

Supporting Information

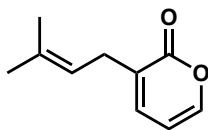
Table of Contents

1. Materials and Methods.....	2
2. Experimental Procedures & Characterization.....	3
3. Ring Expansion Reactions of Compound 3	6
4. X-ray Crystallographic Data.....	6
5. References.....	8
6. Crude ¹ H NMR of Compound 1	9
7. ¹ H and ¹³ C NMR Spectra.....	10

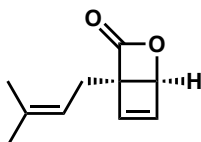
1- Materials & Methods

Unless otherwise stated, all reactions were performed in flame-dried glassware under nitrogen atmosphere using dry, deoxygenated solvents. Solvents were dried in a JC Meyer solvent system. Ethyl diazoacetate (Sigma-Aldrich), 1,8-diazabicyclo[5.4.0]undec-7-ene (TCI), and diisobutylaluminum hydride (Sigma-Aldrich) were used as purchased. Other chemicals were synthesized using published procedures.¹⁻³ Photochemistry was performed in a Rayonet RPR-200 photochemical reactor. 300nm bulbs were purchased from Rayonet (model RPR-3000A). Disposable Pyrex tubes were used for photochemistry (Fisherbrand borosilicate glass, 18x150mm). Thin layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25mm) and visualized by UV fluorescence quenching, *p*-anisaldehyde, KMnO₄, or cerium-ammonium-molybdate (CAM) staining. SiliaFlash P60 Silica gel (230–400 mesh) was used for flash chromatography. ¹H and ¹³C NMR spectra were recorded on a Bruker DRX-500 (¹H), Bruker AV-400 (¹H), and Bruker AV-500 (¹H, ¹³C). All ¹H NMR spectra are reported relative to CDCl₃ (7.26ppm). Data for ¹H NMR spectra are as follows: s = singlet, d = doublet, t = triplet, dd = doublet, ddd = doublet of doublet of doublet, qd = quartet of doublet, m = multiplet. All ¹³C NMR spectra are reported relative to CDCl₃ (77.16 ppm). IR spectra were recorded on a Perkin Elmer 100 spectrometer and are reported in terms of absorption frequency (cm⁻¹). High resolution mass spectra (HR-MS) were recorded on an Agilent 7250 Quadrupole TOF GC-MS (compound **3** and **4**), Waters LCT Premier TOF-ESI Mass Spectrometer (compound **5**), and a Thermo Scientific Q Exactive Plus Hybrid Quadrupole-Orbitrap Mass Spectrometer (compound **1**). Crystallographic data were obtained by the UCLA J.D. McCullough Laboratory of X-ray Crystallography.

2- Experimental Procedures & Characterization

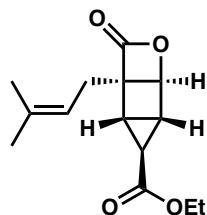


3-prenyl-2H-pyran-2-one 2. Prepared according to literature.¹ All spectra matched the reported literature.



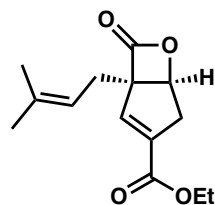
Oxabicyclo[2.2.0]hexenone 4. To a degassed solution of benzene (120 mL) in a flame-dried round bottom flask under N₂ was added prenyl pyrone **2** (750 mg, 4.57 mmol). The solution was divided into six oven-dried Pyrex tubes capped with a septum and further sparged with N₂ for 10 minutes with vigorous stirring. The tubes were then irradiated at 300nm at room temperature for 24 hours or until complete. The reaction was monitored by ¹H NMR by taking crude aliquots. Once complete, the solutions were combined and yield of product was 83% (620 mg, 3.78 mmol) by ¹H NMR. The material was carried further to the next step without any further purification or concentration due to its instability. Note: extensive removal of solvent was avoided due to reported explosions of similar photo-pyrones.⁴

¹H NMR (500 MHz, CDCl₃) δ 6.73 (dd, J = 4.2, 2.3 Hz, 1H), 6.57 (d, J = 2.5 Hz, 1H), 5.16 (d, J = 4.3, 1H), 5.17–5.11 (m, 2H), 2.62 (dd, J = 15.2, 7.5 Hz, 1H), 2.51 (dd, J = 15.3, 7.3 Hz, 1H), 1.72 (s, 3H), 1.64 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.3, 145.0, 140.2, 136.1, 117.1, 74.5, 70.9, 25.8, 24.9, 18.0; FTIR (Neat Film NaCl) 2917, 1808, 1274, 828, 734 cm⁻¹; HRMS: (MS-EI) m/z calc'd for C₁₀H₁₂O₂: 164.0832; measured 164.0835.



Housane 3. To a flame-dried flask equipped with a magnetic stir bar was added bicycle **4** (84 mg, 0.51 mmol) as a 0.03M solution in benzene (15 mL) under N₂ atmosphere. 15 mL of dry DCE was subsequently added to this, followed by Rh₂(esp)₂ (12 mg, 15.3 μmol, 0.03 equiv). To this homogeneous solution was added ethyl diazoacetate (EDA) (1.75 g, 15.4 mmol, 30 equiv) dropwise by syringe pump over 6 hours at room temperature. The green-yellow reaction solution was allowed to stir overnight, concentrated by rotary evaporation, and loaded directly onto a silica column for purification (5% → 15% ethyl acetate in hexanes on SiO₂). Further purification was often deemed necessary, which was accomplished by column chromatography eluting with DCM on SiO₂ affording 28mg (22% yield) of **3** as a white solid.

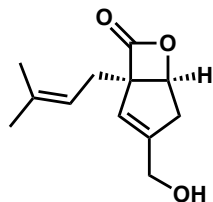
¹H NMR (500 MHz, CDCl₃) δ 5.07 (t, J = 7.5 Hz, 1H), 4.57 (d, J = 4.3 Hz, 1H), 4.19–4.13 (q, J = 7.1 Hz, 2H), 2.73 (d, J = 3.7 Hz, 1H), 2.67 (dd, J = 4.4, 3.7 Hz, 1H), 2.46 (dd, J = 15.3, 7.6 Hz, 1H), 2.25 (dd, J = 15.2, 7.4 Hz, 1H), 2.13 (s, 1H), 1.27 (t, 7.1 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.9, 169.1, 136.4, 116.5, 74.5, 69.3, 61.3, 30.0, 29.1, 29.0, 25.8, 25.2, 18.0, 14.2; FTIR (Neat Film NaCl) 2981, 2917, 1824, 1727, 1447, 1383, 1266, 1182, 1035, 909 cm⁻¹; HR-MS (MS-EI) m/z calc'd for C₁₄H₁₈O₄: 250.1205; measured 250.1195.



