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Supplementary Information

Mechanistic insights into the malonoyl peroxide *syn*-dihydroxylation of alkenes

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Safety Warning!

Peroxides are particularly dangerous. These procedures should be carried out by knowledgeable laboratory workers. DSC data for cyclopropyl malonoyl peroxide **1** is given in Tomkinson *et al.*, *J. Am. Chem. Soc.*, **2010**, *132*, 14409 (page S89, Supporting Information) and shows an onset temperature of 114.5 °C.

General Techniques

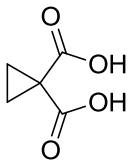
Commercially available solvents and reagents were used without further purification or drying and all reactions performed under an air atmosphere unless otherwise stated. Flash chromatography was carried out using Merck Kieselgel 60 H silica or Matrex silica 60. Analytical thin layer chromatography was carried out using aluminium-backed plates coated with Merck Kieselgel 60 GF254 that were visualised under UV light (at 254 nm). Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III 400 MHz, Bruker Avance DRX 500 MHz or Bruker Avance II 600 MHz spectrometer. NMR spectra were recorded in $CDCl_3$ at 25 °C unless stated otherwise and were reported in δ-units (ppm) relative to residual solvent peaks ($CHCl_3$, δ = 7.26 for protons and δ = 77.16 for carbon atoms; DMSO-d_6, δ = 2.50 for protons and δ = 39.52 for carbon atoms); *J* values were recorded in Hz and multiplicities were expressed by the usual conventions. ^{13}C NMR (DEPTQ-135) spectra show quaternary carbons. Low-resolution mass spectra (MS) were determined using an Agilent 6130 single quadrupole with an APCI/electrospray dual source or ThermoQuest Finnigan LCQ DUO electrospray. ESI refers to electrospray ionization, CI refers to chemical ionization (ammonia), EI refers to electron ionization, APCI refers to atmospheric pressure chemical ionisation, NSI refers to nanospray ionisation and ASAP refers to atmospheric solids analysis probe. High-resolution mass spectra were obtained courtesy of the EPSRC Mass Spectrometry Service at University of Wales, Swansea, U.K. using the ionization methods specified. *In vacuo* refers to evaporation at reduced pressure using a rotary evaporator and diaphragm pump, followed by the removal of trace volatiles using a vacuum (oil) pump. Melting points were determined using a Stuart SMP11 and are uncorrected. Infrared spectra were determined on neat samples using a Shimadzu IRAffinity-1 equipped with an ATR (Attenuated Total Reflectance) accessory, and were reported in cm^{-1}. GC–MS was performed using an Agilent 7890A GC system, equipped with a 30 m DB5MS column connected to a 5975C inert XL CI MSD with Triple-Axis Detector. Single-crystal diffraction data were measured on Oxford Diffraction Xcalibur E and Gemini S instruments. The structures were refined to convergence on F^2 and against all independent reflections by full-matrix least-squares, using the SHELXL-97 program.[1] Selected parameters are given on pages S119–S122 and full details are given in the deposited cif files. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Experimental Procedures and Analytical Data

General Procedure (A) for Dicarboxylic Acid Synthesis[2]

Benzyltriethyl ammonium chloride (0.10 mol, 1 equiv) was added to a stirring solution of 50% (by w.t.) aqueous NaOH (200 mL). Diethyl malonate (0.10 mol, 1 equiv) and dibromoalkane (0.15 mol, 1.5 equiv) were pre-mixed and added to the reaction vessel in one portion. The resulting heterogeneous mixture was stirred vigorously with an overhead mechanical stirrer at room temperature for *n* hours. The reaction was diluted with water (100 mL) and washed with diethyl ether (2 × 100 mL) to remove unreacted starting material. The aqueous phase was acidified to pH 1 with concentrated HCl before being extracted with ethyl acetate (3 × 50 mL), washed with brine (1 × 50 mL), dried over $MgSO_4$ and concentrated to dryness by rotary evaporation to afford the target 1,1-dicarboxylic acids. No further purification was necessary.

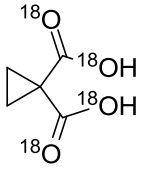
Cyclopropane-1,1-dicarboxylic acid[3] 5



Reaction of diethyl malonate (15.2 mL, 0.10 mol) and 1,2-dibromoethane (12.9 mL, 0.15 mol) in a rapidly stirring mixture of 50% aq. NaOH (200 mL) and benzyltriethyl ammonium chloride (22.8 g, 0.10 mol) according to General Procedure **A** for 4 h at 25 ºC gave the title compound **5** as a colourless solid (6.7 g, 53.2 mmol, 53%).

Colourless solid; m.p. 128–130 °C; IR (neat)/cm^{-1}: 2849, 1713, 1166; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.31 (s, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.0, 27.3, 16.5; LRMS (ESI) *m/z* 112.0 $[M - H_2O]^+$; HRMS (EI) calculated for $C_5H_6O_4$ $[M]^+$ 130.0266, found 130.0268.

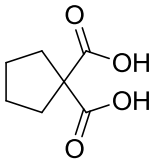
^{18}O-Enriched cyclopropane-1,1-dicarboxylic acid 27



Cyclopropane-1,1-dicarboxylic acid **5** (289 mg, 2.24 mmol, 1.0 equiv) and $^{18}OH_2$ (97% ^{18}O incorporation, 1.00 mL, 56 mmol, 25.0 equiv) were stirred in a sealed sample vial for 15 days at 25 ºC. The solution was transferred to a 5 mL round bottom flask and the water removed by rotary evaporation. The compound was dissolved in fresh $^{18}OH_2$ (97% ^{18}O incorporation, 1.00 mL, 56 mmol, 25.0 equiv) and stirred for a further 15 days at 25 ºC, following levels of ^{18}O incorporation by electrospray ionisation mass spectrometry. Removal of solvent by rotary evaporation gave the ^{18}O-enriched title compound as a colourless solid (292 mg).

Colourless solid; See analytical data for cyclopropane-1,1-dicarboxylic acid **5**. LRMS (ESI) *m/z* 136.9 and 134.9 $[M - H]^-$.

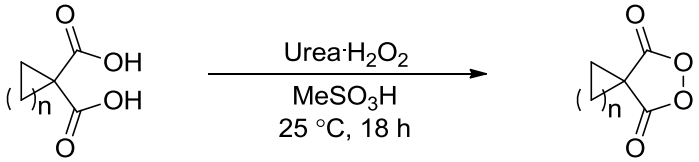
Cyclopentane-1,1-dicarboxylic acid[3] S-63



Reaction of diethyl malonate (10.0 mL, 66.0 mmol) and 1,4-dibromobutane (11.8 mL, 99.0 mmol) in a rapidly stirring mixture of 50% aq. NaOH (130 mL) and benzyltriethyl ammonium chloride (15.1 g, 66.0 mol) according to General Procedure **A** for 5 h at 25 ºC gave the title compound **S-63** as a colourless solid (8.1 g, 51.1 mmol, 77%).

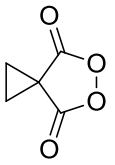
Colourless solid; m.p. 165 °C; IR (neat)/cm^{-1}: 2968, 2878, 1689, 1269, 1190; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.03–2.00 (m, 4H), 1.58–1.54 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.0, 60.0, 34.1, 25.2; LRMS (CI) *m/z* 176.3 $[M + NH_4]^+$; HRMS (ES) calculated for $C_7H_{14}O_4N$ $[M + NH_4]^+$ 176.0917, found 176.0917.

General Procedure B for Peroxide Synthesis



Cycloalkane-1,1-dicarboxylic acid (23.1 mmol, 1 equiv) was stirred in methanesulfonic acid (25 mL) for 10 minutes before addition of urea hydrogen peroxide (6.50 g, 69.2 mmol, 3 equiv) portionwise over 5 minutes. After stirring for 18 hours at 25 °C the contents of the reaction flask were poured into a mixture of ice (50 g) and ethyl acetate (25 mL). The phases were separated and the aqueous phase extracted using ethyl acetate (3 × 30 mL). The combined organic phases were washed with sodium hydrogen carbonate (3 × 20 mL) followed by brine (30 mL). Drying over $MgSO_4$, filtration and removal of solvent by rotary evaporation (caution!) afforded the corresponding malonoyl peroxide as colourless crystals (75–82%) with no need for purification.

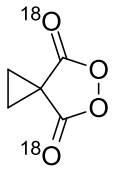
Cyclopropyl malonoyl peroxide[3] 1



Reaction of cyclopropane-1,1-dicarboxylic acid **5** (3.00 g, 23.1 mmol) and urea hydrogen peroxide (6.50 g, 69.2 mmol) in methanesulfonic acid (25 mL) according to General Procedure **B** for 18 h at 25 ºC gave the title compound **1** as a colourless solid (2.43 g, 19.0 mmol, 82%).

Colourless solid; m.p. 70–72 °C; IR (neat)/cm^{-1}: 3021, 1828, 1796, 1087; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.10 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 23.8, 19.9. Unable to obtain low or high resolution mass spectrometry data for malonoyl peroxides using in-house or Swansea National Mass Spectrometry Service.

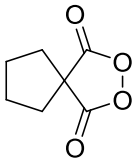
^{18}O-Enriched cyclopropyl malonoyl peroxide 28



Reaction of ^{18}O-enriched cyclopropane-1,1-dicarboxylic acid **27** (279 mg, 2.02 mmol, 1 equiv) and urea hydrogen peroxide (570 mg, 6.07 mmol, 3 equiv) in methanesulfonic acid (2 mL) according to General Procedure **B** for 18 h at 25 ºC gave the title compound **28** as a colourless solid (204 mg, 1.55 mmol, 77%).

See analytical data for cyclopropyl malonoyl peroxide **1**. Unable to obtain low or high resolution mass spectrometry data for malonoyl peroxides using in-house or Swansea National Mass Spectrometry Service.

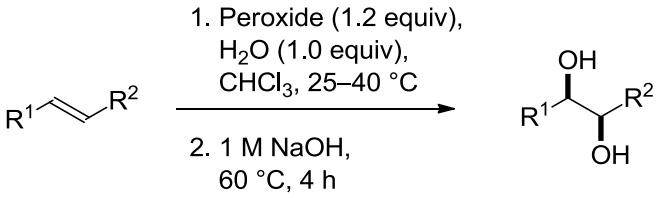
Cyclopentyl malonoyl peroxide[3] 62



Reaction of cyclopentane-1,1-dicarboxylic acid **S-63** (3.65 g, 23.1 mmol) and urea hydrogen peroxide (6.50 g, 69.2 mmol) in methanesulfonic acid (25 mL) according to General Procedure **B** for 18 h at 25 ºC gave the title compound as a colourless solid (2.88 g, 18.5 mmol, 80%).

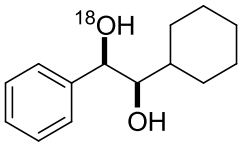
Colourless solid; m.p. 41 °C; IR (neat)/cm^{-1}: 2973, 1797, 1712, 1265; ^{1}H NMR (400 MHz, $CDCl_3$) 2.27–2.23 (m, 4H), 2.01–1.98 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) 175.8, 46.9, 37.7, 26.8. Unable to obtain low or high resolution mass spectrometry data for malonoyl peroxides using in-house or Swansea National Mass Spectrometry Service.

General Procedure C for Alkene Dihydroxylation



Alkene (1.20 mmol, 1 equiv) was added in one portion to a solution of malonoyl peroxide (1.44 mmol, 1.2 equiv), H_2O (22 μL, 1.20 mmol, 1 equiv) and chloroform (2 mL) and stirred at either 25 or 40 °C. On consumption of alkene (TLC analysis – 100% petroleum ether) the reaction mixture was evaporated to dryness *in vacuo* and 1M NaOH (10 mL) was added. The reaction mixture was stirred at 60 °C for 4 h and allowed to cool to room temperature before the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine (1 × 10 mL), dried ($MgSO_4$) and the solvent removed by rotary evaporation to afford the target diol. Diacid **5** was recovered by acidifying the aqueous phase to pH 1 by dropwise addition of concentrated HCl with stirring at 0–5 °C. Extraction with ethyl acetate (3 × 20 mL), washing with brine (1 × 10 mL) and drying over $MgSO_4$ then removal of solvent by rotary evaporation afforded the diacid as a colourless solid (80–90%).

***rel*-(1*R*,2*R*)-^{18}O-Labelled-*rel*-(1*R*,2*R*)-1-cyclohexyl-2-phenylethane-1,2-diol 30**

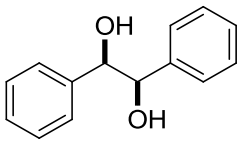


Reaction of (*E*)-(2-cyclohexylvinyl)benzene **29** (58 mg, 0.31 mmol, 1 equiv), H_2O (6 µL, 0.31 mmol, 1 equiv) and ^{18}O-labelled cyclopropyl malonoyl peroxide **1** (49 mg, 3.71 mmol) in $CHCl_3$ (1 mL) according to General Procedure **C** for 24 h at 40 ºC (crude diol 25:1 *syn*:*anti*) and purification by silica gel flash chromatography (1:2 diethyl ether:petroleum ether) gave the title compound as a colourless solid (62 mg, 0.28 mmol, 90%).

Colourless solid; m.p. 83–84 °C; IR (neat)/cm^{-1}: 3271, 3030, 2920, 2853, 1450, 1162; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.17 (m, 5H), 4.62 (d, *J* = 5.7 Hz, 1H), 3.39 (app t, *J* = 5.7 Hz, 1H), 2.18 (bs, 2H), 1.77–1.52 (m, 5H), 1.25–1.04 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 128.7, 128.0, 126.7, 80.2, 74.5, 39.4, 30.3, 27.5, 26.5, 26.4, 26.2; LRMS (EI) *m/z* 222.2 $[M]^+$; HRMS (EI) calculated for $C_{14}H_{20}{}^{16}O^{18}O$ $[M]^+$ 222.1506, found 222.1516.

(Non ^{18}O-labelled: LRMS (EI) *m/z* 220.2 $[M]^+$)

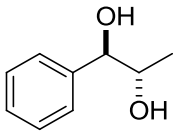
***rel*-(1*R*,2*R*)-1,2-Bisphenylethane-1,2-diol[3] 42**



Reaction of (*E*)-stilbene **13** (3.00 g, 16.7 mmol), H_2O (300 µL, 16.7 mmol, 1 equiv) and cyclopropyl malonoyl peroxide **1** (2.56 g, 20.0 mmol, 1.2 equiv) in $CHCl_3$ (25 mL) according to General Procedure **C** for 24 h at 40 ºC (crude diol 33:1 *syn*:*anti*) and purification by silica gel flash chromatography (1:4 diethyl ether:petroleum ether) gave the title compound as a colourless solid (3.07 g, 14.4 mmol, 86%).

Colourless solid; m.p. 104–105 °C; IR (neat)/cm^{-1}: 3389, 3060, 2922, 2852, 1068; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.23 (m, 6H), 7.14–7.11 (m, 4H), 4.70 (s, 2H), 2.89 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 128.3, 128.1, 127.1, 79.3; LRMS (APCI) *m/z* 196.1 $[M - H_2O]^+$; HRMS (CI) calculated for $C_{14}H_{14}O_2Na$ $[M + Na]^+$ 237.0886, found 237.0887.

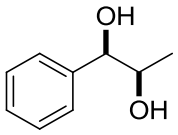
***rel*-(1*R*,2*S*)-1-Phenylpropane-1,2-diol[4] 51**



Reaction of *trans*-β-methylstyrene **46** (155 µL, 1.20 mmol, 1 equiv), H_2O (22 µL, 1.20 mmol, 1 equiv) and cyclopropyl malonoyl peroxide **1** (184 mg, 1.44 mmol, 1.2 equiv) in $CHCl_3$ (2 mL) according to General Procedure **C** for 24 h at 40 ºC (crude diol 16:1 *syn*:*anti*) and purification by silica gel flash chromatography (1:2 diethyl ether:petroleum ether) gave the title compound as a colourless solid (168 mg, 1.10 mmol, 92%).

Colourless solid; m.p. 87 °C; IR (neat)/cm^{-1}: 3408, 3242, 3067, 3040, 2968, 2927, 2891, 1034, 1018; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.28 (m, 5H), 4.66 (dd, *J* = 3.6, 3.6 Hz, 1H), 4.03–3.96 (m, 1H), 2.65 (d, *J* = 3.6 Hz, 1H), 2.11 (d, *J* = 4.6 Hz, 1H), 1.07 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 128.5, 127.9, 126.8, 77.6, 71.4, 17.4; LRMS (ESI) *m/z* 135.1 $[M - OH]^+$; HRMS (ESI) calculated for $C_9H_{11}O$ $[M - OH]^+$ 135.0804, found 135.0800.

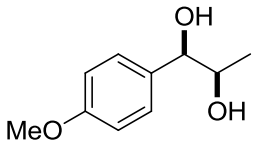
***rel*-(1*R*,2*R*)-1-Phenylpropane-1,2-diol[3] 52**



Reaction of *trans*-β-methylstyrene **44** (155 µL, 1.20 mmol, 1 equiv), H_2O (22 µL, 1.20 mmol, 1 equiv) and cyclopropyl malonoyl peroxide **1** (184 mg, 1.44 mmol, 1.2 equiv) in $CHCl_3$ (2 mL) according to General Procedure **C** for 24 h at 40 ºC (crude diol 16:1 *syn*:*anti*) and purification by silica gel flash chromatography (1:2 diethyl ether:petroleum ether) gave the title compound as a colourless solid (168 mg, 1.10 mmol, 92%).

Colourless solid; m.p. 51–53 °C; IR (neat)/cm^{-1}: 3435, 1714, 1520, 1392, 1061, 1024; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.27 (m, 5H), 4.30 (dd, *J* = 7.5, 2.6 Hz, 1H), 3.82–3.80 (m, 1H), 3.48 (d, *J* = 2.6 Hz, 1H), 3.23 (d, *J* = 2.0 Hz, 1H), 1.00 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 128.6, 128.2, 127.0, 79.6, 72.3, 18.8; LRMS (ESI) *m/z* 134.1 $[M - H_2O]^+$; HRMS (ESI) calculated for $C_9H_{10}O$ $[M - H_2O]^+$ 134.0732, found 134.0730.

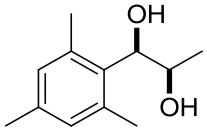
***rel*-(1*R*,2*R*)-1-(4-Methoxyphenyl)propane-1,2-diol[3] 54**



Reaction of *trans*-anethole (180 µL, 1.20 mmol, 1 equiv), H_2O (22 µL, 1.20 mmol, 1 equiv) and cyclopropyl malonoyl peroxide **1** (184 mg, 1.44 mmol, 1.2 equiv) in $CHCl_3$ (2 mL) according to General Procedure **C** for 2 h at 40 ºC (crude diol 5.5:1 *syn*:*anti*) and purification by silica gel flash chromatography (1:2 diethyl ether:petroleum ether) gave the title compound as a colourless solid (166 mg, 0.912 mmol, 76%).

Colourless solid; m.p. 64–65 °C; IR (neat)/cm^{-1}: 3390, 2979, 2901, 1485, 1397, 1065, 1048; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.27 (d, *J* = 7.5 Hz, 1H), 3.81–3.77 (m, 4H), 3.00 (bs, 1H), 2.90 (bs, 1H), 1.00 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 133.3, 128.2, 114.0, 79.2, 72.4, 55.4, 18.9; LRMS (EI) *m/z* 182.1 $[M]^+$; HRMS (EI) calculated for $C_{10}H_{14}O_3$ $[M]^+$ 182.0943, found 182.0940.

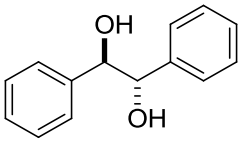
***rel*-(1*R*,2*R*)-1-Mesitylpropane-1,2-diol[3] 55**



Reaction of *E*-1-mesitylpropene (192 mg, 1.20 mmol, 1 equiv), H_2O (22 µL, 1.20 mmol, 1 equiv) and cyclopropyl malonoyl peroxide **1** (184 mg, 1.44 mmol, 1.2 equiv) in $CHCl_3$ (2 mL) according to General Procedure **C** for 24 h at 40 ºC (crude diol >50:1 *syn*:*anti*) and purification by silica gel flash chromatography (2:1 ethyl acetate:petroleum ether) gave the title compound as a colourless solid (217 mg, 1.12 mmol, 93%).

Colourless solid; m.p. 83–85 °C; IR (neat)/cm^{-1}: 3390, 2971, 2934, 1040, 1016; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.82 (s, 2H), 4.86 (d, *J* = 9.1 Hz, 1H), 4.35–4.26 (dq, *J* = 9.1 Hz, 6.4 Hz, 1H), 2.67 (bs, 2H), 2.41 (s, 6H), 2.25 (s, 3H), 1.01 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 137.3, 137.0, 133.4, 130.4, 76.5, 70.0, 21.3, 20.9, 18.8; LRMS (EI) *m/z* 194.1 $[M]^+$; HRMS (EI) calculated for $C_{12}H_{18}O_2$ $[M]^+$ 194.1307, found 194.1309.

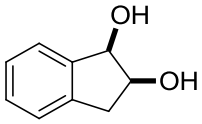
***rel*-(1*R*,2*S*)-1,2-Diphenylethane-1,2-diol[3] 56**



Reaction of (*Z*)-stilbene **13** (3.00 g, 16.7 mmol), H_2O (300 µL, 16.7 mmol, 1 equiv) and cyclopropyl malonoyl peroxide **1** (2.56 g, 20.0 mmol, 1.2 equiv) in $CHCl_3$ (25 mL) according to General Procedure **C** for 24 h at 40 ºC (crude diol 3:1 *syn*:*anti*) and purification by silica gel flash chromatography (1:4 diethyl ether:petroleum ether) gave the title compound as a colourless solid (3.07 g, 14.4 mmol, 86%).

Colourless solid; m.p. 133 °C; IR (neat)/cm^{-1}: 3320, 2943, 2861, 1054; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.24 (m, 10H), 4.82 (s, 2H), 2.25 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 128.4, 128.3, 127.2, 78.2; LRMS (ESI) *m/z* 196.1 $[M - H_2O]^+$; HRMS (ESI) calculated for $C_{14}H_{12}O$ $[M - H_2O]^+$ 196.0888, found 196.0886.

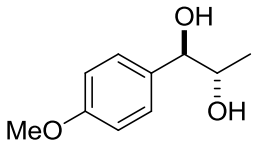
***rel*-(1*R*,2*S*)-2,3-Dihydro-1*H*-indene-1,2-diol[3] 57**



Reaction of indene (140 µL, 1.20 mmol, 1 equiv), H_2O (22 µL, 1.20 mmol, 1 equiv) and cyclopropyl malonoyl peroxide **1** (184 mg, 1.44 mmol, 1.2 equiv) in $CHCl_3$ (2 mL) according to General Procedure **C** for 24 h at 40 ºC (crude diol >50:1 *syn*:*anti*) and purification by silica gel flash chromatography (1:2 diethyl ether:petroleum ether) gave the title compound as a colourless solid 104 mg, 0.70 mmol, 58%).

Colourless solid; m.p. 88–90 °C; IR (neat)/cm^{-1}: 3395, 3058, 2924, 1060, 1041; ^{1}H NMR (400 MHz, $CDCl_3$) 7.44–7.42 (m, 1H), 7.30–7.23 (m, 3H), 5.00 (dd, *J* = 6.9, 5.2 Hz, 1H), 4.52–4.47 (m, 1H), 3.12 (dd, *J* = 16.3, 5.7 Hz, 1H), 2.95 (dd, *J* = 16.3, 3.5 Hz, 1H), 2.58 (d, *J* = 7.3 Hz, 1H), 2.49 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 142.1, 140.3, 128.8, 127.2, 125.4, 125.2, 76.0, 73.5, 38.5; LRMS (EI) *m/z* 150.1 $[M]^+$; HRMS (EI) calculated for $C_9H_{10}O_2$ $[M]^+$ 150.0681, found 150.0684.

***rel*-(1*R*,2*R*)-1-(4-Methoxyphenyl)propane-1,2-diol[5] S-66**



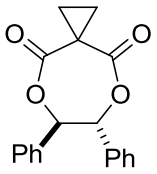
Reaction of *trans*-anethole (180 µL, 1.20 mmol, 1 equiv), H_2O (22 µL, 1.20 mmol, 1 equiv) and cyclopropyl malonoyl peroxide **1** (184 mg, 1.44 mmol, 1.2 equiv) in $CHCl_3$ (2 mL) according to General Procedure **C** for 2 h at 40 ºC (crude diol 5.5:1 *syn*:*anti*) and purification by silica gel flash chromatography (1:2 diethyl ether:petroleum ether) gave the title compound as a colourless solid (166 mg, 0.912 mmol, 76%).

Colourless solid; m.p. 92–93 °C; IR (neat)/cm^{-1}: 3393, 2976, 2920, 1480, 1391, 1056, 1042; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 4.60 (dd, *J* = 3.8, 3.8 Hz, 1H), , 4.02–3.95 (m, 1H), 3.81 (s, 3H), 2.30 (d, *J* = 3.3 Hz, 1H), 1.86 (d, *J* = 4.7 Hz, 1H), 1.10 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 132.5, 128.1, 114.0, 77.4, 71.4, 55.4, 17.7; LRMS (EI) *m/z* 182.1 $[M]^+$; HRMS (EI) calculated for $C_{10}H_{14}O_3$ $[M]^+$ 182.0943, found 182.0941.

Isolation of reaction intermediates 14, 15, 58, 59 and 61 in the dihydroxylation of stilbene.

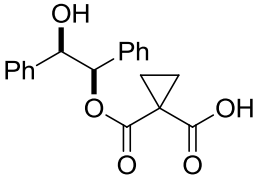
(*E*)-Stilbene **13** (3.00 g, 16.7 mmol), H_2O (300 µL, 16.7 mmol, 1 equiv) and cyclopropyl malonoyl peroxide **1** (2.56 g, 20.0 mmol, 1.2 equiv) were stirred in $CHCl_3$ (25 mL) according to General Procedure **C** for 24 h at 40 ºC but the hydrolysis step using 1M NaOH was not performed. Solvent was removed *in vacuo* and compounds **14, 15** and **61** were separated by silica gel flash chromatography using a solvent gradient; Diphenyl acetaldehyde **61** (1:4 diethyl ether:petroleum ether, R_f 0.48), *syn*-7-membered ring **14** (1:2 Et_2O:petroleum ether, R_f 0.40) and predominantly *syn*-hydroxyester **15** (1:1 diethyl ether:petroleum ether, R_f 0.12). Compounds **14** and **15** were then crystallised by vapour diffusion crystallisation (chloroform:petroleum ether b.p. 30–40 °C) to give colourless needles. The *anti*-7-membered ring **59** and *anti*-hydroxy ester **58** were isolated from an identical reaction using (*Z*)-stilbene. Silica gel column chromatography and two vapour diffusion recrystallisations (chloroform:petroleum ether b.p. 30–40 °C) were required to isolate **58** and **59** as single diastereomers.

***rel*-(6*R*,7*R*)-6,7-Diphenyl-5,8-dioxaspiro[2.6]nonane-4,9-dione 14**



Colourless solid; m.p. 122–124 °C; IR (neat)/cm^{-1}: 3067, 3030, 2920, 1722, 1707, 1339, 1190, 1066; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.19 (m, 6H), 7.07–7.04 (m, 4H), 5.82 (s, 2H), 2.08 (dd, *J* = 9.8, 3.7 Hz, 2H), 1.86 (dd, *J* = 9.8, 3.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 134.8, 129.2, 128.7, 127.4, 84.8, 29.1, 23.2; Unable to get LRMS or HRMS either in-house or from the National Mass Spectrometry Service, Swansea.

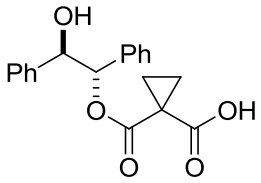
1-(((*rel*-1*R*,2*R*)-2-Hydroxy-1,2-diphenylethoxy)carbonyl)cyclopropanecarboxylic acid 15



Colourless solid; m.p. 117–119 °C; IR (neat)/cm^{-1}: 3377, 3059, 3034, 2913, 2851, 1740, 1686, 1192, 1130; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.23 (m, 6H), 7.13–7.05 (m, 4H), 5.91

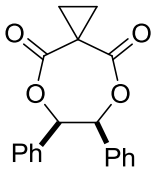
(d, *J* = 7.4 Hz, 1H), 4.92 (d, *J* = 7.4 Hz, 1H), 1.86–1.77 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 171.3, 138.7, 135.6, 128.9, 128.6, 128.5, 128.4, 127.2, 127.0, 82.0, 76.7, 25.7, 22.1, 21.7; HRMS (NSI) calculated for $C_{19}H_{17}O_5$ $[M + H]^+$ 327.1081, found 327.1087.

1-(((*rel*-1*S*,2*R*)-2-Hydroxy-1,2-diphenylethoxy)carbonyl)cyclopropanecarboxylic acid 58



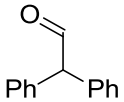
Colourless solid; m.p. 109–110 °C; IR (neat)/cm^{-1}: 3458, 3064, 3032, 2918, 1757, 1734, 1649, 1207, 1169; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.33 (m, 6H), 7.24–7.22 (m, 4H), 5.88 (d, *J* = 6.7 Hz, 1H), 4.91 (d, *J* = 6.7 Hz, 1H), 1.77–1.64 (m, 3H), 1.52–1.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 170.6, 139.2, 135.7, 129.2, 128.8, 128.7, 128.5, 127.5, 127.0, 80.9, 76.1, 25.3, 22.2, 21.9; HRMS (NSI) calculated for $C_{19}H_{19}O_5$ $[M + H]^+$ 327.1227, found 327.1231.

***rel*-(6*R*,7*S*)-6,7-Diphenyl-5,8-dioxaspiro[2.6]nonane-4,9-dione 59**



Colourless solid; m.p. 154–155 °C; IR (neat)/cm^{-1}: 3062, 3022, 2932, 1726, 1706, 1339, 1192, 1067; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.25 (m, 6H), 7.04–7.01 (m, 4H), 6.00 (s, 2H), 2.16 (app. t, *J* = 9.1 Hz, 2H), 1.83 (dd, *J* = 9.7, 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 132.9, 129.2, 128.4, 127.2, 82.8, 29.1, 25.5, 23.0; HRMS (NSI) calculated for $C_{19}H_{17}O_4$ $[M + H]^+$ 309.1121, found 309.1120.

2,2-Diphenylacetaldehyde[6] 61

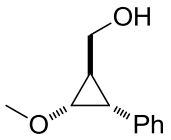


Colourless oil; IR (neat)/cm^{-1}: 3059, 3028, 1724; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (d, *J* = 2.4 Hz, 1H), 7.47–7.31 (m, 10H), 4.98 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 136.3, 129.2, 129.0, 127.6, 64.0; HRMS (CI) calculated for $C_{14}H_{16}NO$ $[M + NH_4]^+$ 214.1226, found 214.1224.

Synthesis of Alkenes

Synthesis of Radical Clock 23

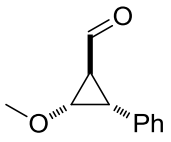
(*trans,trans*-2-Methoxy-3-phenylcyclopropyl)methanol[7]



cis-β-Methoxystyrene (3.4 mL, 25.6 mmol) was added to a suspension of anhydrous copper sulfate (420 mg, 2.6 mmol) in anhydrous benzene (10 mL). The mixture was heated to 75 °C. Whilst stirring rapidly a solution of ethyl diazoacetate (87%, 6.21 mL, 51.2 mmol) in anhydrous benzene (20 mL) was added drop wise over 3 h. Stirring was continued for 1 h at 75 °C before cooling to ambient temperature and stirring for a further 16 h. The contents of the reaction flask were poured onto water (50 mL) and the aqueous layer was extracted with diethyl ether (2 x 50 mL). The combined organics were washed with water (3 x 50 mL) and brine (2 x 50 mL) and then dried over magnesium sulfate. The solvent was removed under reduced pressure to give a brown oil. The oil was subjected to flash chromatography (10% ethyl acetate in petroleum ether) to yield a colourless oil (2.8 g, a mixture of ethyl *trans,trans*-2-methoxy-3-phenylcyclopropanecarboxylate and diethyl fumarate). The oil was dissolved in anhydrous diethyl ether (100 mL) and cooled to 0 °C. Lithium aluminium hydride (950 mg, 25.0 mmol) was added in portions and the mixture was heated under reflux for 18 h. The reaction was cooled to 0 °C and quenched with ice (2 g) and 0.5 M sodium hydroxide solution (8 mL). After stirring for 15 minutes the contents of the flask were filtered through celite. The filter and flask were washed with diethyl ether (60 mL) and the combined organics washed with water (50 mL) and brine (50 mL) and then dried over magnesium sulfate. The solvent was removed under reduced pressure to give the *title compound* as a colourless oil (1.71 g, 38%).

Colourless oil; υ_{max} (ATR)/cm^{-1} 3379, 3061, 3024, 2990, 2934, 2874, 2826; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.19 (5H, m), 3.75–3.60 (2H, m), 3.40 (1H, dd, *J* = 6.6, 3.2 Hz), 3.18 (3H, s), 1.99 (1H, app. t, *J* = 6.6 Hz), 1.84–1.77 (1H, m), 1.61 (1H, br. s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 128.1, 128.1, 125.9, 64.2, 64.0, 58.3, 28.8, 27.9; *m*/*z* (CI): 161.0 [M - H_2O + H]$^+$; HRMS (APCI) calculated for $C_{11}H_{13}O$ 161.0961 [M - H_2O + H]$^+$, found 161.0959.

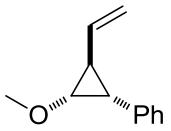
***trans,trans*-2-Methoxy-3-phenylcyclopropanecarbaldehyde[7]**



Oxalyl chloride (610 µL, 7.23 mmol) was added to anhydrous dichloromethane (20 mL). The mixture was cooled to -78 °C and dimethyl sulfoxide (1.10 mL, 15.8 mmol) was added drop wise. The mixture was stirred for 10 minutes and a solution of triethylamine (4.60 mL, 32.8 mmol) and (*trans,trans*-2-methoxy-3-phenylcyclopropyl)methanol (1.17 g, 6.57 mmol) in dichloromethane (15 mL) was added drop wise over 15 minutes. The reaction was monitored by TLC and upon complete consumption of starting alcohol (approx. 30 minutes) the reaction was allowed to warm to ambient temperature. Water (15 mL) and diethyl ether (20 mL) were added and the mixture was poured into a separatory funnel. The layers were separated and the aqueous layer was extracted with diethyl ether (2 x 20 mL). The combined organics were washed with water (20 mL) and brine (20 mL) and then dried over sodium sulfate. The solvent was removed under reduced pressure to give a brown oil (1.16 g, quant.).

Brown oil; υ_{max} (ATR)/cm^{-1} 3059, 3028, 2990, 2936, 2830, 1701; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (1H, d, *J* = 2.7 Hz), 7.37–7.25 (5H, m), 3.95 (1H, dd, *J* = 7.1, 2.6 Hz), 3.37 (3H, s), 2.99–2.94 (1H, m), 2.62–2.58 (1H, m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6, 134.5, 128.5, 128.4, 127.1, 68.5, 59.1, 38.0, 34.4; *m*/*z* (CI): 177.0 $[M + H]^+$; HRMS (APCI) calculated for $C_{11}H_{13}O_2$ 177.0910 $[M + H]^+$, found 177.0909.

(*trans,trans*-2-Methoxy-3-phenylcyclopropyl)ethylene 23[7]



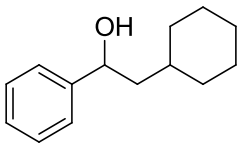
Methyltriphenylphosphonium bromide (3.93 g, 11.0 mmol) was added to anhydrous THF (26 mL). The suspension was cooled to 0 °C and 1.7 M *n*-butyllithium in hexane (4.40 mL) was added. The mixture was stirred for 15 minutes, over which time a pale yellow colour developed. A solution of *trans,trans*-2-methoxy-3-phenylcyclopropanecarbaldehyde (1.14 g, 6.48 mmol) in anhydrous THF (8 mL) was added drop wise and the mixture was stirred at ambient temperature. The reaction was monitored by TLC and upon complete consumption

of starting aldehyde (approximately 1 h) the reaction mixture was poured into a separatory funnel containing a mixture of ammonium chloride (20 mL) and diethyl ether (20 mL). The layers were separated and the aqueous layer was further extracted with diethyl ether (2 x 20 mL). The combined organics were washed with brine (30 mL) and dried over sodium sulfate. The solvent was removed under reduced pressure and the residue purified by flash chromatography (3% ethyl acetate in petroleum ether) to give the *title compound* as a colourless oil (835 mg, 73%).

Colourless oil; υ_{max} (ATR)/cm^{-1} 3084, 3061, 3026, 2982, 2934, 2826; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.15 (5H, m), 5.66 (1H, ddd, J = 17.2, 10.4, 7.7 Hz), 5.13–5.07 (1H, m), 5.00–4.96 (1H, m), 3.43 (1H, dd, *J* = 6.6, 3.3 Hz), 3.20 (3H, s), 2.10 (1H, app t, *J* = 6.6 Hz), 2.06–2.00 (1H, m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7, 137.1, 128.1, 128.1, 126.0, 113.8, 66.9, 58.4, 31.9, 30.4; *m/z* (CI): 175.0 $[M + H]^+$; HRMS (APCI) calculated for $C_{12}H_{15}O$ 175.1117 $[M + H]^+$, found 175.1116.

Synthesis of (*E*)-(2-Cyclohexylvinyl)benzene 29

2-Cyclohexyl-1-phenylethanol S-67

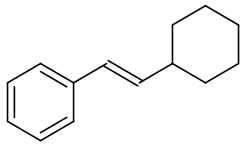


A dry 100 mL 3–necked flask equipped with a reflux condenser was flushed with nitrogen gas before being charged with magnesium turnings (0.79 g, 32.9 mmol) and dry tetrahydrofuran (15 mL). (Bromomethyl)cyclohexane (3.94 mL, 28.2 mmol) was added and the solution heated under reflux. After 30 min. the resulting solution was cooled to 0–5 °C using an ice bath before a solution of benzaldehyde (1.91 mL, 18.8 mmol) in dry tetrahydrofuran (20 mL) was added dropwise *via* syringe. The reaction was stirred at room temperature for 5 hours then cooled to 0–5 °C and carefully quenched by dropwise addition of water, before solvent was removed by rotary evaporation. H_2O (100 mL) and ethyl acetate (100 mL) were added followed by ethylenediaminetetraacetic acid (EDTA) (30 g), and the solution stirred for 1 hour until both phases were clear. The phases were separated and the aqueous phase extracted with ethyl acetate (3 × 30 mL) before the combined organic phases were washed with brine (1 × 50 mL), dried over $MgSO_4$ and solvent removed by rotary evaporation to give a yellow oil. Purification by silica flash column chromatography (1:8

ethyl acetate:petroleum ether) gave the title compound **S-67** as a colourless solid (2.09 g, 55%).

Colourless solid; m.p. 53–54 °C; IR (neat)/cm^{-1}: 3237, 2918, 2845, 1454, 1445; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.34 (m, 4H), 7.30–7.26 (m, 1H), 4.78 (dd, *J* = 8.7, 5.1 Hz, 1H), 1.90 (bs, 1H), 1.84–1.64 (m, 6H), 1.56–1.38 (m, 2H), 1.30–1.15 (m, 3H), 1.02–0.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 128.6, 127.6, 126.0, 72.2, 47.2, 34.3, 34.1, 33.0, 26.6, 26.4, 26.3; LRMS (EI) *m/z* 204.2 $[M]^+$; HRMS (ASAP) calculated for $C_{14}H_{24}NO$ $[M + NH_4]^+$ 222.1852, found 222.1852.

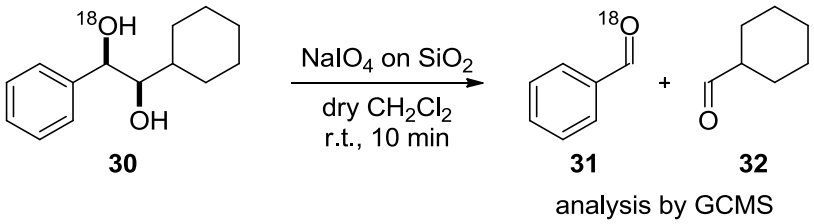
(*E*)-(2-Cyclohexylvinyl)benzene[8] 29



2-Cyclohexyl-1-phenylethanol **S-67** (1.75 g, 8.59 mmol), *p*-toluenesulfonic acid monohydrate (0.21 g, 1.12 mmol) and toluene (30 mL) were added to a 50 mL round bottom flask equipped with a Dean–Stark condenser. The reaction mixture was heated under reflux for 2.5 hours before 5 drops of triethylamine were added to quench the reaction. H_2O (30 mL) was added and the phases separated before the aqueous phase was extracted with diethyl ether (2 × 20 mL). The combined organic phases were washed with brine (1 × 30 mL), dried over $MgSO_4$ and solvent removed by rotary evaporation to give a pale yellow oil. Purification by silica flash column chromatography (petroleum ether) gave the title compound **29** as a colourless oil (1.46 g, 91%).

Colourless oil; IR (neat)/cm^{-1}: 3024, 2920, 2849, 1447; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.39 (m, 2H), 7.35–7.31 (m, 2H), 7.25–7.21 (m, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.23 (dd, *J* = 16.0, 6.9 Hz, 1H), 2.23–2.13 (m, 1H), 1.87–1.72 (m, 5H), 1.42–1.18 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 136.9, 128.6, 127.3, 126.8, 126.0, 41.3, 33.1, 26.3, 26.2; LRMS (EI) *m/z* 186.1 $[M]^+$; HRMS (ASAP) calculated for $C_{14}H_{19}$ $[M + H]^+$ 187.1481, found 187.1480.

Oxidative cleavage of diol[9]

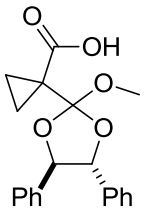


Preparation of $NaIO_4$ on silica: A mixture of sodium metaperiodate (0.514 g, 2.40 mmol) and water (1.00 mL) was stirred at 75 ºC until homogeneous. To the hot aqueous solution was added silica gel (2.00 g). The mixture was stirred and crushed manually at 75 ºC using a spatula until a free-flowing colourless powder formed. The resulting powder was dried (80 ºC at 0.1 Torr) for 4 hours before use.

Anhydrous sodium metaperiodate on silica (150 mg) and anhydrous dichloromethane (500 µL) were added to a small sample vial and stirred vigorously. A solution of diol **30** (10 mg, 0.046 mmol) in anhydrous dichloromethane (500 µL) was added to the reaction vessel in one portion. After 10 minutes, diol **30** had cleanly converted into the two aldehydes **31** and **32** by TLC analysis (1:5 ethyl acetate:petroleum ether). The characteristic almond-like smelling solution of the two aldehydes was filtered through a small sinter funnel and directly analysed by GCMS (see Supplementary Information pages S115–S117).

Synthesis of orthoester 41

1-((*rel*-4*R*,5*R*)-2-Methoxy-4,5-diphenyl-1,3-dioxolan-2-yl) cyclopropanecarboxylic acid 43

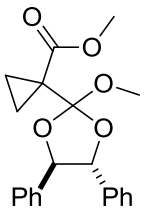


Cyclopropyl malonoyl peroxide **1** (166 mg, 1.30 mmol, 1 equiv) was dissolved in chloroform (2.6 mL) in a 5 mL round bottom flask and the solution dried over activated 3Å molecular sieves for 2 hours. Methanol (100 µL) was also dried over activated 3Å molecular sieves for 2 hours in a separate vessel. *Trans*-stilbene (234 mg, 1.30 mmol, 1 equiv) was weighed into a dry 10 mL round bottom flask followed by addition of the dry peroxide solution and dry methanol (53 µL, 1.30 mmol, 1 equiv) in quick succession. The flask was sealed under nitrogen and stirred for 20 hours at 40 °C. Solvent was removed by rotary evaporation to produce a colourless gum (440 mg). Attempts to purify the compound by silica gel chromatography or crystallisation proved unsuccessful. Due to the relatively clean conversion of the reaction, identification of most of the minor co-products within the reaction mixture and comparison with a similar orthoester in the literature,[10] we were able to assign both the ^{1}H and ^{13}C NMR spectra of the crude reaction mixture with reasonable confidence (see Supplementary Information pages S101–S102 for ^{1}H and ^{13}C DEPT-Q 135 spectra of the crude reaction mixture).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (bs, 1H), 7.37–7.34 (m, 5H), 7.31–7.29 (m, 2H), 7.24–7.21 (m, 3H), 5.13 (d, J = 9.0 Hz, 1H), 4.90 (d, J = 9.0 Hz, 1H), 3.63 (s, 3H), 1.51–1.42 (m, 3H), 1.35–1.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 135.8, 135.5, 128.90, 128.87, 128.8, 126.9, 126.7, 120.5, 87.3, 85.3, 50.8, 28.6, 14.3, 13.4.

Methylation of orthoester 43

Methyl 1-((*rel*-4*R*,5*R*)-2-methoxy-4,5-diphenyl-1,3-dioxolan-2-yl) cyclopropane carboxylate 44



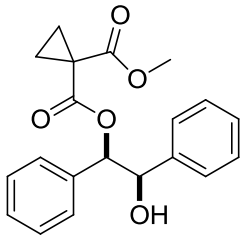
CAUTION! Generation of diazomethane is dangerous due to high risk of explosion. Standard safety protocols for generating diazomethane should be followed and the procedures only carried out by experienced synthetic chemists.

The crude reaction mixture containing orthoester **43** (440 mg) was dissolved in diethyl ether (10 mL). Diazomethane was generated by careful addition of *N*-nitroso-*N*-methylurea (excess, approximately 250 mg) to an unstirred biphasic solution of 40% by w.t. aqueous potassium hydroxide (3 mL) and diethyl ether (10 mL) at 0–5 °C in a clean, scratch-free, glass sample vial without a ground glass joint. Nitrogen was gently bubbled through the yellow diazomethane-diethyl ether solution and the outlet flow passed through the diethyl ether solution containing **43** using a plastic cannula. The reaction was deemed complete when the product flask held a slight yellow colour indicating excess diazomethane present. Both flasks were cooled to 0–5 °C and excess diazomethane quenched by drop wise addition of the minimum amount of acetic acid until no yellow colour remained. Diethyl ether and methyl acetate (formed during quenching of diazomethane with acetic acid) were removed by rotary evaporation and the resulting residue purified by silica gel column chromatography (1:3 diethyl ether: petroleum ether) to afford the title compound **44** as a colourless oil (189 mg, 0.53 mmol, 41%).

Colourless oil; IR (neat)/cm^{-1}: 3062, 3032, 2951, 2909, 2837, 1719, 1319, 1213, 1119, 1078, 1009; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.23 (m, 10H), 5.09 (d, *J* = 9.0 Hz, 1H), 4.89 (d, *J* = 9.0 Hz, 1H), 3.75 (s, 3H), 3.58 (s, 3H), 1.44–1.29 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 136.6, 136.3, 128.72, 128.68, 126.94, 126.87, 120.8, 87.1, 85.4, 52.4, 50.7, 29.0, 13.9, 13.0; LRMS (ESI) *m/z* 377.1 $[M + Na]^+$; HRMS (NSI) calculated for $C_{21}H_{22}O_5Na$ $[M + Na]^+$ 377.1359, found 377.1353.

Independent synthesis of methyl ester 45

1-(*rel*-(1*R*,2*R*)-2-Hydroxy-1,2-diphenylethyl) 1-methyl cyclopropane-1,1-dicarboxylate 45

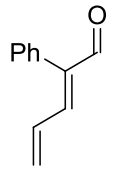


Syn-hydroxy ester **15** (30 mg, 0.092 mmol) was methylated using the diazomethane generation method described above for orthoester **44** (see Supplementary Information page S23); *N*-nitroso-*N*-methylurea (excess, approximately 40 mg), aqueous potassium hydroxide (40% by w.t., 0.5 mL) and diethyl ether (2 x 2 mL). Purification of the crude reaction mixture by silica gel column chromatography (1:1 diethyl ether:petroleum ether) afforded the title compound **45** as a colourless oil (23 mg, 0.068 mmol, 74%).

