Tandem Iridium-Catalyzed Alkene Isomerization-Cope Rearrangement of ω-diene Epoxides for the Stereoselective Synthesis of Acyclic 1,6-Dicarbonyl Compounds

Rahul Suresh, Itai Massad, and Ilan Marek*

Schulich Faculty of Chemistry, Technion - Israel Institute of Technology, Technion City, Haifa, 32000, Israel

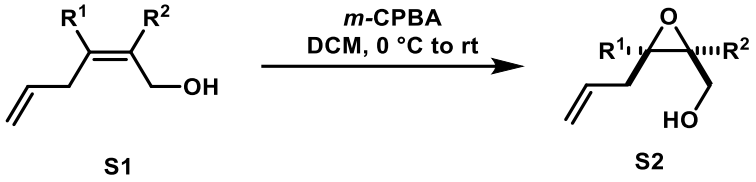
Supporting information

1. General experimental detail

Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of argon. Et_2O and THF were dried from Pure-Solv® Purification System (Innovative Technology©). DCM, Chlorobenzene and DCE were distilled from CaH_2. Toluene, 2-MeTHF and MTBE were distilled from sodium and benzophenone. All other commercially obtained reagents were used as received. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates, (0.25 mm) and visualized by exposure to UV light (254 nm) or stained with anisaldehyde, phosphomolybdic acid, or potassium permanganate. Purification by column chromatography was performed using Fluka silica gel 60 Å (40- 63 μm, 230-400 mesh). ^{1}H-NMR spectra were recorded on Bruker spectrometers (AVIII 400 and AVIII 300) and are reported relative to deuterated solvent signals. Chemical shifts are reported in parts per million (ppm) with respect to the residual solvent signal $CDCl_3$ (1H NMR: δ = 7.26; 13C NMR: δ = 77.00). Peak multiplicities are reported as follows: s = singlet, bs = broad singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, m = multiplet. High-resolution mass spectra (HRMS) were obtained by the mass spectrometry facility at the Technion. Diastereomeric ratio were obtained by analysing the crude nmr spectrum.

2. Preparation of substrates

- **General procedure for epoxidation of allylic alcohols (S1):**

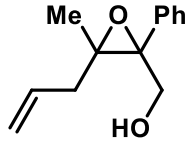


S1 S2

To a stirred solution of allyl alcohol (**S1,** 1.0 equiv.) in DCM (0.3 M) at 0 °C, was added *m*-CPBA (1.1 equiv.) in one portion. The reaction was stirred for 3 hours at 0 °C followed by warming up to room temperature. The reaction mixture was directly poured into a separation funnel and was washed with $NaHCO_3$ (10 mL/mmol, 3 times). The combined aqueous layer was then extracted with DCM (3 mL/mmol). The combined organic layer was dried with Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified further by silica gel (230-400 mesh) column chromatography to obtain the desired product **S2**.

Various (**S1**) were obtained by prepared as previously described in the literature. [1–3]

(3-Allyl-3-methyl-2-phenyloxiran-2-yl)methanol (S2a): liquid, (77% yield).

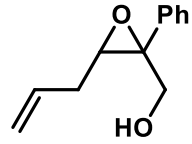


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.50 – 7.26 (m, 5H), 5.91 (ddt, J = 17.1, 10.2, 6.9 Hz, 1H), 5.55 – 4.82 (m, 2H), 4.11 (dd, J = 12.0, 6.0 Hz, 1H), 3.95 (dd, J = 12.0, 6.7 Hz, 1H), 2.72 – 2.57 (m, 1H), 2.49 (dd, J = 14.8, 7.0 Hz, 1H), 1.00 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 137.96, 133.45, 128.29, 127.59, 126.84, 117.98, 69.38, 66.28, 64.99, 39.06, 19.64.

HRMS (APCI): m/z calculated for C13H17O2 [M+H]+: 205.1223, found 205.1209.

(3-Allyl-2-phenyloxiran-2-yl)methanol (S2b): liquid, (87% yield).

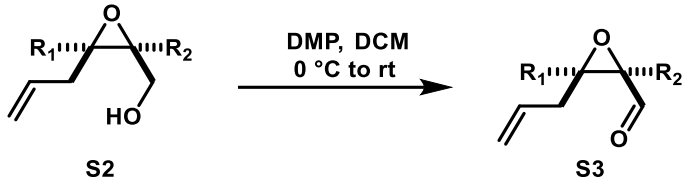


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.40 (m, 2H), 7.40 – 7.33 (m, 2H), 7.33 – 7.28 (m, 1H), 5.92 (ddt, J = 16.9, 10.3, 6.4 Hz, 1H), 5.29 – 5.13 (m, 2H), 4.23 (dd, J = 12.2, 6.0 Hz, 1H), 4.09 – 3.95 (m, 1H), 3.07 (t, J = 6.5 Hz, 1H), 2.63 (dtt, J = 14.3, 6.4, 1.6 Hz, 1H), 2.57 – 2.39 (m, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 138.98, 133.21, 128.52, 127.86, 125.84, 117.55, 65.19, 63.62, 63.14, 32.90.

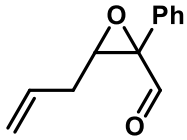
HRMS (APCI): m/z calculated for C12H15O2 [M+H]+: 191.1067, found 191.1088.

- **General procedure for oxidation of epoxyalcohols (S2):**



To a stirred solution of allyl alcohol (**S2,** 1.0 equiv.) in DCM (0.1 M) at 0 °C, was added Dess–Martin periodinane (DMP) (1.05 equiv.) in one portion. The reaction was stirred for 15 minutes at 0 °C followed by stirring at room temperature for 5 hours. The reaction mixture mixture was directly poured into a separation funnel and was washed with (1:1) saturated solution of $NaHCO_3$ and $Na_2S_2O_3$ (10 mL/mmol, 3 times). The combined organic layer was extracted with DCM, combined organic layers were concentrated in vacuo and this crude product was filtered over fluorosil to obtain the desired product **S3**. This aldehyde was used directly without further purification.

3-Allyl-2-phenyloxirane-2-carbaldehyde (S3a): liquid, (92% yield).

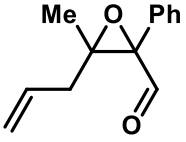


^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.75 (s, 1H), 7.52 – 7.47 (m, 2H), 7.43 – 7.33 (m, 3H), 5.88 (ddt, J = 16.9, 10.2, 6.5 Hz, 1H), 5.30 – 5.10 (m, 2H), 3.30 (t, J = 6.5 Hz, 1H), 2.74 – 2.60 (m, 1H), 2.50 (dtt, J = 15.6, 6.5, 1.4 Hz, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 197.39, 133.54, 131.95, 128.57, 128.51, 126.60, 118.42, 66.52, 65.74, 32.49.

HRMS (APCI): m/z calculated for C12H13O2 [M+H]+: 189.0916, found 189.0918.

3-Allyl-3-methyl-2-phenyloxirane-2-carbaldehyde (S3b): liquid, (quantitative yield).



^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.79 (s, 1H), 7.48 – 7.31 (m, 5H), 5.83 (ddt, J = 17.2, 10.4, 6.9 Hz, 1H), 5.24 – 5.12 (m, 2H), 2.64 (ddt, J = 14.8, 6.8, 1.4 Hz, 1H), 2.47 (dd, J = 14.8, 7.1 Hz, 1H), 1.06 (d, J = 0.6 Hz, 3H).

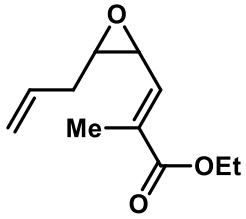
^{13}C-NMR (101 MHz, $CDCl_3$): δ 198.13, 132.42, 132.23, 128.36, 128.30, 127.41, 118.91, 71.44, 69.14, 38.70, 19.01.

HRMS (APCI): m/z calculated for C13H15O2 [M+H]+: 203.1067, found 203.1067.

- **General procedure for Wittig reaction of epoxyaldehydes (S3):**

To a stirred solution of the epoxy aldehyde (**S3,** 1.0 equiv.) in DCM (0.2 M) at 0 °C, was added stabilized ylide (1.2 equiv.) in one portion. The reaction mixture was then warmed to room temperature and stirred for 5 hours. Then the reaction mixture was dried in vacuo followed by purified by silica gel (230-400 mesh) column chromatography (2-3%EtOAc/Hexanes) to obtain the desired product **1**.

Ethyl (E)-3-(3-allyloxiran-2-yl)-2-methylacrylate (1a): (52% yield, liquid).

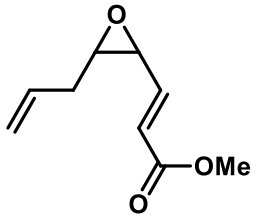


^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.64 – 6.43 (m, 1H), 5.83 (ddt, J = 17.0, 10.2, 6.6 Hz, 1H), 5.25 – 5.06 (m, 2H), 4.21 (qd, J = 7.1, 3.6 Hz, 2H), 3.67 (dd, J = 7.9, 4.3 Hz, 1H), 3.26 (td, J = 6.3, 4.3 Hz, 1H), 2.53 – 2.36 (m, 1H), 2.36 – 2.10 (m, 1H), 1.99 (d, J = 1.5 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 166.98, 134.86, 133.53, 132.96, 117.66, 60.89, 57.93, 53.11, 33.10, 14.19, 13.00.

HRMS (TOFMS): m/z calculated for C11H17O3 [M+H]+: 197.1178, found 197.1175.

Methyl (E)-3-(3-allyloxiran-2-yl)acrylate (1b): (54% yield, liquid).

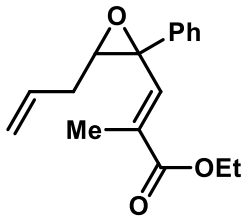


^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.84 (dd, J = 15.6, 6.4 Hz, 1H), 6.15 (dd, J = 15.7, 1.0 Hz, 1H), 5.80 (ddt, J = 16.8, 10.1, 6.5 Hz, 1H), 5.24 – 5.07 (m, 2H), 3.75 (s, 3H), 3.57 (ddd, J = 6.4, 4.4, 1.0 Hz, 1H), 3.31 – 3.21 (m, 1H), 2.45 – 2.32 (m, 1H), 2.22 (ddt, J = 15.2, 7.7, 1.5 Hz, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 165.97, 141.84, 132.75, 125.03, 117.85, 58.46, 55.03, 51.82, 32.04.

HRMS (APCI): m/z calculated for C9H13O3 [M+H]+: 169.0859, found 169.0893.

Ethyl (E)-3-(3-allyl-2-phenyloxiran-2-yl)-2-methylacrylate (1d): (65% yield, liquid).

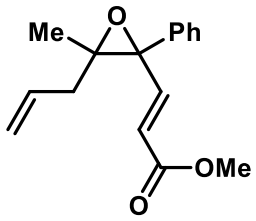


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.27 (m, 5H), 7.11 (d, J = 1.5 Hz, 1H), 5.90 (ddt, J = 17.0, 10.3, 6.5 Hz, 1H), 5.28 – 5.00 (m, 2H), 4.24 (qd, J = 7.1, 3.9 Hz, 2H), 3.19 (dd, J = 6.7, 5.5 Hz, 1H), 2.36 (qt, J = 6.5, 1.4 Hz, 2H), 1.93 (d, J = 1.4 Hz, 3H), 1.32 (t, J = 7.1 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 167.50, 139.06, 134.65, 134.62, 133.07, 128.53, 127.92, 125.74, 117.61, 66.07, 61.86, 60.98, 34.48, 14.50, 14.20.

HRMS (APCI): m/z calculated for C17H21O3 [M+H]+: 273.1485, found 273.1460.

Methyl (E)-3-(3-allyl-3-methyl-2-phenyloxiran-2-yl)acrylate (1e): (92% yield, liquid).

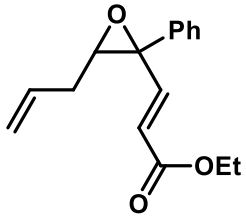


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.29 (m, 5H), 7.25 (d, J = 15.5 Hz, 1H), 6.01 (d, J = 15.5 Hz, 1H), 5.82 (ddt, J = 18.6, 9.4, 7.0 Hz, 1H), 5.49 – 4.83 (m, 2H), 3.72 (s, 3H), 2.49 (ddt, J = 14.3, 7.0, 1.3 Hz, 1H), 2.42 – 2.27 (m, 1H), 1.04 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 166.42, 145.65, 137.07, 133.11, 128.46, 127.70, 126.73, 123.14, 118.35, 68.90, 68.82, 51.69, 38.28, 18.90.

HRMS (APCI): m/z calculated for C16H19O3 [M+H]+: 259.1359, found 259.1329.

Ethyl (E)-3-(3-allyl-2-phenyloxiran-2-yl)acrylate (1h): (58% yield, liquid).

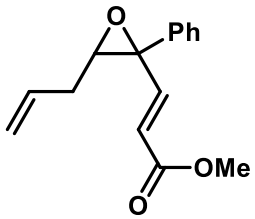


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.31 (m, 5H), 7.28 (d, J = 15.5 Hz, 1H), 6.04 (d, J = 15.5 Hz, 1H), 5.85 (ddt, J = 16.8, 10.3, 6.5 Hz, 1H), 5.21 – 5.13 (m, 2H), 4.21 (qd, J = 7.2, 1.0 Hz, 2H), 3.26 (t, J = 6.4 Hz, 1H), 2.47 (dtt, J = 15.5, 6.4, 1.4 Hz, 1H), 2.41 – 2.27 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 165.83, 142.87, 138.18, 132.67, 128.58, 128.11, 126.25, 124.88, 117.81, 66.83, 63.53, 60.66, 32.53, 14.19.

HRMS (TOFMS): m/z calculated for C16H18O3 [M+Na]+: 281.1154, found 281.1159.

Methyl (E)-3-(3-allyl-2-phenyloxiran-2-yl)acrylate (1i): (59% yield, liquid).

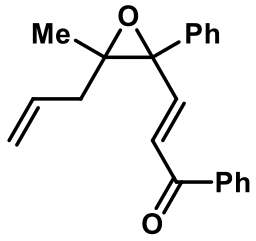


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.22 (m, 5H), 7.21 (d, J = 7.4 Hz, 1H), 6.00 (d, J = 15.5 Hz, 1H), 5.79 (ddt, J = 16.9, 10.3, 6.5 Hz, 1H), 5.14 – 5.08z (m, 2H), 3.69 (s, 3H), 3.20 (t, J = 6.4 Hz, 1H), 2.41 (dtt, J = 15.5, 6.3, 1.4 Hz, 1H), 2.33 – 2.20 (m, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 166.26, 143.17, 138.11, 132.63, 128.60, 128.14, 126.21, 124.37, 117.83, 66.87, 63.51, 51.76, 32.50.

HRMS (APCI): m/z calculated for C15H17O3 [M+H]+: 245.1178, found 245.1158.

Methyl (E)-3-(3-allyl-2-phenyloxiran-2-yl)acrylate (1k): (86% yield, liquid).

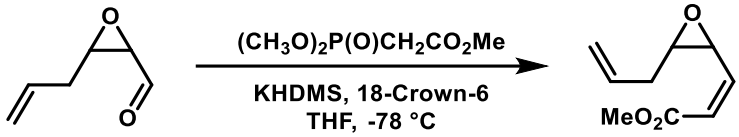


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.96 – 7.89 (m, 2H), 7.60 – 7.52 (m, 1H), 7.49 – 7.43 (m, 2H), 7.38 (q, J = 5.4 Hz, 5H), 7.34 – 7.28 (m, 1H), 7.12 (d, J = 15.1 Hz, 1H), 5.85 (ddt, J = 16.0, 11.3, 7.0 Hz, 1H), 5.23 – 5.08 (m, 2H), 2.52 (ddt, J = 14.4, 7.0, 1.4 Hz, 1H), 2.41 (dd, J = 14.5, 7.0 Hz, 1H), 1.08 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 189.55, 145.29, 137.50, 137.26, 133.13, 133.04, 128.61, 128.60, 128.50, 127.70, 126.72, 126.62, 118.40, 69.54, 69.30, 38.36, 18.86.

HRMS (APCI): m/z calculated for C21H21O2 [M+H]+: 305.1536, found 305.1553.

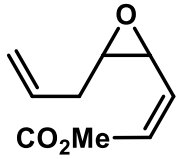
- **Procedure for Horner-Wadsworth-Emmons Olefination of epoxyaldehyde:**



1c

In an oven dried three neck round bottom flask, trimethyl phosphonoacetate (710mg, 3.9 mmol, 1.1 equiv.) and 18-crown-6 (4.7gm, 17.8 mmol, 5.0 equiv.) was taken in freshly distilled THF (70 mL), cooled to -78 °C and solution of potassium-bis(trimethylsilyl)amide (5.6mL, 3.9 mmol, 1.1 equiv.) in toluene was added over 10 min. After an additional 10 min, a solution of aldehyde (400 mg, 3.56 mmol, 1.0 equiv.) in freshly distilled THF (1.5 mL) was transferred to the reaction mixture. and stirred for 30 minutes at -78 °C, a saturated solution of NH4Cl (30 mL) was added, warmed to room temperature and extracted with EtOAc (3 x 30 mL). The combined organic layers were dried over anhydrous Na2SO4, filtered, and concentrated. Purification of the crude product by silica gel (230-400 mesh) column chromatography (2-3%EtOAc/Hexanes) to obtain the desired product **1C** (353 mg, 2.1 mmol, 59%) as a colourless oil.[4]

Methyl (Z)-3-(3-allyloxiran-2-yl)acrylate (1c):

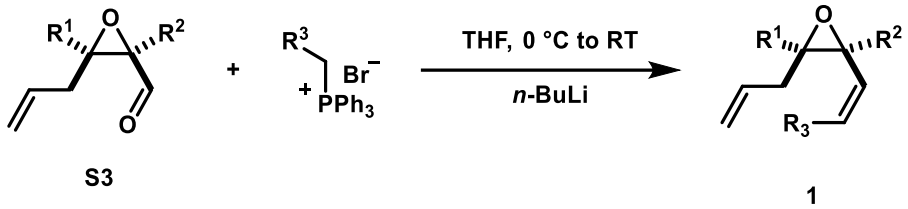


^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.12 – 6.01 (m, 2H), 5.82 (ddt, J = 16.9, 10.3, 6.5 Hz, 1H), 5.31 – 4.90 (m, 2H), 4.47 (td, J = 4.4, 2.0 Hz, 1H), 3.76 (s, 3H), 3.37 – 3.26 (m, 1H), 2.35 (dtt, J = 14.9, 6.7, 1.5 Hz, 1H), 2.24 (dtt, J = 15.4, 6.2, 1.5 Hz, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 166.11, 144.54, 132.86, 124.02, 117.56, 58.16, 53.52, 51.55, 33.24.

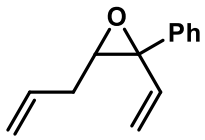
HRMS (APCI): m/z calculated for C9H13O3 [M+H]+: 169.0859, found 169.0865.

- **General procedure for Wittig reaction of epoxyaldehydes (S3):**



In an oven dried round bottom flask, alkyltriphenylphosphonium bromide (1.2 equiv.) was taken in freshly distilled THF (1.6 mL/mmol) under argon atmosphere. The resulting suspension was cooled to 0 °C and *n*-BuLi (1.2 equiv.) was added. The resulting suspension was stirred at 0 °C for 45 min. To this suspension, a solution of aldehyde **S3** (1.0 equiv.) in freshly distilled THF (0.7 mL/mmol) was added dropwise. The resulting mixture was allowed to attain ambient temperature and stirred for 4 h at this temperature. Sat. NH_4Cl (10 mL/mmol) was added to the reaction mixture and extracted with EtOAc (3 × 10 mL/mmol). The combined organic layer was dried over anhydrous Na_2SO_4 and purified by silica gel (230-400 mesh) column chromatography (2-3%EtOAc/Hexanes) to obtain the desired product **1**.[5]

3-Allyl-2-phenyl-2-vinyloxirane (1f): liquid (33% yield, liquid)

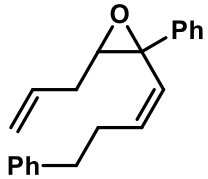


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.32 (m, 4H), 7.32 – 7.28 (m, 1H), 6.22 (dd, J = 17.1, 10.8 Hz, 1H), 5.88 (ddt, J = 16.9, 10.3, 6.5 Hz, 1H), 5.62 – 5.26 (m, 2H), 5.24 – 5.00 (m, 2H), 3.17 (t, J = 6.3 Hz, 1H), 2.63 – 2.42 (m, 1H), 2.37 (dtt, J = 14.9, 6.6, 1.5 Hz, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 139.71, 133.42, 133.21, 128.31, 127.61, 126.34, 119.48, 117.35, 65.87, 64.29, 32.62.

HRMS (APCI): m/z calculated for C13H15O [M+H]+: 187.1117, found 187.1123.

(Z)-3-Allyl-2-phenyl-2-(4-phenylbut-1-en-1-yl)oxirane (1g): (28% yield, liquid)

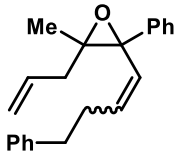


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.27 (m, 5H), 7.25 – 7.21 (m, 2H), 7.19 – 7.13 (m, 1H), 7.12 – 7.07 (m, 2H), 5.98 – 5.79 (m, 3H), 5.25 – 5.02 (m, 2H), 3.09 (t, J = 6.1 Hz, 1H), 2.67 – 2.32 (m, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 141.56, 140.85, 136.49, 133.53, 128.44, 128.31, 128.25, 127.45, 125.82, 125.79, 124.73, 117.19, 65.75, 61.91, 35.19, 34.32, 31.04.

HRMS (APCI): m/z calculated for C21H23O [M+H]+: 291.1743, found 291.1769.

2-Allyl-2-methyl-3-phenyl-3-(4-phenylbut-1-en-1-yl)oxirane (1j): (32% yield, liquid)

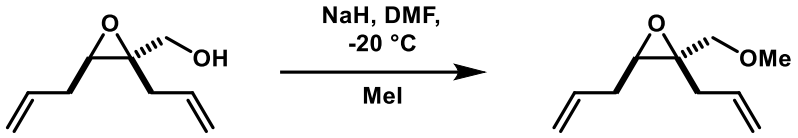


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.30 (m, 3H), 7.29 – 7.22 (m, 4H), 7.19 – 7.10 (m, 3H), 6.00 – 5.56 (m, 3H), 5.21 – 5.04 (m, 2H), 2.70 – 2.27 (m, 6H), 0.98 (d, J = 9.8 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 141.79, 141.56, 140.35, 134.32, 134.22, 133.86, 128.71, 128.44, 128.40, 128.28, 128.23, 128.05, 127.17, 126.98, 126.86, 126.44, 125.81, 125.74, 117.82, 117.67, 69.23, 68.39, 67.42, 65.52, 39.82, 38.46, 35.45, 35.27, 34.28, 30.51, 19.15, 17.68.

HRMS (APCI): m/z calculated for C22H25O [M+H]+: 305.1900, found 305.1881.

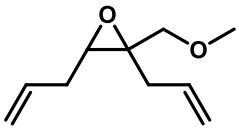
- **Procedure for methyl protection of epoxyalcohol.**[6]



3a

In an over dried 50 mL round bottom flask, alcohol (400mg, 2.6 mmol, 1 equiv.) was taken in DMF under argon atmosphere. To this, dry DMF (8.9mL) was added followed by cooling the reaction to -20 C and then NaH (60%, 94mg, 3.9 mmol, 1.5 equiv.) was added. After 20 minutes, MeI (0.401mL, 6.5mmol, 2.5 equiv) was added and was warmed to room temperature. After 3 hours, the reaction was quenched with Sat. NH_4Cl (10mL) and the mixture was extracted with EtOAc (10mL) three times. The combined organic layer were washed with brine and dried over anhydrous Na_2SO_4 and purified by silica gel (230-400 mesh) column chromatography (3%EtOAc/Hexanes) to obtain the desired product (280mg, 64% yield, 1.66 mmol, liquid).

2,3-Diallyl-2-(methoxymethyl)oxirane (3a):

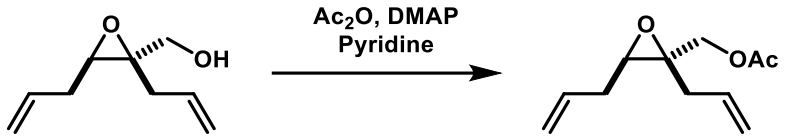


^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.85 (dddt, J = 19.8, 17.2, 10.2, 6.8 Hz, 2H), 5.28 – 4.96 (m, 4H), 3.49 (d, J = 11.1 Hz, 1H), 3.38 (d, J = 11.1 Hz, 1H), 3.35 (s, 3H), 3.00 (t, J = 6.4 Hz, 1H), 2.58 – 2.48 (m, 1H), 2.46 – 2.22 (m, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 133.50, 132.94, 118.25, 117.40, 74.36, 61.64, 59.45, 59.23, 33.39, 32.60.

HRMS (APCI): m/z calculated for C10H17O2 [M+H]+: 169.1223, found 169.1228.

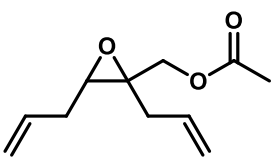
- **Procedure for acetyl protection of epoxyalcohol:**



3b

In an over dried 50 mL round bottom flask, alcohol (400mg, 2.6 mmol, 1 equiv.) was taken in pyridine (5.3mL) followed by Ac_2O (0.53mL, 5.6 mmol, 2 equiv.) and DMAP (32mg, 0.26mmol, 0.1 equiv.). Then solvent was removed in vacuo and the reaction mixture was further purified by silica gel (230-400 mesh) column chromatography (4 %EtOAc/Hexanes) to obtain the desired product (320 mg, 64% yield, 1.63 mmol, liquid).

(2,3-Diallyloxiran-2-yl)methyl acetate (3b):



^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.95 – 5.69 (m, 2H), 5.25 – 5.04 (m, 4H), 4.23 (d, J = 12.0 Hz, 1H), 4.01 (d, J = 12.1 Hz, 1H), 3.02 (t, J = 6.4 Hz, 1H), 2.54 (ddt, J = 14.9, 7.1, 1.4 Hz, 1H), 2.47 – 2.21 (m, 3H), 2.08 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 133.44, 132.88, 118.20, 117.35, 74.31, 61.59, 59.39, 59.17, 33.33, 32.55.

HRMS (APCI): m/z calculated for C11H17O3 [M+H]+: 197.1172, found 197.1173.

- **Procedure for TBDMS protection of epoxyalcohol:**

3c

To a stirring solution of allylic alcohol (400mg, 2.6 mmol, 1 equiv.) and imidazole (0.165 g, 2.5 mmol, 0.95 equiv) in DCM (5mL), was added TBSCl (0.377g, 2.5 mmol, 0.95 equiv.) at rt in one portion. The solution was stirred overnight at rt, followed by addition of 20 ml of saturated ammonium chloride solution. The resulting mixture was allowed to stir until two clear phases emerged and then transferred to a separatory funnel. The aqueous phase was extracted with DCM (3X10 ml) and the combined organic fractions dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was further purified by silica gel (230-400 mesh) column chromatography (4 %EtOAc/Hexanes) to obtain the desired product (480mg, 68% yield, 1.78 mmol, liquid).

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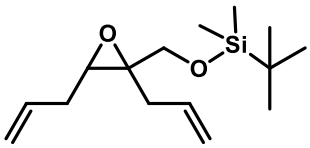
(*tert*-Butyl((2,3-diallyloxiran-2-yl)methoxy)dimethylsilane (3c):



^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.00 – 5.73 (m, 2H), 5.28 – 5.00 (m, 4H), 3.63 (d, J = 2.2 Hz, 2H), 2.99 (t, J = 6.4 Hz, 1H), 2.60 – 2.46 (m, 1H), 2.46 – 2.21 (m, 3H), 0.89 (s, 9H), 0.05 (d, J = 4.2 Hz, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 133.67, 133.19, 117.98, 117.16, 65.28, 62.85, 59.51, 33.14, 32.62, 25.88, 18.32, -5.39.

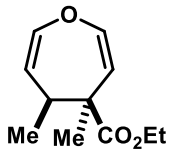
HRMS (TOFMS): m/z calculated for C15H28O2Si [M+Na]+: 291.1756, found 291.1765.

3. General procedure for the iridium-catalyzed isomerization-Cope rearrangement of ω-diene epoxides

Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (11.1 mg, 0.0125 mmol) was placed in a flame-dried Schlenk tube under argon flow utilizing Argon pants. PCy_3 (8.41 mg, 0.03 mmol) and $[Ir(cod)Cl]_2$ (3.36 mg, 0.5 µmol) was subsequently added under argon flow and the solids stirred for 1 minute at room temperature before PhCl (1 mL) was added. Upon complete dissolution of the solids (resulting in an orange-reddish solution. The resulting mixture was then stirred vigorously under argon flow for 5 minutes, followed by addition of the neat starting material (**1**, 0.3 mmol or 0.5 mmol) under argon flow using a microsyringe and heating of the reaction mixture to 120 °C or 140 °C using an oil bath. After 24 hours, the mixture was cooled to room temperature and diluted with 2 ml of petroleum ether. The mixture was then stirred at rt for 5 minutes to yield a cloudy yellow solution which was then filtered on a pad of basic aluminum oxide and concentrated in vacuo to yield the crude reaction mixture as pale-yellow oil which was further purified by silica gel (230-400 mesh) column chromatography (1-2.5 %EtOAc/Hexanes) to obtain the desired product.

Note: the quality of the Ir precatalyst often effects the reaction rate, with the best reactivity obtained with $(Ir(cod)Cl)_2$ purchased from Strem

Ethyl (syn)-4,5-dimethyl-4,5-dihydrooxepine-4-carboxylate (2a): liquid.



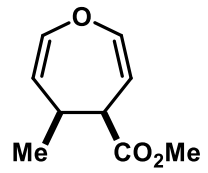
81% yield (79 mg, 0.405 mmol on 0.5 mmol scale).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.16 (dd, J = 8.8, 7.7 Hz, 2H), 5.36 (dd, J = 7.9, 1.3 Hz, 1H), 4.89 (t, J = 7.8 Hz, 1H), 4.16 (dd, J = 7.1, 1.4 Hz, 2H), 2.68 (ddd, J = 8.1, 6.8, 1.3 Hz, 1H), 1.36 (s, 3H), 1.29 – 1.24 (m, 3H), 0.99 (d, J = 6.8 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 175.43, 141.03, 140.19, 110.16, 108.77, 60.89, 50.95, 40.72, 28.15, 20.14, 14.20.

HRMS (APCI): m/z calculated for C11H17O3 [M+H]+: 197.1172, found 197.1163.

Methyl (syn)-5-methyl-4,5-dihydrooxepine-4-carboxylate (2b): liquid.



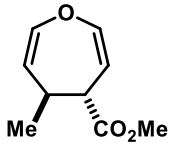
64% yield (53 mg, 0.315 mmol on 0.5 mmol scale).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.26 (dd, J = 7.6, 2.1 Hz, 1H), 6.19 – 6.08 (m, 1H), 5.13 (ddd, J = 7.5, 4.7, 0.8 Hz, 1H), 4.87 (t, J = 7.3 Hz, 1H), 3.70 (s, 3H), 3.58 (ddd, J = 5.0, 3.1, 2.1 Hz, 1H), 3.02 – 2.79 (m, 1H), 1.03 (d, J = 7.0 Hz, 3H).

^{13}C-NMR (101MHz, $CDCl_3$): δ 172.73, 142.48, 141.41, 112.08, 103.76, 52.01, 47.88, 35.21, 19.14.

HRMS (APCI): m/z calculated for C9H13O3 [M+H]+: 169.0859, found 169.0850.

Methyl (anti)-5-methyl-4,5-dihydrooxepine-4-carboxylate (2c): liquid.



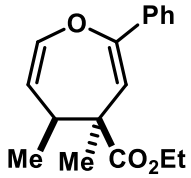
62% yield (35 mg, 0.208 mmol on 0.3 mmol scale).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.28 (dd, J = 7.6, 1.4 Hz, 1H), 6.12 (dd, J = 7.6, 1.1 Hz, 1H), 4.78 (dt, J = 7.6, 5.9 Hz, 2H), 3.70 (s, 3H), 3.19 (td, J = 6.0, 1.4 Hz, 1H), 2.90 – 2.73 (m, 1H), 1.09 (d, J = 7.0 Hz, 3H).

^{13}C-NMR (101MHz, $CDCl_3$): δ 173.56, 143.16, 141.20, 112.31, 103.90, 51.97, 50.47, 35.05, 21.58.

HRMS (APCI): m/z calculated for C9H13O3 [M+H]+: 169.0859, found 169.0853.

Ethyl (syn)-4,5-dimethyl-2-phenyl-4,5-dihydrooxepine-4-carboxylate (2d): liquid.



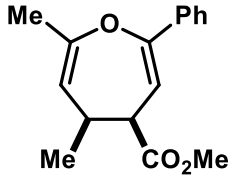
92% yield (75 mg, 0.275 mmol on 0.3 mmol scale).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 7.5 Hz, 2H), 7.33 (q, J = 6.2, 5.3 Hz, 3H), 6.51 – 6.31 (m, 1H), 6.27 (s, 1H), 4.90 (t, J = 7.4 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 2.74 (p, J = 7.2 Hz, 1H), 1.50 (s, 3H), 1.29 (td, J = 7.1, 2.1 Hz, 3H), 1.06 – 0.96 (m, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): 13C NMR (101 MHz, CDCl3) δ 175.76, 150.79, 140.46, 137.00, 128.17, 128.14, 125.56, 110.28, 107.74, 61.01, 50.47, 40.65, 26.08, 20.83, 14.24.

HRMS (TOFMS): m/z calculated for C16H20O4 [M+Na]+: 291.1743, found 291.1718.

Methyl (syn)-5,7-dimethyl-2-phenyl-4,5-dihydrooxepine-4-carboxylate (2e): liquid.



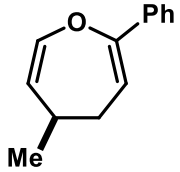
91% yield (70mg, 0.272 mmol on 0.3 mmol scale).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.61 – 7.59 (m, 2H), 7.37 – 7.29 (m, 3H), 6.08 (dd, J = 5.7, 0.7 Hz, 1H), 4.80 (dd, J = 6.5, 1.0 Hz, 1H), 3.93 (dd, J = 5.7, 3.1 Hz, 1H), 3.75 (s, 3H), 2.91 (tt, J = 6.9, 2.9 Hz, 1H), 1.97 (s, 3H), 1.01 (d, J = 6.9 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 173.29, 153.45, 150.32, 136.09, 128.26, 128.24, 125.23, 109.42, 104.86, 52.06, 46.41, 34.82, 22.50, 18.74.

HRMS (APCI): m/z calculated for C16H19O3 [M+H]+: 259.1329, found 259.1318.

5-Methyl-2-phenyl-4,5-dihydrooxepine (2f): liquid (69% yield). liquid.



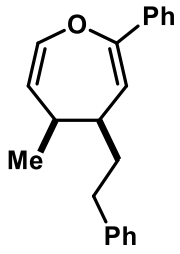
78% yield (44 mg, 0.236 mmol on 0.3 mmol scale).

^{1}H-NMR (400 MHz, $CDCl_3$): 1H NMR (400 MHz, Chloroform-d) δ 7.56 – 7.50 (m, 2H), 7.36 – 7.27 (m, 3H), 6.37 (dt, J = 7.7, 1.6 Hz, 1H), 5.72 (dd, J = 7.8, 6.1 Hz, 1H), 4.70 (dd, J = 7.6, 3.5 Hz, 1H), 2.62 – 2.51 (m, 1H), 2.51 – 2.29 (m, 2H), 1.08 (dd, J = 6.9, 1.1 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 154.62, 141.31, 136.57, 128.19, 127.88, 125.03, 115.13, 107.13, 33.52, 32.23, 23.19.

HRMS (TOFMS): m/z calculated for C13H15O [M+H]+: 187.1123, found 187.1129.

5-Methyl (syn)--4-phenethyl-2-phenyl-4,5-dihydrooxepine (2g): liquid.



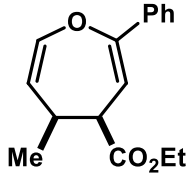
46% yield (40 mg, 0.137 mmol on 0.3 mmol scale).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.56 (dt, *J* = 8.1, 1.7 Hz, 2H), 7.35 (td, *J* = 7.7, 7.3, 1.6 Hz, 2H), 7.29 (td, *J* = 7.1, 1.6 Hz, 3H), 7.24 – 7.17 (m, 3H), 6.42 – 6.32 (m, 1H), 5.69 (dd, *J* = 7.6, 1.8 Hz, 1H), 4.77 (ddt, *J* = 8.3, 5.8, 1.4 Hz, 1H), 2.85 – 2.74 (m, 1H), 2.68 (dtd, *J* = 14.9, 8.2, 7.5, 3.9 Hz, 1H), 2.38 (ddt, *J* = 18.2, 13.7, 6.4 Hz, 2H), 2.05 – 1.83 (m, 2H), 1.12 (dd, *J* = 6.8, 1.8 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 153.15, 142.61, 140.86, 136.92, 129.76, 128.66, 128.46, 128.39, 128.21, 127.97, 126.48, 125.76, 125.29, 112.57, 110.22, 43.03, 36.95, 36.81, 33.82, 23.11.

HRMS (APCI): m/z calculated for C21H23O [M+H]+: 291.1743, found 291.1718.

Ethyl (syn)-5-methyl-2-phenyl-4,5-dihydrooxepine-4-carboxylate (2h): liquid.



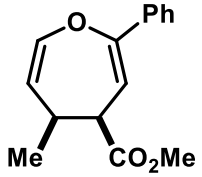
93% yield (72 mg, 0.278 mmol on 0.3 mmol scale).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.63 – 7.56 (m, 2H), 7.38 – 7.30 (m, 3H), 6.43 (dd, J = 7.6, 1.1 Hz, 1H), 6.11 (dd, J = 5.6, 0.7 Hz, 1H), 4.89 (dd, J = 7.6, 6.6 Hz, 1H), 4.22 (qd, J = 7.1, 2.7 Hz, 2H), 3.94 (dd, J = 5.6, 3.0 Hz, 1H), 2.98 (tdt, J = 6.8, 3.1, 0.9 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.06 (d, J = 6.9 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 172.51, 153.72, 141.97, 135.82, 128.28, 128.19, 125.25, 112.98, 104.44, 60.89, 46.81, 35.33, 18.99, 14.27.

