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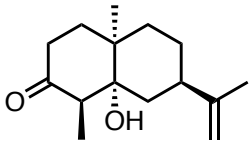
1. Materials and Methods

Unless otherwise stated, each reaction was performed in flame-dried glassware fitted with a rubber septum, under an argon atmosphere, and stirred with a Teflon-coated magnetic stirrer bars. Liquid reagents and solvents were transferred *via* syringe using standard Schlenk techniques. Methanol (MeOH) was distilled over magnesium under an argon atmosphere. Dichloromethane and triethylamine were distilled over calcium hydride under an argon atmosphere. Tetrahydrofuran, benzene, toluene, and diethyl ether were distilled over sodium/benzophenone ketyl under an argon atmosphere. All other solvents and reagents were used as received from commercial sources, unless otherwise noted. Reaction temperatures above 23 °C refer to oil bath temperatures. Thin layer chromatography (TLC) was performed using SiliCycle silica gel 60 F-254 precoated plates (0.25 mm) and visualized under UV irradiation, with a cerium ammonium molybdate (CAM) stain or a potassium permanganate ($KMnO_4$) stain. SiliCycle Silica-P silica gel (particle size 40–63 μm) was used for flash column chromatography. ^1H and ^{13}C NMR spectra were recorded using Bruker AV-500, DRX-500, and AV-400 MHz spectrometers, with ^{13}C NMR spectroscopic operating frequencies of 125, 125, and 100 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) relative to the signal of the residual protonated solvent: $CDCl_3$ signal (δ = 7.26 for ^1H NMR; δ = 77.2 for ^{13}C NMR), C_6D_6 signal (δ = 7.16 for ^1H NMR; δ = 128.1 for ^{13}C NMR), DMSO-d_6 (δ = 2.50 for ^1H NMR; δ = 39.5 for ^{13}C NMR). Data for ^1H NMR spectra are reported as follows: chemical shift, multiplicity, coupling constant(s) (Hz), and number of hydrogen atoms. Data for ^{13}C NMR spectra are reported in terms of chemical shift. The following abbreviations are used to describe the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; quint = quintet; m = multiplet; br = broad. Melting points (MP) are uncorrected and were recorded using an Electrothermal® capillary melting point apparatus. IR spectra were recorded using a Jasco FTIR-4100 spectrometer equippedwith an ATR attachment; the selected signals are reported in cm^{-1}. Optical rotations were recorded using an Autopol IV polarimeter and a 100-mm cell, at concentrations close to 1 g/100 mL. HRMS (ESI) was performed using a Waters LCT Premier spectrometer equipped with ACQUITY UPLC system and autosampler. HRMS (DART) was performed using a Thermo Fisher Scientific Exactive Plus spectrometer equipped with an IonSense ID-CUBE DART source. X-ray crystallographic data were collected using a Bruker SMART CCD-based diffractometer equipped with a low-temperature apparatus operated at 100 K. Ozonolysis experiments were performed using a Globalozone GO-D3G (3 g/h) ozone generator (2.0 L/min, 50% power, O_2 feed gas).

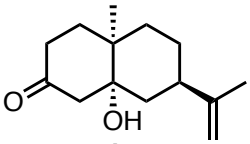
Caution: Ozone is an extremely toxic and reactive oxidant that can react with some compounds to form explosive and shock-sensitive products. Although we have not encountered any ozone-related safety issues in our laboratory, reactions with ozone should be performed only by properly trained individuals in a well-ventilated fume hood (use of a blast-shield is also recommended, especially for reactions performed on larger scales).

2. Starting Material Preparation

Substrates **1d**, **1f**, **1m**, **1o**, **1p**, and **1q** were purchased commercially and used as received.

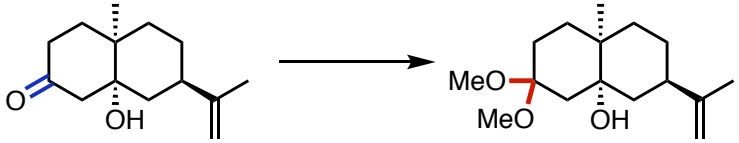


1a



1b

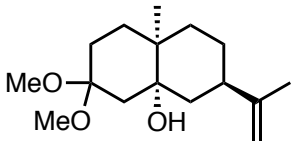
Substrates **1a** and **1b** were prepared following literature procedures.[1]



1b **1c**

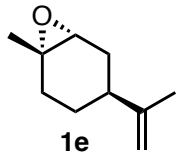
Substrate **1c** was prepared from the hydroxy ketone **1b** following a procedure adapted from the literature.[2]

A round-bottom flask equipped with a magnetic stirrer bar was charged with the ketone **1b** (222 mg, 1.00 mmol, 1.00 equiv), anhydrous MeOH (10.0 mL, 0.100 M), trimethyl orthoformate (165 µL, 0.150 mmol, 1.50 equiv), and 0.1 mol % HCl. The mixture was stirred at ambient temperature for approximately 3 h. Upon completion of the reaction (as indicated by TLC), 0.15 mol % sodium bicarbonate was added. The mixture was concentrated under reduced pressure. Purification of the residue by flash column chromatography (SiO_2) provided the ketal **1c**.



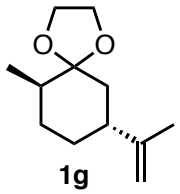
1c

*1.0 mmol scale reaction
Yield: 96% (257 mg).
Physical State: white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.70 (s, 2H), 3.17 (s, 3H), 3.14 (s, 3H), 2.33–2.07 (m, 2H), 1.98–1.78 (m, 3H), 1.72 (s, 3H), 1.70–1.16 (m, 8H), 1.11–0.97 (m, 1H), 0.99 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 150.1, 108.5, 100.9, 73.9, 47.6, 47.5, 42.6, 40.1, 39.0, 36.9, 36.2, 30.5, 28.5, 26.4, 22.0, 21.1.
MP: 63–64 ˚C.
IR (neat, ATR): ν_{max} 3476, 3081, 2956, 2931, 2868, 1106, 1046 cm^{-1}.
Optical Rotation: $[\alpha]_D^{20.4}$ 52.8 (*c* 1.00, $CHCl_3$).
HRMS (DART): calc'd for $C_{15}H_{25}O_2$ $[M - OCH_3]^+$ *m*/*z* 237.1849, found 237.1842.
R_f = 0.43 (20% EtOAc/hexanes).
Purification: FCC (SiO_2, 10 → 20% EtOAc/hexanes).



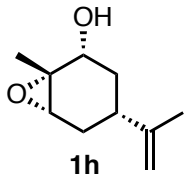
1e

Substrate **1e** was obtained in pure cis form following a literature procedure.[3]

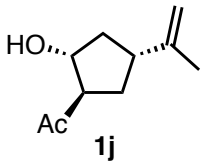


1g

Substrate **1g** was prepared following a literature procedure.[4]

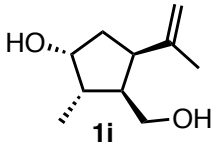


1h



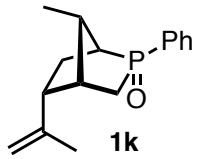
1j

Substrates **1h** and **1j** were prepared following literature procedures.[5]



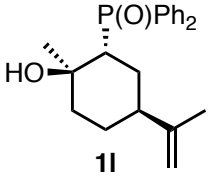
1i

Substrate **1i** was prepared following a literature procedure.[6]



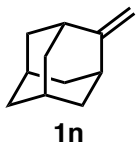
1k

Substrate **1k** was prepared following a literature procedure.[7]



1l

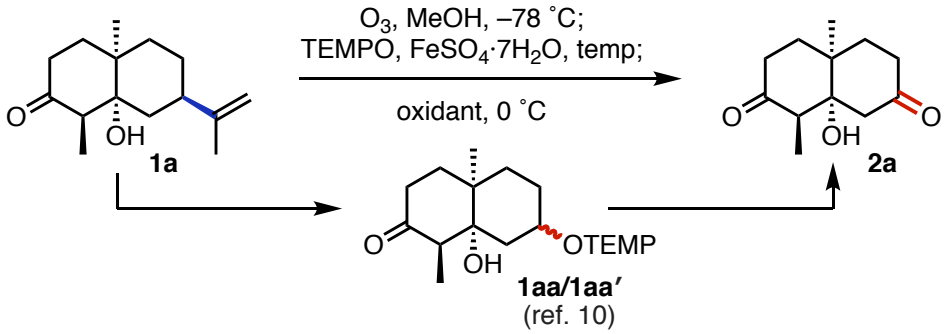
Substrate **1l** was prepared following a literature procedure.[8]



1n

Substrate **1n** was prepared following a literature procedure.[9]

3. Reaction Optimization



A 10-mL vial equipped with a magnetic stirrer bar was charged with the hydroxy ketone **1a** (23.6 mg, 0.100 mmol, 1.0 equiv) and MeOH (4.00 mL, 0.025 M), then placed in a dry-ice/acetone bath and cooled at –78 ˚C while open to air. Ozone was bubbled through the solution until complete consumption of the starting material had occurred (as indicated by TLC with CAM stain). The solution was then sparged with argon for 2 minutes to expel excess ozone. TEMPO (dissolved in 0.500 mL of MeOH) was added at the specified temperature and then ferrous sulfate heptahydrate (33.4 mg, 0.120 mmol, 1.2 equiv) was added.

Entries 1–6: Upon complete consumption of the intermediate α-alkoxy hydroperoxides (as indicated by TLC), 1-chloro-2,4-dinitrobenzene (20.3 mg, 0.100 mmol, 1.0 equiv) was added to the reaction mixture. The mixture was then cooled to 0 ˚C in an ice-water bath, and 10% saturated aqueous sodium thiosulfate (4.0 mL) was added. After warming to room temperature and stirring for 15 minutes, the MeOH/water layer was extracted with dichloromethane (3 × 3.0 mL). The combined organic fractions were transferred to a vial, and the 10% saturated aqueous sodium thiosulfate (4.0 mL) was added, followed by 1.0 M HCl (0.50 mL). After vigorously stirring for 10 min, the organic layer was separated, washed with brine (5.0 mL), dried, and concentrated. The crude product was dissolved in deuterated chloroform, then filtered directly into an NMR tube for analysis.

Entries 7–15: Upon complete consumption of the intermediate α-alkoxy hydroperoxide (as indicated by TLC), the reaction mixture was cooled to 0 ˚C in an ice-water bath and the oxidant was added in a single portion. After stirring for 30 minutes at 0 ˚C, 10% saturated aqueous sodium thiosulfate (2.00 mL) was added, followed by saturated aqueous sodium bicarbonate (2.00 mL). The mixture was warmed to room temperature, then extracted with dichloromethane (3 × 3.00 mL). The combined organic fractions were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by flash column chromatography (SiO_2; 30 → 40% EtOAc/hexanes).

Table S1. Optimization of reaction conditions

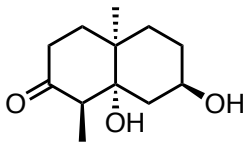
entry	TEMPO (equiv)	oxidant (equiv)	temp (˚C)	% yield 1aa+1aa′[a]	% yield 2a[b]
1	1.5	–	–78 to rt	91	–
2[c]	1.5	–	–78 to rt	94	–
3[c]	1.5	–	0	85	–

4[c]	1.5	–	rt	92	–
5[c]	1.0	–	–78 to rt	79	–
6[c]	2.0	–	–78 to rt	93	–
7[c]	1.5	*m*CPBA (1.2)	–78 to rt	–	33
8[c]	1.5	H_2O_2 (1.2)	–78 to rt	–	trace
9[c]	1.5	UHP (1.2)	–78 to rt	–	0
10[c]	1.5	MMPP (1.2)	–78 to rt	–	53
11[c]	1.5	Oxone™ (1.2)	–78 to rt	–	trace
12[c]	1.5	MMPP (1.5)	–78 to rt	–	62
13[c]	1.5	MMPP (2.0)	–78 to rt	–	78
14[c]	**1.5**	**MMPP (2.5)**	**–78 to rt**	**–**	**84**
15[c]	1.5	MMPP (3.0)	–78 to rt	–	81
16[d]	–	O_2	0 to rt	–	24[e]

[a]Yield determined by ^{1}H NMR spectroscopic analysis using 1-chloro-2,4-dinitrobenzene as an internal standard. [b]Isolated yield. [c]Ferrous sulfate heptahydrate was added as a 5% wt/vol aqueous solution. [d]After ozonolysis, the reaction was bubbled with O_2 for 20 min, then 2.5 equiv ferrous sulfate heptahydrate and 2.5 equiv $PhSiH_3$ were added at 0 ˚C.[11] [e]Approximately 40 mg of **SI-I/SI-I′** was also obtained.

Note: Some additional oxidants (listed below) are known for *N*-oxidation of amines, but were not tested because of their limited availability (e.g., only peracetic acid is commercially available), difficult preparation, and/or safety issues related to their handling (e.g., peroxy acids are potentially explosive).

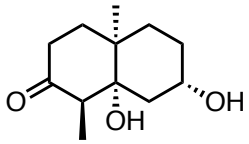
· trifluoroperacetic acid[12]
· DMDO (dimethyldioxirane)[13]
· (±)-*trans*-2-(phenylsulfonyl)-3-phenyloxaziridine[14]
· peracetic acid[15]
· monoperoxysulfuric acid (Caro's acid)[16]



SI-I

*0.5 mmol scale reaction
Yield: 34% (36 mg).
Physical State: white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.92 (dddd, *J* = 11.3, 11.3, 4.8, 4.8 Hz, 1H), 2.77 (q, *J* = 6.6 Hz, 1H), 2.56 (dddd, *J* = 14.2, 14.2, 7.0, 1.0 Hz, 1H), 2.34 (ddd, *J* = 14.2, 5.0, 1.8 Hz, 1H), 2.13 (ddd, *J* = 14.1, 14.1, 5.1 Hz, 1H), 1.95–1.79 (m, 3H), 1.54–1.38 (m, 5H), 1.22 (s, 3H), 1.08 (dd, *J* = 13.6, 11.4 Hz, 1H), 1.05 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 209.9, 79.3, 67.4, 51.9, 37.7, 37.6, 37.4, 33.9, 31.6, 30.2, 21.2, 6.6.
MP: 188 ˚C (decomp).
IR (neat, ATR): ν_{max} 3391, 2967, 2925, 2882, 1704, 1258, 1061, 976 cm^{-1}.

Optical Rotation: $[\alpha]_D^{21.1}$ 26.5 (*c* 0.20, $CHCl_3$).
HRMS (ESI-TOF): calc'd for $C_{12}H_{19}O_2$ $[M - OH]^+$ *m*/*z* 195.1380, found 195.1384.
R_f = 0.09 (50% EtOAc/hexanes).
Purification: FCC (SiO_2, 20 → 100% EtOAc/hexanes).

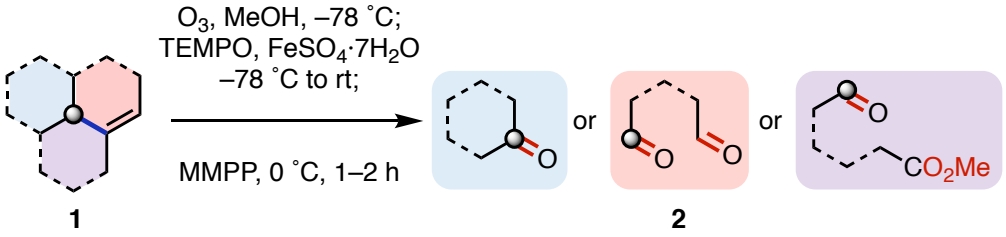


SI-I′

*0.5 mmol scale reaction
Yield: 4% (4 mg).
Physical State: colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.22–4.15 (m, 1H), 3.98 (br s, 1H), 2.81 (d, *J* = 6.6 Hz, 1H), 2.59 (dddd, *J* = 14.2, 14.2, 7.1, 1.1 Hz, 1H), 2.32 (ddd, *J* = 14.2, 5.0, 1.8 Hz, 1H), 2.14 (br s, 1H), 2.13 (ddd, *J* = 14.2, 14.2, 4.6 Hz, 1H), 1.92 (ddd, *J* = 14.1, 14.1, 5.1 Hz, 1H), 1.86 (ddd, *J* = 15.1, 2.7, 2.7 Hz, 1H), 1.77 (dddd, *J* = 14.4, 14.4, 4.4, 2.9 Hz, 1H), 1.71–1.63 (m, 1H), 1.47 (ddd, *J* = 13.9, 7.1, 1.9 Hz, 1H), 1.27 (s, 3H), 1.25–1.19 (m, 2H), 1.06 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 211.0, 78.3, 67.6, 51.1, 38.4, 37.8, 32.5, 31.2, 29.3, 28.0, 21.9, 6.8.
IR (neat, ATR): ν_{max} 3377, 2951, 2932, 2861, 1707, 1263 cm^{-1}.
Optical Rotation: $[\alpha]_D^{21.0}$ 17.0 (*c* 0.10, $CHCl_3$).
HRMS (ESI-TOF): calc'd for $C_{12}H_{19}O_2$ $[M - OH]^+$ *m*/*z* 195.1380, found 195.1388.
R_f = 0.48 (50% EtOAc/hexanes).
Purification: FCC (SiO_2, 20 → 100% EtOAc/hexanes).

4. Experimental Procedures and Characterization Data

4.1. General Procedure for Oxodealkenylation

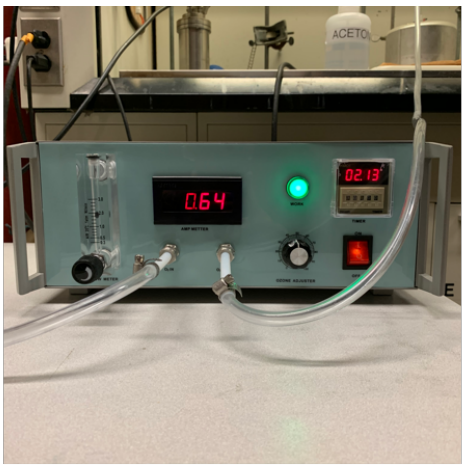


A round-bottom flask equipped with a magnetic stirrer bar was charged with the alkene **1** (1.0 equiv) and MeOH (0.025 M), then cooled to –78 ˚C in a dry-ice/acetone bath while open to the air. Ozone was bubbled through the solution until complete consumption of the starting material had occurred (as indicated by TLC and/or a blue color in the reaction solution). The solution was then sparged with argon for 5 min to expel excess ozone. TEMPO (1.5 equiv; dissolved in a minimal amount of MeOH) was added, followed by freshly prepared[a] aqueous ferrous sulfate heptahydrate (5% wt/vol, 1.2 equiv). The flask was removed from the cooling bath and warmed to room temperature.[b] Upon complete conversion of the α-alkoxy hydroperoxides to the intermediate TEMPO-adducts (as indicated by TLC), the flask was cooled to 0 ˚C with an ice-water bath. MMPP (2.5 equiv) was added portionwise over 10 min (generally resulting in an orange suspension).[c] Upon its completion (as indicated by TLC, generally between 1–2 h), the reaction was quenched by the addition of 10% saturated aqueous sodium thiosulfate and saturated aqueous sodium bicarbonate. The mixture was then warmed to room temperature and transferred to a separatory funnel. The MeOH/water suspension was extracted with EtOAc (3×) and the combined organic fractions washed with brine, dried (anhydrous sodium sulfate), filtered, and concentrated under reduced pressure. Purification of the residue through flash column chromatography (SiO_2) provided the carbonyl product **2**.

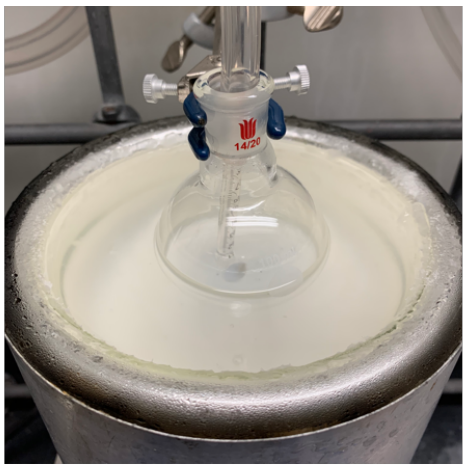
[a]Commercially available ferrous sulfate heptahydrate (from Alfa Aesar, 98%) was dissolved in water approximately 10 min prior to use. This precaution minimized any potential aerobic oxidation of ferrous to ferric species in the aqueous solution.
[b]Conversion of the α-alkoxy hydroperoxide to the intermediate TEMPO adduct was often complete before the mixture reached room temperature. In these cases, the 0 ˚C cooling bath was applied (because prolonged stirring facilitated acetalization/ketalization of the ketone/aldehyde intermediates).
[c]In some cases (noted with each entry), an additional 0.5 equiv of MMPP was added after stirring for 1 h.

Any modification of the above procedure is described below with the specific entry.

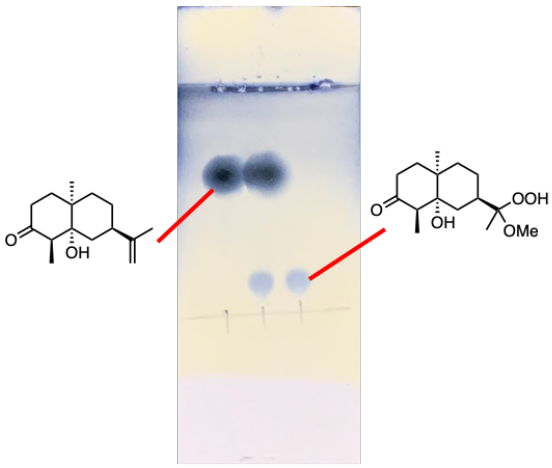
4.2. Graphical Procedure for Oxodealkenylation



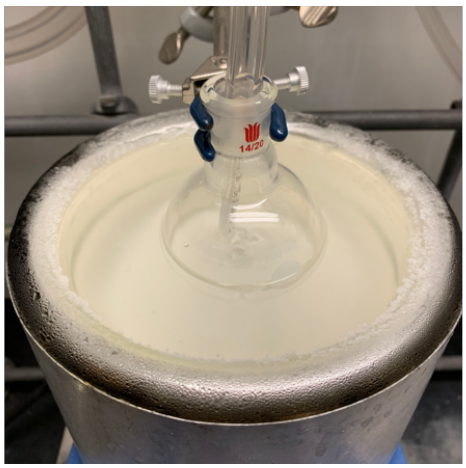
2.0 L/min O_2, 50% power setting



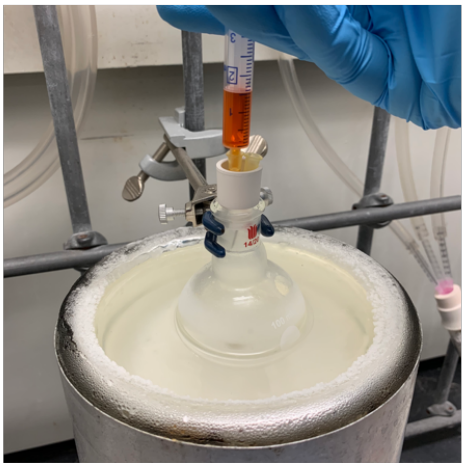
Ozonolysis at –78 °C until SM consumed



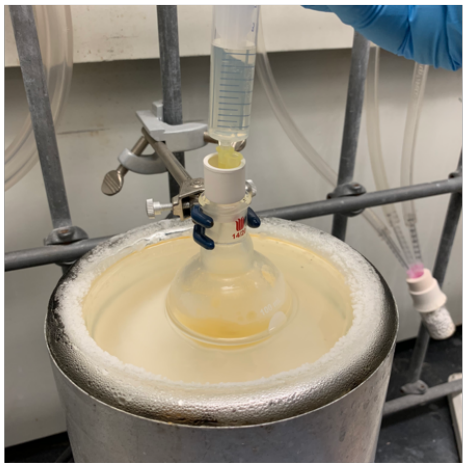
TLC after ozonolysis (30% EA/HEX)



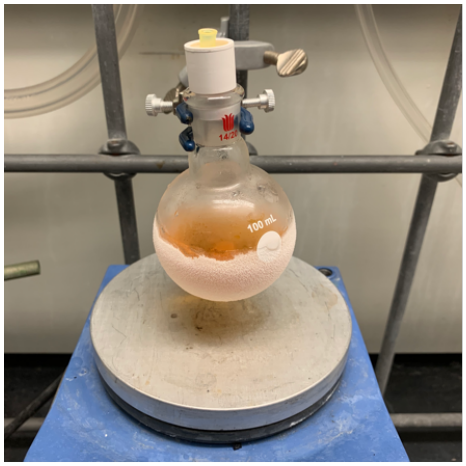
Argon sparge



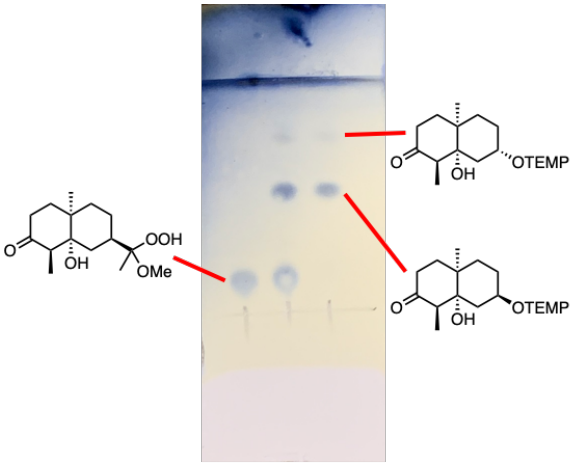
TEMPO addition (dissolved in MeOH)



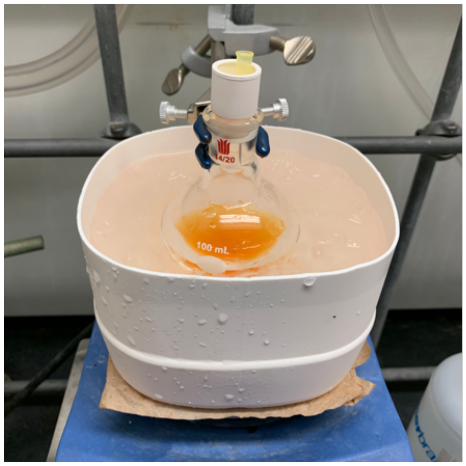
Aqueous (5 wt/vol%) $FeSO_4 \cdot 7H_2O$ addition



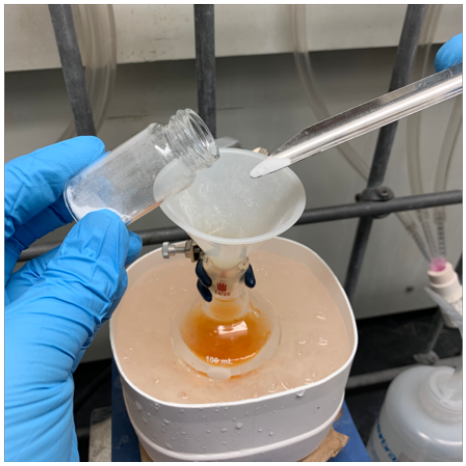
Cooling bath removed



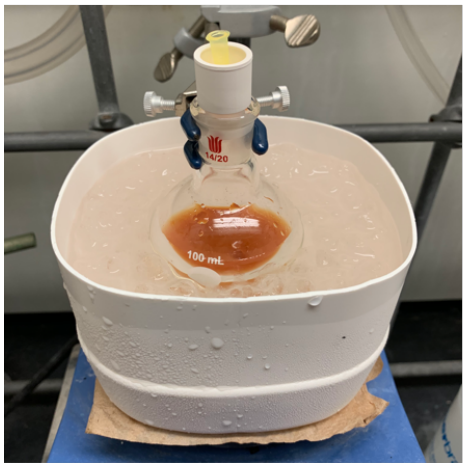
TLC after TEMPO and Fe^{II} addition (30% EA/HEX)



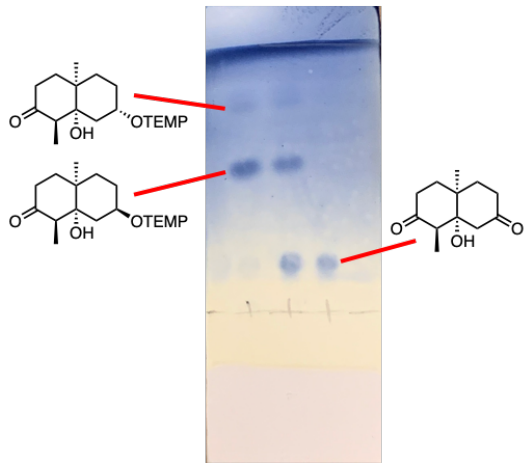
Cooling to 0 ˚C with ice-water bath



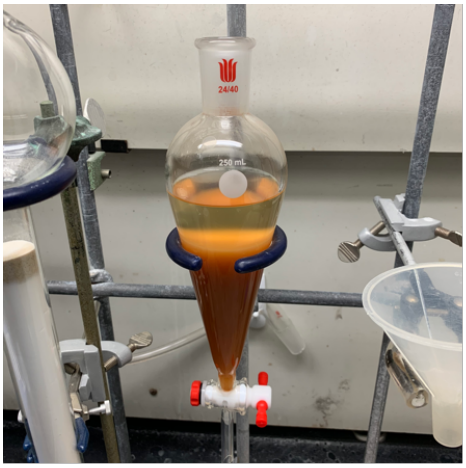
Portion-wise addition of MMPP over 10 min



Reaction mixture after MMPP addition

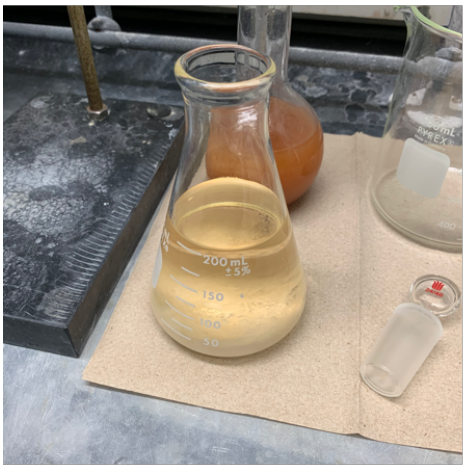


TLC after 2 h stirring

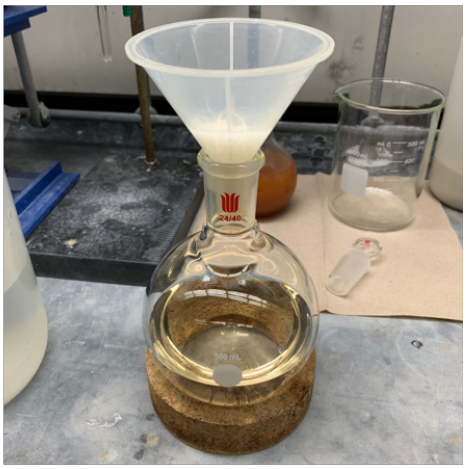


Extraction with ethyl acetate
(orange color from TEMPO)

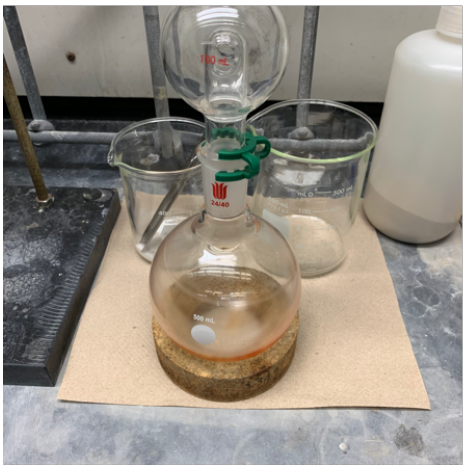
Brine wash



Drying with Na_2SO_4

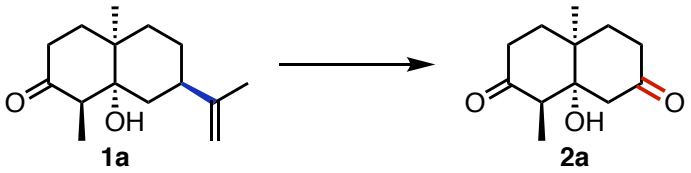


Dried organic layer filtered into RBF



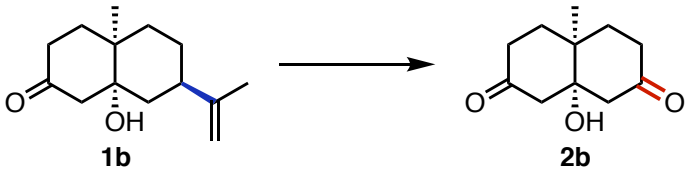
Crude reaction concentrated

4.3. Characterization Data



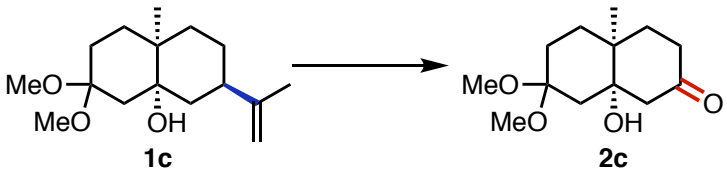
1a **2a**

*1.0 mmol scale reaction
Yield: 87% (183 mg).
Physical State: white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 2.83 (q, *J* = 6.7 Hz, 1H), 2.67 (dddd, *J* = 14.2, 14.2, 7.2, 0.7 Hz, 1H), 2.53–2.43 (m, 2H), 2.34–2.29 (m, 2H), 2.29–2.18 (m, 2H), 2.17–2.12 (m, 1H), 1.70 (dddd, *J* = 13.8, 11.8, 7.0, 1.6 Hz, 1H), 1.33 (s, 3H), 1.02 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 209.4, 209.2, 81.5, 51.7, 45.2, 37.7, 37.4, 37.2, 35.0, 31.0, 20.7, 6.3.
MP: 153–155 ˚C.
IR (neat, ATR): ν_{max} 3459, 2971, 2921, 2850, 1708, 1053 cm^{-1}.
Optical Rotation: $[\alpha]_D^{21.4}$ 31.6 (*c* 0.50, $CHCl_3$).
HRMS (DART): calc'd for $C_{12}H_{17}O_2$ $[M - OH]^+$ *m/z* 193.1223, found 193.1221.
***R*$_f$** = 0.41 (50% EtOAc/hexanes).
Purification: FCC (SiO_2, 30 → 50% EtOAc/hexanes).



1b **2b**

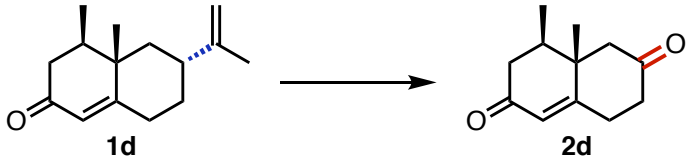
*1.0 mmol scale reaction
Yield: 75% (147 mg).
Physical State: white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 2.55–2.36 (m, 8H), 1.98 (dd, *J* = 7.1, 7.1 Hz, 4H), 1.93 (br s, 1H), 1.30 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 208.1, 79.0, 51.8, 37.5, 37.0, 32.9, 20.5.
MP: 182 ˚C (decomposition).
IR (neat, ATR): ν_{max} 3378, 2956, 2939, 2921, 1708, 1432, 1276 cm^{-1}.
HRMS (DART): calc'd for $C_{11}H_{15}O_2$ $[M + H]^+$ *m/z* 179.1067, found 179.1062.
***R*$_f$** = 0.35 (50% EtOAc/hexanes).
Purification: trituration (pentane).



1c **2c**

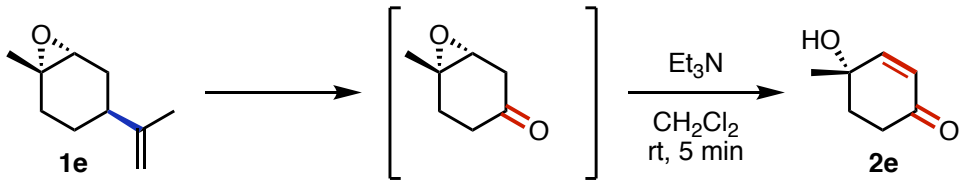
*0.5 mmol scale reaction
Yield: 95% (115 mg).
Physical State: white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.41 (br s, 1H), 3.21 (s, 3H), 3.18 (s, 3H), 2.78–2.67 (m, 1H), 2.53 (ddd, J = 14.2, 14.2, 7.0 Hz, 1H), 2.37–2.12 (m, 2H), 2.01–1.80 (m, 3H), 1.79–1.67 (m, 1H), 1.62–1.42 (m, 3H), 1.39–1.29 (m, 1H), 1.20 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 209.7, 100.8, 75.0, 51.9, 47.9, 47.4, 39.6, 37.5, 37.4, 31.4, 31.2, 26.5, 21.2.
MP: 109–110 ˚C.
IR (neat, ATR): ν_{max} 3473, 2956, 2931, 1714, 1177, 1110, 1078, 1046, 849 cm^{-1}.
Optical Rotation: $[\alpha]_D^{20.6}$ –21.1 (c 1.00, $CHCl_3$).
HRMS (DART): calc'd for $C_{13}H_{21}O_3$ $[M - OH]^+$ m/z 225.1485, found 225.1477.
R_f = 0.36 (30% EtOAc/hexanes).
Purification: FCC (SiO_2, 20 → 30% EtOAc/hexanes).



