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Supporting Information

Electrocatalytic Activation of Donor–Acceptor Cyclopropanes and Cyclobutanes: An Alternative C(sp^3)–C(sp^3) Cleavage Mode

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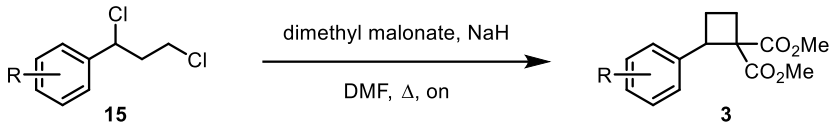
1. General Experimental

All solvents were distilled before use and stored over molecular sieves unless otherwise stated. For electrochemical reactions commercially available hexafluoroisopropanol (HFIP, 99%) and acetonitrile (MeCN, *p.a.*) were used. Oxygen 4.5 that was used for electrochemical reactions, was provided by *Westfalen*. Glassy Carbon electrodes were obtained from *IKA*. Air- and moisture-sensitive reactions were carried out in oven-dried or flame-dried glassware, septum-capped under atmospheric pressure of argon. Commercially available compounds were used without further purification unless otherwise stated. For all purifications by column chromatography silica gel Geduran Si 60 (40-63 µm pore size) from *Merck* and mixtures of pentane/ethyl acetate were used.

Proton (^{1}H), carbon (^{13}C) and fluorine (^{19}F) NMR spectra were recorded on a *Bruker* AVIII400, *Bruker* AVIIIHD500 or *Bruker* AVII600 instrument using the residual signals from $CHCl_3$, δ = 7.26 ppm and δ = 77.16 ppm or CD_3OD δ = 3.31 ppm and δ = 49.00 ppm, as internal reference for ^{1}H and ^{13}C chemical shifts, respectively. Additionally, tetramethylsilane (TMS; δ = 0.00 ppm; 0.03%) was added to NMR samples. The following abbreviations were used for ^{1}H and ^{13}C NMR chemical shifts: s = singlet, d = doublet, t = triplet, m = multiplet. The chemical shift δ is given in ppm. ESI-HRMS was carried out on an FTICR instrument and EI-HRMS was carried out on a *Jeol* AccuTOF GC JMS-T100GC instrument. IR spectra were recorded on an ATR spectrometer Tensor 27 from *Bruker.* IR data is reported as follows: w = weak, m = medium, s = strong, br = broad or combinations thereof. Melting points of solid products were recorded on a *Büchi* Melting Point M-560. Cyclic voltammetry was performed with a *Gamry* Instrument Interface 1010 Potentiostat/Galvanostat/ZRA). A self-made three-electrode setup with two platinum wires (0.5 mm diameter) as working and counter electrodes and a silver wire (0.5 mm diameter) as a quasi-reference electrode was used. For all electrochemical reactions an *IKA* ElectraSyn 2.0 apparatus was used. Exact reaction conditions are given in the following procedures.

2. General Procedures

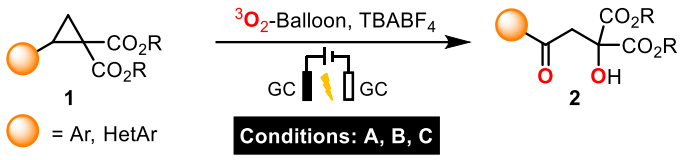
General procedures (GP1) for the cyclization of dichlorides to D–A cycblobutanes (D–A CBs)



General procedure GP1:

GP1 is based on a known literature procedure.[1] NaH (60% in mineral oil, 1.05 eq.) was added at rt to a solution of dichloride (1.0 eq.) and dimethyl malonate (1.10 eq.) in DMF (5 mL per mmol) and the reaction mixture was refluxed at 100 °C for 1 h. Another portion of NaH (60% in mineral oil, 1.05 eq.) was added at 100 °C and the mixture was further refluxed overnight. After cooling to room temperature, H_2O and Et_2O were added and the phases were separated. The aq. phase was extracted with Et_2O and the combined organic layers were washed with aq. sat. NaCl solution and dried over anhydrous Na_2SO_4. Removal of the solvents *in vacuo* and subsequent purification by column chromatography afforded the desired cyclobutanes **3**.

General procedures (GP2-A/B/C) for the electrochemical conversion of D–A cyclopropanes (D–A CPs) to β-hydroxy ketones



General procedure GP2-A (Conditions A):

In a 5 mL ElectraSyn vial cyclopropane **1** (150 µmol, 1.00 eq.) and $TBABF_4$ (0.02 M) were dissolved in HFIP (3 mL) and the solution was saturated with oxygen for 5 minutes. The solution was electrolyzed at a glassy carbon anode and a glassy carbon cathode at a constant potential of +2.4 V. The vial was refilled with HFIP (1.5 mL) 5 min after the

electrolysis was started. After full conversion was observed, the reaction mixture was concentrated *in vacuo* and the remaining residue was adsorbed on silica gel. The desired products **2** were purified by column chromatography.

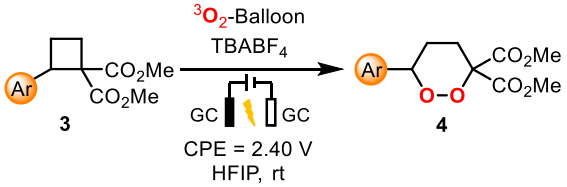
General procedure GP2-B (Conditions B):

In a 10 mL ElectraSyn vial cyclopropane **1** (150 µmol, 1.00 eq.), DDQ (150 µmol, 1.0 eq.) or CoTPP (3.75 µmol, 2.5 mol%) and $TBABF_4$ (0.02 M) were dissolved in MeCN (6 mL) and the solution was saturated with oxygen for 5 minutes. The solution was electrolyzed at a glassy carbon anode and a glassy carbon cathode at a constant potential of +1.3 V (for DDQ) or +2.0 V (for CoTPP). After full conversion was observed, the reaction mixture was concentrated *in vacuo* and the remaining residue was adsorbed on silica gel. The desired products **2** were purified by column chromatograph.

General procedure GP2-C (Conditions C):

In a 5 mL ElectraSyn vial cyclopropane **1** (150 µmol, 1.00 eq.), DDQ (150 µmol, 1.00 eq.) and $TBABF_4$ (0.02 M) were dissolved in HFIP (3 mL) and the solution was saturated with oxygen for 5 minutes. The solution was electrolyzed at a glassy carbon anode and a glassy carbon cathode at a constant potential of +1.3 V. The vial was refilled with HFIP (1.5 mL) 5 min after the electrolysis was started. After full conversion was observed, the reaction mixture was concentrated *in vacuo* and the remaining residue was adsorbed on silica gel. The desired products **2** were purified by column chromatograph.

General procedure (GP3) for the electrochemical conversion of D–A cyclobutanes (D–A CBs) to dioxanes

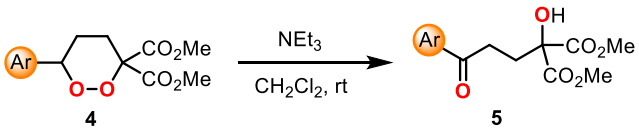


General procedure GP3:

In a 5 mL ElectraSyn vial cyclobutane **3** (100 µmol, 1.00 eq.) and $TBABF_4$ (0.02 M) were dissolved in HFIP (3 mL) and the solution was saturated with oxygen for 5 minutes. The solution was electrolyzed at a glassy carbon anode and a glassy cathode at a constant

potential of +2.4 V. The vial was refilled with HFIP (1.5 mL) 5 min after the electrolysis was started. After full conversion was observed, the reaction mixture was concentrated *in vacuo* and the remaining residue was adsorbed on silica gel. The desired products **4** were purified by column chromatography using pentane/ethyl acetate mixtures.

General procedure (GP4) for the conversion of dioxanes to γ-hydroxy ketones



4 **5**

General procedure GP4:

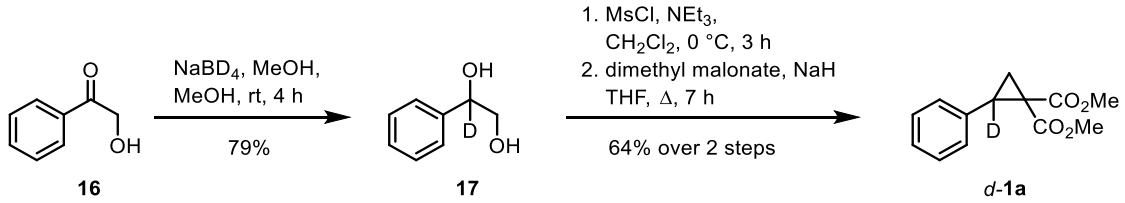
To a solution of dioxane **4** (1.00 eq.) in CH_2Cl_2 (1 mL per 25 µmol) was added NEt_3 (1.20 eq.) at room temperature and the resulting mixture was stirred until full conversion was observed. The reaction mixture was concentrated *in vacuo* and the remaining residue was adsorbed on silica gel. The desired products **5** were purified by column chromatography using pentane/ethyl acetate mixtures.

3. Synthesis of Starting Materials

3.1 Synthesis of D–A cyclopropanes

All non-deuterated D–A CPs **1a** – **1p** were prepared following literature procedures.[2,3] The analytical data were in accordance with those reported in the literature.[4]

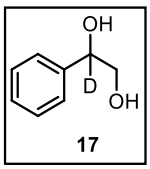
3.2 Synthesis of deuterated D–A cyclopropanes



16 **17** ***d*-1a**

Scheme S1. Synthesis of deuterated D–A CP ***d*-1a.**

1-Phenylethane-1-*d*-1,2-diol (17)



17

Diol **17** was prepared following a literature procedure.[5] $NaBD_4$ (169 mg, 4.04 mmol, 1.10 eq.) was added to a solution of ketone **16** (500 mg, 3.67 mmol, 1.0 eq.) in MeOH (20 mL) at 0 °C and the resulting mixture was stirred at rt for 4 h. The reaction was stopped by the addition of H_2O and EtOAc and the phases were separated. The aq. phase was extracted with EtOAc (2×20 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. Removal of the solvents *in vacuo* afforded diol **17** (405 mg, 2.91 mmol, 79%) as a colourless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.39 – 7.28 (m, 5H), 3.76 (d, J = 11.3 Hz, 1H), 3.66 (d, J = 11.3 Hz, 1H), 2.32 (br, 2H).

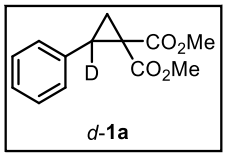
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 140.6, 128.7 (2C), 128.2, 126.2 (2C), 74.4 (t, J = 22.2 Hz, 1C), 68.1.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3337 (br, s), 3029 (w), 2026 (w), 2869 (w), 1493 (w), 1448 (m), 1393 (m), 1126 (m), 993 (s), 698 (s).

HRMS (ESI): $C_8H_9DO_2$ (139.07) calculated: 162.06358, found: 162.06368, $[M+Na]^+$.

m. p.: 66 °C.

Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate-2-*d* (*d*-1a)



d-**1a**

Deuterated CP *d*-**1a** was prepared following a literature procedure.[6] NEt_3 (790 mg, 1.08 mL, 7.80 mmol, 3.0 eq.) was added dropwise to a solution of diol **17** (362 mg, 3.67 mmol, 1.0 eq.) in CH_2Cl_2 (5 mL) at rt and the reaction mixture was cooled to 0 °C. A solution of MsCl (745 mg, 503 µL, 6.05 mmol, 2.50 eq.) in CH_2Cl_2 (5 mL) was added over the course of 90 min and the mixture was stirred for further 3 h at 0 °C. The reaction was stopped by the addition of aq. HCl (2 M) solution and the phases were separated. The aq. phase was extracted with CH_2Cl_2 (3 × 10 mL), the combined organic layers were washed with aq. HCl (2 M, 15 mL) solution, aq. sat. $NaHCO_3$ solution (15 mL) and aq. sat. NaCl solution (15 mL) and dried over anhydrous Na_2SO_4. Removal of the solvents *in vacuo* and subsequent column chromatography (SiO_2, PE/EtoAc 2:1) afforded the dimesylated compound with minor impurities. The white solid was used in the next step without further purification.

To a suspension of NaH (60% in mineral oil, 148 mg, 3.71 mmol, 2.10 eq.) in THF (30 mL) was added dimethyl malonate (490 mg, 426 µL, 3.71 mmol, 2.10 eq.) and the resulting mixture was stirred for 20 min at 0 °C. At 0 °C a solution of the dimesylate (521 mg 1.76 mmol, 1.0 eq.) in THF (10 mL) was added before the reaction mixture was refluxed at 85 °C for 17 h. After cooling to rt the reaction was stopped by the addition of H_2O and EtOAc and the phases were separated. The aq. phase was extracted with EtOAc (3 x 25 mL), the combined organic layers were washed with aq. NaOH (1 M, 25 mL) solution, H_2O (25 ml) and aq. sat. NaCl solution (25 mL) and dried over anhydrous Na_2SO_4. Removal of the solvents *in vacuo* and subsequent column chromatography (SiO_2, PE/EtoAc 15:1 → 10:1) afforded the desired compound *d*-**1a** (264 mg, 1.12 mmol, 64% over 2 steps) as a pale yellow solid.

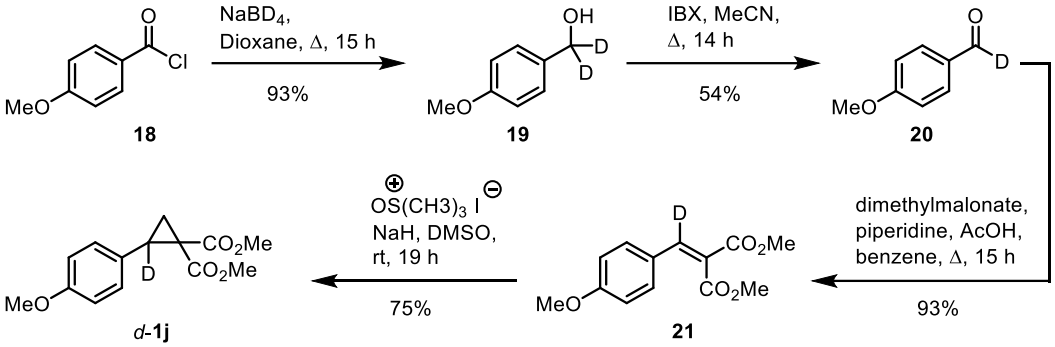
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.30 – 7.18 (m, 5H), 3.80 (s, 3H), 3.37 (s, 3H), 2.20 (d, *J* = 11.3 Hz, 1H), 1.75 (d, *J* = 11.3 Hz, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.4, 170.2, 134.7, 128.6 (2C), 128.6 (2C), 127.5, 52.9, 52.3, 37.3, 32.4 (t, *J* = 22.2 Hz, 1C), 19.2.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2323 (s), 1730 (s), 1499 (w), 1438 (m), 1330 (m), 1271 (s), 1197 (w), 1175 (w), 1072 (m), 904 (w), 786 (w).

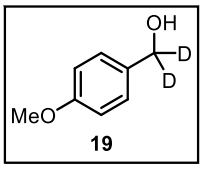
HRMS (ESI): $C_{13}H_{13}DO_4$ (235.09) calculated: 258.08471, found: 258.08464, $[M+Na]^+$.

m. p.: 44 °C.



Scheme S2. Synthesis of deuterated D–A CP *d*-**1j**.

(4-Methoxyphenyl)methan-*d*$_2$-ol (19)

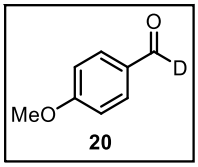


Deuterated alcohol **19** was prepared following a literature procedure.[7] To a solution of acyl chloride **18** (1.00 g, 5.86 mmol, 1.0 eq.) in dioxane (20 mL) was added $NaBD_4$ (368 mg, 8.79 mmol, 1.5 eq.) and the reaction mixture was refluxed at 105 °C for 15 h. The reaction was stopped by the addition of H_2O and EtOAc at rt and the phases were separated. The aq. phase was extracted with EtOAc (3 × 20 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. Removal of the solvents *in vacuo* and subsequent column chromatography (SiO_2, PE/EtoAc 5:1) afforded deuterated alcohol **19** (766 mg, 5.46 mmol, 93%) as a colourless liquid.

^{1}H-NMR (400 MHz, CDCl3): δ = 7.32 – 7.27 (m, 2H), 6.92 – 6.87 (m, 2H), 3.81 (s, 3H), 1.58 (br, s, 1H).

The analytical data were in accordance with those reported in the literature.[7]

Methoxybenzaldehyde-1-*d* (20)

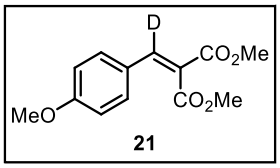


20

IBX (4.55 g, 16.3 mmol, 3.0 eq.) was added at rt to a solution of alcohol **19** (760 mg, 5.42 mmol, 1.0 eq.) in MeCN (30 mL) and the resulting mixture was refluxed for 14 h at 85 °C. After cooling to rt, the suspension was filtered through a celite pad which was washed multiple times with EtOAc. Removal of the solvents *in vacuo* and subsequent column chromatography (SiO_2, PE/EtoAc 20:1) afforded deuterated aldehyde **20** (400 mg, 2.92 mmol, 54%) as a yellow liquid.

^{1}H-NMR (400 MHz, CDCl3): δ = 7.87 – 7.82 (m, 2H), 7.03 – 6.98 (m, 2H), 3.89 (s, 3H).
*Deuterated aldehyde **20** is commercially available from a variety of suppliers (CAS: 19486-71-6).*

Dimethyl 2-((4-methoxyphenyl)methylene-*d*)malonate (21)



21

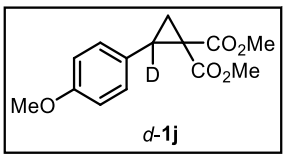
Deuterated CP **21** was prepared following a literature procedure.[3] A solution of compound **20** (400 mg, 2.92 mmol, 1.0 eq.), dimethyl malonate (463 mg, 403 µL, 3.50 mmol, 1.20 eq.), piperidine (25 mg, 30 µL, 292 µmol, 10 mol%) and conc. AcOH (17.5 mg, 16.7 µL, 292 µmol, 10 mol%) in benzene (15 mL) was refluxed at 115 °C for 15 h using a Dean-Stark apparatus. After cooling to rt, the solvents were removed *in vacuo* and the desired product **21** was purified by column chromatography (SiO_2, PE/EtoAc 20:1→10:1). Malonate **21** (684 mg, 2.73 mmol, 93%) was obtained as a colourless liquid.

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.40 – 7.37 (m, 2H), 6.90 – 6.88 (m, 2H), 3.86 (s, 3H), 3.83 (s, 3H), 3.83 (s, 3H).
^{13}C-NMR (151 MHz, $CDCl_3$): δ = 167.8, 164.9, 161.9, 142.4 (t, *J* = 23.9 Hz, 1C), 131.7 (2C), 125.3, 122.77, 114.53 (C2), 55.5, 52.7, 52.6.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1717 (m), 1599 (m), 1511 (w), 1436 (w), 1312 (m), 1256 (s), 1209 (s), 1170 (s), 1091 (s), 1025 (w).

HRMS (ESI): $C_{13}H_{13}DO_5$ (251.09) calculated: 252.09768, found: 274.09777, $[M+H]^+$.

Dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate-2-*d* (*d*-1j)



d-**1j**

Deuterated CP *d*-**1j** was prepared following a literature procedure.[3] A solution of compound **21** (660 mg, 2.63 mmol, 1.0 eq.) in DMSO (4 mL) was added to a suspension of NaH (60% in mineral oil, 121 mg, 3.02 mmol,1.15 eq.) and trimethylsulfoxonium iodide (637 mg, 2.89 mmol, 1.10 eq.) in DMSO (4 mL) and the reaction mixture was stirred for 19 h at rt. The reaction was stopped by the addition of H_2O and EtOAc and the phases were separated. The aq. phase was extracted with EtOAc (3 × 20 mL), the combined organic layers were washed with H_2O (3 × 30 mL) and were dried over anhydrous Na_2SO_4. Removal of the solvents *in vacuo* and subsequent column chromatography (SiO_2, PE/EtoAc 5:1) afforded cyclopropane *d*-**1j** (526 mg, 1.97 mmol, 75%) as a colourless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.12 – 7.09 (m, 2H), 6.81 – 6.78 (m, 2H), 3.78 (s, 3H), 3.77 (s, 3H), 3.38 (s, 3H), 2.15 (d, *J* = 2.15 Hz, 1H), 1.71 (d, *J* = 2.15 Hz, 1H).

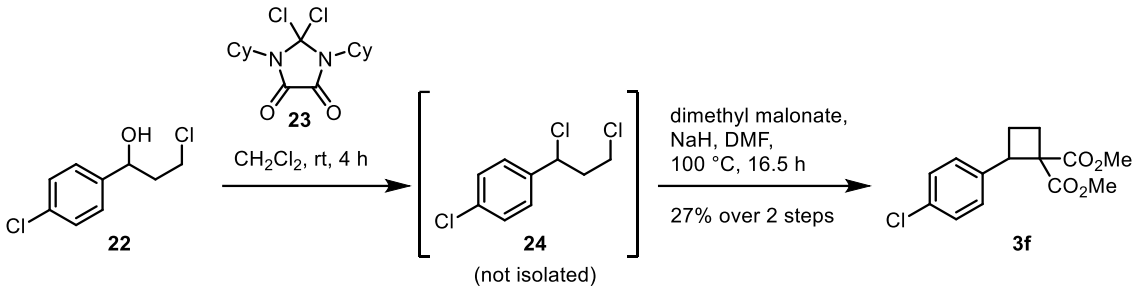
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 170.5, 167.3, 159.1, 129.7 (2C), 126.5, 113.7 (2C), 55.3, 52.9, 52.4, 37.2, 32.1 (t, *J* = 22.2 Hz, 1C) , 19.3.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1725 (s), 1613 (w), 1515 (m), 1439 (m), 1340 (m), 1252 (s), 1181 (s), 1118 (s), 1072 (w), 1031 (m).

HRMS (ESI): $C_{14}H_{15}DO_5$ (265.10) calculated: 266.11333, found: 266.11338, $[M+H]^+$.

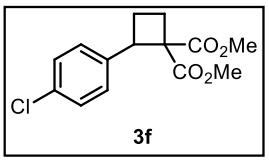
3.3 Synthesis of D-A cyclobutanes

Non-deuterated D–A CBs **3a**, **3d**, **3e** and **3g** were prepared following a literature procedure.[1] The analytical data were in accordance with those reported in the literature.[1,8]



Scheme S3. Synthesis of D–A CB **4f**.

Dimethyl 2-(4-chlorophenyl)cyclobutane-1,1-dicarboxylate (3f)



To a solution of alcohol **22** (1.78 g, 8.72 mmol, 1.0 eq.) in CH_2Cl_2 (20 mL) was added chlorinating agent **23** (3.47 g, 10.5 mmol, 1.20 eq.) and the reaction mixture was stirred for 4 h at rt. After removal of the solvents *in vacuo* dichloride **24** was obtained and was used without further purification in the next step.

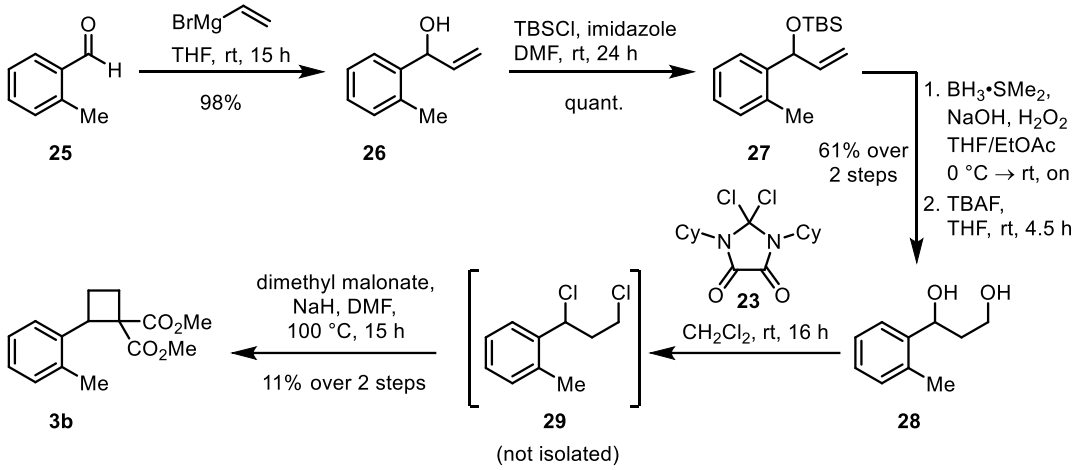
Previously obtained material **24** (1.95 g, 8.72 mmol, 1.0 eq.), dimethyl malonate (1.15 g, 1.00 mL, 9.59 mmol, 1.10 eq.) and NaH (60% in mineral oil, 733 mg, 18.3 mmol, 2.10 eq., 2 portions) were reacted according to **GP1**. Column chromatography (SiO_2, PE/EtOAc 100:1 → 50:1) afforded cyclobutane **3f** (645 mg, 2.28 mmol, 27% over 2 steps) as a pale yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.27– 7.21 (m, 4H), 4.32 (t, *J* = 9.7 Hz, 1H), 3.78 (s, 3H), 3.29 (s, 3H), 2.71 – 2.66 (m, 1H), 2.61 – 2.53 (m, 1H), 2.31 – 2.25 (m, 1H), 2.20 – 2.14 (m, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 172.2, 169.8, 137.7, 132.9, 129.1 (2C), 128.3 (2C), 59.7, 52.8, 52.2, 44.6, 25.8, 20.9.

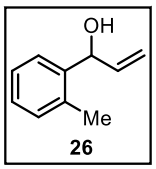
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2954 (w), 1731 (s), 1491 (w), 1438 (m), 1271 (s), 1199 (s), 1104 (s), 1034 (w), 833 (m), 729 (m).

HRMS (ESI): $C_{14}H_{15}ClO_4$ (282.06) calculated: 321.09204, found: 321.09214, $[M+K]^+$.



Scheme S4. Synthesis of deuterated D–A CB **3b**.

1-(*o*-Tolyl)prop-2-en-1-ol (26)

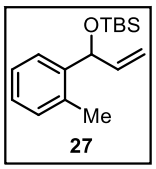


Alcohol **26** was prepared following a literature procedure.[9] To a solution of aldehyde **25** (2.00 g, 16.6 mmol, 1.0 eq.) in THF (25 mL) was added vinylmagnesium bromide (1 M in THF, 20 mL, 19.9 mmol, 1.20 eq.) at 0 °C and the reaction mixture was stirred for 15 h at rt. The reaction was stopped by the addition of aq. sat. NH_4Cl solution and EtOAc and the phases were separated. The aq. phase was extracted with EtOAc (3 × 30 mL), the combined organic layers were washed with of aq. sat. NaCl solution (50 mL) and were dried over anhydrous Na_2SO_4. Removal of the solvents *in vacuo* afforded the desired compound **26** (2.43 g, 16.3 mmol, 98%) as a yellow liquid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.47 – 7.44 (m, 1H), 7.25 – 7.13 (m, 3H), 6.04 (ddd, *J* = 17.2, 10.3, 5.7 Hz, 1H), 5.43 (dt, *J* = 5.7, 1.4 Hz, 1H), 5.32 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.21 (dt, *J* = 10.3, 1.4 Hz, 1H), 2.37 (s, 3H), 1.74 (br, s, 1H).

The analytical data were in accordance with those reported in the literature.[9]

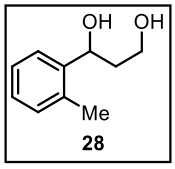
tert-Butyldimethyl((1-(_o_-tolyl)allyl)oxy)silane (27)



27

TBSCl (2.03 g, 13.5 mmol, 1.50 eq.) was added to a solution of alcohol **26** (1.33 g, 9.00 mmol,1.0 eq.) and imidazole (1.23 g, 18 mmol, 2.0 eq.) in DMF (6 mL) and the reaction mixture was stirred for 24 h at rt. The reaction was stopped by the addition of H_2O and EtOAc and the phases were separated. The aq. phase was extracted with EtOAc (3 × 10 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. Removal of the solvents *in vacuo* and subsequent column chromatography (SiO_2, PE/EtoAc 20:1) afforded the desired compound **27** with minor impurities as a colourless liquid. **27** was used in the next step without further purification.

1-(_o_-Tolyl)propane-1,3-diol (28)



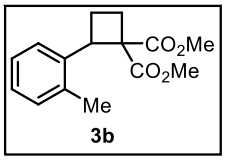
28

Alkene **27** was converted following a literature procedure.[10] To a solution of alkene **27** (500 mg, 1.90 mmol,1.0 eq.) in THF (7 mL) was added BH•SMe_2 (2 M in THF, 1.05 mL, 2.09 mmol, 1.10 eq.) at 0 °C and the reaction mixture was stirred for 3.5 h at rt. EtOAc (20 mL), NaOH (4.5 mL) and H_2O_2 (30%, 4.5 mL) were added dropwise at 0 °C and mixture was stirred for another 21 h at rt. The reaction was stopped by the addition of H_2O and the phases were separated. The aq. phase was extracted with EtOAc (3 × 15 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. Removal of the solvents *in vacuo* and purification by column chromatography (SiO_2, PE/EtoAc 10:1 → 2:1) afforded the desired compound with minor impurities as a colourless liquid. The obtained material was used in the next step without further purification.

TBAF (1 M in THF, 4.45 mL, 4.45 mmol) was added to a solution of the obtained product from the hydroboration (1.36 g, 4.99 mmol, 1.0 eq.) in THF (15 mL) and the reaction mixture was stirred for 4.5 h at rt. Removal of the solvents *in vacuo* and purification by column chromatography (SiO_2, PE/EtoAc 2:1 → 1:2) afforded the desired compound **28** (505 mg, 3.04 mmol, 61% over 3 steps) as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.55 – 7.51 (m, 1H), 7.28 – 7.12 (m, 3H), 5.21 (dd, *J* = 8.2, 4.0 Hz, 1H), 3.90 (t, *J* = 5.4 Hz, 1H), 2.48 (br, s, 2H), 2.33 (s, 3H), 2.02 – 1.85 (m, 2H).
The analytical data were in accordance with those reported in the literature.[11]

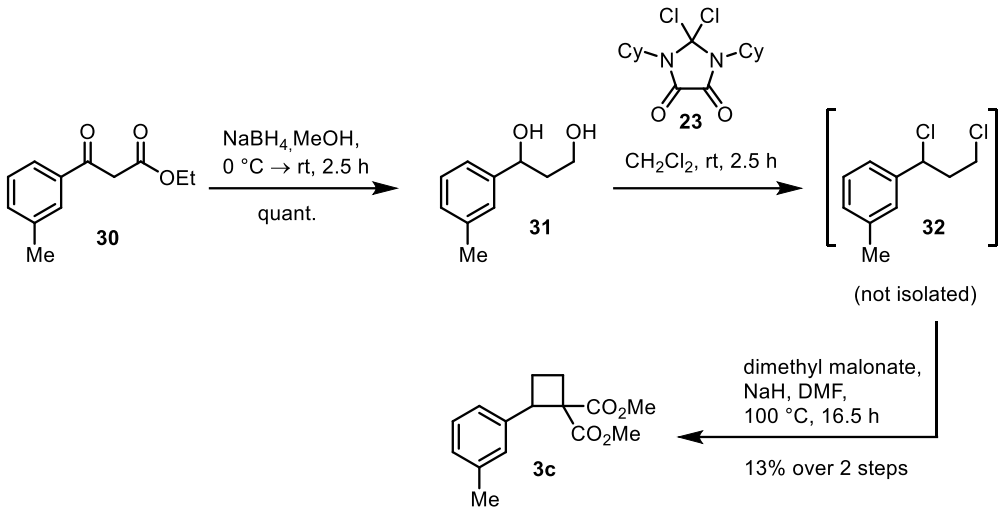
Dimethyl 2-(*o*-tolyl)cyclobutane-1,1-dicarboxylate (3b)



3b

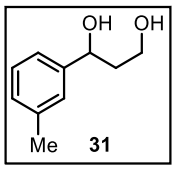
To a solution of diol **28** (498 mg, 3.00 mmol, 1.0 eq.) in CH_2Cl_2 (10 mL) was added chlorinating agent **23** (2.49 g, 7.49 mmol, 2.50 eq.) and the reaction mixture was stirred for 16 h at rt. After removal of the solvents *in vacuo* dichloride **29** was obtained and was used without further purification in the next step.
Previously obtained material **29** (606 mg, 3.00 mmol, 1.0 eq.), dimethyl malonate (436 mg, 380 µL, 3.30 mmol, 1.10 eq.) and NaH (60% in mineral oil, 252 mg, 6.30 mmol, 2.10 eq., 2 portions) were reacted according to **GP1**. Column chromatography (SiO_2, PE/EtOAc 100:1 $\rightarrow$ 50:1) afforded cyclobutane **3b** (89 mg, 340 µmol, 11% over 2 steps) as a colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.28 – 7.25 (br, m, 1H), 7.17 – 7.09 (m, 3H), 4.68 – 4.62 (m, 1H), 3.75 (s, 3H), 3.18 (s, 3H), 2.92 – 2.83 (m, 1H), 2.59 – 2.50 (m, 1H), 2.39 (s, 3H), 2.30 – 2.21 (m, 2H).
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 172.2, 169.8, 137.7, 137.6, 130.3, 127.1, 126.5, 125.8, 59.6, 52.7, 51.9, 41.2, 25.8, 21.6, 20.2.
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2996 (w), 2952 (w), 1727 (s), 1491 (w), 1434 (m), 1263 (s), 1198 (s), 1179 (m), 1101 (s), 747 (m).
HRMS (ESI): $C_{15}H_{18}O_4$ (262.12) calculated: 301.08367, found: 301.08369, $[M+K]^+$.



Scheme S3. Synthesis of D–A CB **3c**.

1-(*m*-Tolyl)propane-1,3-diol (31)

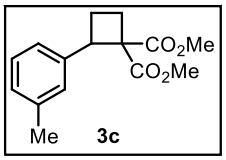


Diol **31** was prepared following a literature procedure.[12] $NaBH_4$ (523 mg, 13.8 mmol, 3.0 eq.) was added at 0 °C to a solution of compound **30** (1.00 g, 4.85 mmol, 1.0 eq.) in MeOH (10 mL) and the reaction mixture was stirred for 2.5 h at rt. The reaction was stopped by the addition of H_2O and EtOAc and the phases were separated. The aq. phase was extracted with EtOAc (3 × 15 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. Removal of the solvents *in vacuo* and purification by column chromatography (SiO_2, PE/EtoAc 3:1 → 2:1) afforded the desired compound **31** (806 mg, 4.85 mmol, quant.) as a colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.27 – 7.07 (m, 4H), 4.93 (dd, *J* = 8.6, 3.9 Hz, 1H), 3.86 (t, *J* = 5.5, Hz, 1H), 2.54 (br, s, 2H), 2.36 (s, 3H), 2.08 – 1.87 (m, 2H).

The analytical data were in accordance with those reported in the literature.[11]

Dimethyl 2-(*m*-tolyl)cyclobutane-1,1-dicarboxylate (3c)



To a solution of diol **31** (798 mg, 4.80 mmol, 1.0 eq.) in CH_2Cl_2 (15 mL) was added chlorinating agent **23** (3.75 g, 11.3 mmol, 2.50 eq.) and the reaction mixture was stirred for 2.5 h at rt. After removal of the solvents *in vacuo* dichloride **32** was obtained and was used without further purification in the next step.

Previously obtained material **32** (975 mg, 3.80 mmol, 1.0 eq.), dimethyl malonate (698 mg, 607 µL, 5.28 mmol, 1.10 eq.) and NaH (60% in mineral oil, 404 mg, 10.1 mmol, 2.10 eq., 2 portions) were reacted according to **GP1**. Column chromatography (SiO_2, PE/EtOAc 100:1 $\rightarrow$ 50:1) afforded cyclobutane **3c** (148 mg, 640 µmol, 13% over 2 steps) as a colourless oil.

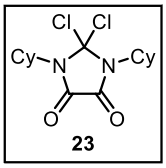
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.19 – 7.15 (m, 1H), 7.09 – 7.01 (m, 3H), 4.33 (t, *J* = 9.5 Hz, 1H), 3.77 (s, 3H), 3.26 (s, 3H), 2.74 – 2.55 (m, 2H), 2.32 (s, 3H), 2.28 – 2.12 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 172.3, 169.9, 139.2, 137.7, 128.5, 128.1, 127.8, 124.7, 59.8, 52.6, 52.0, 45.2, 25.9, 21.6, 21.0.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2996 (w), 2951 (w), 1726 (s), 1489 (w), 1435 (m), 1266 (s), 1197 (s), 1104 (s), 1039 (w), 700 (m).

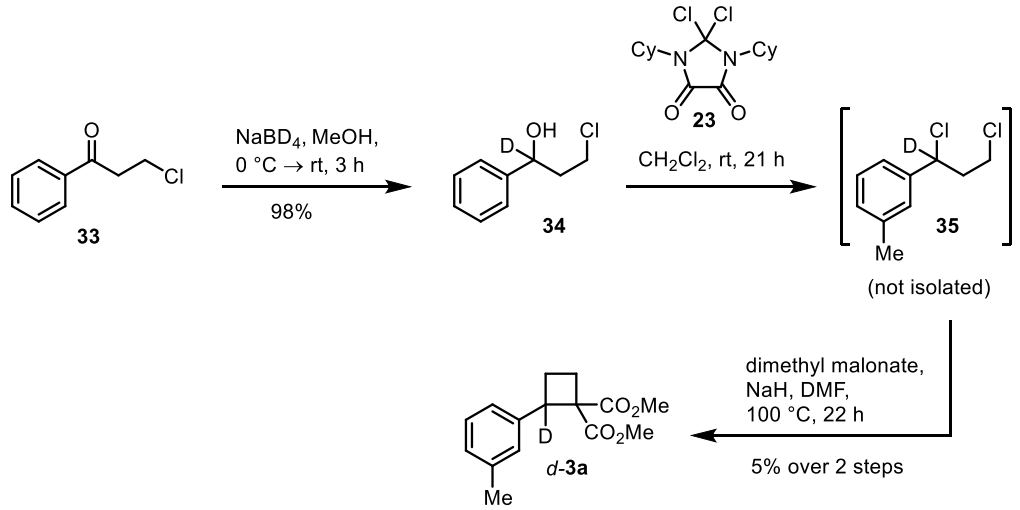
HRMS (ESI): $C_{15}H_{18}O_4$ (262.12) calculated: 301.08367, found: 301.08372, $[M+K]^+$.

2,2-Dichloro-1,3-dicyclohexylimidazolidine-4,5-dione (23)



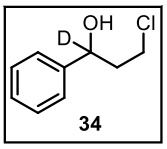
Chlorinating agent **23** was prepared following a literature procedure.[13] Oxyalyl chloride (14.0 g, 9.43 mL, 105 mmol, 1.05 eq.) was added to a solution of DCC (20.6 g, 100 mmol, 1.0 eq.) in CH_2Cl_2 (200 mL) dropwise over 25 min at 0 °C and the reaction mixture was stirred for 3.5 h at rt. After the solvent was removed *in vacuo*, the remaining solid was washed with petrol ether (5 x 100 mL) and dried *in vacuo*. The obtained chlorinating agent **23** (40.1 g, 120 mmol, 94%) was used without further purification.

3.4 Synthesis of deuterated D-A cyclobutane *d*-3a



Scheme S4. Synthesis of deuterated D–A *d*-**3a**.

3-Chloro-1-phenylpropan-1-*d*-1-ol (34)

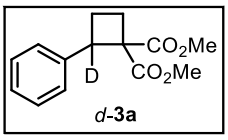


Alcohol **34** was prepared following a literature procedure.[14] $NaBD_4$ (203 mg, 4.89 mmol, 1.10 eq.) was added at 0 °C to a solution of compound **33** (1.00 g, 4.85 mmol, 1.0 eq.) in MeOH (20 mL) and the reaction mixture was stirred for 3 h at rt. The reaction was stopped by the addition of H_2O and EtOAc and the phases were separated. The aq. phase was extracted with EtOAc (2 × 15 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. Removal of the solvents *in vacuo* and purification by column chromatography (SiO_2, PE/EtoAc 10:1) afforded the desired compound **34** (783 mg, 4.56 mmol, 98%) as a yellow liquid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.39 – 7.28 (m, 5H), 3.75 (ddd, *J* = 10.9, 8.2, 5.6 Hz, 1H), 3.57 (ddd, *J* = 10.9, 5.9 Hz, 1H), 2.29 – 2.21 (m, 1H), 2.13 – 2.06 (m, 1H), 1.80 (br, s, 1H).
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 143.8, 128.8 (2C), 128.1, 125.9 (2C), 71.1 (t, *J* = 22.2 Hz, 1C), 41.8, 41.5.
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3365 (br), 3028 (w), 2963 (w), 1493 (w), 1447 (m), 1299 (m), 1197 (s), 1174 (w), 1073 (s), 768 (s).

HRMS (GC/EI): $C_9H_{10}DClO$ (171.05) calculated: 171.05612, found: 171.05745, $[M+H]^+$.

Dimethyl 2-phenylcyclobutane-1,1-dicarboxylate-2-*d* (*d*-3a)



d-**3a**

To a solution of diol **34** (760 mg, 4.42 mmol, 1.0 eq.) in CH_2Cl_2 (20 mL) was added chlorinating agent **23** (2.51 g, 7.51 mmol, 1.70 eq.) and the reaction mixture was stirred for 21 h at rt. After removal of the solvents *in vacuo* dichloride **35** was obtained and was used without further purification in the next step.

Previously obtained material **35** (840 mg, 4.42 mmol, 1.0 eq.), dimethyl malonate (642 mg, 558 µL, 4.86 mmol, 1.10 eq.) and NaH (60% in mineral oil, 371 mg, 9.28 mmol, 2.10 eq., 2 portions) were reacted according to **GP1**. Column chromatography (SiO_2, PE/EtOAc 100:1 $\rightarrow$ 50:1) afforded cyclobutane *d*-**3a** (53.0 mg, 213 µmol, 5% over 2 steps) as a colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.39 – 7.27 (m, 4H), 7.26 – 7.18 (m, 1H),3.78 (s, 3H), 3.24 (s, 3H), 2.75 – 2.68 (m, 1H), 2.66 – 2.56 (m, 1H), 2.32 – 2.23 (m, 1H), 2.21 – 2.13 (m, 1H).

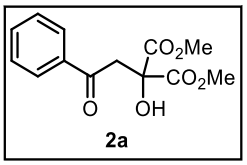
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 172.2, 169.9, 139.2, 128.2 (2C), 127.7 (2C), 127.1, 59.8, 52.6, 52.0, 44.9 (t, *J* = 21.2 Hz, 1C, 25.8, 20.7.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2997 (w), 2952 (w), 1727 (s), 1495 (w), 1438 (m), 1263 (s), 1195 (m), 1108 (s), 1032 (w), 697 (m).