HRMS (APCI): m/z calculated for C16H19O3 [M+H]+: 259.1329, found 259.1315.

Methyl (syn)-5-methyl-2-phenyl-4,5-dihydrooxepine-4-carboxylate (2i): liquid.



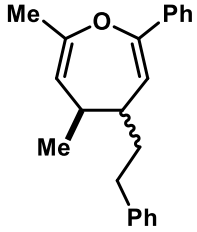
91% yield (67 mg, 0.274 mmol on 0.3 mmol scale).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.57 (m, 2H), 7.38 – 7.27 (m, 3H), 6.43 (dd, J = 7.6, 1.1 Hz, 1H), 6.10 (d, J = 5.6 Hz, 1H), 4.89 (dd, J = 7.6, 6.6 Hz, 1H), 3.97 (dd, J = 5.7, 3.0 Hz, 1H), 3.76 (s, 3H), 3.05 – 2.90 (m, 1H), 1.05 (d, J = 6.8 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 13C NMR (101 MHz, CDCl3) δ 173.06, 153.87, 142.04, 135.85, 128.38, 128.26, 125.32, 113.03, 104.35, 52.16, 46.86, 35.34, 19.12.

HRMS (APCI): m/z calculated for C15H17O3 [M+H]+: 245.1172, found 245.1166.

2,4-Mimethyl-5-phenethyl-7-phenyl-4,5-dihydrooxepine (2j): liquid.



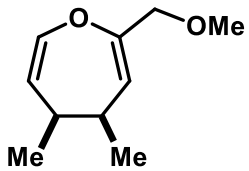
56% yield (51 mg, 0.167 mmol on 0.3 mmol scale).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.57 (ddt, J = 6.6, 5.5, 1.4 Hz, 4H), 7.38 – 7.27 (m, 11H), 7.25 – 7.17 (m, 6H), 5.65 (d, J = 6.9 Hz, 1H), 5.56 (d, J = 6.1 Hz, 1H), 4.71 (d, J = 5.7 Hz, 2H), 2.86 (s, 1H), 2.83 – 2.61 (m, 4H), 2.52 (s, 1H), 2.41 – 2.28 (m, 2H), 1.96 (s, 6H), 1.94 – 1.68 (m, 4H), 1.09 (d, J = 6.5 Hz, 3H), 1.00 (d, J = 7.0 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 152.57, 152.41, 149.41, 149.30, 142.66, 142.48, 137.15, 136.67, 129.70, 128.59, 128.40, 128.35, 128.31, 128.15, 128.14, 127.78, 125.74, 125.66, 125.17, 125.04, 111.98, 110.45, 110.37, 109.53, 42.46, 36.72, 35.90, 35.10, 34.41, 33.57, 22.38, 22.24.

HRMS (APCI): m/z calculated for C22H25O [M+H]+: 305.1900, found 305.1884.

(syn)-2-(Methoxymethyl)-4,5-dimethyl-4,5-dihydrooxepine (2l): liquid.



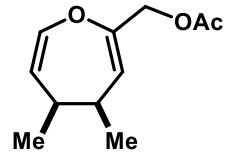
91% yield (46mg, 0.273 mmol on 0.3 mmol scale).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.16 (dd, J = 7.5, 1.4 Hz, 1H), 4.94 (d, J = 5.9 Hz, 1H), 4.68 (dd, J = 7.5, 5.7 Hz, 1H), 3.83 (d, J = 12.1 Hz, 1H), 3.76 (d, J = 12.1 Hz, 1H), 3.35 (s, 3H), 2.68 (pd, J = 6.9, 2.8 Hz, 1H), 2.59 – 2.44 (m, 1H), 1.01 (t, J = 7.1 Hz, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 149.06, 140.57, 113.44, 113.18, 74.03, 57.80, 36.80, 36.06, 18.53, 18.28.

HRMS (APCI): m/z calculated for C10H17O2 [M+H]+: 169.1223, found 169.1230

((syn)-4,5-Dimethyl-4,5-dihydrooxepin-2-yl)methyl acetate (2m): liquid.



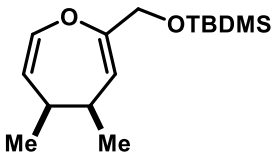
81% yield (48mg, 0.244 mmol on 0.3 mmol scale).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.14 (dd, J = 7.5, 1.4 Hz, 1H), 5.00 (d, J = 6.0 Hz, 1H), 4.70 (dd, J = 7.5, 5.7 Hz, 1H), 4.44 (s, 2H), 2.68 (dq, J = 10.6, 3.9, 3.4 Hz, 1H), 2.55 (dddd, J = 7.1, 5.8, 3.1, 1.5 Hz, 1H), 2.09 (s, 3H), 1.01 (dd, J = 8.2, 7.0 Hz, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 170.78, 147.53, 140.46, 114.88, 113.47, 65.99, 53.42, 36.58, 36.18, 18.47, 18.13.

HRMS (APCI): m/z calculated for C11H17O3 [M+H]+: 197.1172, found 197.1173.

tert-Butyl(((syn)-4,5-dimethyl-4,5-dihydrooxepin-2-yl)methoxy)dimethylsilane (2n): liquid.



78% yield (44 mg, 0.236 mmol on 0.3 mmol scale).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.12 (dd, J = 7.5, 1.4 Hz, 1H), 4.93 (d, J = 6.0 Hz, 1H), 4.65 (dd, J = 7.5, 5.6 Hz, 1H), 3.99 (s, 2H), 2.74 – 2.60 (m, 1H), 2.60 – 2.45 (m, 1H), 0.99 (t, J = 7.3 Hz, 6H), 0.91 (s, 9H), 0.08 (s, 6H);

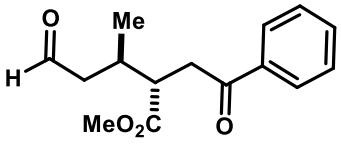
^{13}C-NMR (101 MHz, $CDCl_3$): δ 151.60, 140.47, 113.15, 109.67, 64.00, 36.82, 35.83, 25.95, 18.54, 18.45, 18.25, -5.14, -5.17.

HRMS (APCI): m/z calculated for C15H29O2Si [M+H]+: 269.1931, found 269.1957.

4. General procedure for the hydrolysis of the oxepines using palladium.

In an oven dried Schlenk tube, $Pd(Cl)_2(CH_3CN)_2$ (0.05 equiv.) was taken under argon atmosphere, followed by addition of the substrate (1.0 equiv.) in freshly distilled CH_3CN (0.1M). This solution was stirred at room temperature followed by the addition of distilled H_2O (10 equiv) and heating it to 50 C. This solution was stirred for 24 hours and then cooled to room temperature followed by filtering it over a pad of basic aluminum oxide and concentrated in vacuo to yield the crude reaction mixture which was further purified by silica gel (230-400 mesh) column chromatography (8.5- 12% EtOAc/Hexanes) to obtain the desired product.[7]

Methyl (anti)-3-methyl-5-oxo-2-(2-oxo-2-phenylethyl)pentanoate (4a): liquid.



85% yield (111 mg, 0.423 mmol on 0.5 mmol scale).

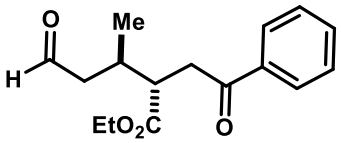
^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.75 (s, 1H), 8.06 – 7.86 (m, 2H), 7.71 – 7.51 (m, 1H), 7.46 (dd, J = 8.4, 7.1 Hz, 2H), 3.69 (s, 3H),

3.52 (dd, J = 17.7, 10.1 Hz, 1H), 3.09 (ddd, J = 10.1, 5.1, 3.6 Hz, 1H), 2.98 (dd, J = 17.7, 3.7 Hz, 1H), 2.65 – 2.53 (m, 2H), 2.34 (ddd, J = 18.0, 9.8, 2.1 Hz, 1H), 1.04 (d, J = 6.7 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 201.01, 197.93, 174.53, 136.42, 133.32, 128.60, 127.99, 51.88, 48.29, 44.87, 37.28, 29.42, 17.79.

HRMS (TOFMS): m/z calculated for C15H18O4 [M+Na]+: 285.1103, found 285.1115.

Ethyl (anti)-3-methyl-5-oxo-2-(2-oxo-2-phenylethyl)pentanoate (4b): liquid.



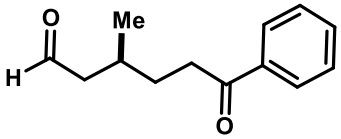
71% yield (38 mg, 0.138 mmol on 0.194 mmol scale).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.77 (d, J = 1.1 Hz, 1H), 8.08 – 7.87 (m, 2H), 7.62 – 7.51 (m, 1H), 7.47 (dd, J = 8.3, 6.9 Hz, 2H), 4.16 (qd, J = 7.1, 1.4 Hz, 2H), 3.53 (dd, J = 17.6, 10.1 Hz, 1H), 3.09 (ddd, J = 10.0, 5.0, 3.7 Hz, 1H), 2.96 (dd, J = 17.7, 3.7 Hz, 1H), 2.67 – 2.55 (m, 2H), 2.35 (ddd, J = 17.9, 9.8, 2.2 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H), 1.05 (d, J = 6.7 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 201.10, 198.01, 173.99, 136.55, 133.29, 128.61, 128.02, 60.79, 48.33, 45.02, 37.22, 29.48, 17.76, 14.19.

HRMS (TOFMS): m/z calculated for C16H20O4 [M+Na]+: 299.1259, found 299.1274.

3-Methyl-6-oxo-6-phenylhexanalpentanoate (4c): liquid.

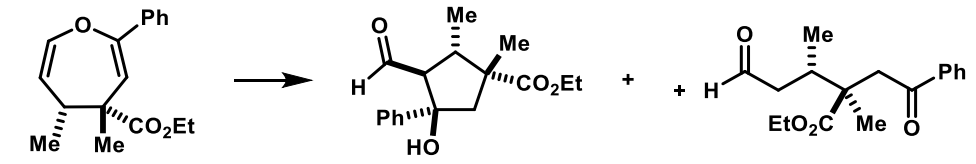


72% yield (19 mg, 0.093 mmol on 0.129 mmol scale).

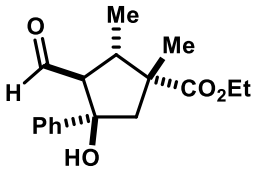
^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.78 (t, J = 2.1 Hz, 1H), 8.04 – 7.91 (m, 2H), 7.61 – 7.52 (m, 1H), 7.51 – 7.41 (m, 2H), 3.11 – 2.94 (m, 2H), 2.48 (ddd, J = 16.4, 5.7, 1.8 Hz, 1H), 2.32 (ddd, J = 16.4, 7.8, 2.4 Hz, 1H), 2.24 – 2.11 (m, 1H), 1.83 (dddd, J = 14.1, 8.6, 6.7, 5.6 Hz, 1H), 1.67 (dtd, J = 14.3, 8.2, 6.5 Hz, 1H), 1.03 (d, J = 6.7 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 202.42, 199.81, 136.79, 133.05, 128.59, 127.97, 50.90, 35.96, 30.94, 27.70, 19.78.

HRMS (TOFMS): m/z calculated for C13H16O2 [M+Na]+: 227.1048, found 227.1053



Ethyl-3-formyl-4-hydroxy-1,2-dimethyl-4 phenylcyclopentanecarboxylate (5a): liquid.

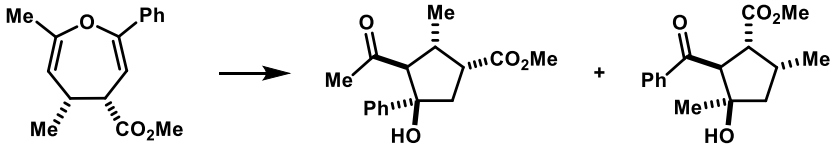


61% yield (65 mg, 0.224 mmol on 0.367 mmol scale).

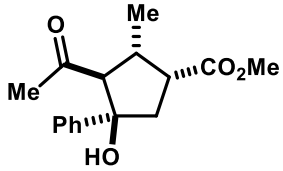
^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.12 (d, J = 1.2 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.33 (dd, J = 8.6, 6.9 Hz, 2H), 7.25 – 7.17 (m, 1H), 5.69 (s, 1H), 4.25 (qq, J = 10.8, 7.1 Hz, 2H), 3.06 (dd, J = 11.9, 1.1 Hz, 1H), 2.57 (d, J = 15.1 Hz, 1H), 2.46 (dq, J = 11.8, 6.8 Hz, 1H), 2.24 (d, J = 15.1 Hz, 1H), 1.40 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H), 1.04 (d, J = 6.8 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 201.06, 178.90, 143.99, 128.37, 127.03, 125.29, 81.74, 73.74, 61.58, 57.09, 52.27, 46.74, 22.59, 14.44, 14.21.

HRMS (TOFMS): m/z calculated for C17H22O4 [M+Na]+: 313.1416, found 313.1433.



Methyl-3-acetyl-4-hydroxy-2-methyl-4-phenylcyclopentane-1-carboxylate(6a): white solid.



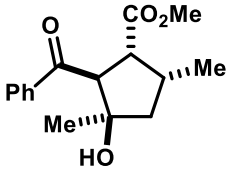
52% yield (36 mg, 0.130 mmol on 0.252 mmol scale).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.35 (m, 2H), 7.29 (dd, J = 8.6, 6.8 Hz, 2H), 7.23 – 7.17 (m, 1H), 5.42 (s, 1H), 3.78 (s, 3H), 3.18 – 3.09 (m, 2H), 2.95 (dt, J = 11.8, 6.8 Hz, 1H), 2.43 (dd, J = 14.9, 6.9 Hz, 1H), 2.34 (d, J = 14.9 Hz, 1H), 1.61 (s, 3H), 1.02 (d, J = 6.7 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 207.17, 178.70, 144.32, 127.84, 126.86, 125.45, 83.74, 74.70, 52.11, 48.50, 48.03, 40.43, 30.60, 16.01.

HRMS (APCI): m/z calculated for C16H21O4 [M+H]+: 277.1434, found 277.1464.

Methyl-3-acetyl-4-hydroxy-2-methyl-4-phenylcyclopentane-1-carboxylate (6b): liquid.



34% yield (24 mg, 0.087 mmol on 0.252 mmol scale).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.06 – 7.97 (m, 2H), 7.67 – 7.55 (m, 1H), 7.48 (t, J = 7.6 Hz, 2H), 4.26 (d, J = 10.1 Hz, 1H), 3.88 (d, J = 1.8 Hz, 1H),

3.61 (s, 3H), 3.55 (t, J = 10.2 Hz, 1H), 2.90 (tdd, J = 10.1, 8.5, 4.9 Hz, 1H), 2.12 (dd, J = 13.2, 7.1 Hz, 1H), 1.56 – 1.45 (m, 1H), 1.29 (s, 3H), 0.99 (d, J = 7.1 Hz, 3H).

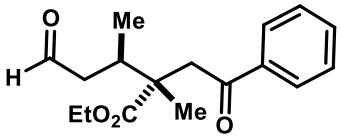
^{13}C-NMR (101 MHz, $CDCl_3$): δ 204.60, 174.27, 137.71, 133.83, 128.77, 128.72, 80.60, 55.28, 51.53, 51.46, 49.97, 33.74, 26.75, 17.02.

HRMS (APCI): m/z calculated for C16H21O4 [M+H]+: 277.1434, found 277.1459.

5. Procedure for the hydrolysis of oxepine using aq. HCl.

In a 25mL round bottom flask, oxepine (100 mg, 0.367 mmol) was taken in 1.5 mL THF. To this stirred solution, 1.5 mL HCl (6M aq.) was added, and the resulting mixture was further stirred for 6 hours. The reaction was quenched by slow addition of sat. $NaHCO_3$ solution (10mL) and then was extracted with CH_2Cl_2 (15 mL) three times. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4 and purified by silica gel (230-400 mesh) column chromatography (12%EtOAc/Hexanes) to obtain the desired product (56 mg, 0.193 mmol) in 53 percent yield.

Ethyl (anti)-2,3-dimethyl-5-oxo-2-(2-oxo-2-phenylethyl)pentanoate (4d): liquid.



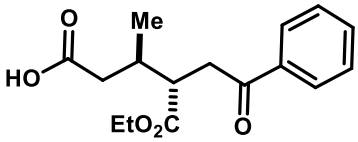
53% yield (56 mg, 0.193 mmol on 0.367 mmol scale).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.74 (d, J = 2.5 Hz, 1H), 7.97 – 7.87 (m, 2H), 7.61 – 7.51 (m, 1H), 7.46 (dd, J = 8.4, 7.1 Hz, 2H), 4.12 (q, J = 7.1 Hz, 2H), 3.47 (d, J = 17.5 Hz, 1H), 3.16 (d, J = 17.6 Hz, 1H), 2.61 (dd, J = 16.8, 2.9 Hz, 1H), 2.50 (ddt, J = 9.8, 6.8, 3.4 Hz, 1H), 2.28 (ddd, J = 16.9, 9.8, 2.6 Hz, 1H), 1.25 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H), 1.01 (d, J = 6.8 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 201.41, 197.35, 175.92, 136.99, 133.19, 128.60, 127.86, 60.69, 46.90, 46.44, 46.06, 34.71, 17.02, 15.34, 14.08.

HRMS (TOFMS): m/z calculated for C17H22O4 [M+Na]+: 313.1416, found 313.1425.

(Anti)-4-(ethoxycarbonyl)-3-methyl-6-oxo-6-phenylhexanoic acid (7): solid.



The aldehyde (**4b**) was oxidized to the carboxylic acid derivative (**7**) and then crystallized.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.05 – 7.89 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 4.25 – 4.07 (m, 2H), 3.55 (dd, J = 17.7, 10.3 Hz, 1H), 3.14 (dt, J = 10.2, 4.2 Hz, 1H), 2.96 (dd, J = 17.7, 3.6 Hz, 1H), 2.52 (ddd, J = 16.6, 11.2, 5.3 Hz, 2H), 2.31 – 2.19 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H), 1.08 (d, J = 6.6 Hz, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 198.10, 177.97, 173.98, 136.46, 133.14, 128.47, 127.91, 60.68, 44.64, 38.72, 36.75, 31.52, 17.21, 14.05.

HRMS (TOFMS): m/z calculated for C16H21O5 [M+Na]+: 293.1384, found 293.1376.

6. References

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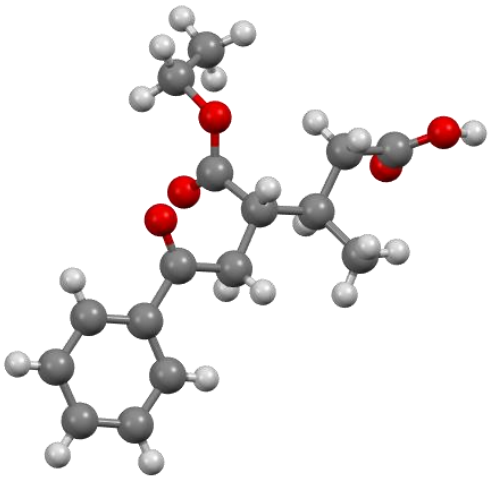
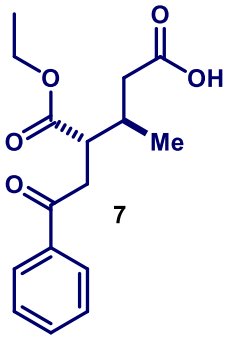
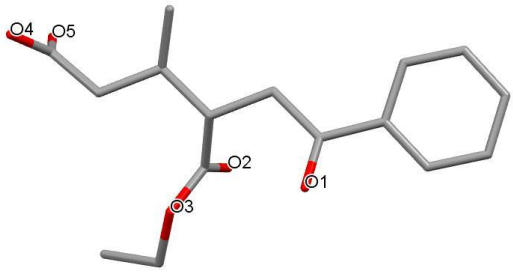
7. Crystal data and structure refinement

Crystal data and structure refinement for Marek167b.	
Identification code	Marek167b
Empirical formula	$C_{16}H_{20}O_5$
Formula weight	292.32
Temperature/K	200.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.000(3)
b/Å	5.5870(9)
c/Å	15.124(2)
α/°	90
β/°	94.465(4)
γ/°	90
Volume/Å^3	1516.4(4)
Z	4
ρ_{calc}g/cm^3	1.280
μ/mm^{-1}	0.095
F(000)	624.0
Crystal size/mm^3	0.24 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.54 to 49.104
Index ranges	$-21 \leq h \leq 20$, $-5 \leq k \leq 6$, $-17 \leq l \leq 17$
Reflections collected	9217
Independent reflections	2499 [R_{int} = 0.0544, R_{sigma} = 0.0617]
Data/restraints/parameters	2499/175/196
Goodness-of-fit on F^2	1.019
Final R indexes [I>=2σ (I)]	R_1 = 0.0511, wR_2 = 0.1154
Final R indexes [all data]	R_1 = 0.1014, wR_2 = 0.1325
Largest diff. peak/hole / e Å^{-3}	0.29/-0.20

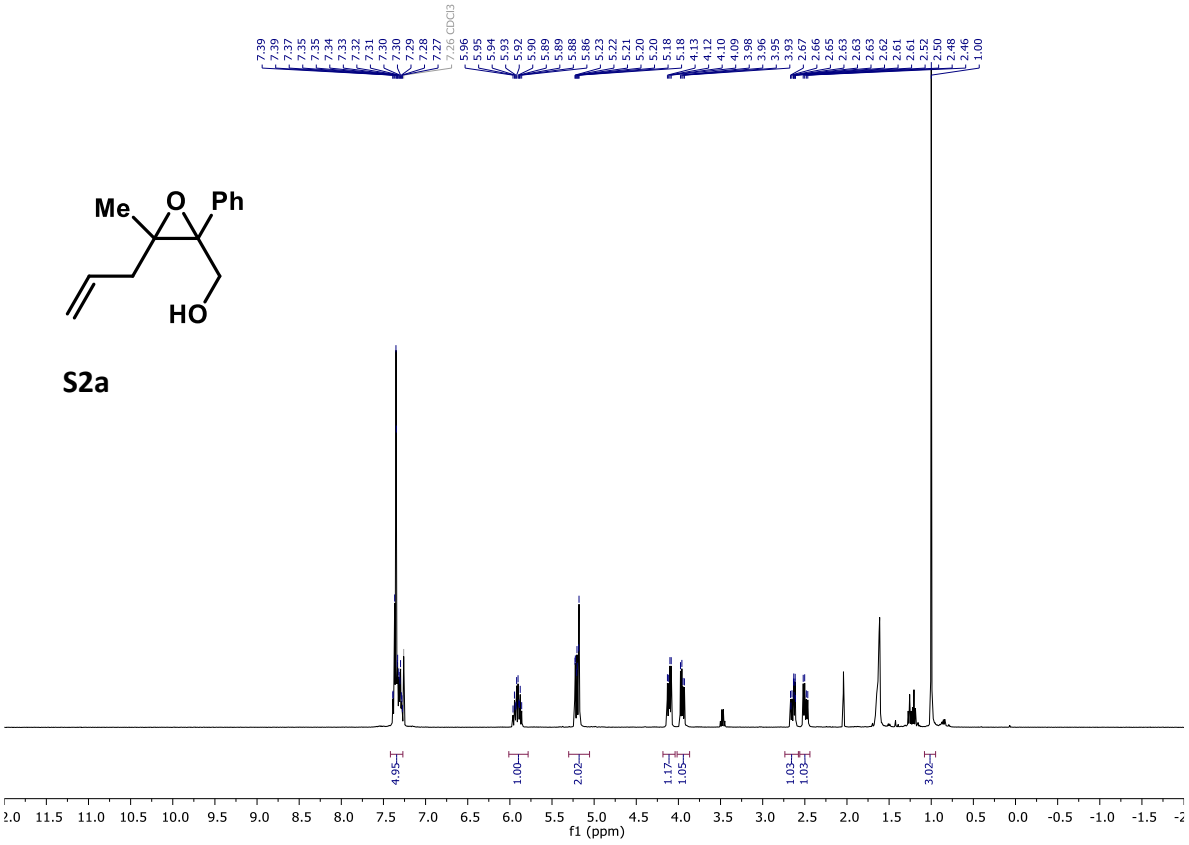


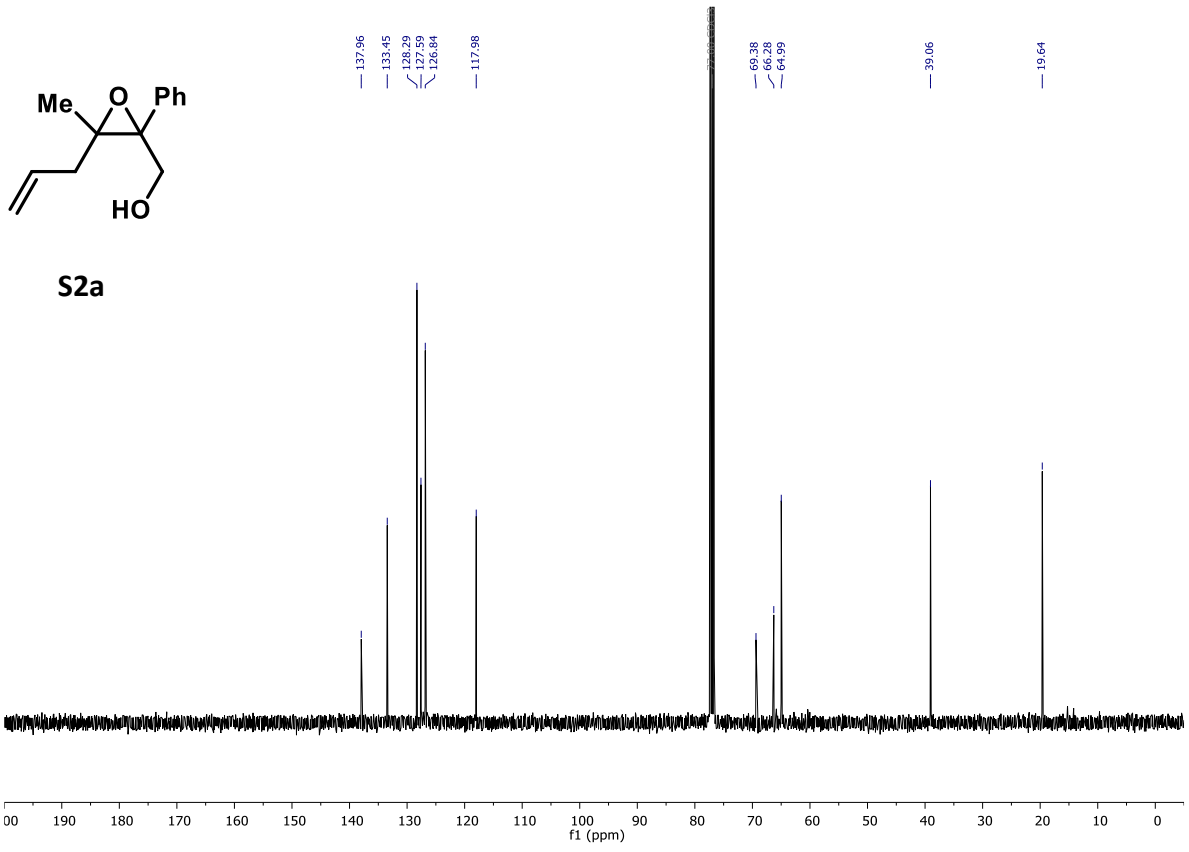


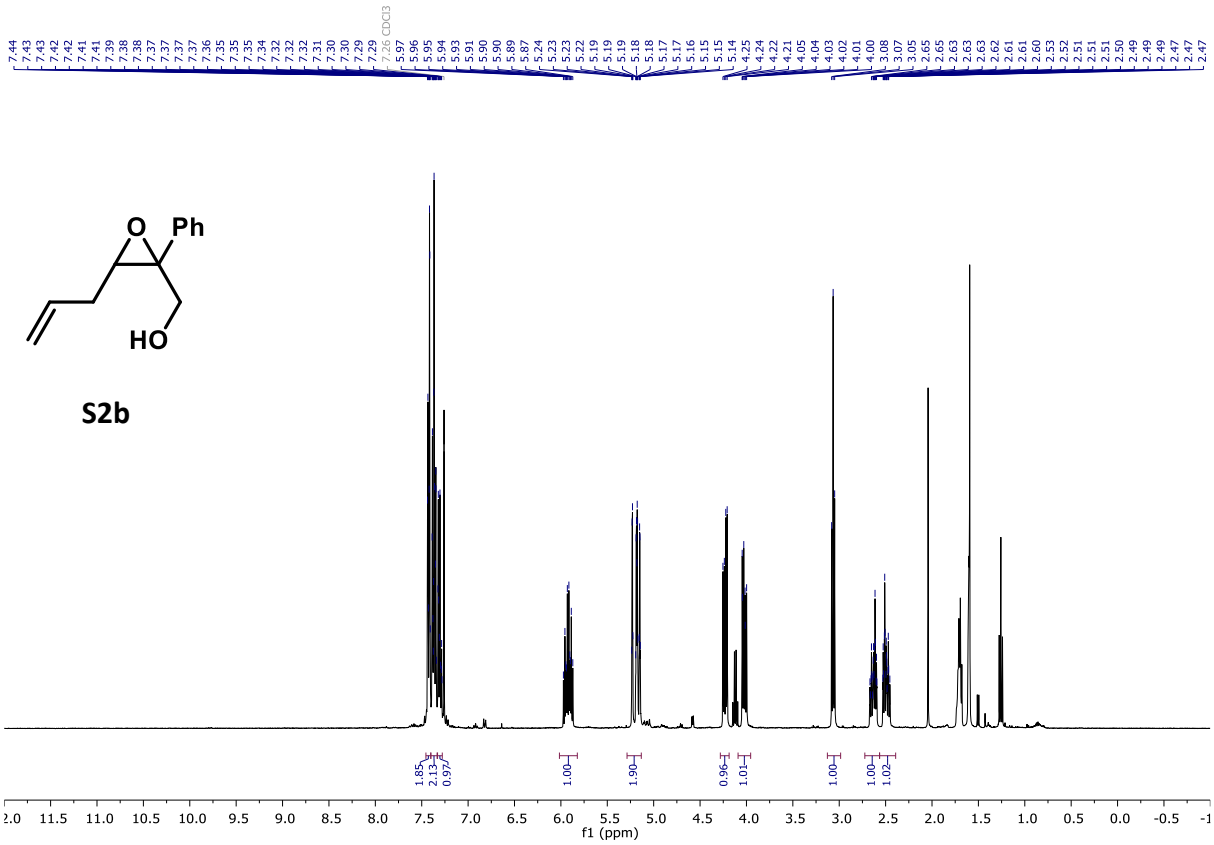
7

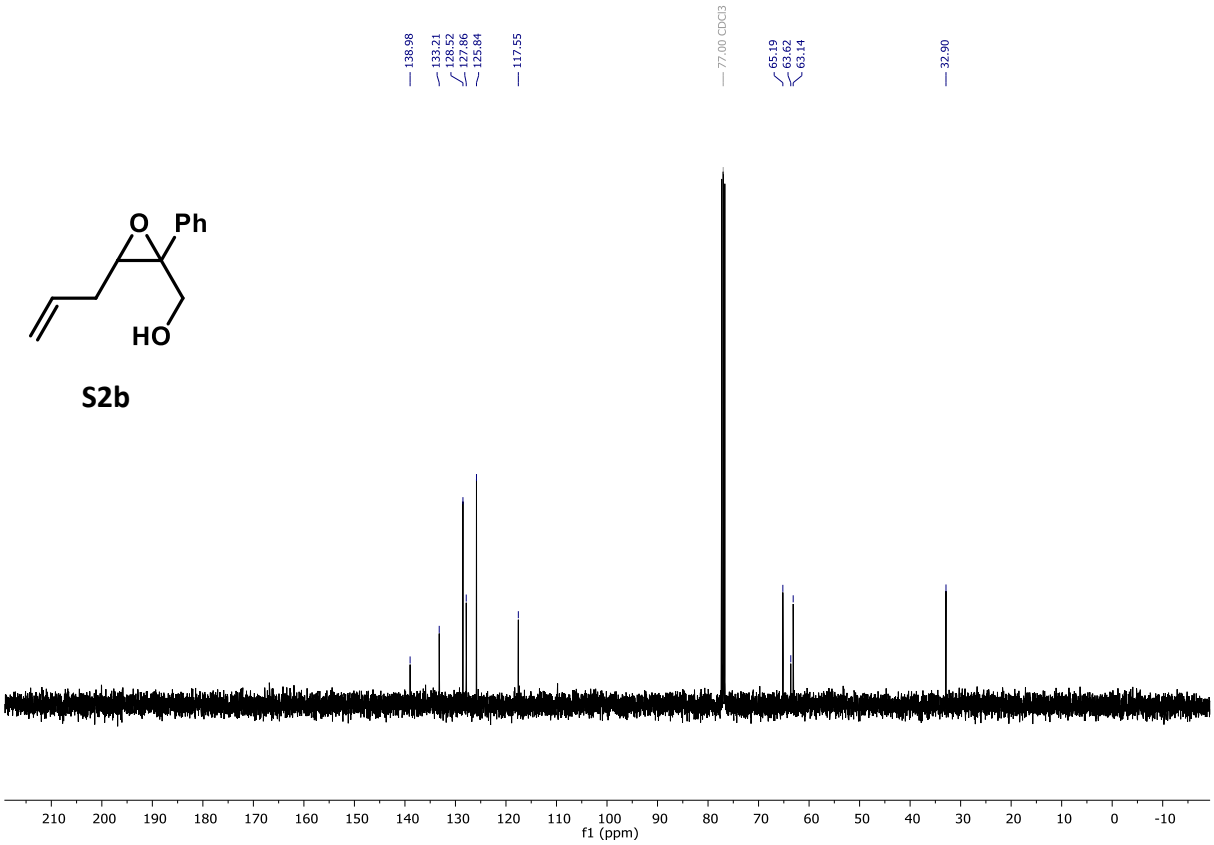


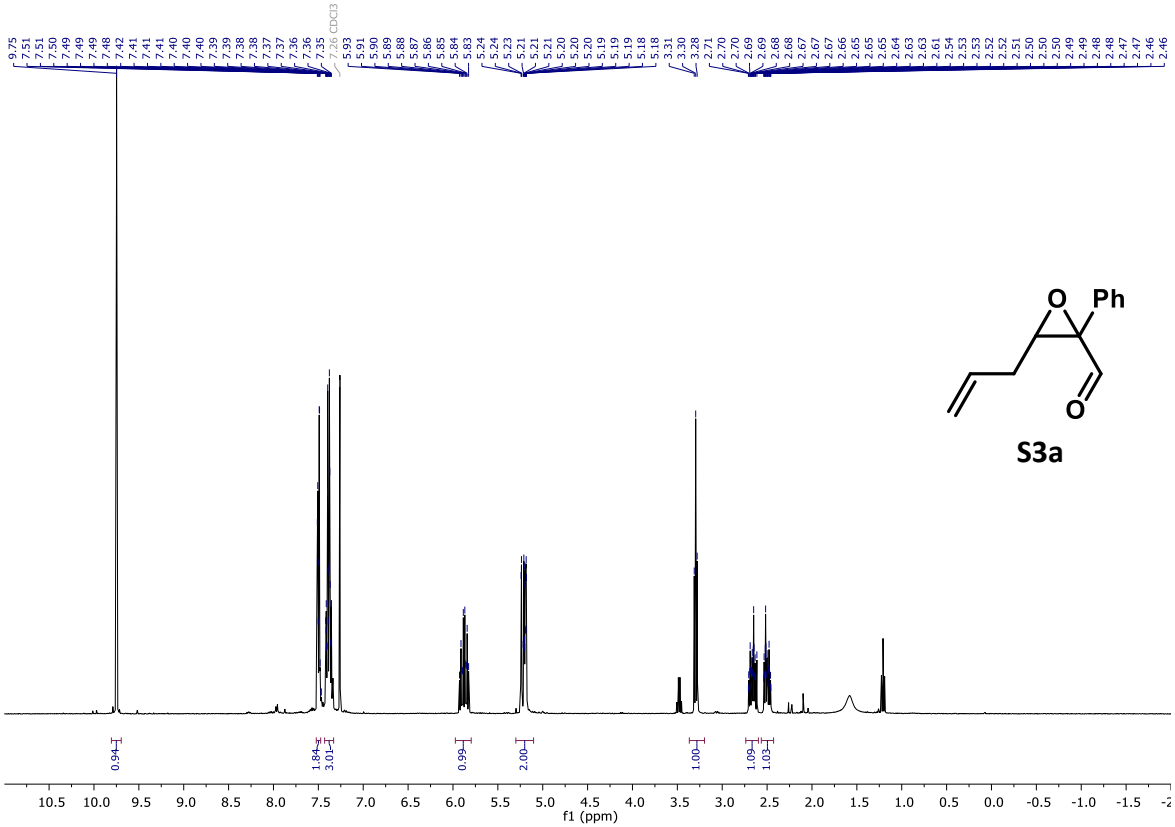
8. NMR Spectra



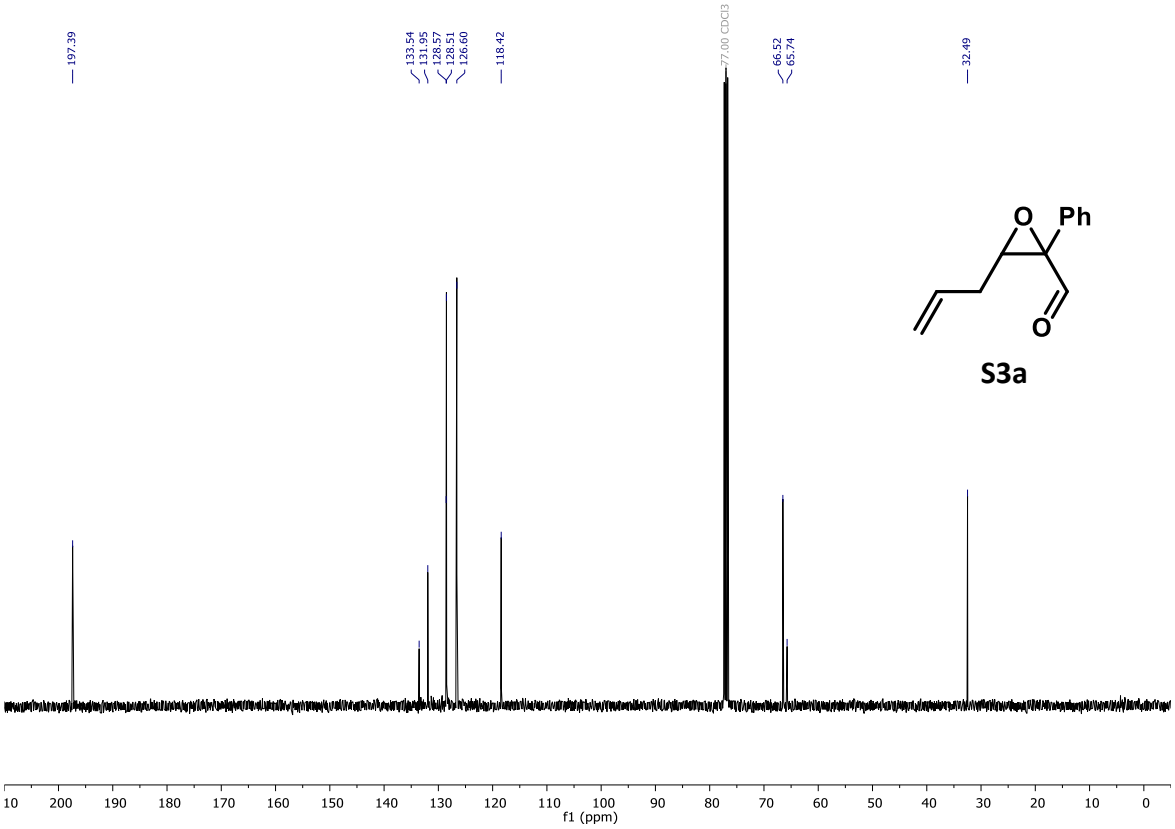



O
Ph
HO
S2b
f1 (ppm)