Colourless oil; IR (neat)/cm^{-1}: 3491, 3062, 3036, 2953, 1716, 1209, 1132, 907; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.21 (m, 6H), 7.13–7.07 (m, 4H), 5.80 (d, *J* = 8.4 Hz, 1H), 4.95 (dd, *J* = 8.4, 2.1 Hz, 1H), 3.99 (d, *J* = 2.1 Hz, 1H), 3.79 (s, 3H), 1.67–1.61 (m, 2H), 1.46–1.42 (m, 1H), 1.31–1.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 168.7, 138.4, 136.3, 128.4, 128.2, 128.1, 127.38, 127.35, 82.4, 77.4, 52.8, 28.2, 17.5, 17.0; HRMS (NSI) calculated for $C_{20}H_{21}O_5$ $[M + H]^+$ 341.1384, found 341.1385.

Reaction of peroxide 1 with radical clock alkene 23

2-Phenylpenta-2,4-dienal 25[11]



(*trans*,*trans*-2-Methoxy-3-phenylcyclopropyl)ethylene **23** (49 mg, 0.28 mmol) was dissolved in deuterated chloroform (0.5 mL). Deuterium oxide (5 µL, 0.28 mmol) was added followed by cyclopropyl malonyl peroxide **1** (36 mg, 0.28 mmol). The reaction mixture was heated to 40 °C for 96 h. 40 µL Of reaction mixture was added to 0.5 mL $CDCl_3$ and analysed by ^1H NMR spectroscopy. Complete consumption of starting materials was observed. To the NMR tube trifluoroacetic acid (40 µL, 0.52 mmol) was added. The tube was shaken and heated to 40 °C for 18 h over which time all of the intermediates cleanly converted to 2-phenylpenta-2,4-dienal, cyclopropane-1,1-dicarboxylic acid and methanol (Figure S2). The reaction intermediates also decompose on silica. A sample of 2-phenylpenta-2,4-dienal for analysis was isolated from the crude reaction mixture using preparative TLC (20% ethyl acetate in petroleum ether, R_f = 0.54).

Colourless oil; υ_{max} (ATR)/cm^{-1} 2957, 2924, 2853, 1686; ^1H NMR (400 MHz, $CDCl_3$) δ 9.69 (1H, s), 7.45–7.34 (3H, m), 7.24–7.20 (2H, m), 7.07 (1H, d, *J* = 11.2 Hz), 6.72 (1H, ddd, J = 16.9, 11.2, 10.0 Hz), 5.86–5.80 (1H, m), 5.63–5.59 (1H, m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 149.5, 142.2, 133.1, 132.4, 129.9, 128.4, 128.4, 128.0; *m*/*z* (CI): 158.9 $[M + H]^+$; HRMS (APCI) calculated for $C_{11}H_{11}O$ 159.0804 $[M + H]^+$, found 159.0801.

Reaction of **23** with the peroxide **1** under standard reaction conditions led to a complex reaction mixture. The ^{1}H NMR spectra for this reaction mixture prior to the addition of TFA is shown at the bottom of Figure S2 (p S27). This confirms the consumption of both **23** and **1**. It is possible that cyclopropane ring opening of the Newcomb clock could occur either before or after the addition of TFA. Potential intermediates for this reaction are collected in Figure S1. Each of these intermediates could converge onto the observed product **25**. Due to the complex nature of this reaction mixture we did not fully purify and characterise the intermediates and reacted them immediately with TFA.

It is important to note that along with dioxygenation products aliphatic alkenes have the potential to form allylic alcohol products (for examples see *J. Org. Chem*. 2012, **77**, 921). Whilst the cyclopropyl ring of the Newcomb clock **23** would disfavour allylic alcohol formation, as we have not characterised the intermediates within this transformation (as noted above) the uncertainty of results obtained with this mechanistic probe should be considered.

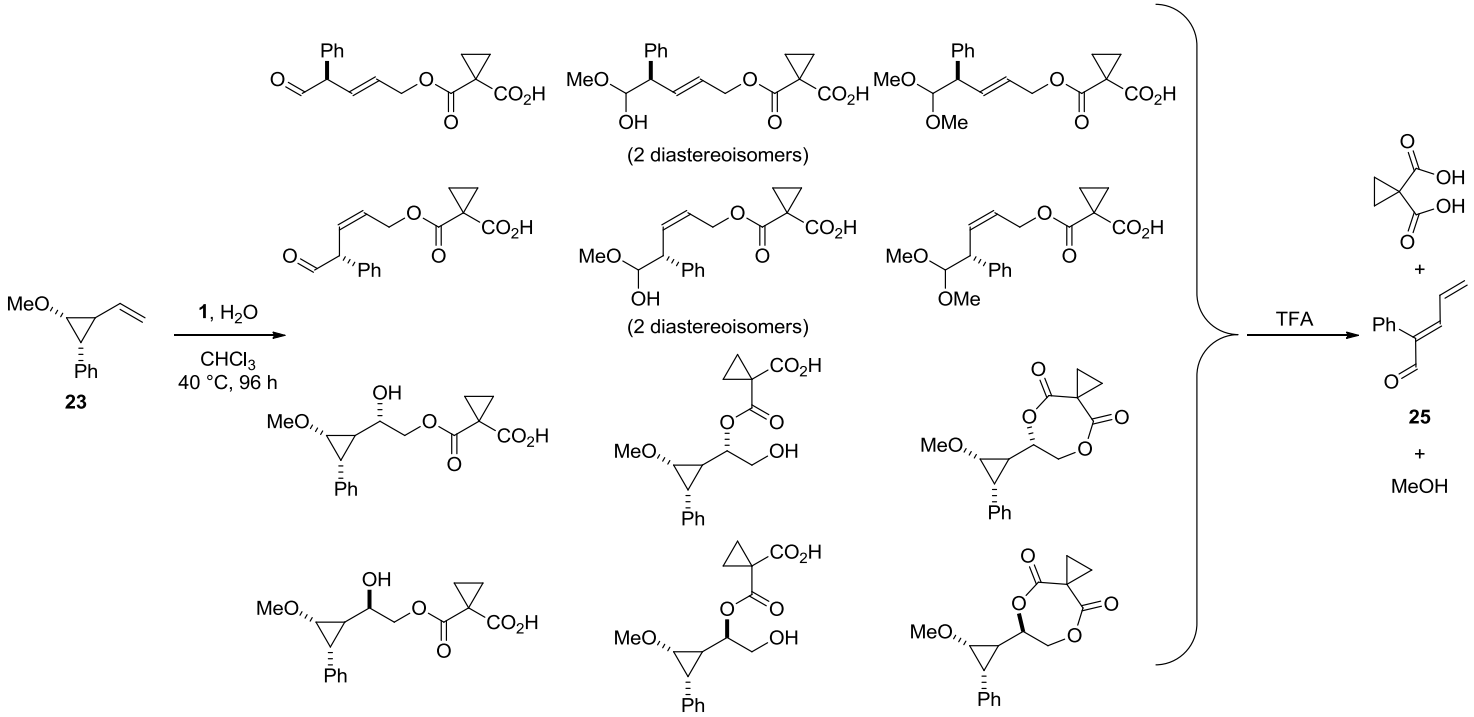


Figure S1. Potential intermediates in the reaction between **1** and **23**.

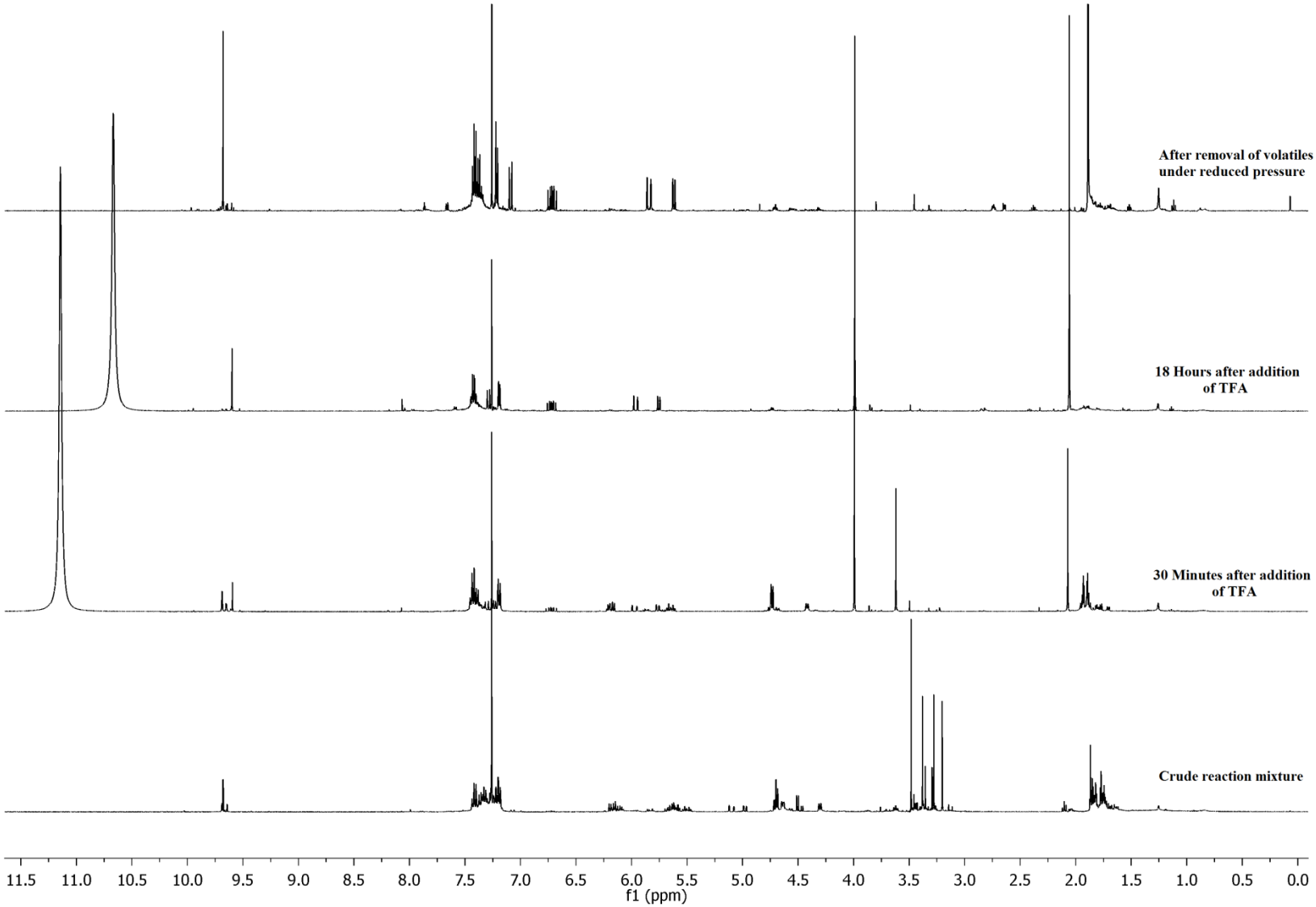
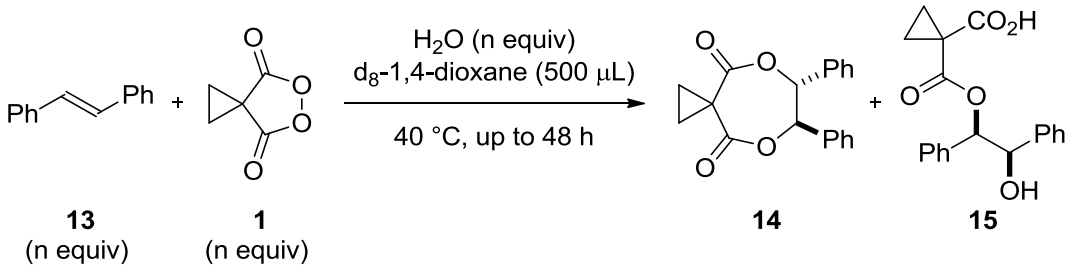


Figure S2. ^{1}H NMR spectra from reaction of alkene **23** with peroxide **1**.

Reaction Kinetics

Kinetic Order of Reaction: Kinetic data was obtained using homogeneous solutions of *trans*-stilbene **13** (n mmol), peroxide **1** (n mmol), and water (n mmol) in d_8-1,4-dioxane (500 µL) in an NMR tube (Scheme S1). Clean conversion of starting materials to dioxygenated products **14** and **15** (Figure S3) allowed integration of the ^{1}H NMR spectra to be used as a means of measuring accurate conversion, and therefore concentration of reagents and products, at known time intervals (Figure S4).



Scheme S1. Homogeneous reaction conditions used to obtain kinetic data.

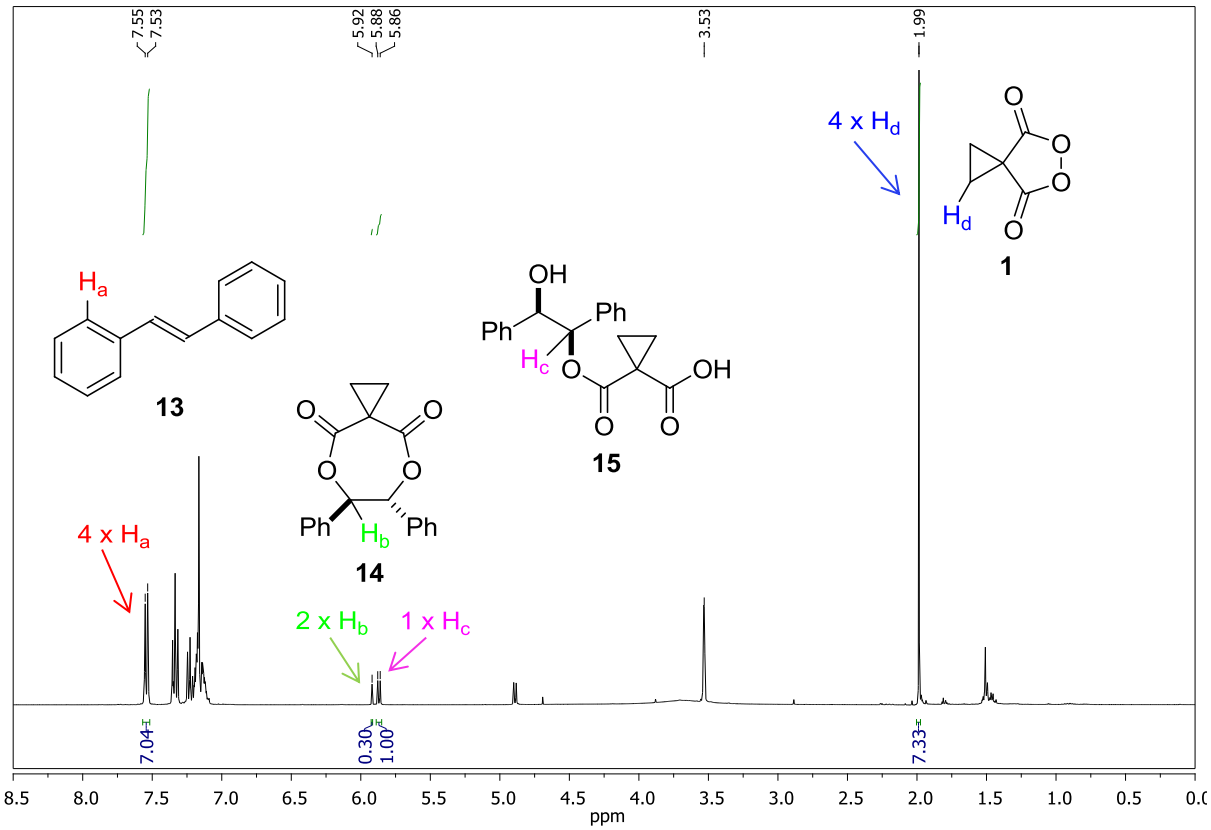


Figure S3. ^{1}H NMR spectrum of the dihydroxylation reaction at t = 4 hours showing the signals used to follow reaction conversion.

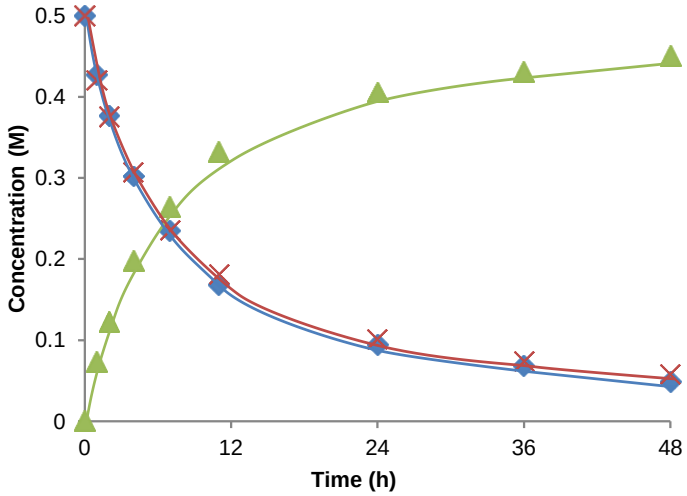


Figure S4. Reaction profile of the cyclopropyl malonoyl peroxide **1** (X, 0.5 M) mediated dihydroxylation of stilbene **13** (♦, 0.5 M) in the presence of one equivalent of water (0.5 M) leading to products **14** and **15** (▲).

The reaction order in stilbene **13** (0.25 M) was determined using an excess of peroxide **1** (0.5 M) and water (0.5 M) under the conditions shown in Scheme S1, and the concentration of stilbene **13** followed over time (24 hours, 93% conversion). A linear correlation was observed in the logarithmic plot of stilbene **13** concentration against time, showing a first-order dependence in stilbene **13** (Figure S5).

The reaction order in peroxide **1** (0.25 M) was determined in the same way using an excess of stilbene **13** (0.5 M) and water (0.5 M) and followed for 24 hours (94% conversion). A linear correlation was observed in the logarithmic plot of peroxide **1** concentration against time, showing a first-order dependence in peroxide **1** (Figure S6).

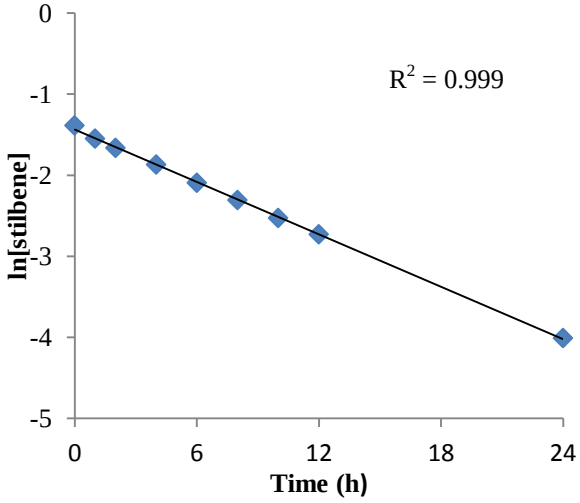


Figure S5. Logarithmic plot of stilbene **13** concentration against time.

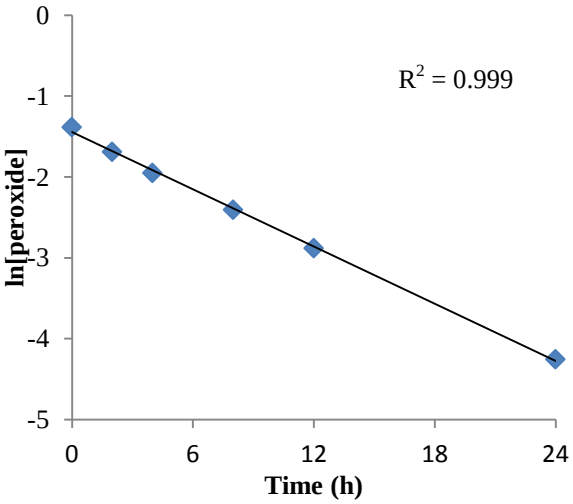


Figure S6. Logarithmic plot of peroxide **1** concentration against time.

Determining the kinetic order in water proved complex due to its dual role as a stoichiometric reagent and catalyst within the dihydroxylation reaction. It should be noted that reaction of alkenes with peroxide **1** proceeds in the absence of water to produce 7-membered 7-membered ring **14** and a complex mixture of unidentifiable co-products, presumably arising from decomposition of dioxonium intermediate **37**. Previous work (stilbene **13** (0.385 M), peroxide **1** (0.77 M), water (n M) in d_8-dioxane at 40 °C) had shown that increasing the concentration of water produced a small increase in the rate of reaction (Figure S7).[12] This was attributed to water's ability to hydrogen bond to the peroxide **1**, activating it toward nucleophilic attack by the alkene.

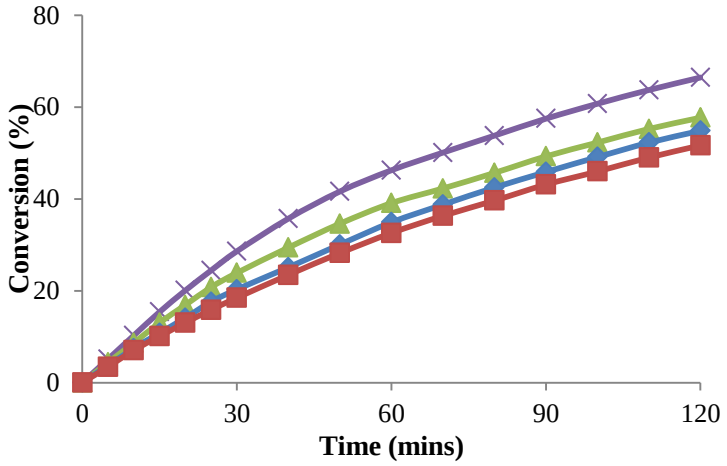


Figure S7. Conversion with increasing water equivalents (1 (■), 2 (♦), 5 (▲) and 10 (×)) against time.

Doubling the concentration of water (from 0.385 M to 0.77 M, 1 to 2 equiv respectively) only increased the initial rate of reaction by a factor of 1.06, consistent with water exerting a small catalytic effect.

With the approximation that the reaction is zero-order in water, the overall dihydroxylation reaction can be considered pseudo-second-order, being first-order in both alkene and peroxide as shown by equation S1.

$$\text{Rate} = k[\text{alkene}][\text{peroxide}] \qquad \textbf{Equation S1}$$

When equal concentrations (0.5 M) of all starting materials are used, [alkene] = [peroxide] so equation S1 can be re-written as:

$$\text{Rate} = k[\text{alkene}]^2 \qquad \textbf{Equation S2}$$

Therefore the plot of 1/[alkene] against time (48 hours, 90% conversion) gives a linear relationship (Figure S8) with a second-order rate constant, k = 0.32 $M^{-1} \cdot hr^{-1}$ (or $k = 8.89 \times 10^{-5}$ $M^{-1} \cdot s^{-1}$).

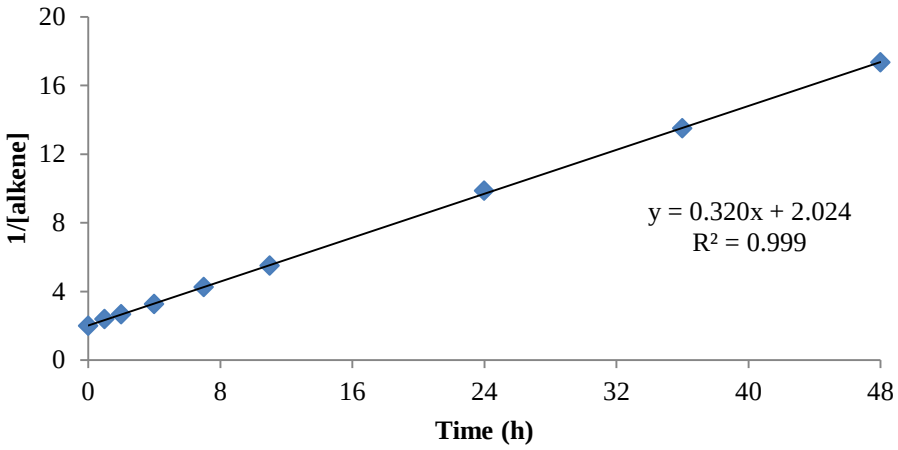
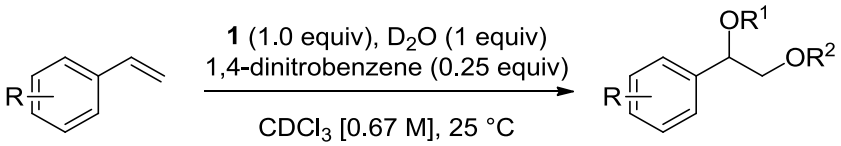


Figure S8. Linear plot of 1/[alkene] against time showing second-order kinetics of the dihydroxylation reaction.

Hammett Analysis



Scheme S2. Reaction conditions for Hammett analysis.

Cyclopropyl malonoyl peroxide **1** (0.341 g, 2.67 mmol, 1 equiv) and 1,4-dinitrobenzene (0.112 g, 0.668 mmol, 0.25 equiv) were dissolved in $CDCl_3$ (4 mL) at 25 °C in a 10 mL round-bottom flask with stirring (Scheme S2). 40 µL of the homogeneous solution was removed and added to an NMR tube containing $CDCl_3$ (500 µL) and the ratio of internal standard (1,4-dinitrobenzene) to cyclopropyl malonoyl peroxide **1** was determined by integration of the ^{1}H NMR spectra. D_2O (48 µL, 2.67 mmol, 1 equiv) and alkene (2.67 mmol, 1 equiv) were added to the reaction vessel and timing commenced immediately. Samples were removed for ^{1}H NMR analysis (as above; 40 µL of reaction mixture added to 500 µL $CDCl_3$ in NMR tube) at known time intervals.

The rate of reaction was monitored by consumption of cyclopropyl malonoyl peroxide **1** relative to the internal standard (1,4-dinitrobenzene) by integration of the corresponding ^{1}H NMR signals:

Cyclopropyl malonoyl peroxide **1**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.11 (s, 4H)

1,4-Dinitrobenzene: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 4H)

The conversion versus time data plotted in Figure S9 is an average of two runs for alkenes **16**–**22** using the method described in Scheme S2.

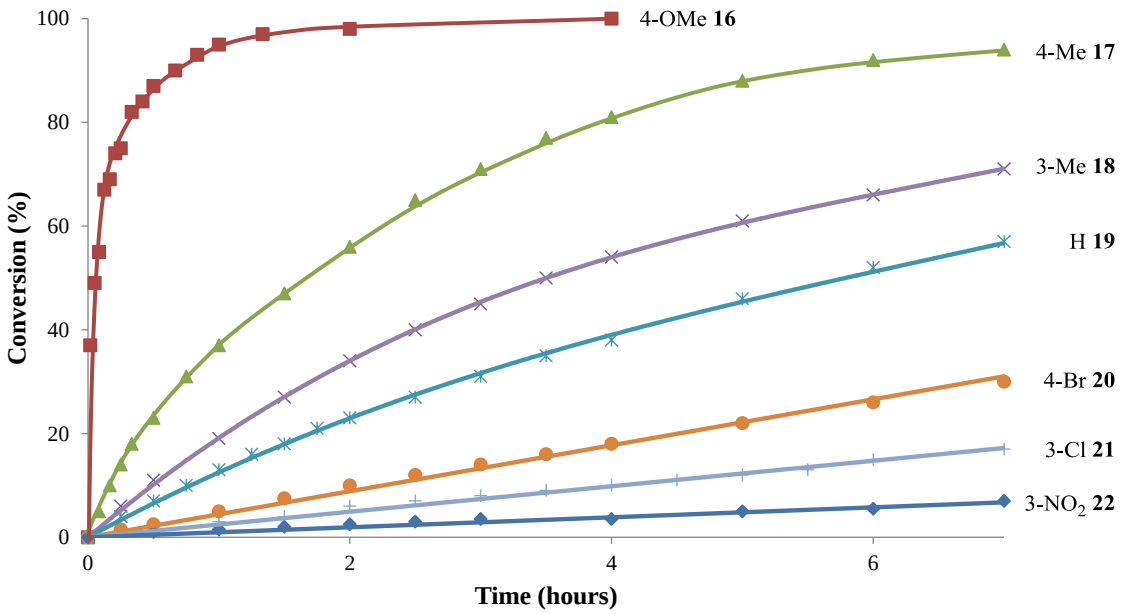


Figure S9. Plot of conversion against time for the reaction of peroxide **1** with substituted styrenes **16**–**22**.

Initial rates of reaction were derived from Figure S9 and used to construct Hammett plots (Figures 10 and 11) based on literature σ or σ^+ values (Table S1).[13]

Styrene	Initial rate ($M \cdot s^{-1}$)	σ	σ^+
4-OMe **16**	4.13×10^{-3}	-0.27	-0.78
4-Me **17**	1.12×10^{-4}	-0.17	-0.31
3-Me **18**	4.17×10^{-5}	-0.07	-0.07
H **19**	2.55×10^{-5}	0	0
4-Br **20**	9.33×10^{-6}	0.23	0.15
3-Cl **21**	4.92×10^{-6}	0.37	0.40
3-NO_2 **22**	1.81×10^{-6}	0.71	0.67

Table S1. Initial rate of reaction between peroxide **1** and styrenes **16**–**22** and the corresponding σ and σ^+ constants.

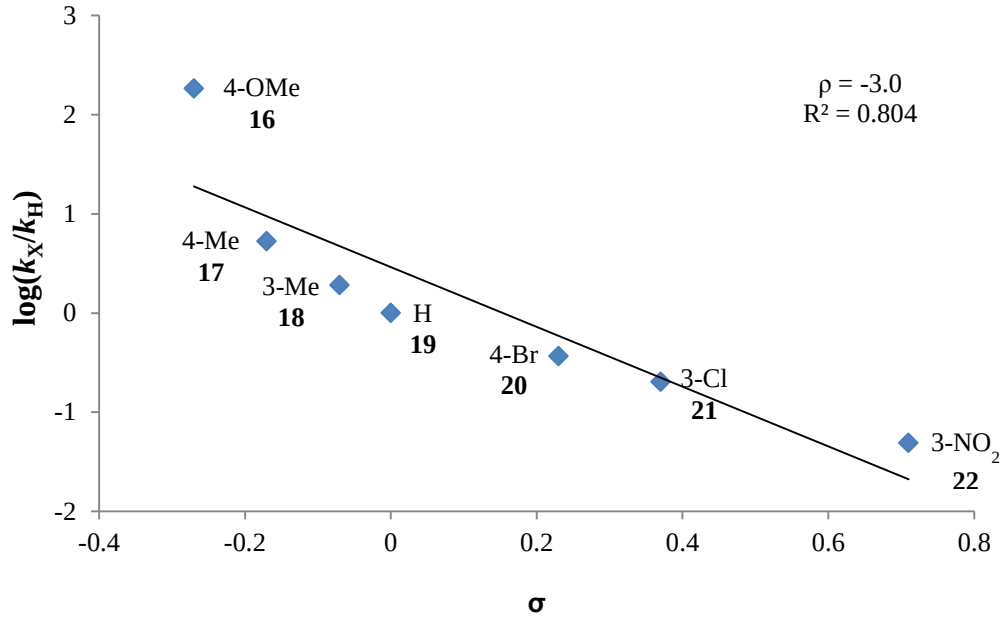


Figure S10. Curved Hammett plot for the reaction of peroxide **1** with substituted styrenes **16**–**22** using σ parameters.

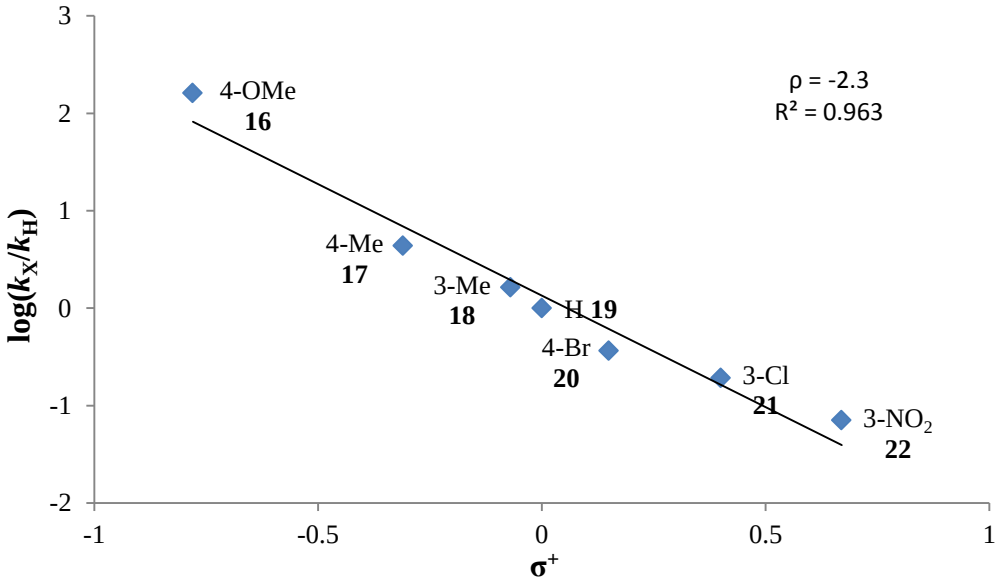


Figure S11. Linear Hammett plot for the reaction of peroxide **1** with substituted styrenes **16**–**22** using σ^+ parameters.

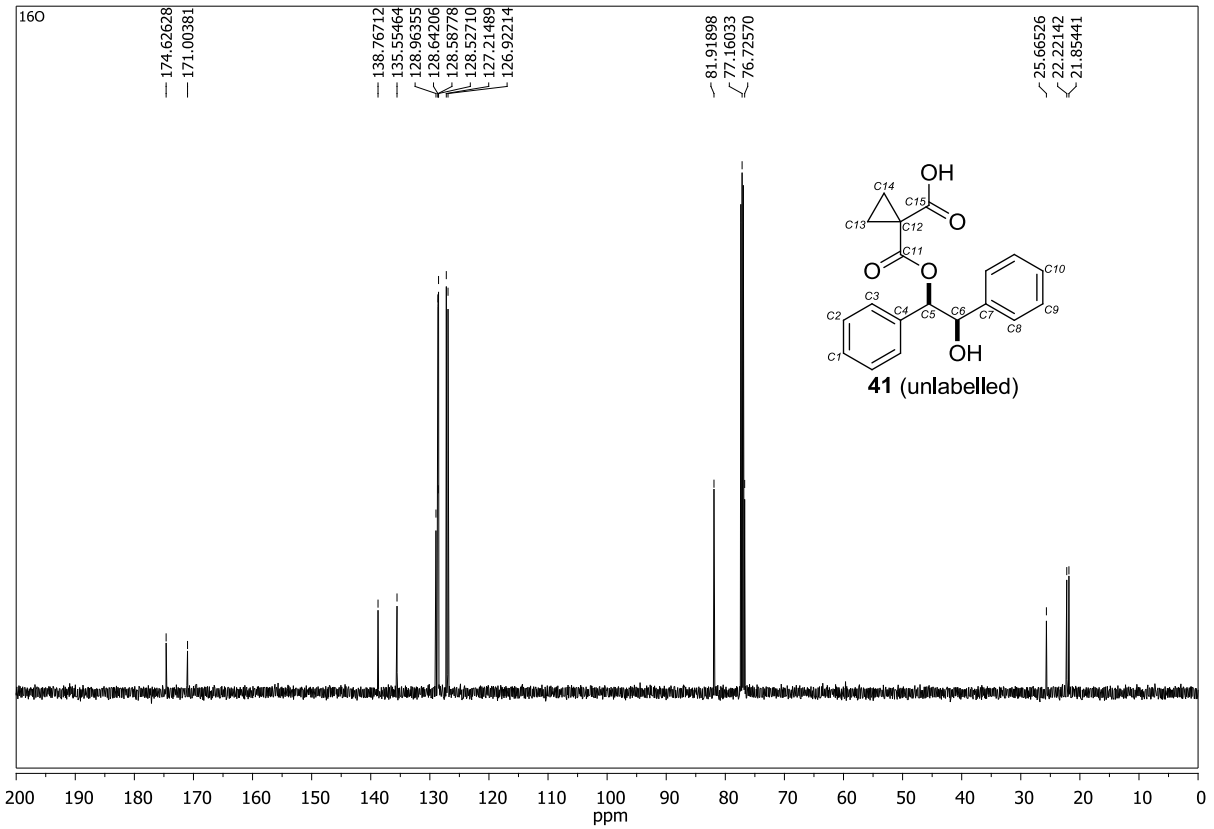
^{18}O-Induced ^{13}C NMR Shift

(*E*)-Stilbene **13** (360 mg, 2 mmol), H_2O (36 µL, 2 mmol, 1 equiv) and cyclopropyl malonoyl peroxide **1** (307 mg, 2 mmol, 1.2 equiv) were stirred in anhydrous $CHCl_3$ (3 mL) according to General Procedure **C** for 24 h at 40 ºC but the hydrolysis step using 1M NaOH was not performed. Solvent was removed *in vacuo* and compound **41** isolated by silica gel flash chromatography (1:1 diethyl ether:petroleum ether, R_f 0.12). Two crystallisations by vapour diffusion crystallisation (chloroform:petroleum ether b.p. 30–40 °C) gave pure **41** as colourless needles. H_2O was replaced with $^{18}OH_2$ (97% ^{18}O, 36 µL, 2 mmol, 1 equiv) and the procedure repeated to afford ^{18}O-labelled **41**.

[0.10 M] solutions of both unlabelled- and ^{18}O-labelled **41** in $CDCl_3$ were prepared and 0.60 mL of each solution was added to separate NMR tubes. ^{13}C NMR data was obtained using a Bruker Avance II 600 MHz spectrometer and the chemical shift values (ppm) were reported to 5 decimal places. The spectra were corrected to $CDCl_3$, δ = 77.16000 (see Table S2). The difference in δ values for each carbon were calculated and reported in ppb.

Carbon #	**^{16}0**	**^{16}O corrected to $CDCl_3$**	**^{18}0**	**^{18}O corrected to $CDCl_3$**	Δδ ppm	Δδ ppb
$CDCl_3$	*77.16033*	*77.16000*	*77.15953*	*77.16000*	*N/A*	*N/A*
11	**174.62628**	**174.62595**	**174.58778**	**174.58825**	**0.0385**	**38.5**
15	**171.00381**	**171.00348**	**171.00800**	**171.00847**	**-0.00419**	**-4.19**
7	138.76712	138.76679	138.76622	138.76669	0.0009	0.9
4	135.55464	135.55431	135.55453	135.55500	0.00011	0.11
1/10	128.96355	128.96322	128.96100	128.96147	0.00255	2.55
2/9	128.64206	128.64173	128.63983	128.64030	0.00223	2.23
1/10	128.58778	128.58745	128.58464	128.58511	0.00314	3.14
2/9	128.52710	128.52677	128.52433	128.52480	0.00277	2.77
3	127.21489	127.21456	127.21382	127.21429	0.00107	1.07
8	126.92214	126.92181	126.92115	126.92162	0.00099	0.99
5	81.91898	81.91865	81.91493	81.91540	0.00405	4.05
6	76.72570	76.72537	76.72165	76.72212	0.00405	4.05
12	**25.66526**	**25.66493**	**25.65508**	**25.65555**	**0.01018**	**10.18**
13/14	22.22142	22.22109	22.21777	22.21824	0.00365	3.65
13/14	21.85441	21.85408	21.85163	21.85210	0.00278	2.78

Table S2. ^{18}O-induced ^{13}C NMR shift data for unlabelled/^{18}O-labelled **41**.



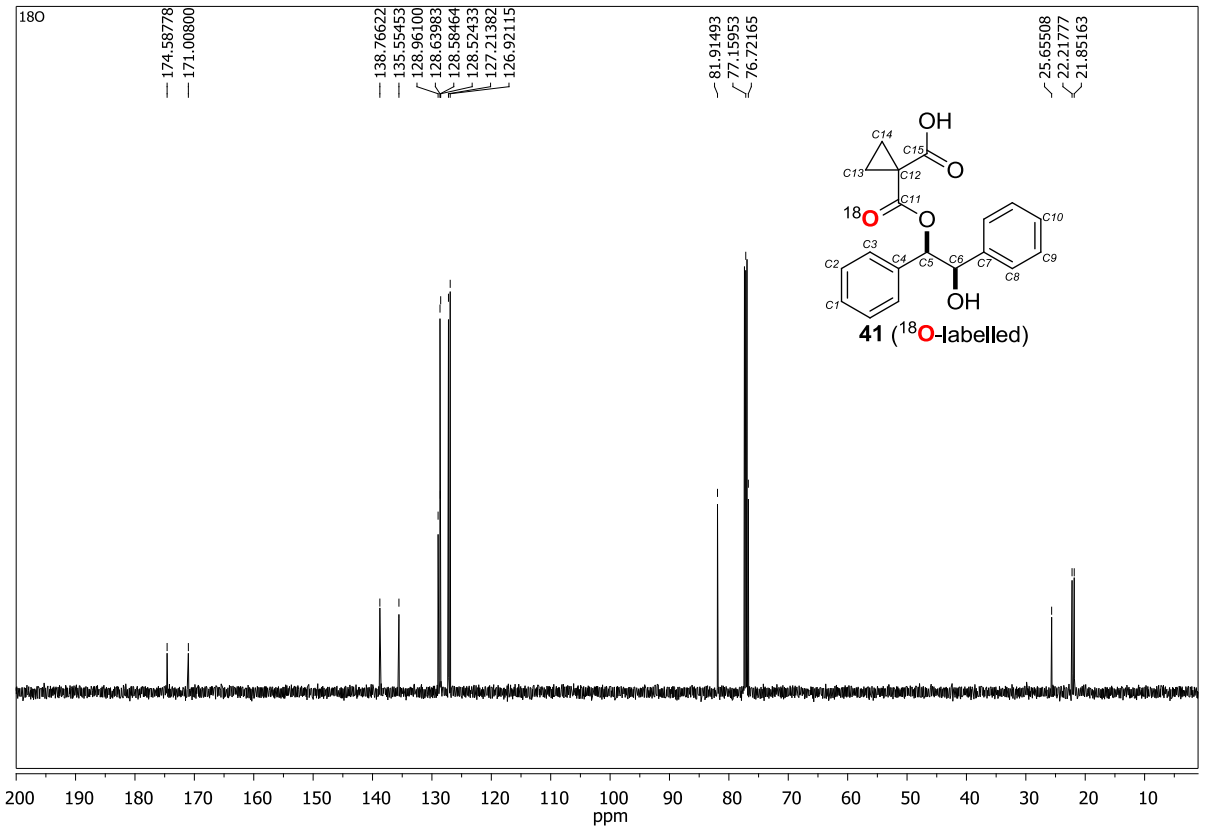


Figure S12. ^{13}C NMR of unlabelled **41** (top) and ^{18}O-labelled **41** (bottom).

DFT Calculations

DFT calculations were performed using the Gaussian09 suite of programs.[14] Although widely used for organic systems, B3LYP[15] has been shown to be particularly successful at calculating O—O, C—O and O—H bond energies[16] and hence was chosen for this study. Transition states and local minima were found at the B3LYP/6-31G level of theory. The obtained geometries were then re-optimised where necessary and characterised using frequency calculations at the B3LYP/6-31+G** level of theory with chloroform PCM solvation. A classical approach was used when analysing frequency data whereby fully converged local minima (reactants and intermediates) contain no imaginary frequencies and first order saddle points (transition states, TS's) possess one imaginary frequency (which when animated moves in the anticipated direction).

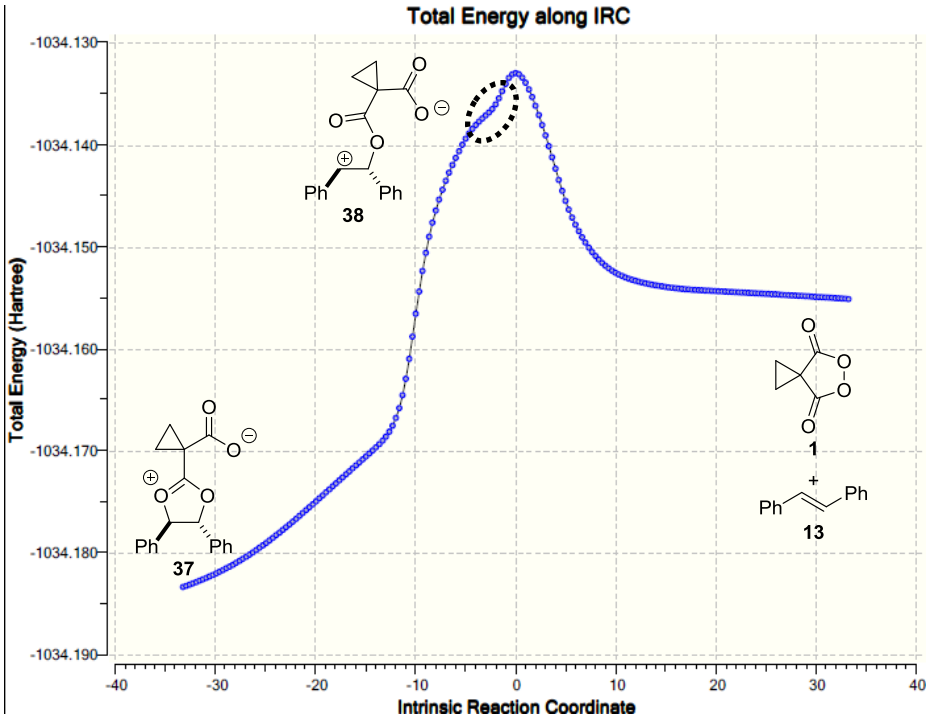


Figure S13. IRC plot for **TS1** *via* intermediate **38**.

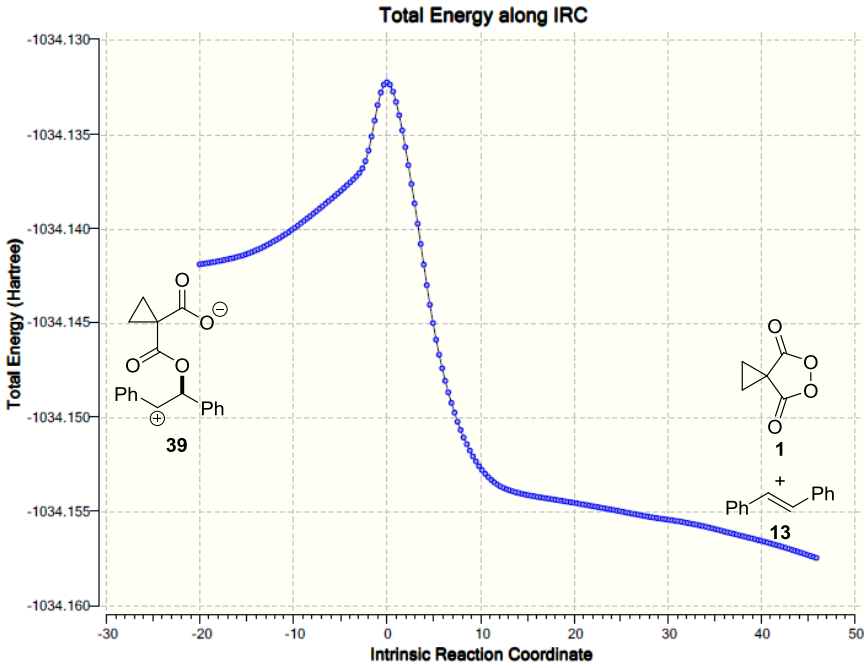


Figure S14. IRC plot for **TS2** leading to open chain zwitterion **39**.

Each transition state was further characterised by following the intrinsic reaction coordinate (B3LYP/6-31G) (Figures S13 and S14). From this it was clear that each transition state led to a different intermediate. **TS1** formed cyclic intermediate **37** (Figure S13) whereas **TS2** formed an open-chain intermediate **39** (Figure S14). Formation of **37** could be due to a concerted reaction process. Upon closer inspection of the reaction coordinate path it was clear that a high-energy intermediate was present which reaffirms a concerted mechanism is not occurring. The relative energy of **38** was derived from a non-optimised structure as attempts to optimise this derivative from **TS1** all led to ring closure (Figure S13).