HRMS (ESI): $C_{14}H_{15}DO_4$ (249.11) calculated: 272.10036, found: 272.10051, $[M+Na]^+$.

4. Electrochemical Synthesis of β-Hydroxy Ketones

Dimethyl 2-hydroxy-2-(2-oxo-2-phenylethyl)malonate (2a)



2a

Cyclopropane **1a** (35.9 mg, 153 µmol, 1.0 eq.) was reacted according to **GP2-A**. Column chromatography (SiO_2, PE/EtOAc 4:1) afforded the desired product **2a** (36.0 mg, 135 µmol, 88%) as a white solid.

Scale-up reaction: In a 20 mL ElectraSyn vial cyclopropane **1a** (722 mg, 3.08 mmol, 1.00 eq.) and $TBABF_4$ (0.02 M) were dissolved in HFIP (15 mL) and the solution was saturated with oxygen for 15 minutes. The solution was electrolyzed at a glassy carbon anode and a glassy cathode at a constant potential of +2.4 V for 22.5 h. The reaction mixture was concentrated *in vacuo* and the remaining residue was adsorbed on silica gel. Purification by column chromatography (SiO_2, PE/EtOAc 4:1 $\rightarrow$ 3:1) afforded the desired product **2a** (685 mg, 2.57 mmol, 83%) as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.98 – 7.94 (m, 2H), 7.62 – 7.58 (m, 1H), 7.50 – 7.45 (m, 2H), 4.30 (br, s, 1H), 3.86 (s, 2H), 3.85 (s, 6H).

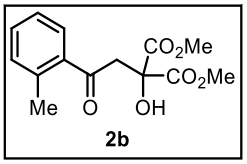
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 196.5, 170.2 (2C), 136.3, 134.0, 128.9 (2C), 128.4 (2C), 77.0, 53.8 (2C), 43.9.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3453 (br), 2963 (w), 2929 (w), 1727 (s), 1675 (m), 1594 (w), 1439 (m), 1212 (s), 1141 (s), 1073 (m).

HRMS (ESI): $C_{13}H_{14}O_6$ (266.07) calcd.: 289.06826 found: 289.06839, $[M+Na]^+$.

m. p.: 90 °C

Dimethyl 2-hydroxy-2-(2-oxo-2-(*o*-tolyl)ethyl)malonate (2b)



2b

Cyclopropane **1b** (36.8 mg, 148 µmol, 1.0 eq.) was reacted according to **GP2-A**. Column chromatography (SiO_2, PE/EtOAc 4:1) afforded the desired product **2b** (35.2 mg, 126 µmol, 85%) as a colourless oil.

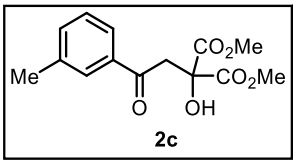
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.72 – 7.70 (m, 1H), 7.42 – 7.38 (m, 1H), 7.30 – 7.24 (m, 2H), 4.32 (br, s, 1H), 3.85 (s, 6H), 3.78 (s, 2H), 2.50 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 200.1, 170.3 (2C), 139.1, 136.7, 132.3, 132.2, 129.1, 126.0, 77.2, 53.8 (2C), 43.4, 21.6.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3484 (br), 2958 (w), 2851 (w), 1744 (s), 1688 (m), 1570 (w), 1441 (m), 1236 (s), 1135 (m), 1075 (w).

HRMS (ESI): $C_{14}H_{16}O_6$ (280.09) calcd.: 281.10196 found: 281.10205, $[M+H]^+$.

Dimethyl 2-hydroxy-2-(2-oxo-2-(*m*-tolyl)ethyl)malonate (2c)



2c

Cyclopropane **1c** (39.2 mg, 158 µmol, 1.0 eq.) was reacted according to **GP2-A**. Column chromatography (SiO_2, PE/EtOAc 4:1) afforded the desired product **2c** (36.0 mg, 128 µmol, 81%) as a colourless oil.

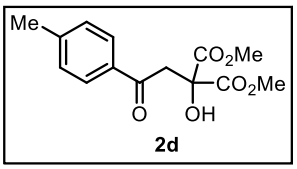
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.78 – 7.74 (m, 2H), 7.42 – 7.34 (m, 2H), 4.31 (br, s, 1H), 3.85 (s, 6H), 3.84 (s, 2H), 2.41 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 196.8, 170.3 (2C), 138.8, 136.3, 134.8, 128.9, 128.8, 125.6, 77.1, 53.8 (2C), 44.0, 21.5.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3488 (br), 2956 (w), 2851 (w), 1743 (s), 1685 (m), 1594 (w), 1438 (m), 1225 (s), 1137 (m), 1076 (w).

HRMS (ESI): $C_{14}H_{16}O_6$ (280.09) calcd.: 303.08391 found: 303.08406, $[M+Na]^+$.

Dimethyl 2-hydroxy-2-(2-oxo-2-(*p*-tolyl)ethyl)malonate (2d)



2d

Cyclopropane **1d** (37.6 mg, 151 µmol, 1.0 eq.) was reacted according to **GP2-A**. Column chromatography (SiO_2, PE/EtOAc 4:1) afforded the desired product **2d** (34.8 mg, 124 µmol, 82%) as a colourless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.87 – 7.84 (m, 2H), 7.29 – 7.26 (m, 2H), 4.32 (br, s, 1H), 3.84 (s, 6H), 3.83 (s, 2H), 2.42 (s, 3H).

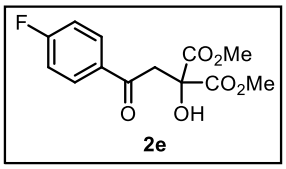
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 196.2, 170.3 (2C), 145.0, 133.8, 129.6 (2C), 128.5 (2C), 77.1, 53.8 (2C), 43.8, 21.9.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3483 (br), 2958 (w), 2849 (w), 1743 (s), 1684 (m), 1607 (w), 1438 (m), 1237 (s), 1139 (m), 1075 (w).

HRMS (ESI): $C_{14}H_{16}O_6$ (280.09) calcd.: 303.08391 found: 303.08411, $[M+Na]^+$.

m. p.: 85 °C

Dimethyl 2-(2-(4-fluorophenyl)-2-oxoethyl)-2-hydroxymalonate (2e)



2e

Cyclopropane **1e** (44.1 mg, 175 µmol, 1.0 eq.) was reacted according to **GP2-A** (*note*: a constant current of *I* = 10 mA was applied instead of a constant potential of *U* = 2.4 V). Column chromatography (SiO_2, PE/EtOAc 4:1) afforded the desired product **2e** (39.9 mg, 141 µmol, 80%) as a colourless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.02 – 7.96 (m, 2H), 7.18 – 7.12 (m, 2H), 3.85 (s, 6H), 3.82 (s, 2H).

No O*H*-signal was observed.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 194.9, 170.2 (2C), 166.3 (d, *J* = 256.1 Hz, 1C), 132.8 (d, *J* = 3.0 Hz, 1C), 131.1 (d, *J* = 9.5 Hz, 2C), 116.1 (d, *J* = 22.0 Hz, 2C), 77.0, 53.8 (2C), 43.8.

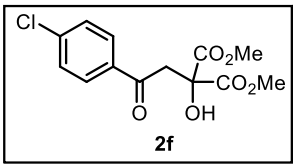
^{19}F-NMR (377 MHz, $CDCl_3$): δ = –104.1 (s, 1F).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3485 (br), 2957 (w), 2853 (w), 1742 (s), 1688 (m), 1597 (m), 1439 (m), 1229 (s), 1138 (m), 1076 (w).

HRMS (ESI): $C_{13}H_{13}FO_6$ (284.06) calcd.: 323.03277 found: 323.03292, $[M+K]^+$.

m. p.: 92 °C

Dimethyl 2-(2-(4-chlorophenyl)-2-oxoethyl)-2-hydroxymalonate (2f)



2f

Cyclopropane **1f** (41.3 mg, 154 µmol, 1.0 eq.) was reacted according to **GP2-A**. Column chromatography (SiO_2, PE/EtOAc 4:1) afforded the desired product **2f** (39.8 mg, 132 µmol, 86%) as a colourless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.92 – 7.88 (m, 2H), 7.47 – 7.43 (m, 2H), 4.25 (br, s, 1H), 3.85 (s, 6H), 3.81 (s, 2H).

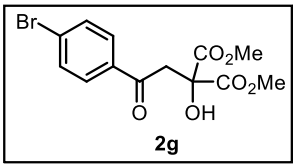
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 195.3, 170.1 (2C), 140.6, 134.7, 129.8 (2C), 129.2 (2C), 76.9, 53.9 (2C), 43.8.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3478 (br), 2958 (w), 2851 (w), 1745 (s), 1689 (m), 15788 (w), 1439 (m), 1238 (s), 1138 (m), 1086 (w).

HRMS (ESI): $C_{13}H_{13}ClO_6$ (300.04) calcd.: 339.00322 found: 339.00321, $[M+K]^+$.

m. p.: 97 °C

Dimethyl 2-(2-(4-bromophenyl)-2-oxoethyl)-2-hydroxymalonate (2g)



2g

Cyclopropane **1g** (49.6 mg, 158 µmol, 1.0 eq.) was reacted according to **GP2-A**. Column chromatography (SiO_2, PE/EtOAc 4:1) afforded the desired product **2g** (44.8 mg, 130 µmol, 82%) as a colourless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.83 – 7.80 (m, 2H), 7.64 – 7.60 (m, 2H), 4.24 (br, s, 1H), 3.85 (s, 6H), 3.81 (s, 2H).

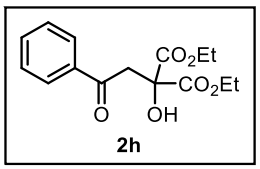
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 195.5, 170.1 (2C), 135.1, 132.2 (2C), 129.9 (2C), 129.3, 76.9, 53.9 (2C), 43.8.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3483 (br), 2956 (w), 2852 (w), 1743 (s), 1688 (m), 1583 (w), 1439 (m), 1235 (s), 1137 (m), 1073 (w).

HRMS (ESI): $C_{13}H_{13}BrO_6$ (343.98) calcd.: 382.95271 found: 382.95274, $[M+K]^+$.

m. p.: 111 °C

Diethyl 2-hydroxy-2-(2-oxo-2-phenylethyl)malonate (2h)



2h

Cyclopropane **1h** (40.0 mg, 152 µmol, 1.0 eq.) was reacted according to **GP2-A**. Column chromatography (SiO_2, PE/EtOAc 4:1) afforded the desired product **2h** (31.3 mg, 106 µmol, 70%) as a colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.98 – 7.95 (m, 2H), 7.61 – 7.57 (m, 1H), 7.50 – 7.45 (m, 2H), 4.30 (q, *J* = 7.1 Hz, 1H), 4.29 (br, s, 1H), 1.29 (t, *J* = 7.1 Hz, 1H).

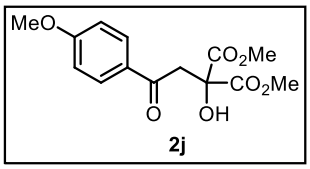
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 196.4, 169.7 (2C), 136.3, 133.7, 128.7 (2C), 128.2 (2C), 76.9, 62.8 (2C), 43.5, 14.0 (2C).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3487 (br), 2983 (w), 2934 (w), 1738 (s), 1688 (m), 1593 (w), 1451 (m), 1229 (s), 1136 (m), 1071 (w).

HRMS (ESI): $C_{15}H_{18}O_6$ (294.11) calcd.: 333.07350 found: 333.07352, $[M+K]^+$.

m. p.: 111 °C

Dimethyl 2-hydroxy-2-(2-(4-methoxyphenyl)-2-oxoethyl)malonate (2j)



2j

Cyclopropane **1j** (37.5 mg, 142 µmol, 1.0 eq.) and CoTPP (3.0 mg, 4.46 µmol, 3.1 mol%) were reacted according to **GP2-B**. Column chromatography (SiO_2, PE/EtOAc 3:1) afforded the desired product **2j** (33.4 mg, 113 µmol, 79%) as a colourless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.95 – 7.92 (m, 2H), 6.95 – 6.92 (m, 2H), 4.37 (br, s, 1H), 3.87 (s, 3H), 3.84 (s, 6H), 3.80 (s, 2H).

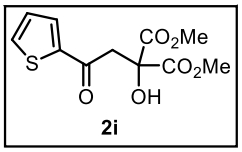
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 195.2, 170.3 (2C), 164.3, 130.7 (2C), 129.4, 114.0 (2C), 77.2, 55.7, 53.7 (2C), 43.5.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3395 (br, m), 2952 (w), 2846 (w), 1739 (s), 1676 (m), 1587 (m), 1445 (m), 1234 (s), 1122 (m), 1038 (m).

HRMS (ESI): $C_{14}H_{16}O_7$ (296.08) calcd.: 319.07882 found: 319.07903, $[M+Na]^+$.

m. p.: 81 °C

Dimethyl 2-hydroxy-2-(2-oxo-2-(thiophen-2-yl)ethyl)malonate (2i)



2i

Cyclopropane **1i** (38.3 mg, 159 µmol, 1.0 eq.) and DDQ (34.3 mg, 151 µmol, 0.95 eq.) were reacted according to **GP2-B**. Column chromatography (SiO_2, PE/EtOAc 4:1) afforded the desired product **2i** (28.1 mg, 103 µmol, 65%) as a colourless solid.

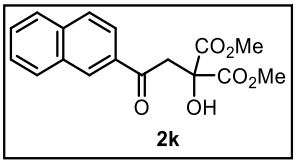
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.77 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.69 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.15 (dd, *J* = 4.9, 3.8 Hz, 1H), 4.29 (br, s, 1H), 3.85 (s, 6H), 3.87 (s, 2H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 189.2, 170.0 (2C), 143.4, 135.0, 133.1, 128.5, 77.0, 53.8 (2C), 44.2.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3479 (br), 2957 (w), 2851 (w), 1741 (s), 1662 (m), 1517 (w), 1438 (m), 1240 (s), 1136 (m), 1031 (w).

HRMS (ESI): $C_{11}H_{12}O_6S$ (272.04) calcd.: 295.02468 found: 295.02480, $[M+Na]^+$.
m. p.: 95 °C

Dimethyl 2-hydroxy-2-(2-(naphthalen-2-yl)-2-oxoethyl)malonate (2k)

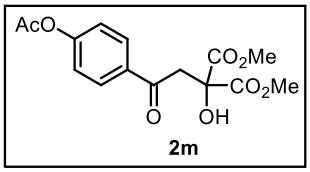


2k

Cyclopropane **1k** (40.4 mg, 142 µmol, 1.0 eq.) and DDQ (33.9 mg, 149 µmol, 1.05 eq.) were reacted according to **GP2-C**. Column chromatography (SiO_2, PE/EtOAc 4:1) afforded the desired product **2k** (18.7 mg, 59.1 µmol, 42%) as a pale yellow oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.50 – 8.49 (m, 1H), 8.02 – 7.96 (m, 2H), 7.91 – 7.87 (m, 2H), 7.69 (dddd, *J* = 21.6, 8.1, 6.9, 1.3 Hz, 2H), 4.36 (br, s, 1H), 4.00 (s, 2H), 3.87 (s, 6H).
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 196.5, 170.3 (2C), 136.0, 133.6, 132.6, 130.6, 129.8, 129.1, 128.8, 128.0, 127.1, 123.7, 77.1, 53.8 (2C), 43.9.
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3484 (br), 2955 (w), 2852 (w), 1741 (s), 1681 (m), 1509 (w), 1437 (m), 1281 (m), 1129 (m), 1025 (w).
HRMS (ESI): $C_{17}H_{16}O_6$ (316.09) calcd.: 339.08391 found: 339.08274, $[M+Na]^+$.
m. p.: 95 °C

Dimethyl 2-(2-(4-acetoxyphenyl)-2-oxoethyl)-2-hydroxymalonate (2m)



2m

Cyclopropane **1m** (41.7 mg, 143 µmol, 1.0 eq.) and DDQ (34.0 mg, 150 µmol, 1.05 eq.) were reacted according to **GP2-C**. Column chromatography (SiO_2, PE/EtOAc 3:1) afforded the desired product **2m** (23.8 mg, 73.4 µmol, 51%) as a colourless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.01 – 7.98 (m, 2H), 7.23 – 7.19 (m, 2H), 3.84 (s, 6H), 3.83 (s, 2H), 2.33 (s, 3H).
No O*H*-signal was observed.

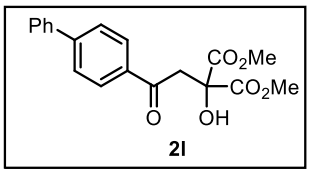
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 195.3, 170.2 (2C), 168.9, 155.1, 133.9, 130.1 (2C), 122.1 (2C), 77.0, 53.8 (2C), 43.9, 21.3.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3474 (br), 2958 (w), 2848 (w), 1744 (s), 1599 (m), 1506 (w), 1437 (m), 1195 (s), 1140 (m), 1039 (w).

HRMS (ESI): $C_{15}H_{16}O_8$ (324.08) calcd.: 347.07374 found: 347.07394, $[M+Na]^+$.

m. p.: 94 °C

Dimethyl 2-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)-2-hydroxymalonate (2l)



2l

Cyclopropane **1l** (46.8 mg, 151 µmol, 1.0 eq.) and DDQ (34.1 mg, 150 µmol, 0.99 eq.) were reacted according to **GP2-C**. Column chromatography (SiO_2, PE/EtOAc 3:1) afforded the desired product **2l** (31.5 mg, 92.3 µmol, 61%) as a colourless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.06 – 8.01 (m, 2H), 7.72 – 7.68 (m, 2H), 7.65 – 7.61 (m, 2H), 7.51 – 7.45 (m, 2H), 7.44 – 7.38 (m, 1H), 4.33 (br, s, 1H), 3.89 (s, 2H), 3.86 (s, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 196.2, 170.3 (2C), 146.7, 139.8, 135.0, 129.2 (2C), 129.0 (2C), 128.6, 127.5 (2C), 127.4 (2C), 77.1, 53.8 (2C), 43.9.

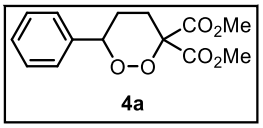
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3453 (br, m), 2959 (w), 2851 (w), 1736 (s), 1603 (m), 1517 (w), 1437 (m), 1212 (m), 1118 (m), 1041 (w).

HRMS (ESI): $C_{19}H_{18}O_6$ (342.11) calcd.: 365.09956 found: 365.09969, $[M+Na]^+$.

m. p.: 151 °C

5. Electrochemical Synthesis of Dioxanes

Dimethyl 6-phenyl-1,2-dioxane-3,3-dicarboxylate (4a)



4a

Cyclobutane **3a** (25 mg, 101 µmol, 1.0 eq.) was reacted according to **GP3**. Column chromatography (SiO_2, PE/EtOAc 4:1) afforded the desired product **4a** (28.0 mg, 99.9 µmol, 99%) as a colourless oil.

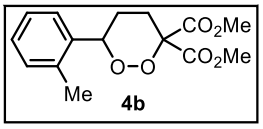
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.37 – 7.28 (m, 5H), 5.24 (dd, *J* = 11.5, 2.5 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 2.75 (ddd, *J* = 13.5, 4.7, 2.6 Hz, 1H), 2.41 – 2.32 (m, 1H), 2.18 (ddd, *J* = 13.5, 12.4, 5.0 Hz, 1H), 2.08 – 2.03 (m, 1H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 167.3, 166.8, 137.2, 129.2, 128.7 (2C), 127.5 (2C), 85.7, 83.2, 53.5, 53.4, 28.3, 26.5.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2957 (w), 2852 (w), 1746 (s), 1496 (m), 1282 (m), 1254 (m), 1223 (m), 1113 (m), 1035 (w), 1008 (m).

HRMS (ESI): $C_{14}H_{16}O_6$ (280.09) calcd.: 303.08391 found: 303.08397, $[M+Na]^+$.

Dimethyl 6-(*o*-tolyl)-1,2-dioxane-3,3-dicarboxylate (4b)



4b

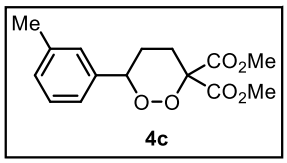
Cyclobutane **3b** (25.9 mg, 98.9 µmol, 1.0 eq.) was reacted according to **GP3**. Column chromatography (SiO_2, PE/EtOAc 4:1) afforded the desired product **4b** (21.9 mg, 74.2 µmol, 75%) as a colourless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.25 – 7.16 (m, 4H), 5.43 (dd, *J* = 11.7, 2.4 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 2.79 (ddd, *J* = 13.5, 4.7, 2.5 Hz, 1H), 2.49 – 2.40 (m, 1H), 2.42 (s, 3H), 2.19 (ddd, *J* = 13.6, 12.6, 5.0 Hz, 1H), 1.99 (ddt, *J* = 13.7, 4.9, 2.4 Hz, 1H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 167.4, 166.8, 137.6, 134.9, 130.8, 129.1, 126.5, 126.2, 85.8, 80.3, 53.5, 53.4, 28.6, 25.6, 19.4.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2955 (w), 2853 (w), 1748 (s), 1439 (m), 1284 (s), 1252 (m), 1219 (m), 1113 (m), 1072 (w), 1007 (m).
HRMS (ESI): $C_{15}H_{18}O_6$ (294.11) calcd.: 317.09956 found: 317.09968, $[M+Na]^+$.

Dimethyl 6-(*m*-tolyl)-1,2-dioxane-3,3-dicarboxylate (4c)

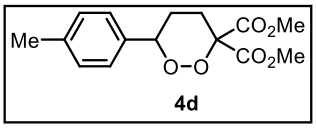


4c

Cyclobutane **3c** (27.2 mg, 104 µmol, 1.0 eq.) was reacted according to **GP3**. Column chromatography (SiO_2, PE/EtOAc 4:1) afforded the desired product **4c** (26.4 mg, 90.3 µmol, 87%) as a pale yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.25 – 7.21 (m, 1H), 7.15 – 7.08 (m, 3H), 5.20 (dd, *J* = 11.4, 2.4 Hz, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 2.74 (ddd, *J* = 13.4, 4.6, 2.6 Hz, 1H), 2.41 – 2.31 (m, 1H), 2.34 (s, 3H), 2.21 – 2.13 (m, 1H), 2.03 (ddt, *J* = 13.4, 4.9, 2.6 Hz, 1H).
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 167.4, 166.9, 138.4, 137.1, 129.9, 128.6, 128.2, 124.6, 85.7, 83.2, 53.5, 53.4, 28.3, 26.5, 21.5.
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2956 (w), 2854 (w), 1744 (s), 1437 (m), 1281 (s), 1252 (m), 1217 (m), 1112 (m), 1042 (w), 1008 (m).
HRMS (ESI): $C_{15}H_{18}O_6$ (294.11) calcd.: 317.09956 found: 317.09958, $[M+Na]^+$.
m. p.: 91 °C

Dimethyl 6-(*p*-tolyl)-1,2-dioxane-3,3-dicarboxylate (4d)



4d

Cyclobutane **3d** (27.0 mg, 104 µmol, 1.0 eq.) was reacted according to **GP3**. Column chromatography (SiO_2, PE/EtOAc 4:1) afforded the desired product **4d** (27.7 mg, 88.6 µmol, 86%) as a pale yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.21 – 7.13 (m, 4H), 5.20 (dd, *J* = 11.5, 2.5 Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 2.74 (ddd, *J* = 13.5, 4.7, 2.6 Hz, 1H), 2.41 – 2.32 (m, 1H), 2.33 (s, 3H), 2.20 – 2.13 (m, 1H), 2.02 (ddt, *J* = 13.6, 5.1, 2.6 Hz, 1H).

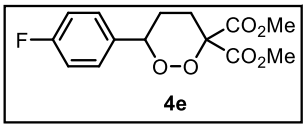
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 167.4, 166.9, 139.2, 134.1, 129.4 (2C), 127.6 (2C), 85.6, 83.0, 53.5, 53.4, 28.3, 26.3, 21.4.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2956 (w), 2855 (w), 1747 (s), 1437 (m), 1282 (s), 1254 (m), 1224 (m), 1121 (m), 1040 (w), 1010 (m).

HRMS (ESI): $C_{15}H_{18}O_6$ (294.11) calcd.: 317.09956 found: 317.09966, $[M+Na]^+$.

m. p.: 90 °C

Dimethyl 6-(4-fluorophenyl)-1,2-dioxane-3,3-dicarboxylate (4e)



4e

Cyclobutane **3e** (27.8 mg, 105 µmol, 1.0 eq.) was reacted according to **GP3**. Column chromatography (SiO_2, PE/EtOAc 4:1) afforded the desired product **4e** (23 mg, 77.4 µmol, 74%) as a pale yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.30 – 7.25 (m, 2H), 7.06 – 7.00 (m, 2H), 5.20 (dd, *J* = 11.4, 2.5 Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 2.74 (ddd, *J* = 13.4, 4.6, 2.7 Hz, 1H), 2.39 – 2.28 (m, 1H), 2.17 (ddd, *J* = 13.4, 12.3, 4.9 Hz, 1H), 2.04 (ddt, *J* = 13.3, 4.9, 2.6 Hz, 1H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 167.3, 166.7, 163.2 (d, *J* = 248.2 Hz, 1C), 132.9 (d, *J* = 3.2 Hz, 1C), 129.5 (d, *J* = 8.4 Hz, 2C), 115.7 (d, *J* = 21.6 Hz, 2C), 85.6, 82.4, 53.5, 53.4, 28.1, 26.5.

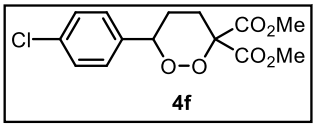
^{19}F-NMR (377 MHz, $CDCl_3$): δ = –112.6 (s, 1F).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2957 (w), 2853 (w), 1749 (s), 1438 (m), 1283 (m), 1256 (m), 1225 (s), 1115 (w), 1037 (m), 1010 (m).

HRMS (ESI): $C_{14}H_{15}FO_6$ (298.08) calcd.: 321.07449 found: 321.07459, $[M+Na]^+$.

m. p.: 115 °C

Dimethyl 6-(4-chlorophenyl)-1,2-dioxane-3,3-dicarboxylate (4f)



4f

Cyclobutane **3f** (28.1 mg, 99.3 µmol, 1.0 eq.) was reacted according to **GP3**. Column chromatography (SiO_2, PE/EtOAc 4:1) afforded the desired product **4f** (21.3 mg, 69.6 µmol, 68%) as a pale yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.33 – 7.30 (m, 2H), 7.24 – 7.21 (m, 2H), 5.20 (dd, *J* = 11.3, 2.5 Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 2.73 (ddd, *J* = 13.5, 4.5, 2.7 Hz, 1H), 2.35 – 2.26 (m, 1H), 2.20 – 2.17 (m, 1H), 2.04 (ddt, *J* = 13.4, 4.9, 2.7 Hz, 1H).

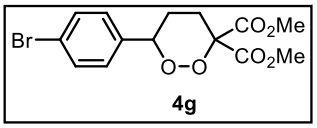
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 167.2, 166.7, 135.6, 135.1, 129.0 (2C), 128.8 (2C), 85.6, 82.3, 53.6, 53.5, 28.0, 26.4.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2956 (w), 2853 (w), 1745 (s), 1437 (m), 1285 (s), 1254 (m), 1223 (m), 1117 (w), 1093 (m), 1011 (m).

HRMS (ESI): $C_{14}H_{15}ClO_6$ (317.05) calcd.: 353.01887 found: 353.01898, $[M+K]^+$.

m. p.: 114 °C

Dimethyl 6-(4-bromophenyl)-1,2-dioxane-3,3-dicarboxylate (4g)



4g

Cyclobutane **3g** (33.7 mg, 104 µmol, 1.0 eq.) was reacted according to **GP3**. Column chromatography (SiO_2, PE/EtOAc 4:1) afforded the desired product **4g** (25 mg, 69.6 µmol, 68%) as a pale yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.50 – 7.46 (m, 2H), 7.18 – 7.14 (m, 2H), 5.18 (dd, *J* = 11.2, 2.6 Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 2.75 – 2.70 (m, 1H), 2.35 – 2.25 (m, 1H), 2.21 – 2.13 (m, 1H), (2.08 – 2.03 (m, 1H)

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 167.2, 166.7, 136.2, 131.9 (2C), 129.1 (2C), 123.3, 85.6, 82.4, 53.5, 53.4, 28.0, 26.4.

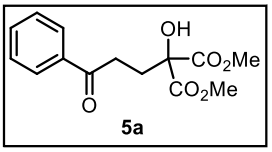
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2956 (w), 2853 (w), 1745 (s), 1437 (m), 1285 (s), 1254 (m), 1223 (m), 1117 (w), 1093 (m), 1011 (m).

HRMS (ESI): $C_{14}H_{15}BrO_6$ (358.00) calcd.: 380.99442 found: 380.99478, $[M+Na]^+$.

m. p.: 124 °C

6. Synthesis of γ-Hydroxy Ketones

Dimethyl 2-hydroxy-2-(3-oxo-3-phenylpropyl)malonate (5a)



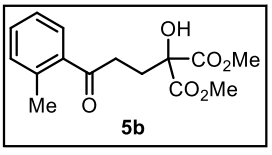
5a

Dioxane **4a** (15 mg, 53.5 µmol, 1.0 eq.) and NEt_3 (6.50 mg, 8.90 µL, 64.2 µmol, 1.20 eq.) were reacted according to **GP4**. Column chromatography (SiO_2, PE/EtOAc 2:1) afforded the desired product **5a** (14.3 mg, 51.0 µmol, 95%) as a white solid.

"*one-pot approach*": Cyclobutane **3a** (25.1 mg, 101 µmol, 1.0 eq.) was reacted according to **GP3** for 16 h. After removal of the solvents, the crude material was dissolved in CH_2Cl_2 and was reacted with NEt_3 (12.1 mg, 16.6 µL, 120 µmol, 1.20 eq.) as described in **GP4**. Column chromatography (SiO_2, PE/EtOAc 4:1) afforded the desired product **5a** (18.0 mg, 64.6 µmol, 64% over 2 steps) as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.98 – 7.94 (m, 2H), 7.59 – 7.54 (m, 1H), 7.49 – 7.43 (m, 2H), 3.92 (br, s, 1H), 3.82 (s, 6H), 3.13 – 3.09 (m, 2H), 2.53 – 2.49 (m, 2H).
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 199.1, 170.1 (2C), 136.7, 133.3, 128.7 (2C), 128.2 (2C), 78.3, 53.7 (2C), 32.8, 29.4.
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3478 (br), 2956 (w), 2854 (w), 1741 (s), 1685 (s), 1446 (m), 1270 (m), 1233 (m), 1074 (m), 1027 (w).
HRMS (ESI): $C_{14}H_{16}O_6$ (280.09) calcd.: 303.08391 found: 303.08405, $[M+Na]^+$.
m. p.: 78 °C

Dimethyl 2-hydroxy-2-(3-oxo-3-(*o*-tolyl)propyl)malonate (5b)



5b

Dioxane **4b** (3.7 mg, 12.5 µmol, 1.0 eq.) and NEt_3 (1.53 mg, 2.09 µL, 15.1 µmol, 1.20 eq.) were reacted according to **GP4**. Column chromatography (SiO_2, PE/EtOAc 2:1) afforded the desired product **5b** (2.50 mg, 8.45 µmol, 68%) as a colourless oil.

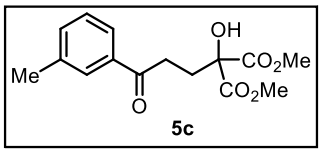
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.66 – 7.64 (m, 1H), 7.37 (td, *J* = 7.5, 1.4 Hz, 1H), 7.27 – 7.23 (m, 2H), 3.88 (br, s, 1H), 3.83 (s, 6H), 3.04 – 3.01 (m, 2H), 2.50 – 2.47 (m, 2H), 2.49 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 202.9, 170.9 (2C), 138.4, 137.6, 132.2, 131.6, 128.8, 125.9, 78.3, 53.7 (2C), 35.6, 29.5, 21.5.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3476 (br), 2955 (w), 2856 (w), 1742 (s), 1686 (m), 1443 (m), 1272 (s), 1232 (s), 1128 (m), 1030 (w).

HRMS (ESI): $C_{15}H_{18}O_6$ (294.11) calcd.: 317.09956 found: 317.09990, $[M+Na]^+$.

Dimethyl 2-hydroxy-2-(3-oxo-3-(*m*-tolyl)propyl)malonate (5c)



5c

Dioxane **4c** (10 mg, 34 µmol, 1.0 eq.) and NEt_3 (4.13 mg, 5.66 µL, 40.8 µmol, 1.20 eq.) were reacted according to **GP4**. Column chromatography (SiO_2, PE/EtOAc 2:1) afforded the desired product **5c** (10 mg, 34 µmol, quant.) as a colourless oil.

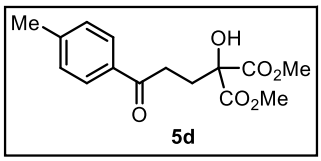
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.78 – 7.72 (m, 2H), 7.39 – 7.31 (m, 2H), 3.93 (br, s, 1H), 3.83 (s, 6H), 3.12 – 3.07 (m, 2H), 2.52 – 2.48 (m, 2H), 2.40 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 199.3, 170.9 (2C), 138.6, 136.8, 134.1, 128.7, 128.6, 125.4, 78.3, 53.7 (2C), 32.8, 29.5, 21.5.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3478 (br), 2955 (w), 2853 (w), 1741 (s), 1683 (m), 1440 (m), 1272 (m), 1236 (s), 1127 (s), 1041 (w).

HRMS (ESI): $C_{15}H_{18}O_6$ (294.11) calcd.: 317.09956 found: 317.09974, $[M+Na]^+$.

Dimethyl 2-hydroxy-2-(3-oxo-3-(*p*-tolyl)propyl)malonate (5d)



Dioxane **4d** (4.40 mg, 15.0 µmol, 1.0 eq.) and NEt_3 (1.82 mg, 2.49 µL, 18.0 µmol, 1.20 eq.) were reacted according to **GP4**. Column chromatography (SiO_2, PE/EtOAc 2:1) afforded the desired product **5d** (4.40 mg, 15.0 µmol, quant.) as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.87 – 7.83 (m, 2H), 7.26 – 7.23 (m, 2H), 3.93 (br, s, 1H), 3.82 (s, 6H), 3.10 – 3.06 (m, 2H), 2.52 – 2.48 (m, 2H), 2.40 (s, 3H).

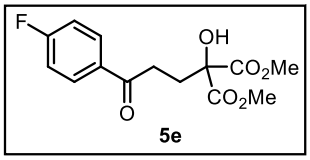
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 198.8, 170.9 (2C), 144.2, 134.3, 129.4 (2C), 128.4 (2C), 78.4, 53.7 (2C), 32.7, 29.5, 21.8.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3475 (br), 2955 (w), 2854 (w), 1742 (s), 1681 (m), 1442 (m), 1271 (s), 1236 (s), 1127 (m), 1032 (w).

HRMS (ESI): $C_{15}H_{18}O_6$ (294.11) calcd.: 317.09956 found: 317.09974, $[M+Na]^+$.

m. p.: 85 °C

Dimethyl 2-(3-(4-fluorophenyl)-3-oxopropyl)-2-hydroxymalonate (5e)



Dioxane **4e** (11.9 mg, 39.9 µmol, 1.0 eq.) and NEt_3 (4.84 mg, 6.63 µL, 47.9 µmol, 1.20 eq.) were reacted according to **GP4**. Column chromatography (SiO_2, PE/EtOAc 2:1) afforded the desired product **5e** (11.8 mg, 39.6 µmol, 99%) as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.01 – 7.96 (m, 2H), 7.15 – 7.09 (m, 2H), 3.89 (br, s, 1H), 3.83 (s, 6H), 3.10 – 3.06 (m, 2H), 2.51 – 2.48 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 197.4, 170.9 (2C), 166.0 (d, *J* = 254.8 Hz, 1C), 133.2 (d, *J* = 3.0 Hz, 1C), 130.9 (d, *J* = 9.3 Hz, 2C), 115.9 (d, *J* = 21.9 Hz, 2C), 78.2, 53.7 (2C), 32.8, 29.4.

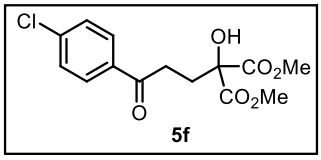
^{19}F-NMR (377 MHz, $CDCl_3$): δ = –105.5 (s, 1F).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3472 (br), 2957 (w), 2856 (w), 1739 (s), 1684 (m), 1441 (m), 1271 (m), 1230 (s), 1128 (m), 1031 (w).

HRMS (ESI): $C_{14}H_{15}FO_6$ (298.08) calcd.: 337.04842 found: 337.04852, $[M+K]^+$.

m. p.: 81 °C

Dimethyl 2-(3-(4-chlorophenyl)-3-oxopropyl)-2-hydroxymalonate (5f)



5f

Dioxane **4f** (7.8 mg, 24.8 µmol, 1.0 eq.) and NEt_3 (3.01 mg, 4.12 µL, 29.7 µmol, 1.20 eq.) were reacted according to **GP4**. Column chromatography (SiO_2, PE/EtOAc 2:1) afforded the desired product **5f** (6.85 mg, 21.8 µmol, 88%) as a white solid.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.91 – 7.88 (m, 2H), 7.44 – 7.41 (m, 2H), 3.87 (br, s, 1H), 3.83 (s, 6H), 3.09 – 3.06 (m, 2H), 2.51 – 2.48 (m, 2H).

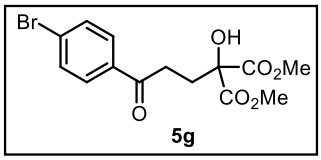
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 197.8, 170.8 (2C), 139.8, 135.0, 129.7 (2C), 129.1 (2C), 78.2, 53.7 (2C), 32.8, 29.3.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3462 (br), 2955 (w), 2855 (w), 1738 (s), 1685 (m), 1441 (m), 1272 (s), 1232 (s), 1128 (s), 1036 (m).

HRMS (ESI): $C_{14}H_{15}ClO_6$ (314.05) calcd.: 353.01888 found: 353.01887, $[M+K]^+$.

m. p.: 82 °C

Dimethyl 2-(3-(4-bromophenyl)-3-oxopropyl)-2-hydroxymalonate (5g)



5g

Dioxane **4g** (11.5 mg, 32.0 µmol, 1.0 eq.) and NEt_3 (4.67 mg, 6.40 µL, 46.1 µmol, 1.20 eq.) were reacted according to **GP4**. Column chromatography (SiO_2, PE/EtOAc 2:1) afforded the desired product **5g** (10.4 mg, 28.9 µmol, 90%) as a white solid.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.83 – 7.80 (m, 2H), 7.61 – 7.58 (m, 2H), 3.87 (br, s, 1H), 3.82 (s, 6H), 3.09 – 3.05 (m, 2H), 2.51 – 2.47s (m, 2H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 198.0, 170.8 (2C), 135.5, 132.1 (2C), 129.8 (2C), 128.5, 78.2, 53.7 (2C), 32.8, 29.3.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3479 (br), 2955 (w), 2852 (w), 1740 (s), 1686 (s), 1441 (m), 1273 (s), 1234 (s), 1128 (s), 1036 (m).

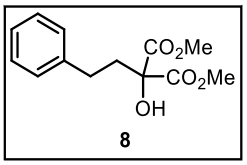
HRMS (ESI): $C_{14}H_{15}BrO_6$ (358.00) calcd.: 380.99442 found: 380.99477, $[M+Na]^+$.

m. p.: 111 °C

7. Synthesis of Follow-up Products

7.1 Products from β-hydroxy ketone 2a

Dimethyl 2-hydroxy-2-phenethylmalonate (8)



8

β-Hydroxy ketone **2a** (100 mg, 376 µmol, 1.0 eq.) and Pd/C (10 wt. % loading, 6 mg, 56.3 µmol, 15 mol%) were evacuated and backfilled with H_2 (3 cycles) before EtOH (5 mL) and EtOAc (1 mL) were added. The reaction mixture was saturated with H_2 gas for 5 min and was stirred for 14 h under an H_2 atmosphere at rt. Filtration through a celite pad and removal of the solvents *in vacuo* afforded product **8** (85 mg, 337 µmol, 90%) as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.26 (m, 2H), 7.21 – 7.16 (m, 3H), 3.84 (br, s, 1H), 3.76 (s, 6H), 2.69 – 2.65 (m, 2H), 2.39 – 2.35 (m, 2H).

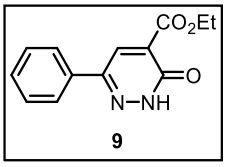
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 171.0 (2C), 140.9, 128.7 (2C), 128.5 (2C), 126.3, 78.7, 53.6 (2C), 36.6, 29.6.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3489 (br), 2955 (w), 2853 (w), 1736 (s), 1438 (m), 1268 (m), 1228 (s), 1201 (s), 1125 (s), 1061 (m).

HRMS (ESI): $C_{13}H_{16}O_5$ (252.09) calcd.: 291.06298 found: 291.06293, $[M+K]^+$.

m. p.: 60 °C

Ethyl 3-oxo-6-phenyl-2,3-dihydropyridazine-4-carboxylate (9)



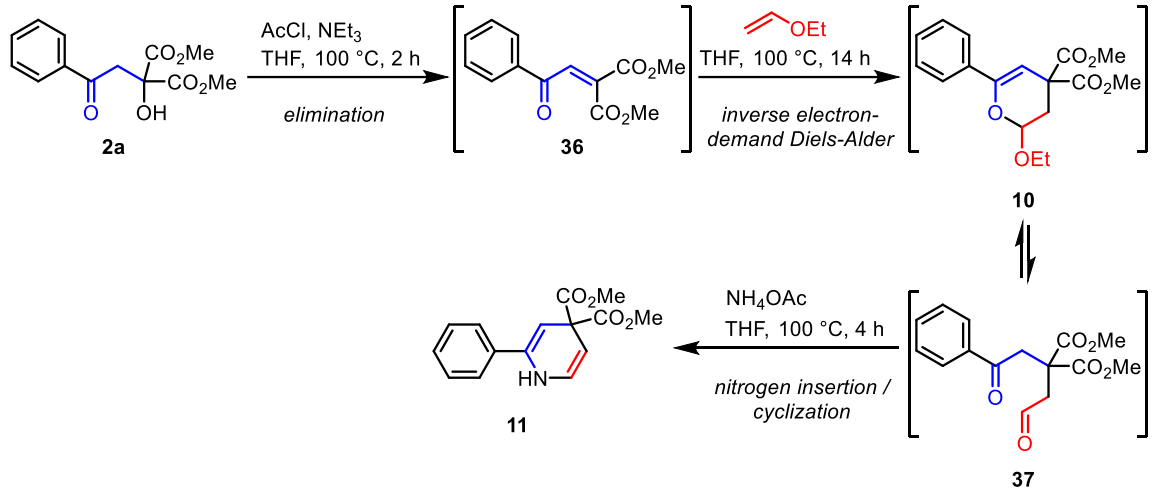
9

In a microwave vial β-hydroxy ketone **1a** (26.2 mg, 100 µmol, 1.0 eq.) and hydrazine hydrochloride (13.7 mg, 200 µmol, 2.0 eq.) were dissolved in EtOH (3 mL). After sealing the vial, the reaction mixture was heated for 24 h at 110 °C. The reaction was stopped by the addition of H_2O and EtOAc at rt and the phases were separated. The aq. phase was extracted with EtOAc (3 × 2 mL) and the organic layer was dried over anhydrous Na_2SO_4.