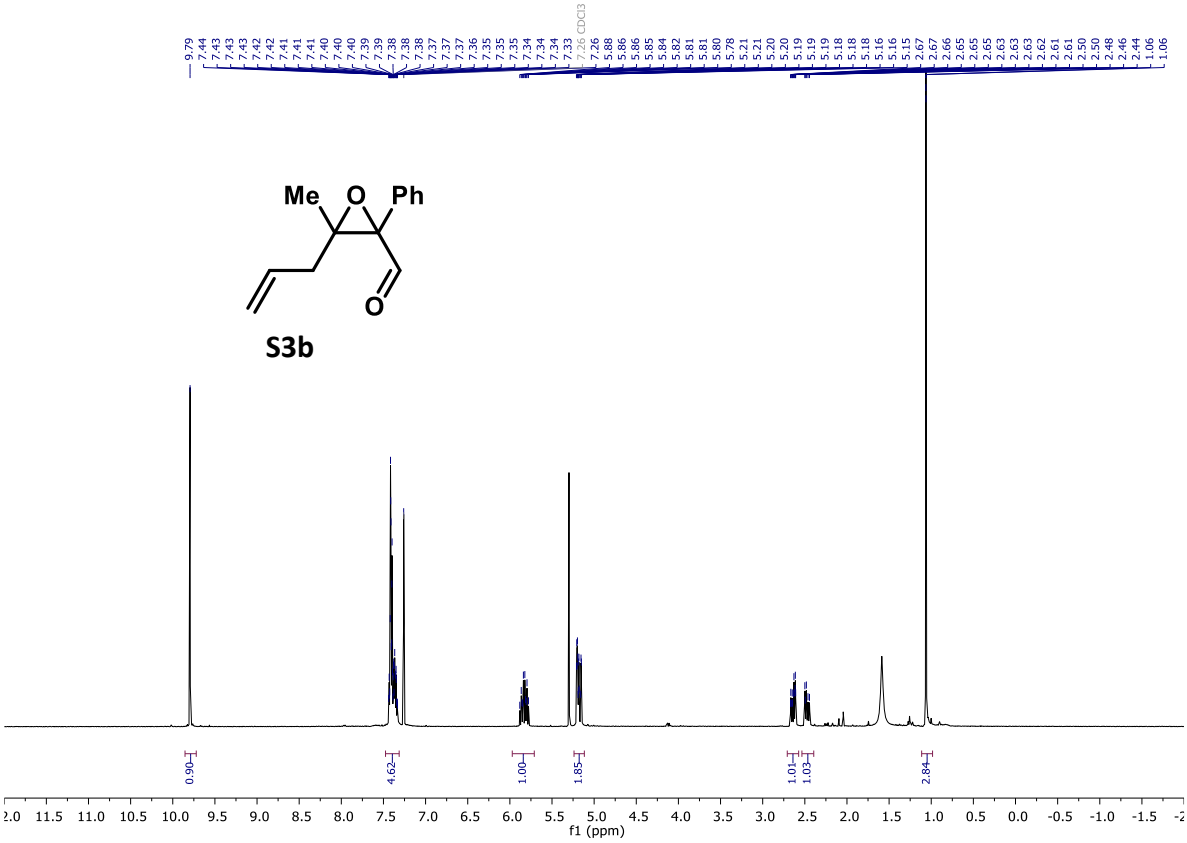

O
Ph
HO
S2b
f1 (ppm)

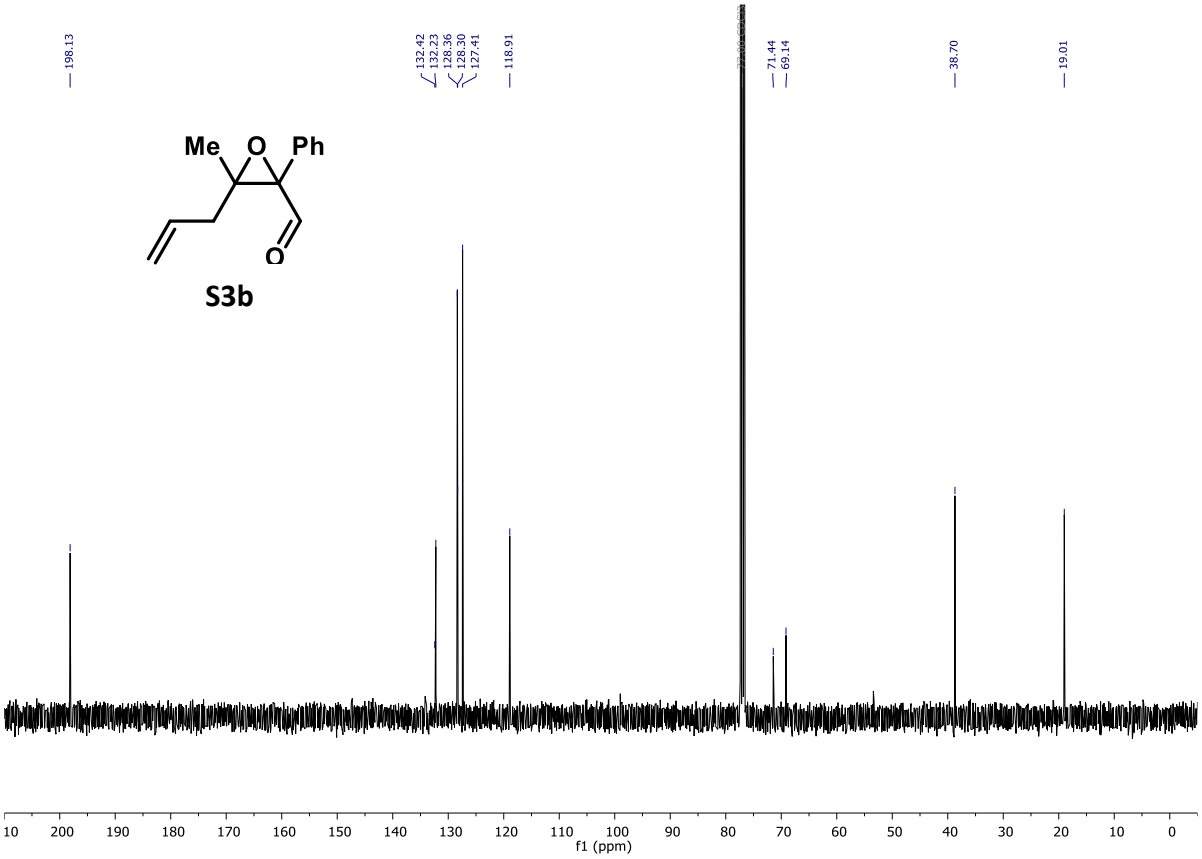

9.75 7.51 7.51 7.50 7.49 7.49 7.49 7.48 7.42 7.41 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.36 7.35 7.26 CDCl3
5.93 5.91 5.90 5.89 5.88 5.87 5.86 5.85 5.84 5.83 5.24 5.24 5.23 5.21 5.21 5.21 5.20 5.20 5.20 5.19 5.19 5.19 5.18 5.18
3.31 3.30 3.28 2.71 2.70 2.70 2.69 2.69 2.68 2.68 2.67 2.67 2.67 2.66 2.65 2.65 2.65 2.64 2.63 2.63 2.61 2.54 2.53 2.53 2.52 2.52 2.51 2.50 2.50 2.50 2.49 2.49 2.48 2.48 2.47 2.47 2.46 2.46
0.94 1.84 3.01 0.99 2.00 1.00 1.09 1.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)
O
Ph
O

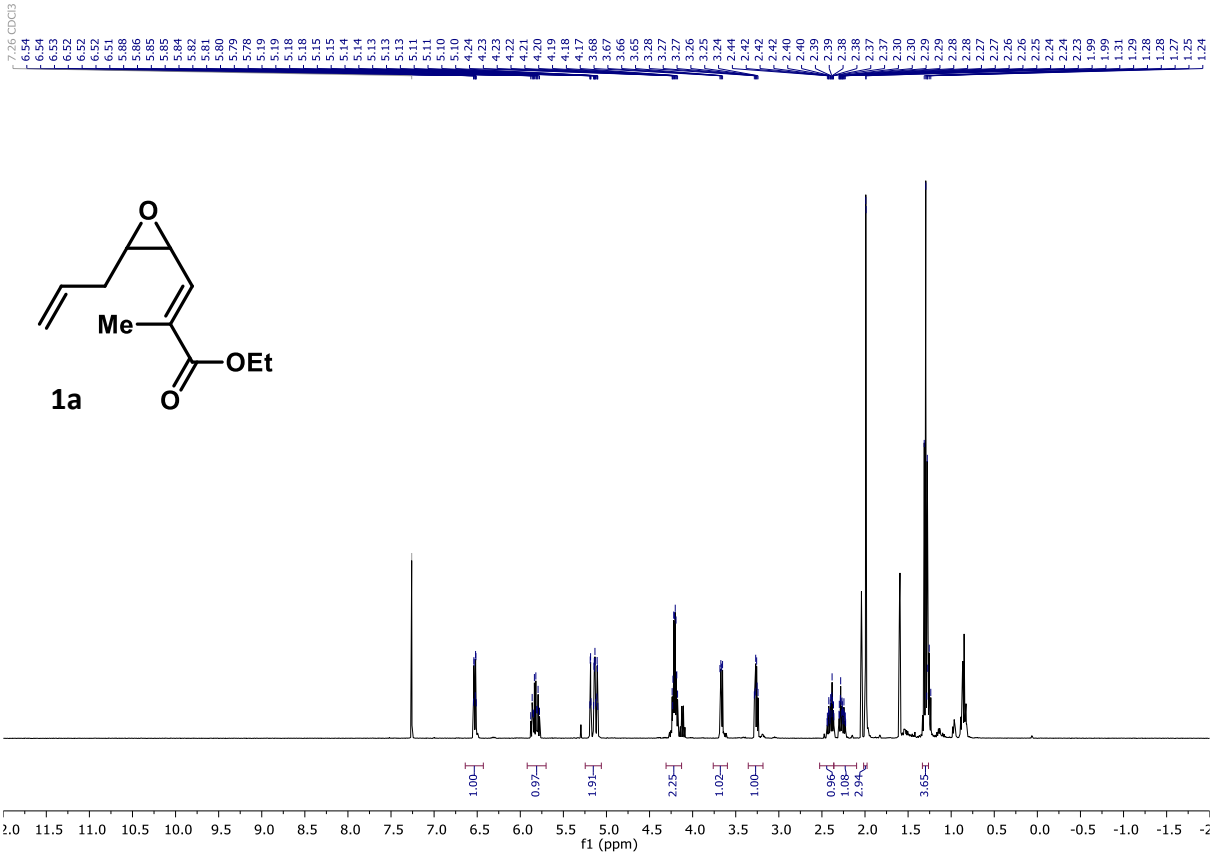
S3a

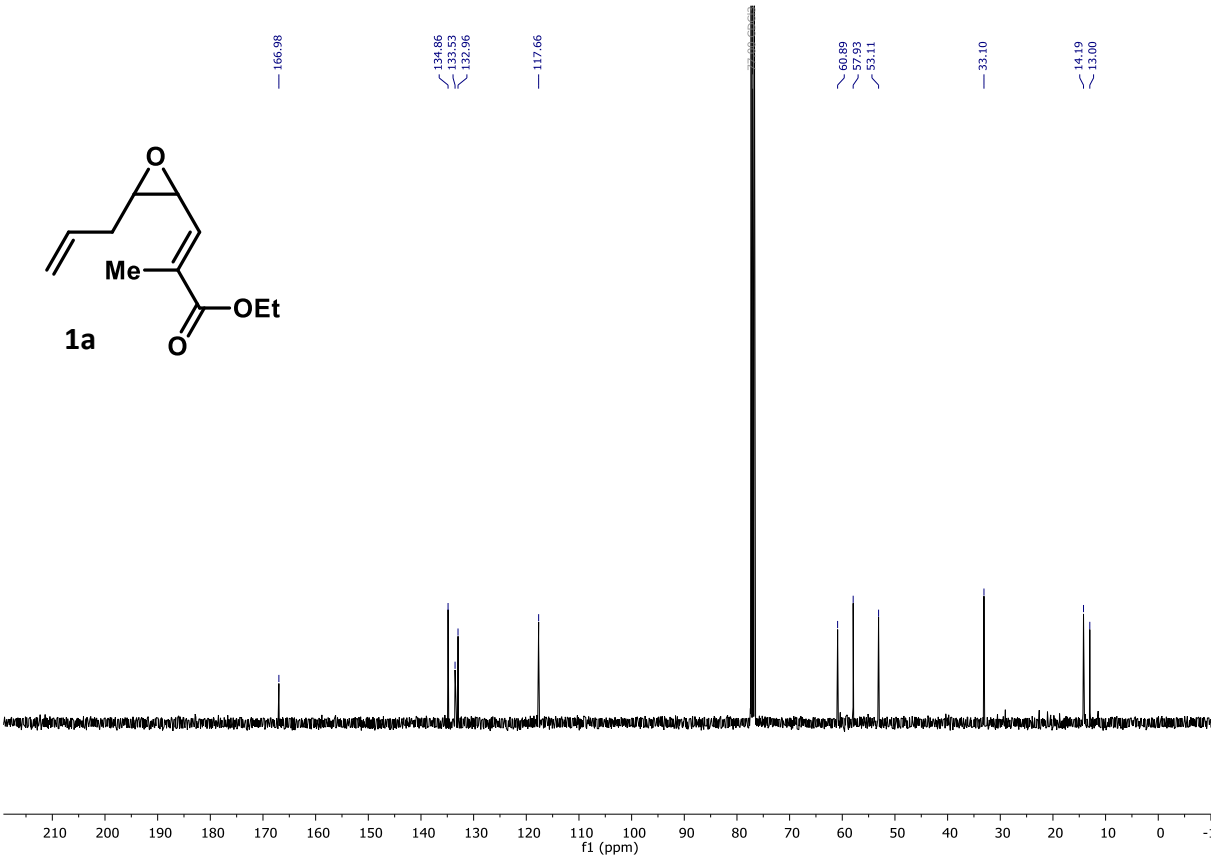

197.39
133.54 131.95 128.57 128.51 126.60
118.42
77.00 CDCl3
66.52 65.74
32.49
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
Ph
O

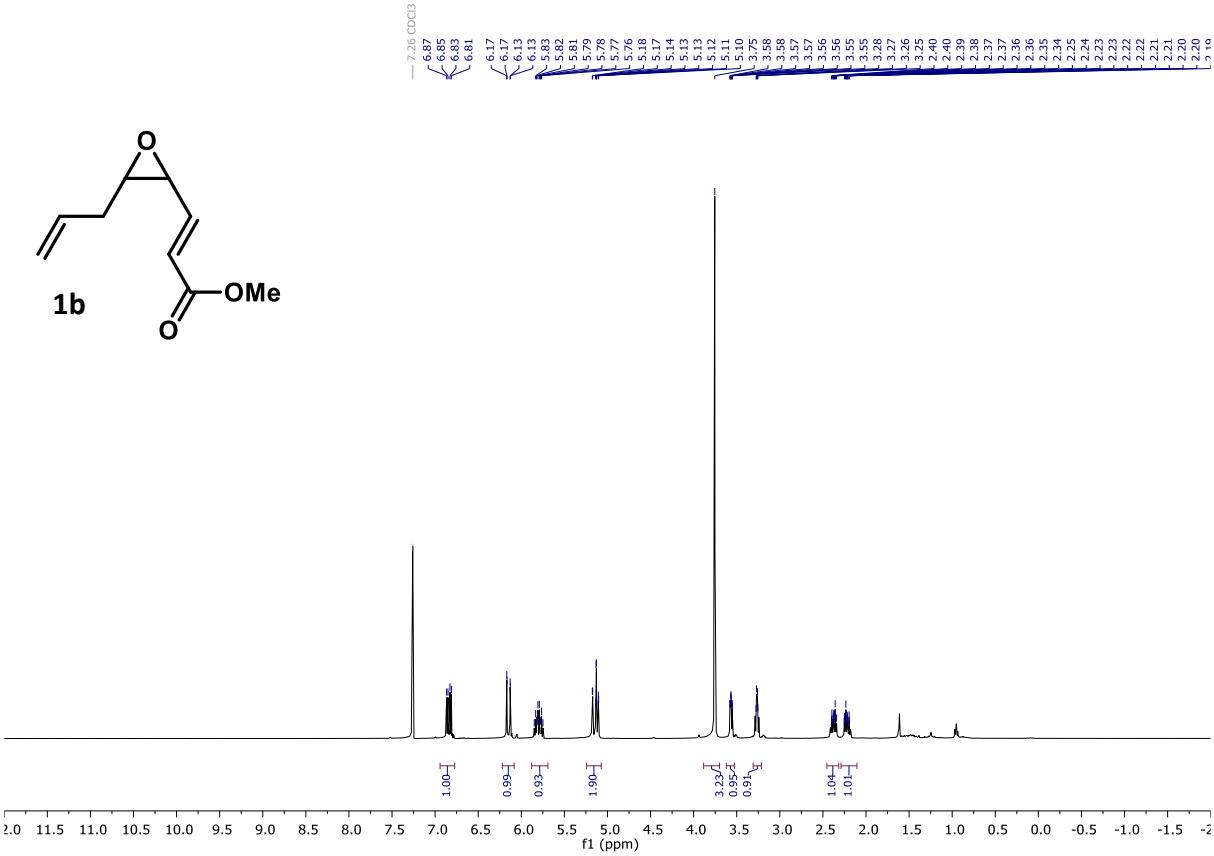
S3a

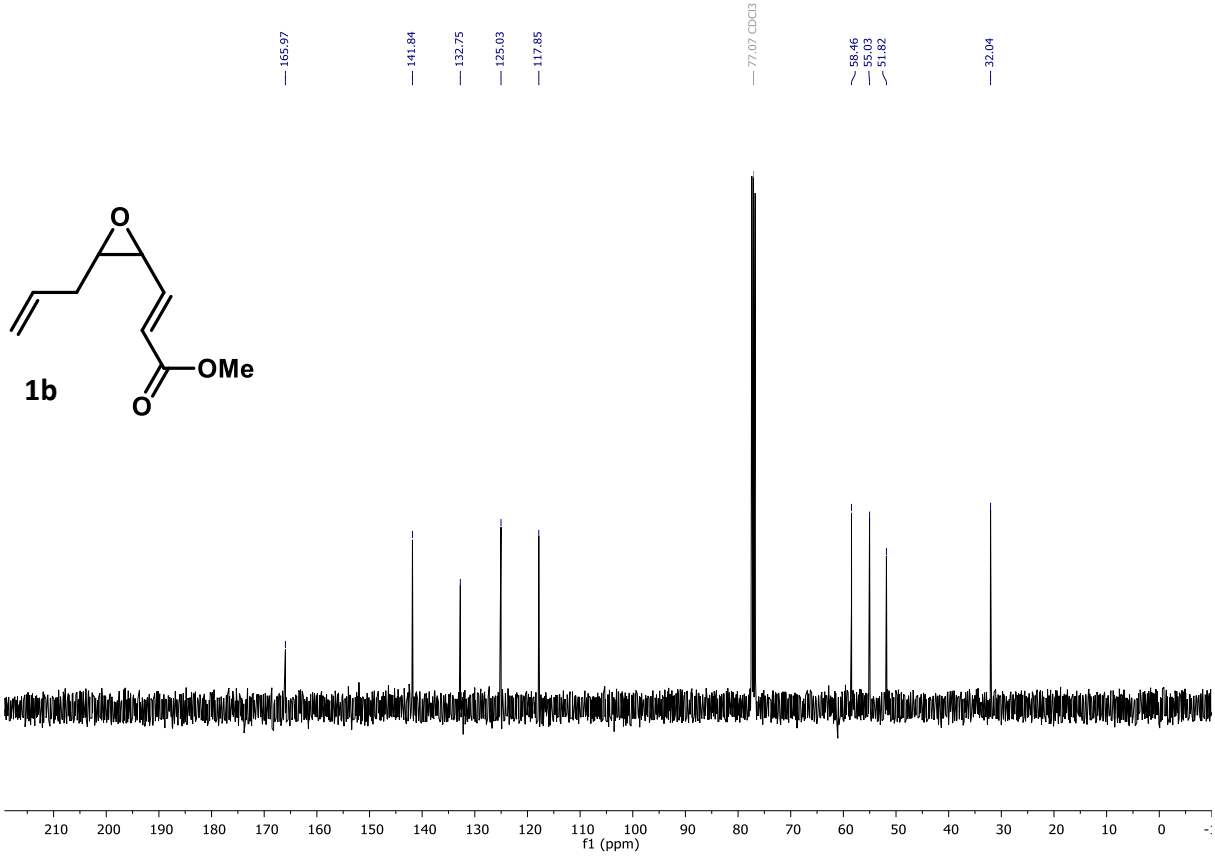

Me
O
Ph
O
S3b
f1 (ppm)

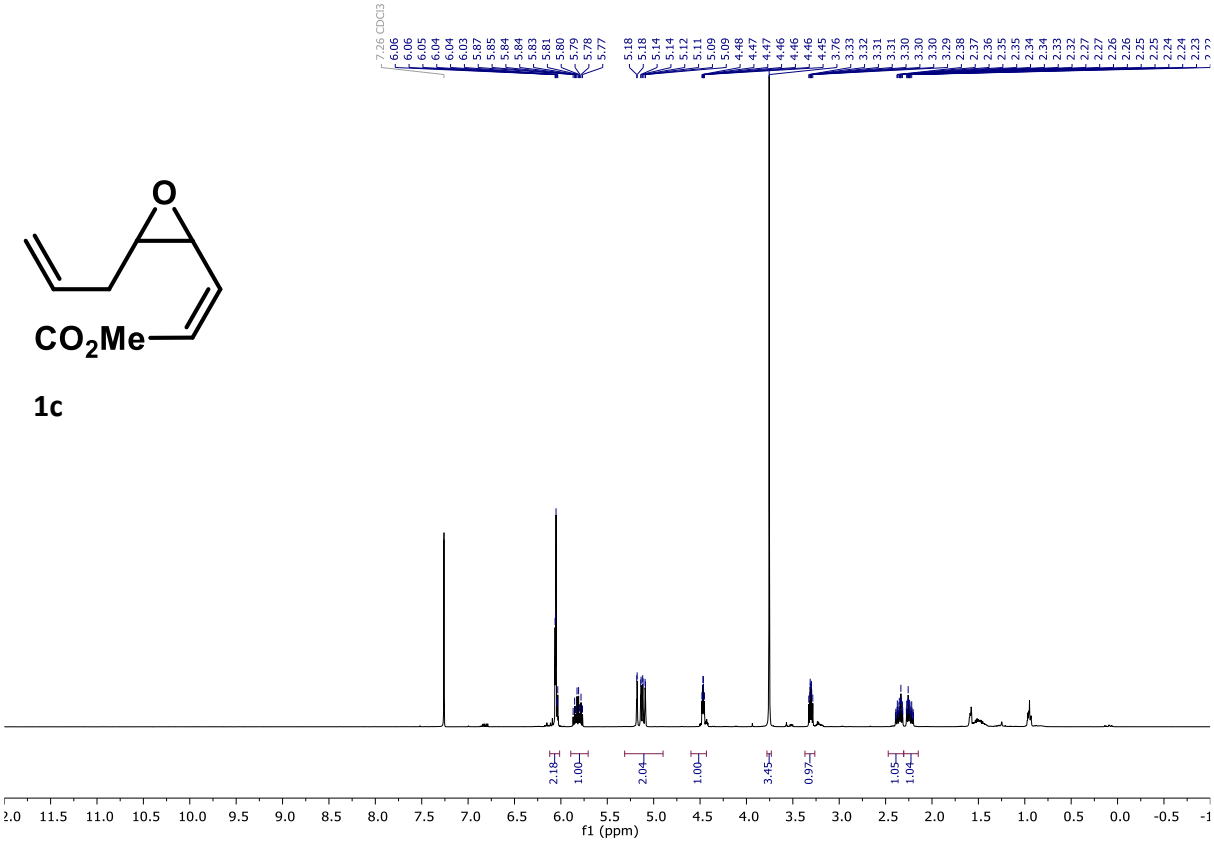

Me
O
Ph
O
S3b
f1 (ppm)

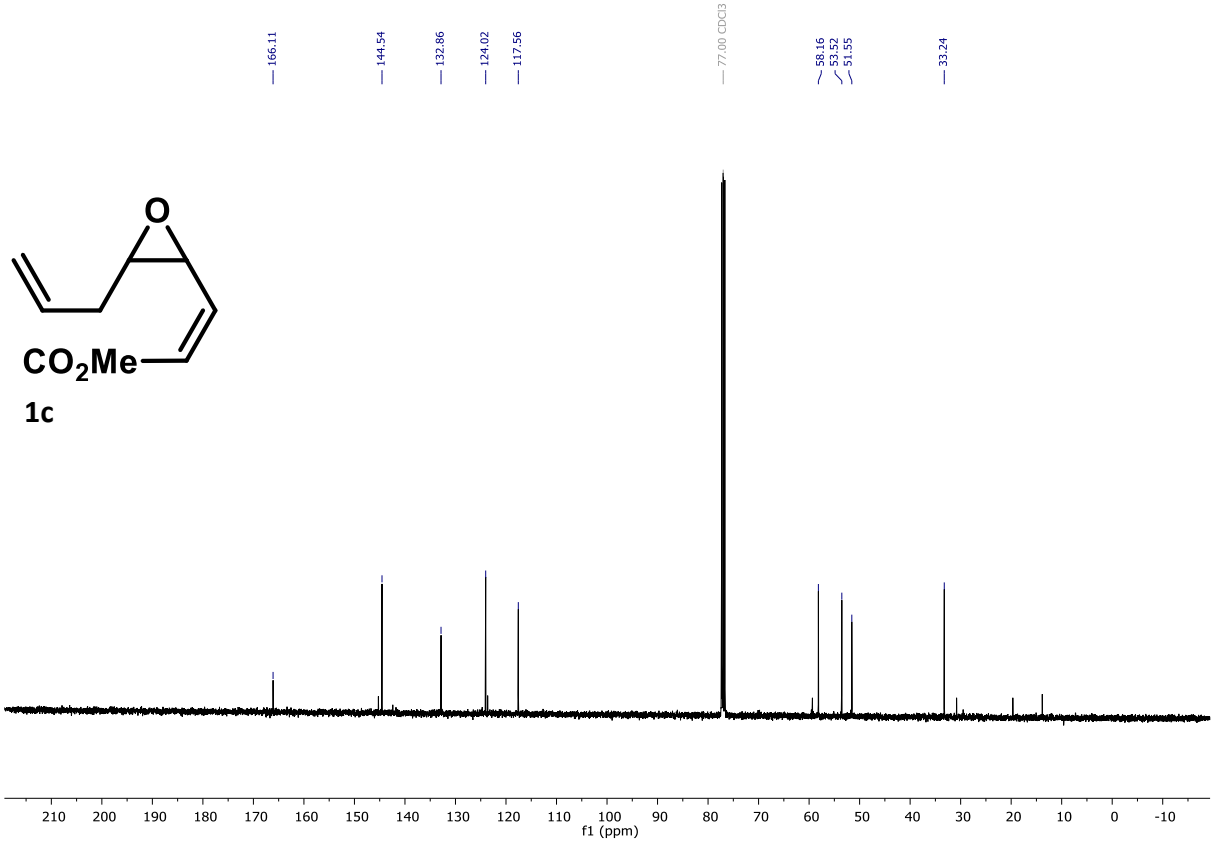

7.26 CDCl3
O
Me
OEt
O
1a
1.00
0.97
1.91
2.25
1.02
1.00
0.96
1.08
2.94
3.65
f1 (ppm)

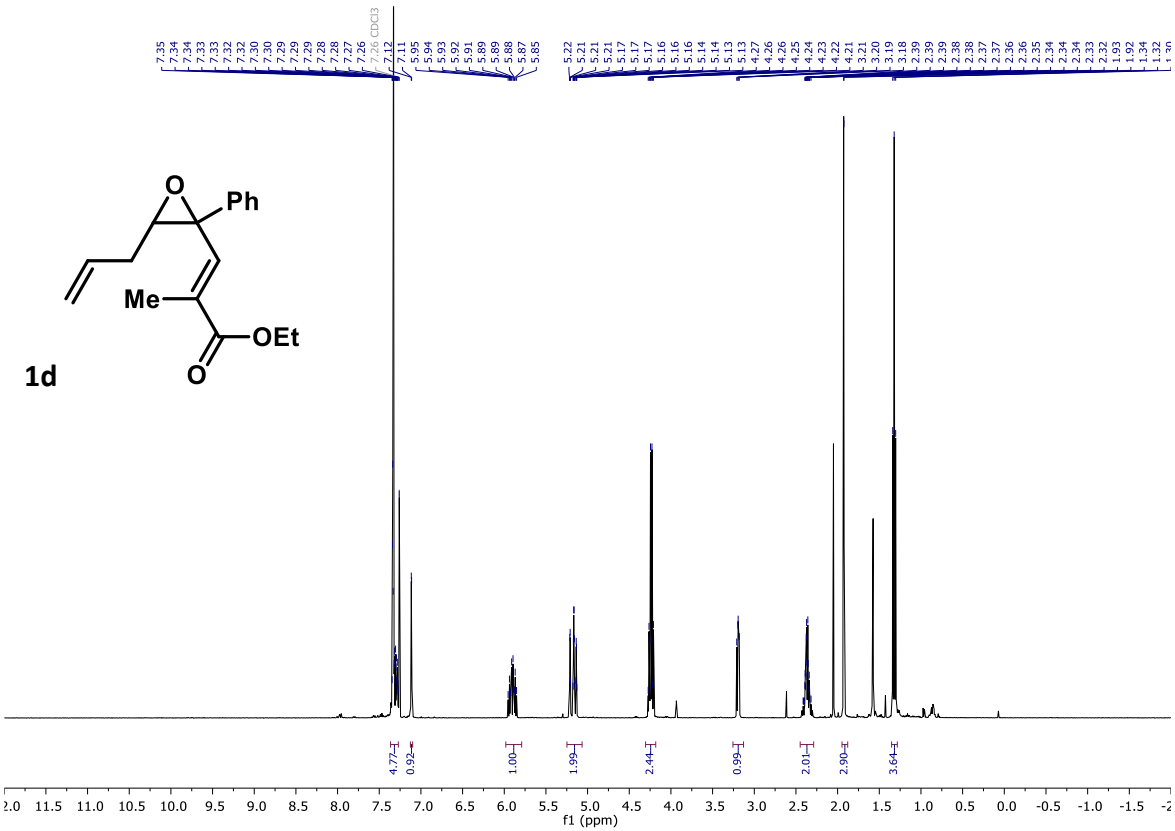

166.98
134.86
133.53
132.96
117.66
60.89
57.93
53.11
33.10
14.19
13.00
O
Me
OEt
O
1a
f1 (ppm)

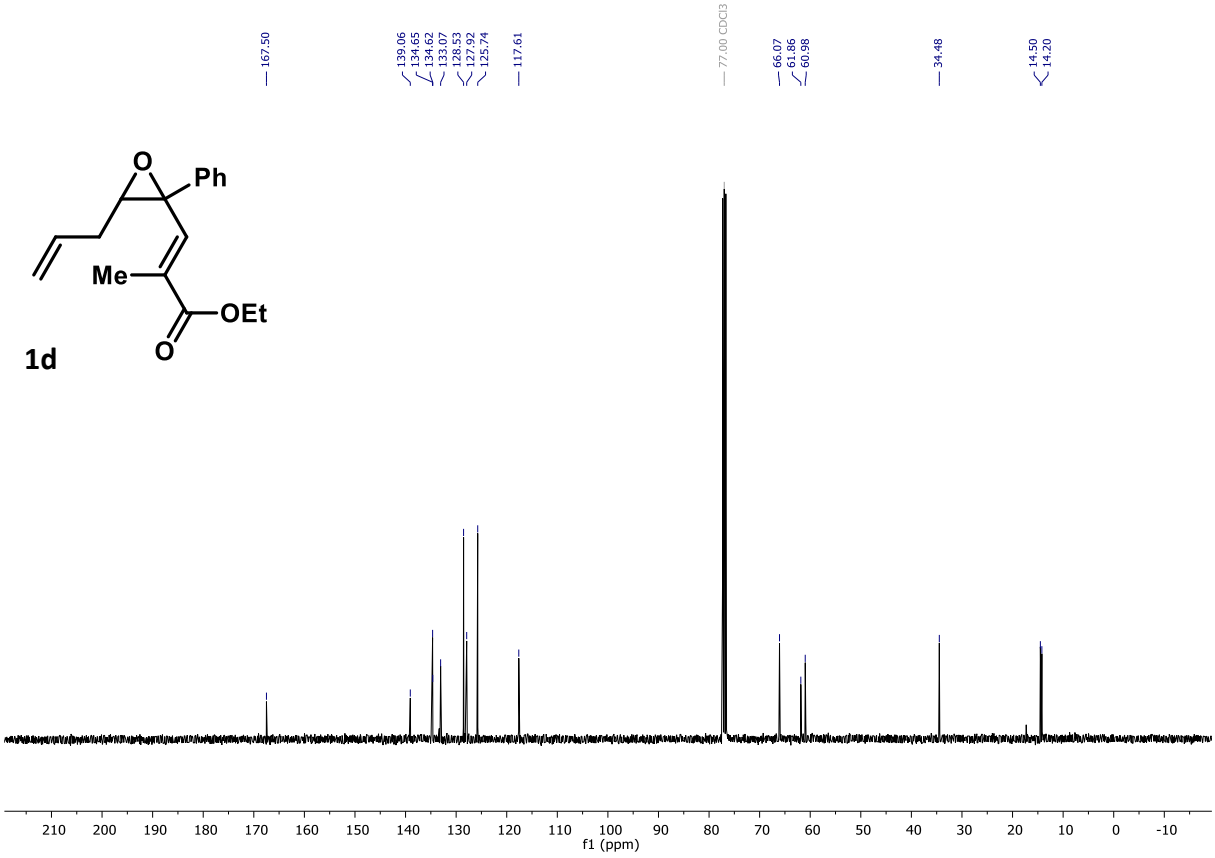

1b
OMe
O
f1 (ppm)

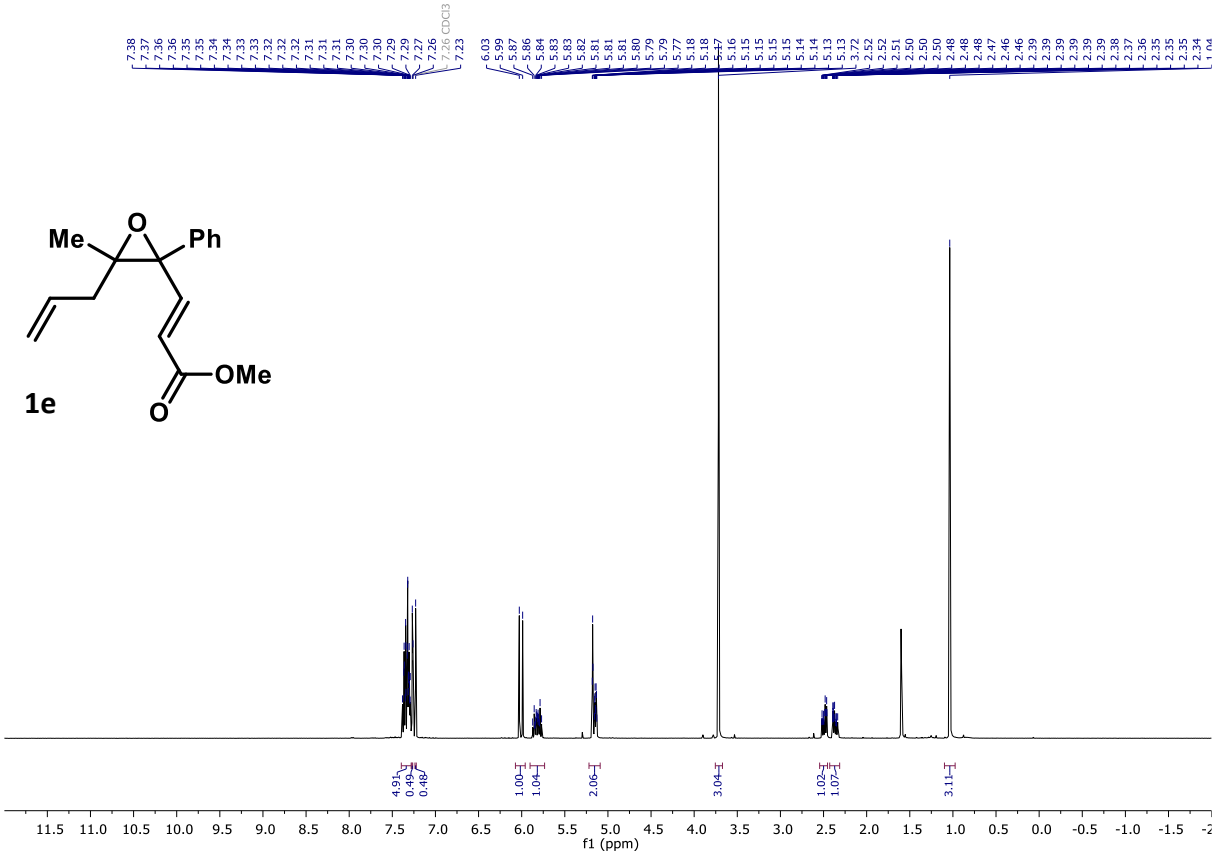

1b
OMe
O
f1 (ppm)

