# Supporting Information

## Construction of Fused- and Spiro- Oxa-[n.2.1] Skeletons by a Tandem Epoxide Rearrangement/Intramolecular [3+2] Cycloaddition of Cyclopropane with Carbonyls

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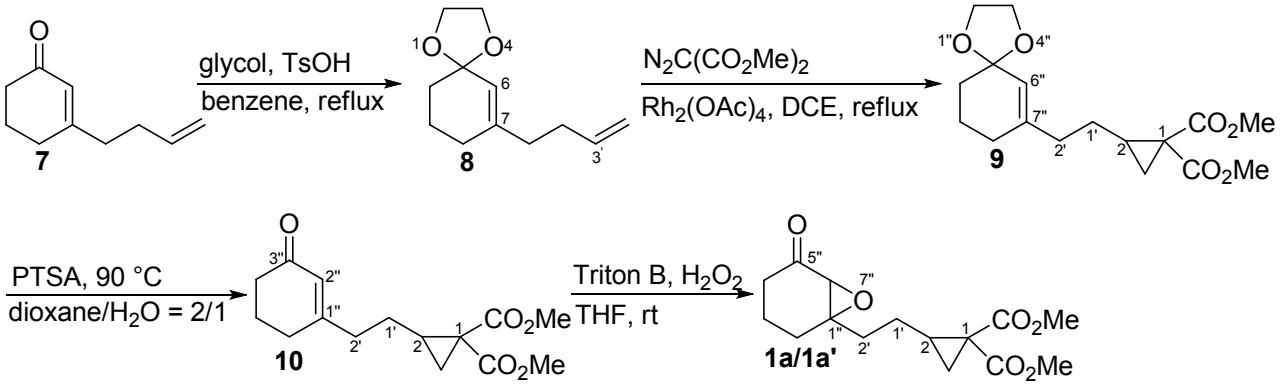
## 1. General information.

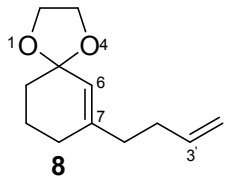
All reactions which required anhydrous conditions proceeded under argon atmosphere. Commercially available reagents were used as received. THF was distilled from sodium benzophenone, while other solvents were dried by distillation over the appropriate drying reagents. Reactions were monitored by TLC on silica gel (GF−254) plates. Column chromatography was performed through silica gel (200–300 mesh). The petroleum ether (PE) used had a b.p. range of 60–90 °C. $^1$H and $^{13}$C NMR (DEPT 135) spectra were recorded on a AM 400 MHz spectrometer ($^1$H at 400 MHz and $^{13}$C at 100 MHz) and a AM 600 MHz spectrometer ($^1$H at 600 MHz and $^{13}$C at 150 MHz). Chemical shifts (δ) were reported in parts per million (ppm) and coupling constants in Hertz (Hz). Tetramethylsilane or residual solvent signals as the internal reference ($CDCl_3$: $\delta_H$ = 7.26, $\delta_C$ = 77.0 ppm; [$D_6$]acetone: $\delta_H$ = 2.04, $\delta_C$ = 29.8 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet). Melting points were determined by use of a Microscope apparatus and are uncorrected. Accurate mass measurements were obtained on a 7.0 T FT-ICR or 4G mass spectrometer or on a double focusing sector-field instrument. Single crystal X-ray diffraction measurements were made on a diffractometer working with graphite monochromated Mo-$K_\alpha$ radiation.

## 2. Preparation of the starting materials

**Scheme 1.1 Preparation of substrate 1a/1a'**

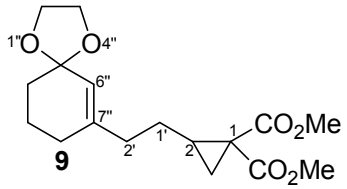



### 7-(But-3-enyl)-1,4-dioxaspiro[4.5]deca-6-ene (8)



To a solution of ketone **7**[1] (3.30 g, 22.0 mmol) in benzene (60 mL) was added glycol (2.45 mL, 44.0 mmol) and *p*-TsOH (189 mg, 1.10 mmol) at rt. The reaction mixture was refluxed for 12 h under a Dean-Stark setup. The mixture was concentrated under reduced pressure. Flash chromatography of the residue over silica gel (petroleum ether/EtOAc 30:1) afforded compound **8** (2.18 g, 51% yield) as a colorless oil, which can be directly used for the next reaction without further purification.

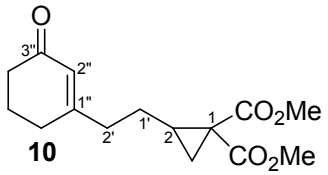
### Dimethyl 2-[2-(1,4-dioxaspiro[4.5]deca-6-en- 7-yl)ethyl]cyclopropane-1,1-dicarboxylate (9)




**9**

To a refluxing solution of $Rh_2(OAc)_4$ (49.0 mg, 0.11 mmol) and compound **8** (2.14 g, 11.0 mmol) in 1,2-dichloroethane (DCE, 40 mL) was added a solution of dimethyl diazomalonate (1.58 g, 10.0 mmol) in DCE (20 mL) via syringe under an argon atmosphere rapidly. The reaction mixture was then refluxed for 3 h and cooled to room temperature. The mixture was filtered and concentrated. Flash chromatography of the residue over silica gel (petroleum ether/EtOAc 15:1) afforded compound **9** (1.65 g, 51% yield) as a colorless oil, which can be directly used for the next reaction without further purification.

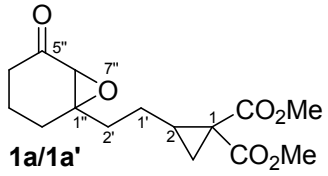
**Dimethyl 2-[2-(3-oxocyclohex-1-enyl)ethyl]cyclopropane-1,1-dicarboxylate (10)**




**10**

To a solution of compound **9** (1.65 g, 5.1 mmol) in a mixture of solvent (1,4-dioxane:water = 2:1) was added *p*-TsOH (131 mg, 0.76 mmol). The reaction mixture was then heated at 90 °C for 9 h and cooled to the room temperature. The reaction mixture was quenched by the addition of brine (50 mL) and extracted with ether (30 mL×3). The combined organic phases was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash chromatography of the residue on silica gel (petroleum ether/ethyl acetate, 15:1) afforded compound **10** (0.93 g, 65% yield) as a colorless oil, which can be directly used for the next reaction without further purification.

**Dimethyl 2-{2-(7-oxa-5-oxobicyclo[4.1.0]heptan-1-yl)ethyl}cyclopropane-1,1-dicarboxylate (1a/1a')**

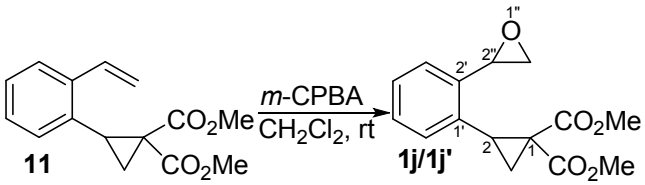



**1a/1a'**

To a solution of compound **10** (0.31 g, 1.10 mmol) in THF (10.0 mL) was added $H_2O_2$ (1.0 mL, 8.80 mmol) and Triton B (0.35 mL, 0.77 mmol) dropwise. The reactiom mixture was stirred at rt until TLC analysis indicated complete conversion to the epoxide **1a**/**1a'**. The reaction mixture was quenched by the addition of water (10.0 mL) and extracted with ether (20 mL×3). The combined organic phases were washed with water (50 mL×5), dried ($Mg_2SO_4$), filtered, and concentrated under reduced pressure to afford the product [0.30 g, 92% yield (**1a/1a**' = 1:1)] as a coloress oil.

The substrates **1b**/**1b'**–**1i**/**1i'** were synthesized according to the procedure given above for compound **1a**/**1a'**.

**Scheme 1.2 Preparation of substrate 1j/1j'**




**Dimethyl 2-[2-(oxiran-2-yl)benzyl]cyclopropane-1,1-dicarboxylate (1j/1j')**

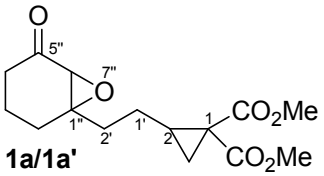
To a solution of compound **11**[2] (0.13 g, 0.50 mmol) in $CH_2Cl_2$ (5.0 mL) was added *m*-chloroperbenzoic acid (0.17 g, 1.0 mmol) slowly, the reactiom mixture was stirred at rt until TLC analysis indicated complete conversion to the epoxide **1j/1j'**. The reaction mixture was quenched by the addition of saturated aqueous $K_2CO_3$ (5.0 mL) and extracted with $CH_2Cl_2$ (5.0 mL×3). The combined organic phases were washed with water (5.0 mL×5), dried ($Mg_2SO_4$), and filtered. Evaporation of the solvent under reduced pressure afforded the product [0.13 g, 92% yield (**1j/1j'** = 1:1)] as a coloress oil.

The substrates **1k/1k'–1n/1n'** were synthesized according to the procedure given above for compound **1j/1j'**.

**Data of compounds 1a/1a'–1n/1n'**

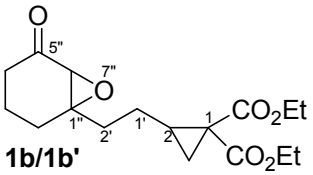
Compounds **1a/1a'–1n/1n'** are all diastereoisomers which could not be isolated by column chromatography under different eluent, but the formation of the products were not affected. The data of the main diasterisomers were reported as below.

**Dimethyl 2-{2-(7-oxa-5-oxobicyclo[4.1.0]heptan-1-yl)ethyl}cyclopropane-1,1-dicarboxylate (1a/1a')**




Coloress oil, 0.30 g, 92% yield (**1a/1a'** = 1:1); $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 3.739/3.735 (s, 3H), 3.694/3.692 (s, 3H), 3.04/3.02 (s, 1H), 2.49/2.44 (t, $J$ = 4.4 Hz, 1H), 2.10–1.97 (m, 2H), 1.93–1.72 (m, 5H), 1.66–1.59 (m, 1H), 1.49–1.44 (m, 1H), 1.43–1.37 (m, 2H), 1.36–1.33 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 206.4/206.3 (C), 170.44/170.39 (C), 168.3 (C), 64.6/64.5 (C), 60.9/60.8 (CH), 52.62/52.60 ($CH_3$), 52.54/52.52 ($CH_3$), 35.8 ($CH_2$), 34.98/34.95 ($CH_2$), 33.9/33.8 (C), 27.8/27.7 (CH), 26.3/26.2 ($CH_2$), 23.82/23.78 ($CH_2$), 21.0 ($CH_2$), 17.2 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{15}H_{21}O_6$ $[M+H]^+$ 297.1333, found 297.1348.

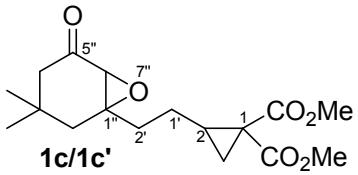
**Diethyl 2-{2-(7-oxa-5-oxobicyclo[4.1.0]heptan-1-yl)ethyl}cyclopropane-1,1-dicarboxylate (1b/1b')**



**1b/1b'**

Coloress oil, 0.33 g, 93% yield (**1b**/**1b'** = 1:1); $^{1}$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 4.24–4.10 (m, 4H), 3.04/3.02 (s, 1H), 2.49/2.44 (t, *J* = 4.4 Hz, 1H), 2.08–2.01 (m, 2H), 1.88–1.72 (m, 5H), 1.63–1.60 (m, 1H), 1.50–1.40 (m, 1H), 1.39–1.29 (m, 3H), 1.28–1.20 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 206.4/206.3 (C), 170.1/170.0 (C), 168.0 (C), 64.6/64.5 (C), 61.43 ($CH_2$), 61.39 ($CH_2$), 60.9/60.8 (CH), 35.8 ($CH_2$), 35.0 ($CH_2$), 34.2/34.1 (C), 27.4/27.3 (CH), 26.32/26.26 ($CH_2$), 23.78/23.75 ($CH_2$), 20.6 ($CH_2$), 17.2 ($CH_2$), 14.1 ($CH_3$), 14.0 ($CH_3$); HRMS (ESI) *m*/*z* calcd for $C_{17}H_{24}NaO_6$ $[M+Na]^+$ 347.1465, found 347.1465.

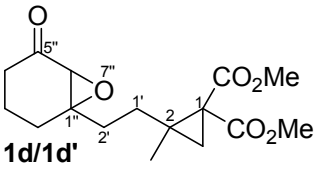
**Dimethyl 2-{2-(3,3-dimethyl-7-oxa-5-oxobicyclo[4.1.0]heptan-1-yl)ethyl}cyclopropane-1,1-dicarboxylate** (**1c**/**1c'**)



**1c/1c'**

Coloress oil, 0.34 g, 96% yield (**1c**/**1c'** = 1:1); $^{1}$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 3.73 (s, 3H), 3.692/3.688 (s, 3H), 3.00/2.97 (s, 1H), 2.59/2.56 (s, 1H), 1.99/1.96 (s, 1H), 1.88–1.83 (m, 1H), 1.79/1.76 (s, 1H), 1.71–1.61 (m, 3H), 1.46–1.34 (m, 4H), 0.98 (s, 3H), 0.85 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 207.5 (C), 170.39/170.37 (C), 168.3 (C), 66.40/66.37 (C), 60.32/60.26 (CH), 52.6 ($CH_3$), 52.5 ($CH_3$), 48.1 ($CH_2$), 41.04/40.95 ($CH_2$), 36.72/36.65 ($CH_2$), 36.12/36.10 (C), 33.9 (C), 30.79/30.78 ($CH_3$), 27.81/27.75 ($CH_3$), 27.65/27.59 (CH), 24.0 ($CH_2$), 21.0 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{17}H_{24}NaO_6$ $[M+Na]^+$ 347.1465, found 347.1469.

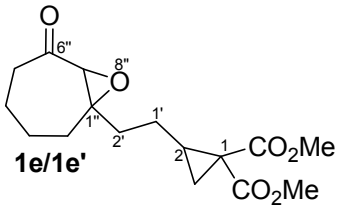
**Dimethyl 2-methyl-2-{2-(7-oxa-5-oxobicyclo[4.1.0]heptan-1-yl)ethyl}cyclopropane-1,1-dicarboxylate** (**1d**/**1d'**)



**1d/1d'**

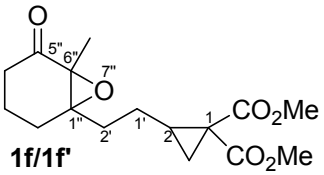
Coloress oil, 0.31 g, 91% yield (**1d**/**1d'** = 1:1); $^{1}$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 3.73 (s, 6H), 3.05/3.04 (s, 1H), 2.51/2.46 (t, *J* = 4.4 Hz, 1H), 2.12–1.99 (m, 2H), 1.94–1.90 (m, 1H), 1.88–1.71 (m, 3H), 1.69–1.61 (m, 3H), 1.47–1.43 (m, 2H), 1.15 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 206.33/206.31 (C), 169.13/169.08 (C), 168.67/168.65 (C), 64.8/64.7 (C), 60.8/60.7 (CH), 52.4 ($CH_3$), 52.3 ($CH_3$), 38.91/38.86 (C), 35.74/35.72 ($CH_2$), 33.0/32.9 ($CH_2$), 32.2/32.1 (C), 29.13/29.10 ($CH_2$), 27.2/27.1 ($CH_2$), 26.3/26.1 ($CH_2$), 19.34/19.32 ($CH_3$), 17.2 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{16}H_{22}NaO_6$ $[M+Na]^+$ 333.1309, found 333.1311.

**Dimethyl 2-{2-(8-oxa-6-oxobicyclo[5.1.0]octa-1-yl)ethyl}cyclopropane-1,1-dicarboxylate (1e/1e')**



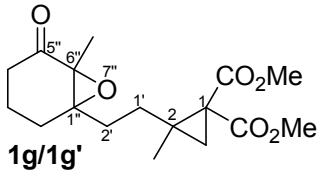

Coloress oil, 0.31 g, 91% yield (**1e**/**1e'** = 1:1); $^{1}$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 3.76/3.75 (s, 3H), 3.712/3.705 (s, 3H), 3.22/3.19 (s, 1H), 2.68–2.64 (m, 1H), 2.27–2.24 (m, 1H), 2.14–2.09 (m, 1H), 1.878–1.63 (m, 7H), 1.46–1.33 (m, 4H), 1.13–1.03 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 210.3/210.2 (C), 170.51/170.45 (C), 168.4 (C), 64.9/64.7 (CH), 63.2/63.1 (C), 52.63 ($CH_3$), 52.58/52.55 ($CH_3$), 40.61/40.57 ($CH_2$), 37.8/37.7 ($CH_2$), 34.0/33.9 (C), 31.3/31.2 ($CH_2$), 27.9/27.8 (CH), 24.7 ($CH_2$), 24.1 ($CH_2$), 23.3 ($CH_2$), 21.1/21.0 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{16}H_{22}NaO_6$ $[M+Na]^+$ 333.1309, found 333.1312.

**Dimethyl 2-{2-(6-methyl-7-oxa-5-oxobicyclo[4.1.0]heptan-1-yl)ethyl}cyclopropane-1,1-dicarboxylate (1f/1f')**




Coloress oil, 0.29 g, 85% yield (**1f**/**1f'** = 1:1); $^{1}$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 3.75 (s, 3H), 3.70 (s, 3H), 2.55/2.51 (t, *J* = 4.8 Hz, 1H), 2.09–2.01 (m, 2H), 1.92–1.67 (m, 6H), 1.61–1.55 (m, 1H), 1.53–1.48 (m, 2H), 1.46–1.40 (m, 1H), 1.37 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 207.2 (C), 170.5 (C), 168.40/168.37 (C), 68.1 (C), 64.8/64.6 (C), 52.6 ($CH_3$), 36.1 ($CH_2$), 34.0/33.9 (C), 32.9/32.8 ($CH_2$), 28.2/28.0 (CH), 27.01/26.97 ($CH_2$), 24.44/24.38 ($CH_2$), 21.04/20.97 ($CH_2$), 17.69/17.66 ($CH_2$), 11.63/11.58 ($CH_3$), one primary carbon signal missing due to signal overlapping; HRMS (ESI) *m*/*z* calcd for $C_{16}H_{22}NaO_6$ $[M+Na]^+$ 333.1309, found 333.1312.

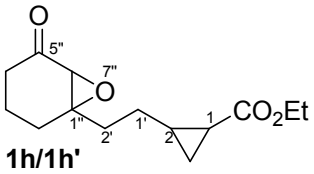
**Dimethyl 2-methyl-2-{2-(6-methyl-7-oxa-5-oxobicyclo[4.1.0]heptan-1-yl)ethyl}cyclopropane-1,1-dicarboxylate (1g/1g')**




Coloress oil, 0.29 g, 80% yield (**1g**/**1g'** = 1.5:1); $^{1}$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 3.74 (s, 3H), 3.72 (s, 3H), 2.57/2.53 (t, *J* = 4.4 Hz, 1H), 2.09–1.98 (m, 2H), 1.94–1.87 (m, 2H), 1.84–1.78 (m, 1H), 1.75–1.71 (m, 1H), 1.68–1.58 (m, 3H), 1.49–1.44 (m, 2H), 1.41/1.39 (s, 3H), 1.18/1.17 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 207.5/207.4 (C), 169.33/169.30 (C), 168.8 (C), 68.6/68.5 (C), 64.8/64.7 (C), 52.6 ($CH_3$), 52.5 ($CH_3$), 39.08/39.05 (C), 36.2 ($CH_2$), 32.52/32.50 (C),

31.3/30.9 ($CH_2$), 29.8/29.5 ($CH_2$), 27.32/27.27 ($CH_2$), 27.03/26.97 ($CH_2$), 19.6 ($CH_3$), 17.8 ($CH_2$), 11.7/11.6 ($CH_3$); HRMS (ESI) *m*/*z* calcd for $C_{17}H_{24}NaO_6$ $[M+Na]^+$ 347.1465, found 347.1473.

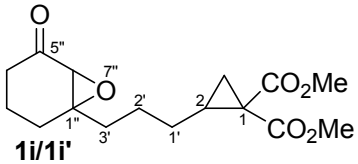
**Ethyl 2-{2-(7-oxa-5-oxobicyclo[4.1.0]heptan-1-yl)ethyl}cyclopropane-1-carboxylate (1h/1h')**



**1h/1h'**

Coloress oil, 0.26 g, 94% yield (**1h**/**1h'** = 1:1); $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 4.13–4.08 (m, 2H), 3.06/3.04/3.02 (s, 1H), 2.51–2.46 (m, 1H), 2.12–2.03 (m, 2H), 1.91–1.82 (m, 1H), 1.80–1.68 (m, 3H), 1.67–1.60 (m, 2H), 1.42–1.34 (m, 2H), 1.27–1.24 (m, 3H), 1.19–1.15 (m, 1H), 1.06–0.89 (m, 1H), 0.69–0.68 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 206.7/206.6/206.43/206.35 (C), 173.9/172.7 (C), 65.0/64.9/64.71/64.68 (C), 61.14/61.05/60.92/60.89 (CH), 60.4/60.3 ($CH_2$), 35.88/35.86/35.34/35.29 ($CH_2$), 28.0/26.5/26.20/26.18 ($CH_2$), 22.4/22.3/22.08/22.06 ($CH_2$), 21.2/21.1/20.3/20.2 (CH), 18.12/18.06 (CH), 17.32/17.27 ($CH_2$), 15.4/15.3 ($CH_2$), 14.3/14.2 ($CH_3$), 13.6/13.5 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{14}H_{20}NaO_4$ $[M+Na]^+$ 275.1254, found 275.1255.

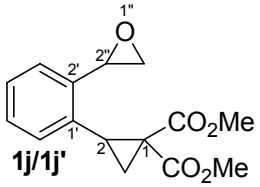
**Dimethyl 2-{3-(7-oxa-5-oxobicyclo[4.1.0]heptan-1-yl)propyl}cyclopropane-1,1-dicarboxylate (1i/1i')**



**1i/1i'**

Coloress oil, 0.33 g, 96% yield (**1i**/**1i'** = 1:1); $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 3.73 (s, 3H), 3.70 (s, 3H), 3.03 (s, 1H), 2.51–2.44 (m, 1H), 2.11–1.98 (m, 2H), 1.96–1.80 (m, 3H), 1.71–1.61 (m, 3H), 1.57–1.46 (m, 2H), 1.44–1.33 (m, 3H), 1.26–1.18 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 206.6 (C), 170.6 (C), 168.5 (C), 65.0 (C), 60.9 (CH), 52.6 ($CH_3$), 52.5 ($CH_3$), 35.9 ($CH_2$), 35.4 ($CH_2$), 33.8 (C), 28.44/28.39 (CH), 28.1 ($CH_2$), 26.32/26.27 ($CH_2$), 23.8 ($CH_2$), 21.1 ($CH_2$), 17.3 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{16}H_{22}NaO_6$ $[M+Na]^+$ 333.1309, found 333.1308.

**Dimethyl 2-[2-(oxiran-2-yl)phenyl]cyclopropane-1,1-dicarboxylate (1j/1j')**

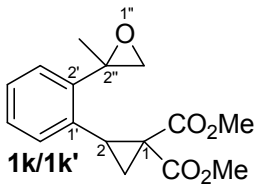


**1j/1j'**

Coloress oil, 0.13 g, 92% yield (**1j**/**1j'** = 2:1); $^1$H NMR (600 MHz, $CDCl_3$, TMS, 25°C) δ 7.28–7.19 (m, 3H), 7.11–7.07 (m, 1H), 4.16–4.15 (m, 1H), 3.81 (s, 3H), 3.41/3.27 (t, *J* = 8.4 Hz, 1H), 3.36/3.30 (s, 3H), 3.19–3.14 (m, 1H), 2.65–2.63 (m, 1H), 2.34–2.32 (m, 1H), 1.79–1.74 (m, 1H); $^{13}$C NMR

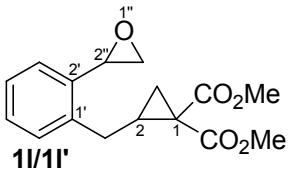
(150 MHz, $CDCl_3$, TMS, 25°C) δ 170.0/169.8 (C), 166.8/166.7 (C), 138.3/138.2 (C), 132.6/132.1 (C), 127.93/127.91 (CH), 127.4 (CH), 127.3/127.2 (CH), 123.9/123.6 (CH), 52.9/52.8 ($CH_3$), 52.3/52.0 ($CH_3$), 50.8/50.6 ($CH_2$), 49.9/49.7 (CH), 36.5/36.4 (C), 30.2/29.5 (CH), 18.6/18.5 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{15}H_{16}NaO_5$ $[M+Na]^+$ 299.0890, found 299.0893.