Purification by column chromatography (SiO_2, PE/EtOAc 2:1) afforded the desired heterocyclic compound **9** (22.3 mg, 91.3 µmol, 81%).

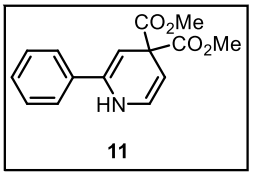
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 12.9 (s, 1H), 8.32 (s, 1H), 7.83 – 7.80 (m, 2H), 7.51 – 7.42 (m, 3H), 4.46 (q, *J* = 7.1 Hz, 1H), 1.43 (t, *J* = 7.1 Hz, 1H).

The analytical data were in accordance with those reported in the literature.[15]



Scheme S5. Sequence leading to the heterocyclic compound **11**.

Dimethyl 2-phenylpyridine-4,4(1*H*)-dicarboxylate (11)



In a capped microwave vial a solution of β-hydroxy ketone **2a** (40.0 mg, 150 µmol, 1.0 eq.), acetyl chloride (59.0 mg, 53.6 µL, 751 µmol, 5.0 eq.) and NEt_3 (152 mg, 210 µL, 1.50 mmol, 10.0 eq.) in THF was stirred at 100 °C for 2 h. After cooling to rt, ethyl vinyl ether (108 mg, 144 µL, 1.50 mmol, 10.0 eq.) was added, the vial was resealed and the resulting mixture was stirred for 14 h at 100 °C. At rt NH_4OAc (115.8 mg, 1.50 mmol, 10 eq.) was added, the vial was again resealed and heated for another 4 h at 100 °C. Removal of the solvents *in vacuo* and subsequent column chromatography (SiO_2, PE/EtOAc 20:1 → 10:1) afforded the desired heterocyclic compound **11** (9 mg, 32.9 µmol, 22% over 3 steps) as a colourless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.22 (br, s, 1H), 7.45 – 7.41 (m, 4H), 7.35 – 7.32 (m, 1H), 6.86 (t, *J* = 2.8 Hz, 1H), 6.50 (t, *J* = 2.8 Hz, 1H) 4.80 (s, 1H), 3.75 (s, 6H).

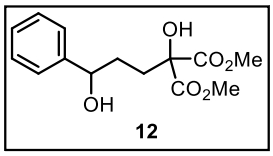
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 169.6 (2C), 132.4, 131.3, 129.1 (2C), 128.0 (2C), 127.6, 118.3, 111.9, 110.6, 52.9 (2C), 49.7.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3375 (br), 2954 (w), 1734 (s), 1684 (w), 1440 (m), 1373 (s), 1304 (m), 1231 (m), 1147 (m), 1022 (m).

HRMS (ESI): $C_{15}H_{15}NO_4$ (273.10) calcd.: 296.08933 found: 296.08919, $[M+Na]^+$.

7.2 Products from dioxane 4a

Dimethyl 2-hydroxy-2-(3-hydroxy-3-phenylpropyl)malonate (12)



12

Dioxane **4a** (12 mg, 43.0 µmol, 1.0 eq.) and Pd/C (10 wt. % loading, 0.60 mg, 6.39 µmol, 16 mol%) were evacuated and backfilled with H_2 (3 cycles) before MeOH (2 mL) was added. The reaction mixture was saturated with H_2 gas for 5 min and was stirred for 17.5 h under an H_2 atmosphere at rt. After filtration through a celite pad and removal of the solvents *in vacuo*, column chromatography (SiO_2, PE/EtOAc 1:1) afforded the desired product **12** (8.20 mg, 29.0 µmol, 68%) as a colourless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.37 – 7.24 (m, 5H), 6.86 (t, *J* = 6.5 Hz, 1H), 3.79 (br, s, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 2.30 – 2.03 (m, 3H), 1.84 – 1.76 (m, 2H), 1.62 (br, s, 1H).

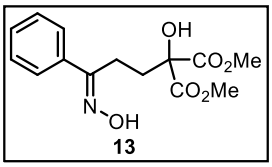
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 171.0, 170.9, 144.2, 128.7 (2C), 127.8, 125.6 (2C), 79.0, 74.2, 53.6, 53.5, 32.9, 31.4.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3383 (br), 2954 (w), 1739 (s), 1492 (w), 1444 (m), 1270 (s), 1231 (s), 1133 (m), 1047 (m), 1022 (w).

HRMS (ESI): $C_{14}H_{18}O_6$ (282.10) calcd.: 321.07350 found: 321.07352, $[M+K]^+$.

7.3 Products from γ-hydroxy ketone 5a

Dimethyl (*E*)-2-hydroxy-2-(3-(hydroxyimino)-3-phenylpropyl)malonate (13)

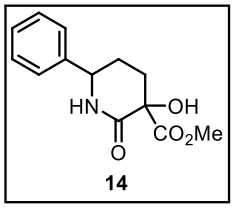


13

Hydroxylamine hydrochloride (27 mg, 390 µmol, 2.0 eq.) was added to a solution of γ-hydroxy ketone **5a** (55 mg, 195 µmol, 1.0 eq.) in pyridine (3 mL) and the resulting mixture was stirred for 21 h at 55 °C. After removal of pyridine *in vacuo,* H_2O and EtOAc were added and the layers were separated. The aq. phase was extracted with EtOAc (2 × 5 mL), the combined organic layers were washed with H_2O (2 × 7 mL) and aq. sat. NaCl solution (7 ml) and were dried over anhydrous Na_2SO_4. Removal of the solvents *in vacuo* and subsequent column chromatography (SiO_2, PE/EtOAc 1:1) afforded a single isomer of oxime **13** (46.7 mg, 158 µmol, 81%) as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.67 – 7.62 (m, 2H), 7.39 – 7.34 (m, 3H), 3.77 (br, s, 6H), 2.83 – 2.79 (m, 2H), 2.20 – 2.16 (m, 2H). No O*H*-signals were observed.
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 172.1 (2C), 158.5, 137.3, 129.9, 129.5 (2C), 127.2 (2C), 80.3, 53.4 (2C), 33.2, 21.1.
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3435 (br), 2955 (w), 1737 (s), 1496 (w), 1444 (m), 1272 (s), 1234 (s), 1133 (s), 985 (m), 932 (m).
HRMS (ESI): $C_{14}H_{17}NO_6$ (295.10) calcd.: 318.09481 found: 318.09481, $[M+Na]^+$.
m. p.: 131 °C

Methyl 3-hydroxy-2-oxo-6-phenylpiperidine-3-carboxylate (14)



14

Oxime **13** (11.1 mg, 37.6 µmol, 1.0 eq.) and Pd/C (10 wt. % loading, 1.00 mg, 9.40 µmol, 25 mol%) were evacuated and backfilled with H_2 (3 cycles) before MeOH (2 mL) was added.

The reaction mixture was saturated with H_2 gas for 5 min and was stirred for 20 h under an H_2 atmosphere at rt. After filtration through a celite pad and removal of the solvents *in vacuo*, column chromatography (SiO_2, PE/EtOAc 1:1) afforded the desired product **14** (7.50 mg, 26.7 µmol, 71%, *d.r.* 9:1) as a colourless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.41 – 7.32 (m, 5H), 6.06 (br, s, 1H), 4.68 – 4.65 (m, 1H), 4.16 (br, s, 1H), 3.87 (s, 3H), 2.42 – 2.37 (m, 1H), 2.27 – 2.22 (m, 1H), 2.13 – 2.06 (m, 1H), 2.05 – 2.02 (m, 1H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 172.4, 170.4, 141.5, 129.1 (2C), 129.5, 126.4 (2C), 74.7, 58.1, 53.4, 30.1, 28.9.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3270 (br), 2928 (w), 1742 (m), 1663 (s), 1446 (m), 1265 (m), 1216 (m), 1185 (s), 1126 (w), 1052 (m).

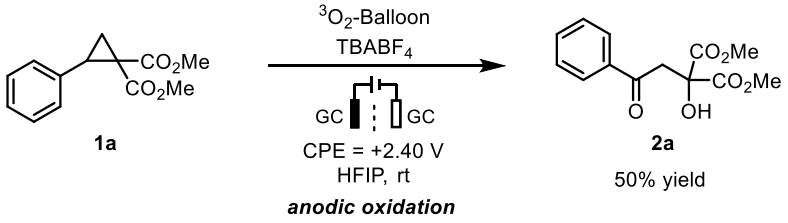
HRMS (ESI): $C_{13}H_{15}NO_4$ (249.10) calcd.: 272.08933 found: 272.08944, $[M+Na]^+$.

8. Mechanistic Experiments

8.1 Divided cell experiments

All divided cell experiments were performed in an IKA Pro-Divide cell. In all cathodic reduction and anodic oxidation reactions, the working chamber (marked with W) was filled with starting material, supporting electrolyte solution (4.5 mL, 0.02 M) and a mediator if needed. The counter chamber (marked with C) was filled with supporting electrolyte solution (4.5 mL, 0.02 M) only. For anodic oxidations positive potentials (working electrode as anode) and for cathodic reductions (working electrode as cathode) negative potentials were applied. Exact reaction conditions are given in the following procedures.

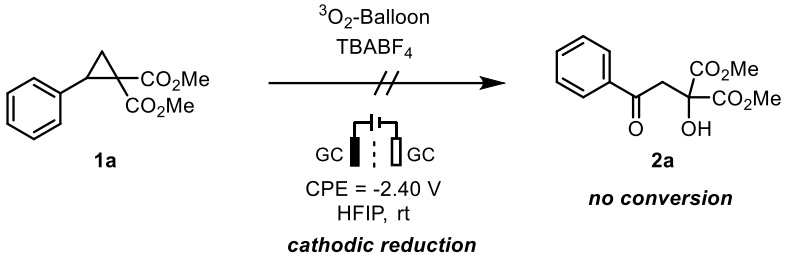
Anodic oxidation of CP 1a



1a **2a** 50% yield

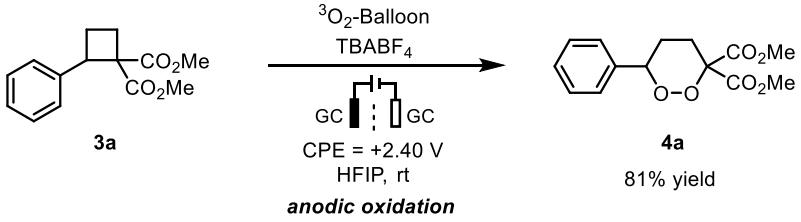
Cyclopropane **1a** (35.1 mg, 150 µmol, 1.00 eq.) and TBABF$_4$ (0.02 M) were filled in the working chamber of an IKA Pro-Divide and were dissolved in HFIP (4.5 mL). The solution was saturated with oxygen for 5 min. The counter chamber was filled with a solution of TBABF$_4$ (0.02 M) in HFIP (4.5 mL). The solutions were electrolyzed at a glassy carbon anode and a glassy carbon cathode at a constant potential of **+2.40 V** for 22 h. The resulting mixture from the working chamber was concentrated *in vacuo* and adsorbed on silica gel. Purification by column chromatography (SiO$_2$, PE/EtOAc 3:1) afforded **2a** (18.7 mg, 74.8 µmol, 50%) as a white solid.

Cathodic reduction of CP 1a



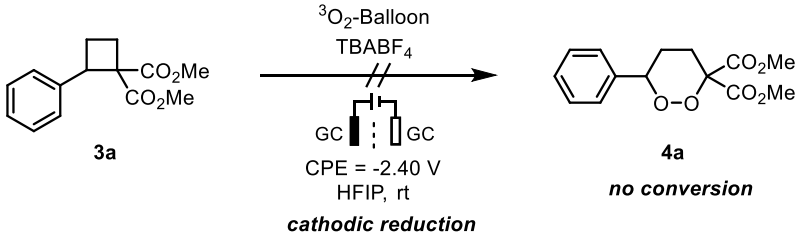
Cyclopropane **1a** (35.1 mg, 150 µmol, 1.00 eq.) and $TBABF_4$ (0.02 M) were filled in the working chamber of an IKA Pro-Divide and were dissolved in HFIP (4.5 mL). The solution was saturated with oxygen for 5 min. The counter chamber was filled with a solution of $TBABF_4$ (0.02 M) in HFIP (4.5 mL). The solutions were electrolyzed at a glassy carbon anode and a glassy carbon cathode at a constant potential of **–2.40 V** for 3 h. No conversion of starting material **1a** was observed.

Anodic oxidation of CB 3a



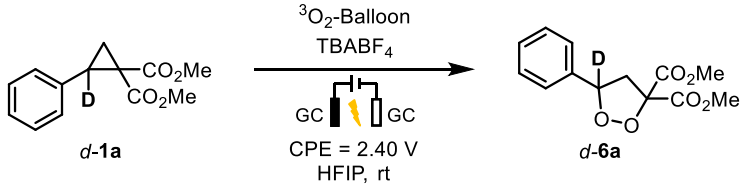
Cyclobutane **3a** (10.8 mg, 43.5 µmol, 1.00 eq.) and $TBABF_4$ (0.02 M) were filled in the working chamber of an IKA Pro-Divide and were dissolved in HFIP (4.5 mL). The solution was saturated with oxygen for 5 min. The counter chamber was filled with a solution of $TBABF_4$ (0.02 M) in HFIP (4.5 mL). The solutions were electrolyzed at a glassy carbon anode and a glassy carbon cathode at a constant potential of **+2.40 V** for 14 h. The resulting mixture from the working chamber was concentrated *in vacuo* and adsorbed on silica gel. Purification by column chromatography (SiO_2, PE/EtOAc 3:1) afforded **4a** (9.88 mg, 35.2 µmol, 81%) as a yellow oil.

Cathodic reduction of CB 3a



Cyclobutane **3a** (10.6 mg, 42.7 µmol, 1.00 eq.) and $TBABF_4$ (0.02 M) were filled in the working chamber of an IKA Pro-Divide and were dissolved in HFIP (4.5 mL). The solution was saturated with oxygen for 5 min. The counter chamber was filled with a solution of $TBABF_4$ (0.02 M) in HFIP (4.5 mL). The solutions were electrolyzed at a glassy carbon anode and a glassy carbon cathode at a constant potential of **–2.40 V** for 3 h. No conversion of starting material **3a** was observed.

8.2 Conversion of deuterated compounds and dioxolane precursors



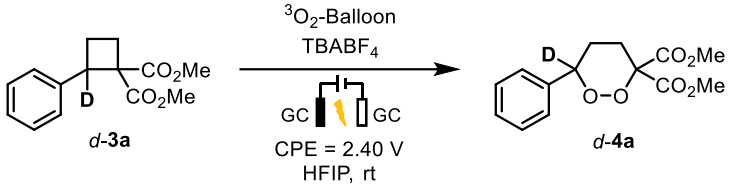
Deuterated cyclopropane *d*-**1a** (22.8 mg, 97.0 µmol, 1.0 eq.) was reacted for 16 h according to **GP2-A**. Column chromatography (SiO_2, PE/EtOAc 4:1) afforded the desired product *d*-**6a** (10 mg, 37.8 µmol, 39%) as a colourless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.42 – 7.33 (m, 5H), 3.88 (s, 3H), 3.86 (s, 3H), 3.54 (d, *J* = 12.9 Hz, 1H), 3.29 (d, *J* = 12.9 Hz, 1H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 167.2, 167.0, 135.0, 129.3, 129.9 (2C), 127.4 (2C), 88.3, 83.5 (t, *J* = 22.4 Hz, 1C), 53.8, 53.7 49.5.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2957 (w), 2853 (w), 1745 (s), 1494 (w), 1442 (m), 1280 (s), 1202 (m), 1082 (m), 1000 (w), 756 (m).

HRMS (GC/EI): $C_{13}H_{13}DO_6$ (267.08) calcd.: 267.08531 found: 267.08535.



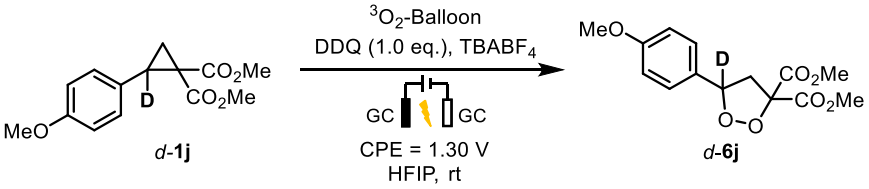
Deuterated cyclobutane *d*-**3a** (19.5 mg, 78.0 µmol, 1.0 eq.) was reacted for 15.5 h according to **GP3**. Column chromatography (SiO_2, PE/EtOAc 4:1) afforded the desired product *d*-**4a** (17.9 mg, 63.2 µmol, 81%) as a yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.36 – 7.28 (m, 5H), 3.88 (s, 3H), 3.83 (s, 3H), 2.74 (ddd, *J* = 13.4, 4.7, 2.6 Hz, 1H), 2.41 – 2.32 (m, 1H), 2.18 (ddd, *J* = 13.4, 12.3, 5.0 Hz, 1H), 2.08 – 2.01 (m, 1H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 167.3, 166.8, 137.2, 129.2, 128.7 (2C), 127.5 (2C), 85.7, 82.7 (t, *J* = 22.6 Hz, 1C), 53.5, 53.4, 28.2, 26.4.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2954 (w), 2854 (w), 1746 (s), 1495 (w), 1440 (m), 1263 (s), 1217 (m), 1068 (m), 1007 (m), 734 (s).

HRMS (ESI): $C_{14}H_{15}DO_6$ (281.10) calcd.: 304.09019 found: 304.09023, $[M+Na]^+$.



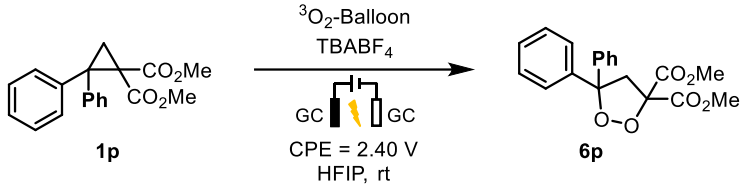
Deuterated cyclopropane *d*-**1j** (26.9 mg, 102 µmol, 1.0 eq.), DDQ (23.3 mg, 103 µmol, 1.01 eq.) and additional H_2O (18 mg, 18 µL, 1.00 mmol, 10.0 eq.) were provided with 3.90 F/mol and reacted according to **GP2-B**. Column chromatography (SiO_2, PE/EtOAc 4:1) afforded the desired product *d*-**1j** (21.4 mg, 72.0 µmol, 71%) as a colourless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.35 – 7.32 (m, 2H), 6.91 – 6.88 (m, 2H), 3.87 (s, 3H), 3.87 (s, 3H), 3.80 (s, 3H), 3.45 (d, *J* = 12.9 Hz, 1H), 3.29 (d, *J* = 12.9 Hz, 1H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 168.1, 167.0, 160.5, 129.2 (2C), 126.1, 114.4 (2C), 88.4, 83.5 (t, *J* = 23.4 Hz, 1C), 55.5, 53.8, 53.8, 49.1.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2925 (w), 2849 (w), 1745 (s), 1514 (w), 1445 (m), 1249 (s), 1184 (m), 1088 (m), 1029 (w), 726 (m).

HRMS (ESI): $C_{14}H_{15}DO_7$ (297.09) calcd.: 336.05904 found: 336.05903.



Cyclopropane **1p** (100 mg, 322 µmol, 1.0 eq.) was reacted for 17 h according to **GP2-A**. Column chromatography (SiO_2, PE/EtOAc 10:1) afforded the desired product **6p** (36.6 mg, 107 µmol, 33%) as a white solid.

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.41 – 7.39 (m, 4H), 7.35 – 7.32 (m, 4H), 7.29 – 7.27 (m, 2H), 3.96 (s, 2H), 3.70 (s, 3H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ = 167.4 (2C), 140.3 (2C), 128.6 (4C), 128.3 (2C), 126.8 (4C), 91.8, 88.6, 54.2, 53.7 (2C).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2955 (w), 2854 (w), 1749 (s), 1493 (w), 1443 (m), 1277 (s), 1168 (m), 1070 (m), 755 (m), 700 (m).

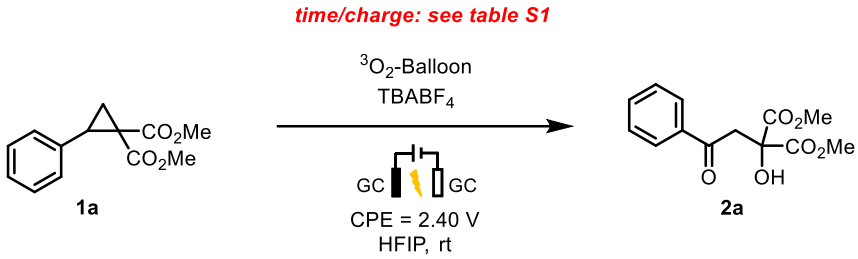
HRMS (ESI): $C_{19}H_{18}O_6$ (342.11) calcd.: 365.09956 found: 365.09956, $[M+Na]^+$.

m. p.: 91 °C

8.3 Chain propagation experiments

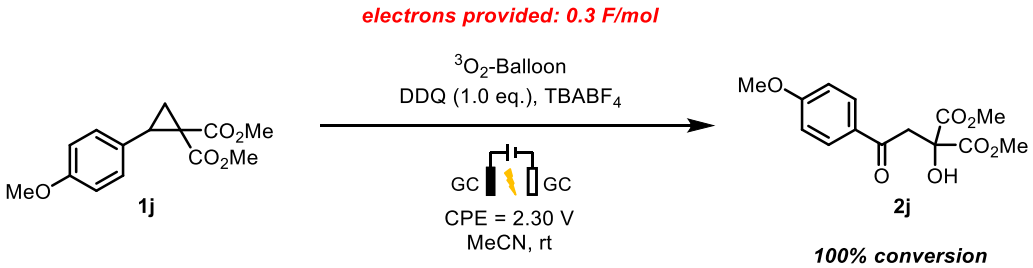
All chain propagation experiments were performed according to **GP2-A** for cyclopropane **1a** and according to **GP2-B** for cyclopropane **1j** in scales of 150 µmol. In order to separate supporting electrolyte from the reaction mixtures, the crude material was pressed through a SiO_2 pad flushing with pentane/ethyl acetate (1:1, 350 mL). All conversion were determined by ^{1}H-NMR spectroscopy after removal of $TBABF_4$ salt. Table S1 shows the results from the time/charge-based conversion of the phenyl cyclopropane **1a** (**GP2-A**). The given theoretical charge value is the amount of coulombs that are needed to reach the observed conversion in a stoichiometric process.

Table S1. Charge-based conversions of **1a** to **2a**.



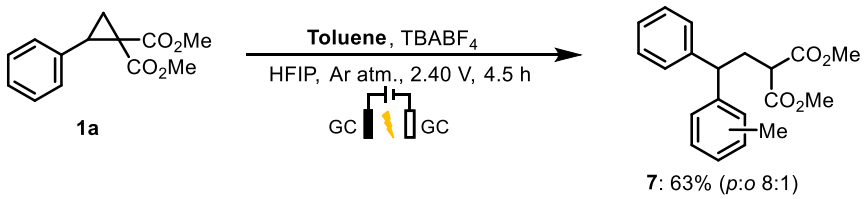
Entry	*Charge Q* [F per mol **1a**]	*Charge Q* [C]	*t* [min]	*observed conv.* [µmol] (%)	*theoretical conv.* [µmol] (%)	*theoretical charge for observesd conv.* [C]
1	0	0	0	0	0	0
2	0.004	0.058	10	34.5 (23)	0.60 (0.04)	3.33
3	0.05	0.72	120	144 (96)	7.50 (5)	13.90
4	**0.1**	**1.45**	**240**	**150 (100)**	**15 (10)**	**14.48**
5	0.3	4.34	720	150 (100)	45 (30)	14.48
6	0.5	7.24	1200	150 (100)	75 (50)	14.48
7	1.0	14.48	2400	150 (100)	150 (100)	14.48

Since the time-based experiments for the conversion of cyclopropane **1a** gave clear indication (see table S1, entry 3 and 4) for chain propagation, cyclobutane **3a** and cyclopropane **1j** were reacted under standard conditions (**GP3** for **3a** and **GP2-B** for **1j**). A total charge of 0.3 F/mol **1j**/**3a** was provided. Also for these reactions a conversion of 100% was observed, indicating that the mediated mechanism is also proceeding via chain propagation.



Scheme S6. Charge-based experiment for cyclopropane **1j**. A total charge of 0.3 F/mol of **1j** was provided.

8.4 Intermediate trapping



In a 5 mL ElectraSyn vial cyclopropane **1a** (24.32 mg, 103 µmol, 1.00 eq.) and $TBABF_4$ (0.03 M) were dissolved in HFIP (4.5 mL; degassed, stored over molecular sieves) and the solution was saturated with argon for 5 minutes. The solution was electrolyzed at a glassy carbon anode and a glassy carbon cathode at a constant potential of +2.40 V for 4.5 h. The reaction mixture was concentrated *in vacuo* and the remaining residue was adsorbed on silica gel. Purification by column chromatography (SiO_2, PE/EtOAc 20:1) afforded **7** (21.4 mg, 64.9 µmol, 63%; *p:o* 8:1) as a colourless oil.

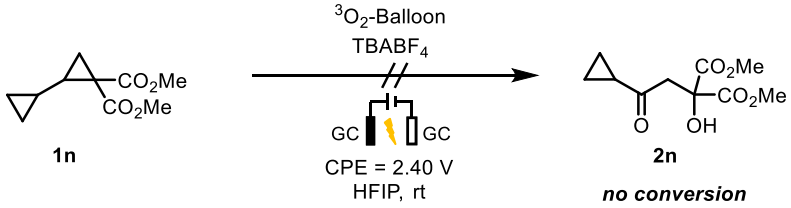
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.30 – 7.26 (m, 2H), 7.24 – 7.22 (m, 2H), 7.20 – 7.16 (m, 1H), 7.13 – 7.08 (m, 4H), 3.91 (t, *J* = 8.1 Hz, 1H), 3.70 (s, 6H), 3.91 (t, *J* = 7.4 Hz, 1H), 2.67 – 2.64 (m, 2H), 2.30 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 169.9, 169.9, 143.7, 140.4, 136.3, 129.5 (2C), 128.7(2C), 127.9 (2C), 127.9 (2C), 126.6, 52.7 (2C), 50.2, 48.4, 34.6, 21.1.

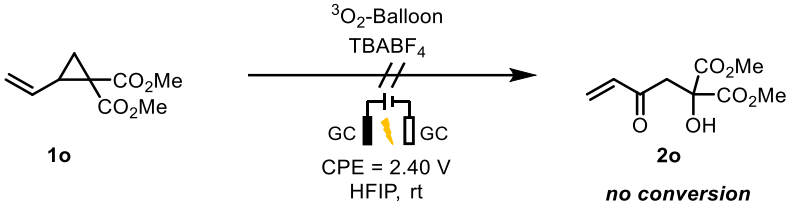
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2953 (w), 1739 (s), 1504 (w), 1442 (m), 1340 (w), 1279 (m), 1230 (m), 1153 (s), 1018 (m), 703 (m).

HRMS (ESI): $C_{20}H_{22}O_4$ (326.15) calcd.: 349.14103 found: 349.14116, $[M+Na]^+$.

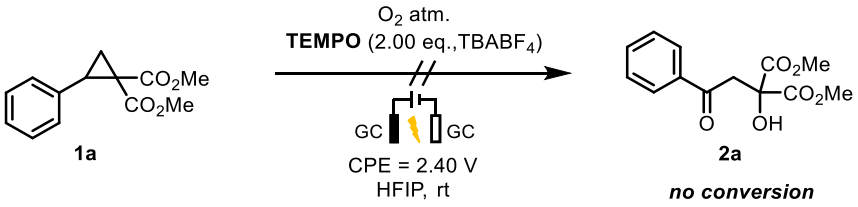
8.5 Inhibition experiments



Cyclopropane **1n** (29.7 mg, 150 µmol, 1.0 eq.) was reacted according to **GP2-A** or **GP2-B**. No conversion of the starting material was observed for either reaction after electrolyzing the solution overnight.



Cyclopropane **1o** (27.6 mg, 150 µmol, 1.0 eq.) was reacted according to **GP2-A** or **GP2-B**. No conversion of the starting material was observed for either reaction after electrolyzing the solution overnight.



In a 5 mL ElectraSyn vial Cyclopropane **1a** (24.5 mg, 105 µmol, 1.0 eq.), TBABF$_4$ (0.02 M) and TEMPO (33.2 mg, 213 µmol, 2.03 eq.) were dissolved in HFIP (4.5 mL) and the resulting solution was left open to air. The reaction mixture was electrolyzed at a glassy carbon anode and a glassy carbon cathode at a constant potential of +2.40 V for 16 h. No conversion of the starting material was observed after reacting for 16 h.

9. Cyclic Voltammetry

The cyclic voltammograms shown in Fig. 1S were recorded using the following conditions: *v* = 100 mv/S, c (cyclopropane) = 0.01 M, *C* (supporting electrolyte $TBABF_4$) = 0.1 M in HFIP or MeCN (stored over molecular sieves and under argon atmosphere).

Ferrocene was added as an internal standard and oxidation potentials were calculated using the local maxima or the points of inflection respectively and are corrected against Fc/Fc^+.

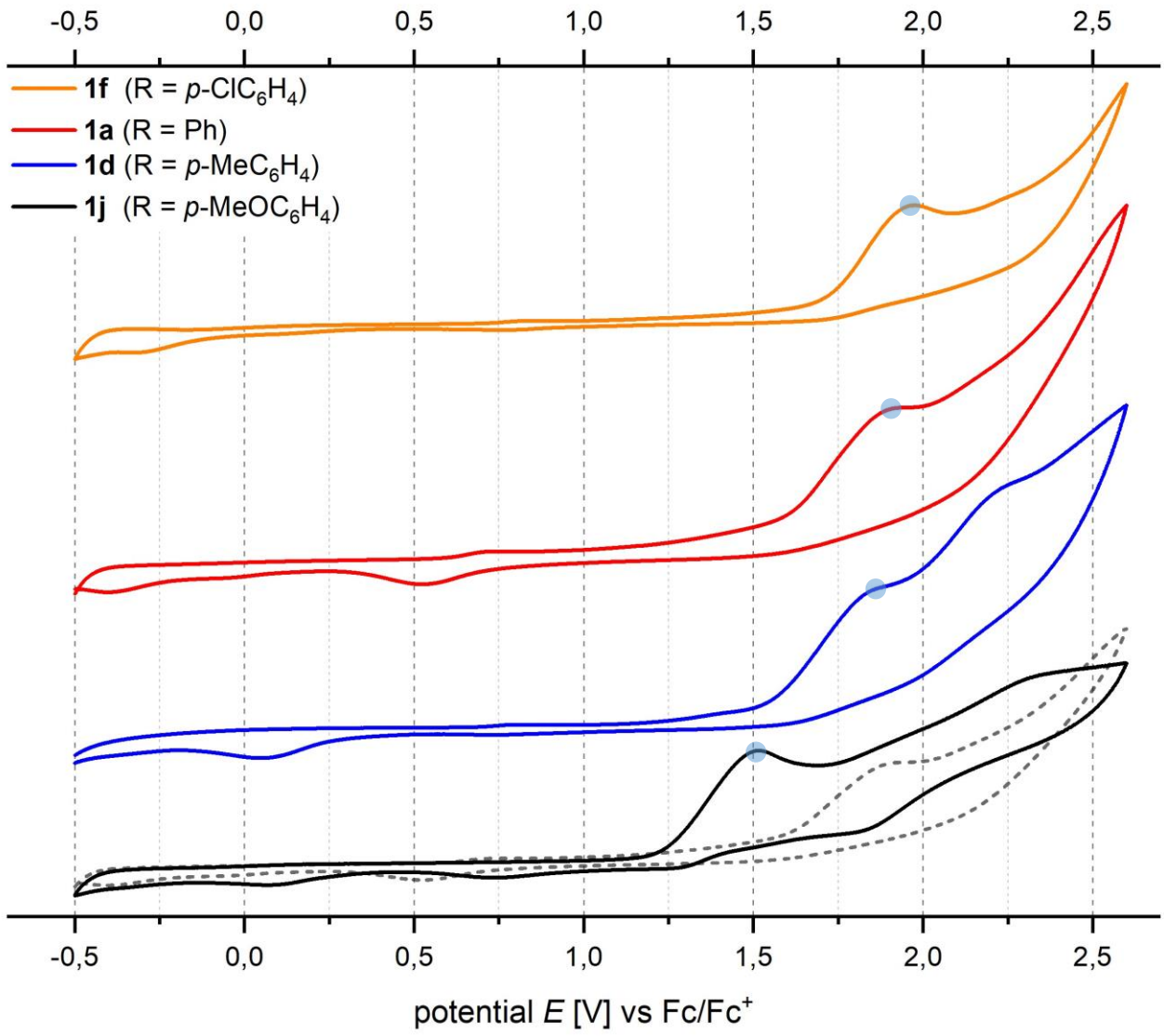


Fig. S1. Cyclic voltammograms for **1fa** (orange), **1a** (red), **1d** (blue), **1j** (black) in HFIP and for **1j** (dashed grey) in MeCN. The depicted voltammograms were obtained using a silver wire reference electrode and are not corrected against the Fc/Fc^+ values.

The cyclic voltammograms give evidence that an irreversible oxidation of cyclopropanes **1** takes place. Since electron-rich arene donors should be easier to oxidize, we expected the

oxidation potentials to shift significantly for different cyclopropanes. As shown in Fig. S1 and table S2 the received data ($E_{ox,1/2}$ ranging from 1.80 – 1.13V) is in accordance with our expectations.

Table S2. Oxidation potentials ($E_{1/2}$ and E_{max}) for **1a**, **1f**, **1d** and **1j** derived from cyclic voltammogram data and corrected against Fc/Fc^+ values.

Oxidation potentials corrected against Fc/Fc^+	**1f** (*p*-ClC_6H_4)	**1a** (Ph)	**1d** (*p*-MeC_6H_4)	**1j** (*p*-$OMeC_6H_4$ in HFIP)	**1j** (*p*-$OMeC_6H_4$ in MeCN)
E_{max} [V]	1.80	1.79	1.74	1.41	1.13
$E_{1/2}$ [V]	1.67	1.65	1.55	1.37	0.95

10. Computational Data

10.1 DFT Calculations

Geometry optimizations of intermediates and Nudged Elastic Band (NEB) calculations for finding the minimum energy path and the saddle point between two minimum structures were performed with ORCA 4.2.1[16] using density-functional theory (DFT) with the TPSSh functional [17] and a def2-TZVP basis set [18]. The conductor-like polarizable continuum model (CPCM)[19] was applied to add implicit solvent. HFIP was used for direct electrolysis (ε = 6.7; r = 3.47) and acetronitrile for mediated electrolysis (ε = 36.6; r = 2.75).

Frequency calculations were performed for each stationary point to confirm that it is a local minimum or first-order saddle point, respectively. NEB was performed using the climbing image method[20] and 15 intermediate images. Shown enthalpies consist of the electronic energy, the zero point energy, thermal vibrational, rotational and translational corrections and a thermal enthalpy correction as provided by ORCA for T = 298.15 K.

Löwdin charges[21] were evaluated to investigate charge distributions within the molecule. For this, the molecule is split into three parts (Fig. S2) and the atomic partial Löwdin charges are summed up for each part to then evaluate the contribution to the total charge deviation compared to the neutral reactant.

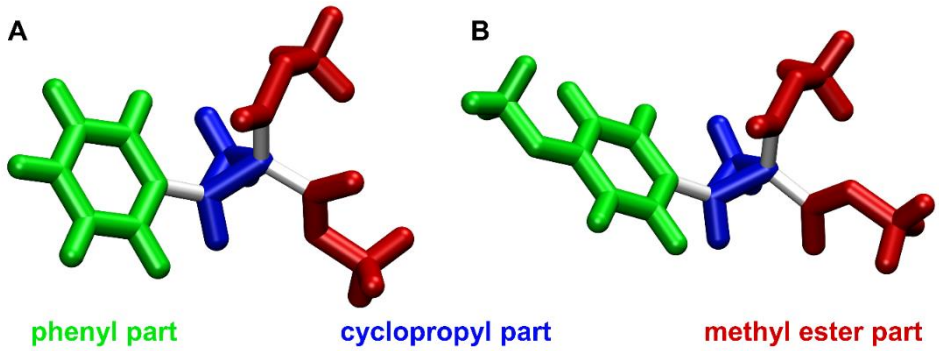


Fig S2. Molecule partitioning for the evaluation of the contribution to the total charge deviation for the direct electrolysis with reactant **1a** (A) and mediated electrolysis with intermediate **1j** (B).

10.2 Supplementary tunneling calculations

After purification dioxolane **6a** by column chromatography the isomerized species **2a** is isolated which results from a ring-opening due to hydrogen transfer. Starting from the deuterated species, this isomerization is not observed and product **6a** is isolated. The very high reaction barrier of 51.33 kcal/mol obtained in the quantum-chemical calculations is an indicator for a possible hydrogen tunneling mechanism through this barrier.

Regarding the dioxane species, here the closed-ring product **4a** represents the isolated product after purification for both the hydrogenated and deuterated species. In this case, a hydrogen transfer and the resulting acyclic isomer **5a** can only be achieved by NEt_3-assisted isomerization with an again high calculated activation barrier of 53.56 kcal/mol.

To get evidence for the hypothesis that tunneling might play a role for this reaction step we applied the Wentzel-Kramers-Brillouin approach (WKB) approximation[22] as described in the review by Kästner[23], which provides the tunneling probability through a potential barrier for certain tunneling energies,

$$\kappa(E_{pt}) = \frac{1}{1 + e^{2\theta(E_{pt})/\hbar}}$$

where the barrier penetration integral is given by

$$\theta(E_{pt}) = \int_{r_a}^{r_b} \sqrt{2m\big(V(r) - E_{pt}\big)dr}$$

The tunneling pre-tunneling energy E_{pt} has to be reached in the so-called pre-tunneling state which represents a molecular configuration favorable for tunneling.[24]

To calculate these tunneling probabilities, the reaction barriers **6a** → **2a** (dioxolane) and **4a** → **5a** (1,2-dioxane) were fitted with a 10th order polynomial (Fig. S3). Note that we only considered the minimum energy paths obtained from the NEB calculations and did not attempt to find the most likely tunneling path.[23] Both barriers share a similar height but the dioxane barrier is broader. This is also reflected when looking at the calculated tunneling probabilities with different pre-tunneling energies (Fig. S4). Because of the barrier width for the dioxane much higher pre-tunneling energies have to be reached to achieve a reasonable tunneling probability compared to the dioxolane species.

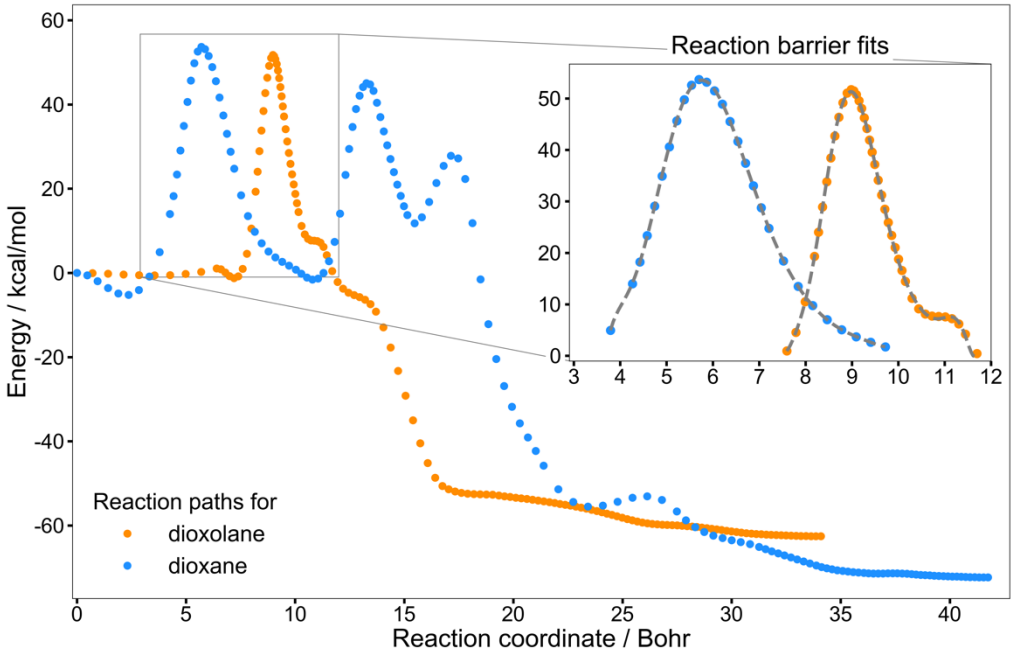


Fig. S3. Minimum energy paths for reaction step F gained from NEB calculations with ORCA for the dioxolane (orange) and the dioxane (blue). Box shows the main reaction barriers with polynomial fits.