Vibralactone ester 5. To a flame dried schlenk flask equipped with a magnetic stir bar under N₂ atmosphere was added housane **3** (135 mg, 0.54 mmol). To this was added dry benzene (35 mL), followed by DBU (123 mg, 0.81 mmol, 1.5 equiv). The reaction flask was heated at 75 °C for 18 hours or until complete by TLC (20% ethyl acetate in hexanes on SiO₂). The slightly yellow/brown-colored reaction solution was then loaded directly onto a silica plug, washed through with DCM, and then concentrated by rotary evaporation. The crude oil was then further purified by column chromatography (20% ethyl acetate in hexanes on SiO₂) to afford 93 mg (69%) of **5** as a colorless oil.

¹H NMR (500 MHz, CDCl₃) δ 6.58 (t, J = 1.9 Hz, 1H), 5.09 (t, J = 7.4 Hz, 1H), 4.82 (d, J = 5.6 Hz, 1H), 4.22 (qd, J = 7.1, 2.5 Hz, 2H), 3.04 (dd, J = 19.3, 1.8 Hz, 1H), 2.94 (ddd, J = 19.3, 5.7, 2.3 Hz, 1H), 2.66 (dd, J = 15.1, 7.4 Hz, 1H), 2.49 (dd, J = 15.1, 7.3 Hz,

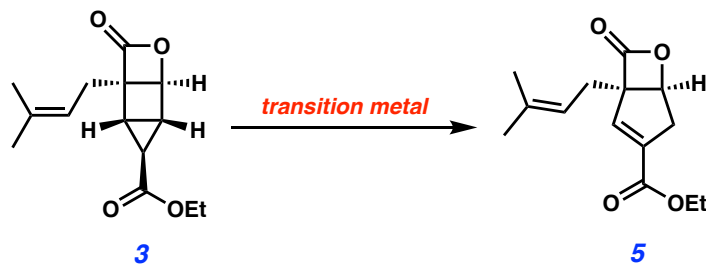
^1H 1.71 (s, 3H), 1.63 (s, 3H), 1.39 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.9, 163.8, 137.7, 137.7, 136.9, 116.6, 78.2, 76.3, 61.1, 36.8, 27.5, 25.9, 18.1, 14.3; FTIR (Neat Film NaCl) 2923, 1823, 1716, 1627; HR-MS (TOF MS-ES) $^+$ m/z calc'd for $\text{C}_{14}\text{H}_{18}\text{O}_4+\text{Na}$: 273.1103; measured: 273.1116.



(±)-vibrallactone 1. To a flame-dried flask equipped with a magnetic stir bar was added **5** as a solution in benzene (24.6 mg, 0.052 M, 1.9 mL). To this was added dry THF (7 mL) and this was cooled to -40 °C. Next, a solution of DIBAL-H in THF (2.9 mL, 0.1M, 0.285 mmol, 2.9 equiv) was added dropwise, and the reaction was allowed to stir for 1 hour. Then the reaction was warmed to 0 °C and stirred for an additional 30 minutes. The reaction flask was then warmed to room temperature and quenched with a solution of acetic acid in ethyl acetate (2.5 mL, 0.23M, 6 equiv). This solution was allowed to stir for 10 minutes, then loaded onto a short silica plug, eluting with 100% ethyl acetate. The eluent was collected and concentrated *in vacuo* and purified by flash chromatography (15% \rightarrow 30% ethyl acetate in hexanes on SiO_2) affording 6.9 mg (34% yield) of (±)-vibrallactone **1** as a colorless oil. Additionally, 7.8 mg (32%) of starting material was also recovered.

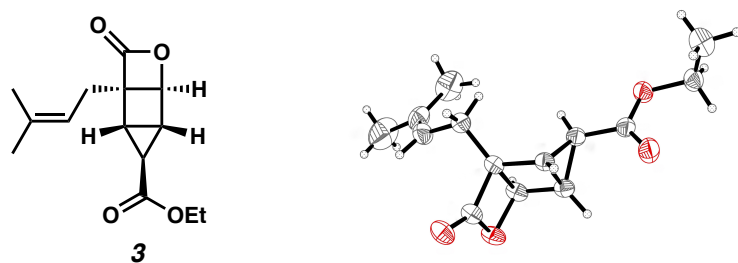
^1H NMR (500 MHz, CDCl_3) δ 5.62 (t, $J = 7.4$, 1H), 5.12 (m, 1H), 4.80 (dd, $J = 4.7$, 1.4 Hz, 1H), 4.25 (d, $J = 4.7$ Hz, 2H), 2.81–2.71 (m, 2H), 2.62 (dd, $J = 15.1$, 7.4 Hz, 1H), 2.43 (dd, $J = 15.1$, 7.4 Hz, 1H), 1.72 (s, 3H), 1.64 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.0, 146.6, 136.1, 122.7, 117.4, 78.5, 75.3, 61.5, 37.5, 27.7, 25.9, 18.1; FTIR (Neat Film NaCl): 3419, 2917, 1815, 1111, 833 cm^{-1} ; HR-MS (MS-ESI) $^+$ m/z calc'd for $\text{C}_{12}\text{H}_{16}\text{O}_3+\text{H}$: 209.1172; measured: 209.1171. Spectroscopic data are consistent with previous reports.^{5–6}

3- Ring expansion reactions of housane 3



A variety of transition metal complexes were employed to promote ring expansion of housane **3** to furnish enoate **5**. In all experiments, no reactivity was observed at low temperatures, while decomposition to unidentifiable complex products was observed at temperatures above 130 °C. Transition metal complexes that were tested include: RhCl(PPh₃)₂(CO), Rh(PPh₃)Cl, Rh₂Cl₂(cod)₂, Rh(acac)(CO)₂, RhCl₃·(H₂O)₃, [Rh(CO)₂Cl]₂, AuCl₃·(H₂O)₃, PdCl₂, Pd(NC-Ph)₂Cl₂, PtCl₂, ZnI₂, and AgBF₄.

4- X-ray crystal structure analysis of housane 3



Note: The crystallographic data have been deposited in the Cambridge Database (CCDC). The deposition number is 1867750.