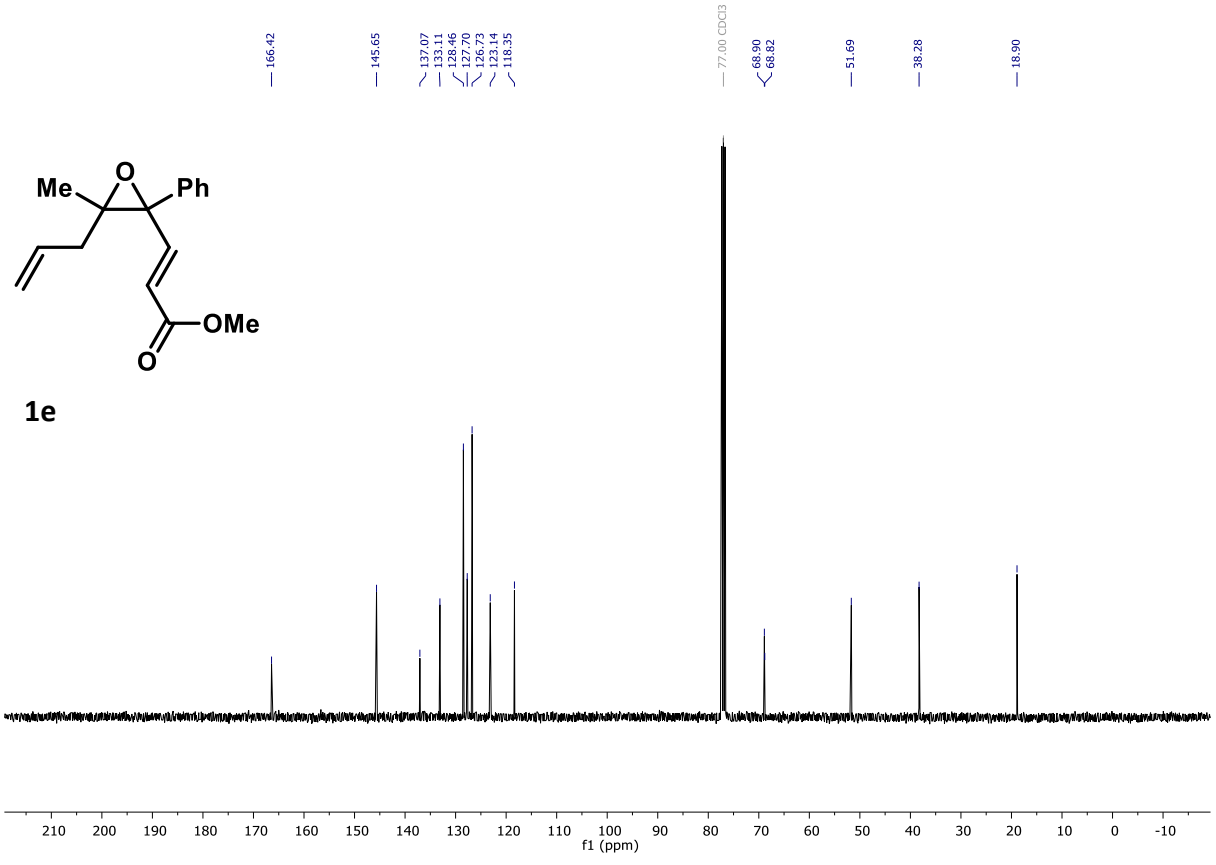

O
CO2Me
1c
f1 (ppm)

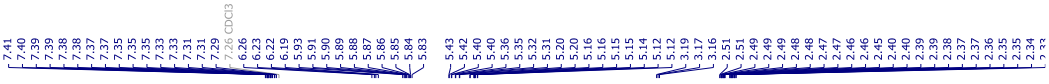

O
CO2Me
1c
f1 (ppm)

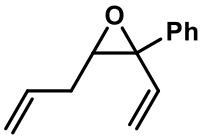

Ph
Me
OEt
O
1d
f1 (ppm)


Ph
Me
OEt
O
1d
f1 (ppm)

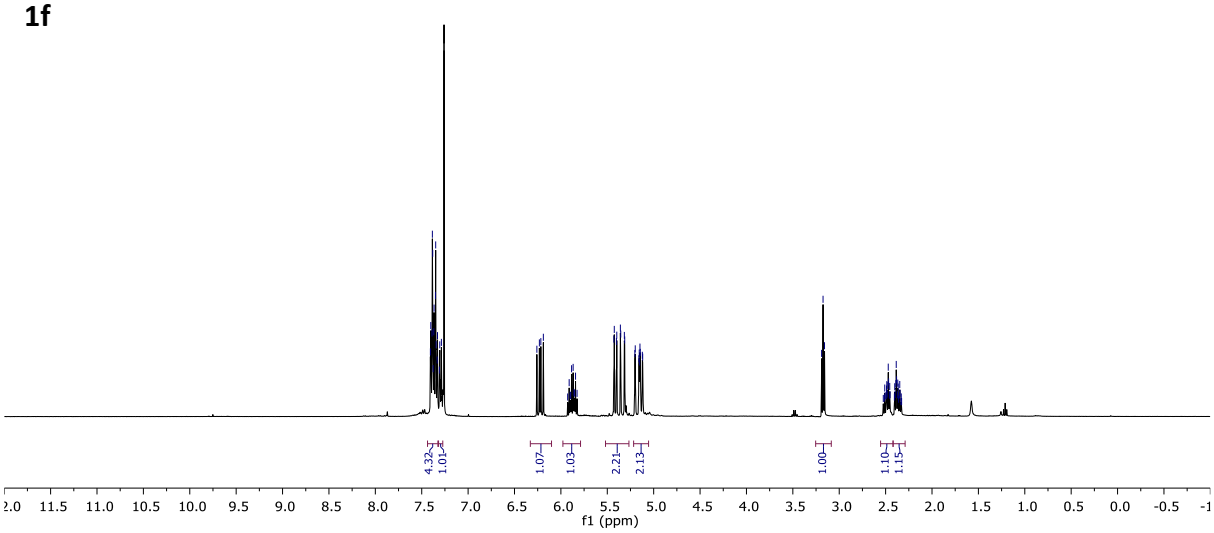

Me
O
Ph
OMe
O
1e
f1 (ppm)

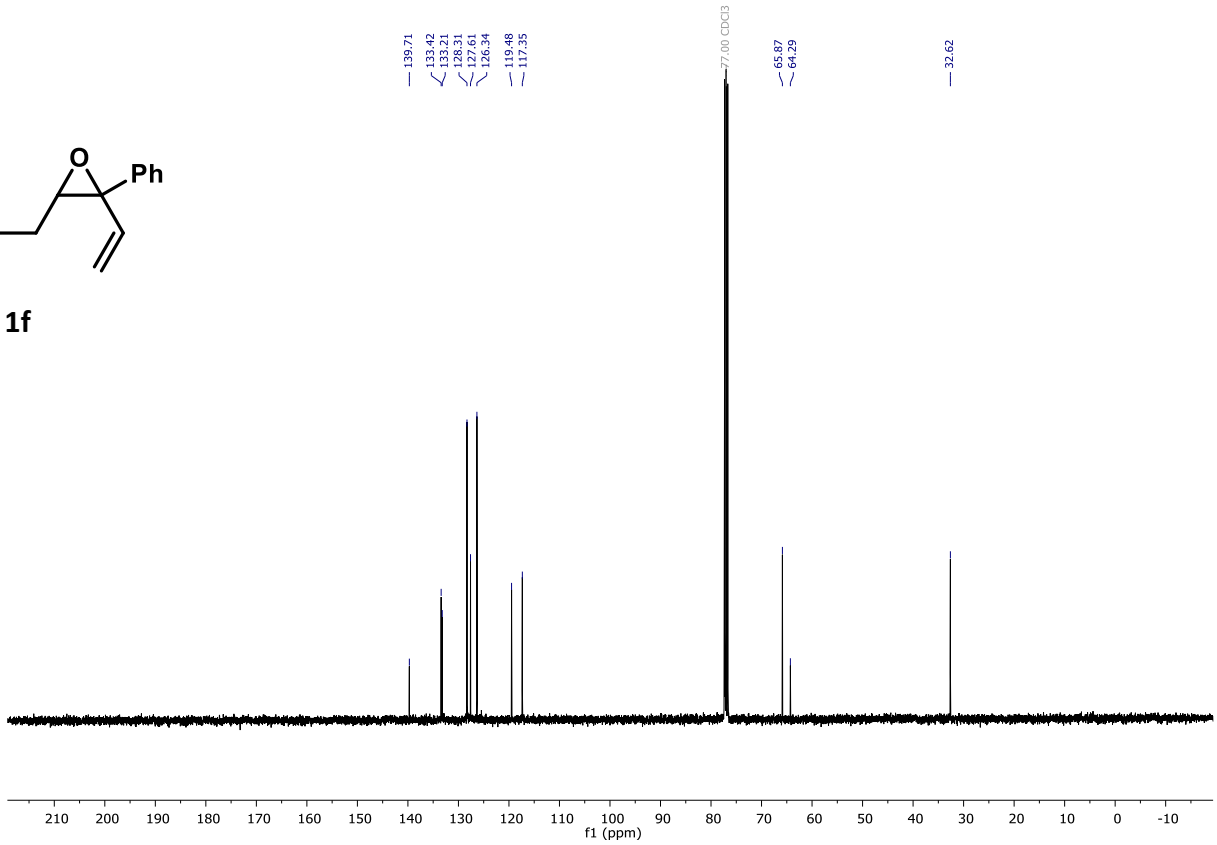

Me
O
Ph
OMe
O
1e
f1 (ppm)




O
Ph

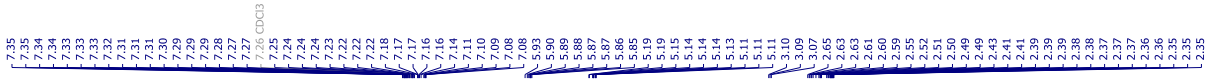
1f

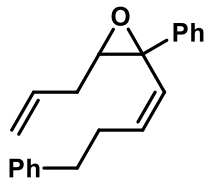

4.32
1.01
1.07
1.03
2.21
2.13
1.00
1.10
1.15
f1 (ppm)


139.71
133.42
133.21
128.31
127.61
126.34
119.48
117.35
77.00 CDCl3
65.87
64.29
32.62
f1 (ppm)

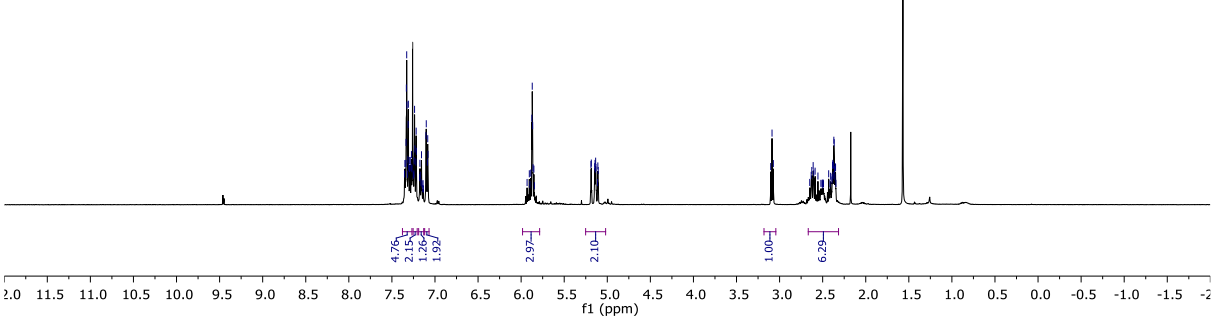
O
Ph

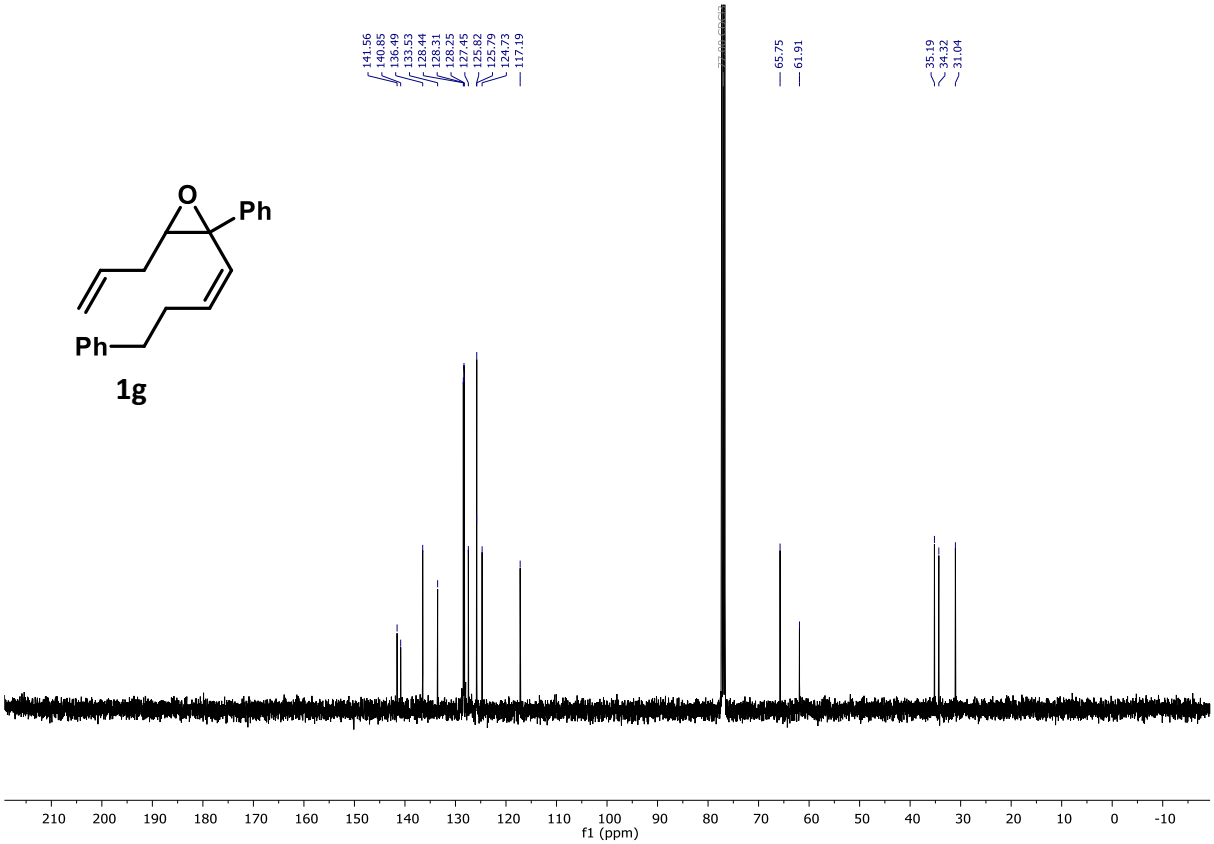
1f



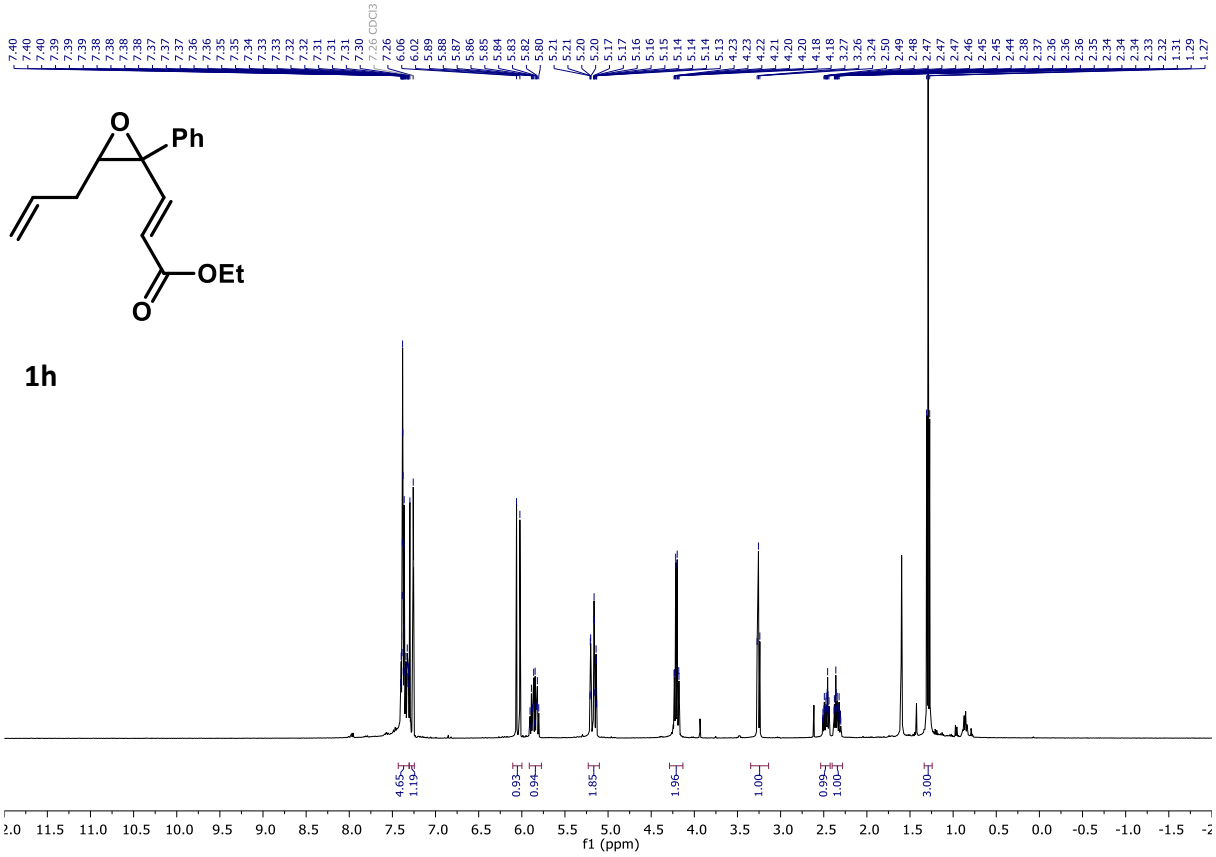


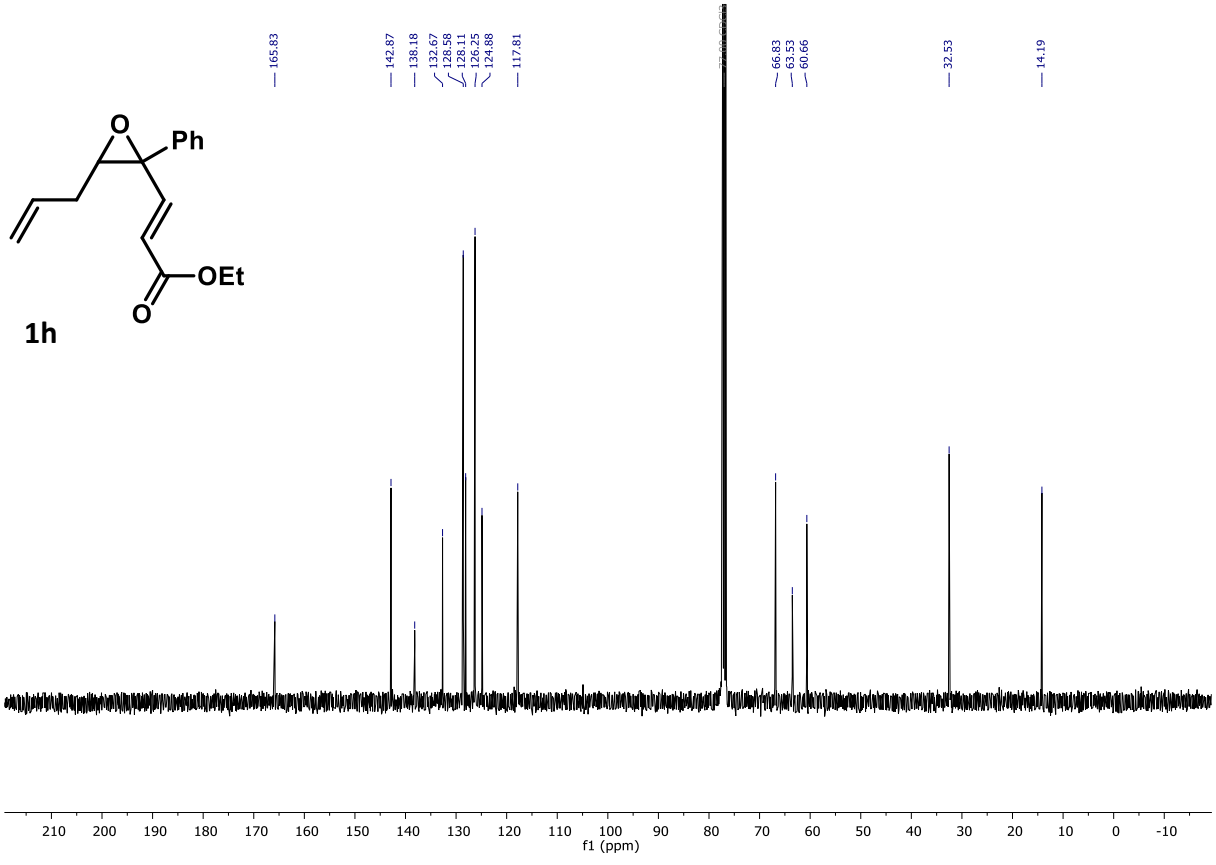
1g

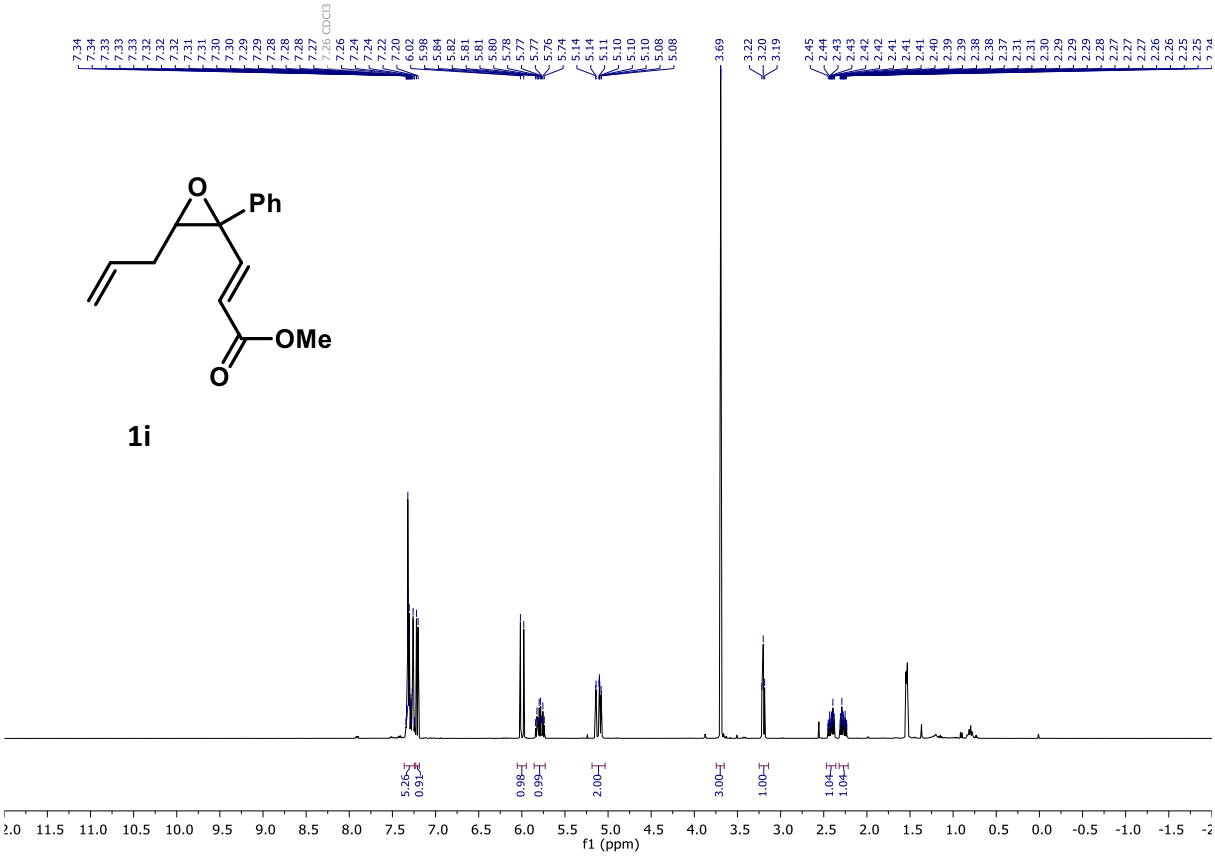


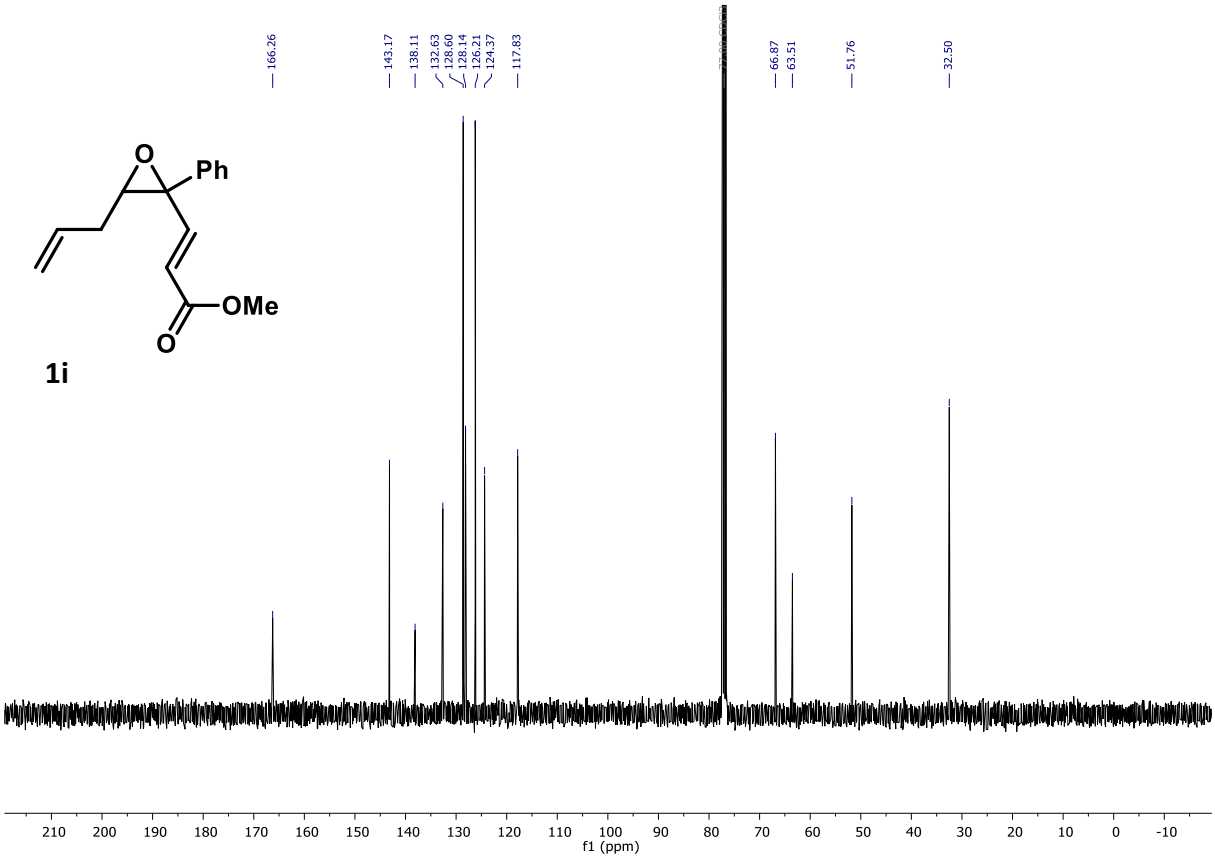


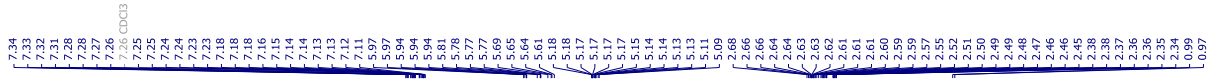
1g

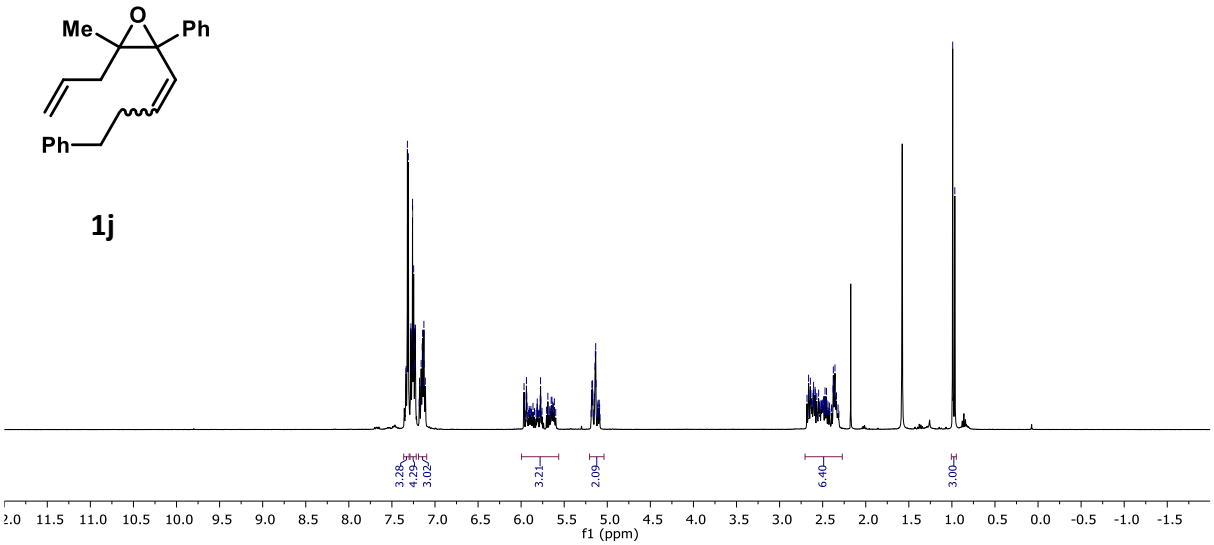

Ph
O
OEt
O
1h
f1 (ppm)

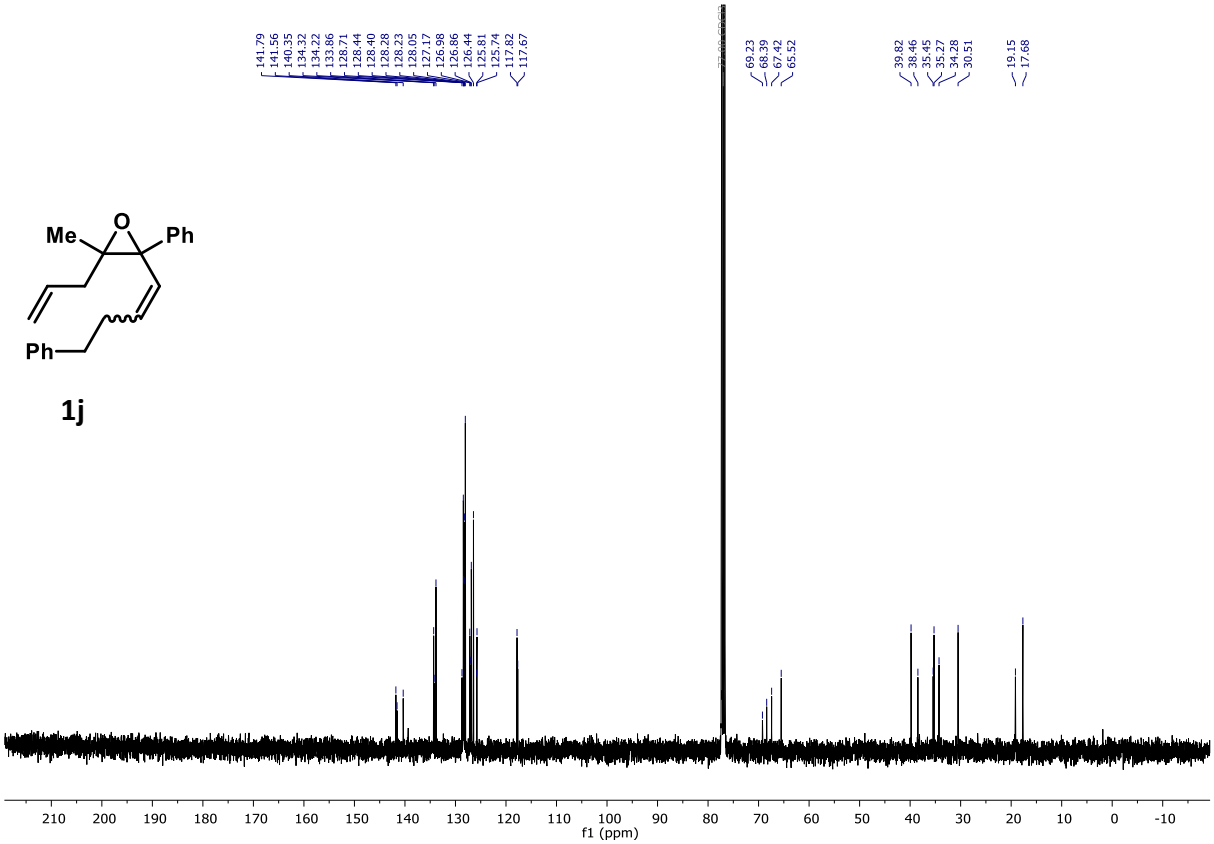

Ph
O
OEt
O
1h
f1 (ppm)

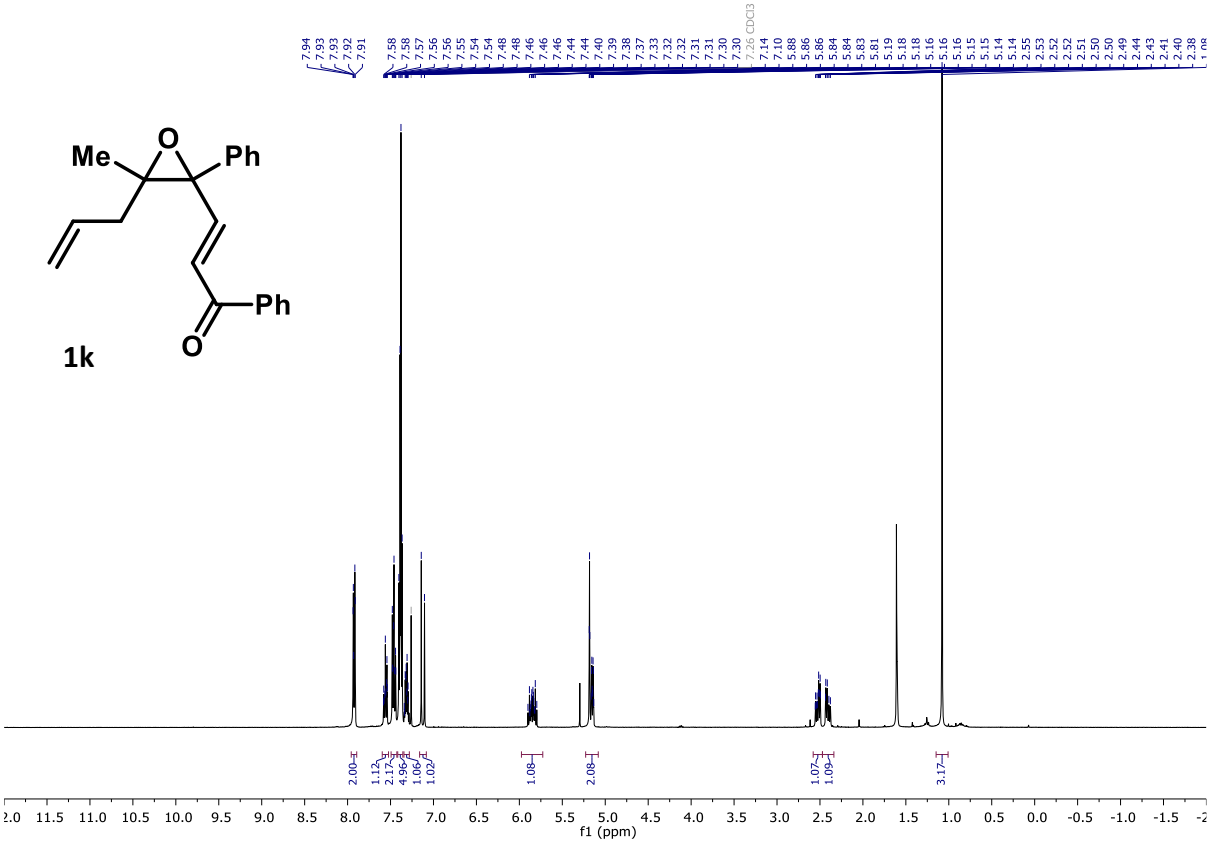

Ph
OMe
O
O
1i
f1 (ppm)