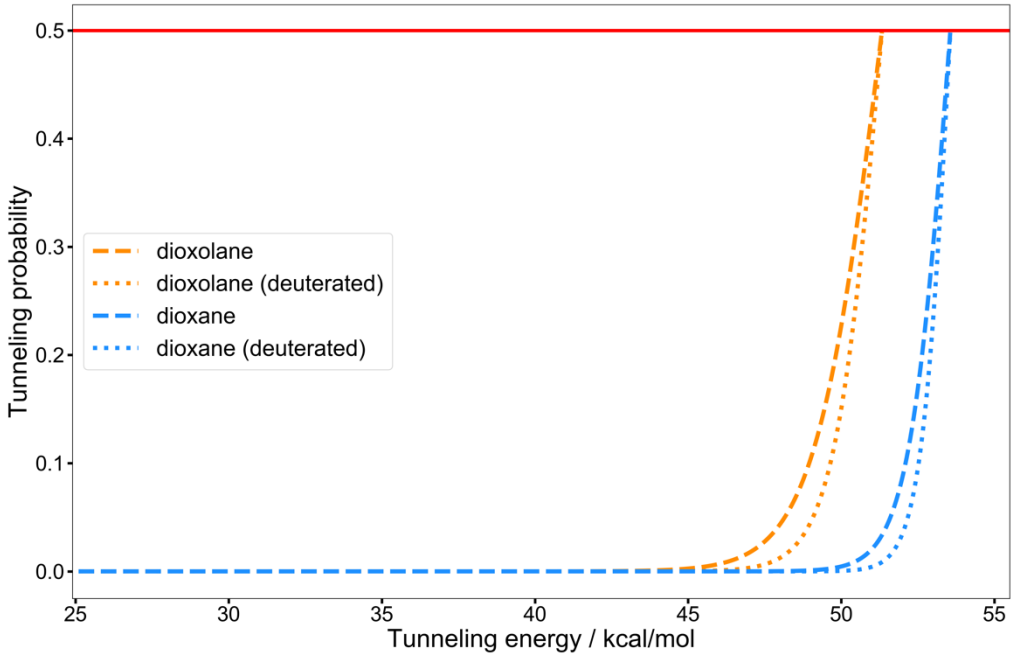


Fig. S4. Tunneling probabilities calculated via WKB approximation for the reaction barriers of the hydrogenated and deuterated dioxolane (orange) and dioxane (blue) species. Maximum tunneling probability 0.5 in the WKB approach indicating the maximum of the reaction barrier is marked by a red line.

To make a statement about the possibility of tunneling in this special case, we employ the following simple model: First, we assume that a pre-tunneling state is thermally populated, i.e., the rate at which the pre-tunneling energy E_{pt} is reached can be calculated as

$$k_1 = A \cdot e^{-\frac{E_{pt}}{R \cdot T}},$$

where the pre-exponential factor A for calculation of reaction rates was set to $10^{12.6}$ s^{-1},[25] R is the ideal gas constant and T is the temperature (298.15 K). To calculate the overall reaction rate for a given pre-tunneling energy E_{pt}, k_1 is multiplied by the tunneling probability κ. Figure S5 plots the resulting overall reaction rates as functions of the pre-tunneling energy.

The maxima of these curves indicate the pre-tunneling energy that yield the largest overall reaction rate when tunneling is considered, whereas the end points of the curves (corresponding to a tunneling energy that is equal to the barrier height) are the reaction rates that are obtained if no tunneling is considered. Simply speaking, the lower the pre-tunneling energy at the maximum, the larger is the overall importance of tunneling for the considered reaction.

For the hydrogenated dioxolane species **6a** an optimal pre-tunneling energy of about 15 kcal/mol is found, for which tunneling increases the overall reaction rate by 9 orders of magnitude. However, this optimal pre-tunneling energy for the deuterated species is much higher with about 28 kcal/mol, with an overall reaction rate that is six orders of magnitude smaller than for the non-deuterated species. This is consistent with the observation that such an isomerization is not found in experiment. For the dioxane **4a**, already in the hydrogenated case the optimal pre-tunneling energy is at approximately 40 kcal/mol, and tunneling only leads to an approximately 8-fold increase of the overall reaction rate. For the deuterated dioxane, the optimal pre-tunneling energy is almost as large as the overall barrier height, i.e., tunneling is not possible in this case.

While we are well aware for the limitations of the simple model we have applied here, the results indicate that a hydrogen tunneling mechanism for the isomerization while purification seems reasonable.

All plots were prepared in Jupyter notebooks using Python and Matplotlib.[26]

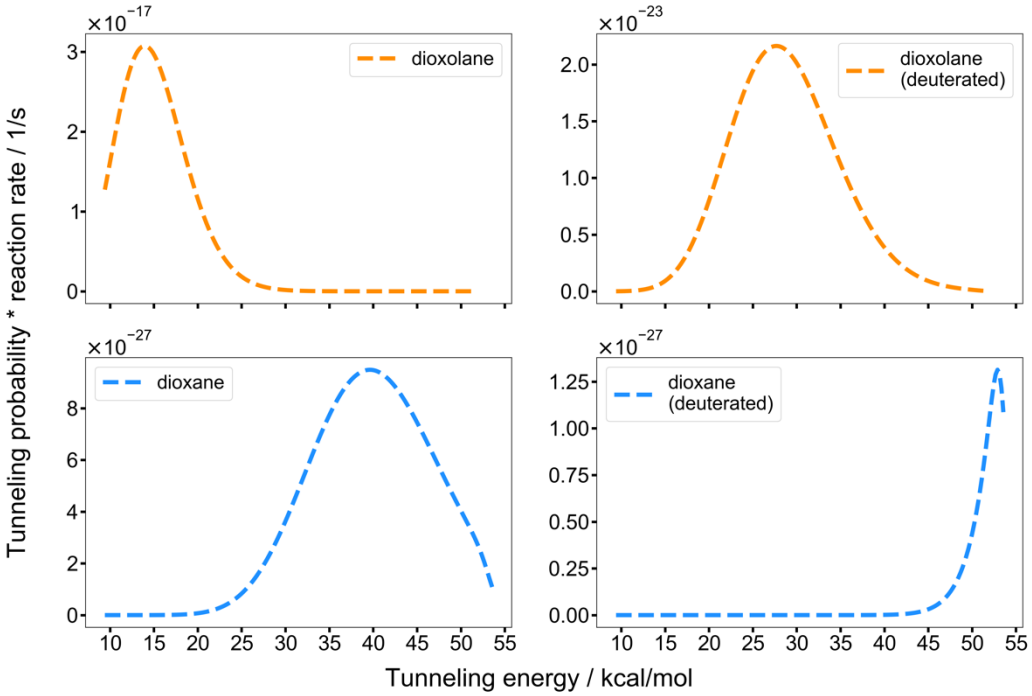


Fig. S5. Reaction rates weighted by tunneling probabilities for hydrogenated and deuterated dioxolane (orange) and dioxane (blue) species. Maxima indicate minimum energy to be reached before tunneling to achieve a positive effect on the reaction rate by hydrogen tunneling.

10.3 Provided files

Coordinates of the optimized intermediates are provided in .xyz files named after the given numbers.

xyz-Coordinates for **1a**

C	-3.37640338717252	-0.15040480550470	0.33396507818104
C	-4.70097445601874	0.19156731972175	0.62043355777160
C	-5.46033582353314	-0.57848828037825	1.49576205539050
C	-4.91106485203786	-1.70971115743943	2.09442247909406
C	-3.59537935989556	-2.06615455798706	1.80811862165150
C	-2.83694851657493	-1.29224680163305	0.93574862455708
H	-5.15649494467438	1.06196632828853	0.16153217246655
H	-6.48599329003432	-0.29623140884633	1.70526494078247
H	-5.50547470365820	-2.31133428138735	2.77313791820399
H	-3.15919481802873	-2.94898760277114	2.26187017184151
H	-1.81360418677733	-1.57656238560884	0.71442103291421
C	-2.51898378618634	0.62218471050201	-0.60882395683315
C	-2.09417171130215	2.08955601012934	-0.34463633645425
H	-2.05594636994308	4.74726030349741	-0.92347332498442

C	-0.67963814056258	2.45689227979577	-0.64192102897572
O	-0.02222398140786	3.20546590286192	0.05885856454376
O	-0.21665113278601	1.87724473396295	-1.75354107670983
C	1.16208409172464	2.17183223561320	-2.09837197659485
C	-2.60370872620606	2.80077983774140	0.88972252005778
O	-2.57462752436692	2.31153837193169	1.99572895381345
O	-3.10402889538539	4.04215406951986	0.75165346093673
C	-3.06476969744154	4.74868506226432	-0.51415372077427
H	-1.70445901152876	0.04318967274774	-1.02737136527175
H	-2.63960434023355	1.80522550806773	-2.48522316841481
H	-3.77226540246864	4.31325372282322	-1.21782047923951
H	-4.06413495551448	2.01142025434413	-1.36257636434706
H	-3.36152501470002	5.76554414419953	-0.27072336924199
H	1.27784689565304	3.24146465594011	-2.26777614382251
H	1.34721132434258	1.61070373753164	-3.00963491357068
H	1.82031928294114	1.84312033636465	-1.29547881781945
C	-3.02849240622223	1.71681004370720	-1.47958977915197

xyz-Coordinates for intermediate **I**

C	-3.326409	-0.149837	0.342385
C	-4.620295	0.296751	0.765485
C	-5.367050	-0.467516	1.621057
C	-4.856165	-1.695499	2.090811
C	-3.584661	-2.159267	1.679945
C	-2.835628	-1.405892	0.817267
H	-5.020718	1.231194	0.397081
H	-6.347558	-0.138054	1.937471
H	-5.448378	-2.294918	2.772093
H	-3.214831	-3.105927	2.050793
H	-1.861093	-1.742596	0.487615
C	-2.497111	0.579636	-0.584972
C	-2.177304	2.118456	-0.392944
H	-1.990877	4.903429	-0.848124
C	-0.737743	2.487486	-0.651657
O	-0.156256	3.289409	0.049366
O	-0.229208	1.861880	-1.701224
C	1.162817	2.158579	-2.021374
C	-2.733767	2.821453	0.839435
O	-2.813697	2.281775	1.918663
O	-3.142772	4.081787	0.696472

C	-3.036432	4.804651	-0.563098
H	-1.638294	0.040415	-0.960531
H	-2.630835	1.667364	-2.503742
H	-3.617930	4.309174	-1.338008
H	-4.107331	1.870867	-1.432976
H	-3.457342	5.782000	-0.347950
H	1.262024	3.219072	-2.244797
H	1.379251	1.549674	-2.893253
H	1.792244	1.881544	-1.177592
C	-3.046288	1.670650	-1.504174

xyz-Coordinates for intermediate **II**

C	-3.314332	-0.237635	0.662208
C	-4.668810	0.146235	0.416787
C	-5.688618	-0.524658	1.045394
C	-5.392356	-1.580840	1.923242
C	-4.074206	-1.974846	2.185444
C	-3.040669	-1.311280	1.567997
H	-4.887702	0.960973	-0.260171
H	-6.719544	-0.246342	0.869632
H	-6.207070	-2.103223	2.411537
H	-3.877593	-2.792082	2.866962
H	-2.009814	-1.591990	1.748458
C	-2.232130	0.361745	0.041731
C	-1.300365	2.547480	-0.605044
H	-3.083430	5.292687	1.730583
C	0.157918	2.376159	-0.746187
O	0.999865	3.162744	-0.359787
O	0.439993	1.201315	-1.337158
C	1.849801	0.905227	-1.512984
C	-1.843617	3.825933	-0.098018
O	-1.284550	4.900229	-0.189105
O	-3.055836	3.646934	0.447091
C	-3.701157	4.845381	0.952977
H	-1.246503	-0.007353	0.313783
H	-1.867580	0.962577	-1.898315
H	-3.851114	5.550512	0.136485
C	-2.249612	1.433437	-0.978911
H	-4.650432	4.504294	1.355385
H	2.303479	1.661770	-2.152033

H	1.873544	-0.071918	-1.986443
H	2.343605	0.884892	-0.542307
H	-3.245675	1.819807	-1.172891

xyz-Coordinates for intermediate **III**

C	-3.368585	-0.697229	1.132526
C	-4.731259	-0.340098	1.386234
C	-5.579684	-1.261223	1.946322
C	-5.101751	-2.542426	2.273988
C	-3.771852	-2.917907	2.042195
C	-2.909661	-2.010671	1.476028
H	-5.091562	0.648196	1.134864
H	-6.613487	-1.008752	2.141770
H	-5.782525	-3.258257	2.720482
H	-3.434572	-3.910999	2.307265
H	-1.876019	-2.268689	1.279949
C	-2.454560	0.161284	0.554204
C	-1.547235	2.508881	0.392421
H	-3.442803	6.028028	-0.433902
C	-0.205280	2.026272	-0.189889
O	0.553574	1.309628	0.417063
O	-0.057372	2.471882	-1.425412
C	1.161262	2.059276	-2.119458
C	-1.830037	3.972450	-0.016197
O	-1.152035	4.886040	0.386978
O	-2.866480	4.061647	-0.832932
C	-3.207357	5.403764	-1.293885
H	-1.450620	-0.232442	0.411206
H	-2.781934	1.471204	-1.023126
H	-2.367905	5.816750	-1.850348
C	-2.700269	1.536138	0.072599
H	-4.075044	5.264077	-1.930941
H	2.023563	2.442852	-1.578052
H	1.080514	2.506280	-3.104369
H	1.190469	0.972866	-2.176206
H	-3.633996	1.957775	0.437530
O	-2.353497	3.008125	2.488138
O	-1.318708	2.500476	1.849331

xyz-Coordinates for intermediate **IV**

C	-3.131731	-0.589312	1.206753
C	-4.018628	0.082519	2.086844
C	-5.024786	-0.619995	2.720485
C	-5.146777	-1.994091	2.500423
C	-4.254516	-2.669323	1.642253
C	-3.239288	-1.975141	1.015268
H	-3.907660	1.145915	2.263190
H	-5.708832	-0.111737	3.387660
H	-5.929886	-2.552464	2.999001
H	-4.371025	-3.733230	1.478381
H	-2.542963	-2.483639	0.359607
C	-2.065750	0.181239	0.505880
C	-1.596960	2.498620	0.084414
H	-4.235360	5.494616	-0.667086
C	-0.229519	2.590846	-0.648018
O	0.301799	3.646455	-0.887971
O	0.242622	1.385794	-0.908017
C	1.565890	1.330571	-1.526536
C	-2.276511	3.877183	0.095051
O	-2.401595	4.557699	1.081896
O	-2.700241	4.154562	-1.125745
C	-3.352236	5.448199	-1.301400
H	-1.351756	-0.470941	0.003898
H	-2.371358	1.123043	-1.430744
H	-2.650467	6.239359	-1.044229
C	-2.505672	1.351428	-0.376945
H	-3.618161	5.482060	-2.352910
H	1.529858	1.840585	-2.486996
H	1.769821	0.271634	-1.647127
H	2.287854	1.801817	-0.862575
H	-3.548847	1.610083	-0.198940
O	-1.293108	0.805750	1.604078
O	-1.316265	2.187895	1.471025

xyz-Coordinates for **6a**

C	-4.40798366907674	-1.42352228868840	-0.40732987511894
C	-5.46059554375528	-2.33583120333868	-0.31195966120103
C	-5.24668770860204	-3.69418365336482	-0.53482744464333
C	-3.97430329398176	-4.15189549003084	-0.86492206395870

C	-2.91763451823248	-3.24765815776514	-0.96301153970403
C	-3.12994961884115	-1.89308507392199	-0.72966597096804
H	-6.45482266160590	-1.97986846320280	-0.06090244275215
H	-6.07319961666119	-4.39139072981625	-0.45405137790257
H	-3.80443289574360	-5.20786621340215	-1.04413132103413
H	-1.92501706969382	-3.60012706593060	-1.22048623679706
H	-2.30165500849907	-1.19784429750226	-0.80961141326463
C	-4.68852175889029	0.04468244496582	-0.20290829268494
O	-0.75350519510591	1.08531400823328	-0.54466668443957
C	-3.05101792961734	1.81504016150447	-0.26982852716715
C	-1.52793112918537	1.87518507297612	-0.06047299143855
C	-3.66125928918466	3.23632084294374	-0.27942525174777
O	-1.20682477616151	2.87417585428843	0.75527906037185
O	-4.25636553080654	3.55178825496274	0.86789296350777
C	0.20510908560277	2.99518679836442	1.09051720483593
C	-4.82811177463649	4.88644547068697	0.94028596466133
H	-2.94880945569974	0.13181077438209	1.11332537114796
O	-3.58620991543737	3.96459731622427	-1.24275430987595
H	-5.60002592908238	4.99295756124540	0.17963600779993
H	-4.04438053535555	5.62776290000892	0.79119261940633
H	-5.24965719248194	4.95639198128278	1.93863587980270
H	0.54035577190993	2.08329570028400	1.58228740399711
H	0.25923285211422	3.84666759774162	1.76216774539640
H	0.77863111708844	3.17162645051229	0.18232974211703
O	-3.25133173878984	1.23098897511635	-1.55074293940305
C	-3.70062085623187	0.80635623716179	0.70634848532155
H	-4.20189949243354	1.30992866465579	1.52764520627859
O	-4.63857527709876	0.78111050006735	-1.46091575582251
H	-5.71956580582305	0.18289154935524	0.12719905527964

xyz-Coordinates for **2a**

C	-4.08203840644541	-1.39359496803499	-0.75889816268480
C	-3.65132794768051	-2.11839692438026	0.35965914573214
C	-4.08974665609194	-3.42276070802365	0.56104804803956
C	-4.95571921820406	-4.01606430400975	-0.35433302407180
C	-5.38860890359507	-3.30174708159487	-1.47241185667521
C	-4.95700087469552	-1.99851975008650	-1.67183135534265
H	-2.97786300089237	-1.67213776649007	1.08086805529006
H	-3.75398858252298	-3.97591760485100	1.43041437226840
H	-5.29339597124229	-5.03440964224967	-0.19809797236970
H	-6.06145994392867	-3.76452386850310	-2.18510024159988

H	-5.28650741241933	-1.43190275761985	-2.53425638235080
C	-3.64739538668248	0.00737460058595	-1.01171497037377
O	-0.05236390722958	2.99594775629513	0.17102600343128
C	-2.09730718570915	1.96657769973228	-0.57043083130749
C	-1.16221670382594	2.60988139927397	0.47862482512526
C	-3.20656834118015	3.00574232269936	-0.88446548586658
O	-1.69603869884559	2.69621358858371	1.68468536867094
O	-4.20103140455541	2.94638216371879	0.00126644765307
C	-0.86797267340472	3.31364401534215	2.71087083105682
C	-5.26894899037072	3.90965586612144	-0.18386299528277
H	-0.52576878652590	2.27215598354302	-1.63197975862204
O	-3.12712584496480	3.81167933104879	-1.78204955436662
H	-5.74259746381675	3.74889650417752	-1.15164148816069
H	-4.86860293522324	4.92111439442153	-0.12492411921349
H	-5.96608806703688	3.71828114960469	0.62688006430080
H	0.04248054357925	2.73087743212373	2.84073146067484
H	-1.47768296040578	3.29435339489797	3.60893345088936
H	-0.62857232734785	4.33468659824578	2.41848298922841
O	-1.33361160501774	1.73437386819758	-1.72641437688158
C	-2.65368125871493	0.63773117517582	-0.04909793612652
H	-3.14678699789313	0.78262371803927	0.91501314155296
O	-4.08595886416582	0.64730526211565	-1.95663196292331
H	-1.81327852294446	-0.04086336810044	0.11426205030579

xyz-Coordinates for **1j**

C	-2.974057	-0.480146	0.152398
C	-4.365592	-0.533544	0.181474
C	-5.051198	-1.251115	1.161535
C	-4.333652	-1.940804	2.138119
C	-2.933462	-1.906847	2.118685
C	-2.271856	-1.187150	1.139019
H	-4.948968	-0.023670	-0.576922
H	-6.133181	-1.270930	1.144545
O	-4.904120	-2.675495	3.135827
H	-2.382057	-2.451412	2.876899
H	-1.186356	-1.172318	1.136686
C	-2.213857	0.254039	-0.898299
C	-1.968787	1.782033	-0.831411
H	-2.413886	4.214178	-1.817464
C	-0.615940	2.204873	-1.297655
O	-0.002047	1.663444	-2.195101

O	-0.160956	3.259658	-0.606591
C	1.148436	3.758702	-0.987119
C	-2.549320	2.576360	0.313727
O	-2.413820	2.258094	1.474696
O	-3.245262	3.696104	0.041070
C	-3.374519	4.215724	-1.305935
H	-1.327244	-0.260371	-1.253993
H	-2.476422	1.167282	-2.903212
H	-4.111000	3.639210	-1.863343
H	-3.920040	1.340117	-1.793914
H	-3.721511	5.237589	-1.175245
H	1.897403	2.985564	-0.820910
H	1.320206	4.614021	-0.340294
H	1.137692	4.056930	-2.034477
C	-2.857979	1.153165	-1.890412
C	-6.335295	-2.748825	3.170921
H	-6.722349	-3.206045	2.256302
H	-6.772031	-1.755367	3.302526
H	-6.573616	-3.375014	4.028053

xyz-Coordinates for intermediate **V**

C	-3.371889	0.023348	0.947878
C	-4.416634	-0.065527	1.874026
C	-5.159822	-1.228935	2.011618
C	-4.857915	-2.347394	1.227523
C	-3.818748	-2.278886	0.296493
C	-3.094667	-1.096134	0.162142
H	-4.649629	0.788067	2.503101
H	-5.968550	-1.291537	2.731274
O	-5.624176	-3.456520	1.440932
H	-3.567547	-3.130939	-0.321390
H	-2.288623	-1.058869	-0.563026
C	-2.545546	1.274910	0.839370
C	-1.541148	3.010146	-0.763372
H	-2.414294	5.905166	1.837433
C	-0.362063	2.751421	-1.542246
O	0.567388	3.517854	-1.805821
O	-0.341953	1.466418	-2.042863
C	0.815041	1.130223	-2.819847
C	-1.733443	4.315231	-0.196562
O	-1.000649	5.304155	-0.255192

O	-2.925528	4.391628	0.493006
C	-3.194914	5.655235	1.117101
H	-2.848154	2.008831	1.588896
H	-2.459141	1.167338	-1.316687
H	-3.264647	6.449886	0.371864
H	-3.585149	2.364651	-0.670170
H	-4.150573	5.529096	1.623030
H	0.910349	1.790631	-3.683275
H	0.655171	0.103747	-3.145384
H	1.721198	1.197453	-2.214669
C	-2.578844	1.948704	-0.568086
C	-5.315182	-4.634687	0.685292
H	-4.292248	-4.965347	0.884731
H	-5.445565	-4.455901	-0.385422
H	-6.021051	-5.390154	1.023590
O	-1.183305	0.903888	1.126605
O	-0.457550	2.048900	1.345522

xyz-Coordinates for intermediate **VI**

C	-3.231505	-0.243041	0.042250
C	-4.603911	0.140302	0.106180
C	-5.537809	-0.620815	0.777873
C	-5.163411	-1.807729	1.428070
C	-3.824894	-2.217643	1.390798
C	-2.890510	-1.450395	0.714464
H	-4.924402	1.057574	-0.371681
H	-6.577087	-0.311300	0.817382
O	-6.163445	-2.488171	2.066641
H	-3.509965	-3.128702	1.883271
H	-1.856883	-1.782343	0.692362
C	-2.237203	0.492573	-0.639205
C	-1.526931	2.897229	-0.884922
H	-3.414842	4.520594	2.237503
C	-0.169372	2.977967	-1.292647
O	0.706938	3.800471	-0.985282
O	0.166151	1.948415	-2.170831
C	1.520361	1.951699	-2.632978
C	-2.038180	3.841341	0.045789
O	-1.473200	4.810052	0.575607
O	-3.370444	3.596038	0.364202
C	-3.958100	4.514612	1.290511

H	-1.224834	0.097014	-0.602858
H	-2.162607	1.586147	-2.458682
H	-3.974810	5.528396	0.883784
H	-3.453690	2.089334	-1.382304
H	-4.976163	4.158910	1.444800
H	1.747029	2.865978	-3.186174
H	1.603957	1.087664	-3.291755
H	2.220389	1.856056	-1.800253
C	-2.412892	1.768989	-1.406268
C	-5.812374	-3.697194	2.749442
H	-5.086371	-3.498695	3.542688
H	-5.406019	-4.434584	2.051805
H	-6.739559	-4.068703	3.180634

xyz-Coordinates for intermediate **VII**

C	-3.308869	-0.204033	1.191462
C	-4.641590	-0.026919	1.571186
C	-5.551544	-1.075670	1.521770
C	-5.136330	-2.339437	1.093810
C	-3.806191	-2.537290	0.715281
C	-2.910434	-1.470921	0.768926
H	-4.975488	0.946742	1.916916
H	-6.583765	-0.932368	1.821818
O	-6.092447	-3.318691	1.085762
H	-3.461309	-3.508226	0.384571
H	-1.875888	-1.635805	0.488749
C	-2.313465	0.956589	1.256860
C	-0.868682	2.527263	0.007677
H	-3.505829	5.307368	1.492172
C	-0.264361	2.981454	-1.344398
O	0.146963	4.107164	-1.555539
O	-0.137466	1.976412	-2.218150
C	0.575020	2.286641	-3.441918
C	-1.474830	3.806079	0.656162
O	-1.060750	4.336933	1.663028
O	-2.535150	4.262291	-0.033591
C	-3.153103	5.468900	0.473952
H	-2.823649	1.783754	1.789608
H	-1.532542	0.622936	-0.724834
H	-2.434781	6.288742	0.455430
H	-2.846110	1.823701	-0.688009

H	-3.985129	5.668149	-0.196128
H	0.056547	3.077106	-3.983705
H	0.573001	1.360870	-4.011696
H	1.593472	2.596485	-3.208998
C	-1.963858	1.451299	-0.160727
C	-5.692725	-4.633207	0.681183
H	-4.915215	-5.024455	1.343313
H	-5.333019	-4.631294	-0.351226
H	-6.588101	-5.246872	0.759092
O	-1.162625	0.557922	1.900196
O	0.180242	2.036480	0.717414

xyz-Coordinates for **6j**

C	-3.44553870218367	-0.19960059124812	1.20570690088133
C	-4.34696122530827	-0.52078395074136	2.22623116675234
C	-5.01591223107486	-1.73464343602622	2.23350387906706
C	-4.78011291643903	-2.66757898582610	1.21727701500917
C	-3.87760852238910	-2.36435651832273	0.19284761500456
C	-3.22404438983543	-1.13568888990565	0.19532403478414
H	-4.52675991135906	0.19020703099255	3.02612286918343
H	-5.71601949503733	-1.98006607035437	3.02386258188494
O	-5.46694941842036	-3.83876774793853	1.30824114191986
H	-3.67879021576411	-3.07212181639575	-0.60104582980746
H	-2.52210377893733	-0.91937681619951	-0.60257051431611
C	-2.71277748086081	1.11192990671065	1.24726427933083
C	-1.41250599596251	2.76138953512538	0.10613014242177
H	-3.13375336722797	6.38806278685016	0.81831680695608
C	-0.49188822947832	2.74007075455959	-1.12846854832965
O	0.28739909823708	3.63611075264740	-1.37788837458821
O	-0.58943458404871	1.60372628843329	-1.80842046611848
C	0.34444612850042	1.43425789284473	-2.90981627852299
C	-1.60362565056488	4.22145453102577	0.55288763223907
O	-1.19895562314046	4.68142456635473	1.59436556587144
O	-2.29233165685190	4.89087971582696	-0.36802457511596
C	-2.53729368900111	6.29655038557224	-0.08835087898694
H	-3.02585338031770	1.68870252564233	2.12289547029018
H	-2.73707787531689	1.37381606297471	-0.90772233168549
H	-1.58754359775080	6.81646986377662	0.02605267572222
H	-3.60144035931283	2.65021879864571	-0.03153457867987
H	-3.08250080699939	6.66215737054721	-0.95357838771038
H	0.19015895215798	2.22460284782959	-3.64298195977061

H	0.10819147632907	0.46039085255971	-3.32833714090079
H	1.36437643790533	1.46074561663200	-2.52896553845339
C	-2.73984196562784	1.98571278623602	-0.00866213230688
C	-5.23140655673752	-4.83511945987734	0.30237746044222
H	-4.18122899070939	-5.13749513430920	0.29787747569857
H	-5.51818742861418	-4.46398196094131	-0.68443055846049
H	-5.85950427478043	-5.67880528021220	0.57925447087352
O	-1.30381518658080	0.80985503759136	1.37400106446574
O	-0.66280511649672	2.10574217891965	1.15767420495524

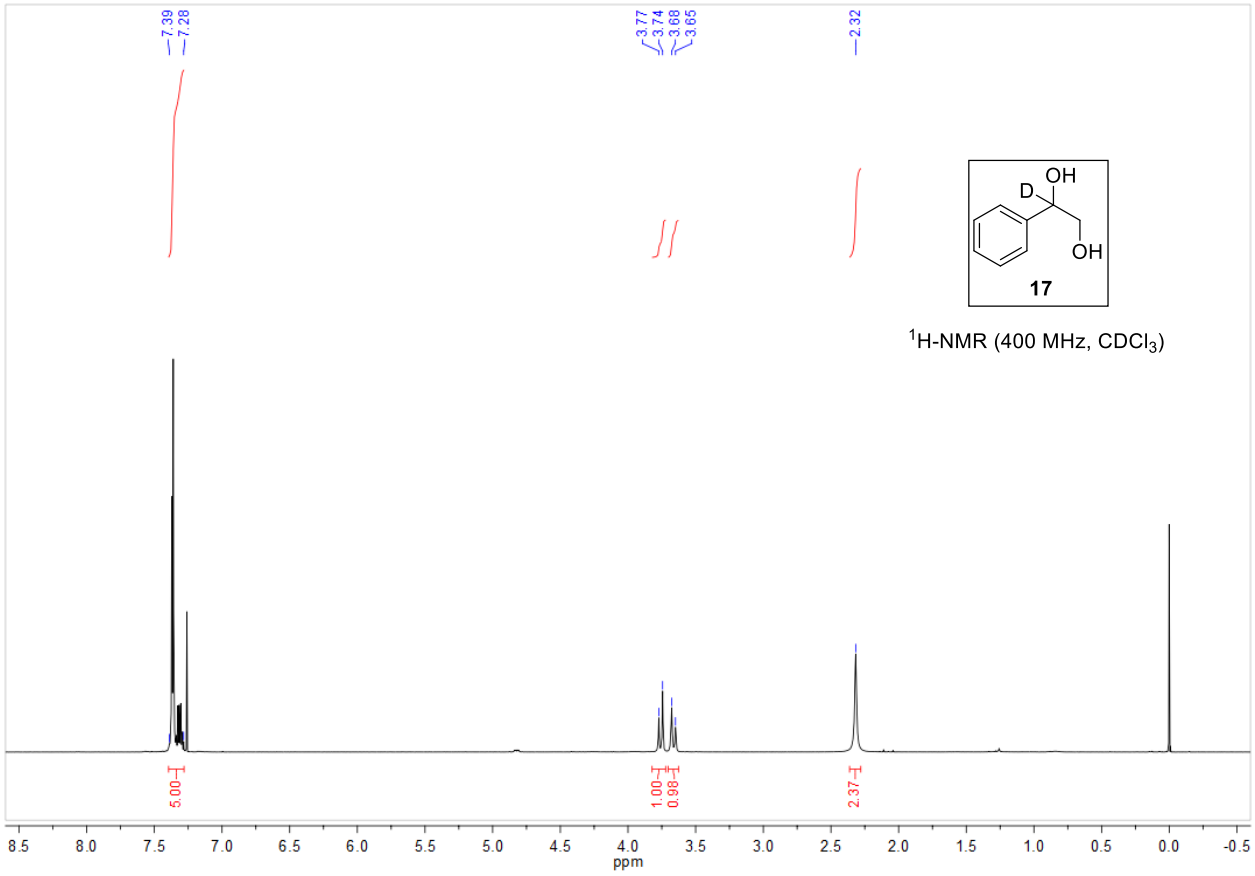
10.4 Energies from DFT calculations

Table S3. Calculated enthalpies and electronic energies.

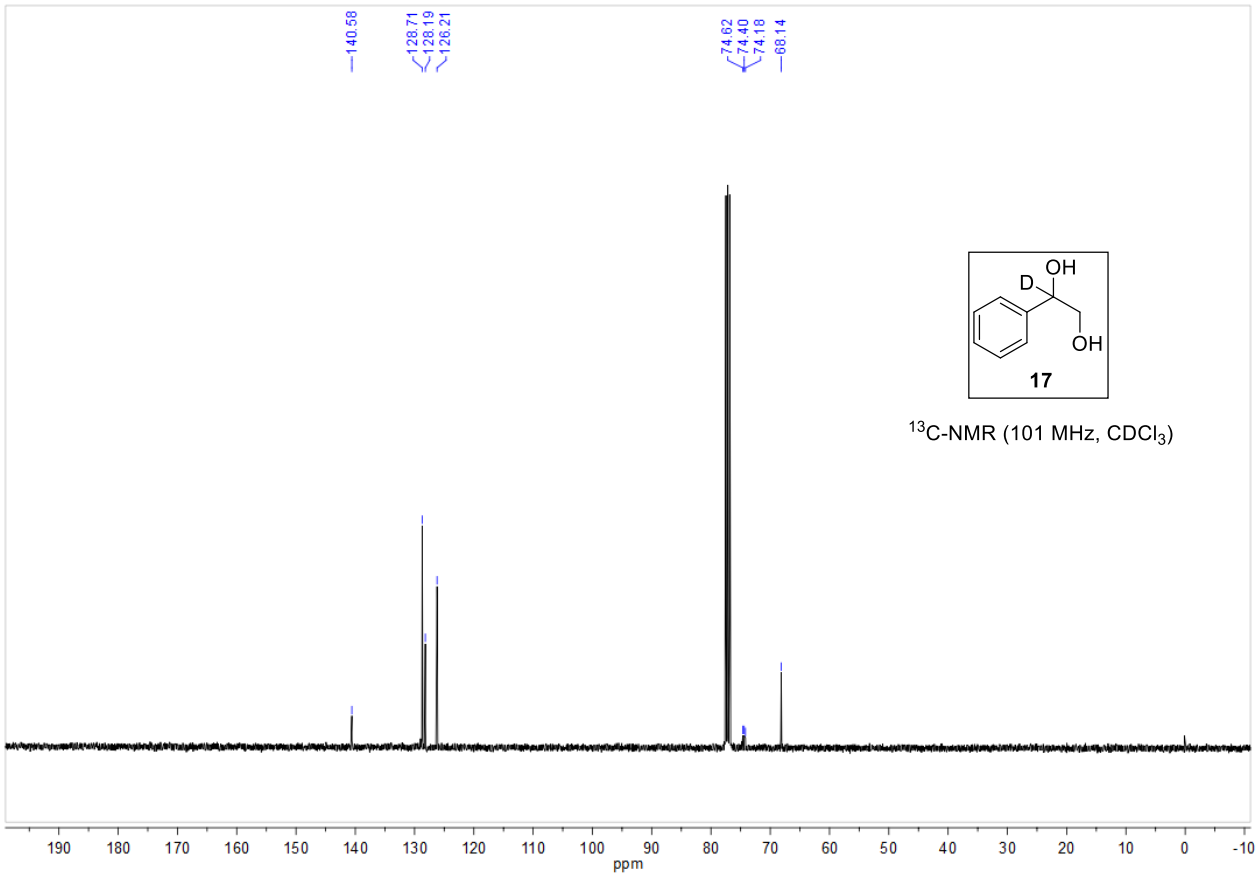
Compound	Enthalpy [kcal/mol]	Electronic energy [Hartree]
1a	-505004.1	-805.051
1j	-576880.6	-919.629
2a	-599462.9	-955.593
6a	-599400.7	-955.495
6j	-671278.4	-1070.073
I	-504856.8	-804.815
II	-504860.7	-804.822
III	-599236.3	-955.231
IV	-599236.3	-955.254
V	-576953.7	-919.741
VI	-671342.3	-1069.869
VII	-671371.2	-1070.219
$^3O_2$	-94366.0	-150.391

11. NMR Data for Synthesized Compounds

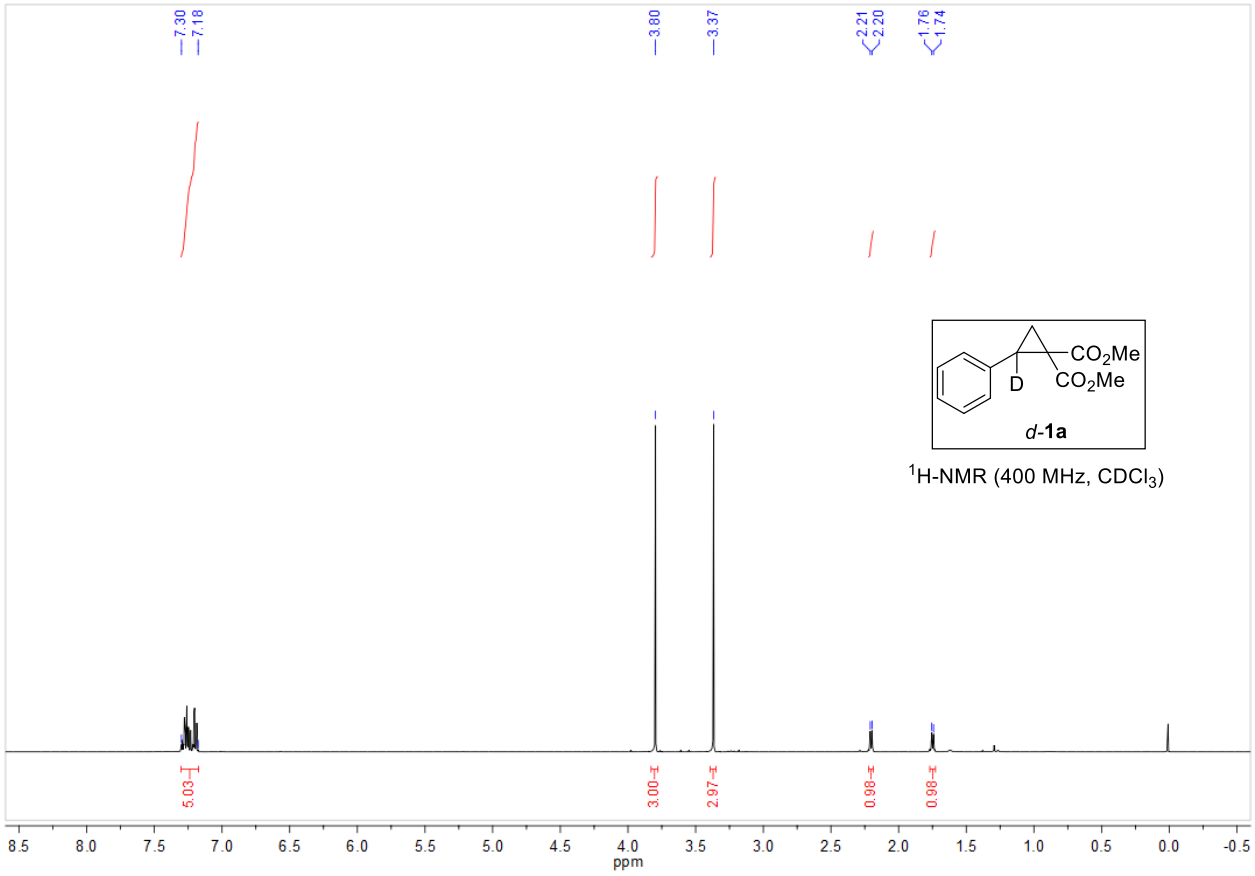
^{1}H, ^{13}C and ^{19}F spectra of compounds that have not been reported in the literature are shown in this chapter. All spectra are marked with the corresponding molecule structure, the frequency and the used deuterated solvent.