Table 1. Crystal data & structure refinement

Refined formula	C ₁₄ H ₁₈ O ₄
Formula weight	250.28
Crystallization solvent	Hexanes
Crystal shape	Platelets
Crystal color	Colorless
Crystal size	0.400 x 0.050 x 0.020 mm

Data Collection

Type of diffractometer	Bruker APEX-II CCD	
Wavelength	CuK α (λ = 1.54178)	
Data collecting temperature	293(2) K	
Theta range for 5987 reflections used in lattice determination	4.05 to 68.74	
Unit cell dimensions	a = 11.867(2) b = 5.3190(10) c = 43.735(8) 2754.3(9) \approx^3	α = 90 β = 93.82(2) γ = 90
Z	8	
Crystal system	monoclinic	
Space group	I 2/a	
Calculated density	1.207 g/cm ³	
Linear absorption coefficient	0.722	
F(000)	1072	
2 θ range for data collection	2.025 to 69.712	
Completeness to theta = 69.712	0.988	
Index ranges	-14 \leq h \leq 13 -6 \leq k \leq 6 -52 \leq l \leq 53	
Data collection scan type	ω and ϕ scan	
Reflections collected	18802	
Independent reflections	2587 [R_{int} = 0.0493, R_{sigma} = 0.0286]	
Reflections > 2 σ (I)	2045	
Average of σ (I)/(net I)	0.0286	
Absorption coefficient	0.722 mm ⁻¹	
Absorption correction	Multi scan	
Max. and min. transmission	0.761 and 0.986	

Structure solution & Refinement

Primary solution method	SHELXL-2014	
Secondary solution method	SHELXL-2014	
Hydrogen placement	geom	
Refinement method	Bruker SHELXTL	
Goodness-of-fit on F ²	1.081	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0610	wR_2 = 0.1511
R indices (all data)	R_1 = 0.0752	wR_2 = 0.1598
Max shift/error	0.000	
Average shift/error	0.000	
Largest diff. peak and hole / e \AA^{-3}	0.286/-0.174	

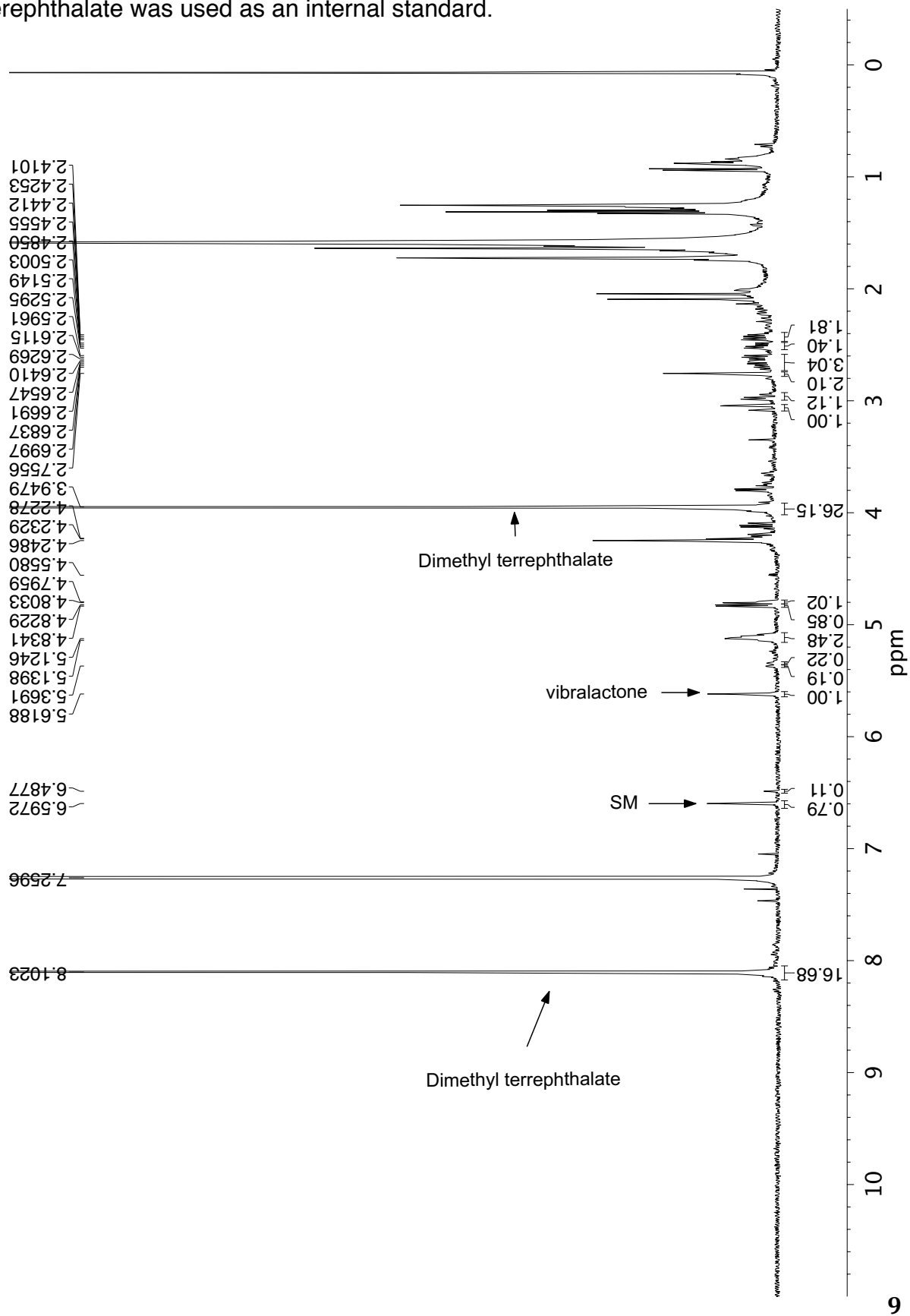
Programs used

Cell refinement	Bruker SAINT
Data collection	Bruker APEX2
Data reduction	Bruker SAINT
Structure solution	SHELXS-97 (Sheldrick 2008)
Structure refinement	SHELXL-2014/6 (Sheldrick, 2014)
Graphics	Bruker SHELXTL