1d **2d**

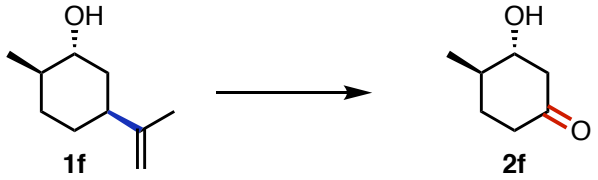
*1.0 mmol scale reaction
Yield: 82% (157 mg).
Physical State: white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.89 (s, 1H), 2.83 (dddd, J = 15.9, 10.9, 7.6, 2.0 Hz, 1H), 2.72 (ddd, J = 15.9, 6.1, 4.2 Hz, 1H), 2.58–2.47 (m, 3H), 2.31–2.11 (m, 4H), 1.06 (s, 3H), 0.94 (d, J = 6.5 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 208.6, 198.4, 165.3, 125.7, 51.3, 42.2, 41.5, 39.8, 39.4, 31.4, 17.9, 14.8.
MP: 102–104 ˚C.
IR (neat, ATR): ν_{max} 3045, 2963, 2918, 1712, 1661, 1301, 1184 cm^{-1}.
Optical Rotation: $[\alpha]_D^{20.7}$ 104.2 (c 1.00, $CHCl_3$).
HRMS (DART): calc'd for $C_{12}H_{17}O_2$ $[M + H]^+$ m/z 193.1223, found 193.1219.
R_f = 0.52 (50% EtOAc/hexanes).
Purification: FCC (SiO_2, 30 → 50% EtOAc/hexanes).
Compound **2d** is known in the literature, but incomplete characterization data has been provided previously.[17]



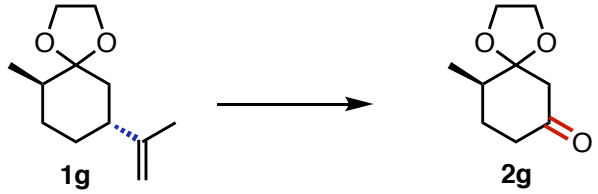
1e **2e**

*1.0 mmol scale reaction
Yield: 81% (102 mg).
Physical State: pale yellow oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.77 (d, J = 10.0 Hz, 1H), 5.89 (d, J = 10.1 Hz, 1H), 2.63 (ddd, J = 17.2, 5.5, 5.5 Hz, 1H), 2.43 (ddd, J = 17.2, 9.0, 5.8 Hz, 1H), 2.21–2.08 (m, 2H), 1.96 (br s, 1H), 1.47 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 199.2, 155.0, 127.8, 68.3, 37.2, 34.8, 27.1.

Optical Rotation: $[\alpha]_D^{20.7}$ –8.7 (*c* 1.00, $CHCl_3$).
***R*f** = 0.28 (50% EtOAc/hexanes).
Purification: FCC (SiO_2, 10 → 50% EtOAc/hexanes).
Note: Extraction performed with CH_2Cl_2. The presumed product formed during the reaction was the corresponding epoxy ketone (R_f = 0.38; 30% EtOAc/hexanes). After extraction, triethylamine (0.15 mL, 1.1 mmol, 1.1 equiv) was added to the organic layer. The mixture was stirred for approximately 5 min and concentrated. The residue was subjected to purification by flash column chromatography to give the enone **2e**.
All characterization data were consistent with those reported in the literature.[18]

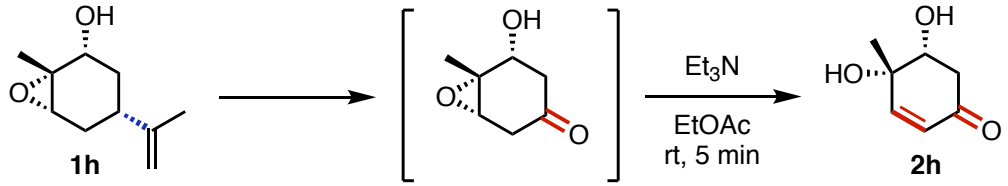


*1.0 mmol scale reaction
Yield: 80% (102 mg).
Physical State: colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.54 (ddd, *J* = 9.5, 9.5, 4.5 Hz, 1H), 2.72 (ddd, *J* = 13.9, 4.5, 1.5 Hz, 1H), 2.44–2.26 (m, 3H), 2.07–1.94 (m, 2H), 1.83–1.73 (m, 1H), 1.40–1.28 (m, 1H), 1.13 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 209.5, 74.8, 49.7, 40.3, 38.2, 29.2, 17.3.
IR (neat, ATR): ν_{max} 3416, 2960, 2925, 2878, 1712, 1460, 1057 cm^{-1}.
Optical Rotation: $[\alpha]_D^{20.8}$ –12.9 (*c* 1.00, $CHCl_3$).
HRMS (DART): calc'd for $C_7H_{13}O_2$ $[M + H]^+$ *m/z* 129.0910, found 129.0906.
***R*f** = 0.25 (30% EtOAc/hexanes).
Purification: FCC (SiO_2, 20 → 50% EtOAc/hexanes).
Note: Extraction performed with CH_2Cl_2.
Compound **2f** is known in the literature, but incomplete characterization data has been provided previously.[19]

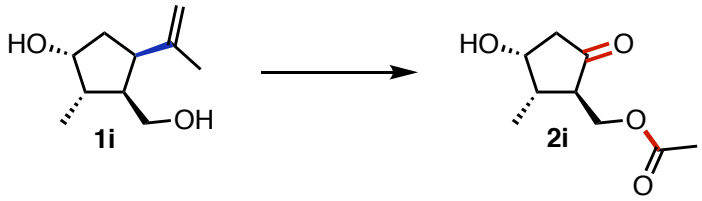


*1.0 mmol scale reaction
Yield: 75% (128 mg).
*5.6 mmol scale reaction
Yield: 75% (714 mg).
Physical State: colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.02–3.90 (m, 4H), 2.61 (dd, *J* = 14.1, 1.9 Hz, 1H), 2.48 (d, *J* = 14.1 Hz, 1H), 2.39 (dddd, *J* = 14.7, 5.2, 4.7, 1.9 Hz, 1H), 2.31 (dddd, *J* = 14.7, 11.2, 6.2, 1.1 Hz, 1H), 2.10 (dddd, *J* = 17.5, 6.6, 6.6, 4.3, 1H), 1.89 (dddd, *J* = 13.5, 6.2, 4.4, 4.4 Hz, 1H), 1.62 (dddd, *J* = 13.5, 11.0, 11.0, 5.4 Hz, 1H), 1.01 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 207.8, 111.2, 65.4, 65.3, 50.8, 39.8, 38.5, 28.2, 13.4.

IR (neat, ATR): ν_{max} 2974, 2942, 2921, 2893, 1718, 1148, 1095, 1018 cm^{-1}.
Optical Rotation: $[\alpha]_D^{20.9}$ 8.4 (*c* 1.00, $CHCl_3$).
HRMS (DART): calc'd for $C_9H_{15}O_3$ $[M + H]^+$ *m/z* 171.1016, found 171.1012.
***R*f** = 0.42 (20% EtOAc/hexanes).
Purification: FCC (SiO_2, 5 → 20% EtOAc/hexanes).
Note: When the reaction was performed on 5.6 mmol scale, a reaction time of approximately 5 h was required.
The racemate of **2g** is known in the literature, but no characterization data has been provided previously.[20]

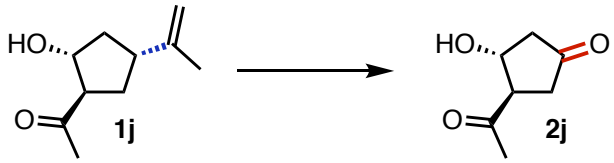


*1.0 mmol scale reaction
Yield: 61% (87 mg).
Physical State: pale yellow oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.68 (dd, *J* = 10.2, 1.2 Hz, 1H), 5.95 (d, *J* = 10.2 Hz, 1H), 4.08–4.01 (m, 1H), 3.06 (br s, 2H), 2.76–2.63 (m, 2H), 1.46 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 197.1, 152.3, 128.2, 73.7, 70.2, 42.8, 25.0.
IR (neat, ATR): ν_{max} 3410, 2974, 2918, 2846, 1676, 1545, 1383, 1053 cm^{-1}.
Optical Rotation: $[\alpha]_D^{21.7}$ 14.8 (*c* 0.50, $CHCl_3$).
HRMS (DART): calc'd for $C_7H_{11}O_3$ $[M + H]^+$ *m/z* 143.0703, found 143.0700.
***R*f** = 0.39 (EtOAc).
Purification: FCC (SiO_2, 80 → 100% EtOAc/hexanes).
Note: The presumed product formed during the reaction was the corresponding epoxy ketone (R_f = 0.21; 50% EtOAc/hexanes). After extraction, triethylamine (0.15 mL, 1.1 mmol, 1.1 equiv) was added to the organic layer. The mixture was stirred for approximately 5 min and concentrated. The residue was subjected to purification by flash column chromatography to give the enone **2h**.

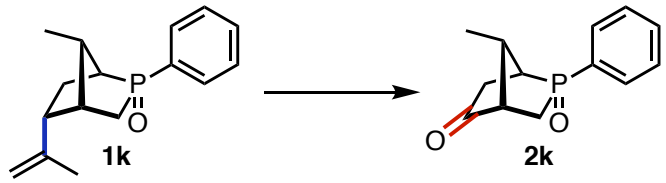


*1.0 mmol scale reaction
Yield: 83% (154 mg).
Physical State: colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.39 (dd, *J* = 3.5, 3.5 Hz, 1H), 4.31 (qd, *J* = 10.8, 3.7 Hz, 2H), 2.47–2.34 (m, 2H), 2.30 (ddd, *J* = 12.0, 3.7, 3.7 Hz, 1H), 2.21–2.11 (m, 1H), 2.01 (s, 3H), 1.89 (br s, 1H), 1.21 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 215.5, 170.8, 70.3, 60.6, 50.6, 48.0, 38.8, 20.7, 13.0.
IR (neat, ATR): ν_{max} 3473, 2963, 2921, 2850, 1743, 1390, 1248, 993 cm^{-1}.
Optical Rotation: $[\alpha]_D^{21.4}$ 103.2 (*c* 0.50, $CHCl_3$).

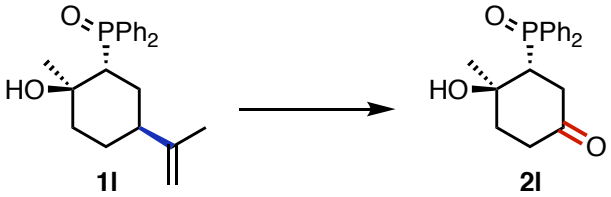
HRMS (DART): calc'd for $C_9H_{13}O_3$ $[M - OH]^+$ *m/z* 169.0859, found 169.0857.
***R*f** = 0.33 (50% EtOAc/hexanes).
Purification: FCC (SiO_2, 30 → 40% EtOAc/hexanes).
Note: After stirring for 1 h, another portion of MMPP (0.5 equiv) was added and the mixture stirred for an additional 1 h (3.0 equiv MMPP total, 2 h total reaction time).



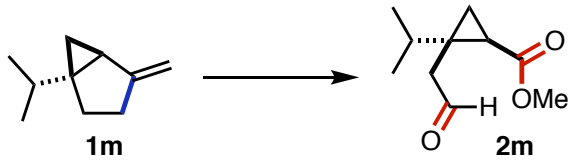
*1.0 mmol scale reaction
Yield: 50% (71 mg).
Physical State: colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.60 (ddd, J = 6.5, 6.5, 6.5 Hz, 1H), 3.25 (ddd, *J* = 8.6, 8.6, 6.2 Hz, 1H), 2.74–2.58 (m, 2H), 2.56 (br s, 1H), 2.44 (dd, *J* = 18.8, 8.7 Hz, 1H), 2.37–2.27 (m, 1H), 2.31 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 212.4, 208.1, 70.8, 56.4, 46.6, 39.3, 30.0.
IR (neat, ATR): ν_{max} 3423, 2918, 2854, 1743, 1704, 1542, 1368 cm^{-1}.
Optical Rotation: $[\alpha]_D^{21.5}$ –58.4 (*c* 0.50, $CHCl_3$).
HRMS (DART): calc'd for $C_7H_9O_2$ $[M - OH]^+$ *m/z* 125.0597, found 125.0594.
***R*f** = 0.58 (EtOAc).
Purification: FCC (SiO_2, 30 → 60% EtOAc/hexanes).



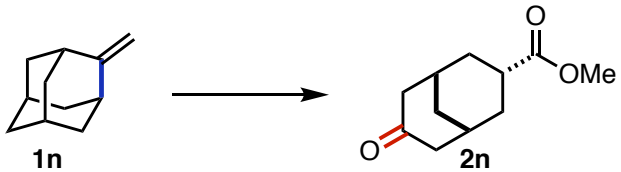
*1.0 mmol scale reaction
Yield: 60% (140 mg).
Physical State: colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88–7.79 (m, 2H), 7.65–7.51 (m, 3H), 3.05 (dd, *J* = 17.6, 17.6 Hz, 1H), 2.79–2.56 (m, 4H), 2.36 (pent, *J* = 7.1 Hz, 1H), 1.89 (dd, *J* = 15.4, 11.9 Hz, 1H), 1.07 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 213.4 (d, J_{CP} = 3.0 Hz), 132.5 (d, J_{CP} = 2.7 Hz), 131.9 (d, J_{CP} = 94.7 Hz), 130.5 (d, J_{CP} = 9.4 Hz), 129.1 (d, J_{CP} = 11.7 Hz), 55.2, 40.8 (d, J_{CP} = 66.3 Hz), 39.8 (d, J_{CP} = 12.2 Hz), 32.2 (d, J_{CP} = 6.5 Hz), 28.3 (d, J_{CP} = 63.9 Hz), 14.1 (d, J_{CP} = 13.7 Hz).
^{31}P NMR (202 MHz, $CDCl_3$): δ 51.9.
IR (neat, ATR): ν_{max} 3434, 2967, 2931, 1750, 1188, 1170, 1120 cm^{-1}.
Optical Rotation: $[\alpha]_D^{21.0}$ –7.4 (*c* 1.00, $CHCl_3$).
HRMS (ESI-TOF): calc'd for $C_{13}H_{16}O_2P$ $[M + H]^+$ *m/z* 235.0882, found 235.0874.
***R*f** = 0.40 (10% methanol/EtOAc).
Purification: FCC (SiO_2, 1 → 5% methanol/EtOAc).



*0.5 mmol scale reaction
Yield: 82% (134 mg).
Physical State: white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80–7.67 (m, 4H), 7.62–7.44 (m, 6H), 5.41 (s, 1H), 3.23 (ddd, *J* = 13.4, 13.4, 3.9 Hz, 1H), 2.52–2.40 (m, 2H), 2.39–2.20 (m, 2H), 2.10–1.99 (m, 2H), 1.53 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 207.5 (d, J_{CP} = 14.4 Hz), 132.6 (d, J_{CP} = 2.8 Hz), 132.5 (d, J_{CP} = 9.1 Hz), 132.4 (d, J_{CP} = 2.8 Hz), 132.3 (d, J_{CP} = 98.2 Hz), 130.7 (d, J_{CP} = 9.2 Hz), 129.2 (d, J_{CP} = 95.6 Hz), 129.1 (d, J_{CP} = 11.7 Hz), 128.7 (d, J_{CP} = 11.6 Hz), 71.9 (d, J_{CP} = 4.4 Hz), 45.6 (d, J_{CP} = 67.5 Hz), 41.3 (d, J_{CP} = 11.8 Hz), 40.3, 38.0, 23.5 (d, J_{CP} = 2.1 Hz).
^{31}P NMR (202 MHz, $CDCl_3$): δ 35.5.
MP: 232–233 ˚C.
IR (neat, ATR): ν_{max} 3342, 2995, 2971, 2918, 1712, 1443, 1163 cm^{-1}.
Optical Rotation: $[\alpha]_D^{21.1}$ –42.9 (*c* 1.00, $CHCl_3$).
HRMS (ESI-TOF): calc'd for $C_{19}H_{22}O_3P$ $[M + H]^+$ *m/z* 329.1301, found 329.1297.
***R*$_f$** = 0.40 (EtOAc).
Purification: trituration (Et_2O).

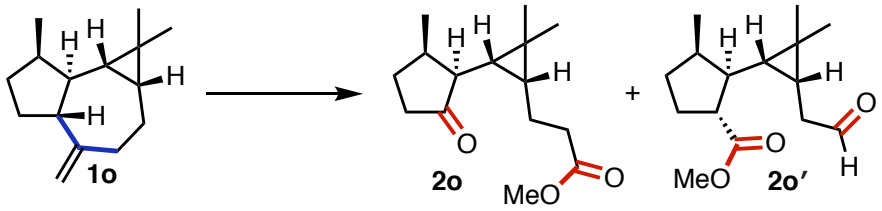


*1.0 mmol scale reaction
Yield: 58% (107 mg).
Physical State: colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.64 (dd, *J* = 2.1, 2.1 Hz, 1H), 3.66 (s, 3H), 2.73 (dd, *J* = 17.6, 2.0 Hz, 1H), 2.58 (dd, *J* = 17.6, 1.9 Hz, 1H), 1.68 (dd, *J* = 8.4, 5.6 Hz, 1H), 1.23–1.12 (m, 2H), 1.07 (dd, *J* = 8.3, 4.8 Hz, 1H), 0.92 (d, *J* = 3.9 Hz, 3H), 0.90 (d, *J* = 3.9 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 202.4, 173.2, 51.9, 41.6, 36.6, 31.3, 24.3, 20.3, 19.6, 19.5.
IR (neat, ATR): ν_{max} 2963, 2882, 1725, 1712, 1446, 1393, 1199, 1174 cm^{-1}.
HRMS (DART): calc'd for $C_{10}H_{17}O_3$ $[M + H]^+$ *m/z* 185.1172, found 185.1169.
***R*$_f$** = 0.42 (10% EtOAc/hexanes).
Purification: FCC (SiO_2, 2 → 5% EtOAc/hexanes).

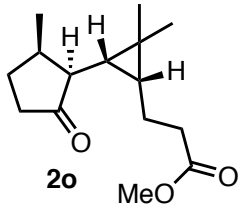


*1.0 mmol scale reaction
Yield: 87% (171 mg).
Physical State: white solid.

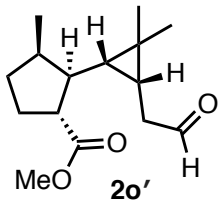
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.65 (s, 3H), 2.62 (t, *J* = 7.3 Hz, 1H), 2.54–2.32 (m, 8H), 1.95–1.73 (m, 4H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 212.2, 175.2, 52.5, 46.8, 35.0, 32.2, 31.0, 29.0.
***R*$_f$** = 0.36 (30% EtOAc/hexanes).
Purification: FCC (SiO_2, 10 → 20% EtOAc/hexanes).
All characterization data were consistent with those reported in the literature.[21]



*1.0 mmol scale reaction
Combined Yield: 82% (206 mg).
Regioisomeric Ratio: 1.3:1 (**2o**/**2o′**, determined from crude ^{1}H NMR spectrum).
Note: After stirring for 1 h, another portion of MMPP (0.5 equiv) was added and the mixture stirred for an additional 1 h (3.0 equiv MMPP total, 2 h total reaction time).

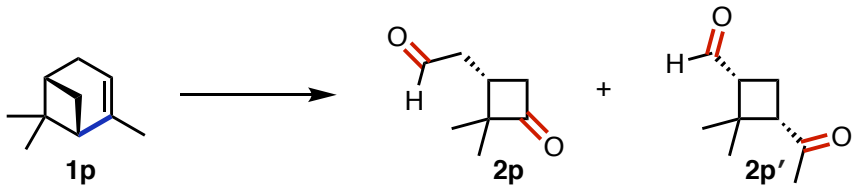


Yield: 45% (114 mg).
Physical State: colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.65 (s, 3H), 2.51 (ddd, *J* = 15.7, 9.9, 5.8 Hz, 1H), 2.50–2.42 (m, 1H), 2.38 (ddd, *J* = 15.9, 9.7, 6.3 Hz, 1H), 2.26–2.18 (m, 2H), 2.06–1.98 (m, 1H), 1.96 (dd, *J* = 10.9, 7.6 Hz, 1H), 1.78–1.65 (m, 2H), 1.58 (dddd, *J* = 14.1, 9.7, 7.5, 6.6 Hz, 1H), 1.06 (s, 3H), 0.96 (s, 3H), 0.96 (d, *J* = 6.4 Hz, 3H), 0.68 (ddd, *J* = 8.8, 7.3, 7.3 Hz, 1H), 0.46 (dd, *J* = 10.8, 9.2 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 221.1, 174.3, 51.5, 50.9, 34.7, 34.1, 33.7, 28.9, 28.0, 26.3, 23.9, 21.0, 17.1, 16.0, 15.8.
IR (neat, ATR): ν_{max} 2963, 2928, 2875, 1733, 1460, 1174, 1146 cm^{-1}.
Optical Rotation: $[\alpha]_D^{21.9}$ –36.5 (*c* 0.20, $CHCl_3$).
HRMS (ESI-TOF): calc'd for $C_{15}H_{24}O_3Na$ $[M + Na]^+$ *m*/*z* 275.1618, found 275.1672.
***R*$_f$** = 0.26 (10% EtOAc/hexanes).
Purification: FCC (SiO_2, 2 → 5% EtOAc/hexanes).



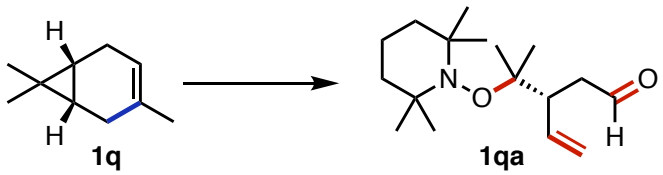
Yield: 37% (92 mg).

Physical State: colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.77 (dd, *J* = 1.4, 1.4 Hz, 1H), 3.64 (s, 3H), 2.61 (ddd, *J* = 9.1, 7.1, 7.1 Hz, 1H), 2.45 (ddd, *J* = 18.5, 6.5, 1.4 Hz, 1H), 2.31 (ddd, *J* = 18.5, 7.8, 1.4 Hz, 1H), 2.18 (sept, *J* = 7.0 Hz, 1H), 2.02 (dddd, *J* = 12.8, 8.9, 8.9, 5.0 Hz, 1H), 1.93–1.84 (m, 2H), 1.76 (*J* = 13.0, 8.9, 7.3, 7.3 Hz, 1H), 1.37 (dddd, *J* = 12.6, 8.2, 7.0, 7.0 Hz, 1H), 1.10 (s, 3H), 0.94 (s, 3H), 0.92 (d, *J* = 7.1 Hz, 3H), 0.92–0.87 (m, 1H), 0.56 (dd, *J* = 11.4, 9.0 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 202.4, 177.4, 51.7, 49.7, 44.0, 40.3, 36.7, 33.2, 28.7, 28.7, 28.6, 19.7, 18.2, 16.2, 16.1.
IR (neat, ATR): ν_{max} 2956, 2931, 2872, 1733, 1712, 1457, 1432, 1372, 1205, 1163 cm^{-1}.
Optical Rotation: $[\alpha]_D^{21.7}$ –16.4 (*c* 0.50, $CHCl_3$).
HRMS (ESI-TOF): calc'd for $C_{15}H_{24}O_3Na$ $[M + Na]^+$ *m/z* 275.1618, found 275.1660.
***R*$_f$** = 0.37 (10% EtOAc/hexanes).
Purification: FCC (SiO_2, 2 → 5% EtOAc/hexanes).

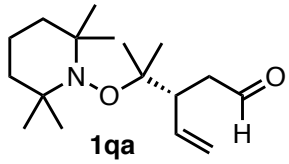


*2.0 mmol scale reaction
Yield: 67% (190 mg).
Regioisomeric Ratio: 5:1 (**2p**/**2p′**, inseparable mixture).
Physical State: colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) 2p: δ 9.84 (s, 1H), 3.27 (dd, *J* = 17.7, 9.2 Hz, 1H), 2.83–2.65 (m, 3H), 2.59–2.50 (m, 1H), 1.25 (s, 3H), 1.05 (s, 3H).
^{1}H NMR (500 MHz, $CDCl_3$) 2p′: δ 9.70 (d, *J* = 1.9 Hz, 1H), 2.99–2.94 (m, 1H), 2.81–2.64 (m, 2H), 2.06 (s, 3H), 1.90–1.84 (m, 1H), 1.49 (s, 3H), 0.99 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) 2p: δ 213.7, 200.6, 61.3, 48.4, 45.5, 30.2, 23.3, 17.5.
^{13}C NMR (125 MHz, $CDCl_3$) 2p′: δ 206.9, 203.1, 53.3, 51.7, 31.2, 30.2, 18.7, 16.9.
IR (neat, ATR): ν_{max} 2967, 2935, 2872, 1775, 1722, 1464, 1383, 1071 cm^{-1}.
Optical Rotation: $[\alpha]_D^{20.0}$ 3.8 (*c* 1.00, $CHCl_3$).
HRMS (DART): calc'd for $C_8H_{13}O_2$ $[M + H]^+$ *m/z* 141.0910, found 141.0907; calc'd for $C_9H_{15}O_2$ $[M + H]^+$ *m/z* 155.1067, found 155.1063.
***R*$_f$** = 0.34 (20% EtOAc/hexanes).
Purification: FCC (SiO_2, 5 → 20% EtOAc/hexanes).
Note: Extraction performed with CH_2Cl_2. Approximately 50 mg of the ester **4** (characterization data are provided in Section 7) was also obtained from the reaction.

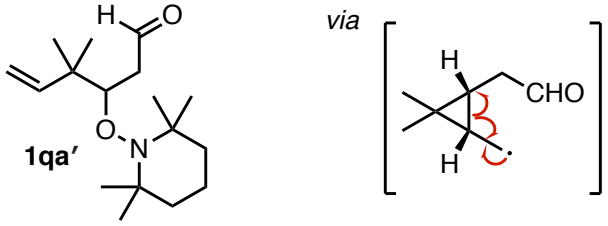
5. Cyclopropylcarbinyl Ring-Opening with 1q



The *O*-alkyl TEMPO adduct **1qa** was synthesized by following the General Procedure found in Section 4.1. After the addition of TEMPO and aqueous ferrous sulfate, the mixture was allowed to warm until the reaction temperature reached 0 ˚C. The reaction was quenched through the addition of 10% saturated aqueous sodium thiosulfate and saturated aqueous sodium bicarbonate. After warming to room temperature, the MeOH/water layer was extracted with EtOAc (3x), washed with brine, dried (anhydrous sodium sulfate), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (SiO_2) provided the pure product **1qa**.

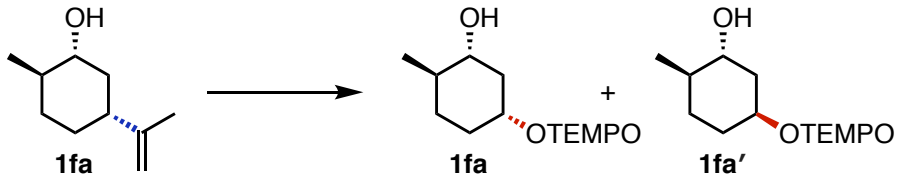


*1.0 mmol scale reaction
Yield: 50% (140 mg).
Physical State: colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.72 (dd, *J* = 3.3, 1.4 Hz, 1H), 5.70 (ddd, *J* = 17.1, 10.3, 8.2 Hz, 1H), 5.13–5.02 (m, 2H), 3.12 (ddd, *J* = 10.8, 8.1, 2.9 Hz, 1H), 2.97 (ddd, *J* = 16.2, 3.1, 1.3 Hz, 1H), 2.41 (ddd, *J* = 16.2, 10.7, 3.4 Hz, 1H), 1.59–1.42 (m, 4H), 1.32–1.24 (m, 2H), 1.26 (s, 3H), 1.18 (s, 3H), 1.14 (s, 3H), 1.14 (s, 3H), 1.07 (s, 3H), 1.06 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 202.9, 138.4, 117.3, 79.6, 59.4, 59.3, 49.1, 43.2, 40.9, 40.8, 35.1, 34.9, 24.1, 23.7, 21.2, 20.6, 17.0.
IR (neat, ATR): ν_{max} 3081, 3006, 2978, 2935, 2875, 2712, 1729, 1468, 1379, 1368, 1127, 919 cm^{-1}.
Optical Rotation: $[\alpha]_D^{22.3}$ 14.3 (*c* 2.00, $CHCl_3$).
HRMS (DART): calc'd for $C_{17}H_{32}NO_2$ $[M + H]^+$ *m*/*z* 282.2428, found 282.2425.
***R*$_f$** = 0.39 (5% EtOAc/hexanes).
Purification: FCC (SiO_2, 3 → 5% EtOAc/hexanes).
Note: An additional product (R_f = 0.30, 5% EtOAc/hexanes) was also formed in this reaction. We presume it was **1qa′**, based on LCMS analysis of the mixture (1.5:1 **1qa**/**1qa′**). Nevertheless, this compound was extremely unstable and decomposed upon attempts at purification.

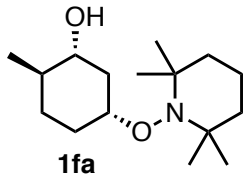


6. Reductive Cleavage of N–O bond of 1fa

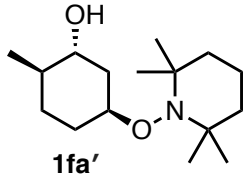
The *O*-alkyl TEMPO adducts **1fa**/**1fa′** were synthesized by following the General Procedure found in Section 4.1. After the addition of TEMPO and aqueous ferrous sulfate, the mixture was allowed to warm until its reaction temperature reached 0 ˚C. The reaction was quenched through the addition of 10% saturated aqueous sodium thiosulfate and saturated aqueous sodium bicarbonate. After warming to room temperature, the MeOH/water layer was extracted with dichloromethane (3×), washed with brine, dried (anhydrous sodium sulfate), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (SiO_2) provided the pure products **1fa** and **1fa′** (1.8:1 *d.r.*).



*0.65 mmol scale reaction
Combined Yield: 92% (161 mg).
Regioisomeric Ratio: 1.8:1 (**1fa**/**1fa′**, determined from crude ^{1}H NMR spectrum).

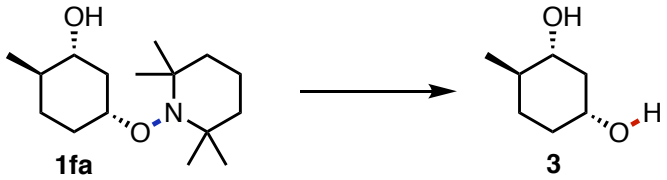


Yield: 59% (103 mg).
Physical State: colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.65 (dddd, *J* = 11.0, 11.0, 4.0, 4.0 Hz, 1H), 3.10 (ddd, *J* = 10.4, 9.9, 3.9 Hz, 1H), 2.48–2.40 (m, 1H), 2.11–2.02 (m, 1H), 1.76 (br s, 1H), 1.71 (dddd, *J* = 13.8, 3.8, 3.8, 3.8 Hz, 1H), 1.65–0.82 (m, 22H), 0.98 (d, *J* = 6.5 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 80.3, 74.7, 59.6, 41.4, 40.1, 39.3, 34.3, 31.8, 29.9, 20.2, 17.8, 17.2.
IR (neat, ATR): ν_{max} 3367, 2974, 2931, 2875, 1457, 1375, 1354, 1135, 1004, 989 cm^{-1}.
Optical Rotation: $[\alpha]_D^{21.2}$ –3.5 (*c* 1.00, $CHCl_3$).
HRMS (ESI-TOF): calc'd for $C_{16}H_{32}NO_2$ $[M + H]^+$ *m*/*z* 270.2428, found 270.2393.
***R*$_f$** = 0.54 (20% EtOAc/hexanes).
Purification: FCC (SiO_2, 5 → 10% EtOAc/hexanes).
Note: 2D NMR experimental data were consistent with the proposed structural assignment of the product.



Yield: 33% (58 mg).

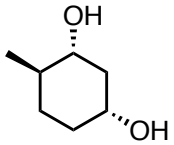
Physical State: white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.09–4.01 (m, 1H), 3.59–3.49 (m, 1H), 2.34–2.24 (m, 1H), 2.02–1.94 (m, 1H), 1.67–1.02 (m, 24H), 1.04 (d, J = 5.7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 79.6, 72.9, 59.6, 40.2, 39.4, 39.3, 34.1, 29.6, 28.1, 20.1, 18.2, 17.0.
MP: 74–75 ˚C.
IR (neat, ATR): ν_{max} 3374, 3003, 2978, 2931, 2872, 1457, 1375, 1358, 1131, 1064, 1032, 986, 756 cm^{-1}.
Optical Rotation: $[\alpha]_D^{21.8}$ –0.4 (*c* 0.50, $CHCl_3$).
HRMS (ESI-TOF): calc'd for $C_{16}H_{32}NO_2$ $[M + H]^+$ *m*/*z* 270.2428, found 270.2398.
***R*$_f$** = 0.47 (20% EtOAc/hexanes).
Purification: FCC (SiO_2, 5 → 10% EtOAc/hexanes).
Note: 2D NMR experimental data were consistent with the proposed structural assignment of the product.



1fa **3**

The diol **3** was synthesized by following a procedure adapted from the literature.[22]

A vial equipped with a magnetic stirrer bar was charged with *O*-alkyl TEMPO adduct **1fa** (54 mg, 0.2 mmol, 1.0 equiv) and acetic acid/THF (1.2:1, 0.1 M). Activated zinc dust (512 mg, 8.0 mmol, 40.0 equiv) was added and the mixture was heated to 50 ˚C. Upon completion of the reaction (as indicated by TLC, 3 h), the mixture was cooled to room temperature and diluted with diethyl ether. The solution was filtered through a plug of silica, which was subsequently washed with EtOAc. The combined organic fractions were concentrated under reduced pressure. Purification by flash column chromatography (SiO_2) provided the pure product **3**.



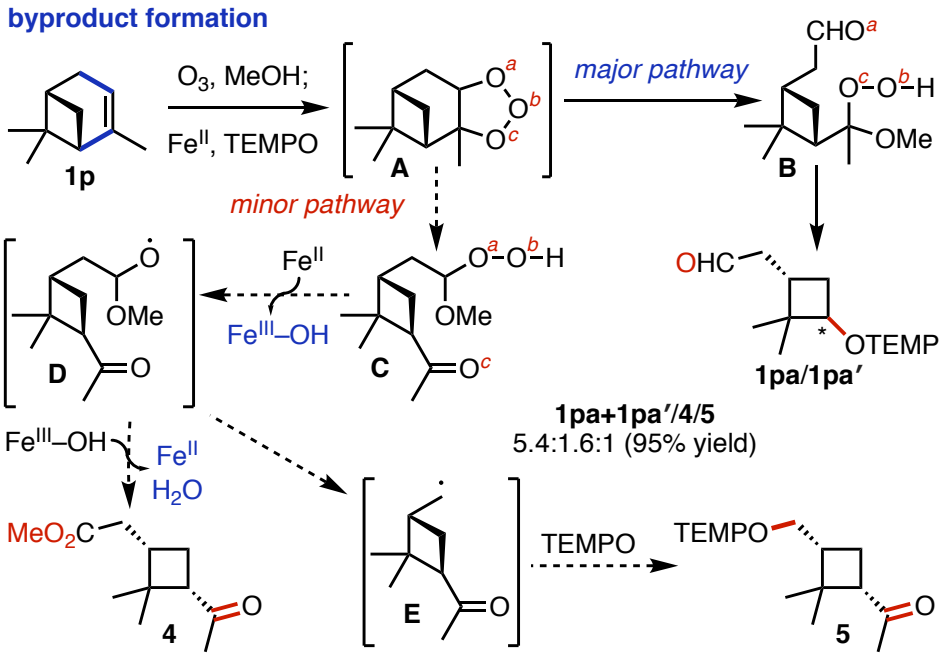
3

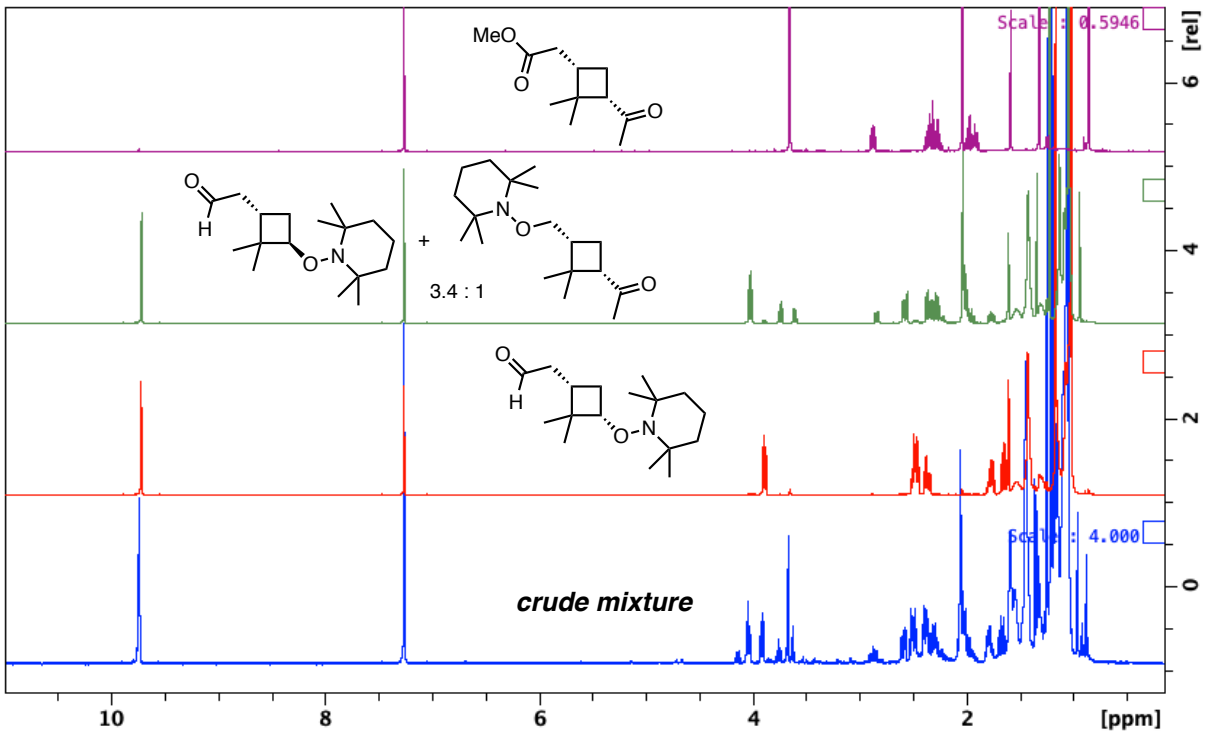
*0.2 mmol scale reaction
Yield: 92% (24 mg).
Physical State: colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.68 (dddd, J = 10.4, 10.4, 4.2, 4.2 Hz, 1H), 3.21 (ddd, J = 9.8, 9.8, 3.9 Hz, 1H), 2.28–2.20 (m, 1H), 1.95–1.87 (m, 1H), 1.76 (dddd, J = 13.8, 4.0, 4.0, 4.0 Hz, 1H), 1.41–1.24 (m, 3H), 1.06–0.95 (m, 1H), 1.01 (d, J = 6.5 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 74.1, 69.1, 43.5, 38.9, 34.4, 29.0, 17.7.
IR (neat, ATR): ν_{max} 3357, 2935, 2907, 2868, 1457, 1364, 1014 cm^{-1}.
Optical Rotation: $[\alpha]_D^{22.0}$ –15.5 (*c* 0.20, $CHCl_3$).
HRMS (DART): calc'd for $C_7H_{14}O_2Na$ $[M + H]^+$ *m*/*z* 153.0886, found 153.0907.
***R*$_f$** = 0.21 (75% EtOAc/hexanes).

