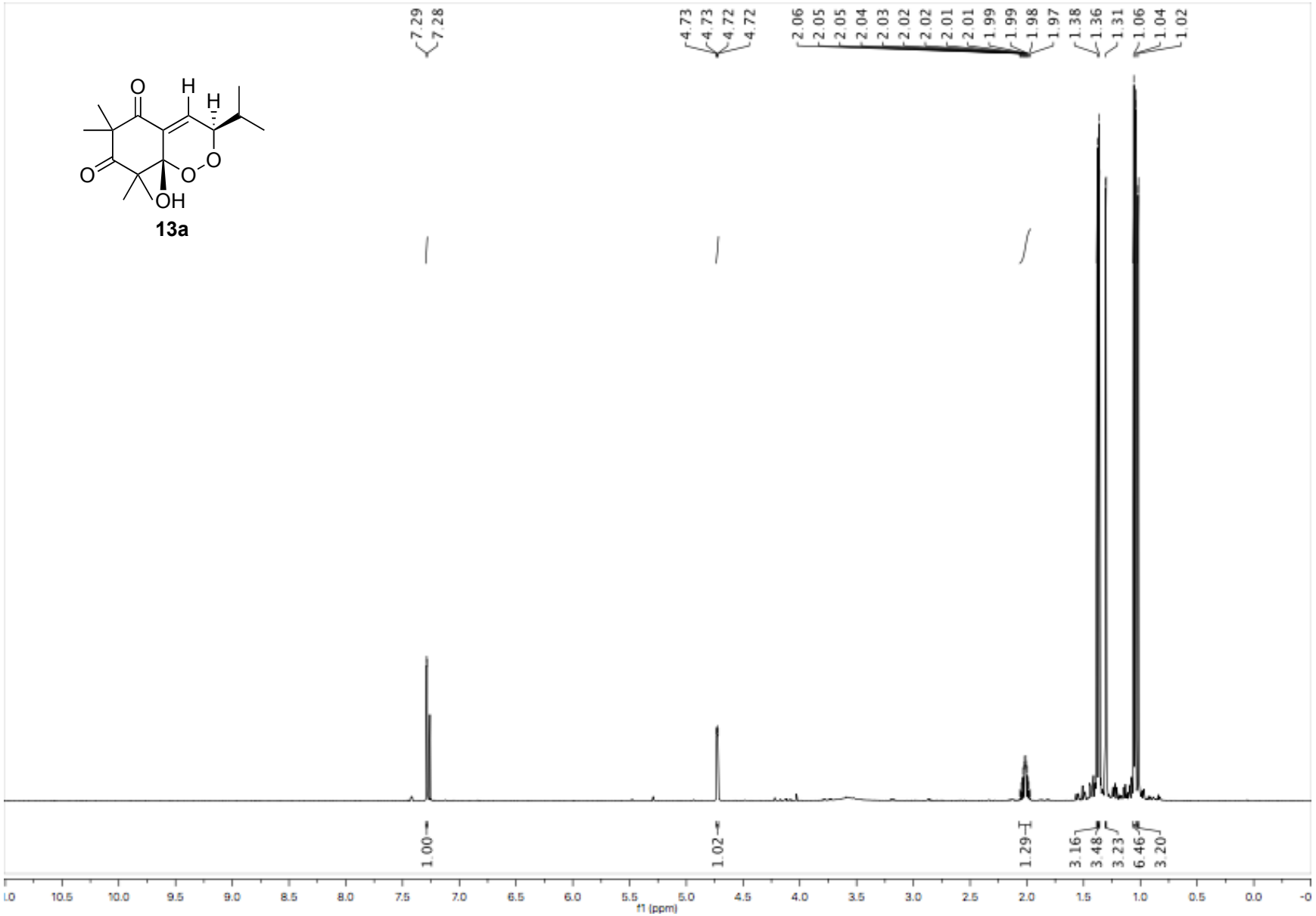


Figure S41. ^{1}H NMR spectrum for *syn*-endoperoxide **13a**

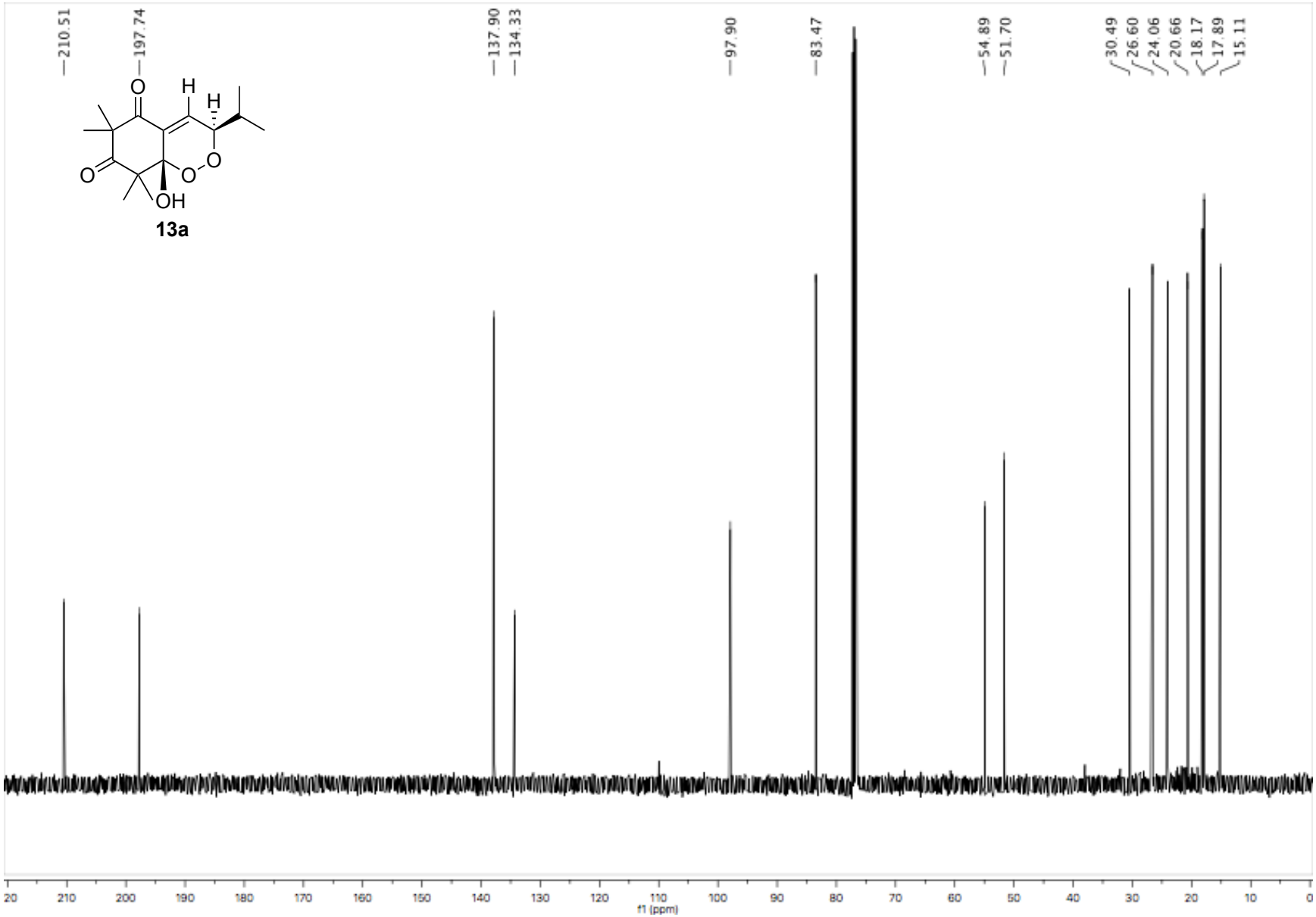


Figure S42. ^{13}C NMR spectrum for *syn*-endoperoxide **13a**

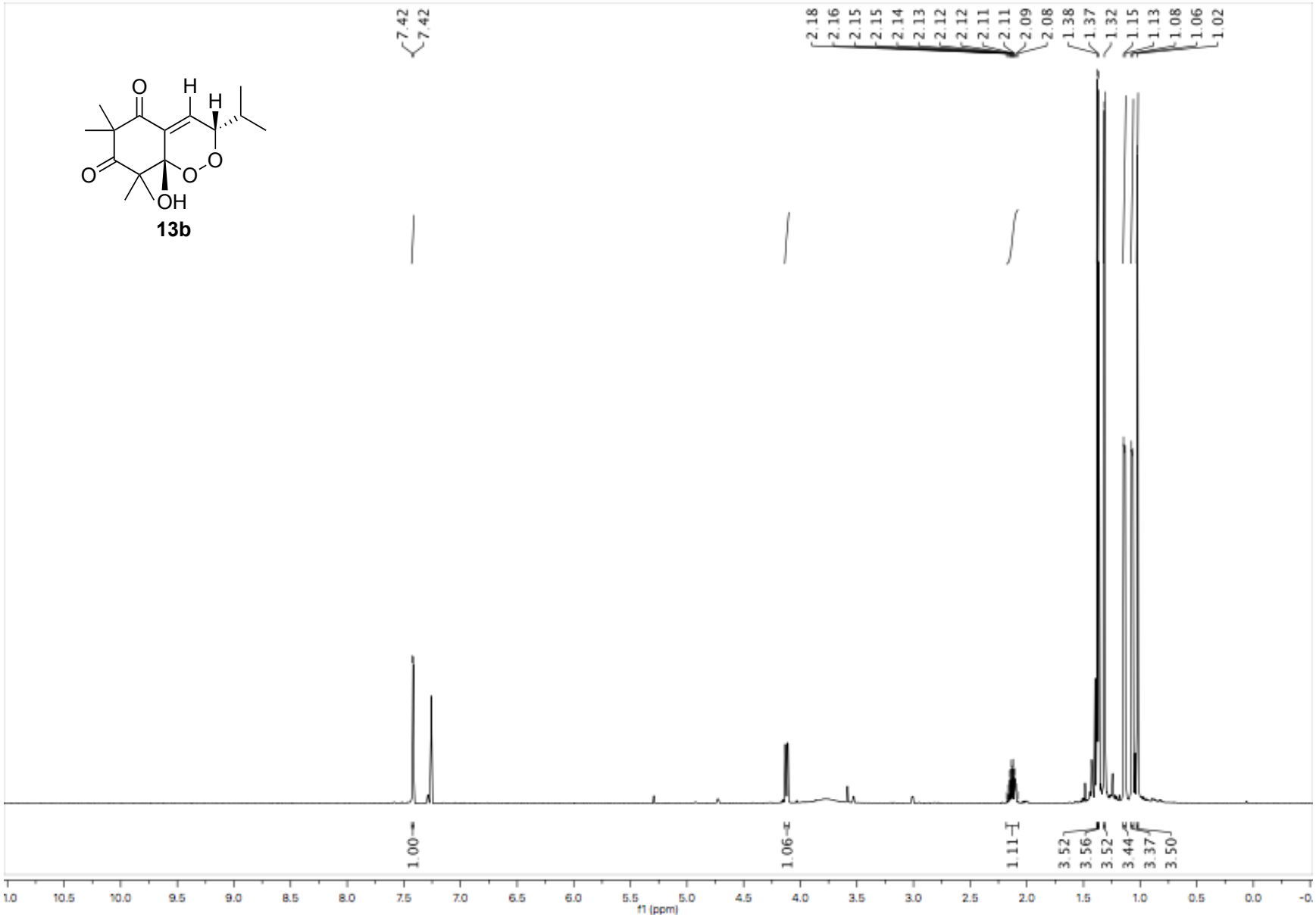


Figure S43. ^{1}H NMR spectrum for *anti*-endoperoxide **13b**

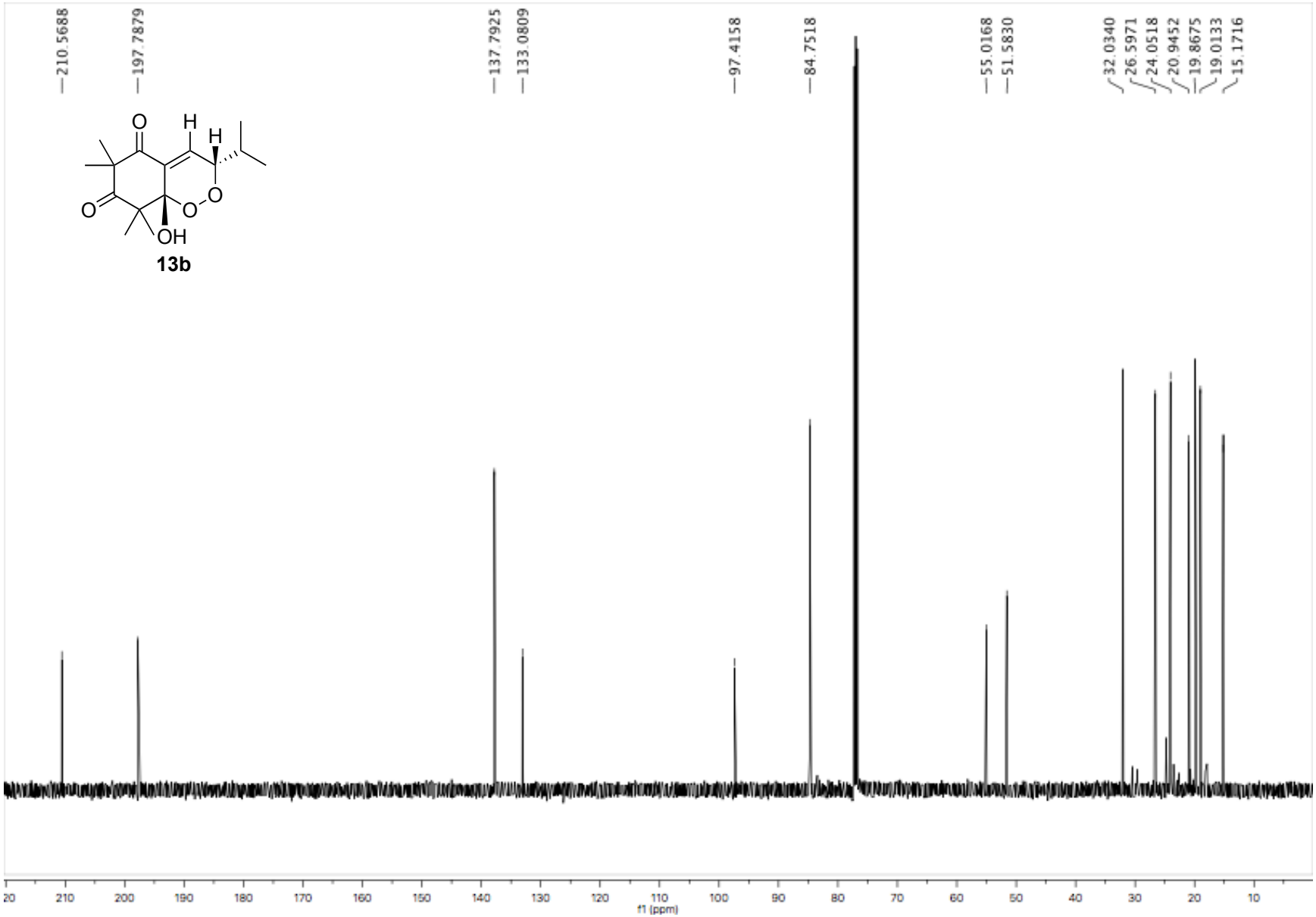


Figure S44. ^{13}C NMR spectrum for *anti*-endoperoxide **13b**

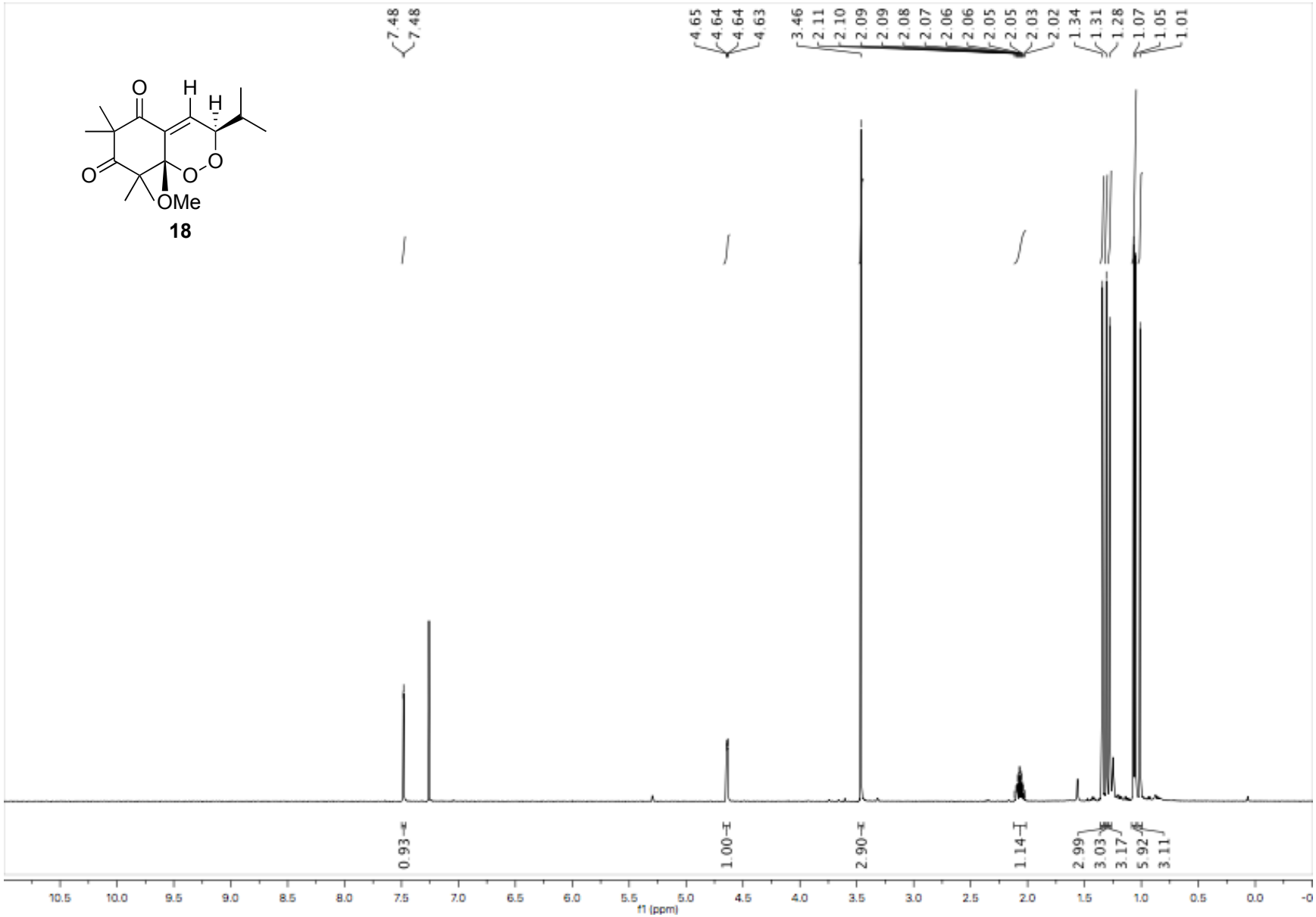


Figure S45. ^{1}H NMR spectrum for endoperoxide methyl-ether **18**

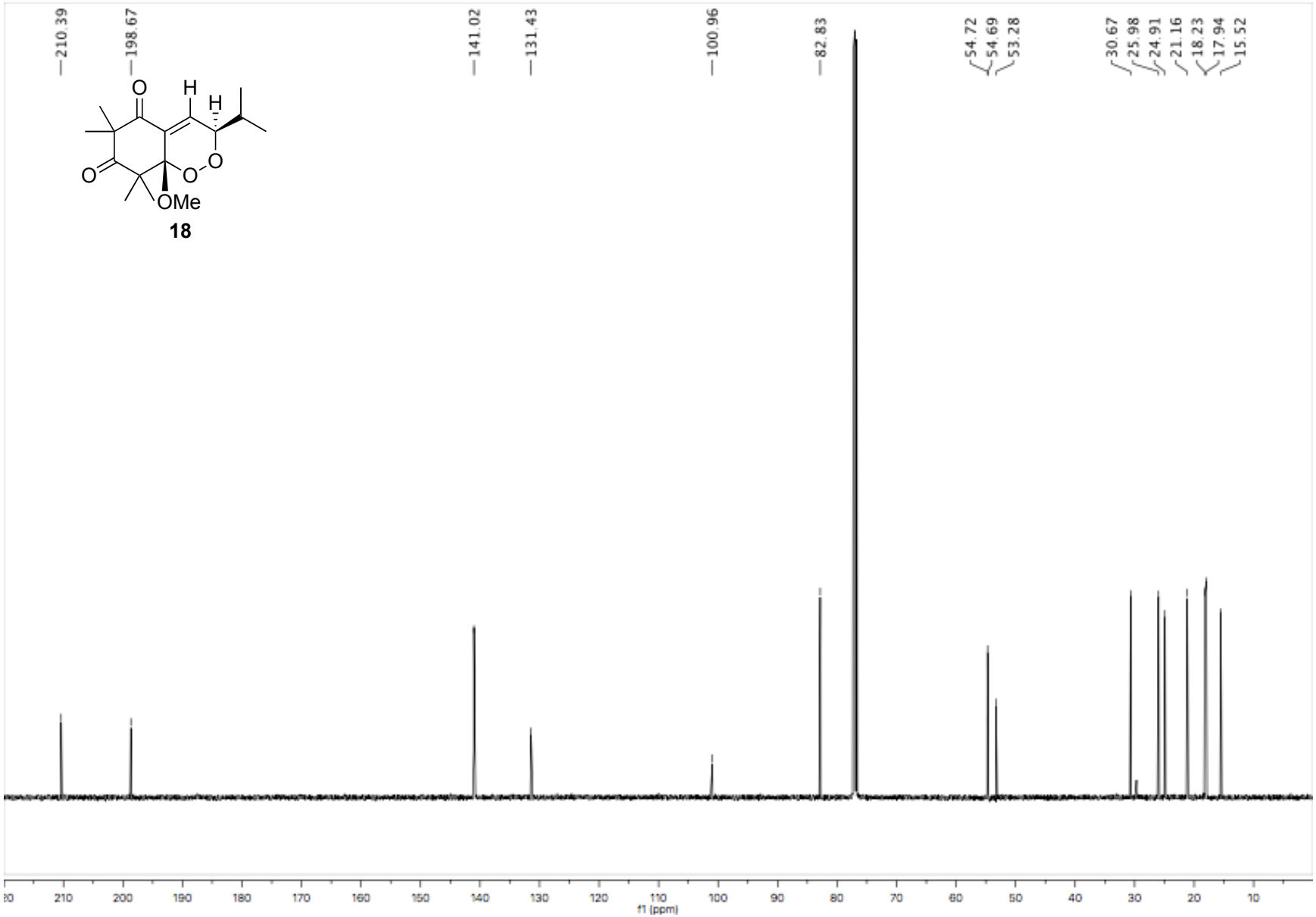


Figure S46. ^{13}C NMR spectrum for endoperoxide methyl-ether **18**

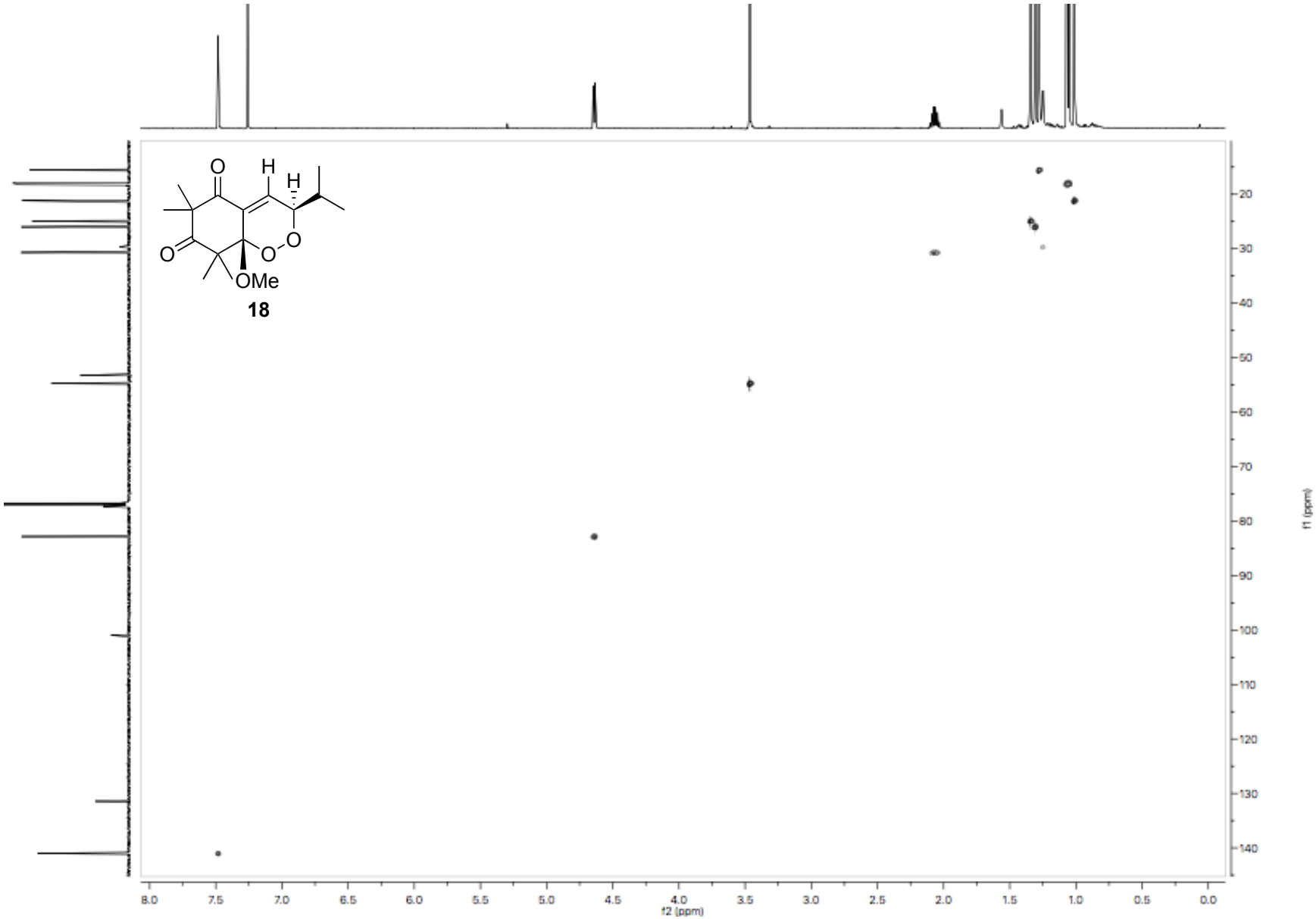


Figure S47. HSQC spectrum for endoperoxide methyl-ether **18**

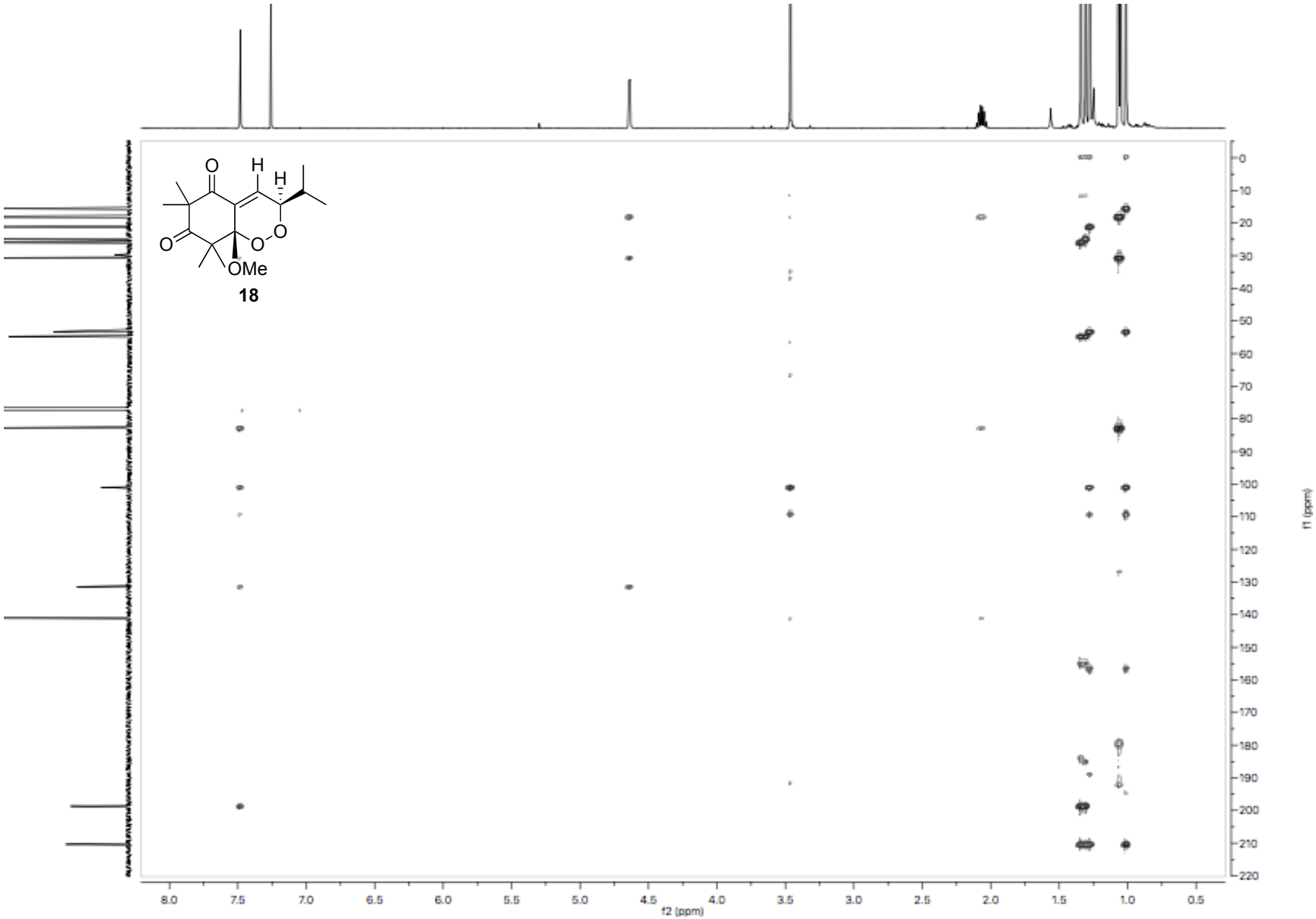


Figure S48. HMBC spectrum for endoperoxide methyl-ether **18**

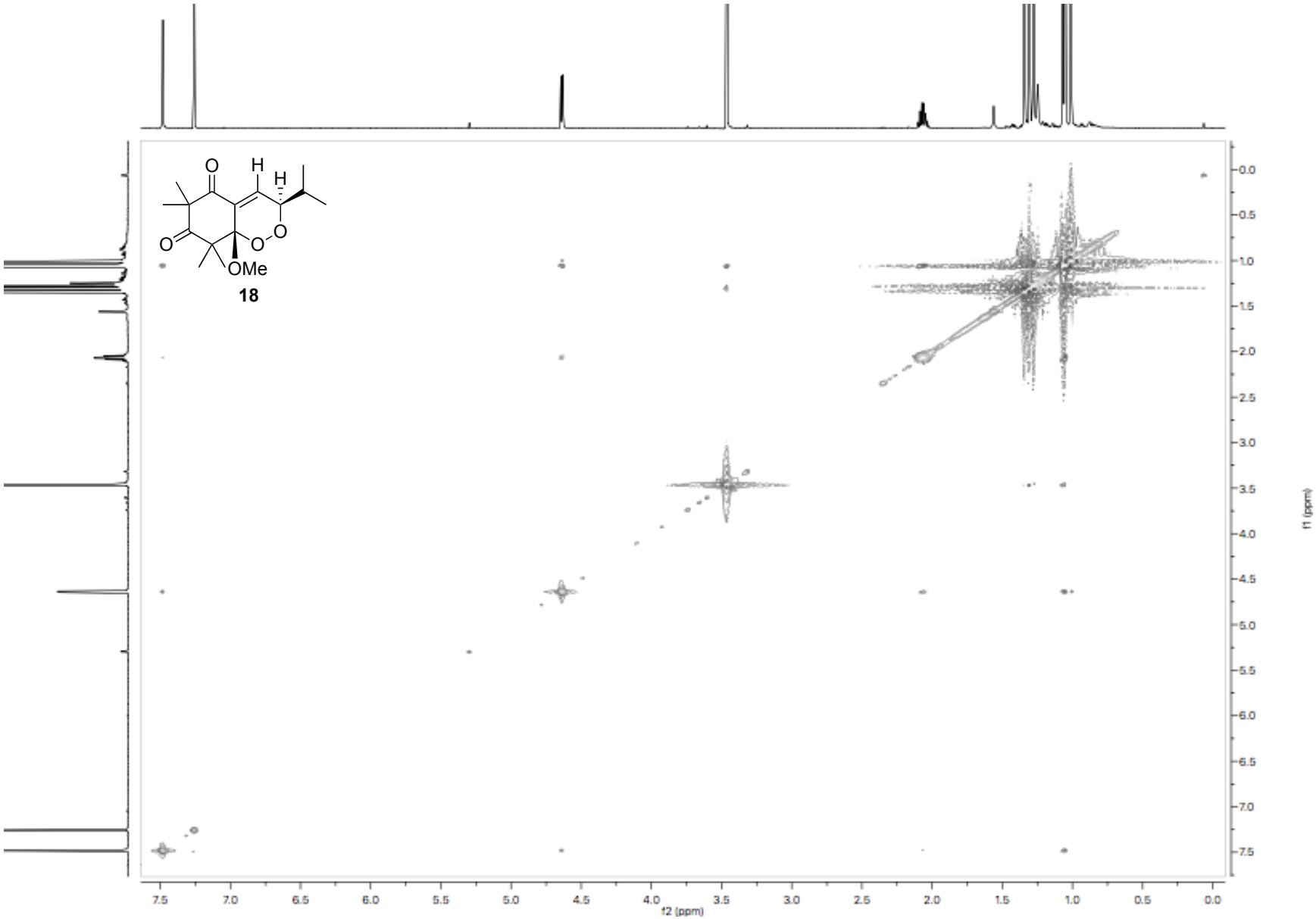


Figure S49. NOESY spectrum for endoperoxide methyl-ether **18**

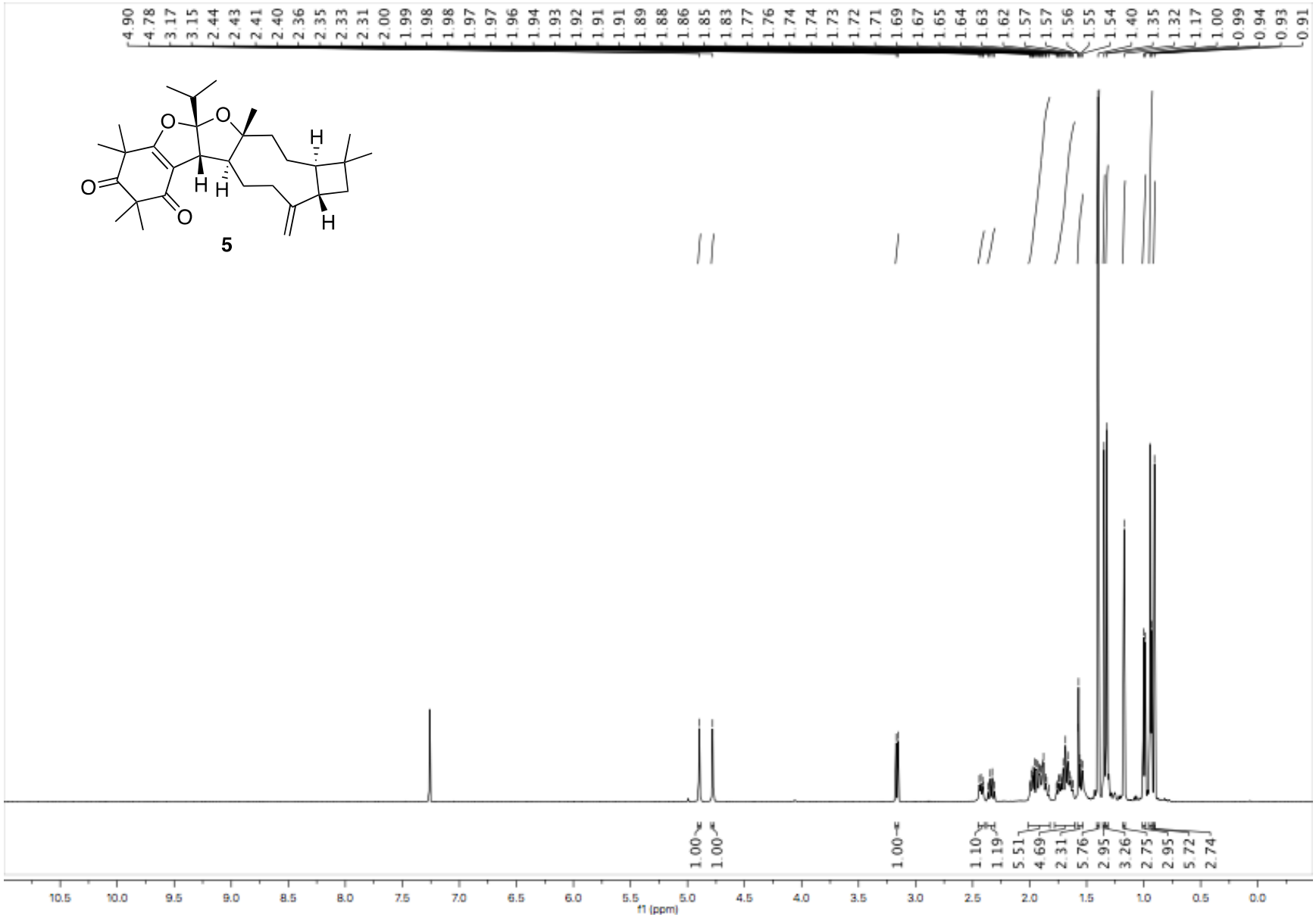


Figure S50. ^{1}H NMR spectrum for synthetic rhodomyrtusial A (**5**)