**Dimethyl 2-[2-(2-methyloxiran-2-yl)phenyl]cyclopropane-1,1-dicarboxylate (1k/1k')**



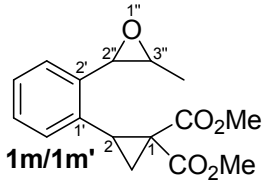

Coloress oil, 0.13 g, 90% yield (**1k**/**1k'** = 3:1); $^1H$ NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 7.46–7.40 (m, 1H), 7.25–7.16 (m, 2H), 6.91–6.89 (m, 1H), 3.80 (s, 3H), 3.47 (t, *J* = 8.8 Hz, 1H), 3.36/3.30 (s, 3H), 3.06–3.02 (m, 1H), 2.91/2.81 (d, *J* = 5.2 Hz, 1H), 2.37–2.34 (m, 1H), 1.80–1.76 (m, 1H), 1.66/1.61 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 170.1/169.9 (C), 166.7/166.6 (C), 142.2/142.0 (C), 130.8/130.7 (C), 127.59/127.52 (CH), 127.5/127.1 (CH), 127.2/126.8 (CH), 125.4/125.1 (CH), 58.0/57.6 (C), 55.2/54.7 ($CH_2$), 52.9 ($CH_3$), 52.2 ($CH_3$), 38.2/38.0 (C), 30.0/29.7 ($CH_3$), 24.1/23.3 (CH), 18.8/18.3 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{16}H_{18}NaO_5$ $[M+Na]^+$ 313.1046, found 313.1047.

**Dimethyl 2-[2-(oxiran-2-yl)benzyl]cyclopropane-1,1-dicarboxylate (1l/1l')**




Coloress oil, 0.13 g, 90% yield (**1l/1l'** = 1:1); $^1H$ NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 7.26–7.24 (m, 4H), 4.00 (t, *J* = 3.2 Hz, 1H), 3.749/3.745 (s, 3H), 3.740/3.736 (s, 3H), 3.18–3.15 (m, 1H), 3.11–2.98 (m, 1H), 2.71–2.68 (m, 1H), 2.66–2.55 (m, 1H), 2.32–2.21 (m, 1H), 1.64–1.60 (m, 1H), 1.53–1.49 (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 170.40/170.36 (C), 168.50 (C), 137.8/137.7 (C), 135.53/135.48 (C), 128.6/128.4 (CH), 128.0/127.9 (CH), 126.92/126.89 (CH), 124.5/124.4 (CH), 52.73/52.71 ($CH_3$), 52.6 ($CH_3$), 50.5/50.2 ($CH_2$), 50.2/50.1 (CH), 34.2/34.1 (C), 30.9/30.8 ($CH_2$), 28.1/27.9 (CH), 21.5 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{16}H_{18}NaO_5$ $[M+Na]^+$ 313.1046, found 313.1052.

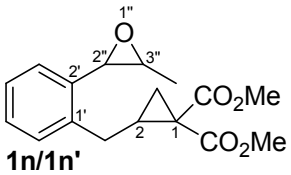
**Dimethyl 2-[2-(3-methyloxiran-2-yl)phenyl]cyclopropane-1,1-dicarboxylate (1m/1m')**




Coloress oil, 0.13 g, 90% yield (**1m**/**1m'** = 3:1); $^1H$ NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 7.27–

7.21 (m, 3H), 7.08–7.06 (m, 1H), 4.26/4.19 (d, $J$ = 4.0 Hz, 1H), 3.81 (s, 3H), 3.46–3.39 (m, 1H), 3.36/3.13 (t, $J$ = 8.4 Hz, 1H ), 3.34/3.33 (s, 3H), 2.35–2.30 (m, 1H), 1.81–1.71 (m, 1H), 1.04 (d, $J$ = 5.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 169.9 (C), 166.9 (C), 136.2/135.8 (C), 132.6 (C), 127.3/127.1 (CH), 126.8/126.6 (CH), 56.1/55.9 (CH), 55.5/54.5 (CH), 52.93/52.89 ($CH_3$), 52.3/52.0 ($CH_3$), 36.8/36.6 (C), 30.2/29.8 (CH), 18.9/18.4 ($CH_2$), 12.8/12.6 ($CH_3$), two tertiary carbon signals missing due to signal overlapping; HRMS (ESI) $m/z$ calcd for $C_{16}H_{18}NaO_5$ $[M+Na]^+$ 313.1046, found 313.1047.

**Dimethyl 2-[2-(3-methyloxiran-2-yl)benzyl]cyclopropane-1,1-dicarboxylate (1n/1n')**



**1n/1n'**

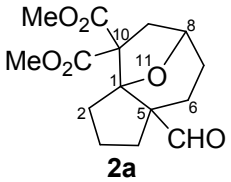
Coloress oil, 0.14 g, 92% yield (**1n**/**1n'** = 1.5:1); $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 7.31–7.21 (m, 4H), 4.07–4.05 (m, 1H), 3.76/3.75 (s, 3H), 3.73/3.71 (s, 3H), 3.43–3.38 (m, 1H), 2.97–2.87 (m, 1H), 2.64–2.51 (m, 1H), 2.27–2.21 (m, 1H), 1.63–1.58 (m, 1H), 1.52–1.48 (m, 1H), 1.02/1.01 (d, $J$ = 4.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 170.4/170.3 (C), 168.5/168.4 (C), 137.3/137.2 (C), 133.4/133.3 (C), 128.3/128.0 (CH), 127.53/127.51 (CH), 126.82/126.79 (CH), 126.19/126.16 (CH), 56.03/56.02 (CH), 54.9/54.7 (CH), 52.7/52.6 ($CH_3$), 52.49/52.47 ($CH_3$), 34.03/34.00 (C), 30.8/30.6 ($CH_2$), 27.8/27.4 (CH), 21.5/21.4 ($CH_2$), 12.8/12.7 ($CH_3$); HRMS (ESI) $m/z$ calcd for $C_{17}H_{20}NaO_5$ $[M+Na]^+$ 327.1203, found 327.1205.

**3**. **Preparation and data of compounds 2a, 3a, 2b, 3b, 2c, 3c, 2d, 3d, 2e, 3e, 2f, 2g, and 2i–2n**

To a solution of epoxide **1a**/**1a'** (44 mg, 0.15 mmol) in $CH_2Cl_2$ (5.0 mL) was added $BF_3$•$Bu_2O$ (0.21 mL, 0.30 mmol) at 0 °C under an argon atmosphere, and the solution was strired at 0 °C for 5 min. The reaction mixture was heated to reflux for 3 h and then cooled to room temperature. The reaction mixture was concentrated under reduced pressure. Flash column chromatography of the residue on silica gel (petroleum ether/ethyl acetate, 10:1) afforded compounds **2a** (19 mg, 43% yield) and **3a** (19 mg, 43% yield) as white solids.

Compounds **2b**, **3b**, **2c**, **3c**, **2d**, **3d**, **2e**, **3e**, **2f**, **2g**, and **2i**–**2n** were synthesized using epoxides **1b**/**1b'**–**1g**/**1g'**, and **1i**/**1i'**–**1n**/**1n'** as sustrates according to the procedure given above for compounds **2a** and **3a**.

**Dimethyl 5-formyl-11-oxatricyclo[6.2.1.0$^{1,5}$]undeca-10,10-dicarboxylate (2a)**

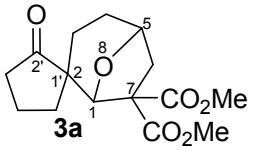


**2a**

White solid, 19 mg, 43% yield; m.p. 76–79 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 9.49 (s, 1H), 4.44–4.42 (m, 1H), 3.73 (s, 3H), 3.65 (s, 3H), 2.73–2.67 (m, 1H), 2.58–2.49 (m, 2H), 2.31–2.23

(m, 1H), 2.15–1.92 (m, 5H), 1.60–1.56 (m, 1H), 1.53–1.52 (m, 1H), 1.49–1.48 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 200.3 (CH), 170.4(C), 168.5 (C), 92.7 (C), 72.4 (CH), 63.1 (C), 59.2 (C), 52.8 ($CH_3$), 52.4 ($CH_3$), 36.4 ($CH_2$), 31.5 ($CH_2$), 30.4 ($CH_2$), 26.2 ($CH_2$), 19.5 ($CH_2$), 17.9 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{15}H_{20}NaO_6$ $[M+Na]^+$ 319.1152, found 319.1164.

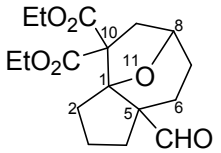
**Dimethyl 8-oxa-2'-oxospiro{bicyclo[3.2.1]octane-2,1'-cyclopentane}-7,7-dicarboxylate** (**3a**)



**3a**

White solid, 19 mg, 43% yield; m.p. 92–94 °C; $^1$H NMR (600 MHz, $CDCl_3$, TMS, 25°C) δ 4.80 (s, 1H), 4.45–4.43 (m, 1H), 3.71 (s, 3H), 3.61 (s, 3H), 2.86 (d, *J* = 14.4 Hz, 1H), 2.79–2.76 (m, 1H), 2.49–2.45 (m, 1H), 2.39–2.36 (m, 1H), 2.28–2.20 (m, 1H), 2.18–2.14 (m, 1H), 2.10–2.08 (m, 1H), 1.89–1.84 (m, 2H), 1.56–1.48 (m, 2H), 1.09–1.06 (m, 1H); $^{13}$C NMR (150 MHz, $CDCl_3$, TMS, 25°C) δ 217.2 (C), 171.6 (C), 166.9 (C), 78.6 (CH), 75.6 (CH), 63.5 (C), 53.13 (C), 53.06 ($CH_3$), 52.3 ($CH_3$), 35.98 ($CH_2$), 35.97 ($CH_2$), 34.4 ($CH_2$), 28.0 ($CH_2$), 22.9 ($CH_2$), 16.5 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{15}H_{20}NaO_6$ $[M+Na]^+$ 319.1152, found 319.1165.

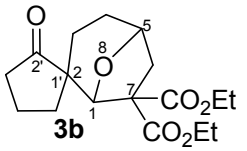
**Diethyl 5-formyl-11-oxatricyclo[6.2.1.0$^{1,5}$]undeca-10,10-dicarboxylate** (**2b**)



**2b**

White solid, 21 mg, 43% yield; m.p. 80–82 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 9.51 (s, 1H), 4.42–4.40 (m, 1H), 4.23–4.11 (m, 3H), 4.04–3.96 (m, 1H), 2.71–2.66 (m, 1H), 2.56–2.47 (m, 2H), 2.29–2.21 (m, 1H), 2.14–2.08 (m, 2H), 2.07–1.90 (m, 3H), 1.57–1.46 (m, 3H), 1.26–1.21 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 200.2 (CH), 169.8 (C), 168.1 (C), 92.5 (C), 72.3 (CH), 63.1 (C), 61.7 ($CH_2$), 61.6 ($CH_2$), 59.2 (C), 36.3 ($CH_2$), 31.5 ($CH_2$), 30.4 ($CH_2$), 26.2 ($CH_2$), 19.6 ($CH_2$), 18.0 ($CH_2$), 14.0 ($CH_3$), 13.6 ($CH_3$); HRMS (ESI) *m*/*z* calcd for $C_{17}H_{24}NaO_6$ $[M+Na]^+$ 347.1465, found 347.1468.

**Diethyl 8-oxa-2'-oxospiro{bicyclo[3.2.1]octane-2,1'-cyclopentane}-7,7-dicarboxylate** (**3b**)

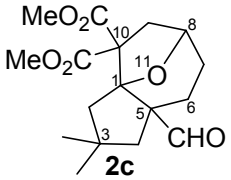


**3b**

White solid, 21 mg, 43% yield; m.p. 85–88 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 4.80 (s, 1H), 4.44–4.42 (m, 1H), 4.24–4.09 (m, 3H), 3.94–3.86 (m, 1H), 2.86–2.77 (m, 2H), 2.44–2.36 (m, 2H), 2.29–2.06 (m, 3H), 1.88–1.82 (m, 2H), 1.54–1.46 (m, 2H), 1.22 (q, *J* = 7.2 Hz, 3H), 1.17 (q, *J* = 7.2 Hz, 3H), 1.08–1.03 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 217.2 (C), 171.1 (C), 166.5 (C), 78.3 (CH), 75.6 (CH), 63.6 (C), 61.9 ($CH_2$), 61.4 ($CH_2$), 53.1 (C), 36.0 ($CH_2$), 35.9 ($CH_2$),

34.3 ($CH_2$), 28.0 ($CH_2$), 22.9 ($CH_2$), 16.4 ($CH_2$), 13.9 ($CH_3$), 13.6 ($CH_3$); HRMS (ESI) *m*/*z* calcd for $C_{17}H_{24}NaO_6$ $[M+Na]^+$ 347.1465, found 347.1466.

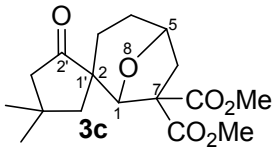
**Dimethyl 3,3-dimethyl-5-formyl-11-oxatricyclo[6.2.1.0$^{1,5}$]undeca-10,10-dicarboxylate** (**2c**)



**2c**

White solid, 22 mg, 45% yield; m.p. 68–70 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 9.67 (s, 1H), 4.42–4.40 (m, 1H), 3.70 (s, 3H), 3.64 (s, 3H), 2.70–2.65 (m, 1H), 2.49–2.43 (m, 2H), 2.09–2.05 (m, 1H), 2.00–1.91 (m, 3H), 1.49–1.41 (m, 3H), 1.24 (s, 3H), 1.19 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 200.5 (CH), 170.2 (C), 168.6 (C), 93.2 (C), 72.1 (CH), 63.6 (C), 61.6 (C), 52.8 ($CH_3$), 52.5 ($CH_3$), 47.0 ($CH_2$), 46.3 ($CH_2$), 36.0 ($CH_2$), 35.6 (C), 32.8 ($CH_3$), 32.3 ($CH_3$), 26.1 ($CH_2$), 18.2 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{17}H_{24}NaO_6$ $[M+Na]^+$ 347.1465, found 347.1475.

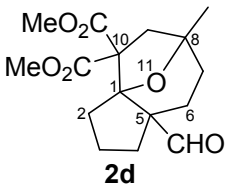
**Dimethyl 4',4'-dimethyl-8-oxa-2'-oxospiro{bicyclo[3.2.1]octane-2,1'-cyclopentane}-7,7-dicarboxylate** (**3c**)



**3c**

White solid, 21 mg, 43% yield; m.p. 93–96 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 4.73 (s, 1H), 4.40–4.38 (m, 1H), 3.71 (s, 3H), 3.64 (s, 3H), 2.85 (d, *J* = 13.6 Hz, 1H), 2.51–2.43 (m, 3H), 2.30–2.22 (dt, *J* = 13.6, 5.2 Hz, 1H), 2.03 (d, *J* = 15.6 Hz, 1H), 1.89–1.80 (m, 1H), 1.70 (d, *J* = 14.0 Hz, 1H), 1.50 (dd, *J* = 13.6, 4.8 Hz, 1H), 1.25 (s, 3H), 1.14 (dd, *J* = 14.0, 4.8 Hz, 1H), 0.93 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 215.6 (C), 171.6 (C), 167.0 (C), 83.0 (CH), 74.9 (CH), 63.4 (C), 53.4 (C), 53.1 ($CH_3$), 52.6 ($CH_2$), 52.4 ($CH_3$), 49.6 ($CH_2$), 36.1 ($CH_2$), 31.5 (C), 30.9 ($CH_3$), 30.1 ($CH_3$), 27.9 ($CH_2$), 24.2 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{17}H_{24}NaO_6$ $[M+Na]^+$ 347.1465, found 347.1473.

**Dimethyl 5-formyl-8-methyl-11-oxatricyclo[6.2.1.0$^{1,5}$]undeca-10,10-dicarboxylate** (**2d**)

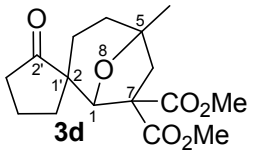


**2d**

White solid, 3 mg, 6% yield; m.p. 73–75 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 9.50 (s, 1H), 3.72 (s, 3H), 3.63 (s, 3H), 2.62 (d, *J* = 13.8 Hz, 1H), 2.54–2.50 (m, 1H), 2.33 (d, *J* = 13.8 Hz, 1H), 2.26–2.18 (m, 1H), 2.07–1.92 (m, 4H), 1.75–1.67 (m, 1H), 1.57–1.51 (m, 3H), 1.38 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 200.3 (CH), 170.4 (C), 168.6 (C), 93.5 (C), 78.1 (C), 63.9 (C), 58.6 (C), 52.8 ($CH_3$), 52.4 ($CH_3$), 41.9 ($CH_2$), 32.5 ($CH_2$), 31.7 ($CH_2$), 30.4 ($CH_2$), 26.6 ($CH_3$),

19.8 ($CH_2$), 19.5 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{16}H_{23}O_6$ $[M+H]^+$ 311.1489, found 311.1502.

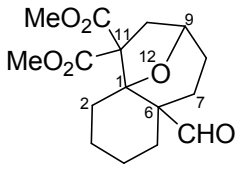
**Dimethyl 5-methyl-8-oxa-2'-oxospiro{bicyclo[3.2.1]octane-2,1'-cyclopentane}-7,7-dicarboxylate (3d)**



**3d**

White solid, 26 mg, 56% yield; m.p. 70–73 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 4.84 (s, 1H), 3.73 (s, 3H), 3.59 (s, 3H), 2.97 (d, *J* = 14.0 Hz, 1H), 2.77–2.72 (m, 1H), 2.43–2.34 (m, 1H), 2.29–2.20 (m, 2H), 2.18–2.01 (m, 2H), 1.91–1.84 (m, 1H), 1.63–1.47 (m, 3H), 1.31 (s, 3H), 1.16–1.11 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 217.4 (C), 171.7 (C), 166.9 (C), 81.3 (C), 79.3 (CH), 64.4 (C), 53.1 ($CH_3$), 52.4 (C), 52.1 ($CH_3$), 41.8 ($CH_2$), 36.0 ($CH_2$), 34.3 ($CH_2$), 34.0 ($CH_2$), 26.7 ($CH_3$), 24.7 ($CH_2$), 16.5 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{16}H_{22}NaO_6$ $[M+Na]^+$ 333.1309, found 333.1321.

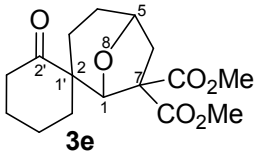
**Dimethyl 6-formyl-12-oxatricyclo[7.2.1.0$^{1,6}$]dodeca-11,11-dicarboxylate (2e)**



**2e**

White solid, 28 mg, 60% yield; m.p. 79–81 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 10.10 (s, 1H), 4.54–4.52 (m, 1H), 3.74 (s, 3H), 3.65 (s, 3H), 2.83–2.77 (m, 1H), 2.50–2.34 (m, 3H), 2.00–1.96 (m, 1H), 1.86–1.67 (m, 3H), 1.63–1.57 (m, 3H), 1.44–1.40 (m, 2H), 1.39–1.29 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 203.4 (CH), 171.3 (C), 169.5 (C), 87.3 (C), 74.5 (CH), 67.5 (C), 52.9 ($CH_3$), 52.3 ($CH_3$), 51.1 (C), 37.8 ($CH_2$), 33.4 ($CH_2$), 29.7 ($CH_2$), 26.9 ($CH_2$), 23.1 ($CH_2$), 22.4 ($CH_2$), 20.7 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{16}H_{22}NaO_6$ $[M+Na]^+$ 333.1309, found 333.1311.

**Dimethyl 8-oxo-2'-oxaspiro{bicyclo[3.2.1]octane-2,1'-cyclohexane}-7,7-dicarboxylate (3e)**

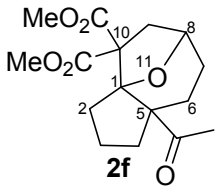


**3e**

White solid, 7 mg, 15% yield; m.p. 74–76 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 5.38 (s, 1H), 4.45–4.44 (m, 1H), 3.74 (s, 3H), 3.53 (s, 3H), 2.89–2.86 (m, 1H), 2.3 (d, *J* = 18.4 Hz, 1H), 2.77–2.61 (m, 1H), 2.44–2.38 (m, 1H), 2.26–2.22 (m, 2H), 2.14–2.11 (m, 1H), 2.10–1.90 (m, 3H), 1.70–1.63 (m, 3H), 1.43–1.38 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 212.7 (C), 171.5 (C), 167.3 (C), 79.7 (CH), 76.1 (CH), 63.8 (C), 53.2 ($CH_3$), 52.2 ($CH_3$), 52.1 (C), 39.6 ($CH_2$), 37.6 ($CH_2$), 36.6 ($CH_2$), 29.5 ($CH_2$), 26.6 ($CH_2$), 22.9 ($CH_2$), 20.7 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{16}H_{22}NaO_6$ $[M+Na]^+$ 333.1309, found 333.1320.

**Dimethyl 5-acetyl-11- oxatricyclo[6.2.1.0$^{1,5}$]undeca-10,10-**

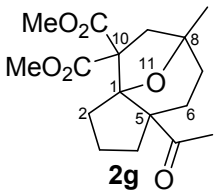
**dicarboxylate (2f)**



**2f**

White solid, 25 mg, 54% yield; m.p. 65–67 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 4.31–4.29 (m, 1H), 3.69 (s, 3H), 3.62 (s, 3H), 2.83–2.75 (m, 2H), 2.71–2.67 (m, 1H), 2.49–2.41 (m, 1H), 2.22–2.15 (m, 2H), 2.06 (s, 3H), 2.05–1.97 (m, 1H), 1.85–1.76 (m, 2H), 1.57–1.49 (m, 2H), 1.46–1.41 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 210.0 (C), 170.9 (C), 170.3 (C), 94.8 (C), 71.8 (CH), 64.2 (C), 60.0 (C), 52.9 ($CH_3$), 52.3 ($CH_3$), 38.6 ($CH_2$), 33.2 ($CH_2$), 31.5 ($CH_2$), 26.8 ($CH_2$), 26.1 ($CH_3$), 22.2 ($CH_2$), 19.8 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{16}H_{22}NaO_6$ $[M+Na]^+$ 333.1309, found 333.1310.

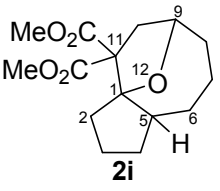
**Dimethyl 5-acetyl-8-methyl-11-oxatricyclo[6.2.1.0$^{1,5}$]undeca-10,10-dicarboxylate (2g)**



**2g**

White solid, 21 mg, 43% yield; m.p. 69–72 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 3.72 (s, 3H), 3.62 (s, 3H), 2.84–2.76 (m, 2H), 2.50–2.42 (m, 2H), 2.18–2.11 (m, 2H), 2.09 (s, 3H), 1.90–1.75 (m, 3H), 1.61–1.52 (m, 2H), 1.47–1.41 (m, 1H), 1.29 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 210.0 (C), 171.0 (C), 170.2 (C), 95.7 (C), 77.2 (C), 65.0 (C), 59.3 (C), 52.8 ($CH_3$), 52.3 ($CH_3$), 44.2 ($CH_2$), 33.5 ($CH_2$), 33.0 ($CH_2$), 31.6 ($CH_2$), 27.1 ($CH_3$), 26.4 ($CH_3$), 24.0 ($CH_2$), 19.8 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{17}H_{24}NaO_6$ $[M+Na]^+$ 347.1465, found 347.1463.

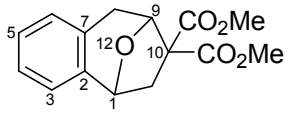
**Dimethyl 12-oxatricyclo[7.2.1.0$^{1,5}$]dodeca-11,11-dicarboxylate (2i)**



**2i**

White solid, 18 mg, 43% yield; m.p. 126–129 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 4.61–4.56 (m, 1H), 3.75 (s, 3H), 3.72 (s, 3H), 2.51–2.46 (m, 1H), 2.32–2.22 (m, 2H), 1.87–1.64 (m, 6H), 1.63–1.60 (m, 2H), 1.59–1.44 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 170.8 (C), 169.8 (C), 94.1 (C), 77.2 (CH), 67.9 (C), 52.4 ($CH_3$), 52.2 ($CH_3$), 50.5 (CH), 37.3 ($CH_2$), 36.0 ($CH_2$), 34.4 ($CH_2$), 32.3 ($CH_2$), 32.1 ($CH_2$), 24.3 ($CH_2$), 23.6 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{15}H_{22}NaO_5$ $[M+Na]^+$ 305.1359, found 305.1361.