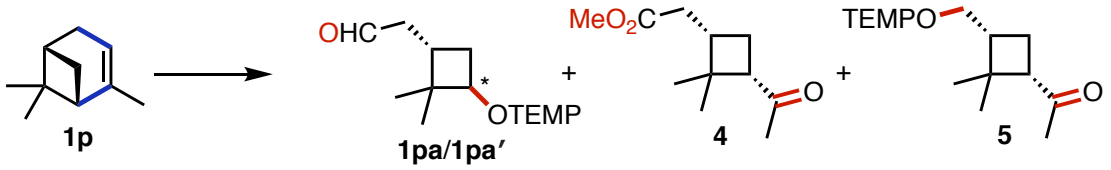
Purification: FCC (SiO_2, 50 $\rightarrow$ 75% EtOAc/hexanes).

7. Byproduct Formation with 1p

Typically, we have found that the combination of Criegee ozonolysis and SET-based fragmentation reactions and subsequent trapping of the alkyl radical intermediate converted the terpenoid starting materials cleanly to their desired products. Nevertheless, in some cases (primarily when employing cycloalkenes) side products were also observed. To investigate the pathways leading to these side products, all of the detectable products were isolated from the reaction of (+)-*α*-pinene (**1p**). Based on NMR spectroscopic and mass spectrometric analyses, the products produced were determined to be the *O*-alkyl TEMPO adducts **1pa** and **1pa′**, the ketoester **4**, and the *O*-alkyl TEMPO adduct **5** (**1pa**+**1pa′**/**4**/**5**, 5.4:1.6:1). These products arose through two possible molozonide (**A**) fragmentation pathways.[23] In the major pathway, the tertiary *α*-alkoxy hydroperoxide **B** is generated. When treated with a ferrous species, the resulting alkoxy radical can undergo *β*-scission smoothly to give the desired *O*-alkyl TEMPO adducts **1pa** and **1pa′** (which upon oxidation provides the carbonyl product **2p**). In the minor pathway, the secondary *α*-alkoxy hydroperoxide **C** is generated. SET-based reduction of the O–O bond provides the alkoxy radical **D**. Subsequent Fe(III)-catalyzed dehydration converts this reactive intermediate to the ketoester **4**.[24] Alternatively, *β*-fragmentation of the alkoxy radical **D** and subsequent trapping of the alkyl radical **E** gives the *O*-alkyl TEMPO adduct **5** (which, upon oxidation, gives the product **2p′**).



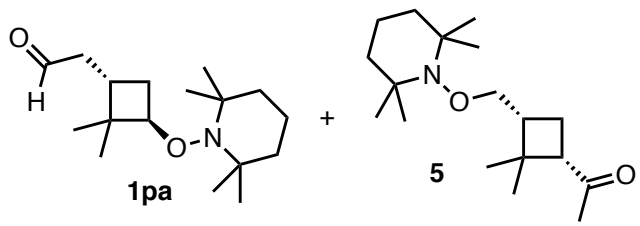




*1.0 mmol scale reaction

Combined Yield: 95% (252 mg).

Regioisomeric Ratio: 5.4:1.6:1.0 (**1pa**+**1pa′**/**4**/**5**, determined from crude ^{1}H NMR spectrum).



Physical State: colorless oil.

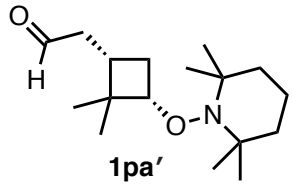
^{1}H NMR (500 MHz, $CDCl_3$) 1pa: δ 9.72 (dd, *J* = 1.9, 1.9 Hz, 1H), 4.06–3.99 (m, 1H), 2.57 (ddd, *J* = 16.4, 6.0, 1.5 Hz, 1H), 2.35 (ddd, *J* = 16.7, 9.5, 2.1 Hz, 1H), 2.32–2.24 (m, 1H), 2.06–1.92 (m, 2H), 1.58–1.00 (m, 18H), 1.22 (s, 3H), 1.04 (s, 3H).

^{1}H NMR (500 MHz, $CDCl_3$) 5: δ 3.74 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.61 (dd, *J* = 9.3, 5.9 Hz, 1H), 2.84 (dd, *J* = 10.3, 7.4 Hz, 1H), 2.24 (dddd, *J* = 8.4, 8.4, 2.5, 2.5 Hz, 1H), 2.04 (s, 3H), 1.77 (ddd, *J* = 11.4, 7.8, 7.8 Hz, 1H), 1.58–1.00 (m, 19H) 1.34 (s, 3H), 0.94 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) 1pa: δ 202.6, 85.1, 60.1, 58.5, 46.2, 44.2, 39.9, 34.5, 34.0, 33.2, 30.9, 24.0, 23.2, 20.2, 17.3.

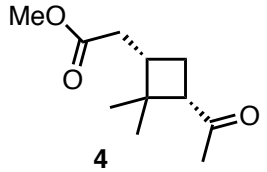
^{13}C NMR (125 MHz, $CDCl_3$) 5: δ 208.1, 77.4, 59.7, 59.5, 54.1, 43.1, 40.7, 39.6, 39.5, 33.4, 32.8, 31.0, 30.1, 20.0, 19.9, 19.8, 17.4, 17.1.

IR (neat, ATR): ν_{max} 2967, 2935, 2872, 2716, 1725, 1708, 1468, 1372, 1358, 1138, 1089, 1036 cm^{-1}.
Optical Rotation: $[\alpha]_D^{21.9}$ –20.6 (*c* 0.50, $CHCl_3$).
HRMS (ESI-TOF): calc'd for $C_{17}H_{32}NO_2$ $[M + H]^+$ *m*/*z* 282.2428, found 282.2408; calc'd for $C_{18}H_{34}NO_2$ $[M + H]^+$ 296.2584, found 296.2562.
R_f = 0.41 (10% EtOAc/hexanes).
Purification: FCC (SiO_2, 5% EtOAc/hexanes).
Note: It was not possible to fully separate the products **1pa** and **5**. The NMR spectra are provided for a mixture of **1pa**/**5** (3.4:1). All characterization data were collected from this mixture. 2D NMR spectroscopic experiments were consistent with the proposed structural assignments of the products.



1pa′

Physical State: colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.72 (dd, *J* = 2.1, 2.1 Hz, 1H), 3.89 (dd, *J* = 8.8, 7.1 Hz, 1H), 2.54–2.43 (m, 2H), 2.36 (ddd, *J* = 16.5, 8.0, 1.8 Hz, 1H), 1.77 (dddd, *J* = 10.6, 7.4, 7.4, 7.4 Hz, 1H), 1.65 (ddd, *J* = 10.6, 10.6, 9.0 Hz, 1H), 1.58–1.23 (m, 6H), 1.20–0.98 (m, 12H), 1.17 (s, 3H), 1.02 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 202.2, 85.2, 60.1, 58.5, 45.9, 44.9, 39.9, 35.6, 34.0, 33.2, 30.5, 28.8, 20.1, 17.3, 16.4.
IR (neat, ATR): ν_{max} 2999, 2967, 2935, 2875, 2719, 1729, 1471, 1379, 1362, 1135, 1039 cm^{-1}.
Optical Rotation: $[\alpha]_D^{22.1}$ 9.0 (*c* 0.20, $CHCl_3$).
HRMS (ESI-TOF): calc'd for $C_{17}H_{32}NO_2$ $[M + H]^+$ *m*/*z* 282.2428, found 282.2433.
R_f = 0.50 (10% EtOAc/hexanes).
Purification: FCC (SiO_2, 5% EtOAc/hexanes).
Note: 2D NMR spectroscopic data were consistent with the proposed structural assignment of the product.

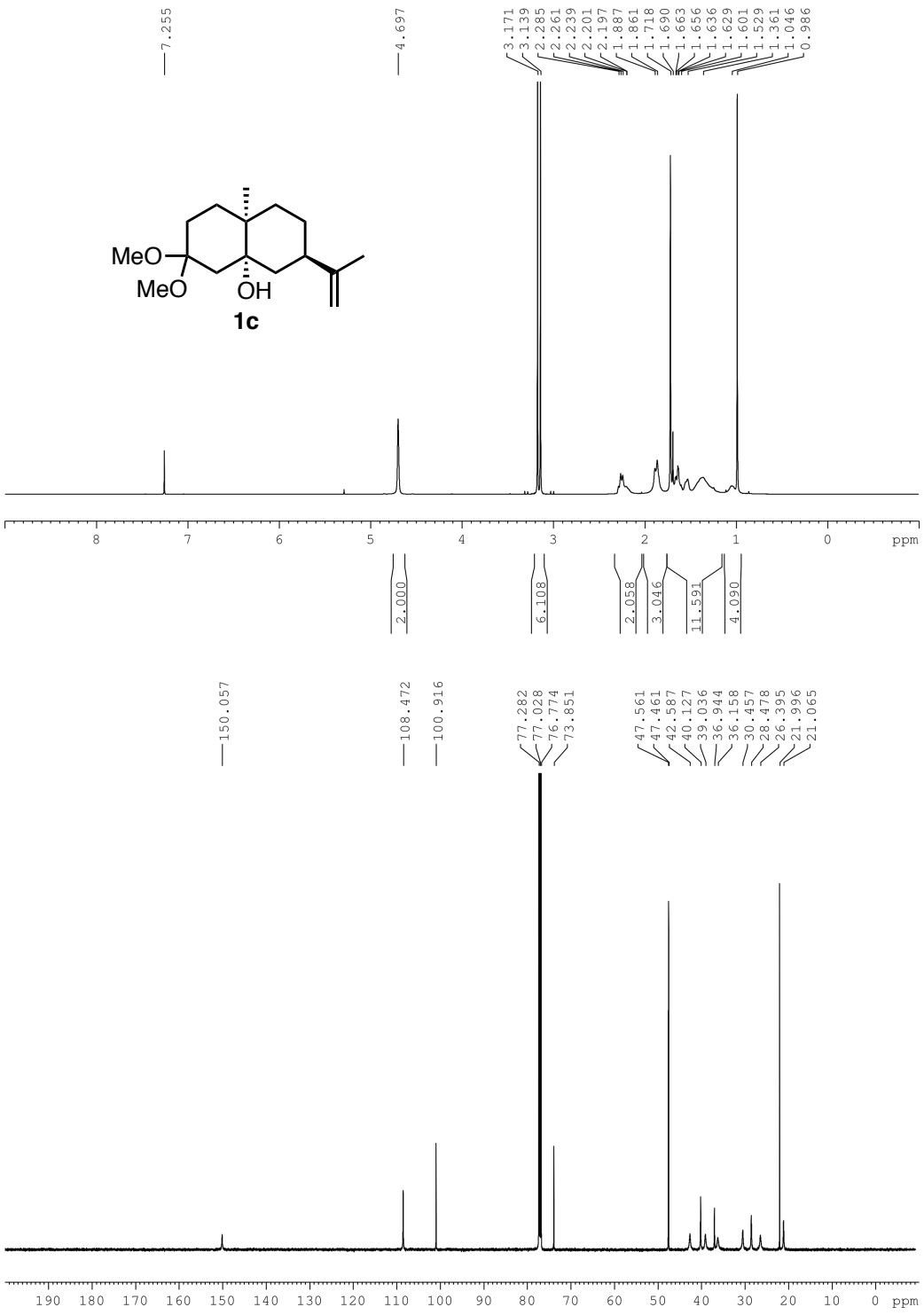


4

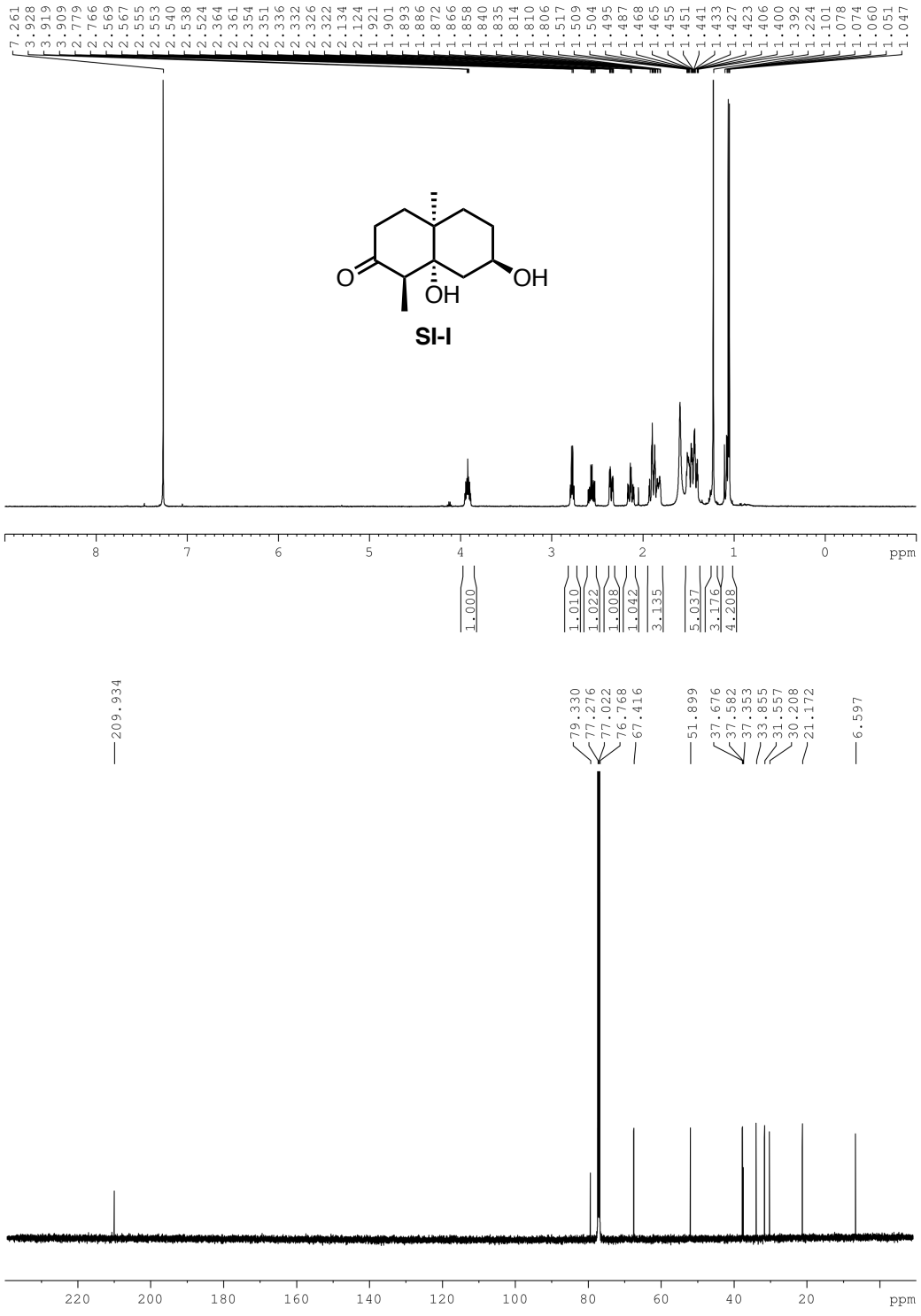
Physical State: colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.65 (s, 3H), 2.88 (dd, *J* = 10.2, 7.6 Hz, 1H), 2.41–2.22 (m, 3H), 2.04 (s, 3H), 2.02–1.93 (m, 1H), 1.91 (ddd, *J* = 11.4, 7.8, 7.8 Hz, 1H), 1.32 (s, 3H), 0.86 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 207.6, 173.2, 54.2, 51.5, 43.3, 38.0, 34.9, 30.2, 30.2, 23.0, 17.3.
IR (neat, ATR): ν_{max} 2999, 2960, 2950, 2907, 2878, 1743, 1704, 1174 cm^{-1}.
Optical Rotation: $[\alpha]_D^{22.1}$ 14.0 (*c* 0.20, $CHCl_3$).
HRMS (DART): calc'd for $C_{11}H_{19}NO_3$ $[M + H]^+$ *m*/*z* 199.1329, found 199.1325.
R_f = 0.21 (10% EtOAc/hexanes).
Purification: FCC (SiO_2, 5% EtOAc/hexanes).

Note: 2D NMR spectroscopic data were consistent with the proposed structural assignment of the product.

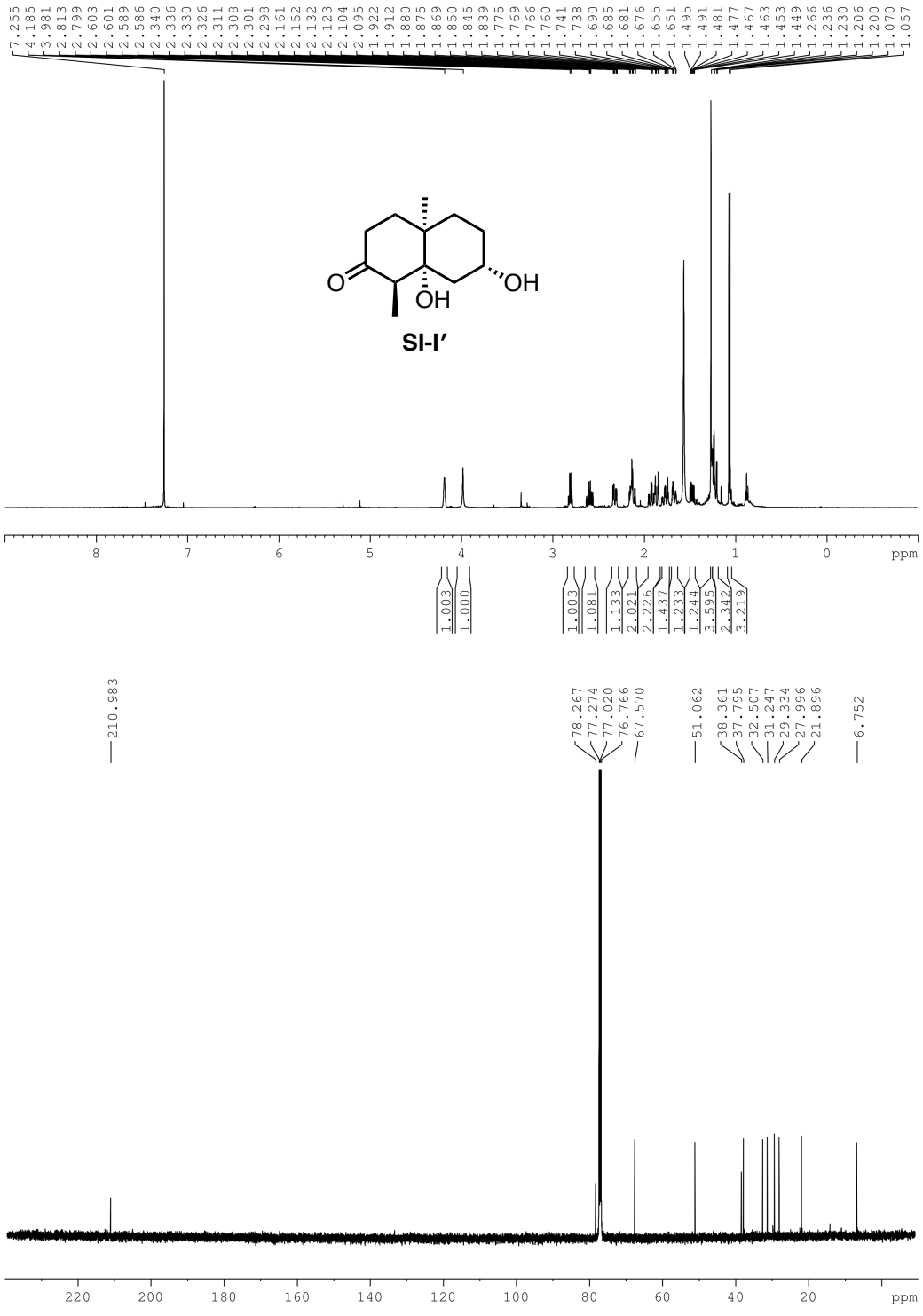
8. Copies of ^{1}H, ^{13}C, and ^{31}P NMR Spectra



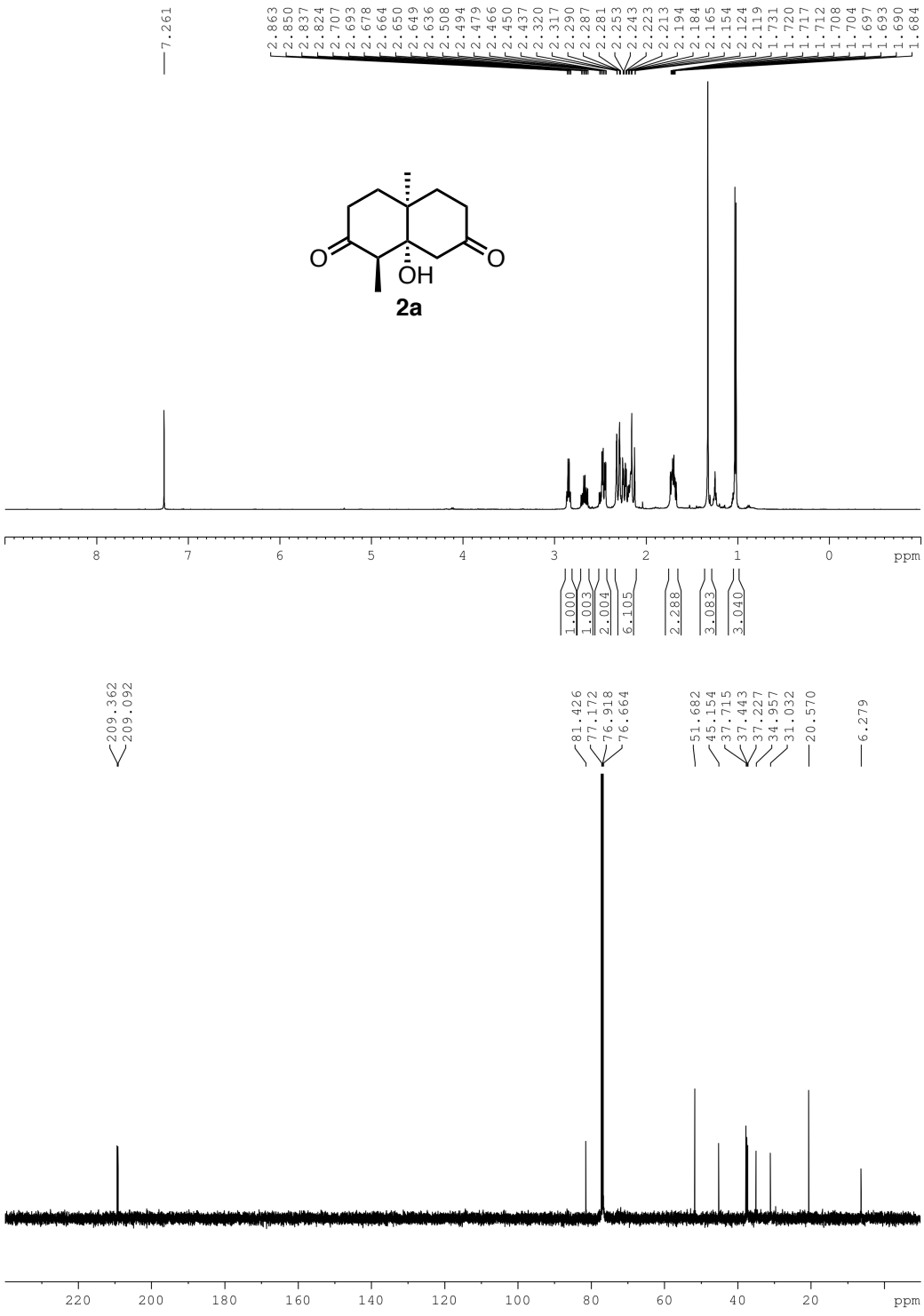
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **1c**



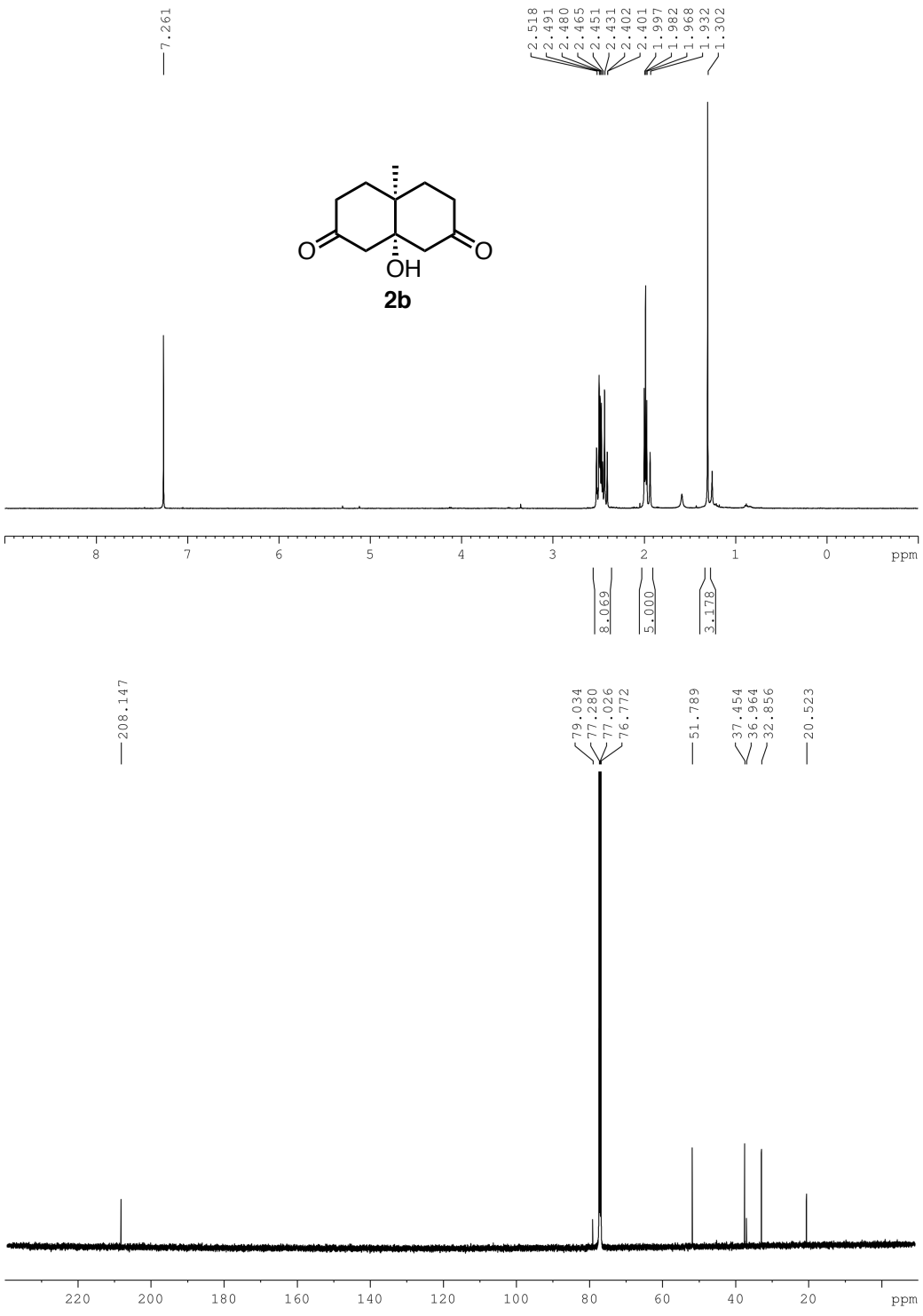
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **SI-I**



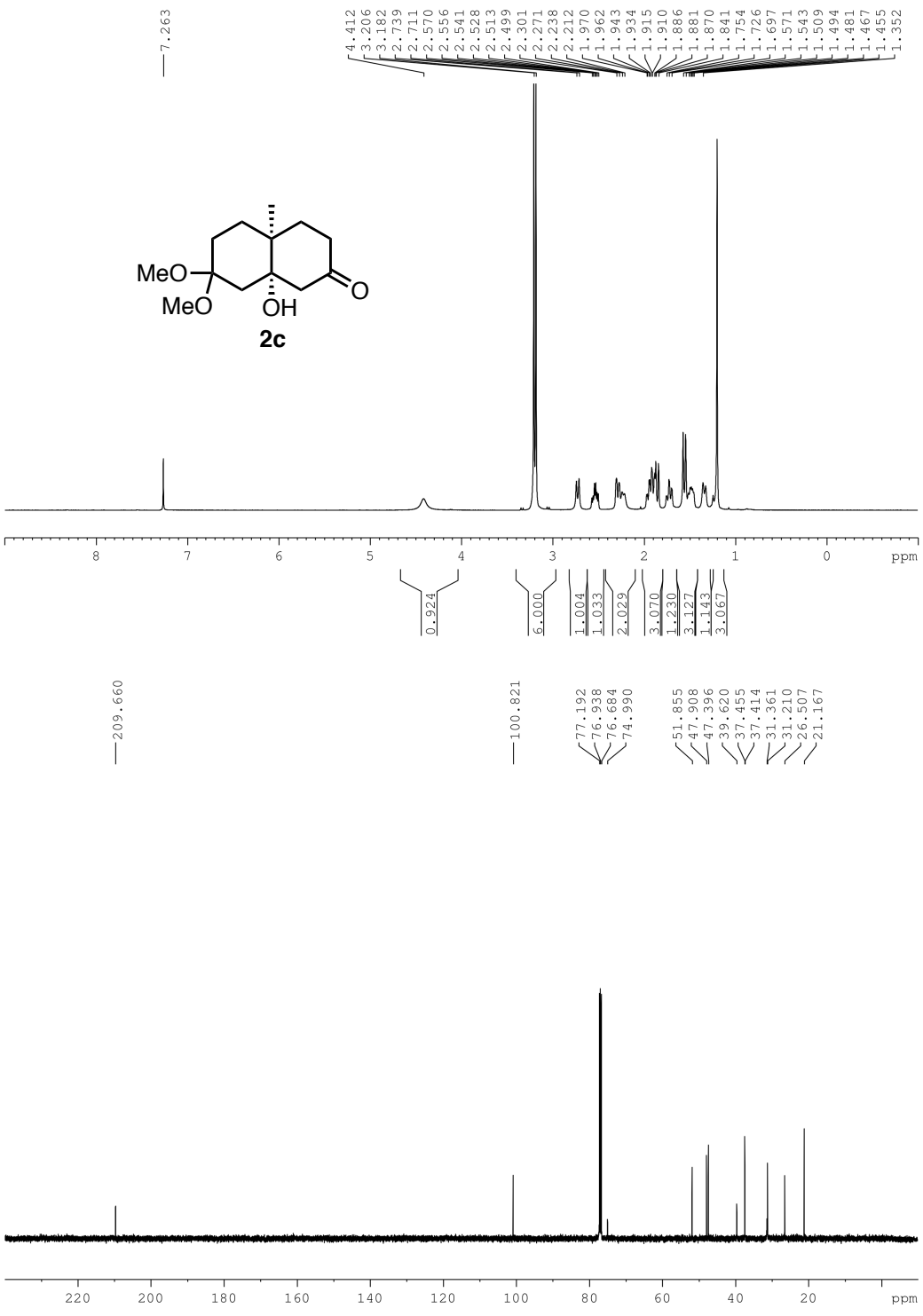
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **SI-I′**



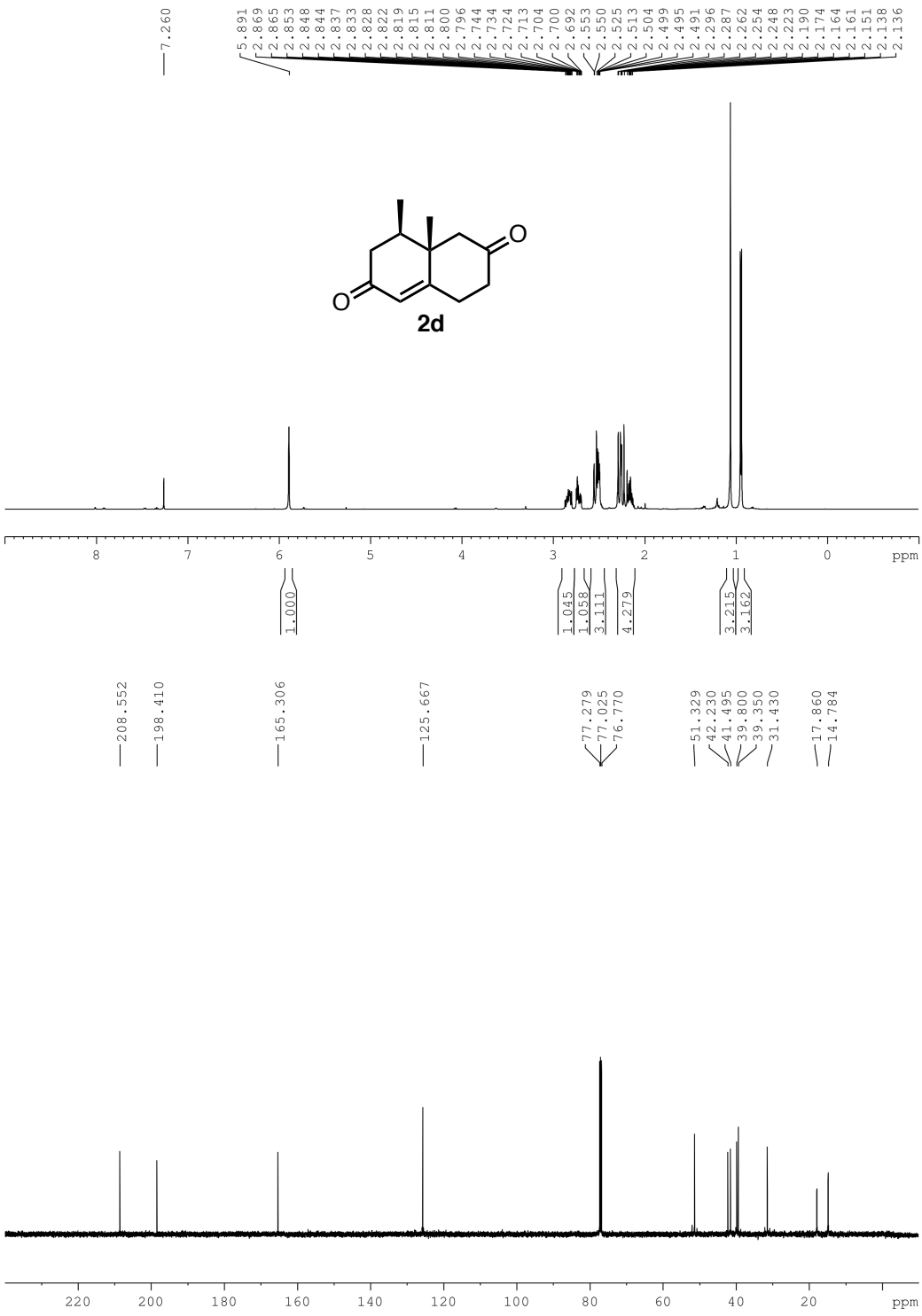
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **2a**