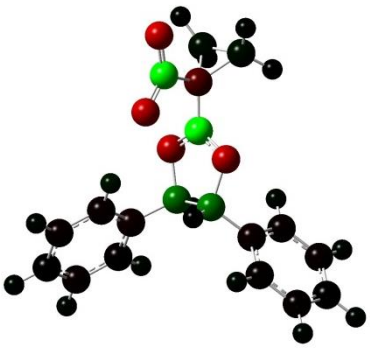


Figure S15. Atomic structure of **37** displaying ATP charge localisation.

The relative energies of **1** and **13** compared to charged species **37** and **39** was somewhat surprising (Figure S16). For **39** it was apparent from comparison of gas-phase and solution-phase energies that the PCM solvation stabilises the zwitterionic species. However, the

relative energy of **37** is similar in gas and solution phase. Closer inspection of **37** revealed three aspects which likely contribute to its stability. Firstly, an anion C—H interaction between the carboxylate and phenyl ring is present (2.25 Å) and secondly, the close proximity of the carboxylate to the oxonium ion (2.90 Å to the oxygen atoms and 2.43 Å to the electrophilic carbon centre). Finally, inspection of the APT (atomic polar tensor) charge distribution reveals extensive charge delocalisation within the carboxylate. Charge delocalisation is also prevalent within the oxonium ion and benzylic carbon sites (Figure S15). A combination of these three factors likely stabilise the zwitterion **37** and this gives rise to its low energy. When a basis set larger than 6-31G is used in the gas phase, upon optimisation, **37** ring closes to form lactone **40**. The gas-phase data presented is based on structures optimised with solvation and then frequency calculations performed at the B3LYP/6-31+G** level.

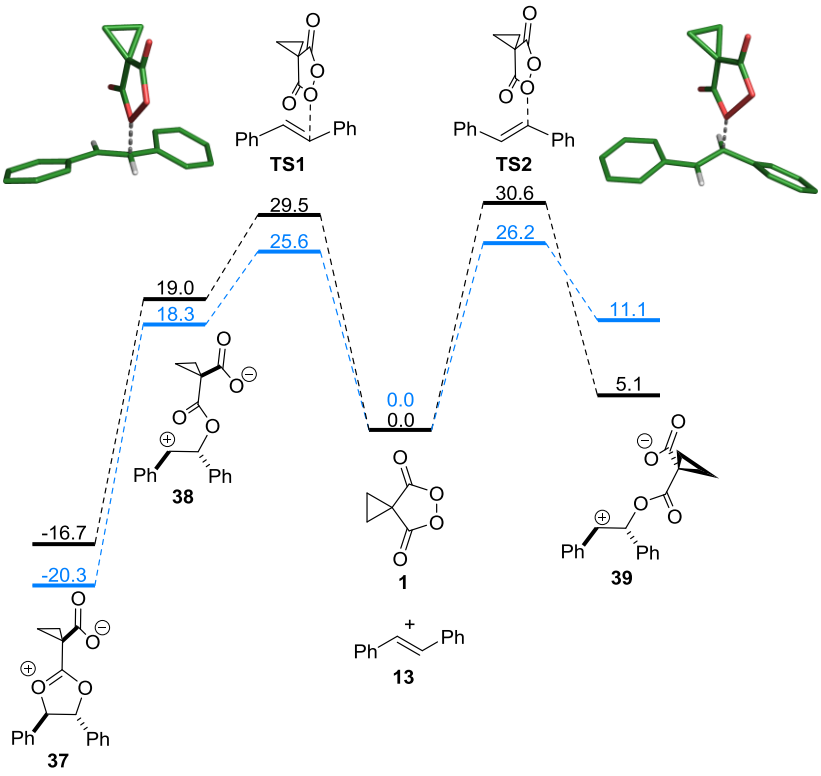


Figure S16. Calculated relative Gibbs free energies (kcal mol^{-1}).
B3LYP/6-31+G** Chloroform PCM (Black), B3LYP/6-31+G** Gas Phase (Blue)

Diradical Mechanism

Local minima and transition states were found using analogous methodology to the ionic investigation. Spin-unrestricted B3LYP (UB3LYP) was used for all calculations involving radical species.

A transition state **TS3** (28.9 kcalmol^{-1}) to form the diradical species **S68** from peroxide **1** was found (Figure S17).

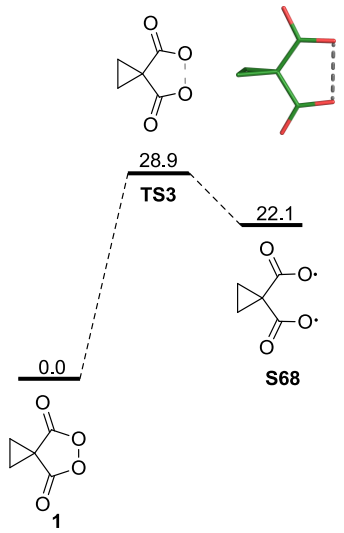


Figure S17. Peroxide Homolytic Cleavage (kcal mol^{-1}).

Apparent transition states for the reaction of diradical **S68** with stilbene were found. However, upon following the IRC it became clear that they were not true transition states for the reaction. Despite extensive searching no transition states were found for a radical pathway.

Single Electron Transfer (SET) Mechanism

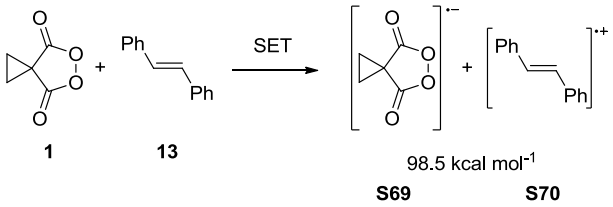


Figure S18. SET Process

	S69	**S70**	Combined
Gas Phase	-4.1	156.0	151.9
Chloroform	-39.0	137.5	98.5

Table S3. Energies of SET Intermediates (kcal mol^{-1})

The combined energies of **S69** and **S70** were found to be significantly higher (98.5 kcal mol^{-1}) compared to the ground state reactants (Table S3). This was found to be solely due to **S70** as **S69** is lower in energy than **1**. Despite the favourable formation of **S69**, it is likely to be highly reactive which could explain why malonyl peroxide **1** is not amenable to mass spectrometric analysis.

Cartesian Coordinates

The number of imaginary frequencies relate to structures optimised at the B3LYP/6-31+G** level with PCM chloroform solvation.

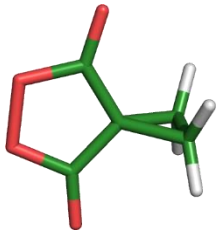
All Gibbs Free Energies are calculated at 298.15 K.

Peroxide 1

Gibbs Free Energies (hartrees):

B3LYP/6-31+G** Chloroform PCM = -493.711605

B3LYP/6-31+G** Gas Phase = -493.703630

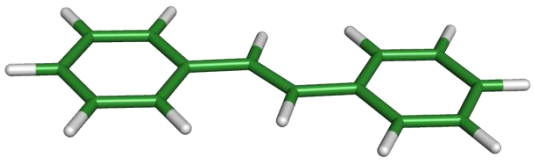


Number of imaginary frequencies=0

O	4.329233	-1.054453	0.938960
C	3.357199	-1.374798	0.304004
O	3.458481	-1.516588	-1.071207
C	1.971279	-1.674410	0.693146
C	1.252665	-2.004729	-0.546396
O	2.147150	-1.909307	-1.601095
C	1.281879	-0.940460	1.855357
C	1.637311	-2.360803	2.028020
O	0.110495	-2.317727	-0.765747
H	1.893070	-0.184030	2.336667
H	0.854075	-3.109242	1.966534
H	2.501626	-2.616002	2.632368
H	0.245499	-0.677258	1.670851

Stilbene 13

Gibbs Free Energies (hartrees):



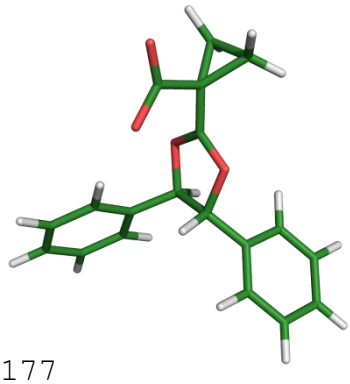
B3LYP/6-31+G** Chloroform PCM = -540.577615

B3LYP/6-31+G** Gas Phase = -540.557129

Number of imaginary frequencies=0

C	3.595168	1.210355	0.004308
C	2.856495	2.396618	0.002866
C	1.461100	2.352577	0.001878
C	0.766074	1.126151	0.002302
C	1.528665	-0.061086	0.003778
C	2.921507	-0.017880	0.004751
C	-0.702319	1.150974	0.001217
C	-1.533857	0.086746	0.001455
C	-3.002229	0.111617	0.000376
C	-3.697314	-1.114761	0.000790
C	-5.092719	-1.158724	-0.000180
C	-5.831318	0.027574	-0.001611
C	-5.157575	1.255783	-0.002056
C	-3.764744	1.298916	-0.001062
H	-5.601240	-2.118634	0.000187
H	-3.131641	-2.043184	0.001896
H	-3.269115	2.264580	-0.001428
H	-5.721854	2.184125	-0.003154
H	-6.916897	-0.001310	-0.002392
H	-1.106520	-0.914518	0.002573
H	-1.129674	2.152233	0.000121
H	0.895371	3.280966	0.000770
H	1.033105	-1.026782	0.004180
H	3.364957	3.356558	0.002500
H	3.485827	-0.946196	0.005839
H	4.680747	1.239302	0.005095

5-Membered Ring Zwitterion 37



Gibbs Free Energies (hartrees):

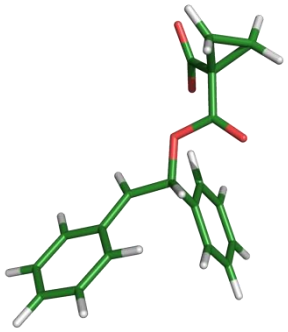
B3LYP/6-31+G** Chloroform PCM = -1034.315781

B3LYP/6-31+G** Gas Phase = -1034.293099

Number of imaginary frequencies=0

C	-4.985331	1.759805	-1.476177
C	-5.326849	0.411642	-1.671942
C	-4.394497	-0.594820	-1.391601
C	-3.117363	-0.258853	-0.933723
C	-2.776896	1.082125	-0.740091
C	-3.713529	2.088104	-1.005503
C	-6.680470	0.034042	-2.201790
O	-7.748362	0.686307	-1.391673
C	-8.575535	1.301973	-2.175912
O	-8.348306	1.164435	-3.443736
C	-7.007563	0.535717	-3.633085
C	-9.666609	2.124430	-1.663528
C	-9.113115	3.581011	-1.524620
O	-9.903505	4.444285	-1.109165
C	-7.054955	-0.497923	-4.720389
C	-7.883524	-1.626751	-4.621991
C	-7.904193	-2.571994	-5.647313
C	-7.090182	-2.403825	-6.773574
C	-6.261739	-1.284081	-6.874840
C	-6.248814	-0.330369	-5.853462
C	-10.663466	1.577117	-0.666011
C	-11.102862	1.874526	-2.071754
O	-7.898155	3.676050	-1.862045
H	-10.568615	0.537401	-0.368020
H	-11.686260	2.771594	-2.249465
H	-1.787306	1.344240	-0.377876
H	-2.396393	-1.042648	-0.722839
H	-6.356727	1.365678	-3.912177
H	-5.716829	2.542299	-1.664848
H	-6.859192	-1.037270	-2.098896
H	-3.454674	3.129999	-0.844218
H	-5.610346	0.544494	-5.937030
H	-8.523135	-1.767448	-3.754847
H	-11.310364	1.038224	-2.732299
H	-5.630990	-1.147469	-7.747630
H	-7.105298	-3.143026	-7.568702
H	-8.553025	-3.438706	-5.568088
H	-10.949730	2.267902	0.119674
H	-4.663202	-1.638378	-1.531955

Open Chain Zwitterion 39



Gibbs Free Energies (hartrees):

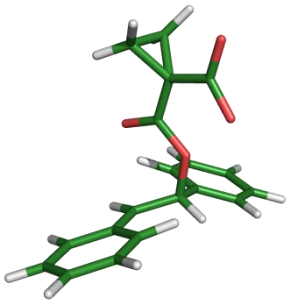
B3LYP/6-31+G** Chloroform PCM = -1034.281123

B3LYP/6-31+G** Gas Phase = -1034.243110

Number of imaginary frequencies=0

C	-1.832752	-0.680824	0.653063
C	-0.917431	-0.951446	-0.383464
C	-1.154917	-2.000616	-1.291976
C	-2.320709	-2.750331	-1.188666
C	-3.243154	-2.473482	-0.167786
C	-3.000469	-1.439755	0.741726
C	0.360371	-0.102479	-0.505604
O	-0.592029	4.236341	2.396801
C	-0.933385	3.264618	1.677194
O	-1.558507	2.223768	2.028667
C	1.162635	-0.926012	0.416664
C	-0.616861	3.379539	0.163874
C	-0.480563	2.123339	-0.619772
O	0.250013	1.188605	0.071724
C	2.091412	-1.937065	0.110787
C	2.555574	-2.192445	-1.214123
C	3.502793	-3.175121	-1.436152
C	4.007470	-3.920385	-0.355190
C	3.571564	-3.682445	0.956431
C	2.623241	-2.700957	1.192408
C	0.257199	4.532990	-0.336472
C	-1.217840	4.566459	-0.572106
O	-0.877656	1.902755	-1.748957
H	0.666249	5.150256	0.455838
H	-1.583567	4.384331	-1.577552
H	-4.151071	-3.063619	-0.088202
H	-2.517824	-3.544788	-1.901275
H	0.955636	-0.731321	1.467479
H	-1.660893	0.160979	1.322953
H	0.709693	-0.056625	-1.536934
H	-3.722923	-1.217588	1.520491
H	2.273135	-2.503231	2.200681
H	2.181411	-1.607142	-2.046259
H	-1.816734	5.237629	0.034347
H	3.975834	-4.262107	1.778826
H	4.752310	-4.688382	-0.539820
H	3.863357	-3.367183	-2.440684
H	0.908157	4.341999	-1.184993
H	-0.444183	-2.212221	-2.085532

High-Energy Zwitterion 38



Gibbs Free Energies (hartrees):

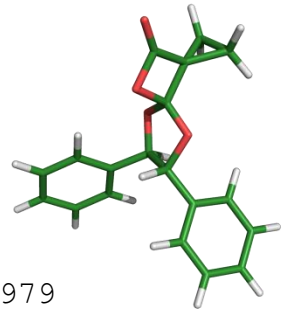
B3LYP/6-31+G** Chloroform PCM = -1034.258963

B3LYP/6-31+G** Gas Phase = -1034.231598

Number of imaginary frequencies=N/A (non-optimised structure)

C	2.295495	-1.717406	-0.976556
C	1.726989	-1.590678	0.303938
C	2.520431	-1.866171	1.431966
C	3.856053	-2.252684	1.288447
C	4.414759	-2.372750	0.011151
C	3.630342	-2.107440	-1.117886
C	0.309710	-1.135252	0.528434
O	0.270815	4.444774	1.107934
C	0.217507	3.184209	0.967921
O	0.022460	2.350634	1.940497
C	-0.728634	-1.579987	-0.409617
C	0.370224	2.599276	-0.429892
C	0.301680	1.137324	-0.609068
O	0.217899	0.441401	0.585554
C	-2.115754	-1.480147	-0.158544
C	-2.647353	-0.861180	1.018602
C	-4.020282	-0.809904	1.220728
C	-4.900295	-1.354662	0.268496
C	-4.401863	-1.950584	-0.903733
C	-3.032703	-2.011030	-1.119126
C	1.311824	3.376482	-1.390669
C	-0.157184	3.471654	-1.593831
O	0.306449	0.553742	-1.713746
H	1.818607	4.210813	-0.919615
H	-0.601733	2.942821	-2.428975
H	5.453008	-2.666910	-0.104067
H	4.457414	-2.453232	2.168955
H	-0.416141	-2.013439	-1.352865
H	1.714119	-1.464579	-1.854890
H	0.024476	-1.315627	1.566246
H	4.061077	-2.191707	-2.110356
H	-2.638753	-2.464319	-2.023387
H	-1.978813	-0.383862	1.725836
H	-0.655756	4.375695	-1.263226
H	-5.087297	-2.356912	-1.639075
H	-5.971427	-1.304006	0.433731
H	-4.415245	-0.331433	2.109784
H	1.896146	2.777334	-2.079664
H	2.093664	-1.759468	2.425087

Lactone 40



Gibbs Free Energies (hartrees):

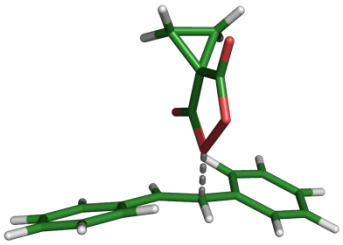
B3LYP/6-31+G** Chloroform PCM = -1034.325054

B3LYP/6-31+G** Gas Phase = -1034.314026

C	0.210243	2.914952	0.718979
C	-0.442784	2.106419	-0.223549
C	-1.521540	2.631205	-0.946301
C	-1.953727	3.942276	-0.723342
C	-1.300787	4.742563	0.217356
C	-0.215552	4.226510	0.935031
C	-0.023864	0.674715	-0.445382
O	1.423273	0.550518	-0.529901
C	1.839539	-0.489328	0.271693
O	0.747920	-1.223951	0.655934
C	-0.376427	-0.303177	0.706616
C	3.095902	-1.249739	-0.112012
C	3.724736	-0.658889	1.103286
O	4.786624	-0.691549	1.671173
C	-1.678828	-1.046090	0.570679
C	-1.881419	-1.970910	-0.465107
C	-3.103092	-2.634143	-0.588499
C	-4.138949	-2.374463	0.316293
C	-3.944007	-1.454085	1.348774
C	-2.716188	-0.797383	1.477858
C	3.697974	-1.467746	-1.477650
C	3.238676	-2.643759	-0.670335
O	2.603965	0.046165	1.470004
H	3.093598	-1.148064	-2.321126
H	3.984512	-3.277239	-0.200163
H	-1.629660	5.763608	0.387021
H	-2.791772	4.337424	-1.289814
H	-0.344508	0.227388	1.664546
H	1.060082	2.523372	1.270051
H	-0.438907	0.305708	-1.388623
H	0.301002	4.846956	1.661488
H	-2.564016	-0.089587	2.288250
H	-1.080492	-2.182626	-1.167363
H	2.316704	-3.141498	-0.954313
H	-4.740972	-1.250990	2.057796
H	-5.089617	-2.890151	0.217815
H	-3.247554	-3.353279	-1.389386
H	4.763574	-1.282634	-1.571112
H	-2.024533	2.014757	-1.686858

	Free energy /hartrees	E_{rel} /kcal mol^{-1}
Lactone **38**	-1034.325054	0
Zwitterion **37**	-1034.315781	5.82

Transition State 1 TS1



Gibbs Free Energies (hartrees):

B3LYP/6-31+G** Chloroform PCM = -1034.242268

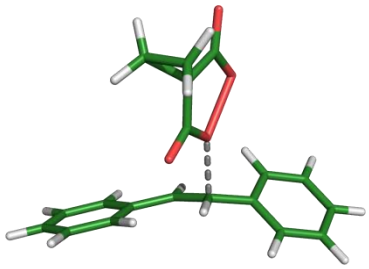
B3LYP/6-31+G** Gas Phase = -1034.219966

Number of imaginary frequencies=1 (-314.94 cm^{-1})

C	-2.293912	-1.739200	0.988099
C	-1.721561	-1.660653	-0.298429
C	-2.533551	-1.918897	-1.420810
C	-3.877236	-2.265691	-1.265956
C	-4.431982	-2.354317	0.016033
C	-3.637688	-2.085966	1.138940
C	-0.302073	-1.323981	-0.530698
O	-0.259046	4.415718	-1.229379
C	-0.221847	3.185596	-0.966165
O	-0.035525	2.252506	-1.877249
C	0.720782	-1.600309	0.410409
C	-0.378499	2.666748	0.432624
C	-0.292808	1.198195	0.581067
O	-0.150461	0.547019	-0.632745
C	2.124570	-1.490542	0.162405
C	2.657548	-0.898531	-1.018207
C	4.033466	-0.835798	-1.209448
C	4.909898	-1.356601	-0.242718
C	4.404009	-1.929011	0.934905
C	3.030184	-1.985893	1.141778
C	-1.322749	3.437631	1.380631
C	0.147740	3.544009	1.584671
O	-0.339392	0.609548	1.680432
H	-1.840715	4.267932	0.913628
H	0.594620	3.014396	2.418140
H	-5.476352	-2.621982	0.139991
H	-4.488703	-2.462091	-2.140362
H	0.428169	-1.916417	1.405541
H	-1.702412	-1.483692	1.858628
H	-0.015165	-1.363357	-1.576659
H	-4.069500	-2.137430	2.133136
H	2.632446	-2.418282	2.054820
H	1.990742	-0.445905	-1.742421
H	0.646630	4.450149	1.259153
H	5.083246	-2.318584	1.685278
H	5.982020	-1.304305	-0.401304
H	4.430738	-0.370213	-2.104639
H	-1.900054	2.832302	2.069987
H	-2.106055	-1.841582	-2.416172

Transition State 2 TS2

Note: For clarity, a mirror image of this structure is used within the main text



Gibbs Free Energies (hartrees):

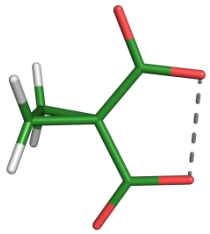
B3LYP/6-31+G** Chloroform PCM = -1034.240511

B3LYP/6-31+G** Gas Phase = -1034.219293

Number of imaginary frequencies=1 (-333.60 cm^{-1})

C	2.363608	-1.666567	-0.944249
C	1.679159	-1.714792	0.285398
C	2.313576	-2.289202	1.402462
C	3.596205	-2.832510	1.287167
C	4.264577	-2.792720	0.058242
C	3.648313	-2.201076	-1.053077
C	0.305397	-1.183489	0.435095
O	1.554815	4.203485	-1.330330
C	1.216555	3.076984	-0.886072
O	1.715564	1.943291	-1.339640
C	-0.707883	-1.527147	-0.491343
C	0.217244	2.910066	0.214256
C	-0.060803	1.514034	0.605433
O	0.566210	0.581150	-0.216890
C	-2.126391	-1.471385	-0.325287
C	-2.768481	-1.045389	0.872848
C	-4.156509	-1.049345	0.961817
C	-4.940098	-1.478197	-0.122016
C	-4.327214	-1.899341	-1.312728
C	-2.941230	-1.894209	-1.415230
C	-0.933011	3.935867	0.309855
C	0.167630	3.991841	1.310118
O	-0.780955	1.187495	1.569819
H	-0.941504	4.668664	-0.489558
H	-0.027085	3.635672	2.315338
H	5.263717	-3.206778	-0.031004
H	4.073927	-3.277268	2.154029
H	-0.361986	-1.876266	-1.462434
H	1.914083	-1.156838	-1.789308
H	0.001118	-0.958806	1.452391
H	4.176217	-2.141578	-1.999002
H	-2.461782	-2.216295	-2.334661
H	-2.175283	-0.672640	1.697052
H	0.918806	4.767012	1.206715
H	-4.933188	-2.225356	-2.150977
H	-6.022107	-1.480628	-0.040150
H	-4.635758	-0.714074	1.875134
H	-1.896322	3.545495	0.618170
H	1.798195	-2.314230	2.358455

Peroxide Homolytic Cleavage Transition State 3 TS3



Gibbs Free Energies (hartrees):

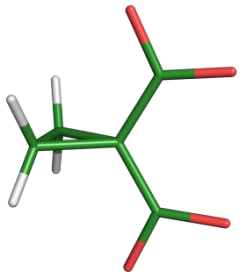
B3LYP/6-31+G** Chloroform PCM = -493.665534

B3LYP/6-31+G** Gas Phase = -493.657960

Number of imaginary frequencies=1(-277.04 cm^{-1})

C	-0.002010	1.581146	-0.748882
C	0.003068	1.587124	0.739924
H	-0.910292	1.845138	-1.278976
H	0.927831	1.794620	-1.263463
H	-0.901454	1.855588	1.274184
H	0.936541	1.804869	1.246088
C	-0.021346	0.227536	0.001096
O	-1.186072	-1.884300	0.012109
O	1.117097	-1.878585	0.001403
C	-1.225172	-0.610694	0.008465
C	1.287777	-0.564089	0.000041
O	-2.399390	-0.030336	0.010901
O	2.373471	0.045690	-0.002362

Diradical S68



Gibbs Free Energies (hartrees):

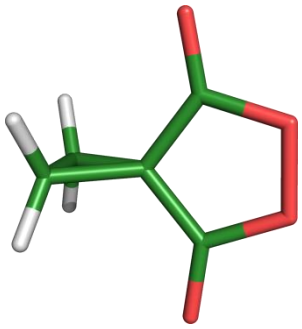
B3LYP/6-31+G** Chloroform PCM = -493.676423

B3LYP/6-31+G** Gas Phase = -493.668946

Number of imaginary frequencies=0

C	-4.139720	0.114807	1.059203
C	-2.695032	-0.097020	0.877329
H	-4.795915	0.025564	0.199817
H	-4.585426	-0.101992	2.024216
H	-2.319478	-0.338569	-0.111365
H	-2.108773	-0.464196	1.713147
C	-3.210997	1.356564	1.037968
O	-3.027746	3.437154	-0.225073
O	-2.783789	3.258549	2.506832
C	-3.241543	2.188665	-0.181885
C	-2.952294	2.014189	2.334884
O	-3.484700	1.734048	-1.337425
O	-2.874274	1.393799	3.434875

Peroxide Radical Anion S69



Gibbs Free Energies (hartrees):

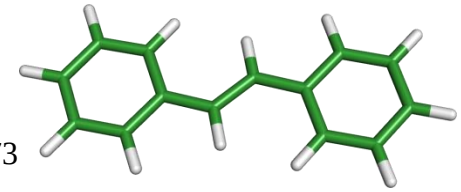
B3LYP/6-31+G** Chloroform PCM = -493.773791

B3LYP/6-31+G** Gas Phase = -493.710226

Number of imaginary frequencies=0

O	4.351997	-1.052222	0.919380
C	3.347018	-1.381481	0.277463
O	3.471361	-1.518398	-1.123455
C	1.974496	-1.674983	0.685551
C	1.279081	-2.000613	-0.558178
O	2.174069	-1.906989	-1.647683
C	1.273236	-0.924348	1.864709
C	1.636604	-2.375979	2.041145
O	0.108402	-2.322588	-0.795438
H	1.873275	-0.176000	2.378482
H	0.838606	-3.115099	2.010505
H	2.485421	-2.621988	2.675991
H	0.226396	-0.669119	1.712989

Stilbene Radical Cation S70



Gibbs Free Energies (hartrees):

B3LYP/6-31+G** Chloroform PCM = -540.358573

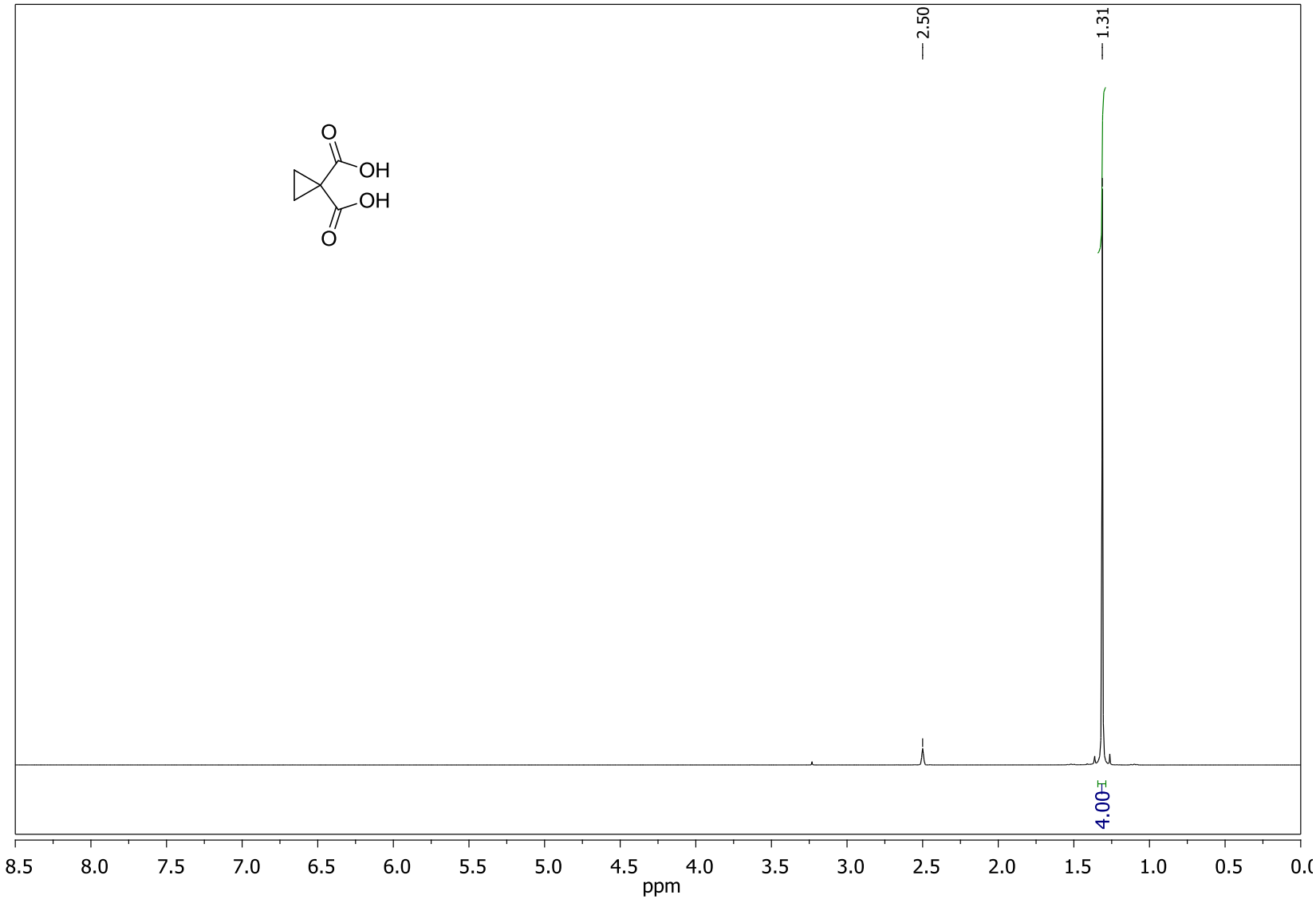
B3LYP/6-31+G** Gas Phase = -540.308553

Number of imaginary frequencies=0

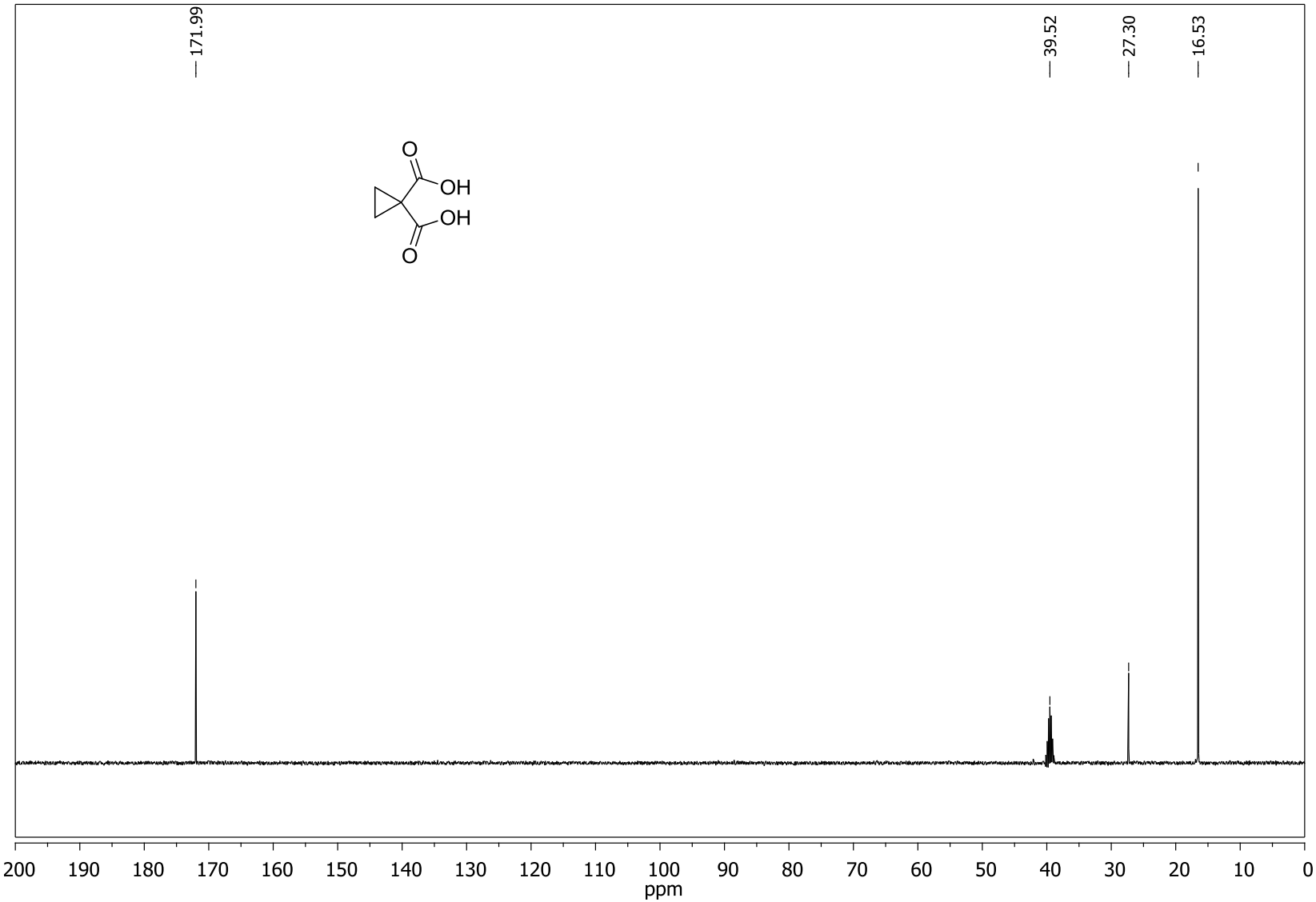
C	3.545331	1.203534	0.004277
C	2.820438	2.407003	0.002770
C	1.436880	2.373131	0.001791
C	0.735168	1.130317	0.002285
C	1.495300	-0.078771	0.003824
C	2.876902	-0.035604	0.004798
C	-0.690828	1.167421	0.001223
C	-1.545326	0.070424	0.001442
C	-2.971321	0.107527	0.000395
C	-3.673036	-1.135286	0.000773
C	-5.056594	-1.169157	-0.000203
C	-5.781484	0.034314	-0.001576
C	-5.113054	1.273452	-0.001966
C	-3.731453	1.316617	-0.001001
H	-5.580107	-2.119274	0.000091
H	-3.105874	-2.061527	0.001841
H	-3.231939	2.278859	-0.001308
H	-5.685162	2.195209	-0.003022
H	-6.866898	0.009617	-0.002342
H	-1.105705	-0.923529	0.002503
H	-1.130448	2.161374	0.000138
H	0.869717	3.299371	0.000626
H	0.995789	-1.041015	0.004245
H	3.343950	3.357121	0.002378
H	3.449011	-0.957361	0.005969
H	4.630745	1.228232	0.005050

^{1}H and ^{13}C Spectra

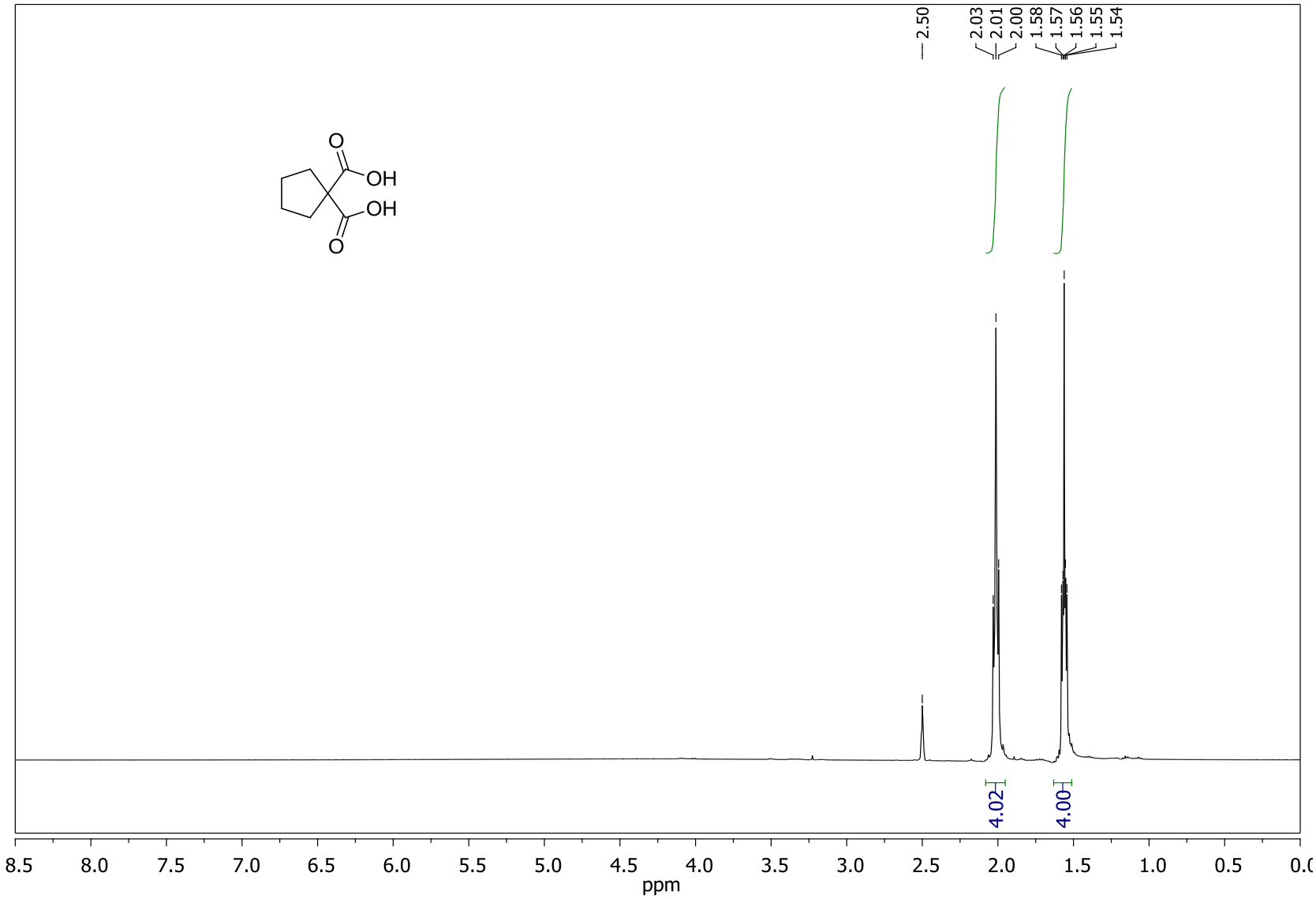
Cyclopropane-1,1-dicarboxylic acid **5**: ^{1}H NMR (400 MHz, DMSO-d_6)



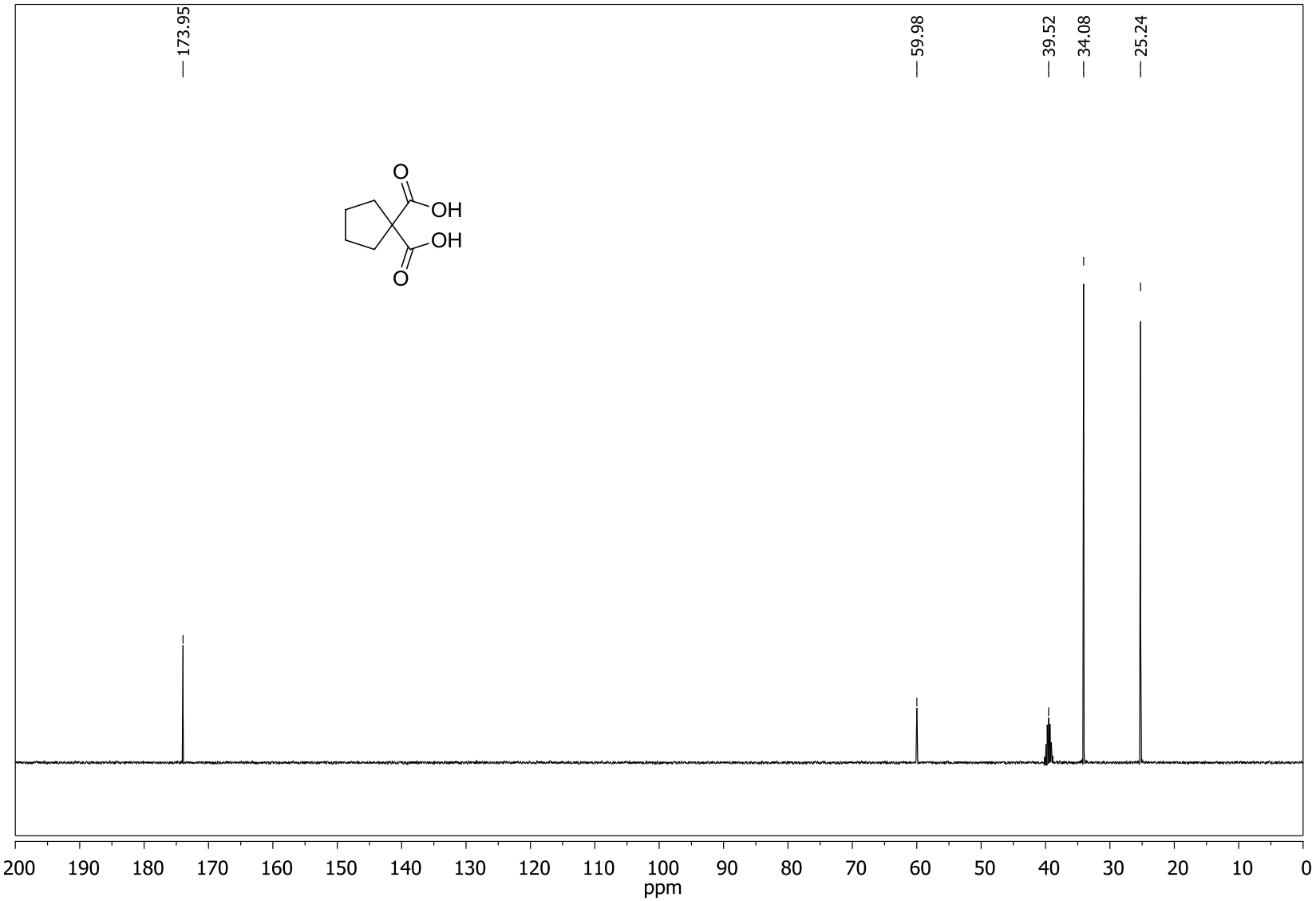
Cyclopropane-1,1-dicarboxylic acid **5**: ^{13}C NMR (100 MHz, DMSO-d_6)



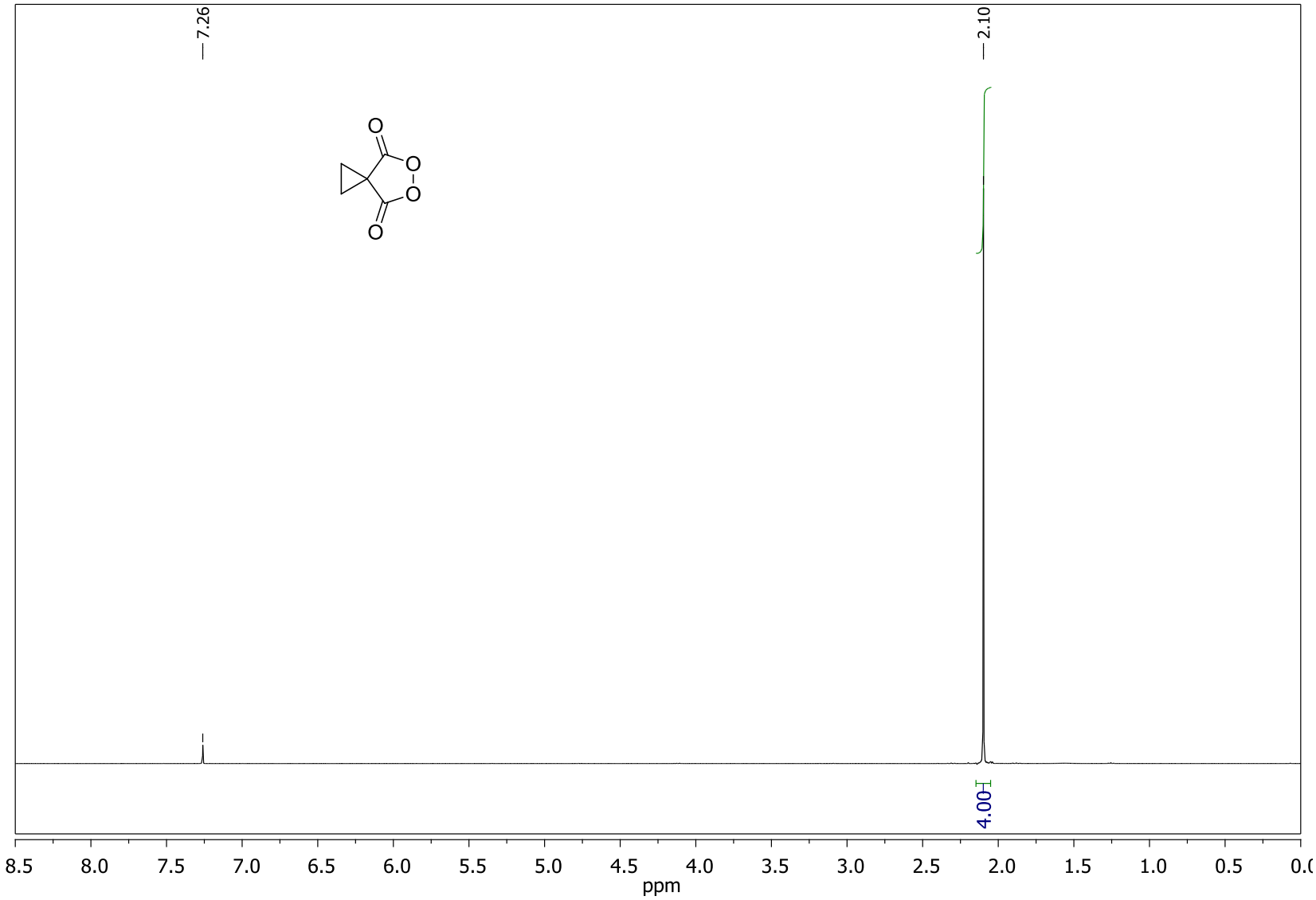
Cyclopentane-1,1-dicarboxylic acid **S-63**: ^{1}H NMR (400 MHz, DMSO-d_6)