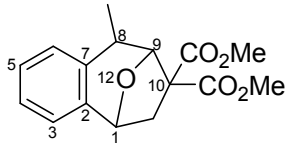
**Dimethyl 12-oxatricyclo[7.2.1.0$^{2,7}$]dodeca-2(7),3,5-triene-10,10-dicarboxylate (2j)**




**2j**

White solid, 38 mg, 92% yield; m.p. 90–93 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 7.18–7.10 (m, 2H), 7.00–6.96 (m, 2H), 5.40 (d, *J* = 6.0 Hz, 1H), 5.10 (d, *J* = 6.8 Hz, 1H), 3.77 (s, 3H), 3.66 (s, 3H), 3.37 (dd, *J* = 17.6, 6.0 Hz, 1H), 2.94 (d, *J* = 13.2 Hz, 1H), 2.59 (dd, *J* = 13.2, 7.2 Hz, 1H), 2.55 (d, *J* = 18.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 171.5 (C), 169.2 (C), 139.6 (C), 130.2 (C), 128.3 (CH), 127.6 (CH), 126.1 (CH), 123.9 (CH), 78.8 (CH), 77.5 (CH), 64.9 (C), 53.1 ($CH_3$), 52.8 ($CH_3$), 44.1 ($CH_2$), 31.1 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{15}H_{16}NaO_5$ $[M+Na]^+$ 299.0890, found 299.0889.

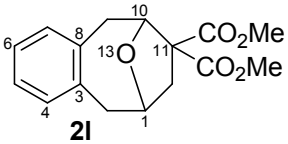
**Dimethyl 8-methyl-12-oxatricyclo[7.2.1.0$^{2,7}$]dodeca-2(7),3,5-triene-10,10-dicarboxylate (2k/2k')**




**2k/2k'**

White solid, 38 mg, 87% yield (**2k**/**2k'** = 2:1); m.p. 126–129 °C; The compounds **2k** and **2k'** could not be isolated by column chromatography under different eluent; $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 7.23–7.11 (m, 3H), 7.02–6.93 (m, 1H), 5.31–5.07 (m, 2H), 3.76 (s, 3H), 3.63/3.61 (s, 3H), 2.94–2.85 (m, 1H), 2.68–2.49 (m, 2H), 1.42/1.21 (d, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 171.9/171.5 (C), 169.1 (C), 138.5 (C), 136.1/135.9 (C), 128.3/127.7 (CH), 127.6/126.2 (CH), 126.3/125.2 (CH), 123.5/123.2 (CH), 84.0/83.8 (CH), 78.5/77.7 (CH), 64.4/62.7 (C), 53.1/53.0 ($CH_3$), 52.7/52.4 ($CH_3$), 45.9/43.7 ($CH_2$), 36.5/35.0 (CH), 23.6/13.5 ($CH_3$); HRMS (ESI) *m*/*z* calcd for $C_{16}H_{18}NaO_5$ $[M+Na]^+$ 313.1046, found 313.1048.

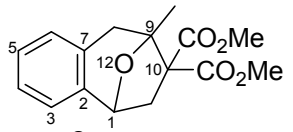
**Dimethyl 13-oxatricyclo[8.2.1.0$^{3,8}$]trideca-3(8),4,6-triene-11,11-dicarboxylate (2l)**




**2l**

White solid, 18 mg, 41% yield; m.p. 82–85 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 7.14–7.06 (m, 3H), 6.97–6.96 (m, 1H), 5.05–5.03 (m, 1H), 4.69–4.65 (m, 1H), 3.73 (s, 3H), 3.48 (s, 3H), 3.41 (d, *J* = 16.0 Hz, 1H), 3.32 (d, *J* = 16.0 Hz, 1H), 3.18 (dd, *J* = 16.0, 4.4 Hz, 1H), 2.85 (dd, *J* = 16.0, 4.8 Hz, 1H), 2.52–2.47 (m, 1H), 2.27 (dd, *J* = 14.0, 2.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 171.7 (C), 168.3 (C), 138.5 (C), 137.6 (C), 131.4 (CH), 131.2 (CH), 126.8 (CH), 126.1 (CH), 79.9 (CH), 75.9 (CH), 65.2 (C), 53.3 ($CH_3$), 52.6 ($CH_3$), 45.1 ($CH_2$), 42.4 ($CH_2$), 36.0 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{16}H_{18}NaO_5$ $[M+Na]^+$ 313.1046, found 313.1046.

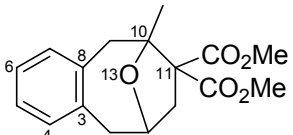
**Dimethyl 9-methyl-12-oxatricyclo[7.2.1.0$^{2,7}$]dodeca-2(7),3,5-triene-10,10-dicarboxylate (2m)**




**2m**

White solid, 38 mg, 87% yield; m.p. 89–92 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 7.15–7.08 (m, 2H), 6.99–6.97 (m, 2H), 5.11 (d, *J* = 7.2 Hz, 1H), 3.77 (s, 3H), 3.65 (s, 3H), 3.32 (d, *J* = 18.0 Hz, 1H), 3.05 (d, *J* = 18.0 Hz, 1H), 3.02 (dd, *J* = 12.8, 7.6 Hz, 1H), 2.62 (dd, *J* = 12.8, 0.8 Hz, 1H), 1.61 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 171.6 (C), 169.9 (C), 140.2 (C), 131.1 (C), 128.1 (CH), 127.2 (CH), 126.0 (CH), 123.1 (CH), 84.7 (C), 76.4 (CH), 66.7 (C), 52.8 ($CH_3$), 52.4 ($CH_3$), 44.6 ($CH_2$), 39.4 ($CH_2$), 24.4 ($CH_3$); HRMS (ESI) *m*/*z* calcd for $C_{16}H_{18}NaO_5$ $[M+Na]^+$ 313.1046, found 333.1055.

**Dimethyl 10-methyl-13-oxatricyclo[8.2.1.0$^{3,8}$]trideca-3(8),4,6-triene-11,11-dicarboxylate** (**2n**)

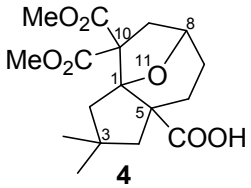



**2n**

White solid, 38 mg, 83% yield; m.p. 92–95 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 7.13–7.05 (m, 2H), 7.02–6.96 (m, 2H), 4.73–4.68 (m, 1H), 3.72 (s, 3H), 3.48 (s, 3H), 3.42 (d, *J* = 14.4 Hz, 1H), 3.31 (d, *J* = 15.2 Hz, 1H), 3.15 (d, *J* = 15.2 Hz, 1H), 2.83 (dd, *J* = 16.0, 5.2 Hz, 1H), 2.68 (dd, *J* = 13.6, 8.8 Hz, 1H), 1.93 (dd, *J* = 13.6, 2.8 Hz, 1H), 1.48 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 171.8 (C), 169.3 (C), 139.5 (C), 137.4 (C), 132.0 (CH), 130.6 (CH), 126.7 (CH), 125.9 (CH), 85.0 (C), 74.7 (CH), 67.4 (C), 52.6 ($CH_3$), 52.1 ($CH_3$), 50.4 ($CH_2$), 44.4 ($CH_2$), 36.8 ($CH_2$), 24.8 ($CH_3$); HRMS (ESI) *m*/*z* calcd for $C_{17}H_{20}NaO_5$ $[M+Na]^+$ 327.1203, found 327.1214.

**4**. **Preparation and data of compound 4**

**Dimethyl 5-carboxyl -3,3-dimethyl-11-oxatricyclo[6.2.1.0$^{1,5}$]undeca-10,10-dicarboxylate** (**4**)

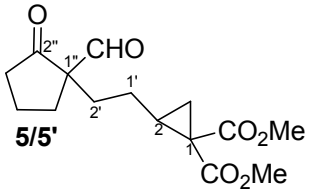



**4**

Coupound **2c** (19 mg, 0.06 mmol) was oxidized in the air for two weeks afforded **4** (20 mg, 99% yield) as a white solid; m.p. 94–97 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 4.35–4.34 (m, 1H), 3.72 (s, 3H), 3.67 (s, 3H), 2.91 (dd, *J* = 14.0, 8.4 Hz, 1H), 2.80 (d, *J* = 14.0 Hz, 1H), 2.62 (dd, *J* = 14.0, 2.8 Hz, 1H), 2.44–2.34 (m, 1H), 2.13–1.93 (m, 3H), 1.78 (dd, *J* = 14.8, 6.0 Hz, 1H), 1.68 (d, *J* = 13.2 Hz, 1H), 1.48 (dd, *J* = 13.6, 7.2 Hz, 1H), 1.16 (s, 3H), 1.08 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 181.4 (C), 170.7 (C), 170.0 (C), 94.4 (C), 71.8 (CH), 64.9 (C), 55.3 (C), 52.7 ($CH_3$), 52.5 ($CH_3$), 48.8 ($CH_2$), 47.8 ($CH_2$), 38.0 ($CH_2$), 35.2 (C), 33.1 ($CH_3$), 31.0 ($CH_3$), 26.3 ($CH_2$), 22.4 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{17}H_{24}NaO_7$ $[M+Na]^+$ 363.1414, found 363.1425.

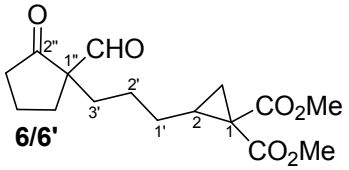
**5**. **Preparation and data of compound 5/5' and 6/6'**

**Dimethyl 2-[2-(1-formyl-2-oxocyclopentyl)propyl]cyclopropane-1,1-dicarboxylate** (**5**/**5'**)




To a solution of epoxide **1a/1a'** (45 mg, 0.15 mmol) in $CH_2Cl_2$ (5.0 mL) was added $BF_3$•$Bu_2O$ (0.10 mL, 0.15 mmol) at 0 °C under an argon atmosphere, and the solution was strired at 0 °C for 5 min. The reaction mixture was quenched by the addition of saturated aqueous $K_2CO_3$ (5.0 mL) and extracted with $CH_2Cl_2$ (5.0 mL×3). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatography of the residue on silica gel (petroleum ether/ethyl acetate, 10:1) afforded compounds **5/5'** [20 mg, 45% yield (**5**/**5'** = 1:1)] as a coloress oil, The pure compound **5** or **5'** could not be isolated by column chromatography under different eluent; $^1$H NMR (400 MHz, acetone-$d_6$, TMS, 25°C) δ 9.40/9.37 (s, 1H), 3.75/3.73 (s, 3H), 3.690/3.689 (s, 3H), 2.51–2.47 (m, 1H), 2.31–2.27 (m, 2H), 2.08–2.04 (m, 2H), 2.01–1.89 (m, 1H), 1.88–1.78 (m, 4H), 1.37–1.28 (m, 3H); $^{13}$C NMR (100 MHz, acetone-$d_6$, TMS, 25°C) δ 214.87/214.85 (C), 199.7/199.6 (CH), 171.0 (C), 168.92/168.88 (C), 67.5 (C), 52.9 ($CH_3$), 52.8 ($CH_3$), 38.8/38.7 ($CH_2$), 34.8 (C), 32.3/32.2 ($CH_2$), 28.82/28.79 ($CH_2$), 28.30/28.27 (CH), 24.63/24.59 ($CH_2$), 20.89/20.88 ($CH_2$), 20.0 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{15}H_{21}O_6$ $[M+H]^+$ 297.1333, found 297.1331.

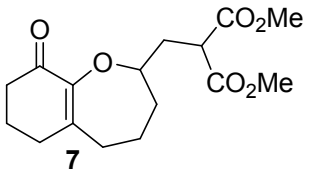
**Dimethyl 2-[3-(1-formyl-2-oxocyclopentyl)propyl]cyclopropane-1,1-dicarboxylate** (**6**/**6'**)




The compounds **6**/**6'** was synthesized according to the procedure given above for compound **5**/**5'** using substrates **1i**/**1i'** as starting material. coloress oil, 45 mg, 96% yield; $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 9.36 (s, 1H), 3.73/3.72 (s, 3H), 3.69 (s, 3H), 2.57–2.51 (m, 1H), 2.31–2.22 (m, 2H), 1.97–1.89 (m, 2H), 1.88–1.80 (m, 2H), 1.79–1.71 (m, 1H), 1.69–1.61 (m, 1H), 1.44–1.18 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 214.81/214.78 (C), 198.5 (CH), 170.6 (C), 168.5 (C), 67.4 (C), 52.6 ($CH_3$), 52.5 ($CH_3$), 38.5 ($CH_2$), 33.8 (C), 32.4 ($CH_2$), 28.8 ($CH_2$), 27.90/27.88 (CH), 27.80 ($CH_2$), 23.78/23.76 ($CH_2$), 21.1 ($CH_2$), 19.3 ($CH_2$); HRMS (ESI) *m*/*z* calcd for $C_{16}H_{22}NaO_6$ $[M+Na]^+$ 333.1309, found 333.1309.

**6**. **Preparation and data of compound 7**

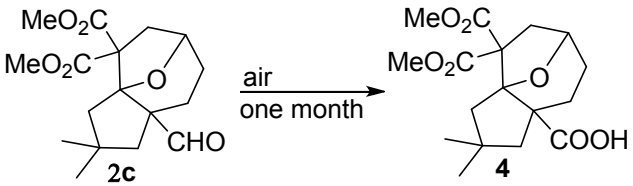
**Dimethyl 2-{(9-oxo-2,3,4,5,6,7,8,9-octahydrobenzo[b]oxepin-2-yl}methyl]malonate** (**7**)



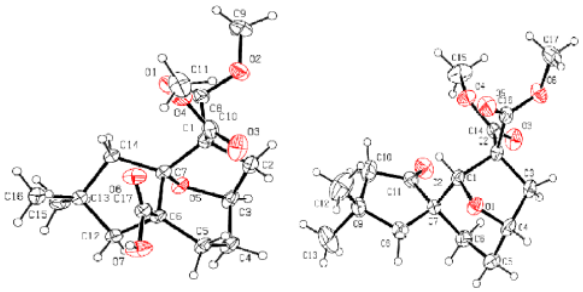

7

To a solution of epoxide **1i/1i'** (47 mg, 0.15 mmol) in 1,2-dichloroethane (5.0 mL) was added $Sc(OTf)_3$ (37 mg, 0.075 mmol) at rt under an argon atmosphere, and the solution was strired at 60 °C for 5 h and then cooled to rt. The reaction mixture was concentrated under reduced pressure. Flash column chromatography of the residue on silica gel (petroleum ether/ethyl acetate, 10:1) afforded compound **7** (17 mg, 36% yield) as a white solid; m.p. 96–99 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25°C) δ 4.44–4.41 (m, 1H), 3.74 (s, 3H), 3.72 (s, 3H), 3.49–3.43 (m, 1H), 2.55–2.48 (m, 1H), 2.41–2.36 (m, 4H), 2.17–2.06 (m, 3H), 1.98–1.84 (m, 4H), 1.75–1.67 (m, 1H), 1.51–1.43 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 25°C) δ 194.1 (C), 170.7 (C), 170.5 (C), 150.5 (C), 147.4 (C), 79.8 (CH), 52.4 ($CH_3$), 47.7 (CH), 37.7 ($CH_2$), 36.8 ($CH_2$), 35.8 ($CH_2$), 33.3 ($CH_2$), 31.8 ($CH_2$), 23.4 ($CH_2$), 22.2 ($CH_2$); HRMS (ESI) *m/z* calcd for $C_{16}H_{23}O_6$ $[M+H]^+$ 311.1489, found 311.1502.

**7**. **Figure 1. Synthesis of compound 4 and the X-ray crystallographic structures of compounds 4 and 3c**




2c 4



4 3c

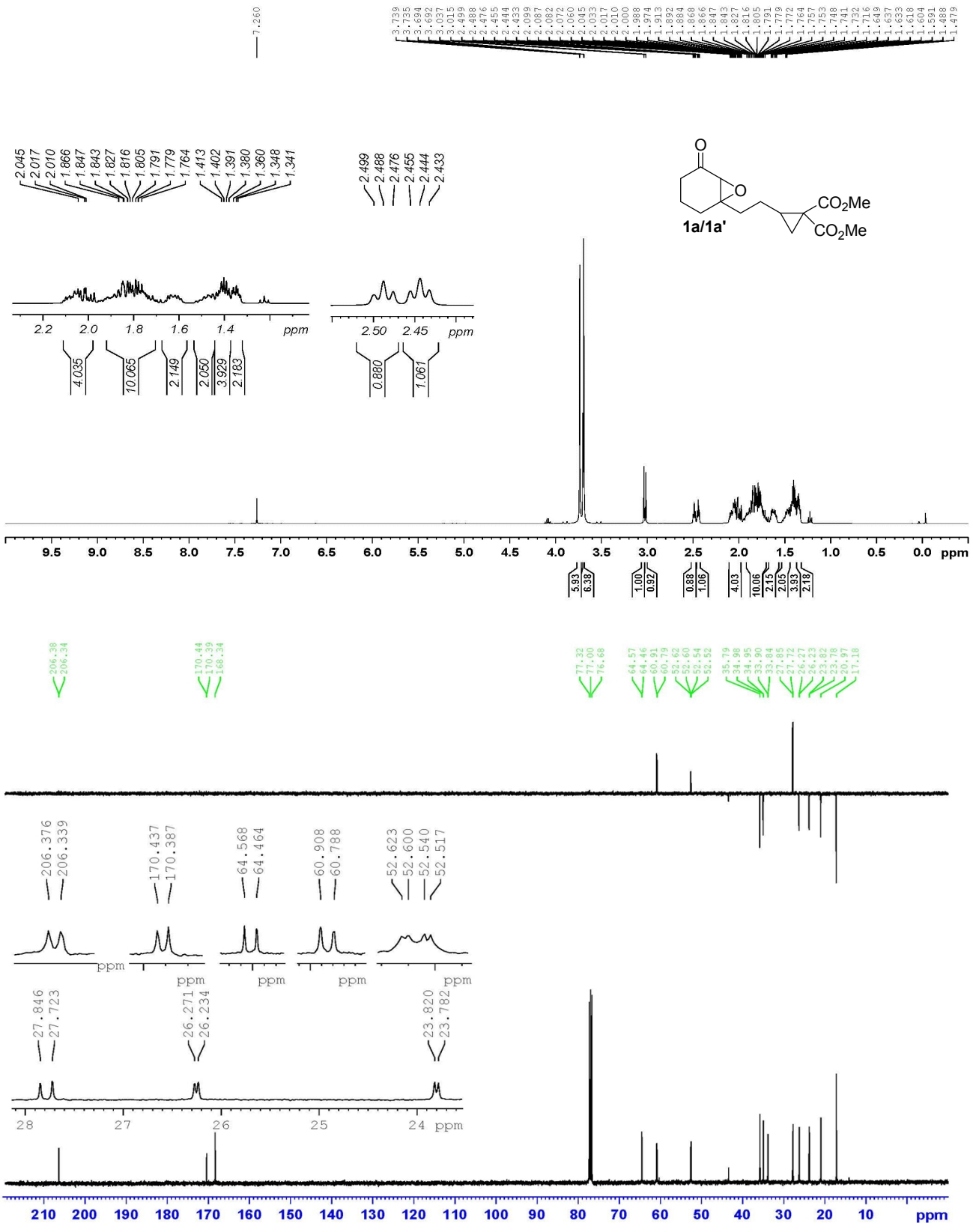
**8**. **References:**

(1) M. D'Augustin, L. Palais, A. Alexakis, *Angew. Chem. Int. Ed.* 2005, **44**, 1376.

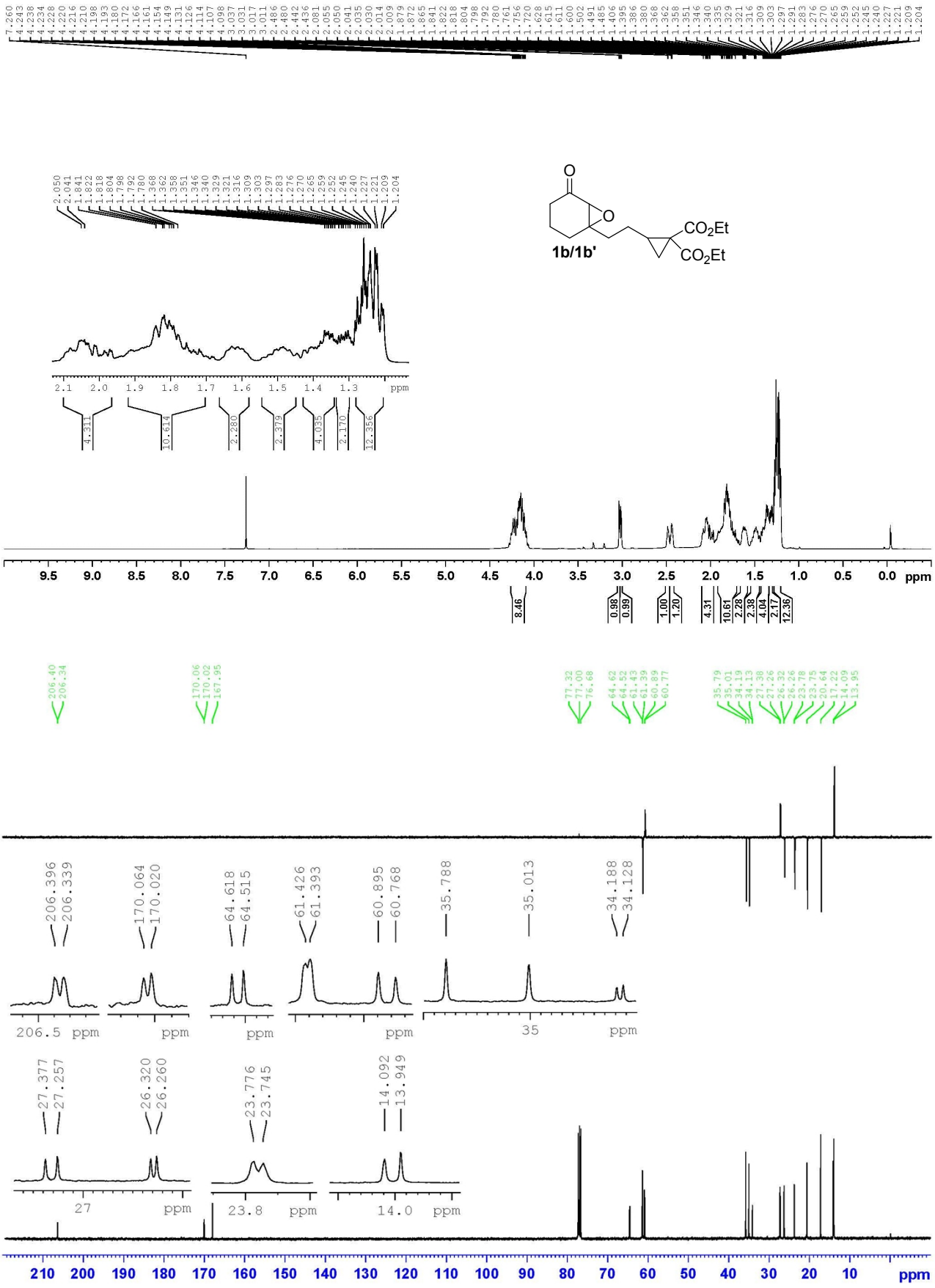
(2) W. Zhu, J. Fang, Y. Liu, J. Ren, Z. Wang, *Angew. Chem. Int. Ed.* 2013, **52**, 2032.