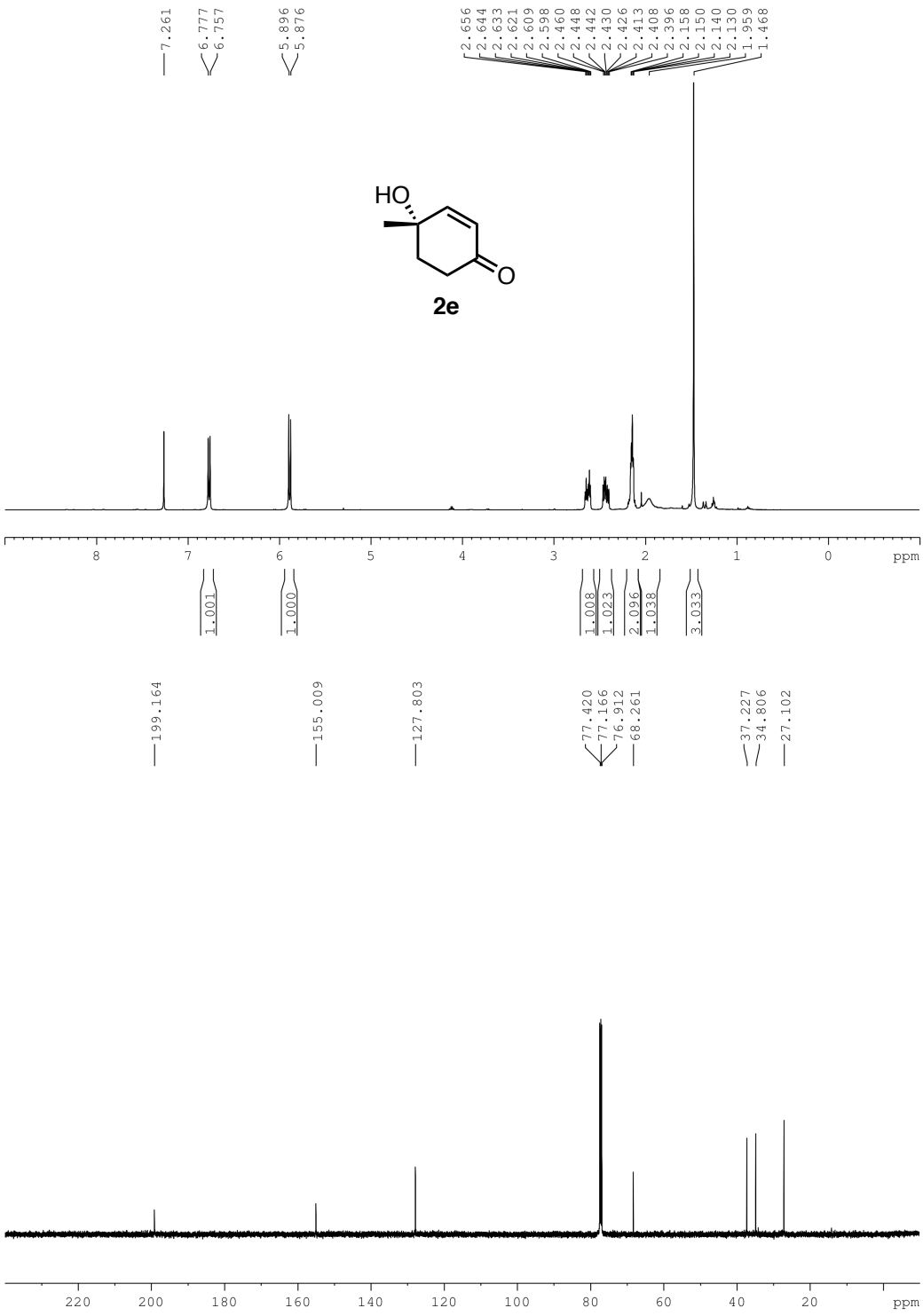
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **2b**



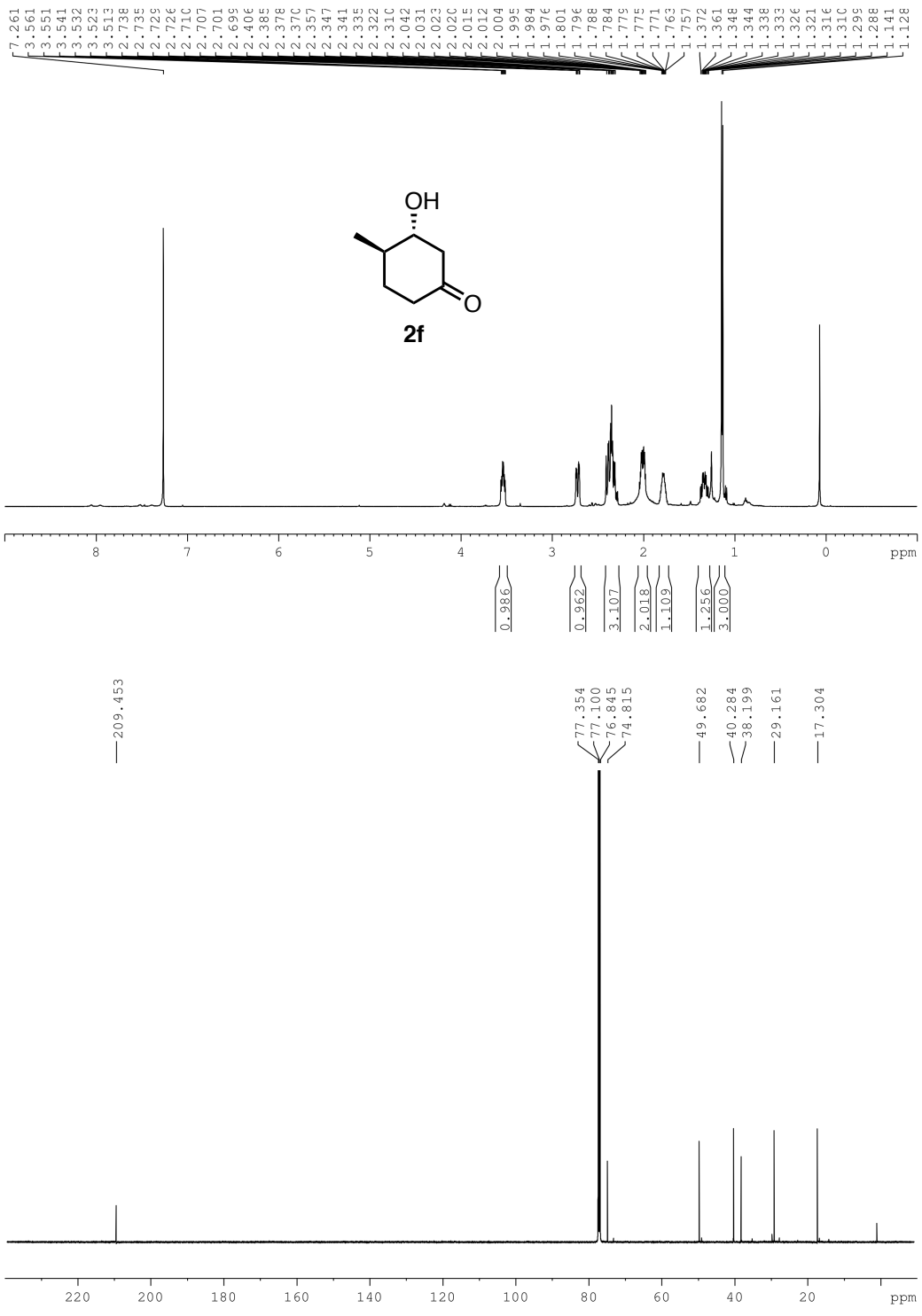
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **2c**



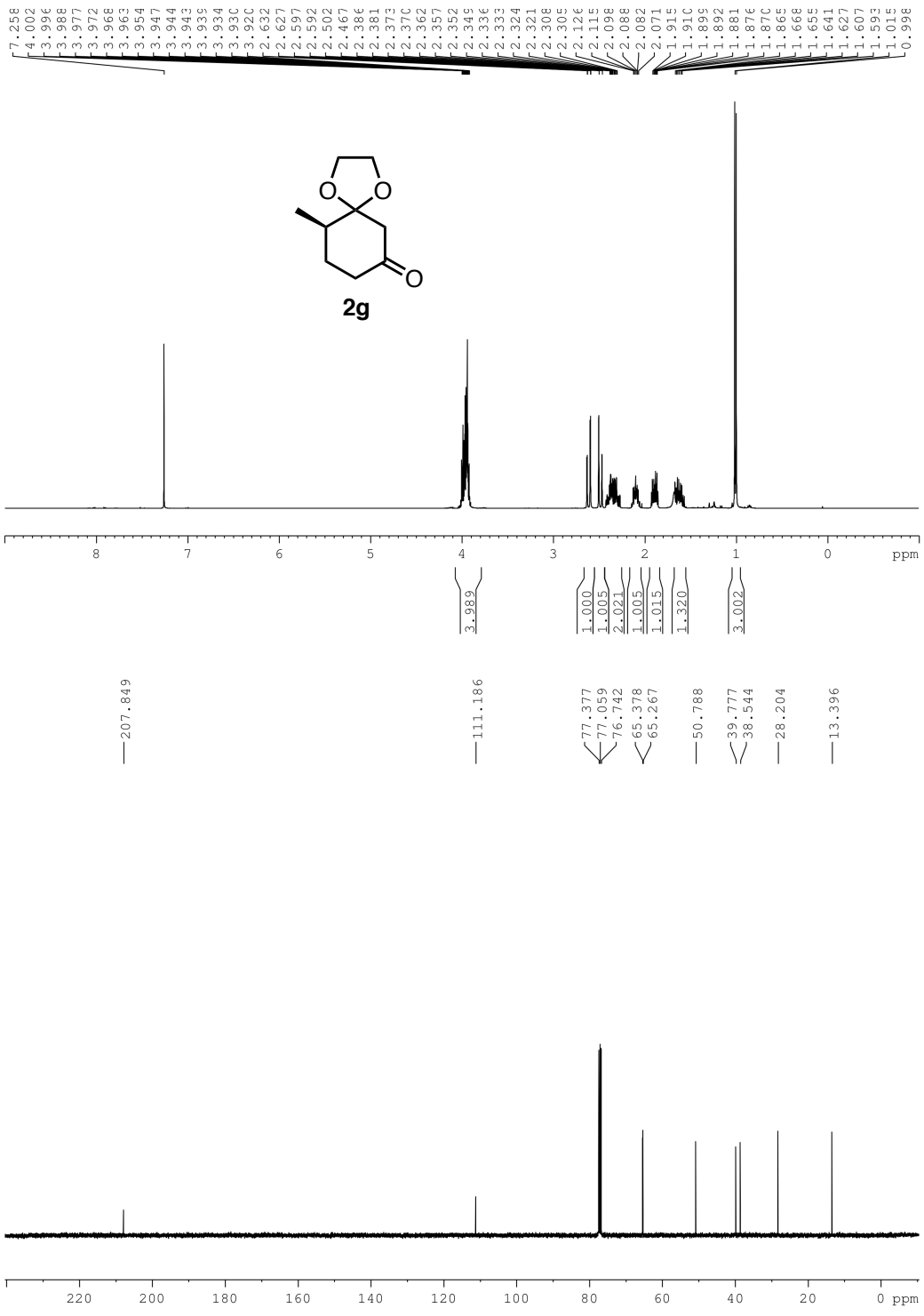
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **2d**



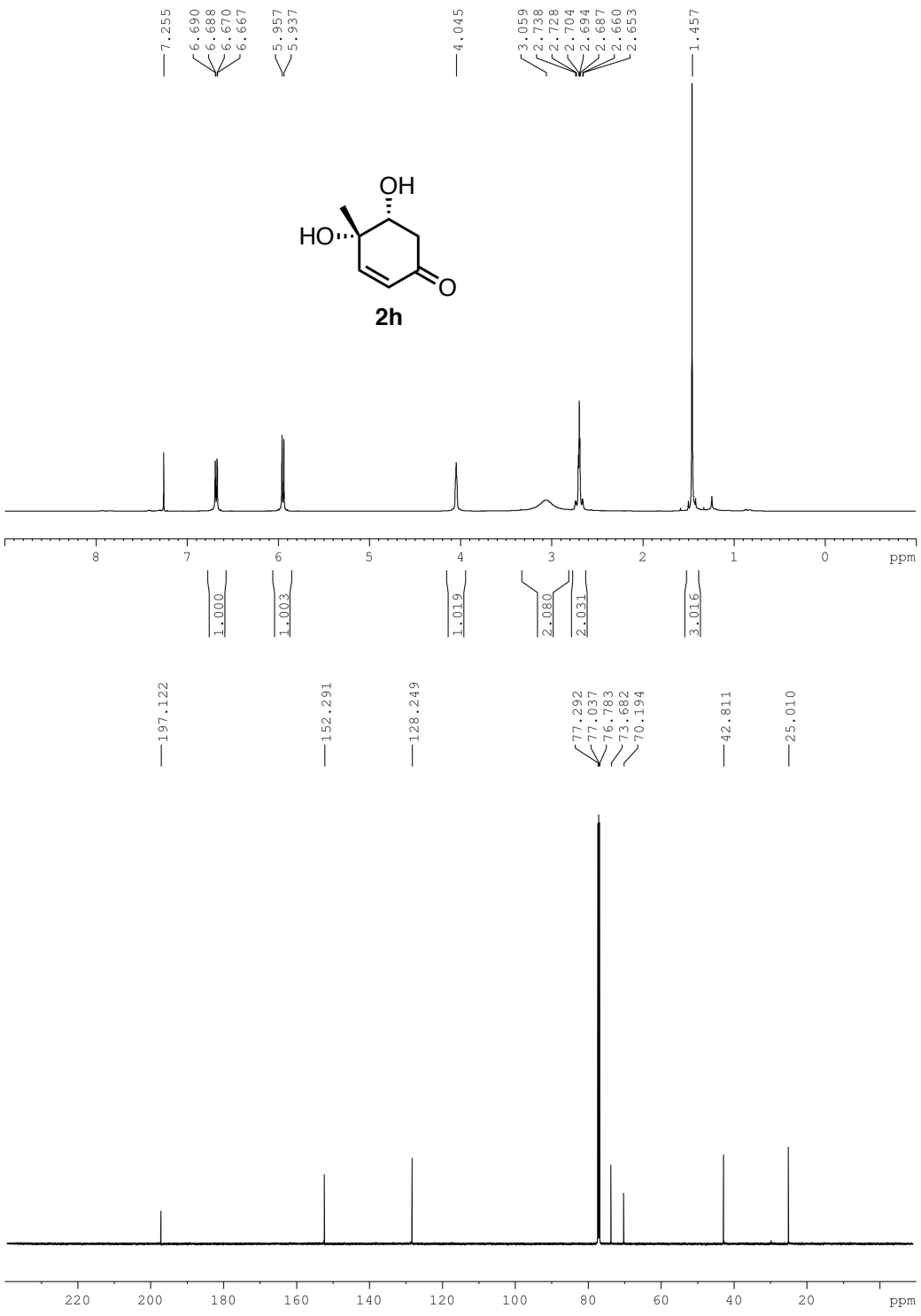
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **2e**



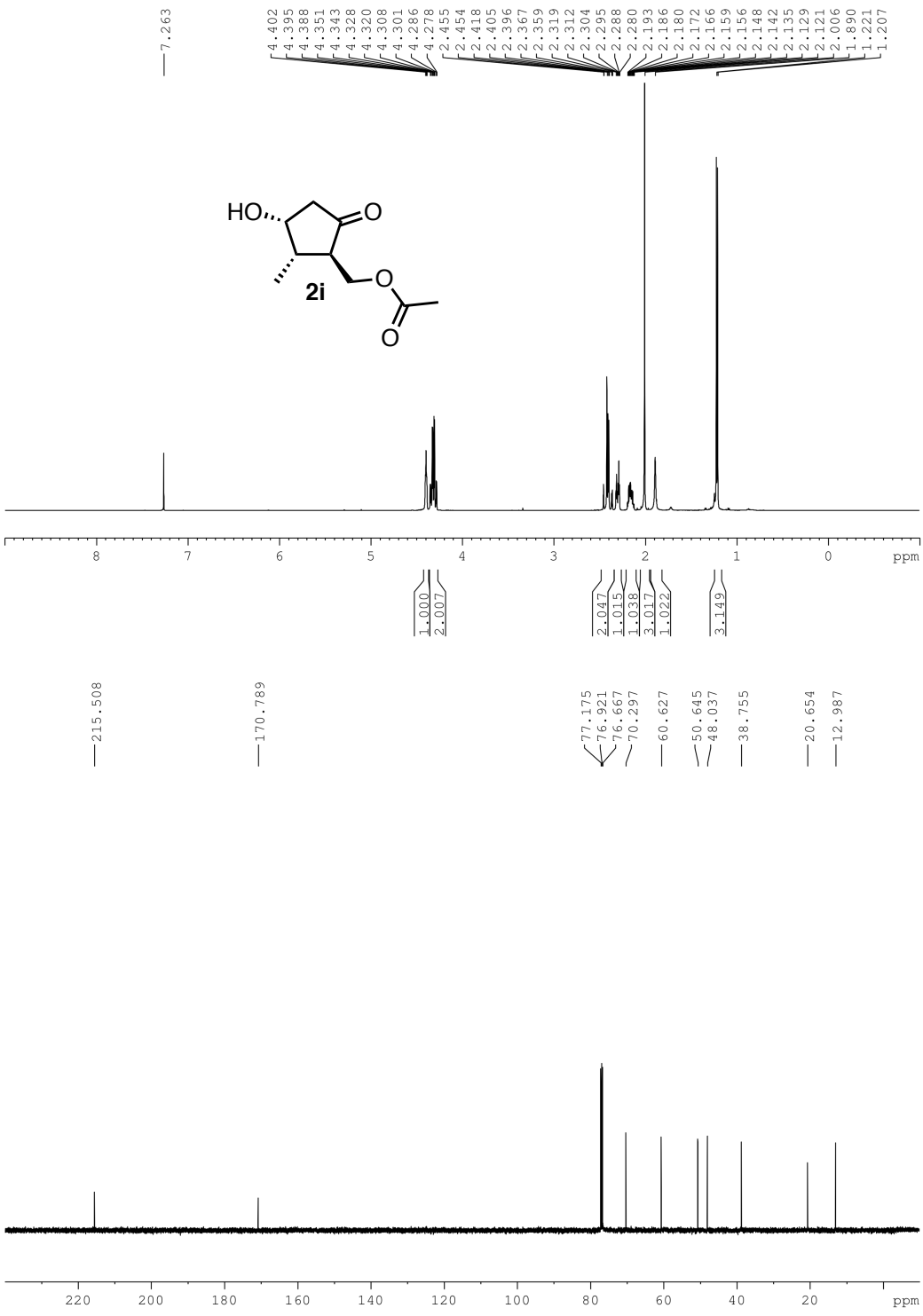
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **2f**



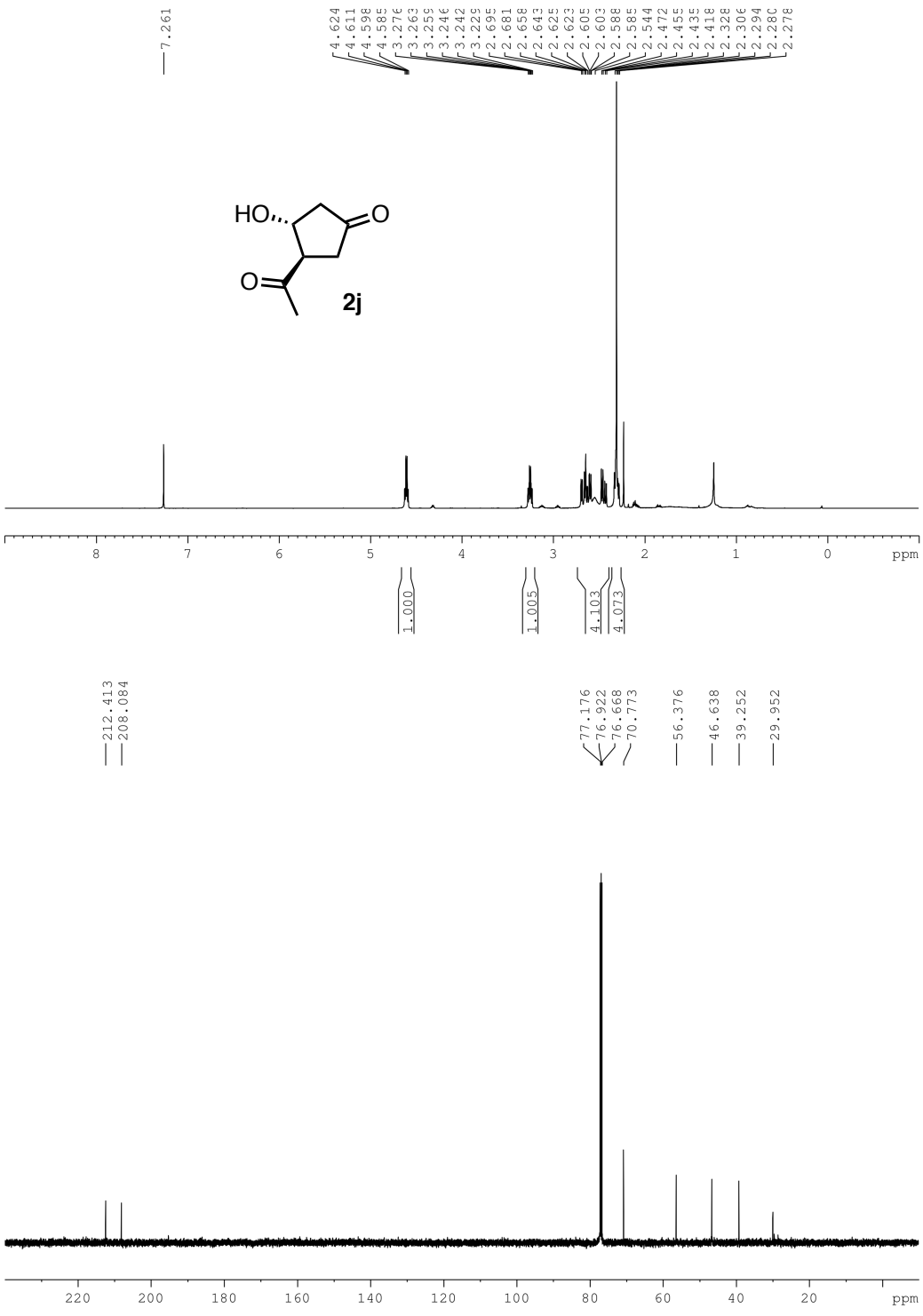
^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR Spectra of **2g**



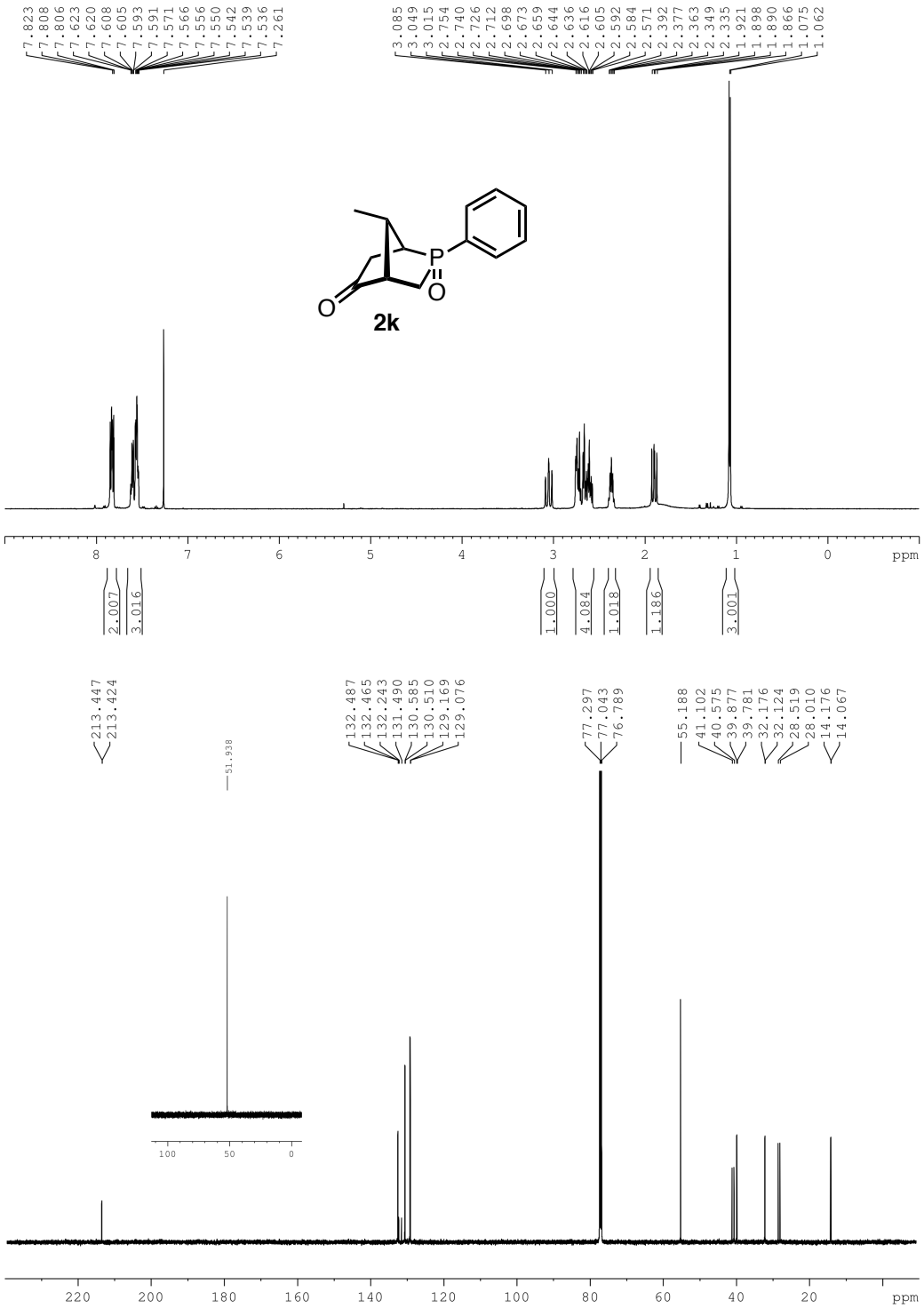
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **2h**



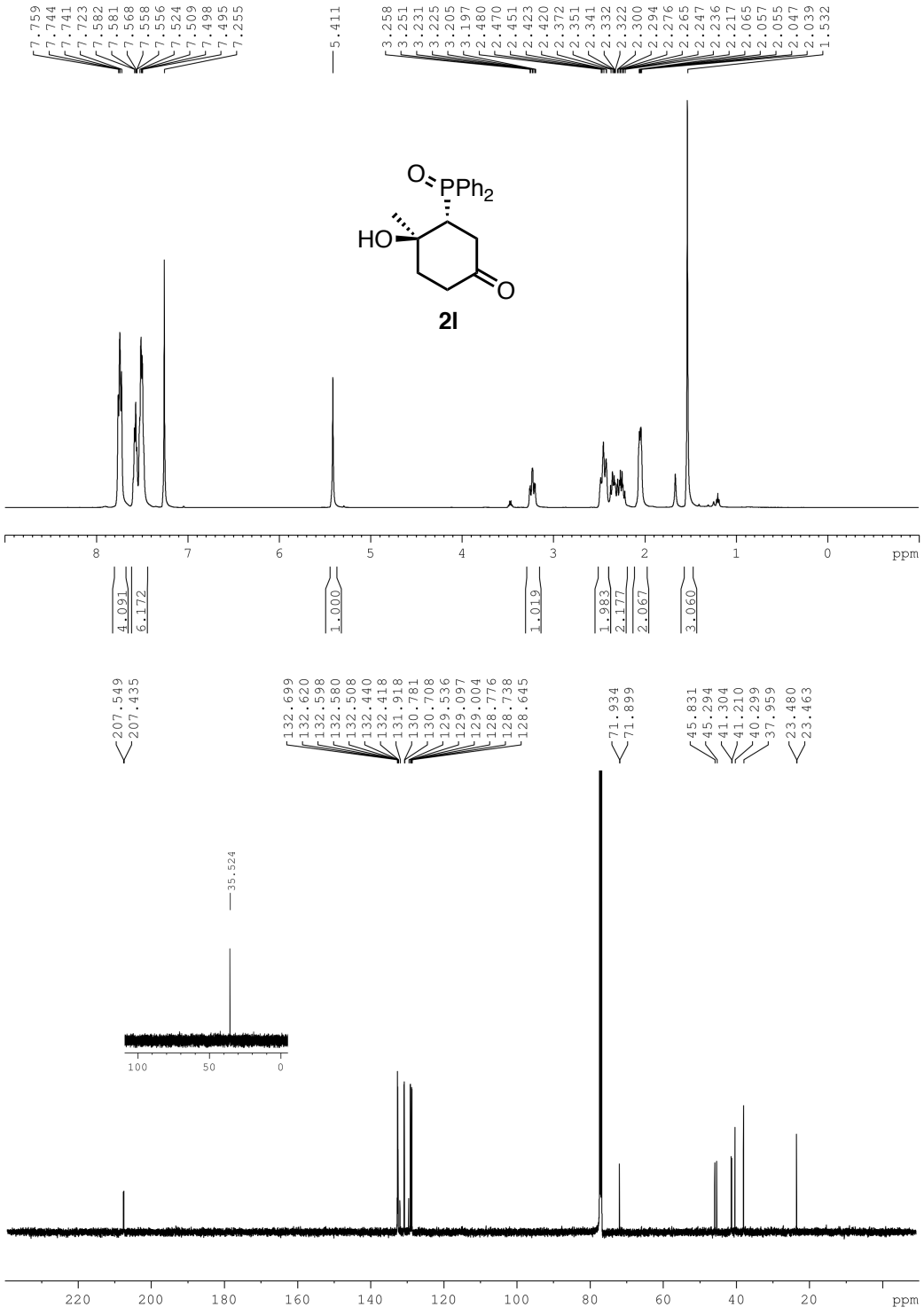
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **2i**



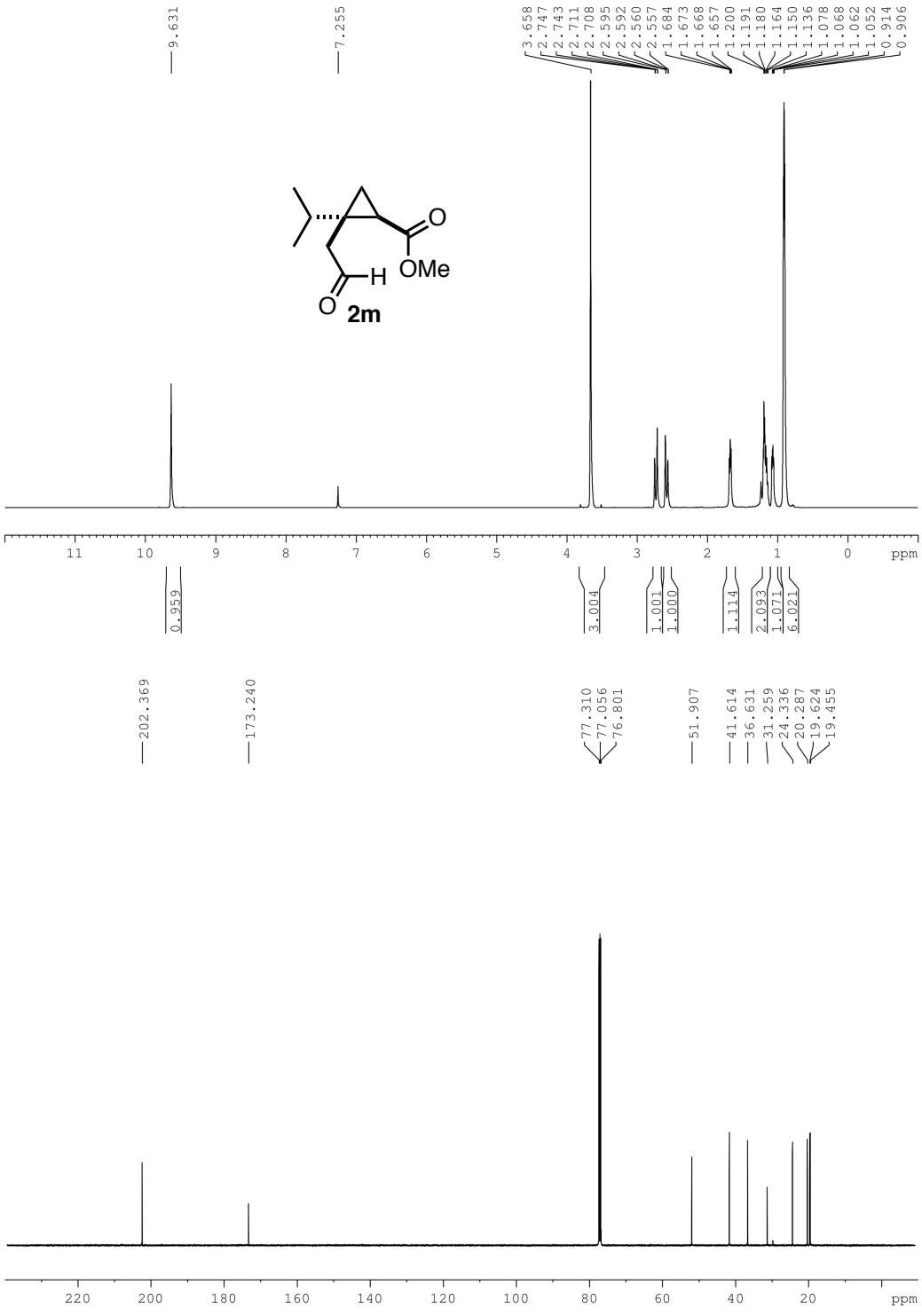
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **2j**



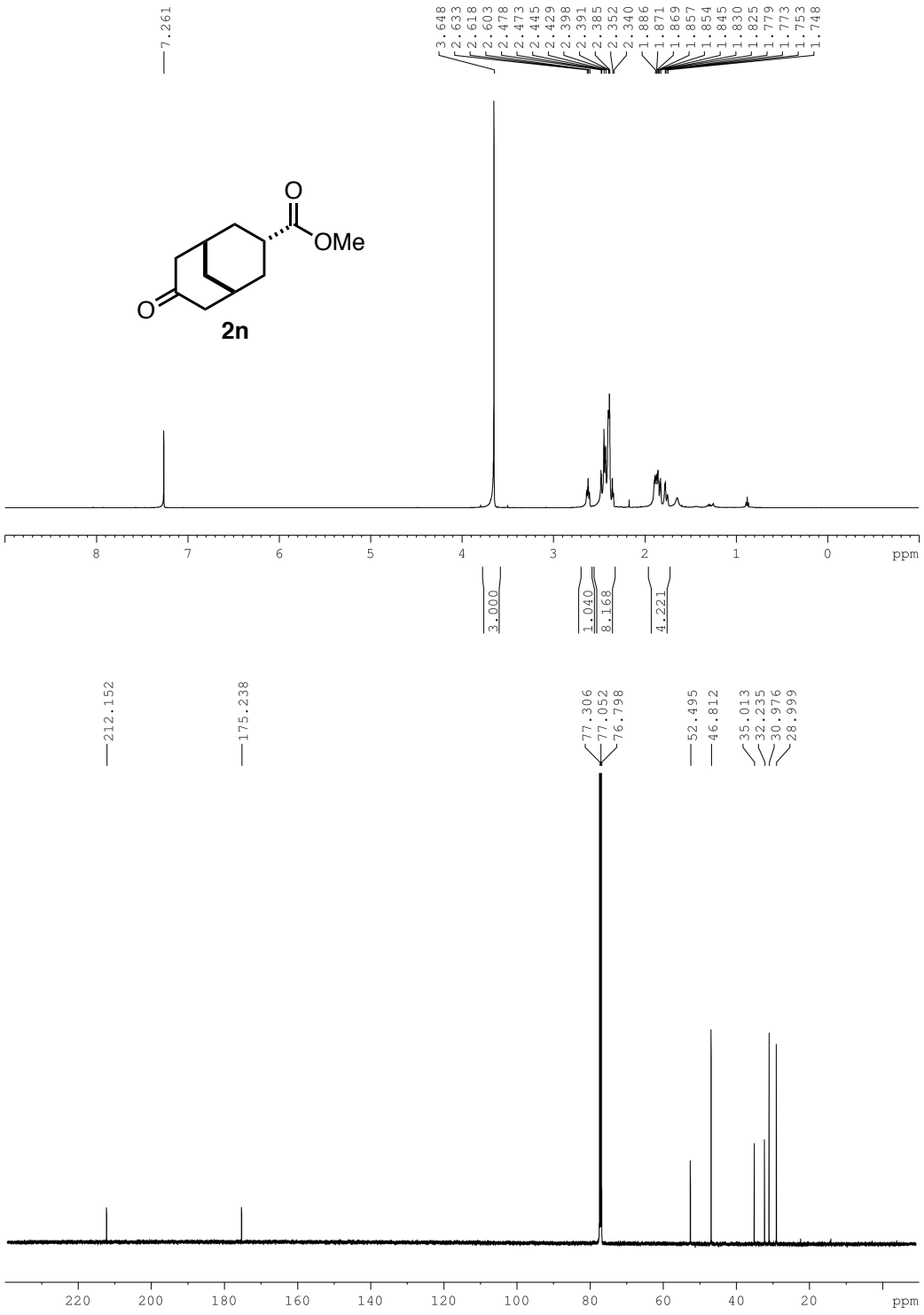
^{1}H (500 MHz, $CDCl_3$), ^{13}C (125 MHz, $CDCl_3$) and ^{31}P (202 MHz, $CDCl_3$) NMR Spectra of **2k**