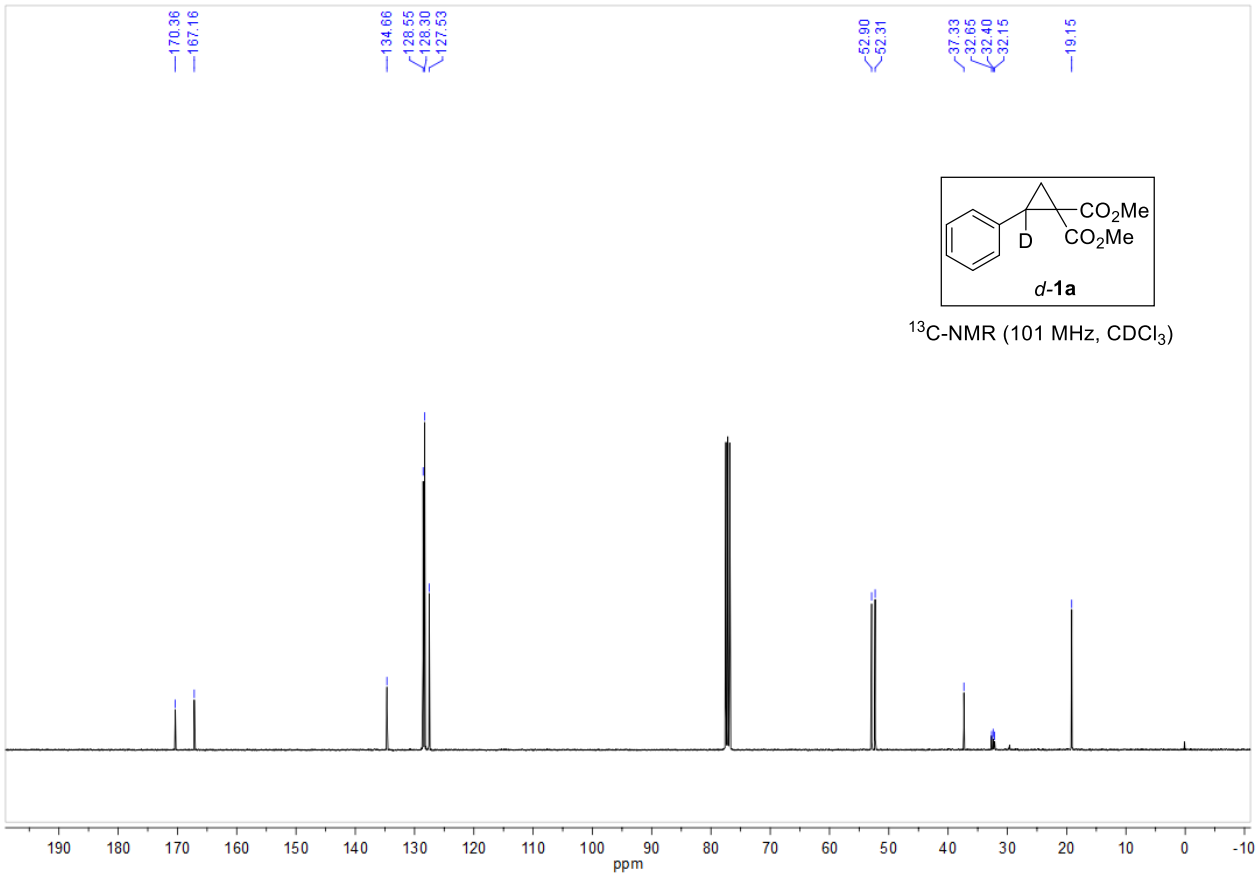
^{1}H-NMR (400 MHz, $CDCl_3$)



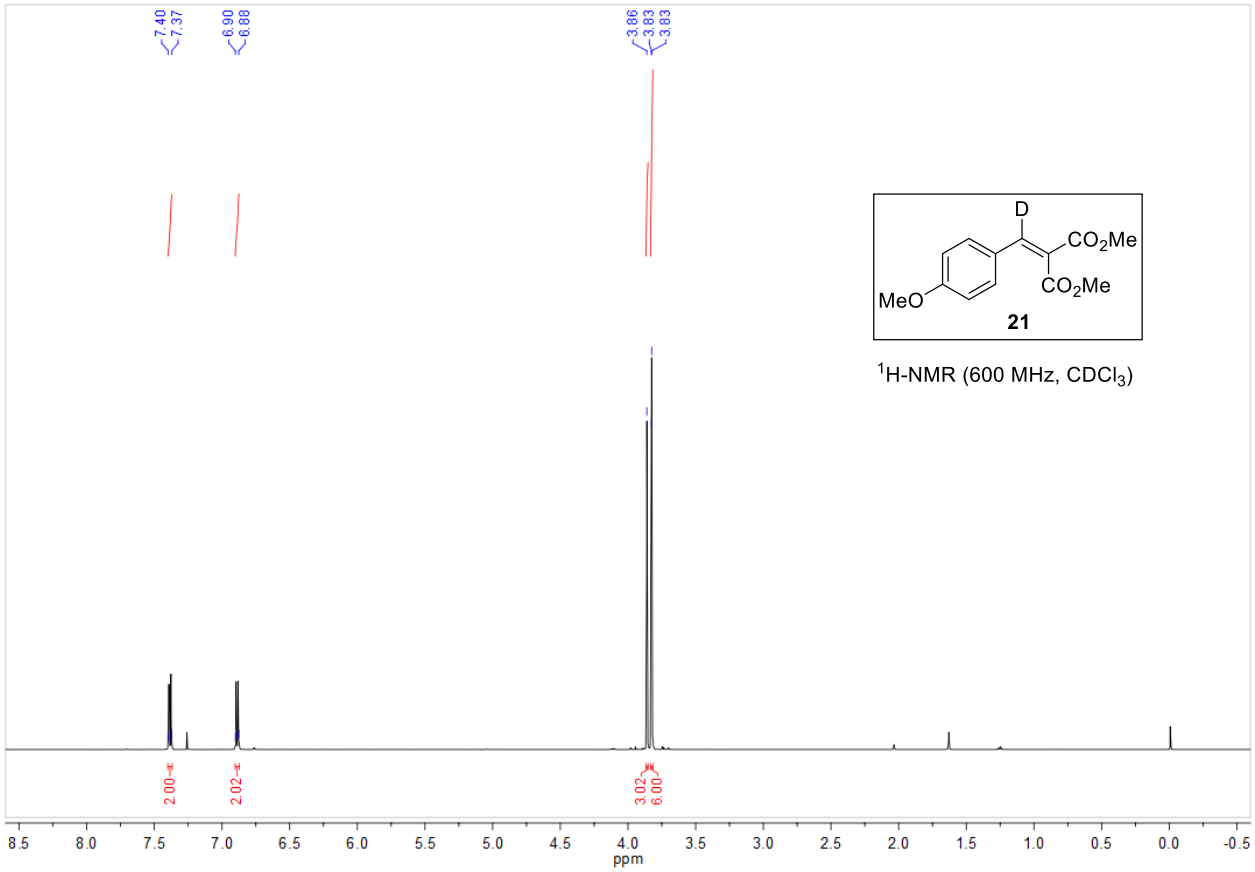
^{13}C-NMR (101 MHz, $CDCl_3$)



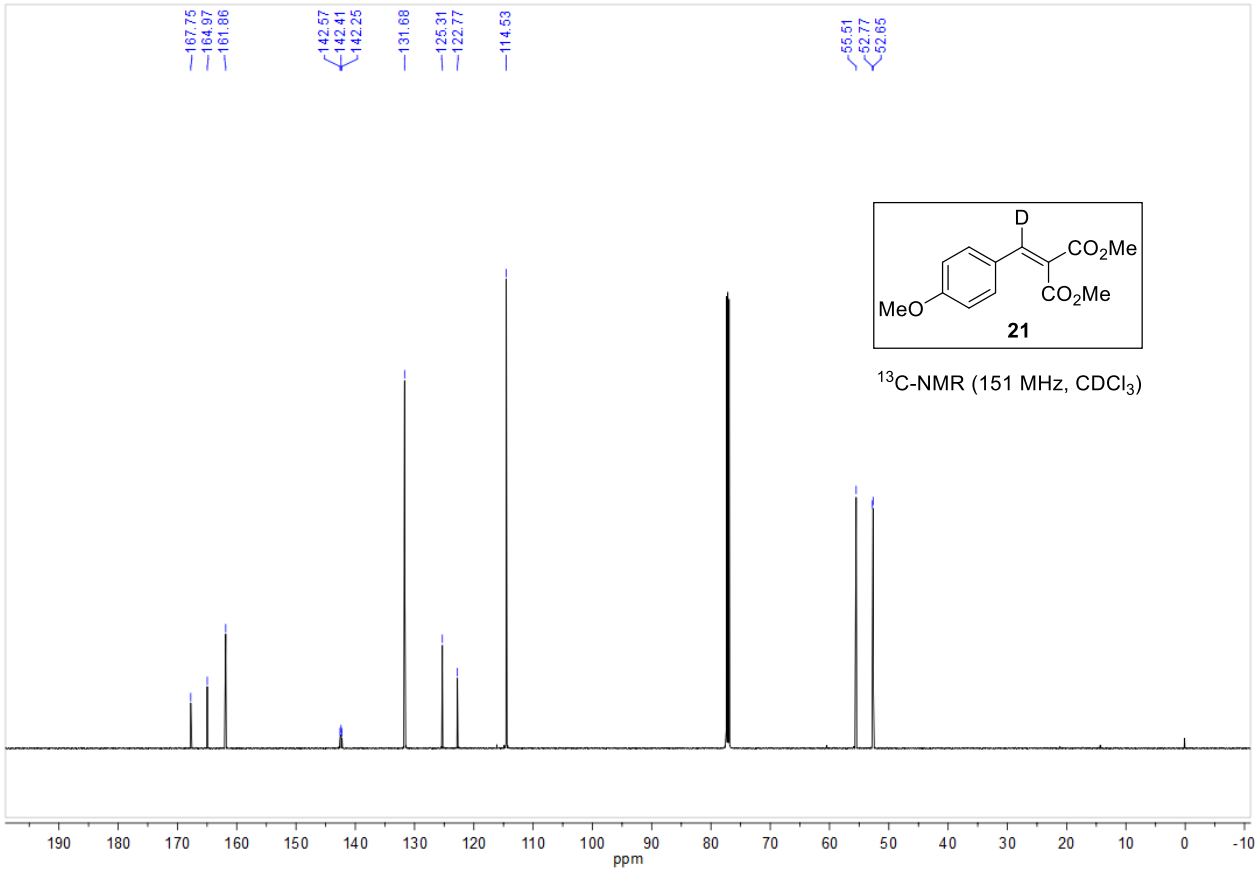
^{1}H-NMR (400 MHz, $CDCl_3$)



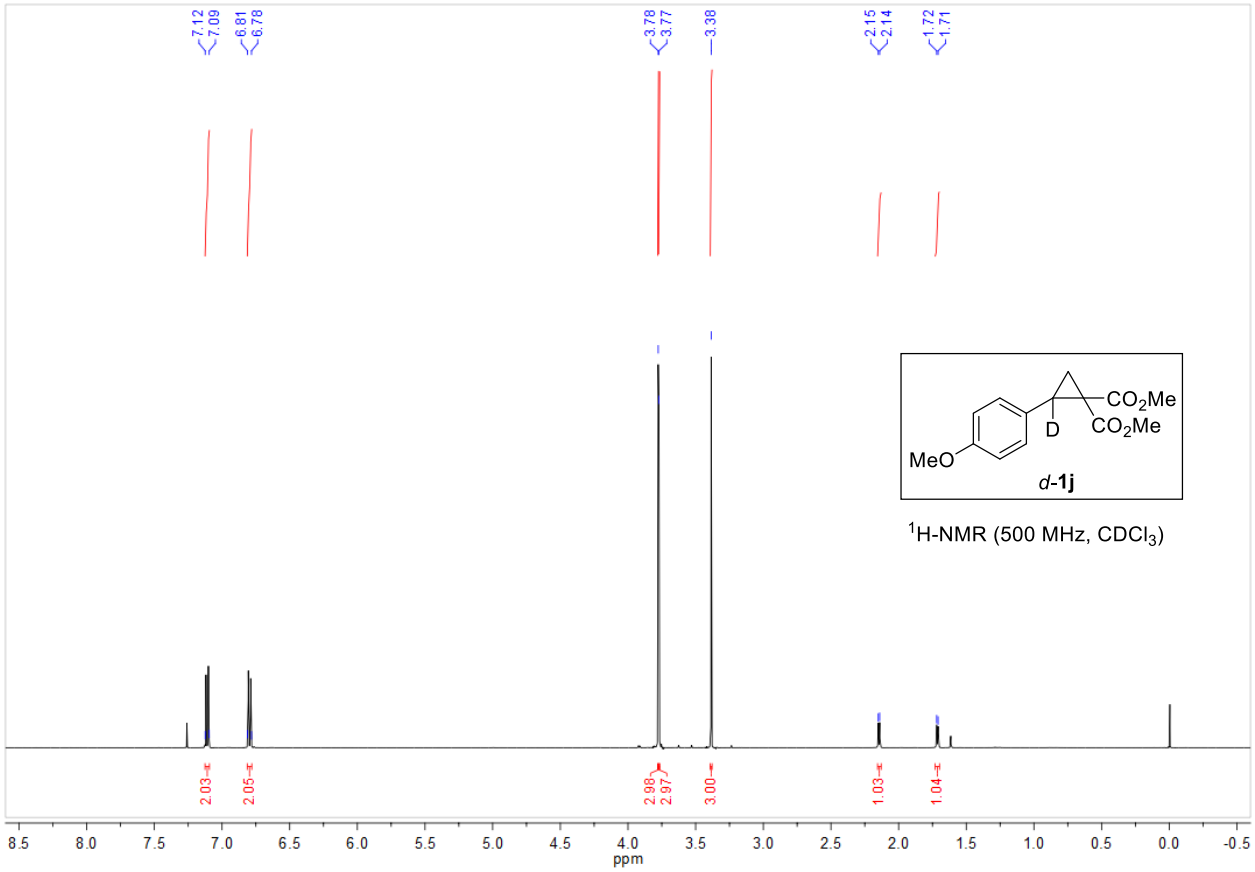
^{13}C-NMR (101 MHz, $CDCl_3$)



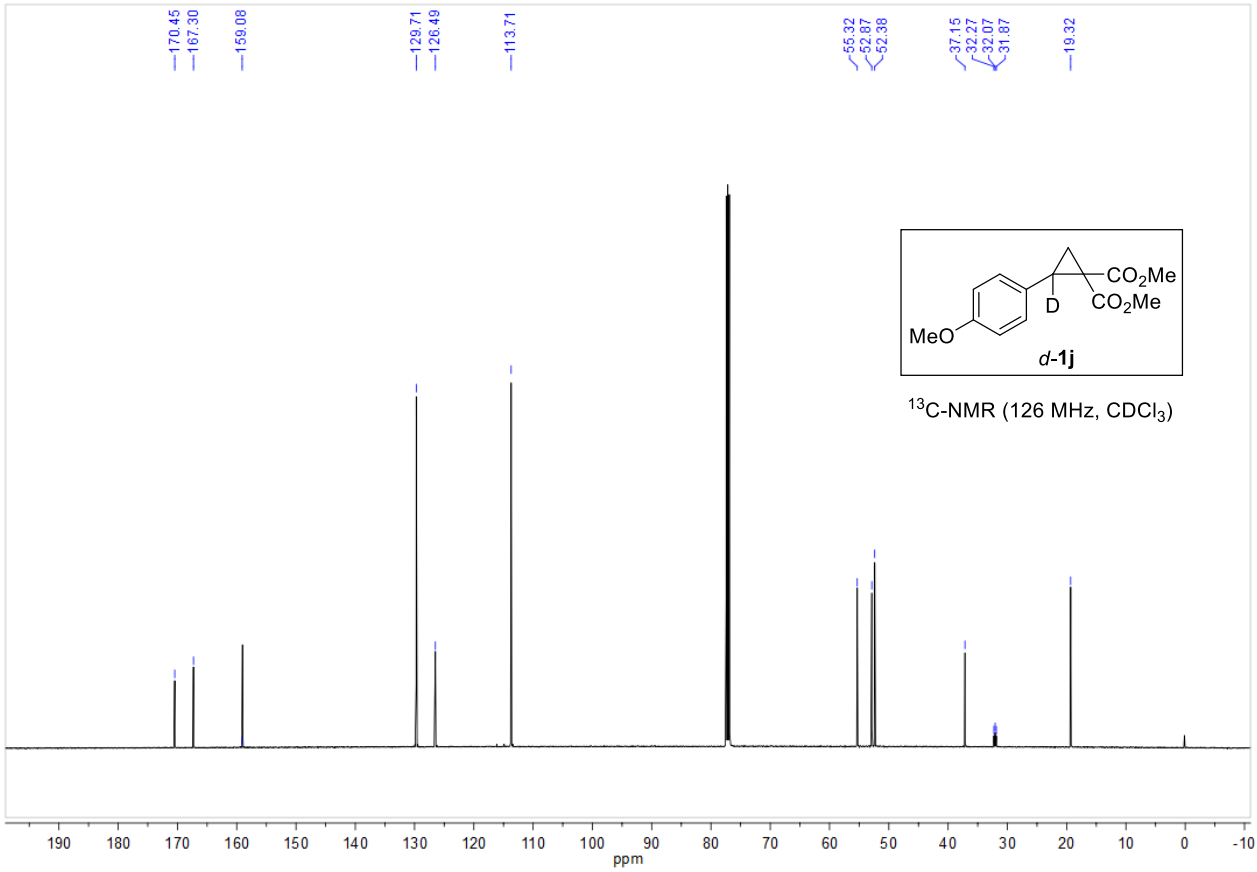
^{1}H-NMR (600 MHz, $CDCl_3$)



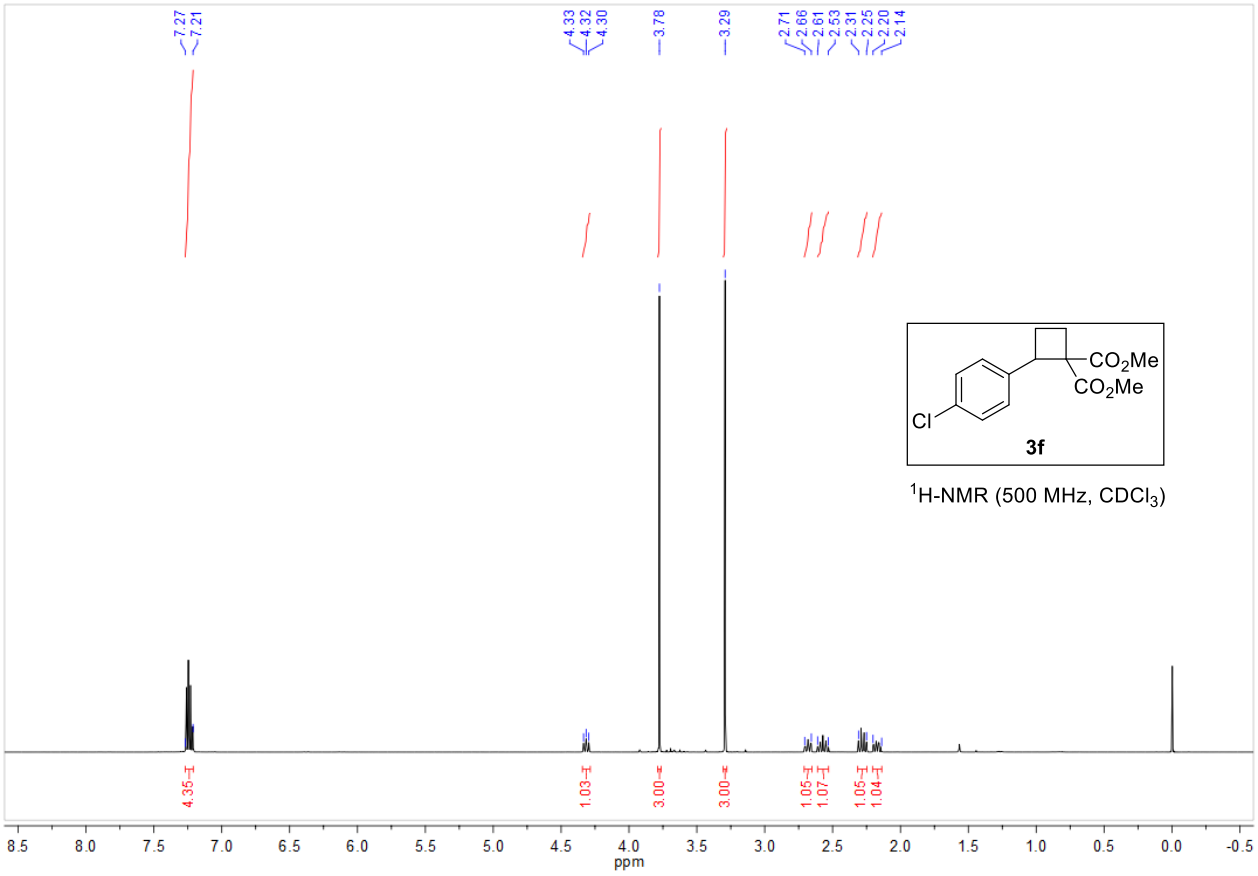
^{13}C-NMR (151 MHz, $CDCl_3$)



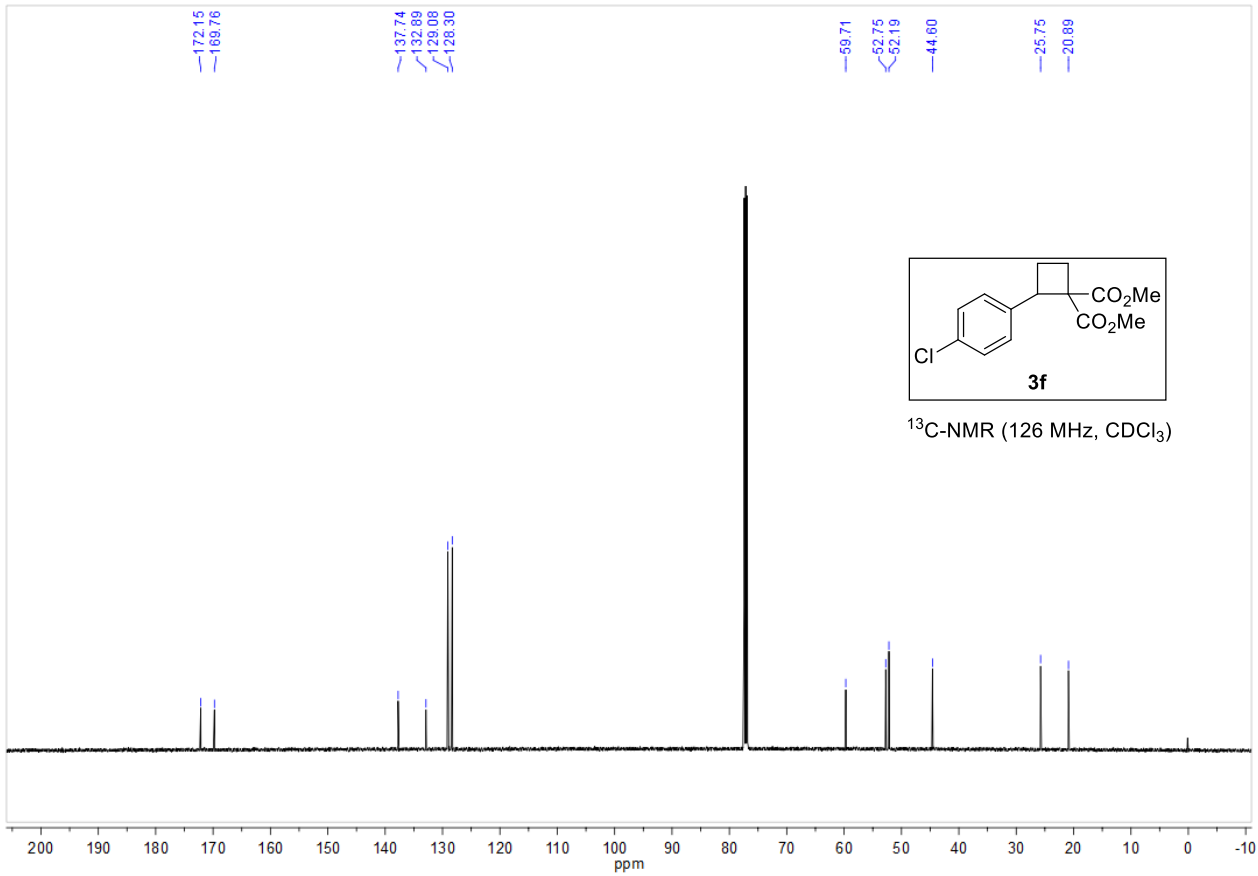
^{1}H-NMR (500 MHz, $CDCl_3$)



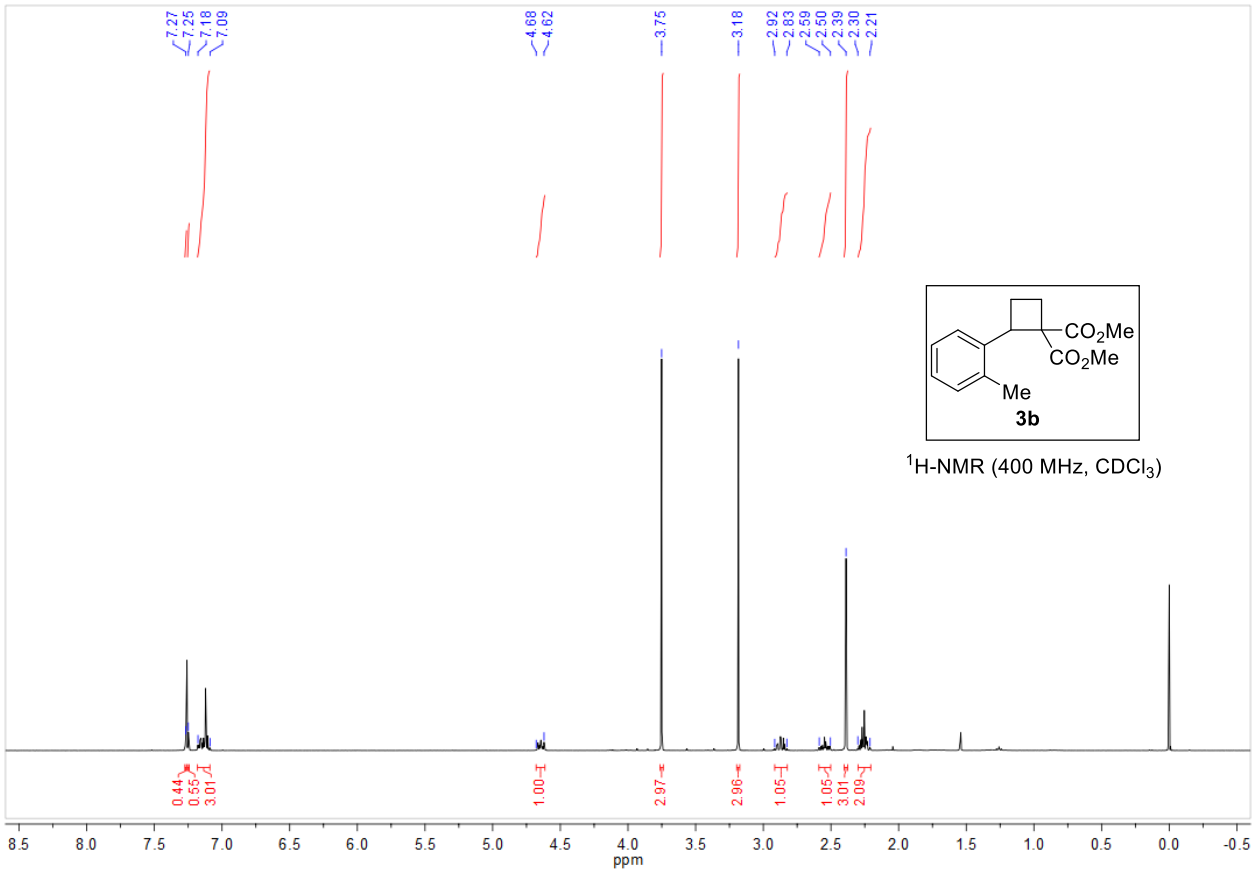
^{13}C-NMR (126 MHz, $CDCl_3$)



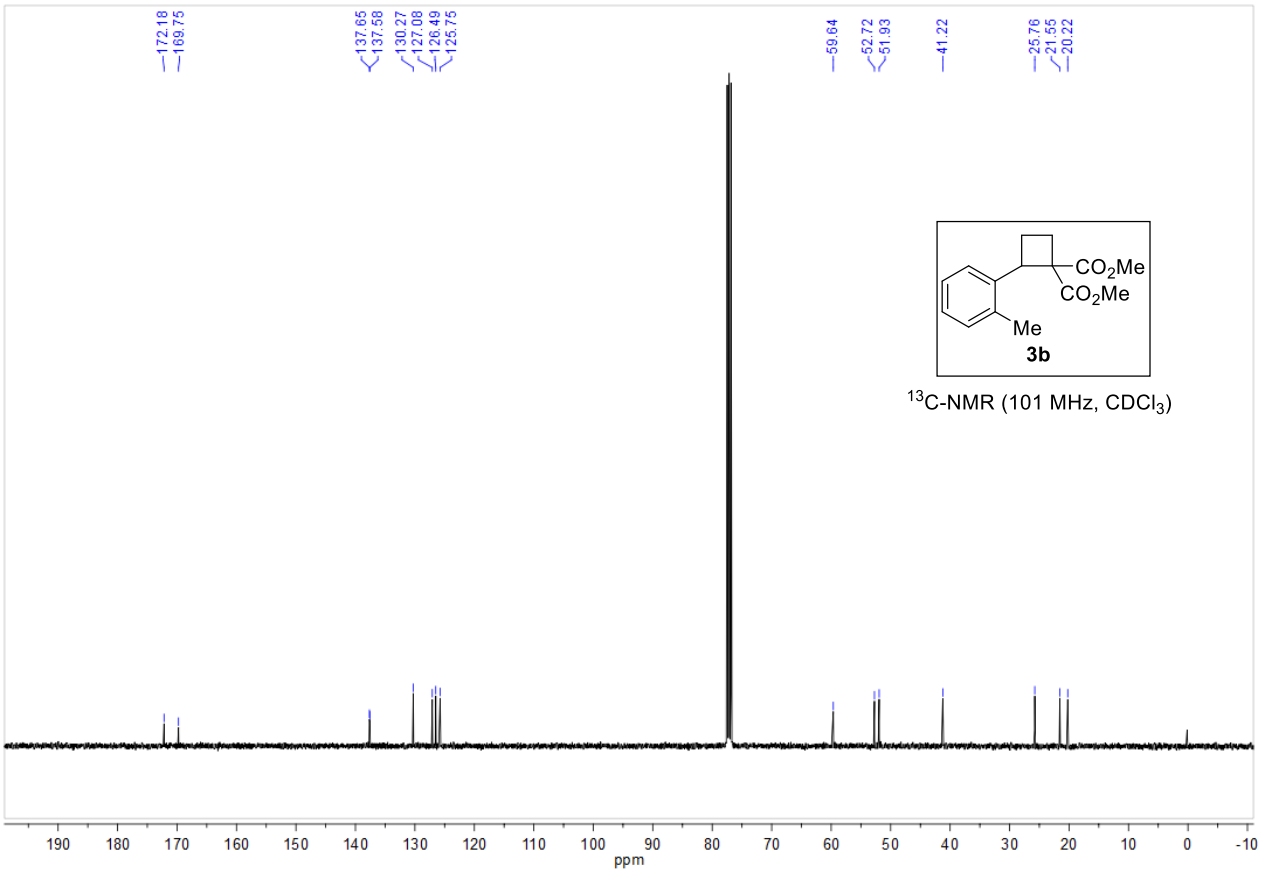
^{1}H-NMR (500 MHz, $CDCl_3$)



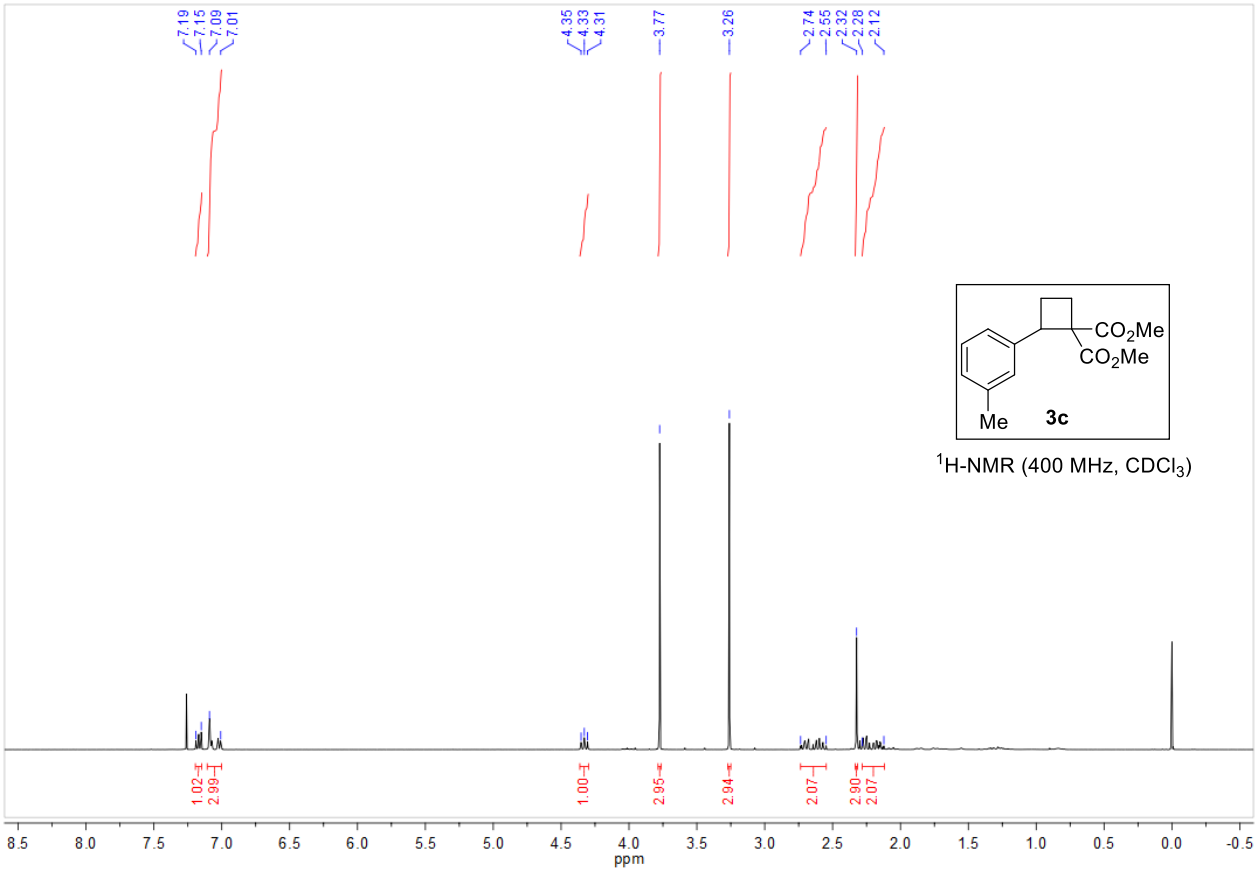
^{13}C-NMR (126 MHz, $CDCl_3$)



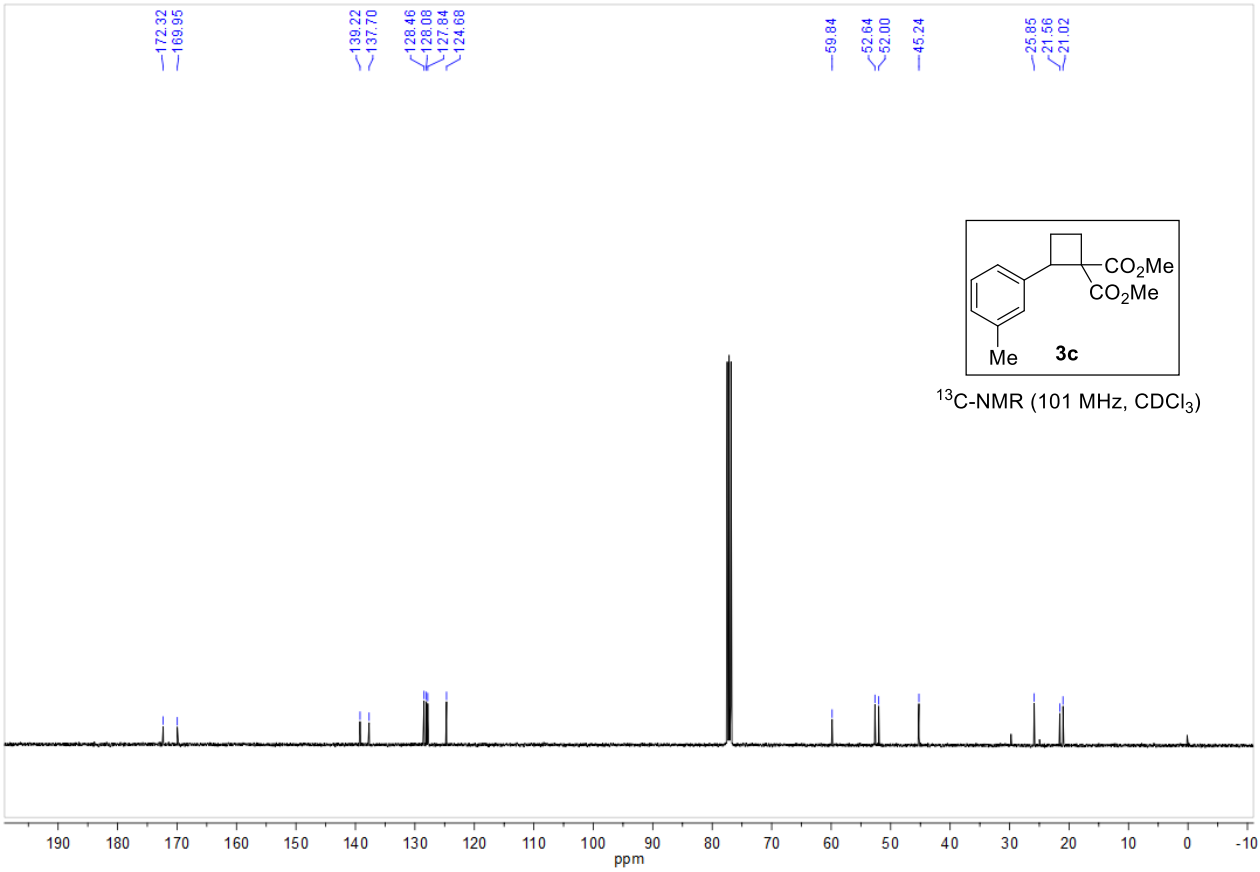
^{1}H-NMR (400 MHz, $CDCl_3$)



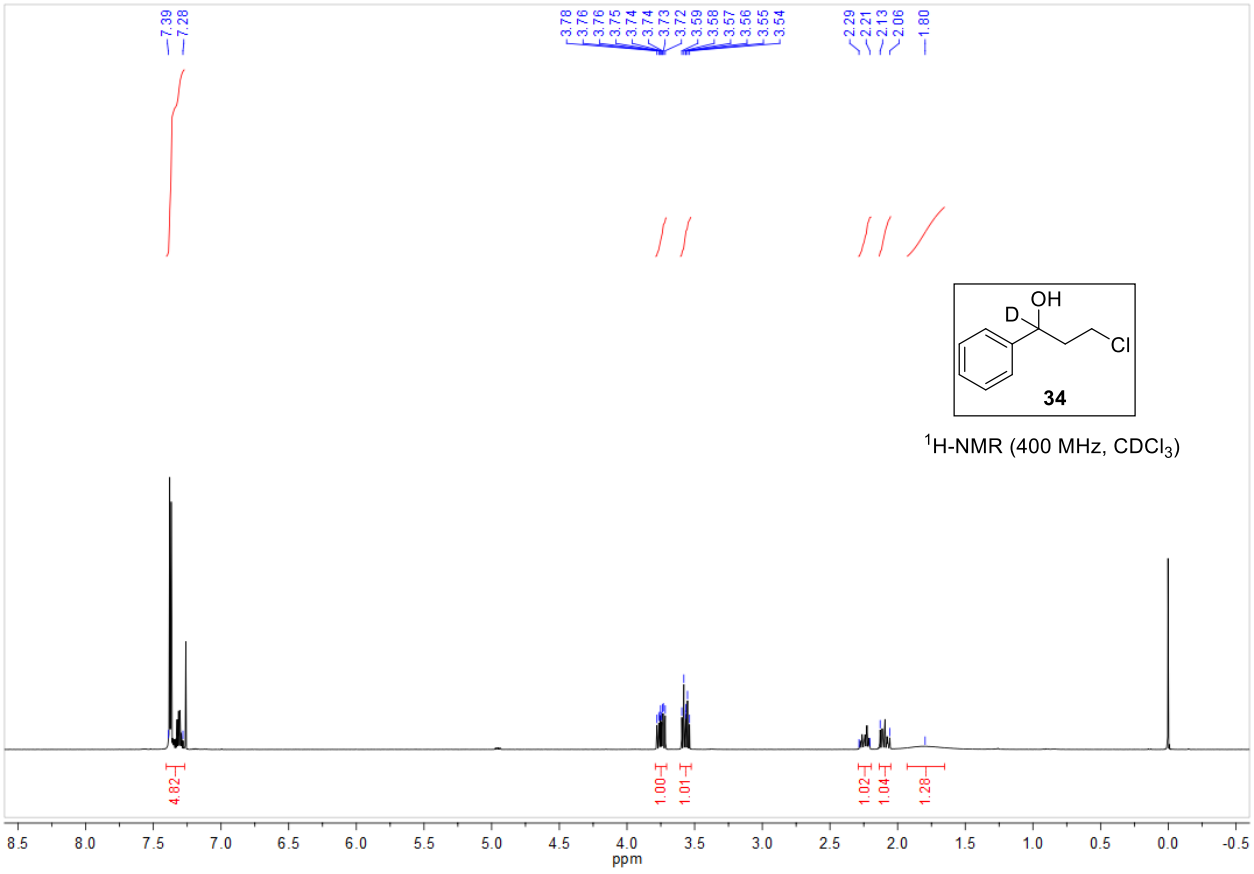
^{13}C-NMR (101 MHz, $CDCl_3$)



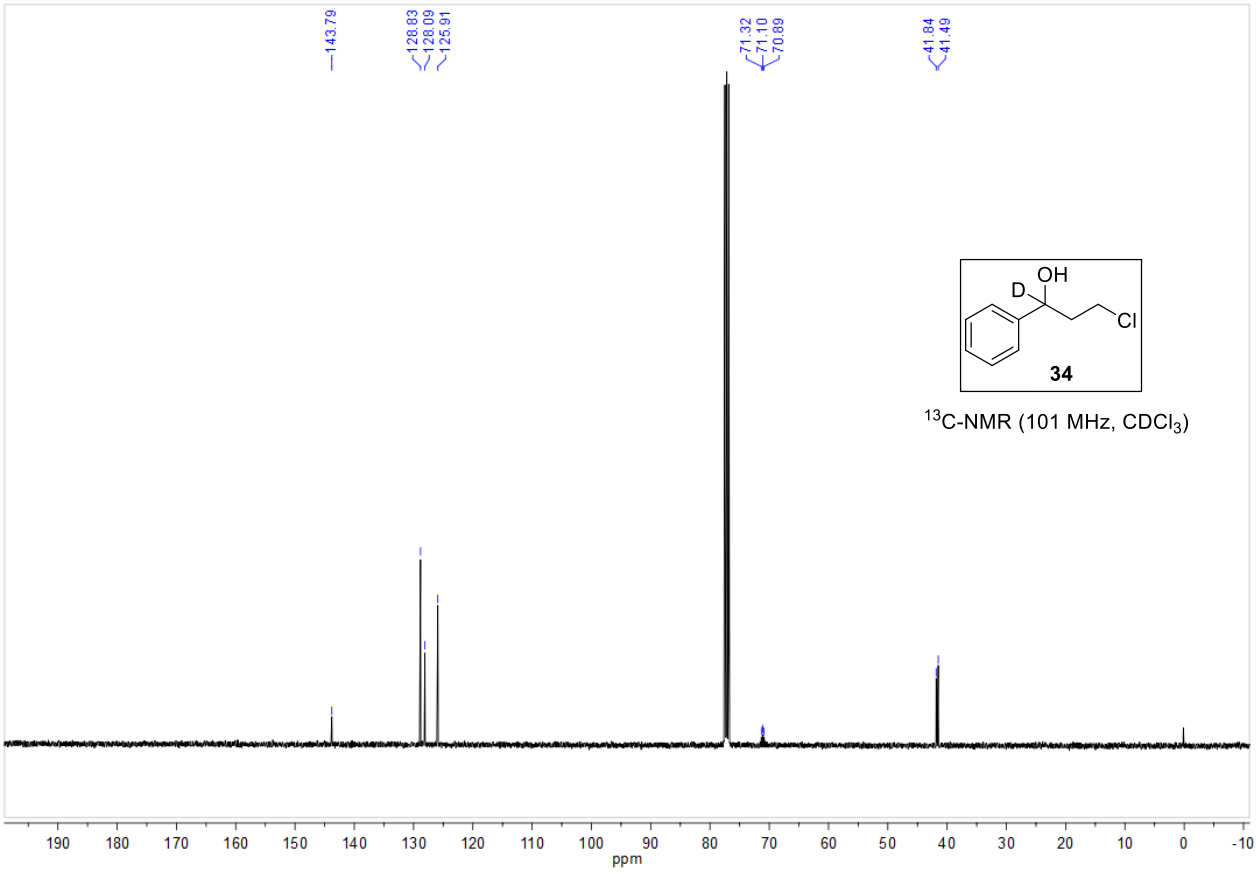
^{1}H-NMR (400 MHz, $CDCl_3$)