## 9. $^{1}$H NMR, $^{13}$C NMR and DEPT spectra of 1a/1a'–1n/1n', 2a, 3a, 2b, 3b, 2c, 3c, 2d, 3d, 2e, 3e, 2f, 2g, 2i–2n, 4, 5/5', 6/6', and 7

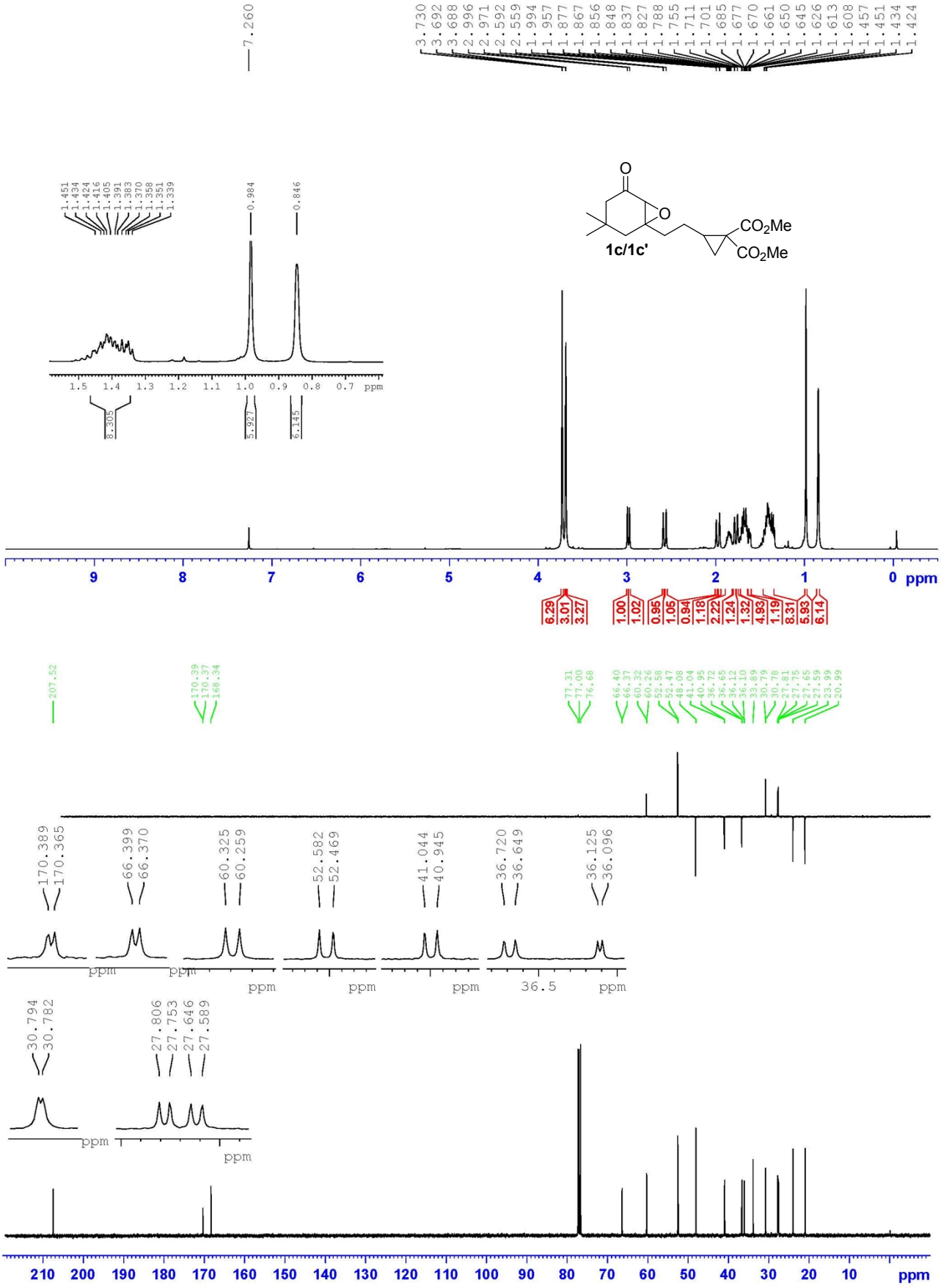
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **1a**/**1a'**



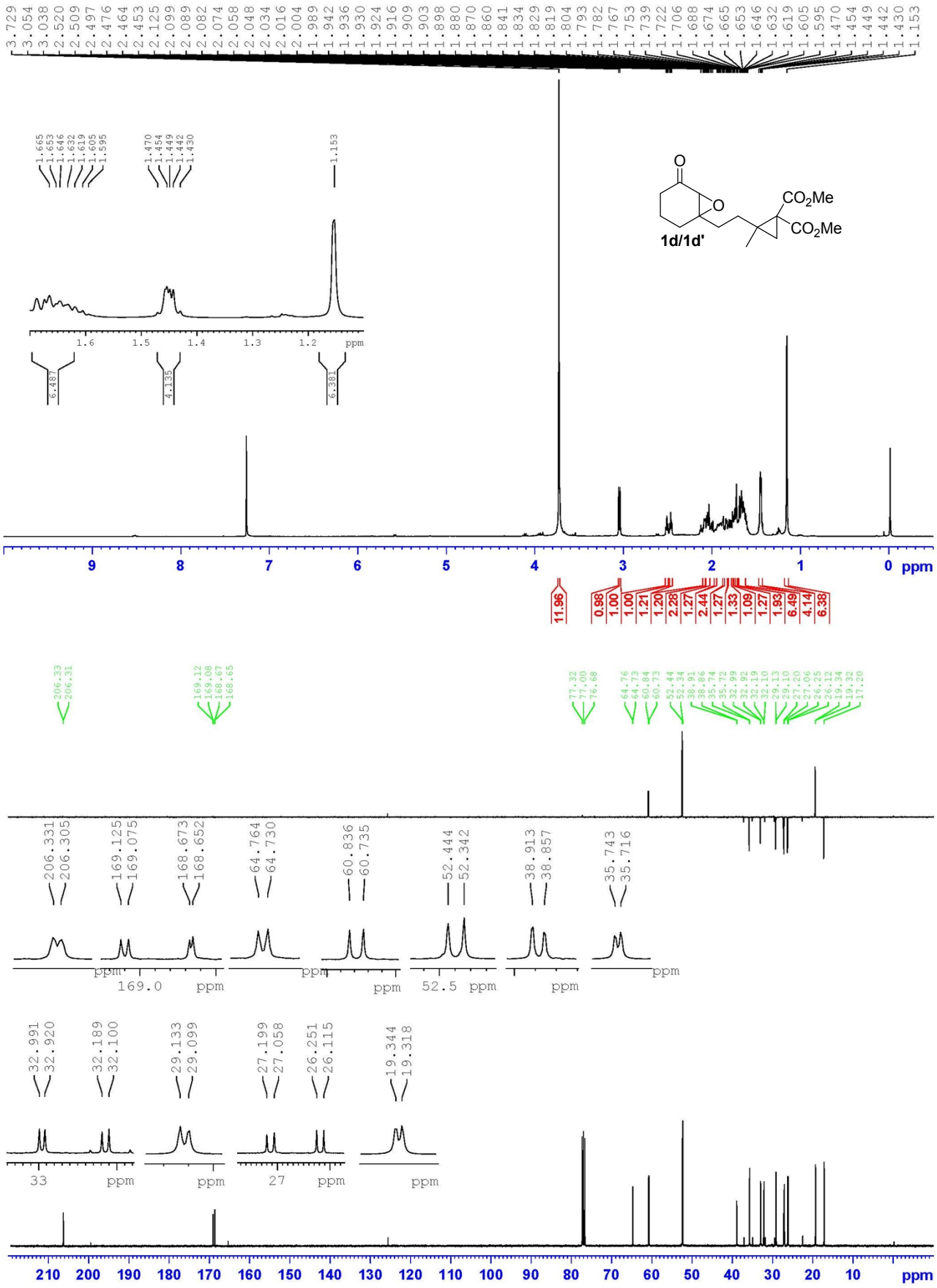
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **1b**/**1b'**



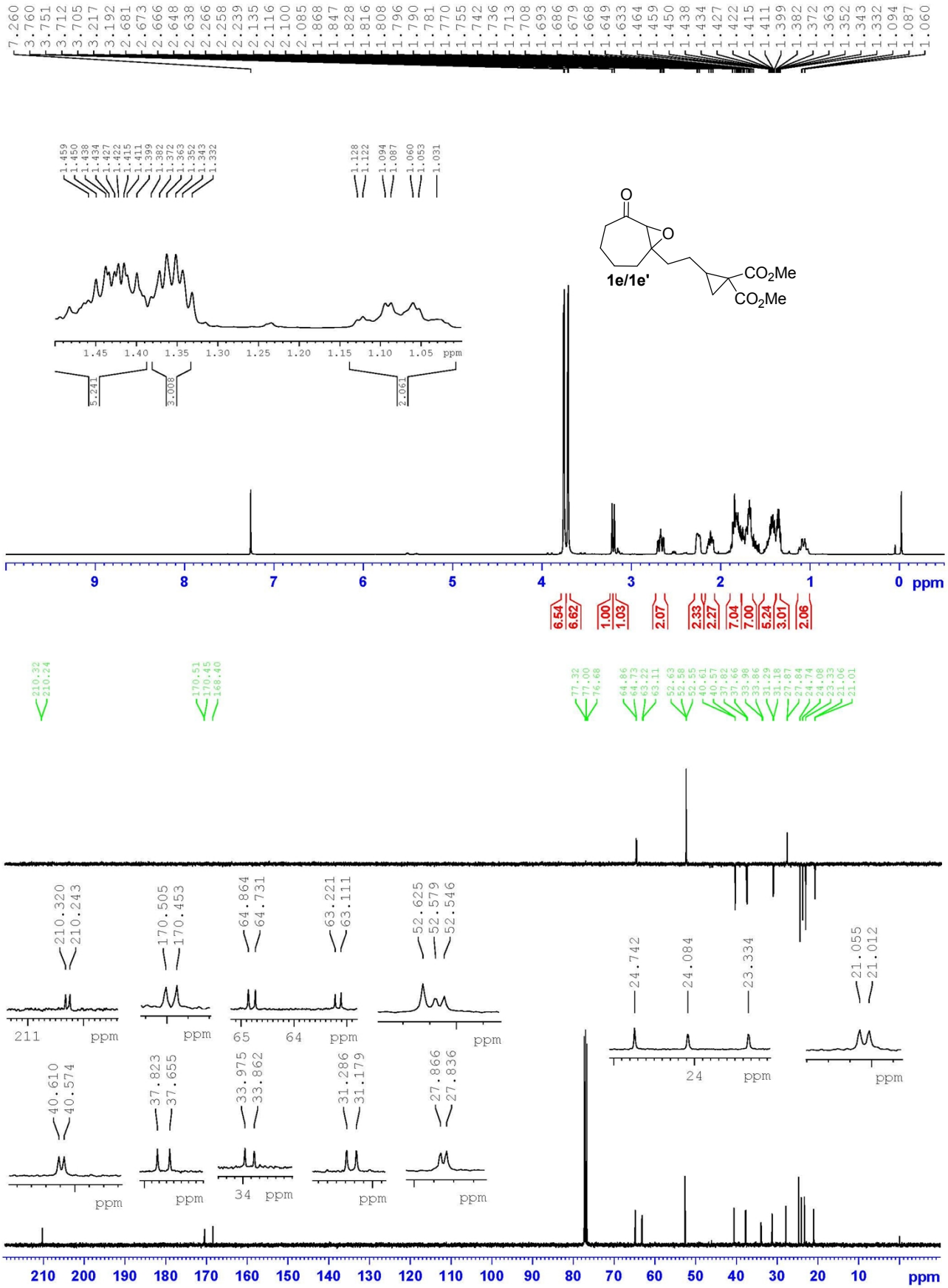
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **1c**/**1c'**



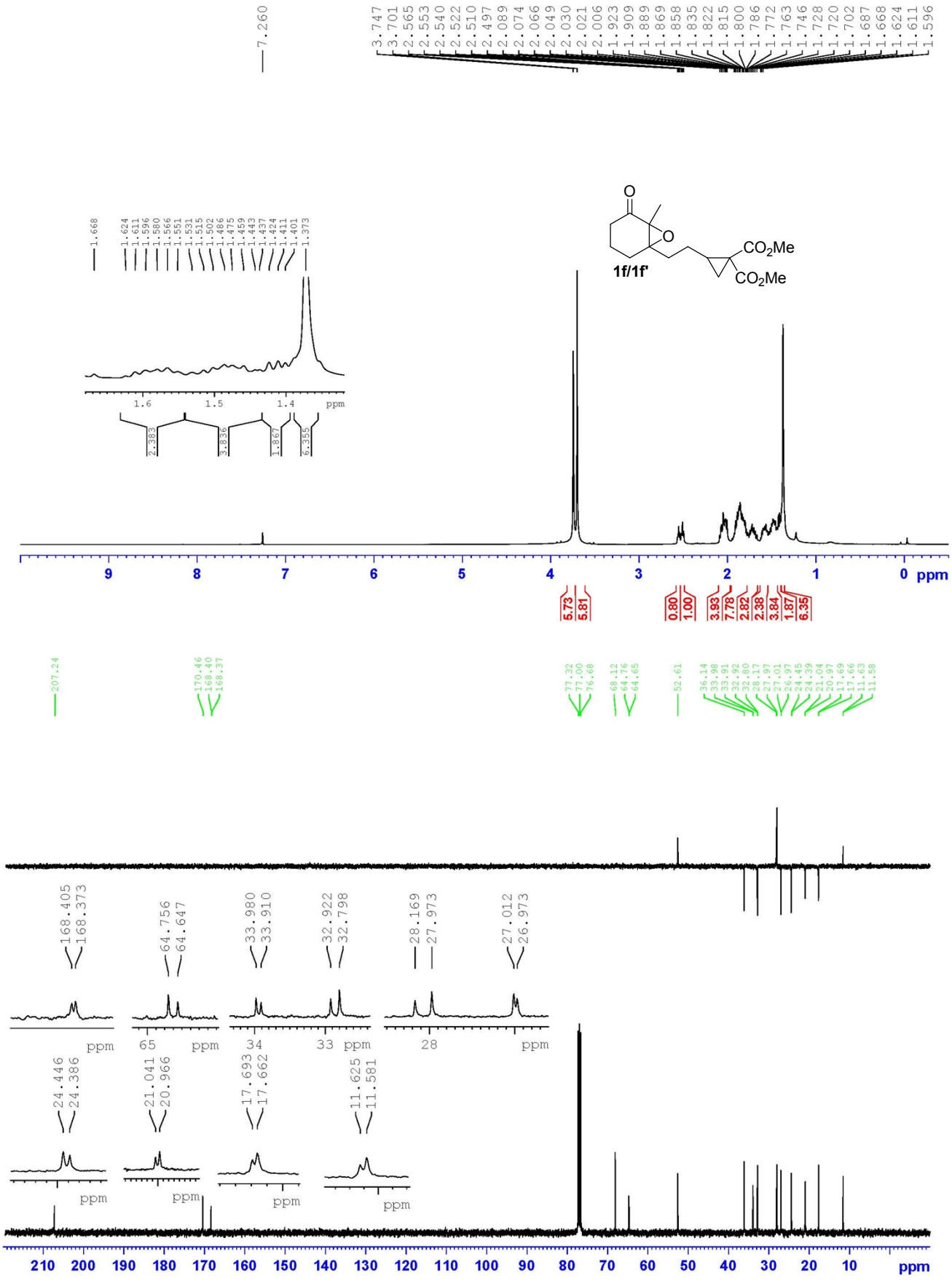
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **1d/1d'**



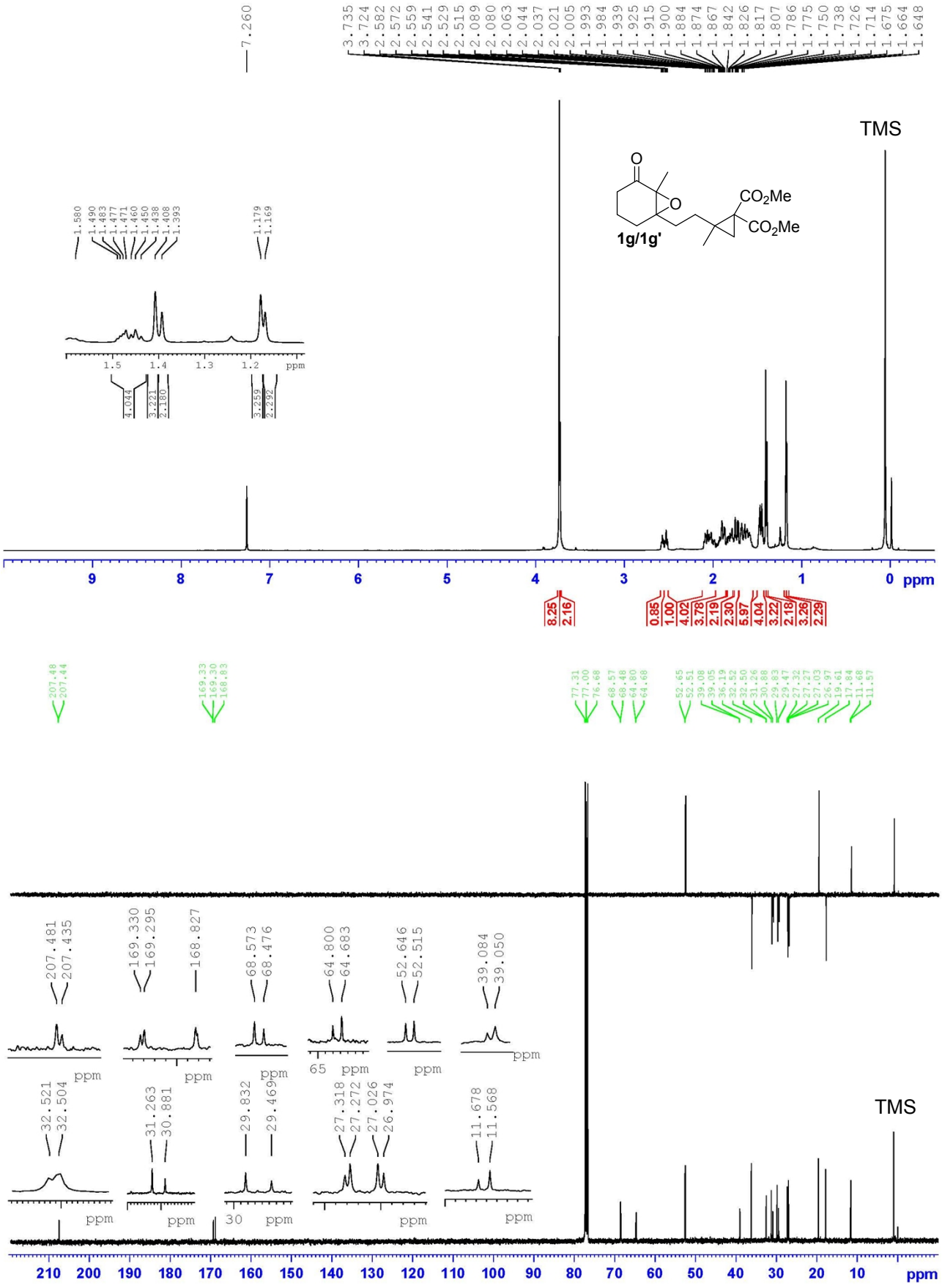
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **1e**/**1e'**



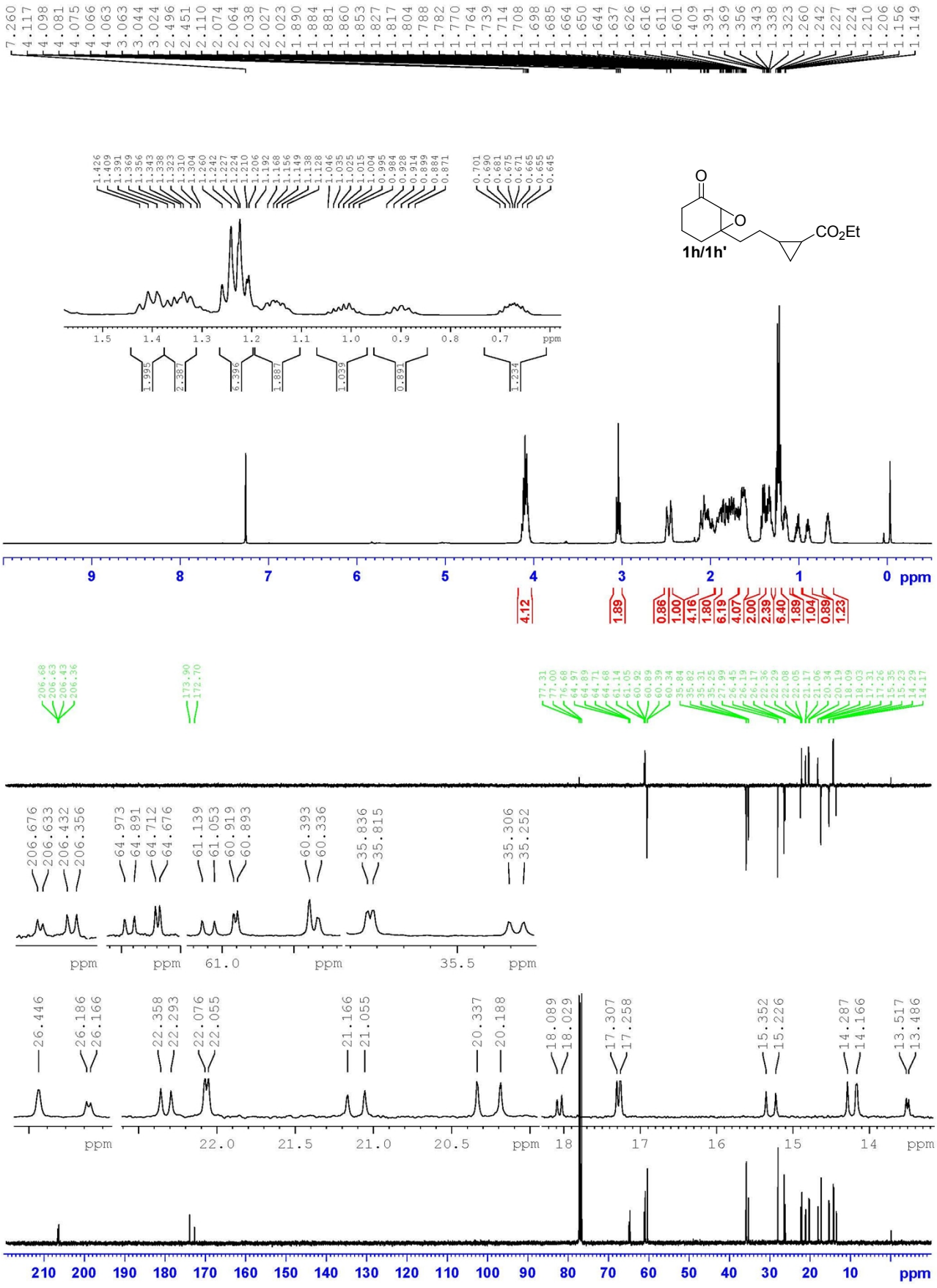
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **1f**/**1f'**



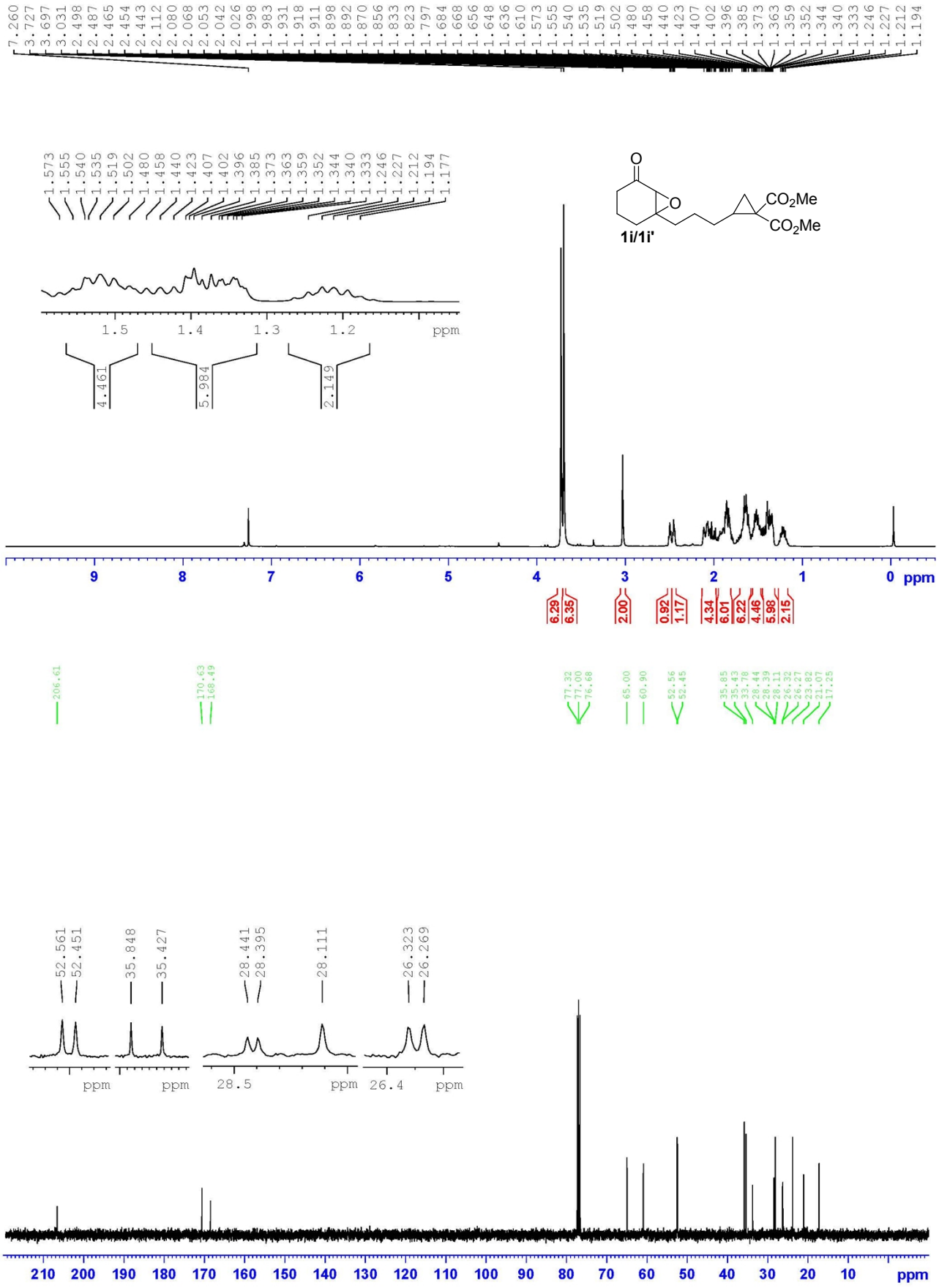
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **1g**/**1g'**