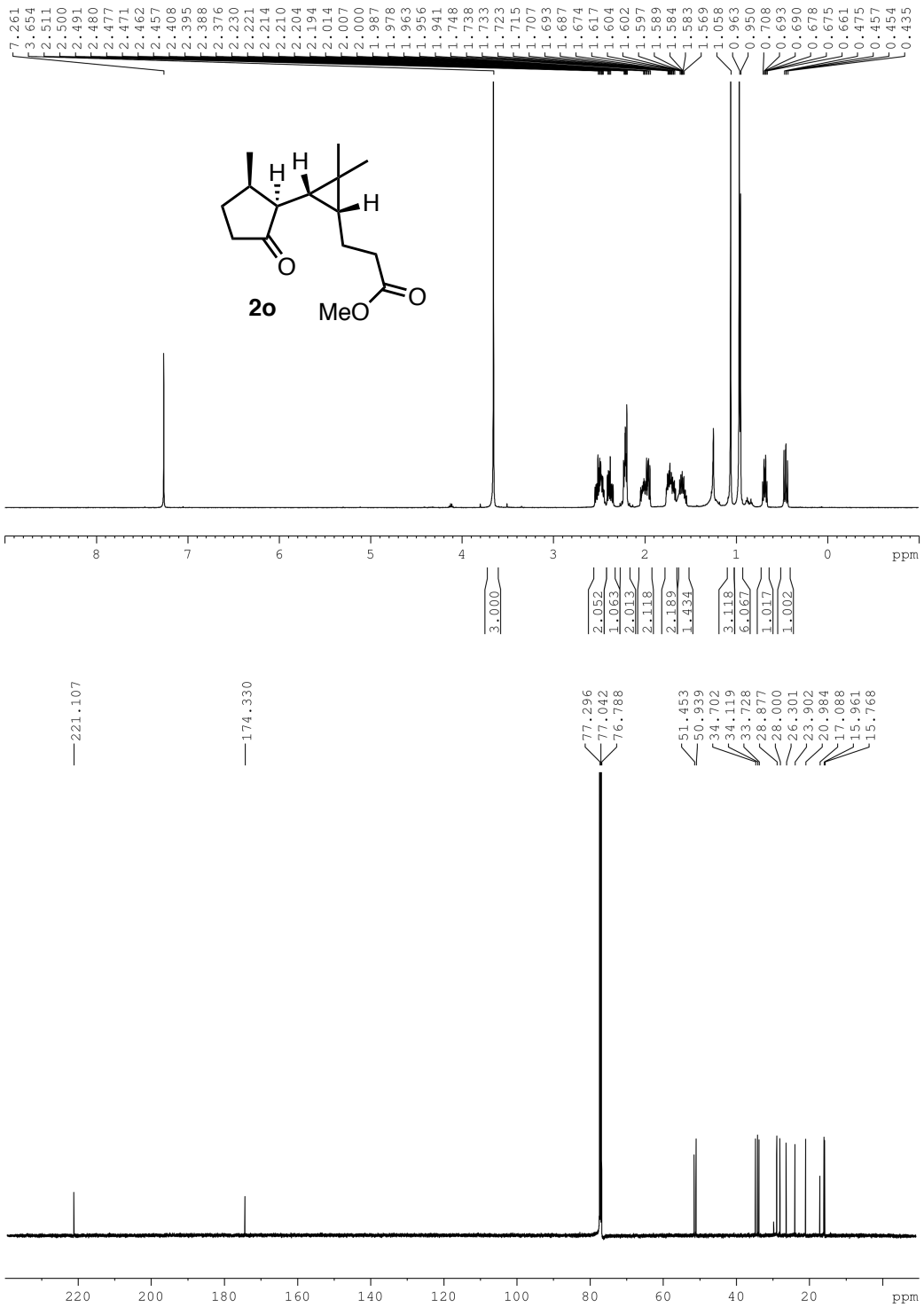
^{1}H (500 MHz, $CDCl_3$), ^{13}C (125 MHz, $CDCl_3$) and ^{31}P (202 MHz, $CDCl_3$) NMR Spectra of **2l**



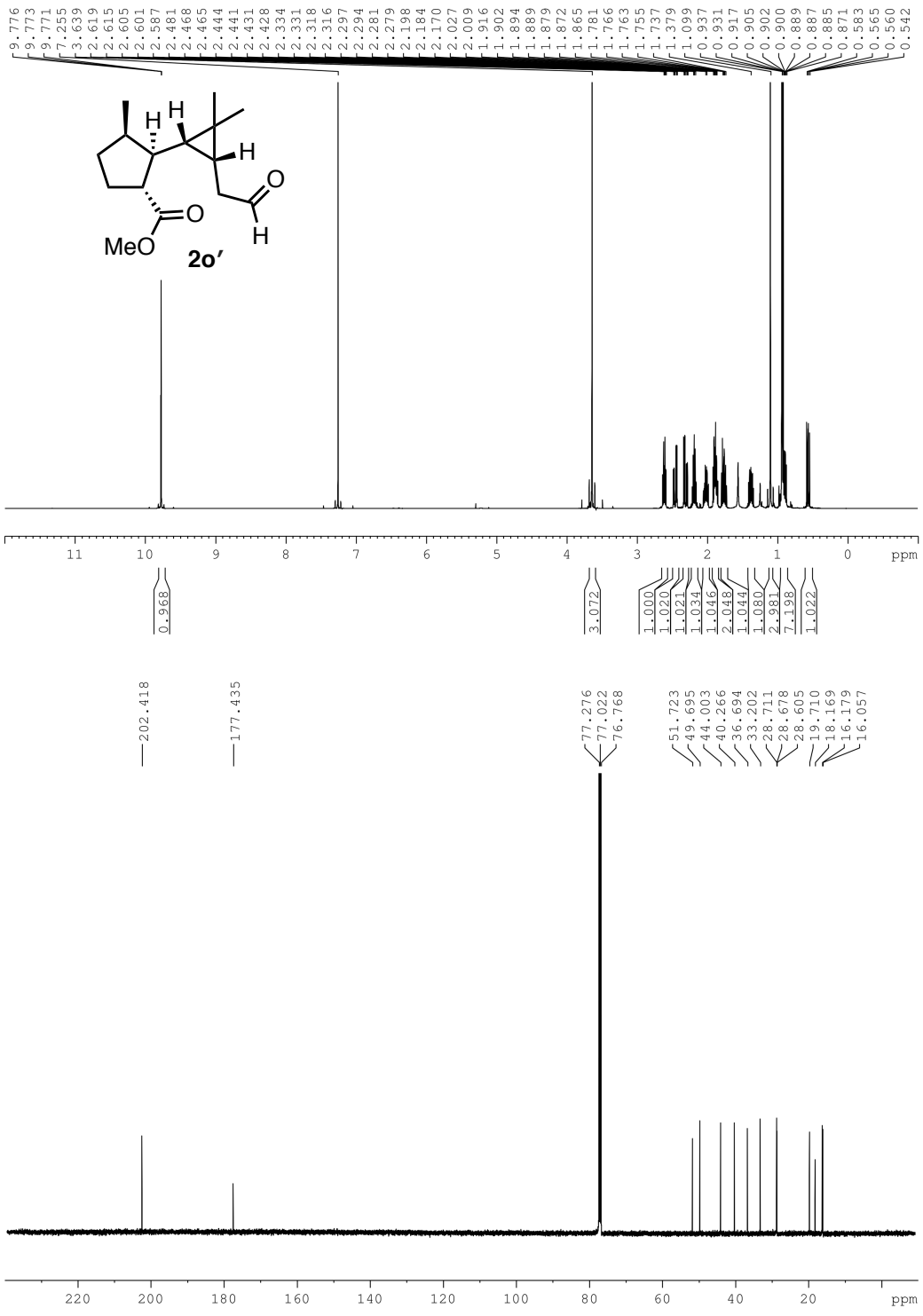
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **2m**



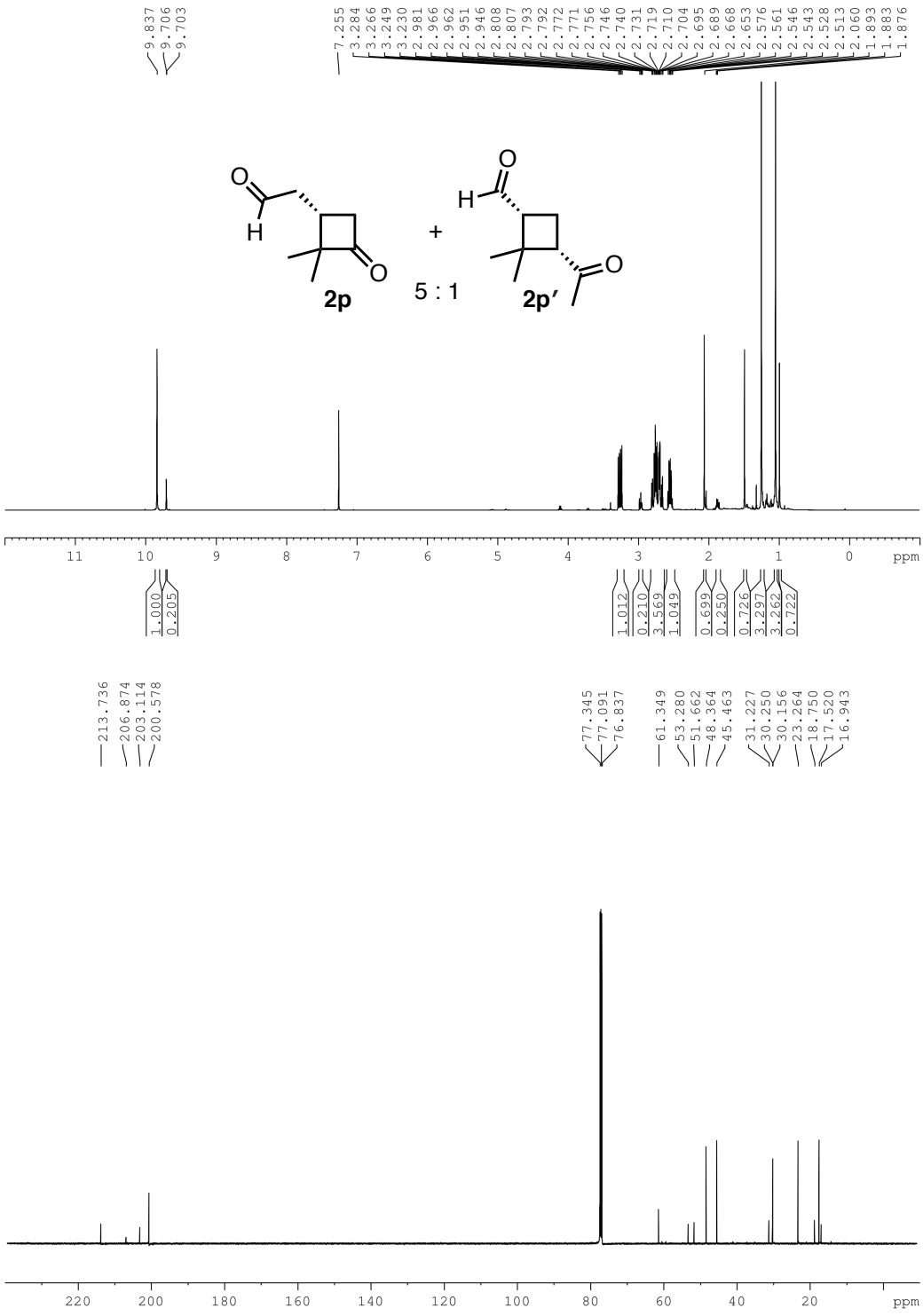
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **2n**



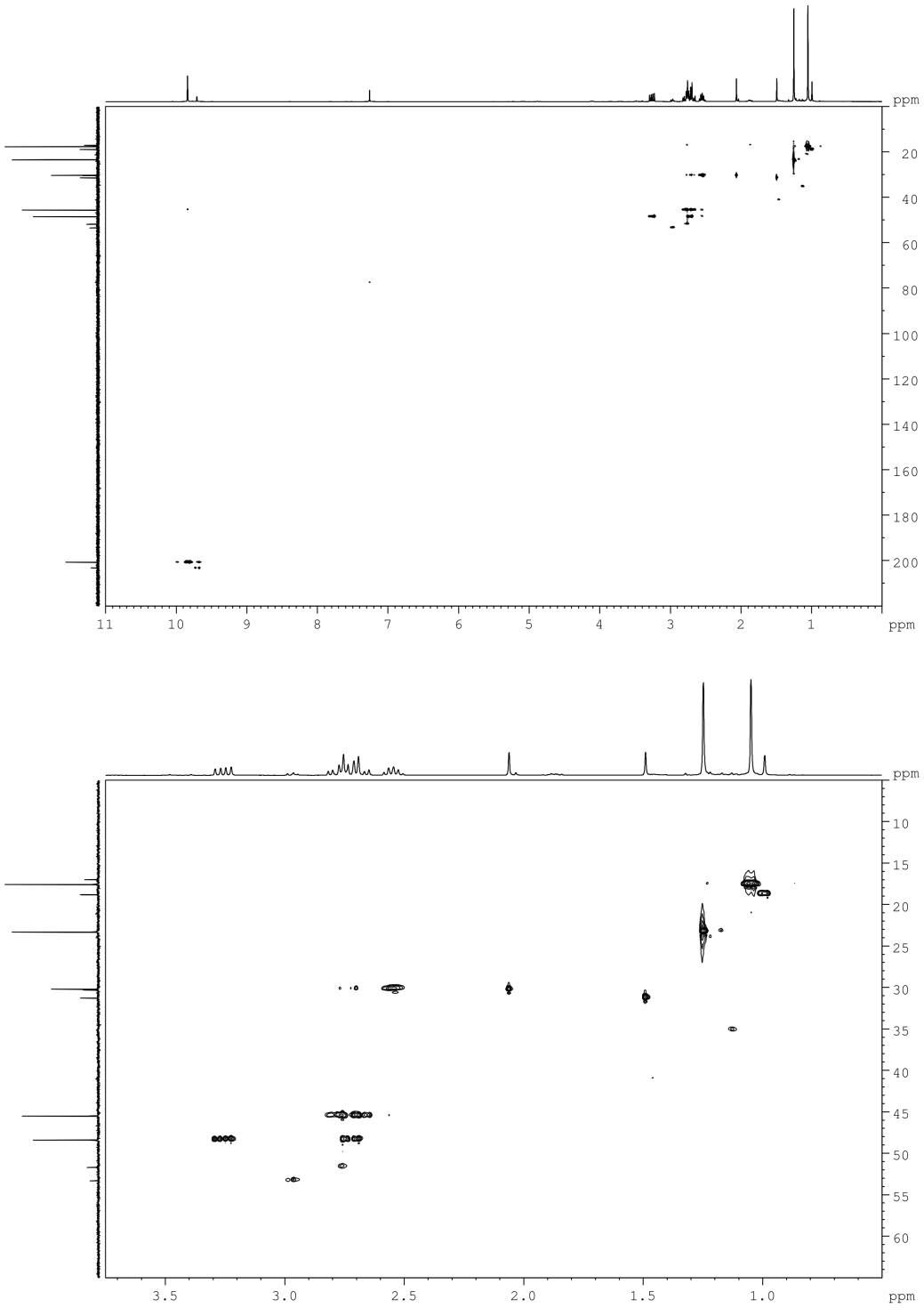
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **2o**



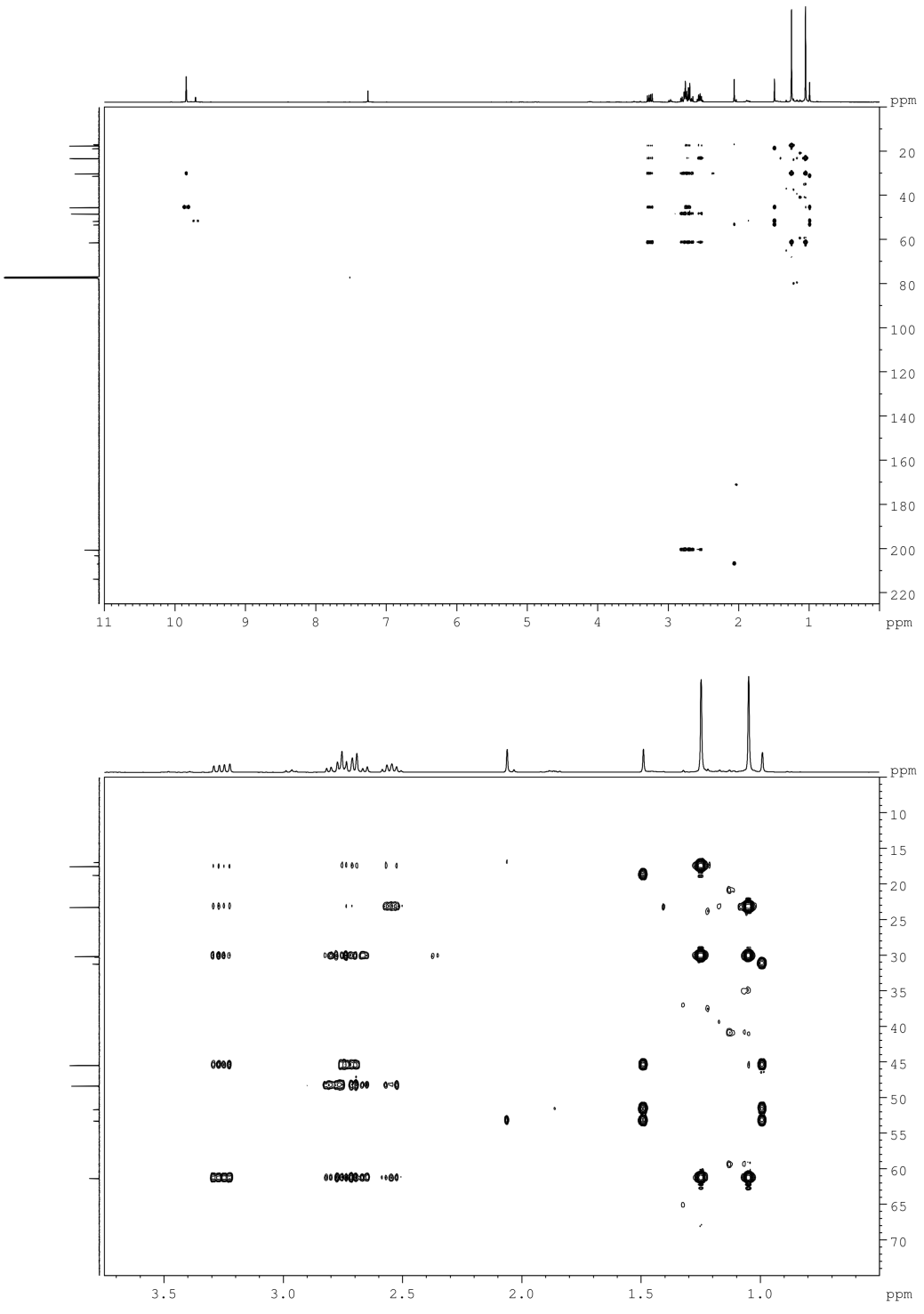
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **2o′**



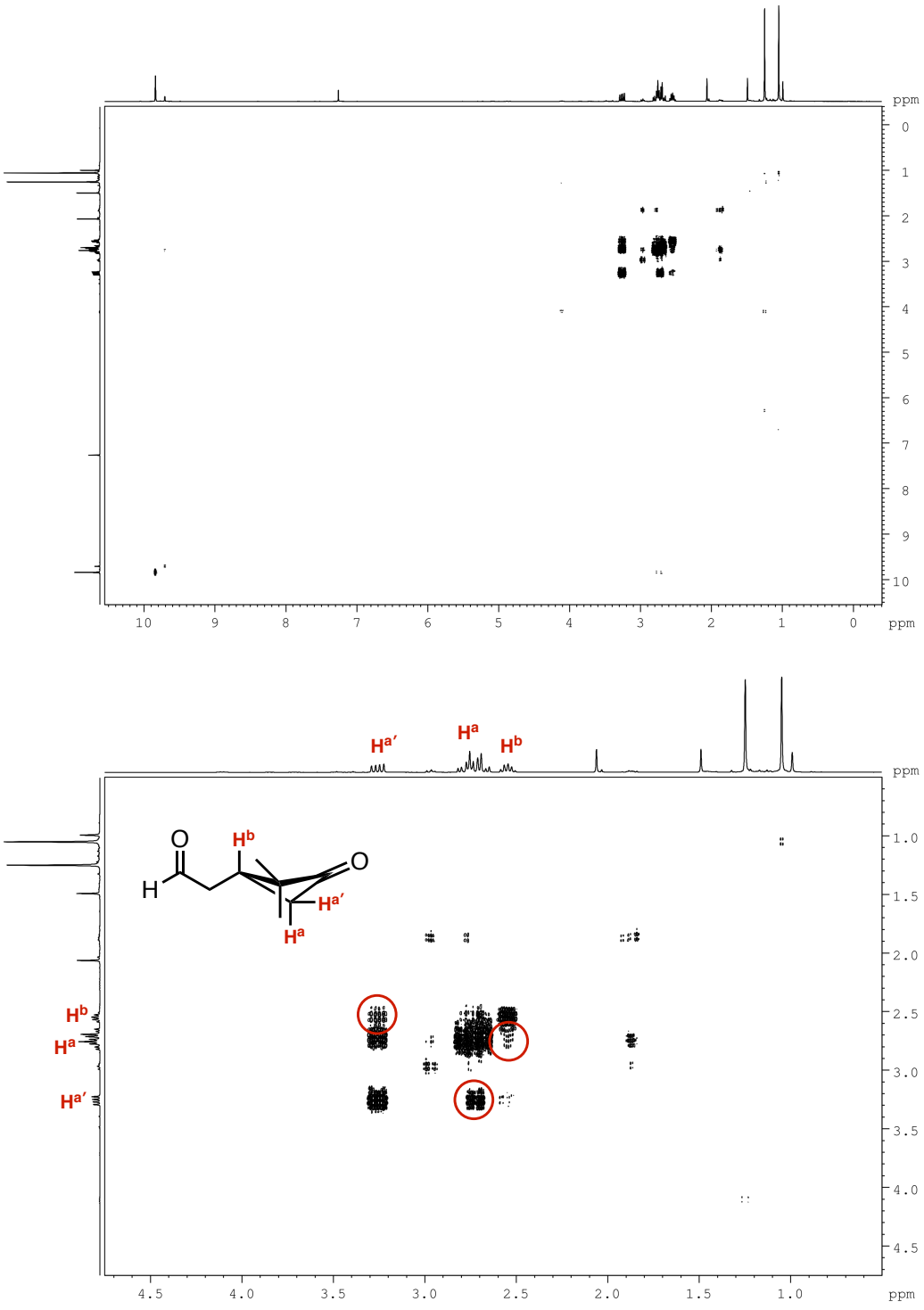
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **2p** and **2p′** (5:1)



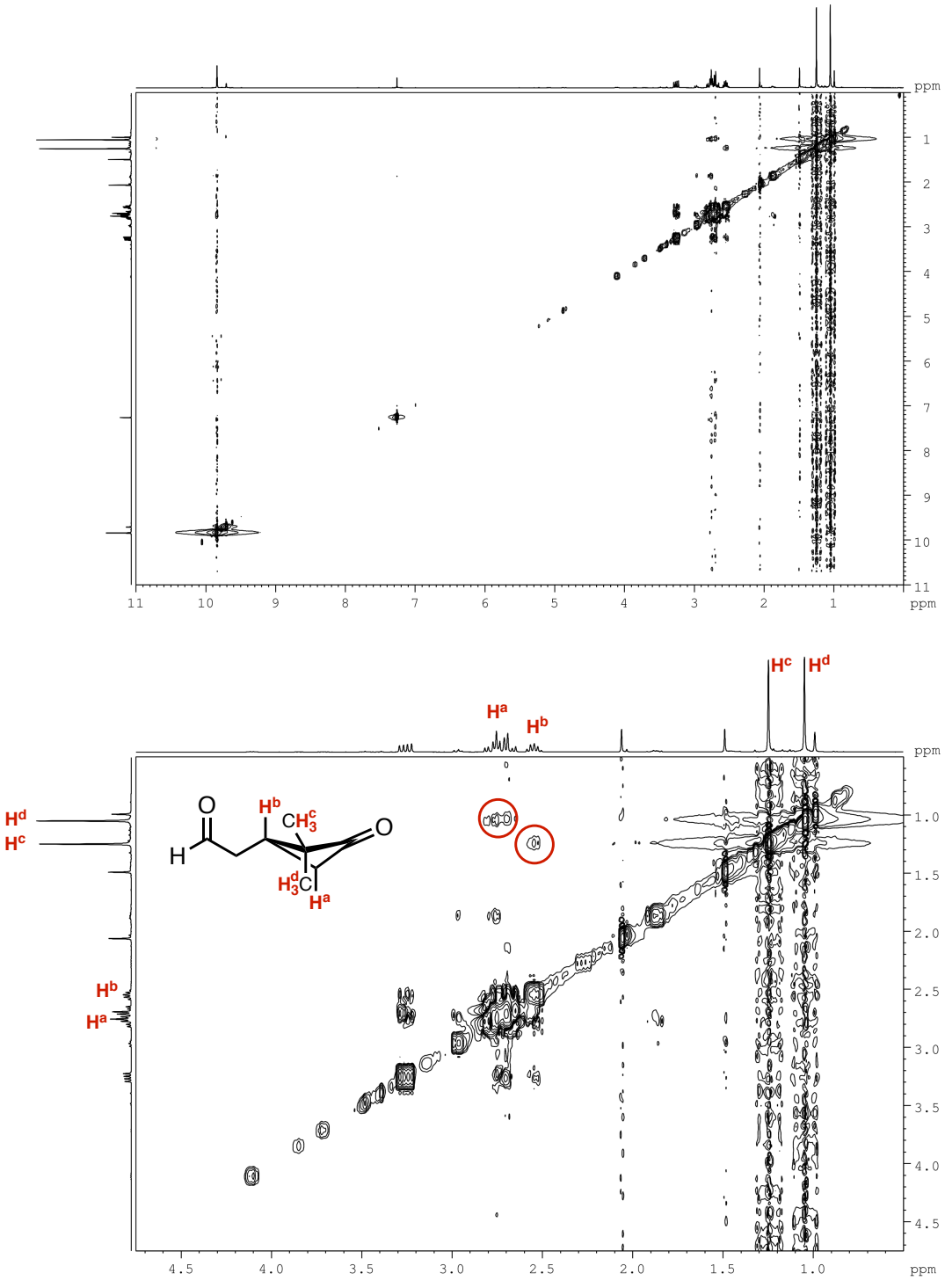
HSQC (400 MHz, $CDCl_3$) NMR Spectrum of **2p** and **2p′** (5:1)



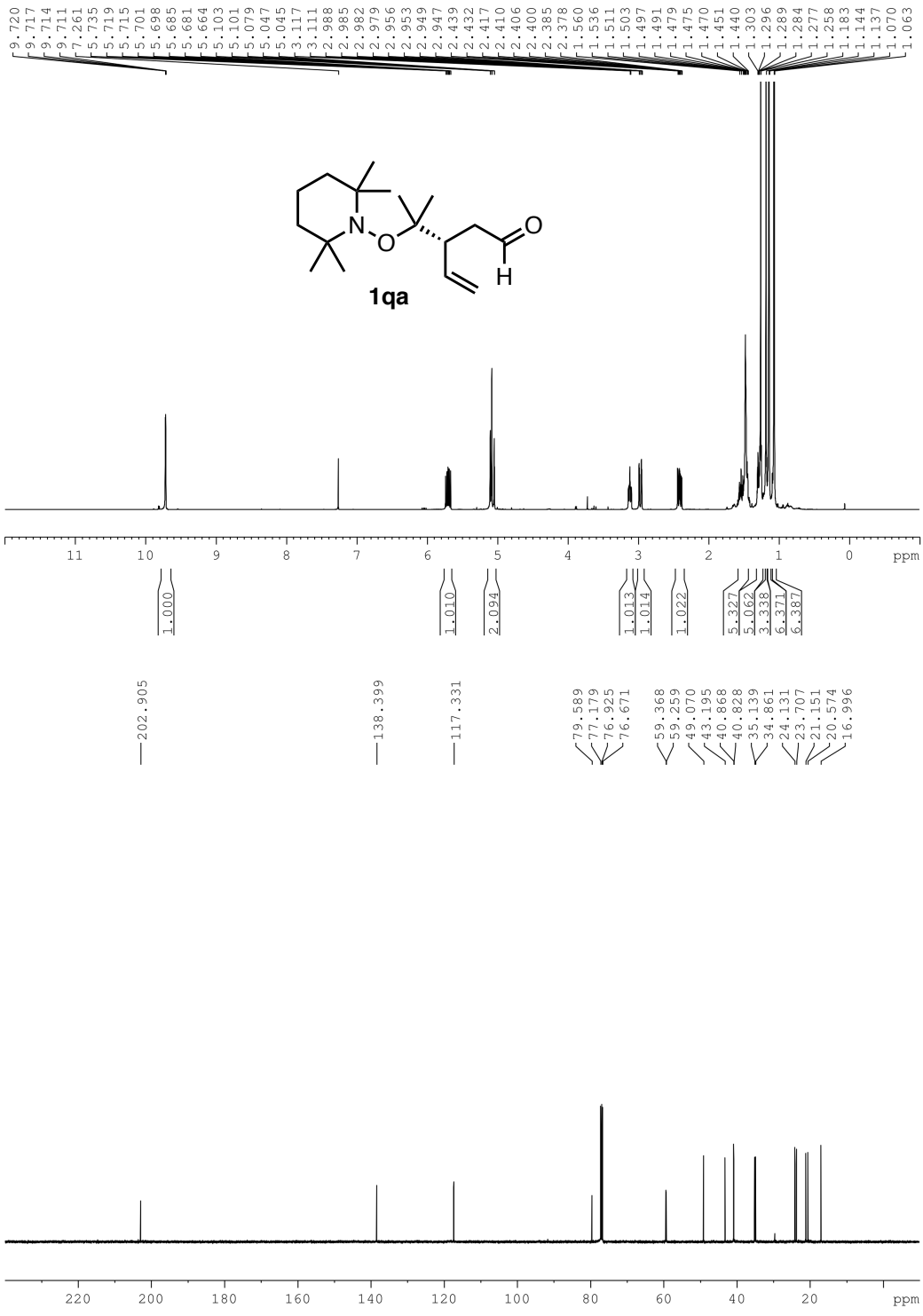
HMBC (400 MHz, $CDCl_3$) NMR Spectrum of **2p** and **2p′** (5:1)



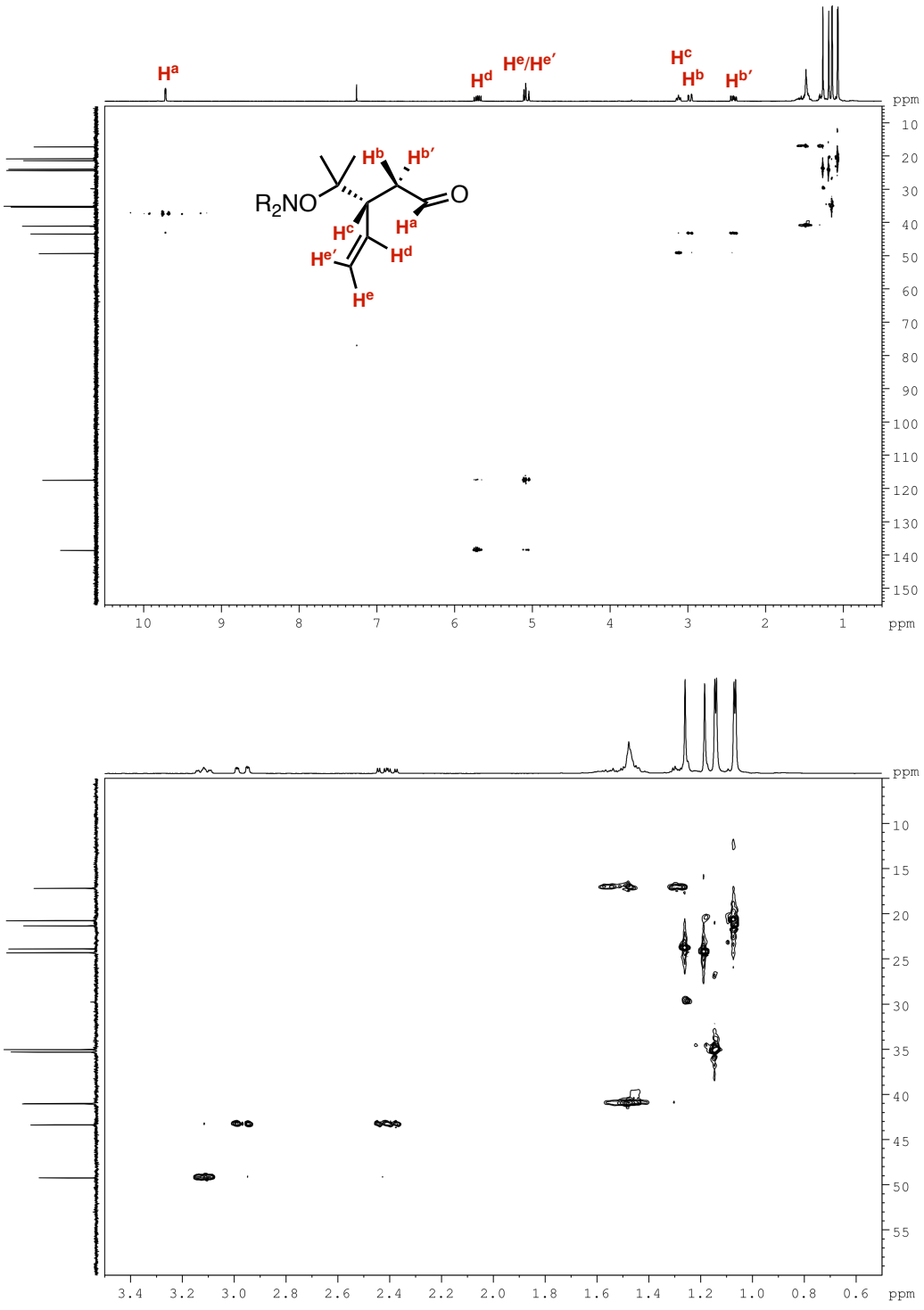
COSY (400 MHz, $CDCl_3$) NMR Spectrum of **2p** and **2p′** (5:1)



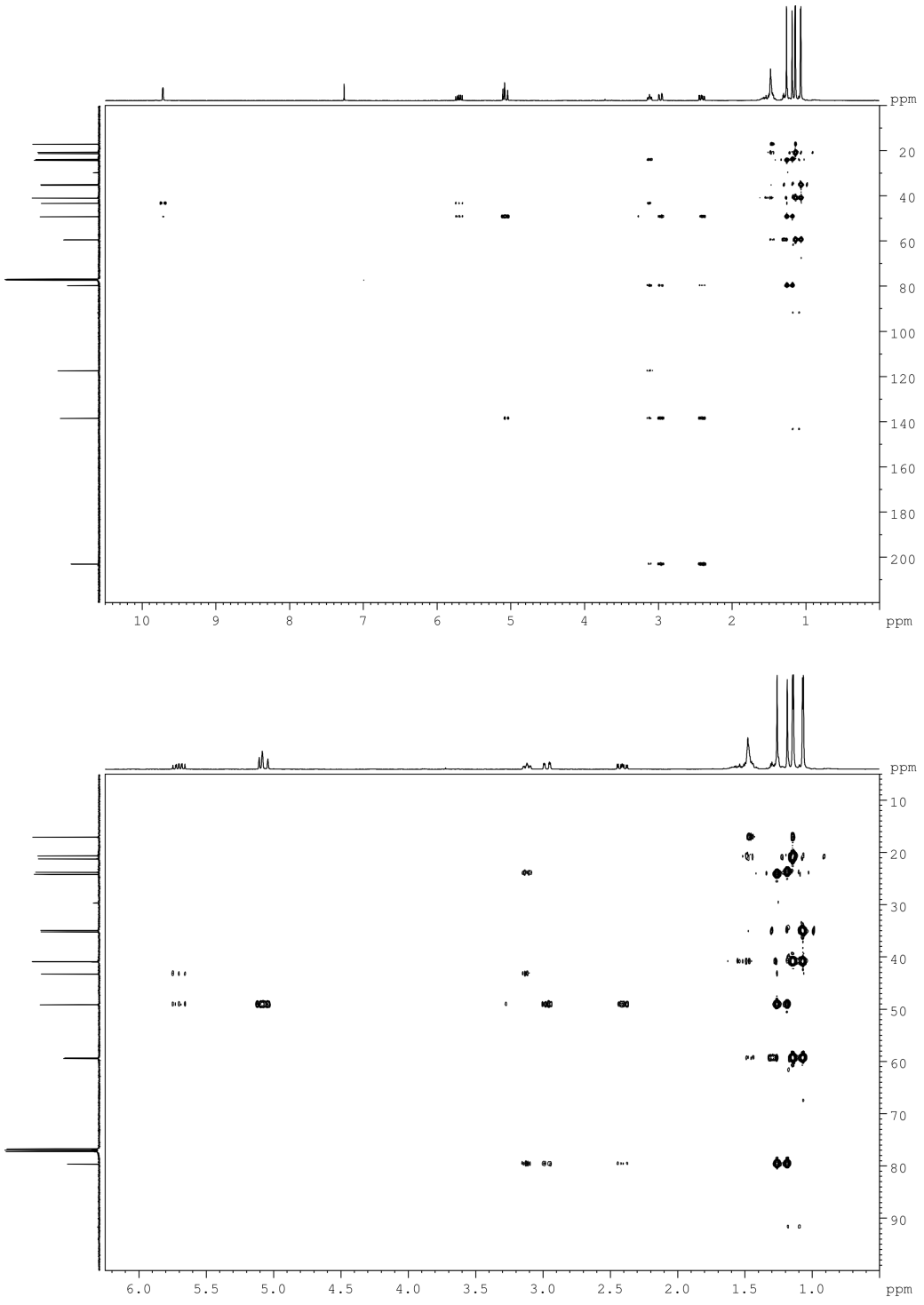
NOESY (400 MHz, $CDCl_3$) NMR Spectrum of **2p** and **2p′** (5:1)