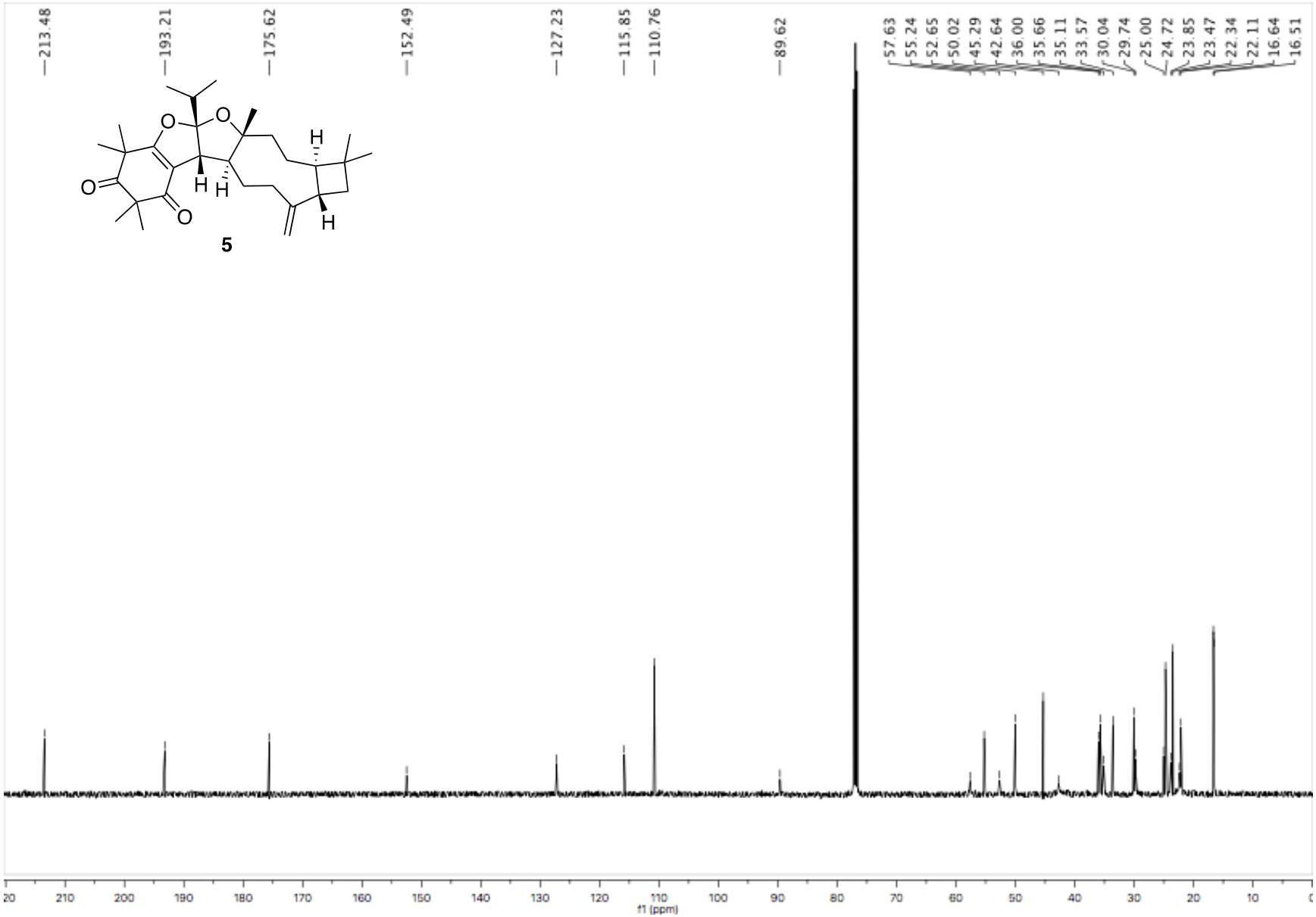


Figure S51. ^{13}C NMR spectrum for synthetic rhodomyrtusial A (**5**)

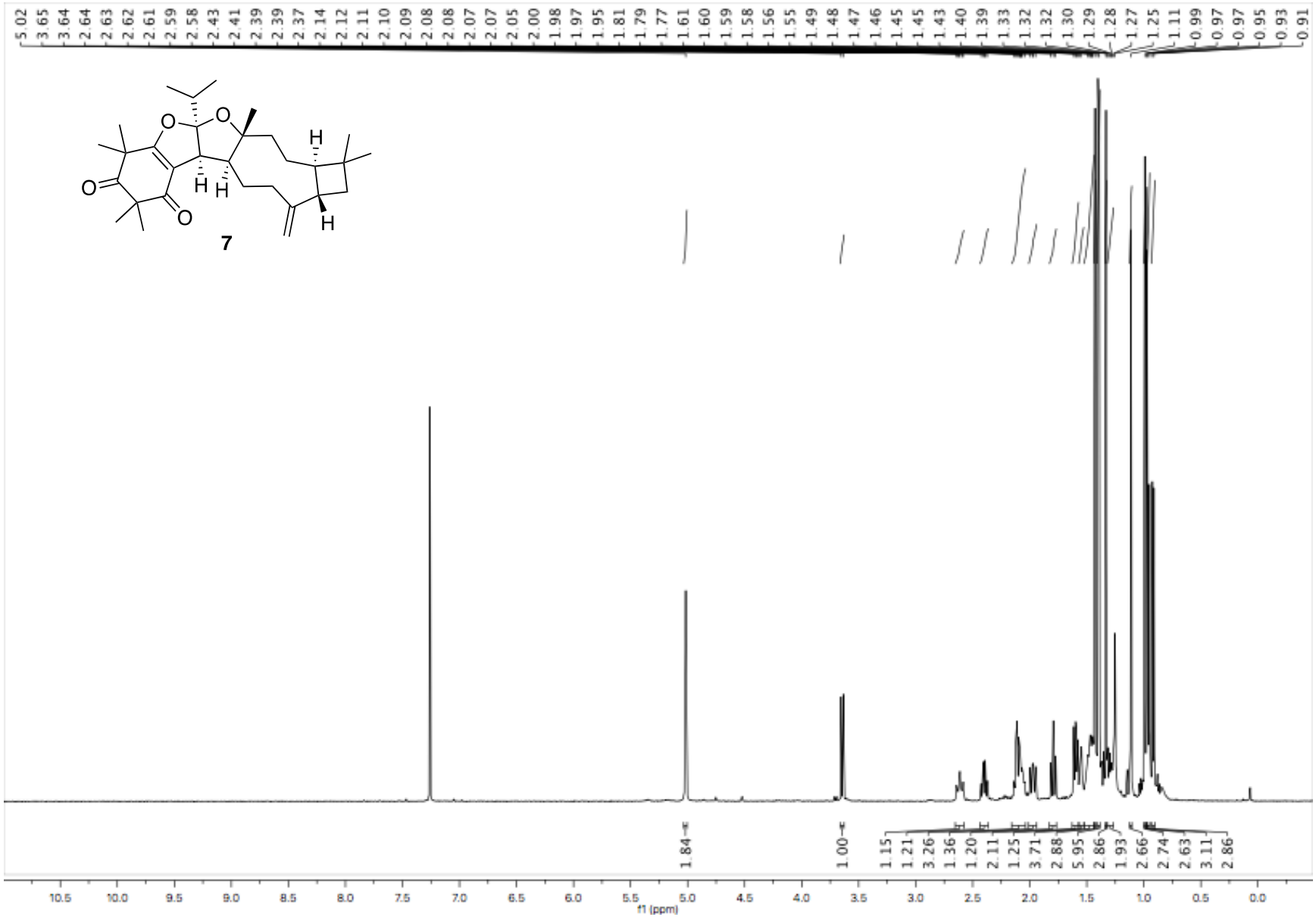


Figure S52. ^{1}H NMR spectrum for synthetic rhodomyrtusial C (**7**)

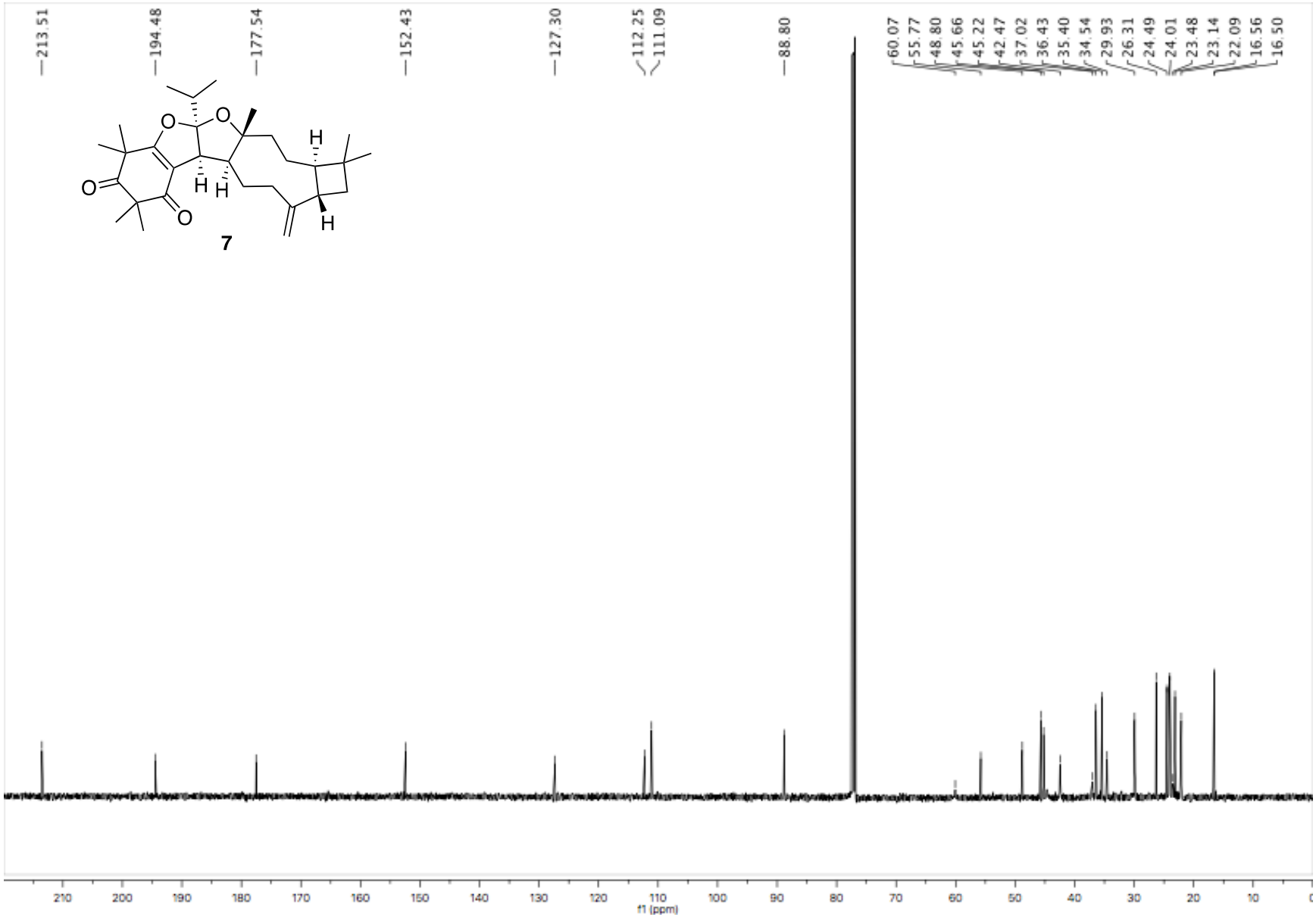


Figure S53. ^{13}C NMR spectrum for synthetic rhodomyrtusial C (**7**)

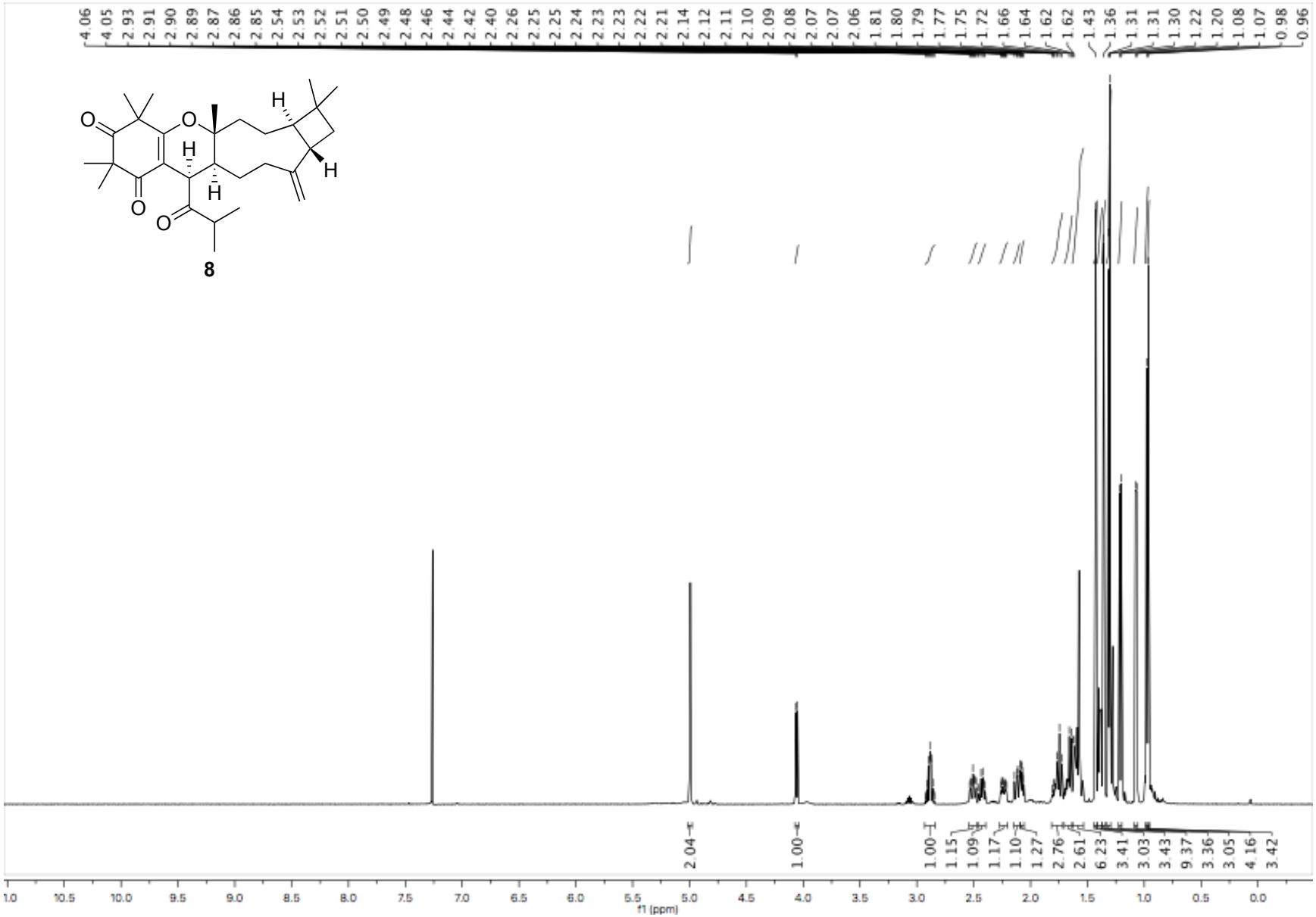


Figure S54. ^{1}H NMR spectrum for synthetic rhotomentodione A (**8**)

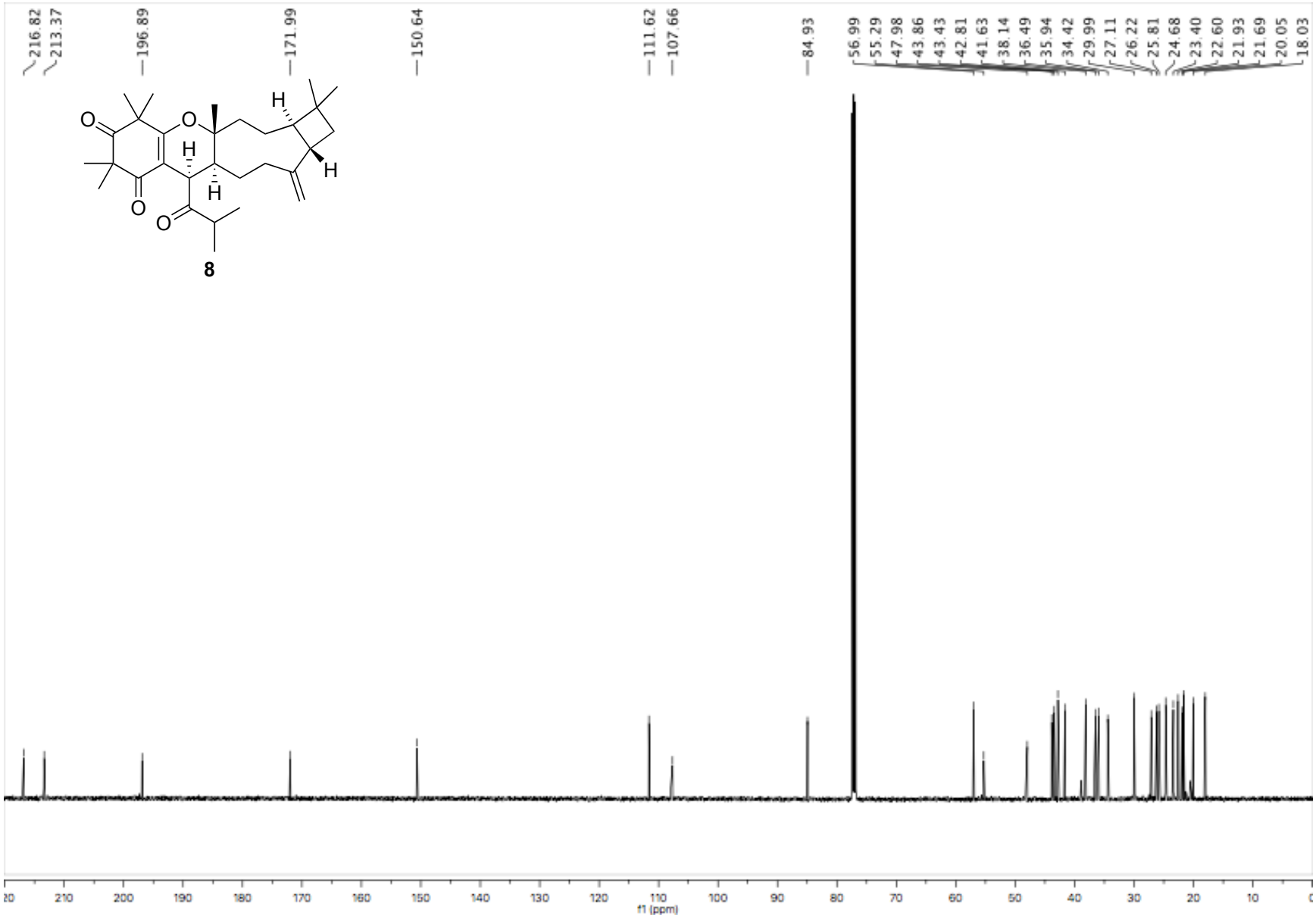


Figure S55. ^{13}C NMR spectrum for synthetic rhotomentodione A (**8**)

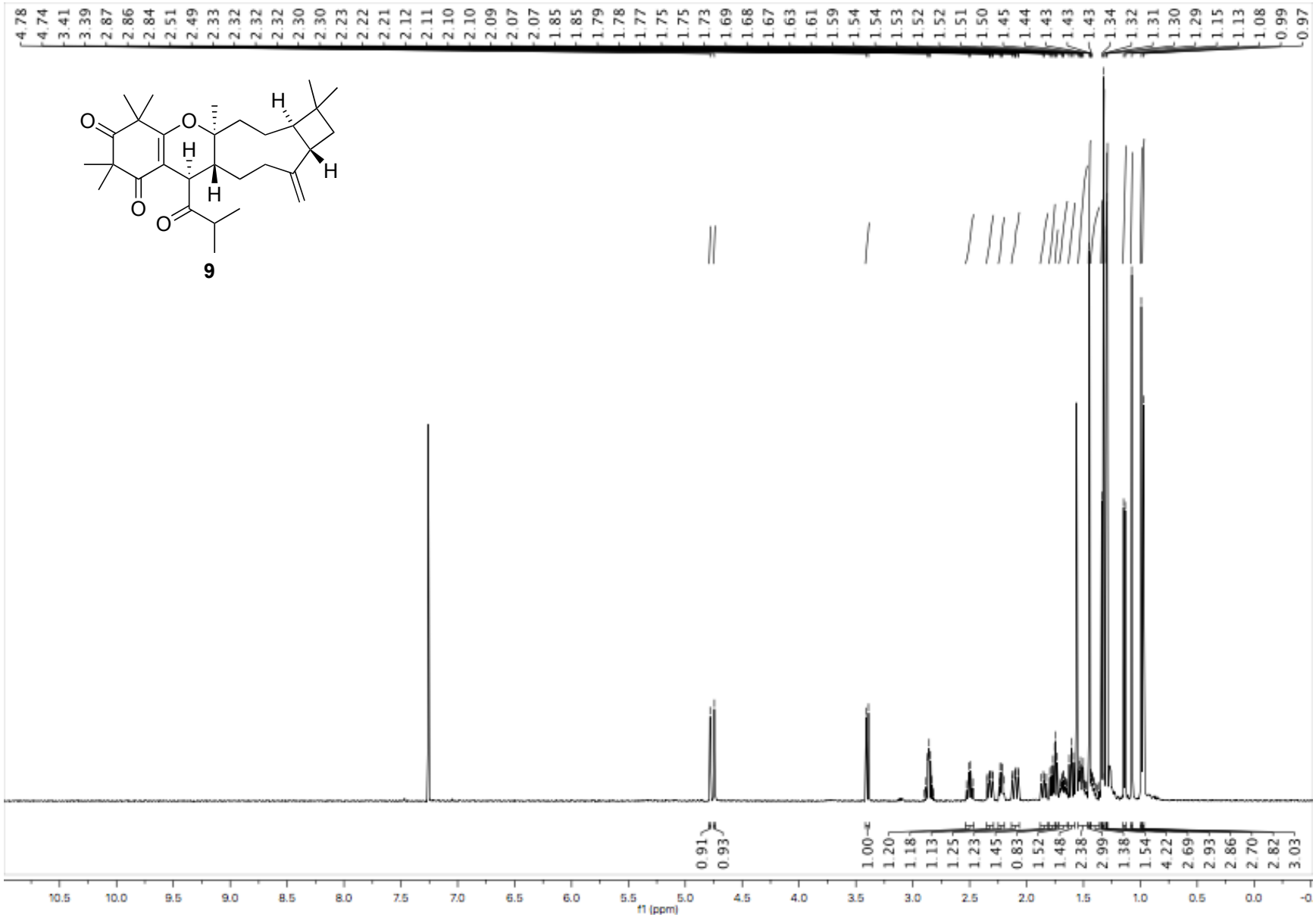


Figure S56. ^{1}H NMR spectrum for synthetic rhotomentodione B (**9**)

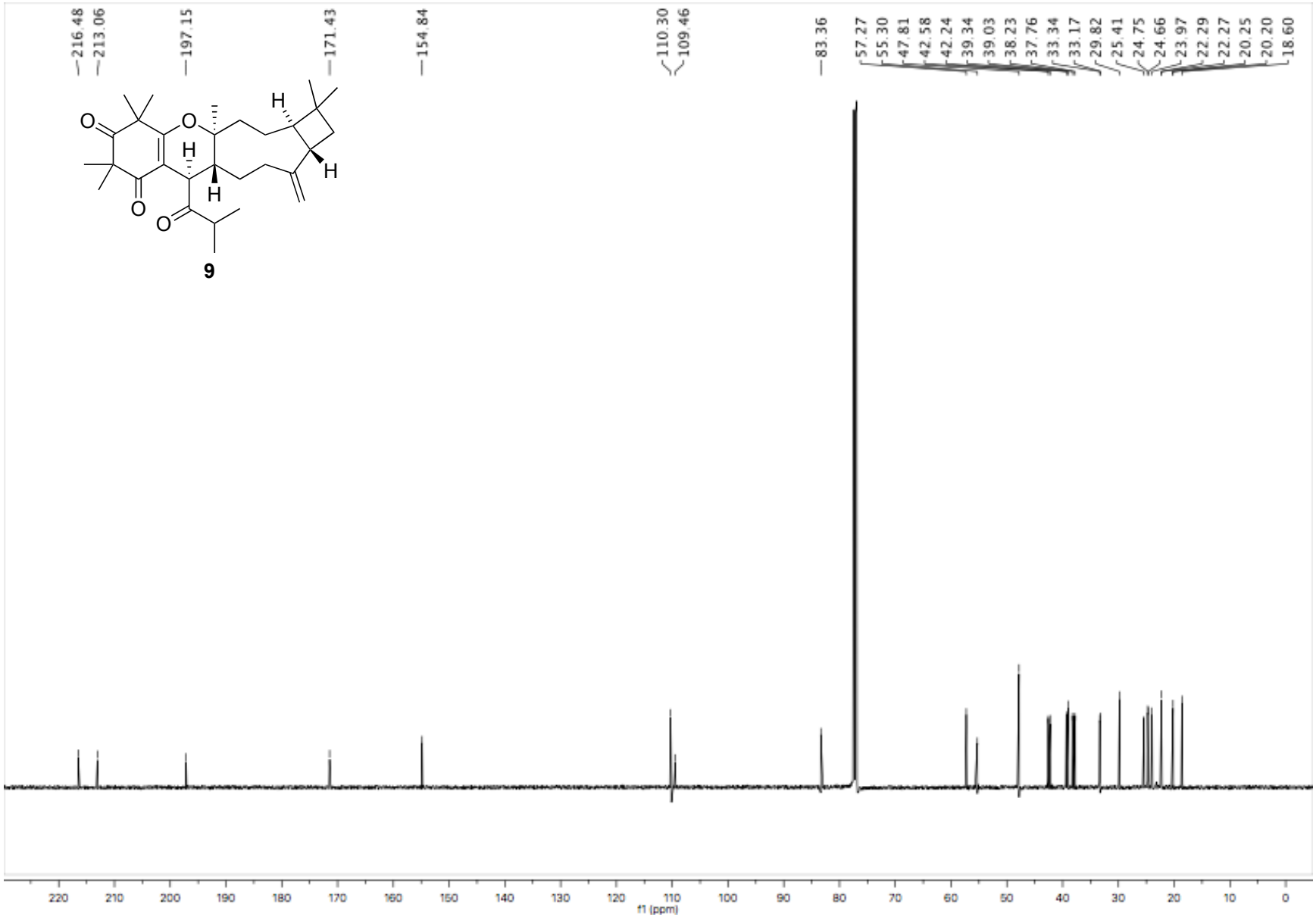


Figure S57. ^{13}C NMR spectrum for synthetic rhotomentodione B (**9**)

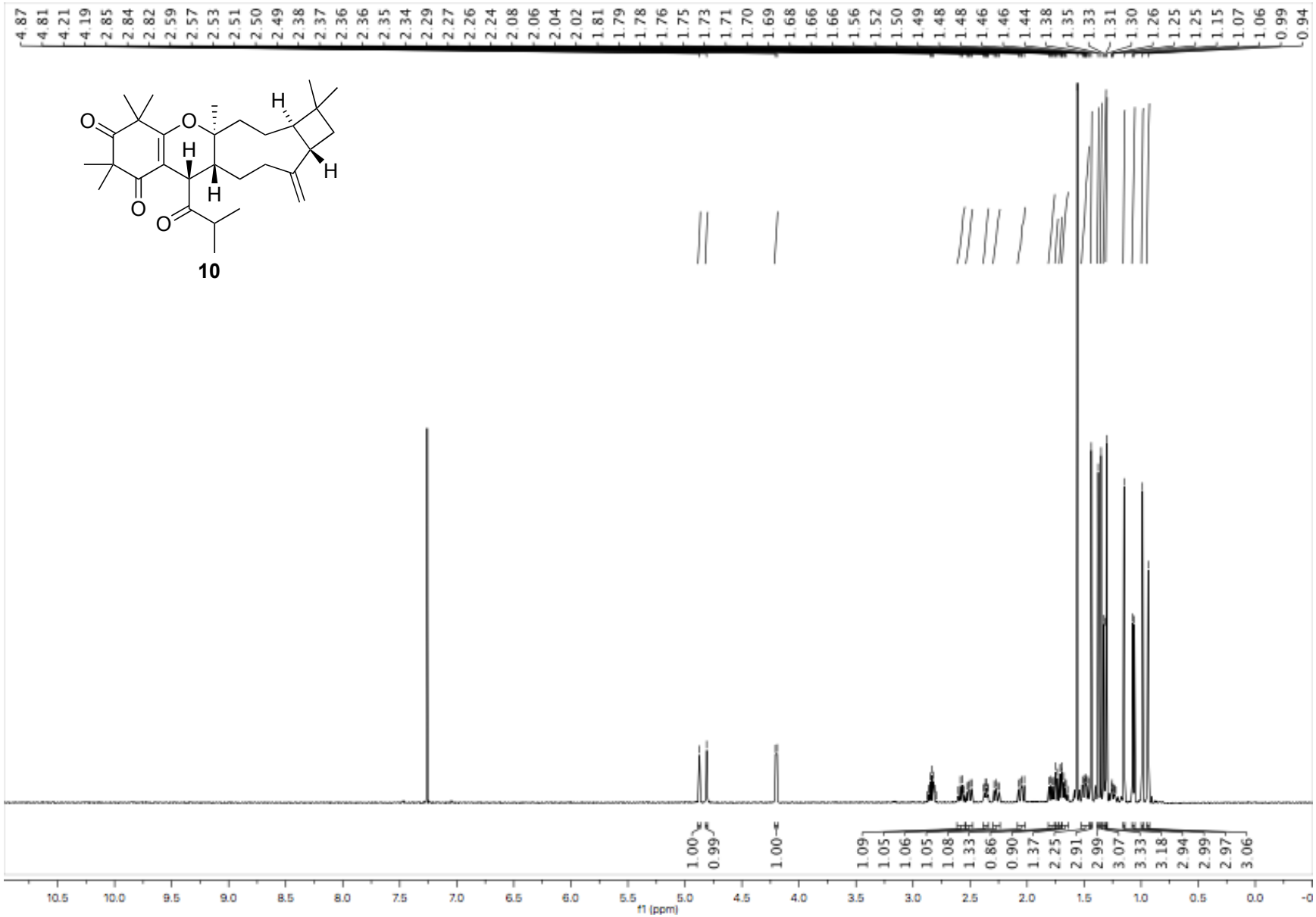


Figure S58. ^{1}H NMR spectrum for synthetic tomentodione Q (**10**)