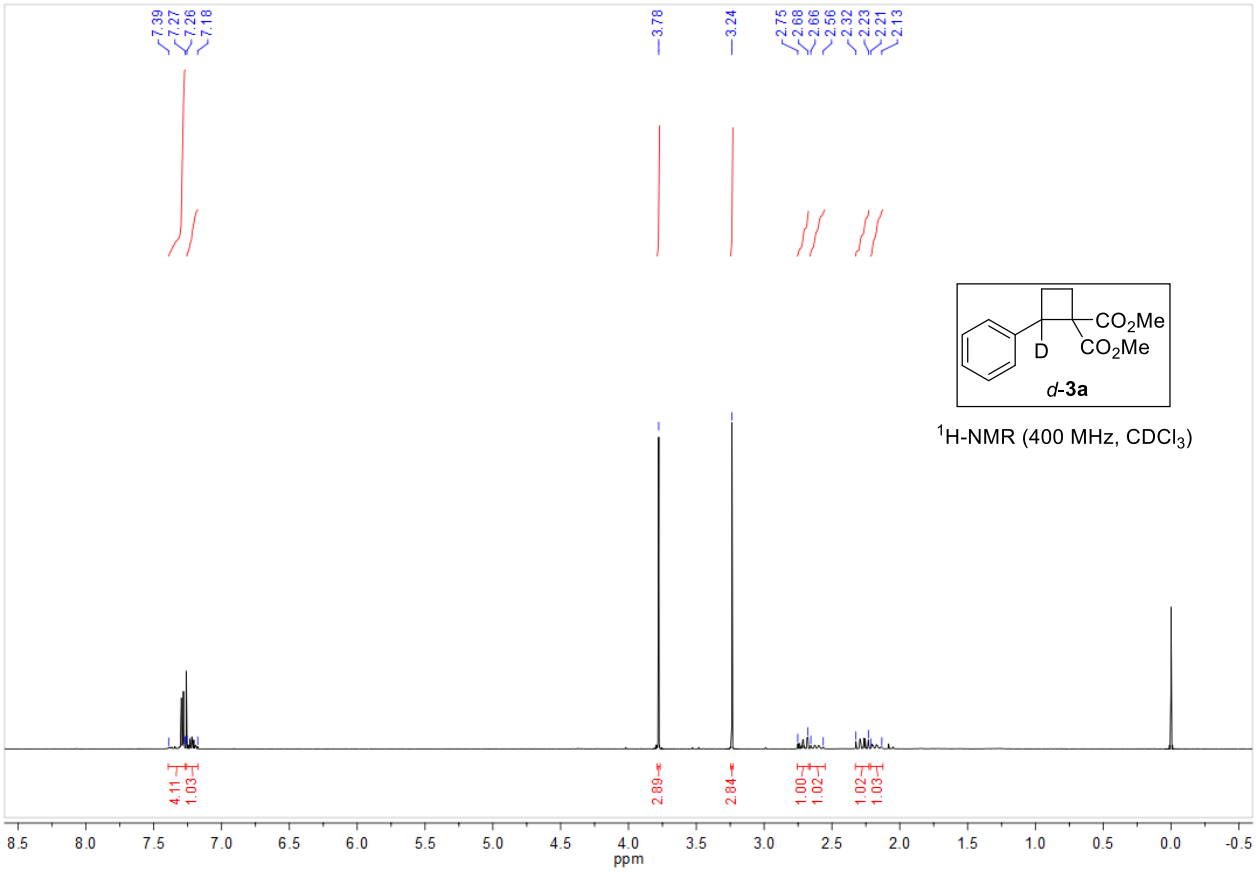
^{13}C-NMR (101 MHz, $CDCl_3$)



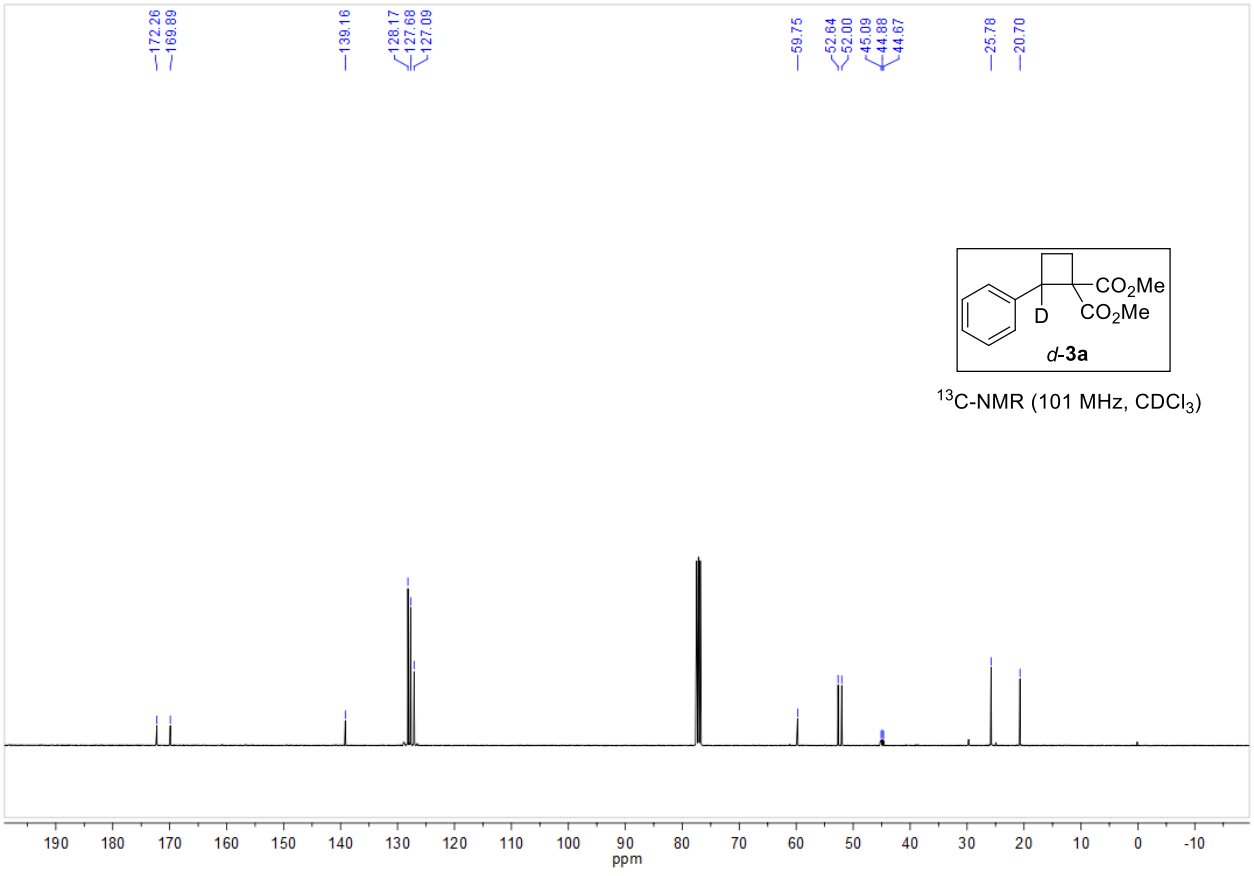
^{1}H-NMR (400 MHz, $CDCl_3$)



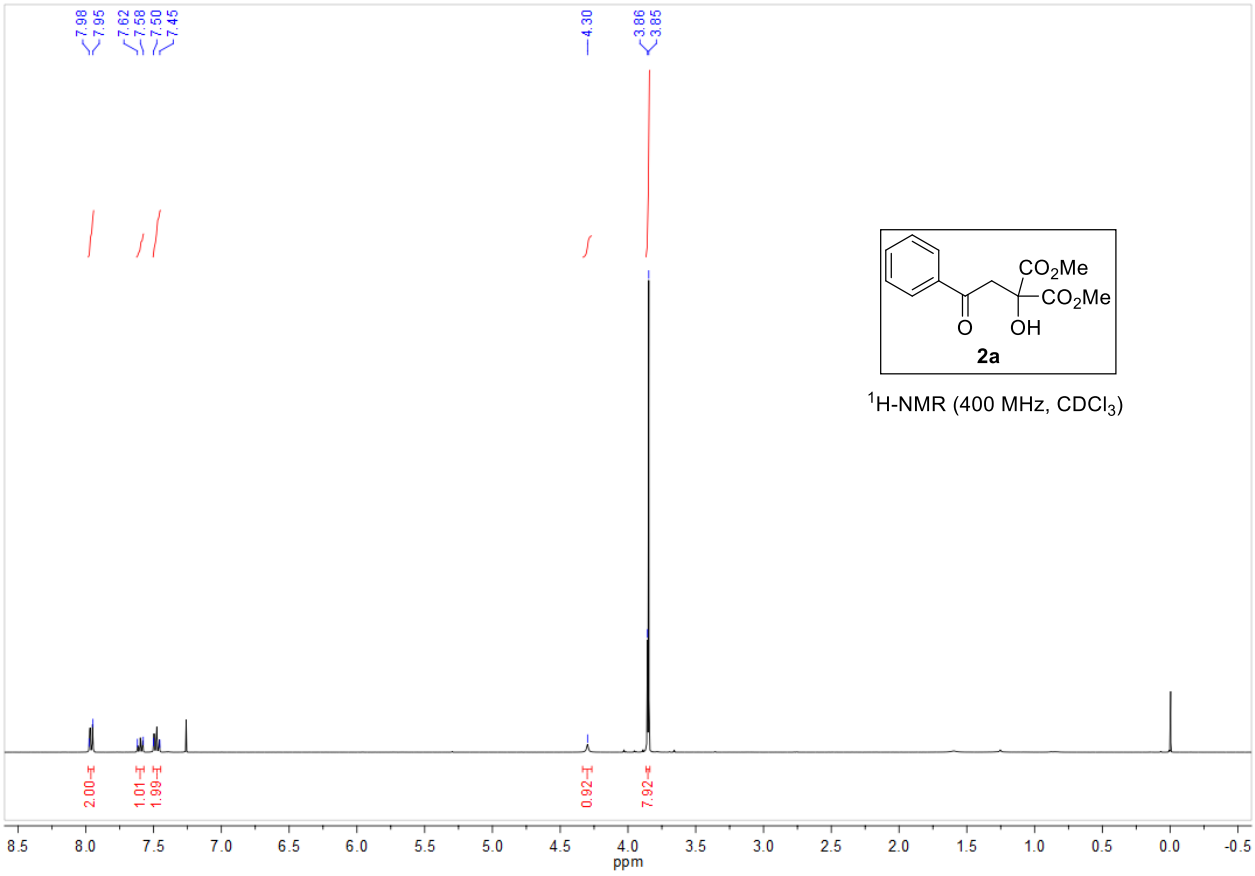
^{13}C-NMR (101 MHz, $CDCl_3$)



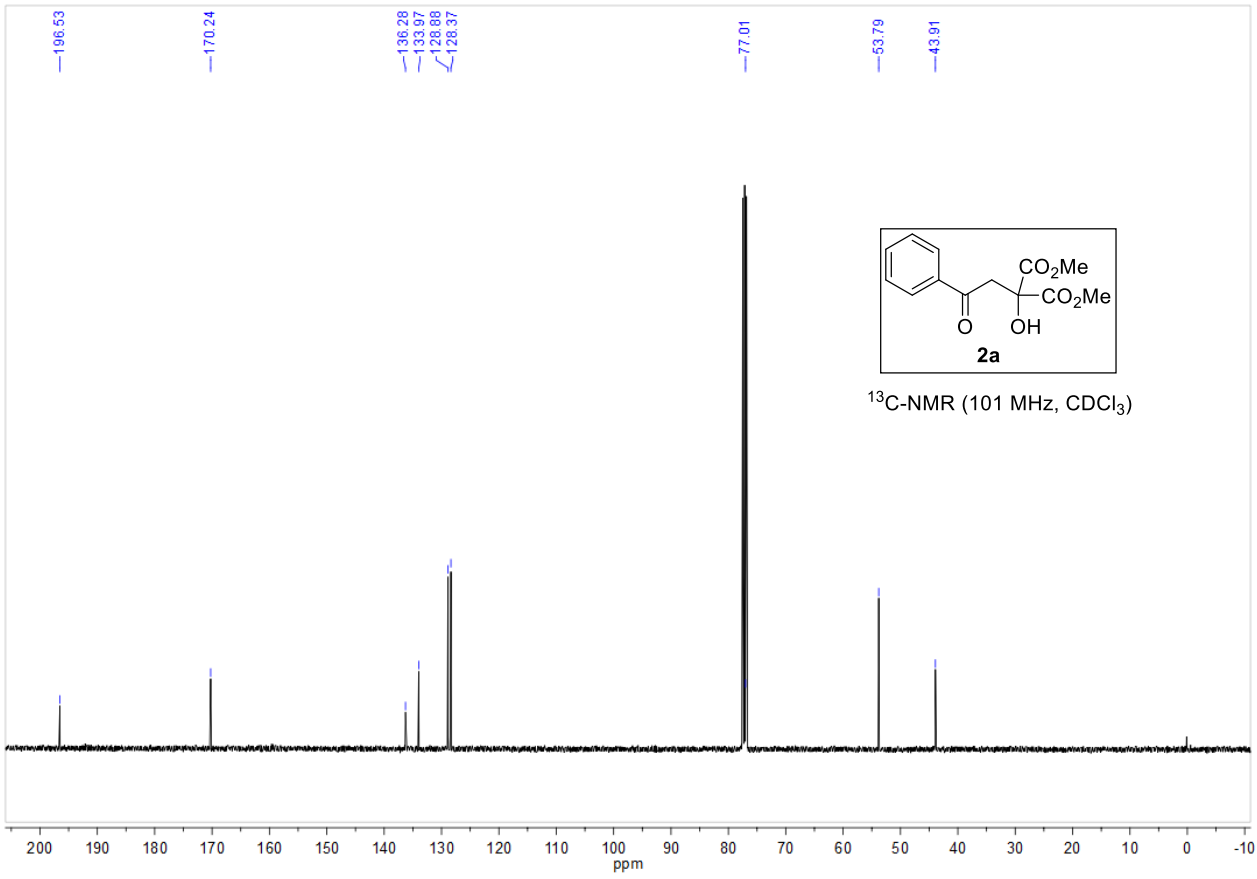
^{1}H-NMR (400 MHz, $CDCl_3$)



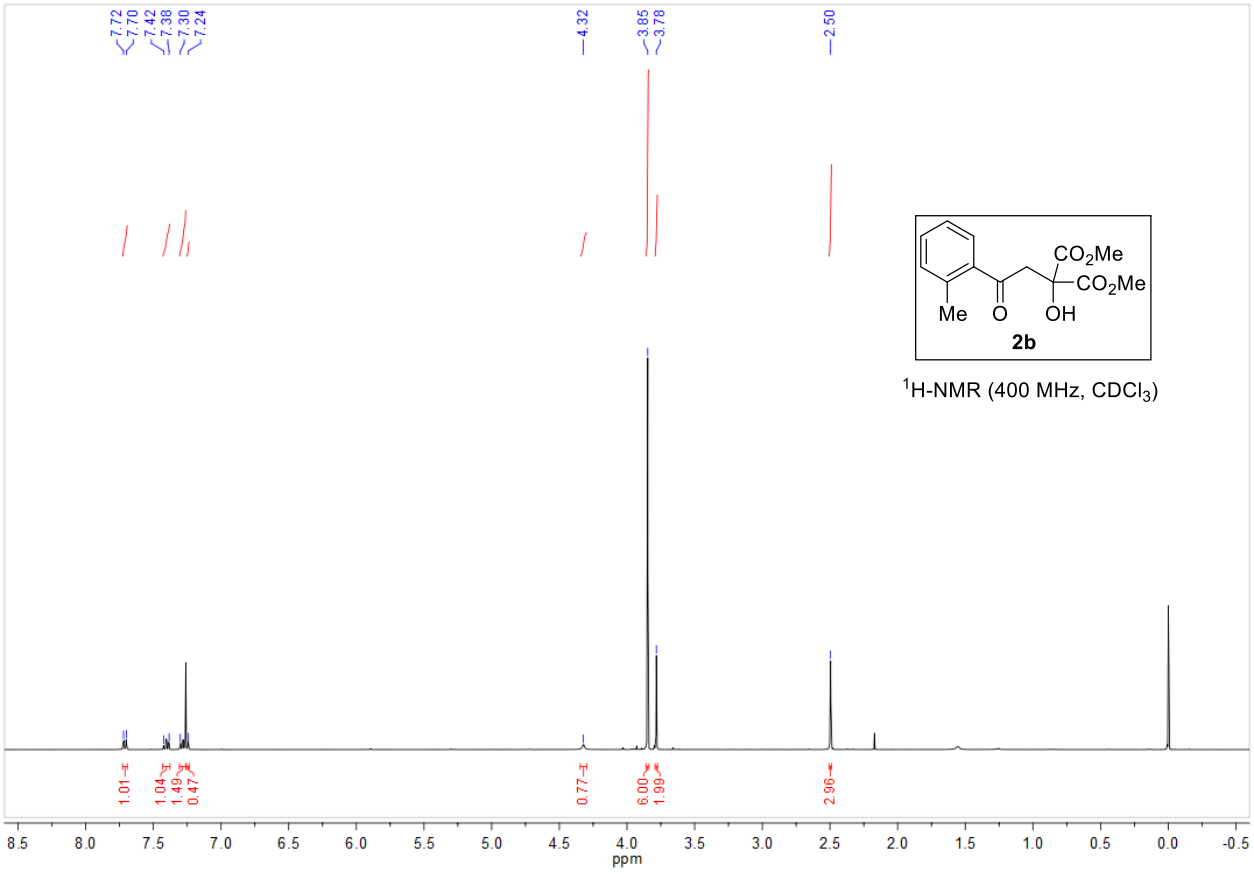
^{13}C-NMR (101 MHz, $CDCl_3$)



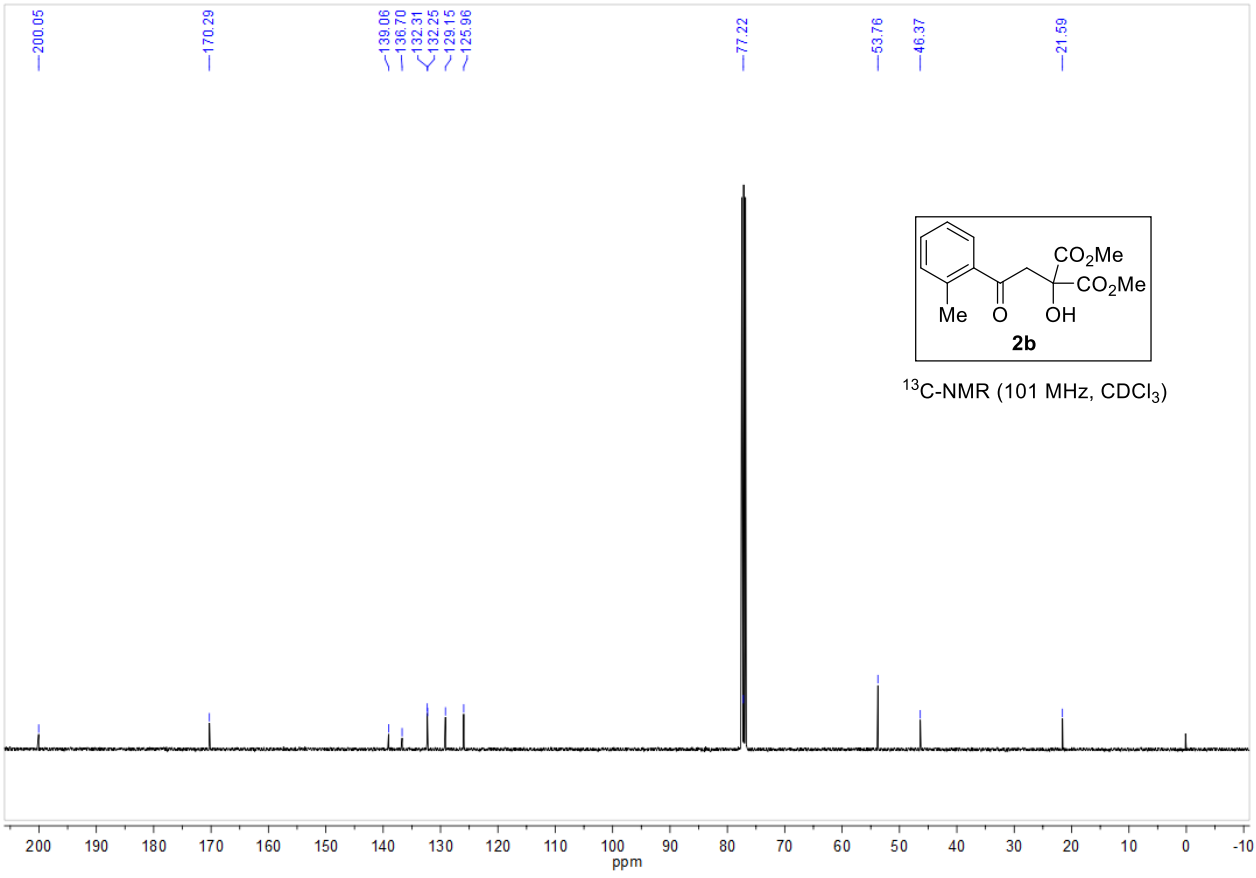
^{1}H-NMR (400 MHz, $CDCl_3$)



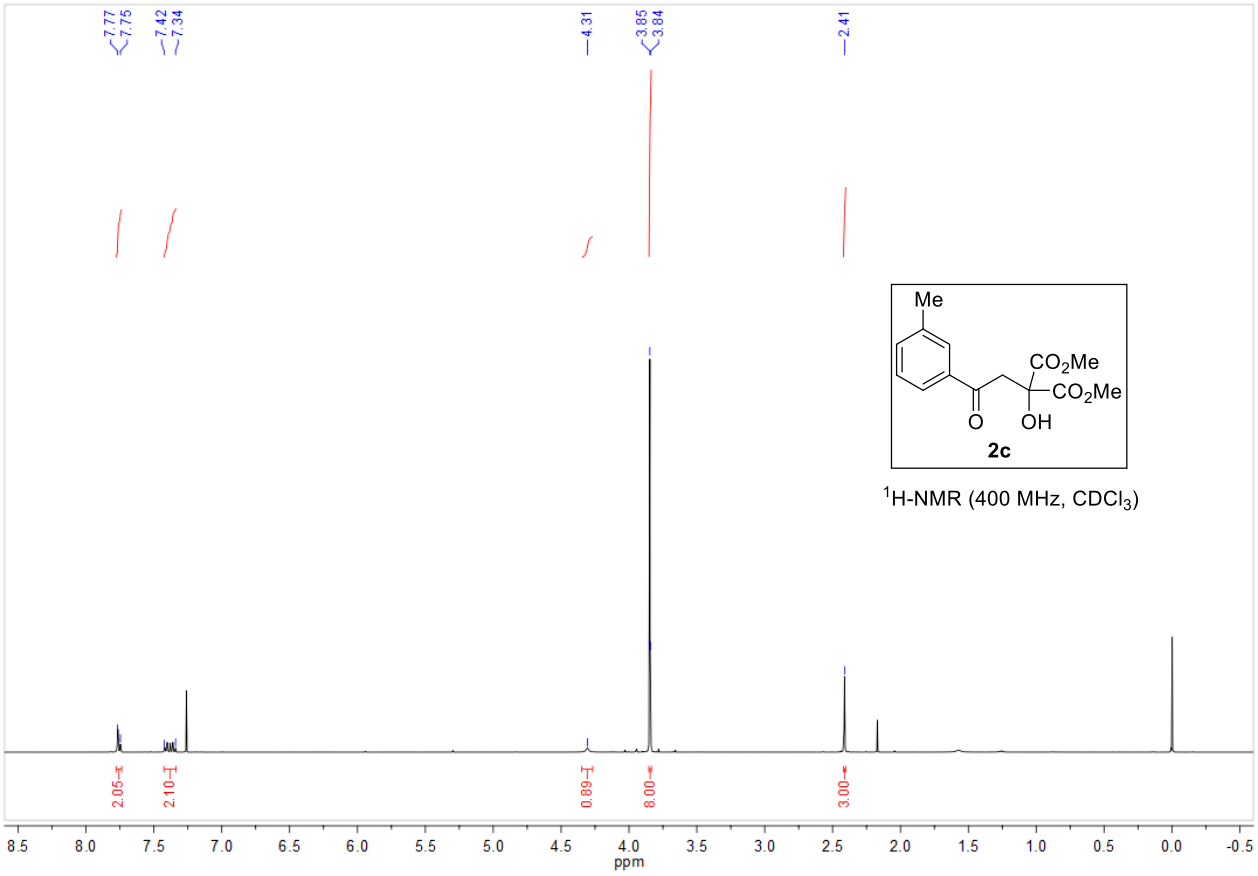
^{13}C-NMR (101 MHz, $CDCl_3$)



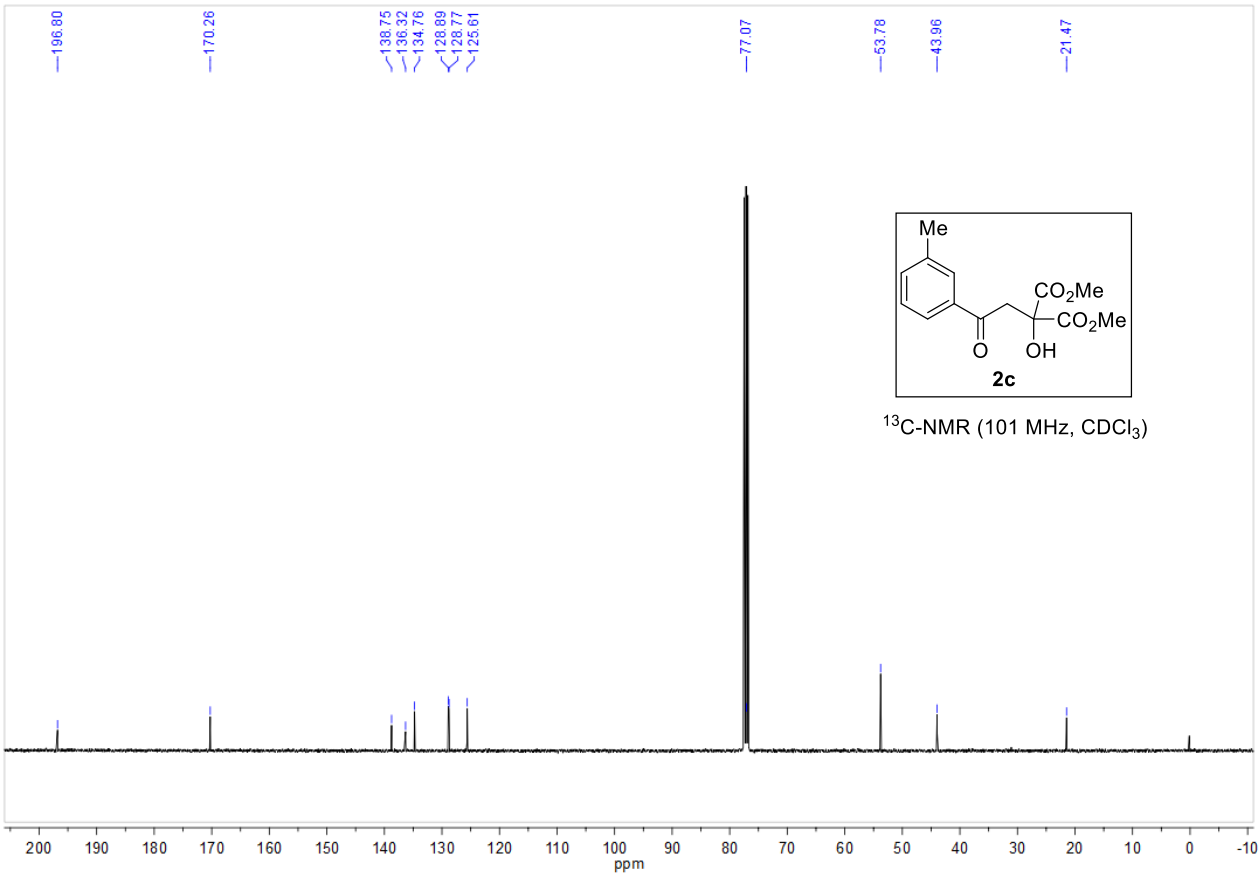
^{1}H-NMR (400 MHz, $CDCl_3$)



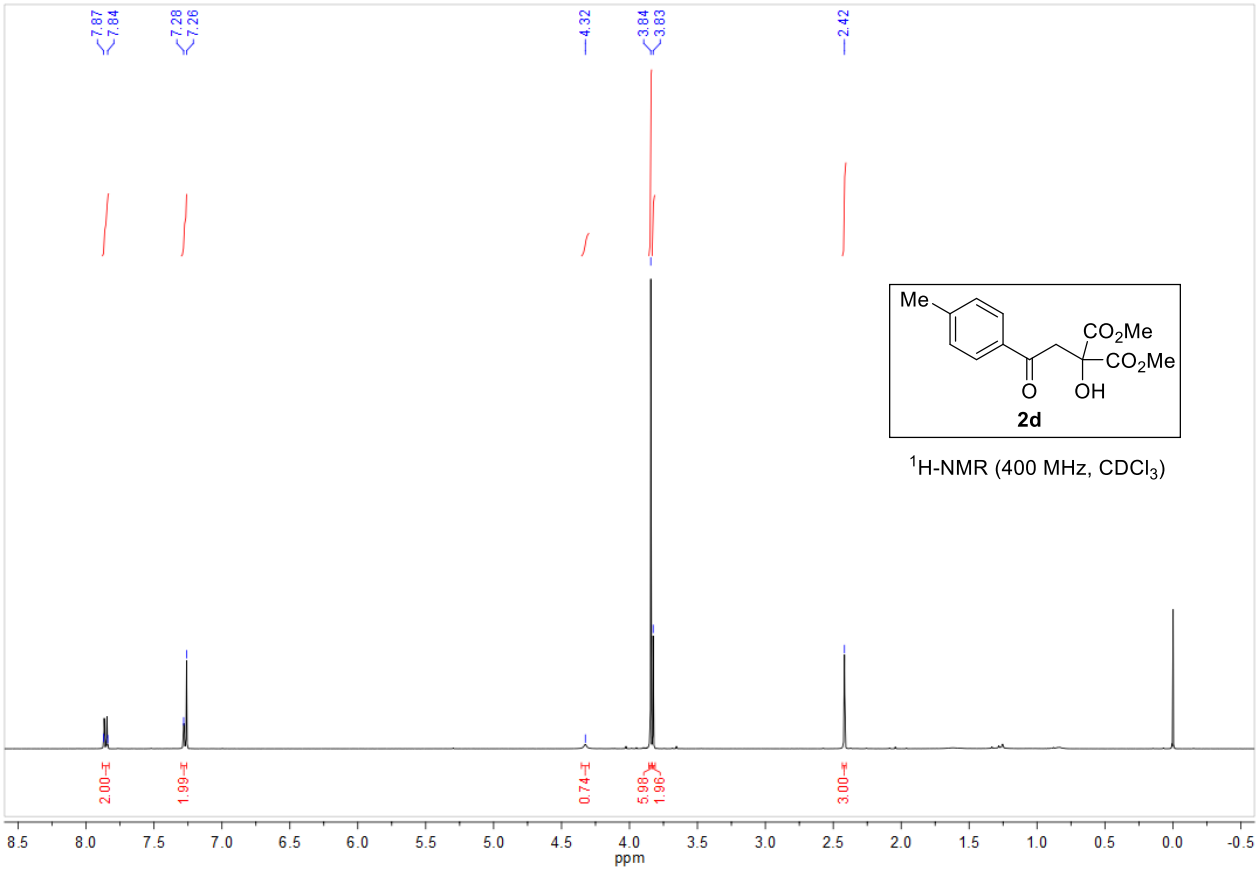
^{13}C-NMR (101 MHz, $CDCl_3$)



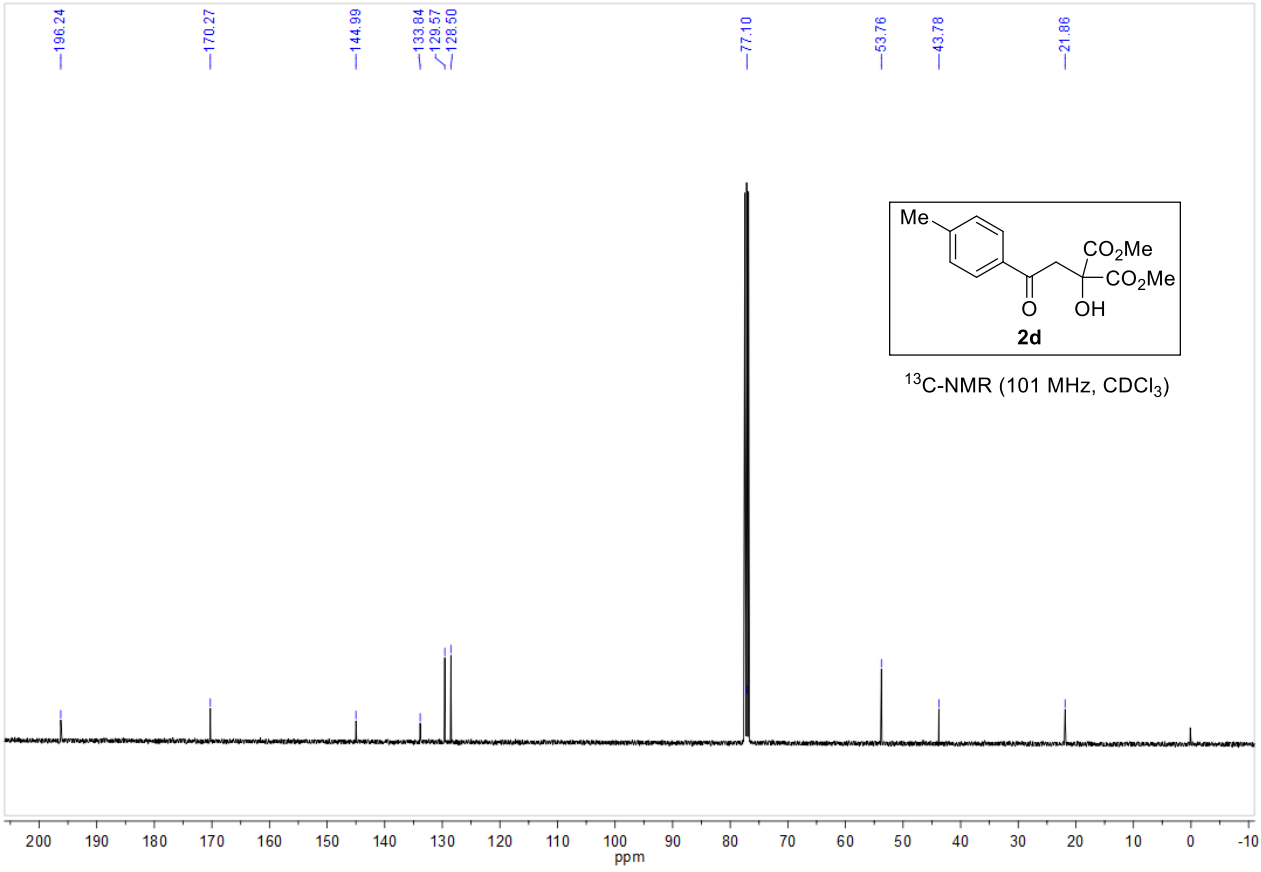
^{1}H-NMR (400 MHz, $CDCl_3$)



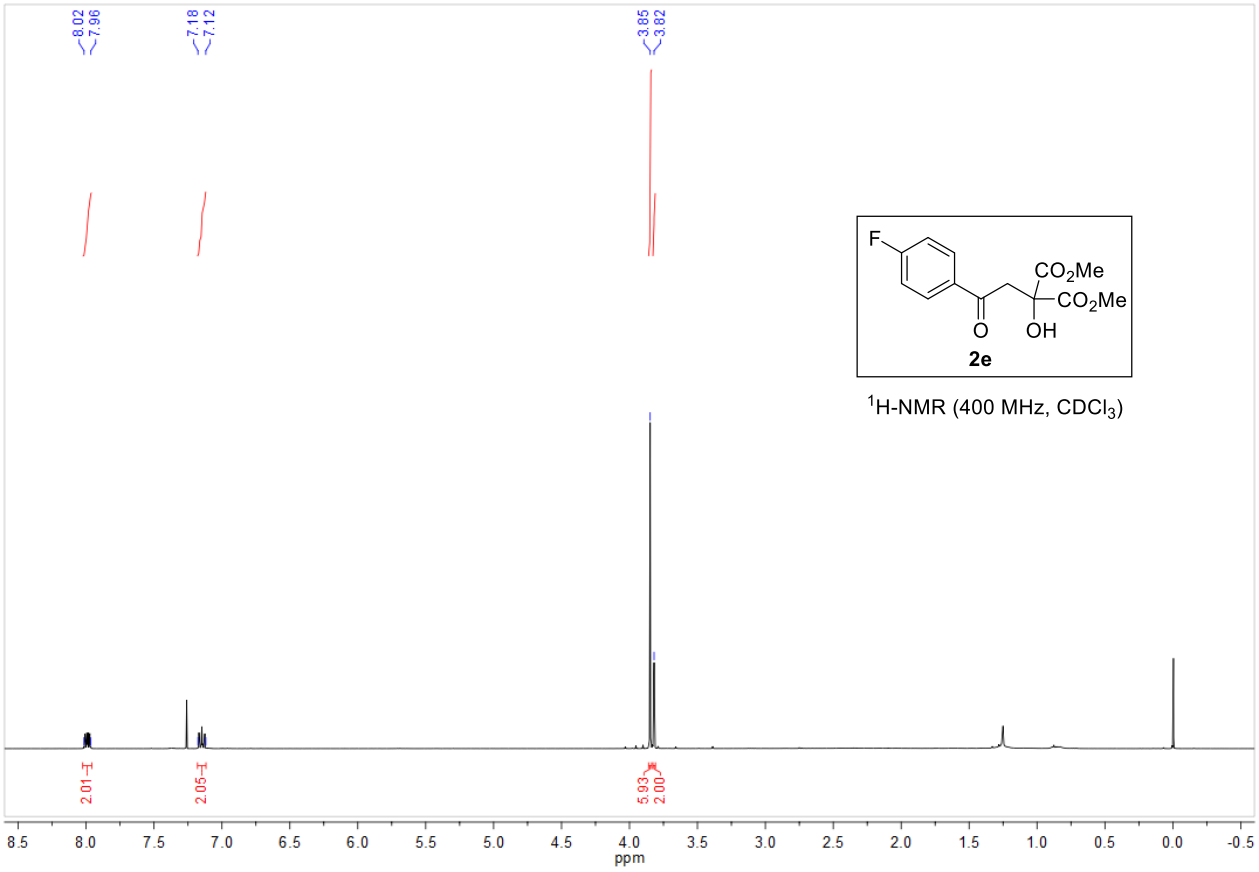
^{13}C-NMR (101 MHz, $CDCl_3$)



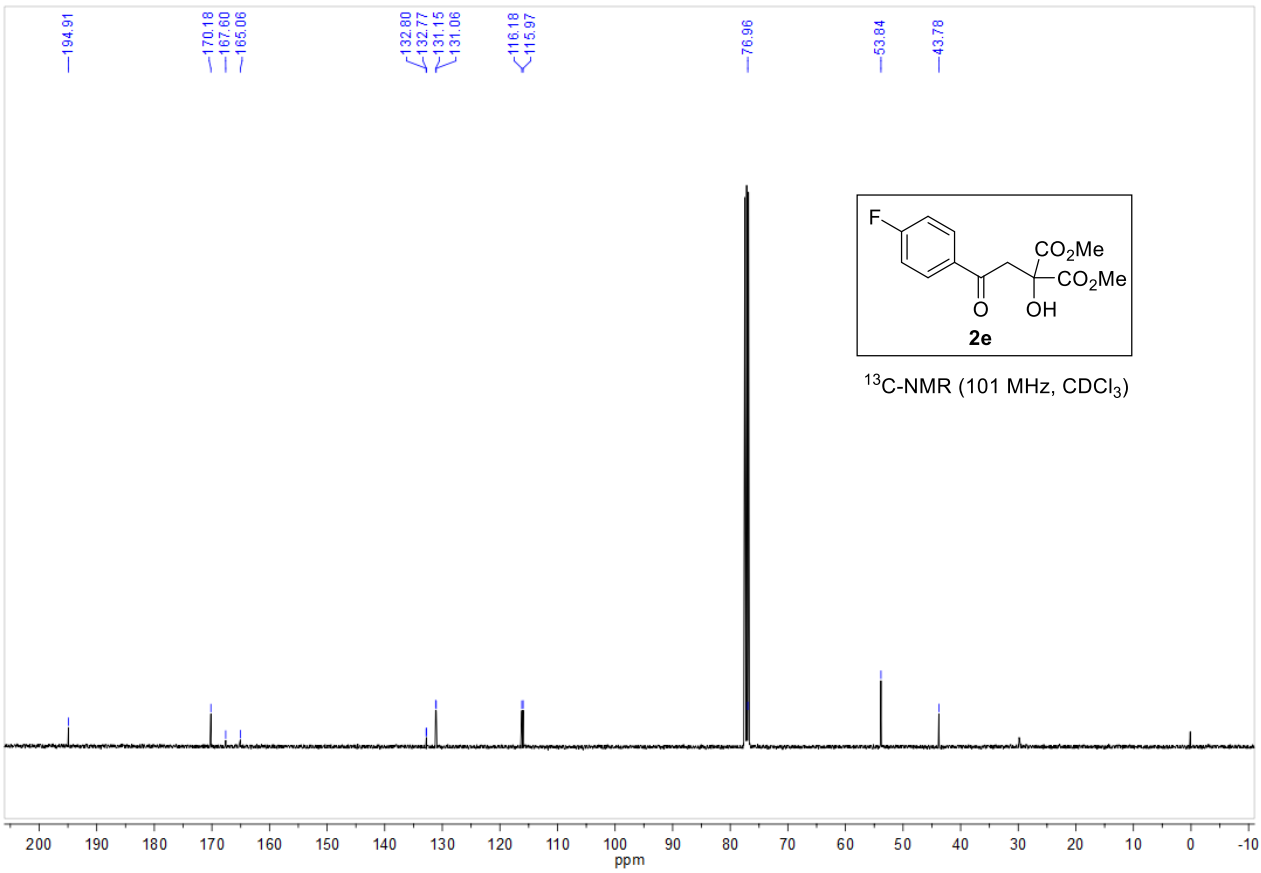
^{1}H-NMR (400 MHz, $CDCl_3$)