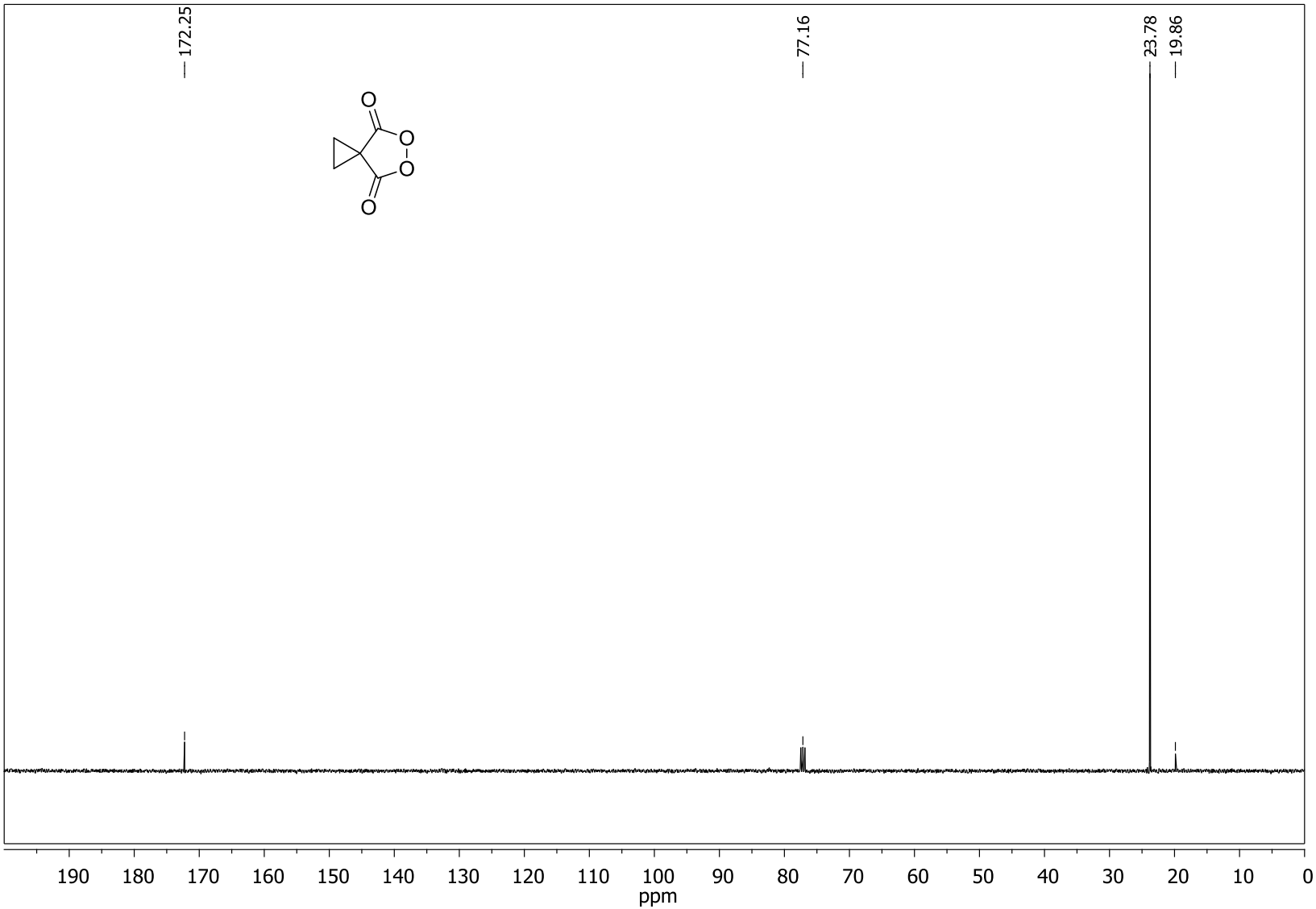
Cyclopentane-1,1-dicarboxylic acid **S-63**: ^{13}C NMR (100 MHz, DMSO-d_6)



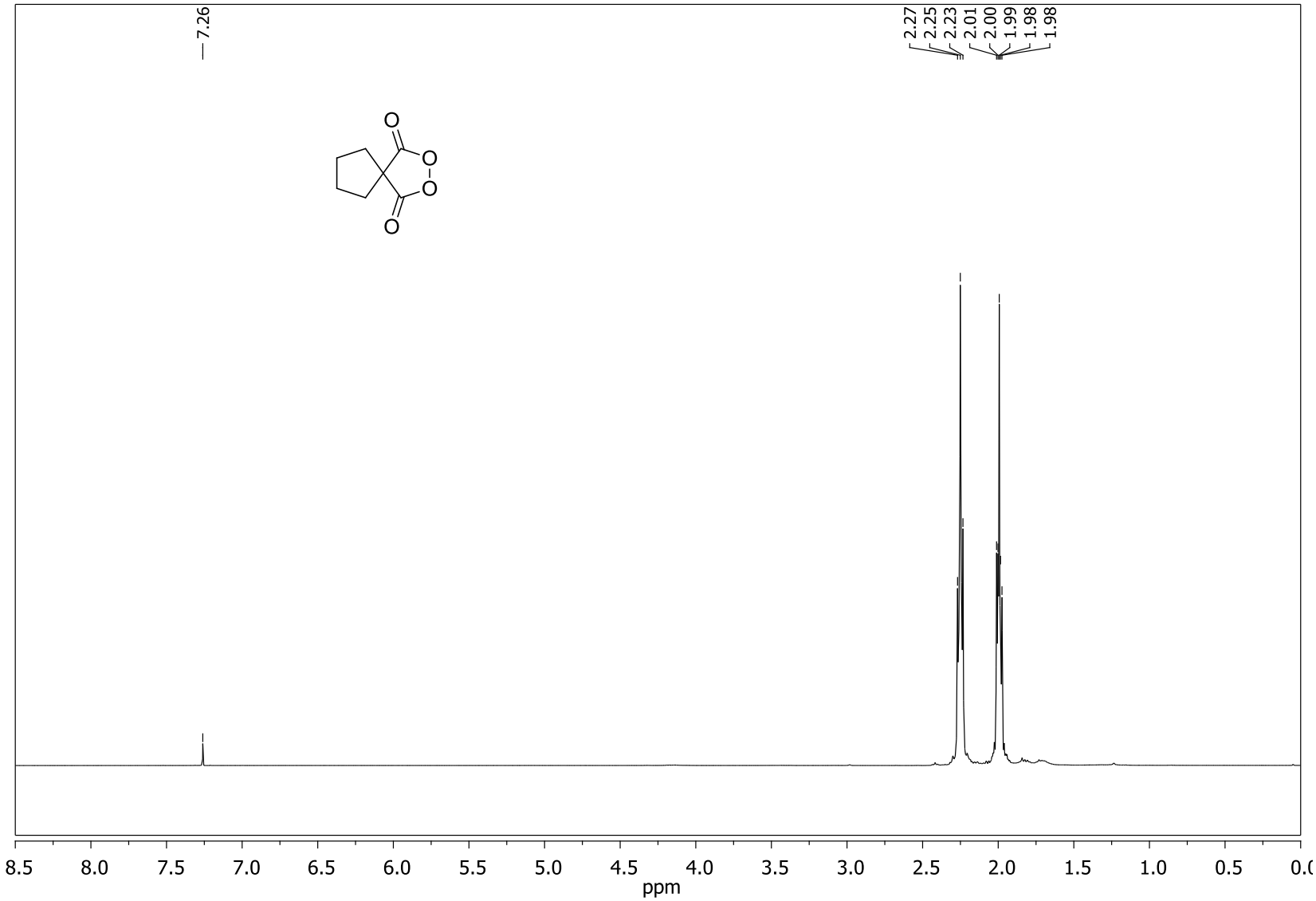
Cyclopropyl malonoyl peroxide **1**: ^{1}H NMR (400 MHz, $CDCl_3$)



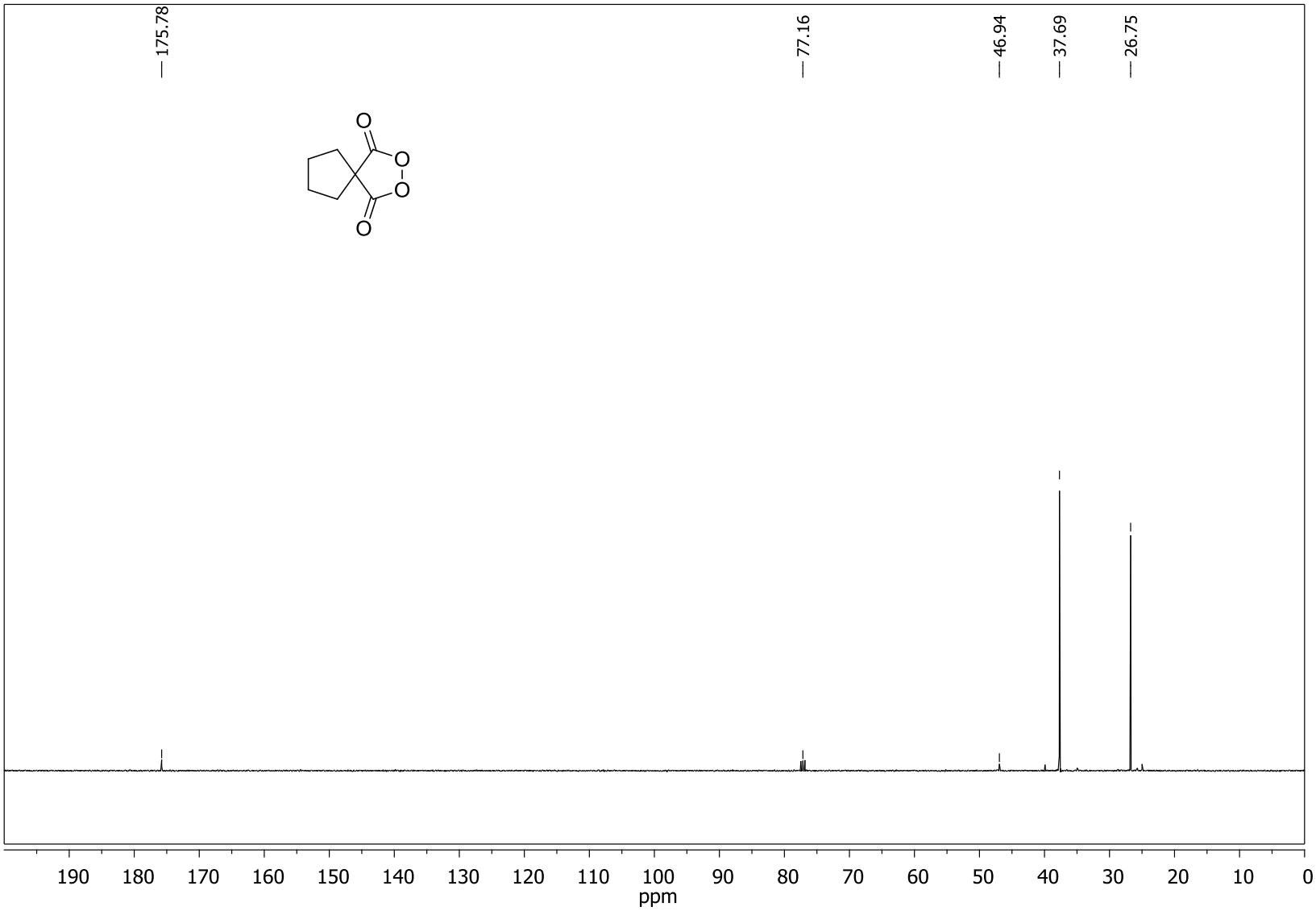
Cyclopropyl malonoyl peroxide **1**: ^{13}C NMR (100 MHz, $CDCl_3$)



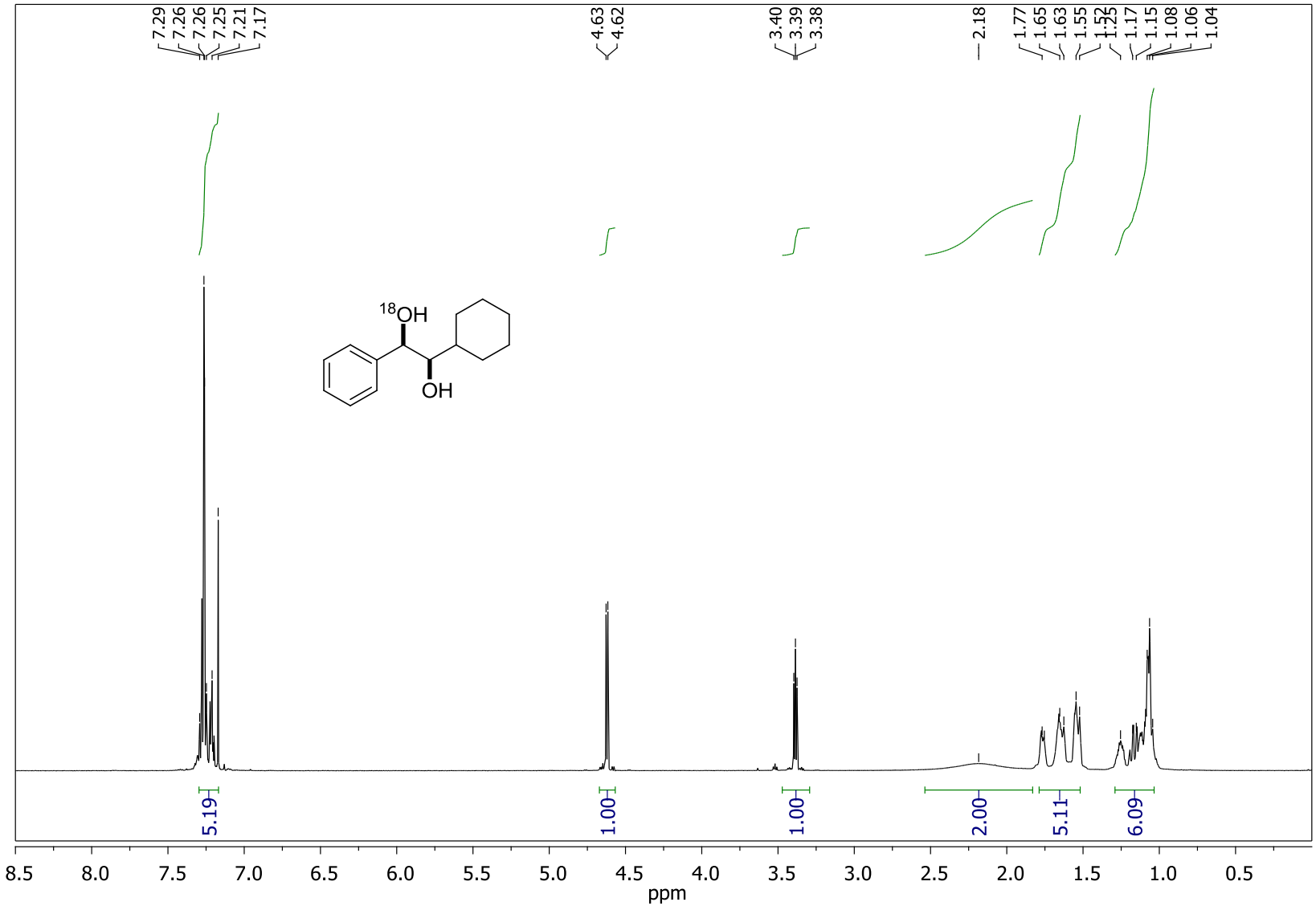
Cyclopentyl malonoyl peroxide **62**: ^{1}H NMR (400 MHz, $CDCl_3$)



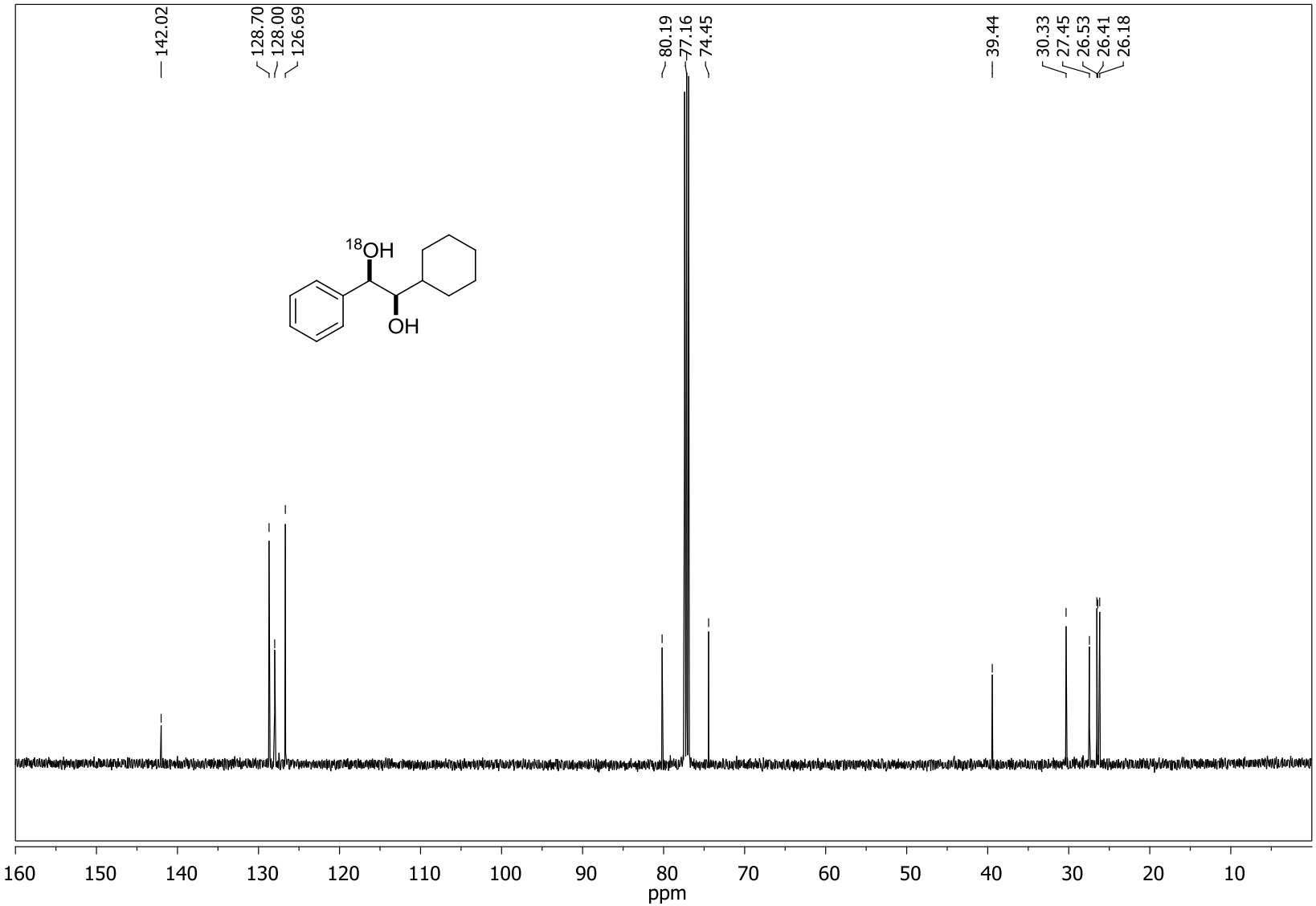
Cyclopentyl malonoyl peroxide **62**: ^{13}C NMR (100 MHz, $CDCl_3$)



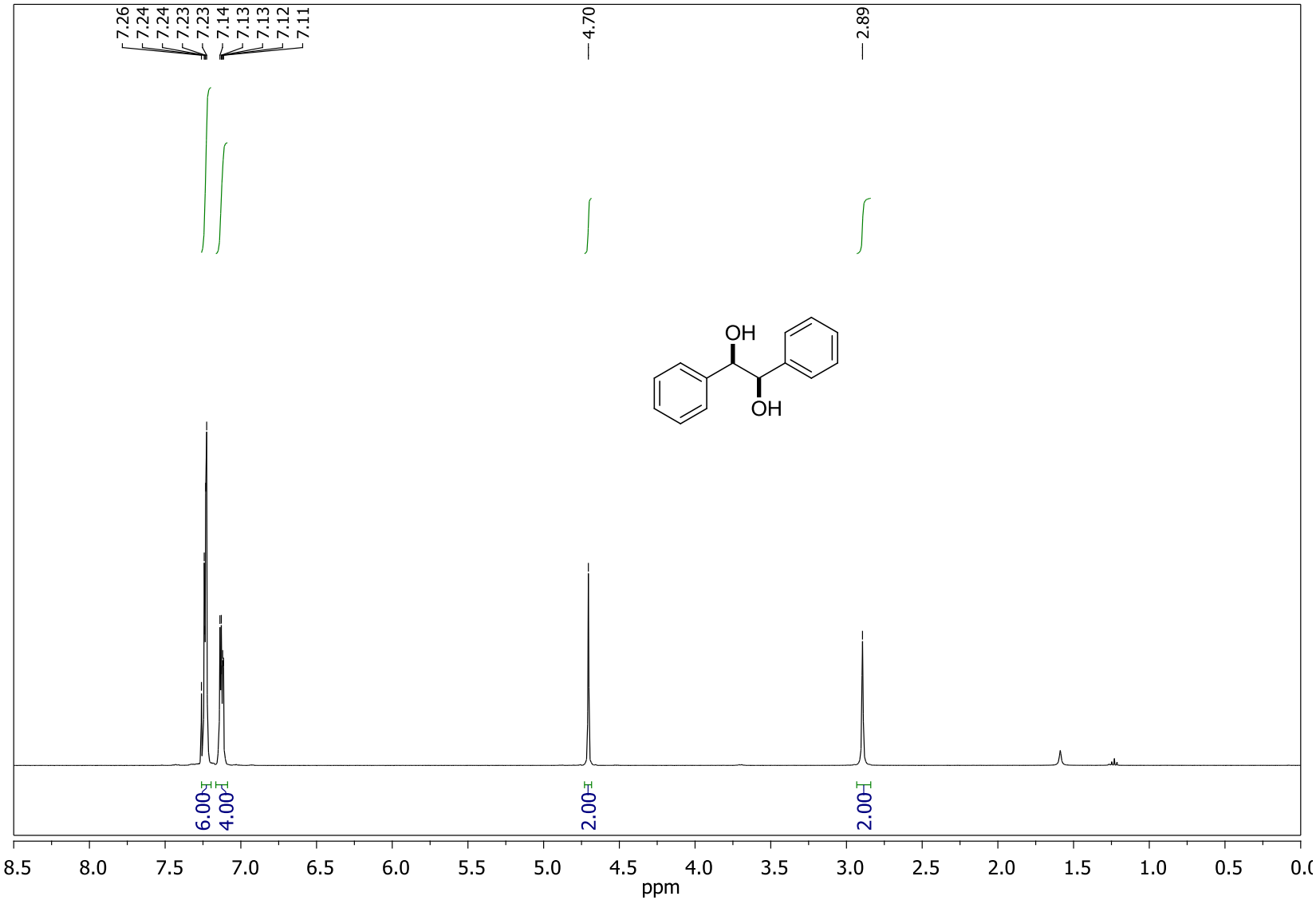
rel-(1*R*,2*R*)-1-Cyclohexyl-2-phenylethane-1,2-diol **30** (25:1 *syn*:*anti*): ^{1}H NMR (500 MHz, $CDCl_3$)



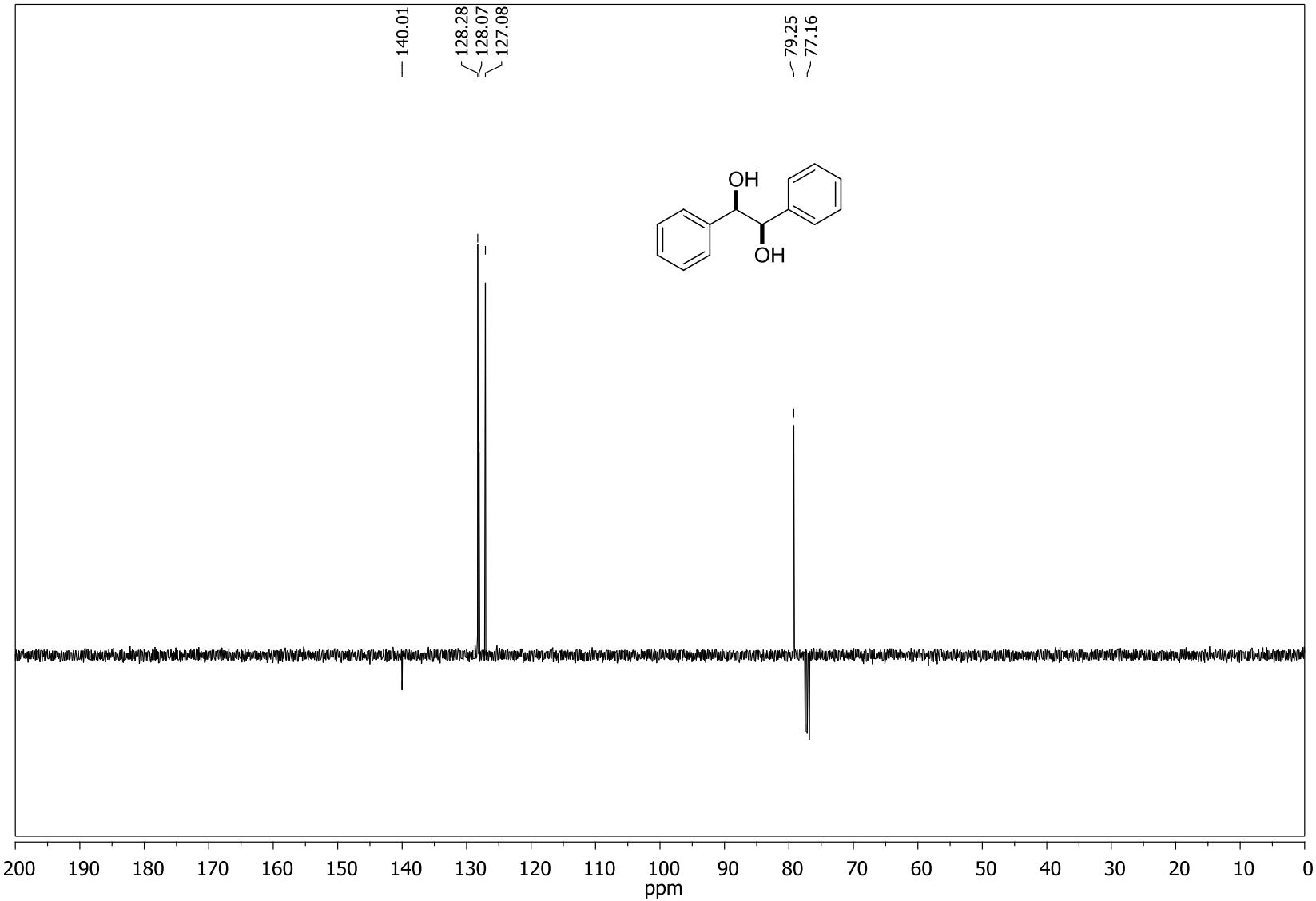
rel-(1*R*,2*R*)-1-Cyclohexyl-2-phenylethane-1,2-diol **30** (25:1 *syn*:*anti*): ^{13}C NMR DEPTQ-135 (125 MHz, $CDCl_3$)



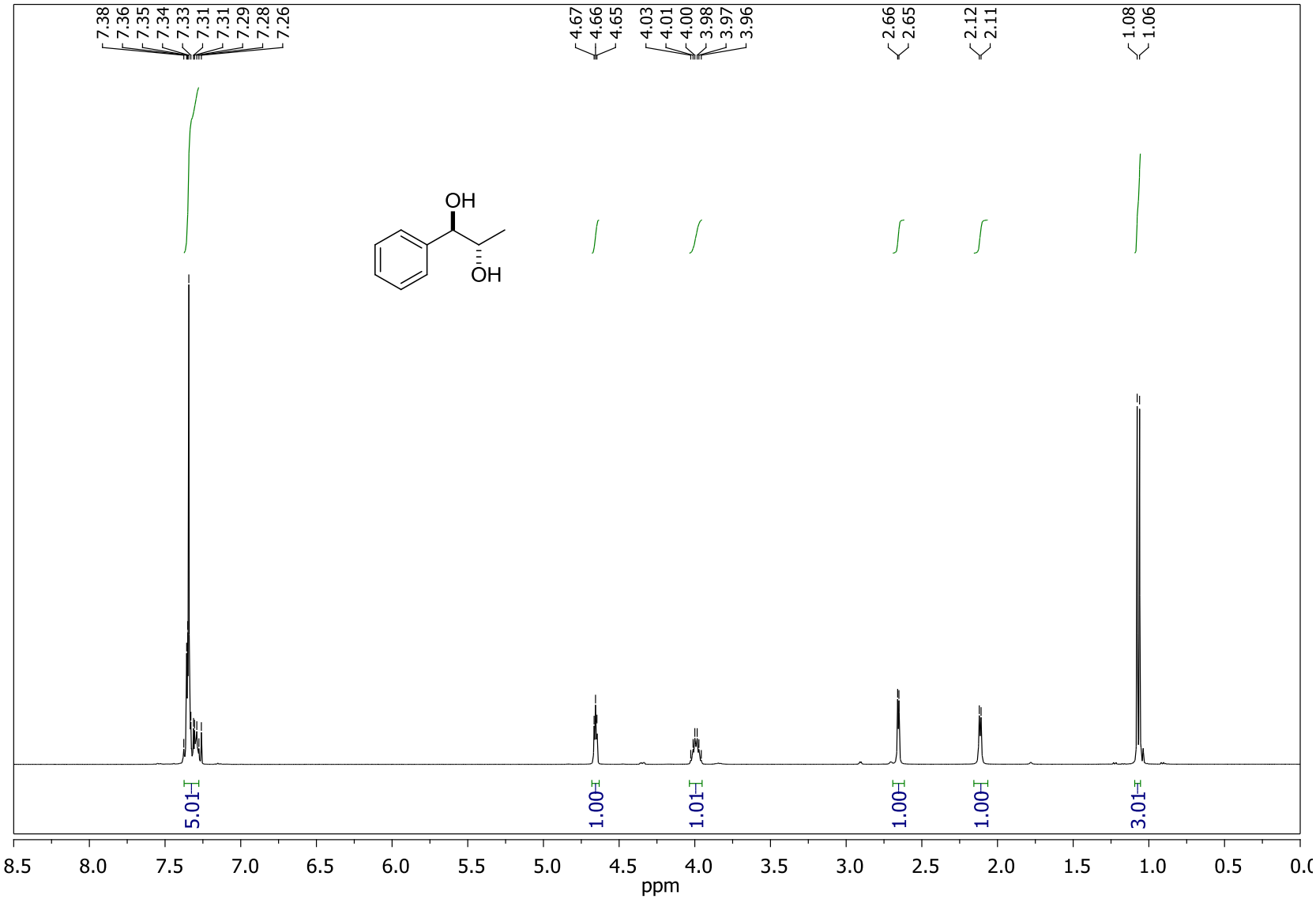
rel-(1*R*,2*R*)-1,2-Diphenylethane-1,2-diol **42**: ^{1}H NMR (400 MHz, $CDCl_3$)



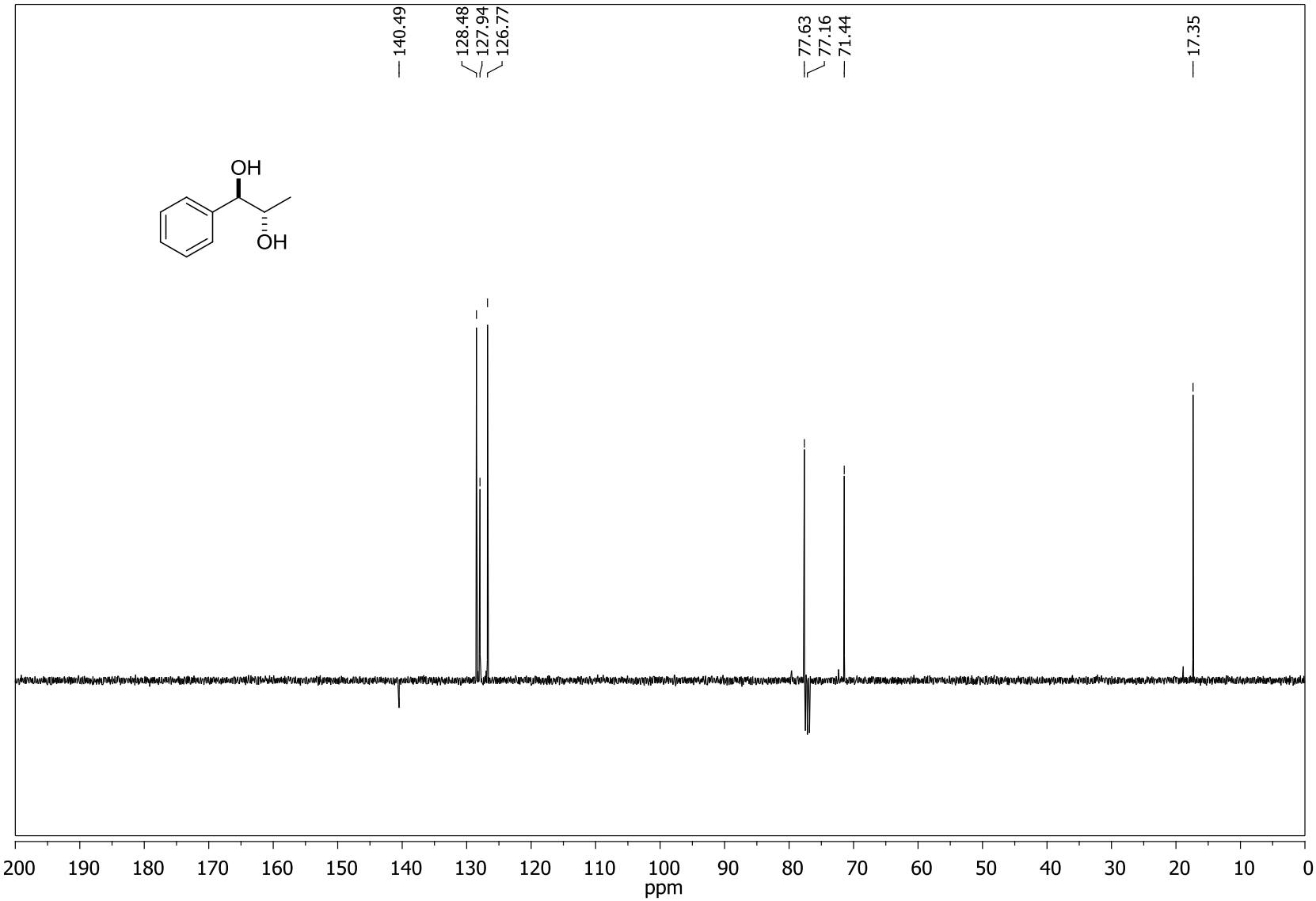
rel-(1*R*,2*R*)-1,2-Diphenylethane-1,2-diol **42**: ^{13}C NMR DEPTQ-135 (100 MHz, $CDCl_3$)



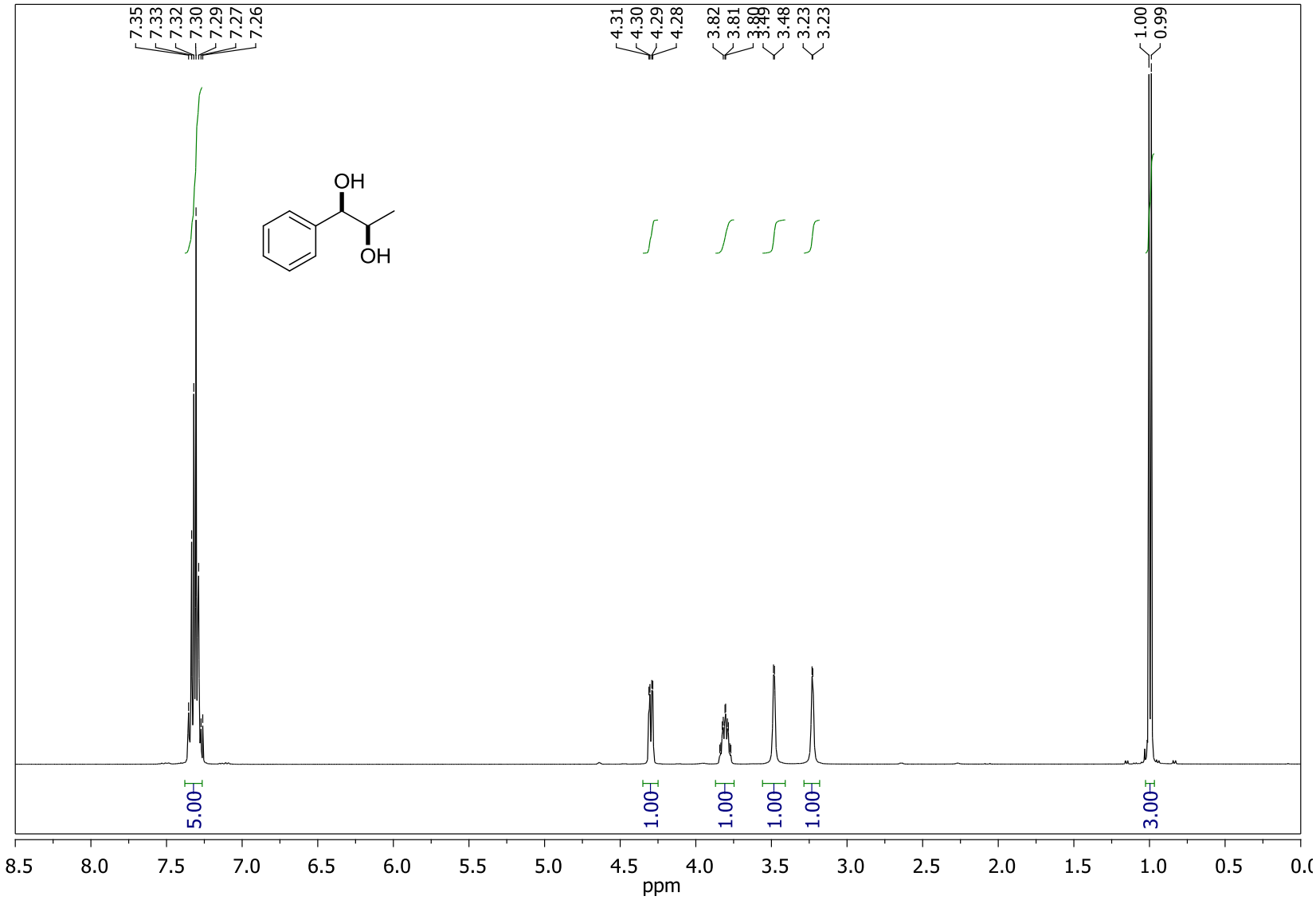
rel-(1*R*,2*S*)-1-Phenylpropane-1,2-diol **51**: ^{1}H NMR (400 MHz, $CDCl_3$)



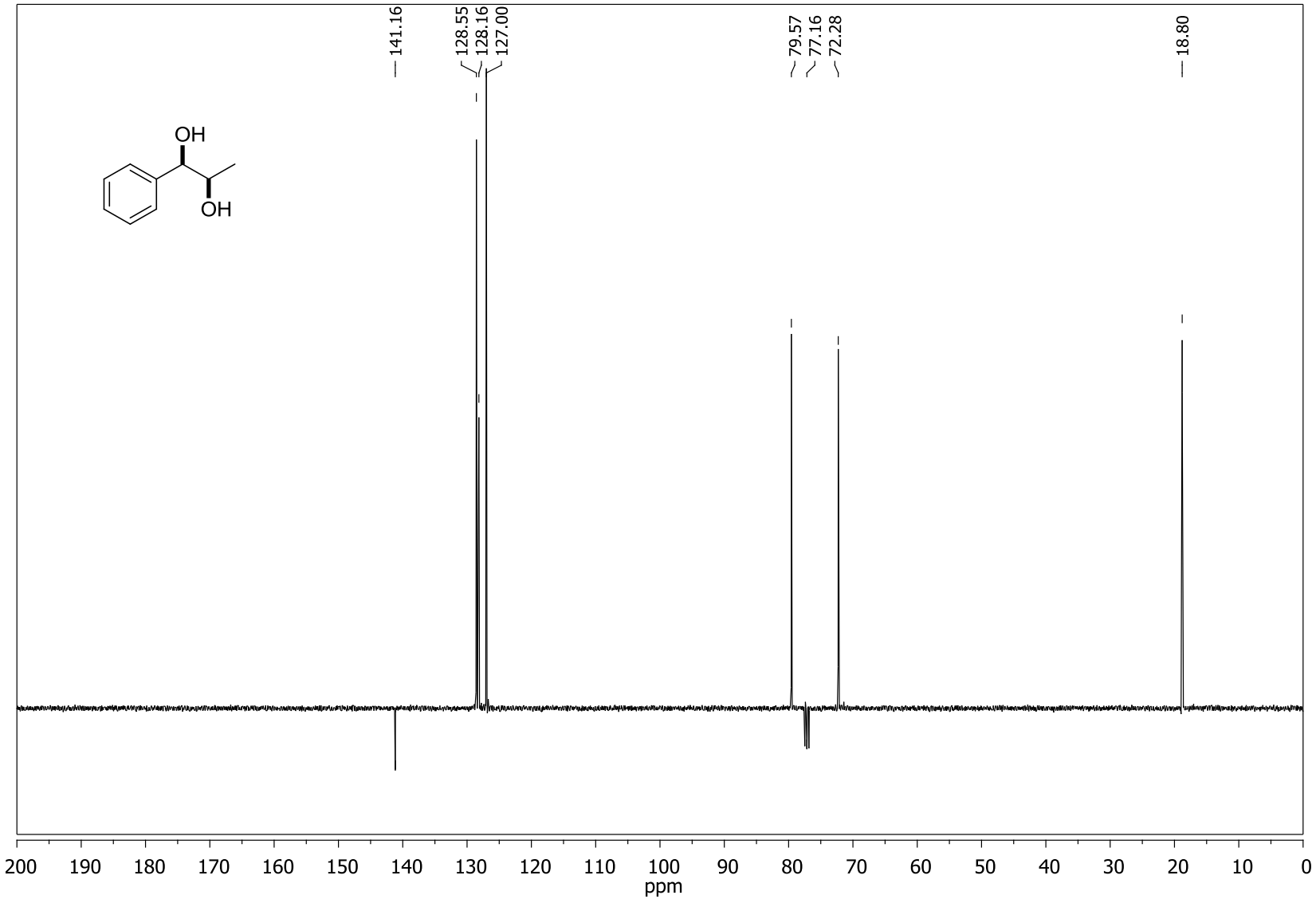
rel-(1*R*,2*S*)-1-Phenylpropane-1,2-diol **51**: ^{13}C NMR DEPTQ-135 (100 MHz, $CDCl_3$)



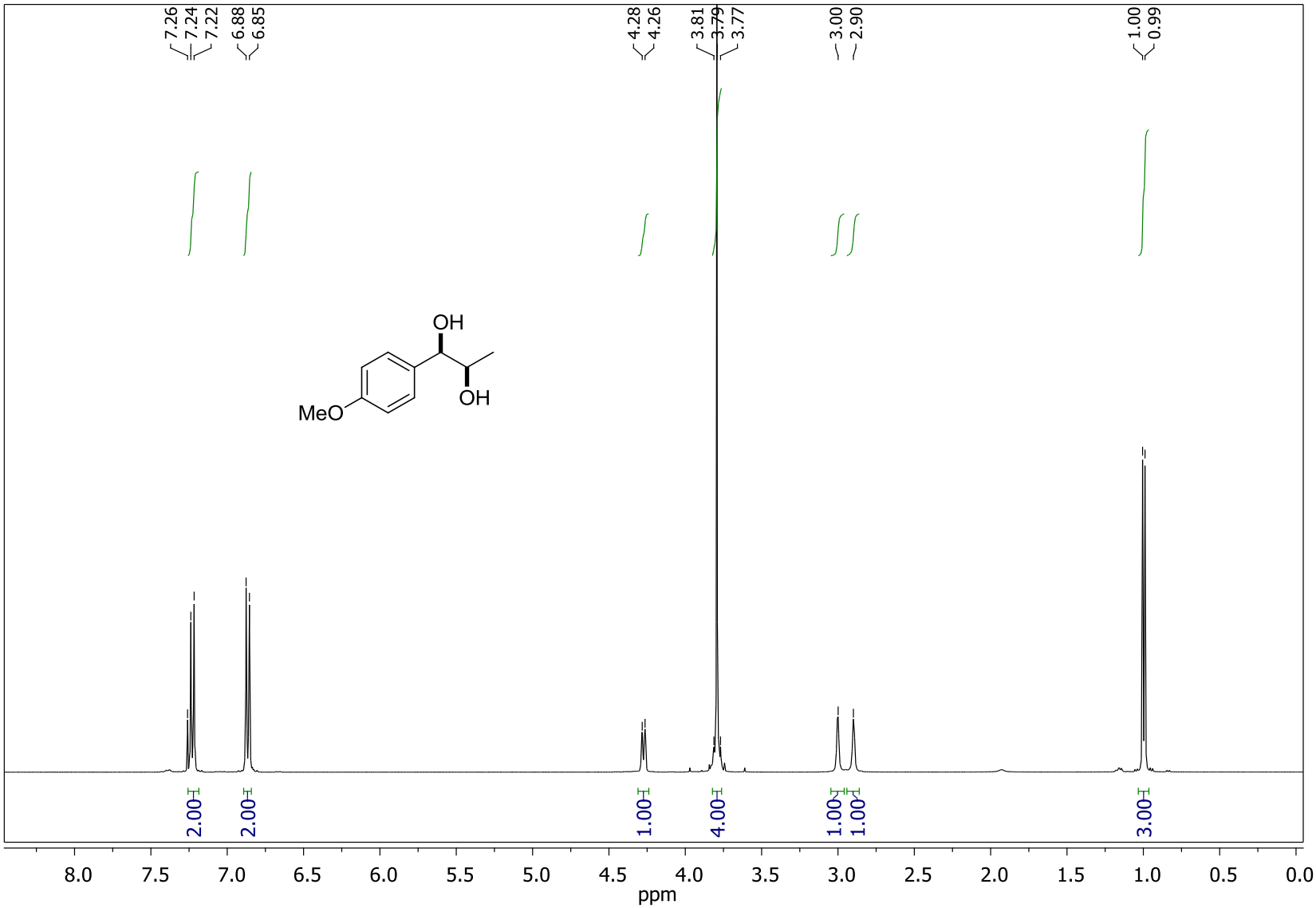
rel-(1*R*,2*R*)-1-Phenylpropane-1,2-diol **52**: ^{1}H NMR (400 MHz, $CDCl_3$)



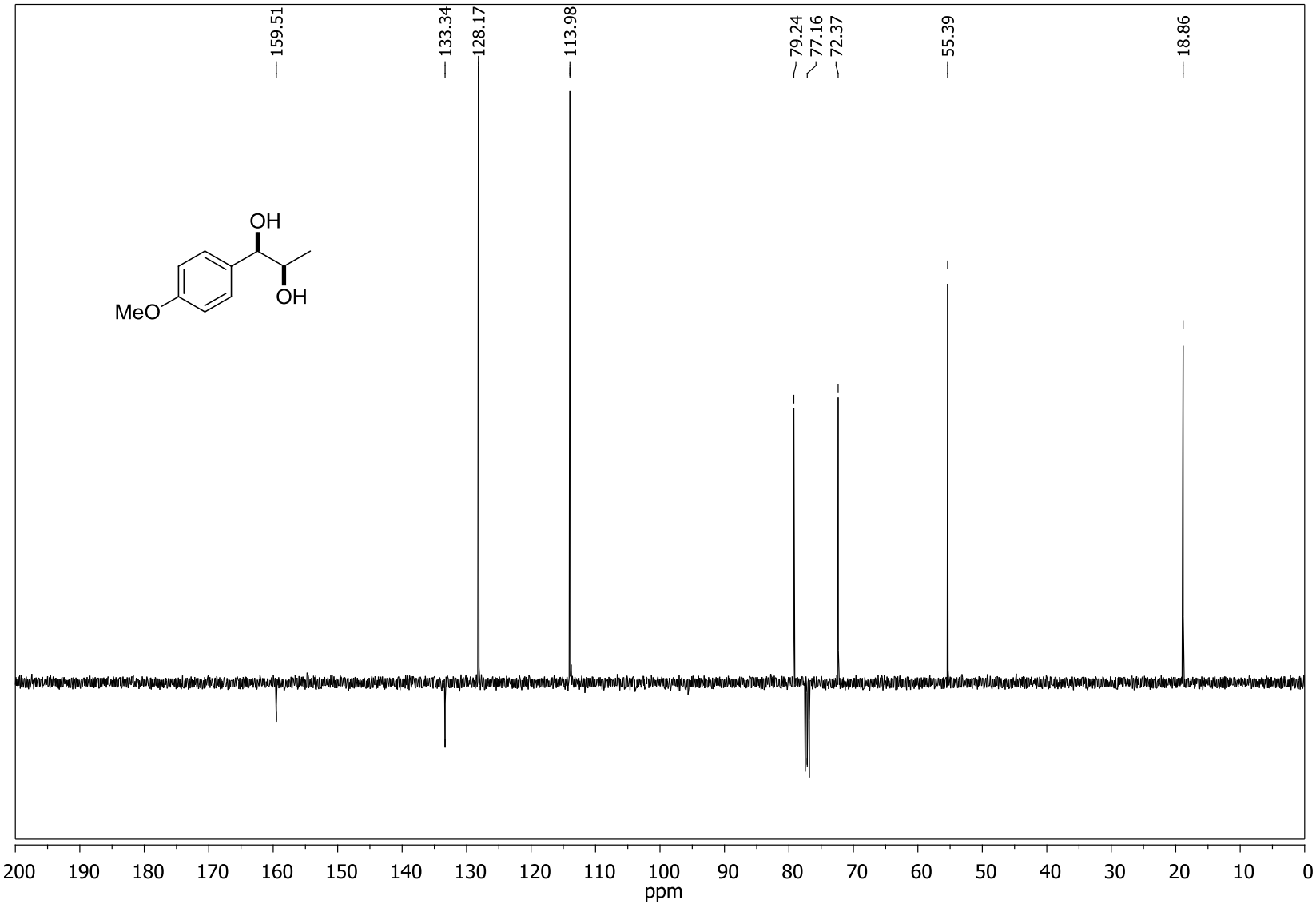
rel-(1*R*,2*R*)-1-Phenylpropane-1,2-diol **52**: ^{13}C NMR DEPTQ-135 (100 MHz, $CDCl_3$)