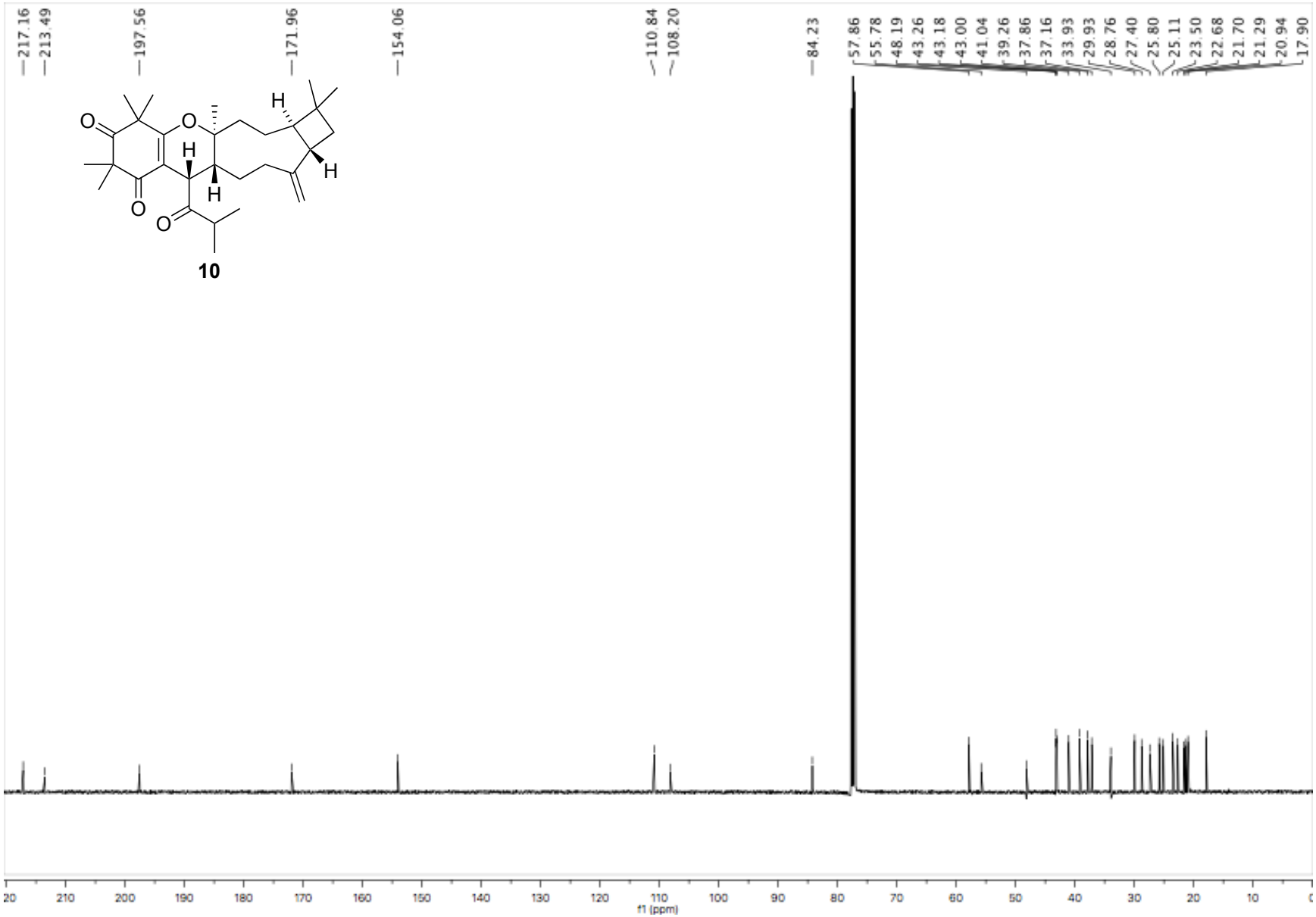


Figure S59. ^{13}C NMR spectrum for synthetic tomentodione Q (**10**)

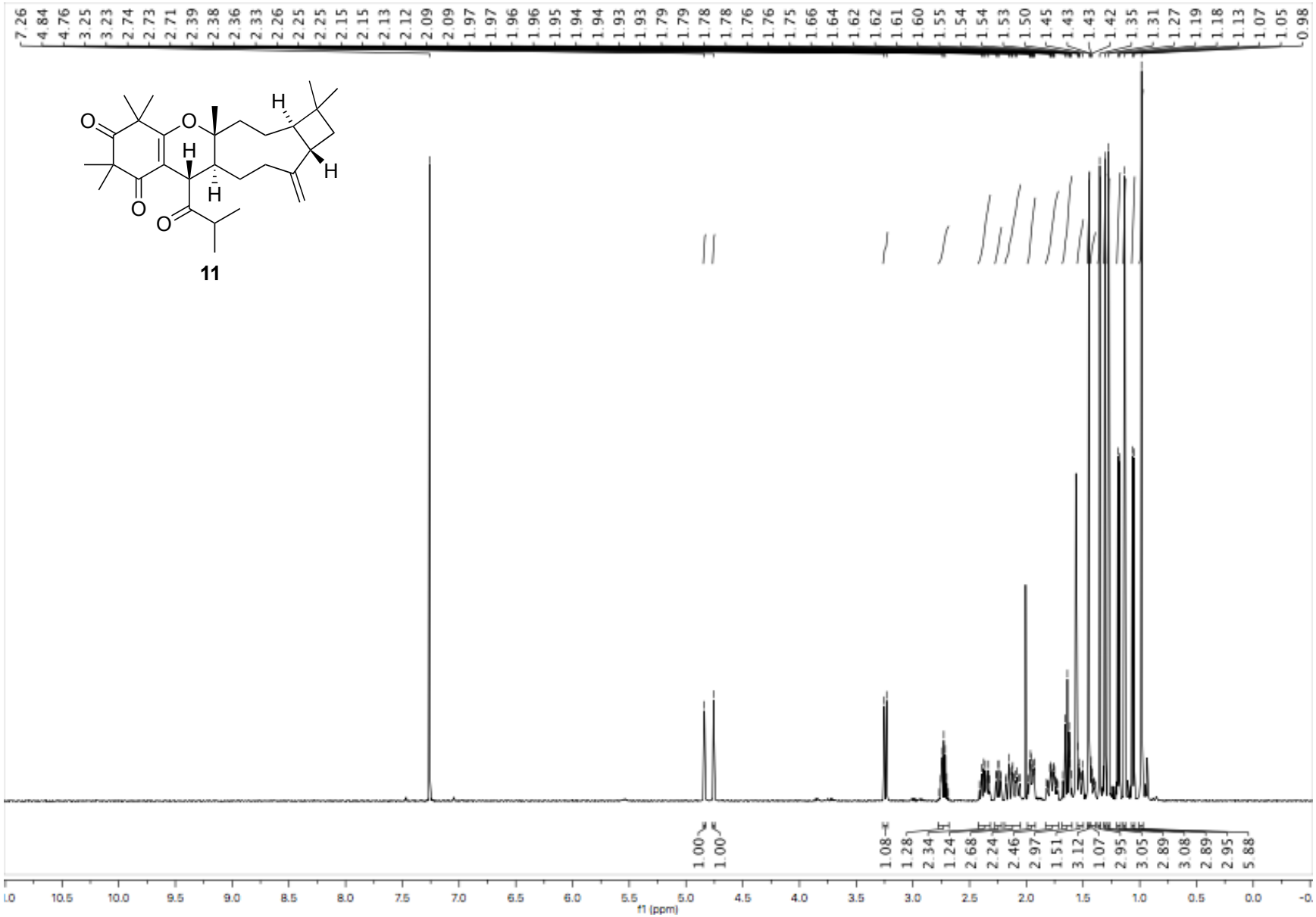


Figure S60. ^{1}H NMR spectrum for synthetic tomentodione Q (**11**)

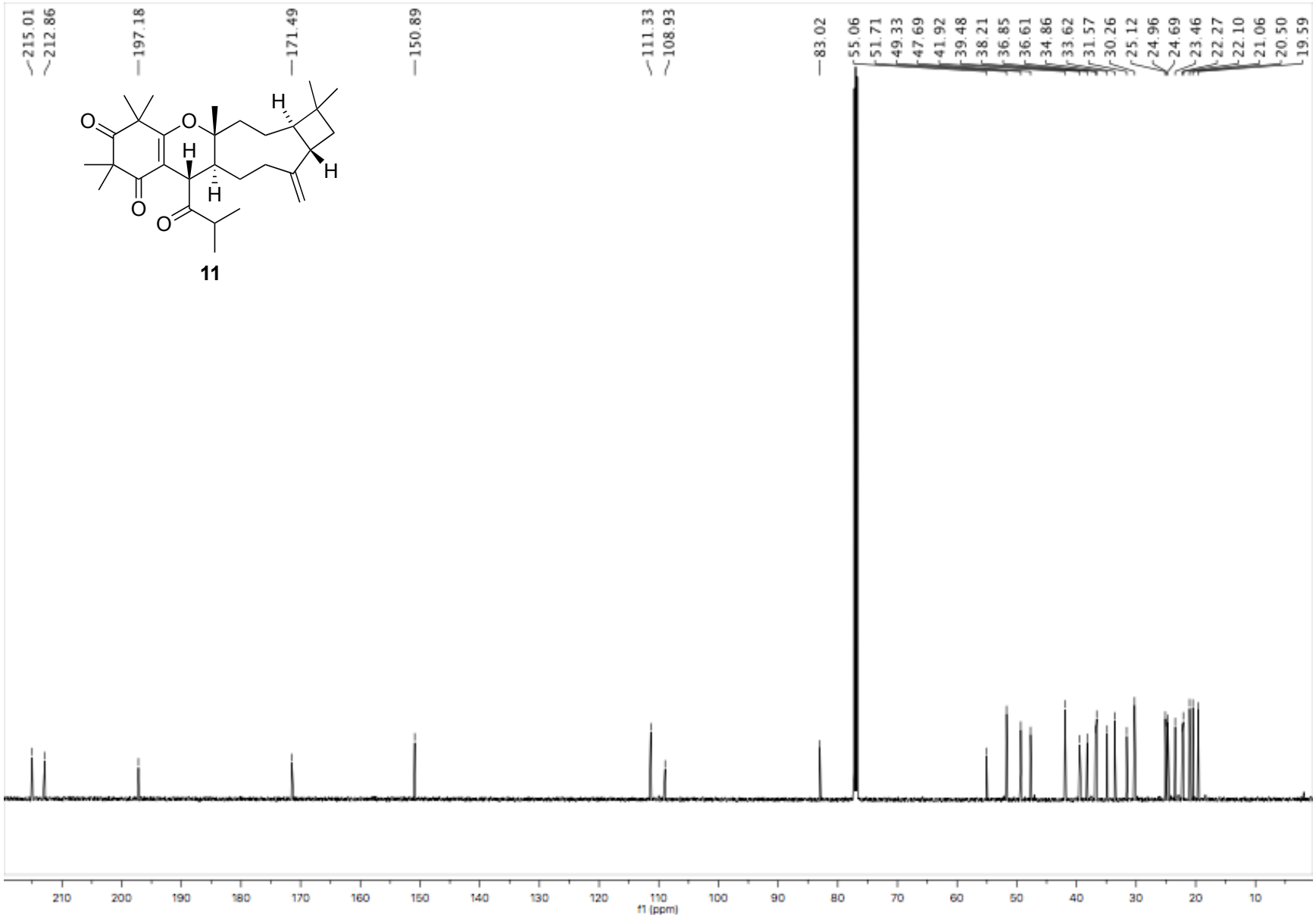


Figure S61. ^{13}C NMR spectrum for synthetic tomentodione Q (**11**)

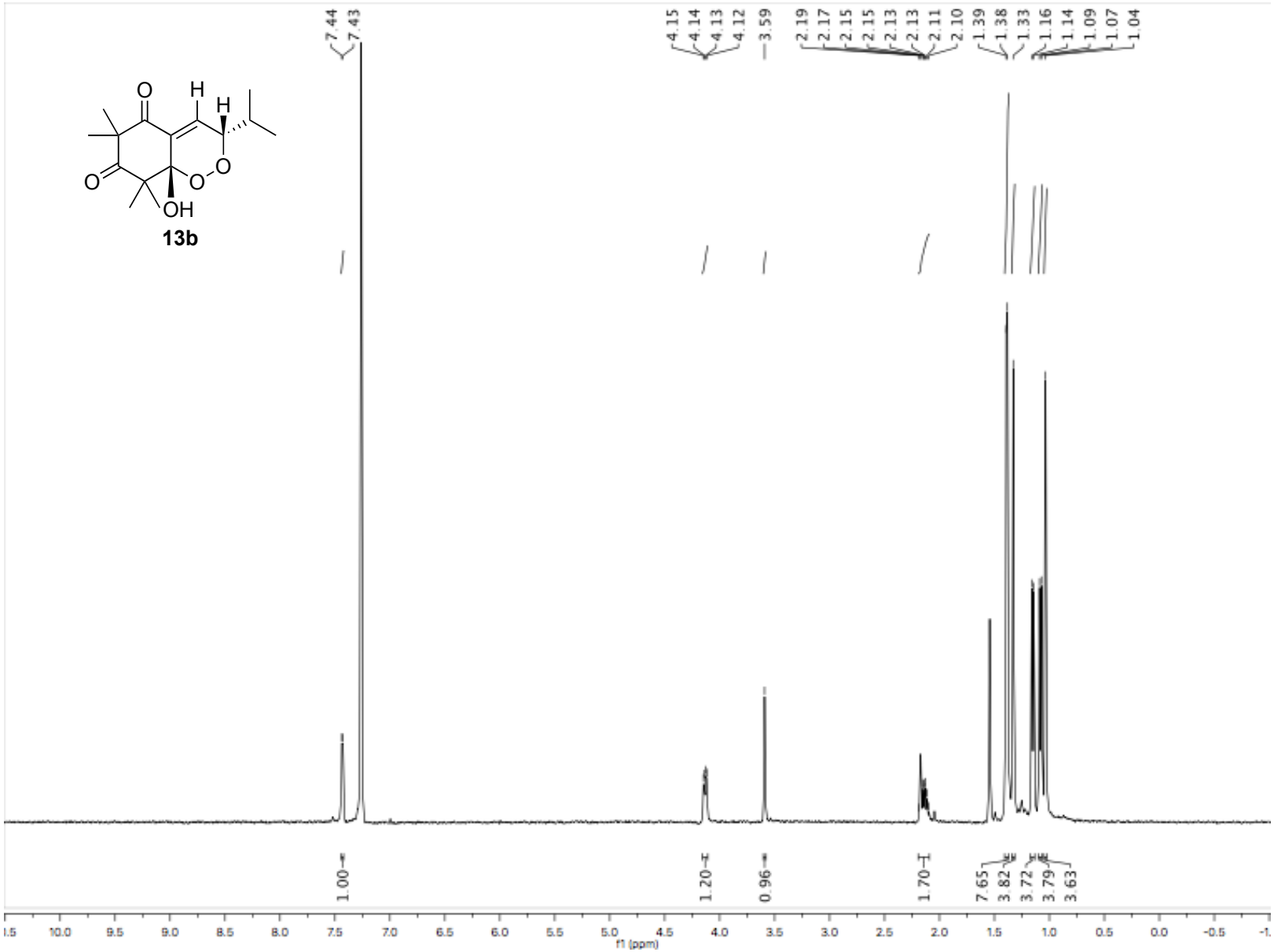


Figure S62. ^{1}H NMR spectrum for pure **13b** (starting material for thermal equilibration experiment)

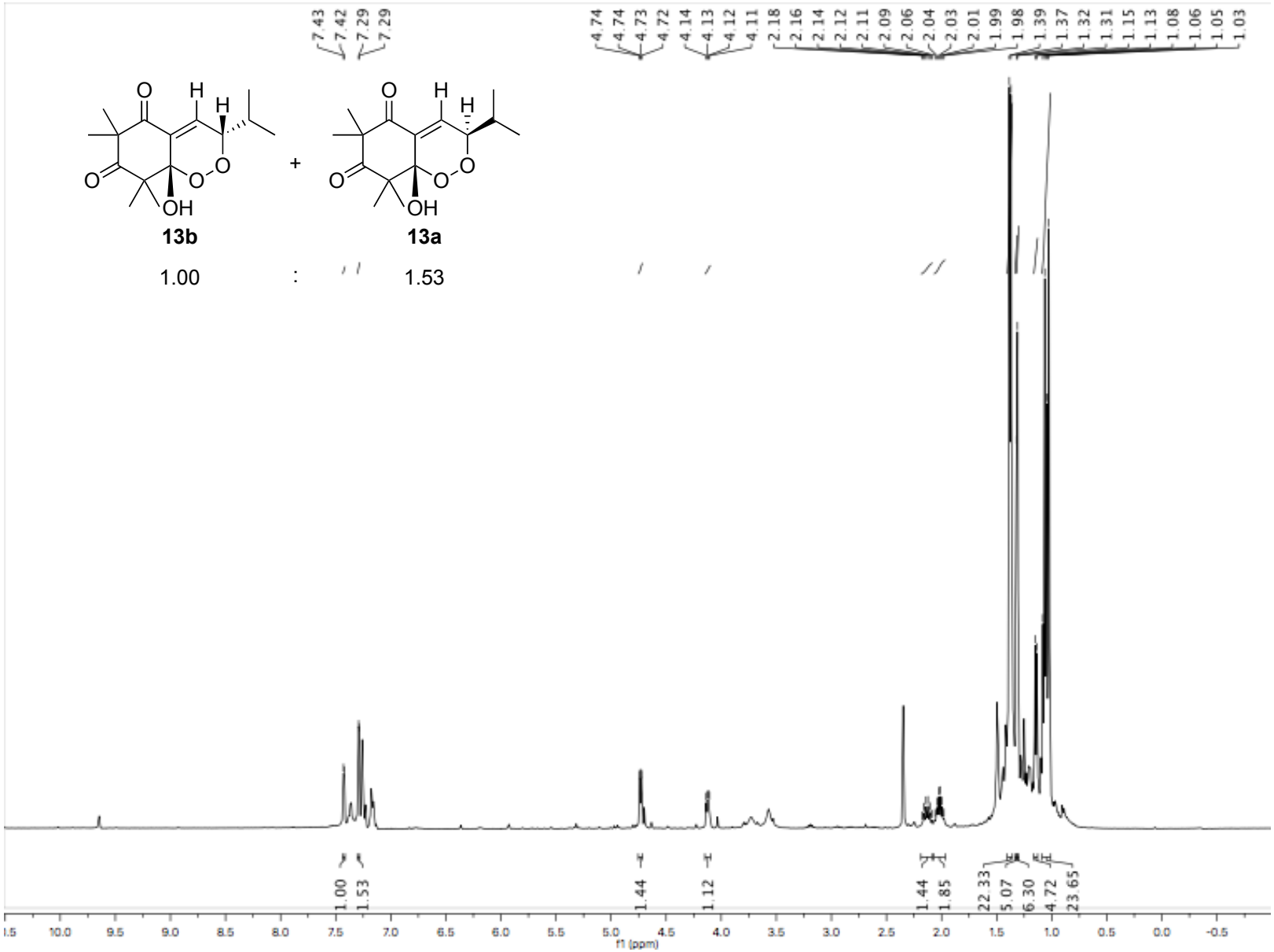


Figure S63. Crude ^{1}H NMR spectrum for thermal equilibration of endoperoxides **13a** and **13b**