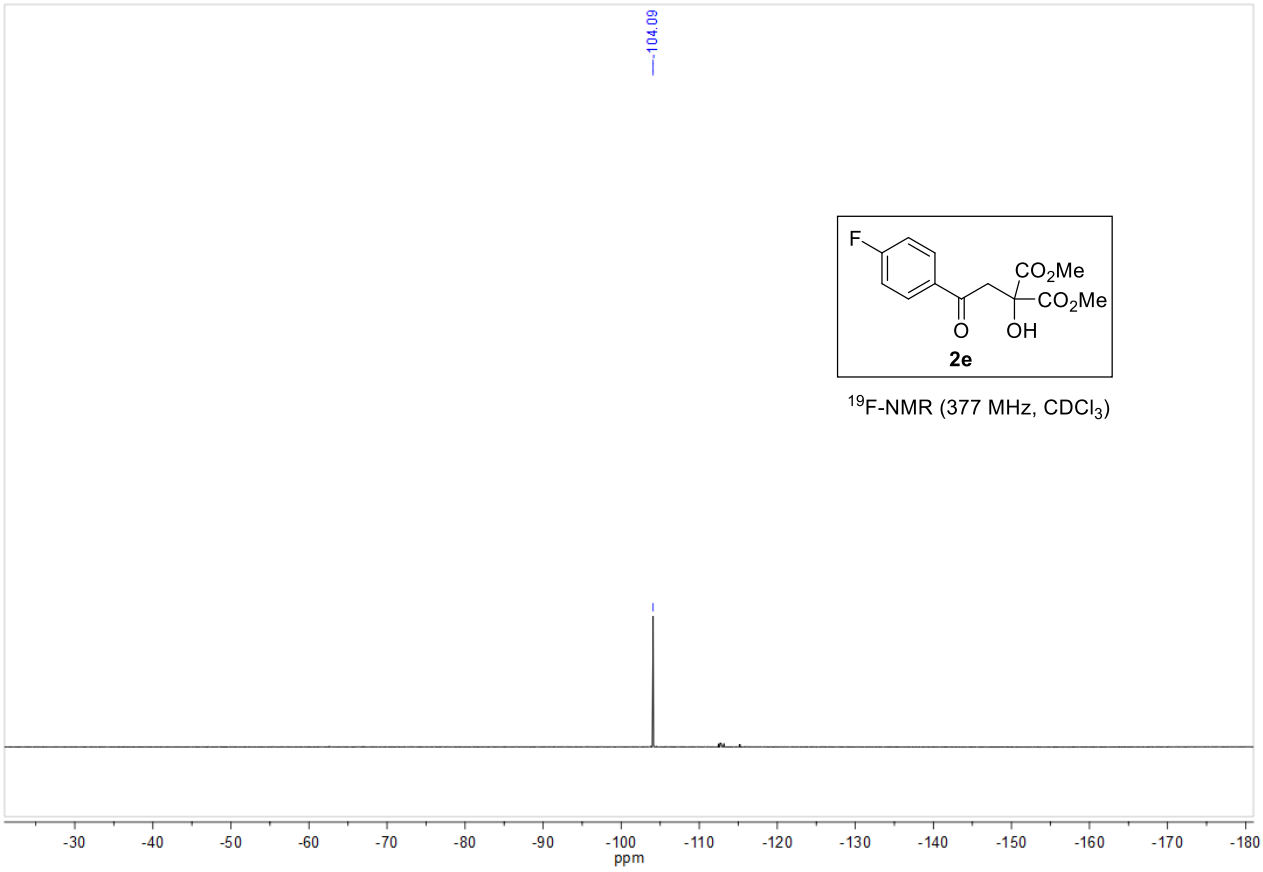
^{13}C-NMR (101 MHz, $CDCl_3$)



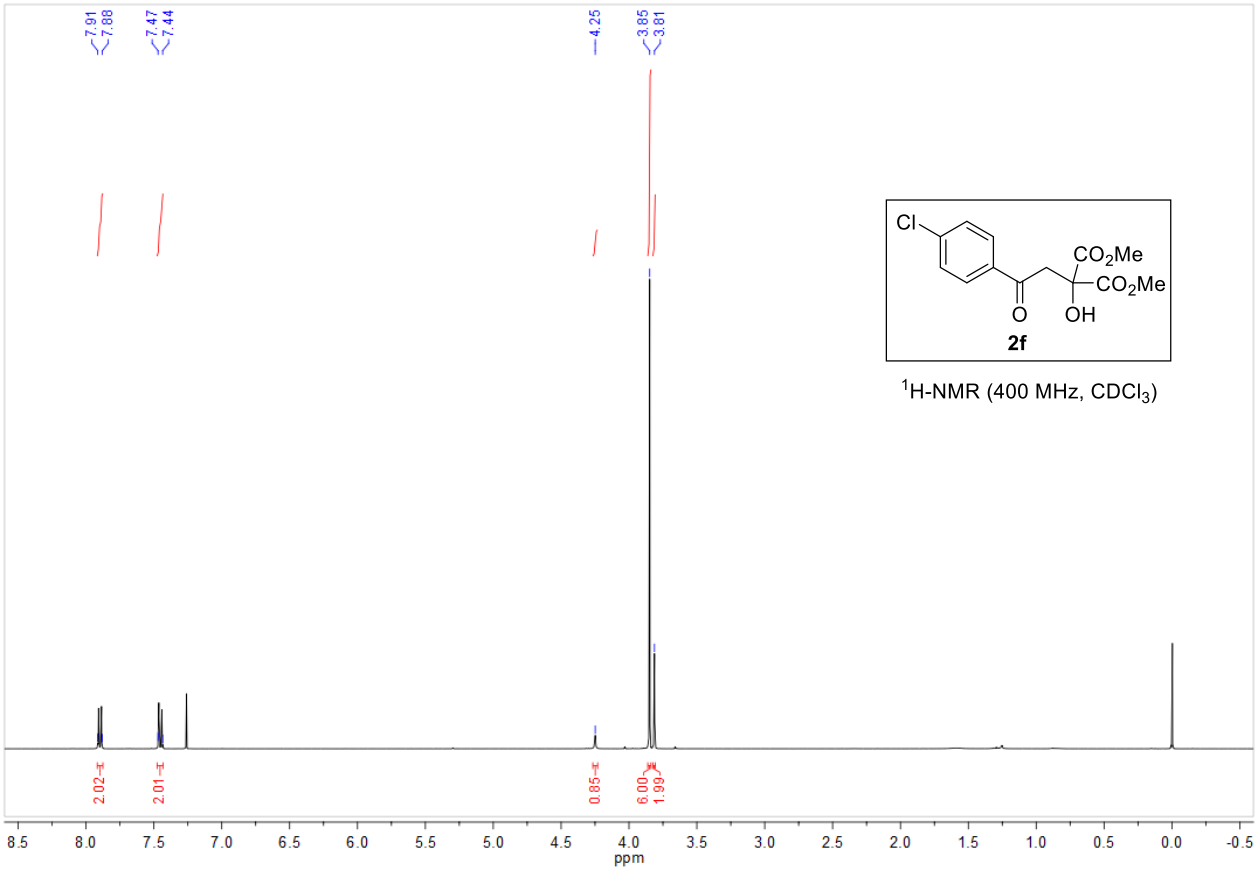
^{1}H-NMR (400 MHz, $CDCl_3$)



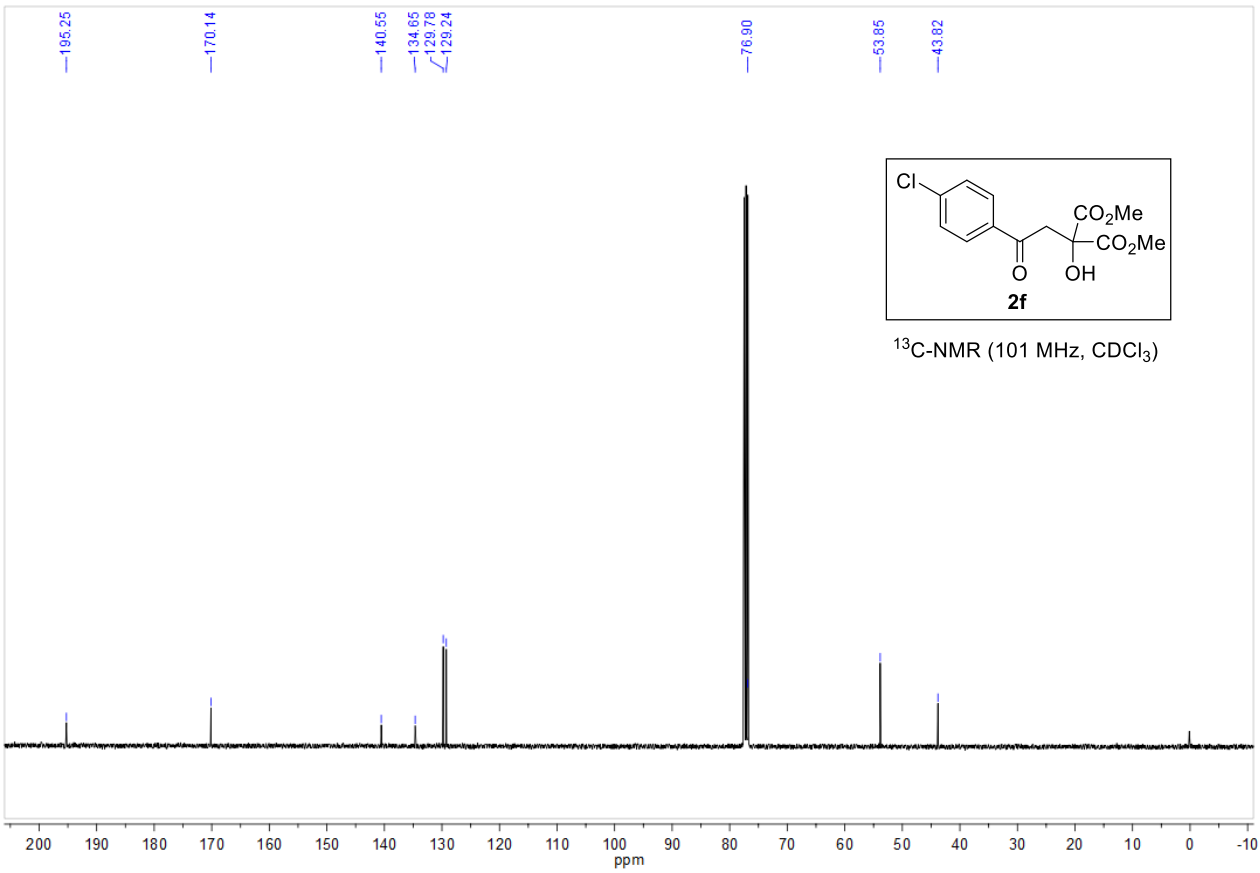
^{13}C-NMR (101 MHz, $CDCl_3$)



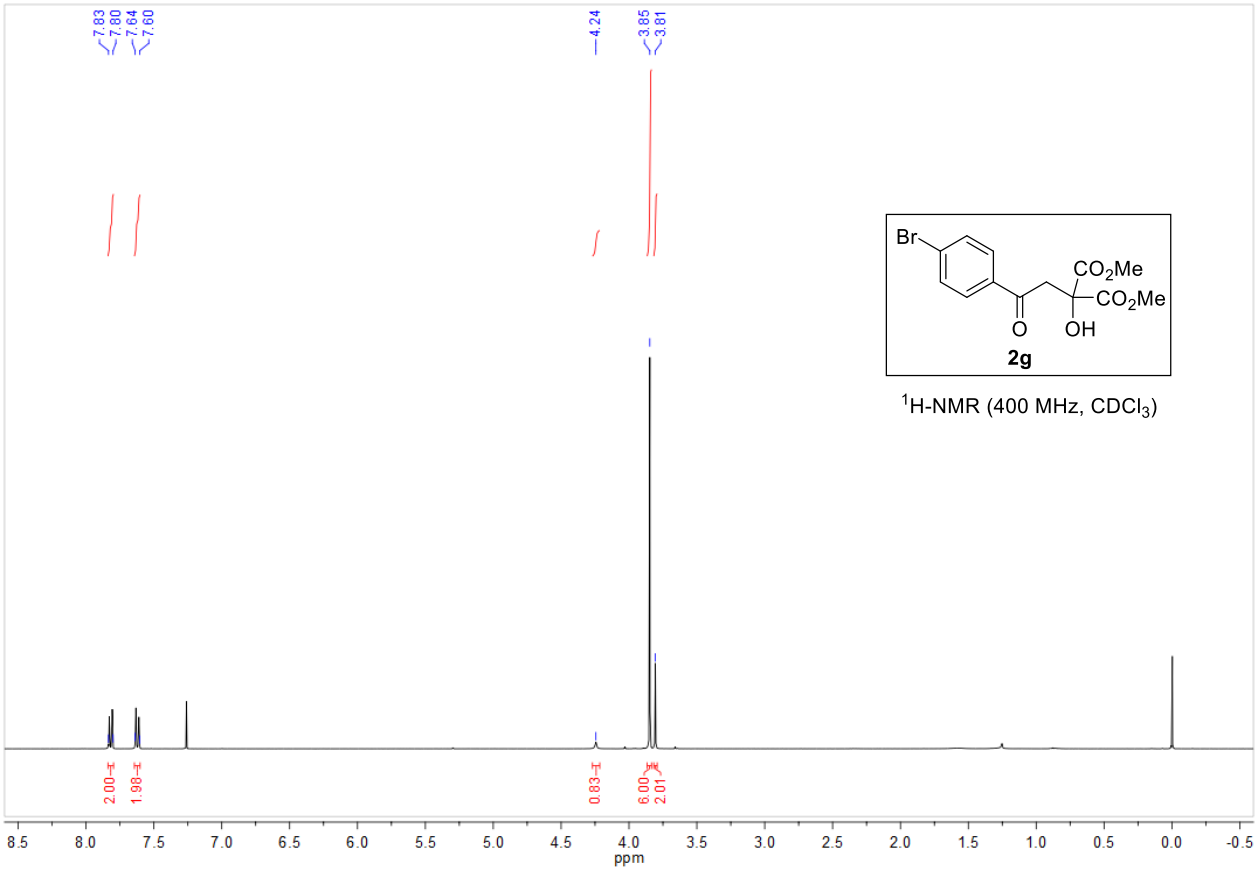
^{19}F-NMR (377 MHz, $CDCl_3$)



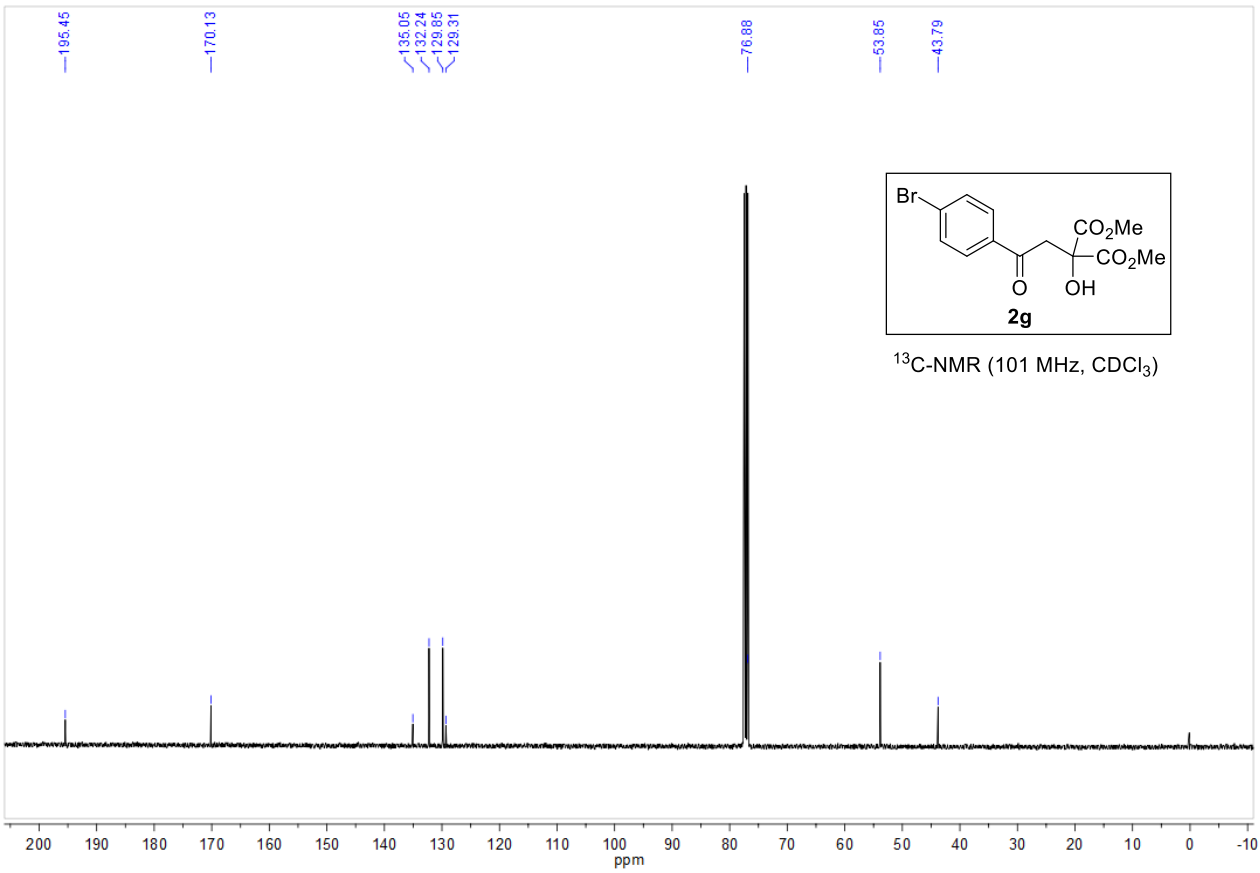
^{1}H-NMR (400 MHz, $CDCl_3$)



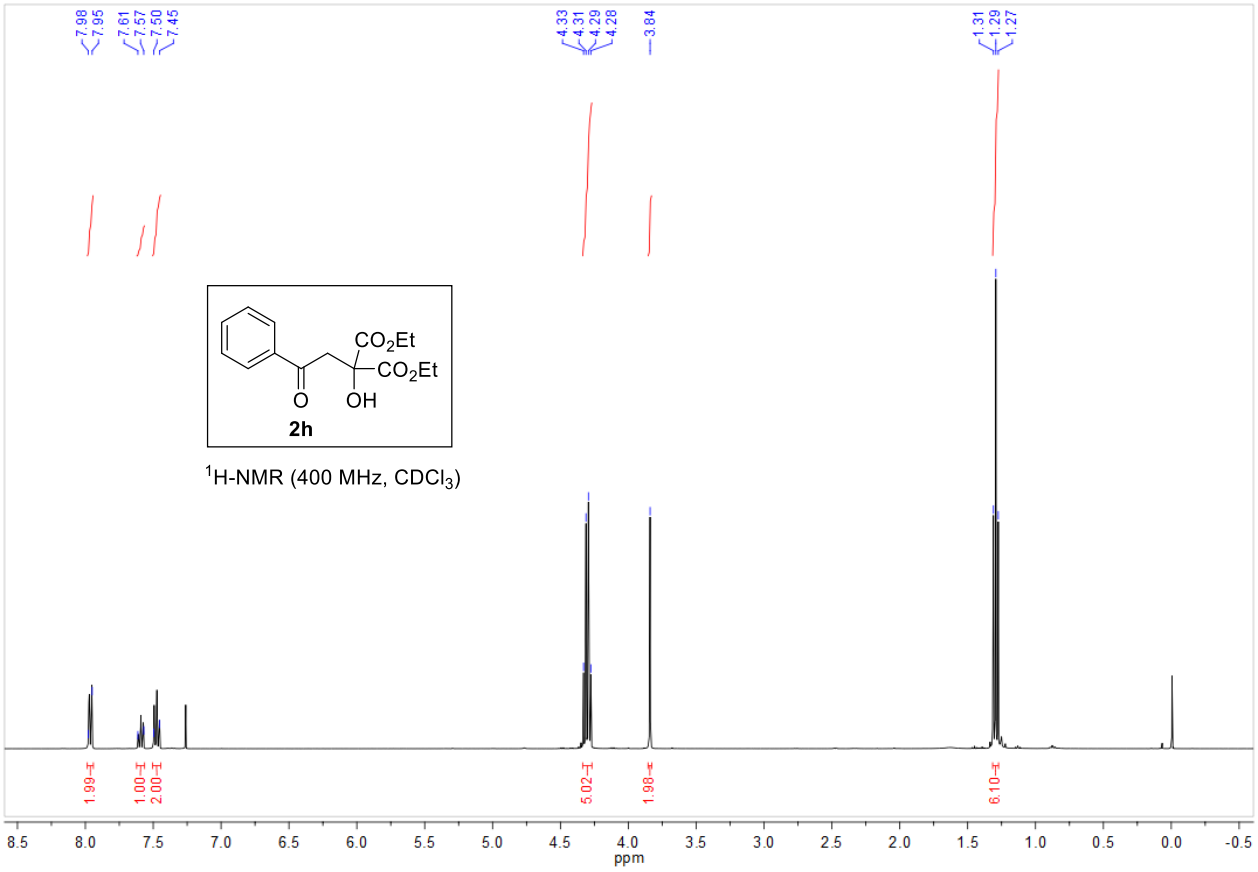
^{13}C-NMR (101 MHz, $CDCl_3$)



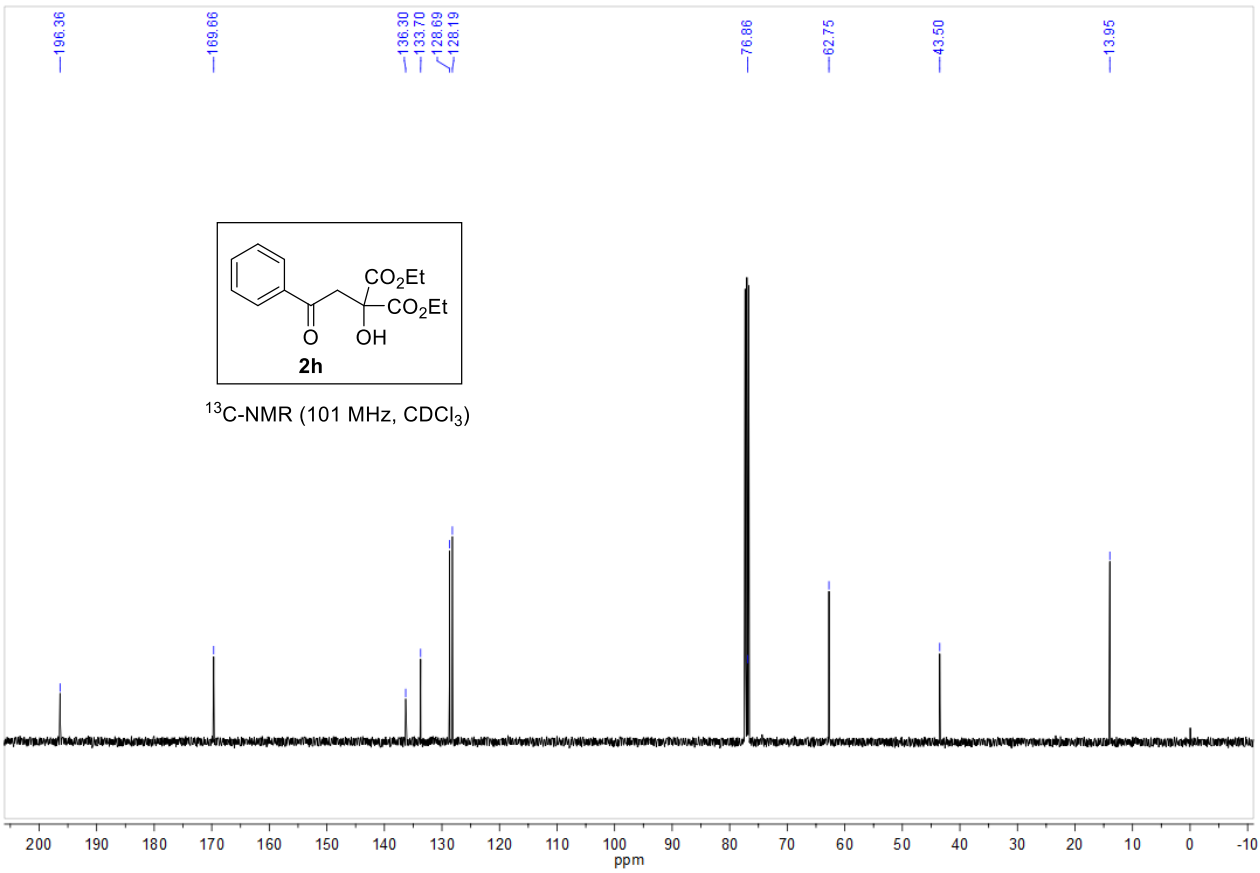
^{1}H-NMR (400 MHz, $CDCl_3$)



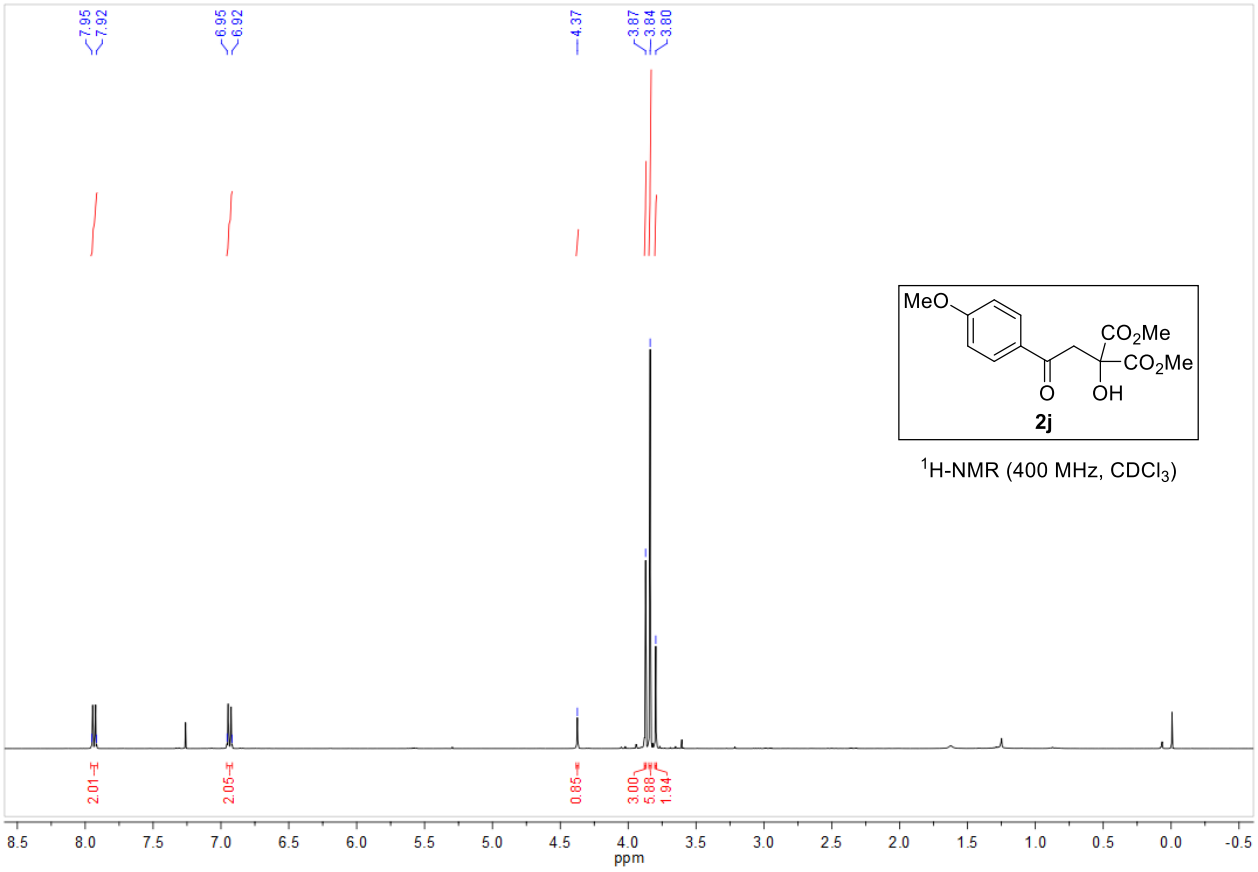
^{13}C-NMR (101 MHz, $CDCl_3$)



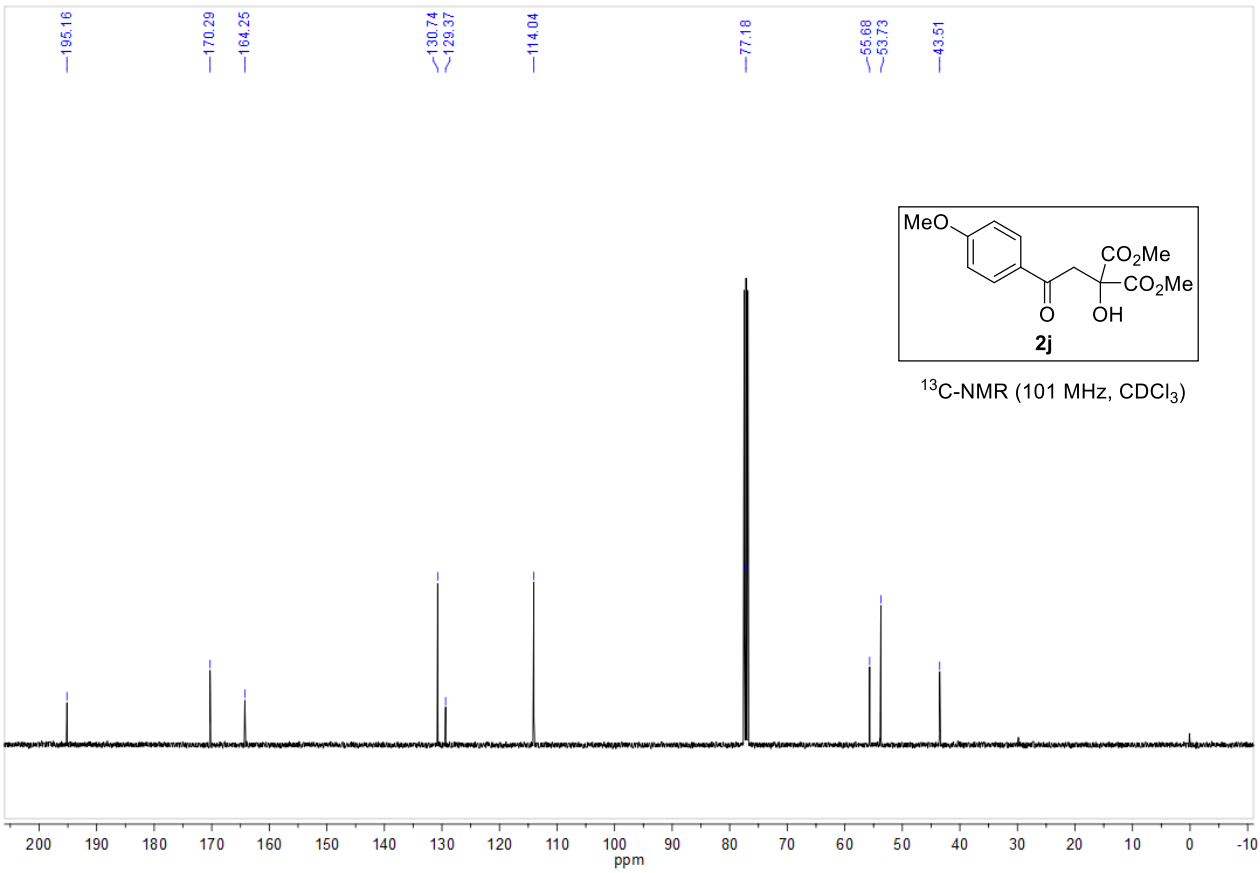
^{1}H-NMR (400 MHz, $CDCl_3$)



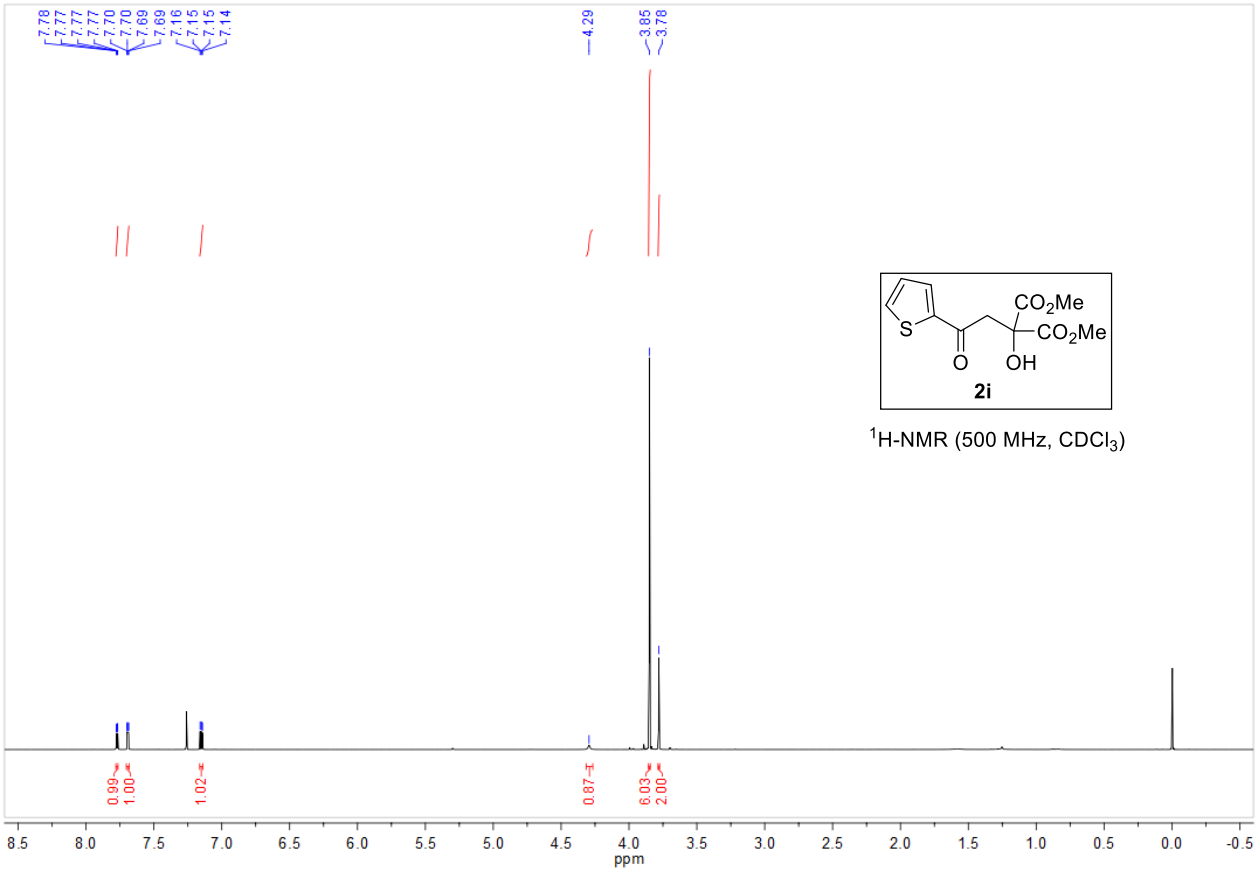
^{13}C-NMR (101 MHz, $CDCl_3$)



^{1}H-NMR (400 MHz, $CDCl_3$)

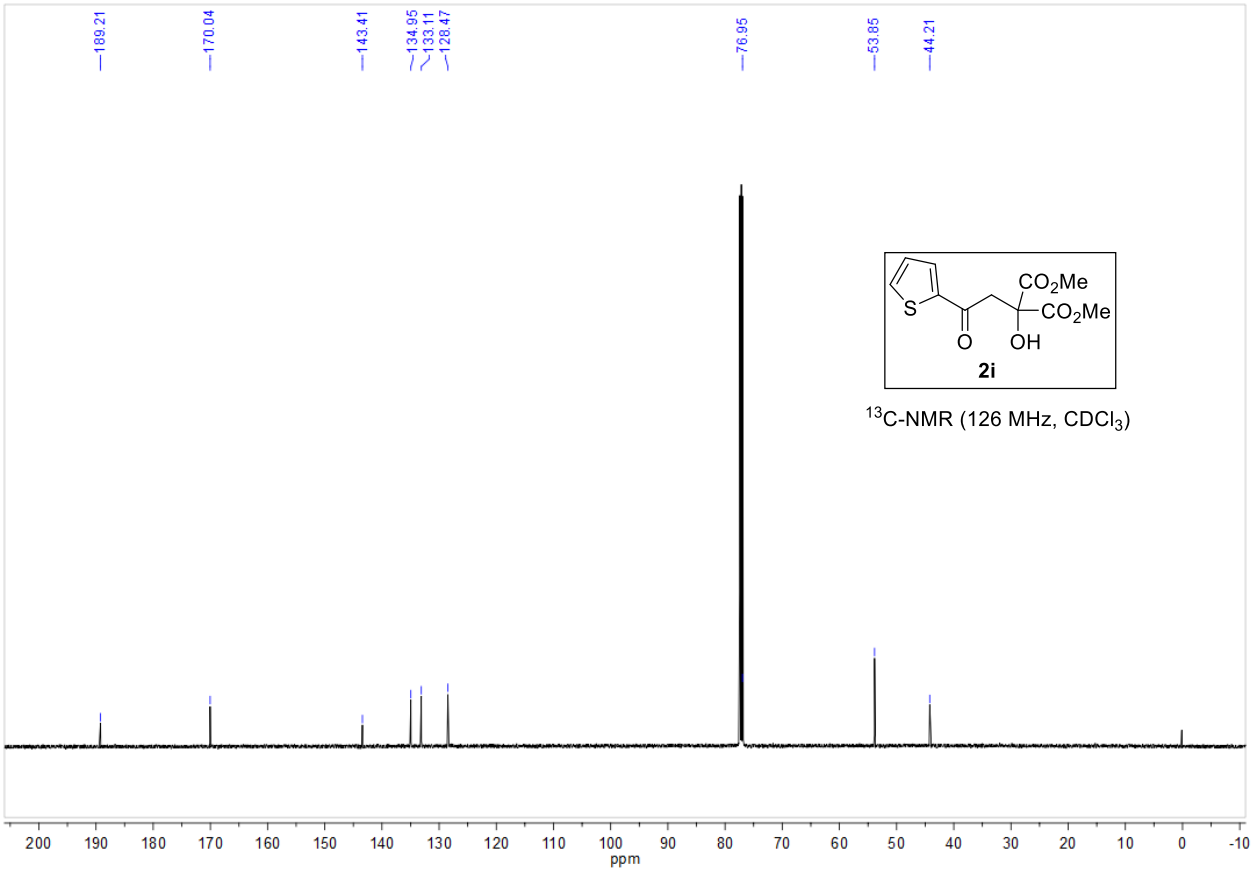


^{13}C-NMR (101 MHz, $CDCl_3$)



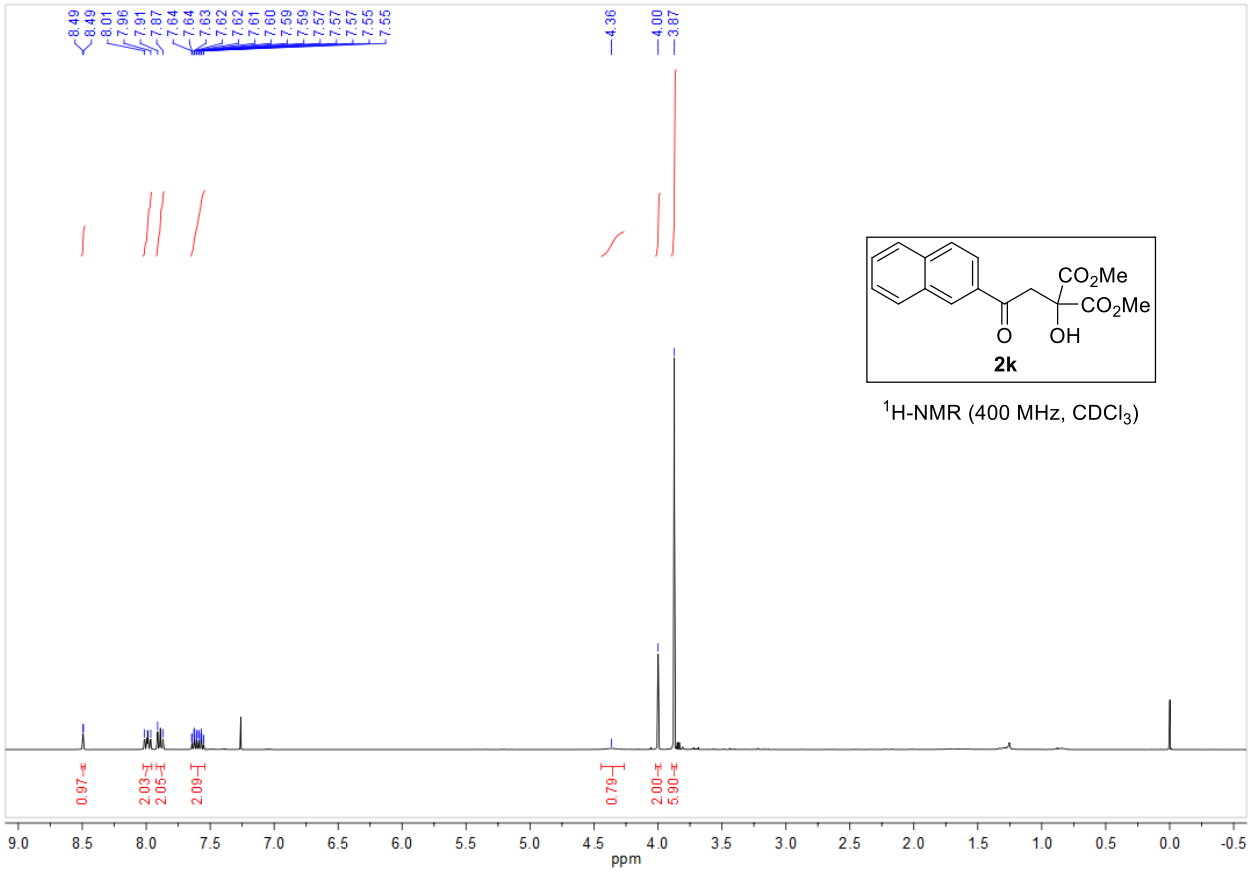
2i

^{1}H-NMR (500 MHz, $CDCl_3$)