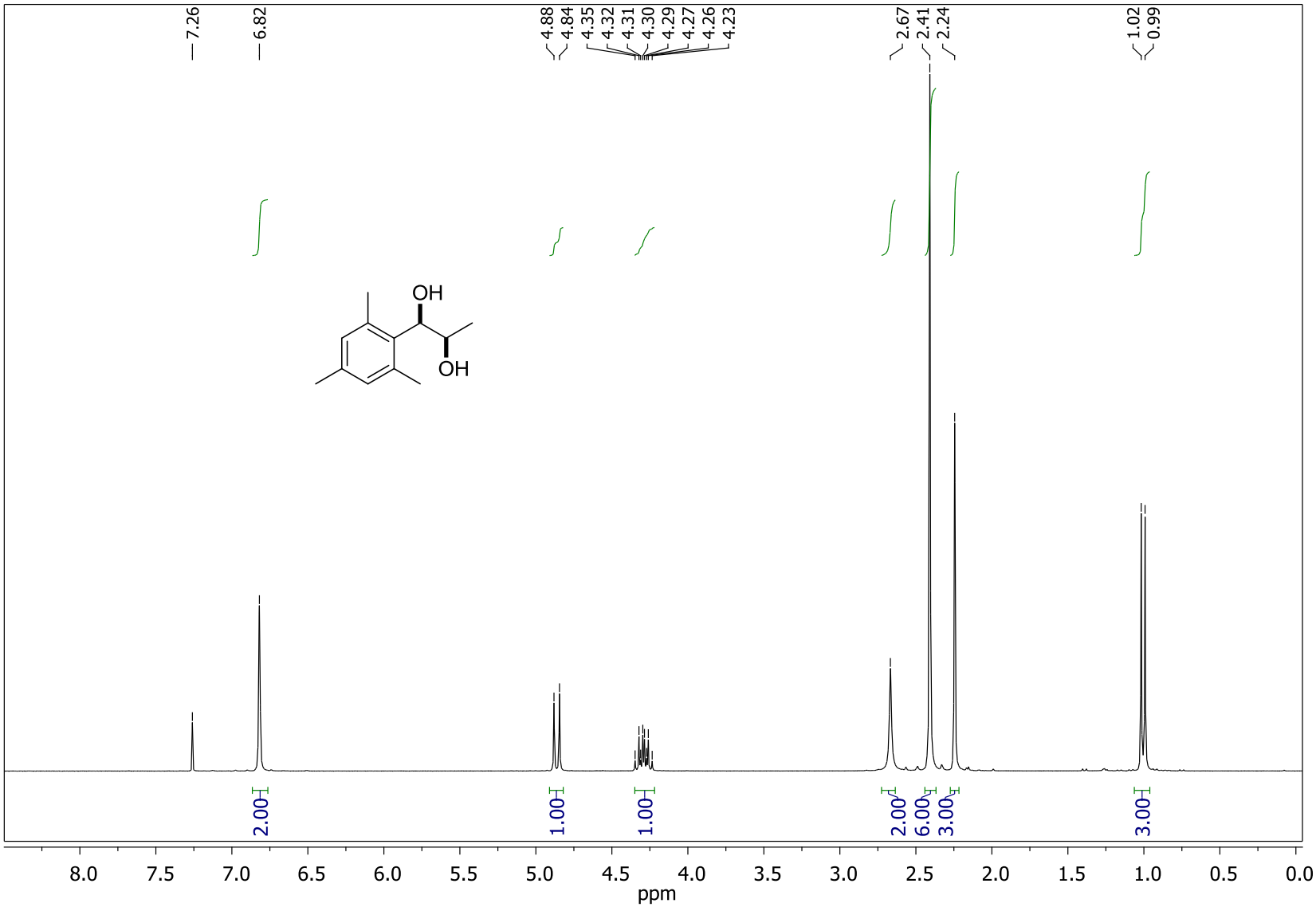
rel-(1*R*,2*R*)-1-(4-Methoxyphenyl)propane-1,2-diol **54**: ^{1}H NMR (400 MHz, $CDCl_3$)



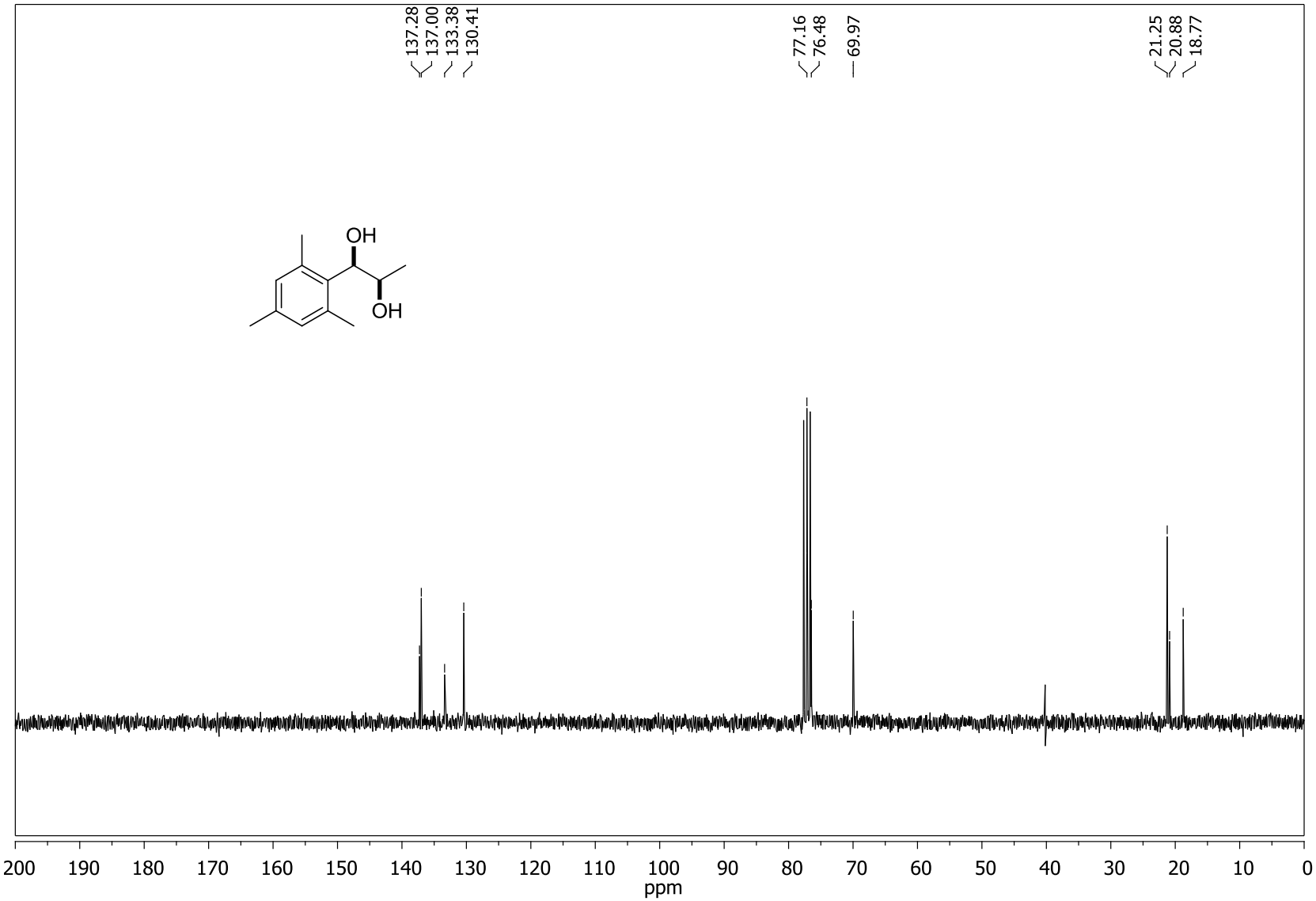
rel-(1*R*,2*R*)-1-(4-Methoxyphenyl)propane-1,2-diol **54**: ^{13}C NMR DEPTQ-135 (100 MHz, $CDCl_3$)



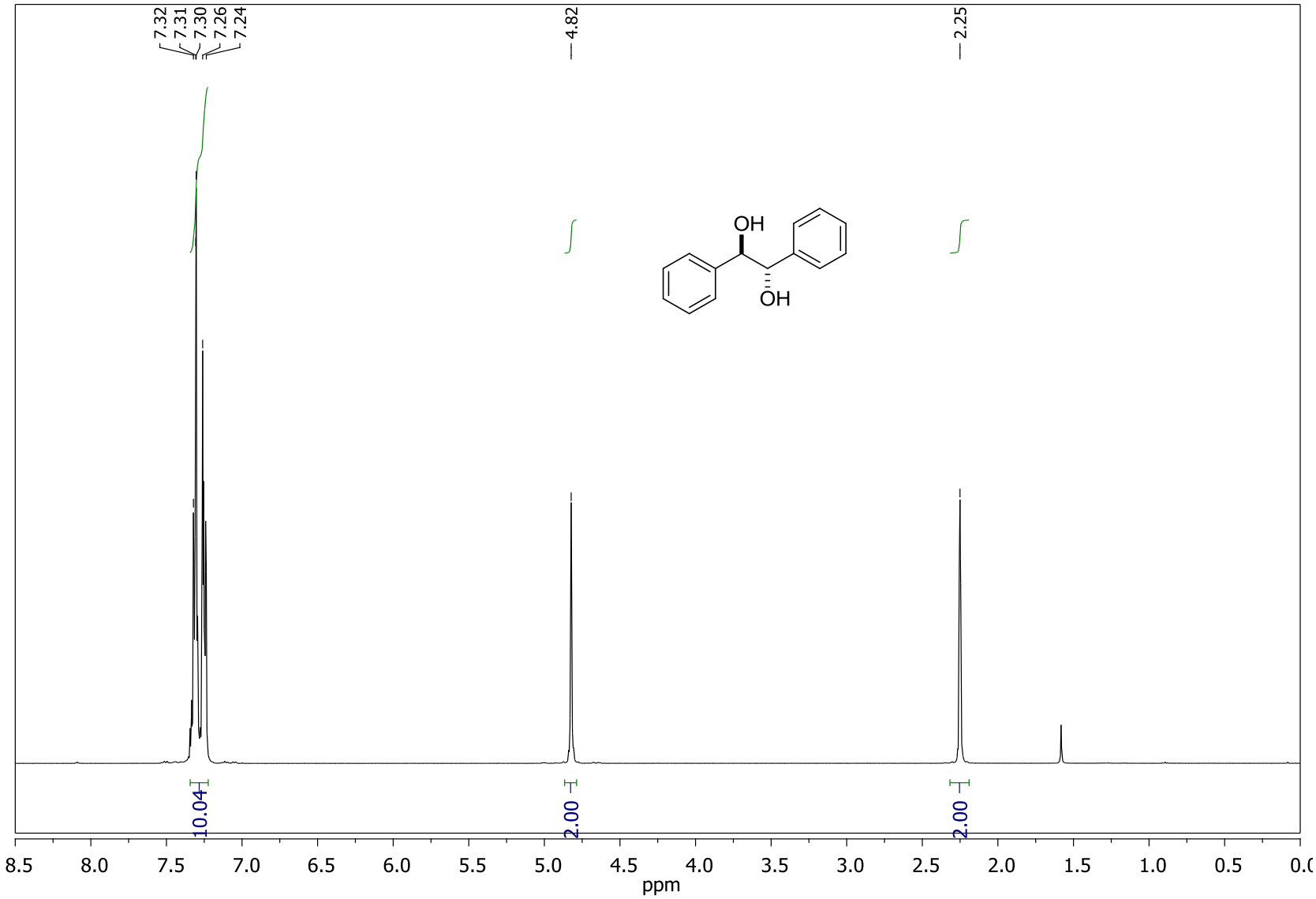
rel-(1*R*,2*R*)-1-Mesitylpropane-1,2-diol **55**: ^{1}H NMR (250 MHz, $CDCl_3$)



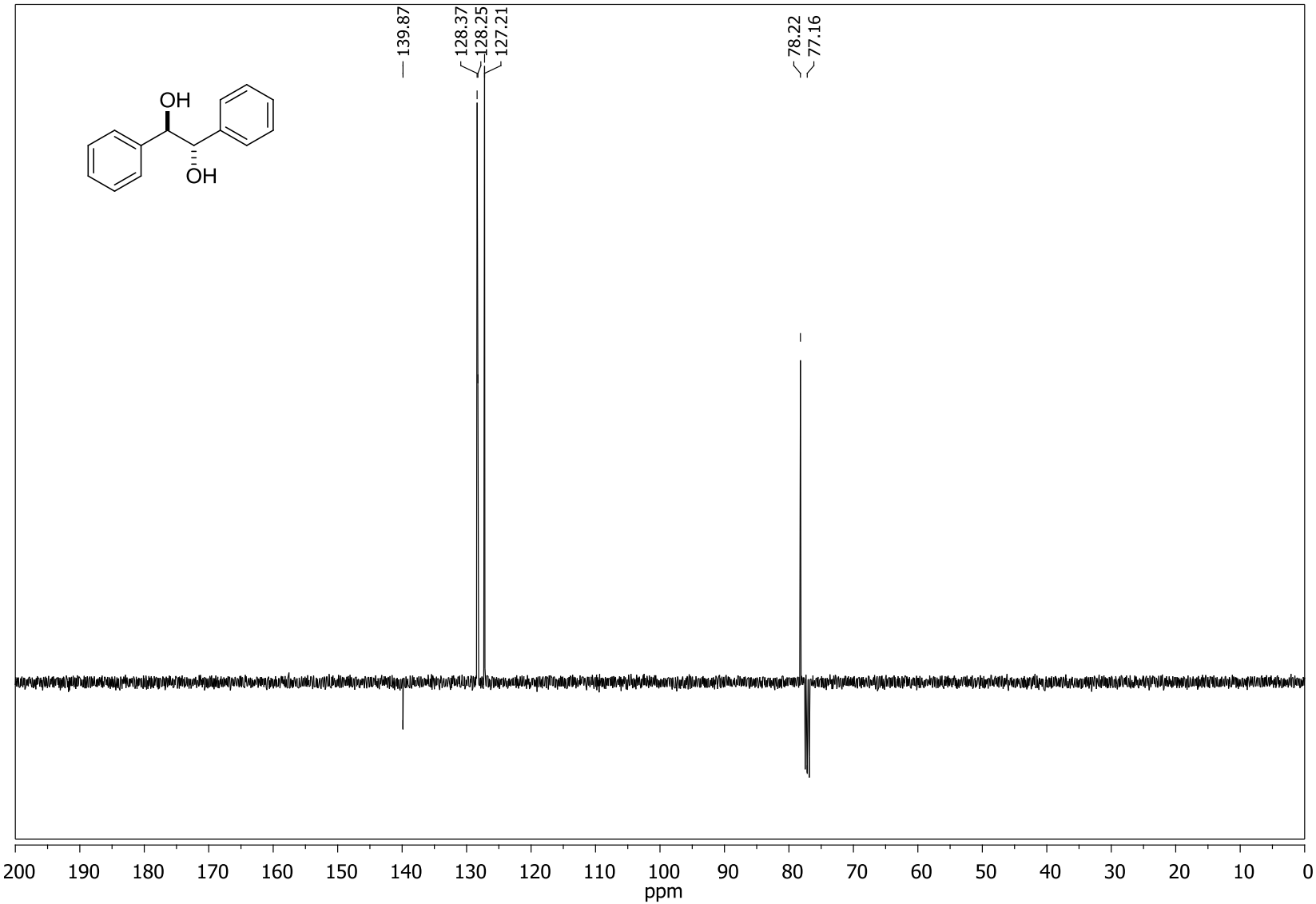
rel-(1*R*,2*R*)-1-Mesitylpropane-1,2-diol **55**: ^{13}C NMR DEPTQ-135 (62.5 MHz, $CDCl_3$)



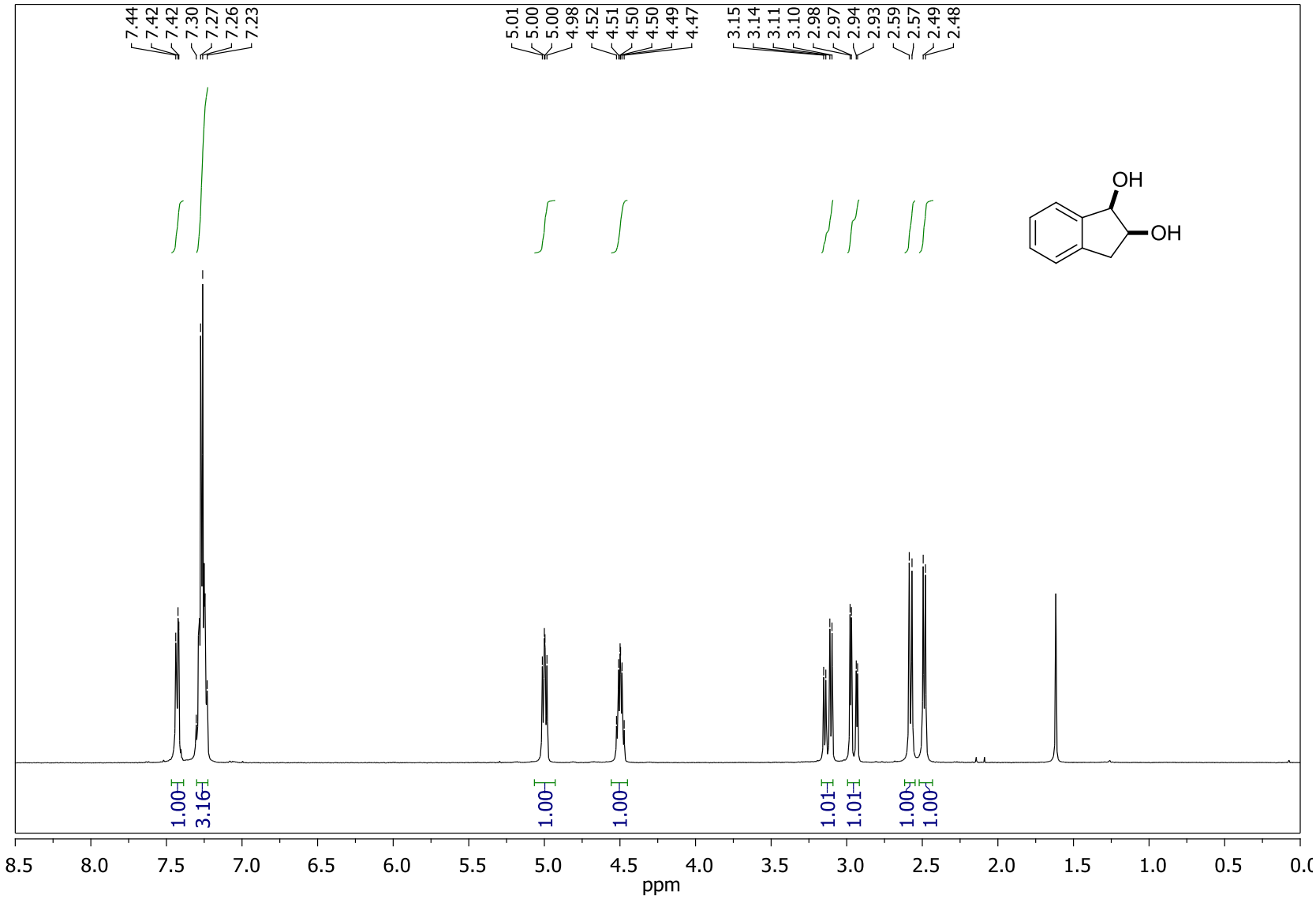
rel-(1*R*,2*S*)-1,2-Diphenylethane-1,2-diol **56**: ^{1}H NMR (400 MHz, $CDCl_3$)



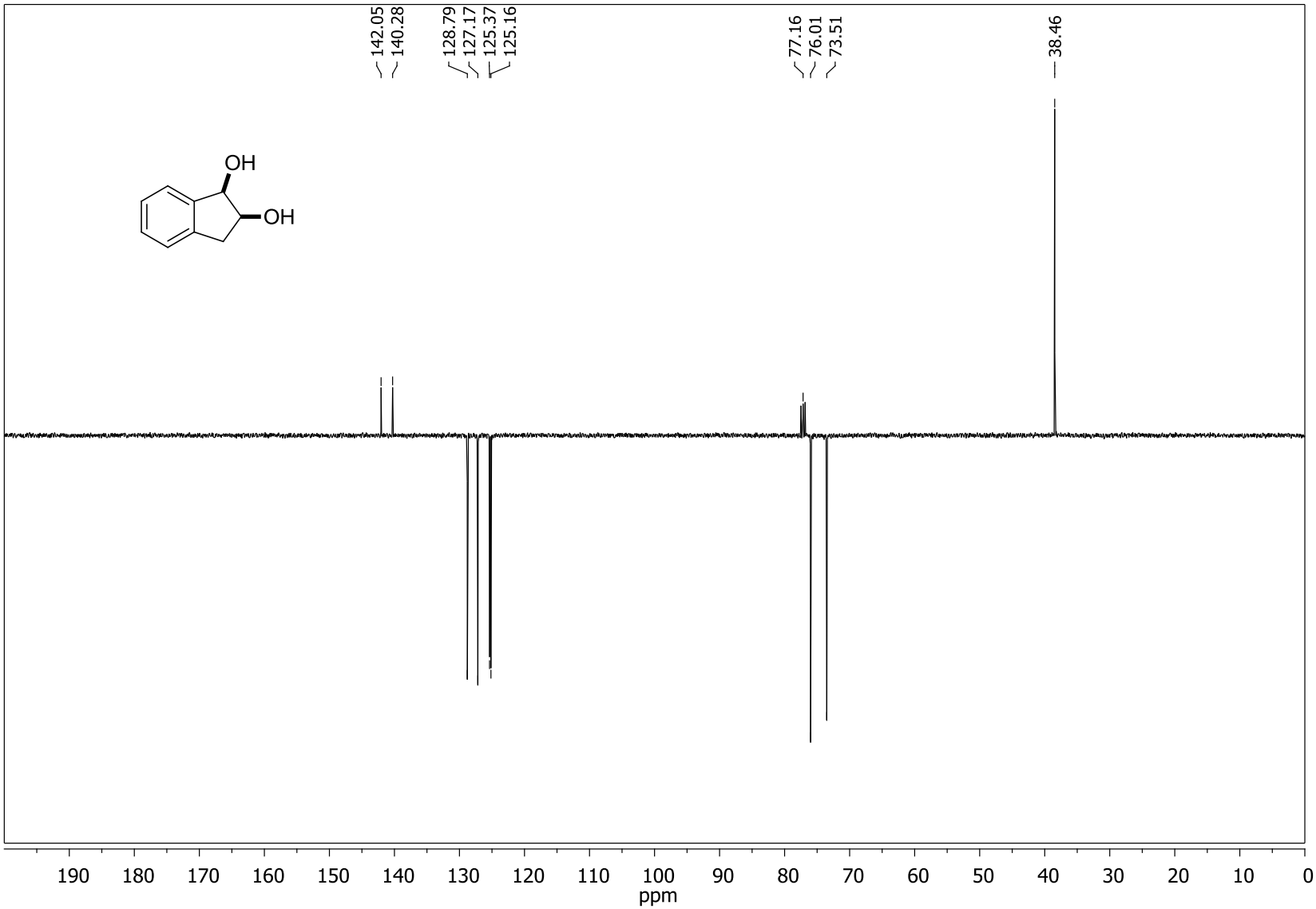
rel-(1*R*,2*S*)-1,2-Diphenylethane-1,2-diol **56**: ^{13}C NMR DEPTQ-135 (100 MHz, $CDCl_3$)



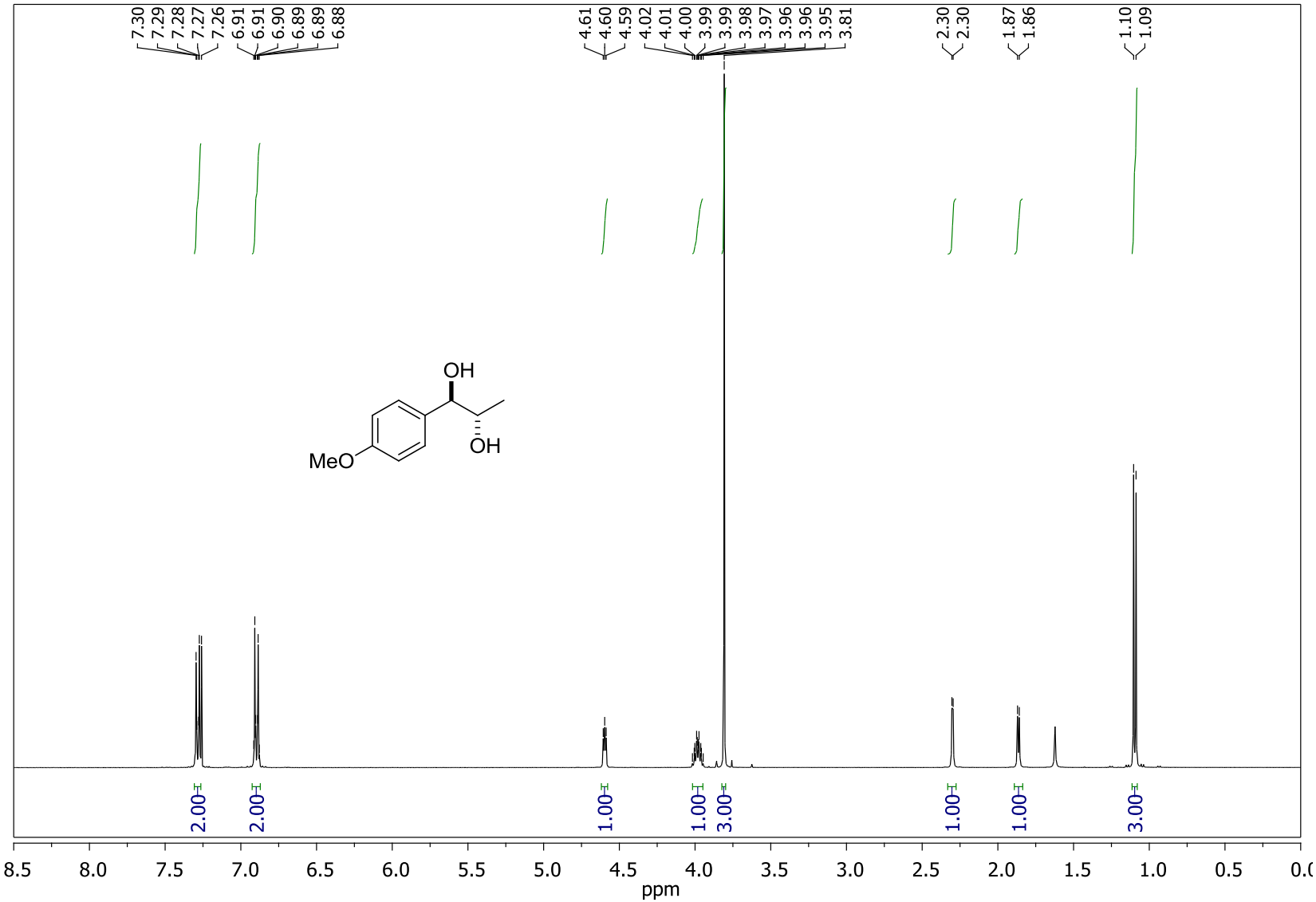
rel-(1*R*,2*S*)-2,3-Dihydro-1*H*-indene-1,2-diol **57**: ^{1}H NMR (400 MHz, $CDCl_3$)



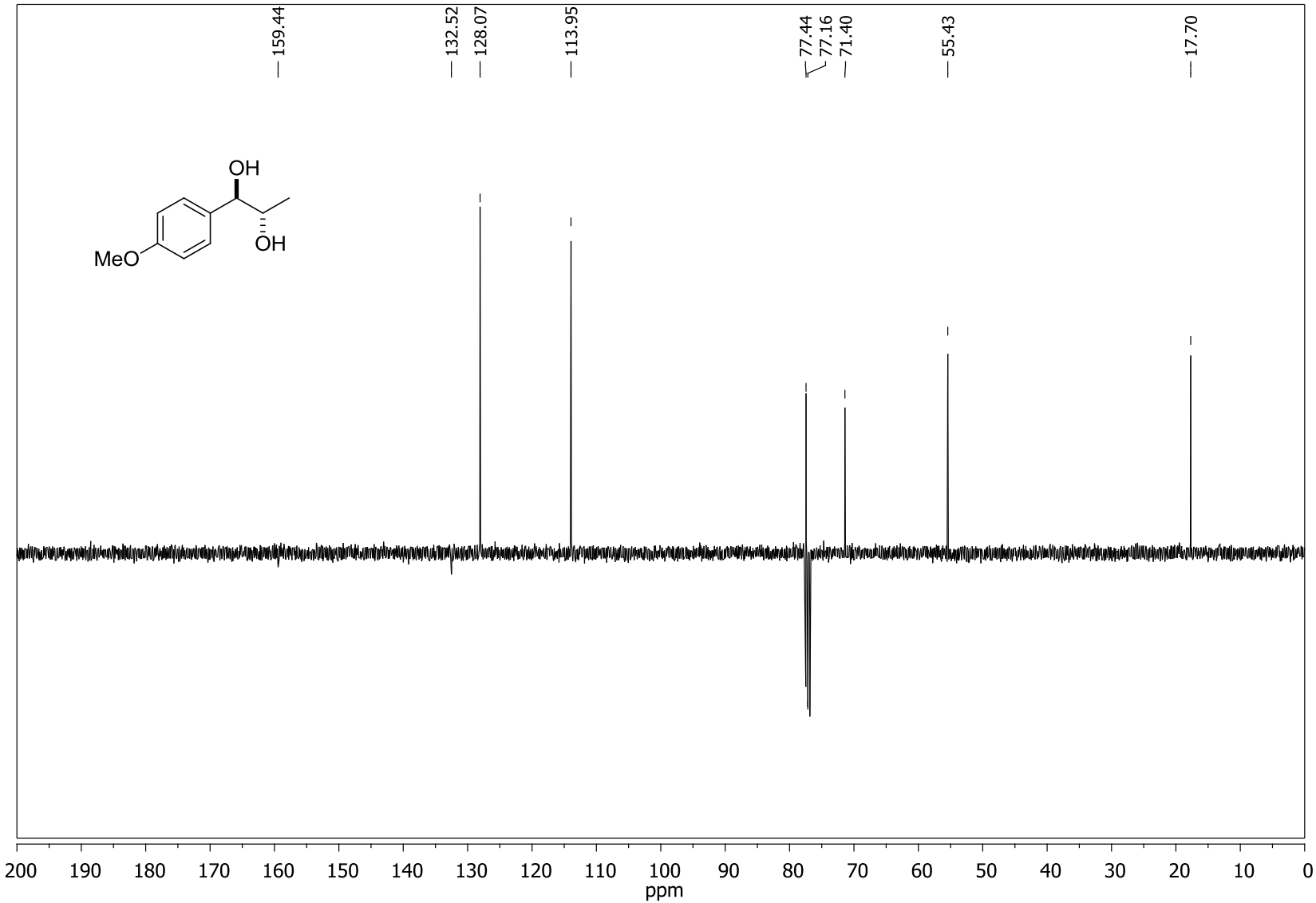
rel-(1*R*,2*S*)-2,3-Dihydro-1*H*-indene-1,2-diol **57**: ^{13}C NMR DEPTQ-135 (100 MHz, $CDCl_3$)



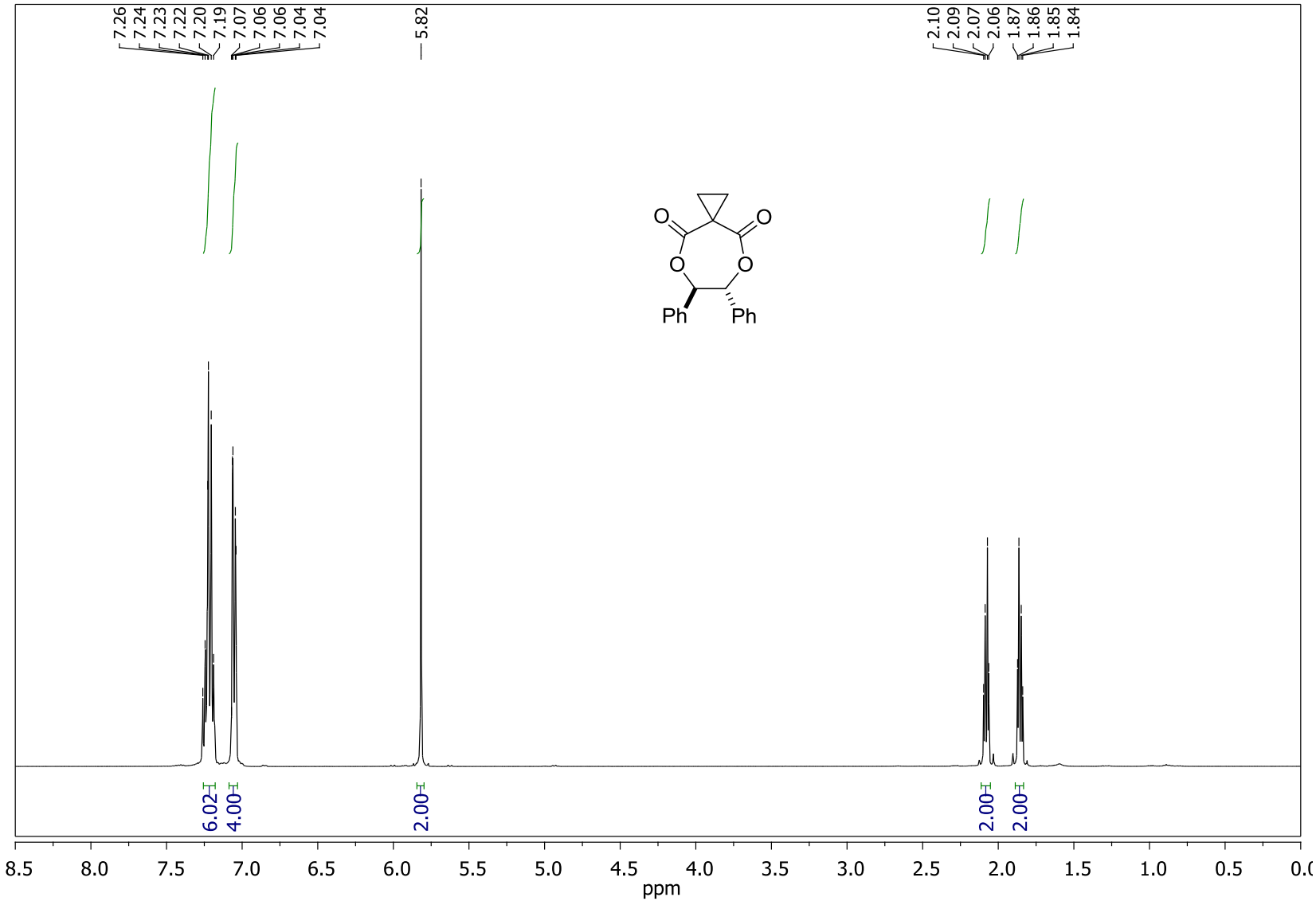
rel-(1*R*,2*S*)-1-(4-Methoxyphenyl)propane-1,2-diol **S66**: ^{1}H NMR (400 MHz, $CDCl_3$)



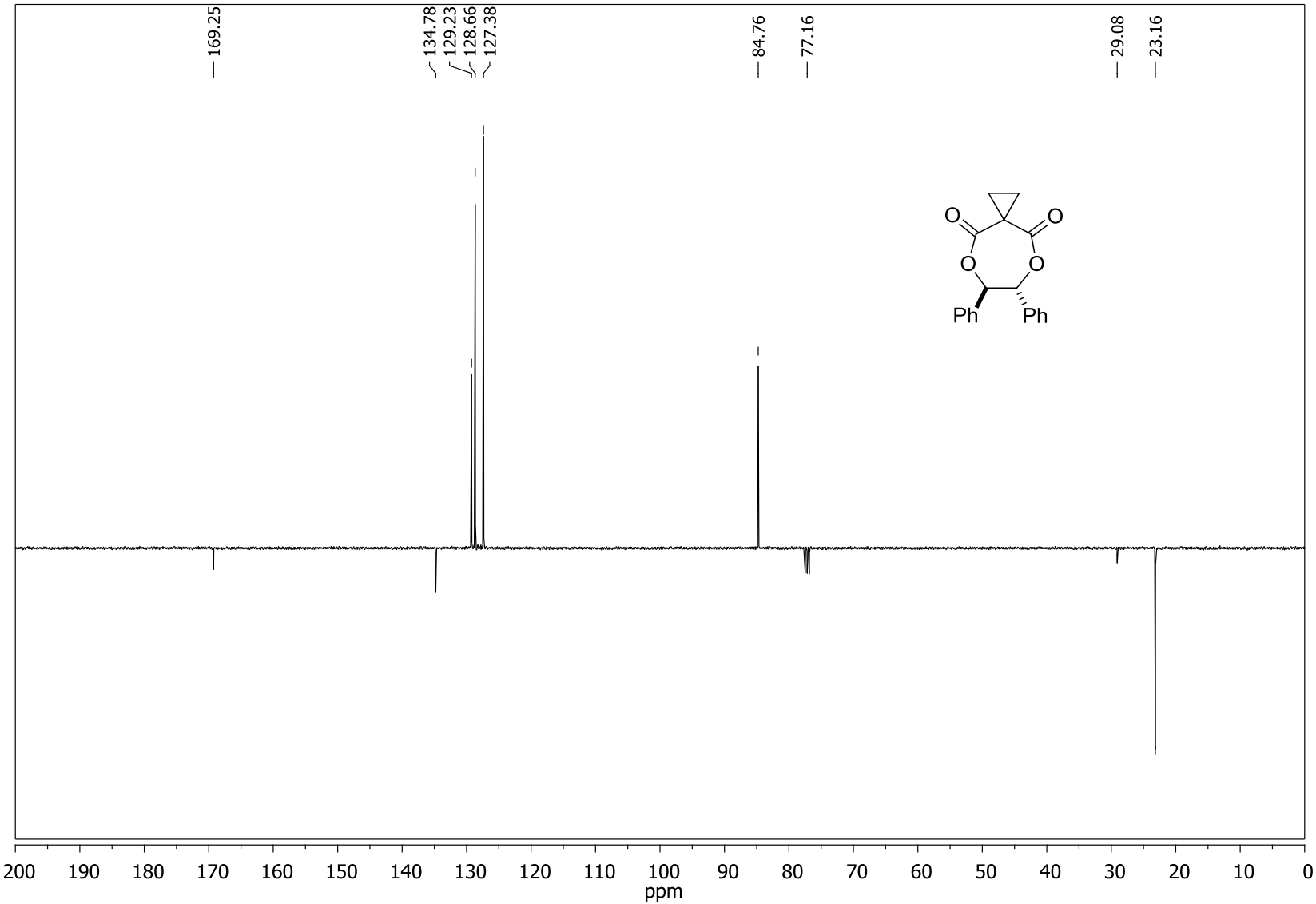
rel-(1*R*,2*S*)-1-(4-Methoxyphenyl)propane-1,2-diol **S66**: ^{13}C NMR DEPTQ-135 (100 MHz, $CDCl_3$)



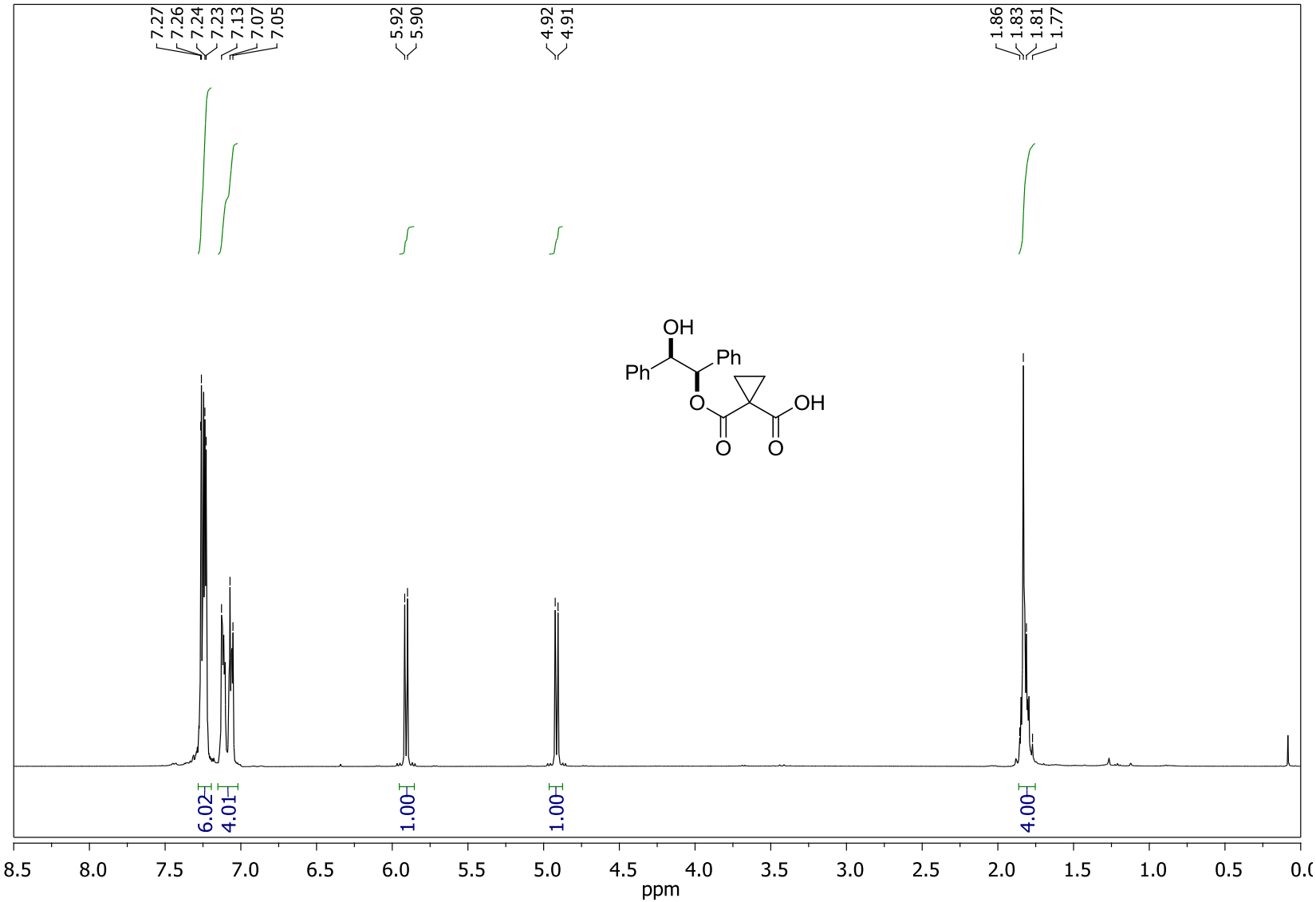
***rel*-(6*R*,7*R*)-6,7-Diphenyl-5,8-dioxaspiro[2.6]nonane-4,9-dione 14** ^{1}H NMR (400 MHz, $CDCl_3$)



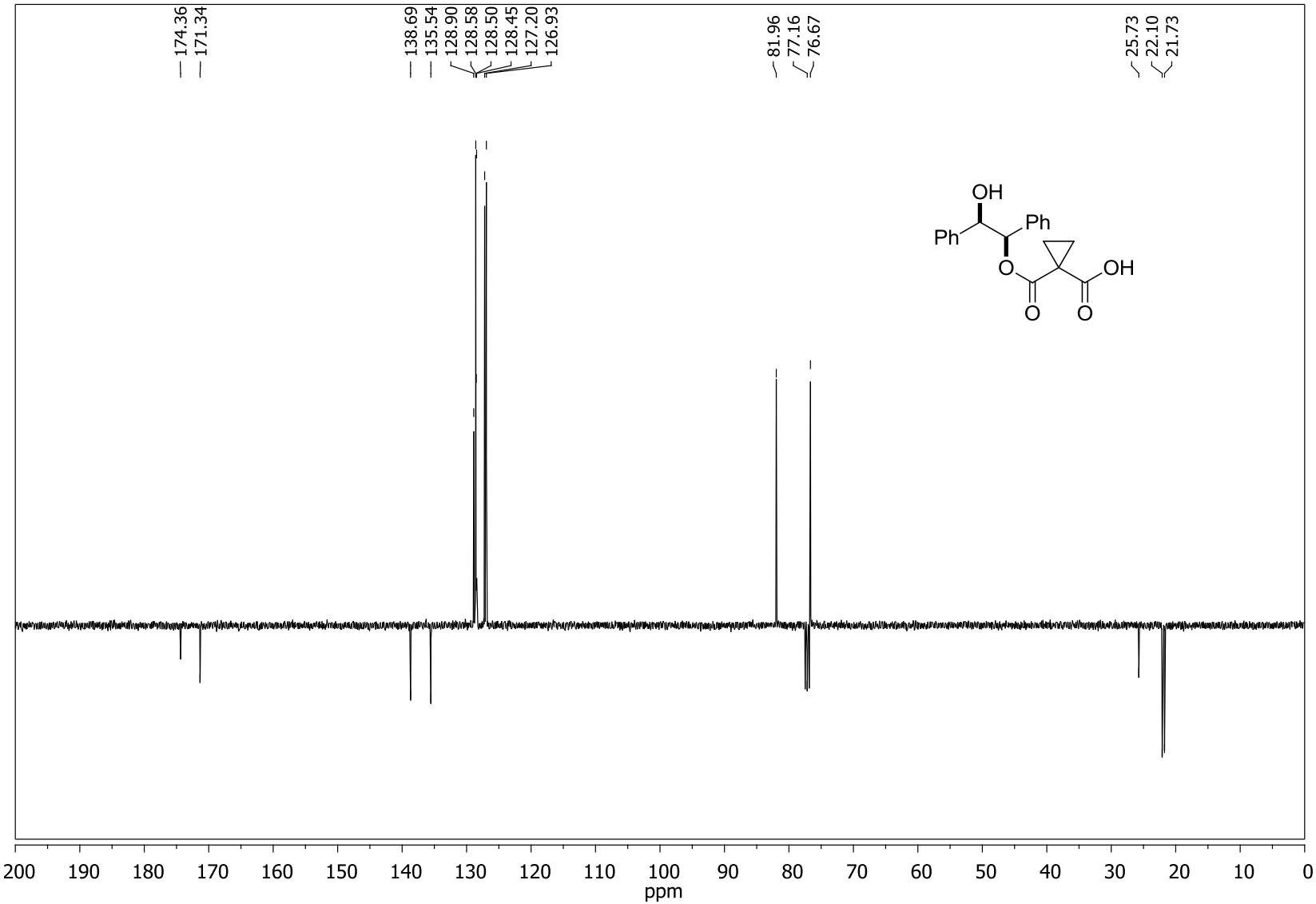
***rel*-(6*R*,7*R*)-6,7-Diphenyl-5,8-dioxaspiro[2.6]nonane-4,9-dione 14**: ^{13}C NMR DEPTQ-135 (100 MHz, $CDCl_3$)