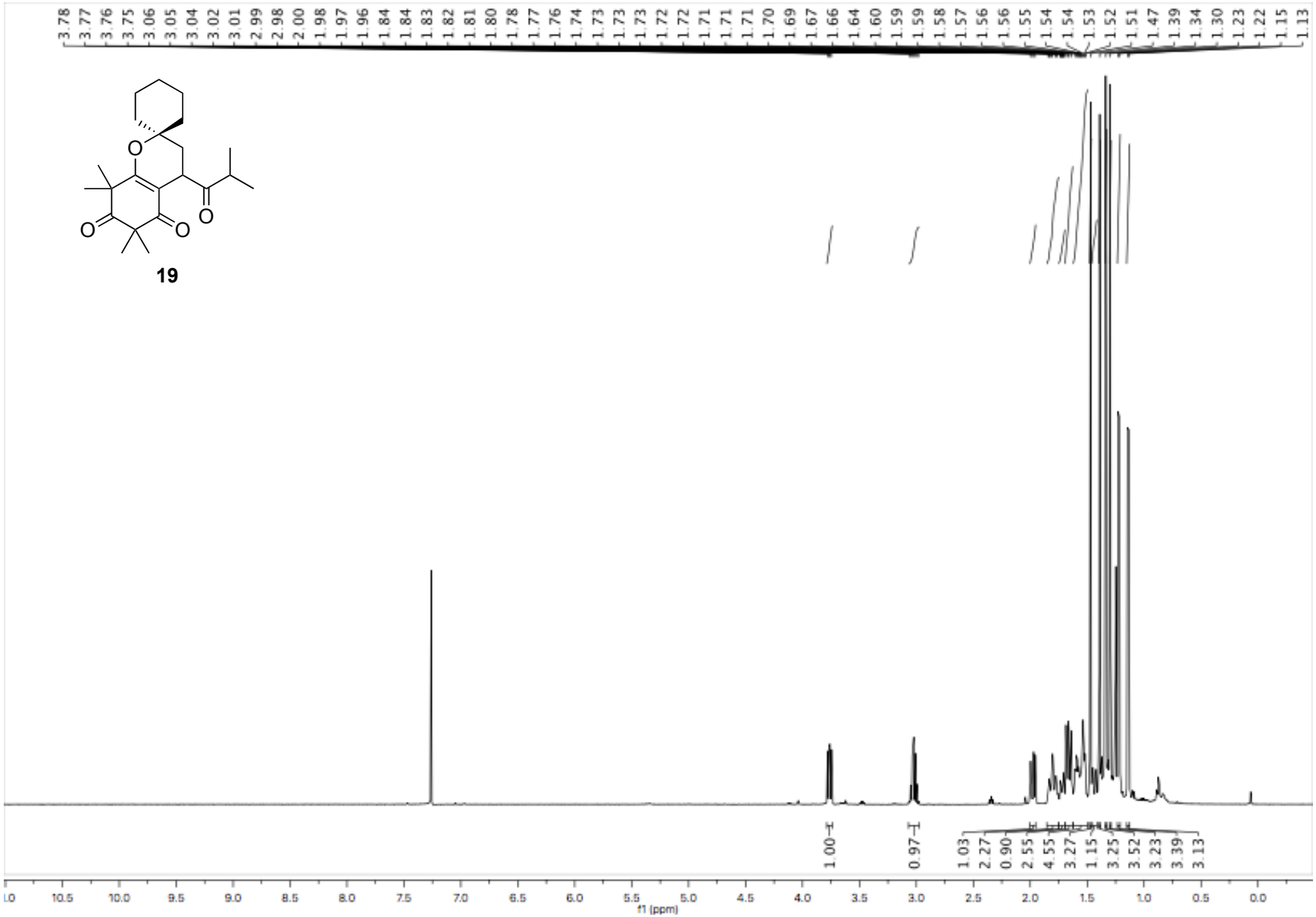


Figure S64. ^{1}H NMR spectrum for spirocycle **19**

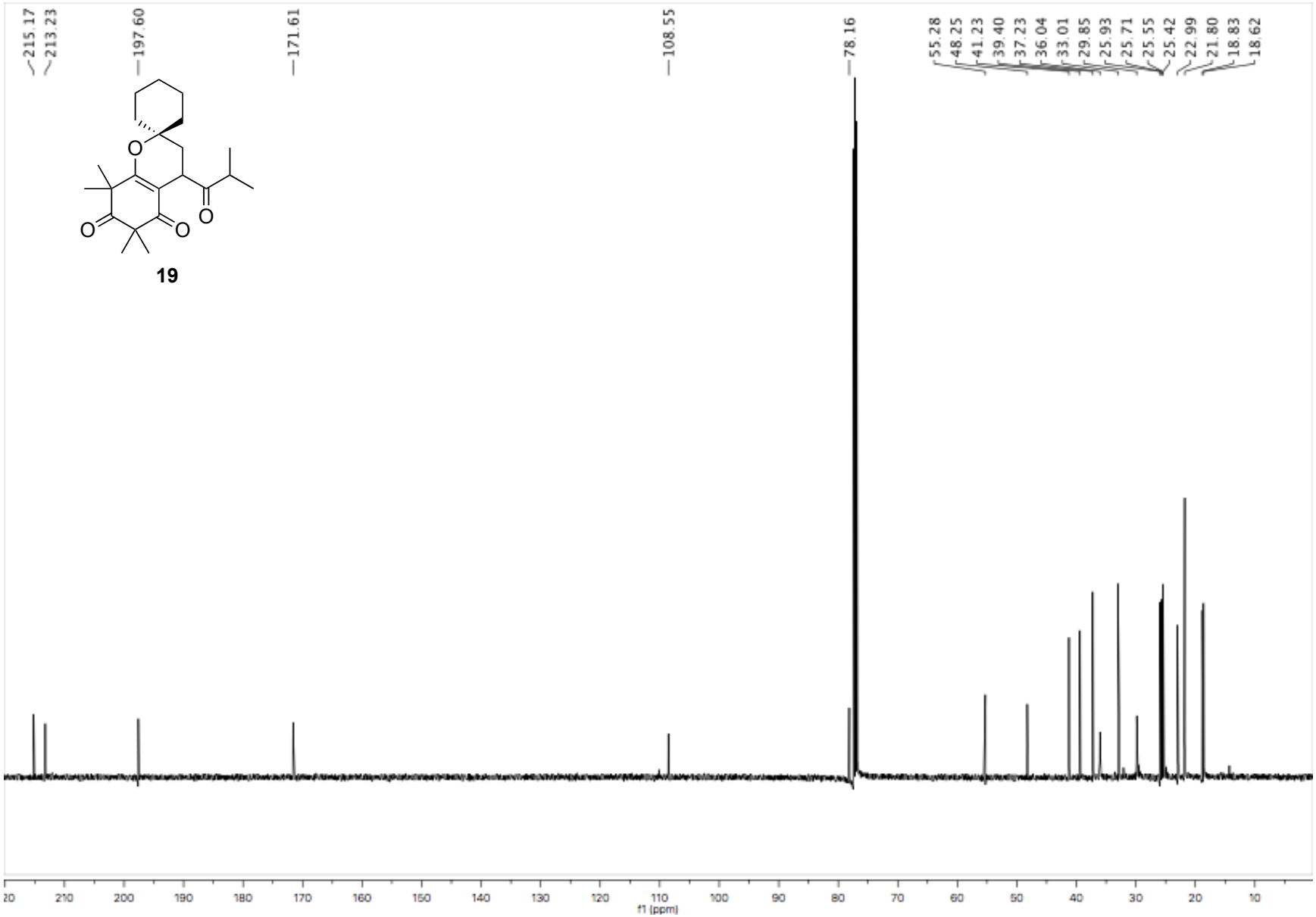


Figure S65. ^{13}C NMR spectrum for spirocycle **19**

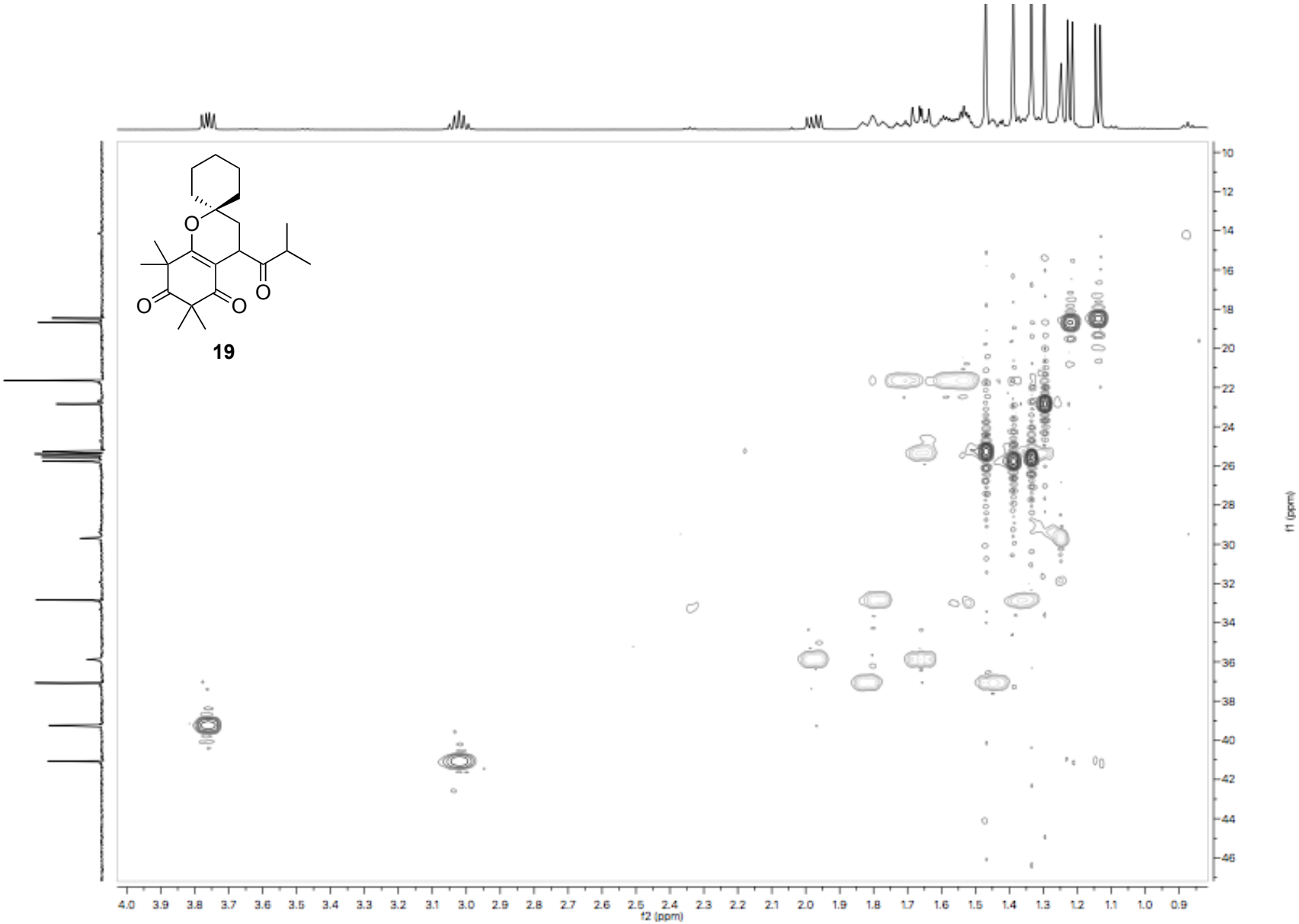


Figure S66. HSQC spectrum for spirocycle **19**

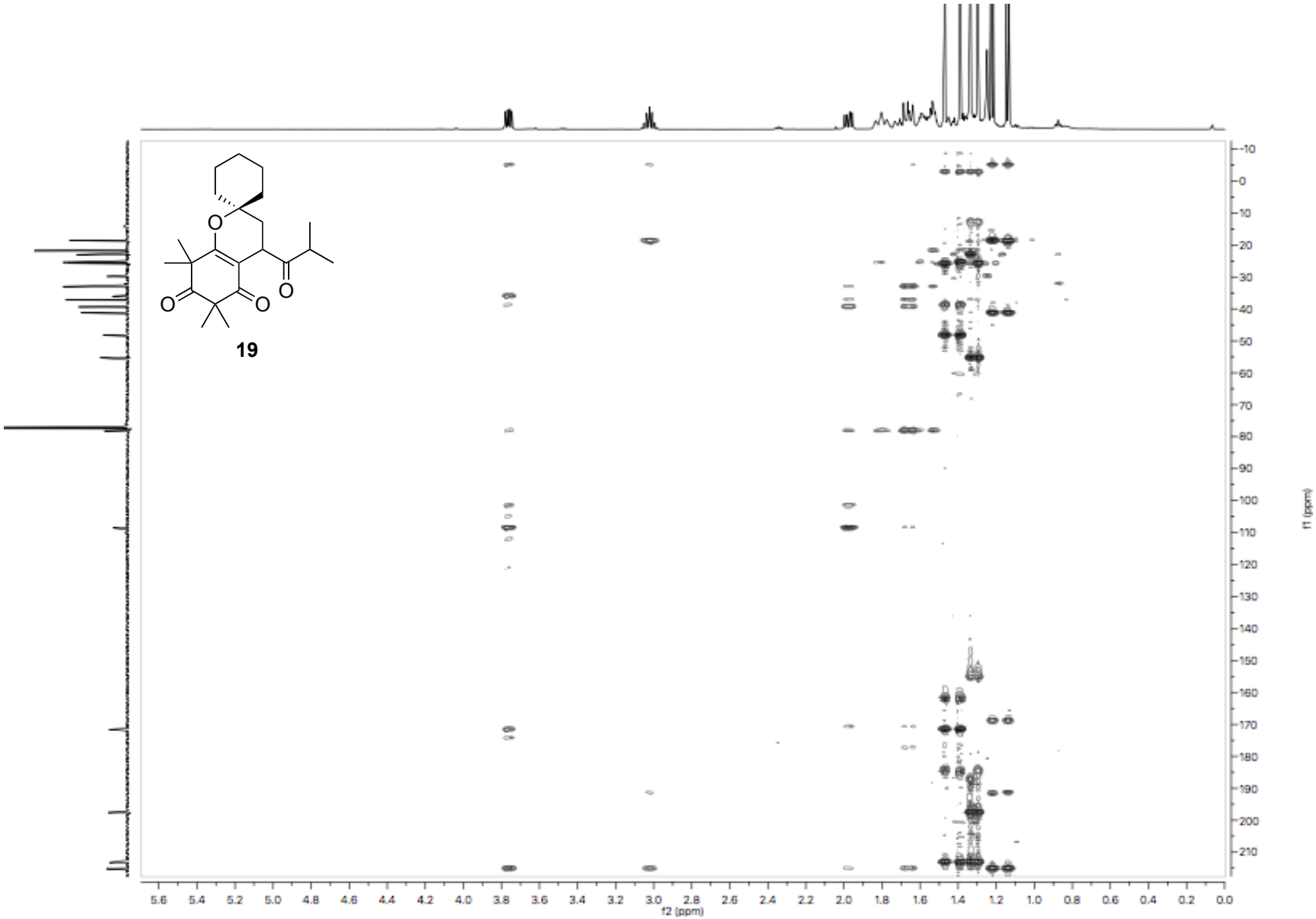


Figure S67. HMBC spectrum for spirocycle **19**

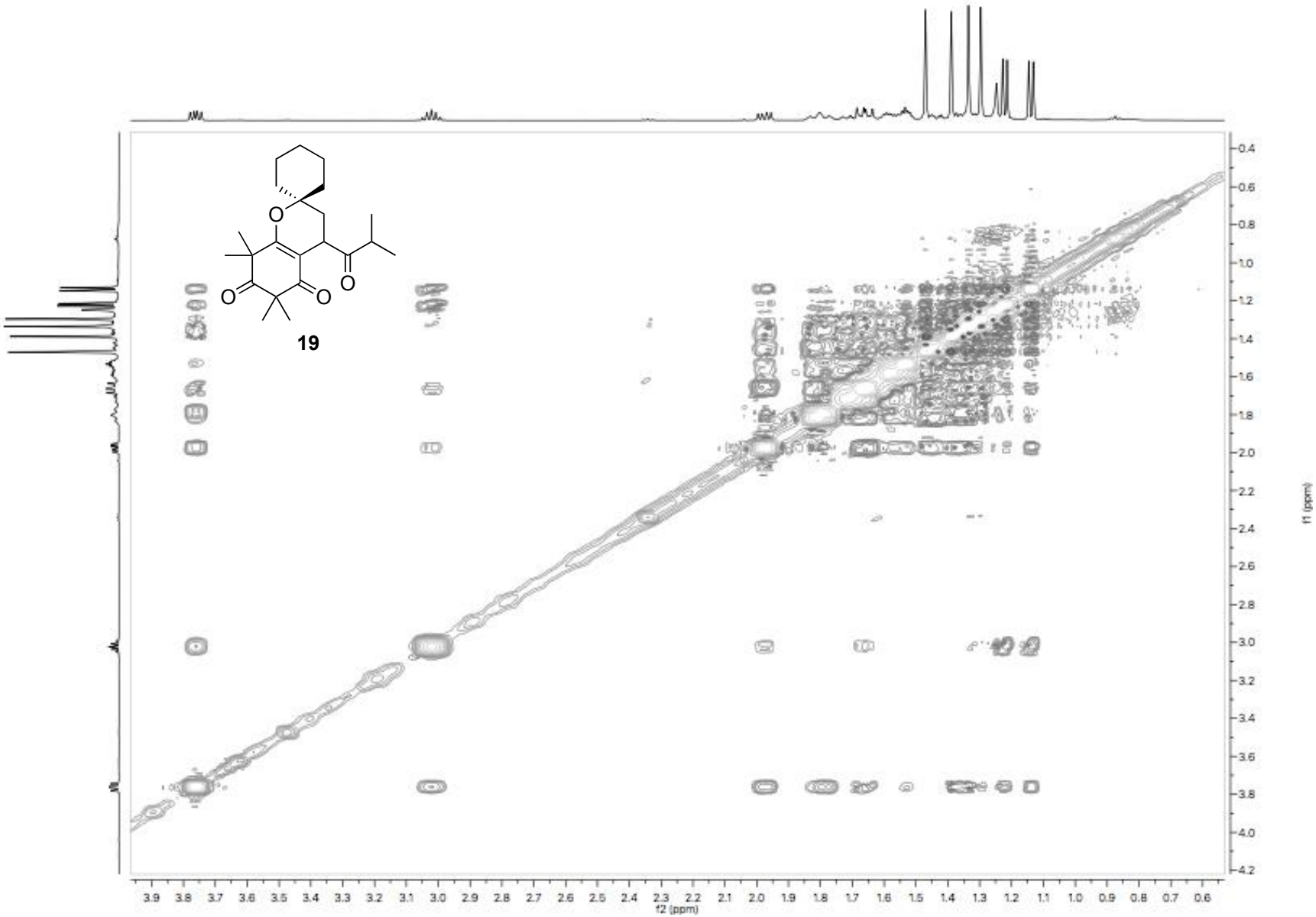


Figure S67. NOESY spectrum for spirocycle **19**

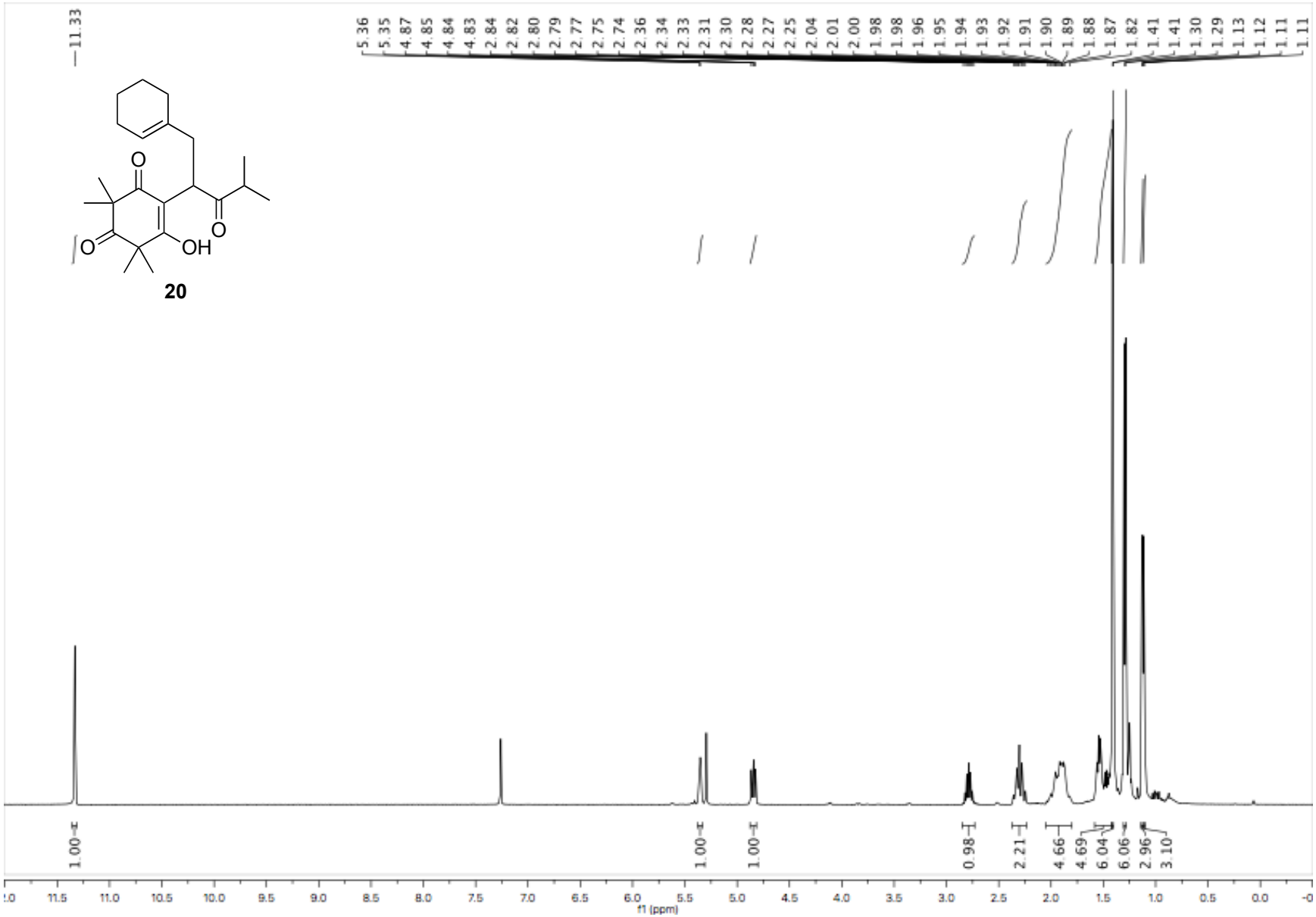


Figure S68. ^{1}H NMR spectrum for ene product **20**

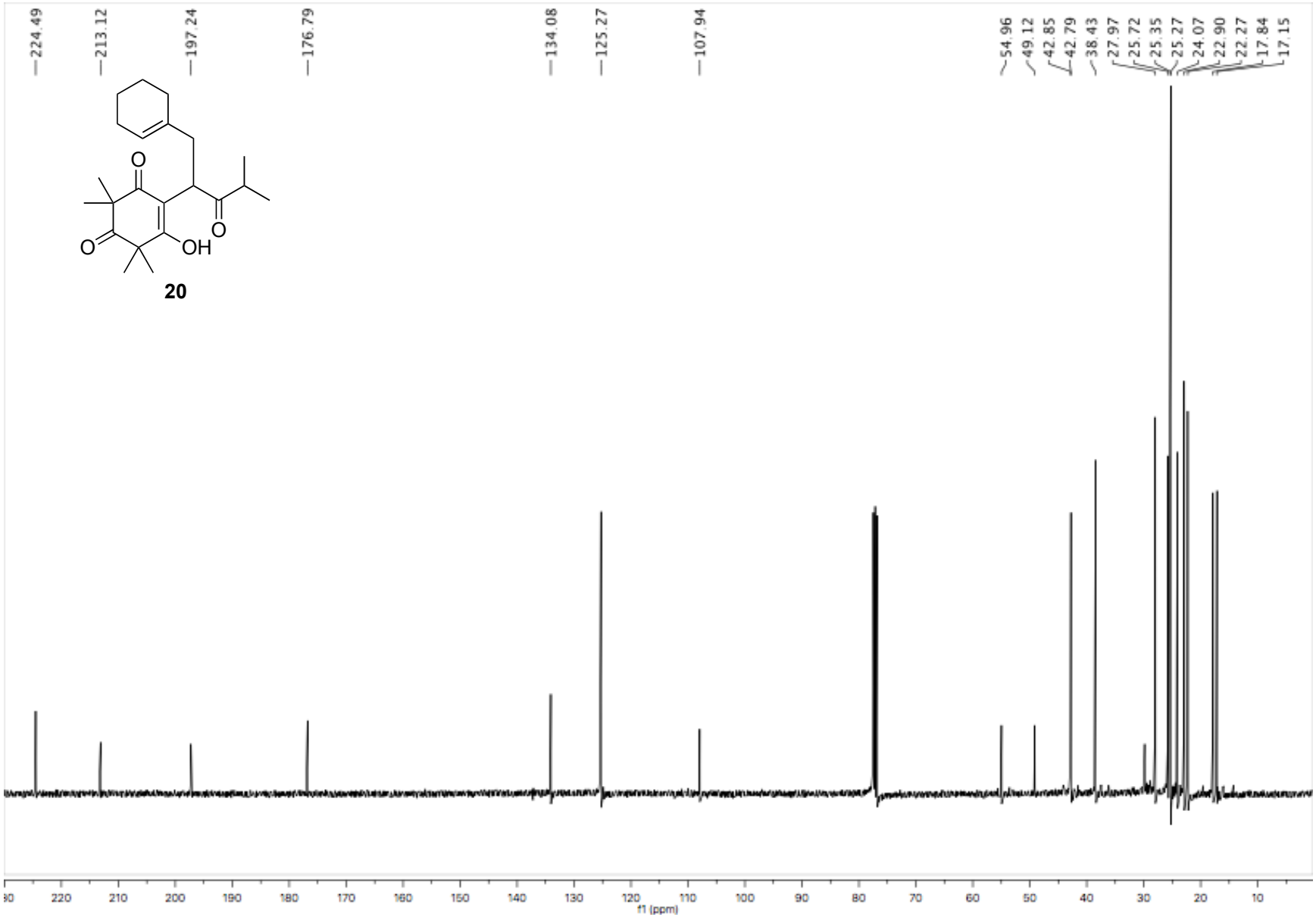


Figure S69. ^{13}C NMR spectrum for ene product **20**

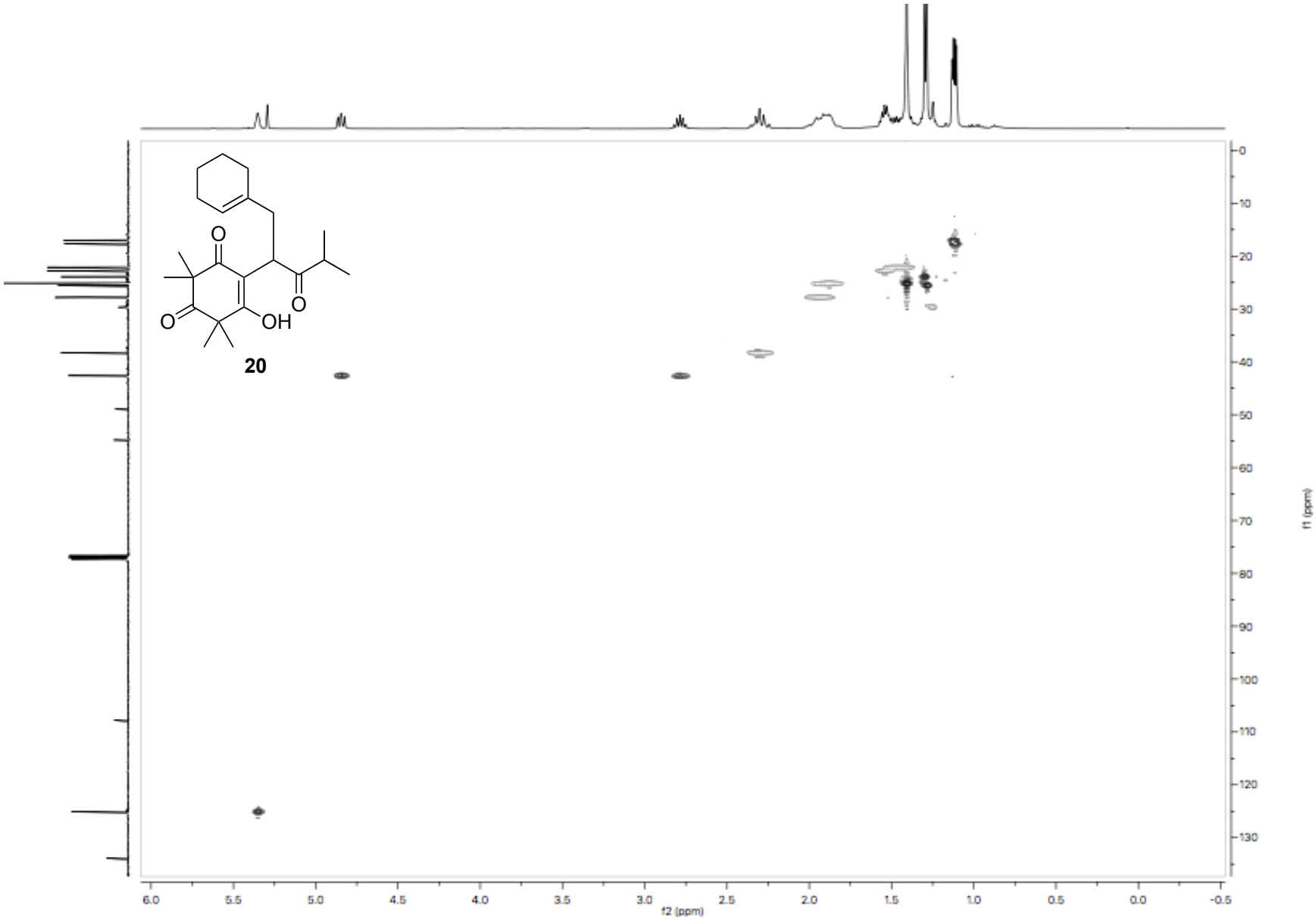


Figure S70. HSQC spectrum for ene product **20**

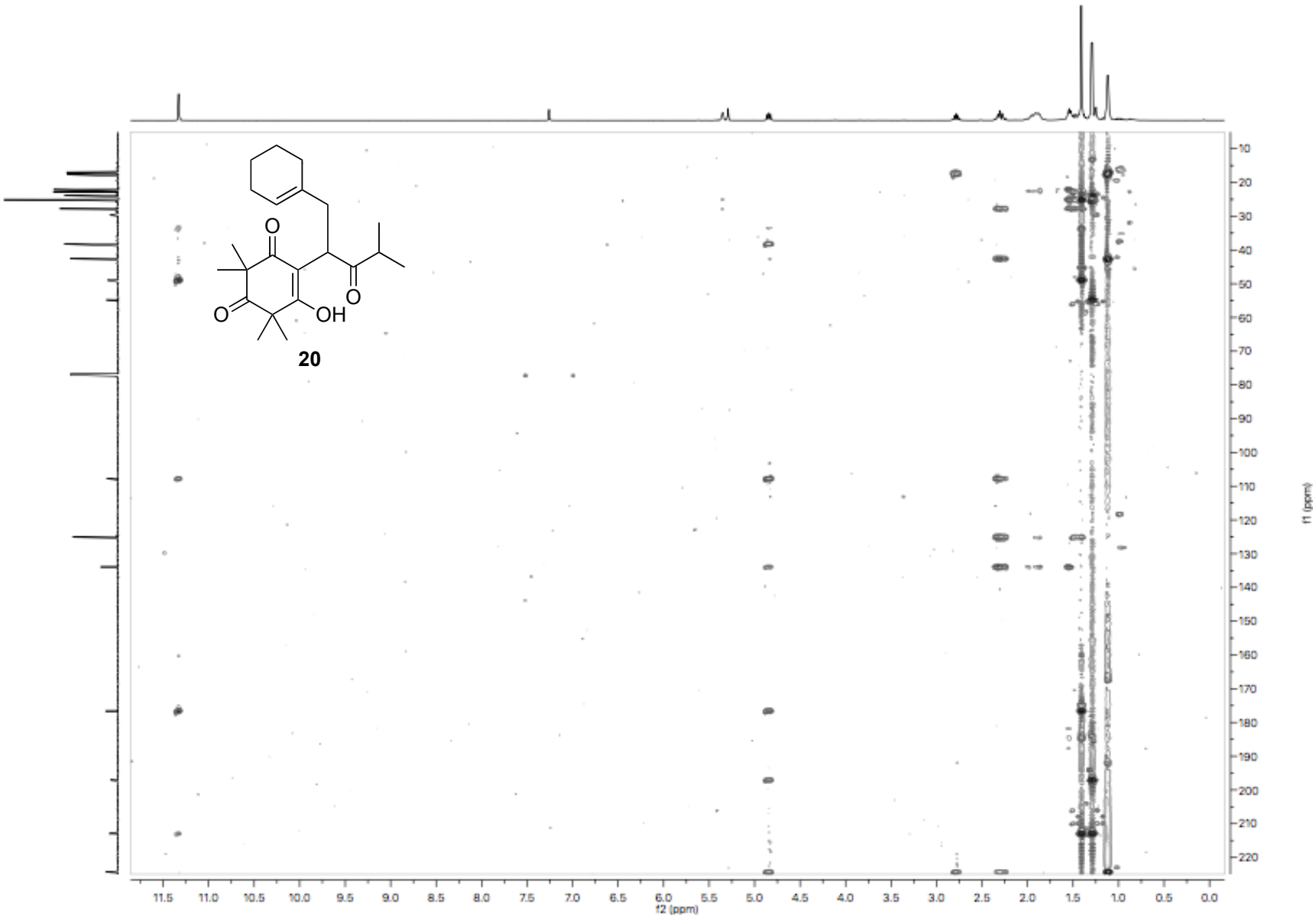


Figure S71. HMBC spectrum for ene product **20**

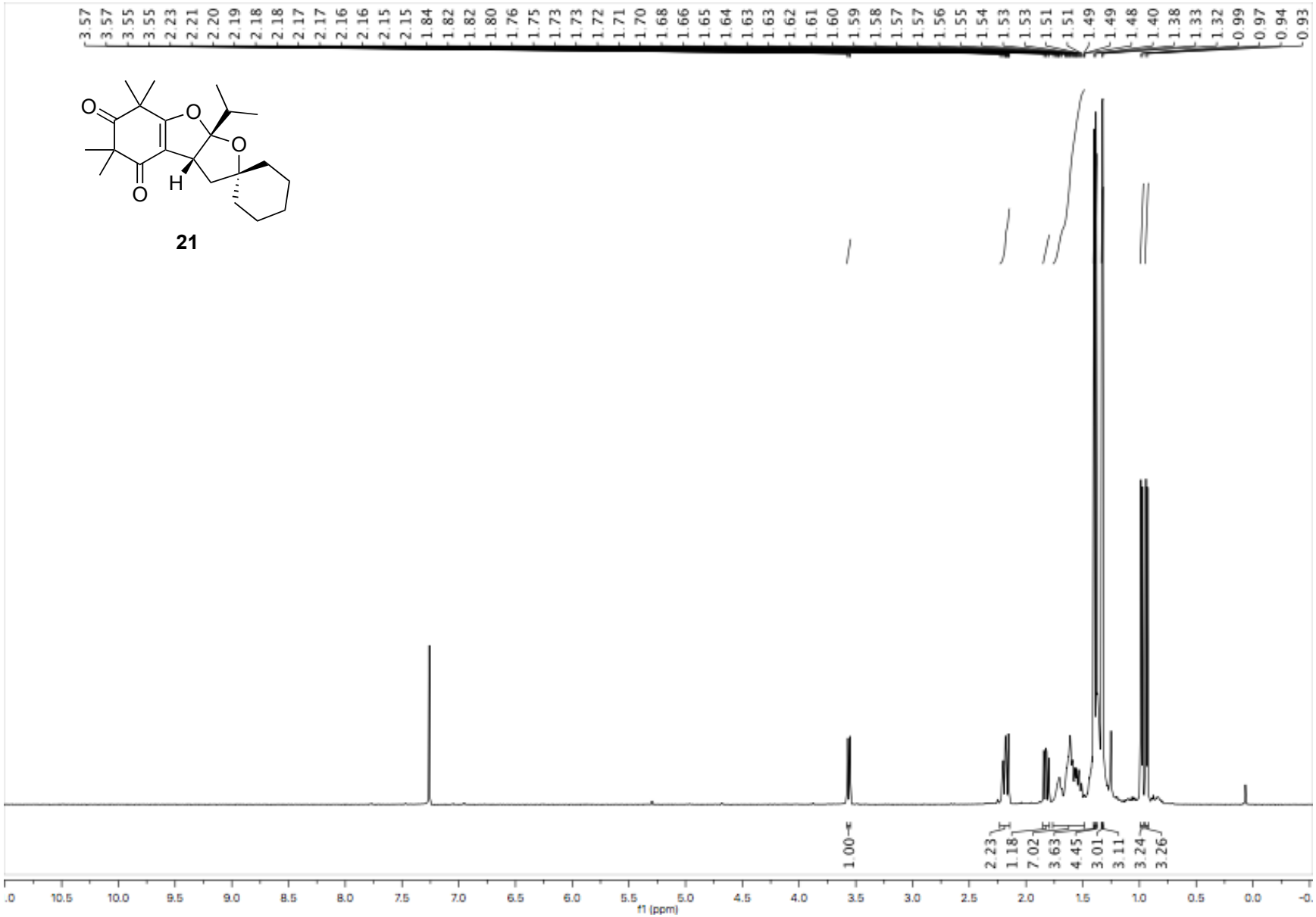


Figure S72. ^{1}H NMR spectrum for spirocycle **21**

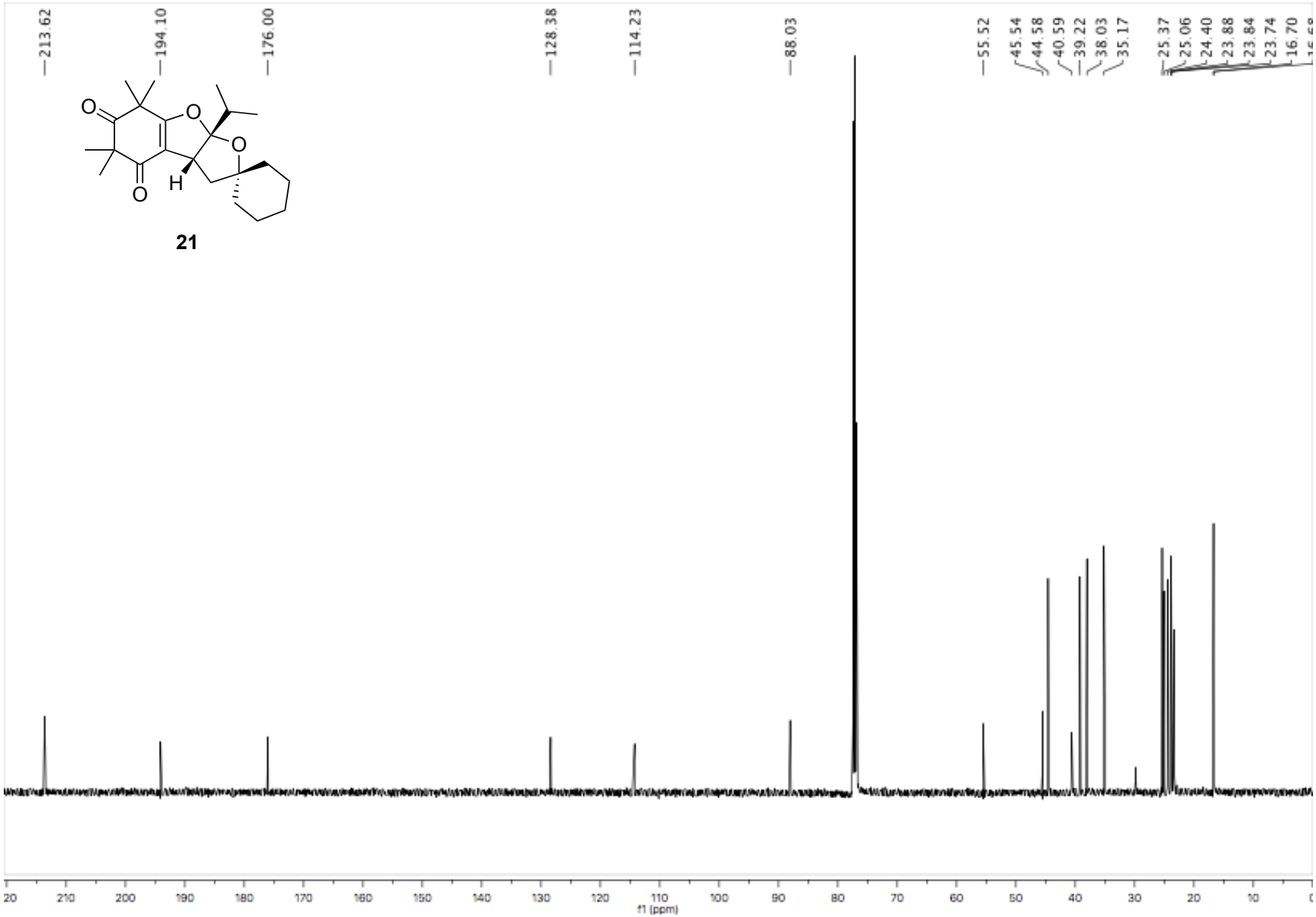


Figure S73. ^{13}C NMR spectrum for spirocycle **21**