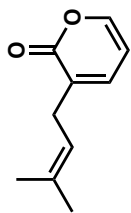
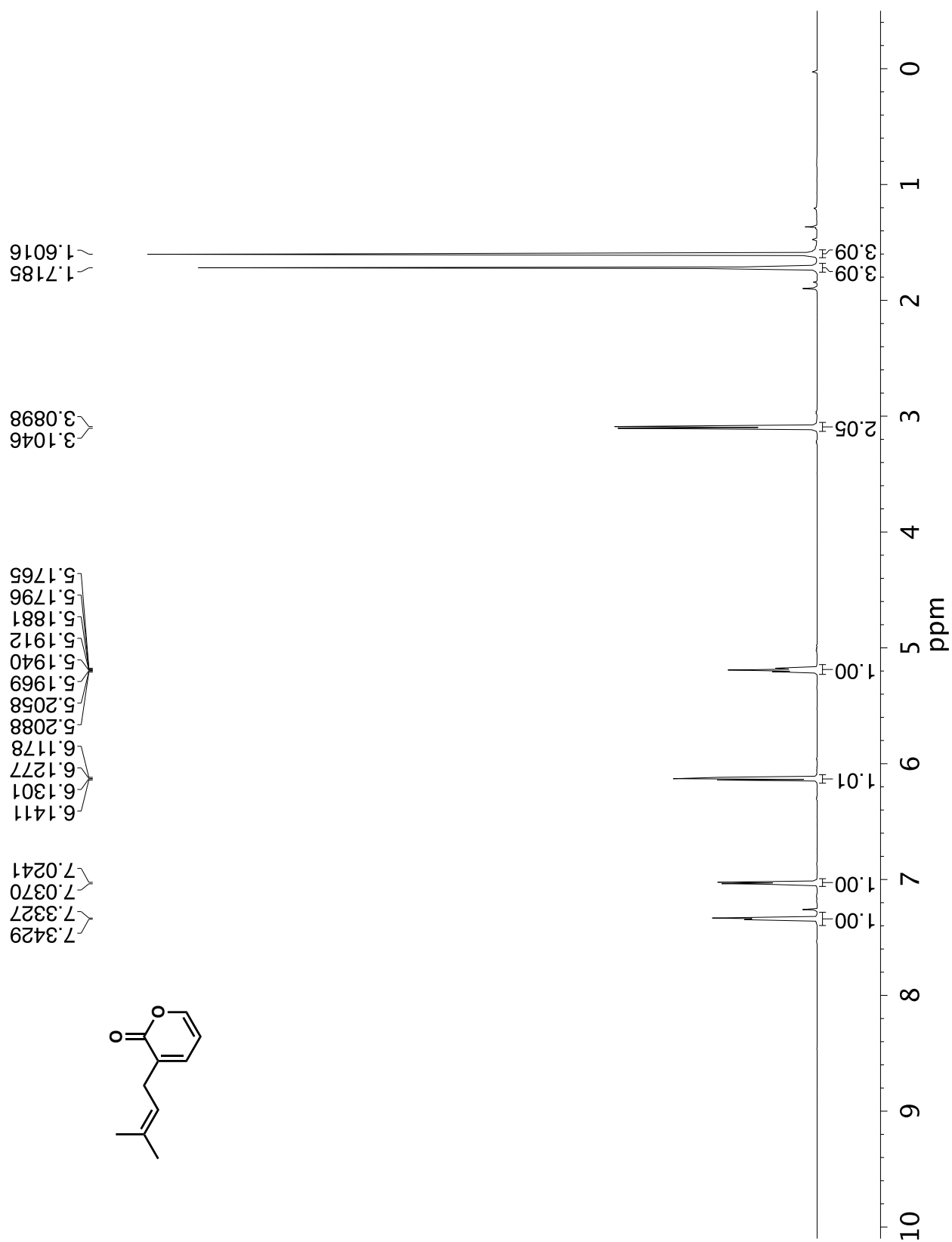
5- References

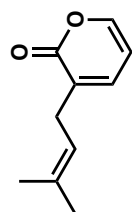
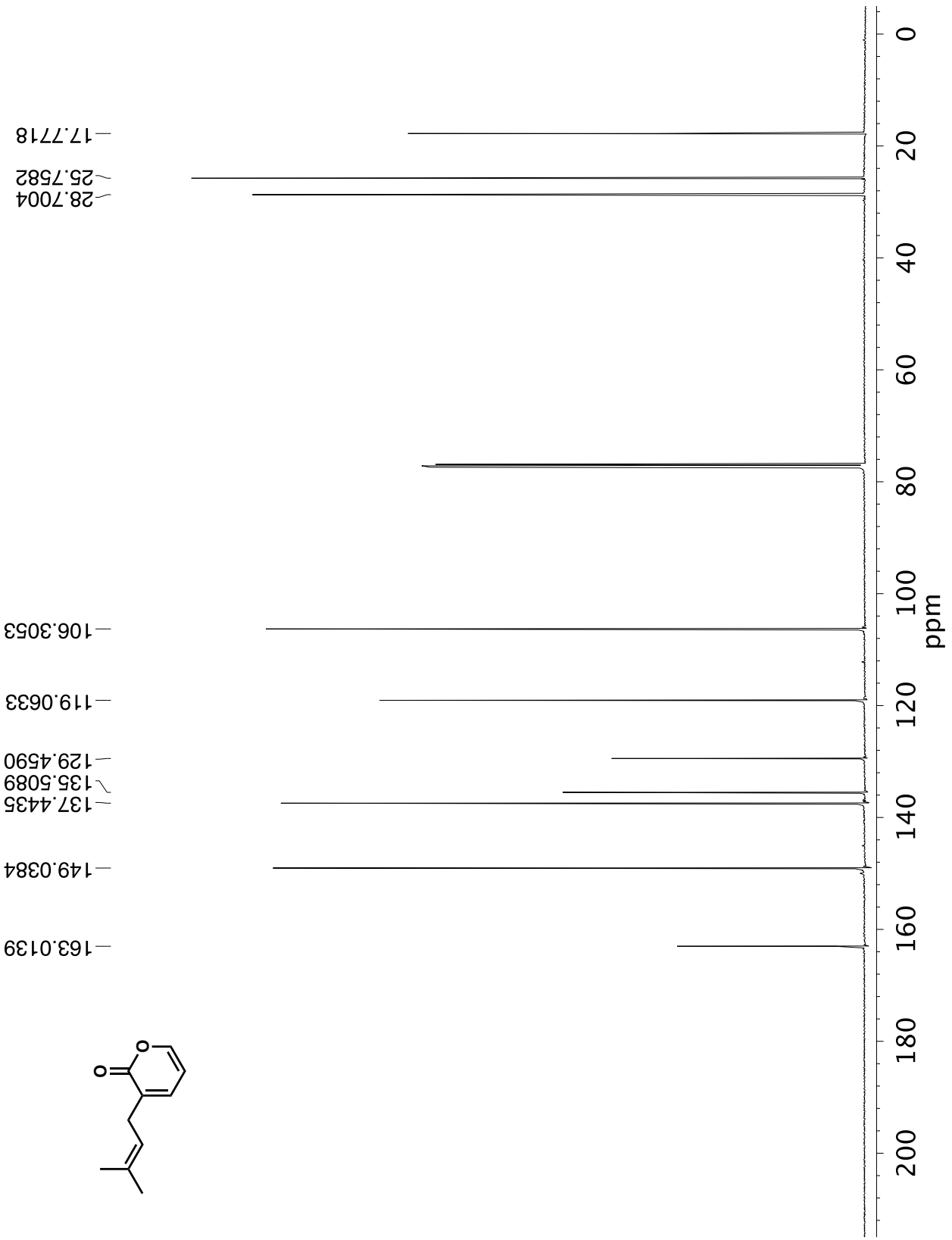
1. Posner, G. H.; Harrison, W.; Wettlaufer, D. G. *J. Org. Chem.* **1985**, *50*, 5041–5044.
2. Frébault, F.; Oliveira, M. T.; Wöstefeld, E.; and Maulide, N. *J. Org. Chem.* **2010**, *75*, 7962–7965.
3. Taber, D. F.; Meagley, R. P.; Louey, J. P.; Rheingold, A. L. *Inorg. Chim. Acta*, **1995**, *239*, 25–28.
4. Corey, E. J.; Streith, J. *J. Am. Chem. Soc.* **1964**, *86*, 950–951.
5. Liu, D.-Z.; Wang, F.; Liao, T.-G.; Tang, J.-G.; Steglich, W.; Zhu, H.-J.; Liu, J.-K. *Org. Lett.* **2006**, *8*, 5749–5752.
6. Zhou, Q.; Snider, B. B. *Org. Lett.* **2008**, *10*, 1401–1404.