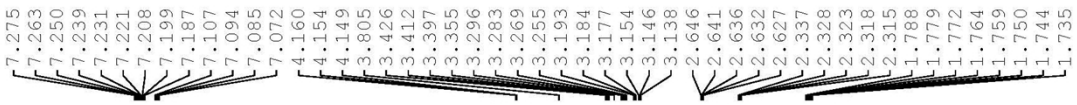
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **1h**/**1h'**

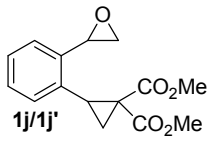


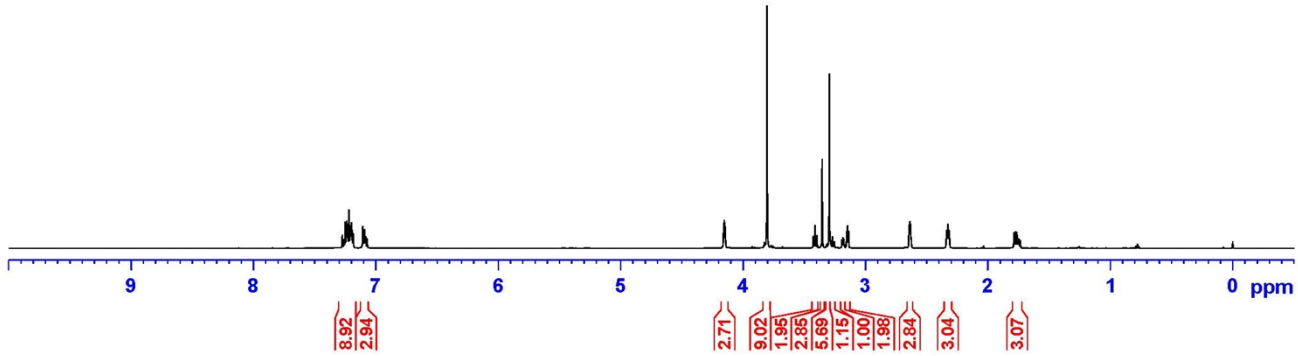
$^{1}$H NMR ($CDCl_3$, 400 MHz) and $^{13}$C NMR ($CDCl_3$, 100 MHz) of **1i**/**1i'**

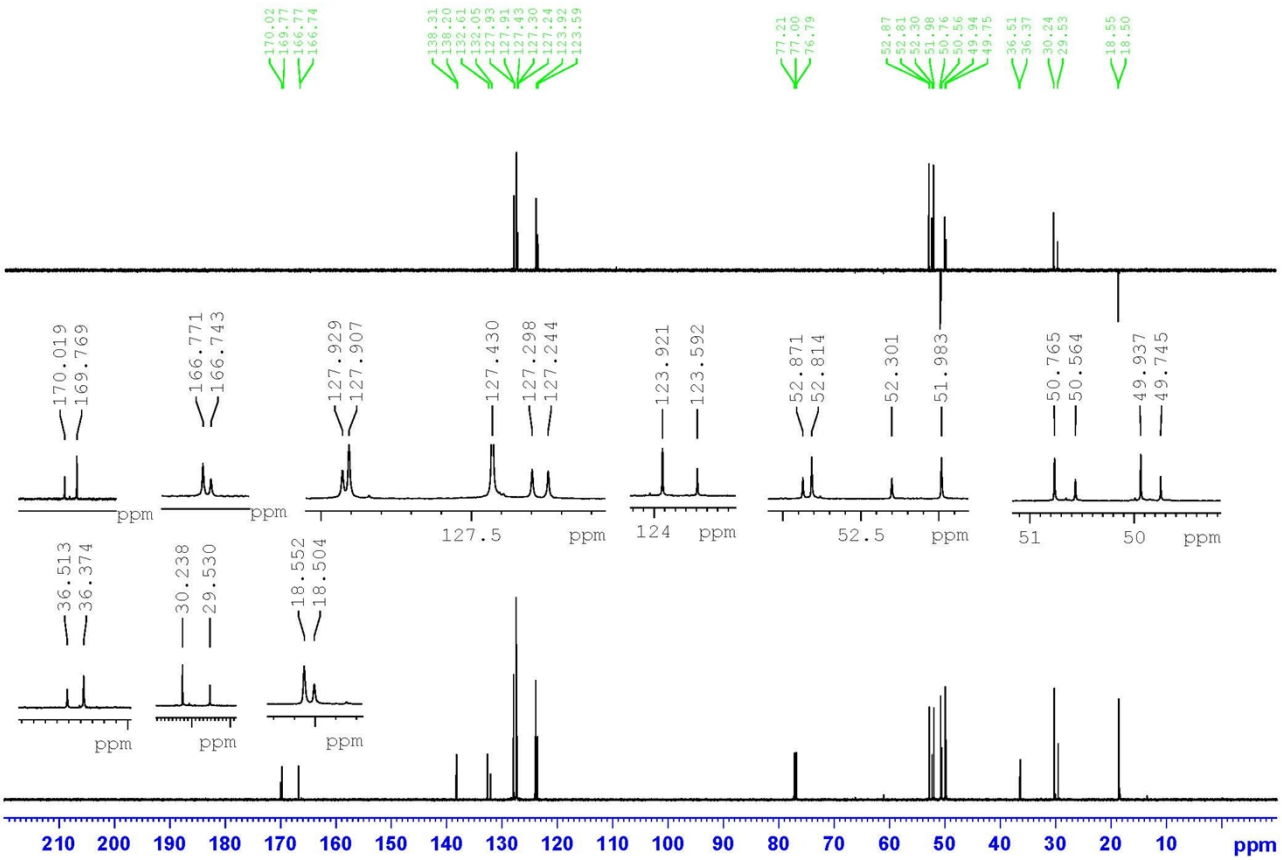


$^{1}$H NMR ($CDCl_3$, 600 MHz), $^{13}$C NMR ($CDCl_3$, 150 MHz) and DEPT 135 of **1j**/**1j'**

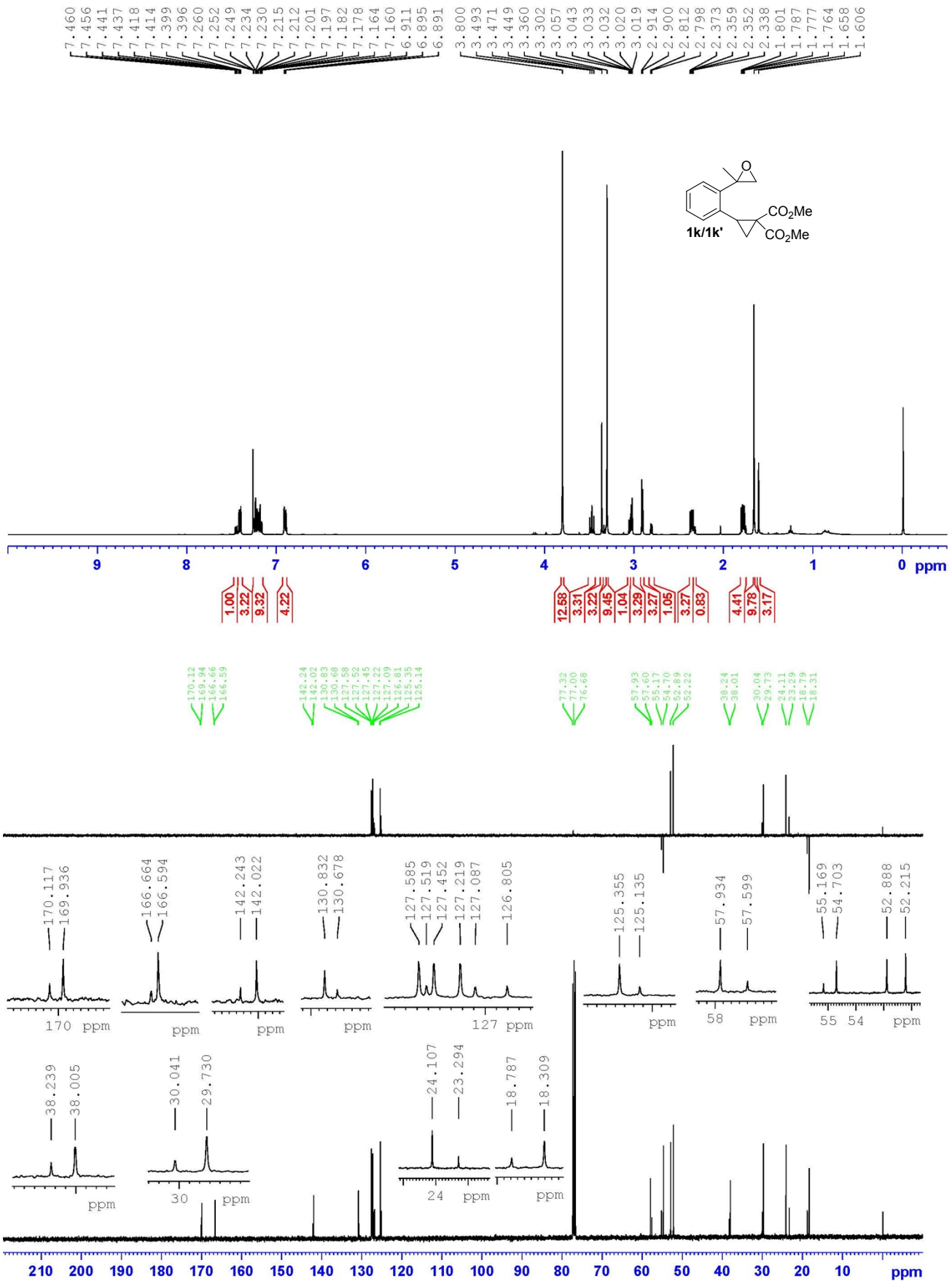


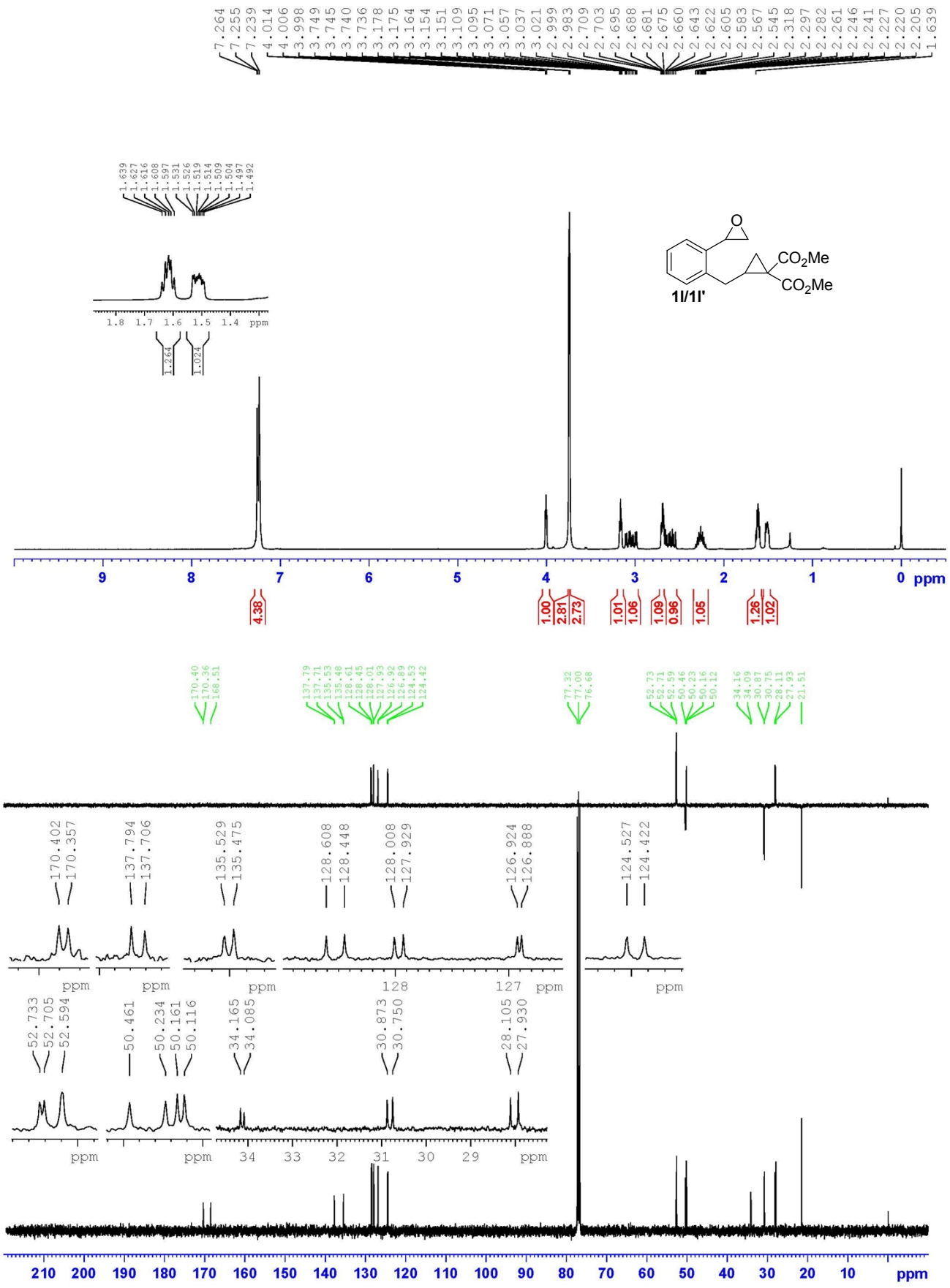



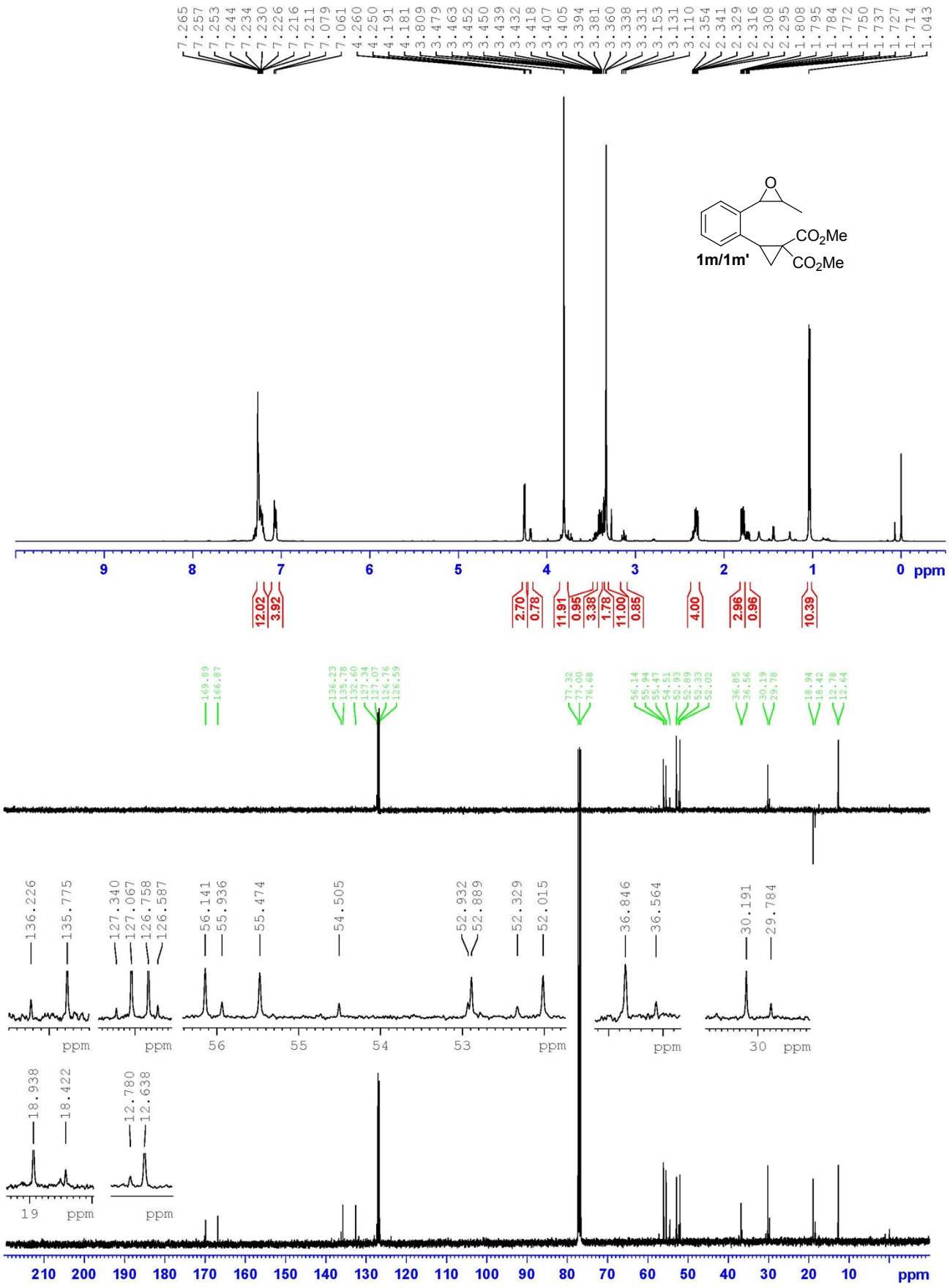
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **1k**/**1k'**



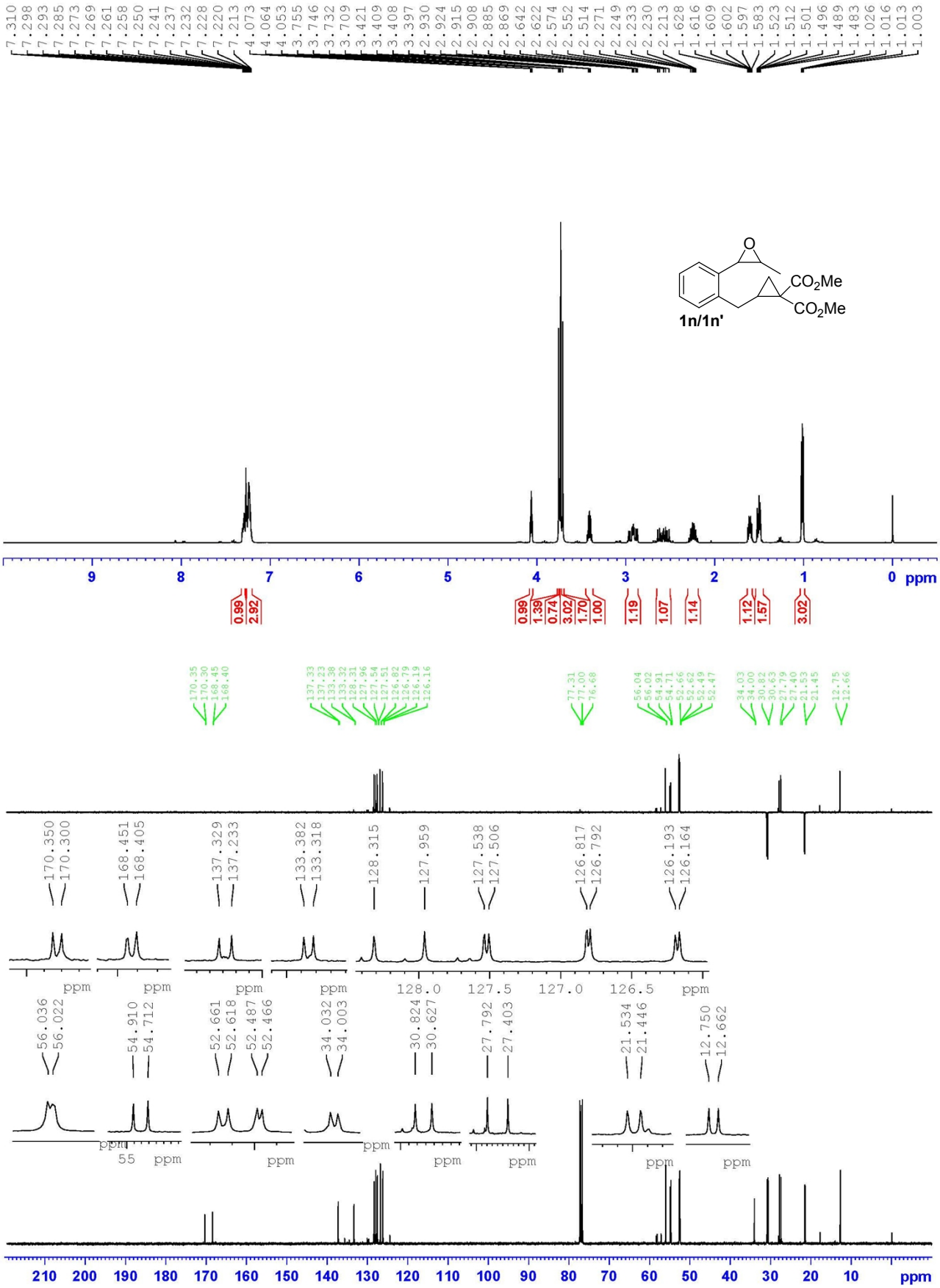
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **1l**/**1l'**



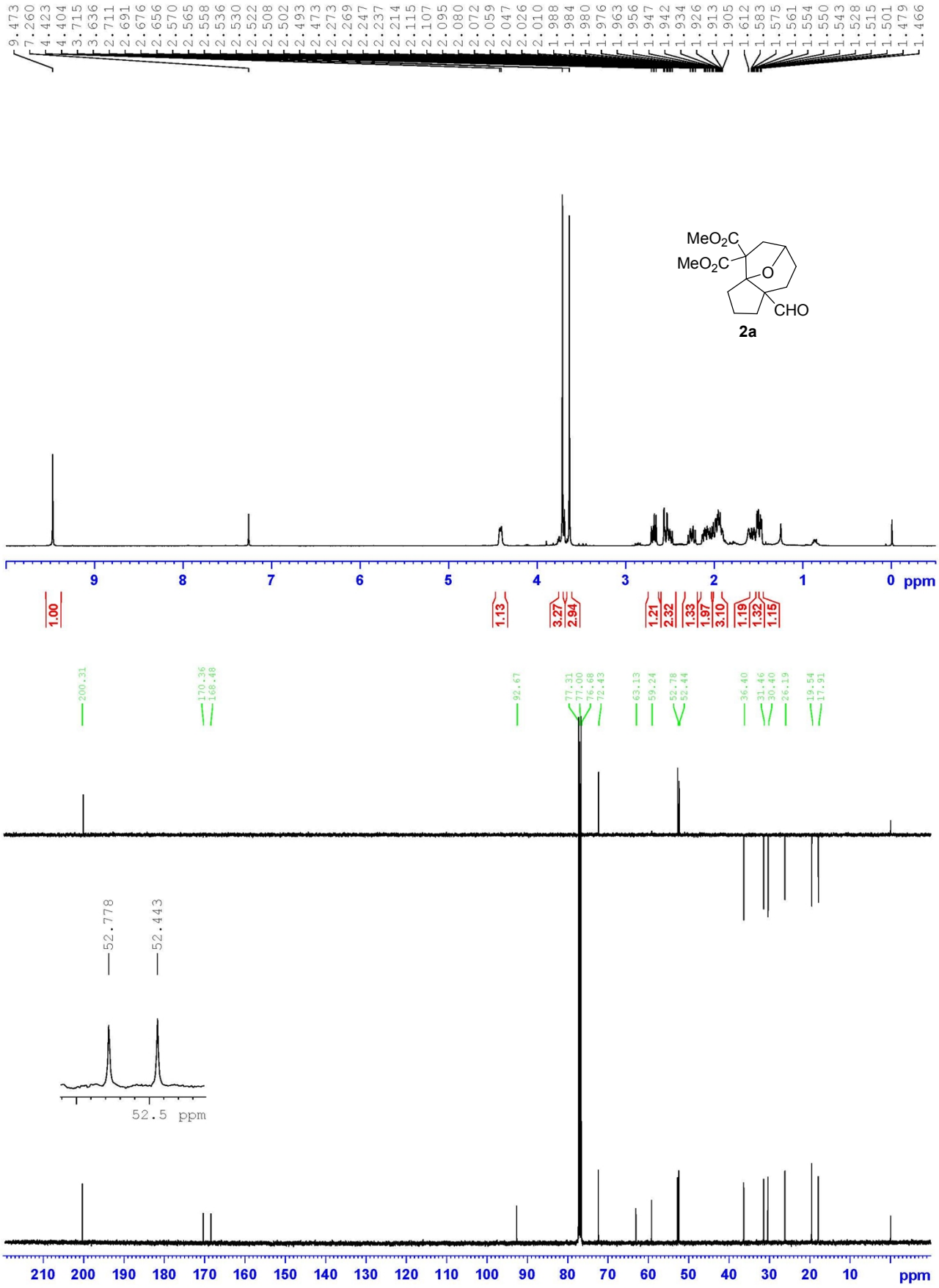
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **1m**/**1m'**



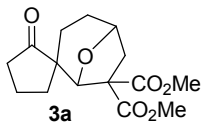
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **1n**/**1n'**