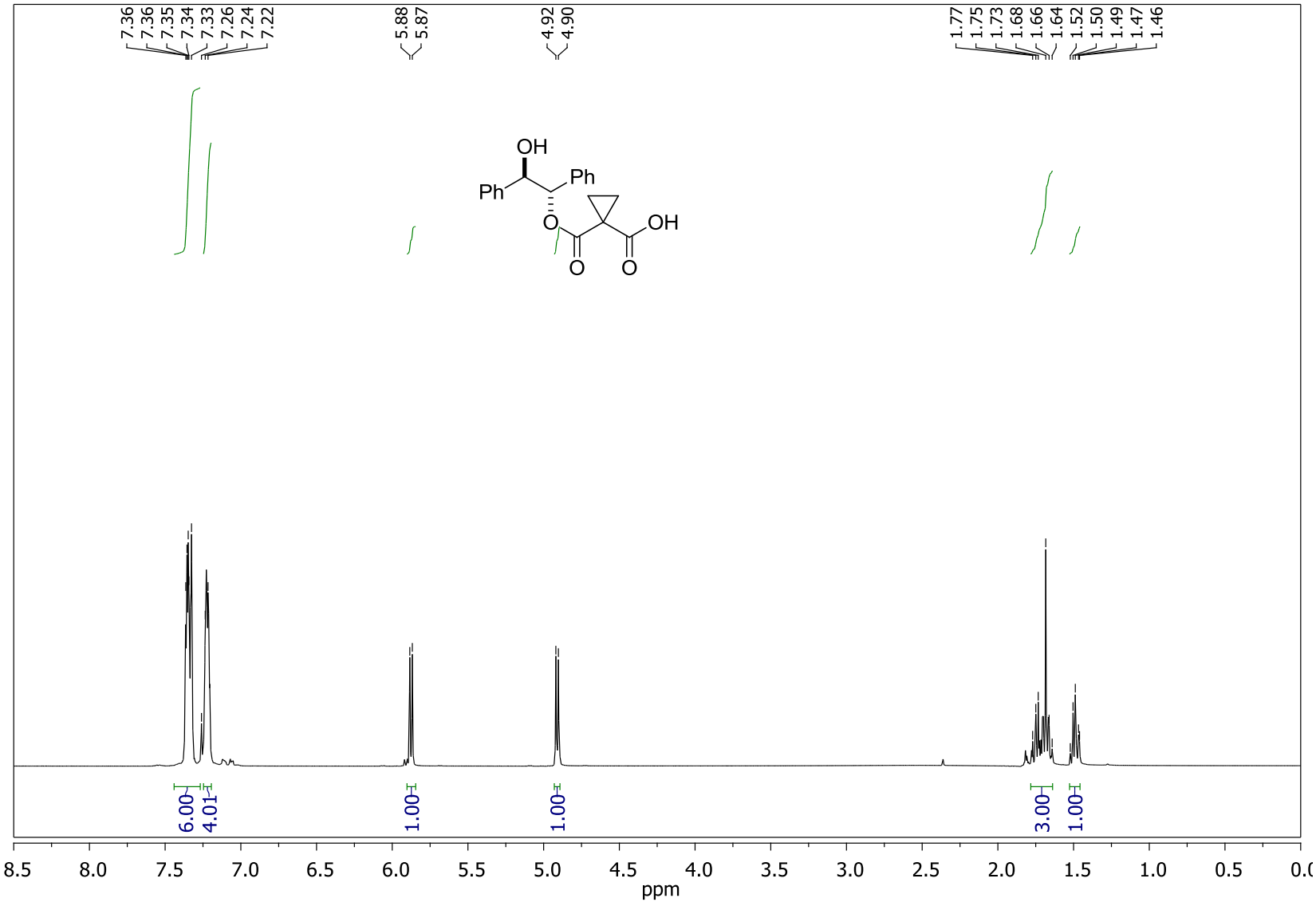
1-(((*rel*-1*R*,2*R*)-2-Hydroxy-1,2-diphenylethoxy)carbonyl)cyclopropanecarboxylic acid 15: ^{1}H NMR (400 MHz, $CDCl_3$)



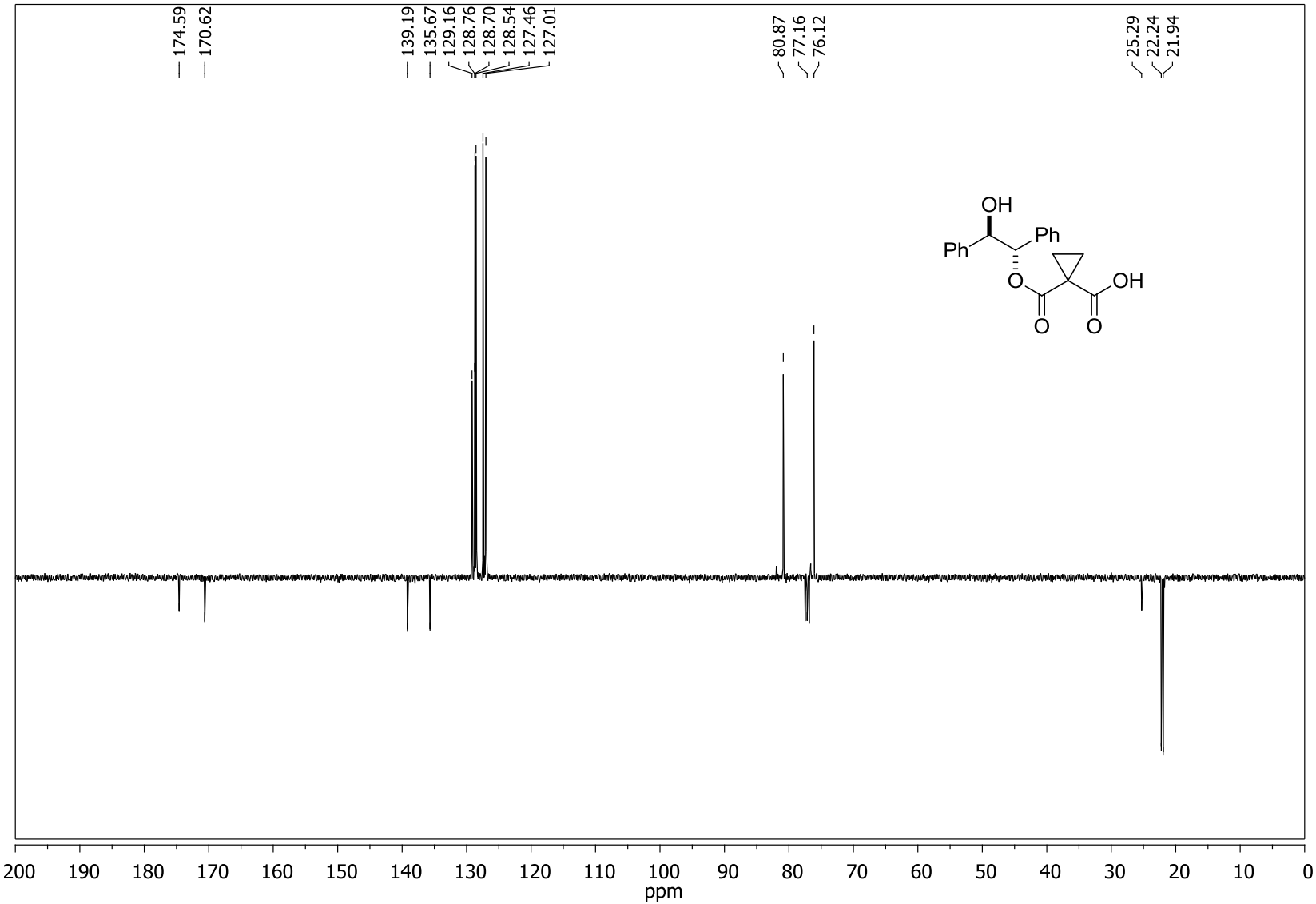
1-(((*rel*-1*R*,2*R*)-2-Hydroxy-1,2-diphenylethoxy)carbonyl)cyclopropanecarboxylic acid 15: ^{1}H NMR DEPTQ-135 (100 MHz, $CDCl_3$)



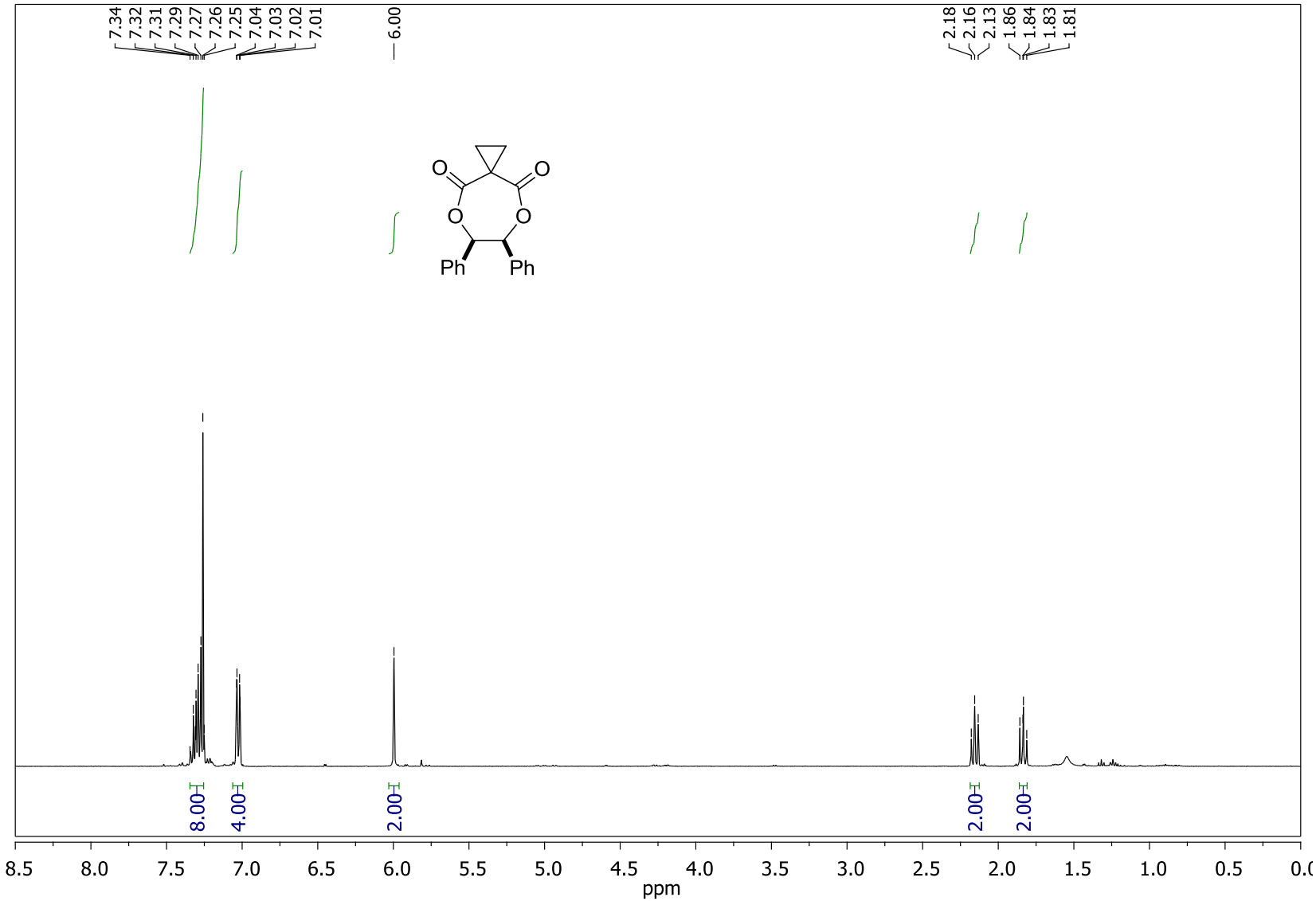
1-(((*rel*-1*S*,2*R*)-2-Hydroxy-1,2-diphenylethoxy)carbonyl)cyclopropanecarboxylic acid 58: ^{1}H NMR (400 MHz, $CDCl_3$)



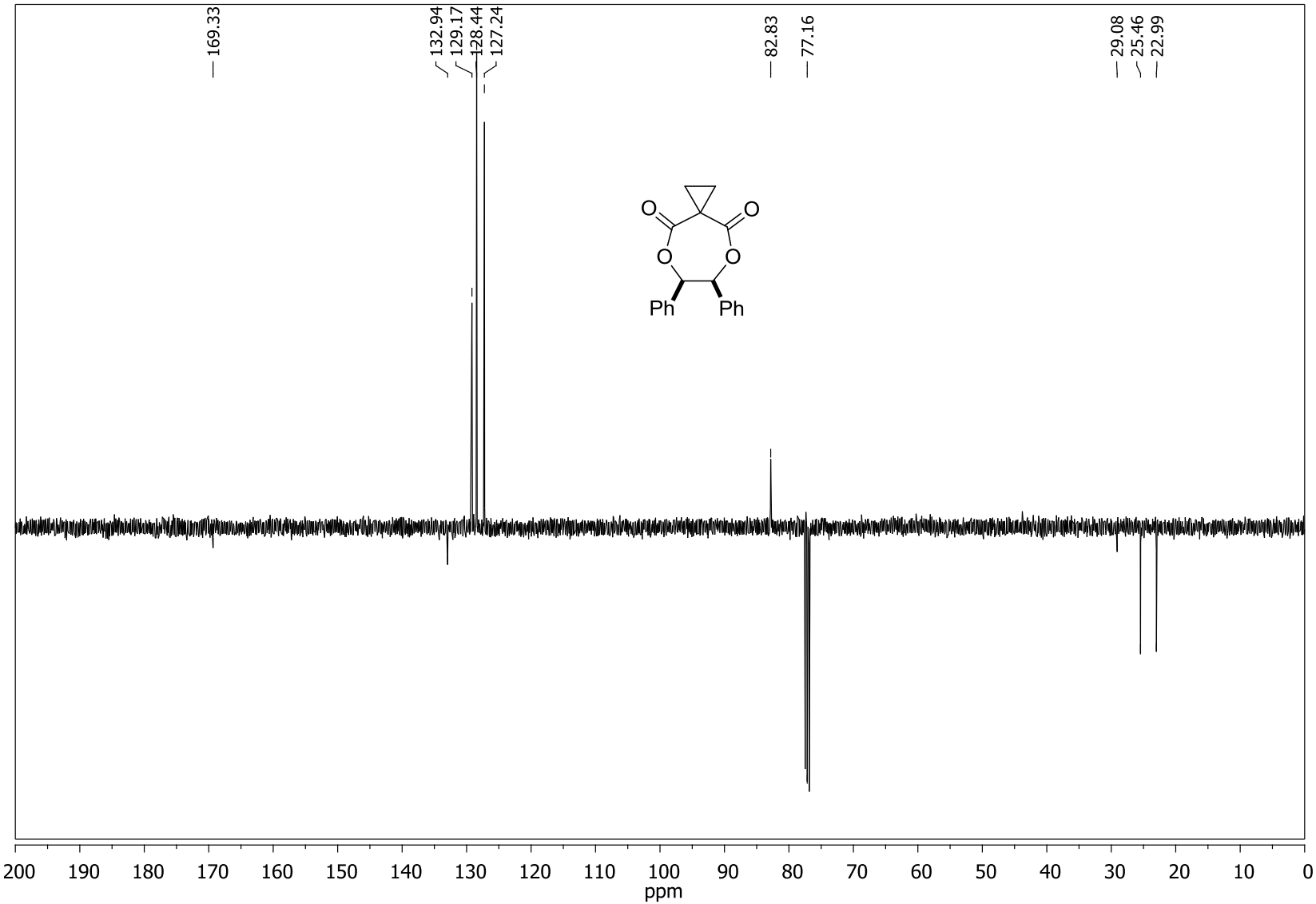
1-(((*rel*-1*S*,2*R*)-2-Hydroxy-1,2-diphenylethoxy)carbonyl)cyclopropanecarboxylic acid 58: ^{13}C NMR DEPTQ-135 (100 MHz, $CDCl_3$)



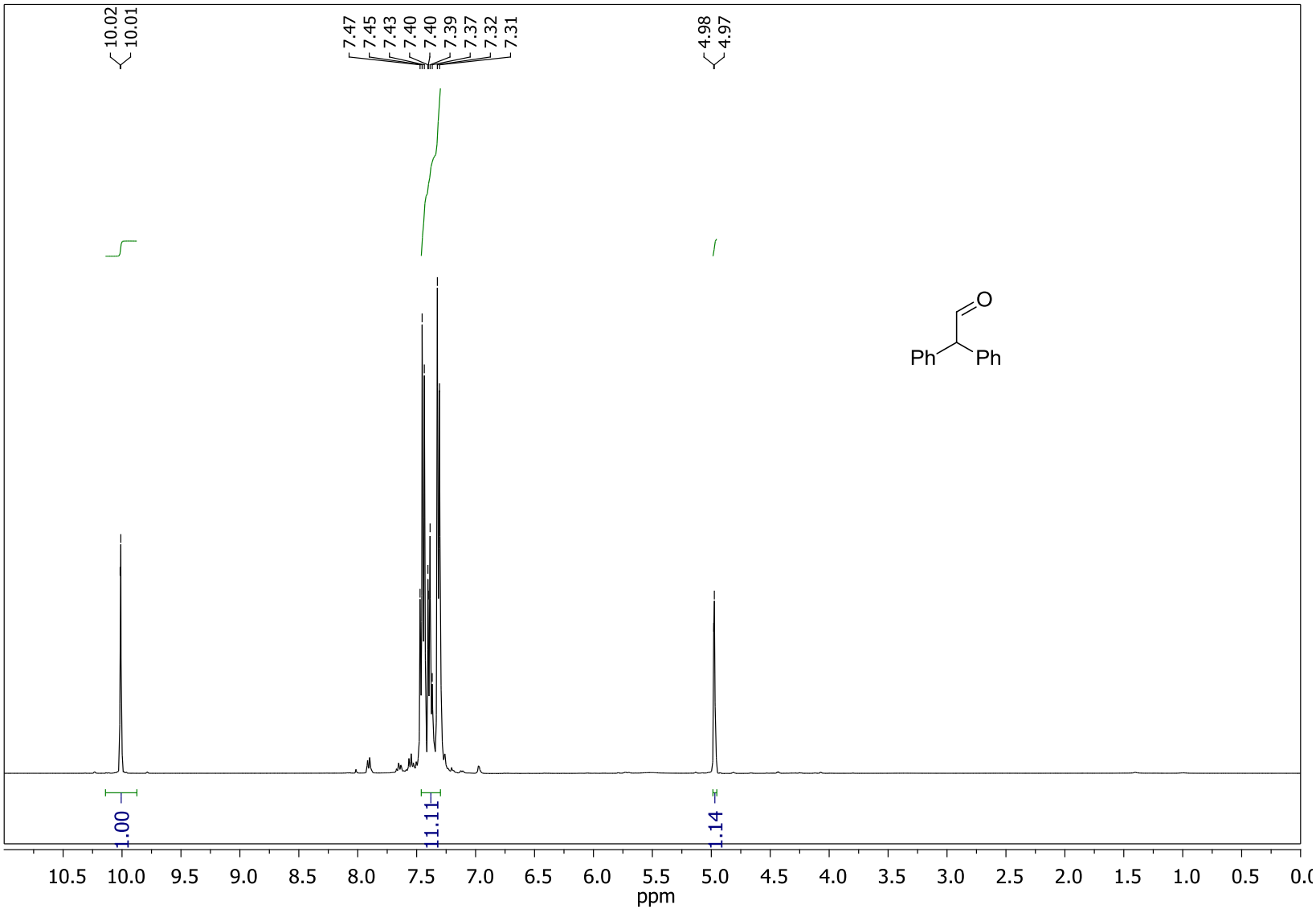
***rel*-(6*R*,7*S*)-6,7-Diphenyl-5,8-dioxaspiro[2.6]nonane-4,9-dione 59**: ^{1}H NMR (400 MHz, $CDCl_3$)



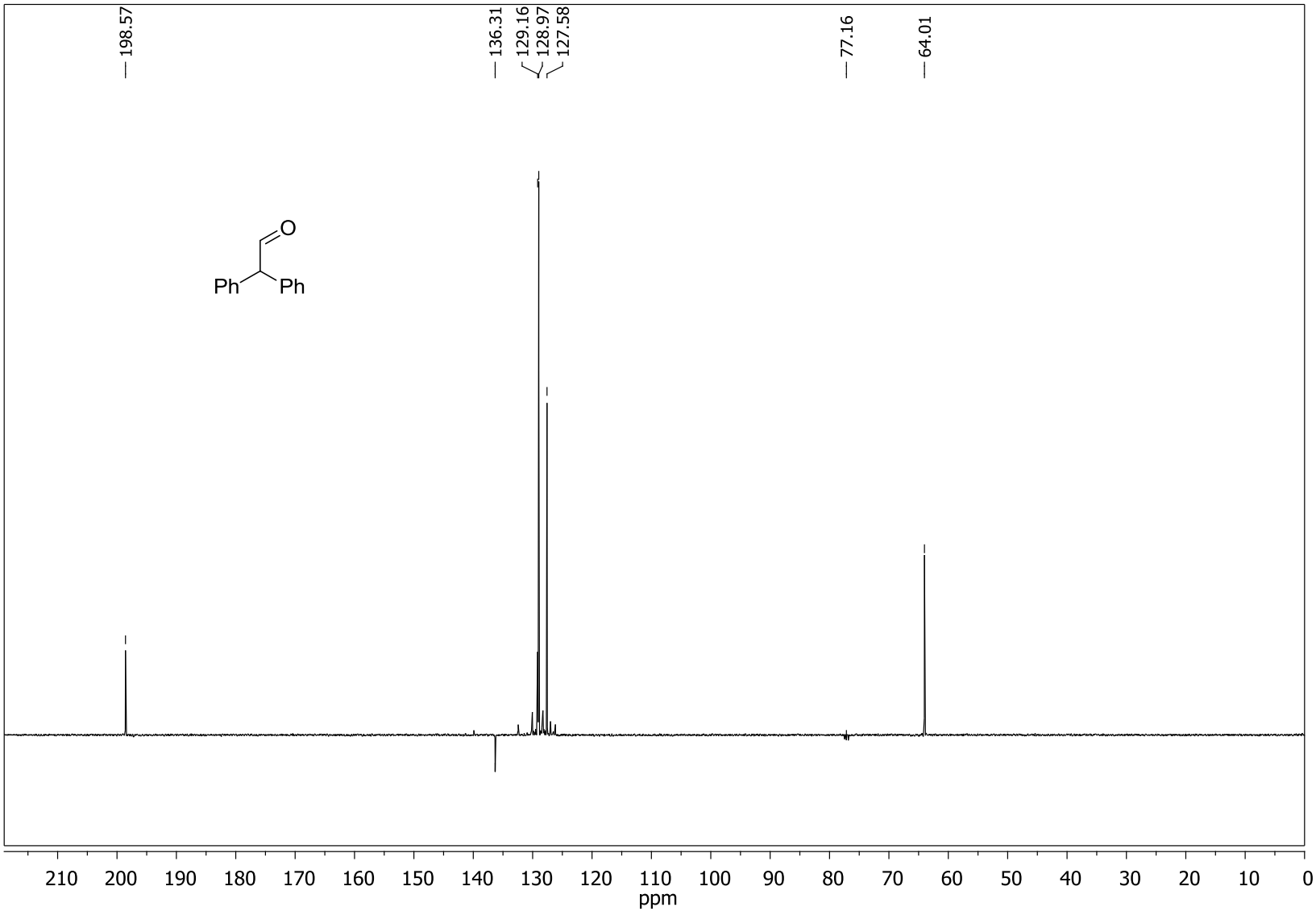
***rel*-(6*R*,7*S*)-6,7-Diphenyl-5,8-dioxaspiro[2.6]nonane-4,9-dione 59**: ^{13}C NMR DEPTQ-135 (100 MHz, $CDCl_3$)



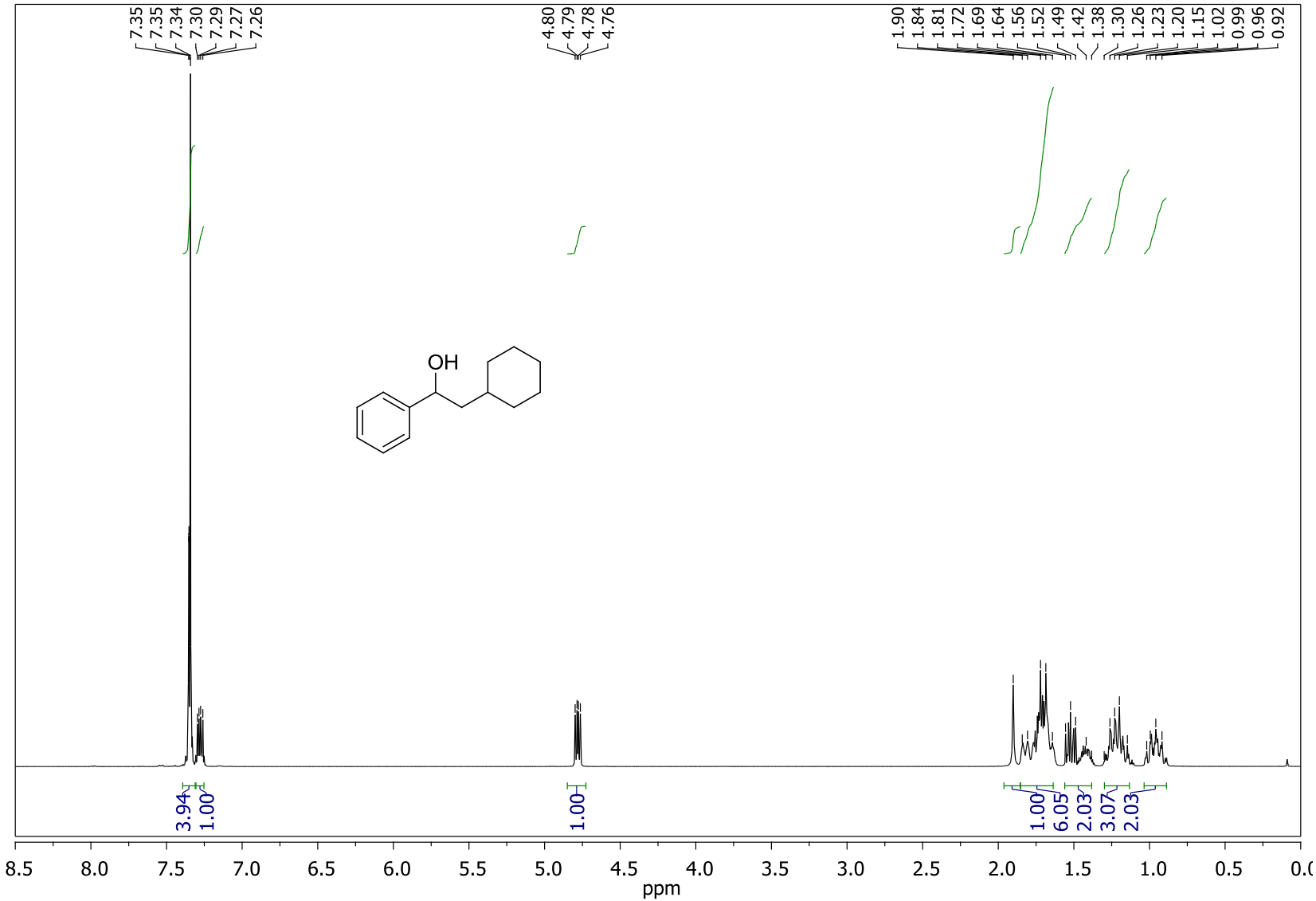
2,2-Diphenylacetaldehyde 61: ^{1}H NMR (400 MHz, $CDCl_3$)



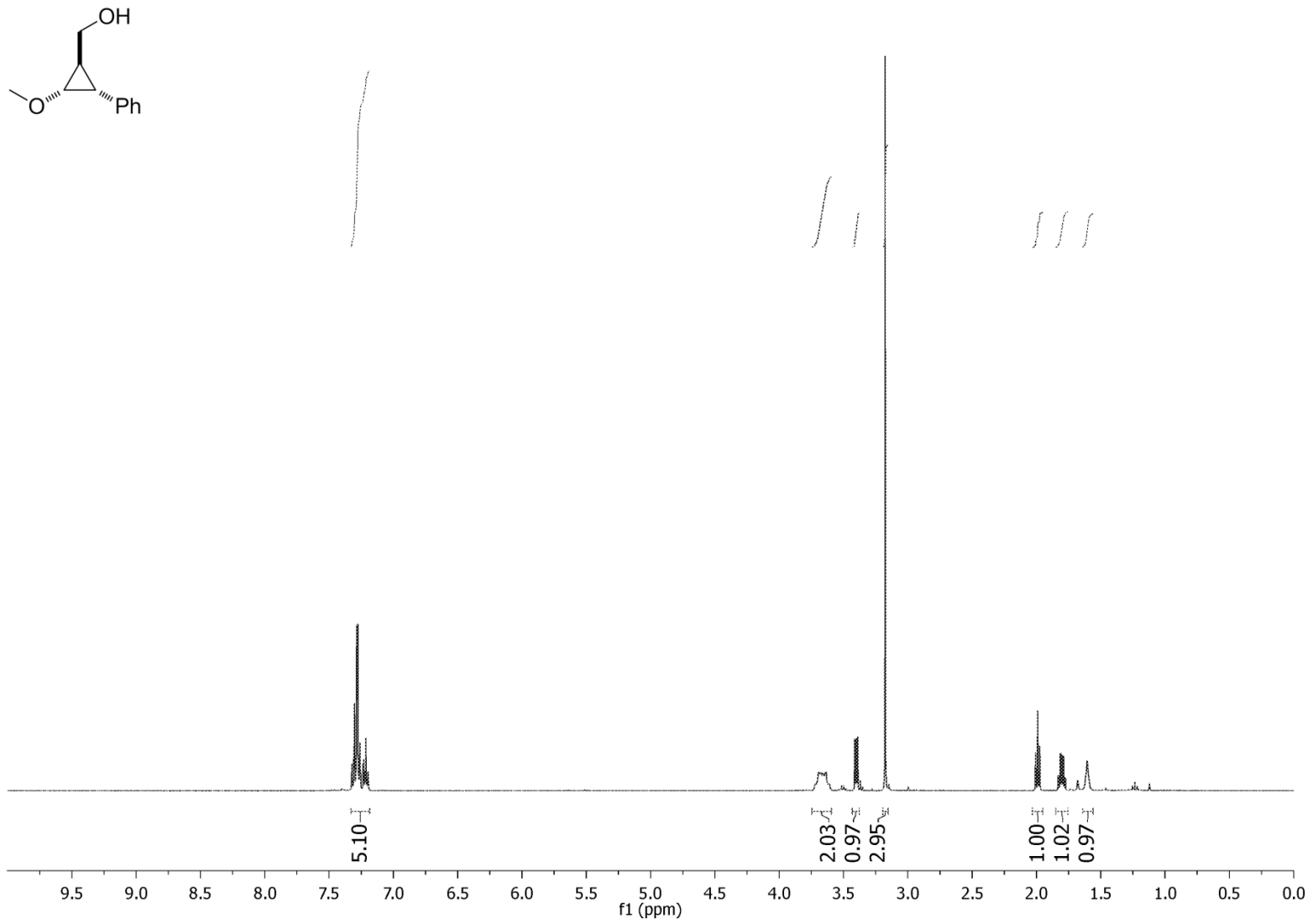
2,2-Diphenylacetaldehyde 61: ^{13}C NMR DEPTQ-135 (100 MHz, $CDCl_3$)



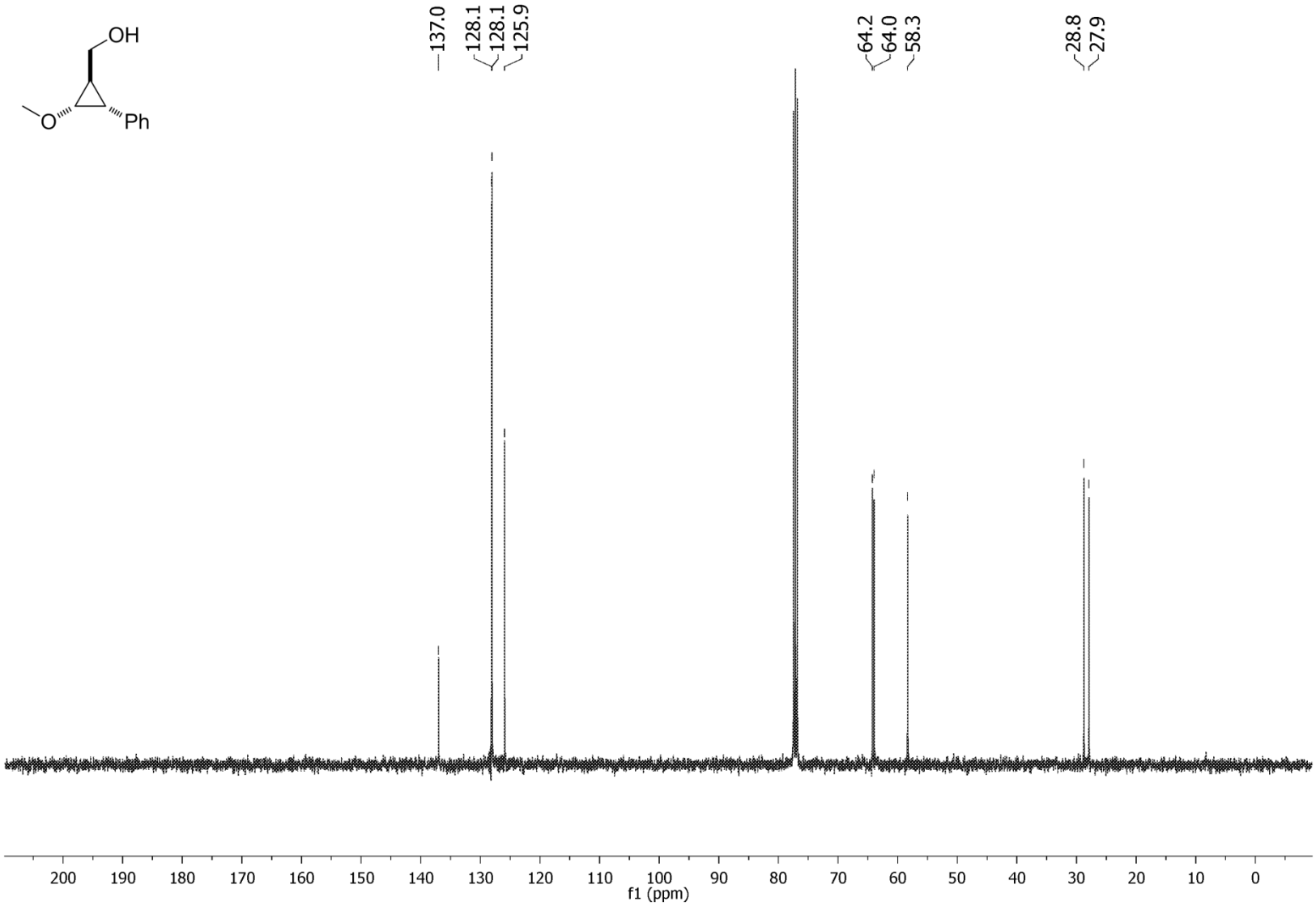
2-Cyclohexyl-1-phenylethanol S67: ^{1}H NMR (400 MHz, $CDCl_3$)



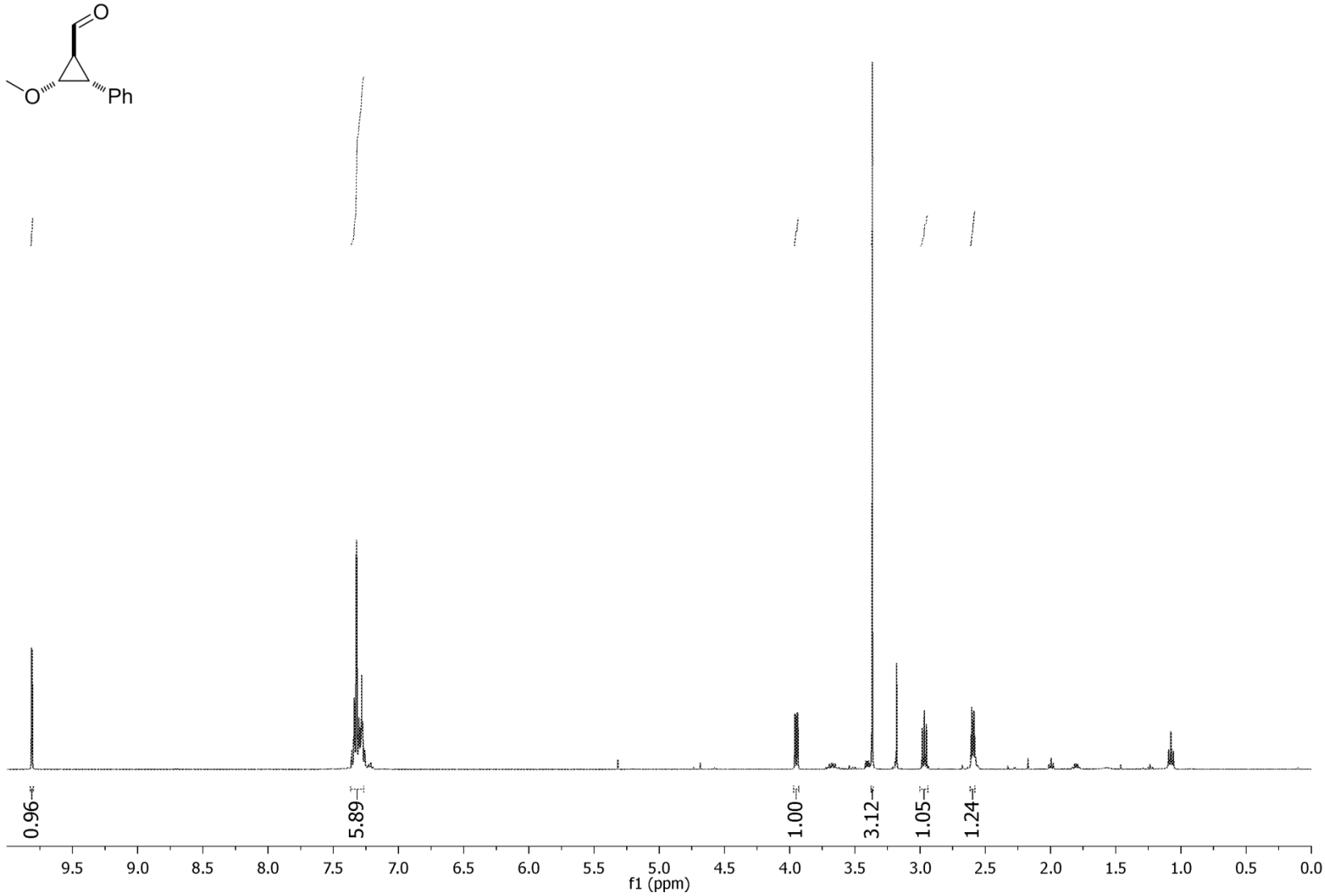
(*trans,trans*-2-Methoxy-3-phenylcyclopropyl)methanol ^{1}H NMR (400 MHz, $CDCl_3$)



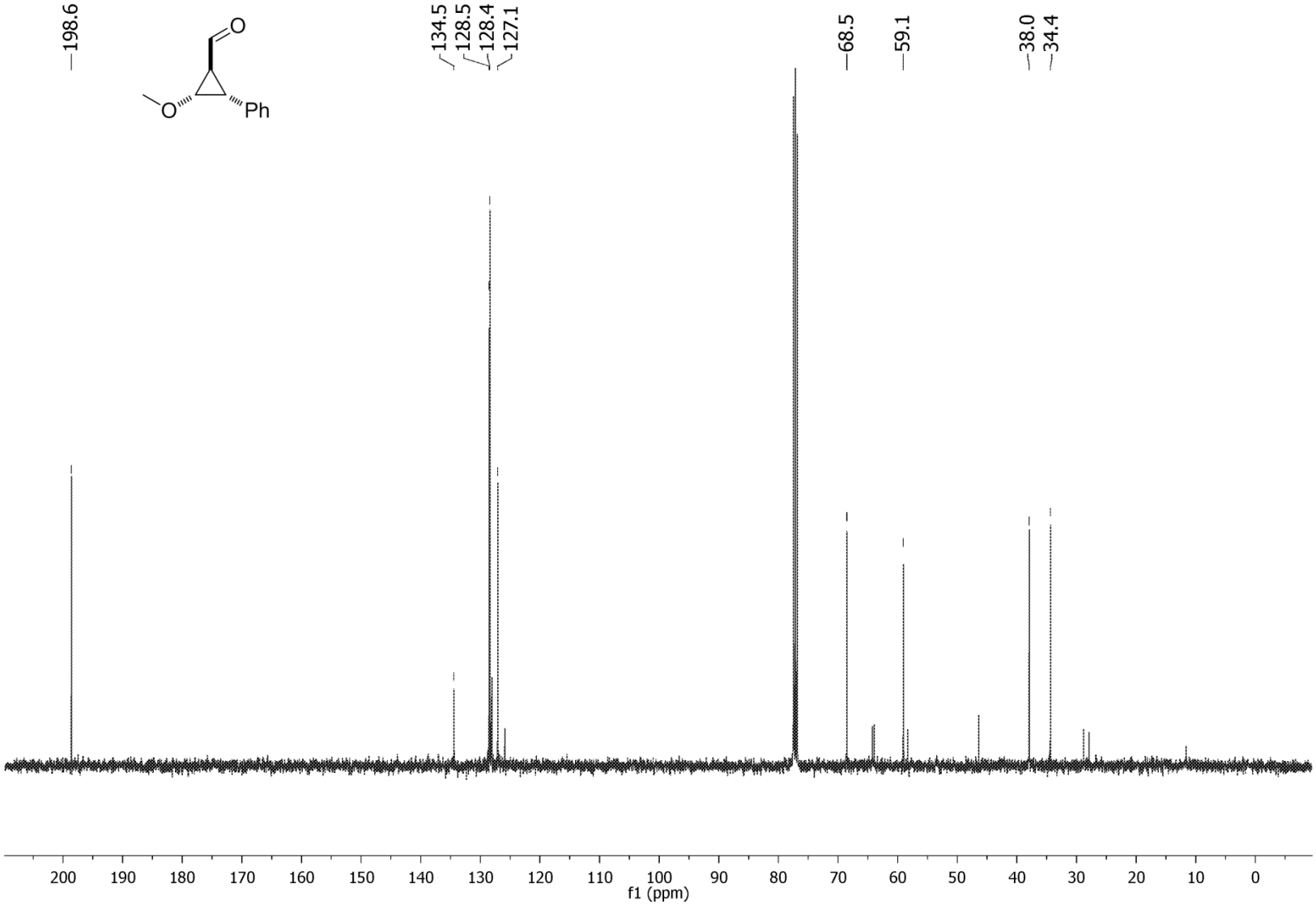
(*trans,trans*-2-Methoxy-3-phenylcyclopropyl)methanol ^{13}C NMR (101 MHz, $CDCl_3$)



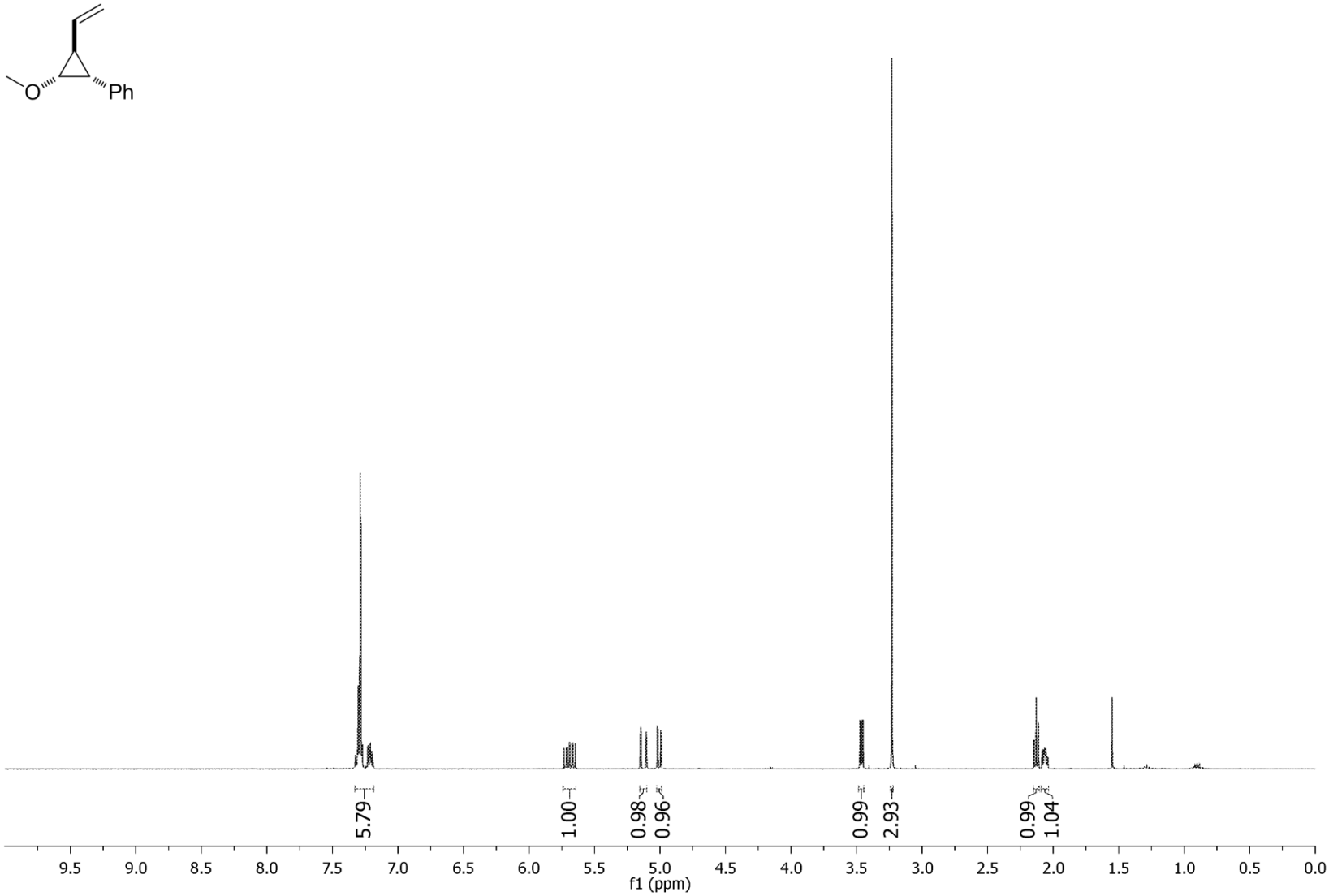
***trans,trans*-2-Methoxy-3-phenylcyclopropanecarbaldehyde** ^{1}H NMR (400 MHz, $CDCl_3$) crude reaction mixture