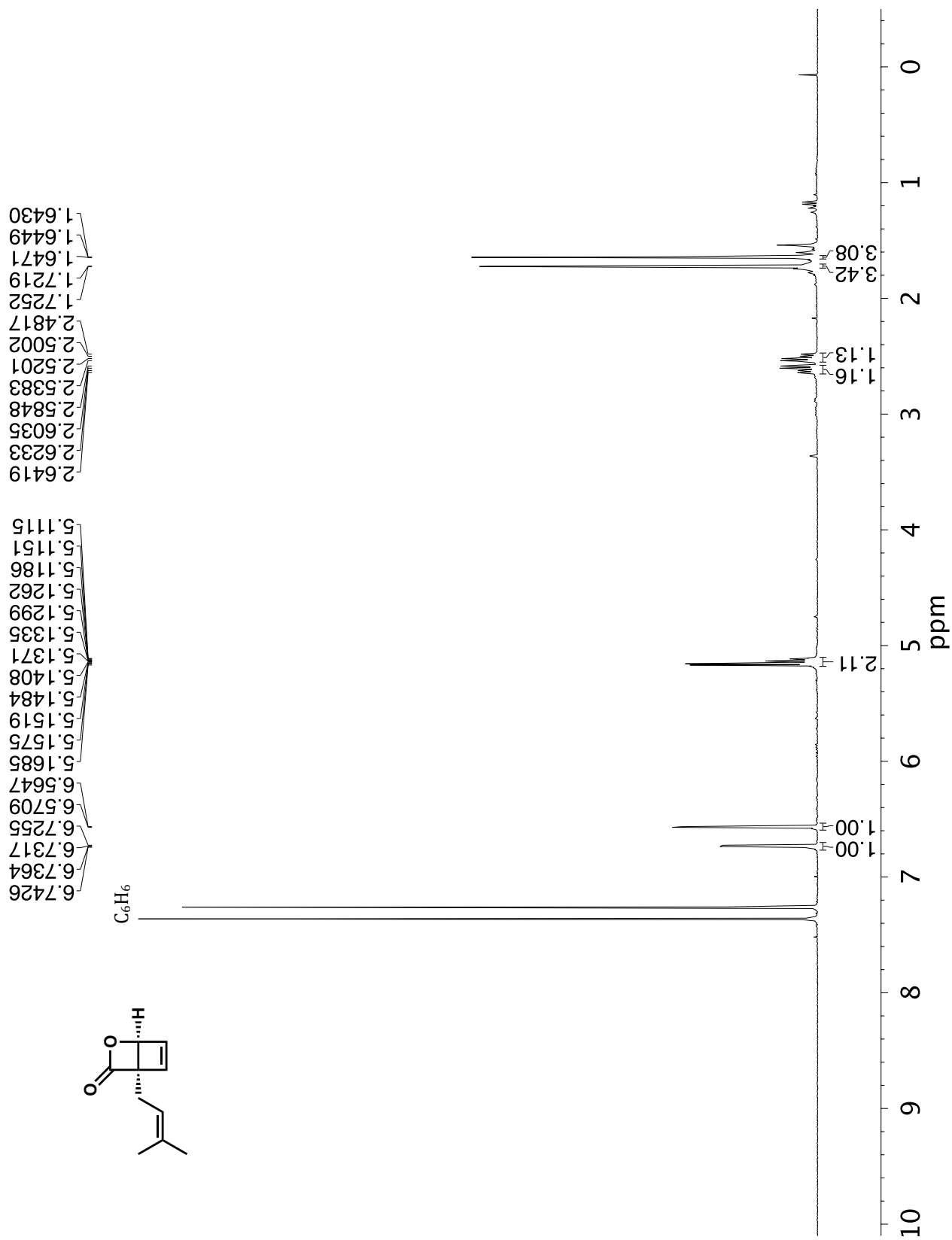
6- Crude ^1H NMR of Compound 1 (vibrallactone). Crude shows starting material (SM) and vibrallactone as major products, along with minor unidentified products. Dimethyl terephthalate was used as an internal standard.