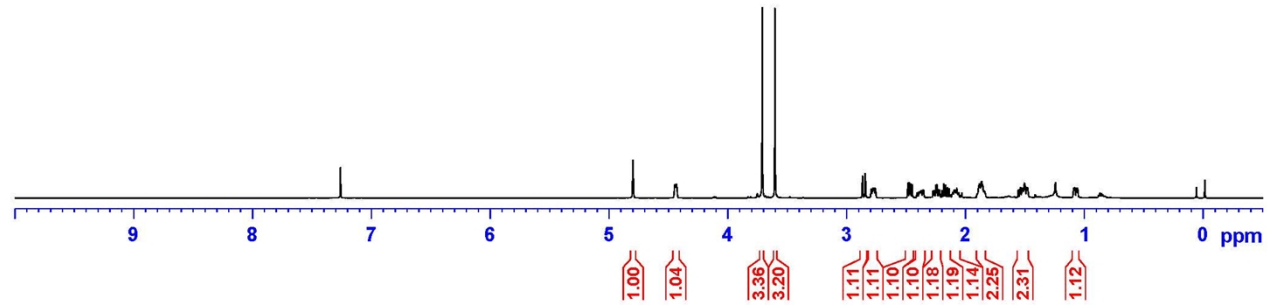
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **2a**



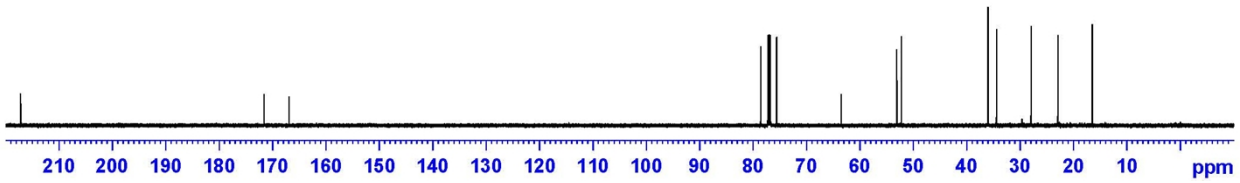
$^{1}$H NMR ($CDCl_3$, 600 MHz), $^{13}$C NMR ($CDCl_3$, 150 MHz) and DEPT 135 of **3a**

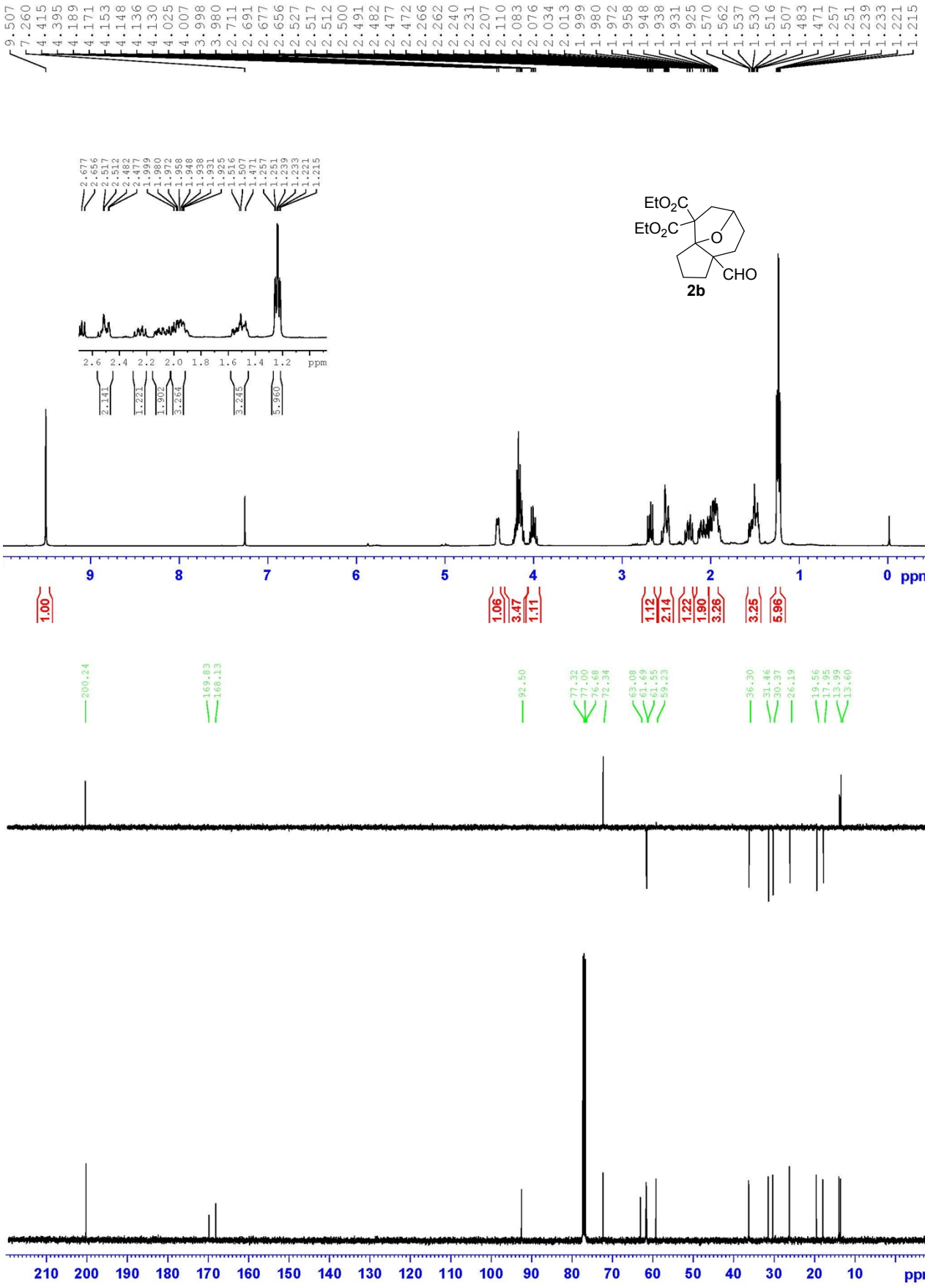

**3a**



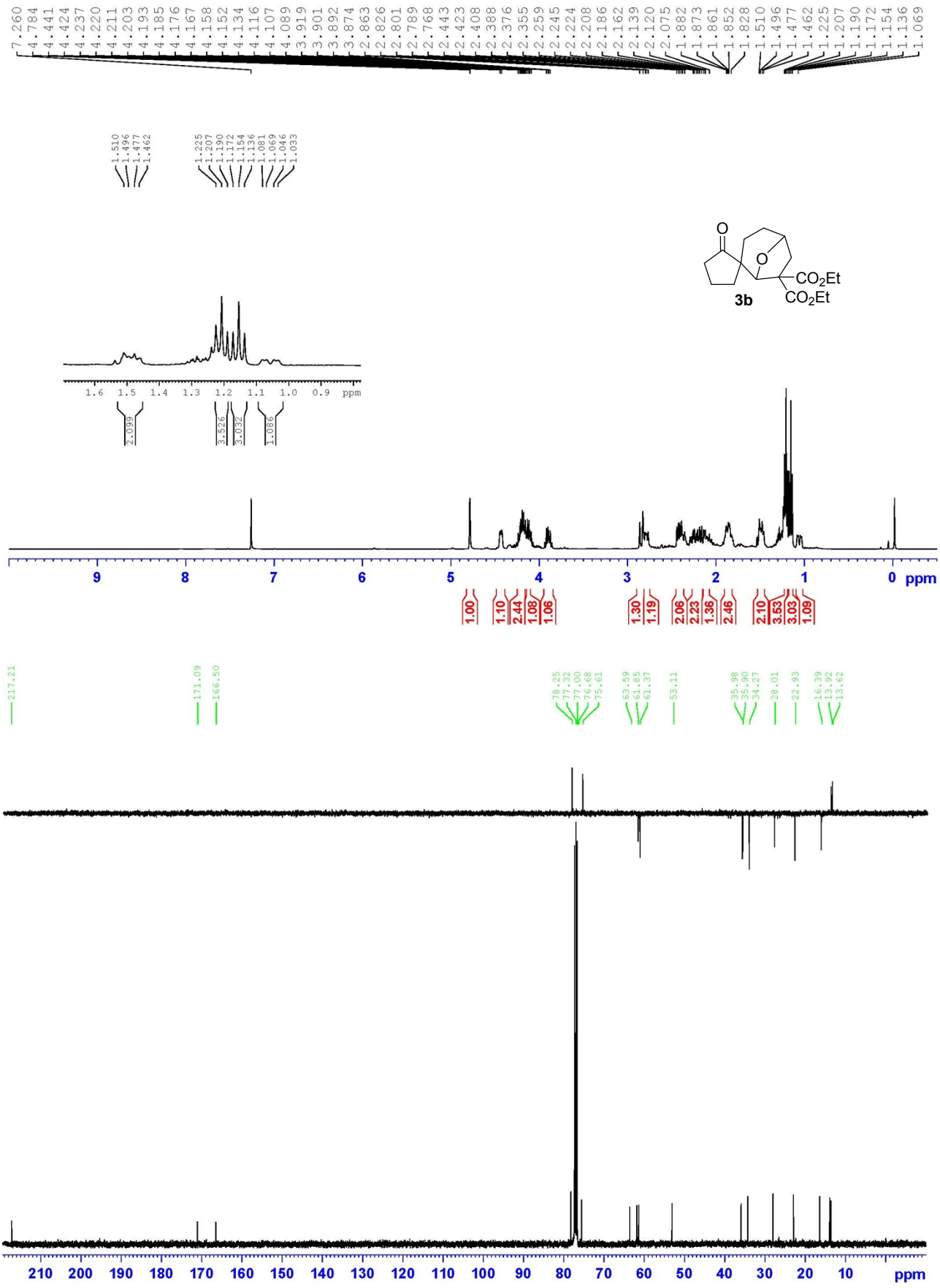




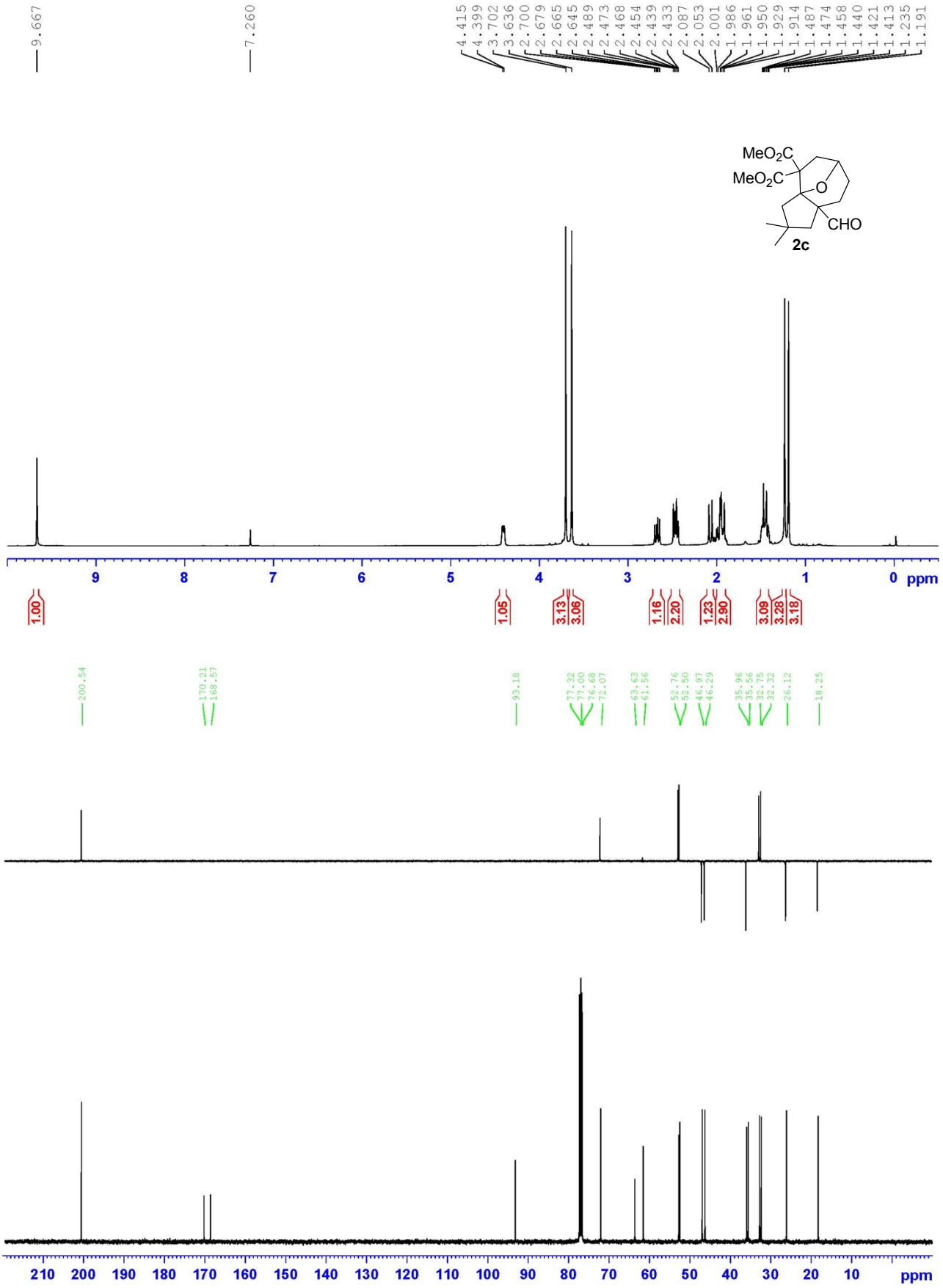
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **2b**



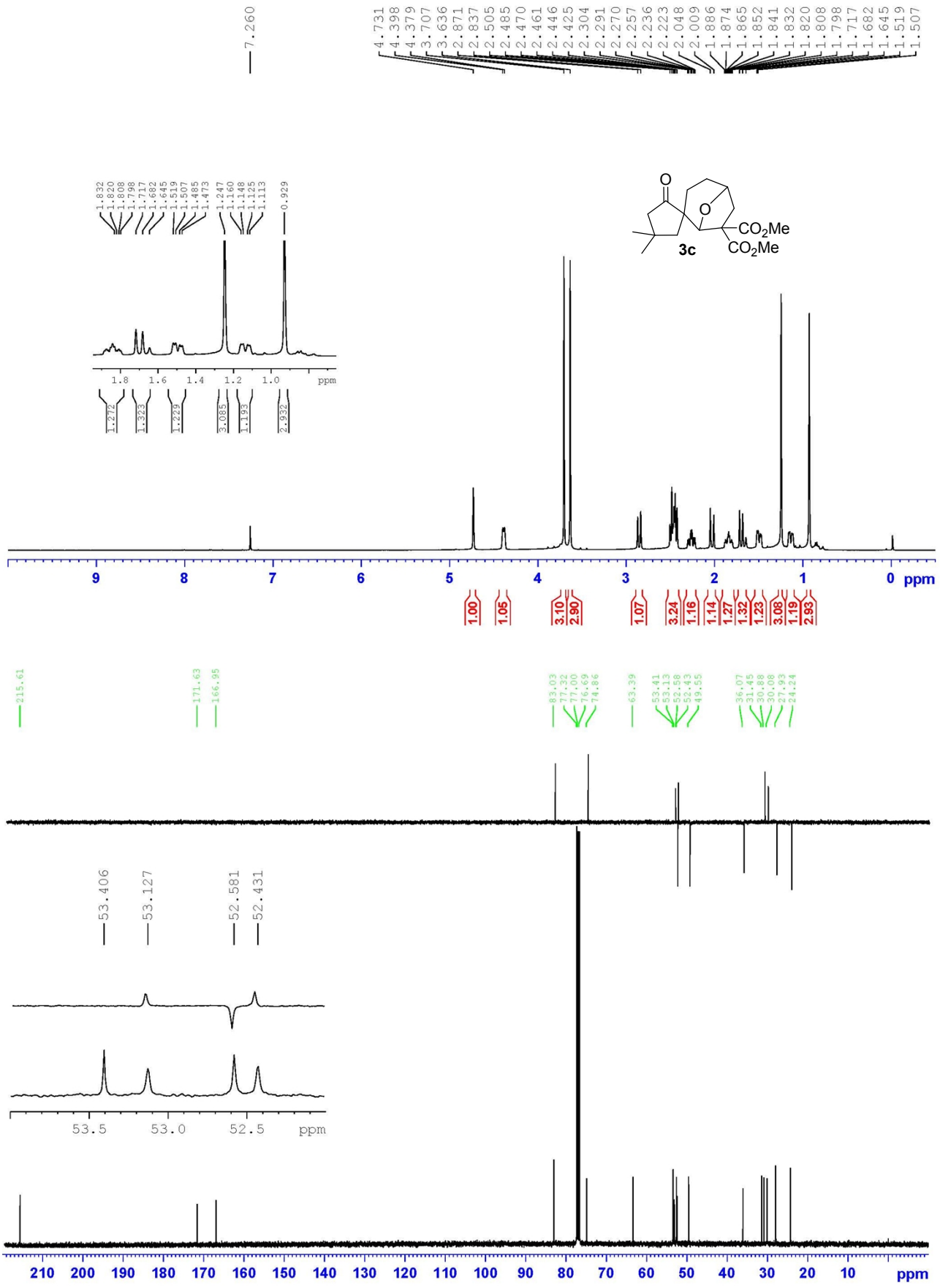
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **3b**



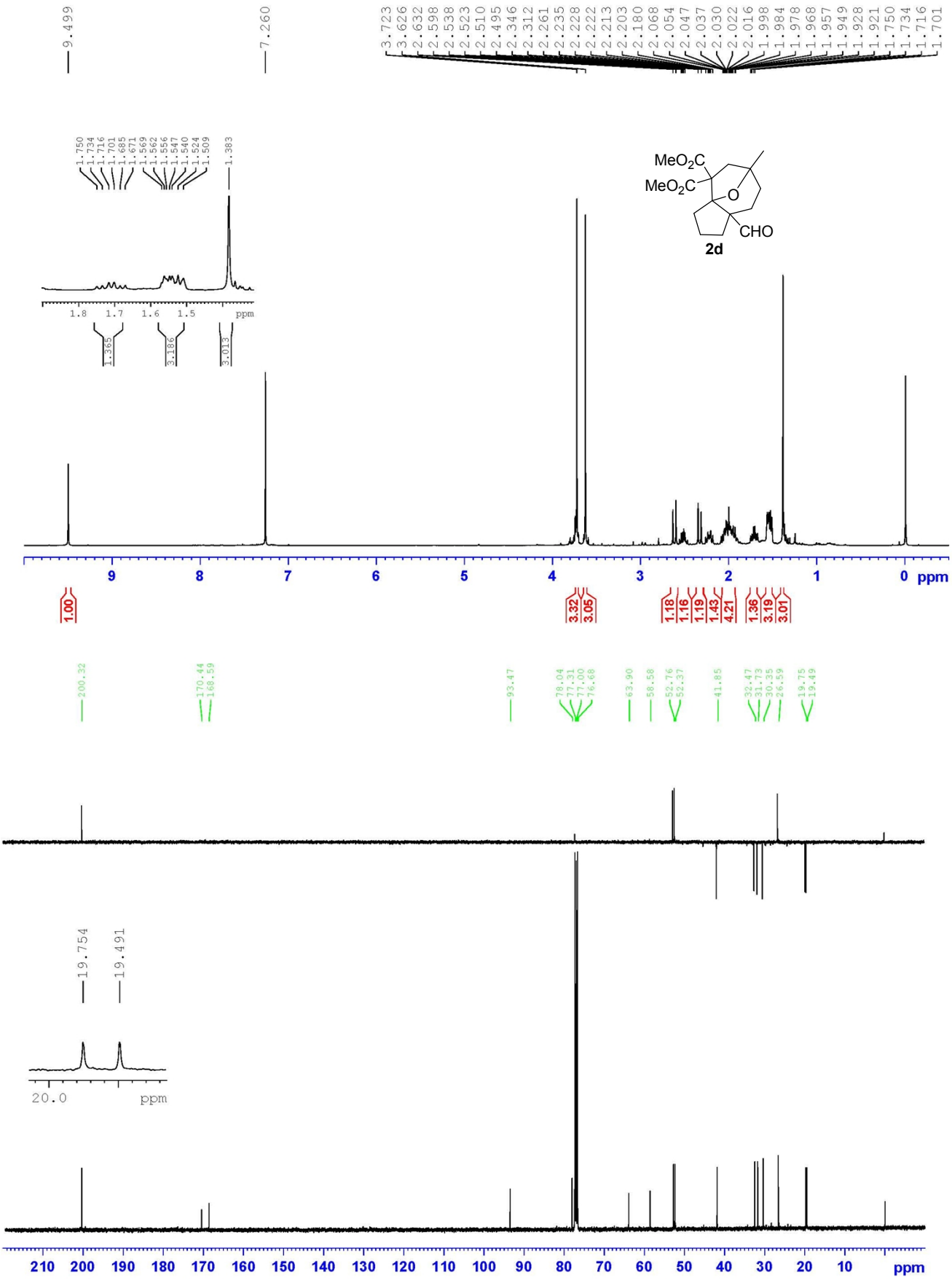
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **2c**



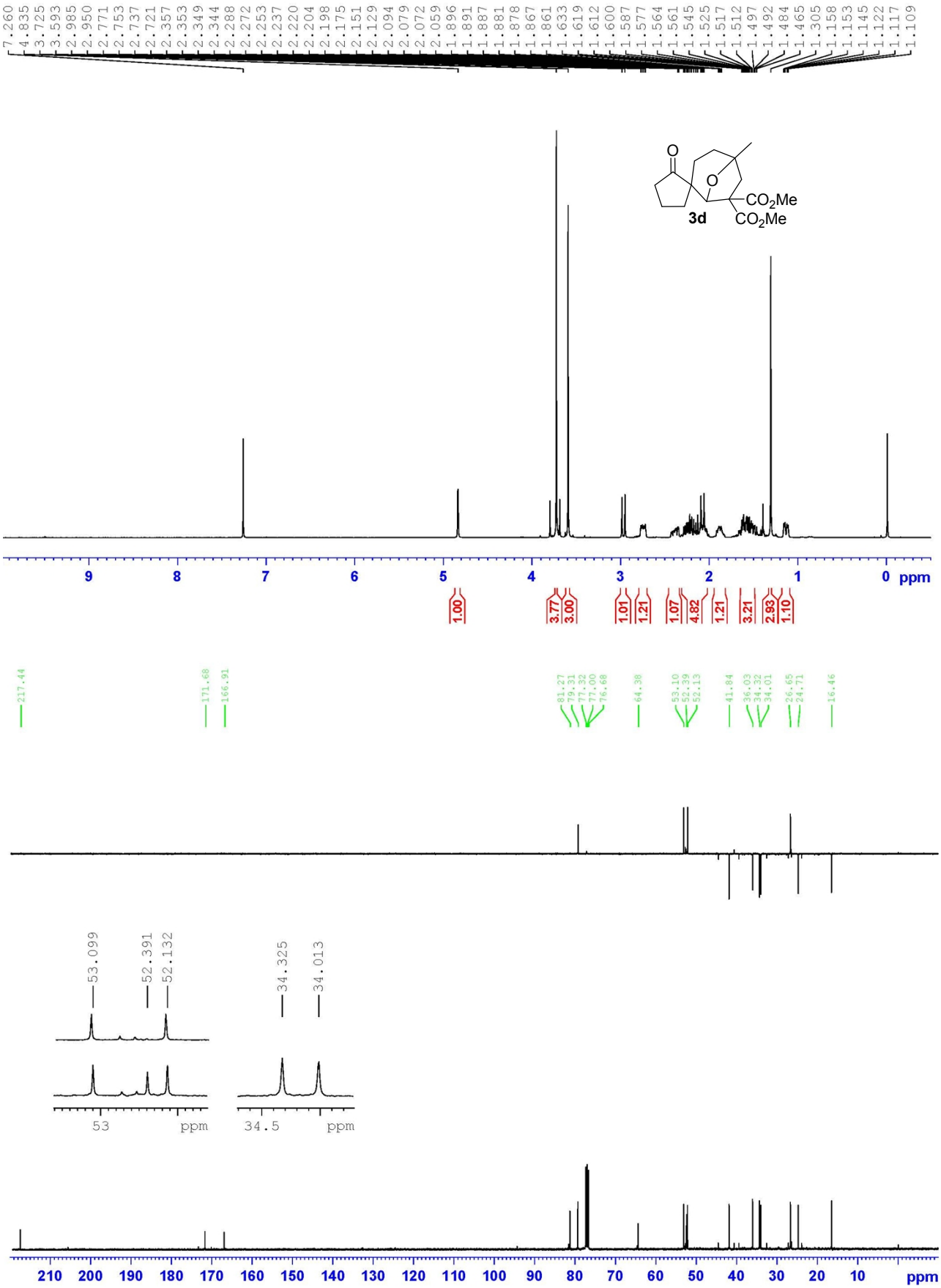
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **3c**