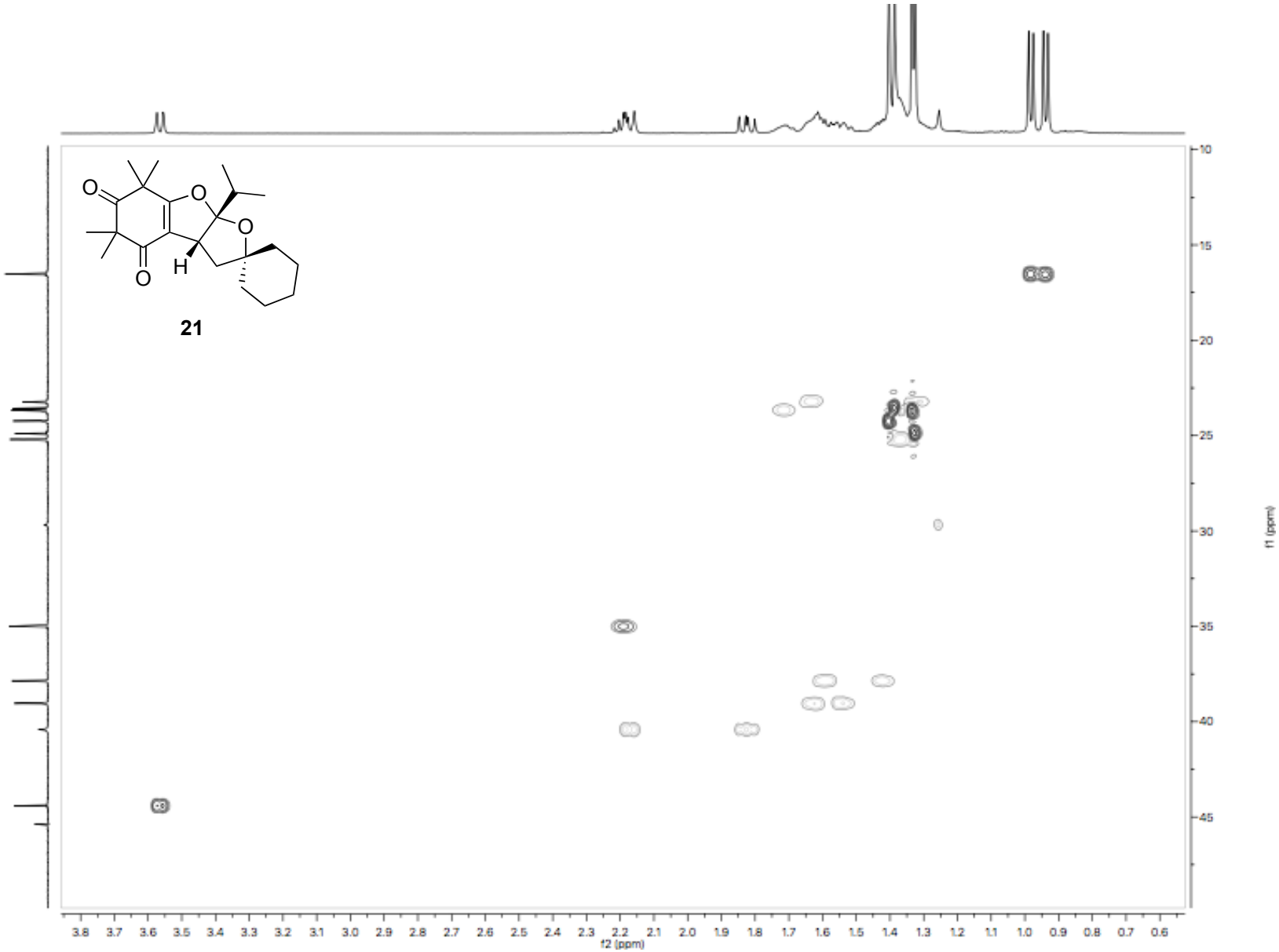


Figure S74. HSQC spectrum for spirocycle **21**

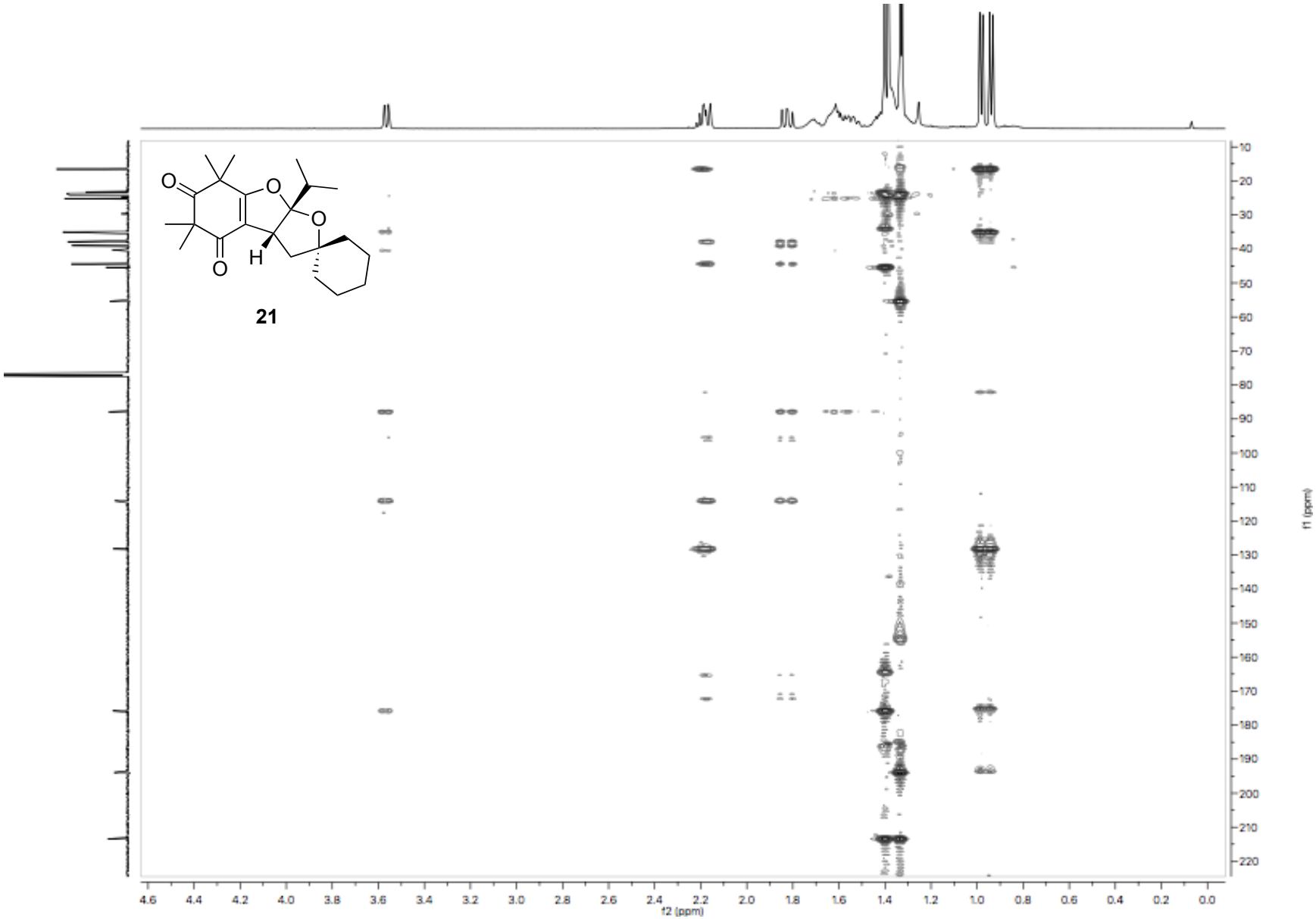


Figure S75. HMBC spectrum for spirocycle **21**

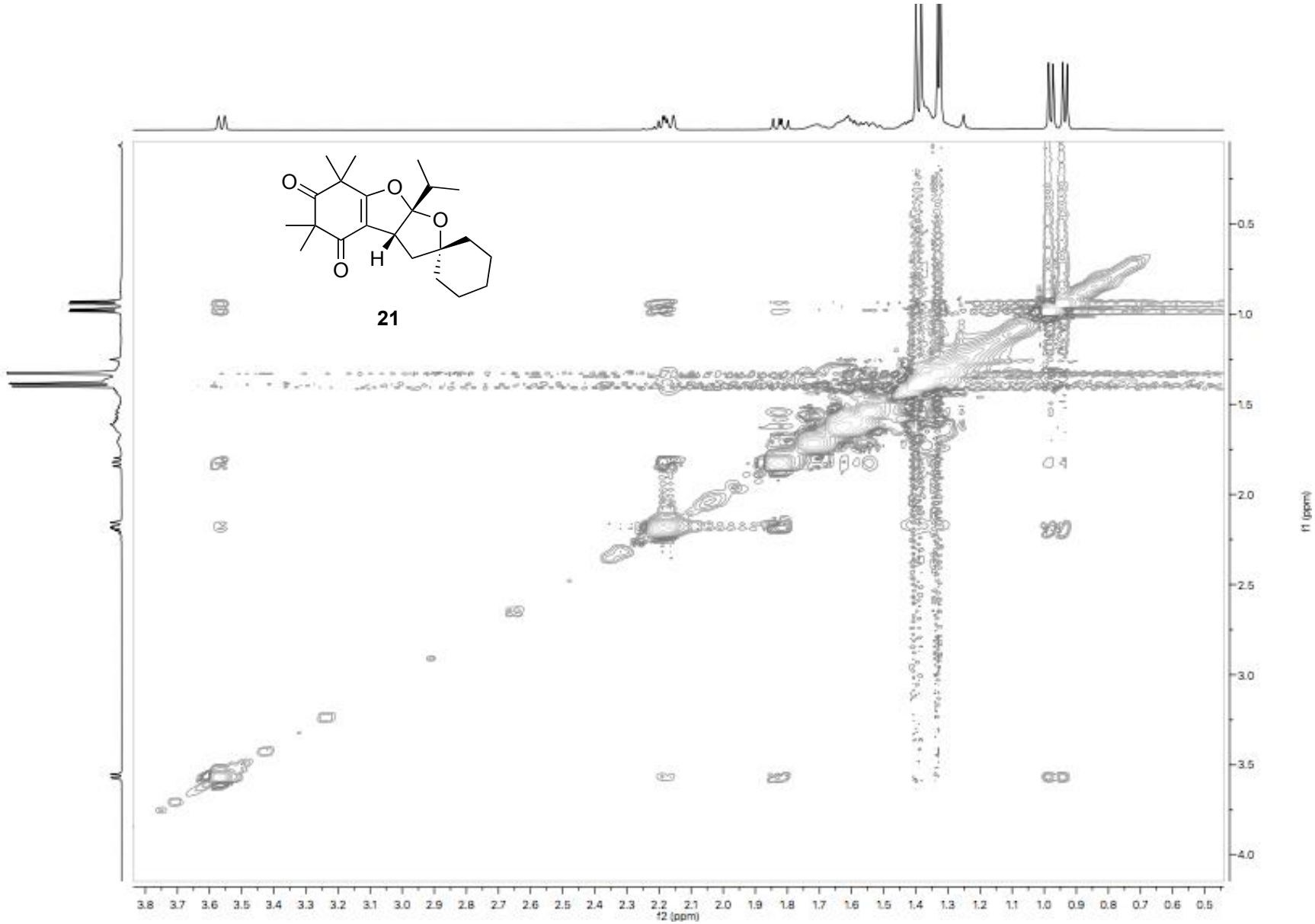


Figure S76. NOESY spectrum for spirocycle **21**

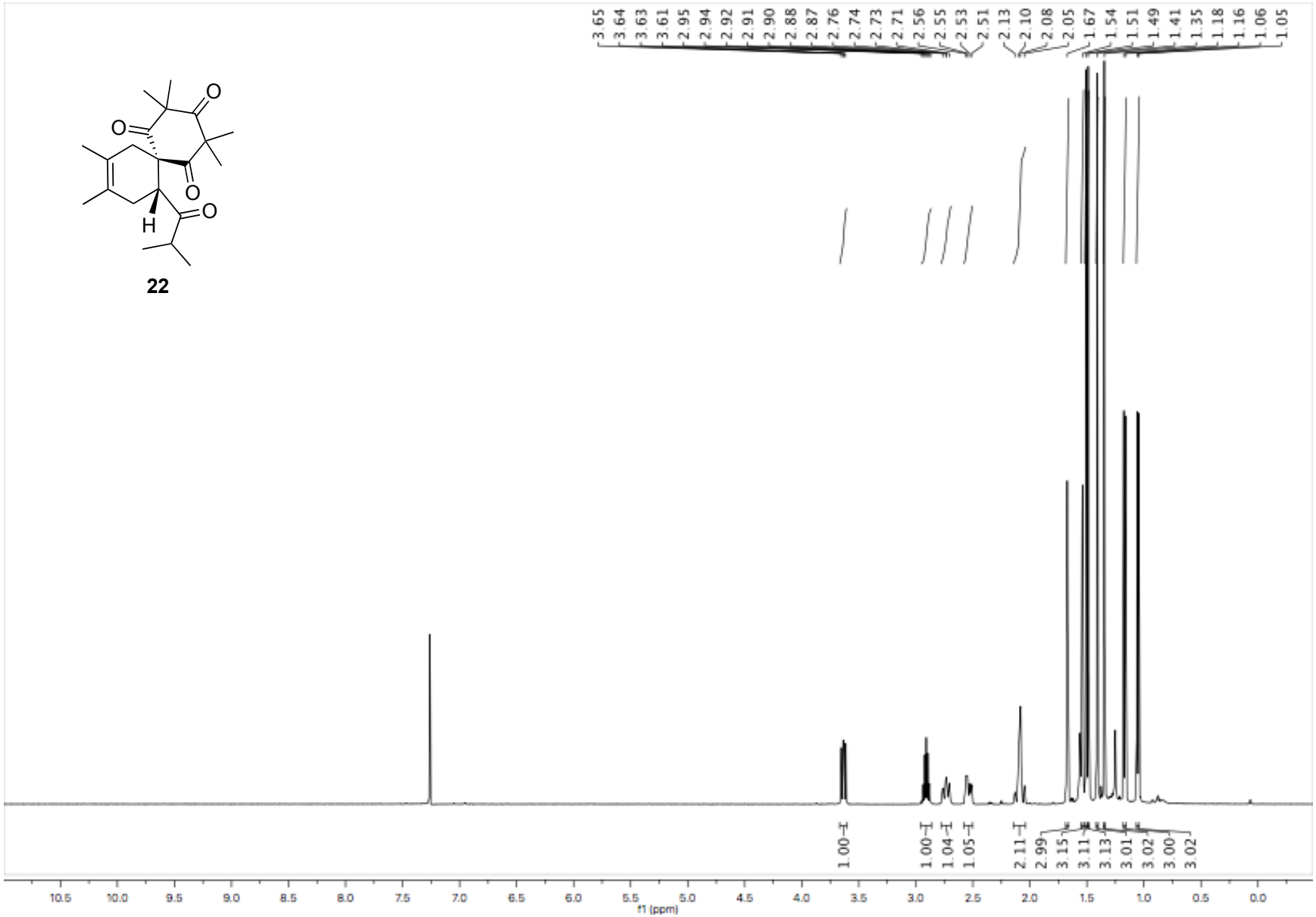


Figure S77. ^{1}H NMR spectrum for spirocycle **22**

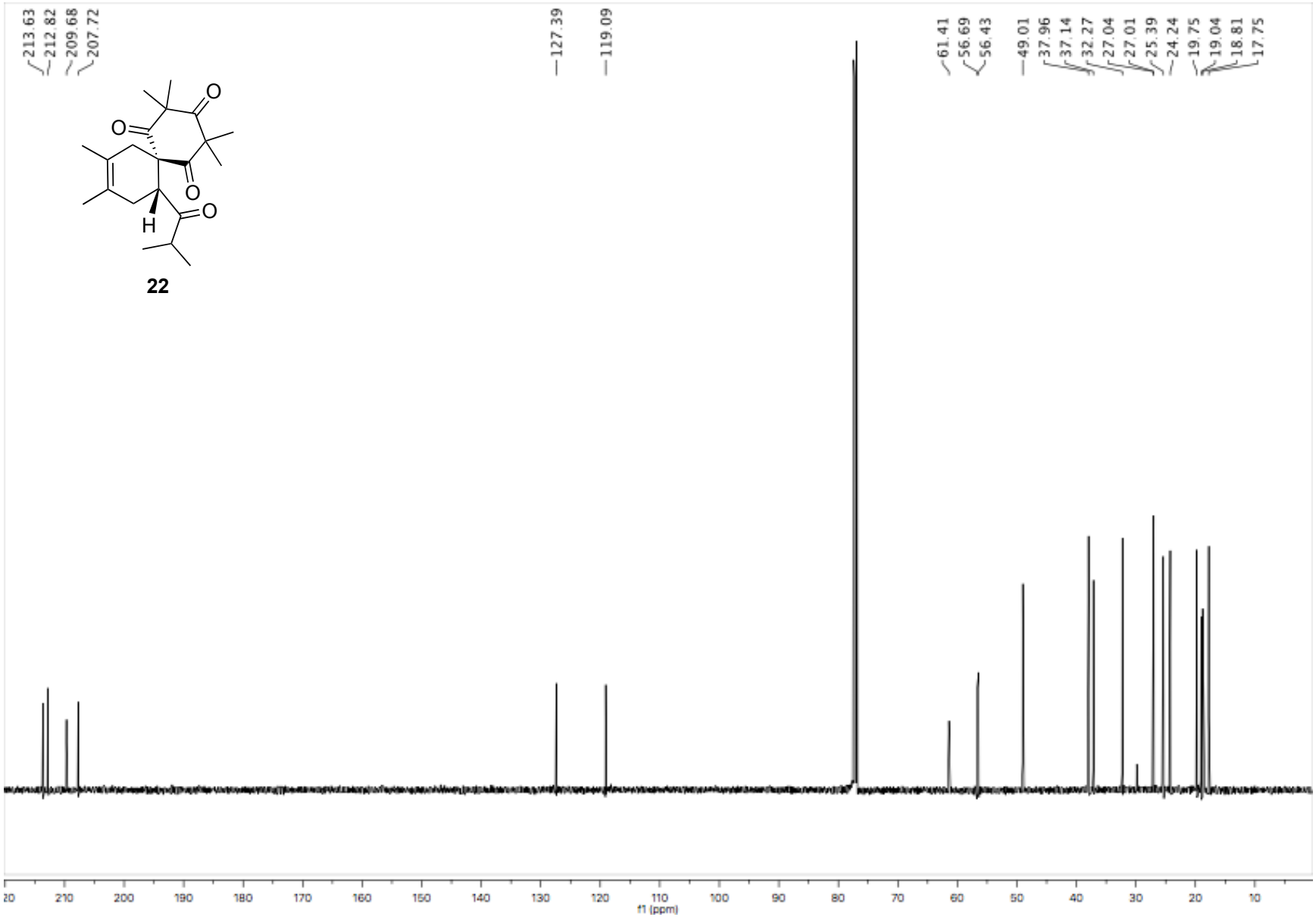


Figure S78. ^{13}C NMR spectrum for spirocycle **22**

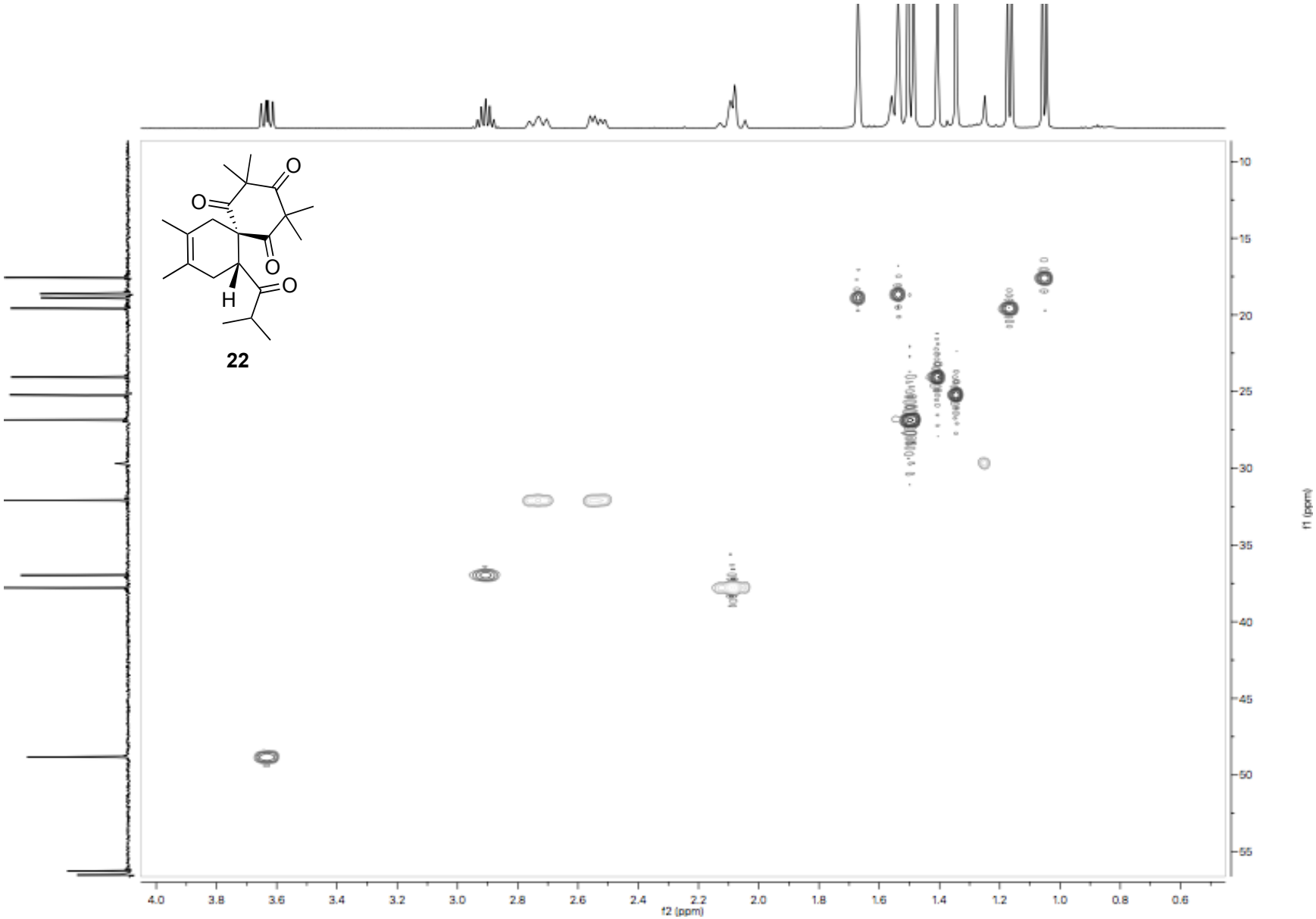


Figure S79. HSQC spectrum for spirocycle **22**

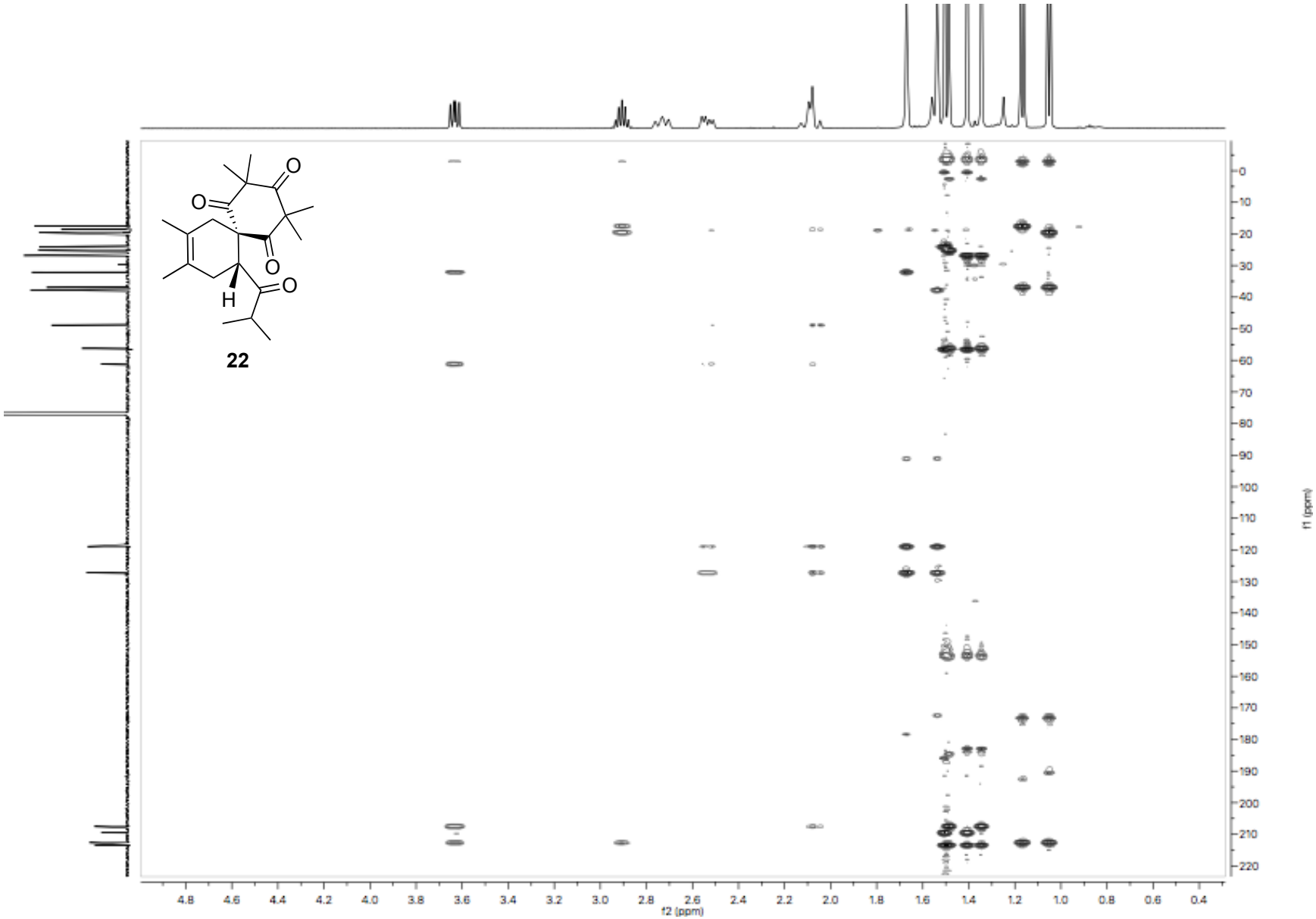


Figure S80. HMBC spectrum for spirocycle **22**

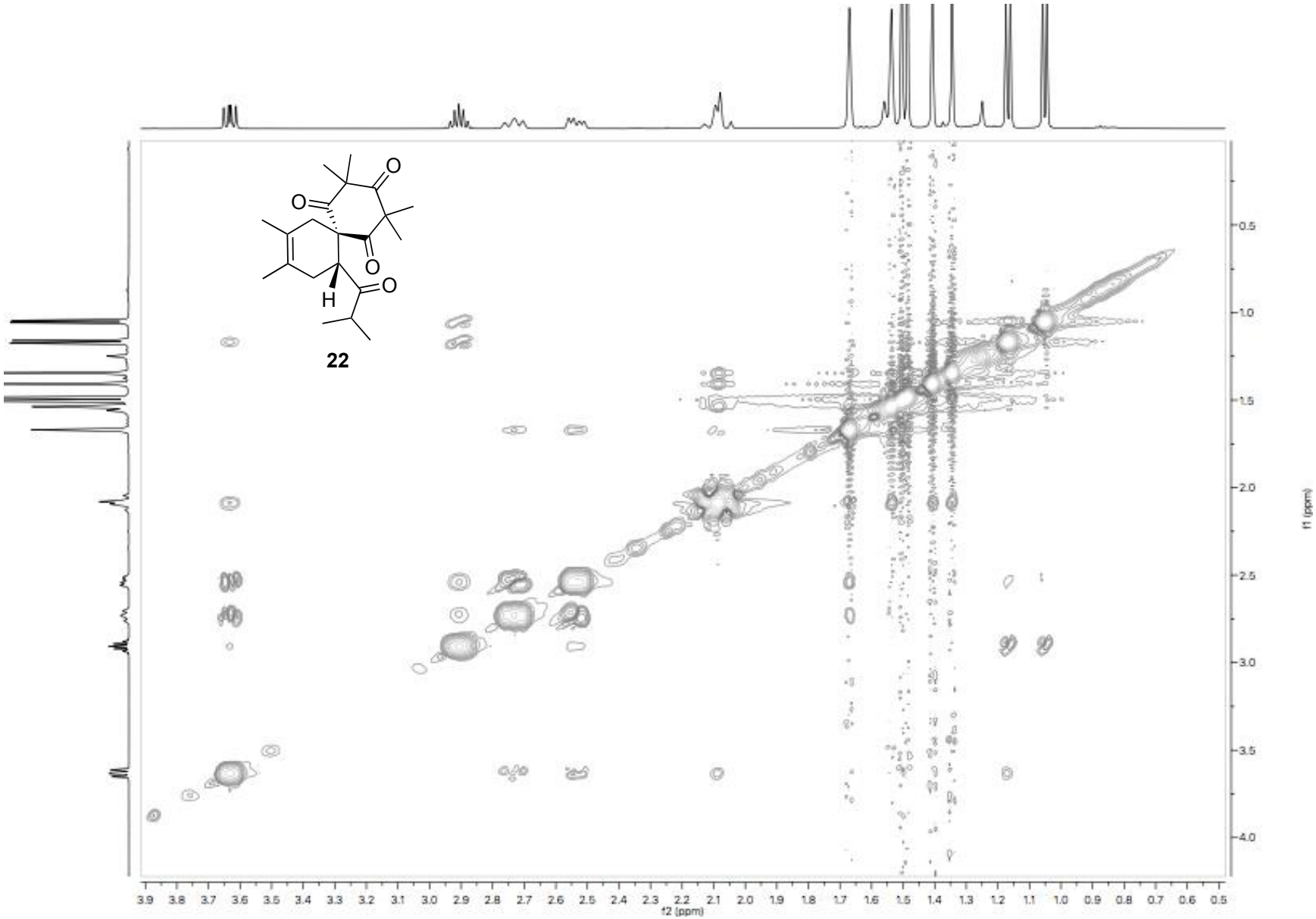


Figure S81. NOESY spectrum for spirocycle **22**

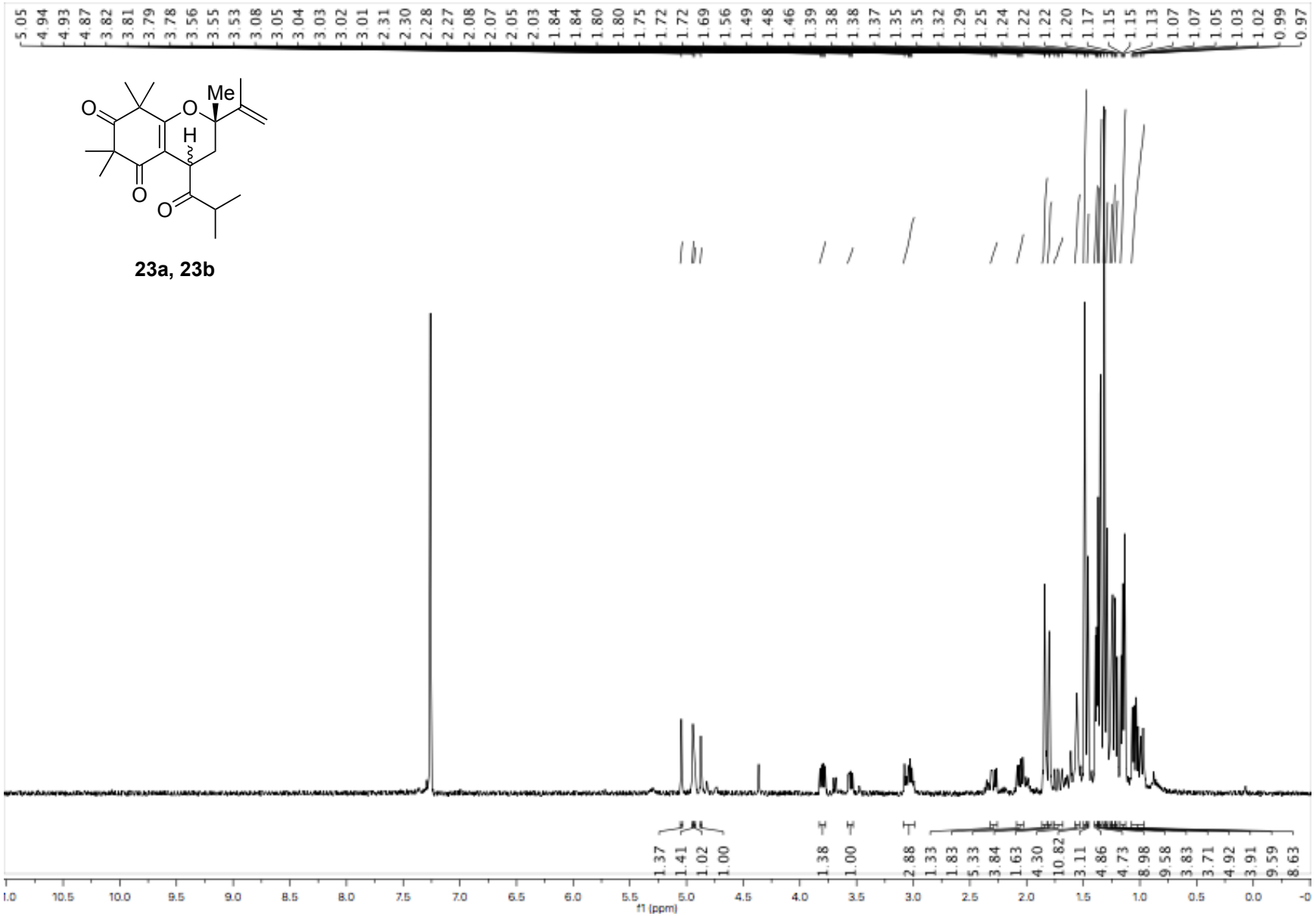


Figure S82. ^{1}H NMR spectrum for dihydropyrans **23a and 23b**

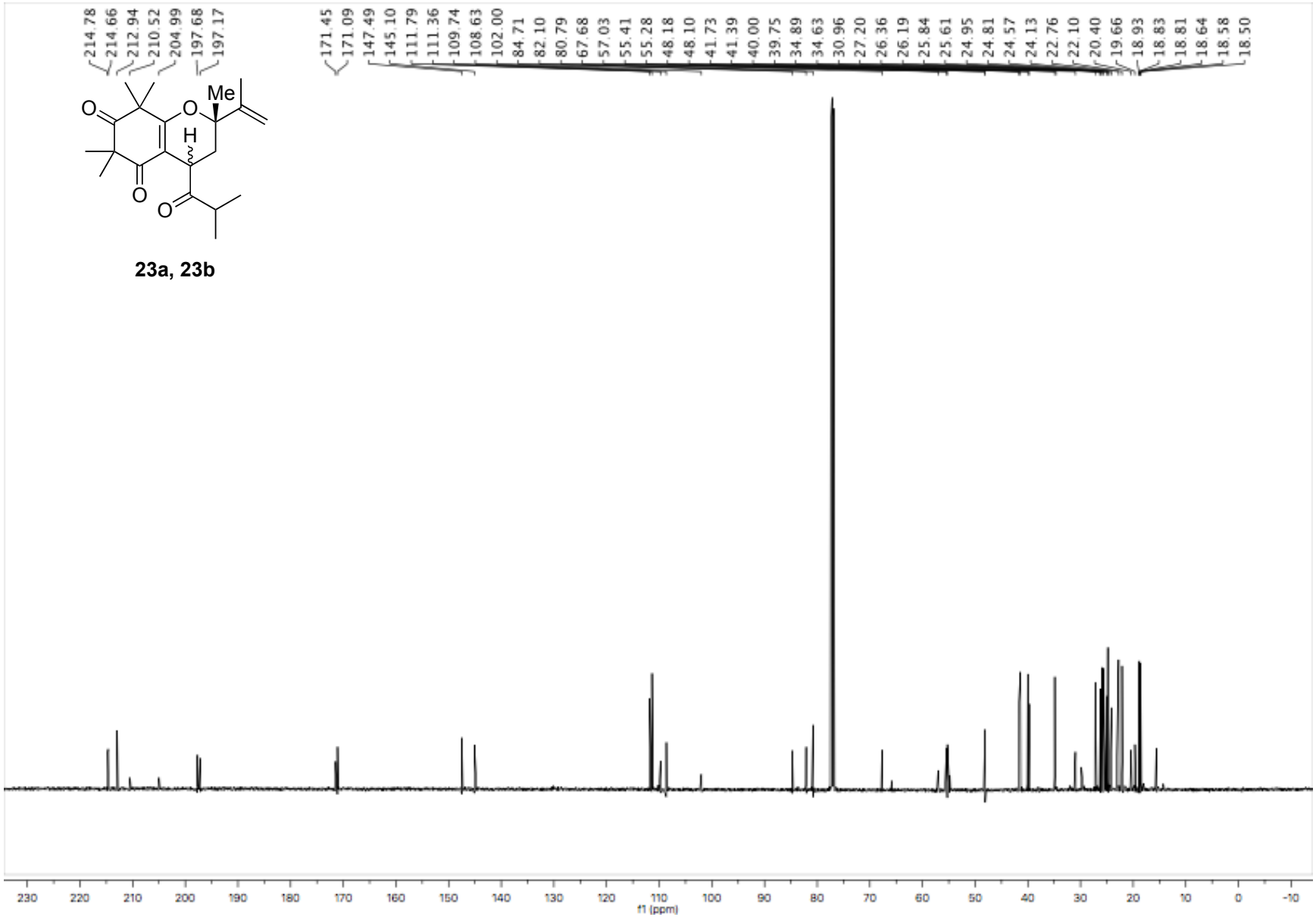


Figure S83. ^{13}C NMR spectrum for dihydropyrans **23a and 23b**

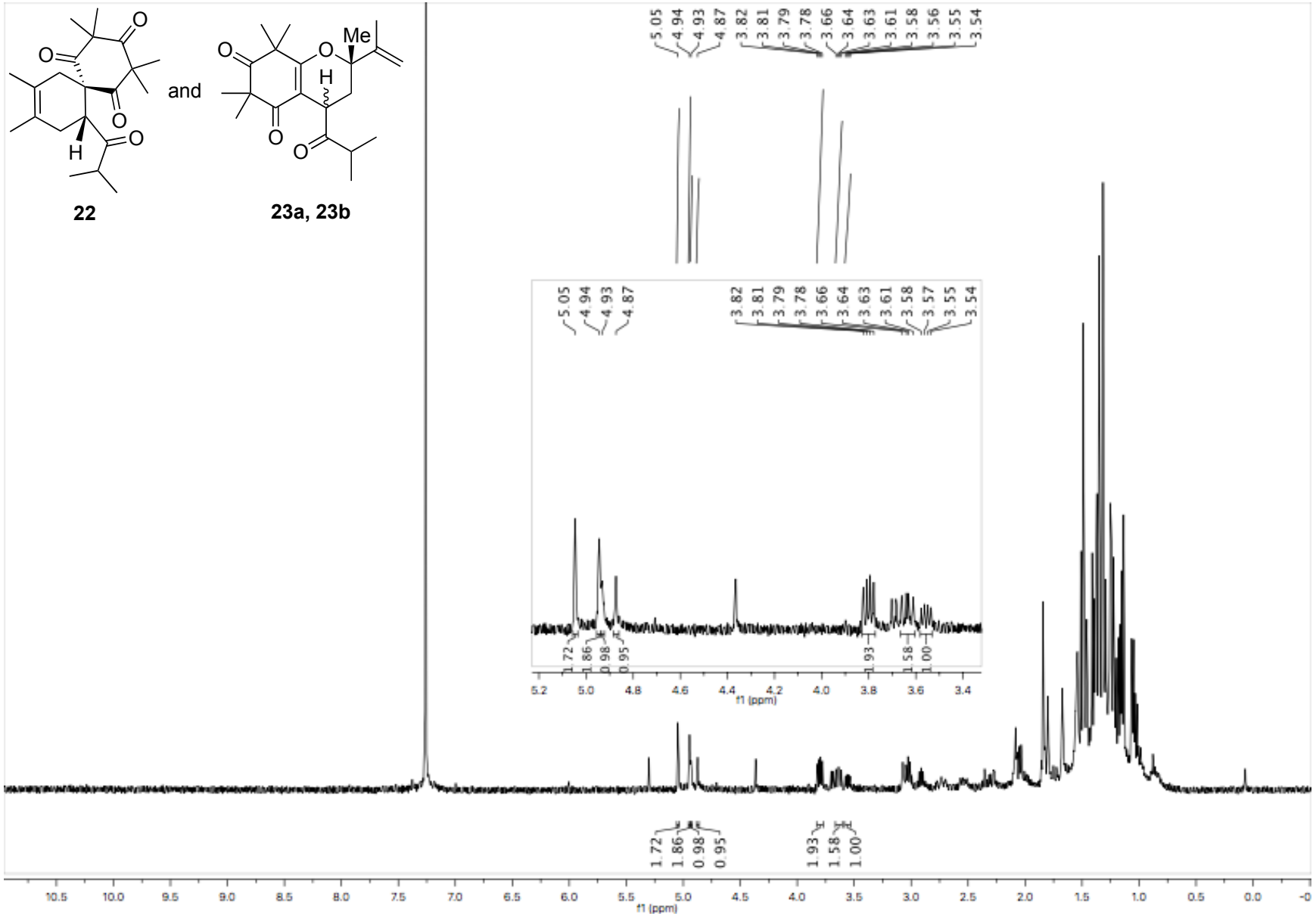