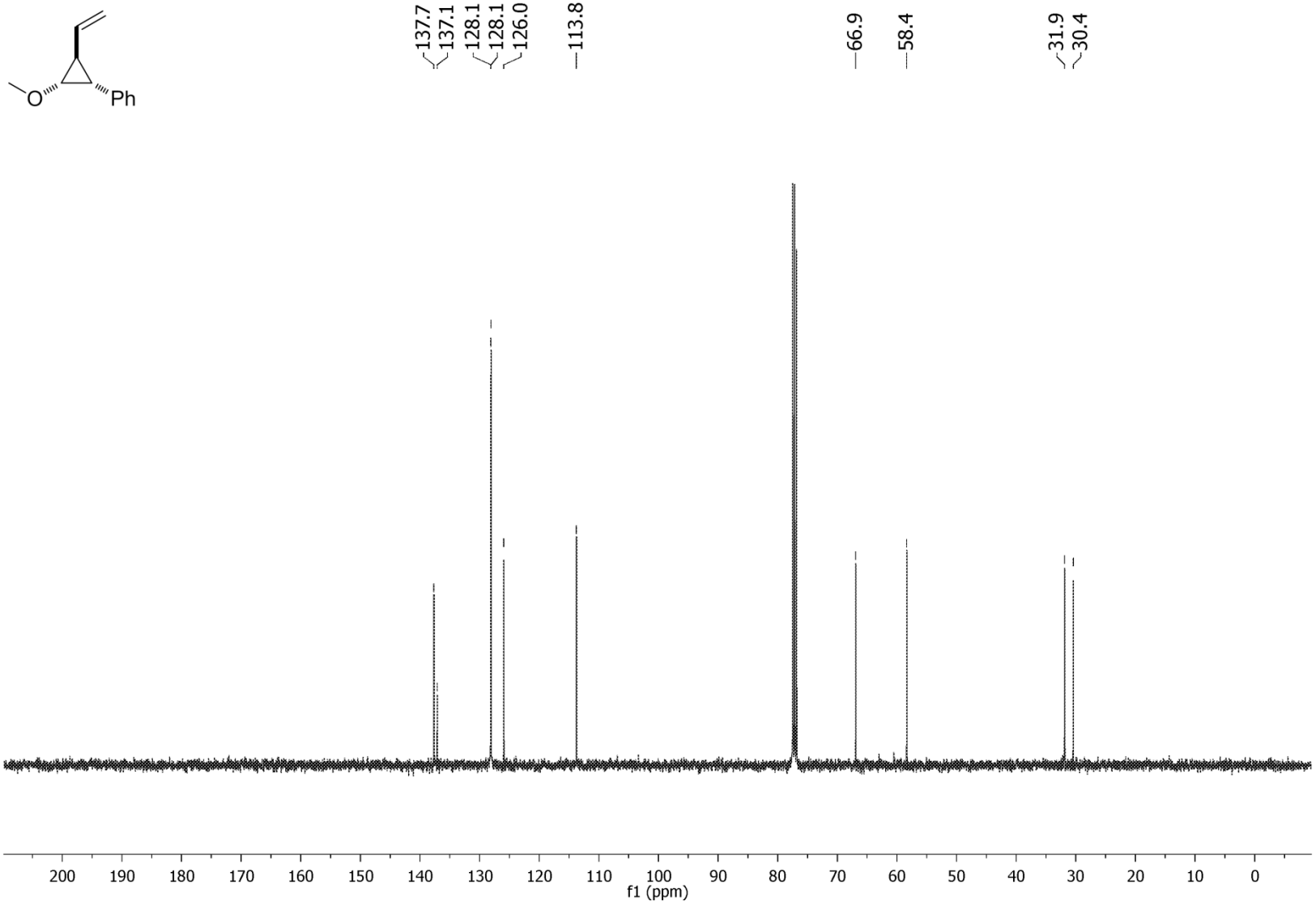
***trans,trans*-2-Methoxy-3-phenylcyclopropanecarbaldehyde** ^{13}C NMR (101 MHz, $CDCl_3$) crude reaction mixture



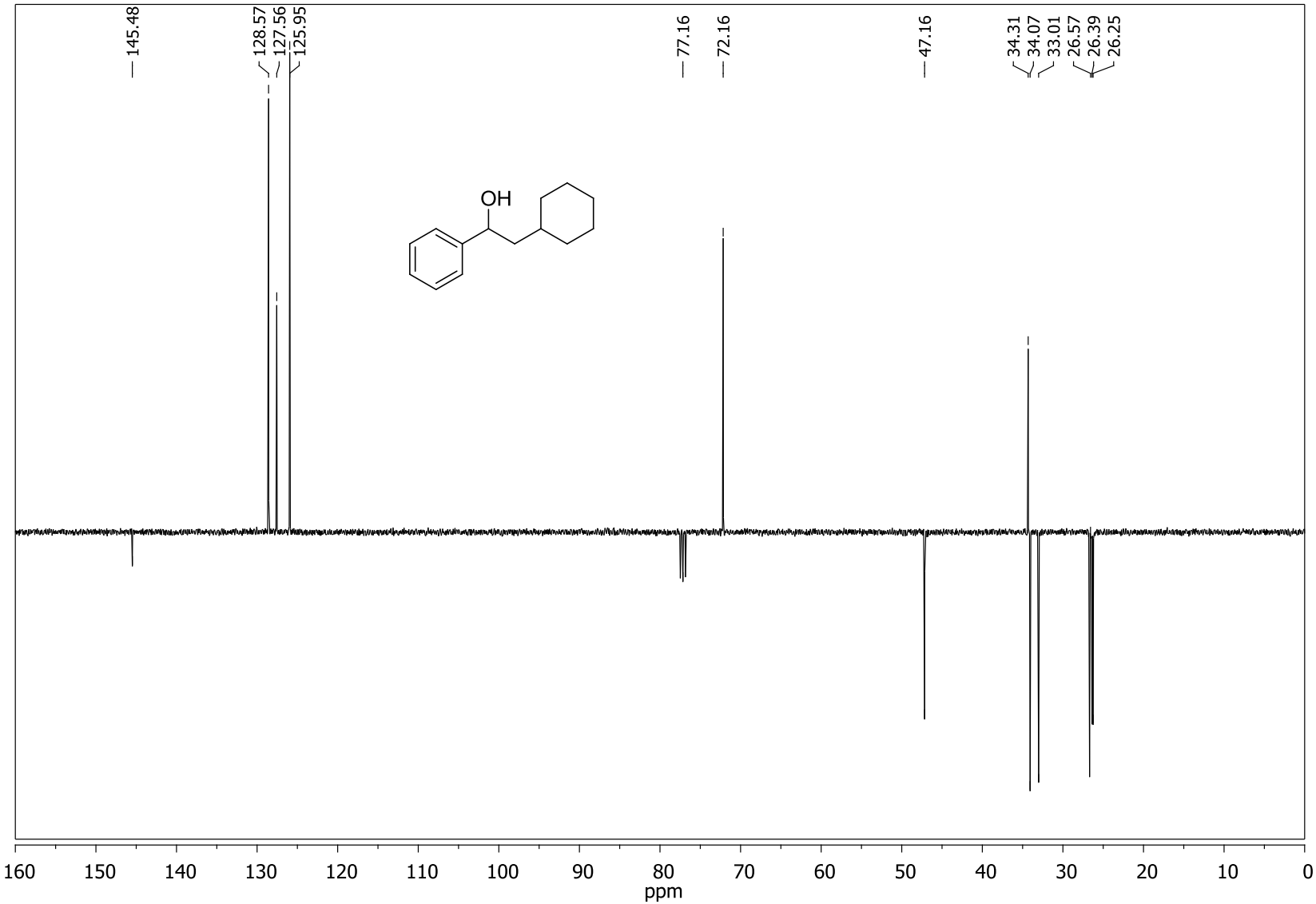
(*trans*,*trans*-2-Methoxy-3-phenylcyclopropyl)ethylene 23 ^{1}H NMR (400 MHz, $CDCl_3$)



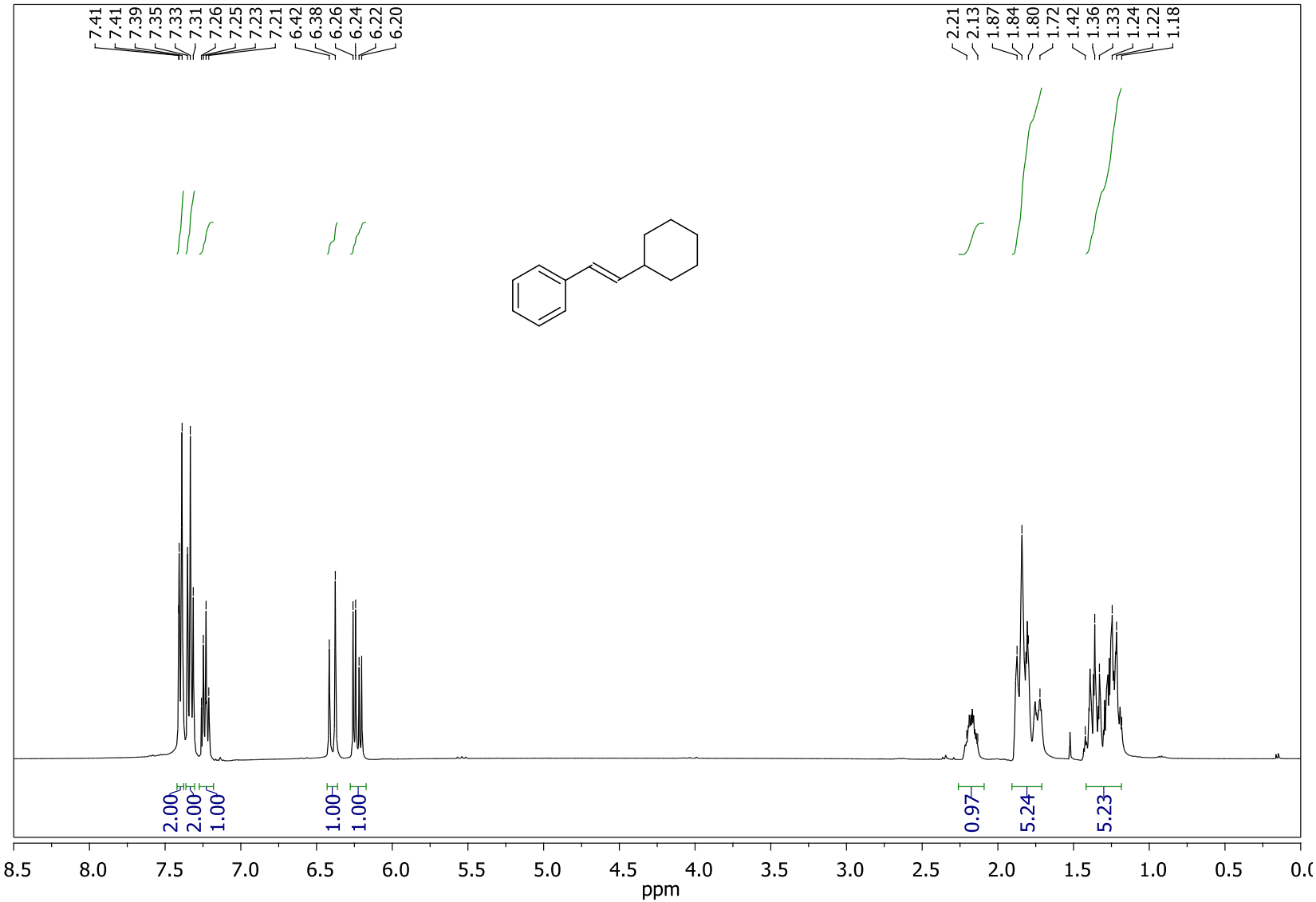
(*trans*,*trans*-2-Methoxy-3-phenylcyclopropyl)ethylene 23 ^{13}C NMR (101 MHz, $CDCl_3$)



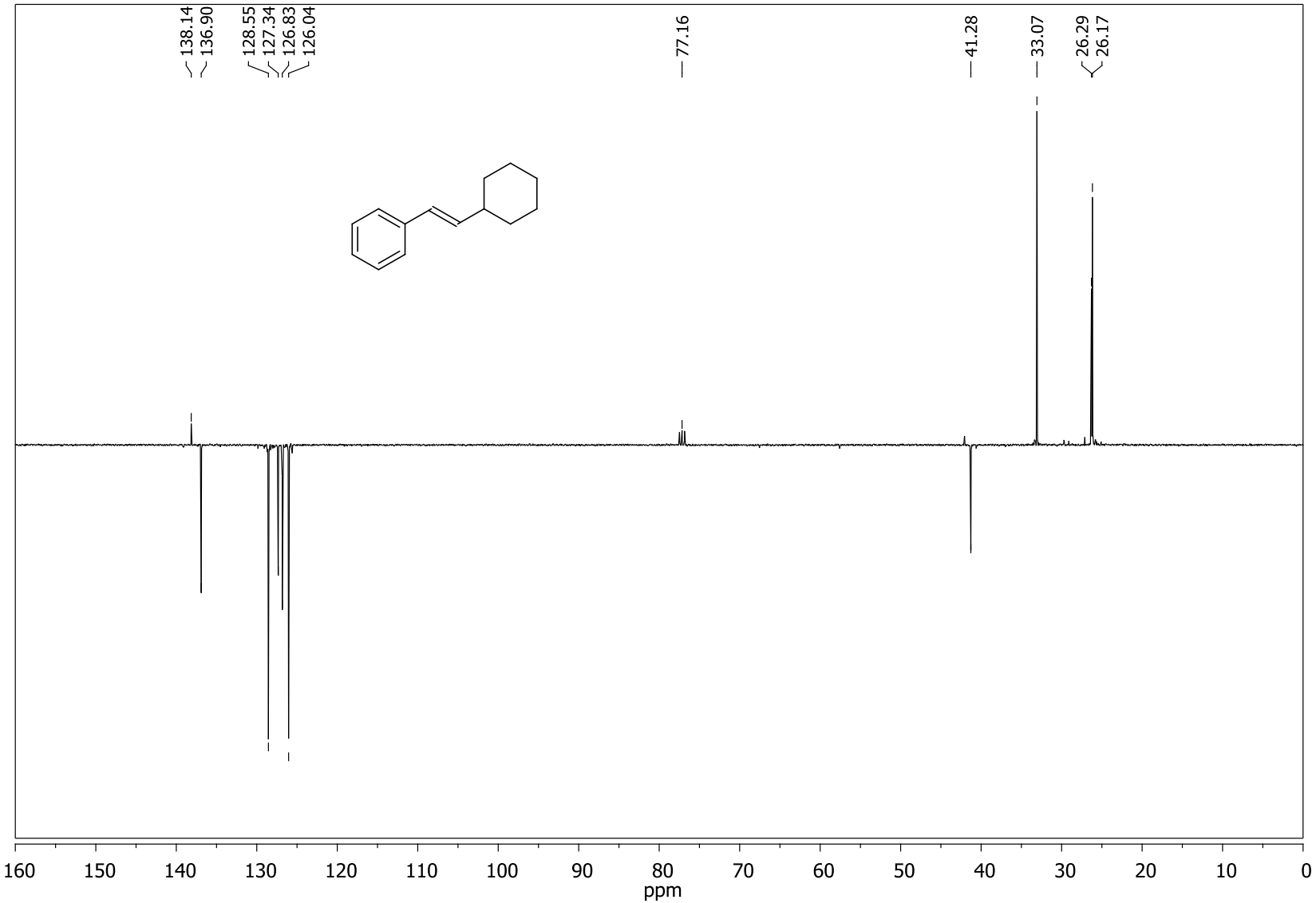
2-Cyclohexyl-1-phenylethanol S67: ^{13}C NMR DEPTQ-135 (100 MHz, $CDCl_3$)



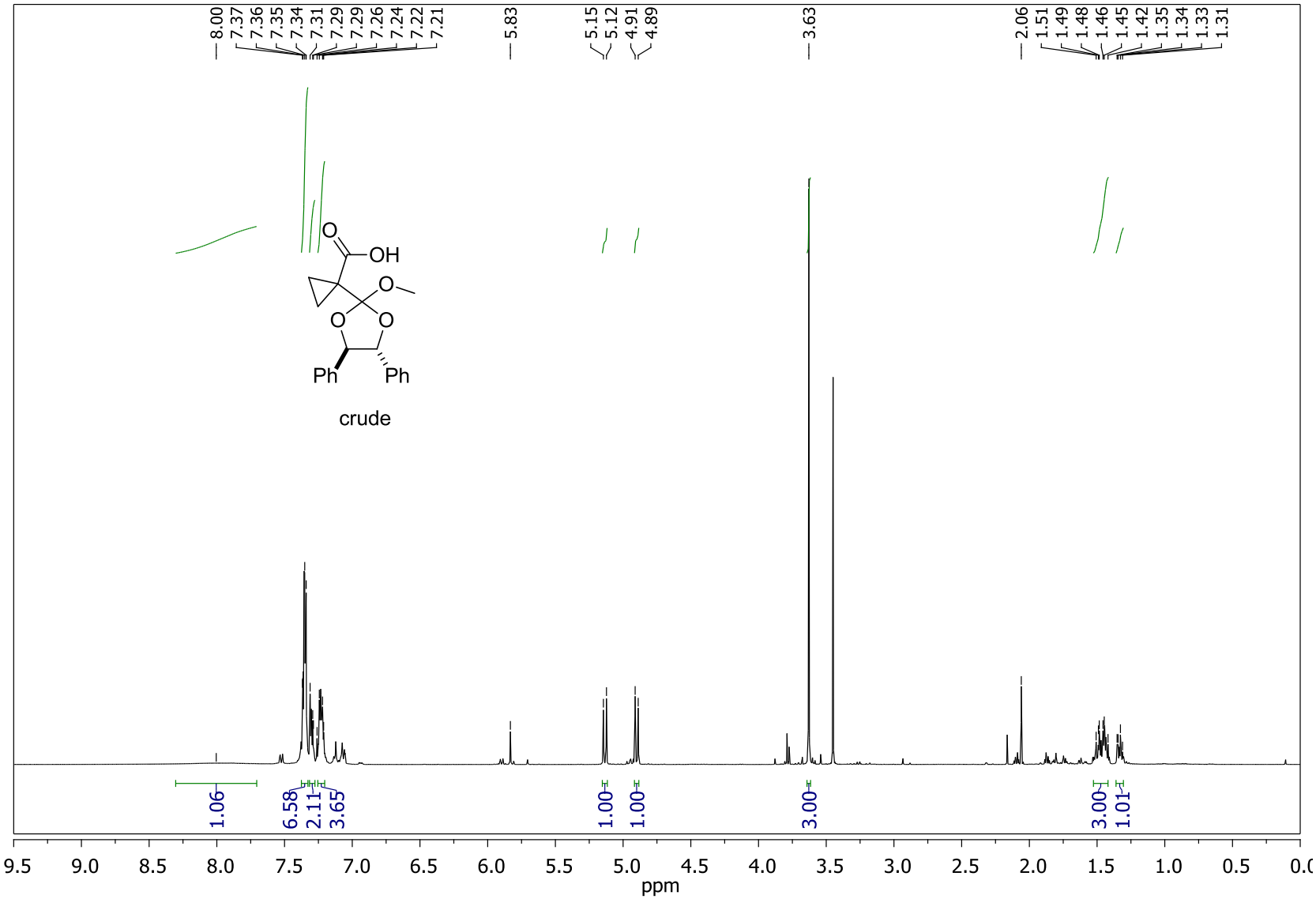
(*E*)-(2-Cyclohexylvinyl)benzene 29: ^{1}H NMR (400 MHz, $CDCl_3$)



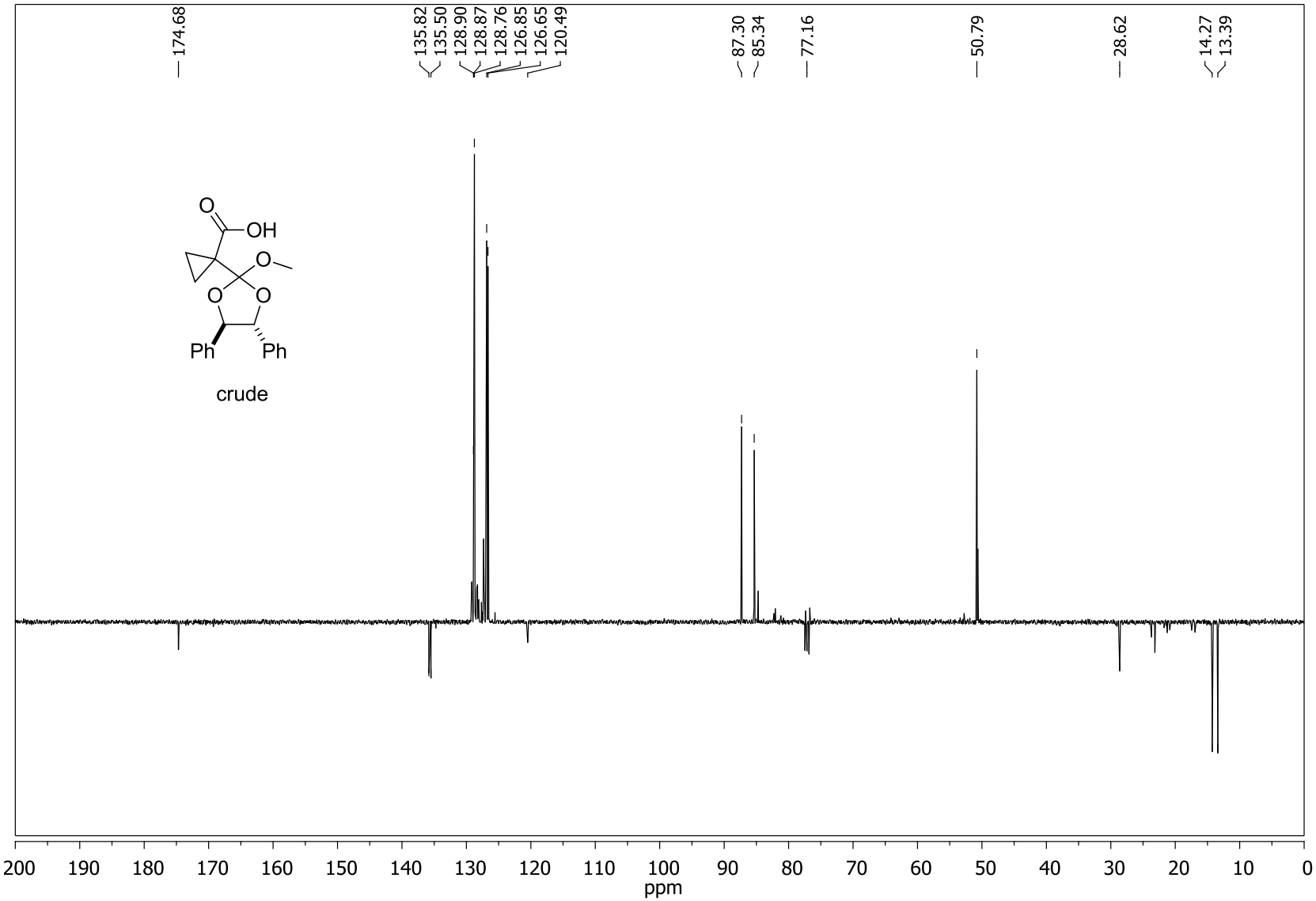
(*E*)-(2-Cyclohexylvinyl)benzene 29: ^{13}C NMR DEPTQ-135 (100 MHz, $CDCl_3$)



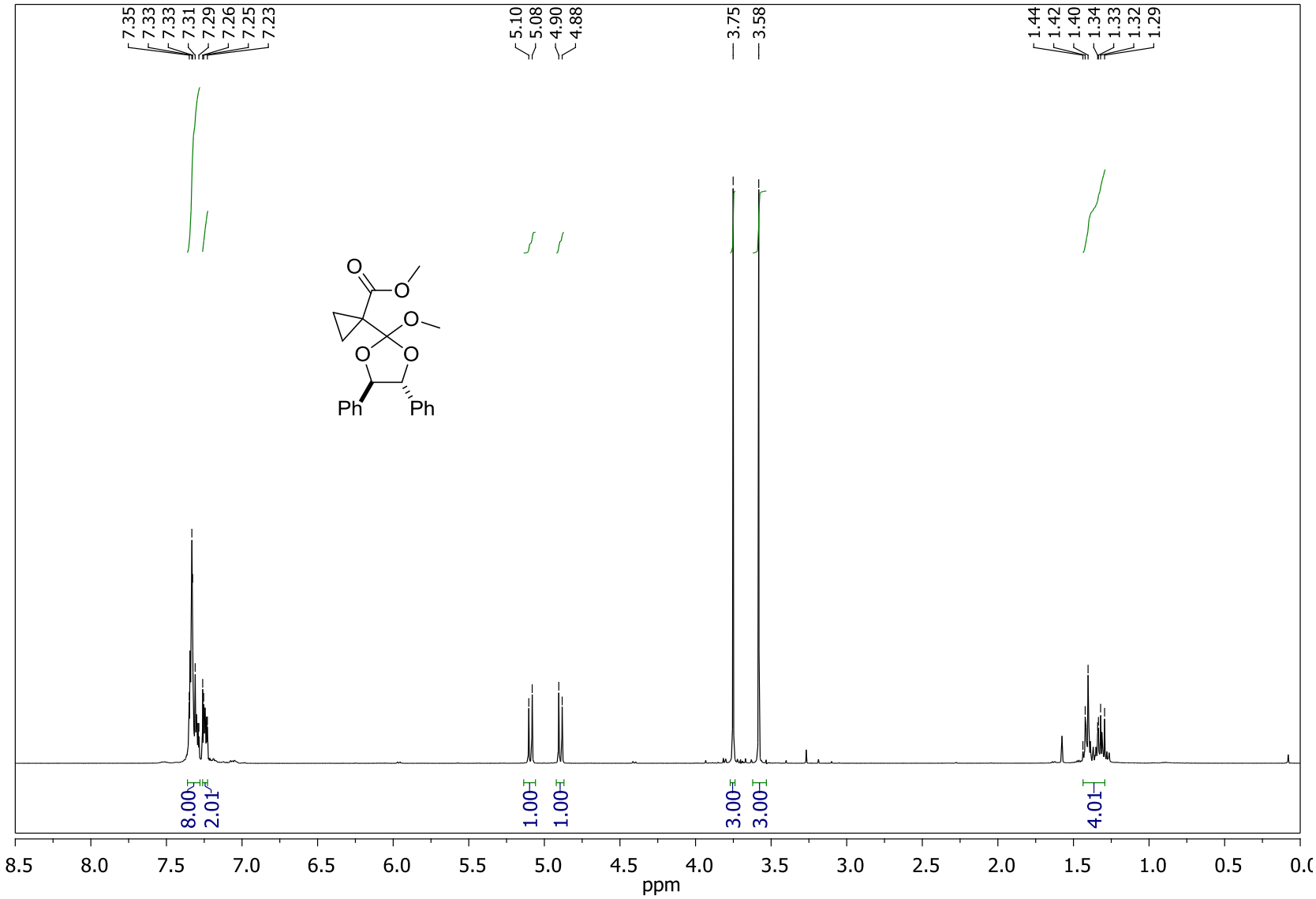
1-((*rel*-4*R*,5*R*)-2-Methoxy-4,5-diphenyl-1,3-dioxolan-2-yl) cyclopropanecarboxylic acid 43: ^{1}H NMR (400 MHz, $CDCl_3$)



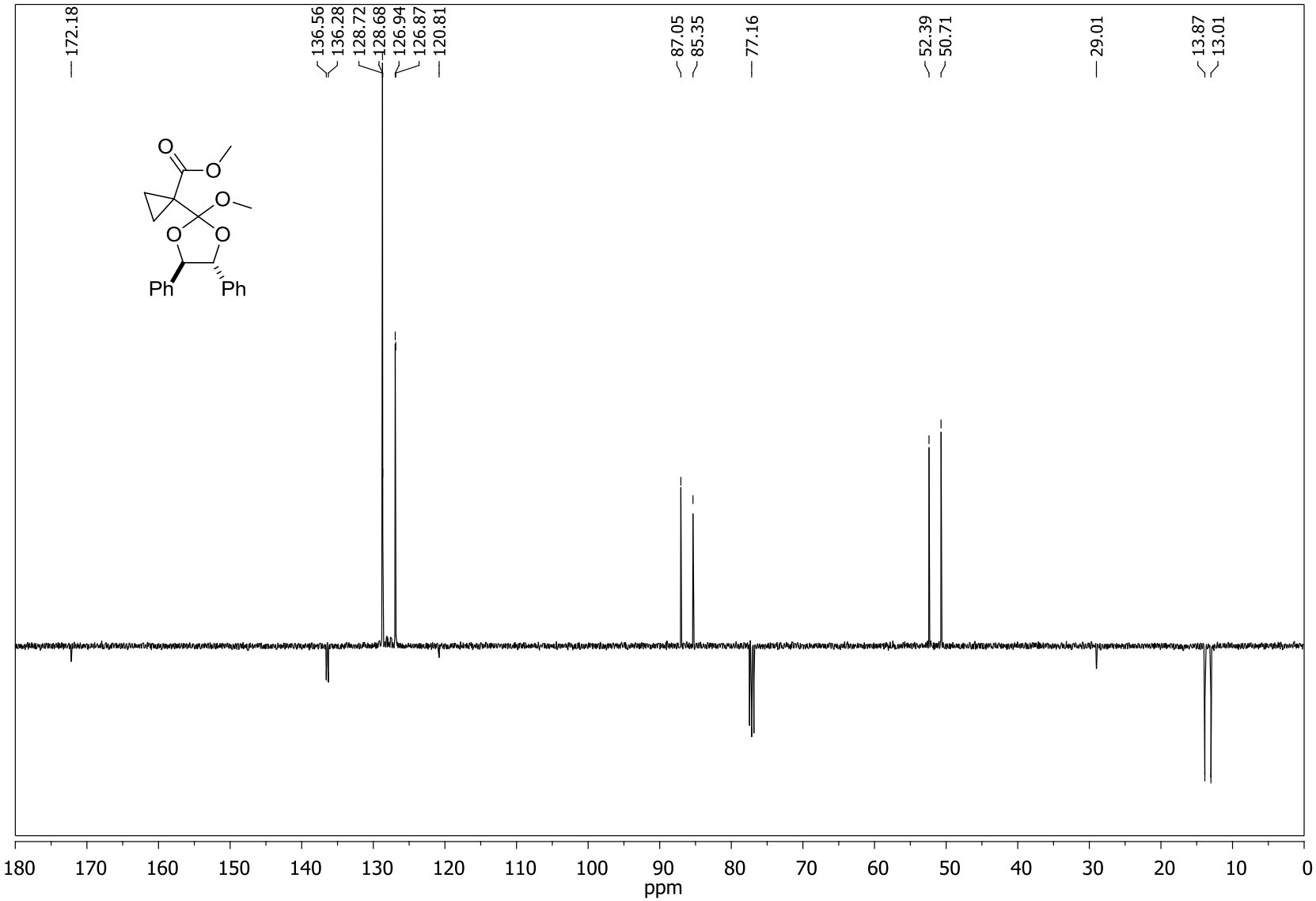
1-((*rel*-4*R*,5*R*)-2-Methoxy-4,5-diphenyl-1,3-dioxolan-2-yl) cyclopropanecarboxylic acid 43: ^{13}C NMR DEPTQ-135 (100 MHz, $CDCl_3$)



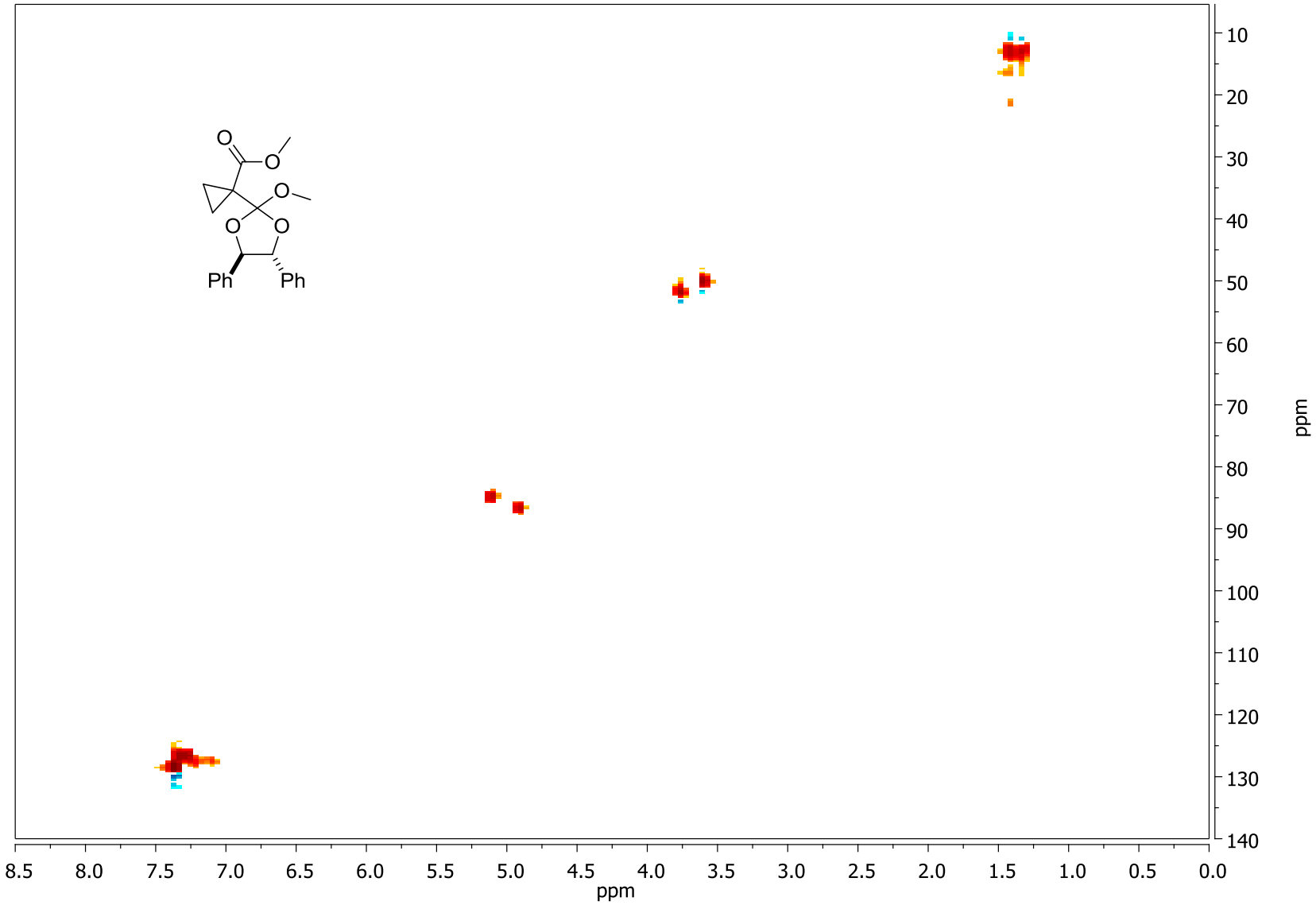
Methyl 1-((*rel*-4*R*,5*R*)-2-methoxy-4,5-diphenyl-1,3-dioxolan-2-yl) cyclopropane carboxylate 44: ^{1}H NMR (400 MHz, $CDCl_3$)



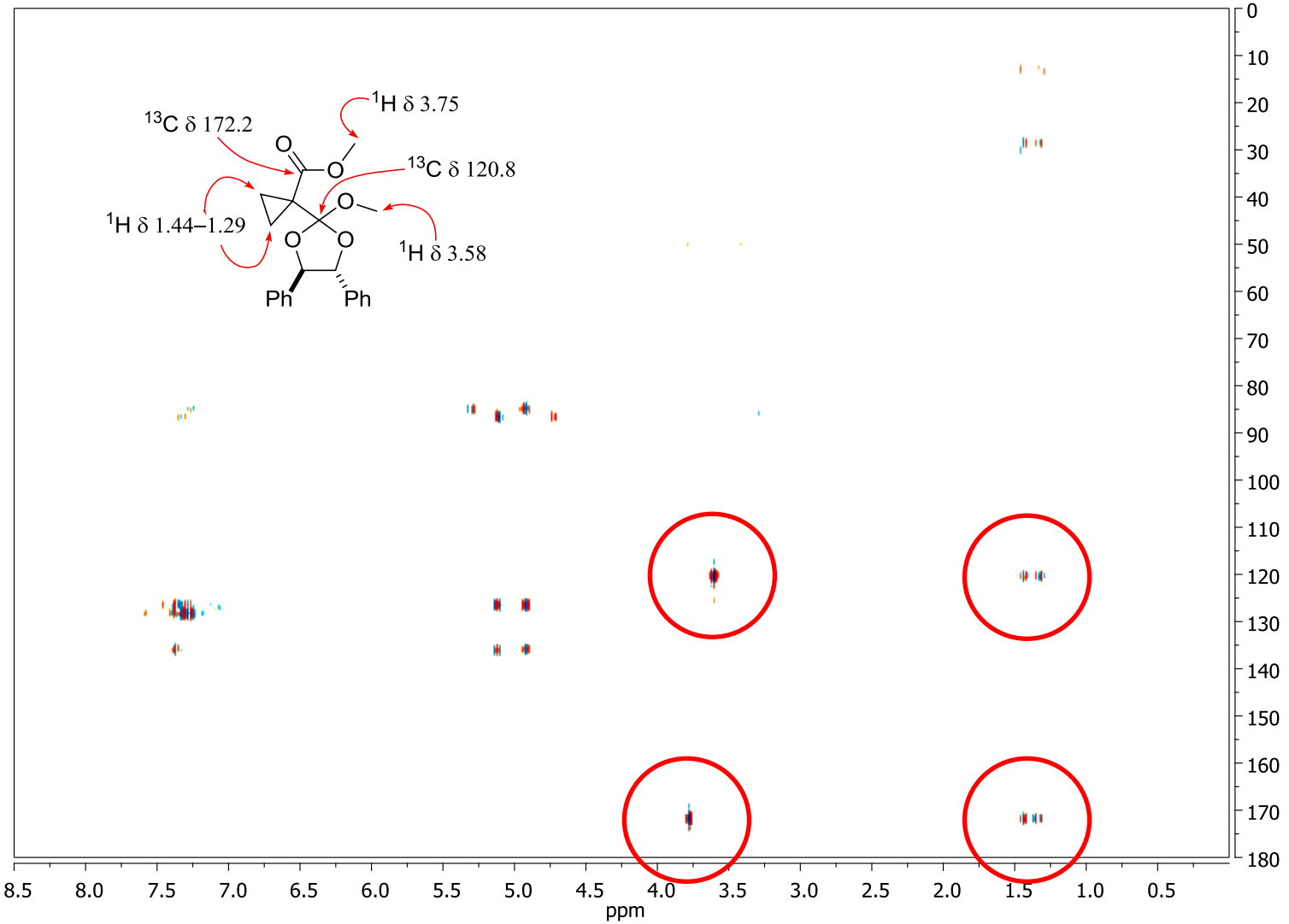
Methyl 1-((*rel*-4*R*,5*R*)-2-methoxy-4,5-diphenyl-1,3-dioxolan-2-yl) cyclopropane carboxylate 44: ^{13}C NMR DEPTQ-135 (100 MHz, $CDCl_3$)



Methyl 1-((*rel*-4*R*,5*R*)-2-methoxy-4,5-diphenyl-1,3-dioxolan-2-yl) cyclopropane carboxylate 44: HSQC (400 MHz, $CDCl_3$)



Methyl 1-((*rel*-4*R*,5*R*)-2-methoxy-4,5-diphenyl-1,3-dioxolan-2-yl) cyclopropane carboxylate 44: HMBC (400 MHz, $CDCl_3$)



Key interactions highlighted using:

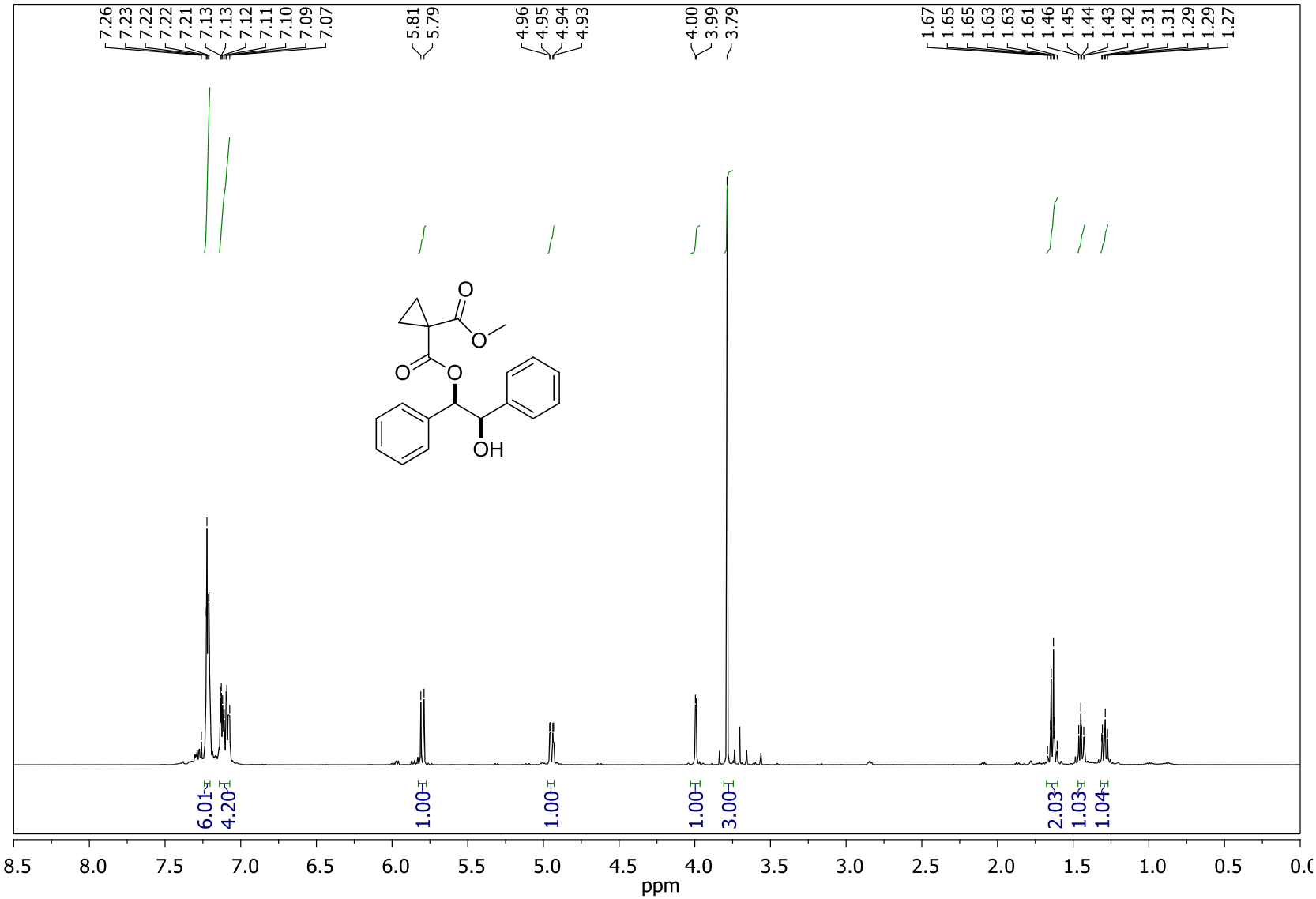
Key signals:

^{13}C DEPTQ-135: Orthoester quaternary carbon (^{13}C δ 120.8) *See Supplementary Information page S104.*

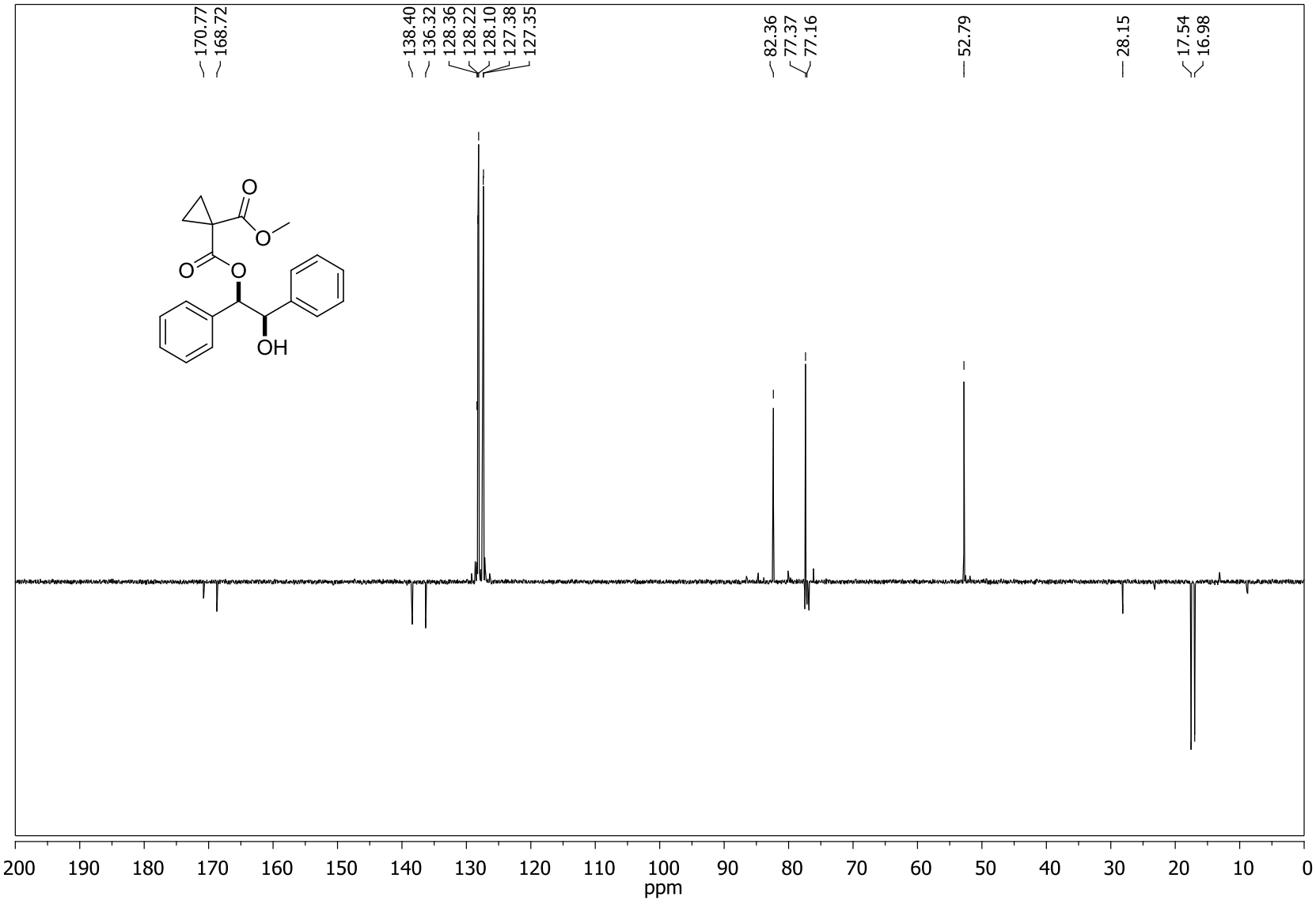
HMBC: Orthoester carbon (^{13}C δ 120.8) interaction with cyclopropane (^{1}H δ 1.44–1.29) and orthoester methoxy group (^{1}H δ 3.58).

HMBC: Carbonyl (^{13}C δ 172.2) interaction with cyclopropane (^{1}H δ 1.44–1.29) and methyl ester methoxy group (^{1}H δ 3.75).