$^{1}$H NMR ($CDCl_3$, 600 MHz) of $^{13}$C NMR ($CDCl_3$, 150 MHz) of **2d**



$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **3d**



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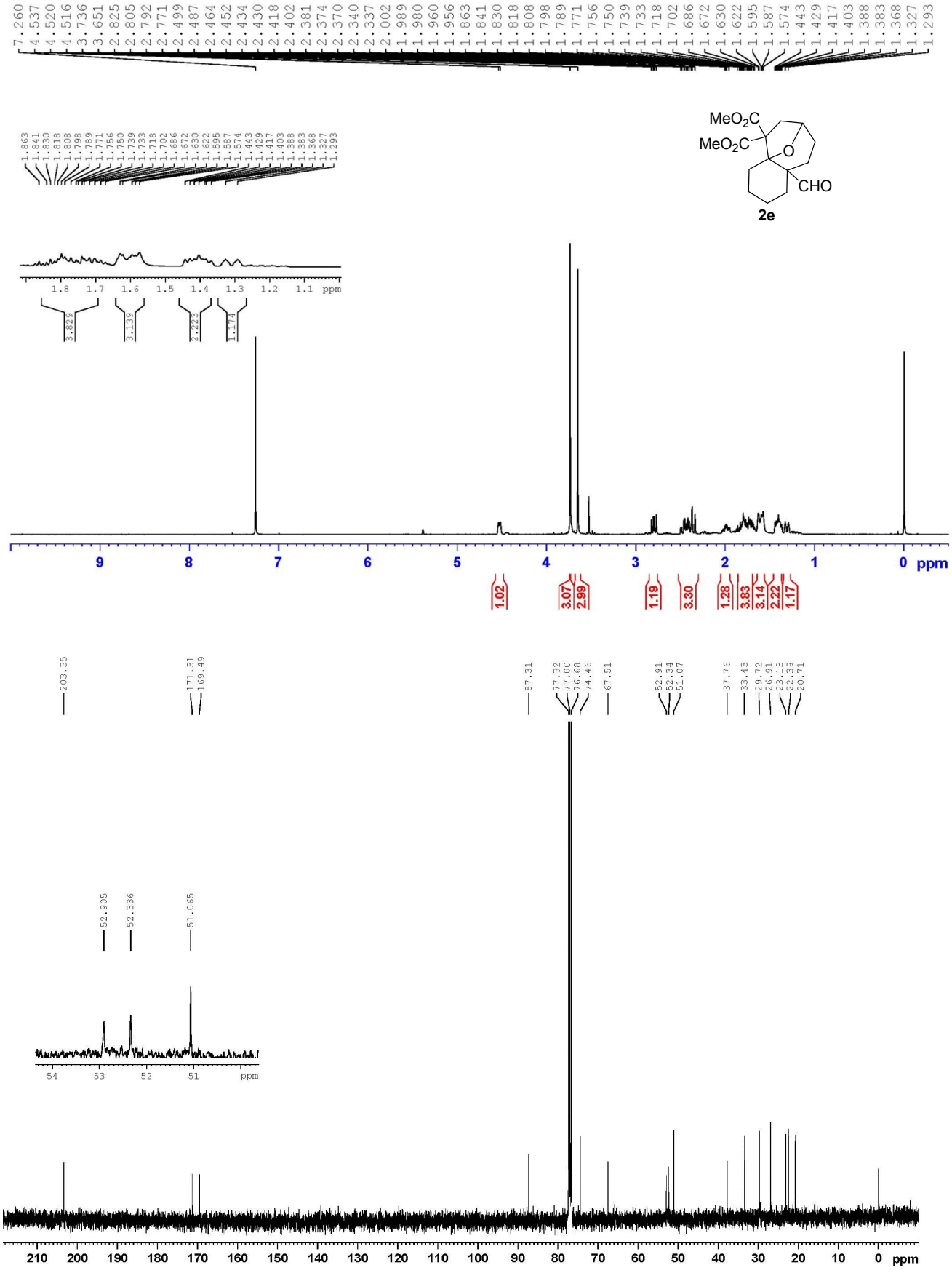

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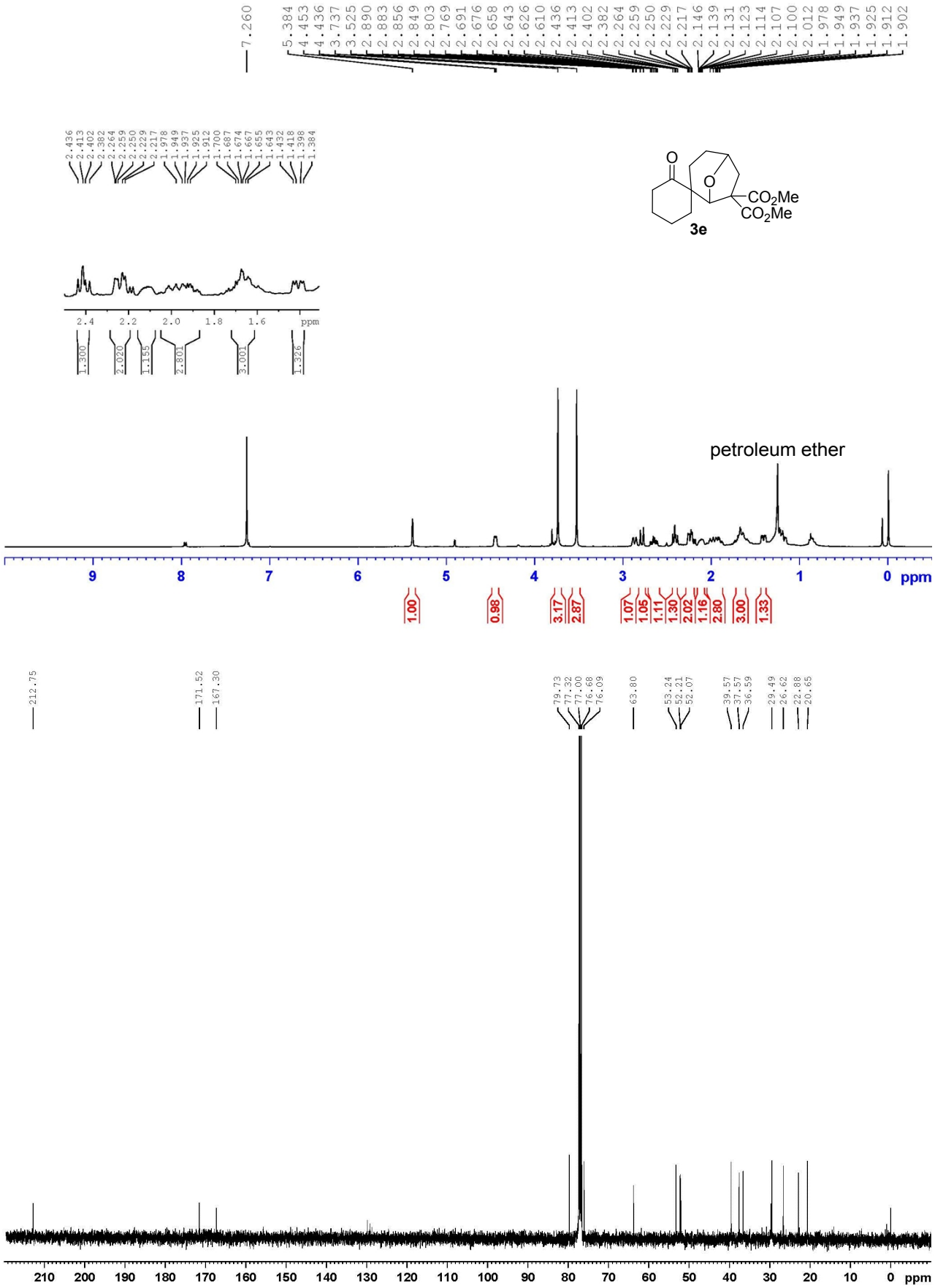
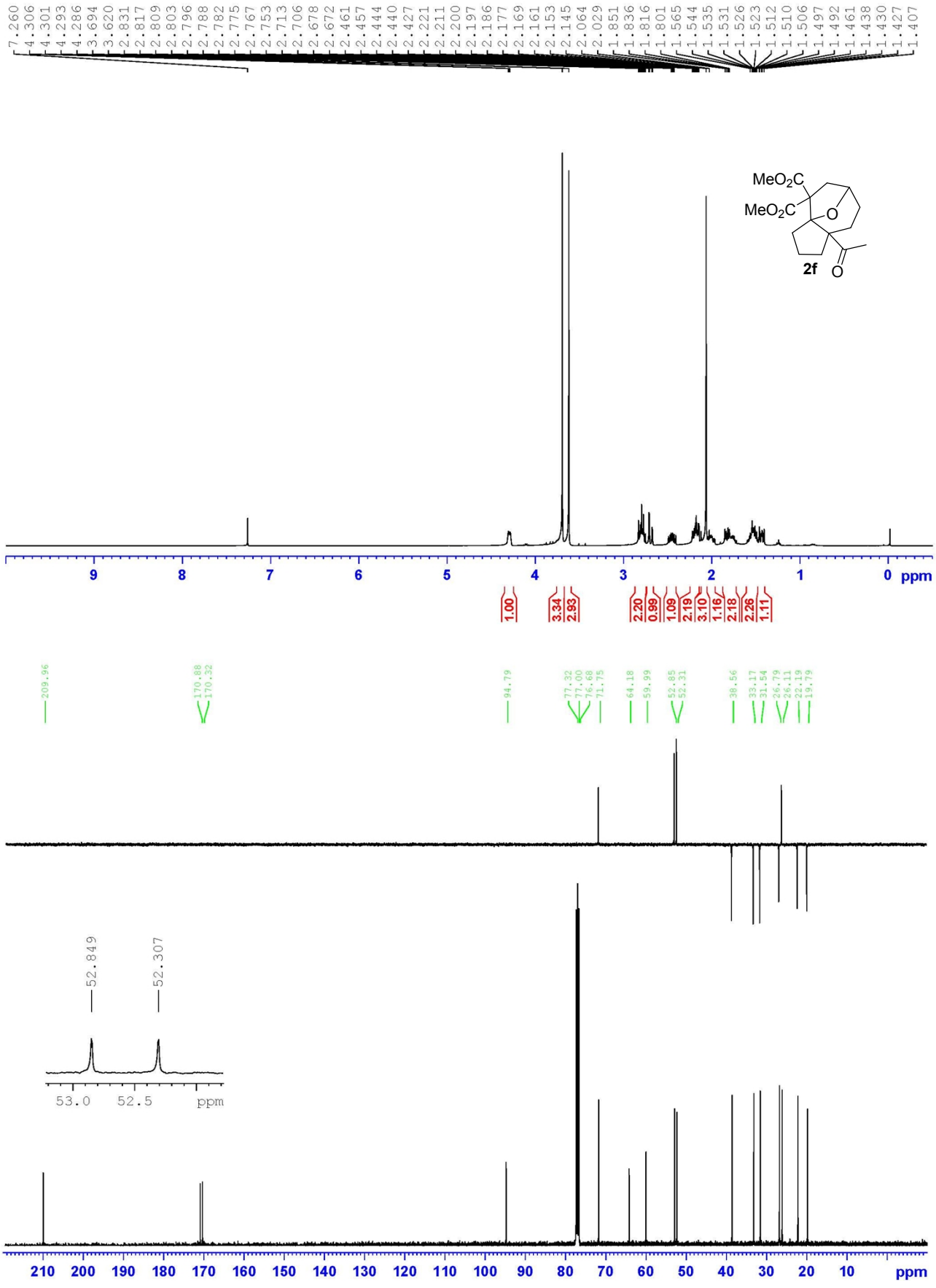
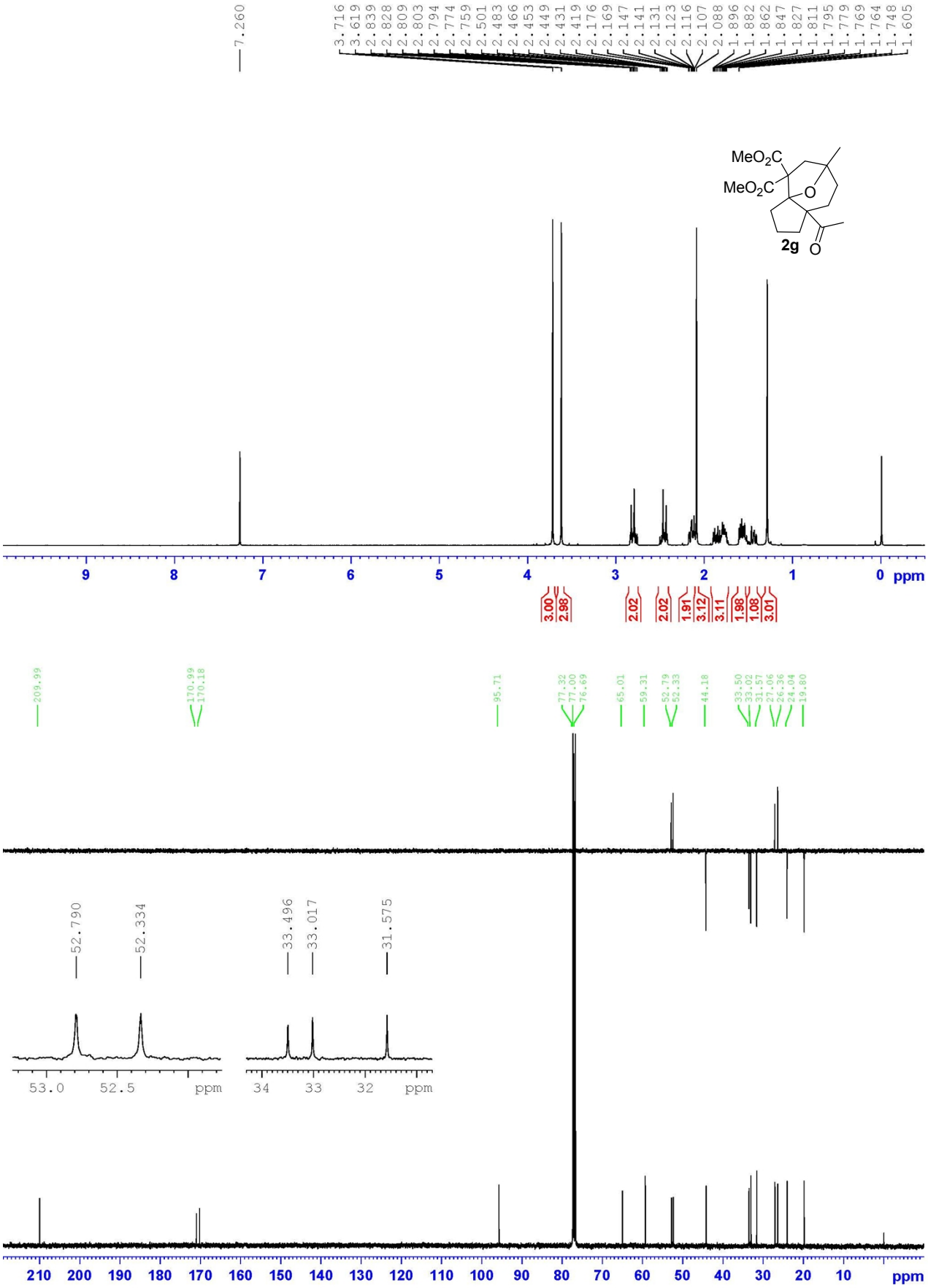


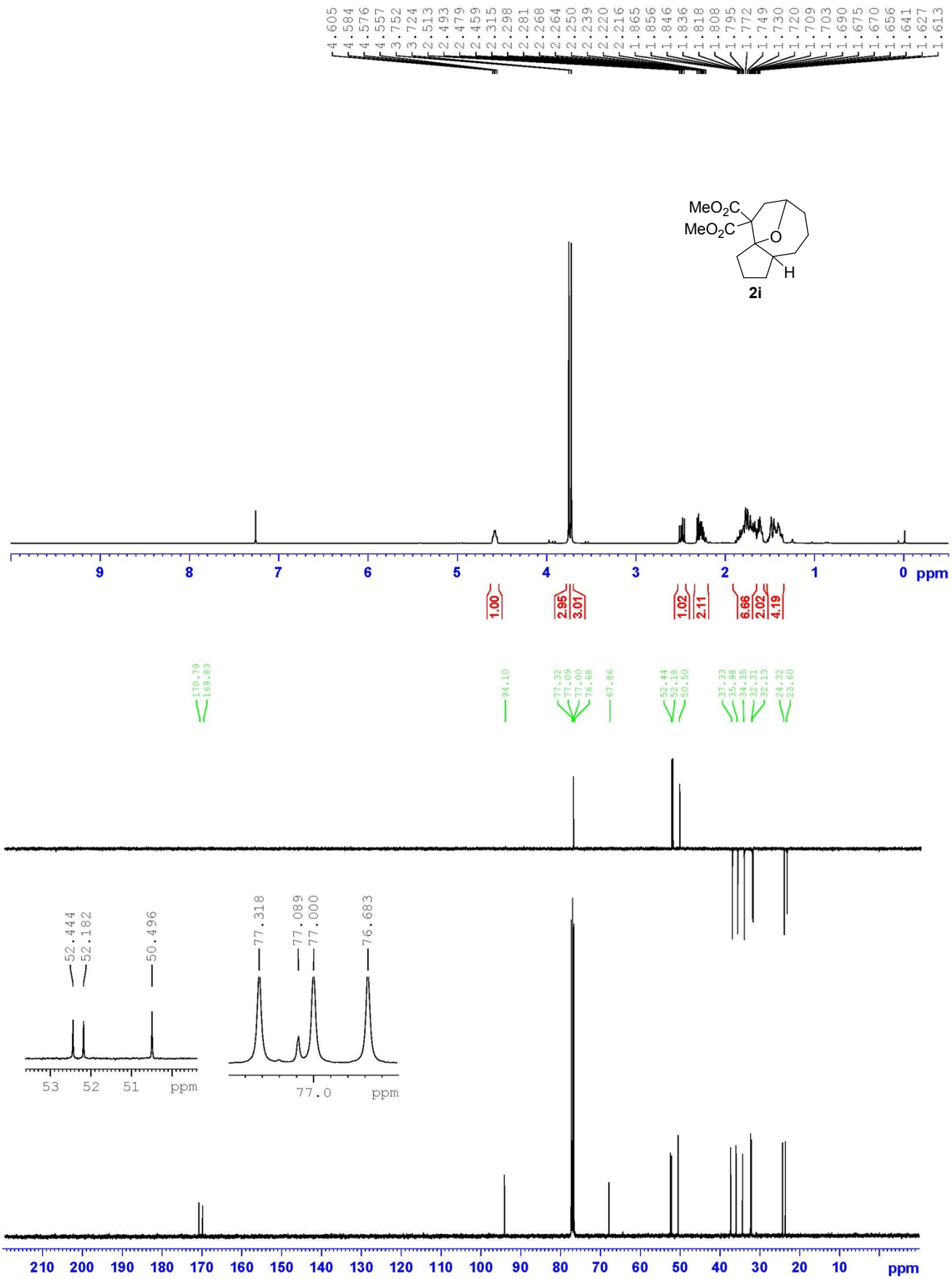
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **2f**



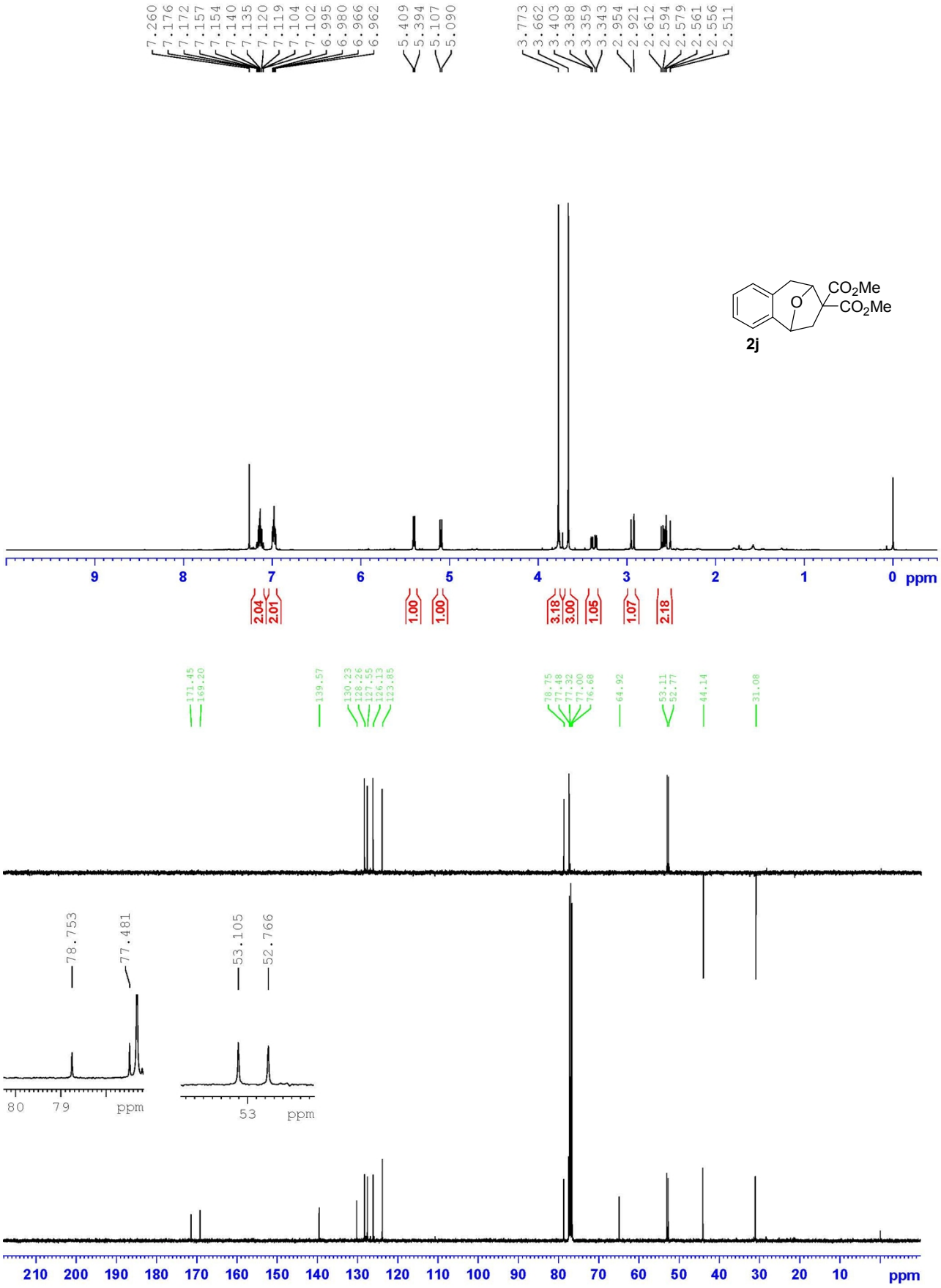
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **2g**



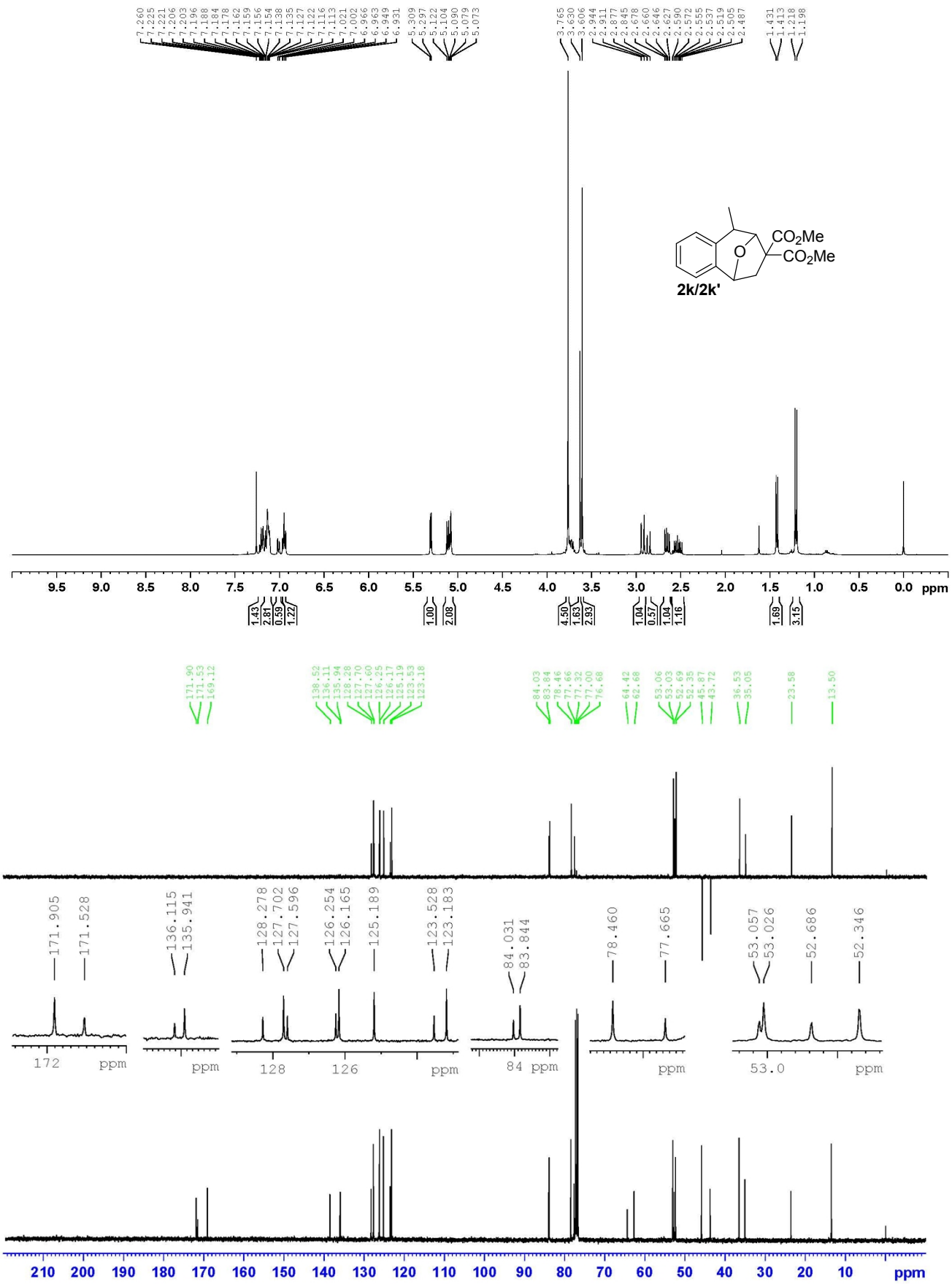
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **2i**