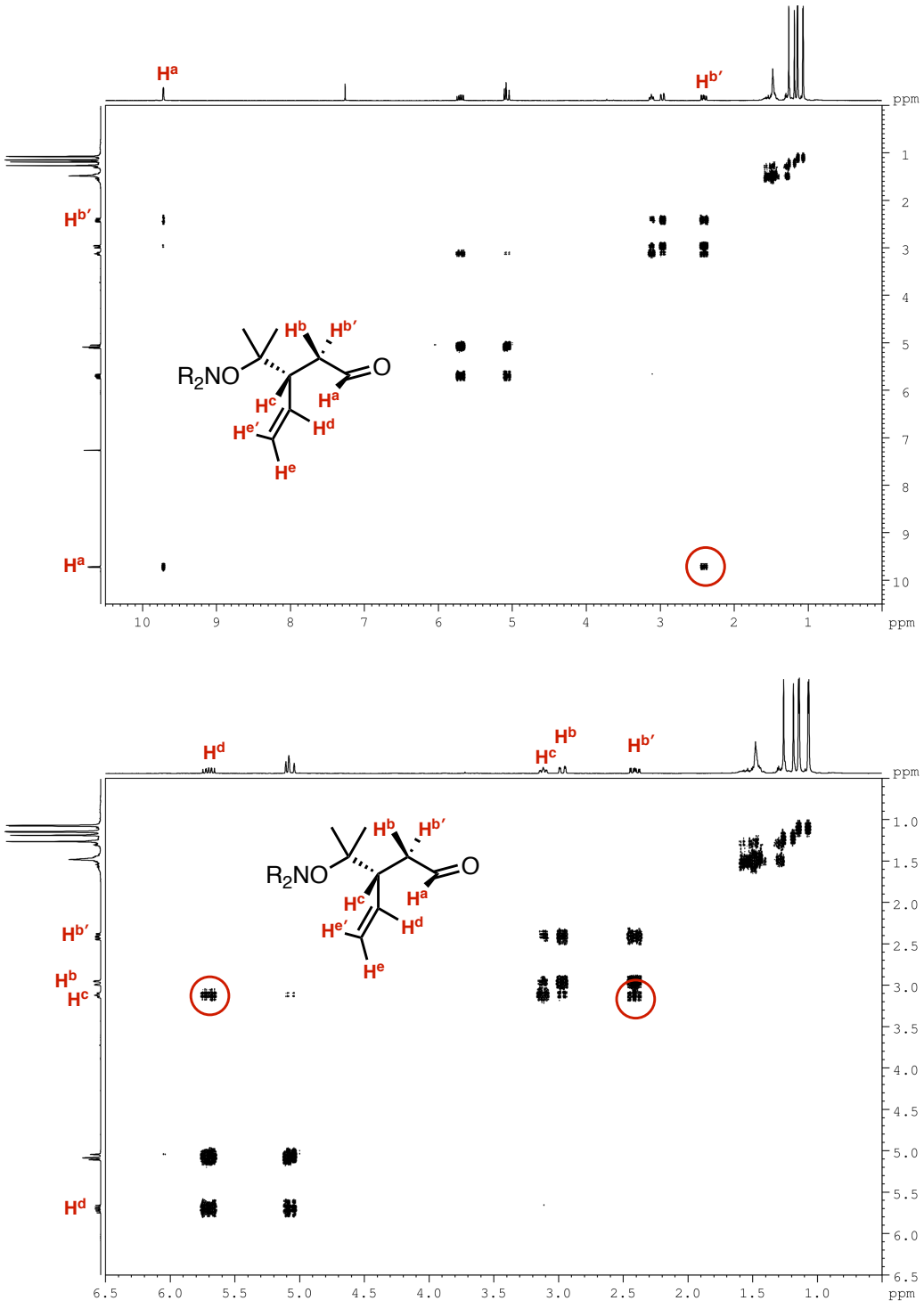
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **1qa**



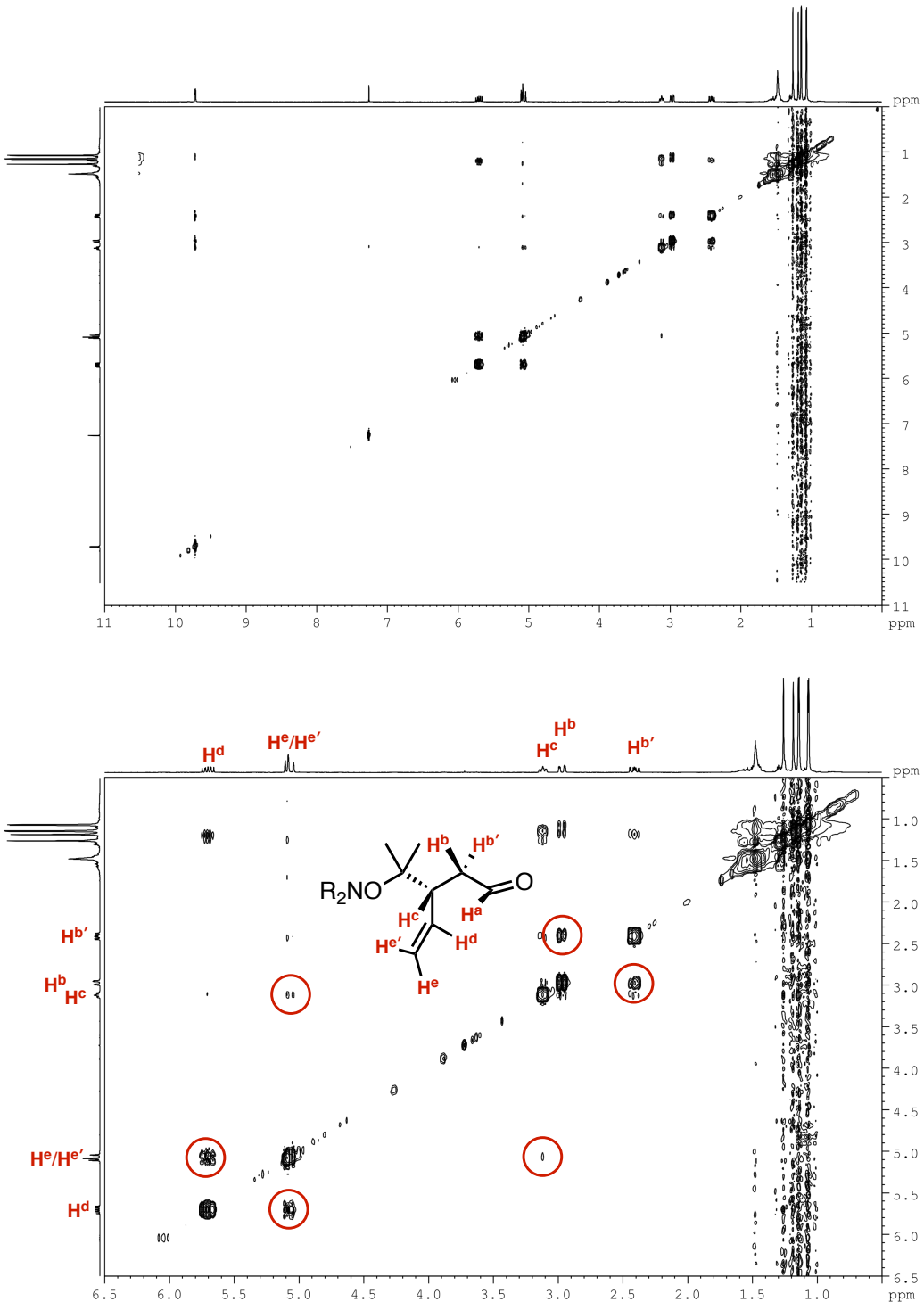
HSQC (400 MHz, $CDCl_3$) NMR Spectrum of **1qa**



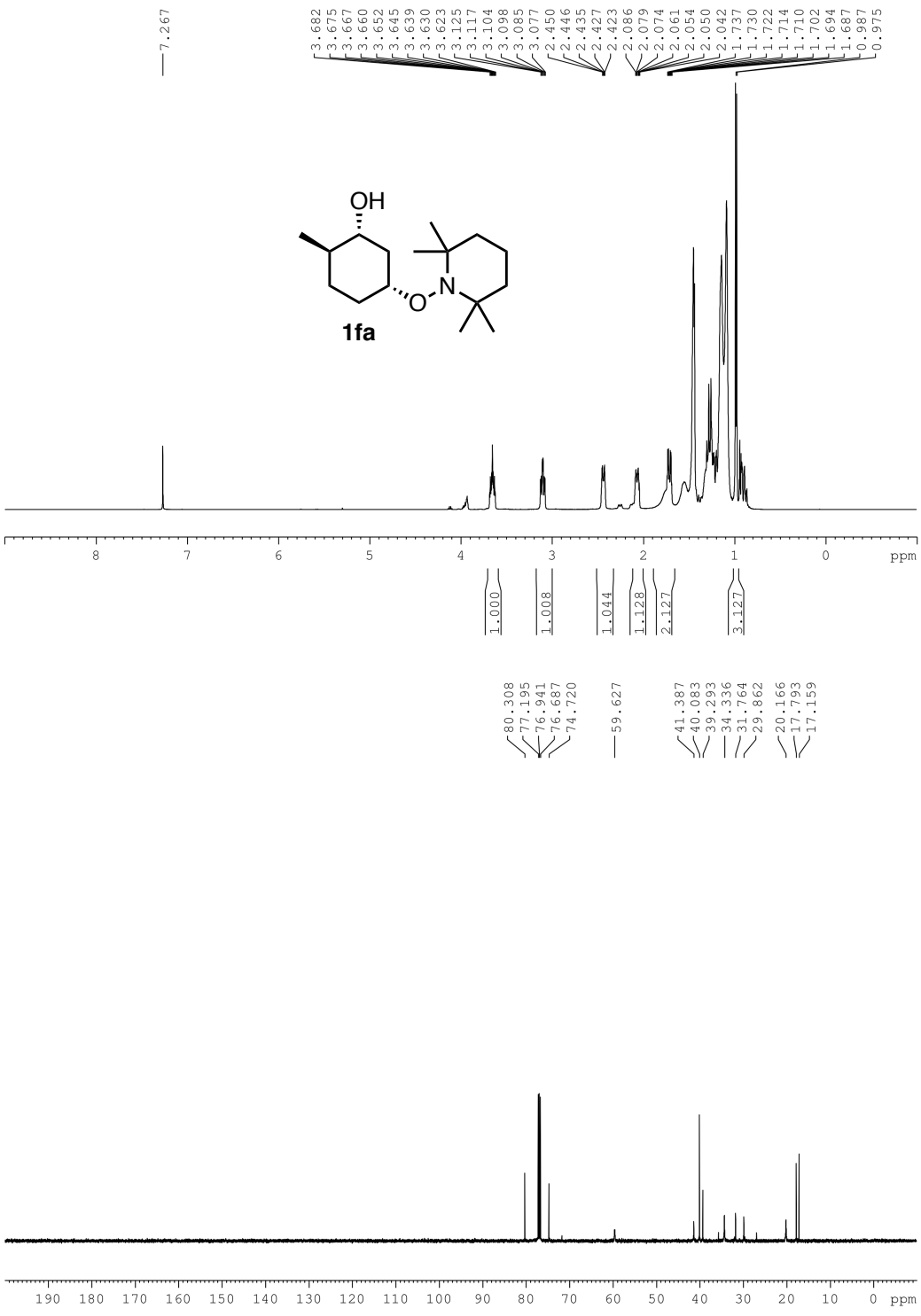
HMBC (400 MHz, $CDCl_3$) NMR Spectrum of **1qa**



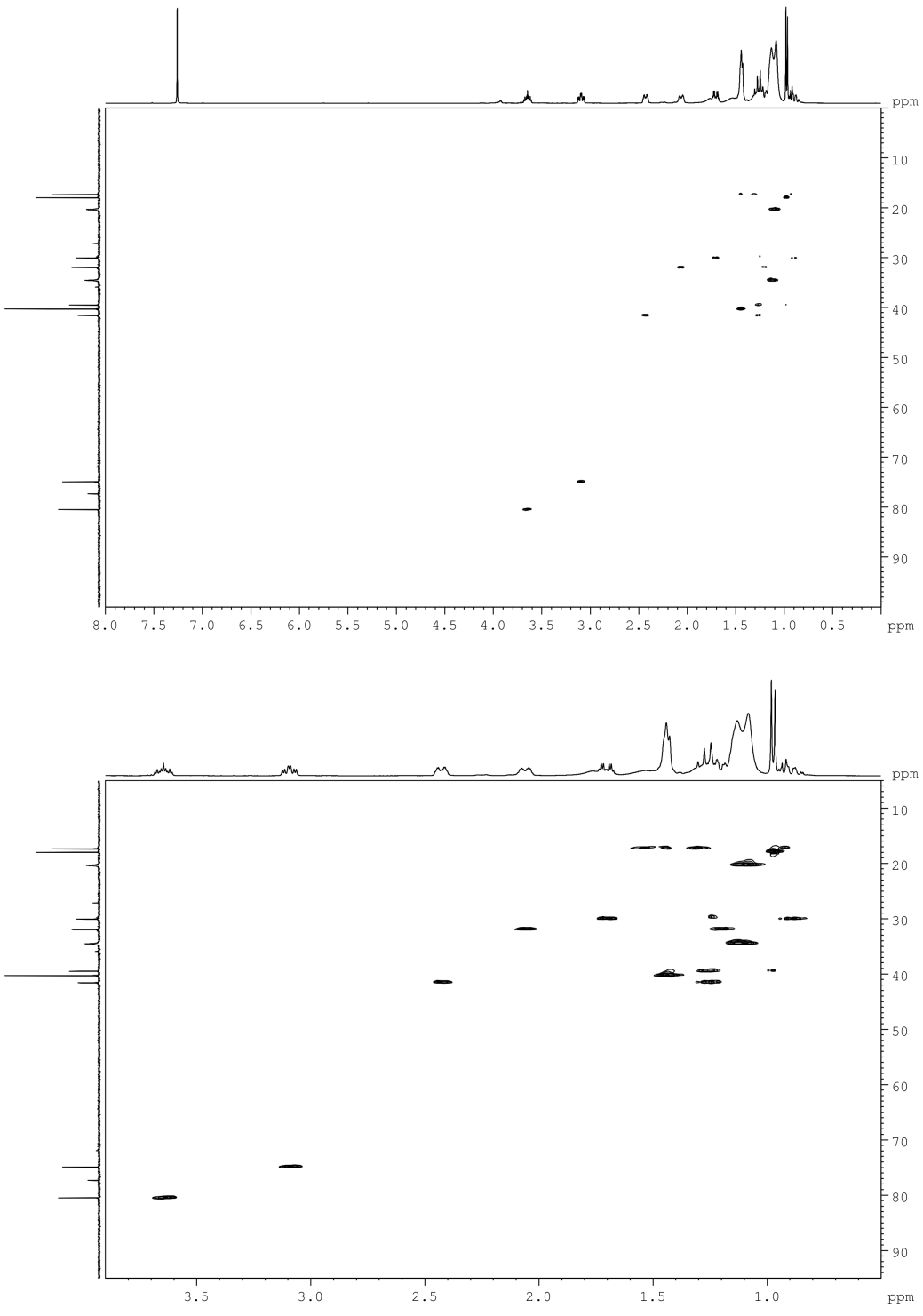
COSY (400 MHz, $CDCl_3$) NMR Spectrum of **1qa**



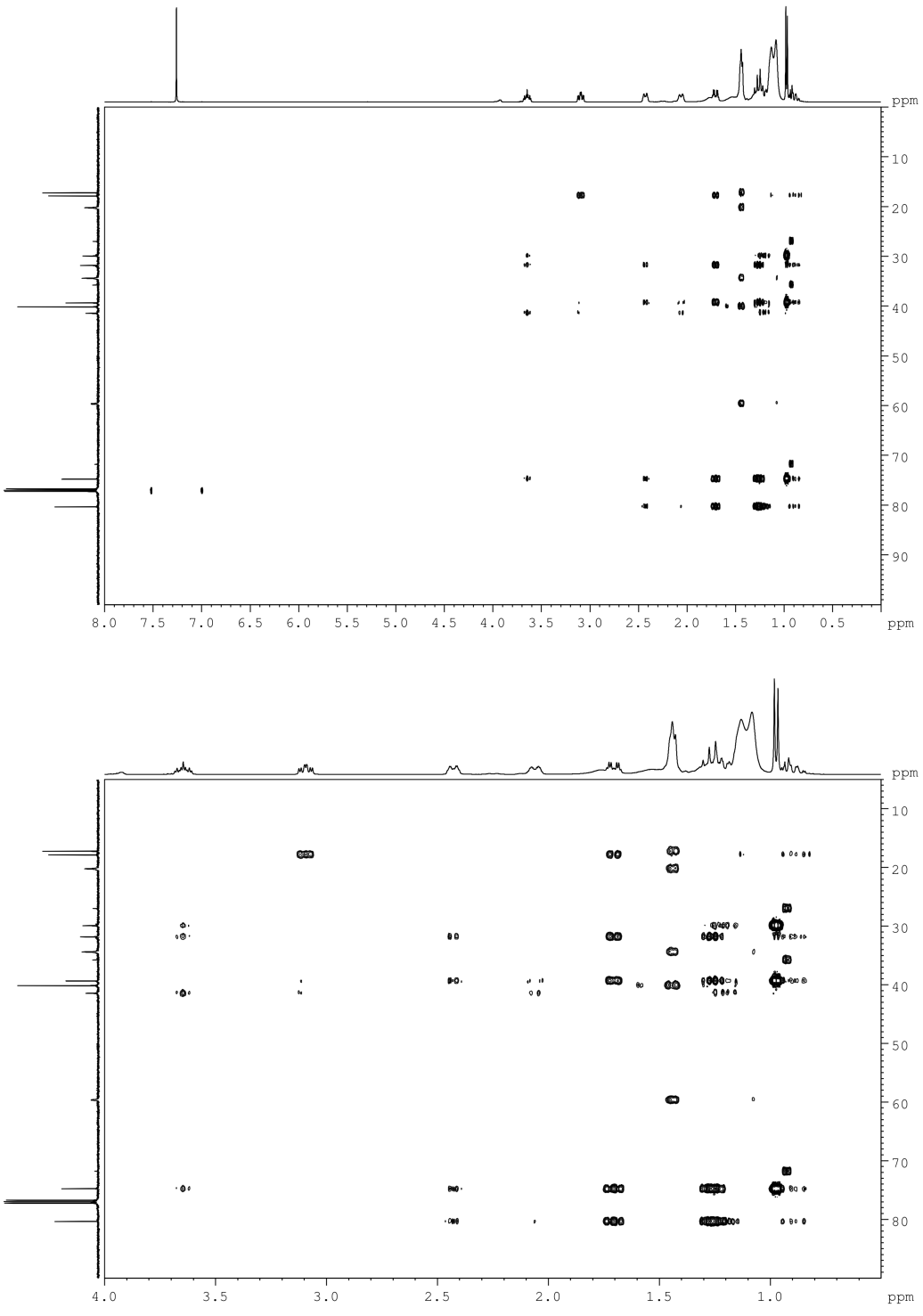
NOESY (400 MHz, $CDCl_3$) NMR Spectrum of **1qa**



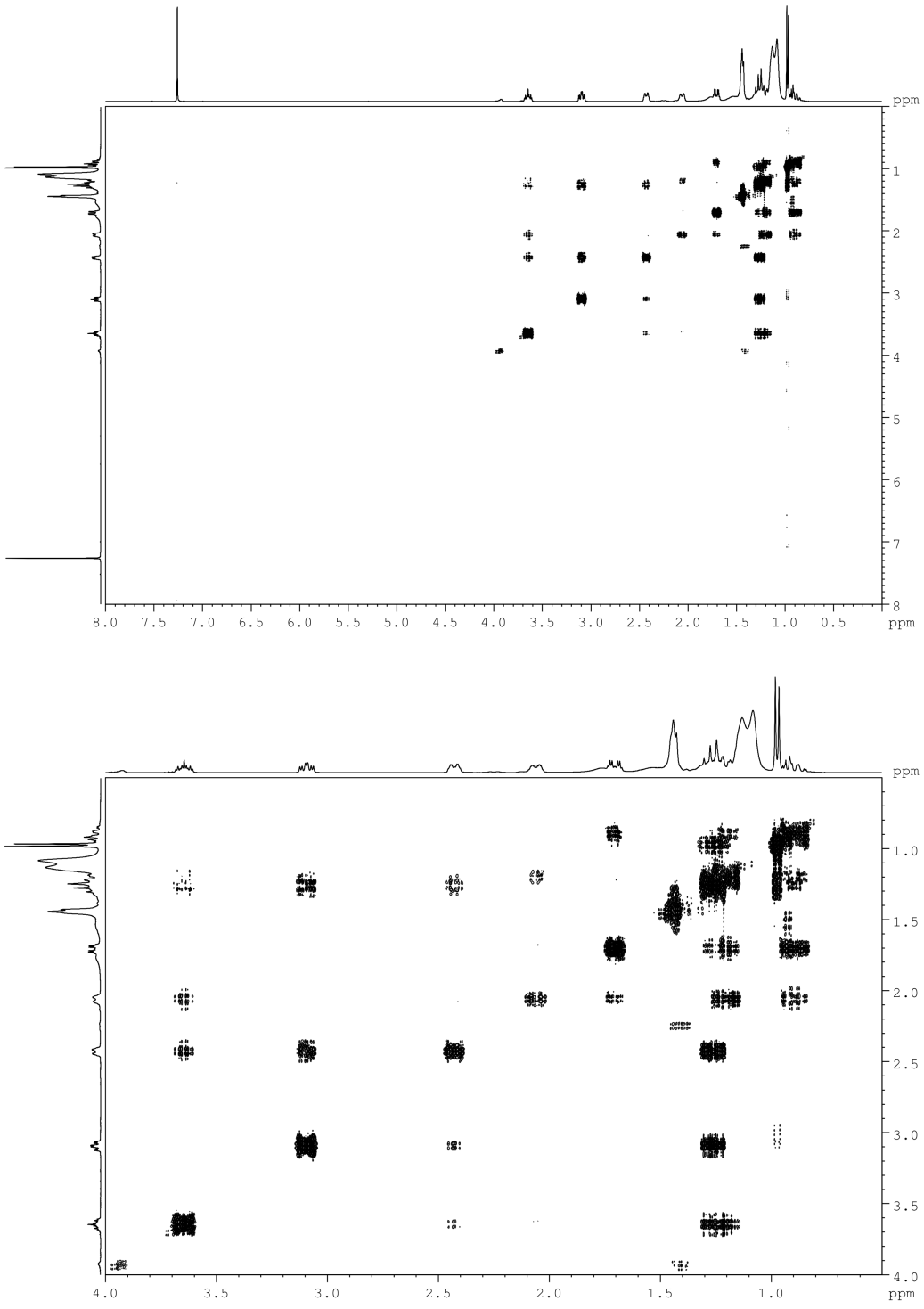
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **1fa**



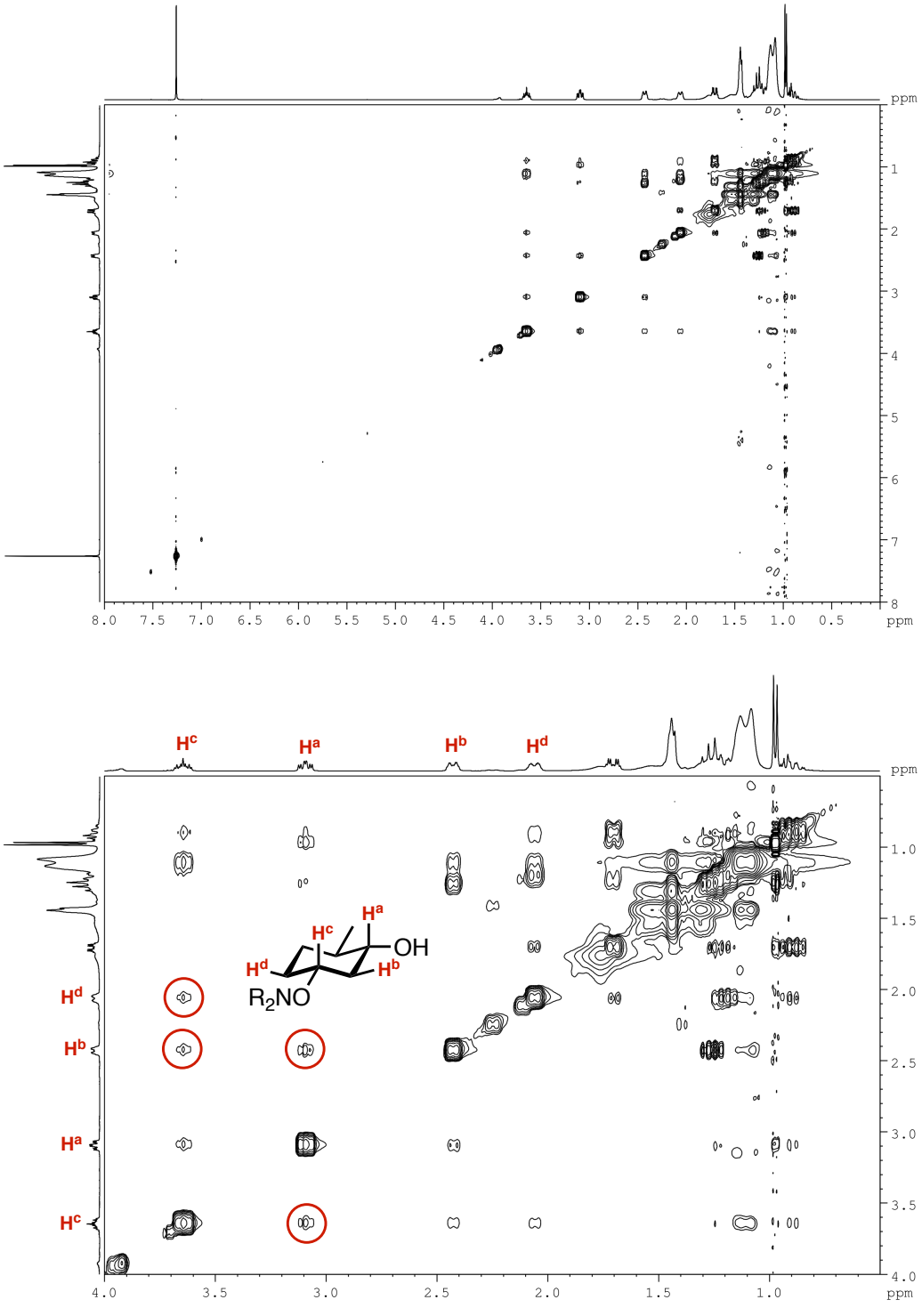
HSQC (400 MHz, $CDCl_3$) NMR Spectrum of **1fa**



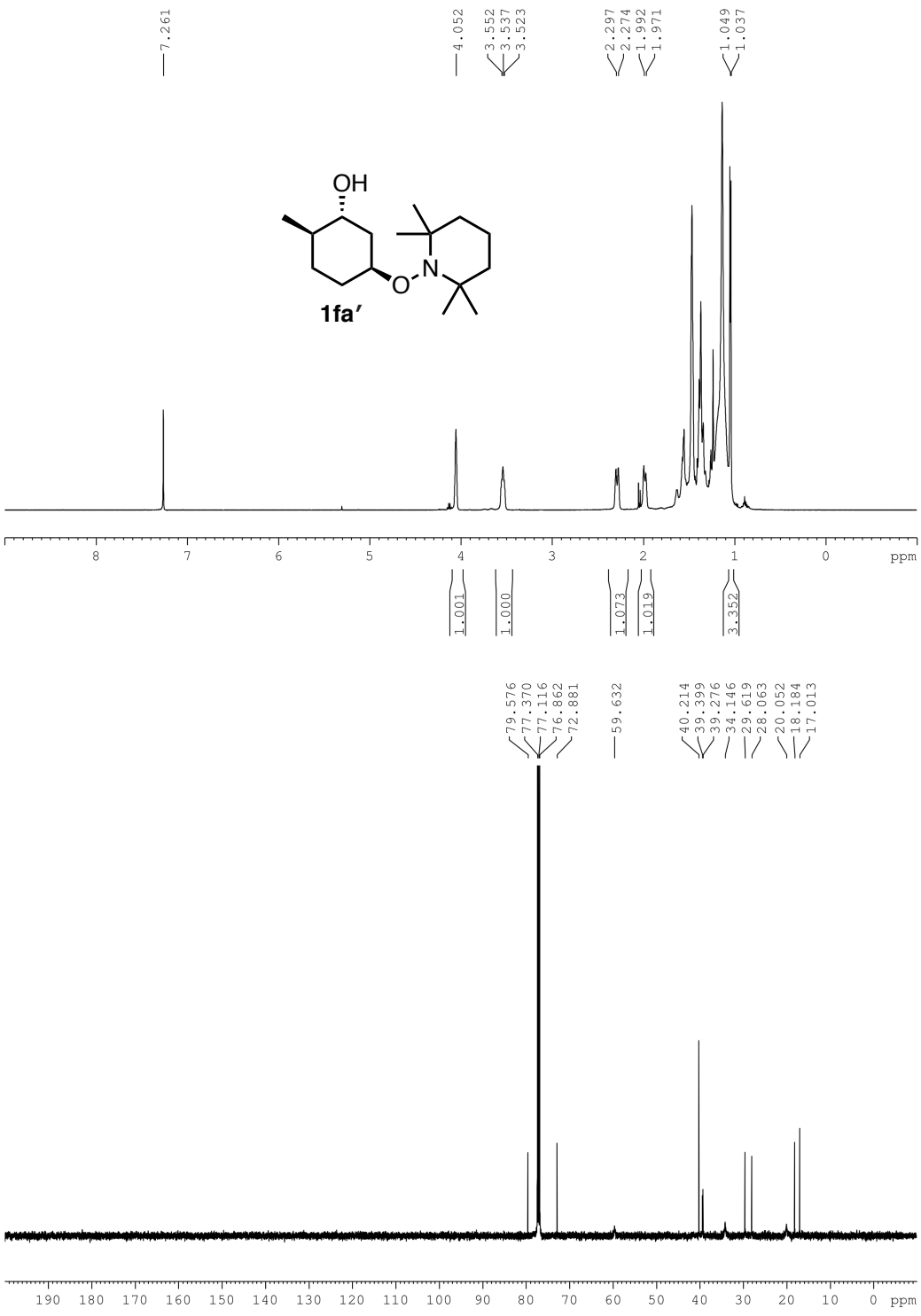
HMBC (400 MHz, $CDCl_3$) NMR Spectrum of **1fa**



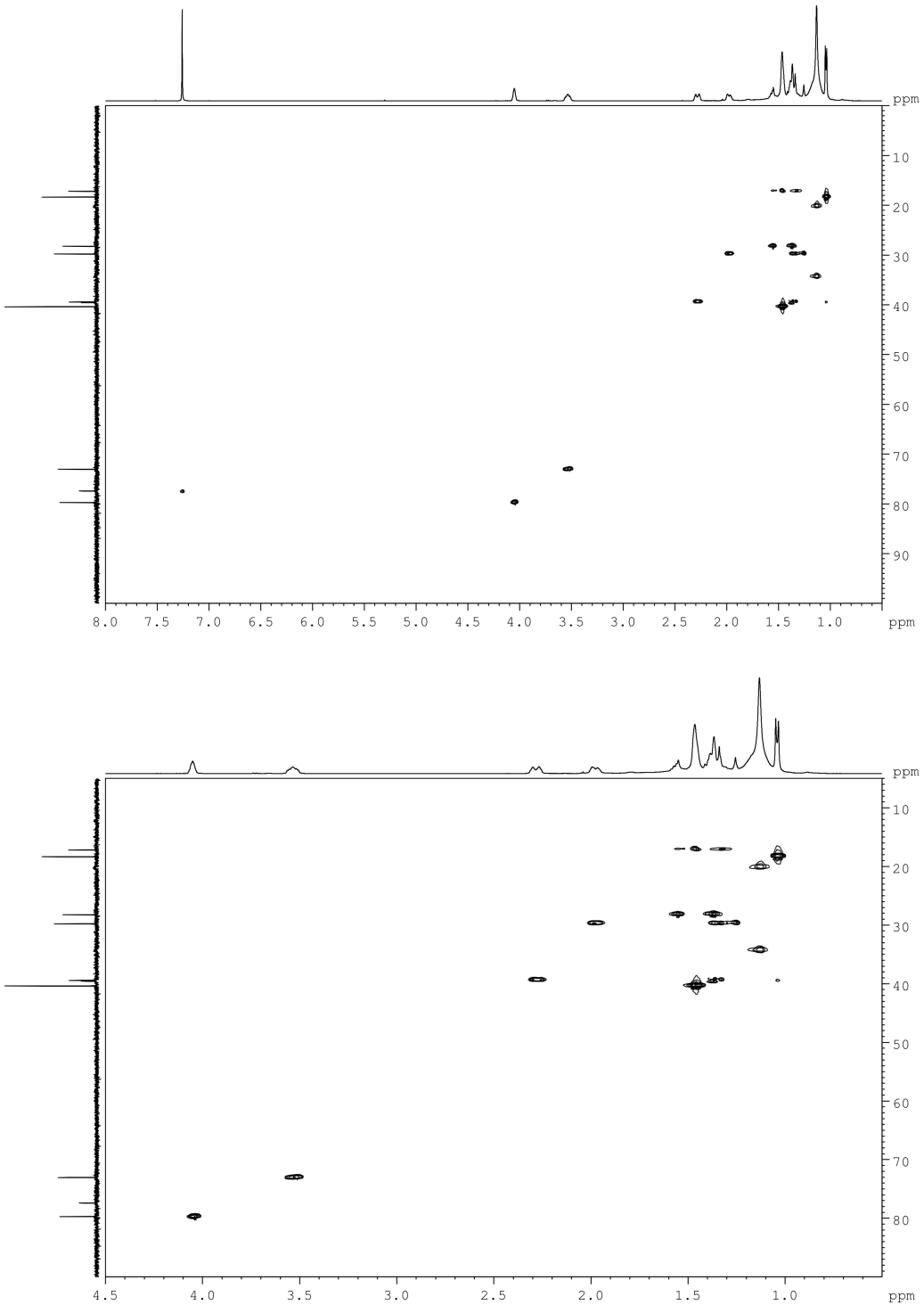
COSY (400 MHz, $CDCl_3$) NMR Spectrum of **1fa**



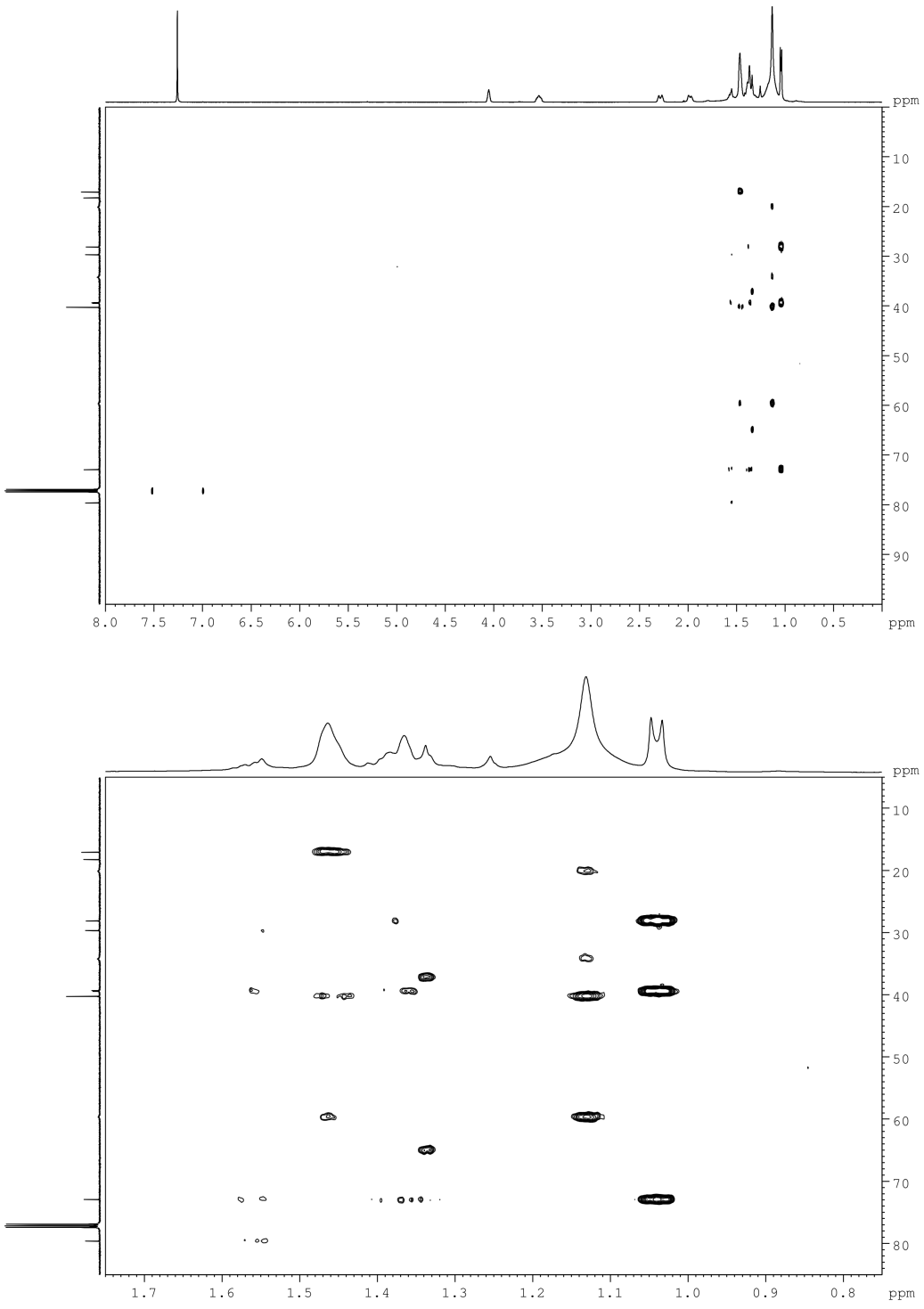
NOESY (400 MHz, $CDCl_3$) NMR Spectrum of **1fa**