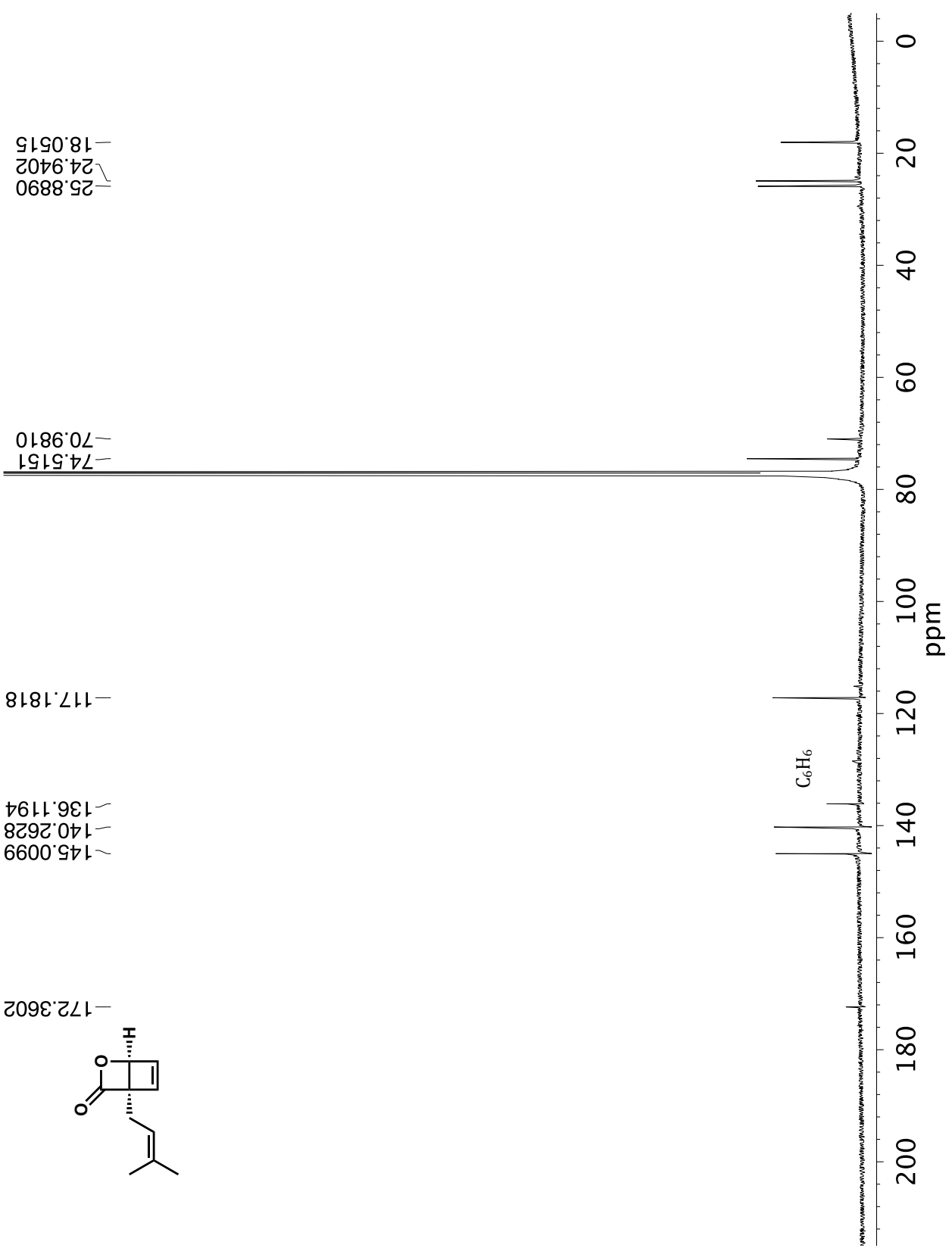


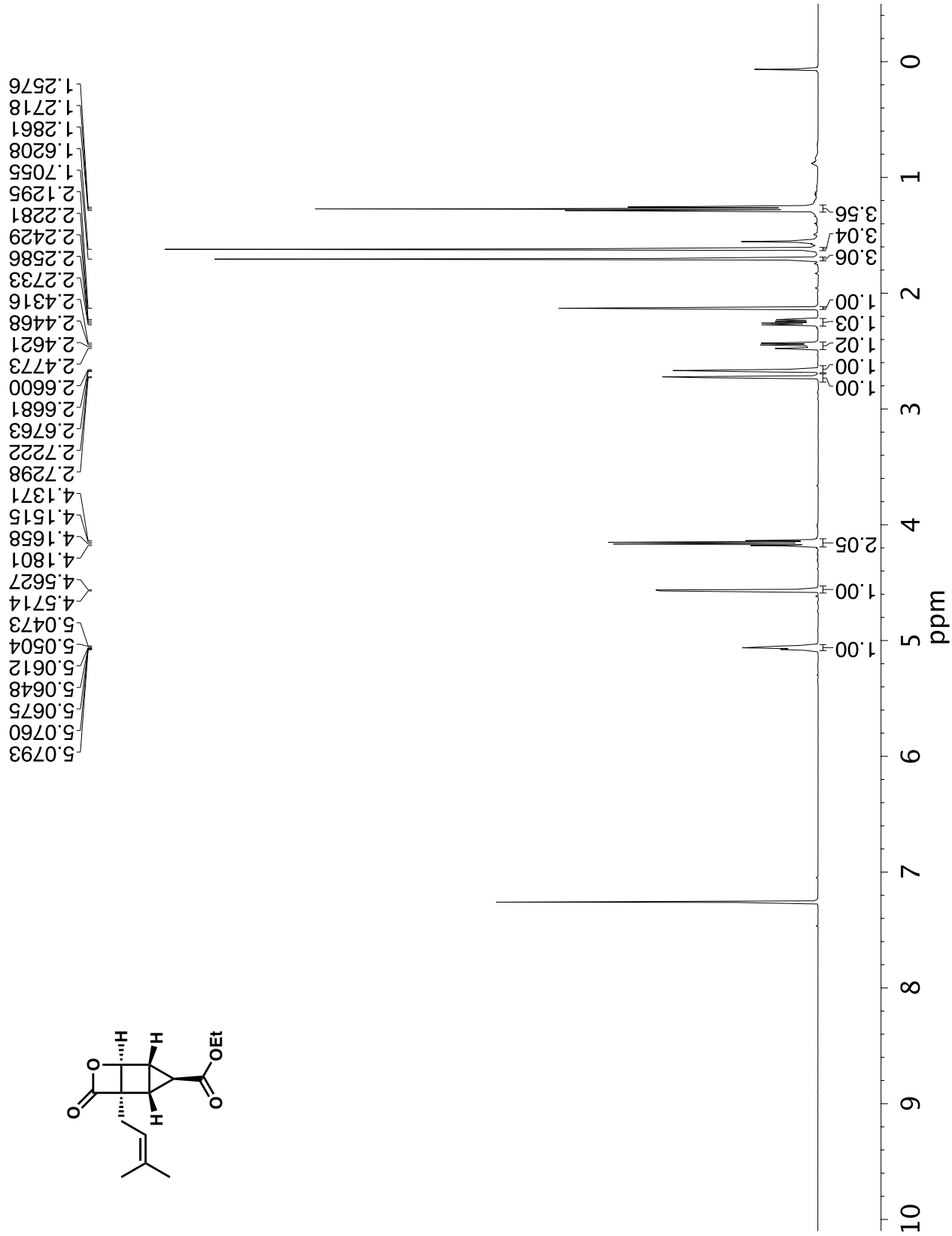
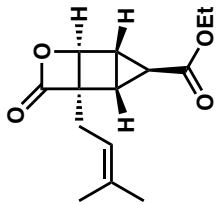
7- ¹H and ¹³C NMR Spectra