Figure S84. Crude ^{1}H NMR for the thermolysis of **23a** and **23b**

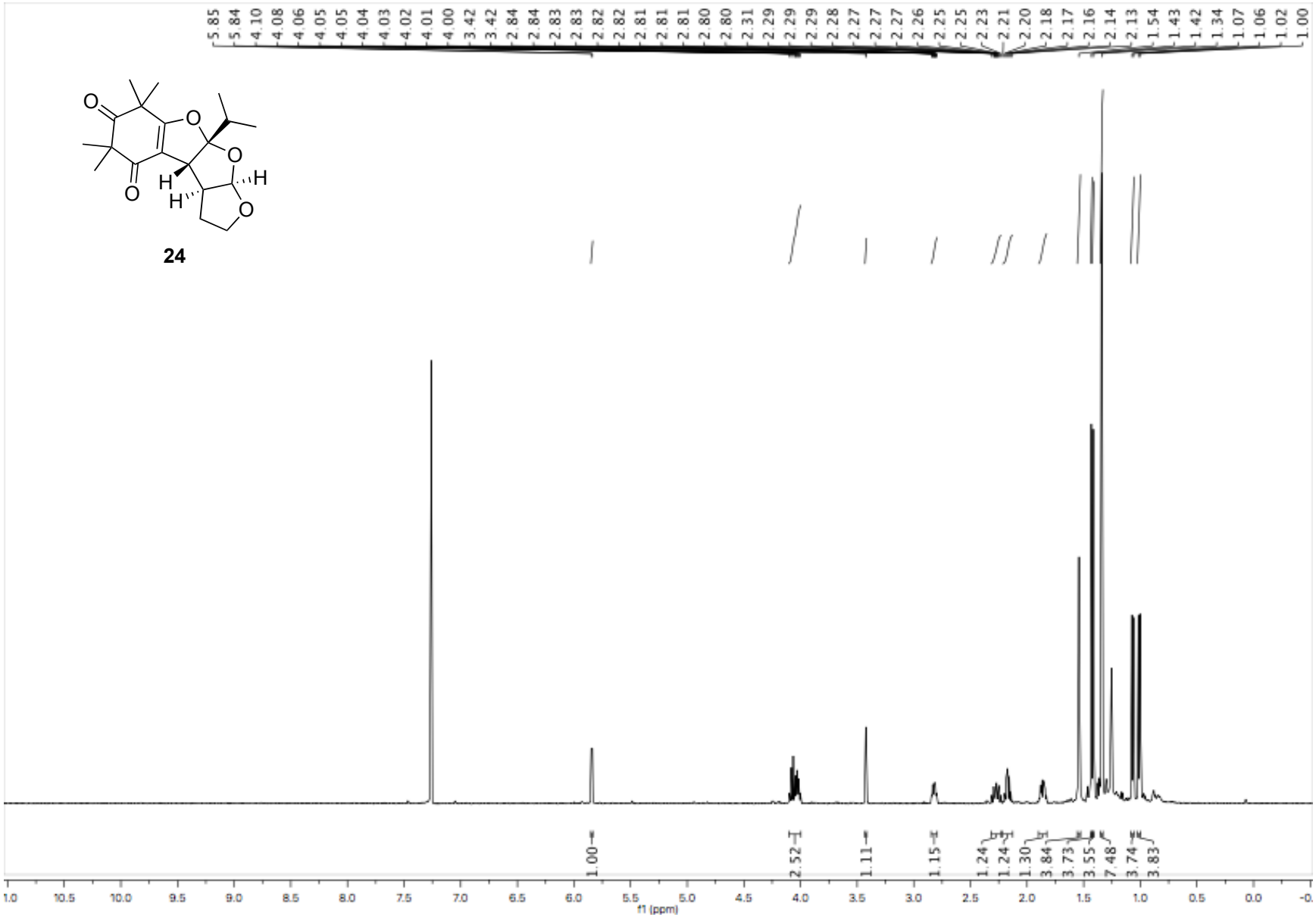


Figure S85. ^{1}H NMR spectrum for *tris*-furan **24**

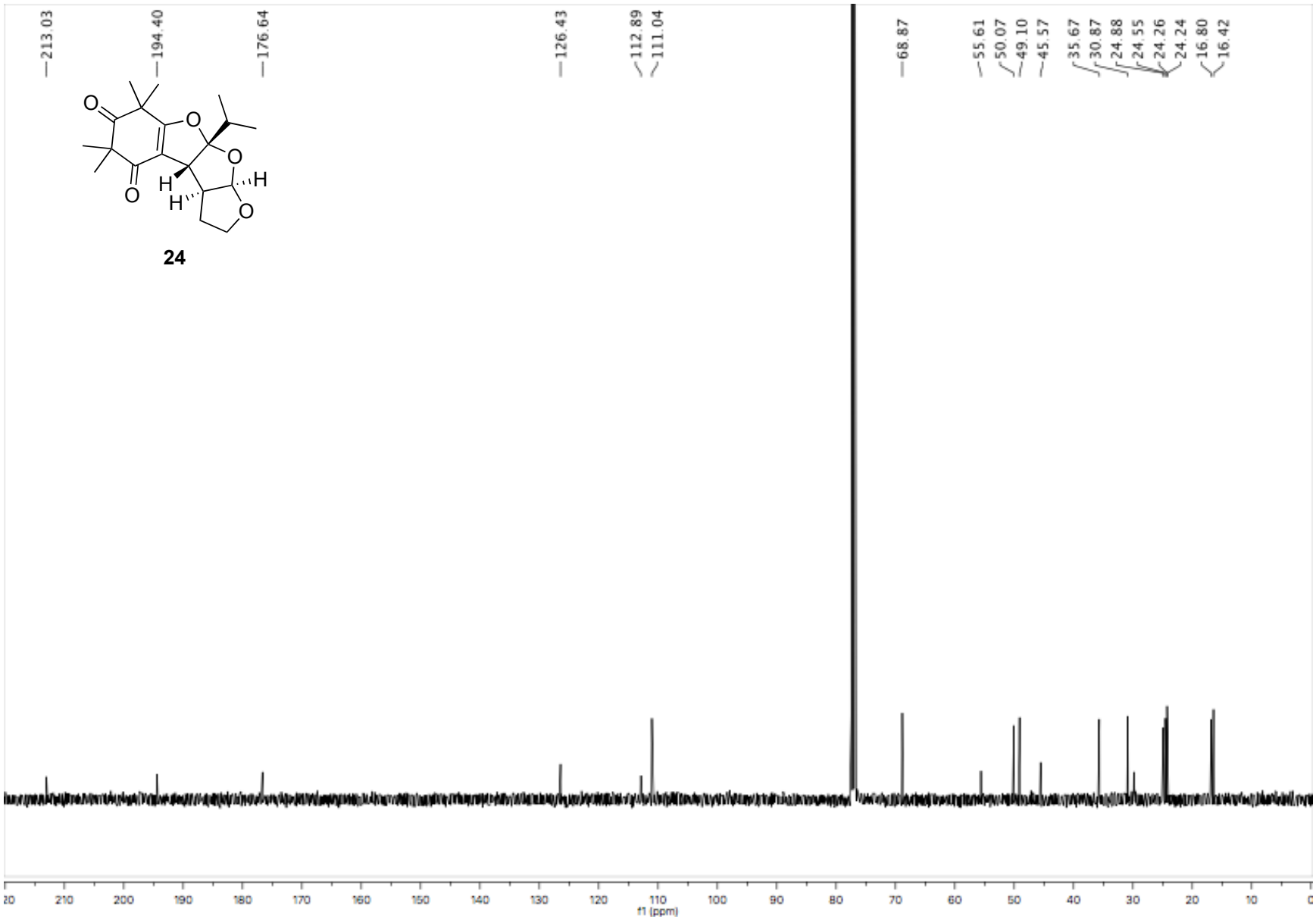


Figure S86. ^{13}C NMR spectrum for *tris*-furan **24**

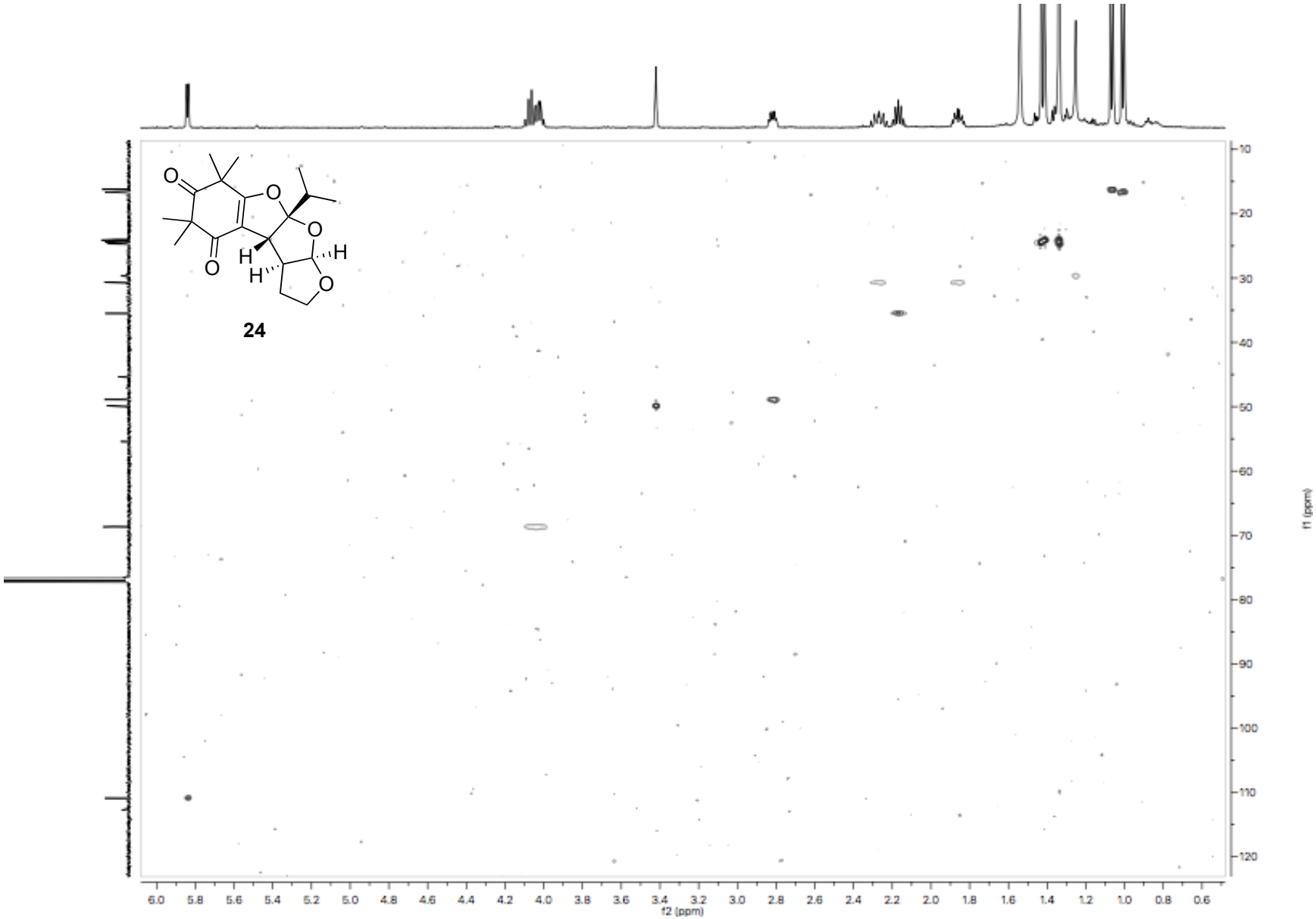


Figure S87. HSQC spectrum for *tris*-furan **24**

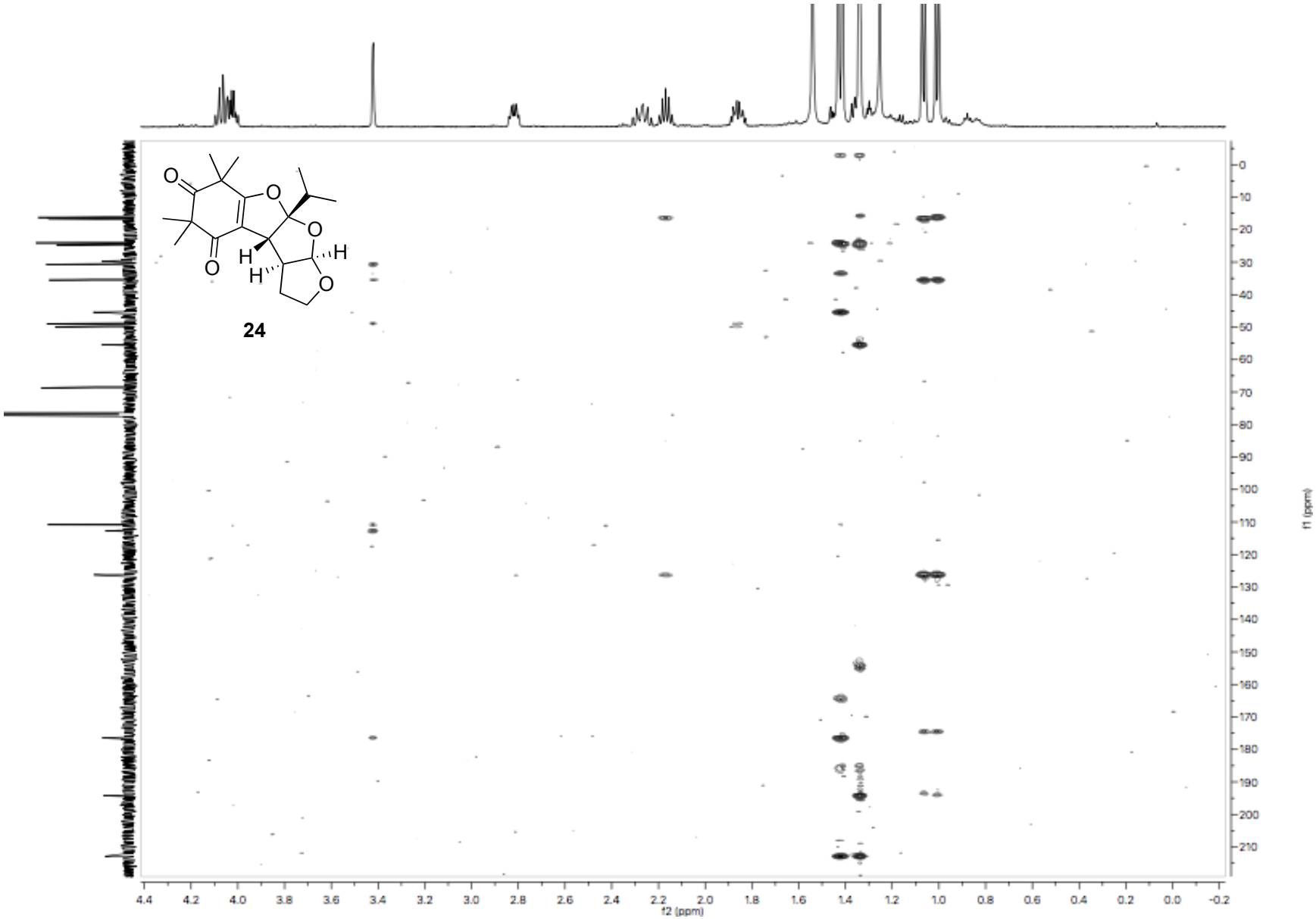


Figure S88. HMBC spectrum for *tris*-furan **24**

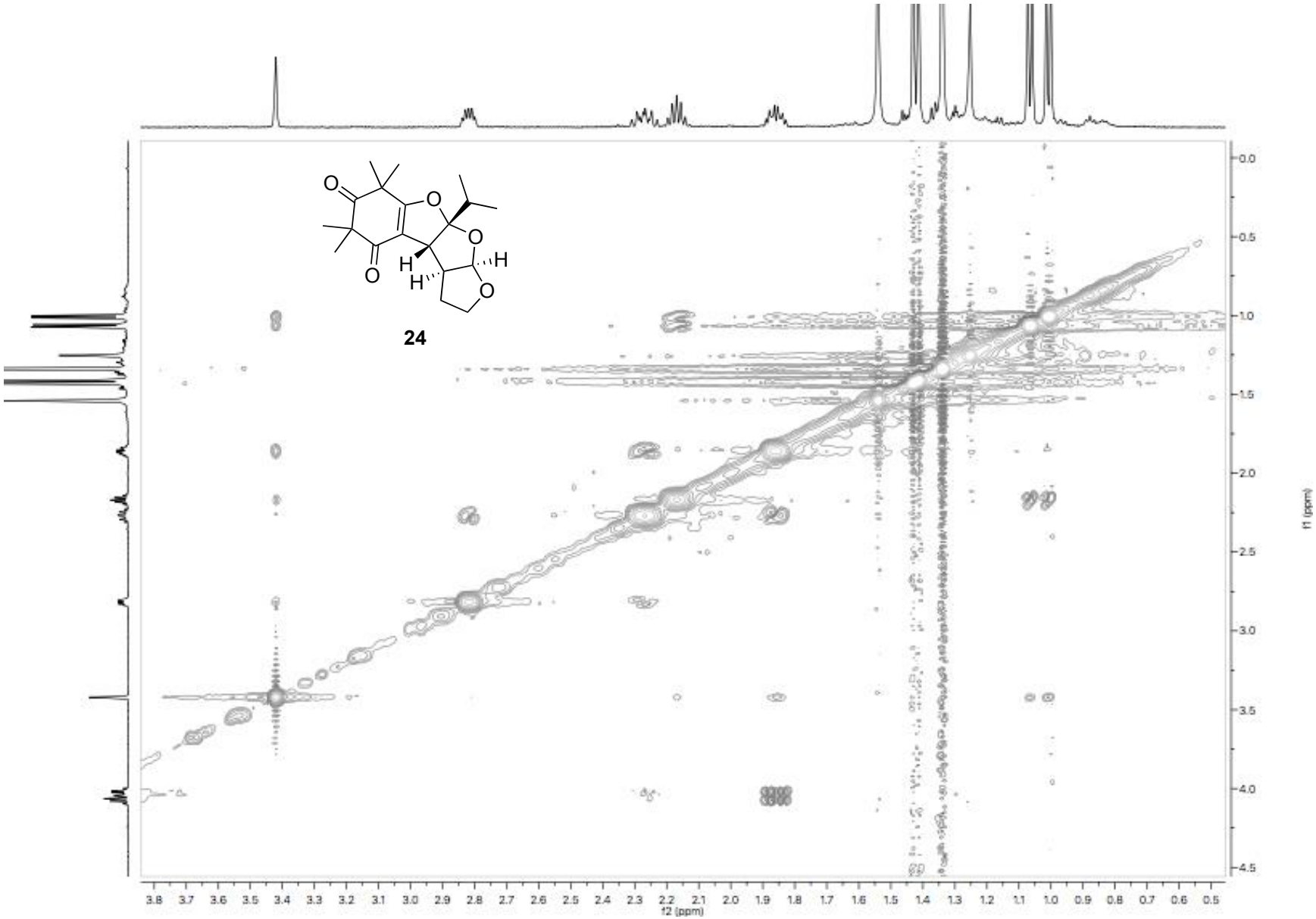


Figure S89. NOESY spectrum for *tris*-furan **24**

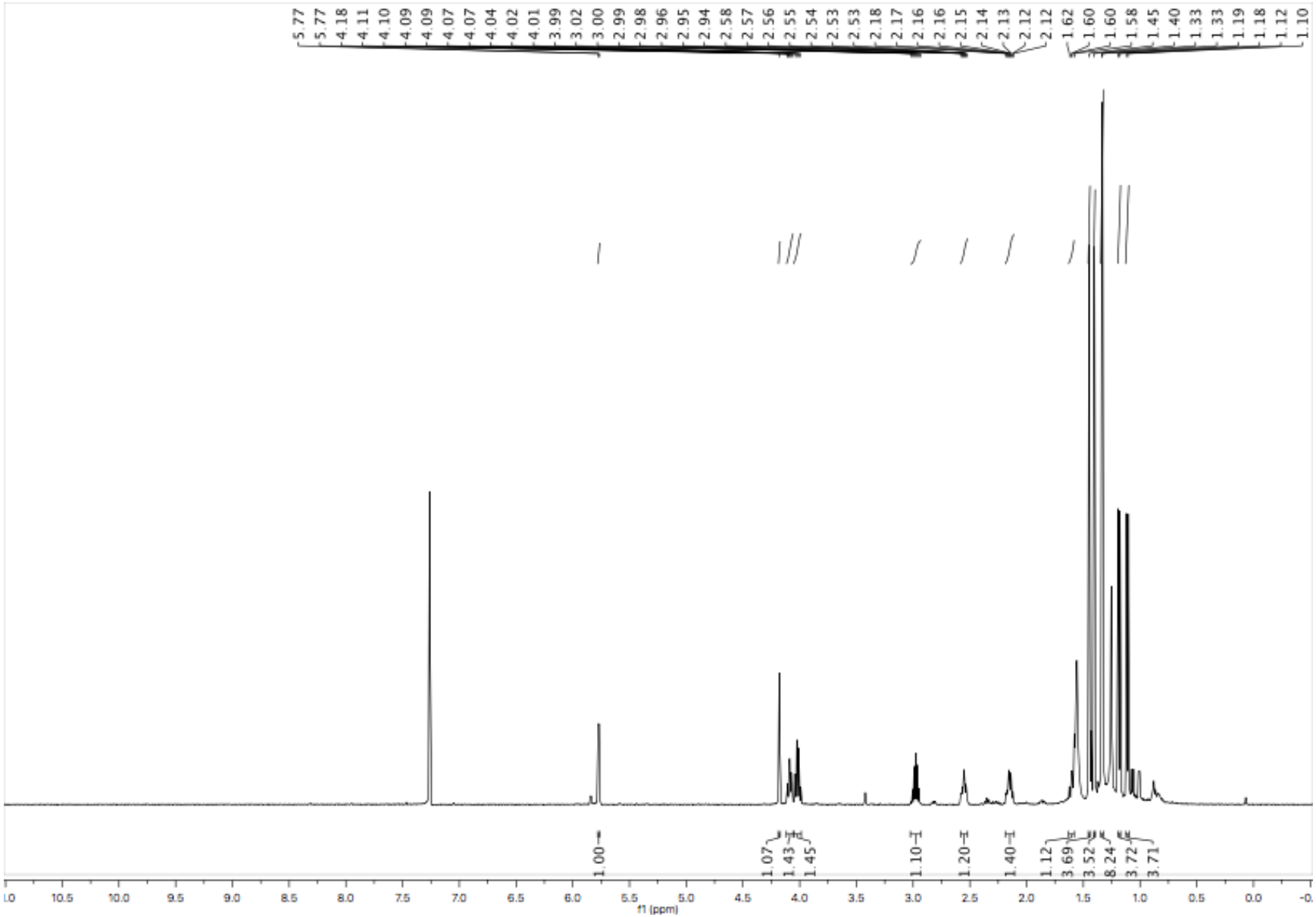


Figure S90. ^{1}H NMR spectrum for dihydropyran **25**

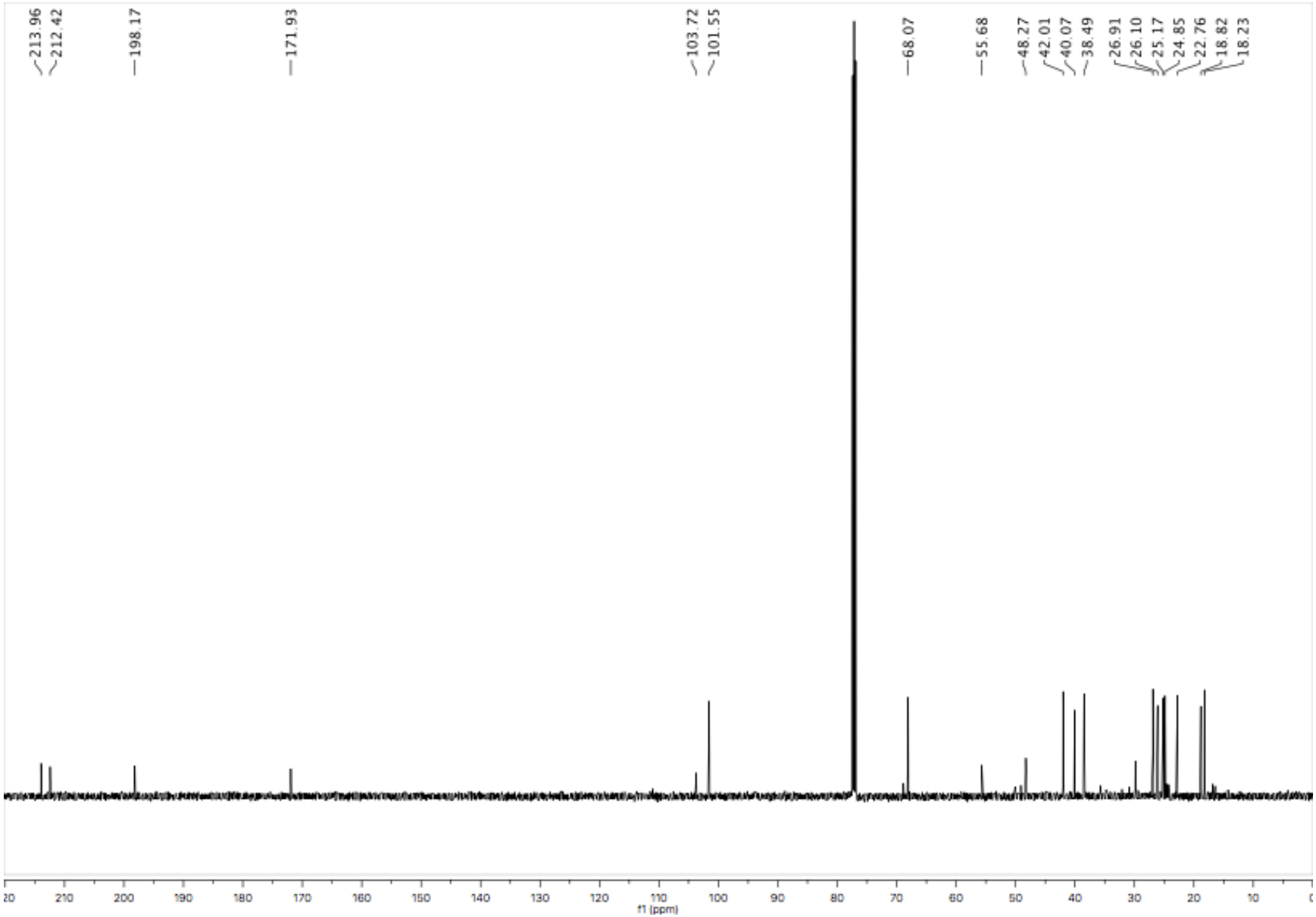


Figure S91. ^{13}C NMR spectrum for dihydropyran **25**

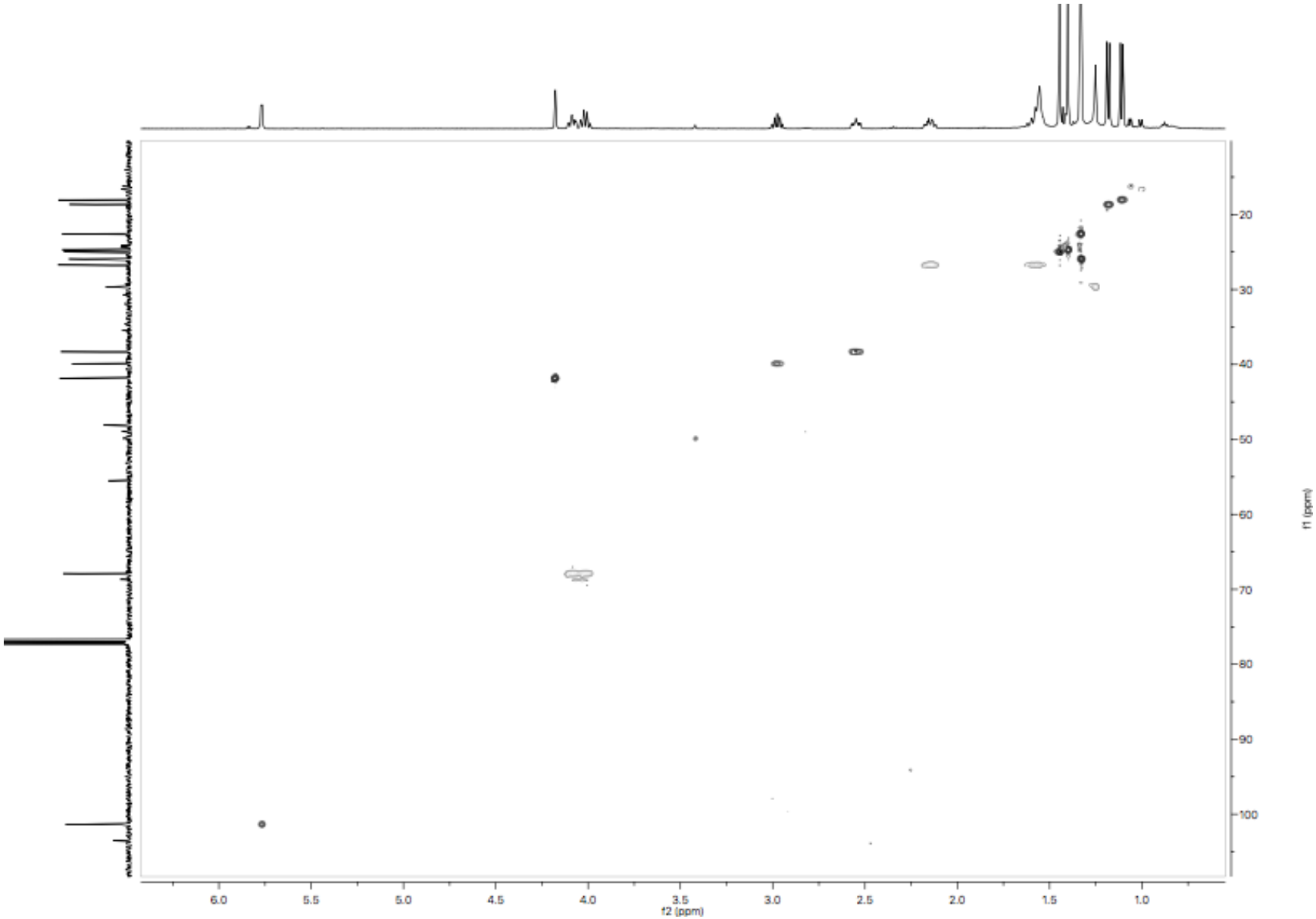


Figure S92. HSQC spectrum for dihydropyran **25**

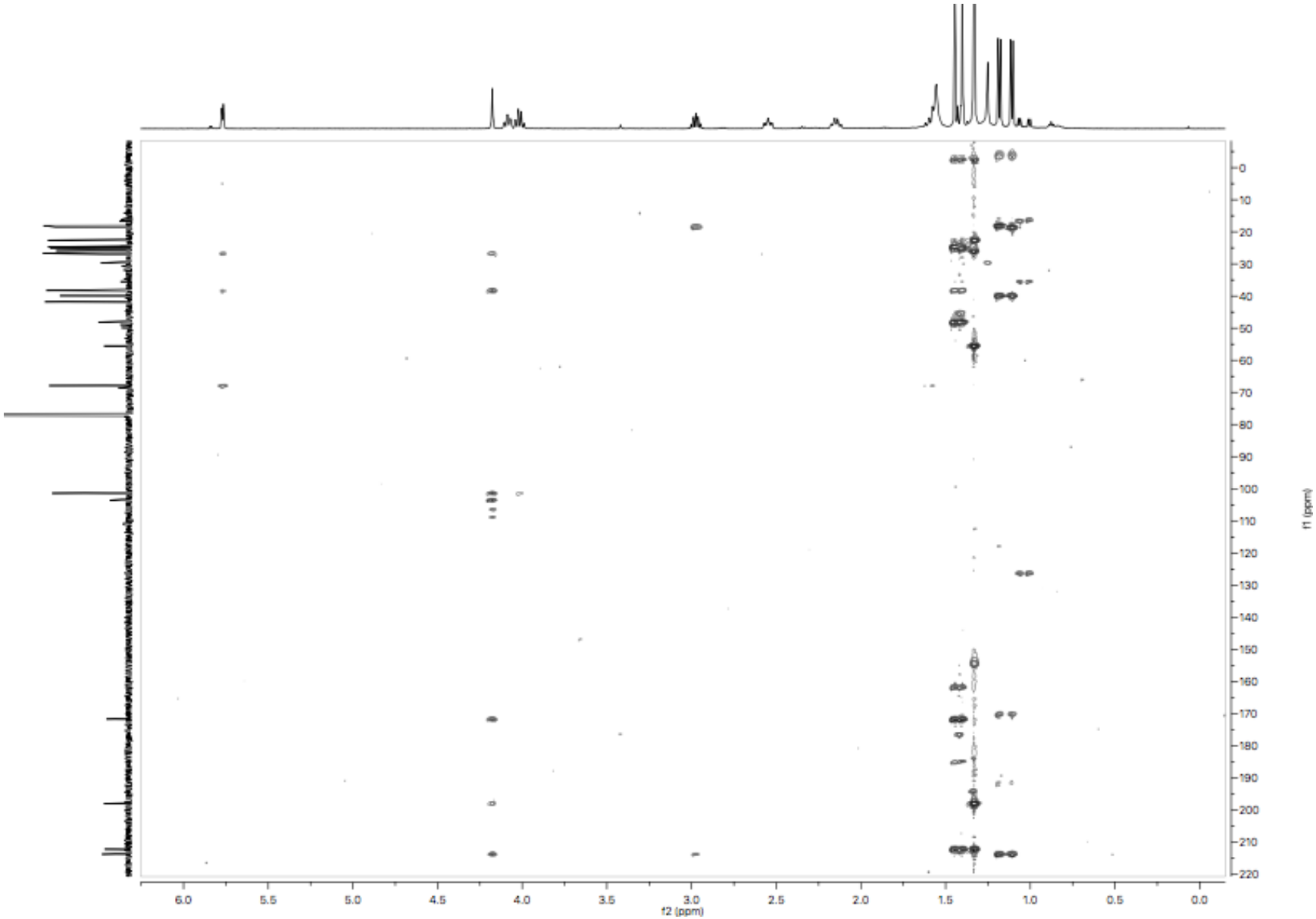


Figure S93. HMBC spectrum for dihydropyran **25**

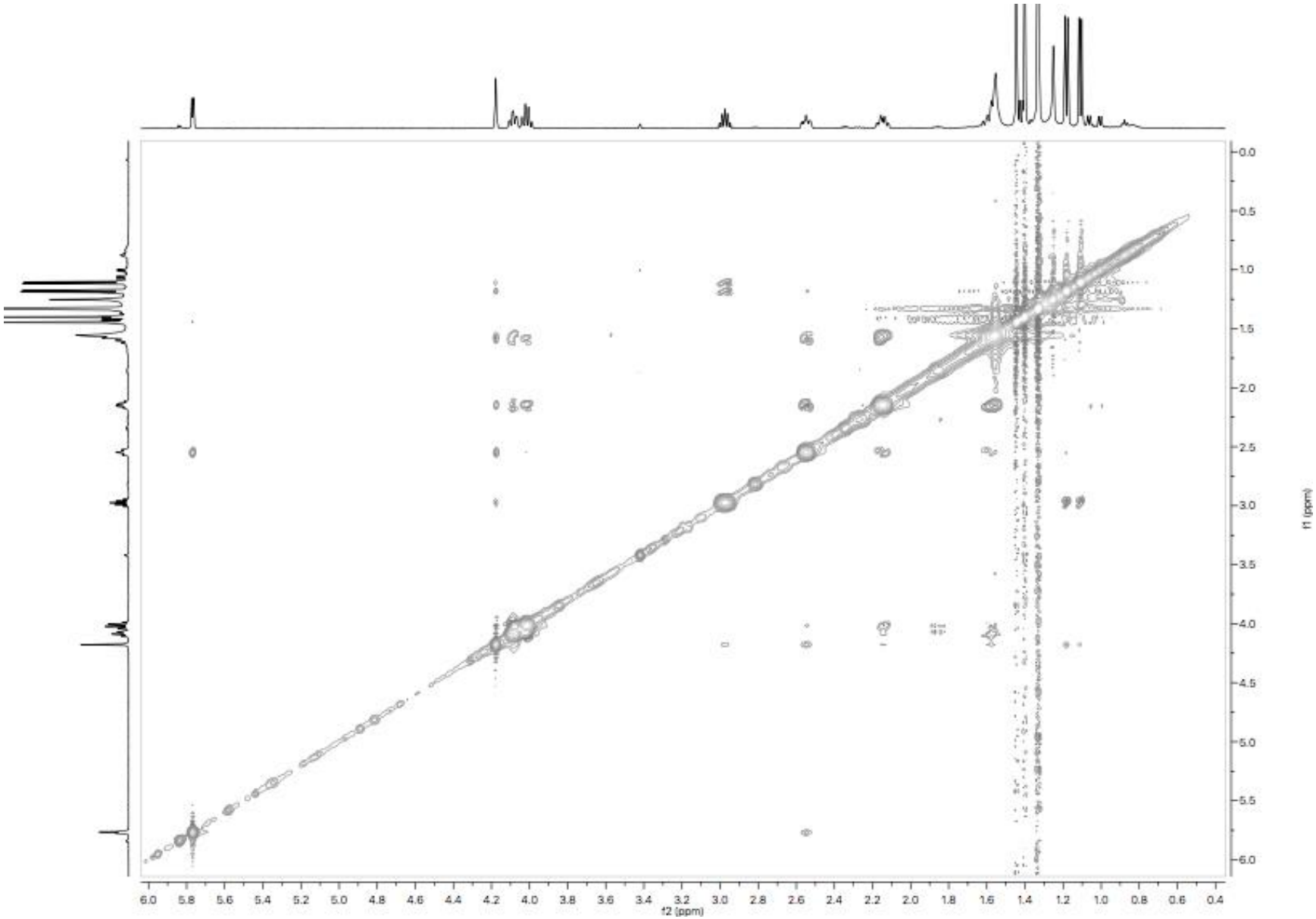
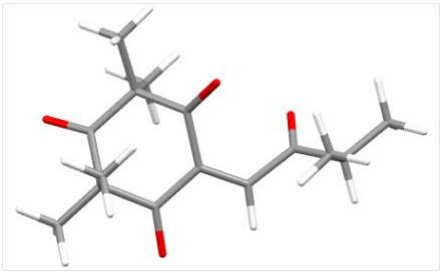