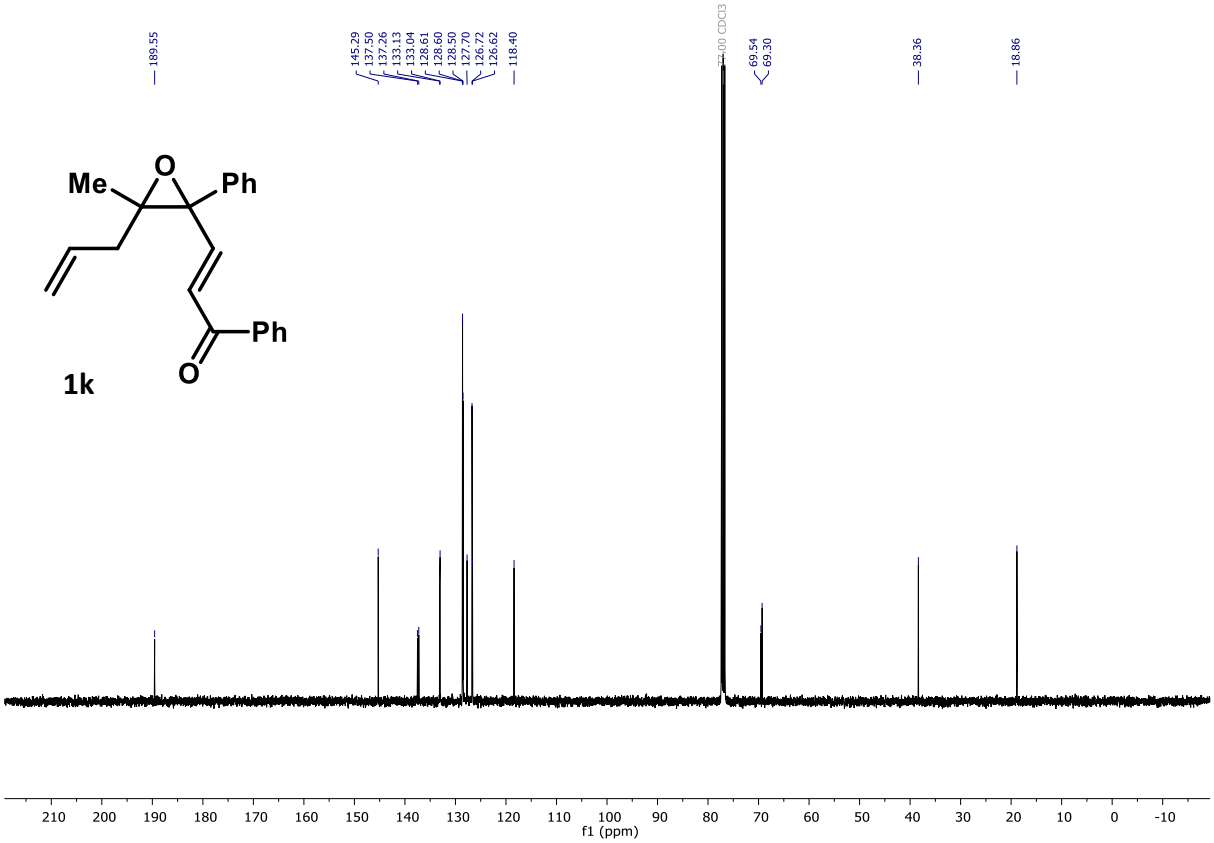

Ph
OMe
O
O
1i
166.26
143.17
138.11
132.63
128.60
128.14
126.21
124.37
117.83
66.87
63.51
51.76
32.50
f1 (ppm)

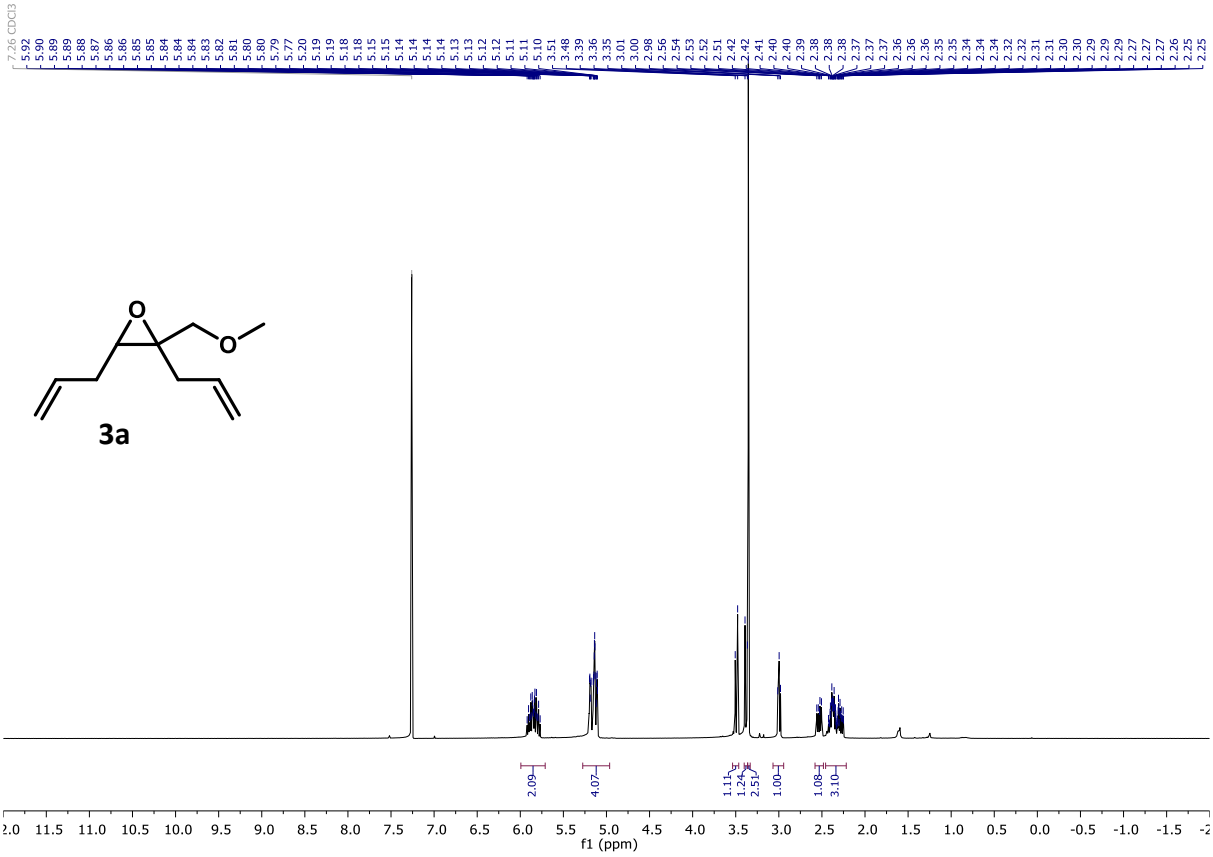


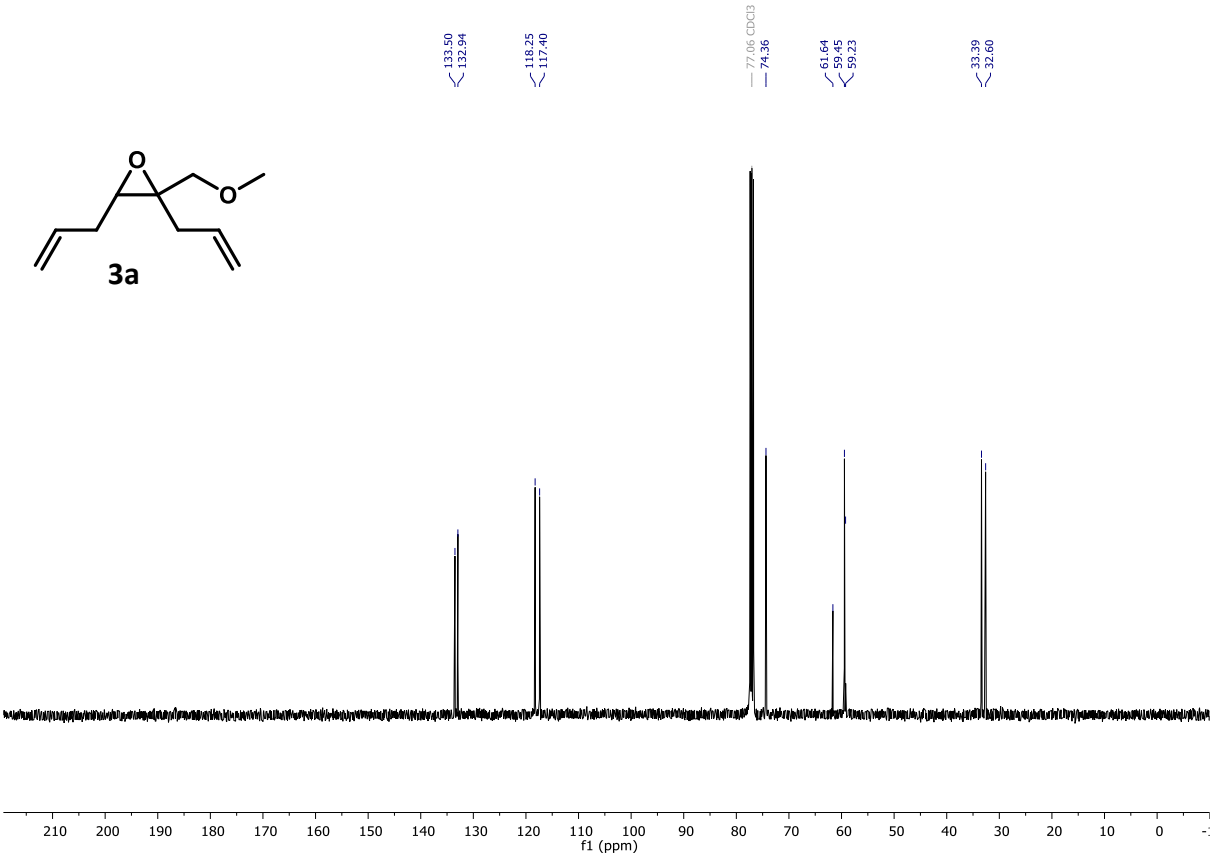

Me
O
Ph
Ph
1j
3.28
4.29
3.02
3.21
2.09
6.40
3.00
f1 (ppm)

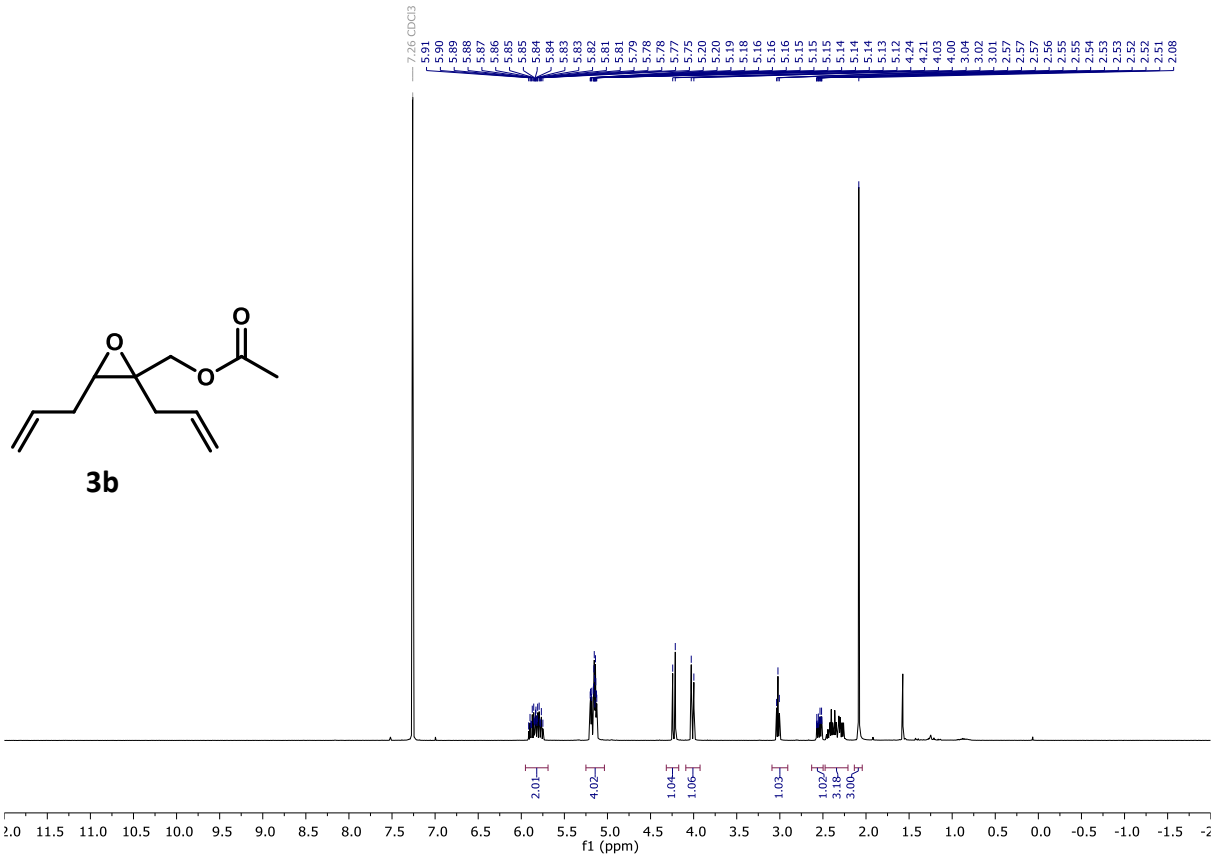

Me
O
Ph
Ph
1j
f1 (ppm)

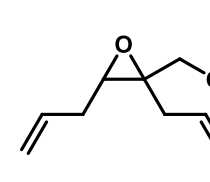

Me
O
Ph
Ph
O
1k
f1 (ppm)


Me
O
Ph
Ph
O
1k
f1 (ppm)


3a
f1 (ppm)


3a
f1 (ppm)

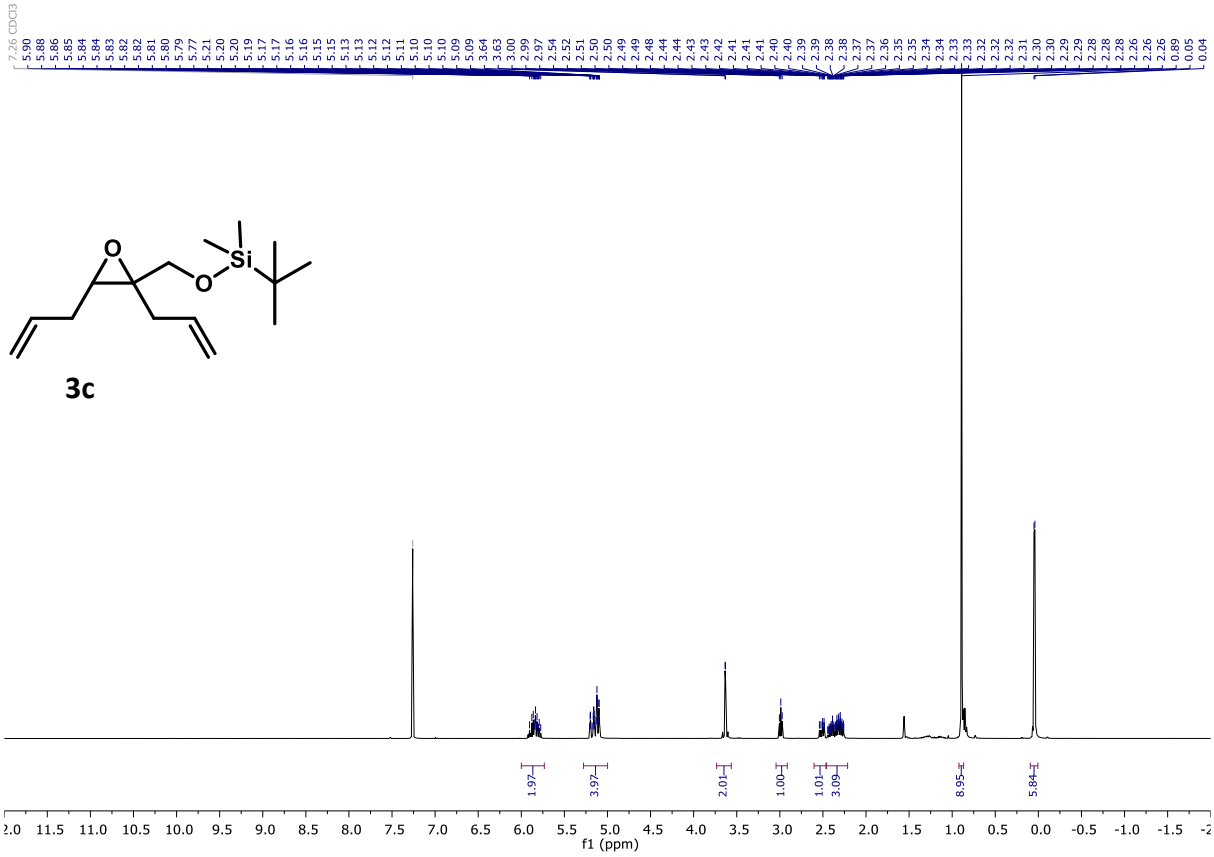

7.26 CDCl3
5.91
5.90
5.89
5.88
5.87
5.86
5.85
5.85
5.84
5.84
5.83
5.83
5.82
5.81
5.81
5.79
5.78
5.78
5.77
5.75
5.20
5.20
5.19
5.18
5.16
5.16
5.15
5.15
5.15
5.14
5.14
5.14
5.13
5.12
4.24
4.21
4.03
4.00
3.04
3.02
3.01
2.57
2.57
2.57
2.56
2.55
2.55
2.54
2.53
2.53
2.52
2.52
2.51
2.08
2.01
4.02
1.04
1.06
1.03
1.02
3.18
3.00
f1 (ppm)

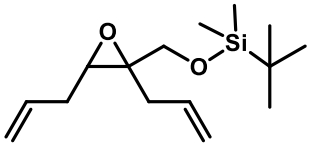


3b

170.61
133.15
132.23
118.76
117.58
77.05 CDCl3
65.95
60.35
60.02
33.55
32.44
20.83
f1 (ppm)

3b

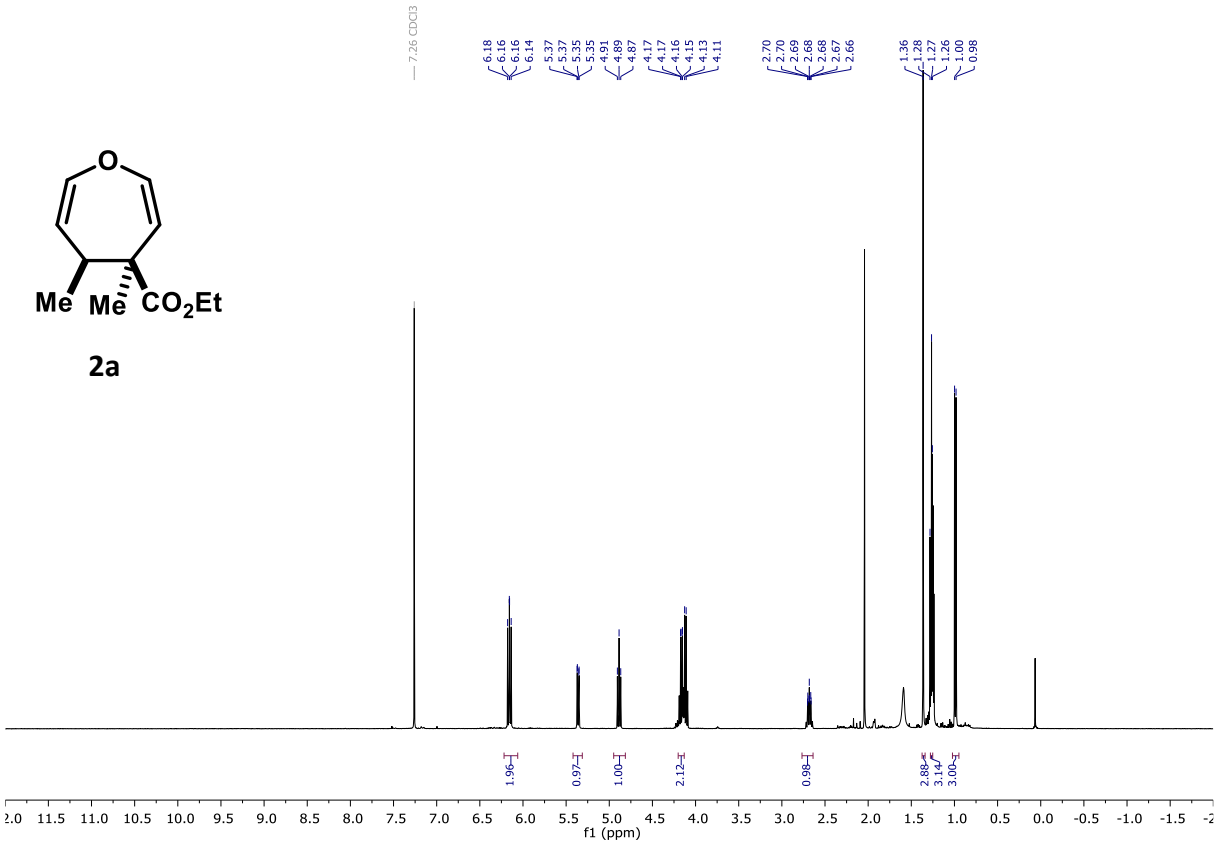

7.26 CDCl3
1.97
3.97
2.01
1.00
1.01
3.09
8.95
5.84
f1 (ppm)



3c

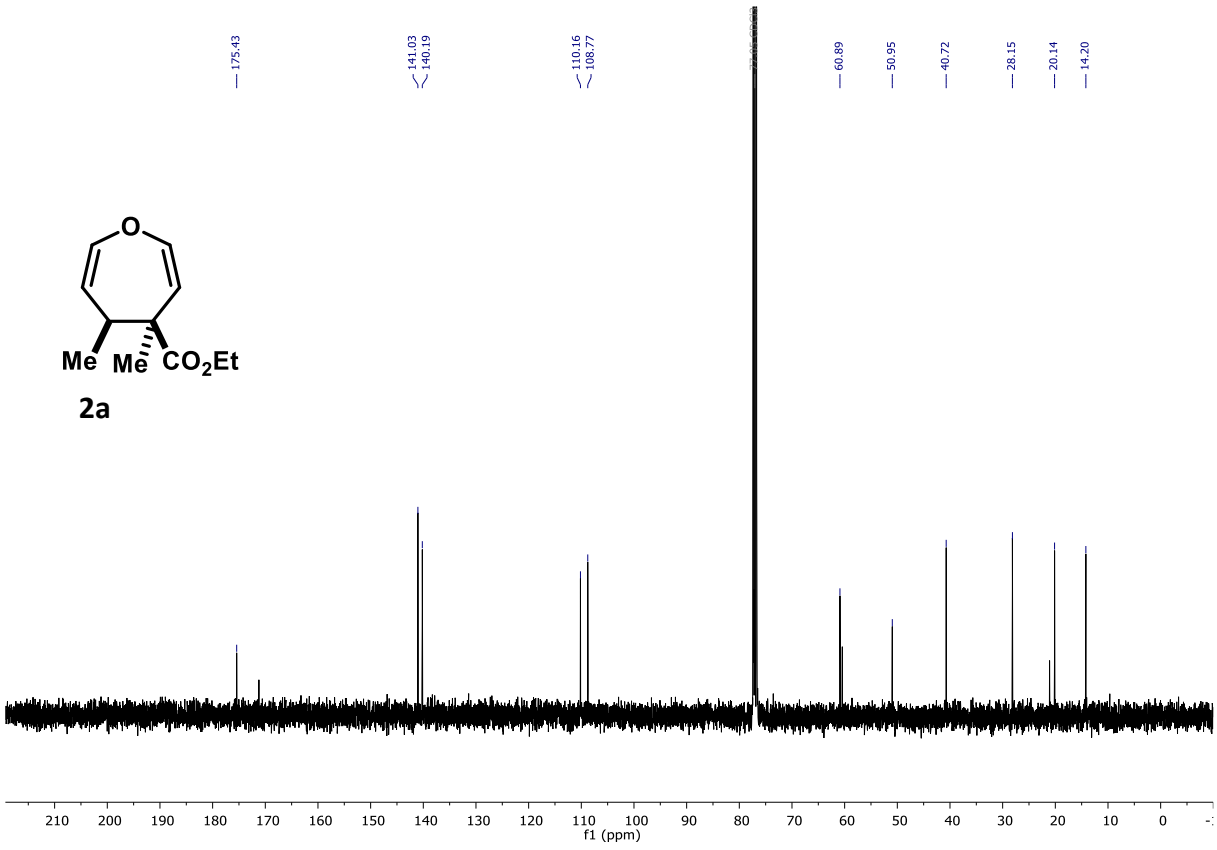
133.67
133.19
117.98
117.16
77.06
65.28
62.85
59.51
33.14
32.62
25.88
18.32
-5.39
f1 (ppm)

3c


7.26 CDCl3
6.18
6.16
6.16
6.14
5.37
5.37
5.35
5.35
4.91
4.89
4.87
4.17
4.17
4.16
4.15
4.13
4.11
2.70
2.70
2.69
2.68
2.68
2.67
2.66
1.36
1.28
1.27
1.26
1.00
0.98
1.96
0.97
1.00
2.12
0.98
2.88
3.14
3.00
f1 (ppm)

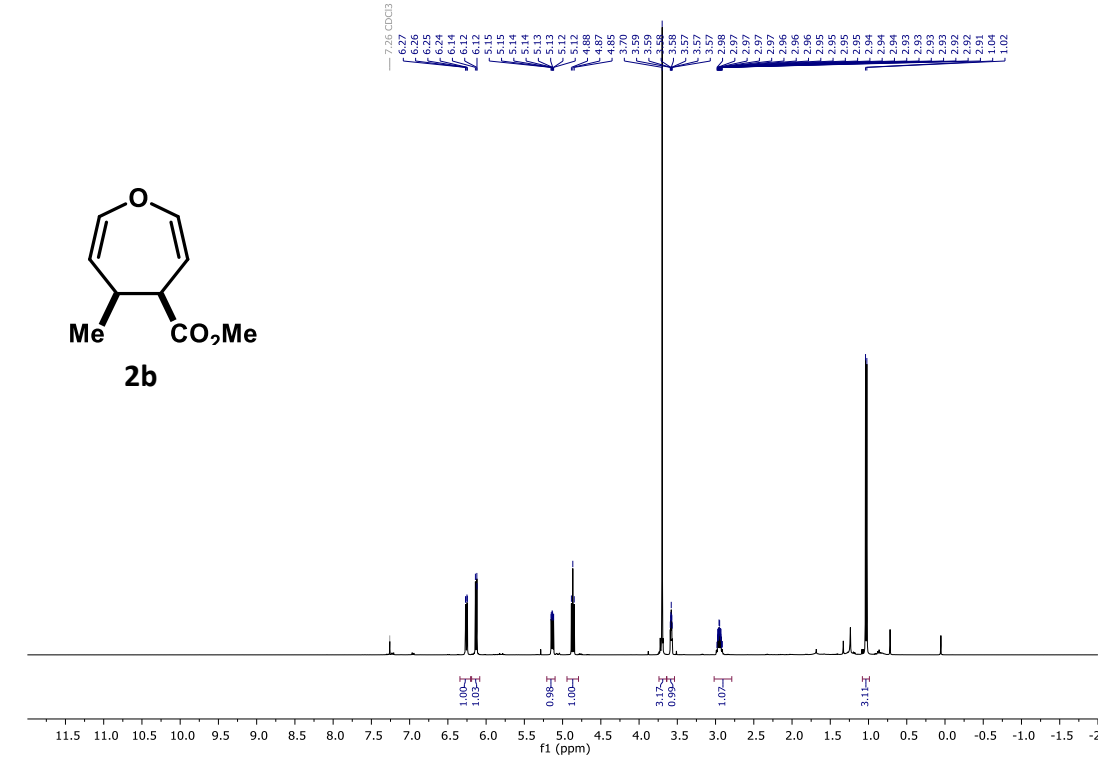
Me
Me
CO2Et

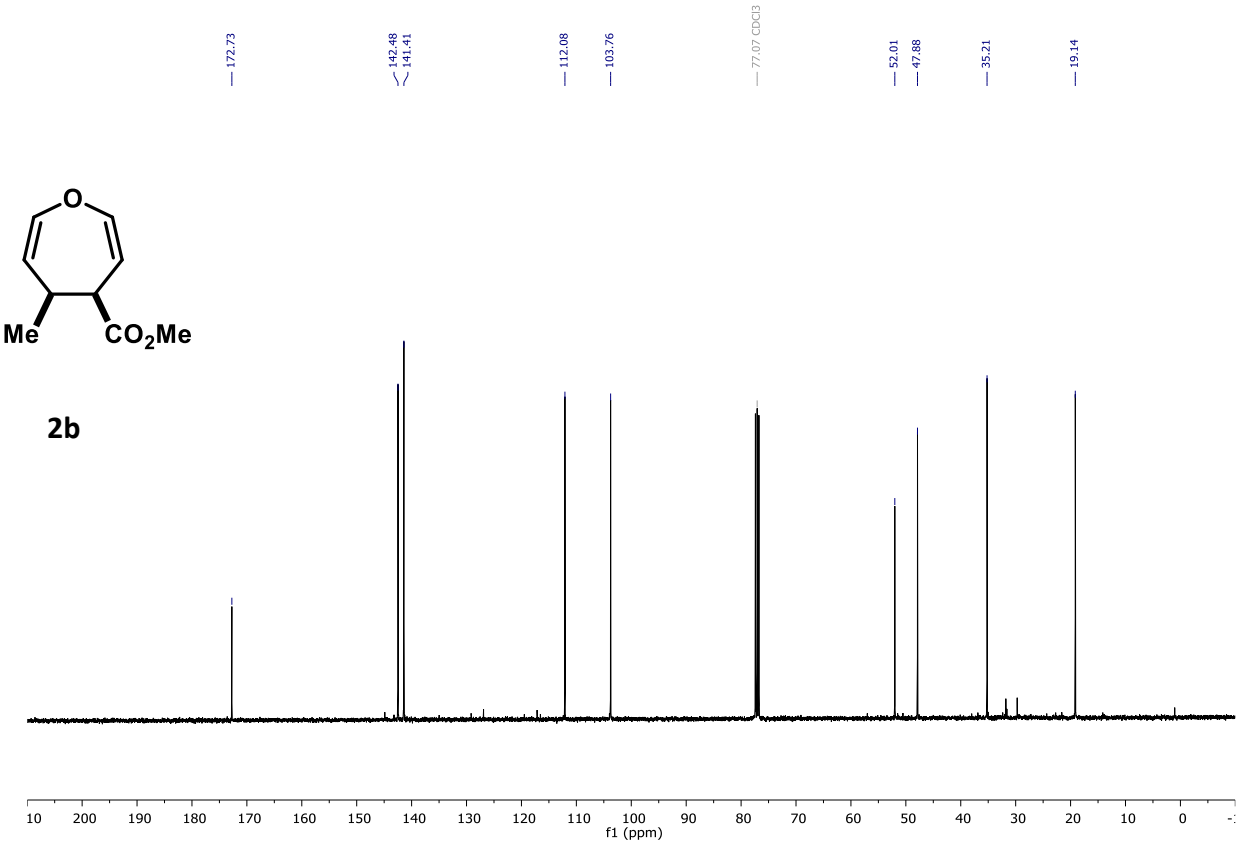
2a

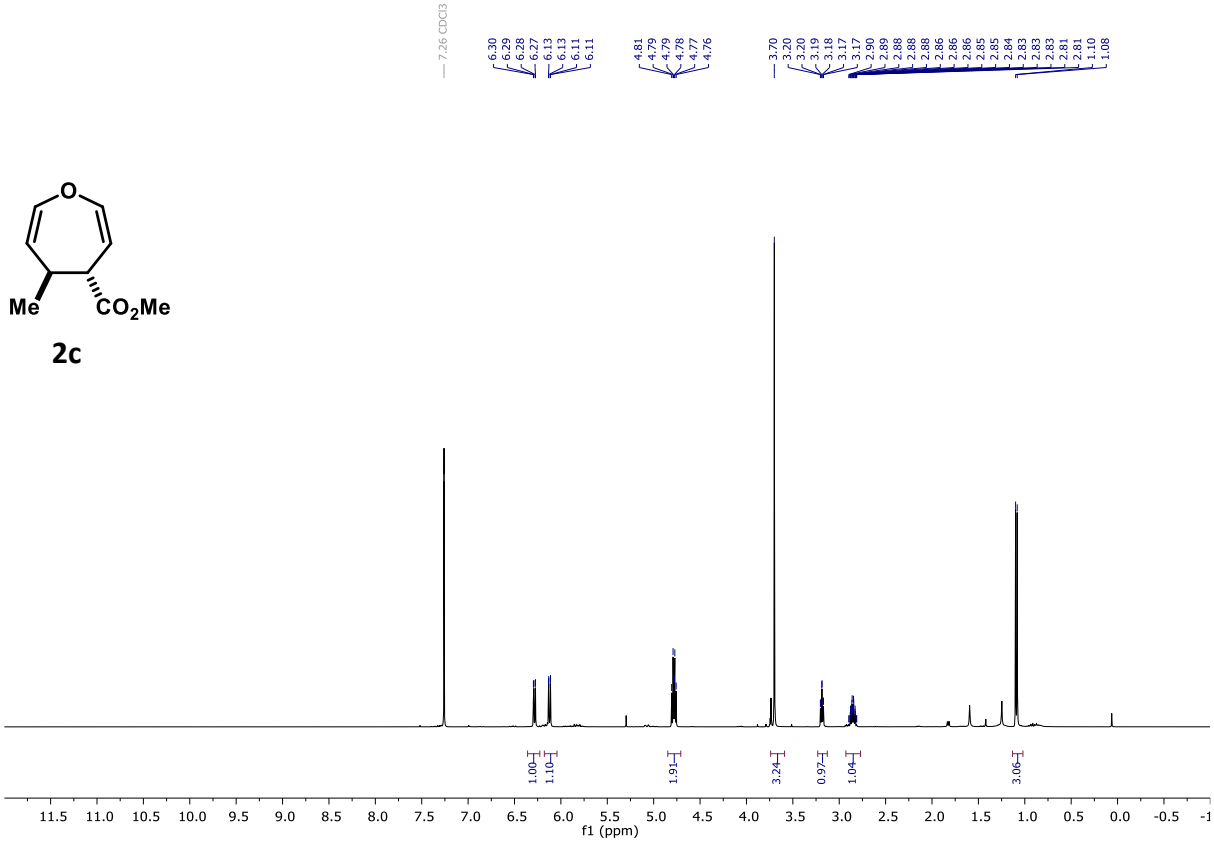

175.43
141.03
140.19
110.16
108.77
60.89
50.95
40.72
28.15
20.14
14.20
f1 (ppm)

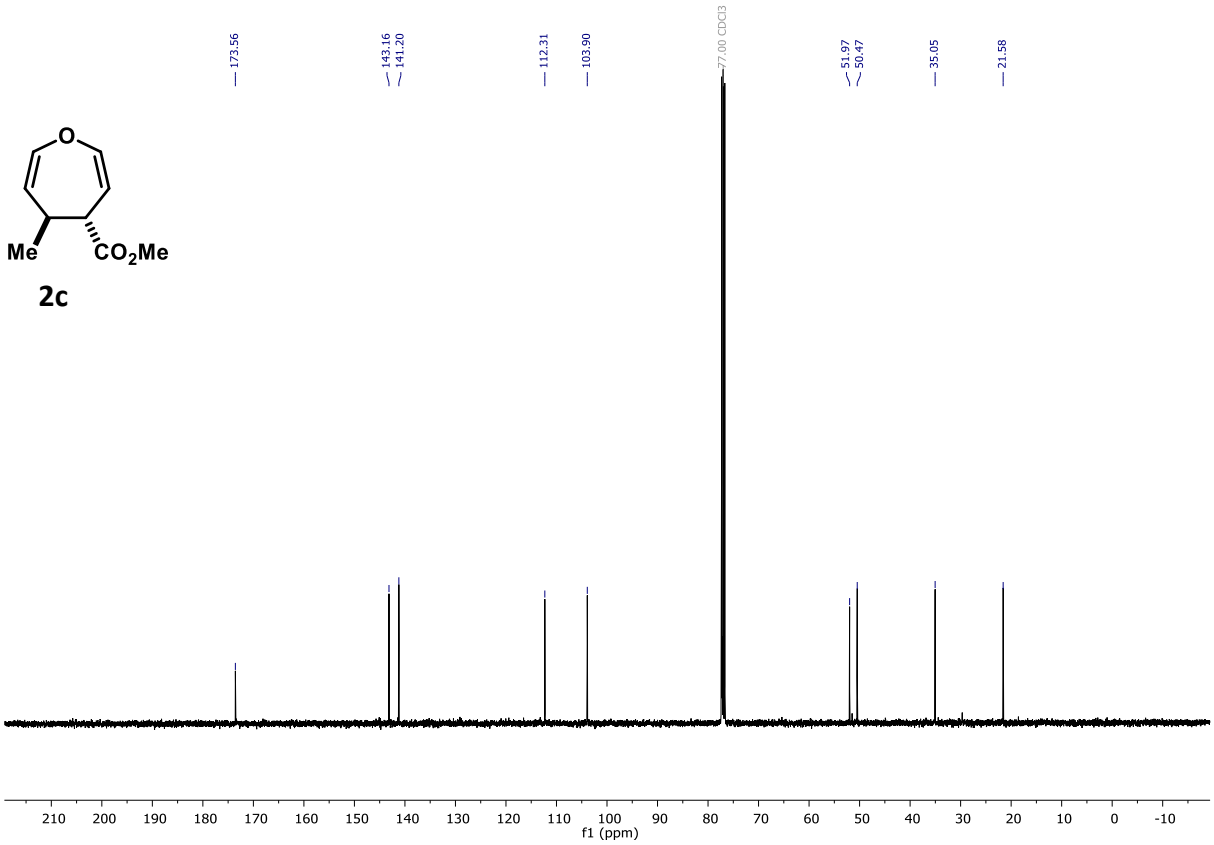
Me
Me
CO2Et

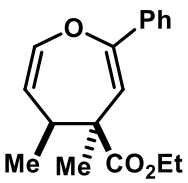
2a


Me
CO2Me
2b
f1 (ppm)


Me
CO2Me
2b
f1 (ppm)