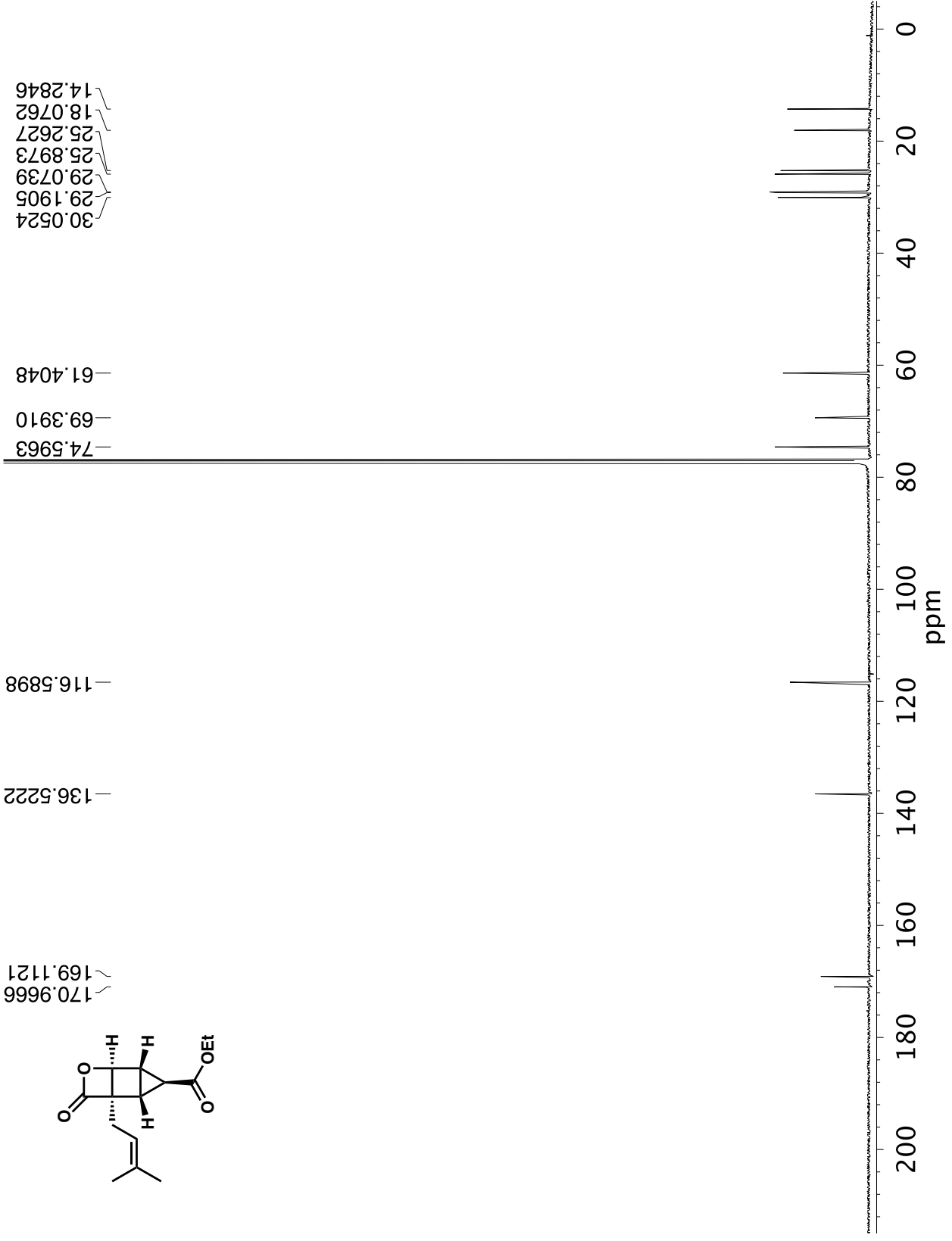


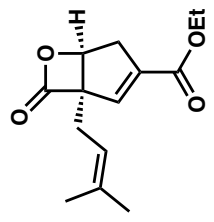
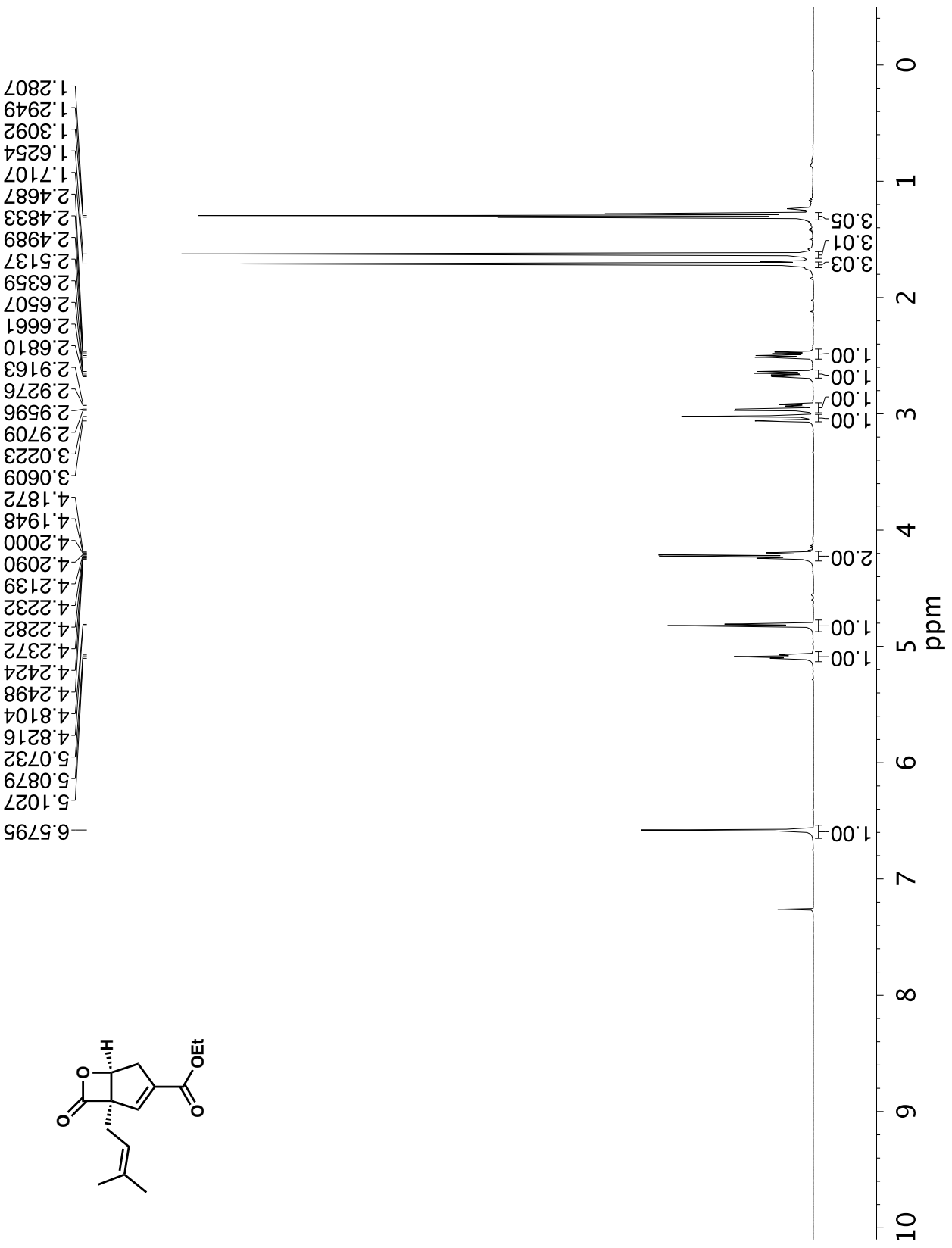