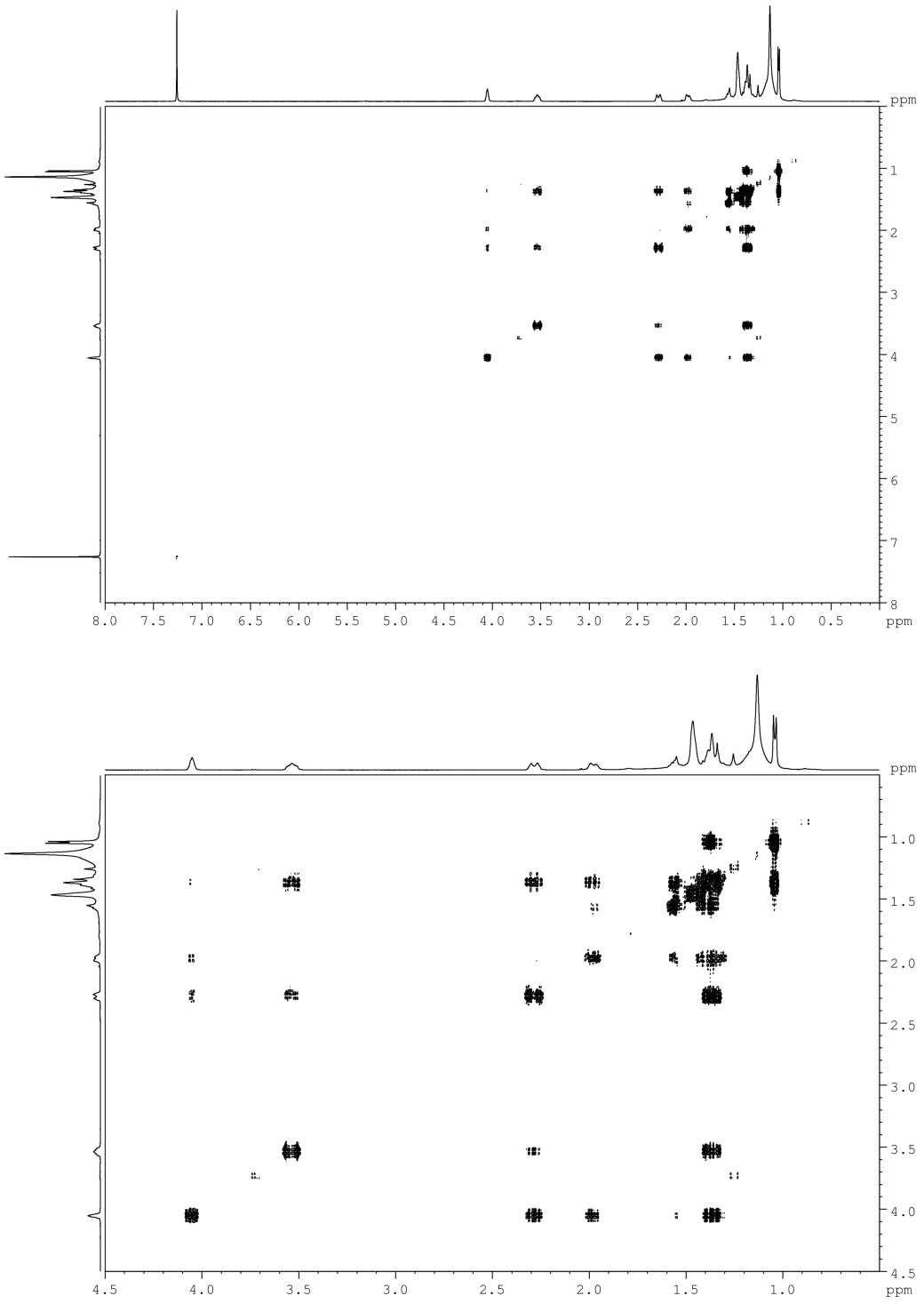
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **1fa′**



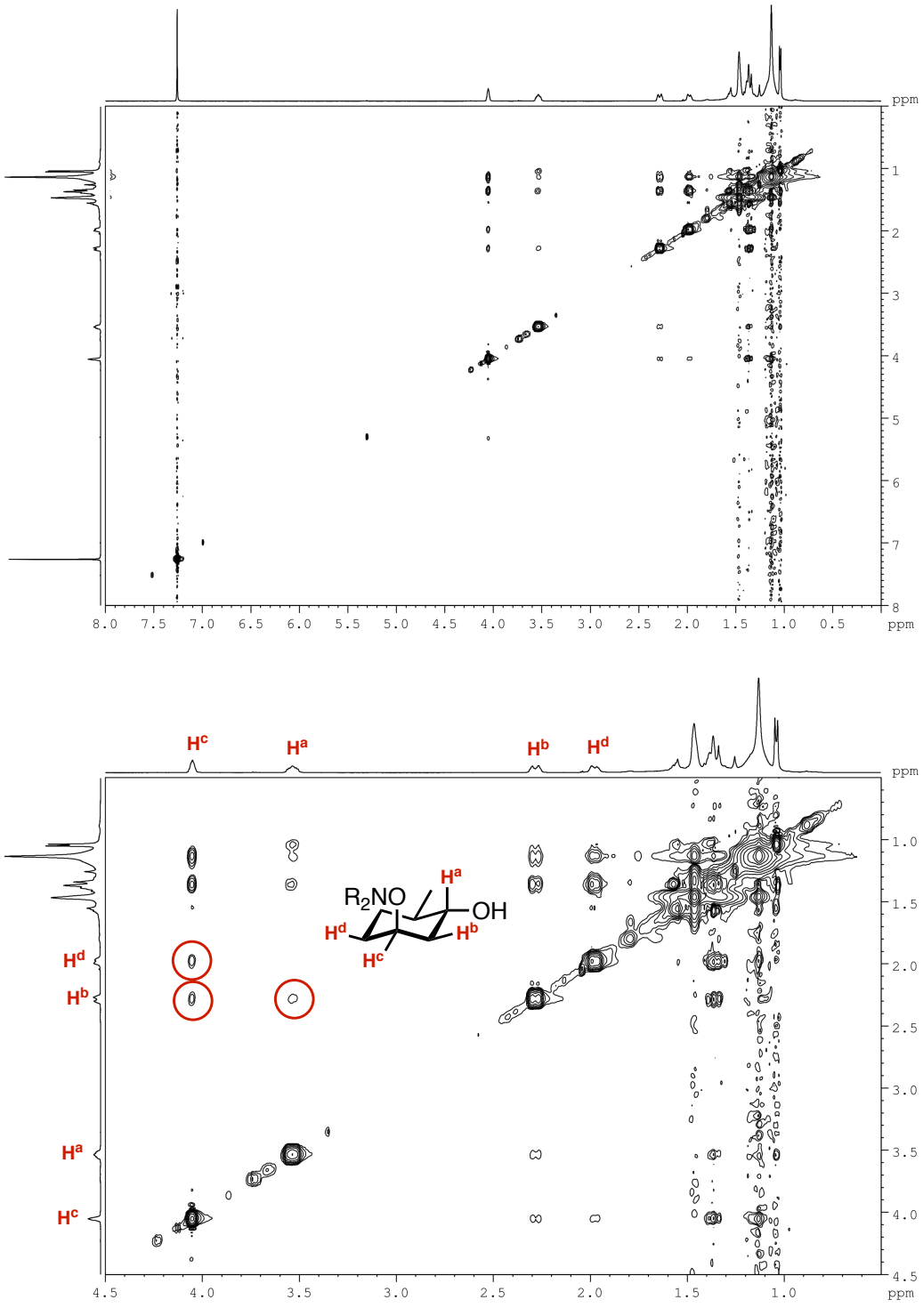
HSQC (400 MHz, $CDCl_3$) NMR Spectrum of **1fa′**



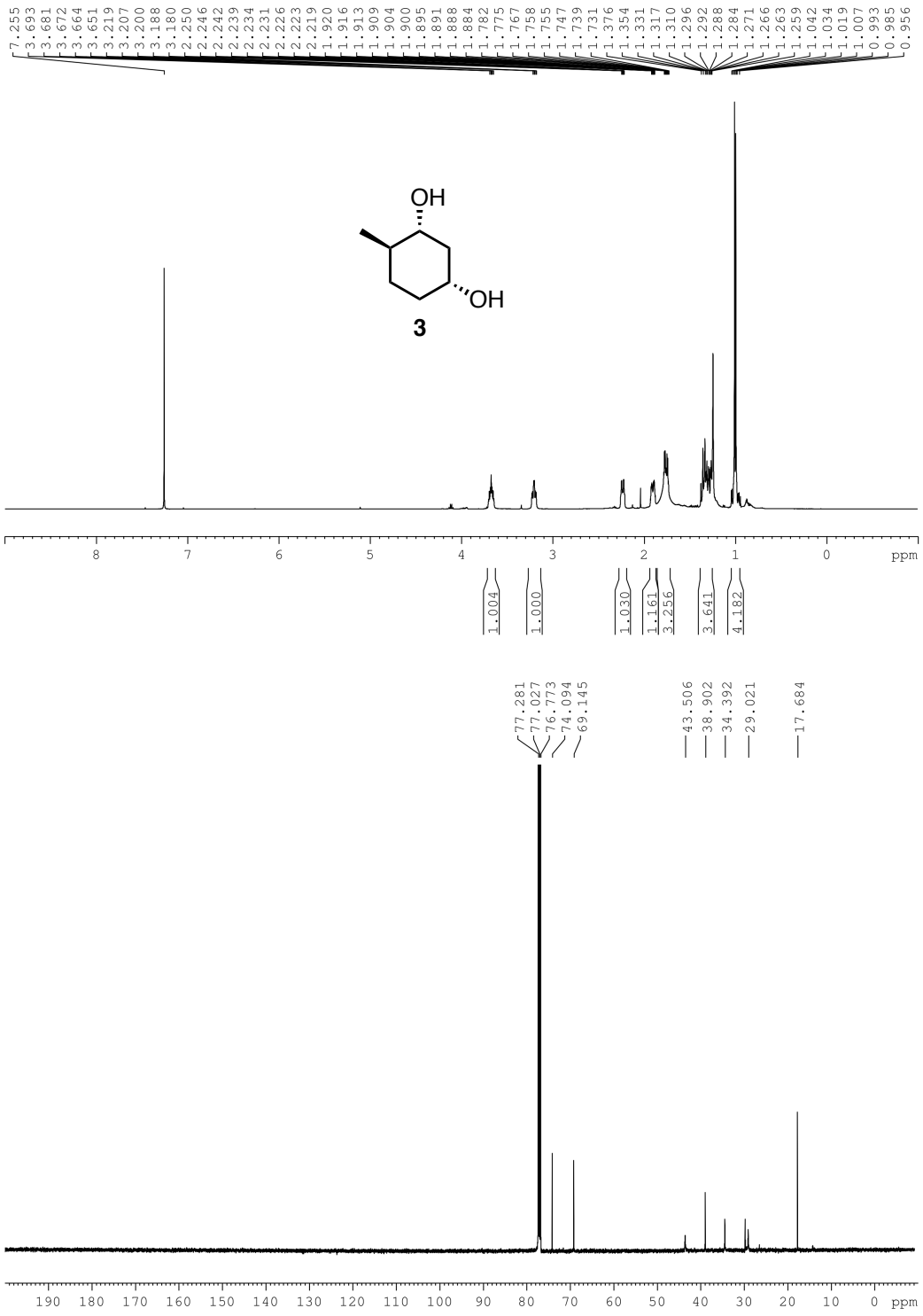
HMBC (400 MHz, $CDCl_3$) NMR Spectrum of **1fa′**



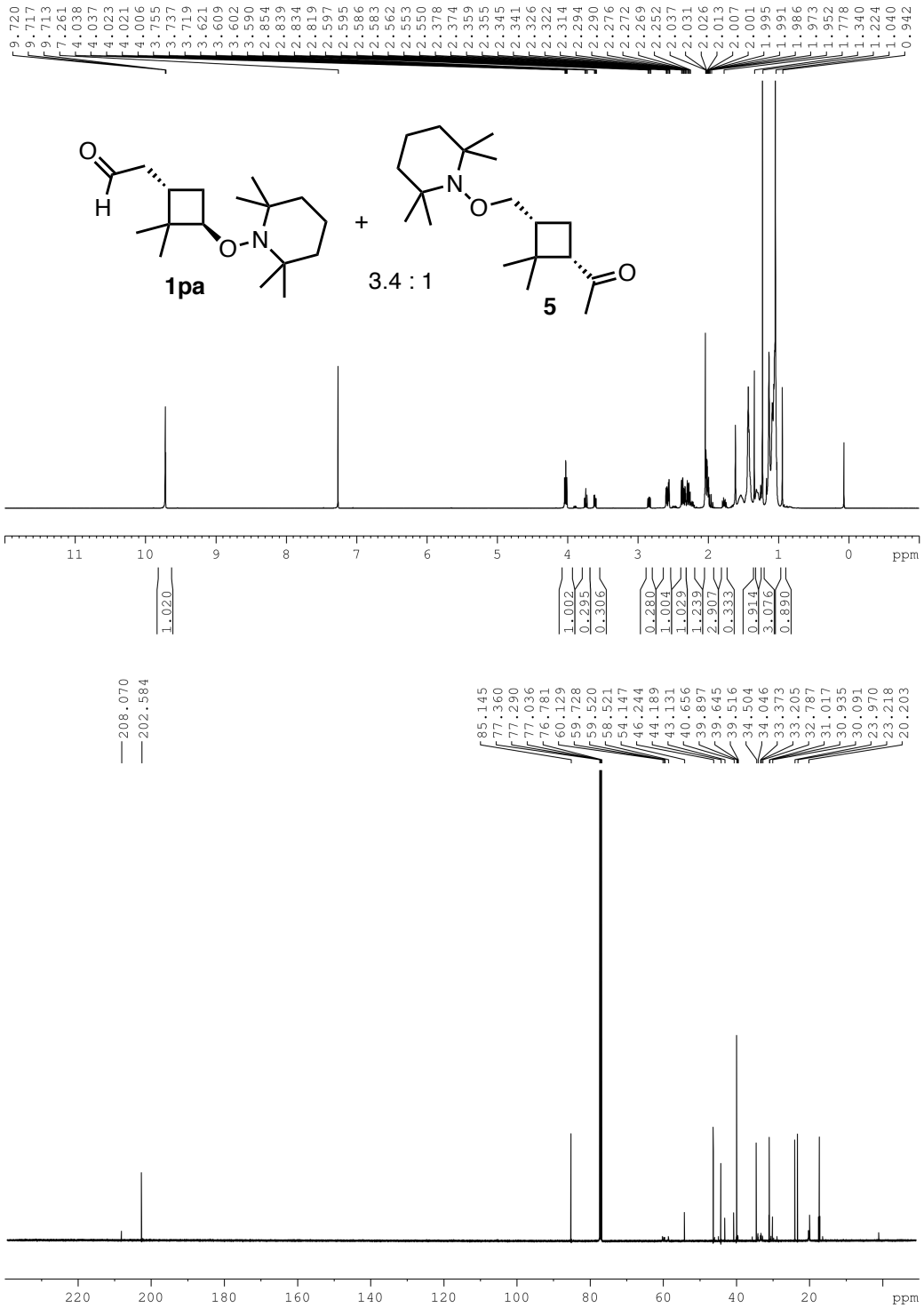
COSY (400 MHz, $CDCl_3$) NMR Spectrum of **1fa′**



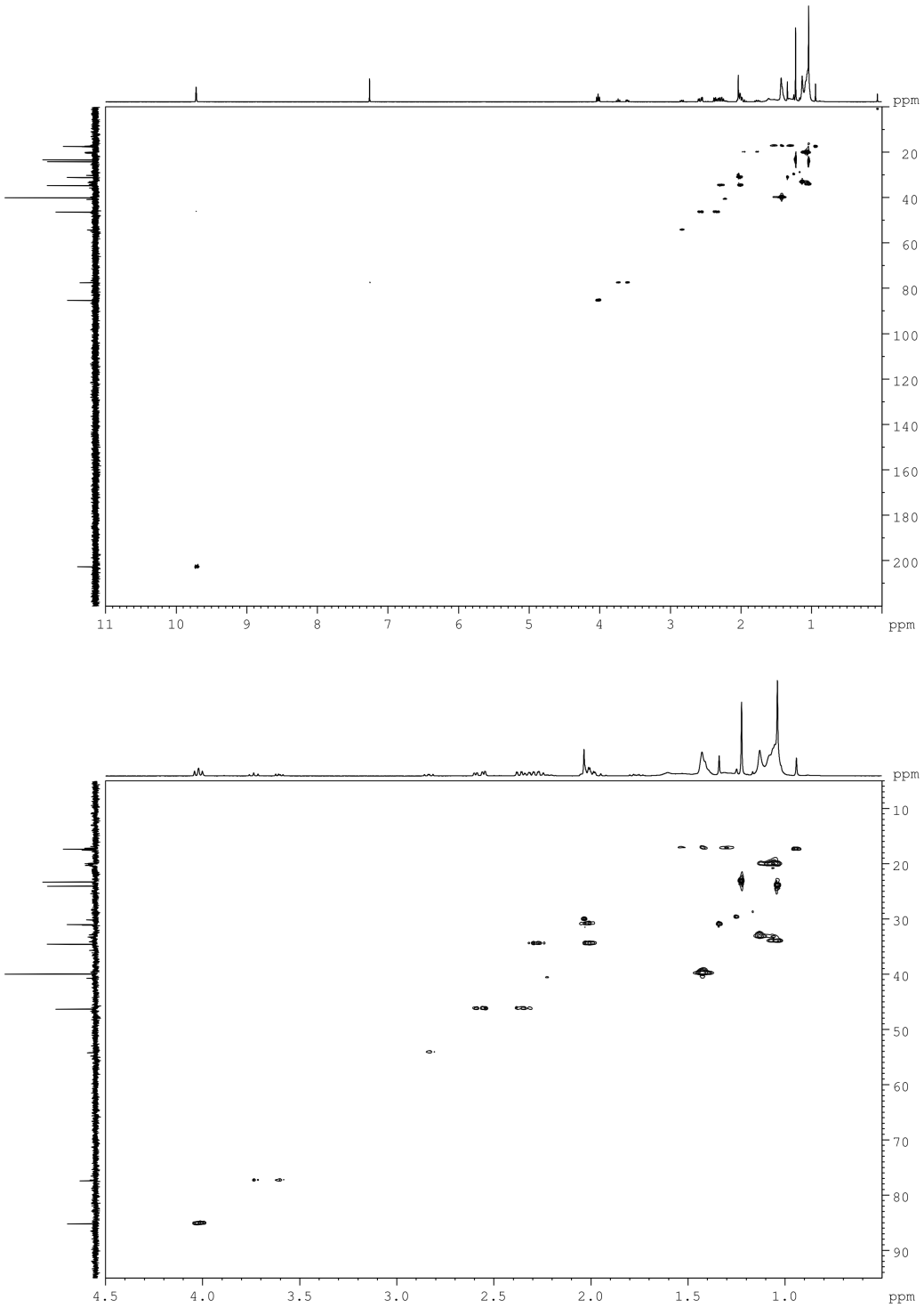
NOESY (400 MHz, $CDCl_3$) NMR Spectrum of **1fa′**



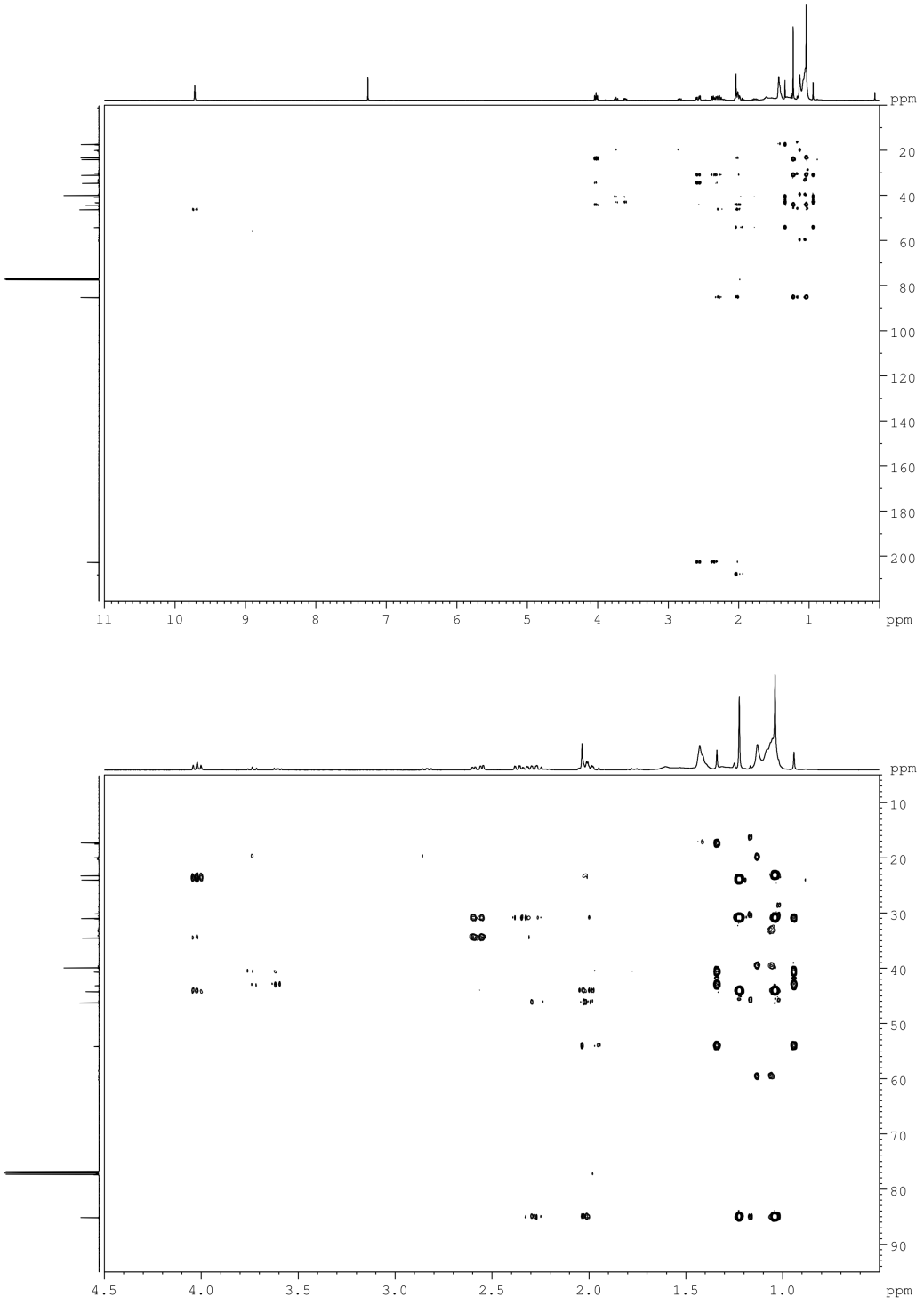
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **3**



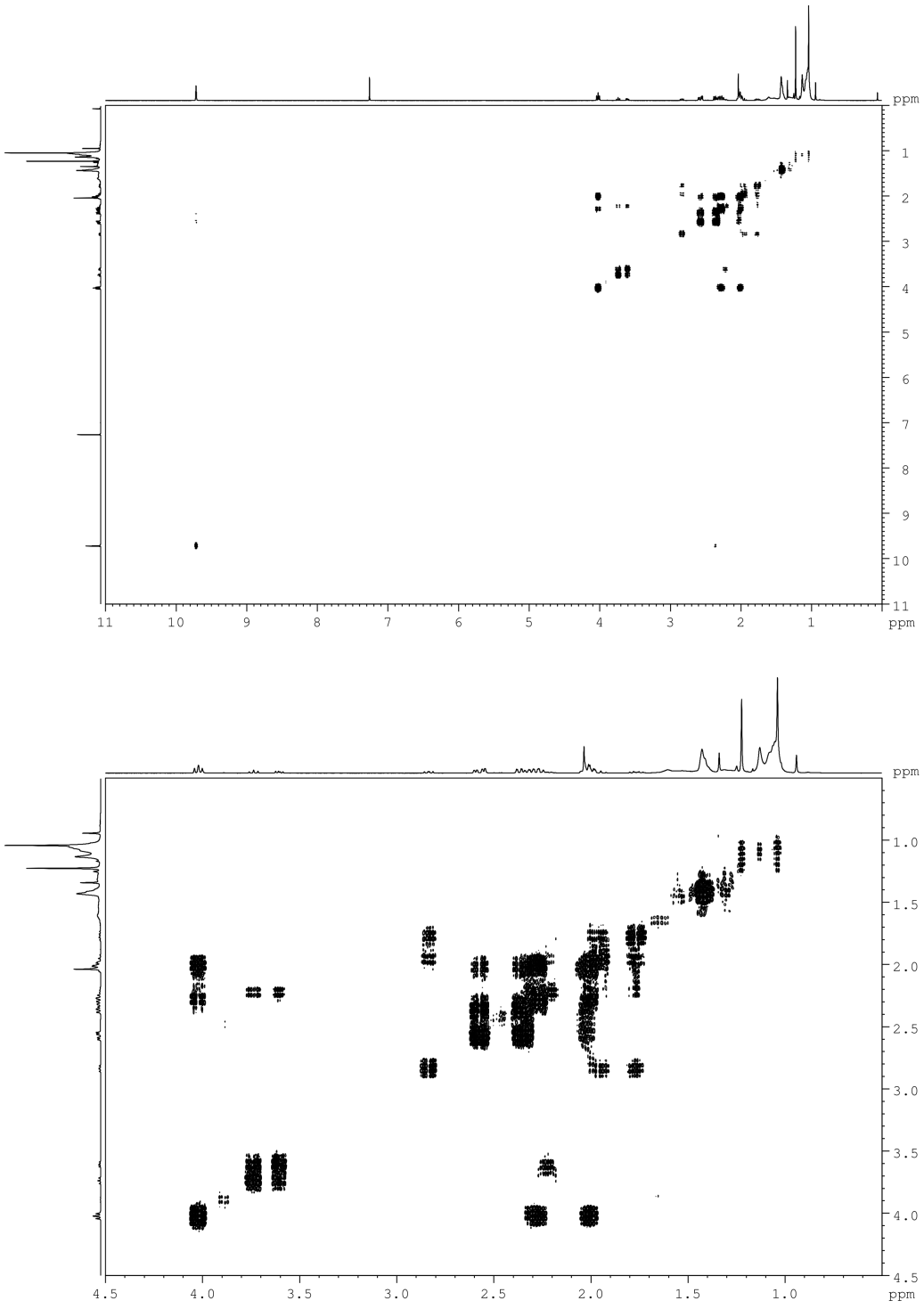
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **1pa** and **5** (3.4:1)



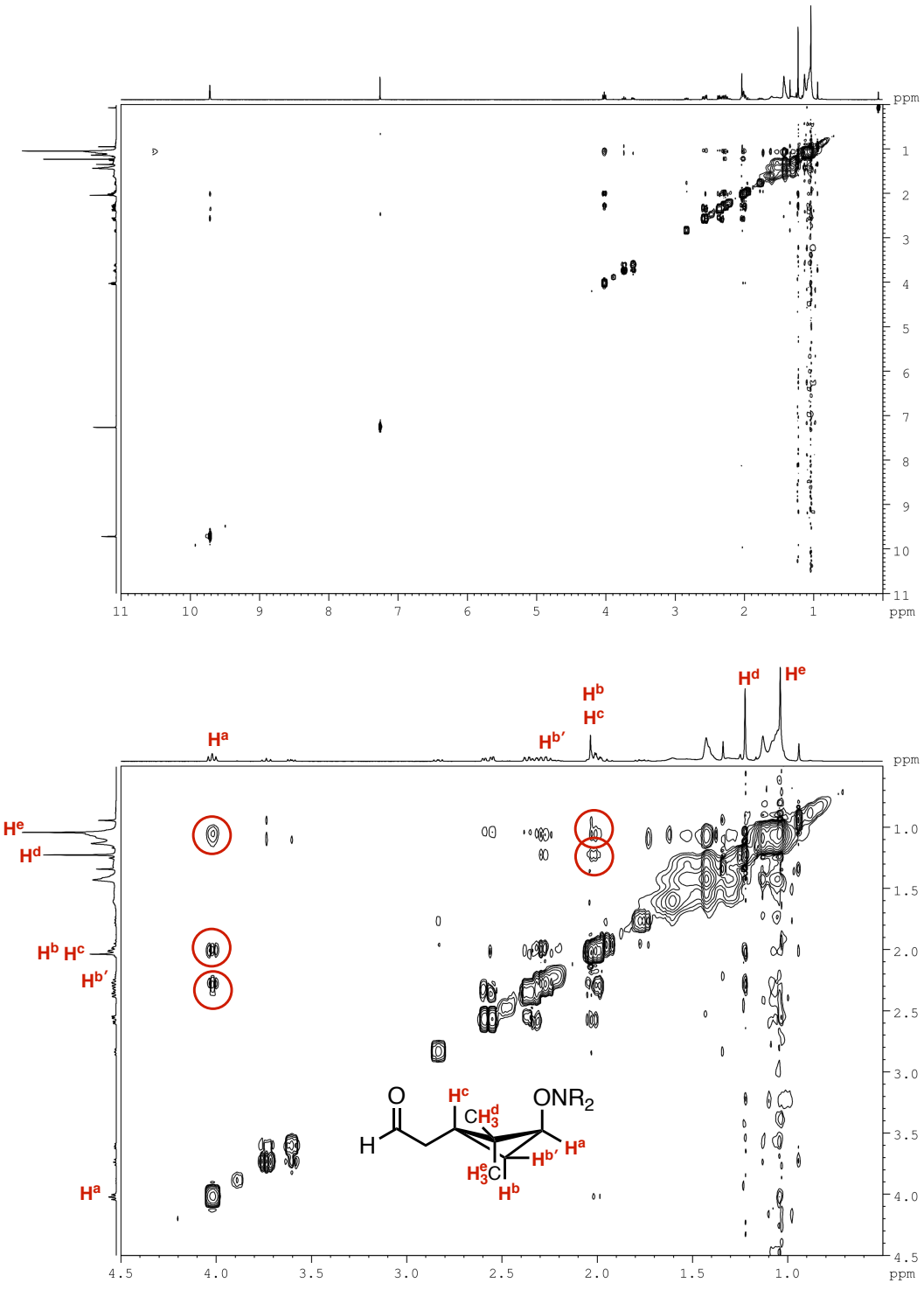
HSQC (400 MHz, $CDCl_3$) NMR Spectrum of **1pa** and **5** (3.4:1)



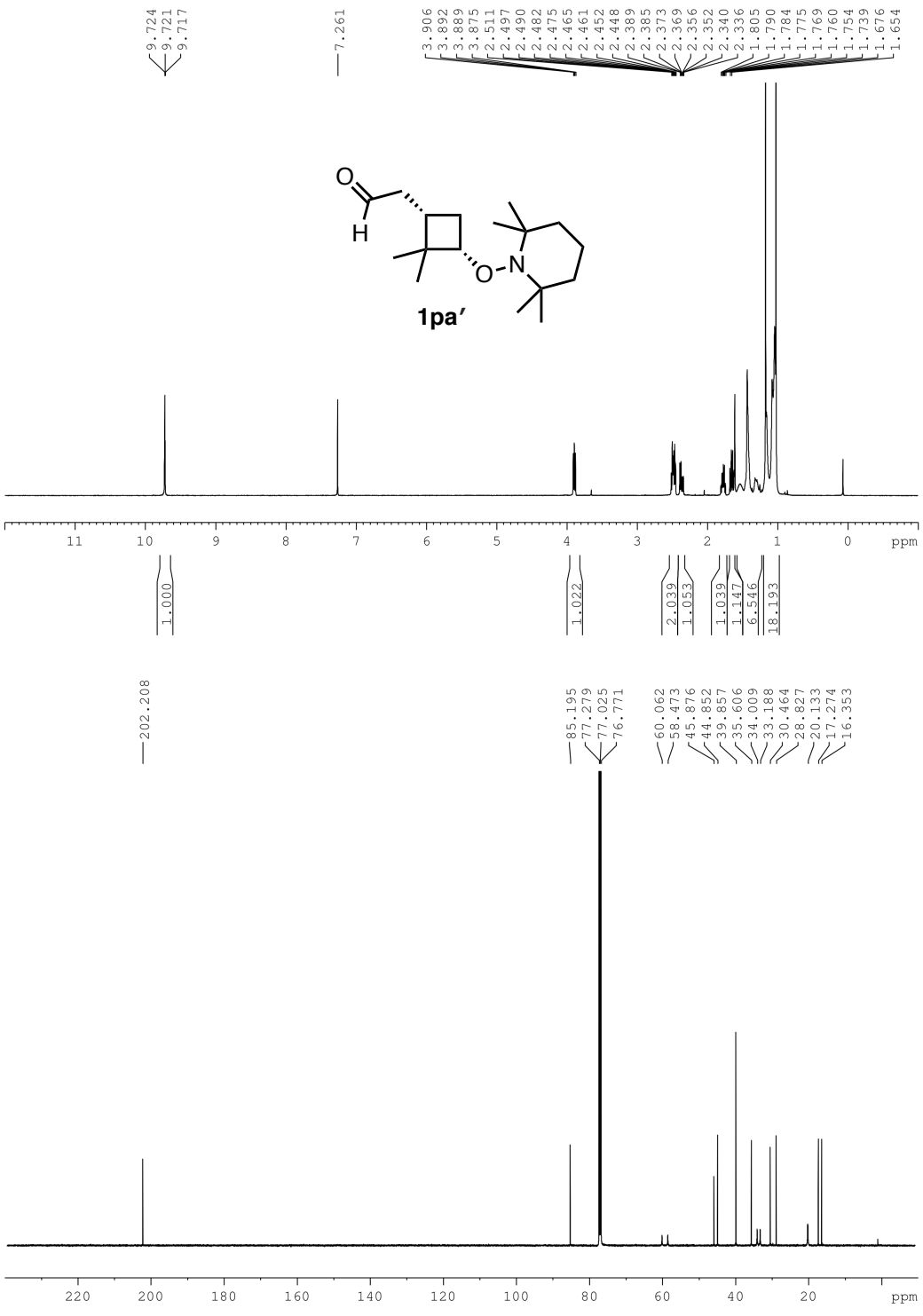
HMBC (400 MHz, $CDCl_3$) NMR Spectrum of **1pa** and **5** (3.4:1)



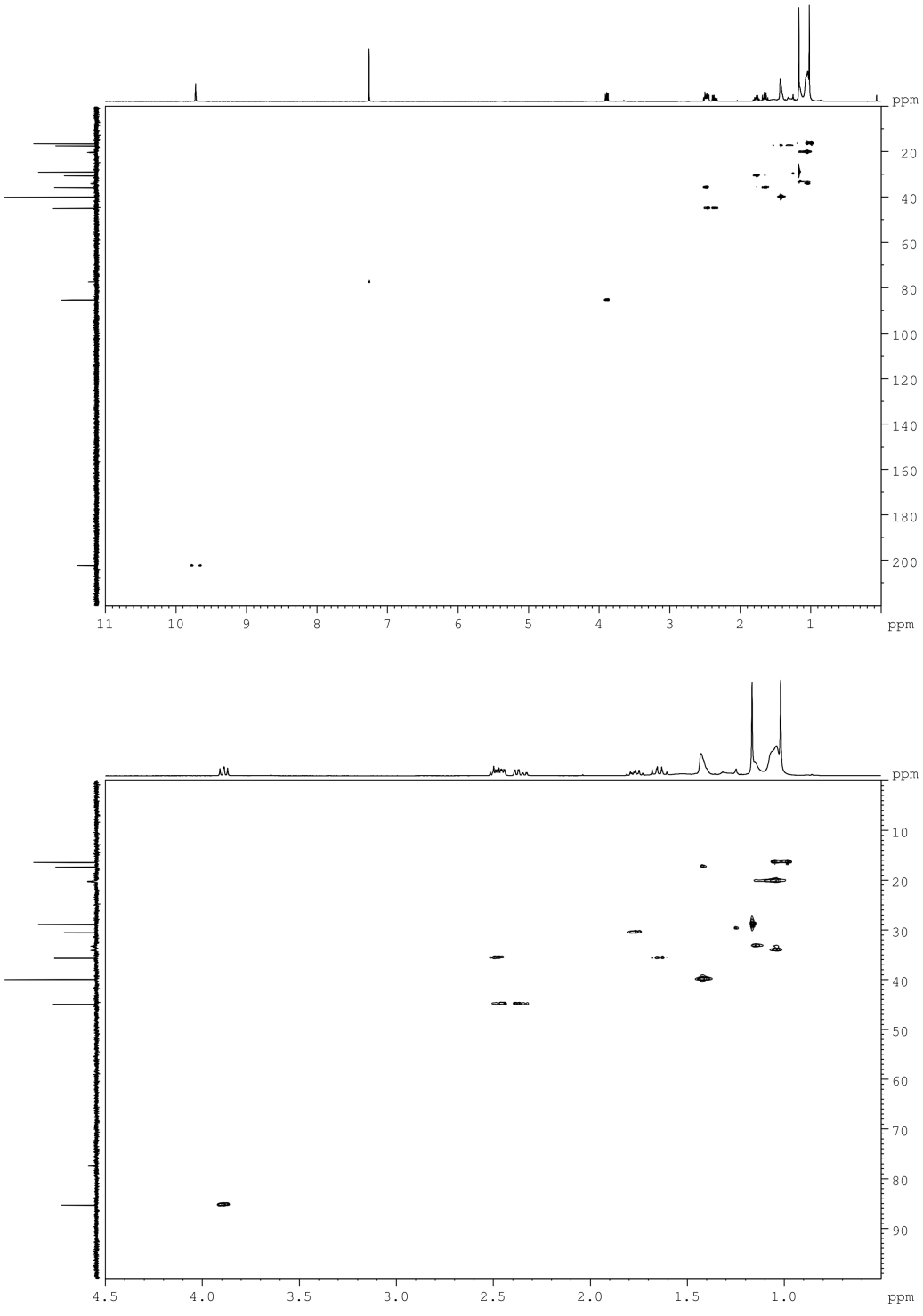
COSY (400 MHz, $CDCl_3$) NMR Spectrum of **1pa** and **5** (3.4:1)