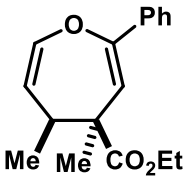

7.26 CDCl3
6.30
6.29
6.28
6.27
6.13
6.13
6.11
6.11
4.81
4.79
4.79
4.78
4.77
4.76
3.70
3.20
3.20
3.19
3.18
3.17
3.17
2.90
2.89
2.88
2.88
2.88
2.86
2.86
2.86
2.85
2.85
2.84
2.83
2.83
2.83
2.81
2.81
1.10
1.08
O
Me
CO2Me
2c
1.00
1.10
1.91
3.24
0.97
1.04
3.06
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


173.56
143.16
141.20
112.31
103.90
77.00 CDCl3
51.97
50.47
35.05
21.58
O
Me
CO2Me
2c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
Ph
Me
Me
CO2Et

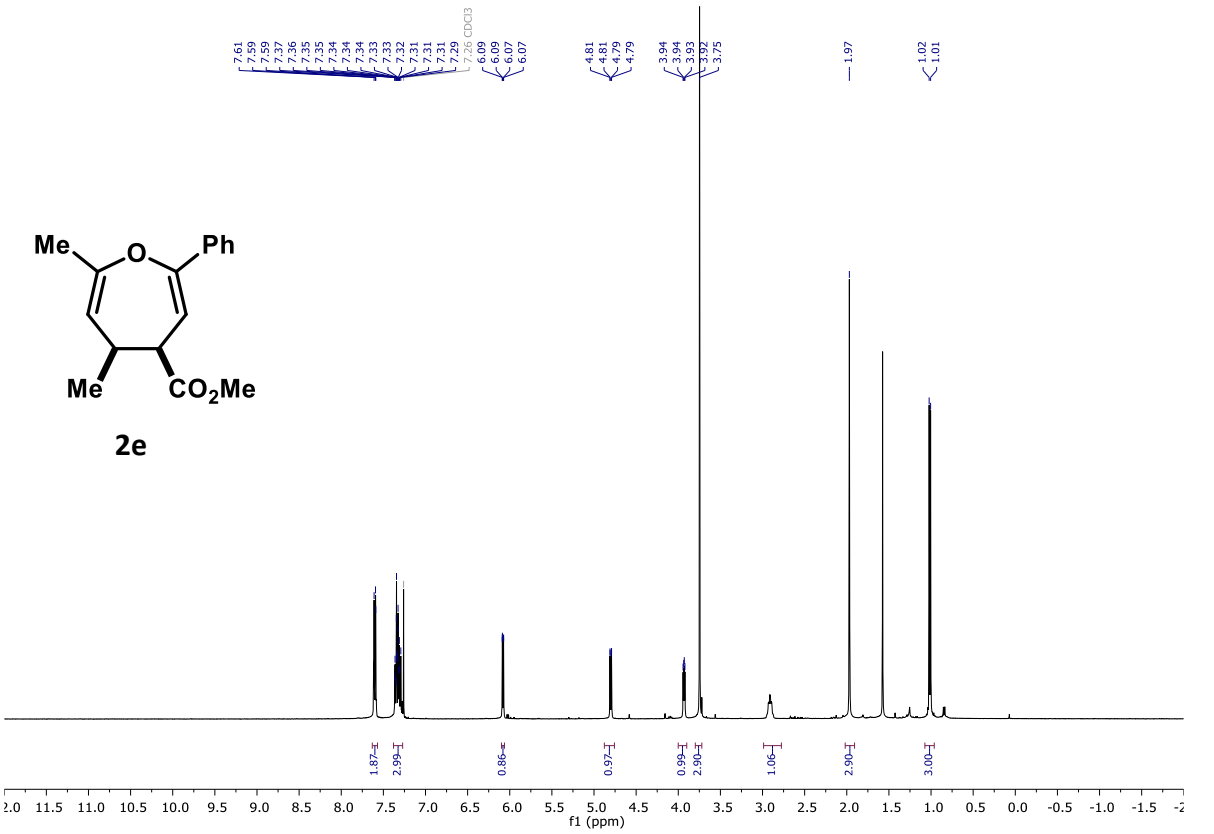
2d

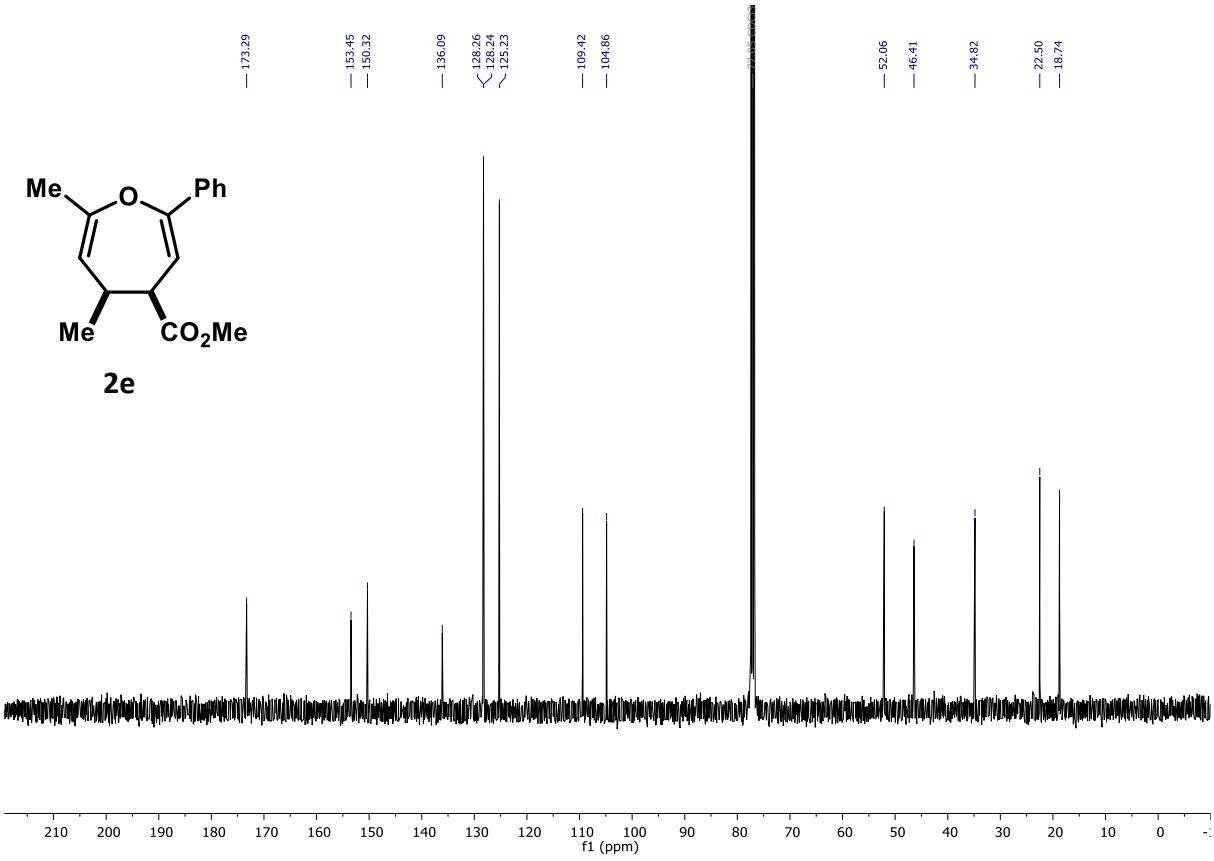
7.62
7.60
7.36
7.34
7.32
7.31
7.26 CDCl3
6.38
6.38
6.36
6.27
4.92
4.90
4.88
4.87
4.24
4.22
4.20
4.18
2.77
2.76
2.74
2.72
2.70
1.50
1.31
1.31
1.30
1.29
1.28
1.27
1.03
1.02
1.01
f1 (ppm)

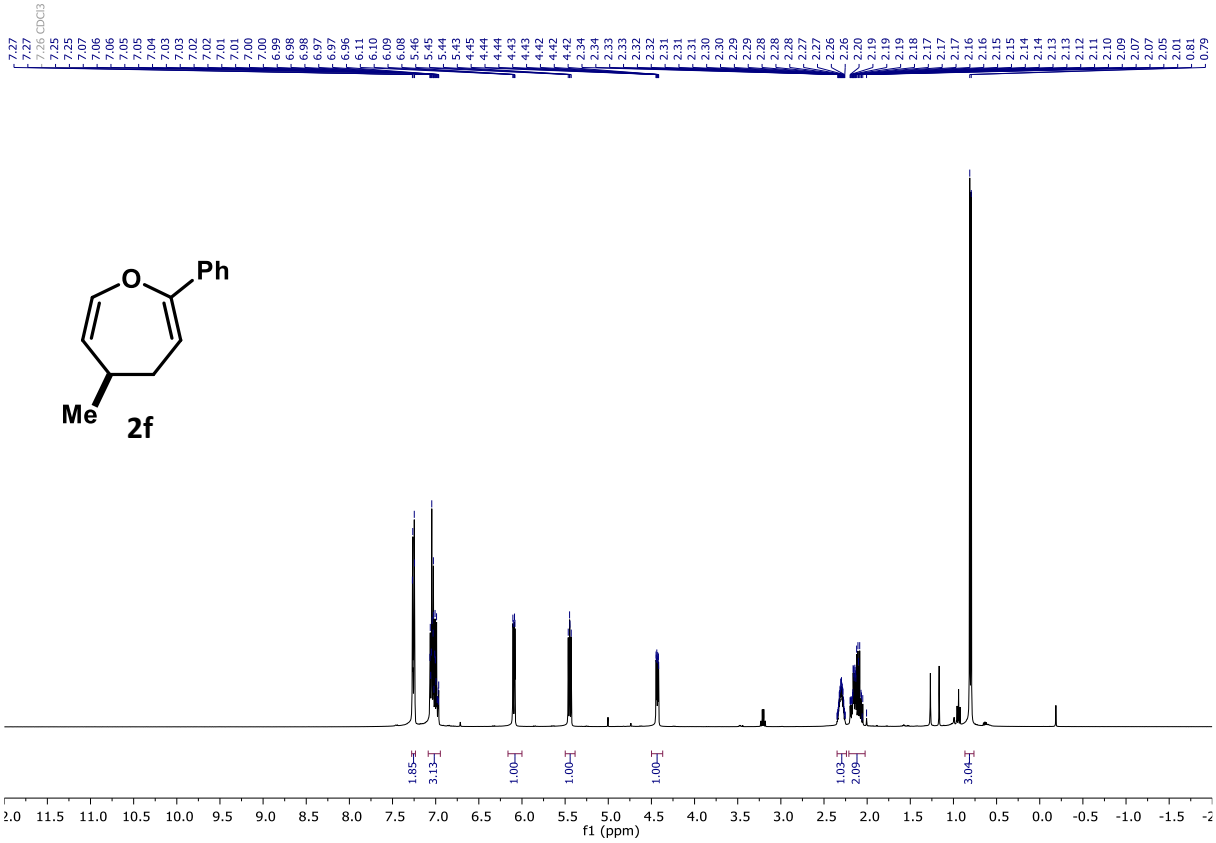

O
Ph
Me
Me
CO2Et

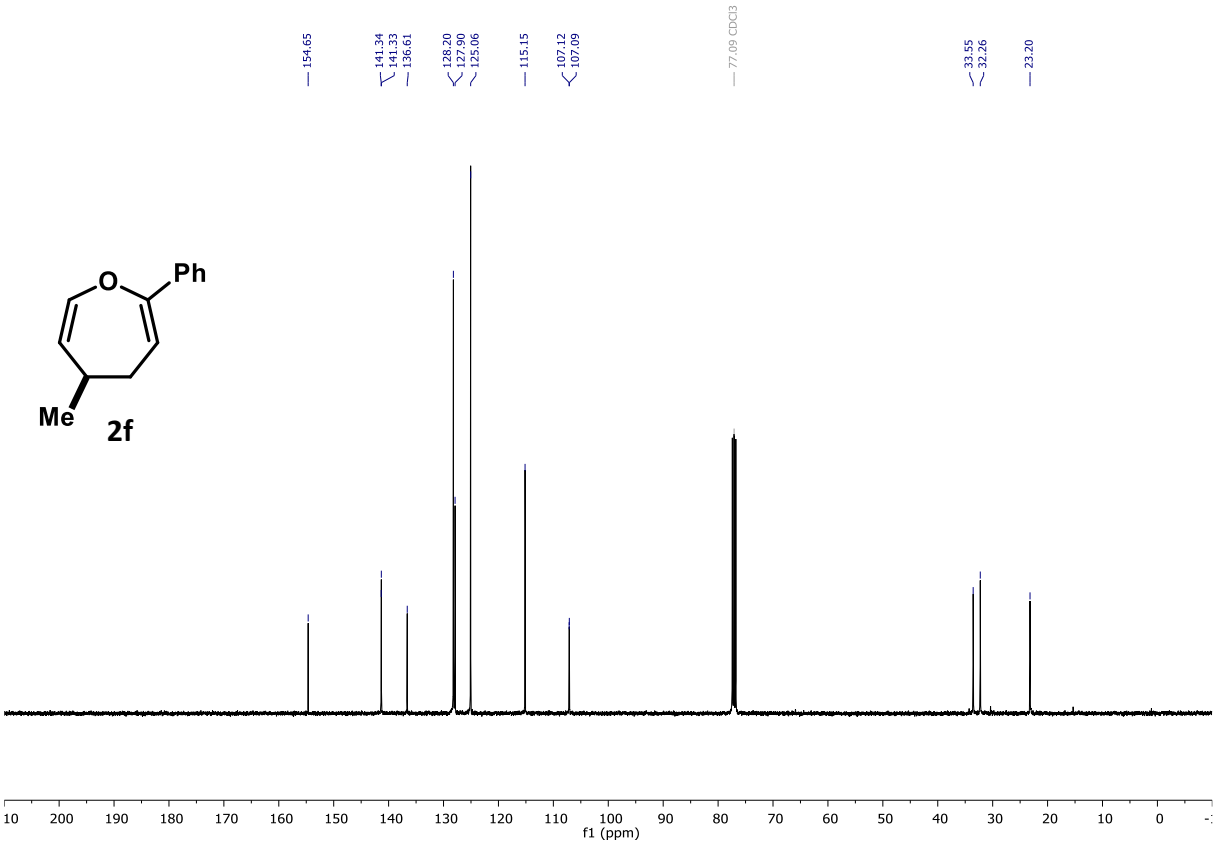
2d

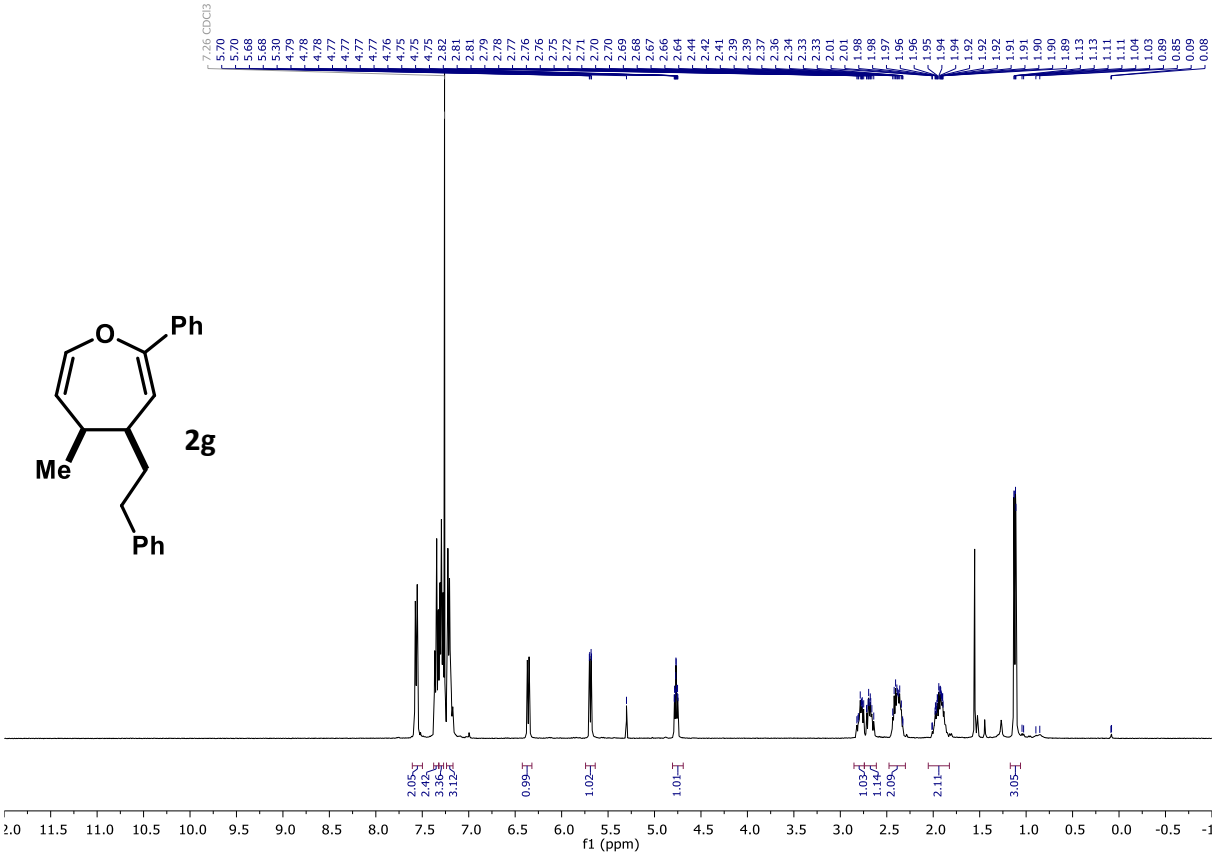
175.76
150.79
140.46
137.00
128.17
128.14
125.56
110.28
107.74
77.05 CDCl3
61.01
50.47
40.65
26.08
20.83
14.24
f1 (ppm)

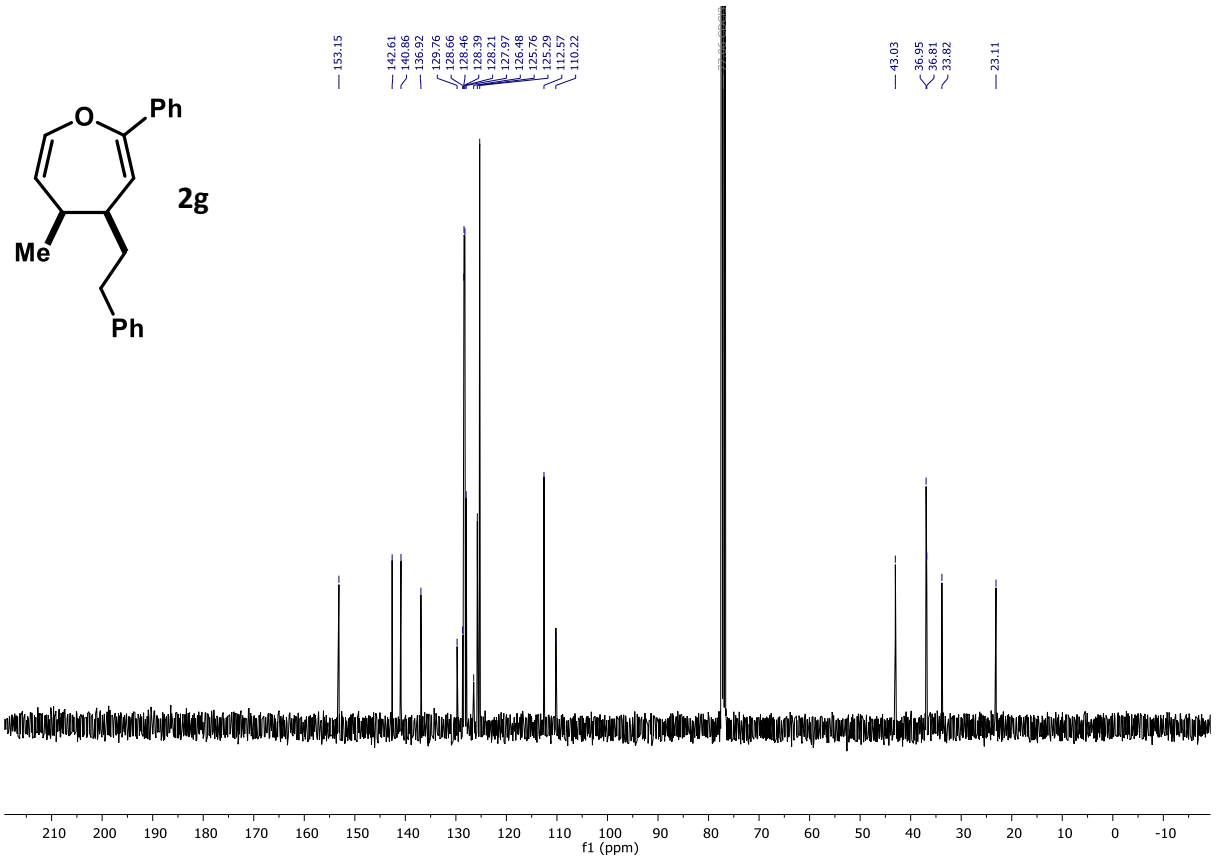

7.61
7.59
7.59
7.37
7.36
7.35
7.35
7.34
7.34
7.34
7.33
7.33
7.32
7.31
7.31
7.31
7.29
7.26 CDCl3
6.09
6.09
6.07
6.07
4.81
4.81
4.79
4.79
3.94
3.94
3.93
3.92
3.75
1.97
1.02
1.01
Me
O
Ph
Me
CO2Me
2e
1.87
2.99
0.86
0.97
0.99
2.90
1.06
2.90
3.00
f1 (ppm)

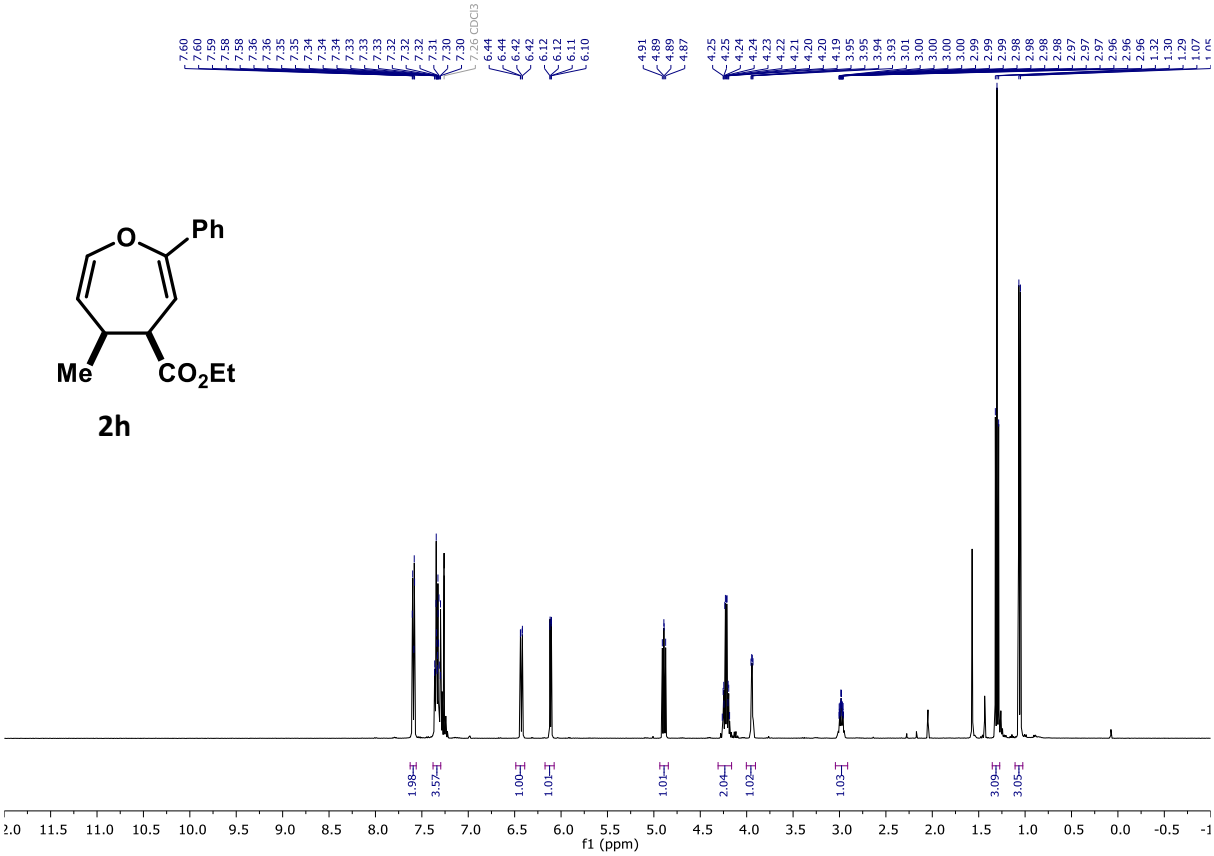

173.29
153.45
150.32
136.09
128.26
128.24
125.23
109.42
104.86
52.06
46.41
34.82
22.50
18.74
Me
O
Ph
Me
CO2Me
2e
f1 (ppm)

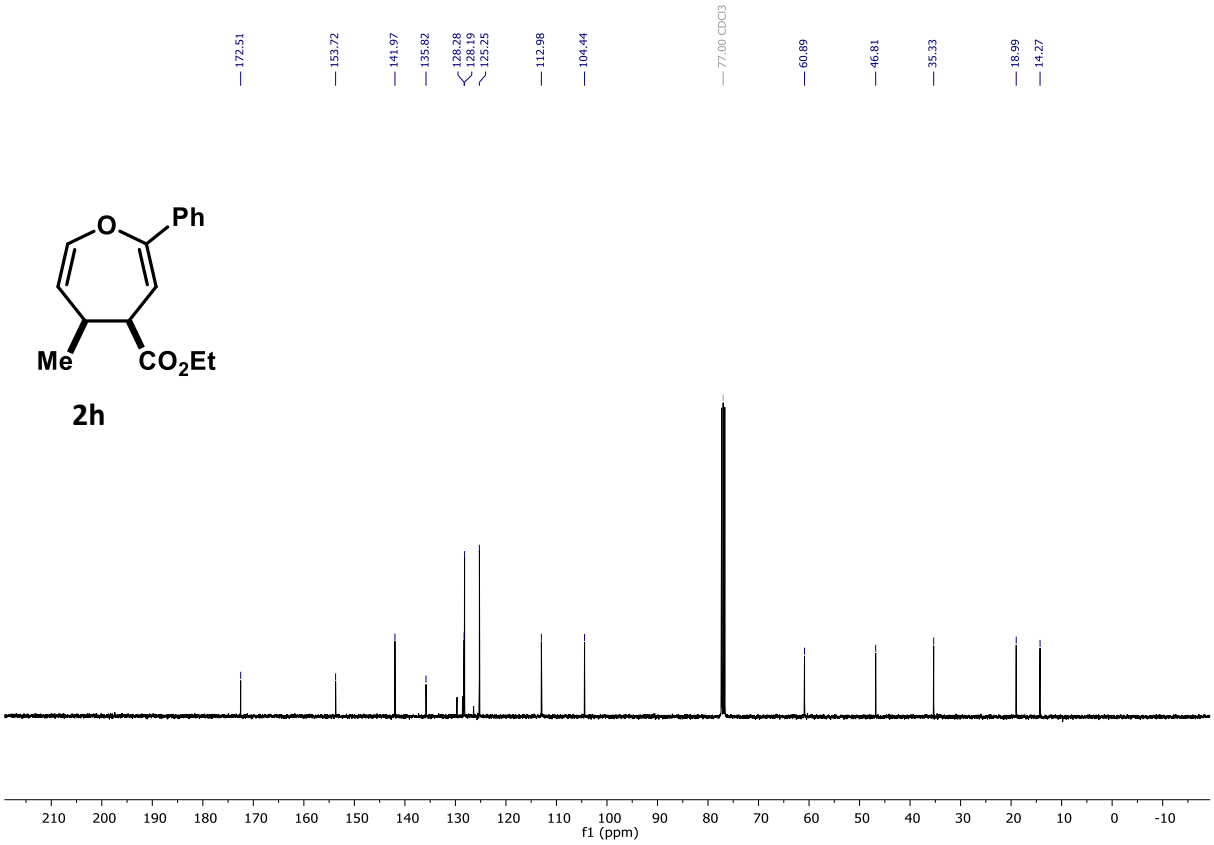

Ph
O
Me
2f
f1 (ppm)

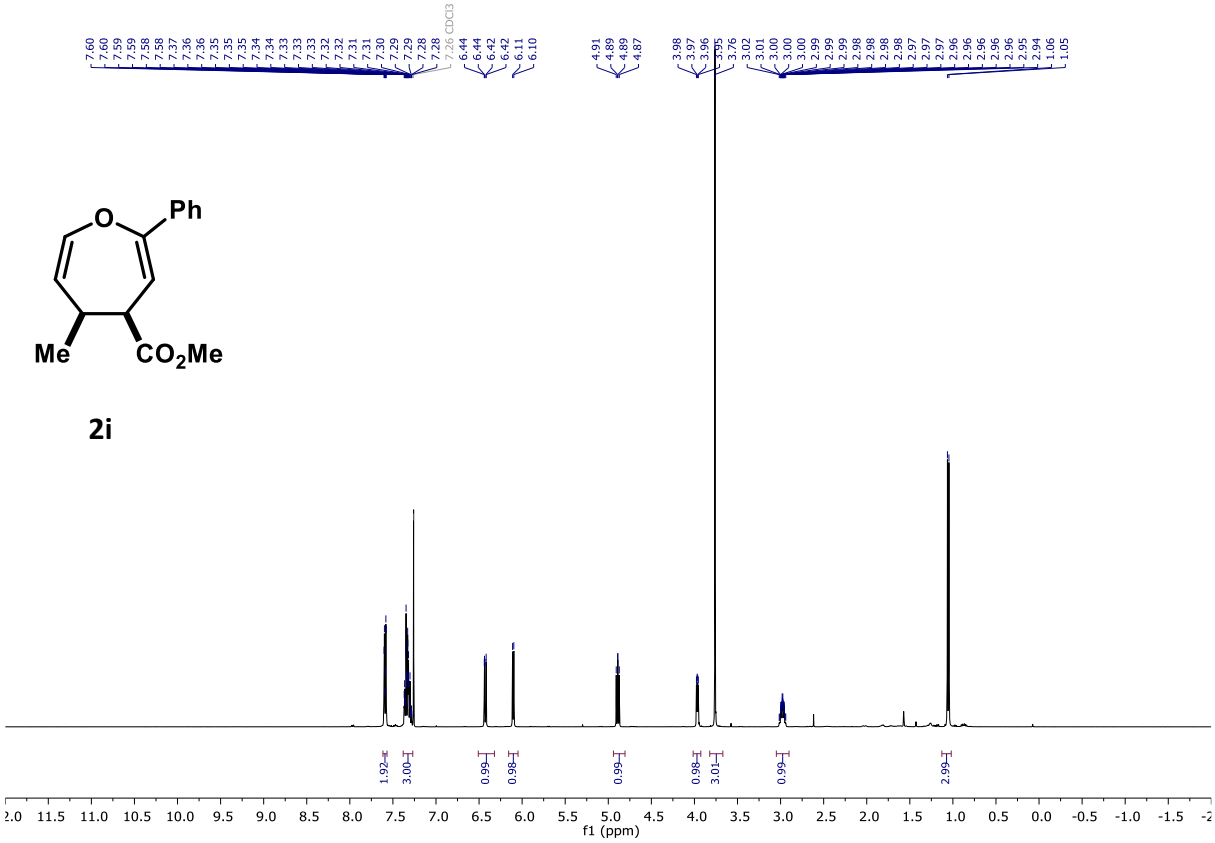

Ph
O
Me
2f
f1 (ppm)

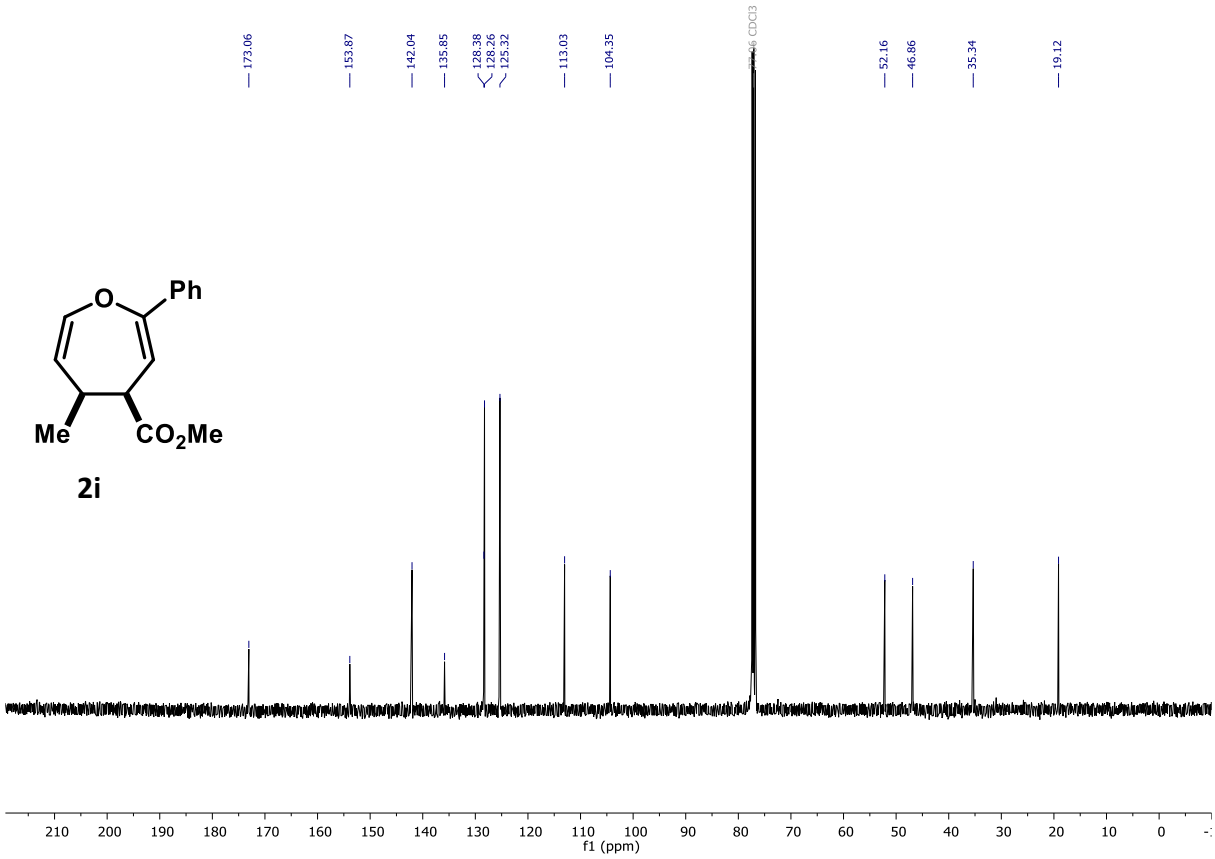

O
Ph
Me
Ph
2g
f1 (ppm)

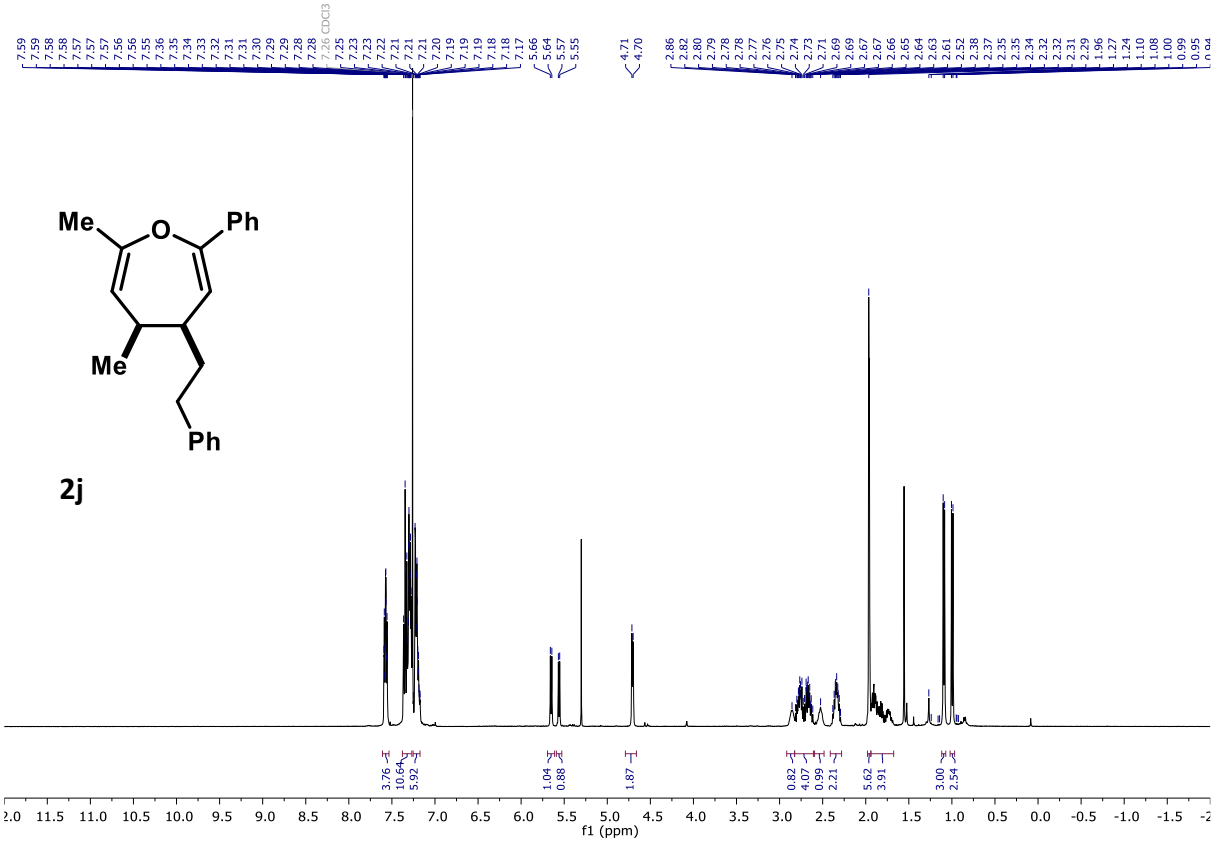

O
Ph
Me
Ph
2g
f1 (ppm)