Figure S94. NOESY spectrum for dihydropyran **25**

V. Computational Studies (Boston University)

A. Computational Methods and Results for Enetrione Minimization (9)

All calculations were performed in the gas phase using Jaguar 9.5 (Schrödinger Release 2017-1)[S4,S5] using the Boston University Shared Computing Cluster (SCC) at the Massachusetts Green High-Performance Computing Center. Ground state structures were first optimized at the STO-3G level of theory for all atoms, then re-optimized at the B3LYP/6-31G** level of theory for all atoms with vibrational frequencies included. Mercury visualization software was used to generate images of optimized structures.[S6]



Charge = 0, multiplicity = 1

SCFE energy: DFT(b3lyp):	-884.54658407484 hartrees
Total internal energy, Utot (SCFE + ZPE + U):	-884.202342 hartrees
Total enthalpy, Htot (Utot + pV):	-884.201398 hartrees
Total Gibbs free energy, Gtot (Htot - T*S):	-884.274091 hartrees

Table S4. Coordinates for DFT-minimized Enetrione (**9**)

O1	-2.8340556069	0.2385831676	-0.8125988843
C2	-2.2411565111	1.1451392127	-0.2541605869
C3	-2.9892230824	2.3152376358	0.4017934965
C4	-4.4176942684	2.4235826001	-0.1377572946
C5	-3.0165813513	2.0242848185	1.9372521275
C6	-2.2299956170	3.6463205131	0.2257451323
C7	-0.6836770329	3.6683092420	0.2918033862
C8	-0.1837530620	4.0674247981	-1.1289496934
C9	-0.2199254254	4.7069383126	1.3250907300
C10	-0.0994274031	2.2898330295	0.5924357935
C11	-0.7456923650	1.1412892228	-0.1221175556
C12	-0.0372988665	0.1310034591	-0.6554549306

C13	1.4650957391	0.0781406419	-0.7263484513
C14	2.1432582483	-1.1485575412	-0.1288140271
C15	1.7796203764	-1.2835984423	1.3653199081
C16	3.6548271949	-1.1125738082	-0.3617753113
O17	2.0676970644	0.9741157355	-1.2897751537
O18	0.8467761315	2.1254602924	1.3426927799
O19	-2.8347218096	4.6864717799	0.0631710774
H20	-4.4160255019	2.6222333563	-1.2123908517
H21	-4.9530930741	1.4876986134	0.0307841099
H22	-4.9426625246	3.2426287952	0.3559611630
H23	-2.0186801481	1.9388627445	2.3774838167
H24	-3.5486817050	2.8313451393	2.4484732086
H25	-3.5486175423	1.0858781910	2.1175511866
H26	-0.4984723579	3.3523760971	-1.8946776599
H27	-0.5903929273	5.0494063311	-1.3812004343f
H28	0.9084665219	4.1087088147	-1.1382543440
H29	-0.5231205743	4.4246191918	2.3374818901
H30	0.8690171377	4.7831332515	1.3149113308
H31	-0.6584980397	5.6777097260	1.0876793702
H32	-0.5974448388	-0.6815748170	-1.1197060898
H33	1.7141927300	-2.0172686074	-0.6543363726
H34	0.7007233583	-1.3882684447	1.5146688962
H35	2.2650558177	-2.1679947735	1.7882697923
H36	2.1084522432	-0.4022339223	1.9228358413
H37	3.8917834540	-1.0173358495	-1.4241478210
H38	4.1045303357	-0.2587188702	0.1529479283
H39	4.1177341667	-2.0278984070	0.0189765303

B. Computational Methods and Results for Reaction Pathways Producing 5–7

All calculations were performed with ORCA[S7] version 4.0.1. Geometries were optimized with the composite PBEh-3c[S8] method developed by Grimme and coworkers. This method contains a modified version of the PBE0[S9] functional and the def2-SV(P)S[10] basis set with dispersion corrections,[S11] BSSE corrections,[S12] and reduced computational cost via the RIJONX[S13] approximation along with the DEF2/J auxiliary basis set.[S14] The method has been shown to give MP2-like performance for certain small-to-medium sized organic molecules.[S8] Each of the reactants and products was confirmed as a minimum based on the lack of imaginary frequencies. Each of the TS structures was confirmed as a saddle point based on the existence of one and only

one imaginary frequency. Thermal contributions to thermodynamic parameters were evaluated at reaction conditions (333.15 K). The equilibrium structures are shown in Tables S6-S14, with visual representations in Figure S95.

The optimized structures were then subjected to single-point energy evaluations at the orbital-optimized spin component scaled MP2 (OO-SCS-MP2[S15]/DEF2-TZVP[S10] level. The RI approximation was employed for the OO-SCS-MP2 correlation calculations with the DEF2/C[S16] auxiliary basis sets. The RIJCOSX approximation[S17] was employed for the SCF cycle of the OO-SCS-MP2 calculations with the DEF2/J auxiliary basis. The results are shown in Table S5, with the OO-SCS-MP2 results summarized in Figure S95. Also included in Table S5 are results for the HDA formation of **10** from **14** + **ββ** for comparison.

Solvent effects were probed by performing the geometry optimizations with implicit solvation using the conductor-like polarizable continuum model[S18] implemented in ORCA. The results were nearly identical to the gas-phase results.

We have ensured that **TS5^c**-**TS7^c** connect the desired reactants and products by performing steepest descent optimization (PBEh-3c) from geometries straddling each of the transition states. The results are shown in Figures S96-S98. The reaction path for **5** and **7** are clearly concerted and asynchronous. The reaction pathway for **6**, however, is not as concerted. The formation of the σ-bond between the isopropyl ketone oxygen and caryophyllene passes through a very broad and shallow region centered at ~2.8 Å. The breadth and shallowness of this region suggests that there are other relaxation pathways that might be available and therefore the transmission coefficient for reaction can be reasonably assumed to be dampened.

Finally, the transition state structures **TS5^c** and **TS6^c** were checked for diradical character by performing CASSCF(12,12)/DEF2-TZVP/RIJCOSX//PBEh-3c calculations. The active space

included the entire π–system on **14**, and the active π/π* bonds on βα/ββ involved in the cycloadditions. The participation of lone pairs on the oxygen atoms was also checked, and they were found to be well-localized with natural orbital occupation numbers (NOON) near 2.00. **TS5^{c}** and **TS6^{c}** each had very little diradical character with the CI wavefunctions dominated by a single determinant (> 79% in each case). The natural orbitals (NO), NOON, and CI expansions are shown in Figures S99-S100.

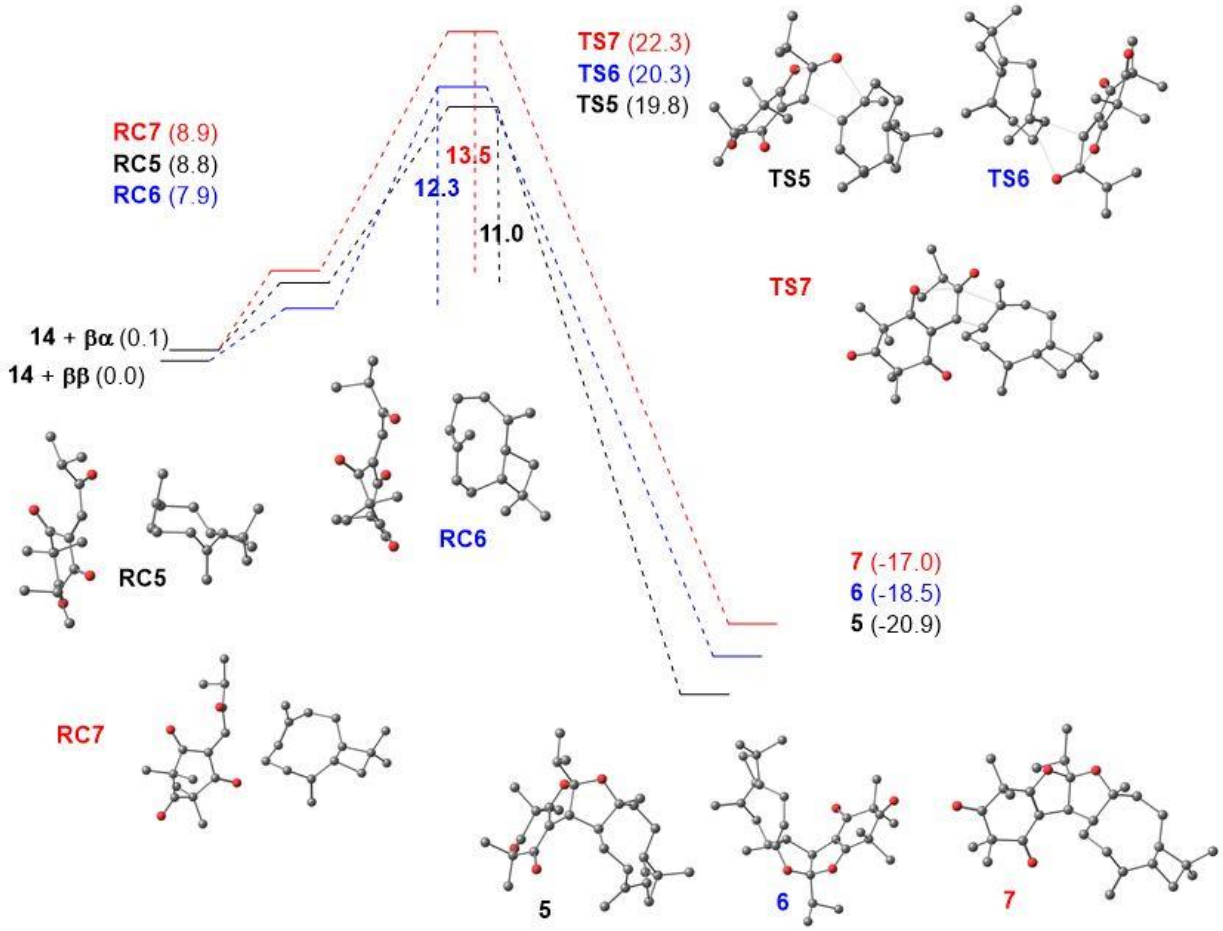


Figure S95. Free energy profile (kcal/mol) for reaction paths connecting **14** + **βα**/**ββ** with

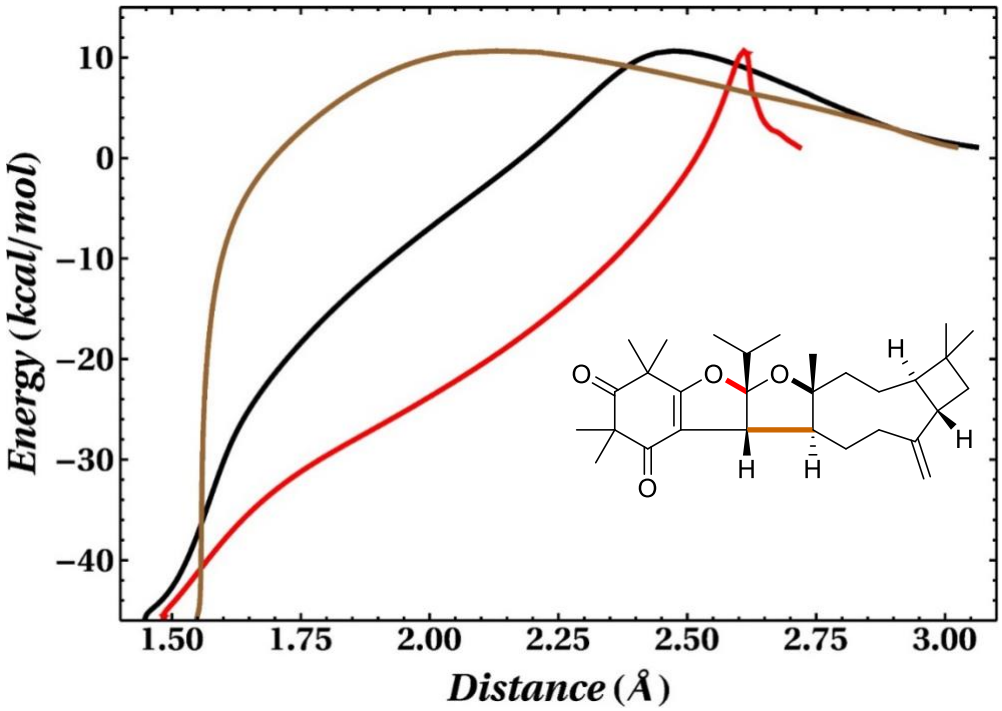


Figure S96. Potential energy surface for the three active bonds in the reaction path for the formation of **5** from **14** + **βα**.

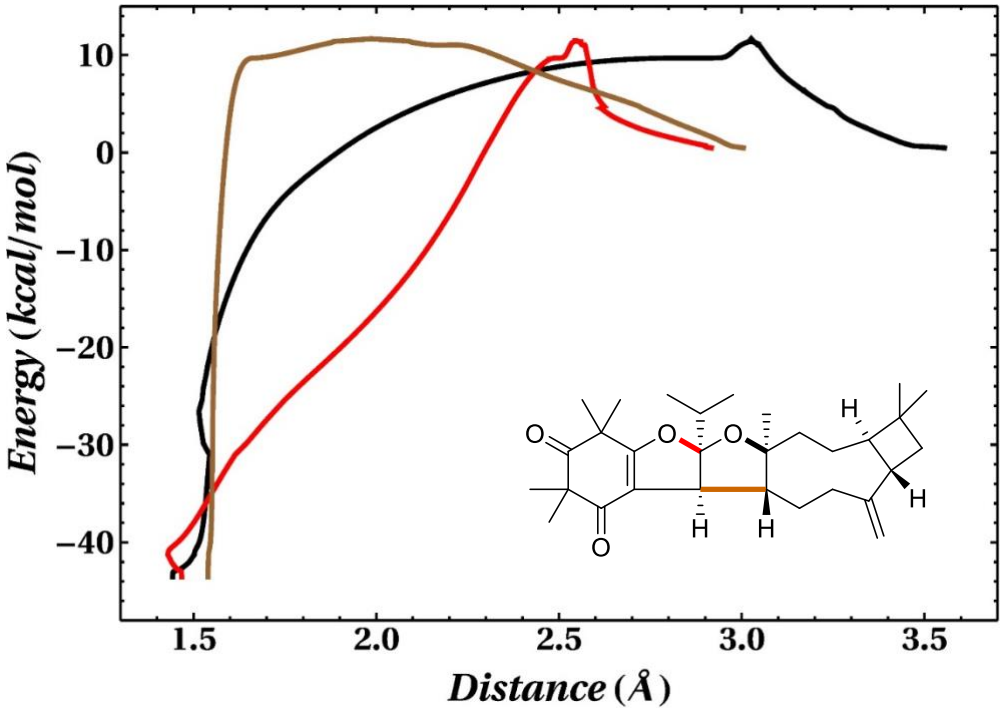


Figure S97. Potential energy surface for the three active bonds in the reaction path for the formation of **6** from **14** + **ββ**.

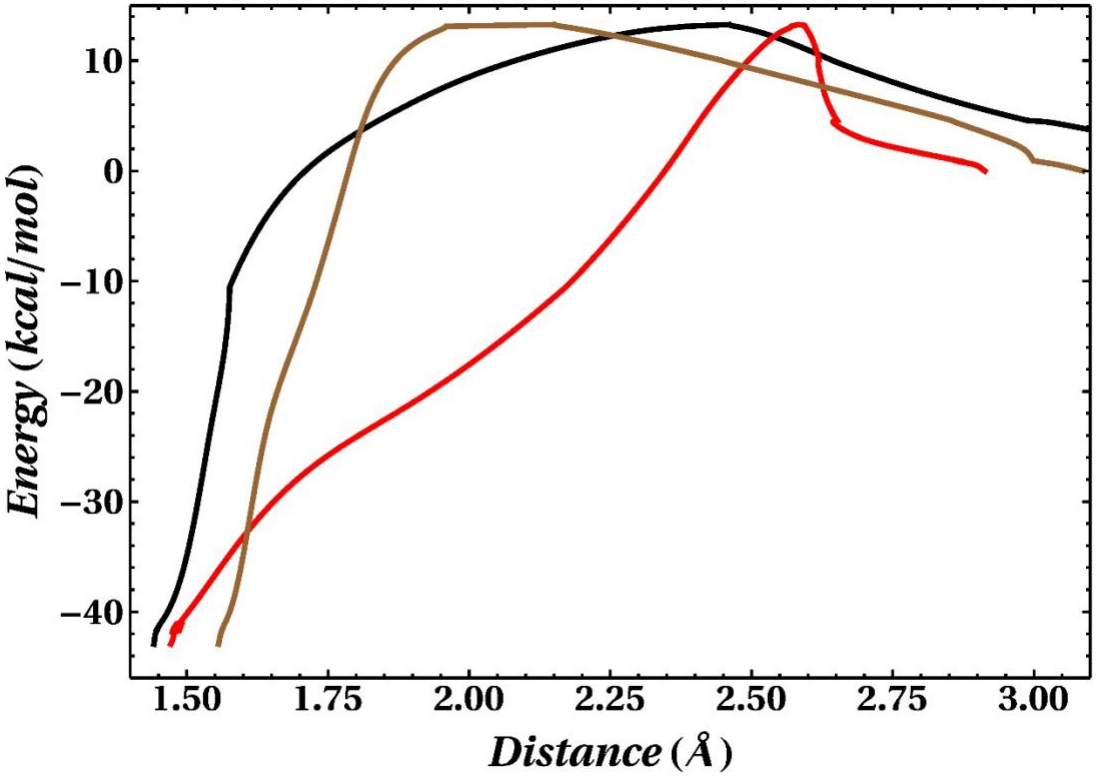


Figure S98. Potential energy surface for the three active bonds in the reaction path for the formation of **7** from **14** + **βα**.

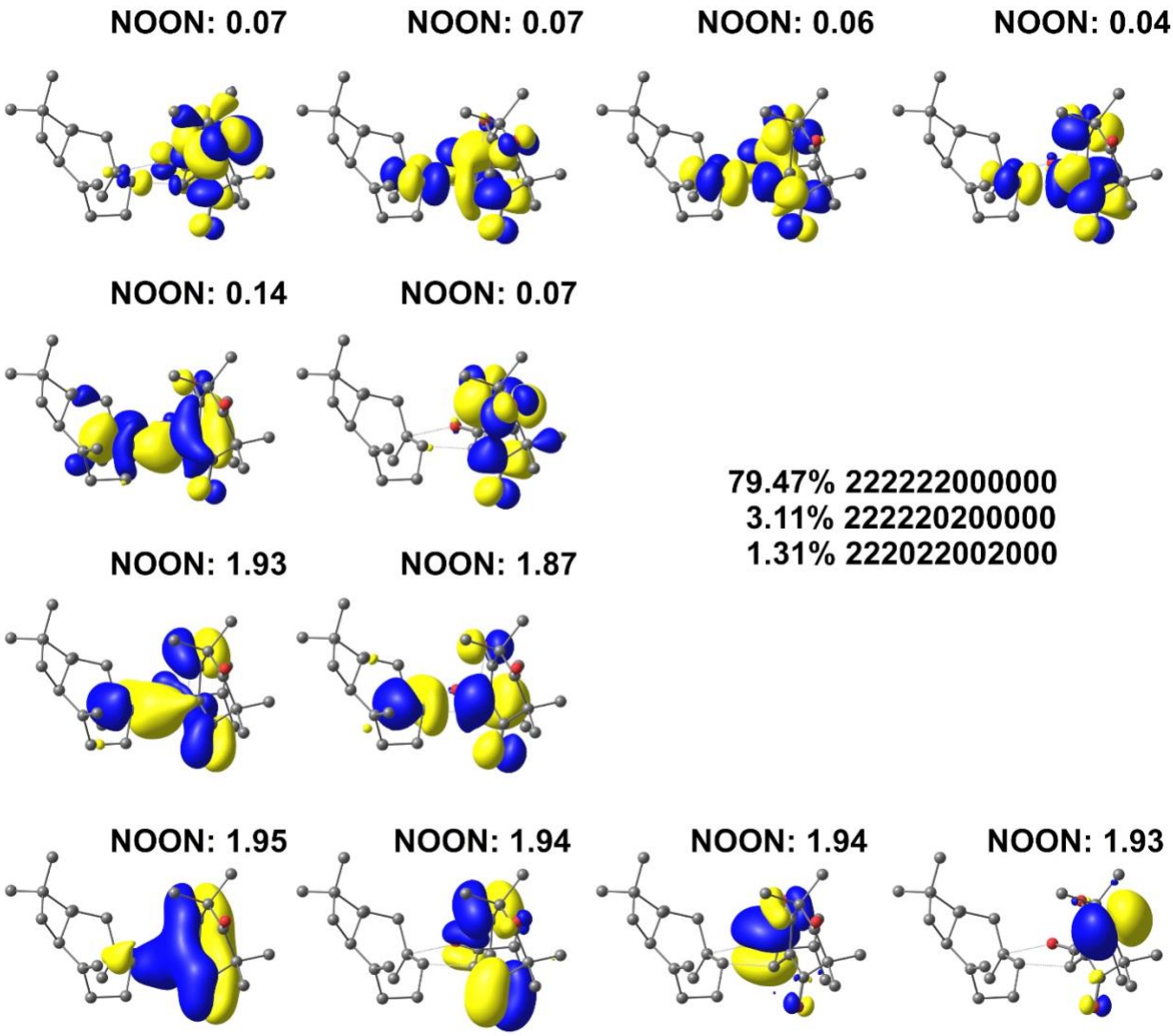


Figure S99. Active space for **TS5**[c] with natural orbital occupation numbers (NOON) and leading CI coefficients for the wavefunction.

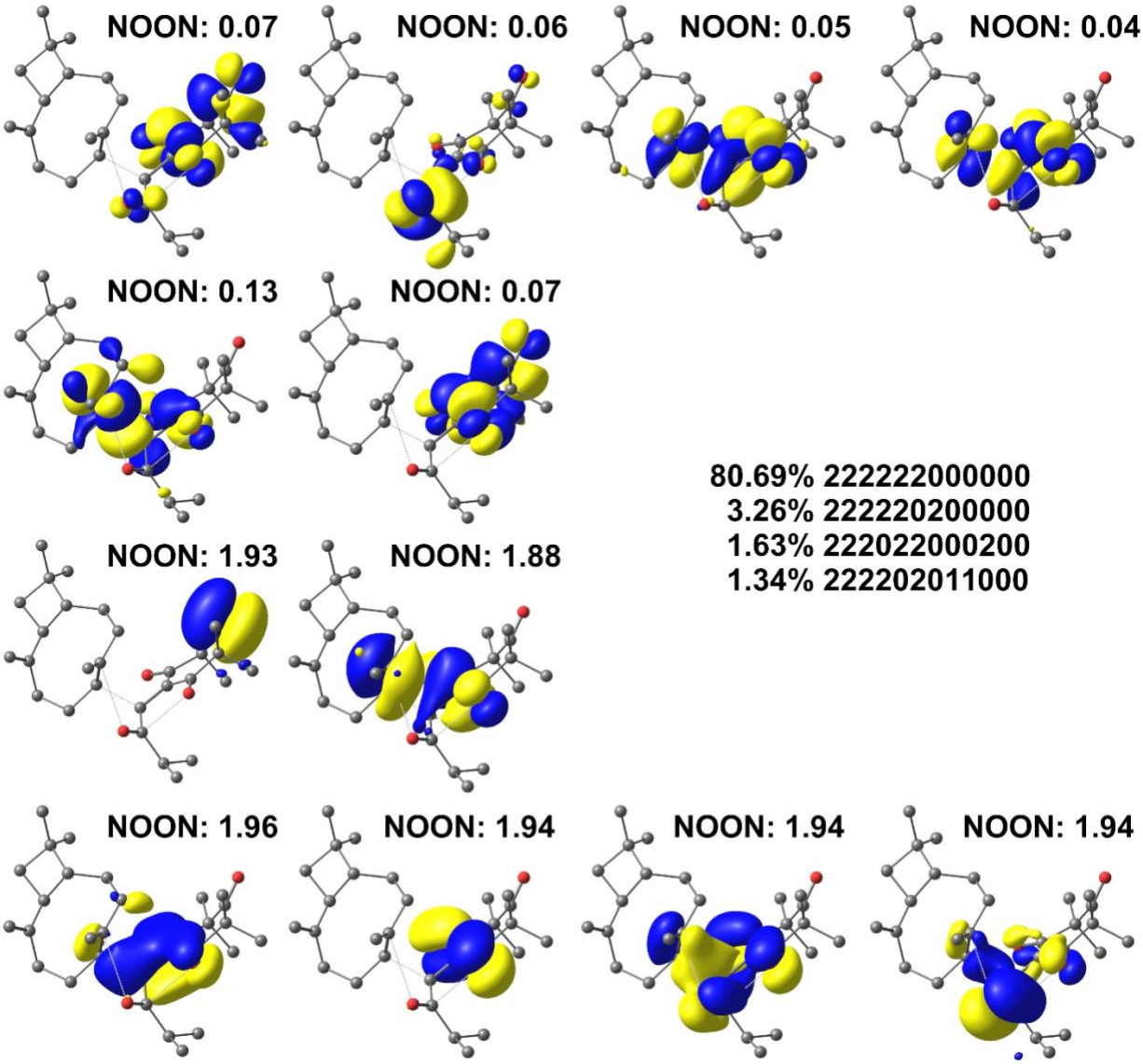


Figure S100. Active space for **TS6^{c}** with natural orbital occupation numbers (NOON) and leading CI coefficients for the wavefunction.

Table S5. Absolute and relative (kcal/mol) energies for examined species.

	Method	E (a.u.)	ΔE[iv]	ZPE[v]	G (a.u)	ΔG[vi]
βα	**PBEh-3c**	-584.7185033	N/A	241.45	-584.398844	N/A
	OO-SCS-MP2 DEF2-TZVP	-584.913384			-584.5937246	
ββ	**PBEh-3c**	-584.7188042	N/A	241.39	-584.3987334	N/A
	OO-SCS-MP2 DEF2-TZVP	-584.9134264			-584.5933556	
14	**PBEh-3c**	-882.64065	N/A	225.18	-882.3604277	N/A
	OO-SCS-MP2 DEF2-TZVP	-883.1478385			-882.8676162	
RC1[i]	**PBEh-3c**	-1467.369302	-6.2	468.65	-1466.742585	9.9
	OO-SCS-MP2 DEF2-TZVP	-1468.072792	-7.2		-1467.446075	8.8
TS1[c]	**PBEh-3c**	-1467.352305	4.5	468.17	-1466.721371	23.9
	OO-SCS-MP2 DEF2-TZVP	-1468.060699	0.4		-1467.429765	19.8
1	**PBEh-3c**	-1467.445284	-53.9	471.32	-1466.804077	-28.0
	OO-SCS-MP2 DEF2-TZVP	-1468.135844	-46.8		-1467.494638	-20.9
RC6[ii]	**PBEh-3c**	-1467.370454	-6.9	468.61	-1466.743817	9.8
	OO-SCS-MP2 DEF2-TZVP	-1468.075249	-8.8		-1467.448612	7.9
TS6[c]	**PBEh-3c**	-1467.351856	4.8	468.07	-1466.719385	25.1
	OO-SCS-MP2 DEF2-TZVP	-1468.06147	-0.1		-1467.428999	20.3
6	**PBEh-3c**	-1467.439874	-50.5	471.53	-1466.797925	-24.1
	OO-SCS-MP2 DEF2-TZVP	-1468.13267	-44.8		-1467.493894	-18.5
RC7[iii]	**PBEh-3c**	-1467.37012	-6.9	468.70	-1466.743657	9.9
	OO-SCS-MP2 DEF2-TZVP	-1468.07335	-7.6		-1467.446888	8.9
TS7[c]	**PBEh-3c**	-1467.348619	6.8	468.25	-1466.715959	27.3
	OO-SCS-MP2 DEF2-TZVP	-1468.058138	2.0		-1467.425478	22.3
7	**PBEh-3c**	-1467.438529	-49.6	471.41	-1466.796722	-23.4
	OO-SCS-MP2 DEF2-TZVP	-1468.130183	-43.2		-1467.488376	-17.0
RC10	**PBEh-3c**	-1467.372468	-8.2	468.87	-1466.744685	9.3
	OO-SCS-MP2 DEF2-TZVP	-1468.078095	-10.6		-1467.450312	6.9
TS10	**PBEh-3c**	-1467.355017	2.8	468.08	-1466.722835	23.0
	OO-SCS-MP2 DEF2-TZVP	-1468.064148	-1.8		-1467.431966	18.4
10	**PBEh-3c**	-1467.419208	-37.5	471.60	-1466.778357	-11.9
	OO-SCS-MP2 DEF2-TZVP	-1468.115670	-34.1		-1467.474820	-8.5

i. (**14**+**βα**) reaction complex for formation of **5**. Coordinates in Table S6.
ii. (**14**+**ββ**) reaction complex for formation of **6**. Coordinates in Table S9.
iii. (**14**+**βα**) reaction complex for formation of **7**. Coordinates in Table S12.
iv. E is electronic energy, $\Delta E\left(^{kcal}/_{mol}\right) = E(X) - E(\mathbf{9}) - E(\beta\beta)$
v. Includes thermal (333.15 K) and non-thermal contributions
vi. $\Delta G\left(^{kcal}/_{mol}\right) = G(X) - G(\mathbf{9}) - G(\beta\beta)$.

Table S6. Coordinates for equilibrium geometry of **RC5**.