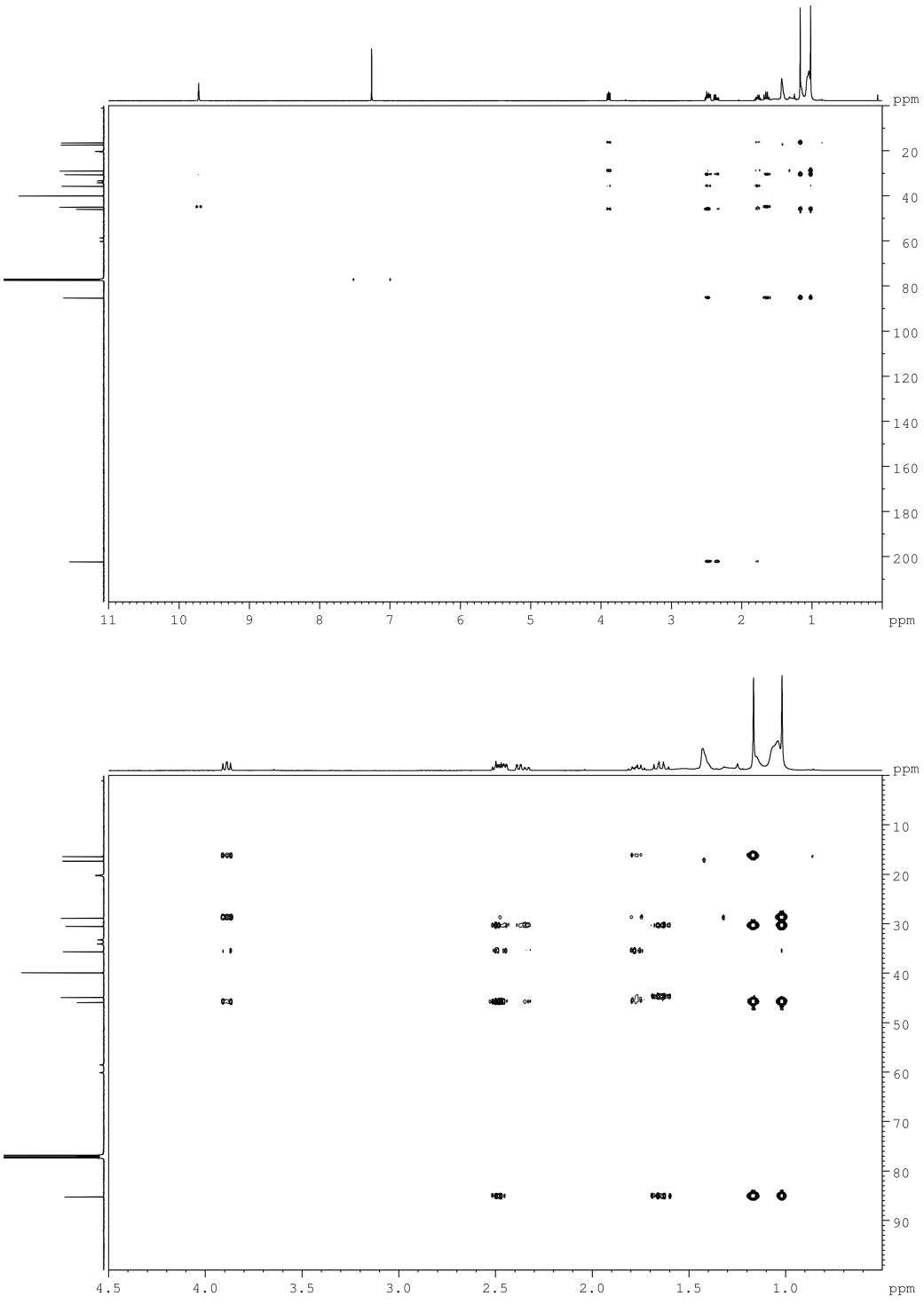
NOESY (400 MHz, $CDCl_3$) NMR Spectrum of **1pa** and **5** (3.4:1)



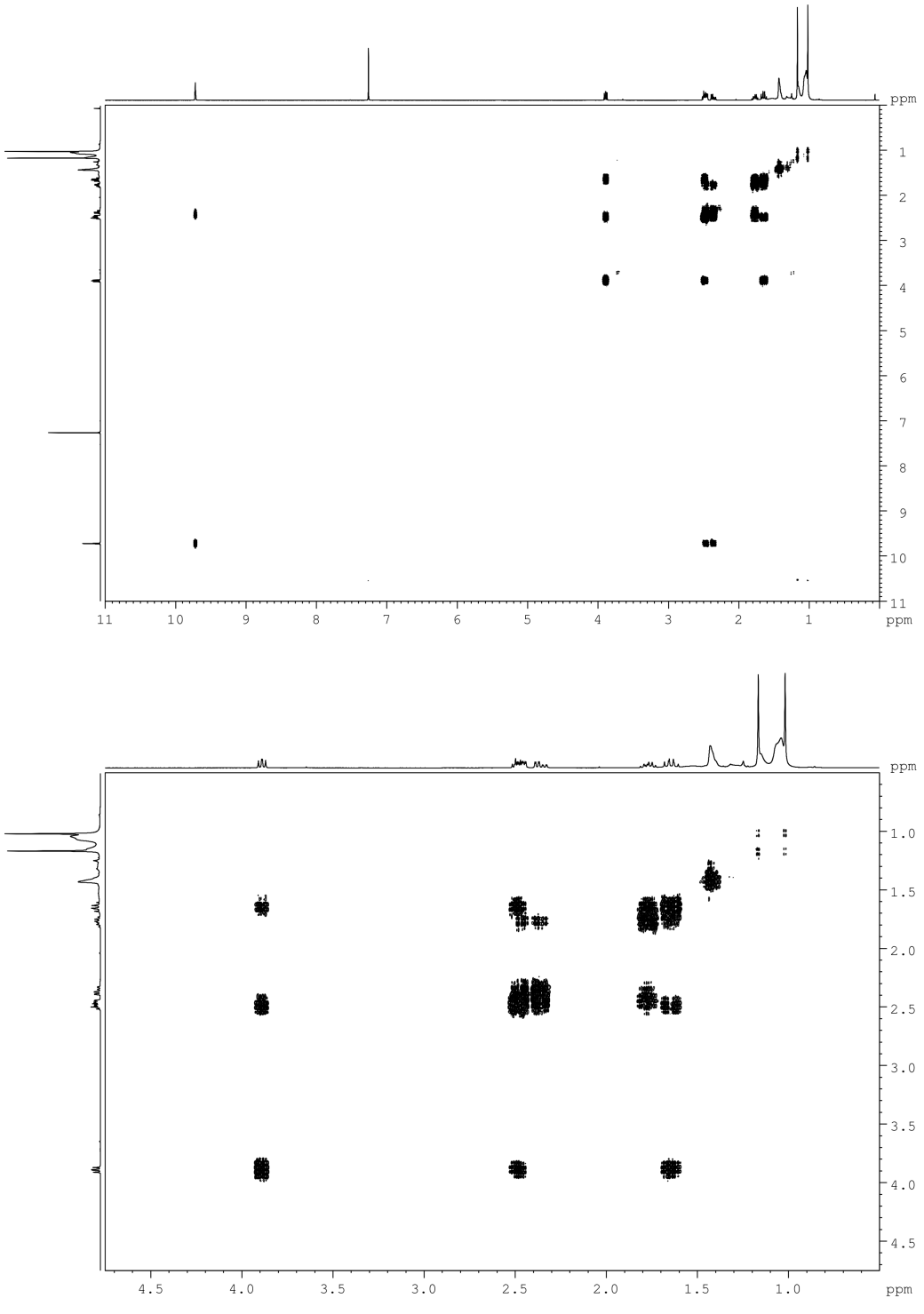
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **1pa′**



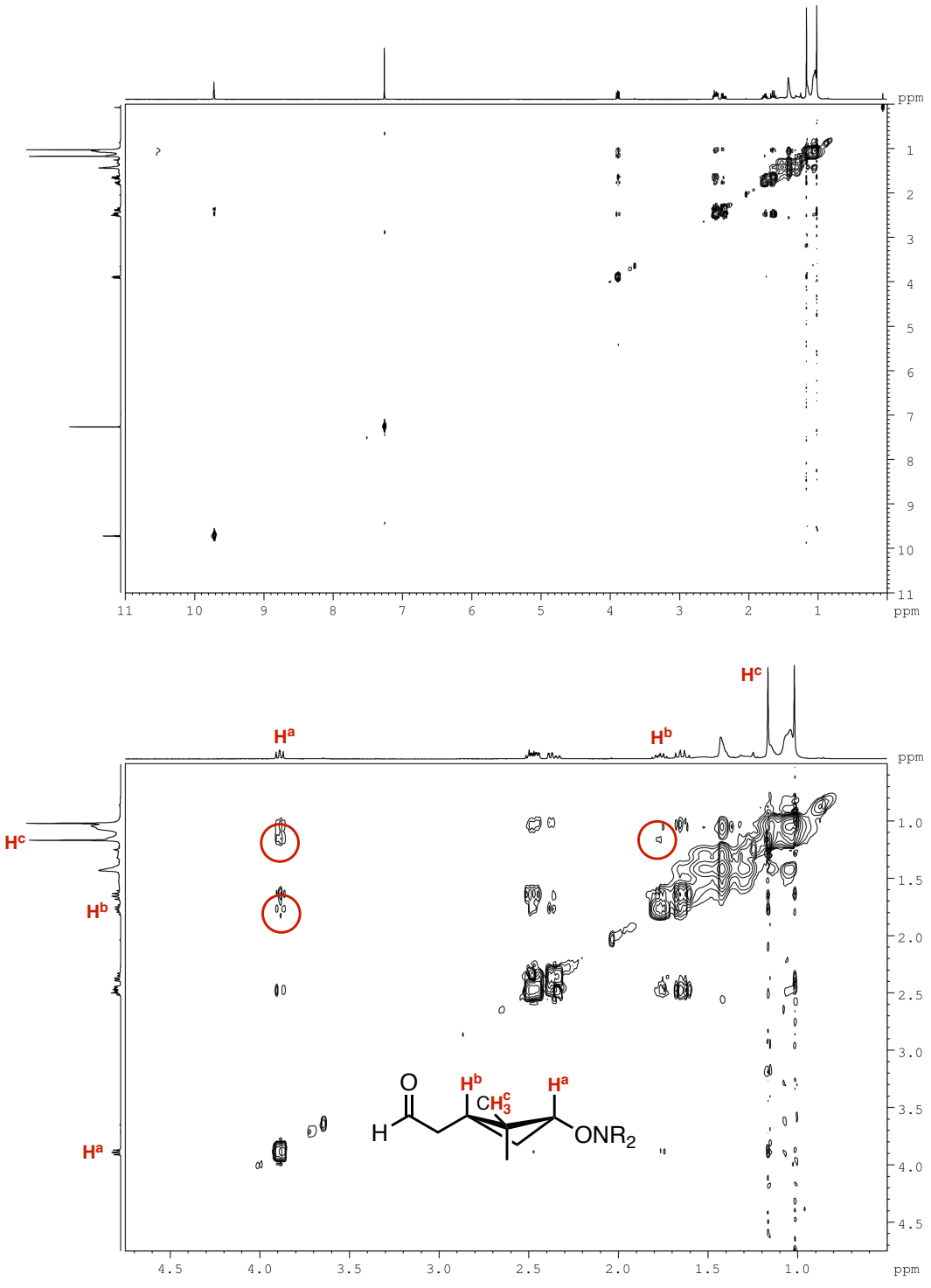
HSQC (400 MHz, $CDCl_3$) NMR Spectrum of **1pa′**



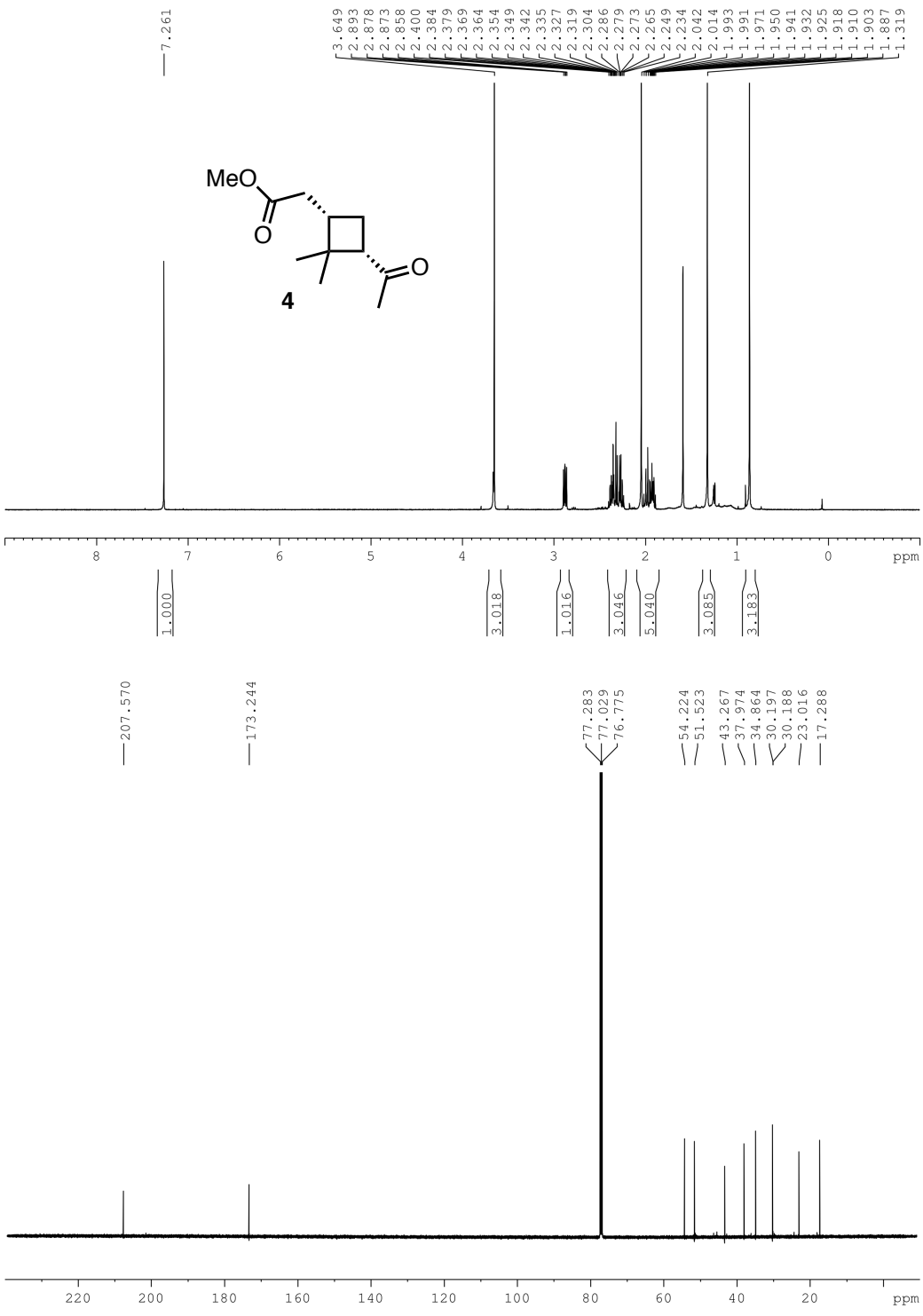
HMBC (400 MHz, $CDCl_3$) NMR Spectrum of **1pa′**



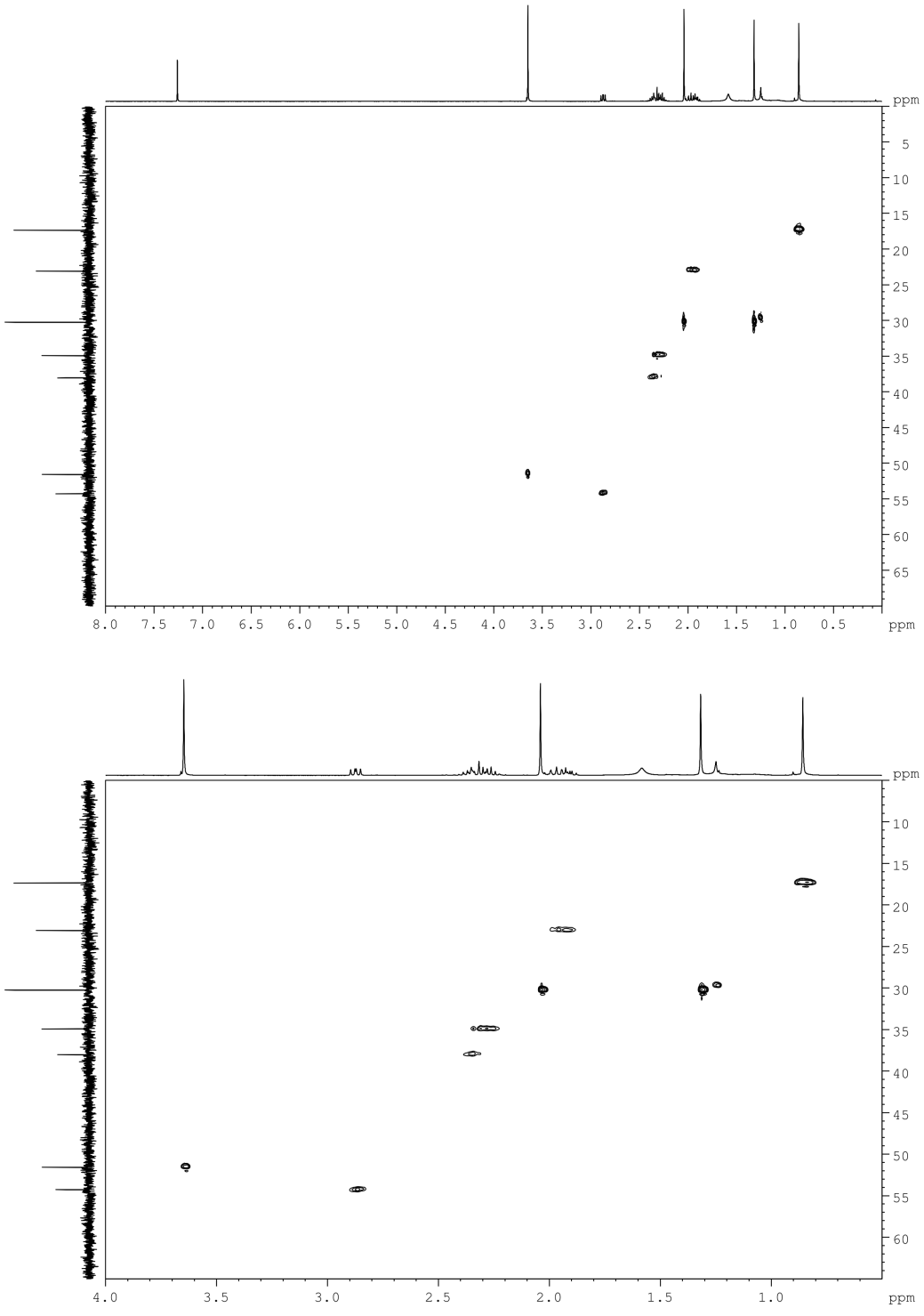
COSY (400 MHz, $CDCl_3$) NMR Spectrum of **1pa′**



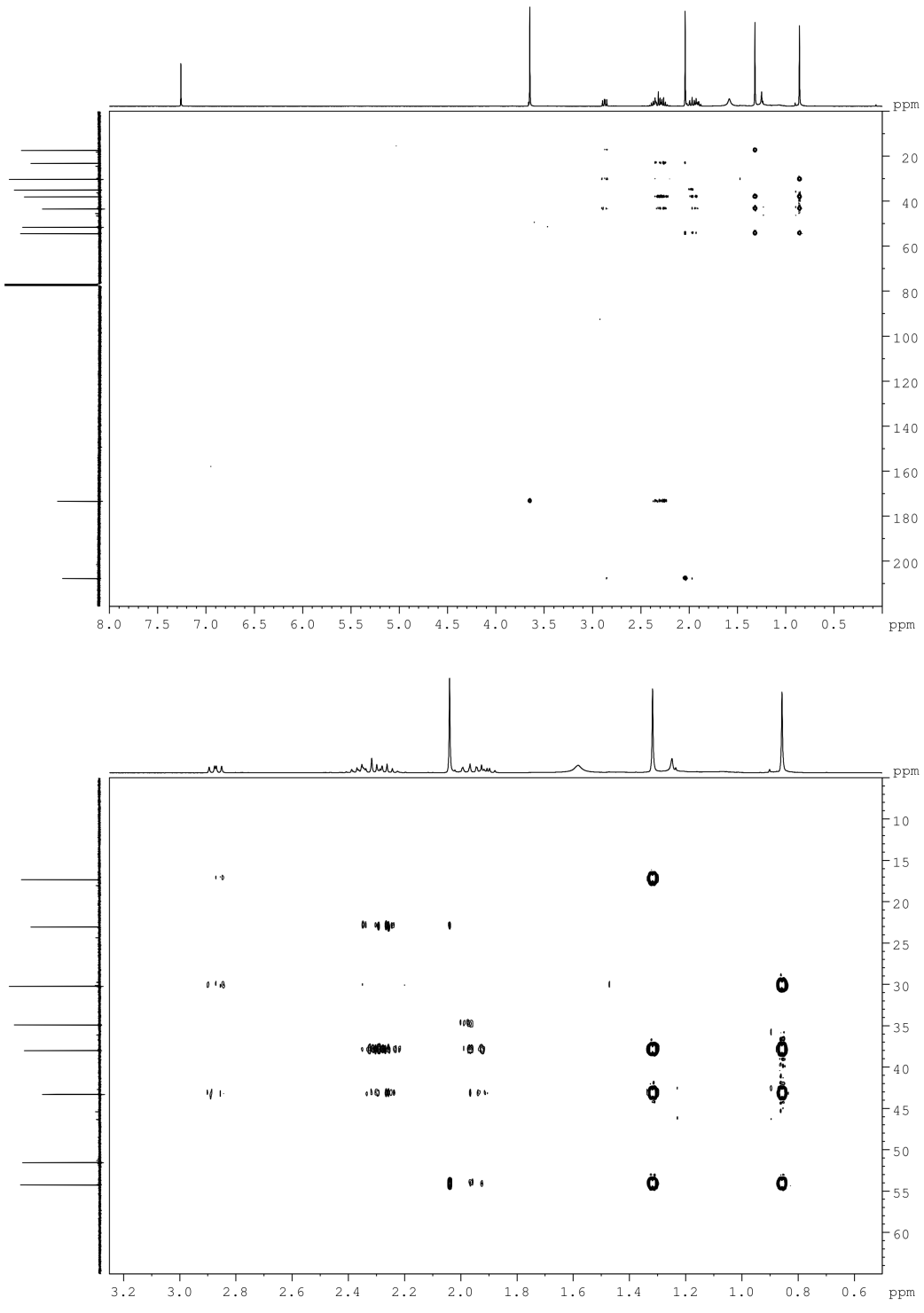
NOESY (400 MHz, $CDCl_3$) NMR Spectrum of **1pa′**



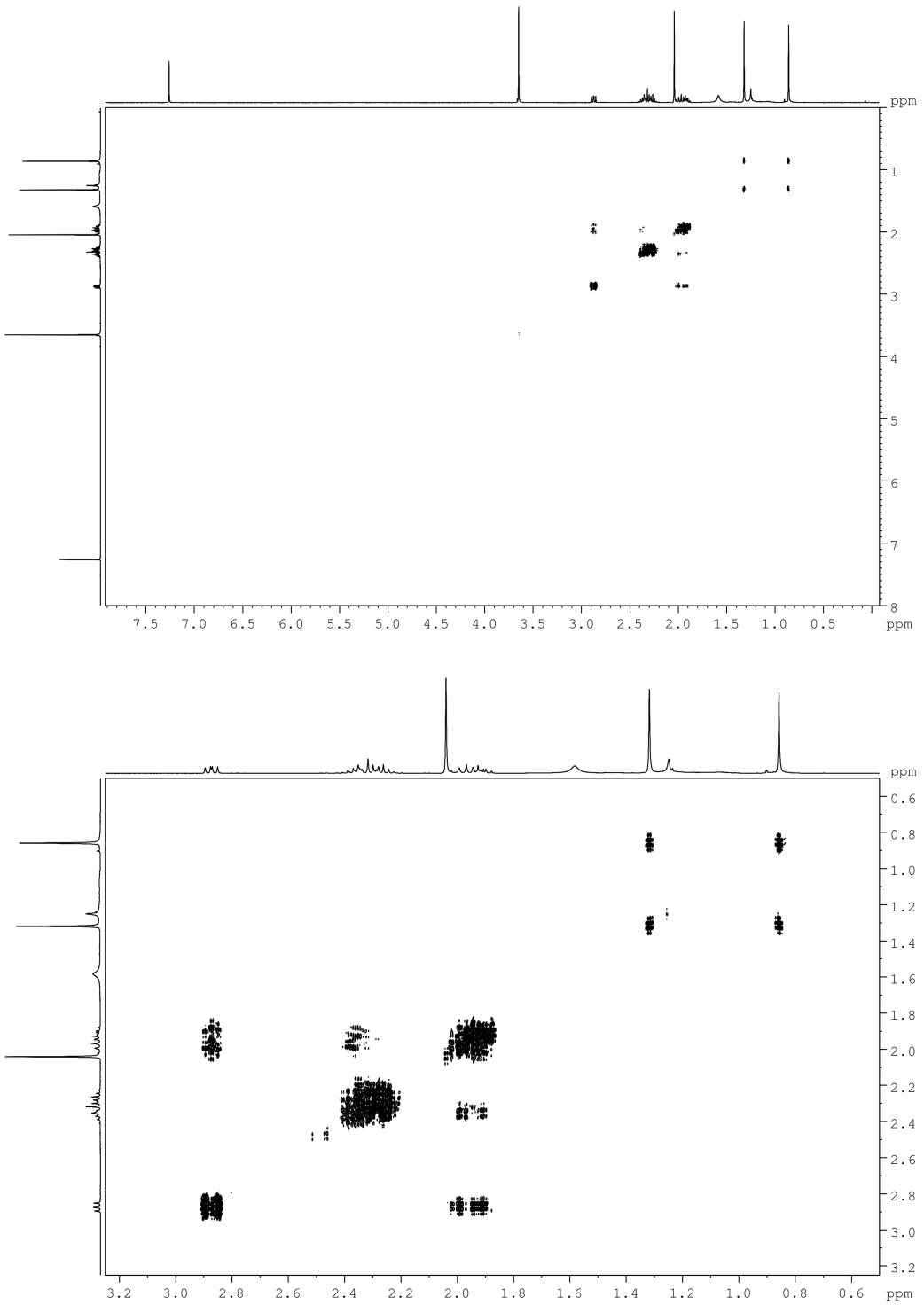
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (125 MHz, $CDCl_3$) NMR Spectra of **4**



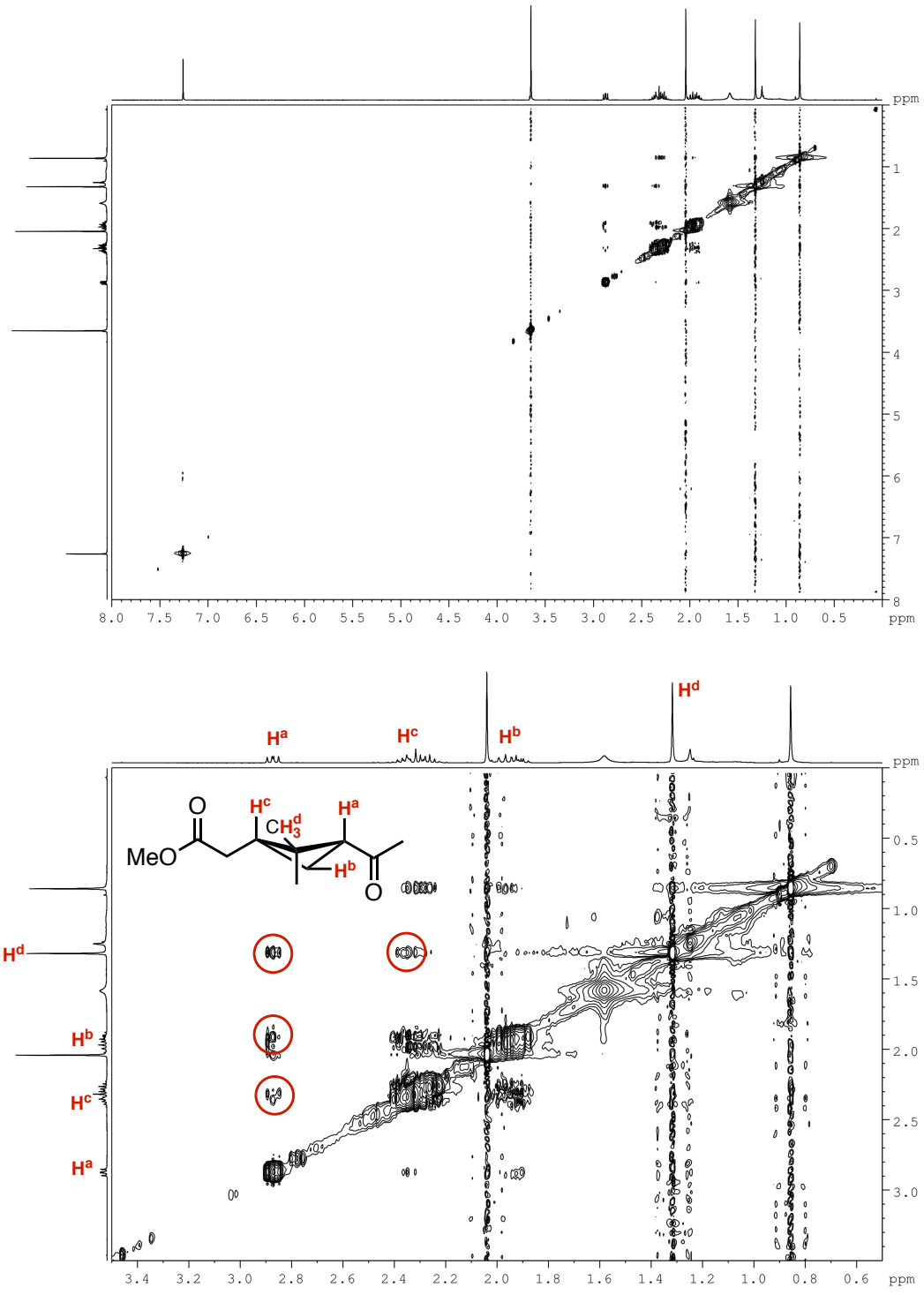
HSQC (400 MHz, $CDCl_3$) NMR Spectrum of **4**



HMBC (400 MHz, $CDCl_3$) NMR Spectrum of **4**



COSY (400 MHz, $CDCl_3$) NMR Spectrum of **4**



NOESY (400 MHz, $CDCl_3$) NMR Spectrum of **4**

9. References

1. Huang, D.; Schuppe, A. W.; Liang, M. Z.; Newhouse, T. R. *Org. Biomol. Chem.* **2016**, *14*, 6197–6200.

2. Dong, J.-L.; Yu, L.-S.-H.; Xie, J.-W. *ACS Omega* **2018**, *3*, 4974–4985.

3. Steiner, D.; Ivision, L.; Goralski, C. T.; Appell, R. B.; Gojkovic, J. R.; Singaram, B. *Tetrahedron: Asymmetry* **2002**, *13*, 2359–2363.

4. Solladie, G.; Hutt, J. *J. Org. Chem.* **1987**, *52*, 3560–3566.

5. Tanveer, K.; Kim, S.-J.; Taylor, M. S. *Org. Lett.* **2018**, *20*, 5327–5331.

6. Yang, H.; Gao, Y.; Qiao, X.; Xie, L.; Xu, X. *Org. Lett.* **2011**, *13*, 3670–3673.

7. Smaligo, A. J.; Vardhineedi, S.; Kwon, O. *ACS Catal.* **2018**, *8*, 5188–5192.

8. Muller, G.; Sainz, D. *J. Organomet. Chem.* **1995**, *495*, 103–111.

9. Yan, T.-H.; Tsai, C.-C.; Chien, C.-T.; Cho, C.-C.; Huang, P.-C. *Org. Lett.* **2004**, *6*, 4961–4963.

10. Smaligo, A. J.; Swain, M.; Quintana, J. C.; Tan, M. F.; Kim, D. A.; Kwon, O. *Science* **2019**, *364*, 681–685.

11. Bao, J.; Tian, H.; Yang, P.; Deng, J.; Gui, J. *ChemRxiv* **2019**, DOI: 10.26434/chemrxiv.8874455.v1.

12. Caster, K. C.; Rao, A. S.; Mohan, H. R.; McGrath, N. A.; Brichacek, M. Trifluoroperacetic acid. In *e-EROS Encyclopedia of Reagents for Organic Synthesis*; Wiley, 2012; DOI: 10.1002/047084289X.rt254.pub2.

13. Crandall, J. K.; Curci, R.; D'Accolti, L.; Fusco, C. Dimethyldioxirane. In *e-EROS Encyclopedia of Reagents for Organic Synthesis*; Wiley, 2005; DOI: 10.1002/047084289X.rd329.pub2.

14. Chen, B.-C.; Davis, F. A. (±)-*trans*-2-(Phenylsulfonyl)-3-phenyloxaziridine. In *e-EROS Encyclopedia of Reagents for Organic Synthesis*; Wiley, 2001; DOI: 10.1002/047084289X.rp115.

15. Rao, A. S.; Mohan, H. R.; Hofferberth, J. E.; Nikonov, G. Peracetic acid. In *e-EROS Encyclopedia of Reagents for Organic Synthesis*; Wiley, 2013; DOI: 10.1002/047084289X.rp034.pub3.

16. Krow, G. R. Monoperoxysulfuric acid. In *e-EROS Encyclopedia of Reagents for Organic Synthesis*; Wiley, 2001; DOI: 10.1002/047084289X.rm288m.

17. McGuire, H. M.; Odom, H. C.; Pinder, A. R. *J. Chem. Soc., Perkin Trans.* **1974**, *1*, 1879–1883.

18. (a) Bueno, A. B.; Carreño, M. C.; Ruano, J. L. G. *Tetrahedron Lett.* **1995**, *36*, 3737–3740. (b) Horn, E. J.; Rosen, B. R.; Chen, Y.; Tang, J.; Chen, K.; Eastgate, M. D.; Baran, P. S. *Nature* **2016**, *533*, 77–81.

19. A. C. Ferretti, H.-W. Man, J. Muslehiddinoglu, J. Xu, K. H.-Y. Yong, M. G. Beauchamps, M. A. Kothare, N. Zhou, N. A. Boersen, Y. Li, R. Hilgraf, M. A. Nagy, D. Zou, L. Huang, Solid forms of 2-(tert-butylamino)-4-((1r,3r,4r)-3-hydroxy-4-methylcyclohexylamino)-pyrimidine-5-carboxamide, compositions thereof and methods of their use. WO 2015116755 A2, January 30, 2014.

20. Vankar, Y. D.; Chaudhuri, N. C.; Rao, C. T. *Tetrahedron Lett.* **1987**, *28*, 551–554.

21. Renzoni, G. E.; Borden, W. T. *J. Org. Chem.* **1983**, *48*, 5231–5236.

22. Jahn, E.; Smrcek, J.; Pohl, R.; Císarová, I.; Jones, P. G.; Jahn, U. *Eur. J. Org. Chem.* **2015**, 7785–7798.

23. (a) Kamens, R.; Jang, M.; Chien, C.-J.; Leach, K. *Environ. Sci. Technol.* **1999**, *33*, 1430–1438. (b) Zhang, D.; Zhang, R. *J. Chem. Phys.* **2005**, *122*, 1–12. (c) Zhang, X.; Chen, Z.; Wang, H.; He, S.; Huang, D. *Atmos. Environ.* **2009**, *43*, 4465–4471.

24. (a) Hartmann, M.; Seiberth, M. *Helv. Chim. Acta.* **1932**, *15*, 1390–1392. (b) Robertson, A. *Nature* **1948**, *162*, 153.