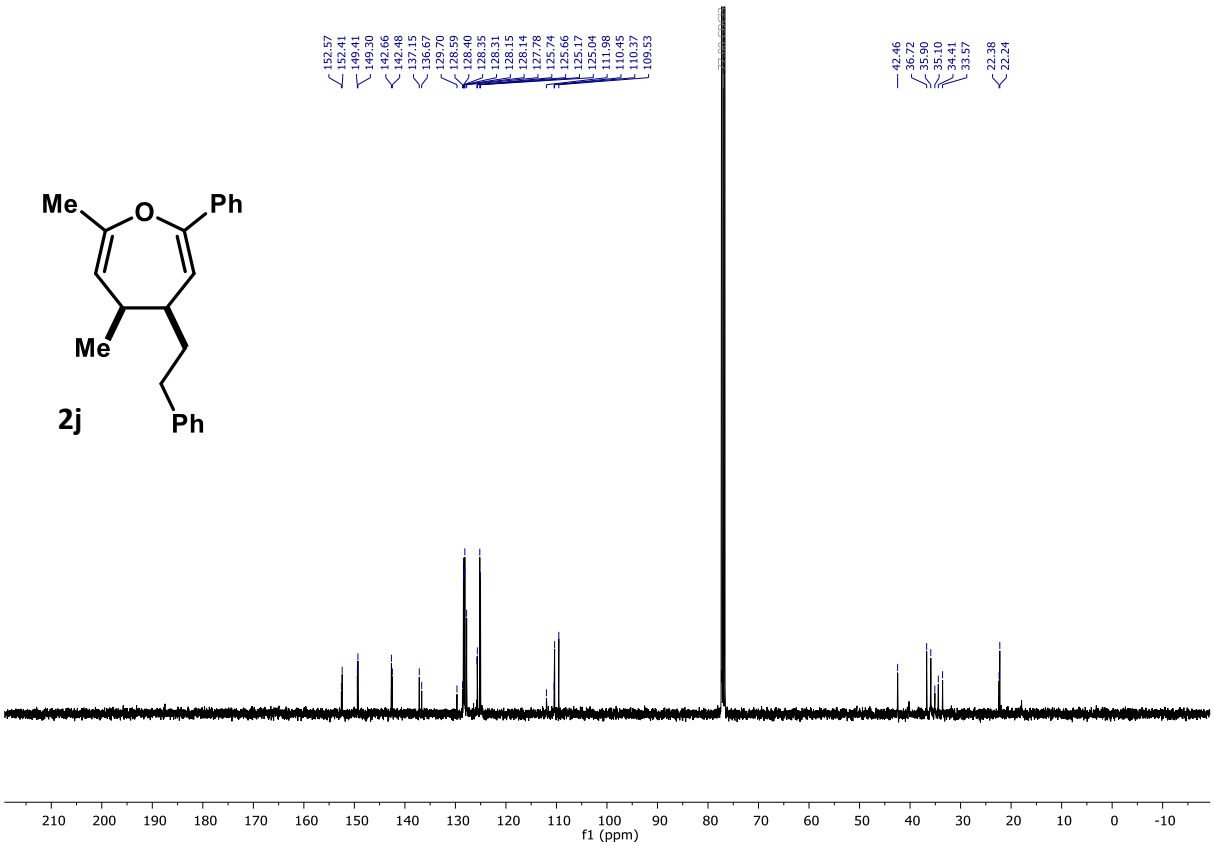

Ph
O
Me
CO2Et
2h
f1 (ppm)

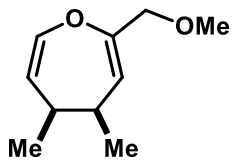

Ph
O
Me
CO2Et
2h
f1 (ppm)


Ph
O
Me
CO2Me
2i
f1 (ppm)


Ph
O
Me
CO2Me
2i
f1 (ppm)

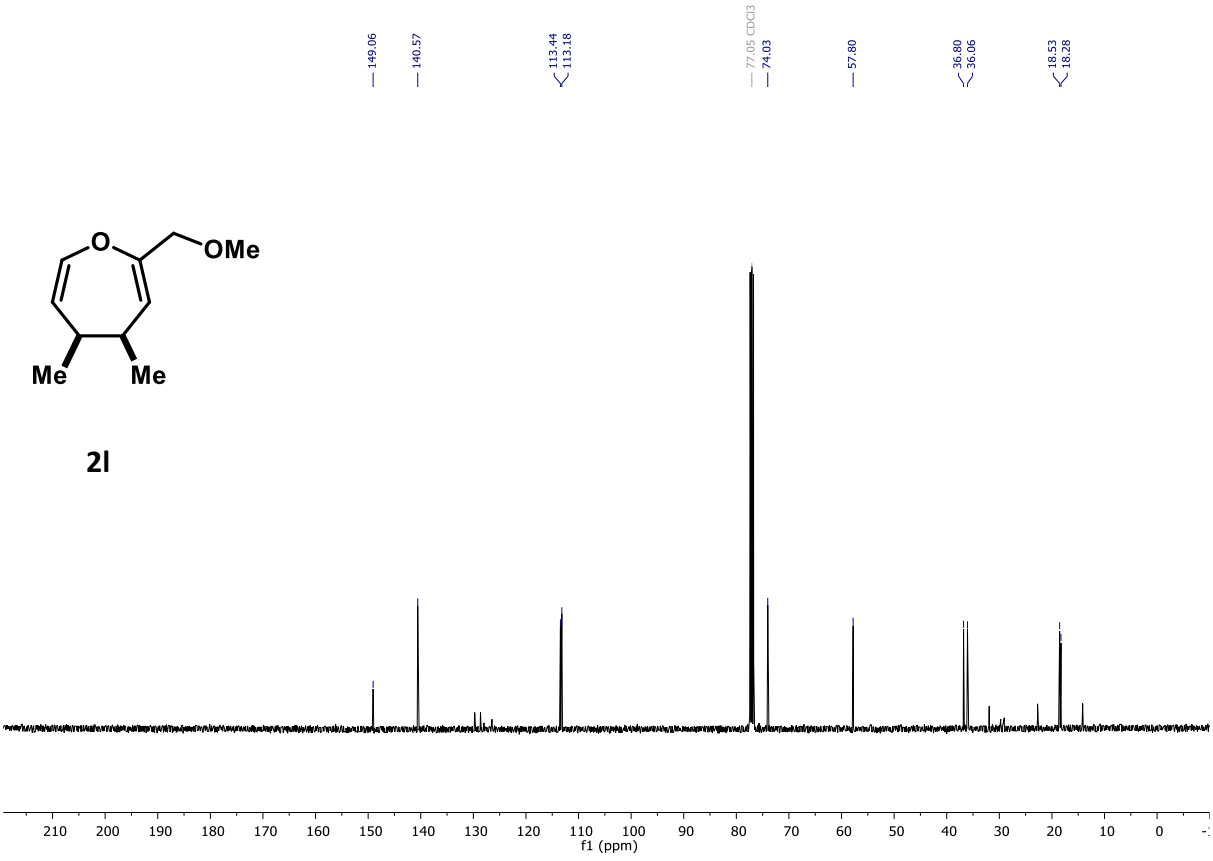

Me
O
Ph
Me
Ph
2j
f1 (ppm)


Me
O
Ph
Me
Ph
2j
f1 (ppm)


O
OMe
Me
Me

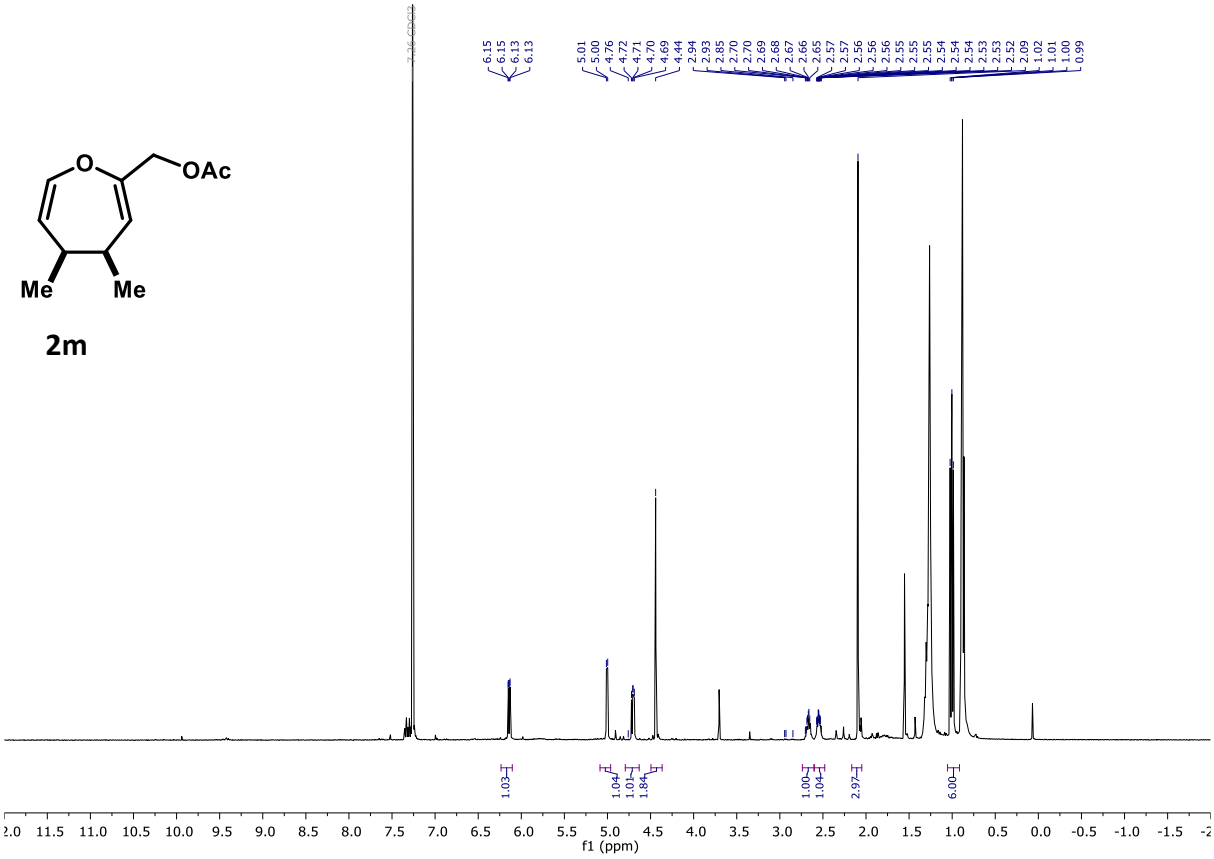
2l

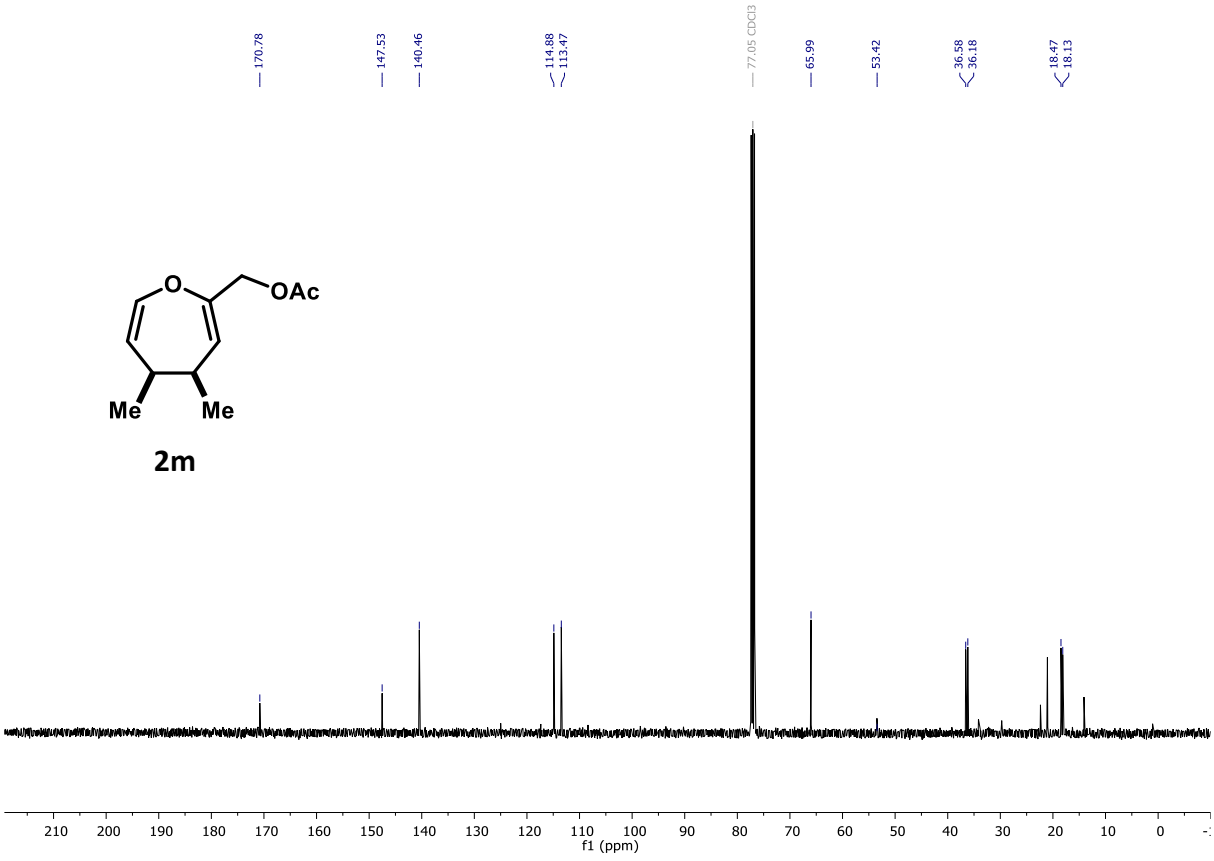
7.26 CDCl3
6.17
6.17
6.16
6.15
4.95
4.93
4.70
4.68
4.68
4.67
3.85
3.82
3.78
3.75
3.35
1.02
1.01
0.99
1.00
1.06
1.02
1.01
1.01
3.36
1.03
1.09
6.34
f1 (ppm)

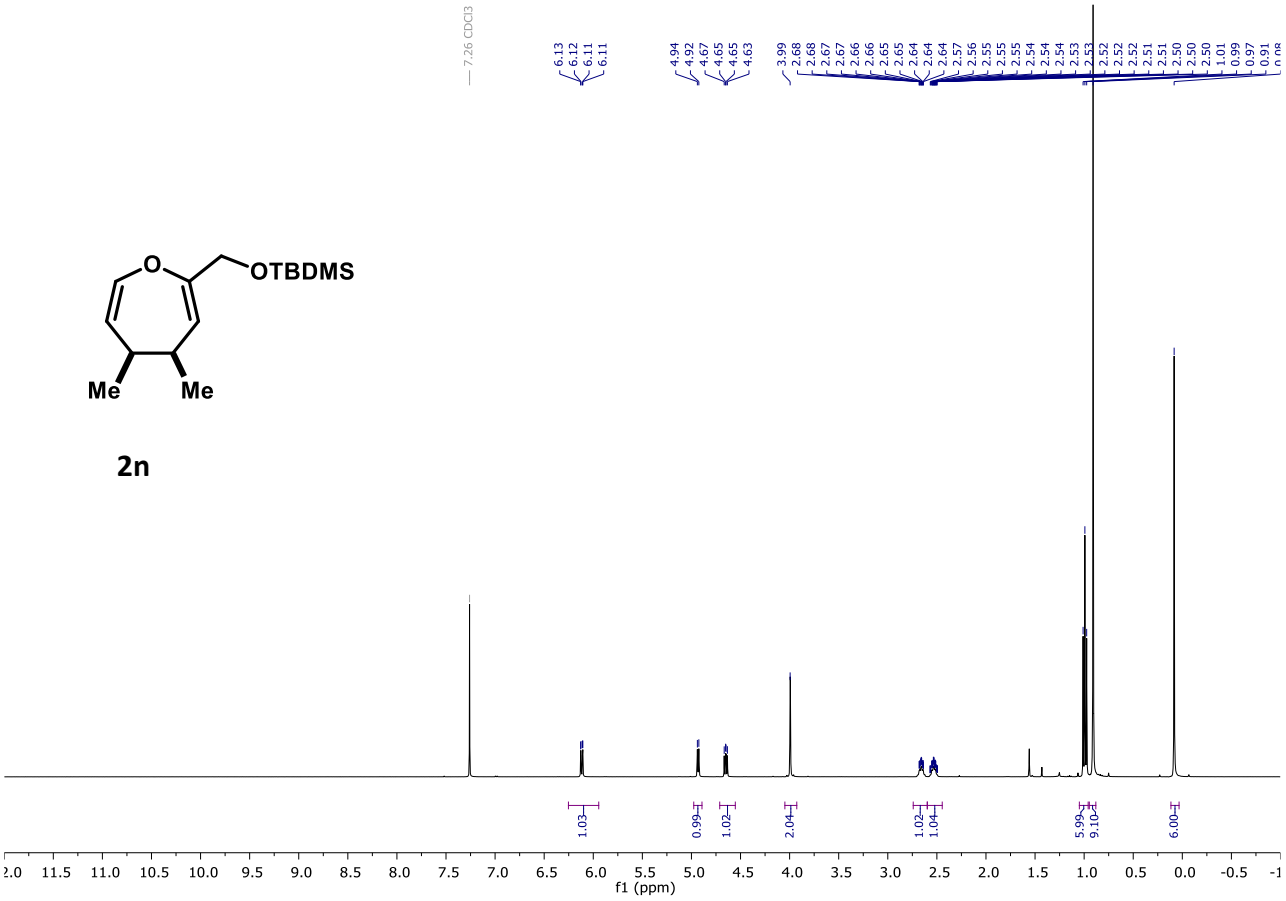

149.06
140.57
113.44
113.18
77.05 CDCl3
74.03
57.80
36.80
36.06
18.53
18.28
f1 (ppm)

O
OMe
Me
Me

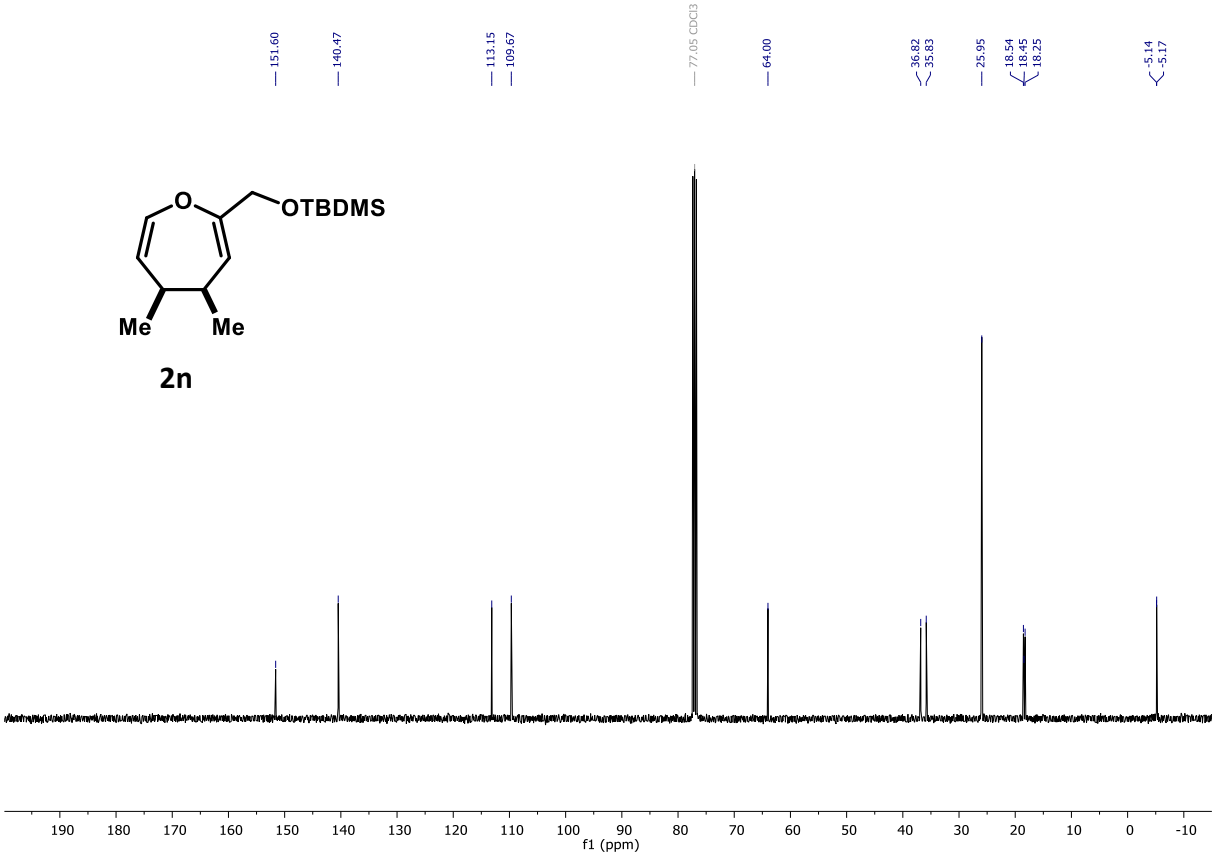
2l


OAc
Me
Me
2m
f1 (ppm)

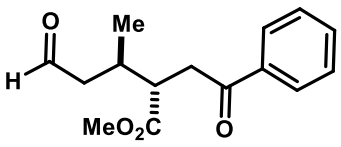

OAc
Me
Me
2m
f1 (ppm)


7.26 CDCl3
6.13
6.12
6.11
6.11
4.94
4.92
4.67
4.65
4.65
4.63
3.99
2.68
2.68
2.67
2.67
2.66
2.66
2.65
2.65
2.64
2.64
2.64
2.57
2.56
2.55
2.55
2.55
2.54
2.54
2.54
2.53
2.53
2.52
2.52
2.52
2.51
2.51
2.50
2.50
2.50
1.01
0.99
0.97
0.91
O
OTBDMS
Me
Me
1.03
0.99
1.02
2.04
1.02
1.04
5.99
9.10
6.00
f1 (ppm)

2n

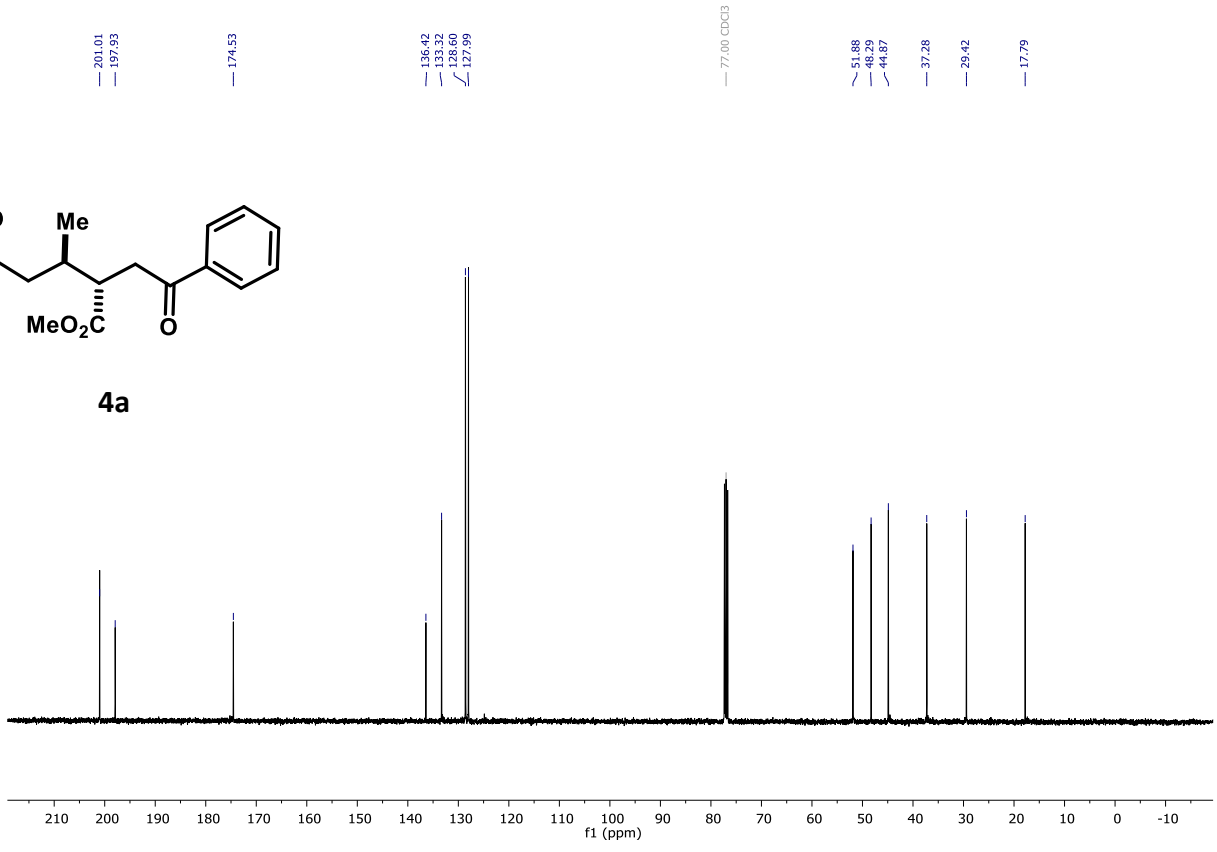

151.60
140.47
113.15
109.67
77.05 CDCl3
64.00
36.82
35.83
25.95
18.54
18.45
18.25
-5.14
-5.17
O
OTBDMS
Me
Me
f1 (ppm)

2n


O
Me
H
MeO2C
O

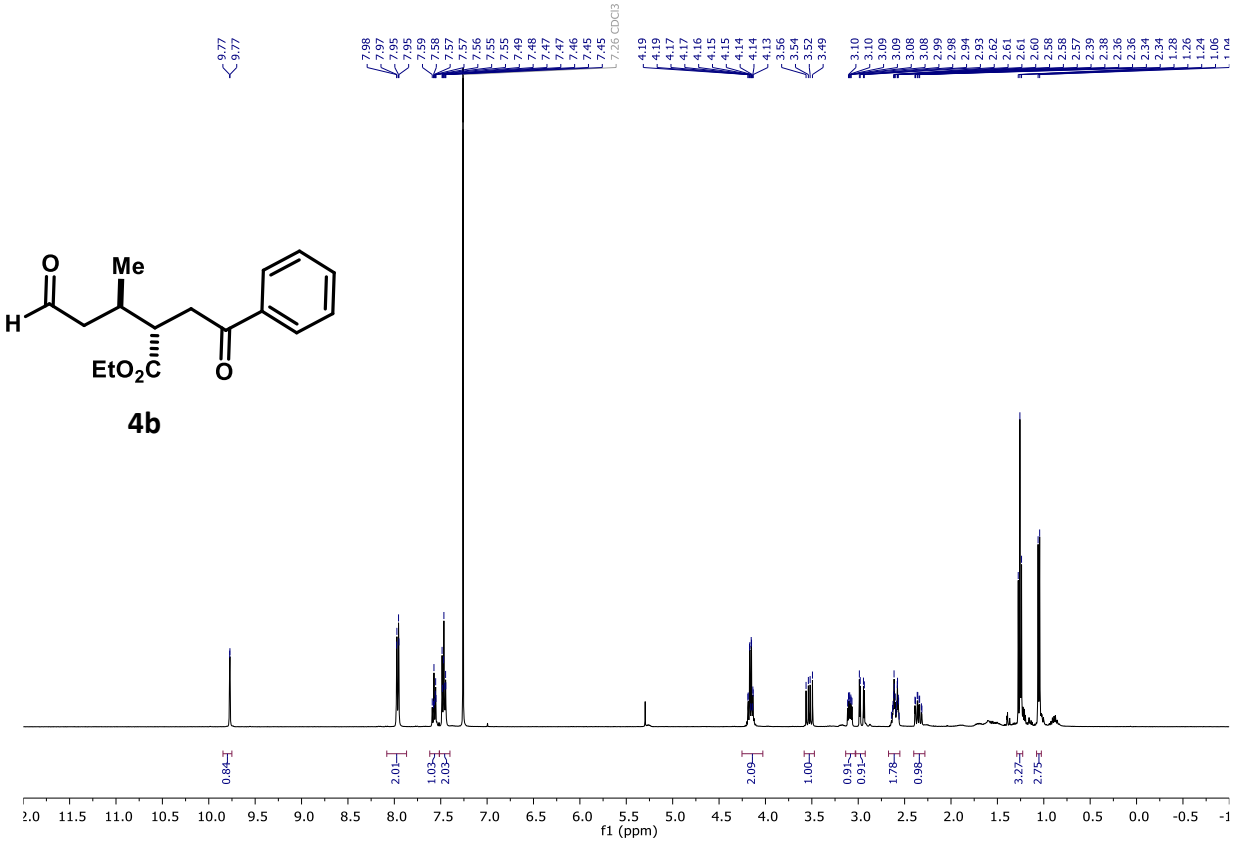
4a

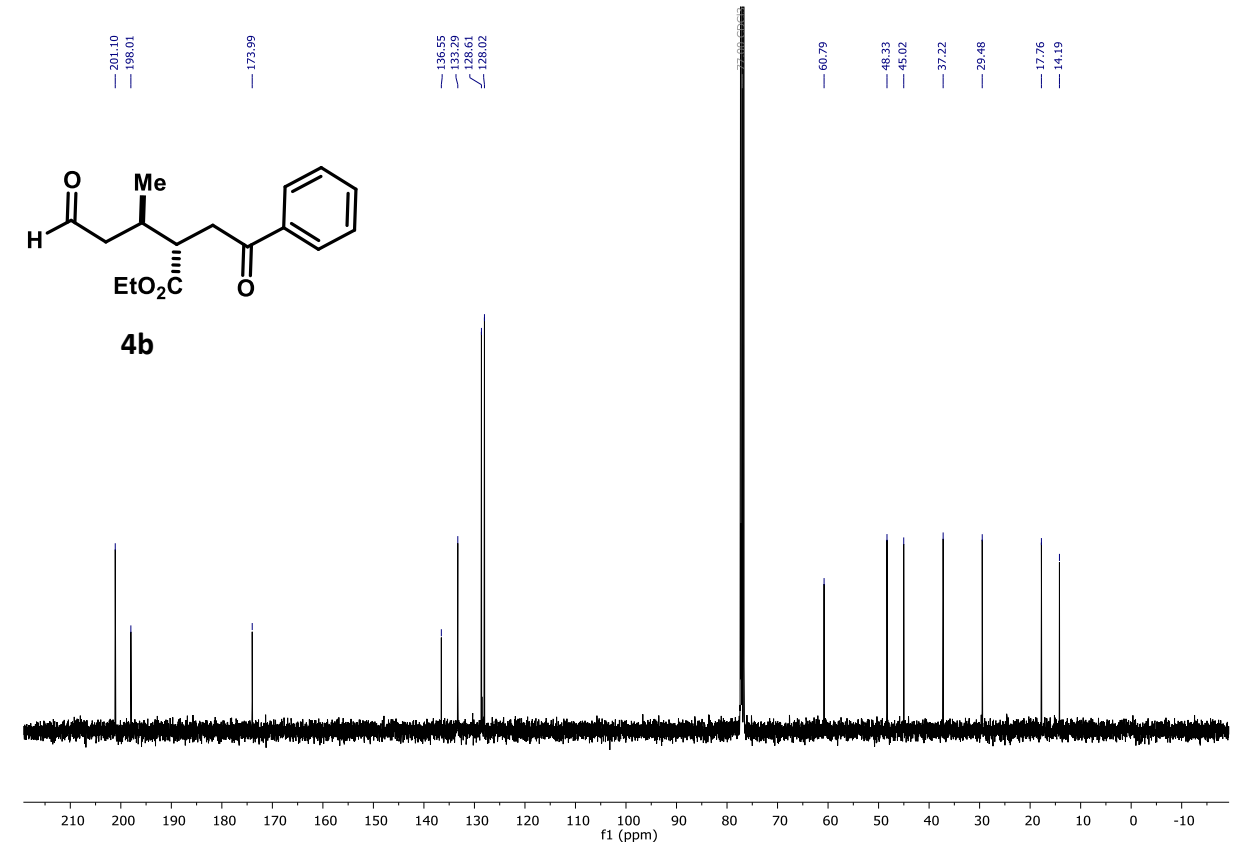
9.75
7.96
7.96
7.96
7.94
7.94
7.59
7.58
7.58
7.58
7.57
7.56
7.56
7.55
7.55
7.54
7.48
7.47
7.46
7.46
7.44
7.44
7.26 CDCl3
3.69
3.55
3.53
3.51
3.48
3.12
3.11
3.10
3.10
3.09
3.08
3.08
3.07
3.01
3.00
2.97
2.96
2.60
2.59
2.58
2.57
2.56
2.56
2.55
2.55
2.38
2.37
2.35
2.35
2.33
2.33
1.05
0.86
2.04
1.04
2.04
2.99
1.08
0.98
1.02
1.93
1.00
3.22
f1 (ppm)

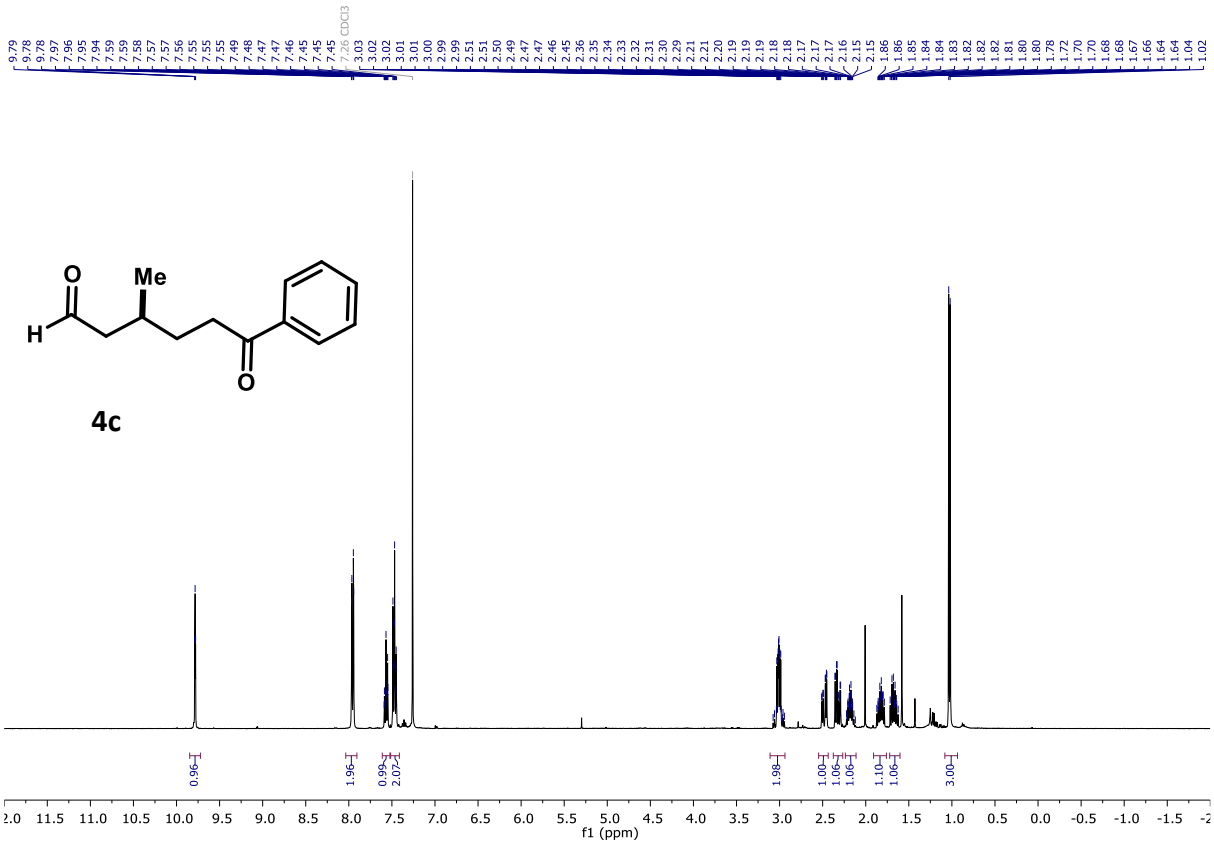

201.01
197.93
174.53
136.42
133.32
128.60
127.99
77.00 CDCl3
51.88
48.29
44.87
37.28
29.42
17.79
f1 (ppm)