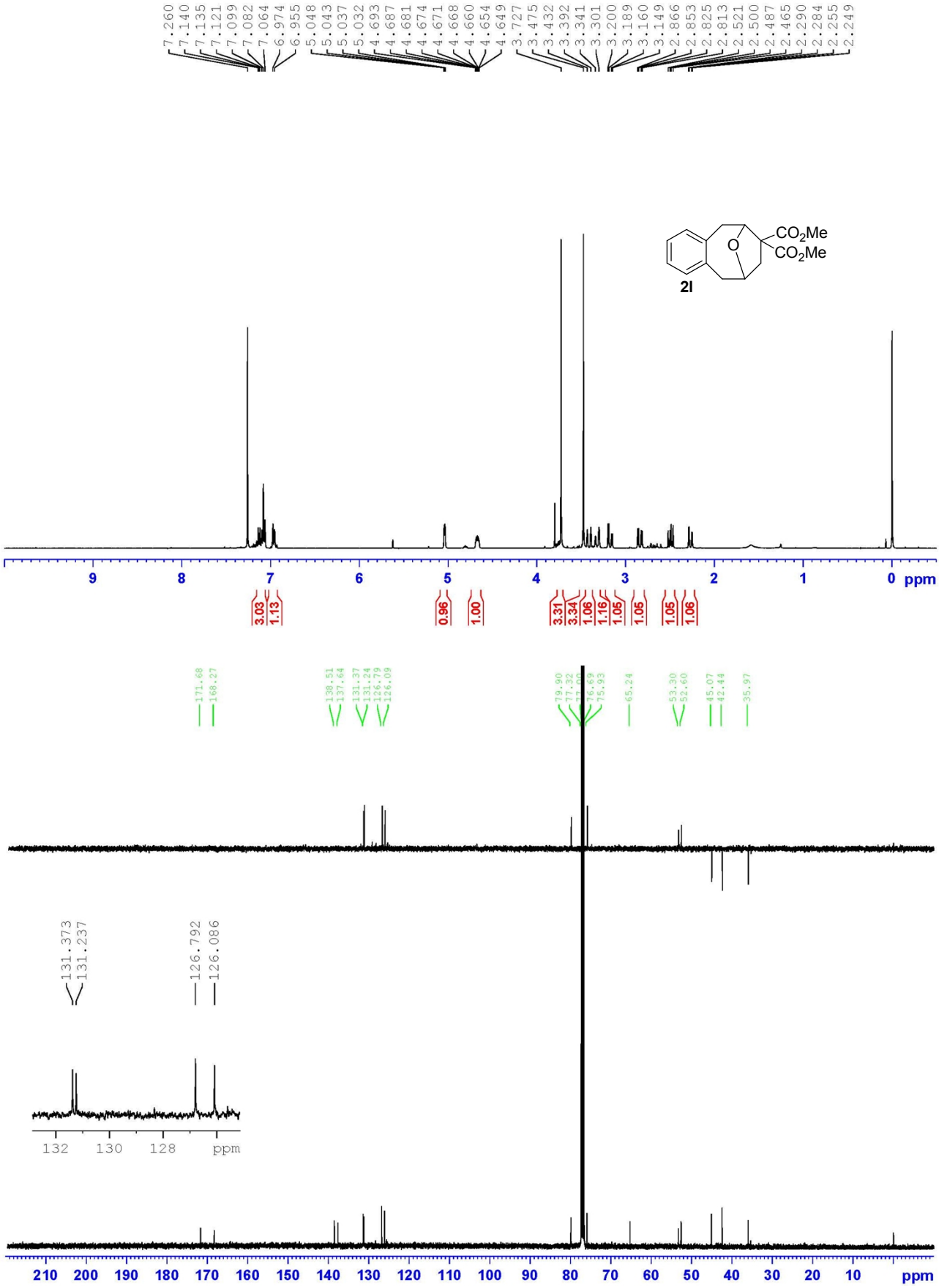
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **2j**



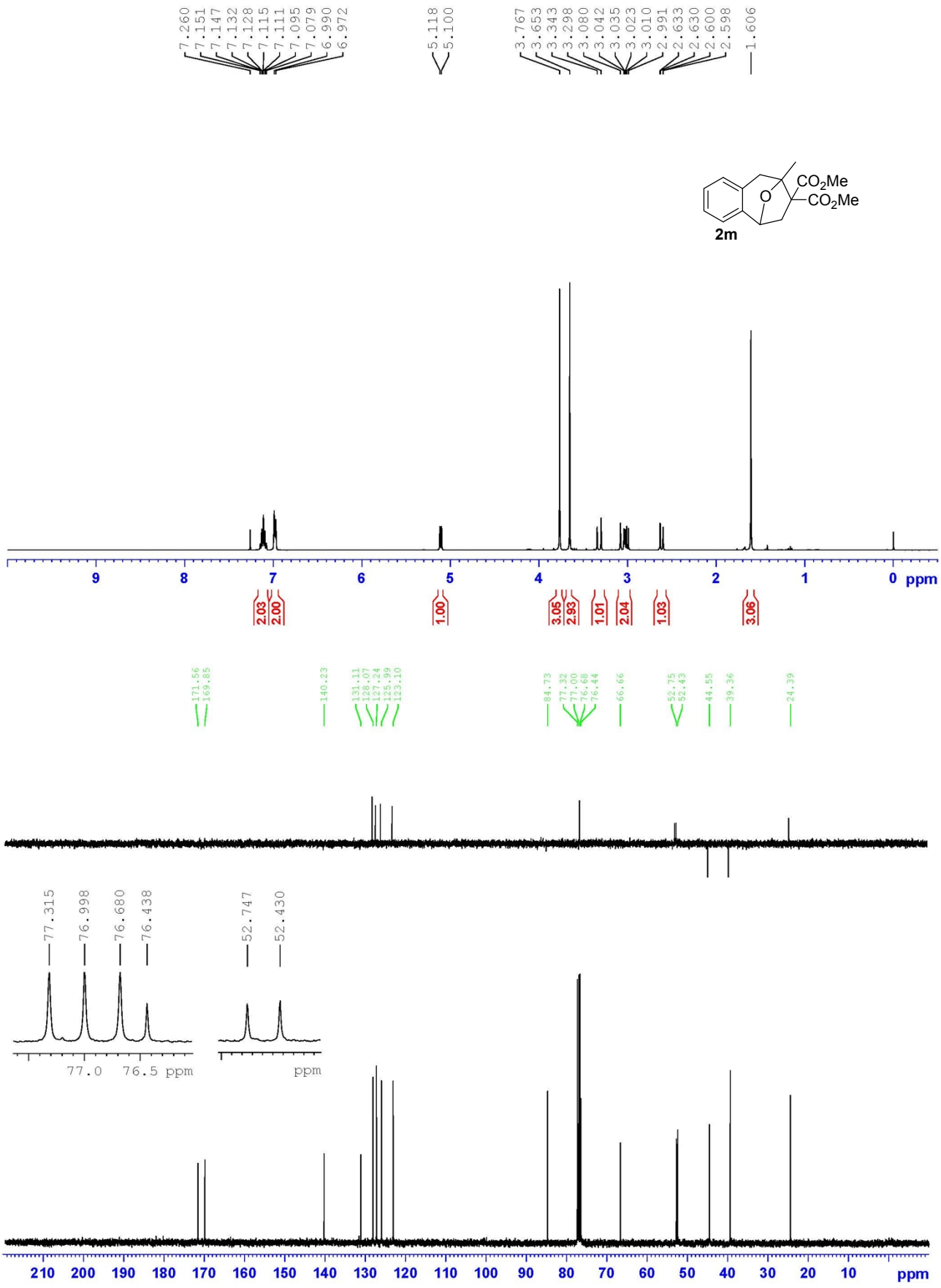
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **2k**/**2k'**



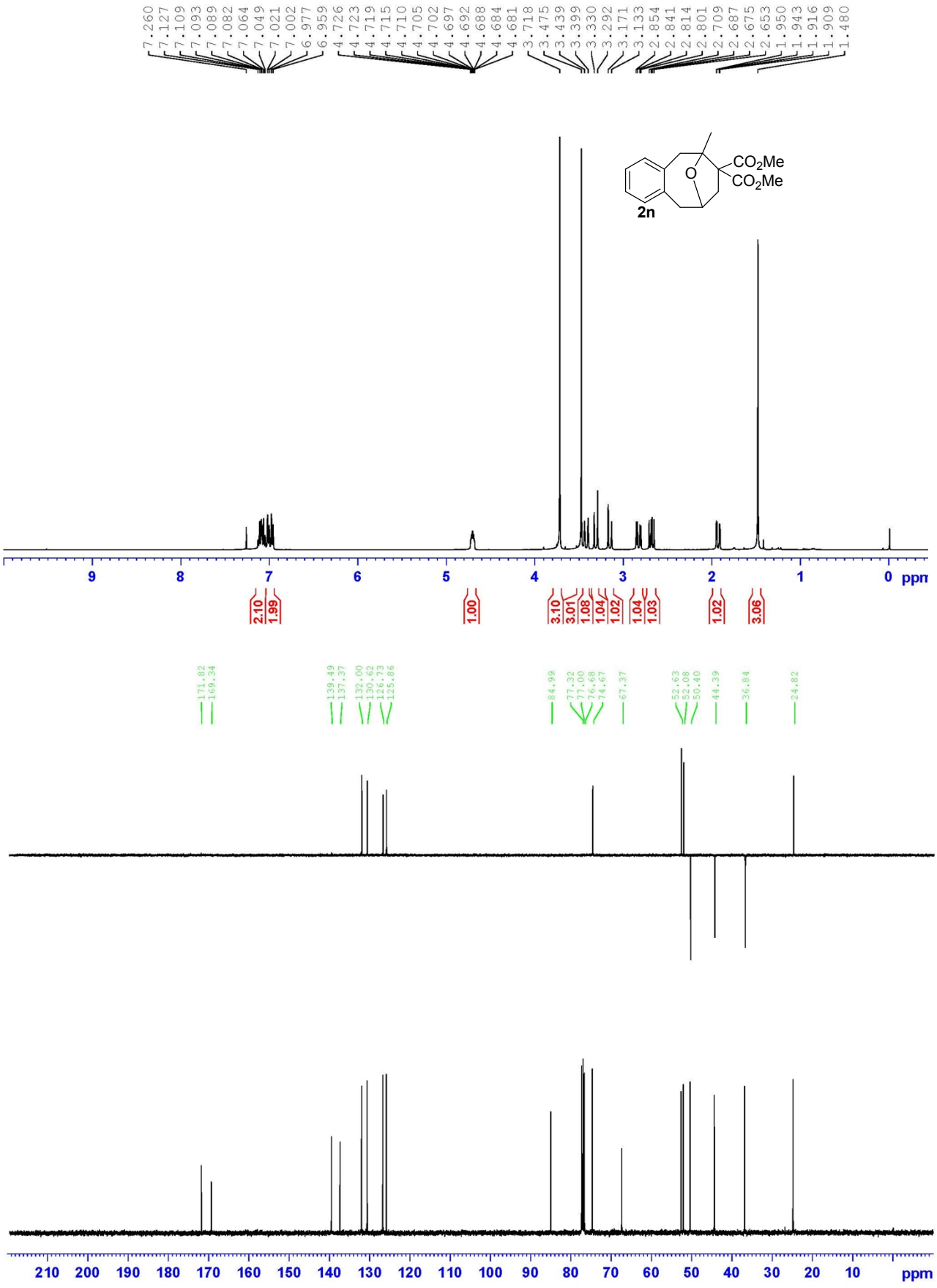
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **2l**



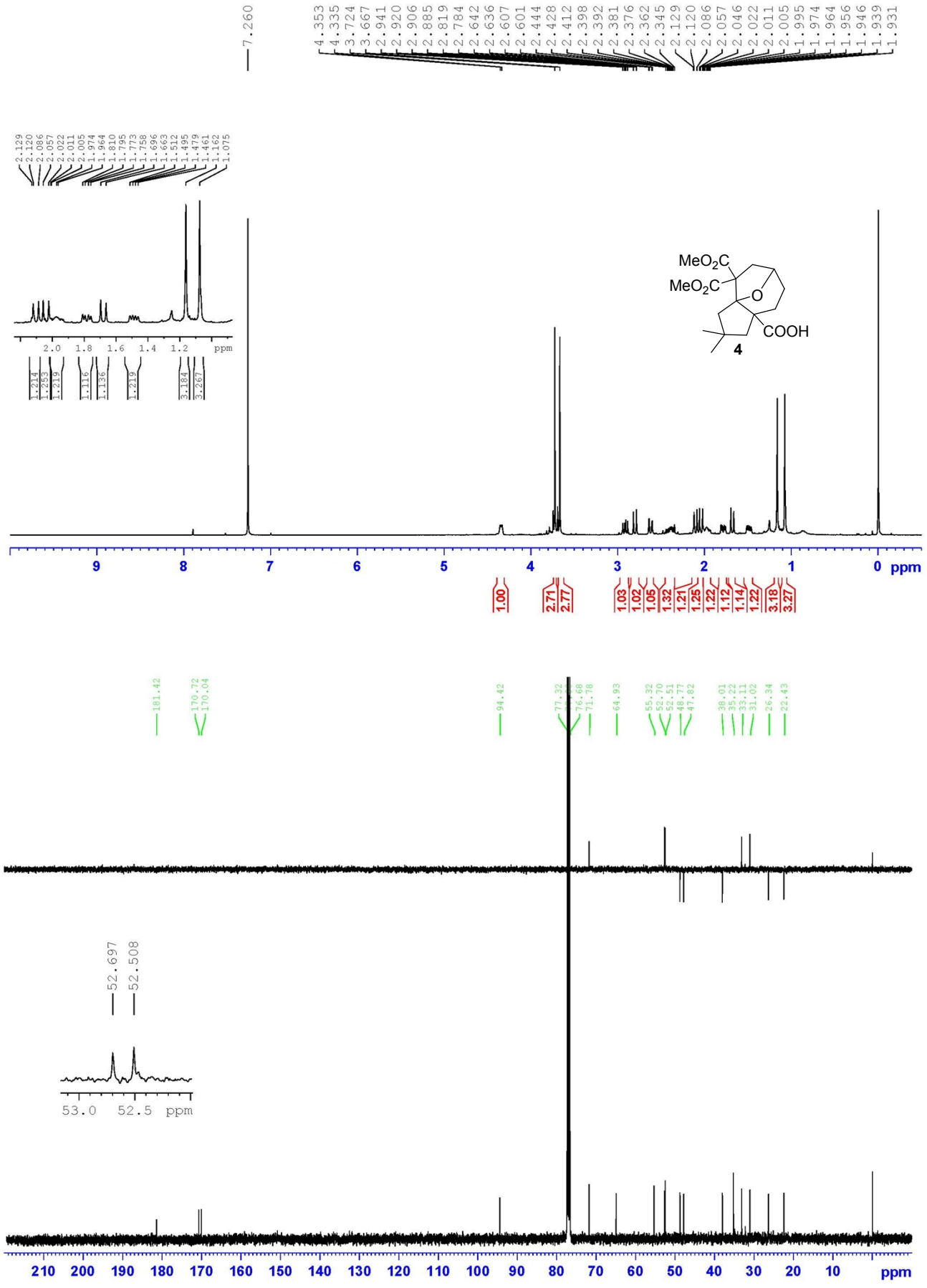
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **2m**



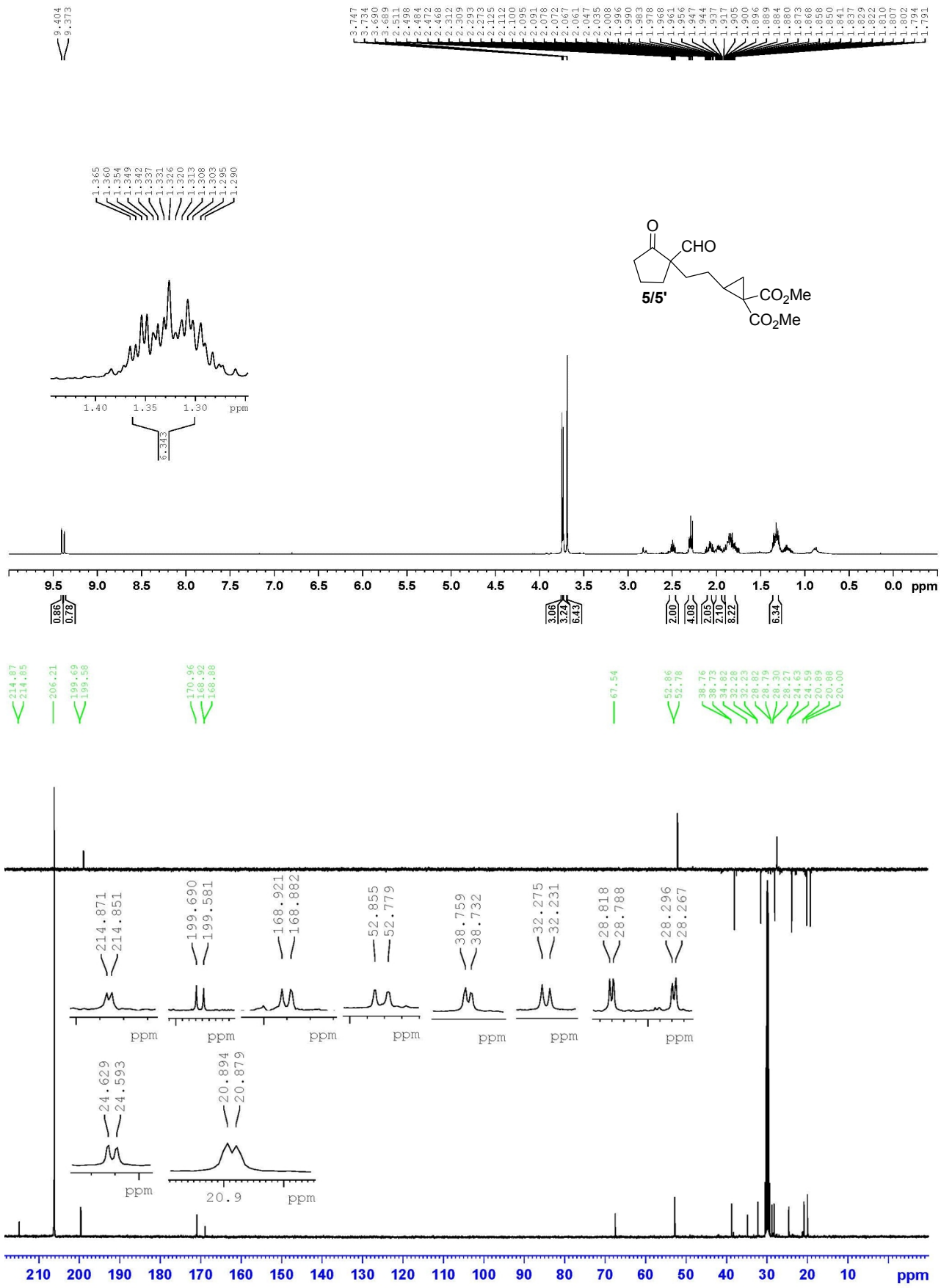
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **2n**



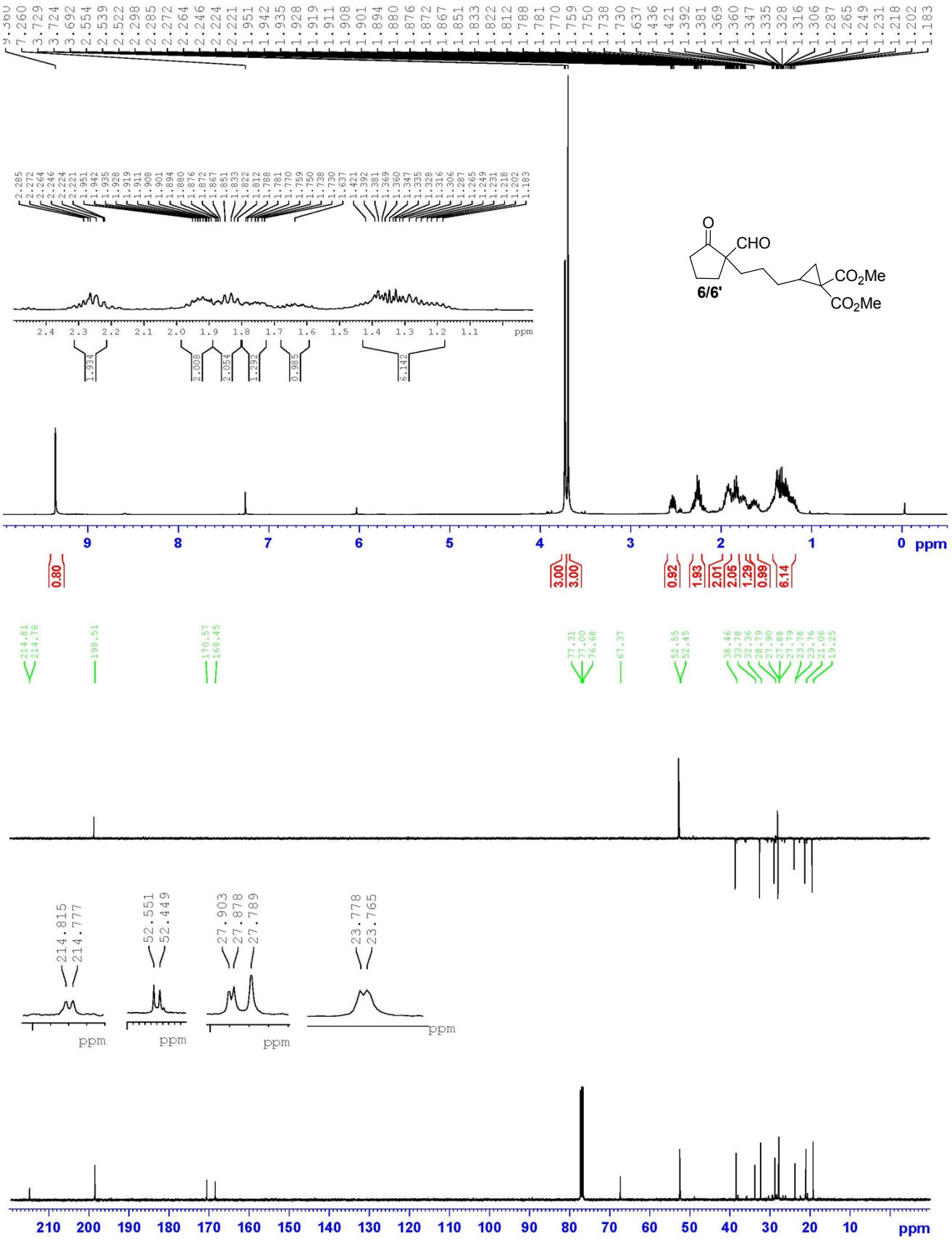
$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **4**



$^{1}$H NMR (acetone-$d_6$, 400 MHz), $^{13}$C NMR (acetone-$d_6$, 100 MHz) and DEPT 135 of **5**/**5'**



$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **6**/**6'**



$^{1}$H NMR ($CDCl_3$, 400 MHz), $^{13}$C NMR ($CDCl_3$, 100 MHz) and DEPT 135 of **7**