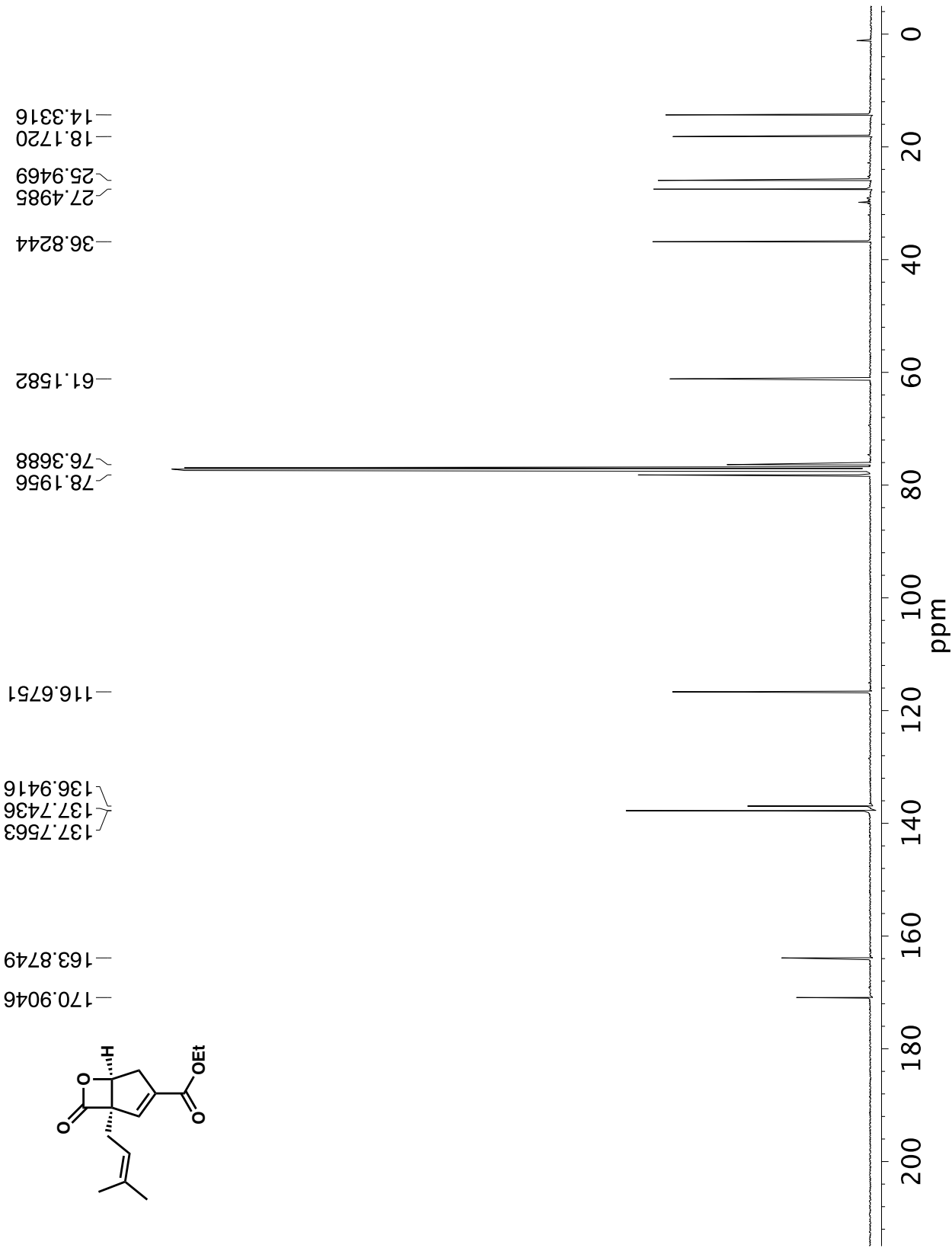


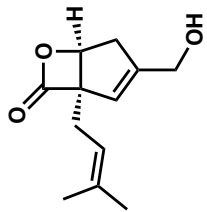




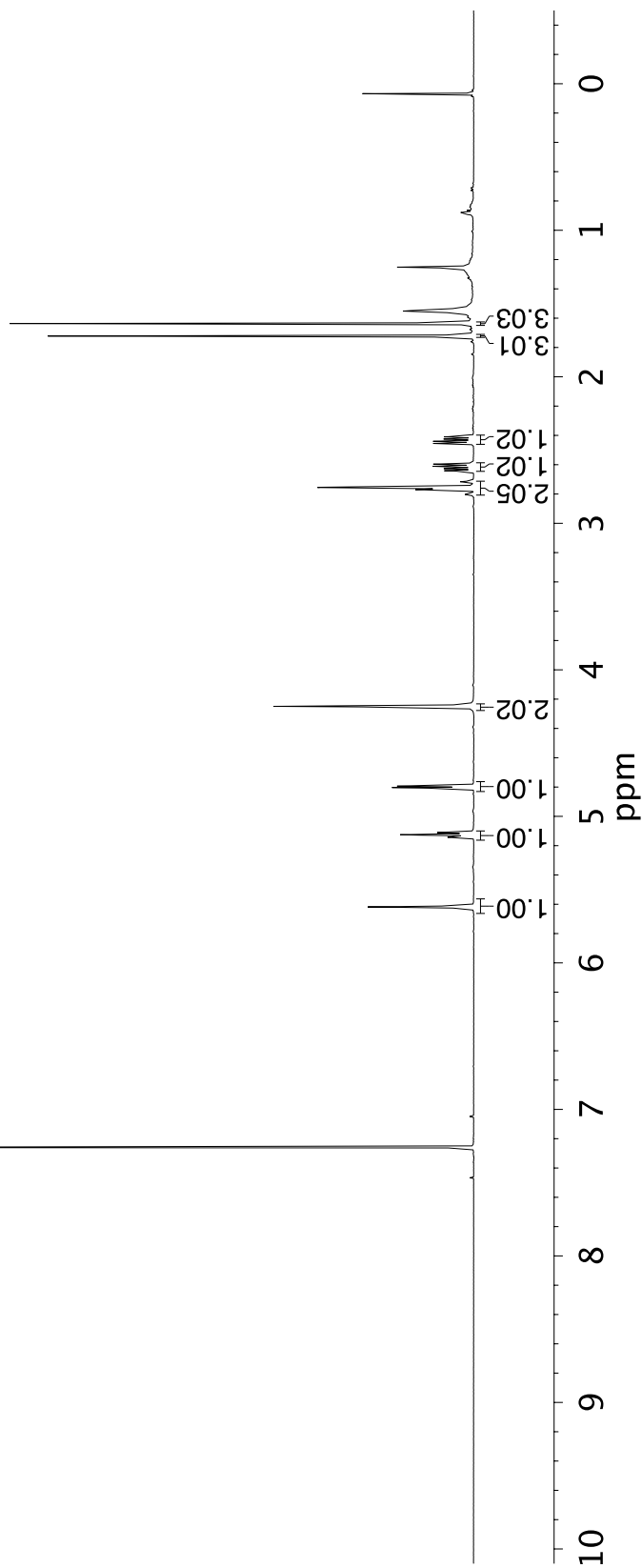


¹H NMR (500 MHz, CDCl₃) of compound 5.





5.6181
5.1401
5.1283
5.1253
5.1225
5.1106
4.8035
4.7939
4.2505
4.2473
2.8075
2.7580
2.7560
2.7540
2.7183
2.7163
2.6412
2.6265
2.6110
2.5962
2.4550
2.4403
2.4248
2.4101
1.7239
1.7218
1.6372



¹H NMR (500 MHz, CDCl₃) of compound 1.