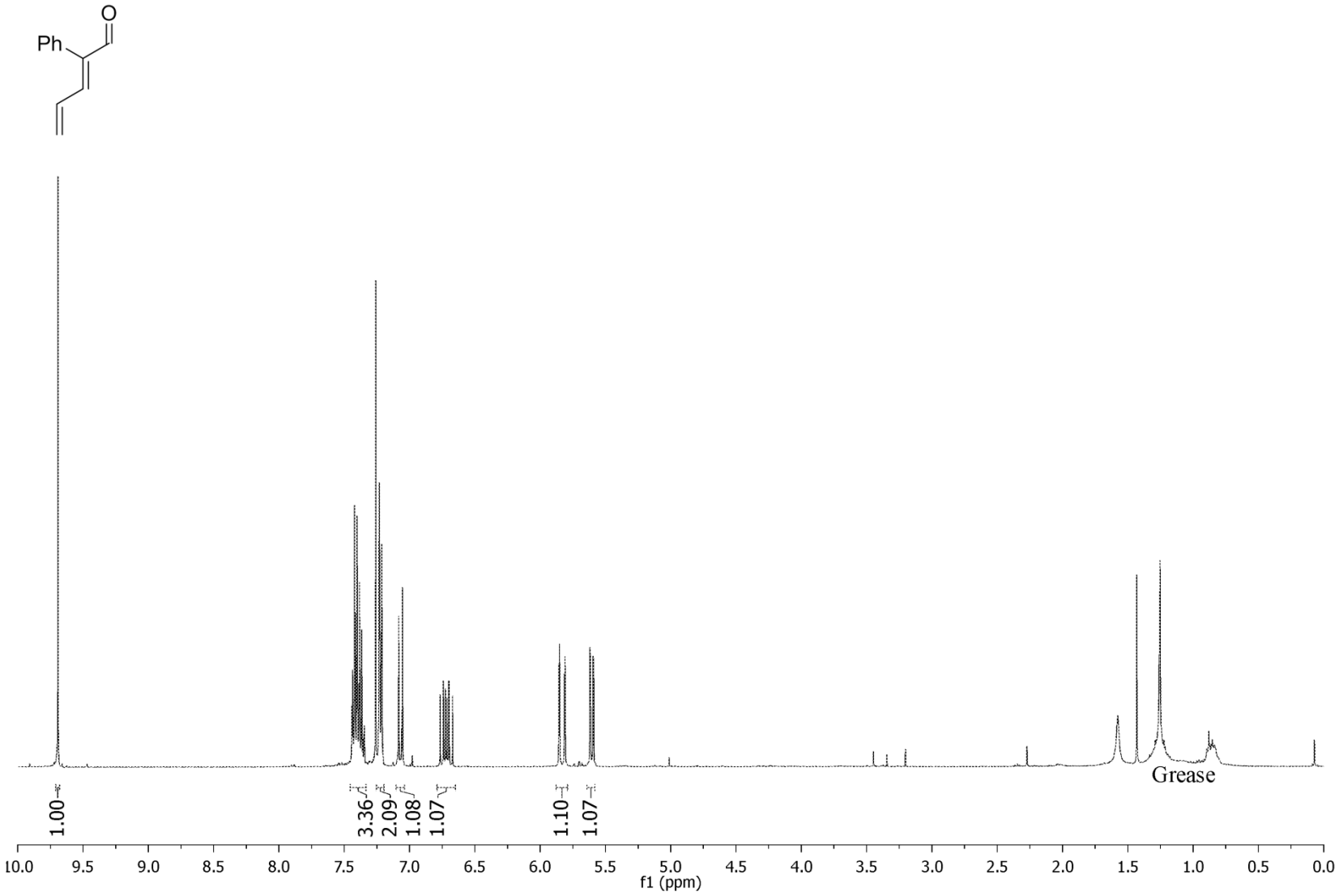
1-(*rel*-(1*R*,2*R*)-2-Hydroxy-1,2-diphenylethyl) 1-methyl cyclopropane-1,1-dicarboxylate 45: ^{1}H NMR (400 MHz, $CDCl_3$)



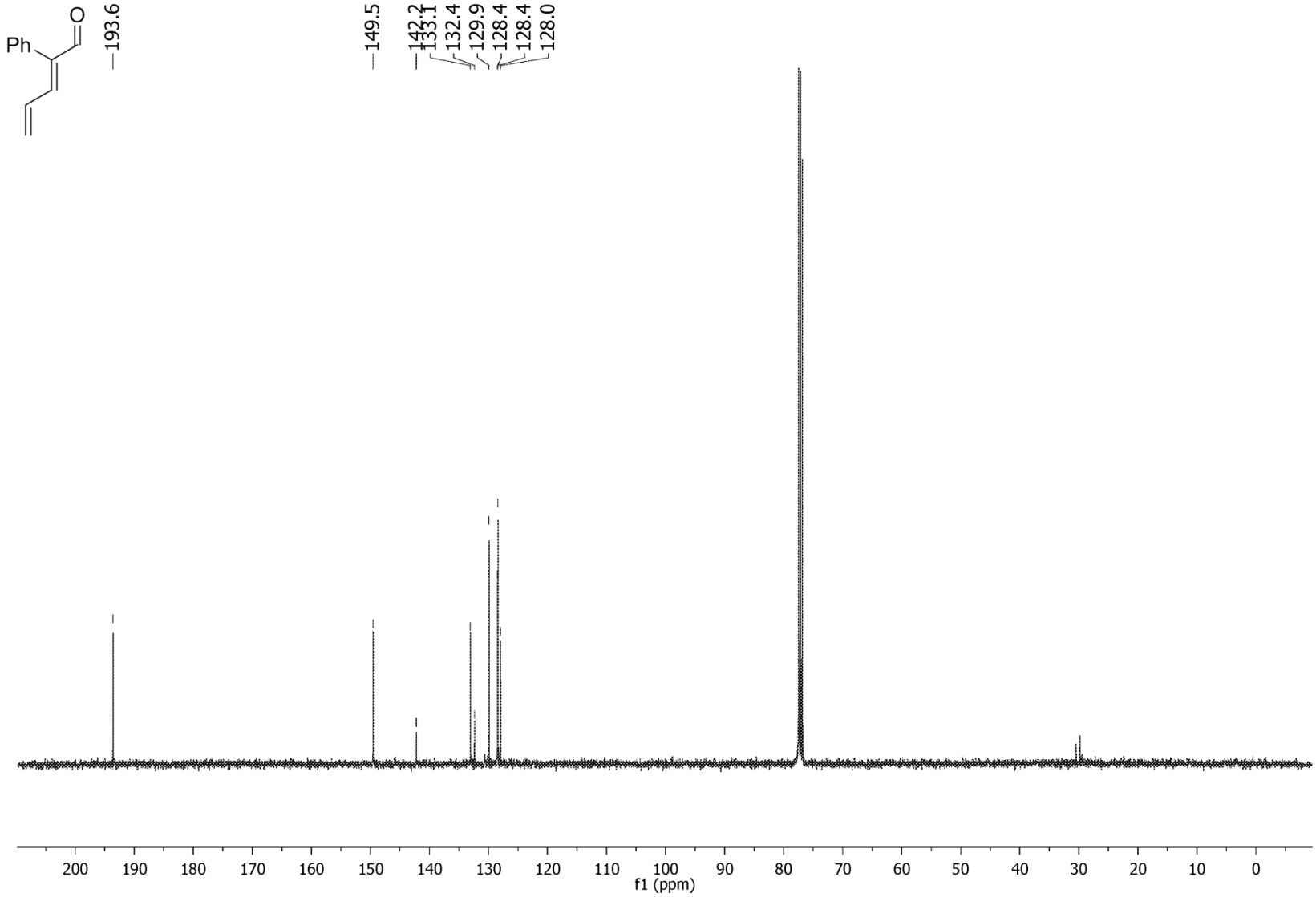
1-(*rel*-(1*R*,2*R*)-2-Hydroxy-1,2-diphenylethyl) 1-methyl cyclopropane-1,1-dicarboxylate 45: ^{13}C NMR DEPTQ-135 (100 MHz, $CDCl_3$)



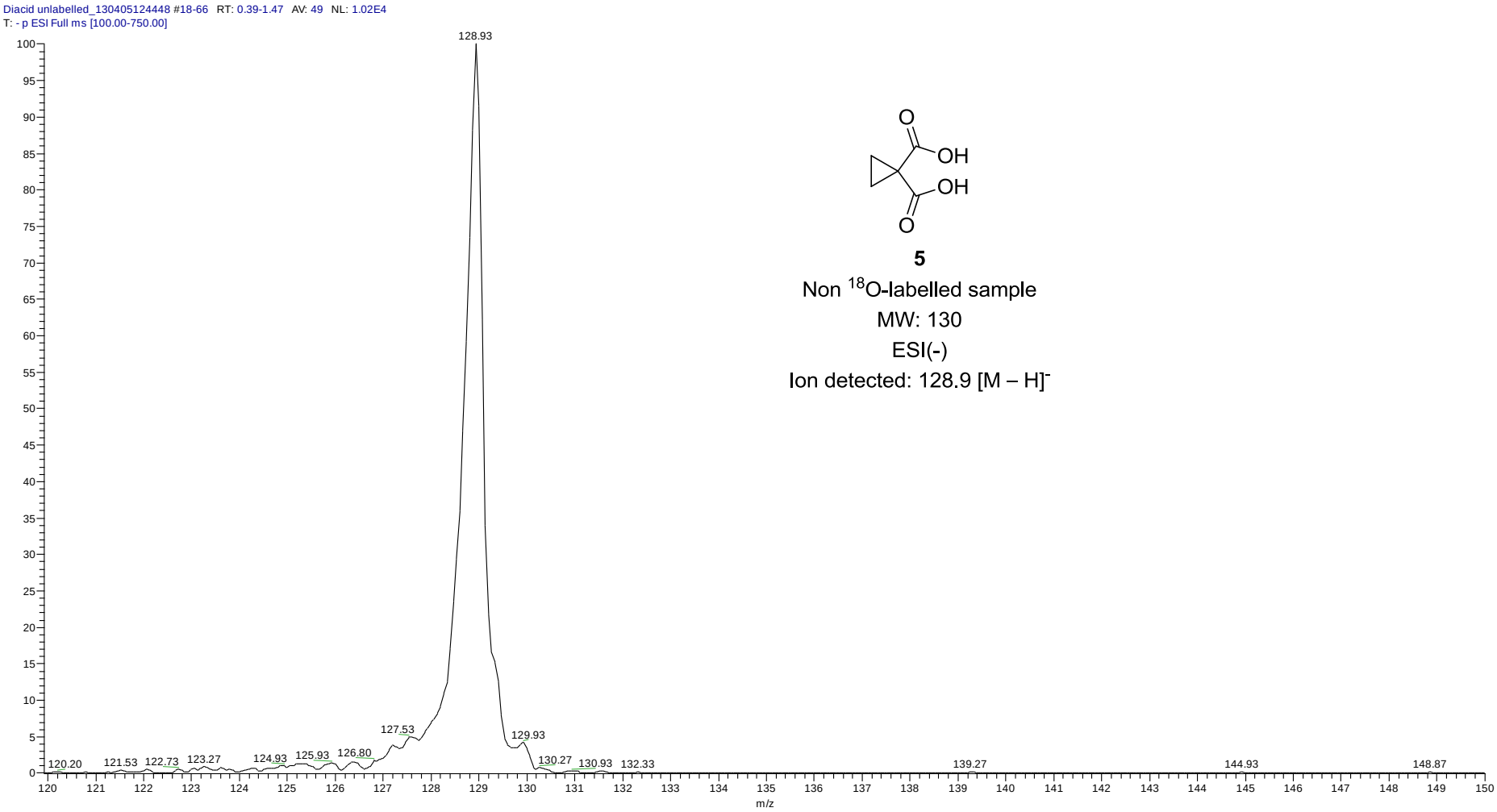
2-Phenylpenta-2,4-dienal 25: ^{1}H NMR (400 MHz, $CDCl_3$)



2-Phenylpenta-2,4-dienal 25: ^{13}C NMR (101 MHz, $CDCl_3$)



Mass Spectrometric Data



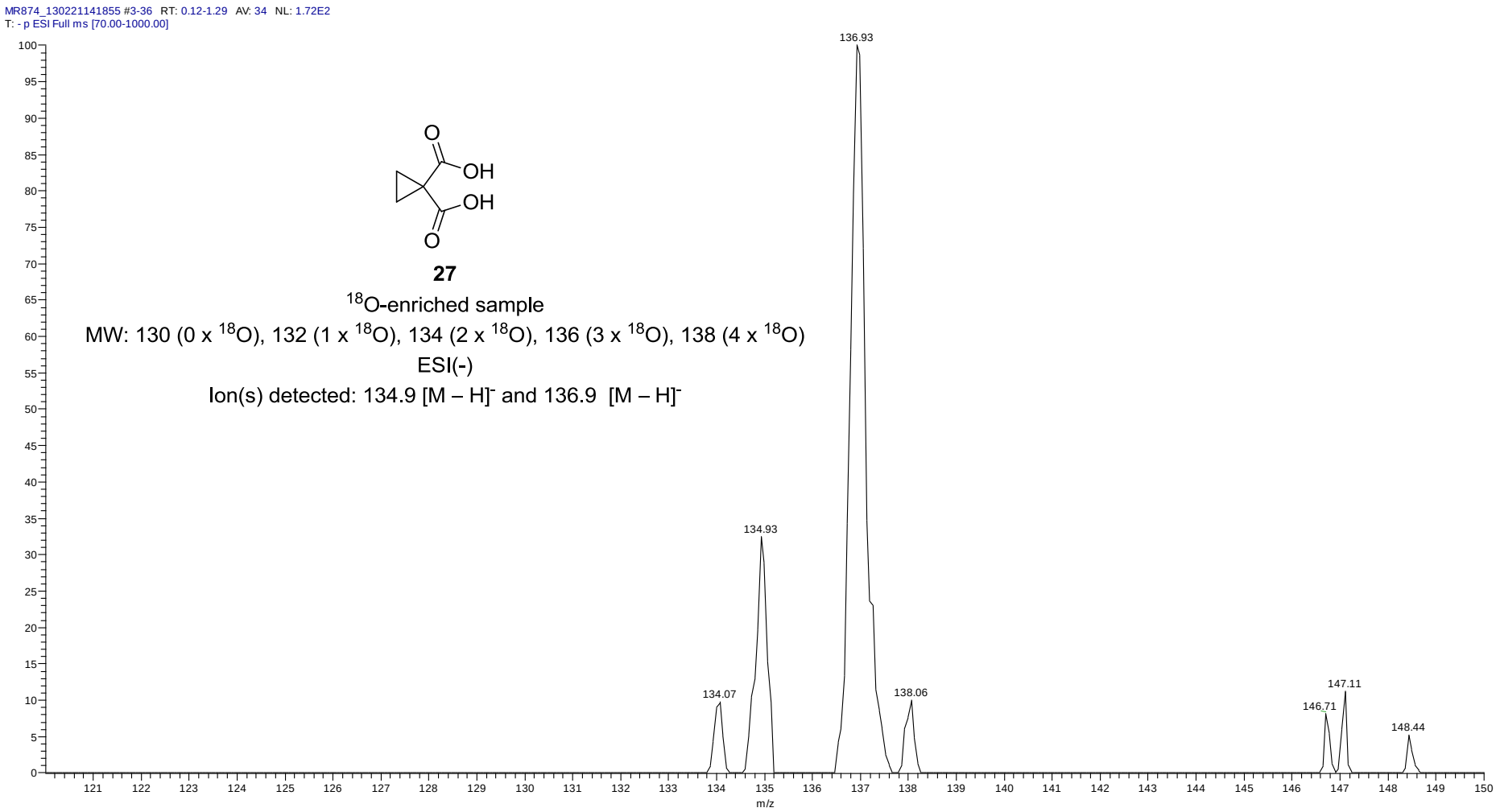
5

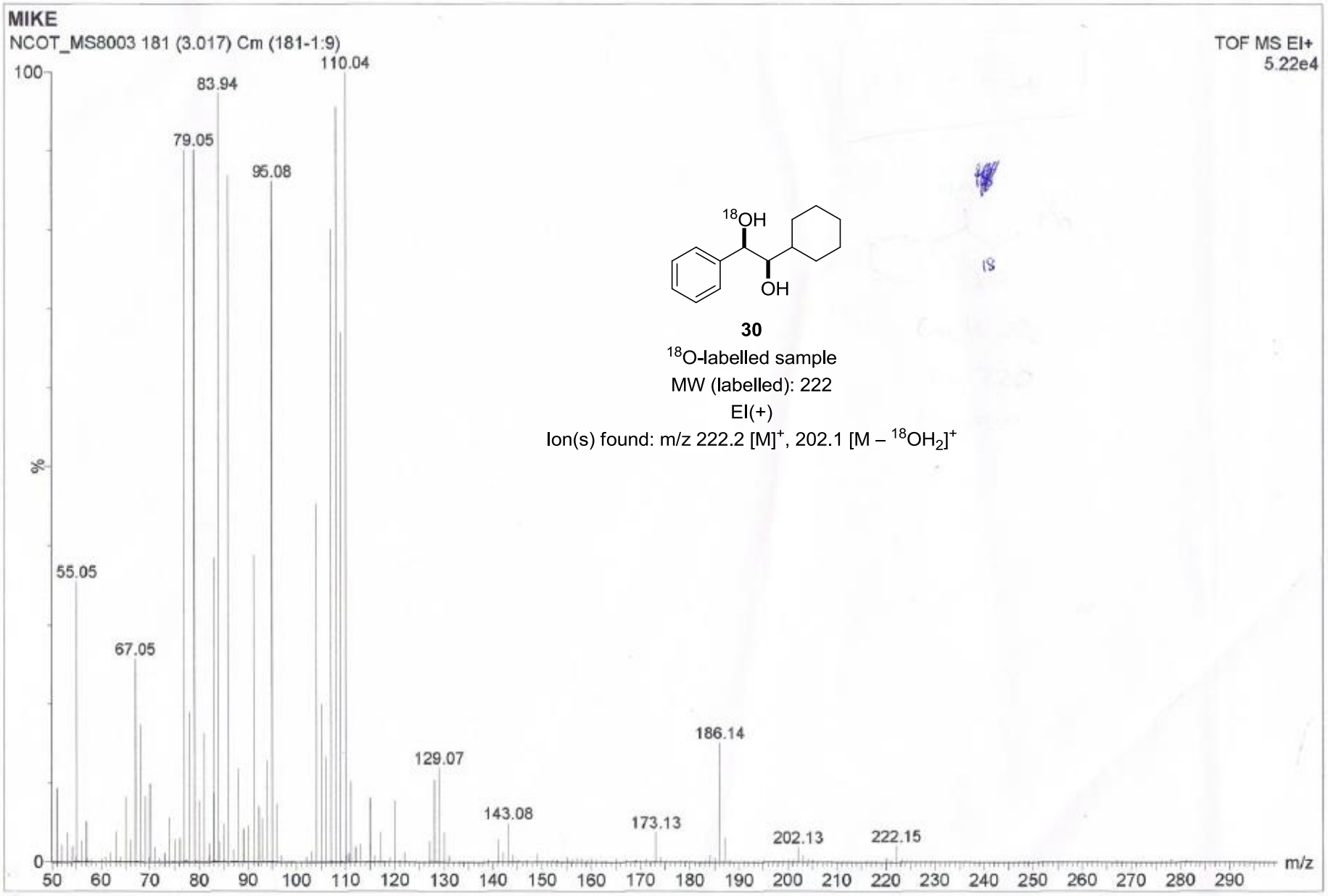
Non ^{18}O-labelled sample

MW: 130

ESI(-)

Ion detected: 128.9 $[M - H]^-$


MR874_130221141855 #3-36 RT: 0.12-1.29 AV: 34 NL: 1.72E2
T: - p ESI Full ms [70.00-1000.00]
O
OH
OH
O
27
18O-enriched sample
MW: 130 (0 x 18O), 132 (1 x 18O), 134 (2 x 18O), 136 (3 x 18O), 138 (4 x 18O)
ESI(-)
Ion(s) detected: 134.9 [M – H]- and 136.9 [M – H]-
136.93
134.93
134.07
138.06
147.11
146.71
148.44
m/z



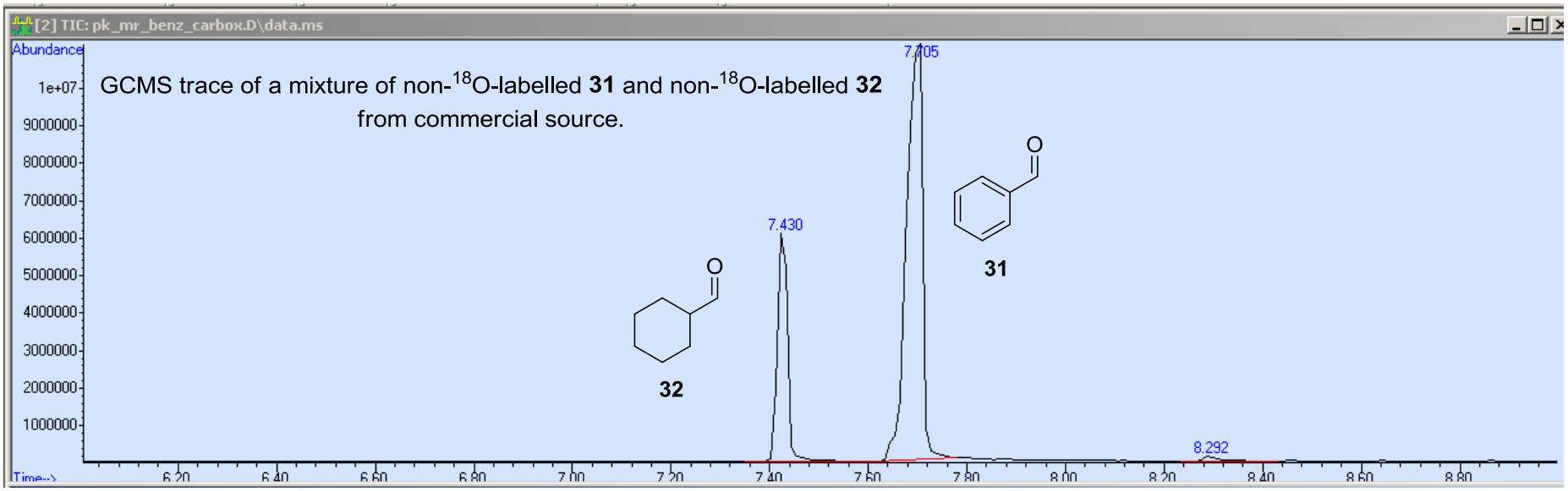
30

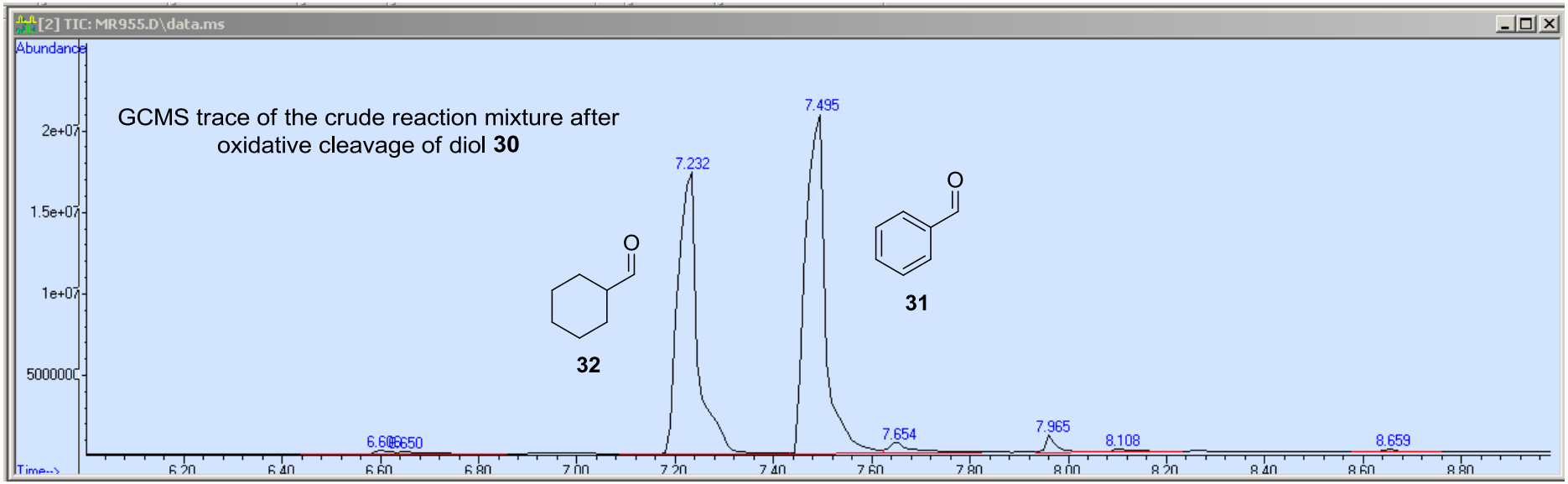
^{18}O-labelled sample

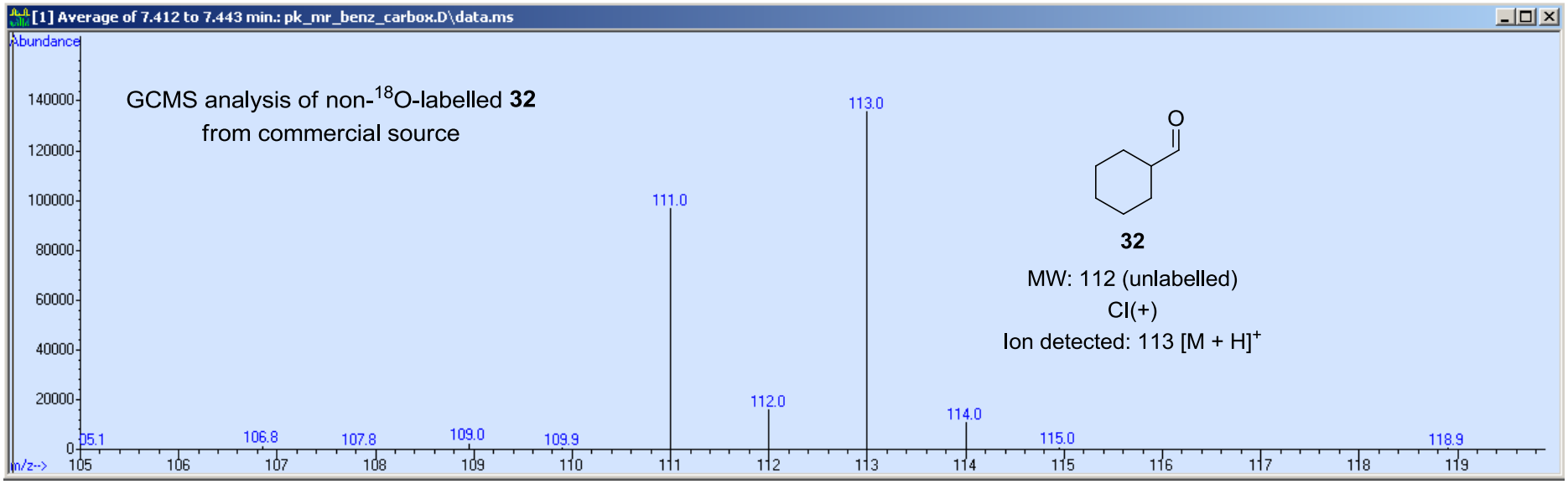
MW (labelled): 222

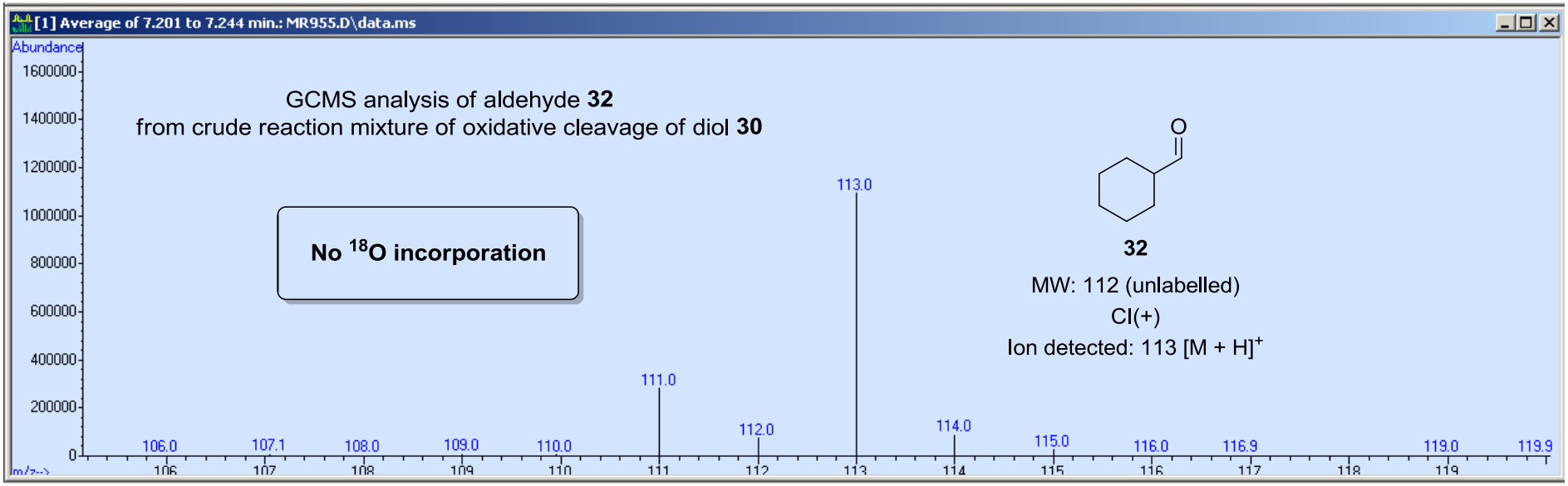
EI(+)

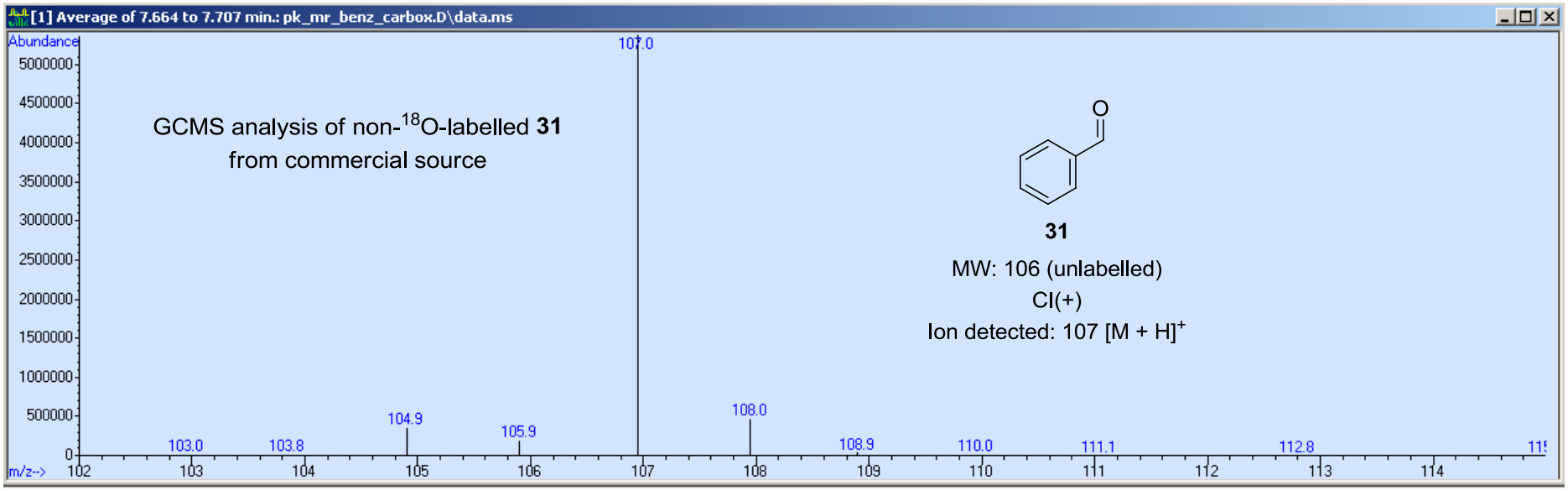
Ion(s) found: m/z 222.2 $[M]^+$, 202.1 $[M - {}^{18}OH_2]^+$

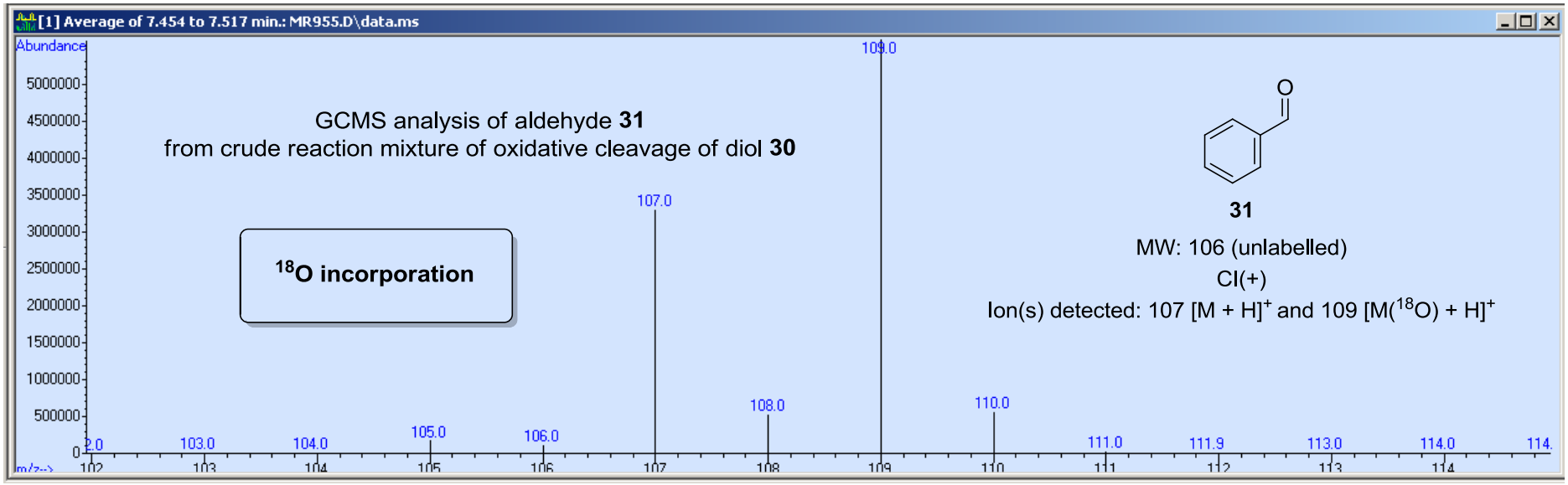

[2] TIC: pk_mr_benz_carbox.D\data.ms
Abundance
GCMS trace of a mixture of non-18O-labelled 31 and non-18O-labelled 32 from commercial source.
7.430
7.705
8.292
32
31
Time-->


[2] TIC: MR955.D\data.ms
Abundance
GCMS trace of the crude reaction mixture after oxidative cleavage of diol 30
7.232
7.495
7.654
7.965
8.108
8.659
32
31
Time-->


[1] Average of 7.412 to 7.443 min.: pk_mr_benz_carbox.D\data.ms
Abundance
GCMS analysis of non-18O-labelled 32
from commercial source
113.0
111.0
112.0
114.0
O
32
MW: 112 (unlabelled)
CI(+)
Ion detected: 113 [M + H]+
m/z-->


[1] Average of 7.201 to 7.244 min.: MR955.D\data.ms
Abundance
GCMS analysis of aldehyde 32
from crude reaction mixture of oxidative cleavage of diol 30
No 18O incorporation
113.0
111.0
112.0
114.0
O
32
MW: 112 (unlabelled)
CI(+)
Ion detected: 113 [M + H]+
m/z-->


[1] Average of 7.664 to 7.707 min.: pk_mr_benz_carbox.D\data.ms
Abundance
GCMS analysis of non-18O-labelled 31
from commercial source
31
MW: 106 (unlabelled)
CI(+)
Ion detected: 107 [M + H]+
m/z-->

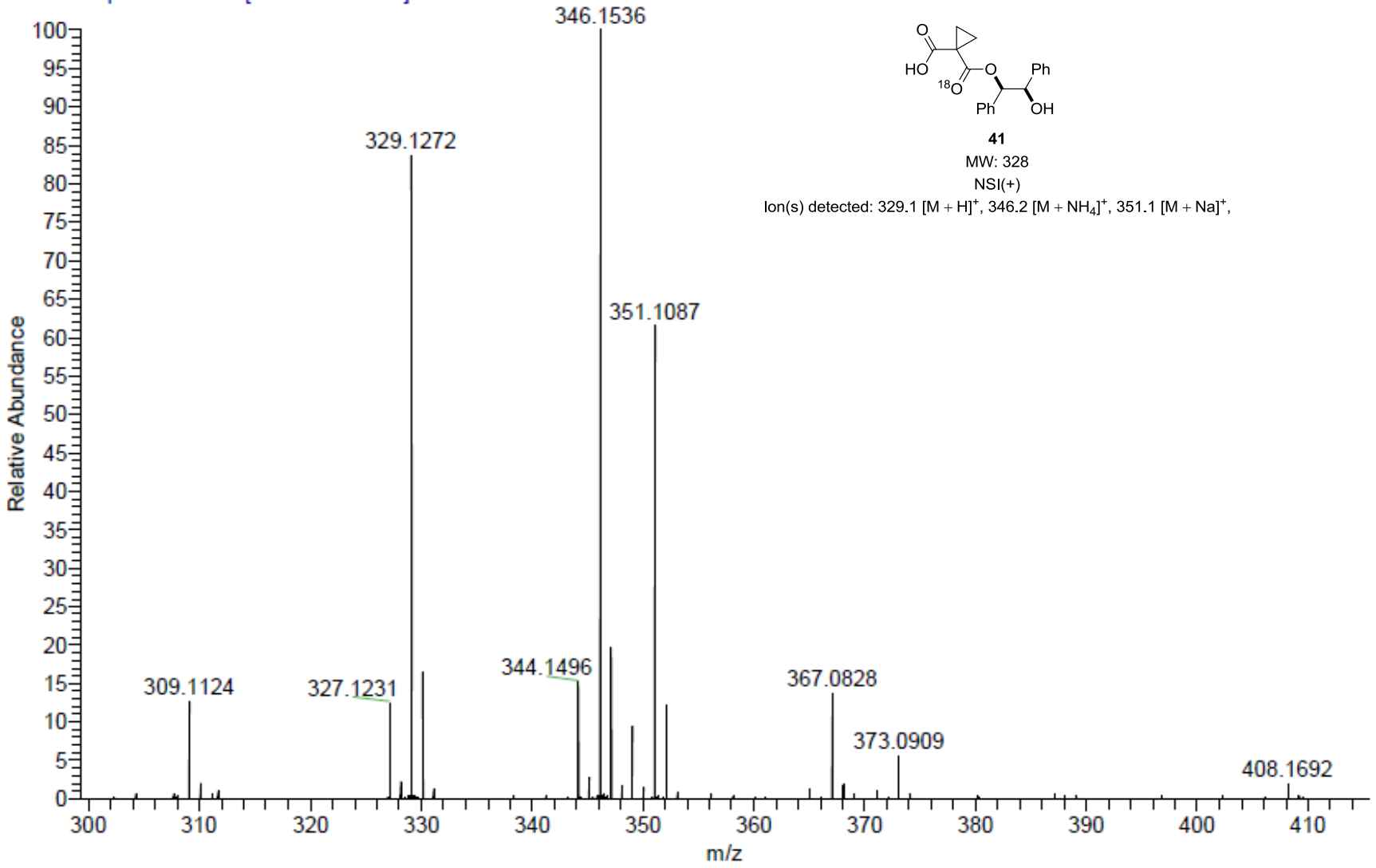

[1] Average of 7.454 to 7.517 min.: MR955.D\data.ms
Abundance
GCMS analysis of aldehyde 31
from crude reaction mixture of oxidative cleavage of diol 30
18O incorporation
31
MW: 106 (unlabelled)
CI(+)
Ion(s) detected: 107 [M + H]+ and 109 [M(18O) + H]+
m/z-->

MR899 MW=?
(MeOH)/MeOH + NH4OAc

EPSRC National Facility Swansea
LTQ Orbitrap XL

Michael Rawling
25/04/2013 14:29:22

STRTOM184-OJ-HNESP #28-50 RT: 0.72-1.28 AV: 22 SM: 7G NL: 1.32E7
T: FTMS + p NSI Full ms [120.00-2000.00]



41

MW: 328

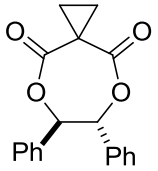
NSI(+)

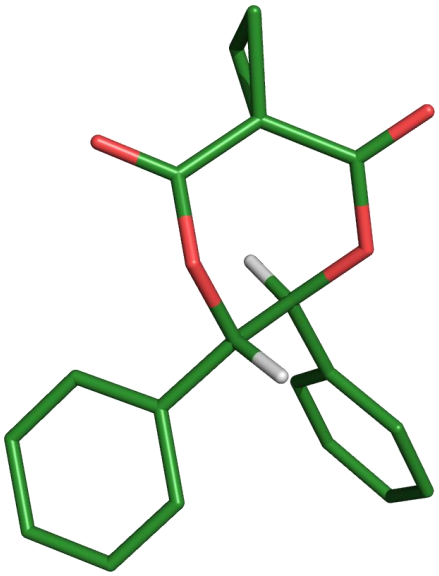
Ion(s) detected: 329.1 $[M + H]^+$, 346.2 $[M + NH_4]^+$, 351.1 $[M + Na]^+$,

X-Ray Crystallographic Data

rel-(6*R*,7*R*)-6,7-diphenyl-5,8-dioxaspiro[2.6]nonane-4,9-dione 14

Available from Cambridge Crystallographic Data Centre as supplementary publication number **CCDC 936075**.

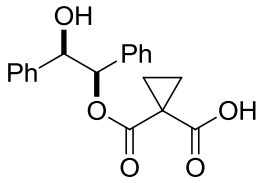


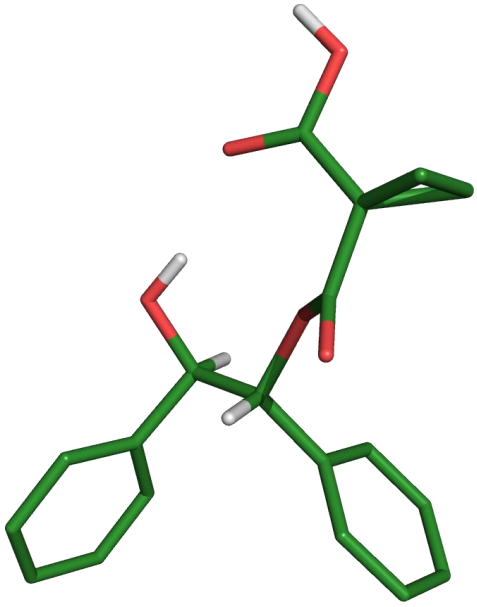


Empirical formula	$C_{19}H_{16}O_4$
M_r (g mol^{-1})	308.32
Crystal system	Monoclinic
Space group	P 2_1/n
a/ Å	9.5528(6)
b/ Å	10.1091(5)
c/ Å	16.1660(9)
β (°)	104.844(5)
V/Å^3	1509.05(15)
Z	4
Temp K	123(2)
2θmax	54
λ/ Å	0.71073
Measured reflections	7058
Unique reflections	3293
R_{int}	0.0348
Observed rflns [$I > 2\sigma(I)$]	2293
μ (mm^{-1})	0.095
No. of parameters	208
R [on *F*, obs rflns only]	0.0515
wR [on F^2, all data]	0.1023
GoF	1.037
Largest diff. peak/hole/e Å^{-3}	0.233/-0.233

1-(((*rel*-1*R*,2*R*)-2-hydroxy-1,2-diphenylethoxy)carbonyl) cyclopropane carboxylic acid 15

Available from Cambridge Crystallographic Data Centre as supplementary publication number **CCDC 936076**.

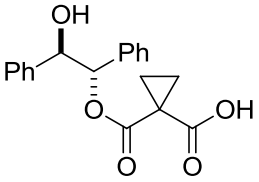




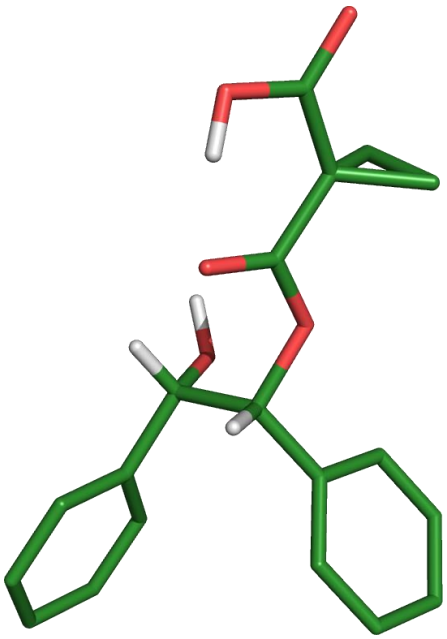
Empirical formula	$C_{19}H_{18}O_5$
M_r (g mol^{-1})	326.33
Crystal system	Monoclinic
Space group	P $2_1/c$
a/ Å	10.7552(7)
b/ Å	10.1502(7)
c/ Å	14.9906(8)
β (°)	93.447(5)
V/Å^3	1633.52(18)
Z	4
Temp K	153(2)
2θmax	55
λ/ Å	0.71073
Measured reflections	13349
Unique reflections	3678
R_{int}	0.0492
Observed rflns [$I > 2\sigma(I)$]	2463
μ (mm^{-1})	0.096
No. of parameters	225
R [on *F*, obs rflns only]	0.0471
wR [on F^2, all data]	0.1191
GoF	1.028
Largest diff. peak/hole/e Å^{-3}	0.224/-0.262

1-(((*rel*-1*S*,2*R*)-2-hydroxy-1,2-diphenylethoxy)carbonyl)cyclopropanecarboxylic acid 58

Available from Cambridge Crystallographic Data Centre as supplementary publication number **CCDC 936077**.

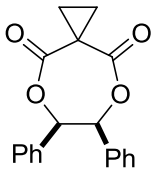


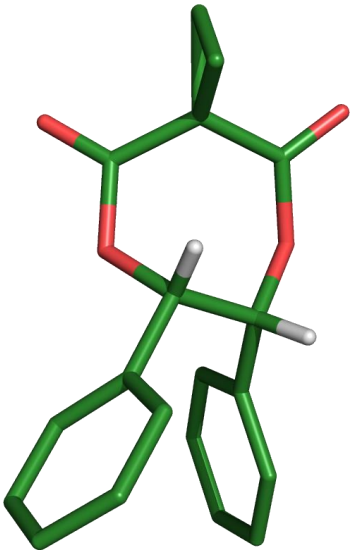
Empirical formula	$C_{19}H_{18}O_5$
M_r (g mol^{-1})	326.33
Crystal system	Orthorhombic
Space group	P $2_12_12_1$
a/ Å	5.6981(7)
b/ Å	8.6185(7)
c/ Å	32.841(7)
β (º)	
V/Å^3	1612.6(4)
Z	4
Temp K	123(2)
2θmax	146.4
λ/ Å	1.5418
Measured reflections	3829
Unique reflections	2650
R_{int}	0.0360
Observed rflns [$I > 2\sigma(I)$]	2185
μ (mm^{-1})	0.804
No. of parameters	223
R [on *F*, obs rflns only]	0.0626
wR [on F^2, all data]	0.1667
GoF	1.063
Largest diff. peak/hole/e Å^{-3}	0.318/-0.232



***rel*-(6*R*,7*S*)-6,7-diphenyl-5,8-dioxaspiro[2.6]nonane-4,9-dione 59**

Available from Cambridge Crystallographic Data Centre as supplementary publication number **CCDC 936074**.





Empirical formula	$C_{19}H_{16}O_4$
M_r (g mol^{-1})	308.32
Crystal system	Monoclinic
Space group	P 2_1/c
a/ Å	13.4714(4)
b/ Å	5.8443(2)
c/ Å	19.1637(6)
β (°)	103.276(3)
V/Å^3	1468.45(8)
Z	4
Temp K	123(2)
2θmax	146.2
λ/ Å	1.5418
Measured reflections	6142
Unique reflections	2878
R_{int}	0.0213
Observed rflns [$I > 2\sigma(I)$]	2434
μ (mm^{-1})	0.799
No. of parameters	208
R [on *F*, obs rflns only]	0.0406
wR [on F^2, all data]	0.1103
GoF	1.036
Largest diff. peak/hole/e Å^{-3}	0.302/-0.227

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