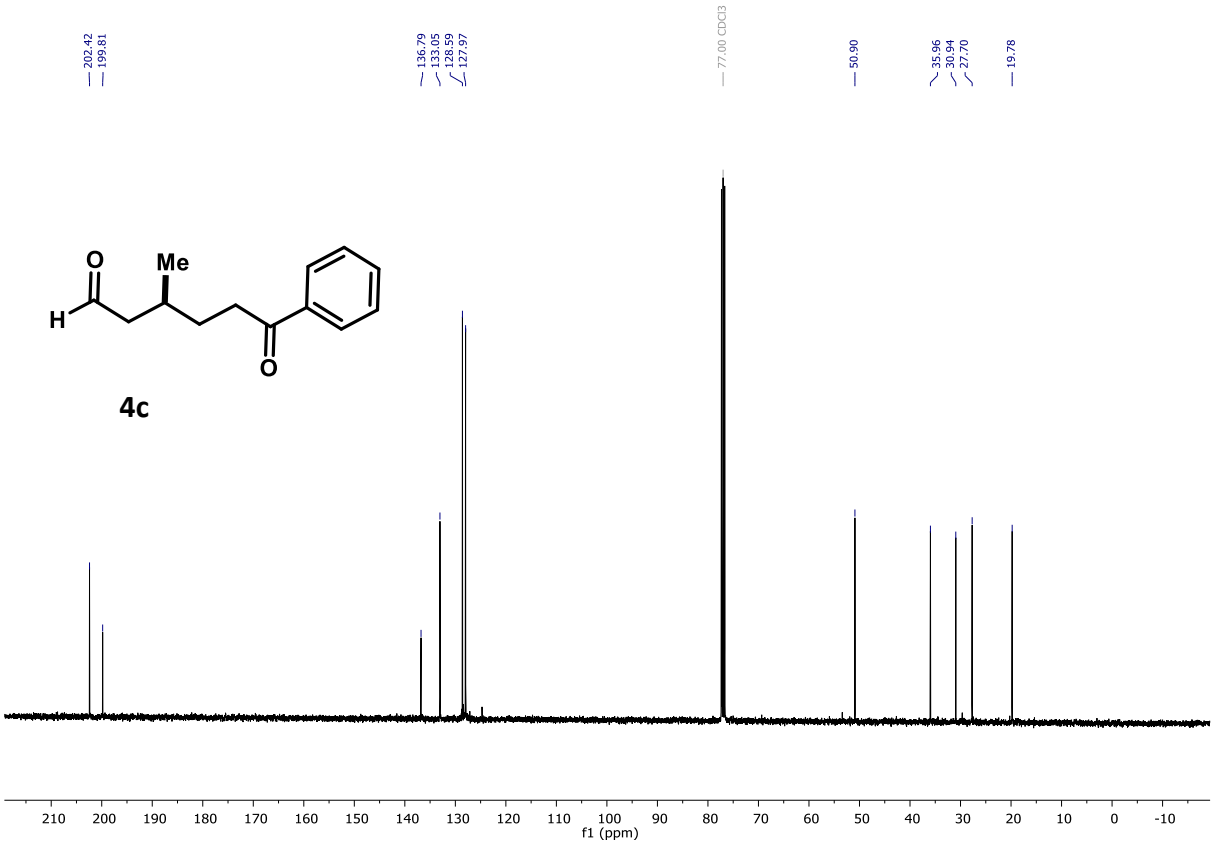
O
Me
H
MeO2C
O

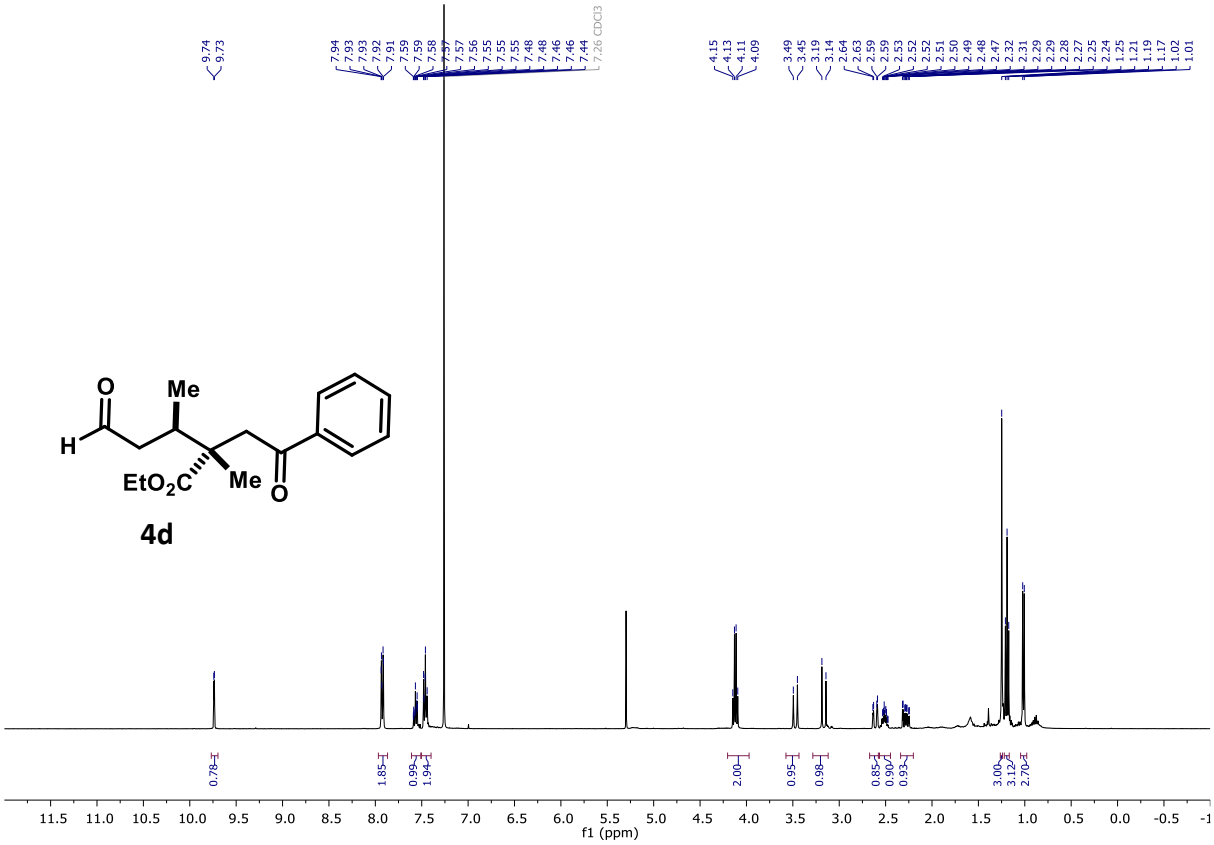
4a


4b
f1 (ppm)


4b
f1 (ppm)


O
Me
H
O
4c
f1 (ppm)


O
Me
H
O
4c
f1 (ppm)


9.74
9.73
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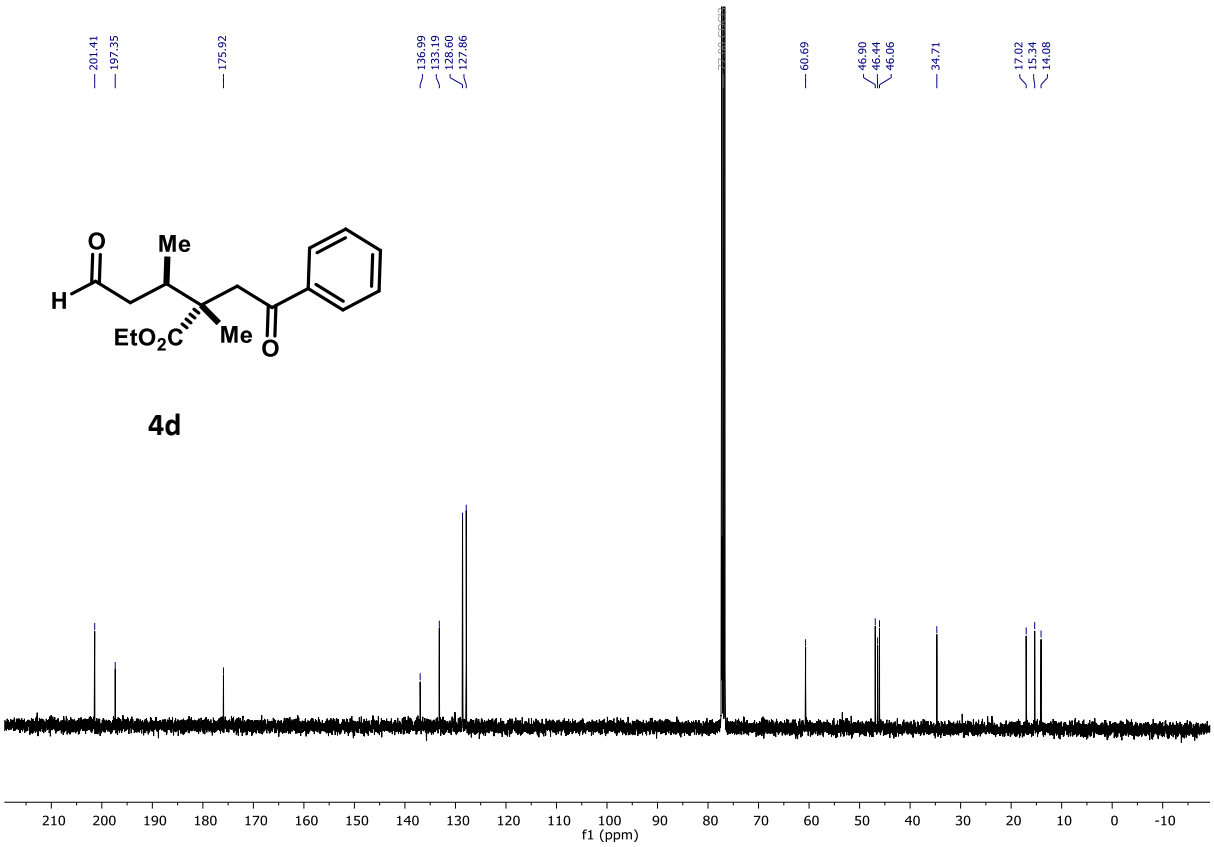
7.93
7.92
7.91
7.59
7.59
7.58
7.57
7.57
7.56
7.55
7.55
7.55
7.48
7.48
7.46
7.46
7.44
7.26 CDCl3
4.15
4.13
4.11
4.09
3.49
3.45
3.19
3.14
2.64
2.63
2.59
2.59
2.59
2.53
2.52
2.52
2.51
2.50
2.49
2.48
2.47
2.32
2.31
2.29
2.29
2.28
2.27
2.25
2.24
1.25
1.21
1.19
1.17
1.02
1.01
0.78
1.85
0.99
1.94
2.00
0.95
0.98
0.85
0.90
0.93
3.00
3.12
2.70
f1 (ppm)

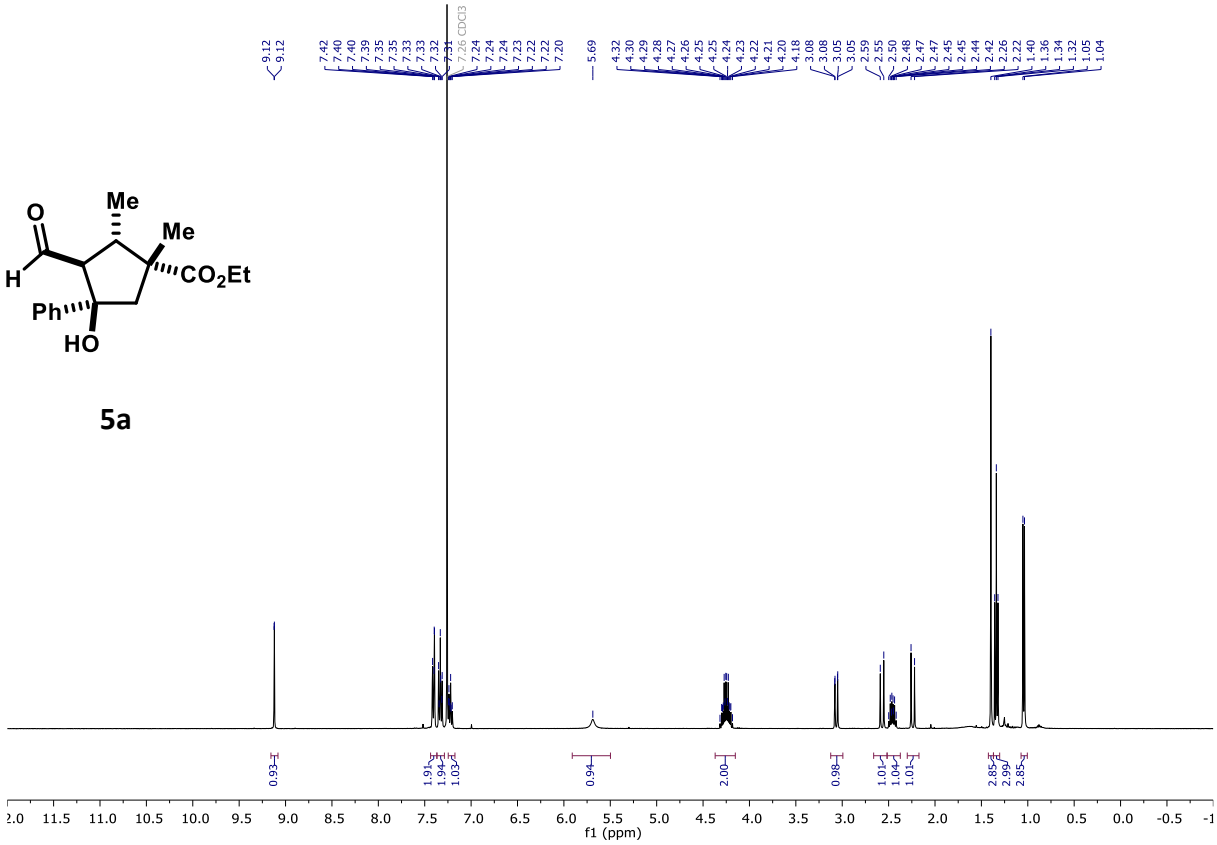
O
Me
H
EtO2C
Me
O

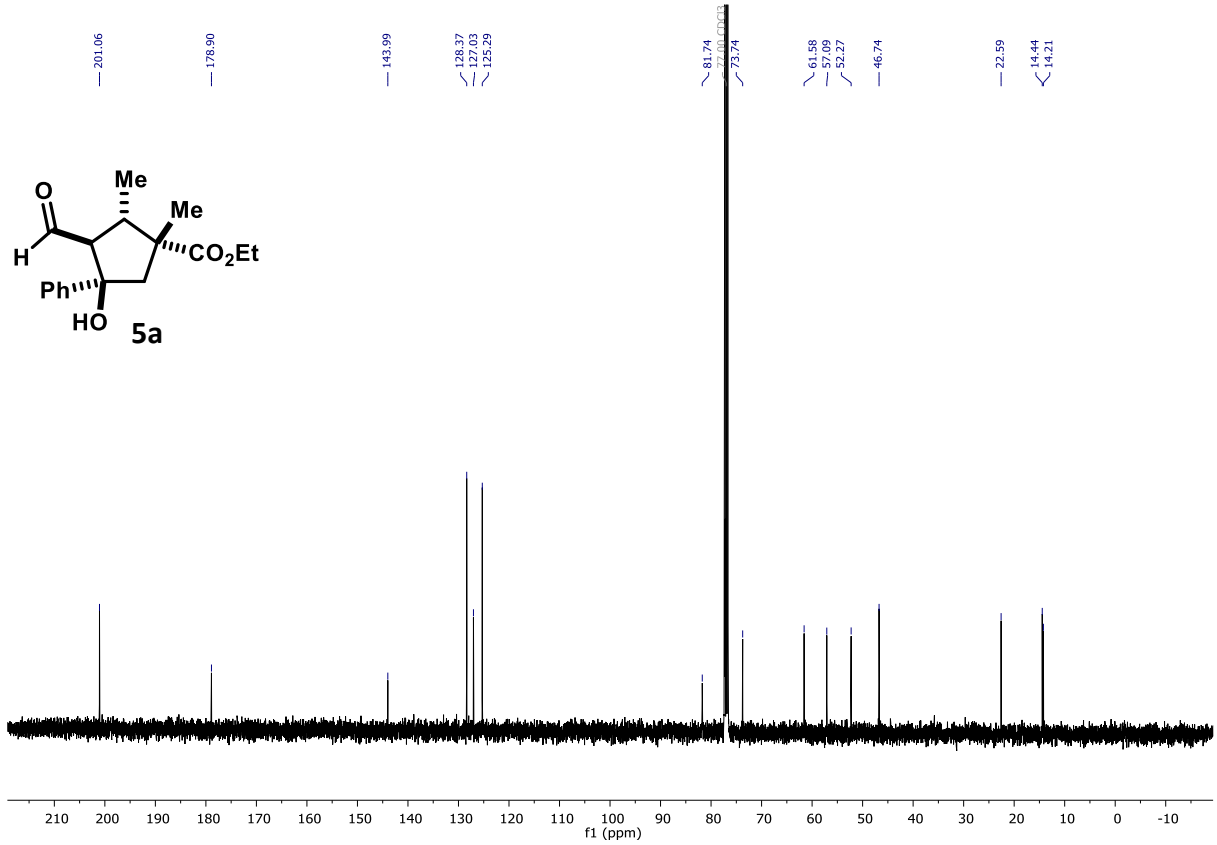
4d

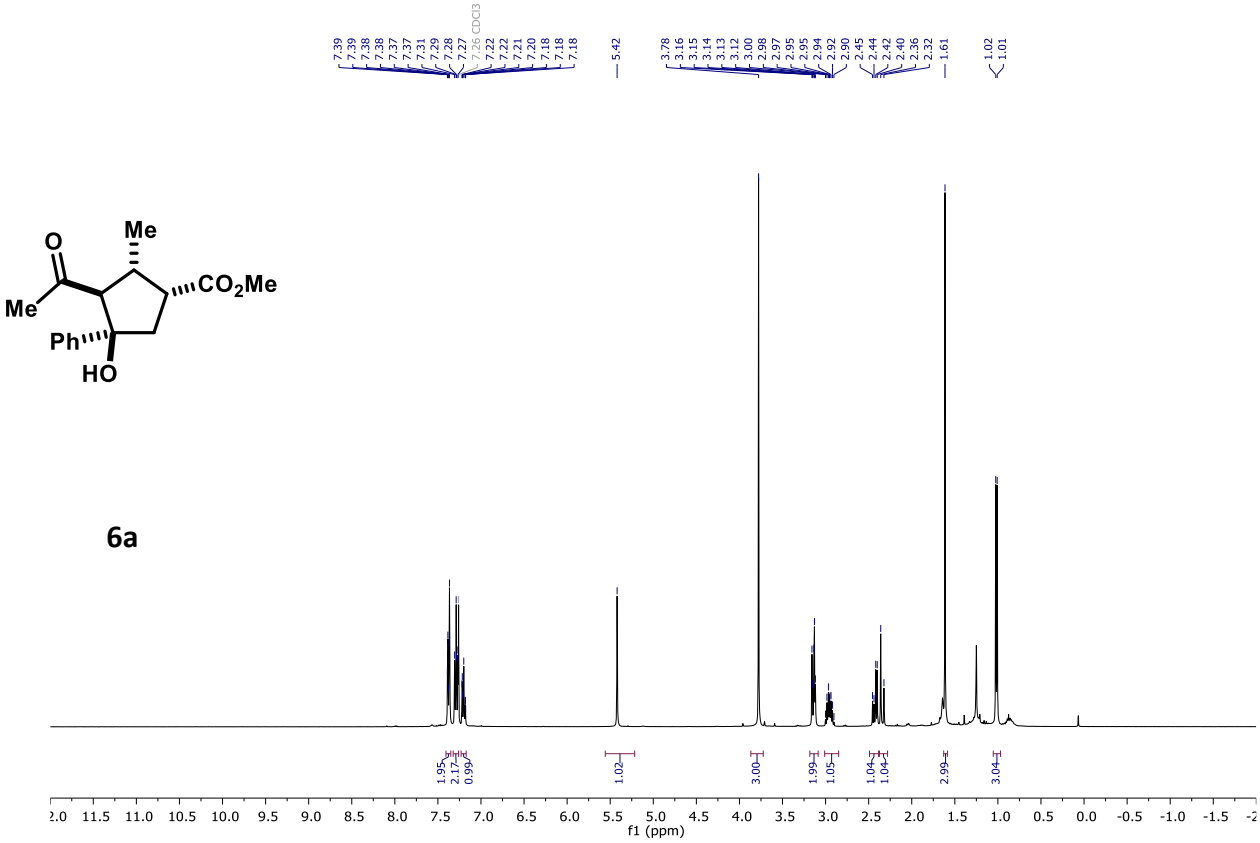

201.41
197.35
175.92
136.99
133.19
128.60
127.86
77.00
60.69
46.90
46.44
46.06
34.71
17.02
15.34
14.08
f1 (ppm)

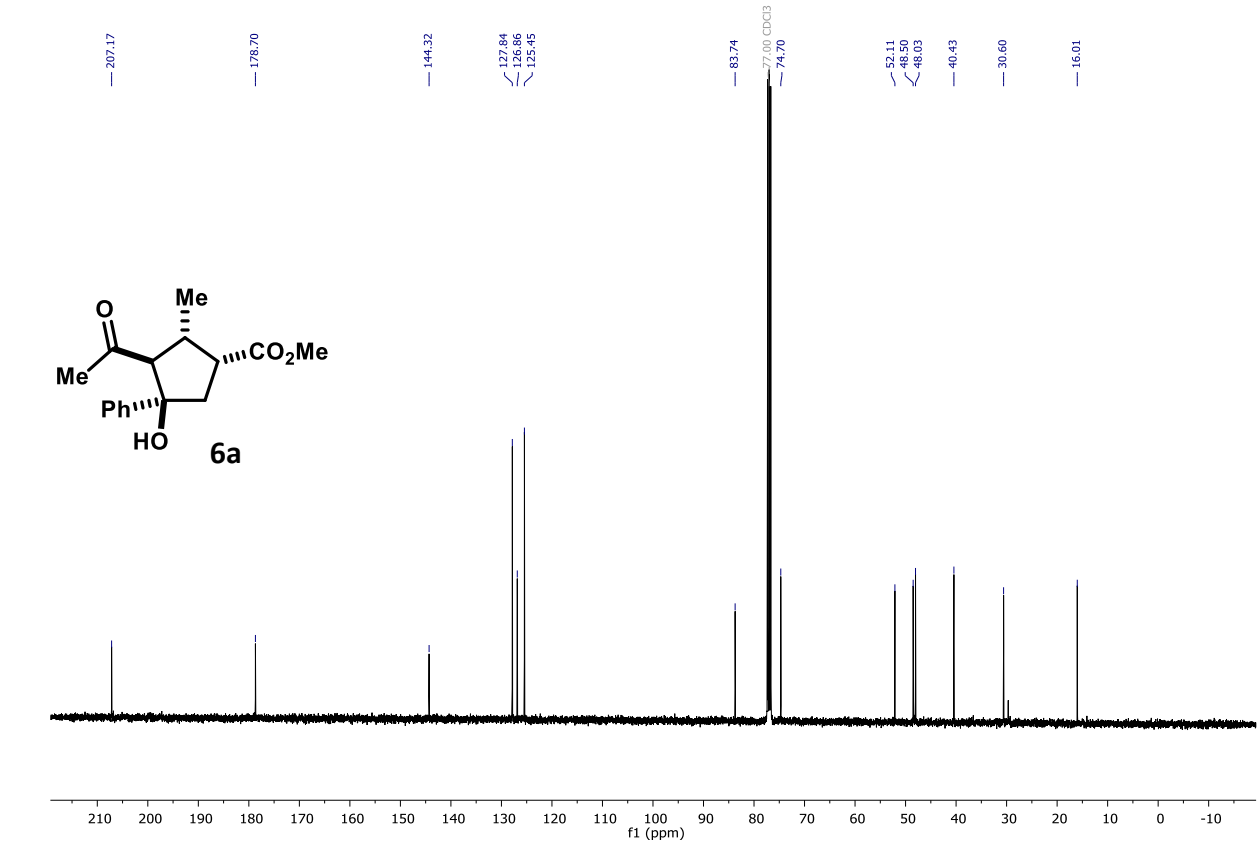
O
Me
H
EtO2C
Me
O

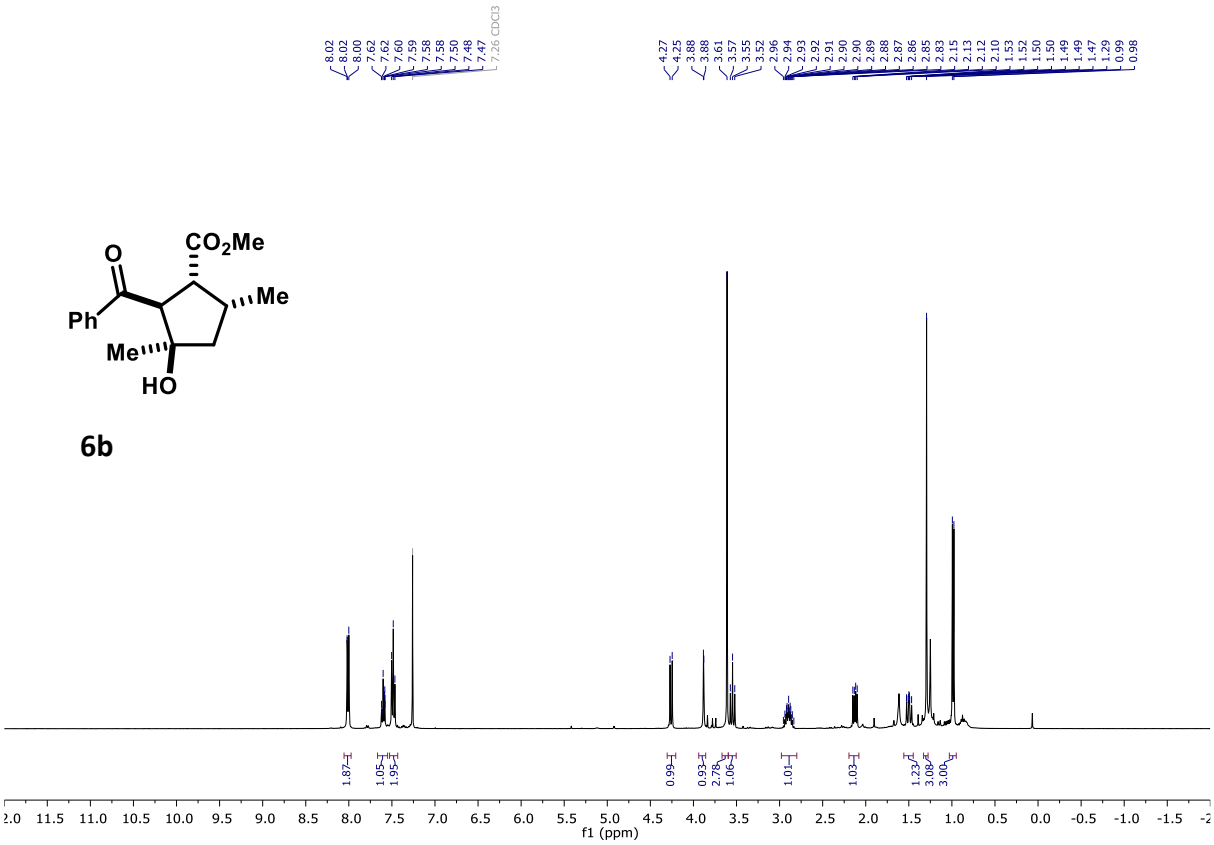
4d

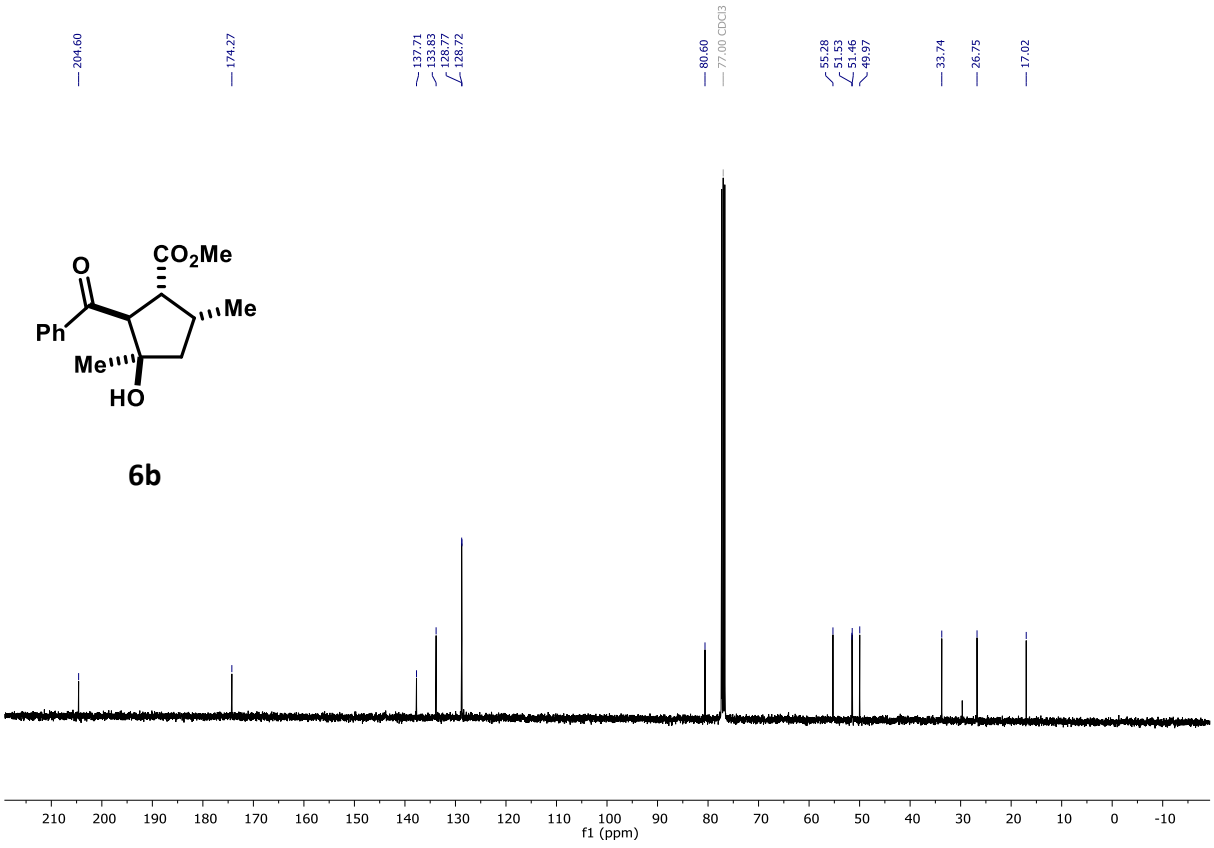

Me
O
Me
H
CO2Et
Ph
HO
5a
f1 (ppm)

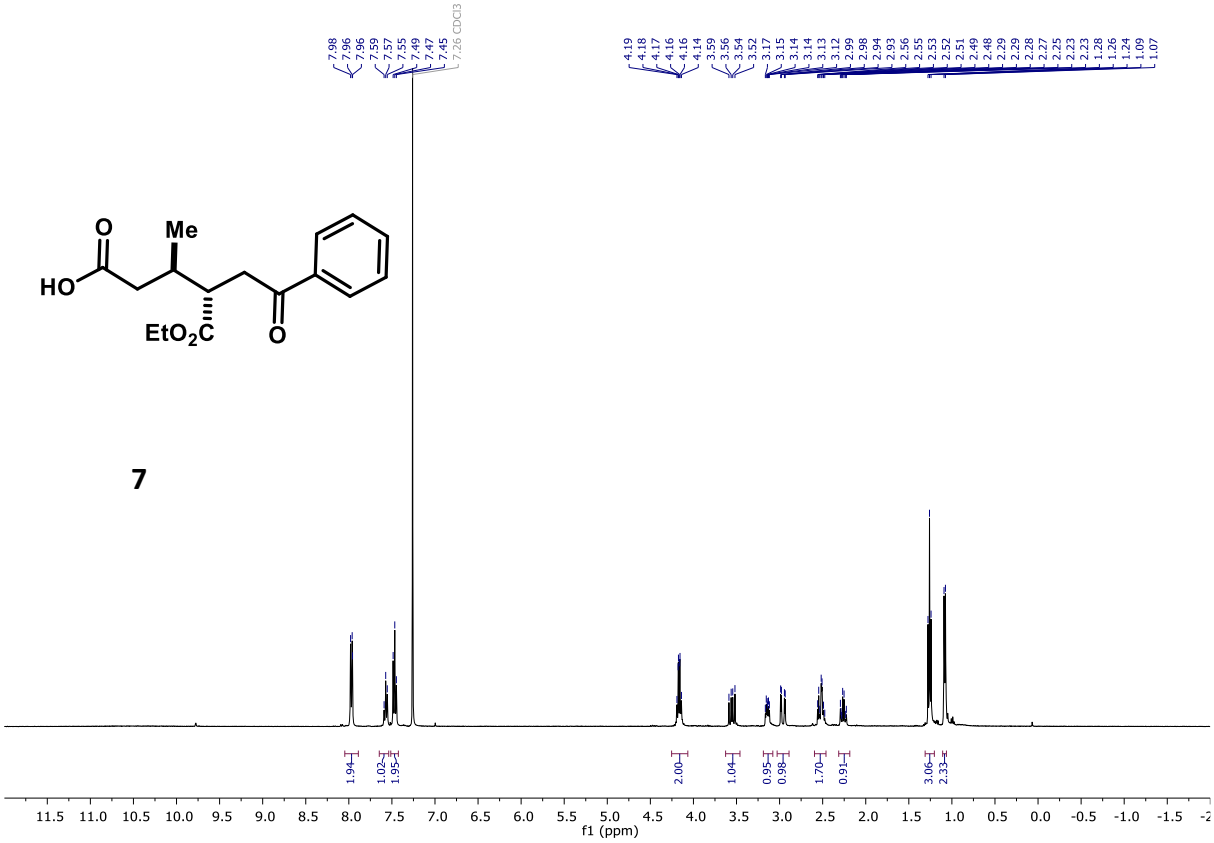

Me
O
Me
H
CO2Et
Ph
HO
5a
f1 (ppm)

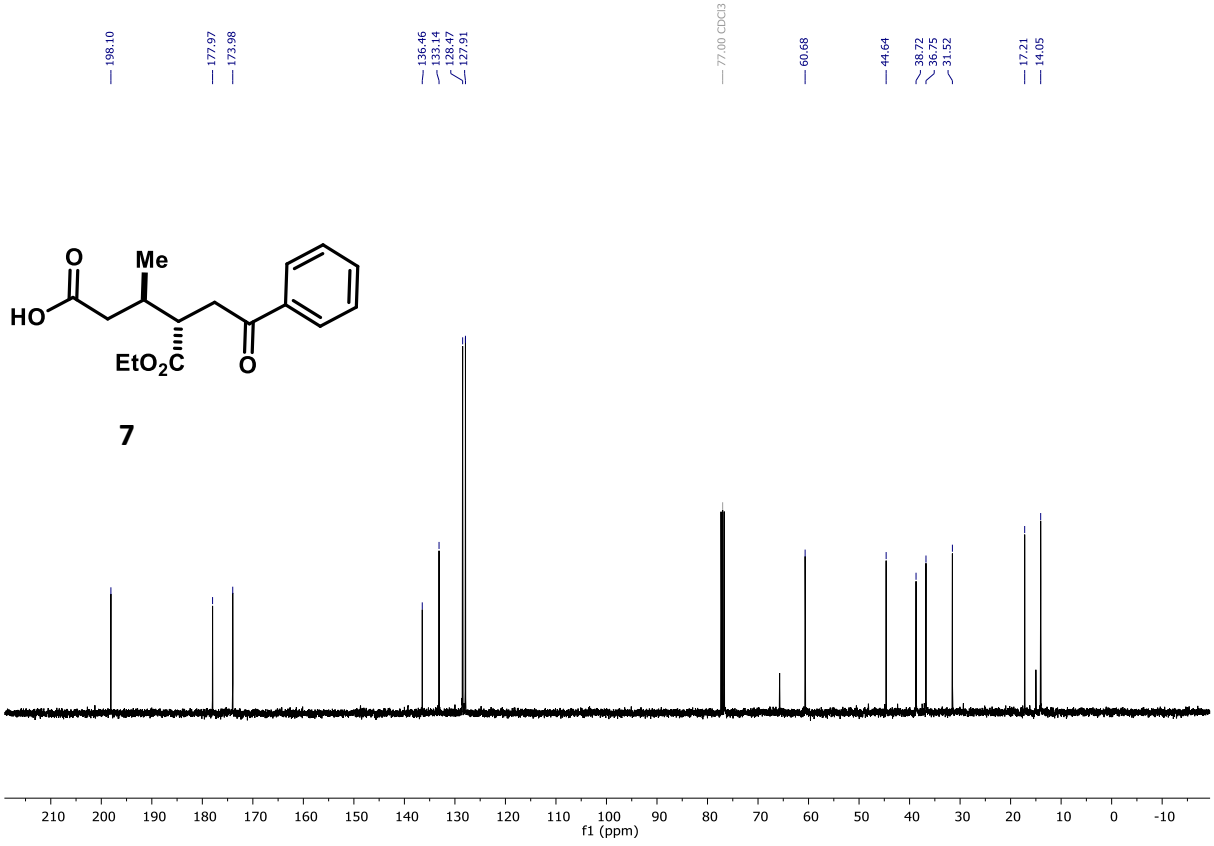

7.39
7.39
7.38
7.38
7.37
7.37
7.31
7.29
7.28
7.27
7.26 CDCl3
7.22
7.22
7.21
7.20
7.18
7.18
7.18
5.42
3.78
3.16
3.15
3.14
3.13
3.12
3.00
2.98
2.97
2.95
2.95
2.94
2.92
2.90
2.45
2.44
2.42
2.40
2.36
2.32
1.61
1.02
1.01
O
Me
Me
CO2Me
Ph
HO
6a
1.95
2.17
0.99
1.02
3.00
1.99
1.05
1.04
1.04
2.99
3.04
f1 (ppm)


207.17
178.70
144.32
127.84
126.86
125.45
83.74
77.00 CDCl3
74.70
52.11
48.50
48.03
40.43
30.60
16.01
O
Me
Me
CO2Me
Ph
HO
6a
f1 (ppm)


8.02
8.02
8.00
7.62
7.62
7.60
7.59
7.58
7.58
7.50
7.48
7.47
7.26 CDCl3
4.27
4.25
3.88
3.88
3.61
3.57
3.55
3.52
2.96
2.94
2.93
2.92
2.91
2.90
2.90
2.89
2.88
2.87
2.86
2.85
2.83
2.15
2.13
2.12
2.10
1.53
1.52
1.50
1.50
1.49
1.49
1.47
1.29
0.99
0.98
O
CO2Me
Ph
Me
Me
HO
6b
1.87
1.05
1.95
0.99
0.93
2.78
1.06
1.01
1.03
1.23
3.08
3.00
f1 (ppm)


204.60
174.27
137.71
133.83
128.77
128.72
80.60
77.00 CDCl3
55.28
51.53
51.46
49.97
33.74
26.75
17.02
O
CO2Me
Ph
Me
Me
HO
6b
f1 (ppm)


7.98
7.96
7.96
7.59
7.57
7.55
7.49
7.47
7.45
7.26 CDCl3
4.19
4.18
4.17
4.16
4.16
4.14
3.59
3.56
3.54
3.52
3.17
3.15
3.14
3.14
3.13
3.12
2.99
2.98
2.94
2.93
2.56
2.55
2.53
2.52
2.51
2.49
2.48
2.29
2.29
2.28
2.27
2.25
2.23
2.23
1.28
1.26
1.24
1.09
1.07
O
Me
HO
EtO2C
O
7
1.94
1.02
1.95
2.00
1.04
0.95
0.98
1.70
0.91
3.06
2.33
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


198.10
177.97
173.98
136.46
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128.47
127.91
77.00 CDCl3
60.68
44.64
38.72
36.75
31.52
17.21
14.05
O
Me
HO
EtO2C
O
7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)