C	1.434039000	-0.645478000	2.766122000
C	0.100741000	-0.278780000	2.188633000
C	-0.804763000	-1.167716000	1.783507000
C	-0.570106000	-2.633272000	1.588548000
C	0.316253000	-2.817551000	0.341186000
C	-0.074651000	-1.871401000	-0.778257000
C	0.757226000	-0.629562000	-1.003061000
C	0.941425000	-0.146512000	-2.456448000
C	0.823103000	1.317682000	-1.994418000
C	2.197490000	1.959416000	-1.848778000
C	-0.090331000	2.213070000	-2.811127000
C	0.221112000	0.800376000	-0.654743000
C	0.625475000	1.556070000	0.605075000
C	-0.118186000	1.171726000	1.889924000
C	-1.139598000	-2.155454000	-1.524279000
H	2.248215000	-0.432188000	2.068014000
H	1.632674000	-0.058547000	3.665152000
H	1.504121000	-1.699660000	3.032170000
H	-1.731859000	-0.786657000	1.367567000
H	-1.525425000	-3.139696000	1.445012000
H	-0.091924000	-3.108137000	2.450977000
H	0.259715000	-3.852492000	-0.004843000
H	1.358215000	-2.641026000	0.618946000
H	1.735922000	-0.770259000	-0.533045000
H	0.112619000	-0.442180000	-3.100559000
H	1.868897000	-0.438832000	-2.952890000
H	2.638721000	2.121525000	-2.834508000
H	2.147819000	2.929093000	-1.349978000
H	2.892324000	1.333790000	-1.285159000
H	-1.069719000	1.753780000	-2.957370000
H	-0.247791000	3.174739000	-2.316609000
H	0.330079000	2.417835000	-3.798413000
H	-0.872577000	0.786957000	-0.735618000
H	0.456905000	2.623144000	0.421649000
H	1.703038000	1.456842000	0.766506000
H	0.220404000	1.806375000	2.712769000
H	-1.185885000	1.367637000	1.757680000
H	-1.488230000	-1.512980000	-2.322334000
H	-1.722747000	-3.052249000	-1.353531000
O	-0.664623000	0.675566000	5.252417000
C	-2.194543000	-1.001113000	4.659788000
C	-1.161630000	-0.380528000	5.545505000
H	-1.903863000	-1.879377000	4.092873000
C	-3.430748000	-0.518857000	4.513040000

C	-0.756475000	-1.199660000	6.749503000
O	-3.529012000	0.825461000	6.438096000
C	-0.147588000	-0.330459000	7.838337000
C	0.211579000	-2.298278000	6.292137000
C	-3.888572000	0.654710000	5.299094000
C	-4.369168000	-1.138875000	3.542237000
H	-1.661304000	-1.681822000	7.134907000
H	0.764125000	0.156940000	7.495020000
H	0.102513000	-0.939916000	8.707029000
H	-0.842411000	0.444524000	8.159200000
H	1.126894000	-1.865367000	5.886670000
H	-0.219903000	-2.948509000	5.529612000
H	0.486488000	-2.929068000	7.137288000
C	-4.750087000	1.650290000	4.548745000
C	-5.773912000	-0.547781000	3.506457000
C	-5.710160000	0.977499000	3.560465000
O	-4.052116000	-2.077027000	2.855170000
C	-3.758733000	2.498980000	3.722488000
C	-5.538157000	2.546693000	5.501609000
C	-6.494204000	-1.013512000	4.795373000
C	-6.546631000	-1.028748000	2.288305000
O	-6.420079000	1.653560000	2.866210000
H	-6.006951000	-0.701084000	5.719743000
H	-6.553123000	-2.101917000	4.808077000
H	-7.511408000	-0.621879000	4.807993000
H	-6.070229000	-0.722264000	1.358477000
H	-7.556763000	-0.624193000	2.293650000
H	-6.613285000	-2.115049000	2.285481000
H	-3.174198000	1.897651000	3.024711000
H	-3.058222000	3.005058000	4.386314000
H	-4.306835000	3.247878000	3.153234000
H	-6.230611000	1.973901000	6.119746000
H	-6.112861000	3.277733000	4.936190000
H	-4.862693000	3.078623000	6.168853000

Table S7. Coordinates for equilibrium geometry of **TS5**[c].

C	1.827203000	-1.658806000	2.689292000
C	0.702430000	-0.697538000	2.513798000
C	-0.582175000	-1.095226000	2.231357000
C	-0.898161000	-2.420198000	1.589708000
C	-0.438303000	-2.416944000	0.126435000
C	-0.935108000	-1.211290000	-0.644559000
C	0.069059000	-0.151083000	-1.000085000
C	-0.235898000	0.849301000	-2.126946000
C	0.530747000	1.938423000	-1.352836000

C	1.979312000	2.031855000	-1.817354000
C	-0.098266000	3.318029000	-1.306239000
C	0.343232000	1.076749000	-0.072316000
C	1.455063000	1.114807000	0.967262000
C	1.054420000	0.748091000	2.407805000
C	-2.220896000	-1.131892000	-0.979715000
H	2.387456000	-1.739461000	1.752107000
H	2.525854000	-1.312634000	3.449019000
H	1.494473000	-2.660356000	2.953492000
H	-1.239015000	-0.290343000	1.921658000
H	-1.971502000	-2.600664000	1.632870000
H	-0.429024000	-3.254931000	2.116437000
H	-0.789375000	-3.332481000	-0.356038000
H	0.653797000	-2.453806000	0.090499000
H	1.025079000	-0.644564000	-1.209307000
H	-1.298105000	1.089761000	-2.192583000
H	0.116226000	0.590647000	-3.126987000
H	2.023585000	2.463747000	-2.819097000
H	2.577469000	2.669193000	-1.163398000
H	2.469282000	1.057613000	-1.864933000
H	-1.146799000	3.266510000	-1.007418000
H	0.417213000	3.964608000	-0.591857000
H	-0.054715000	3.808909000	-2.280937000
H	-0.605642000	1.369670000	0.393765000
H	1.837066000	2.139907000	1.010428000
H	2.302246000	0.503113000	0.641637000
H	1.880270000	0.991780000	3.077890000
H	0.204274000	1.362905000	2.708069000
H	-2.636988000	-0.298402000	-1.528451000
H	-2.918622000	-1.918303000	-0.717487000
O	0.483231000	-0.361185000	4.954292000
C	-1.566015000	-1.313630000	4.107977000
C	-0.672543000	-0.641052000	5.127354000
H	-1.465740000	-2.398916000	4.131554000
C	-2.859990000	-0.853575000	3.877317000
C	-1.291522000	-0.578181000	6.520941000
O	-2.180429000	1.325427000	4.308718000
C	-0.641514000	0.505849000	7.366178000
C	-1.149887000	-1.960461000	7.169302000
C	-3.058148000	0.577097000	3.899711000
C	-3.945167000	-1.782797000	3.615968000
H	-2.357520000	-0.367895000	6.417724000
H	0.417131000	0.308742000	7.529878000
H	-1.128723000	0.554142000	8.340794000
H	-0.737483000	1.481692000	6.892807000
H	-0.101953000	-2.251267000	7.254052000

H	-1.677654000	-2.736414000	6.613209000
H	-1.569517000	-1.941060000	8.175208000
C	-4.305695000	1.163516000	3.253697000
C	-5.359328000	-1.202924000	3.726673000
C	-5.430347000	0.150153000	3.034702000
O	-3.779190000	-2.970812000	3.421400000
C	-3.850790000	1.674810000	1.872240000
C	-4.851814000	2.336582000	4.075743000
C	-5.640207000	-0.973176000	5.229514000
C	-6.396591000	-2.163274000	3.162926000
O	-6.371989000	0.448791000	2.346621000
H	-4.935641000	-0.289046000	5.702904000
H	-5.581746000	-1.924109000	5.760002000
H	-6.645350000	-0.573095000	5.367014000
H	-6.238653000	-2.355625000	2.102845000
H	-7.399152000	-1.756232000	3.280918000
H	-6.349788000	-3.117786000	3.683262000
H	-3.436827000	0.872934000	1.255735000
H	-3.084403000	2.439596000	1.994884000
H	-4.693969000	2.107798000	1.337062000
H	-5.189896000	2.023952000	5.064666000
H	-5.695704000	2.792816000	3.560330000
H	-4.077878000	3.089701000	4.211321000

Table S8. Coordinates for equilibrium geometry of **5**.

C	1.890377000	-1.643747000	2.752187000
C	0.889107000	-0.497965000	2.782945000
C	-0.542856000	-0.846225000	2.271216000
C	-0.765695000	-2.189202000	1.581457000
C	-0.227484000	-2.293139000	0.154906000
C	-0.763734000	-1.230723000	-0.780791000
C	0.246348000	-0.248655000	-1.276682000
C	-0.080808000	0.816711000	-2.331020000
C	0.887256000	1.782561000	-1.611731000
C	2.288068000	1.717139000	-2.206711000
C	0.441769000	3.226049000	-1.472037000
C	0.708183000	0.901302000	-0.342898000
C	1.853205000	0.738579000	0.652369000
C	1.476756000	0.765307000	2.136746000
C	-2.051567000	-1.183516000	-1.106821000
H	2.132344000	-1.953949000	1.738102000
H	2.820953000	-1.335460000	3.230709000
H	1.516748000	-2.516504000	3.287832000
H	-0.848053000	-0.074653000	1.562245000
H	-1.845754000	-2.346883000	1.544508000

H	-0.362067000	-3.006398000	2.186387000
H	-0.485613000	-3.281886000	-0.233301000
H	0.864227000	-2.256624000	0.154496000
H	1.134184000	-0.806446000	-1.598897000
H	-1.111829000	1.168598000	-2.254147000
H	0.123005000	0.571151000	-3.374521000
H	2.294859000	2.160527000	-3.204394000
H	3.010164000	2.270359000	-1.602942000
H	2.657866000	0.694964000	-2.303726000
H	-0.573748000	3.292183000	-1.076936000
H	1.097655000	3.777836000	-0.794031000
H	0.456521000	3.743748000	-2.433648000
H	-0.179852000	1.282525000	0.175415000
H	2.545496000	1.573195000	0.507021000
H	2.441081000	-0.153024000	0.414436000
H	2.374210000	1.015885000	2.709659000
H	0.781147000	1.594639000	2.302055000
H	-2.451763000	-0.431866000	-1.773700000
H	-2.766179000	-1.893338000	-0.709620000
O	0.733363000	-0.184448000	4.183482000
C	-1.453099000	-0.702869000	3.510055000
C	-0.561551000	-0.047161000	4.569871000
H	-1.832401000	-1.673872000	3.834936000
C	-2.532051000	0.314091000	3.331663000
C	-0.748986000	-0.511813000	6.014545000
O	-0.954227000	1.374188000	4.522850000
C	0.020206000	0.355959000	7.008069000
C	-0.349657000	-1.975672000	6.179663000
C	-2.114547000	1.464119000	3.885958000
C	-3.766274000	0.176306000	2.608698000
H	-1.820482000	-0.422660000	6.231437000
H	1.093662000	0.309602000	6.822662000
H	-0.153983000	-0.000142000	8.024032000
H	-0.284316000	1.400249000	6.969838000
H	0.720722000	-2.111433000	6.026072000
H	-0.874707000	-2.639258000	5.491563000
H	-0.584508000	-2.314020000	7.189020000
C	-2.760198000	2.800502000	3.783101000
C	-4.742537000	1.352763000	2.721636000
C	-4.046550000	2.698439000	2.943262000
O	-4.064294000	-0.831509000	2.001292000
C	-1.787352000	3.770322000	3.092122000
C	-3.118719000	3.347753000	5.175578000
C	-5.606356000	1.078447000	3.973848000
C	-5.646343000	1.421881000	1.494678000
O	-4.528777000	3.710874000	2.508357000

H	-5.009294000	0.960974000	4.878216000
H	-6.170686000	0.157426000	3.827345000
H	-6.317421000	1.889992000	4.131328000
H	-5.080586000	1.637002000	0.588396000
H	-6.399364000	2.198455000	1.610874000
H	-6.151258000	0.469099000	1.351695000
H	-1.498697000	3.411009000	2.102951000
H	-0.882319000	3.888110000	3.686234000
H	-2.252354000	4.746541000	2.973996000
H	-3.787356000	2.683007000	5.722043000
H	-3.607161000	4.316396000	5.077277000
H	-2.216256000	3.479786000	5.771667000

Table S9. Coordinates for equilibrium geometry of **RC6**.

C	-1.185038000	1.423438000	2.420184000
C	-0.220084000	0.290920000	2.263565000
C	-0.556282000	-0.999589000	2.239192000
C	-1.930580000	-1.553419000	2.067557000
C	-2.105895000	-1.968022000	0.588937000
C	-1.547732000	-0.935598000	-0.365248000
C	-0.096896000	-1.058549000	-0.762756000
C	0.282124000	-0.917698000	-2.251546000
C	1.601690000	-0.235218000	-1.837006000
C	2.747261000	-1.237726000	-1.766252000
C	2.019614000	0.986456000	-2.633286000
C	0.947898000	0.054027000	-0.456657000
C	1.822871000	0.005801000	0.790087000
C	1.211499000	0.698033000	2.010268000
C	-2.324334000	0.039113000	-0.830423000
H	-0.852734000	2.091475000	3.218201000
H	-1.232096000	2.015740000	1.502774000
H	-2.196529000	1.108697000	2.663509000
H	0.243935000	-1.728542000	2.130411000
H	-2.693304000	-0.817604000	2.322327000
H	-2.105246000	-2.424916000	2.706657000
H	-3.165510000	-2.139940000	0.387577000
H	-1.600787000	-2.923880000	0.423014000
H	0.292608000	-2.009201000	-0.386044000
H	-0.385086000	-0.228597000	-2.772997000
H	0.347917000	-1.836338000	-2.837923000
H	3.633807000	-0.807587000	-1.296394000
H	2.484124000	-2.137096000	-1.206631000
H	3.032984000	-1.554729000	-2.771366000
H	1.200707000	1.702939000	-2.720825000
H	2.858706000	1.500339000	-2.157966000

H	2.332214000	0.716221000	-3.644453000
H	0.445689000	1.028129000	-0.514074000
H	2.779114000	0.493449000	0.571394000
H	2.071607000	-1.031525000	1.031368000
H	1.839305000	0.513276000	2.888608000
H	1.249076000	1.780016000	1.854915000
H	-1.954964000	0.804653000	-1.502037000
H	-3.367987000	0.115505000	-0.551825000
O	-1.082077000	0.687329000	5.874467000
C	0.254955000	-1.159777000	5.332242000
C	-0.937325000	-0.505430000	5.951195000
C	1.519179000	-0.787447000	5.545022000
H	0.060515000	-1.959721000	4.625608000
C	-1.927466000	-1.439482000	6.606837000
O	1.398864000	0.215547000	7.669020000
C	1.884105000	0.231641000	6.566283000
C	2.859229000	1.298271000	6.108589000
C	2.607151000	-1.382750000	4.724608000
C	-3.159980000	-0.705495000	7.108056000
C	-1.227848000	-2.221125000	7.723953000
H	-2.226916000	-2.160956000	5.833929000
H	-2.901248000	0.015259000	7.883356000
H	-3.870210000	-1.414485000	7.533746000
H	-3.664222000	-0.164225000	6.308958000
H	-0.855919000	-1.547675000	8.495640000
H	-0.380166000	-2.800484000	7.356769000
H	-1.926875000	-2.917810000	8.185789000
C	3.854133000	0.764200000	5.071564000
C	3.985050000	-0.747921000	4.880309000
O	2.415988000	-2.321575000	3.992709000
O	4.548720000	1.528532000	4.457368000
C	3.638545000	1.895472000	7.282612000
C	1.996860000	2.394753000	5.452684000
C	4.875509000	-1.076632000	3.691519000
C	4.600500000	-1.337854000	6.171700000
H	4.254493000	1.153521000	7.791789000
H	2.951659000	2.313395000	8.016157000
H	4.290527000	2.691825000	6.927240000
H	1.389131000	2.011799000	4.633412000
H	2.639934000	3.182854000	5.065320000
H	1.320244000	2.822554000	6.191266000
H	4.468862000	-0.683257000	2.760308000
H	4.979442000	-2.154121000	3.581216000
H	5.867008000	-0.648936000	3.827296000
H	3.997675000	-1.179274000	7.066537000
H	5.582446000	-0.898492000	6.348809000

H	4.730098000	-2.413306000	6.051511000

Table S10. Coordinates for equilibrium geometry of **TS6[c]**.

C	-1.673365000	1.386744000	2.258192000
C	-0.515443000	0.461230000	2.304951000
C	-0.574280000	-0.904341000	2.530885000
C	-1.817301000	-1.707183000	2.251954000
C	-1.796140000	-2.213409000	0.796625000
C	-1.391187000	-1.152177000	-0.200521000
C	0.071960000	-1.048277000	-0.548605000
C	0.498934000	-0.974027000	-2.028933000
C	1.662039000	-0.040807000	-1.629089000
C	2.952808000	-0.818700000	-1.403354000
C	1.916494000	1.156389000	-2.524986000
C	0.884446000	0.255433000	-0.317543000
C	1.652783000	0.456028000	0.977634000
C	0.814996000	1.077552000	2.105453000
C	-2.301868000	-0.348997000	-0.744529000
H	-1.566706000	2.138942000	3.043529000
H	-1.649645000	1.919449000	1.304242000
H	-2.639792000	0.912367000	2.370813000
H	0.335405000	-1.440979000	2.269343000
H	-2.716144000	-1.119793000	2.425324000
H	-1.881208000	-2.570935000	2.919675000
H	-2.786719000	-2.602492000	0.552465000
H	-1.106822000	-3.058954000	0.722822000
H	0.607615000	-1.873883000	-0.070615000
H	-0.246870000	-0.456535000	-2.635808000
H	0.748439000	-1.915340000	-2.521798000
H	3.721334000	-0.199093000	-0.937193000
H	2.812260000	-1.696525000	-0.770362000
H	3.352586000	-1.169218000	-2.356841000
H	0.997006000	1.711984000	-2.718582000
H	2.631110000	1.846665000	-2.070409000
H	2.326940000	0.850630000	-3.489712000
H	0.230061000	1.118123000	-0.497958000
H	2.499899000	1.125265000	0.800216000
H	2.087004000	-0.490651000	1.306885000
H	1.368620000	0.947834000	3.053004000
H	0.710403000	2.152513000	1.945324000
H	-2.039347000	0.427566000	-1.453022000
H	-3.353987000	-0.436321000	-0.503631000
O	-2.197155000	0.012029000	4.780188000
C	-0.099131000	-1.091702000	4.450168000

C	-1.301491000	-0.639270000	5.248347000
C	1.196872000	-0.616876000	4.758752000
H	-0.117763000	-2.170293000	4.288197000
C	-1.460958000	-1.281623000	6.631834000
O	0.334563000	1.177980000	5.950464000
C	1.322467000	0.599204000	5.517397000
C	2.697825000	1.210003000	5.775447000
C	2.325047000	-1.402571000	4.312958000
C	-2.237582000	-0.357901000	7.564451000
C	-0.207085000	-1.820848000	7.311795000
H	-2.099265000	-2.150703000	6.412085000
H	-1.651546000	0.531224000	7.794297000
H	-2.457961000	-0.872489000	8.500396000
H	-3.179617000	-0.038021000	7.125828000
H	0.463781000	-1.017225000	7.613253000
H	0.353911000	-2.519548000	6.691946000
H	-0.496947000	-2.356719000	8.216479000
C	3.851425000	0.427734000	5.150361000
C	3.705200000	-1.064718000	4.872614000
O	2.192215000	-2.356122000	3.560431000
O	4.890481000	0.989653000	4.913463000
C	2.929426000	1.289728000	7.296814000
C	2.699028000	2.642043000	5.220308000
C	4.808423000	-1.540192000	3.933027000
C	3.818920000	-1.830832000	6.210225000
H	2.898881000	0.316077000	7.784603000
H	2.157088000	1.911286000	7.747390000
H	3.899810000	1.740629000	7.503646000
H	2.572536000	2.659826000	4.136774000
H	3.639150000	3.138676000	5.450134000
H	1.884877000	3.210606000	5.664987000
H	4.776379000	-1.021985000	2.974720000
H	4.702785000	-2.605140000	3.739271000
H	5.789083000	-1.364498000	4.370754000
H	2.991795000	-1.625901000	6.889051000
H	4.751538000	-1.581439000	6.717506000
H	3.819892000	-2.902103000	6.008299000

Table S11. Coordinates for equilibrium geometry of **6**.

C	-2.550653000	0.189692000	1.514480000
C	-1.301512000	0.431341000	2.349136000
C	-0.325914000	-0.767702000	2.502701000
C	-0.845380000	-2.155302000	2.093126000
C	-0.264529000	-2.657946000	0.765858000
C	-0.487794000	-1.766213000	-0.432227000

C	0.514756000	-0.671115000	-0.691326000
C	0.911203000	-0.340712000	-2.142097000
C	1.066009000	1.141010000	-1.748524000
C	2.512415000	1.472532000	-1.399966000
C	0.509150000	2.168935000	-2.715112000
C	0.177761000	0.841134000	-0.506449000
C	0.497830000	1.582984000	0.783308000
C	-0.589642000	1.711599000	1.852196000
C	-1.524248000	-1.978873000	-1.240226000
H	-3.163738000	1.091706000	1.508372000
H	-2.307208000	-0.060576000	0.485269000
H	-3.163524000	-0.615183000	1.917086000
H	0.563905000	-0.585483000	1.906665000
H	-1.934001000	-2.190514000	2.050439000
H	-0.559921000	-2.883842000	2.855970000
H	-0.687990000	-3.644047000	0.562428000
H	0.810857000	-2.806093000	0.905499000
H	1.423554000	-0.890423000	-0.121370000
H	0.083284000	-0.487719000	-2.837834000
H	1.786654000	-0.855319000	-2.542272000
H	2.606619000	2.463368000	-0.951526000
H	2.954352000	0.754838000	-0.706466000
H	3.124959000	1.466649000	-2.303781000
H	-0.515270000	1.928359000	-3.005292000
H	0.500858000	3.166880000	-2.269823000
H	1.107604000	2.223670000	-3.627194000
H	-0.866770000	1.009934000	-0.792593000
H	0.767245000	2.610271000	0.514231000
H	1.406991000	1.163751000	1.225595000
H	-0.135956000	2.222340000	2.702595000
H	-1.358171000	2.399976000	1.488027000
H	-1.720256000	-1.368759000	-2.112905000
H	-2.229987000	-2.778833000	-1.053905000
O	-1.804196000	0.659025000	3.681337000
C	0.097301000	-0.683680000	3.980036000
C	-0.954266000	0.220899000	4.658227000
C	1.364926000	0.063789000	4.233157000
H	0.132633000	-1.680135000	4.427929000
C	-1.740313000	-0.388862000	5.815858000
O	-0.195536000	1.356843000	5.194894000
C	1.088363000	1.187867000	4.913534000
C	2.045180000	2.247059000	5.334942000
C	2.686349000	-0.316981000	3.816123000
C	-2.848312000	0.532602000	6.317378000
C	-0.831379000	-0.813871000	6.965275000
H	-2.205601000	-1.290492000	5.399753000

H	-2.439801000	1.454672000	6.732569000
H	-3.412735000	0.038974000	7.109443000
H	-3.547289000	0.797848000	5.526772000
H	-0.404990000	0.048714000	7.478484000
H	-0.007825000	-1.451396000	6.639936000
H	-1.402041000	-1.379048000	7.702458000
C	3.453762000	1.924189000	4.805070000
C	3.844979000	0.502336000	4.390965000
O	2.892594000	-1.274874000	3.097556000
O	4.270395000	2.806757000	4.775270000
C	2.102500000	2.326055000	6.872217000
C	1.597280000	3.606561000	4.777899000
C	5.010550000	0.545819000	3.406006000
C	4.291124000	-0.234245000	5.674503000
H	2.378848000	1.374517000	7.325834000
H	1.130244000	2.617171000	7.268861000
H	2.832520000	3.075192000	7.176467000
H	1.555067000	3.600077000	3.688050000
H	2.295304000	4.383489000	5.081291000
H	0.608199000	3.864504000	5.152889000
H	4.747090000	1.081185000	2.493435000
H	5.298116000	-0.465445000	3.127203000
H	5.872549000	1.042204000	3.846275000
H	3.479624000	-0.353500000	6.392864000
H	5.105161000	0.304924000	6.159678000
H	4.650575000	-1.229199000	5.412249000

Table S12. Coordinates for equilibrium geometry of **RC7**.

C	-1.495924524	1.935454395	1.846441962
C	-0.960324580	0.539971338	1.740754118
C	0.303549336	0.207566859	2.002139756
C	1.434514950	1.168611607	2.190868359
C	1.756201352	1.809213295	0.827350604
C	1.701592146	0.797373913	-0.301392986
C	0.480181347	0.766449831	-1.191128203
C	0.688612155	0.421489128	-2.680054867
C	-0.609800568	-0.406555746	-2.680011531
C	-1.768448129	0.390914491	-3.266234345
C	-0.536900055	-1.778216707	-3.325226724
C	-0.560552461	-0.402104657	-1.123438499
C	-1.899381890	-0.281778168	-0.406248426
C	-1.866391761	-0.476998779	1.115321563
C	2.721752903	-0.040263467	-0.470933495
H	-2.435131783	1.949400419	2.404202506
H	-1.716236137	2.355772299	0.861355666
H	-0.812516517	2.613587477	2.352357857
H	0.592604144	-0.832698135	1.882087280
H	2.309992526	0.625917593	2.552541673
H	1.212246998	1.940479860	2.932077322
H	2.741921740	2.279662084	0.862277610
H	1.039415694	2.610836386	0.634293058
H	-0.045971130	1.722380535	-1.102825917
H	1.571082915	-0.197835860	-2.843875753
H	0.741194016	1.264423334	-3.371936594
H	-2.729235181	-0.103176171	-3.109839879
H	-1.840519804	1.394683244	-2.842987286
H	-1.632762405	0.506310573	-4.343658679
H	0.309418224	-2.352096887	-2.943280969
H	-1.443019485	-2.356973775	-3.129727534
H	-0.424115849	-1.703524523	-4.409225702
H	-0.042600249	-1.305190238	-0.778685776
H	-2.574280833	-1.033544571	-0.830356320
H	-2.358122797	0.683999559	-0.636949307
H	-2.887399239	-0.403524387	1.504257725
H	-1.510725880	-1.486941038	1.337996023
H	2.737000922	-0.803226544	-1.238226208
H	3.591989717	-0.004375110	0.173121859
O	-0.619417943	1.740457566	5.197542871
C	0.234821861	-0.433205475	5.020748174
C	-0.840612478	0.563526434	5.319466649
C	1.435291299	-0.464706727	5.601770568
H	0.020766703	-1.138482843	4.224234352

C	-2.183384700	-0.017175716	5.695037615
O	0.980597077	0.722323732	7.587547688
C	1.786560265	0.415238895	6.747035157
C	3.221675366	0.906879405	6.753414251
C	2.490170477	-1.378042261	5.081691088
C	-3.251330912	1.053855310	5.841607180
C	-2.044915656	-0.866155577	6.963041663
H	-2.460607839	-0.691844346	4.872992338
H	-2.996070831	1.761133981	6.630145383
H	-4.206964460	0.596160686	6.098114424
H	-3.389897452	1.618947614	4.921041300
H	-1.739150019	-0.253387566	7.810144610
H	-1.309346901	-1.663125792	6.849624915
H	-2.999723245	-1.332398078	7.204463678
C	4.197839474	-0.262195941	6.603957373
C	3.707941327	-1.571142729	5.973452462
O	2.359754917	-1.966943190	4.037140407
O	5.332554281	-0.160399678	6.983055155
C	3.527207985	1.730710733	7.995347190
C	3.405934559	1.770202203	5.482235509
C	4.834614454	-2.275040736	5.229369537
C	3.235730892	-2.449263242	7.159394702
H	3.391457593	1.153196876	8.908869491
H	2.865906676	2.594081931	8.048963481
H	4.554745461	2.086441811	7.970841699
H	3.320136044	1.199529708	4.556678861
H	4.391838126	2.233000107	5.499856634
H	2.650682840	2.555977494	5.448305118
H	5.181240365	-1.690855341	4.377434746
H	4.499796457	-3.240048363	4.853871496
H	5.681965687	-2.438637944	5.891155497
H	2.444925855	-1.991097585	7.755692788
H	4.078243833	-2.650285786	7.820371765
H	2.860350218	-3.402605561	6.786673758

Table S13. Coordinates for equilibrium geometry of **TS7[c]**.

C	-1.167459994	2.371299897	1.838822643
C	-0.917321915	0.904031778	1.901316583
C	0.289352766	0.361354036	2.291354687
C	1.535341747	1.195576298	2.352072247
C	1.961037399	1.655479778	0.948255410
C	1.861259596	0.552412651	-0.084903718
C	0.715859529	0.595428256	-1.064302485
C	0.916444735	-0.008994061	-2.467029487
C	-0.534235834	-0.526481523	-2.453211573

C	-1.466918170	0.429884450	-3.186738063
C	-0.755313654	-1.948903907	-2.932285301
C	-0.530907002	-0.336209075	-0.909143742
C	-1.835262566	0.119965502	-0.273941835
C	-1.927747188	0.018687965	1.258875265
C	2.763574058	-0.425237092	-0.085675588
H	-2.220374836	2.602885263	1.985911875
H	-0.889538508	2.744588281	0.848034108
H	-0.586303125	2.923183700	2.573468458
H	0.473766637	-0.647520657	1.929412574
H	2.332896489	0.583071011	2.773117466
H	1.419709932	2.057356439	3.012663738
H	2.988545572	2.023455442	0.999081342
H	1.355134003	2.509252265	0.637547602
H	0.374816083	1.631828072	-1.162741265
H	1.637143276	-0.827442482	-2.466823112
H	1.196015449	0.684203103	-3.262316478
H	-2.517794090	0.178121492	-3.031491547
H	-1.327720493	1.468763586	-2.881375464
H	-1.277622015	0.383671547	-4.260976487
H	-0.072788649	-2.644584848	-2.441069274
H	-1.774585089	-2.283793785	-2.724737076
H	-0.597054337	-2.034637448	-4.009529452
H	-0.202741695	-1.272645936	-0.441799176
H	-2.640420328	-0.502240840	-0.677989333
H	-2.070790395	1.141566136	-0.585105799
H	-2.936613490	0.298651654	1.568155107
H	-1.766423707	-1.020821219	1.556759301
H	2.734929230	-1.253970328	-0.780189179
H	3.572934032	-0.444757943	0.633707454
O	-2.024468317	0.957043067	4.056816870
C	-0.059121213	-0.408478118	4.165478037
C	-1.325394669	0.215356313	4.698436570
C	1.144244912	-0.301437509	4.874926127
H	-0.254577075	-1.410502488	3.783807155
C	-1.885732155	-0.358893397	6.011056360
O	0.453973404	1.696936636	5.829272207
C	1.333954336	0.856461200	5.705693941
C	2.681339090	1.043550755	6.397065126
C	2.152637891	-1.320607419	4.694582489
C	-2.538858655	0.743114317	6.843121455
C	-0.983195749	-1.233179128	6.871654451
H	-2.689740593	-1.009548711	5.638989633
H	-1.786496148	1.422963592	7.239247534
H	-3.075230827	0.300731682	7.683186591
H	-3.249616520	1.322880362	6.259016635

H	-0.189509837	-0.661957380	7.351230308
H	-0.525859780	-2.053744113	6.320260615
H	-1.585121039	-1.674957034	7.667006735
C	3.306186778	-0.301679838	6.751615450
C	3.242483065	-1.460987889	5.755600386
O	2.105650661	-2.121204457	3.774542345
O	3.891572757	-0.445988957	7.794199280
C	2.540144454	1.918809168	7.637119486
C	3.619786213	1.745100403	5.390274875
C	4.620504320	-1.615255626	5.095467148
C	2.917105747	-2.749404380	6.531469124
H	1.893430533	1.460896947	8.385137678
H	2.109791475	2.881702021	7.370582328
H	3.510358135	2.089824210	8.099200770
H	3.747710404	1.187268593	4.463635265
H	4.603778249	1.894895109	5.835952473
H	3.211727647	2.723301611	5.134510162
H	4.911225642	-0.734501143	4.522024097
H	4.607969683	-2.465007625	4.415172212
H	5.382325083	-1.788740644	5.854737671
H	1.941228187	-2.692918066	7.017306263
H	3.664706953	-2.927554478	7.301790729
H	2.907200332	-3.597856933	5.849243300

Table S14. Coordinates for equilibrium geometry of **7**.

C	-0.497046485	2.583923573	1.880797377
C	-0.741726203	1.152658387	2.332519448
C	0.490647066	0.212193112	2.425606833
C	1.867783822	0.842772062	2.245469621
C	2.214530250	1.238202091	0.803799835
C	1.903809807	0.152218334	-0.202360091
C	0.709929537	0.351971433	-1.093195899
C	0.614517356	-0.406924358	-2.427094289
C	-0.908652253	-0.535440479	-2.236119003
C	-1.652495165	0.570424027	-2.975234135
C	-1.525637068	-1.885231245	-2.550808321
C	-0.688453332	-0.239821250	-0.723857326
C	-1.774262952	0.555849828	-0.013693458
C	-1.864841762	0.503685266	1.512271493
C	2.666412047	-0.936973171	-0.251723712
H	-1.411810103	3.164019640	2.011784632
H	-0.222986707	2.647522695	0.831052008
H	0.284394400	3.064777815	2.468116640
H	0.407553776	-0.553696998	1.654107634
H	2.605867305	0.098731565	2.544012789

H	2.012578059	1.701139572	2.908224525
H	3.283646829	1.461973803	0.772833765
H	1.716449752	2.163731525	0.517421897
H	0.594169591	1.425177384	-1.282634605
H	1.104742621	-1.380634705	-2.390112763
H	0.970070618	0.116879068	-3.316141107
H	-2.709445244	0.604722603	-2.704566958
H	-1.231869486	1.559534753	-2.784770704
H	-1.598752273	0.400132812	-4.052397638
H	-0.984127930	-2.694442208	-2.057791394
H	-2.565706691	-1.932684265	-2.218629968
H	-1.516883873	-2.086413897	-3.624367136
H	-0.533553713	-1.197628350	-0.212475809
H	-2.732364307	0.164855242	-0.373388714
H	-1.753983598	1.595999264	-0.350770644
H	-2.799271476	0.995570094	1.797761651
H	-1.968974644	-0.542211432	1.825877029
H	2.485243177	-1.752837662	-0.937821239
H	3.510233232	-1.063248480	0.415458414
O	-1.248441176	1.268503043	3.677308818
C	0.288492690	-0.506237957	3.791430022
C	-0.680445617	0.401492097	4.559028215
C	1.464485028	-0.531693308	4.714027311
H	-0.137362059	-1.499075509	3.630559523
C	-1.763101619	-0.284333517	5.395736663
O	0.189930808	1.148364935	5.481407999
C	1.326366612	0.477811910	5.592404621
C	2.335246761	0.926908468	6.591397463
C	2.595727070	-1.411373787	4.683666178
C	-2.654751465	0.724364167	6.115462804
C	-1.220649321	-1.315110430	6.380716111
H	-2.378798852	-0.819184550	4.662377137
H	-2.099951170	1.270892898	6.878674382
H	-3.473660195	0.205530638	6.615108612
H	-3.090878657	1.448082456	5.429402848
H	-0.638620069	-0.850789923	7.178418720
H	-0.596418927	-2.071602510	5.905096295
H	-2.052456502	-1.834976274	6.857450876
C	3.279585458	-0.246754066	6.896434451
C	3.593298875	-1.317765254	5.842913527
O	2.765594427	-2.227975052	3.798644692
O	3.821229748	-0.294355794	7.969419601
C	1.679390558	1.431407580	7.877368020
C	3.172848569	2.062099169	5.964027444
C	4.987187848	-1.012056826	5.268414184
C	3.625502632	-2.688302373	6.535360986

H	1.078820492	0.657963797	8.356667169
H	1.030630142	2.279977951	7.666791474
H	2.438136971	1.749285915	8.588560230
H	3.646537194	1.756349306	5.031655056
H	3.948988637	2.381452922	6.659520790
H	2.534873602	2.919892043	5.749765023
H	5.024111504	-0.051646340	4.751937244
H	5.262405538	-1.784487124	4.552027298
H	5.729813436	-0.997046056	6.065542732
H	2.653623849	-2.948016418	6.958139420
H	4.356040043	-2.694722001	7.341582344
H	3.894691048	-3.457578509	5.814080982

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