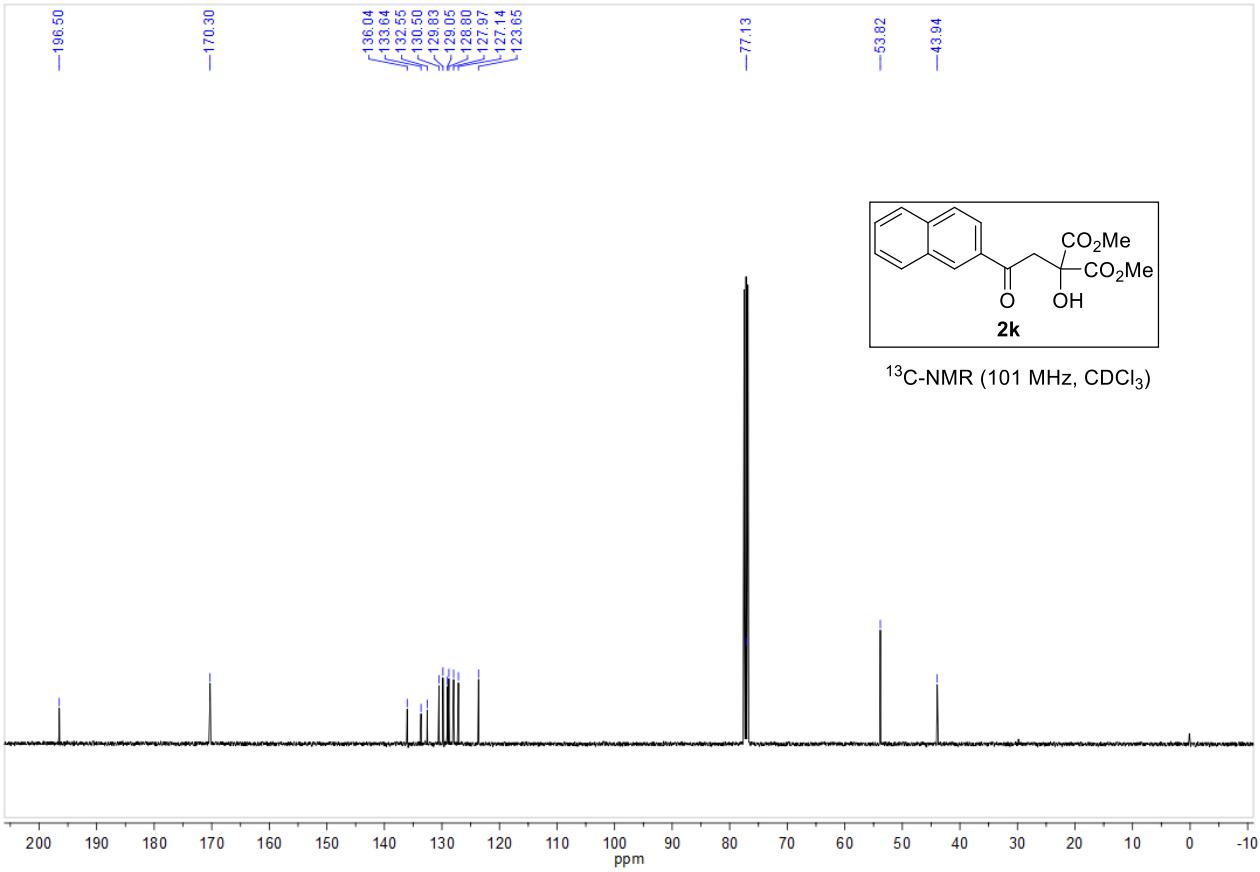
2i

^{13}C-NMR (126 MHz, $CDCl_3$)



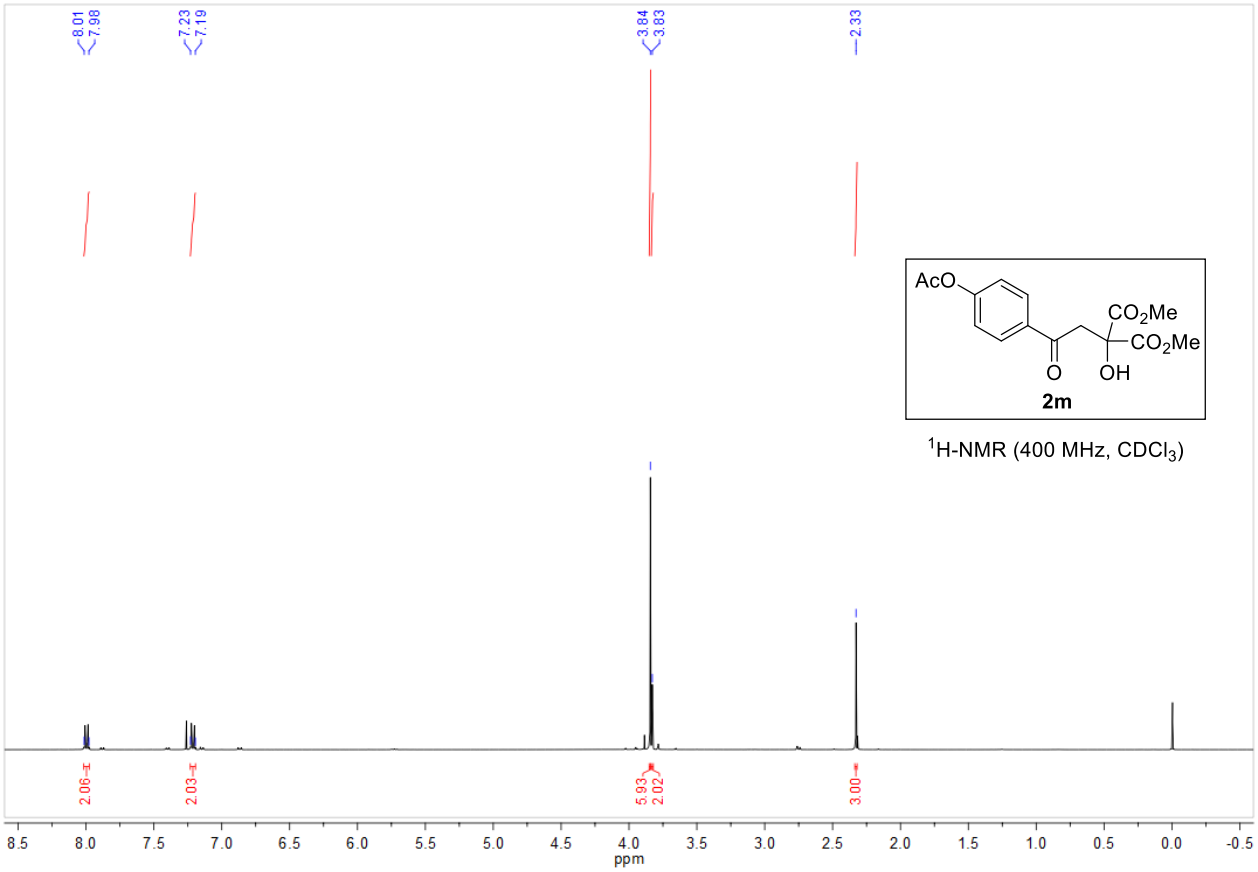
2k

^{1}H-NMR (400 MHz, $CDCl_3$)

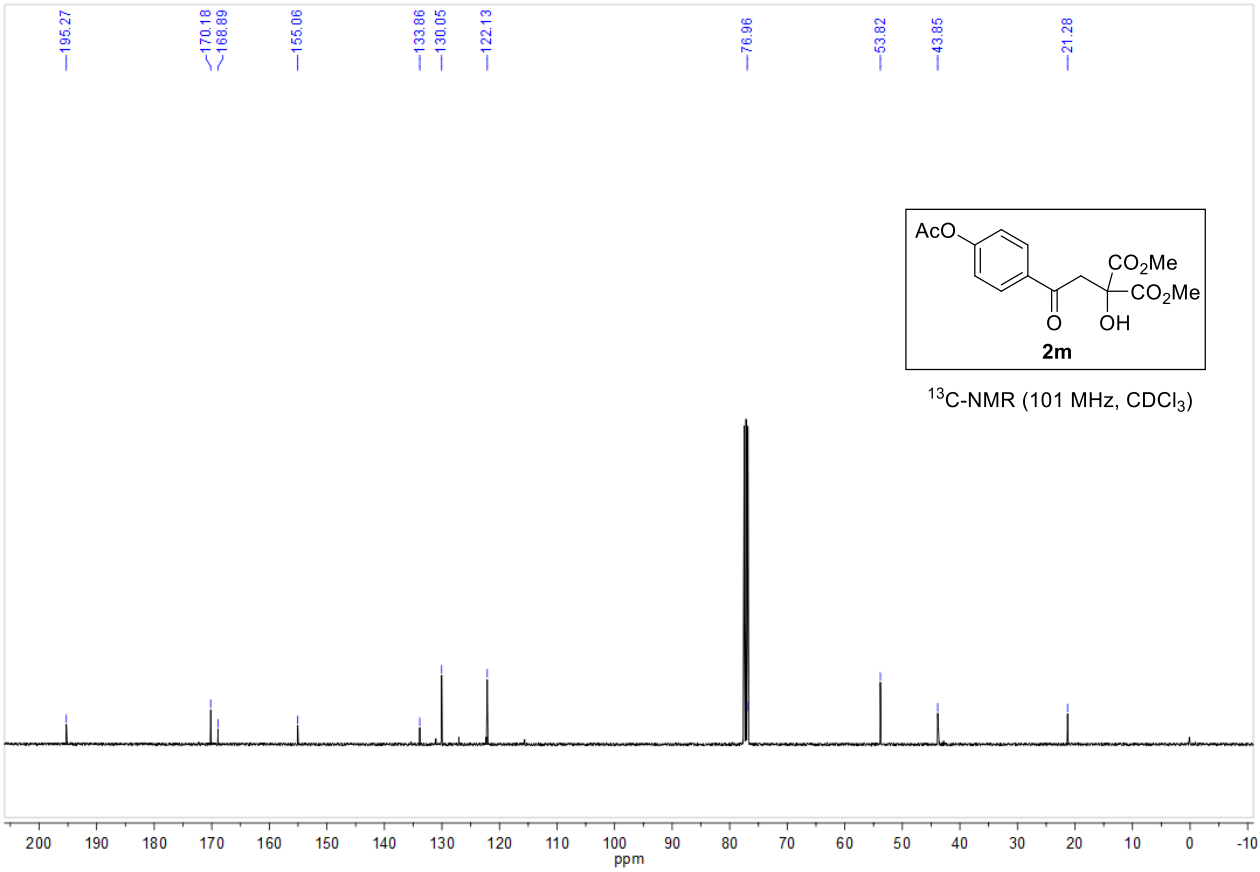


2k

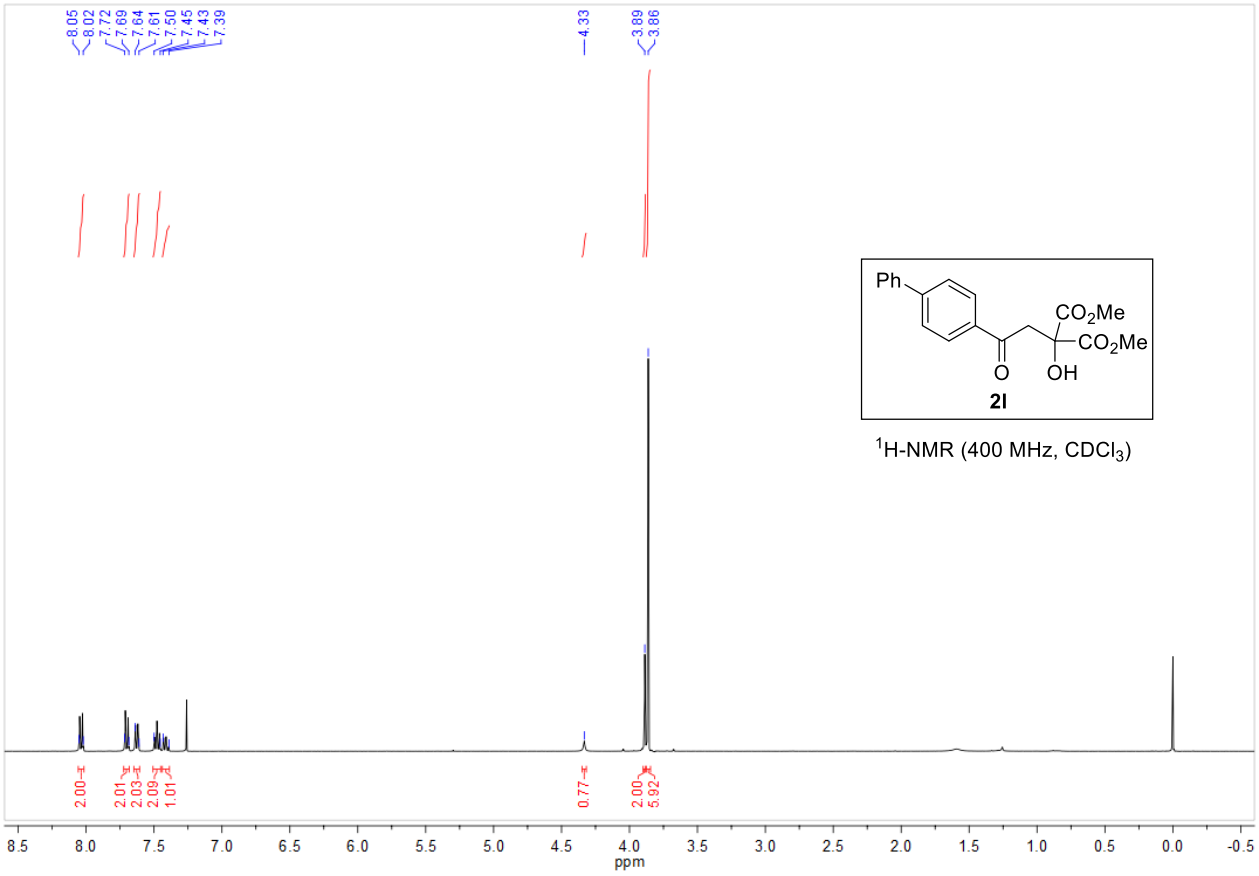
^{13}C-NMR (101 MHz, $CDCl_3$)



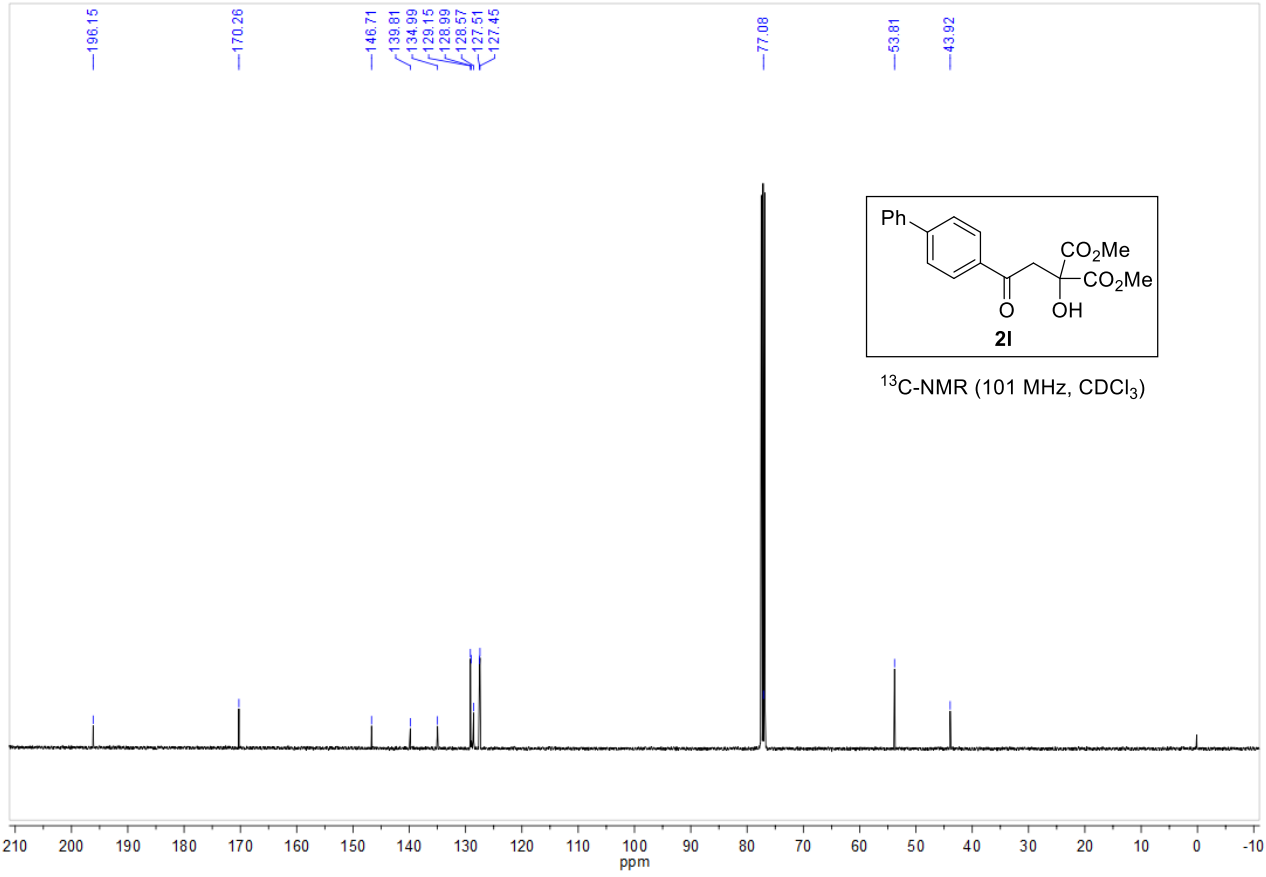
^{1}H-NMR (400 MHz, $CDCl_3$)



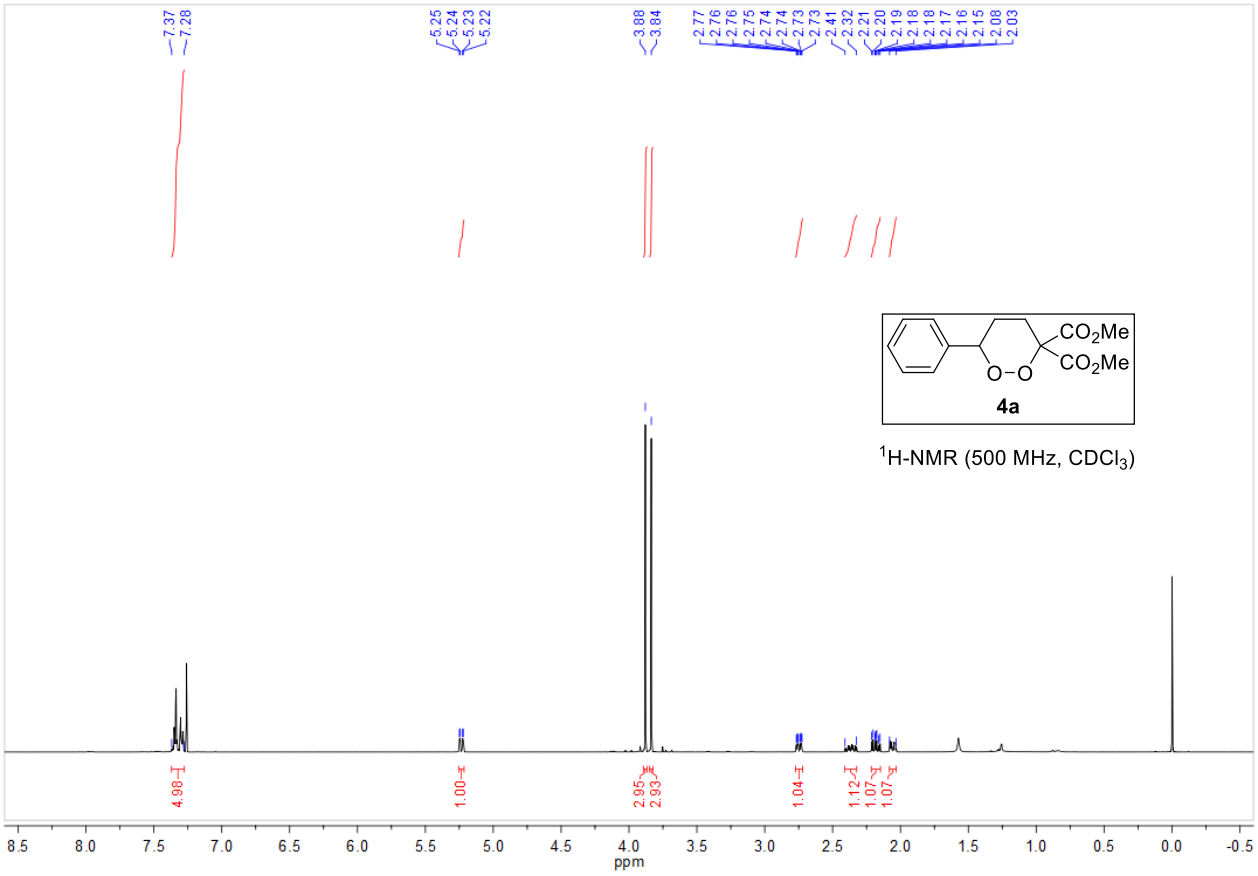
^{13}C-NMR (101 MHz, $CDCl_3$)



^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (101 MHz, $CDCl_3$)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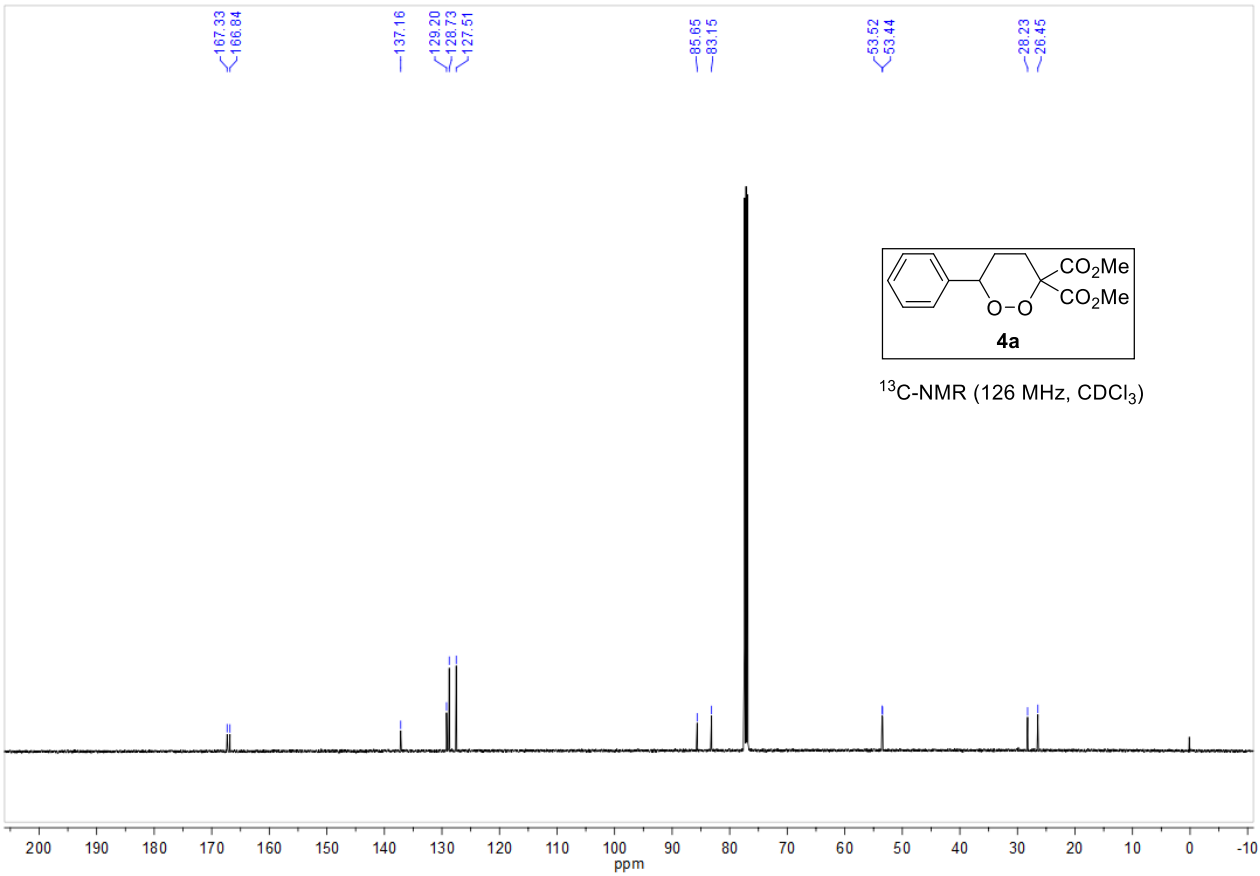
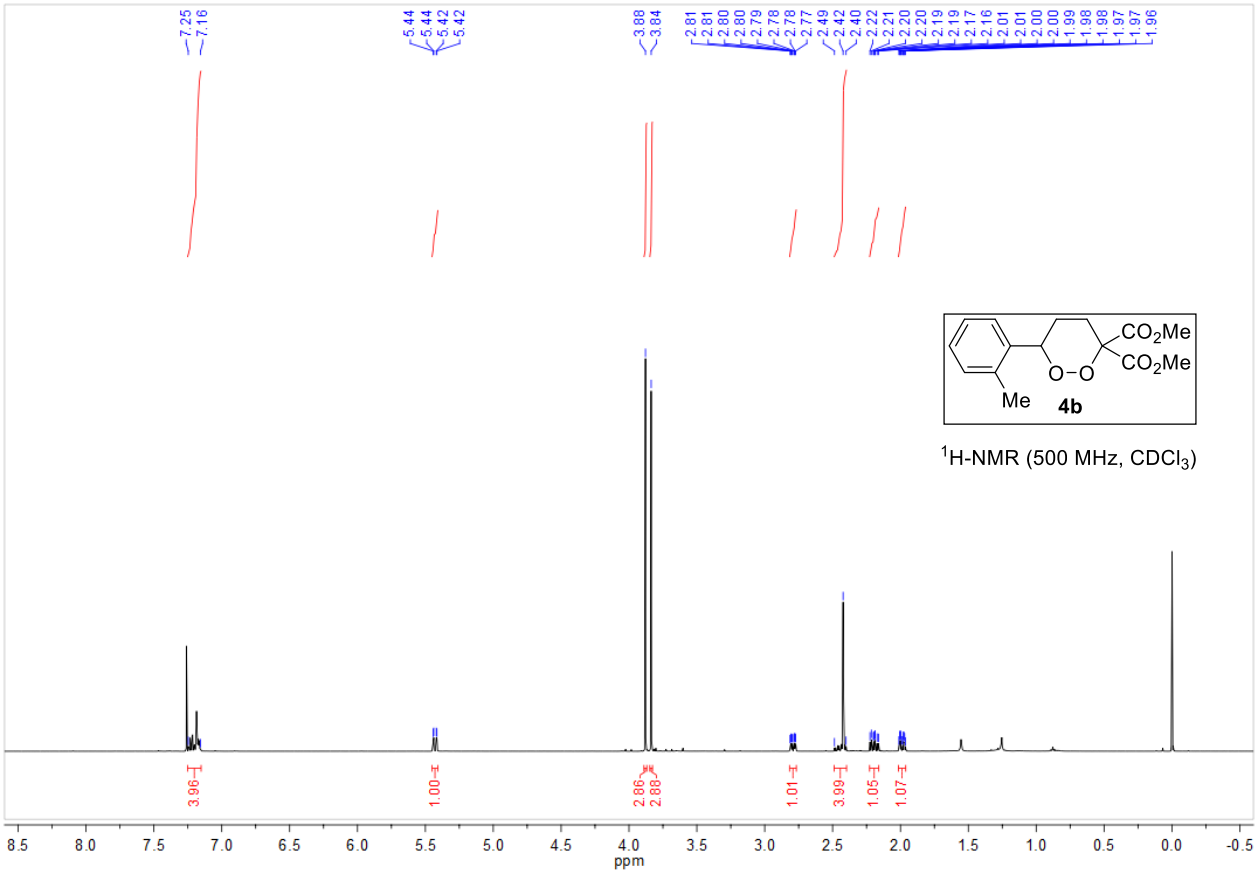
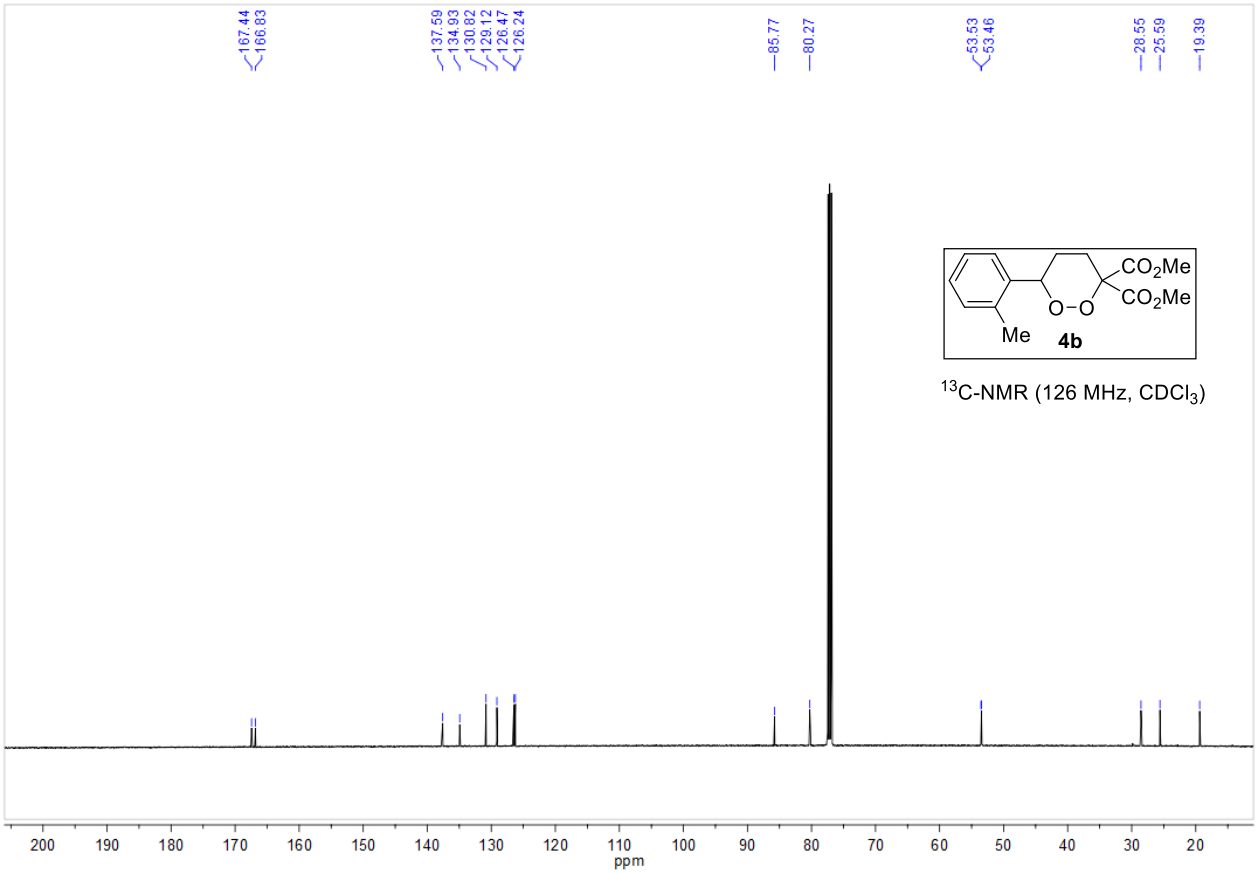
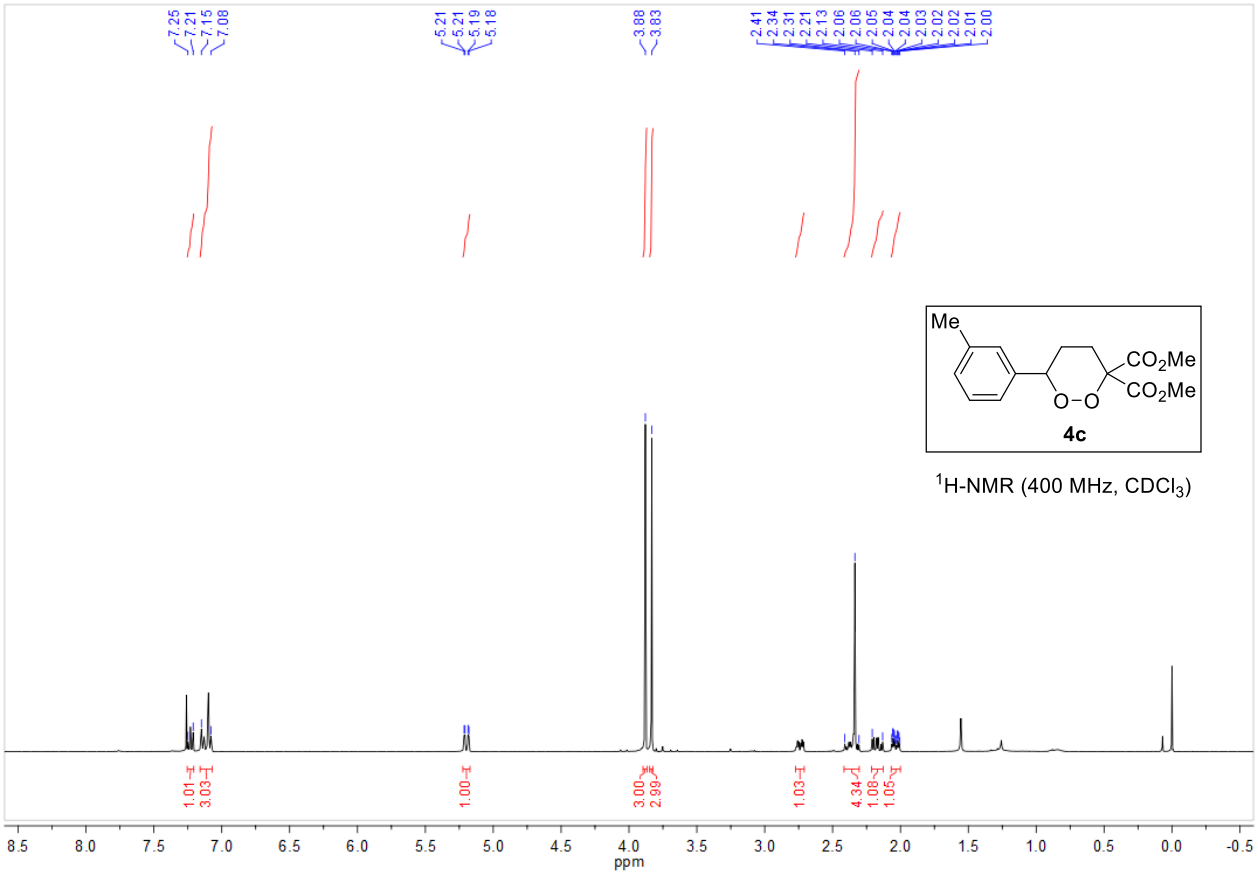
7.28
5.25
5.24
5.23
5.22
3.88
3.84
2.77
2.76
2.76
2.75
2.74
2.74
2.73
2.73
2.41
2.32
2.21
2.20
2.19
2.18
2.18
2.17
2.16
2.15
2.08
2.03
CO2Me
CO2Me
O–O
4a
1H-NMR (500 MHz, CDCl3)
4.98
1.00
2.95
2.93
1.04
1.12
1.07
1.07
ppm

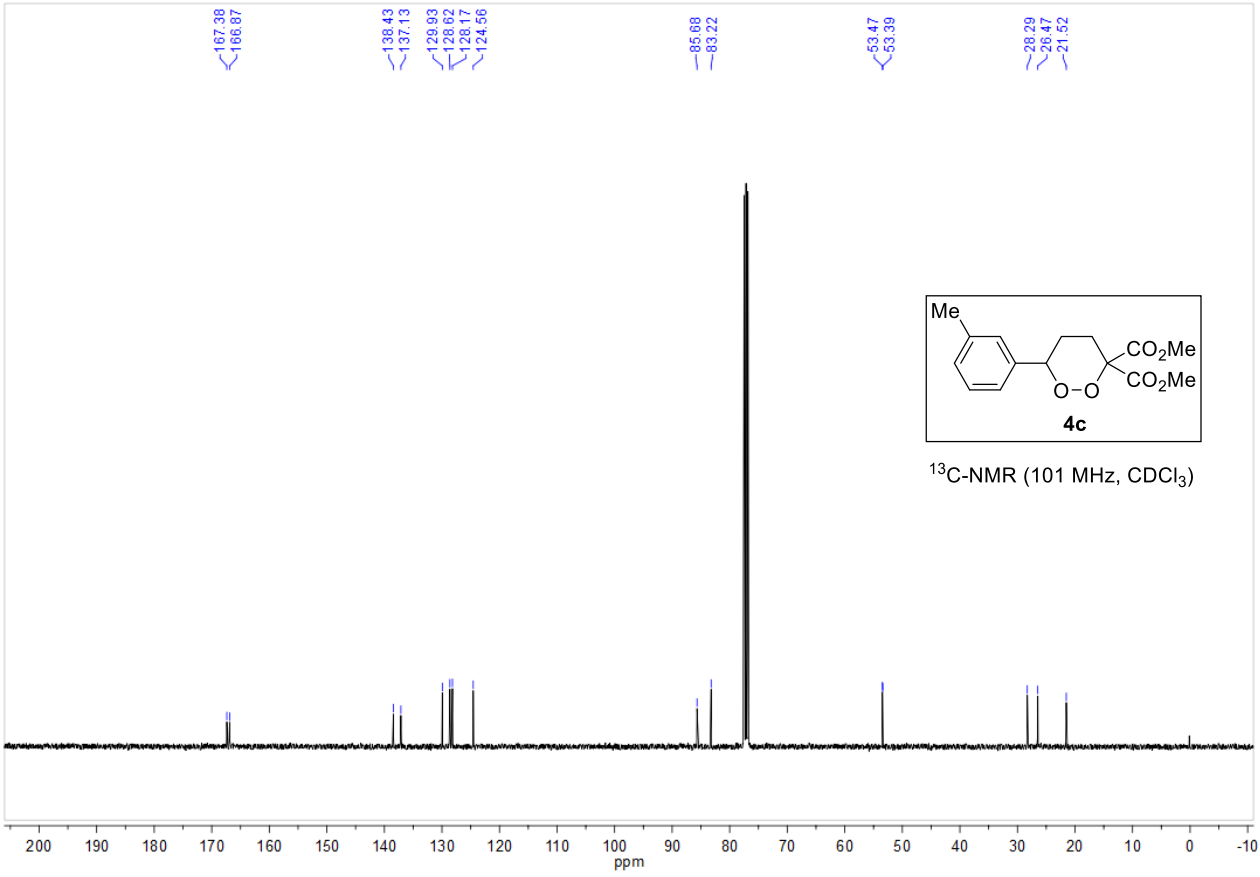

167.33
166.84
137.16
129.20
128.73
127.51
85.65
83.15
53.52
53.44
28.23
26.45
CO2Me
CO2Me
O–O
4a
13C-NMR (126 MHz, CDCl3)
ppm


7.25
7.16
5.44
5.44
5.42
5.42
3.88
3.84
2.81
2.81
2.80
2.80
2.79
2.78
2.78
2.77
2.49
2.42
2.40
2.22
2.21
2.20
2.20
2.19
2.19
2.17
2.16
2.01
2.01
2.00
2.00
1.99
1.98
1.98
1.97
1.97
1.96
CO2Me
CO2Me
O–O
Me
4b
1H-NMR (500 MHz, CDCl3)
3.96
1.00
2.86
2.88
1.01
3.99
1.05
1.07
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
ppm

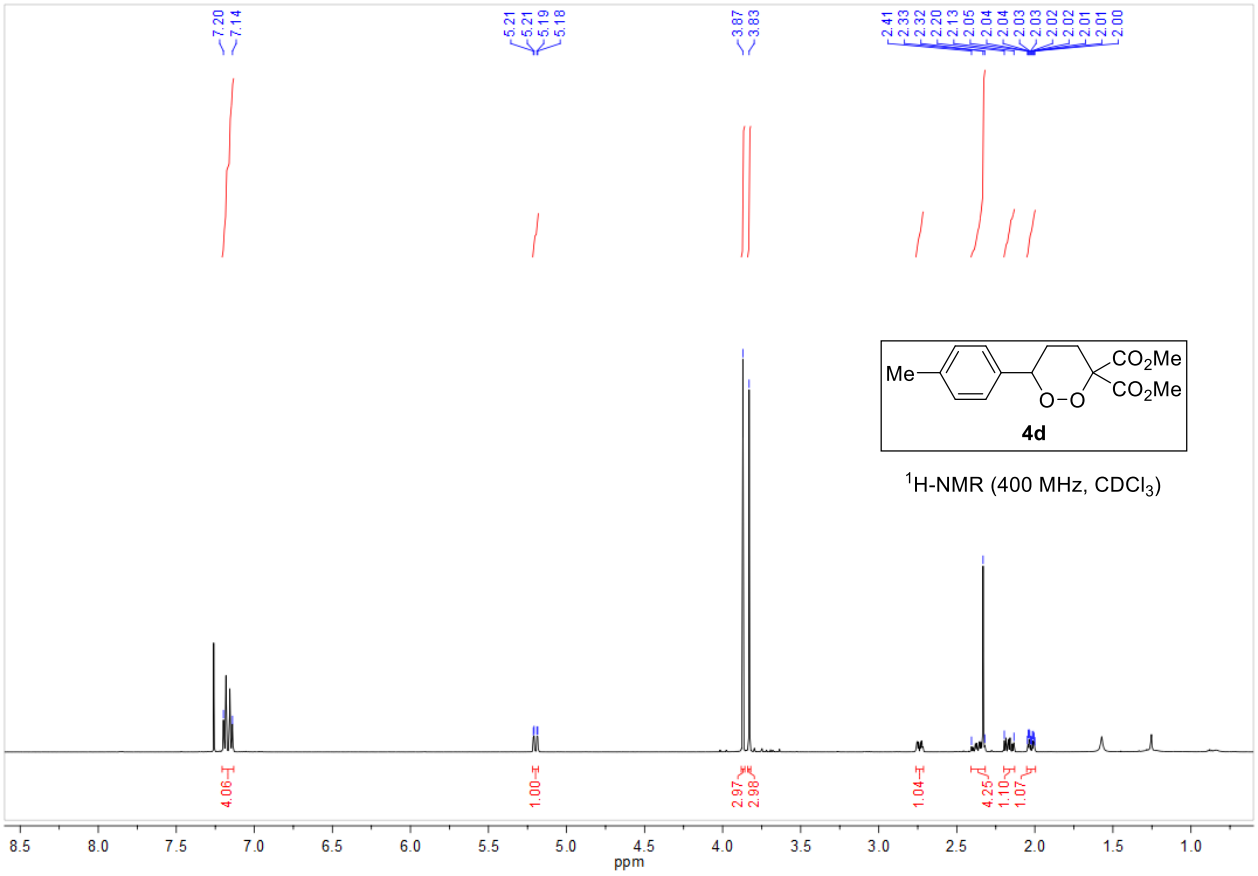

167.44
166.83
137.59
134.93
130.82
129.12
126.47
126.24
85.77
80.27
53.53
53.46
28.55
25.59
19.39
CO2Me
CO2Me
O–O
Me
4b
13C-NMR (126 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



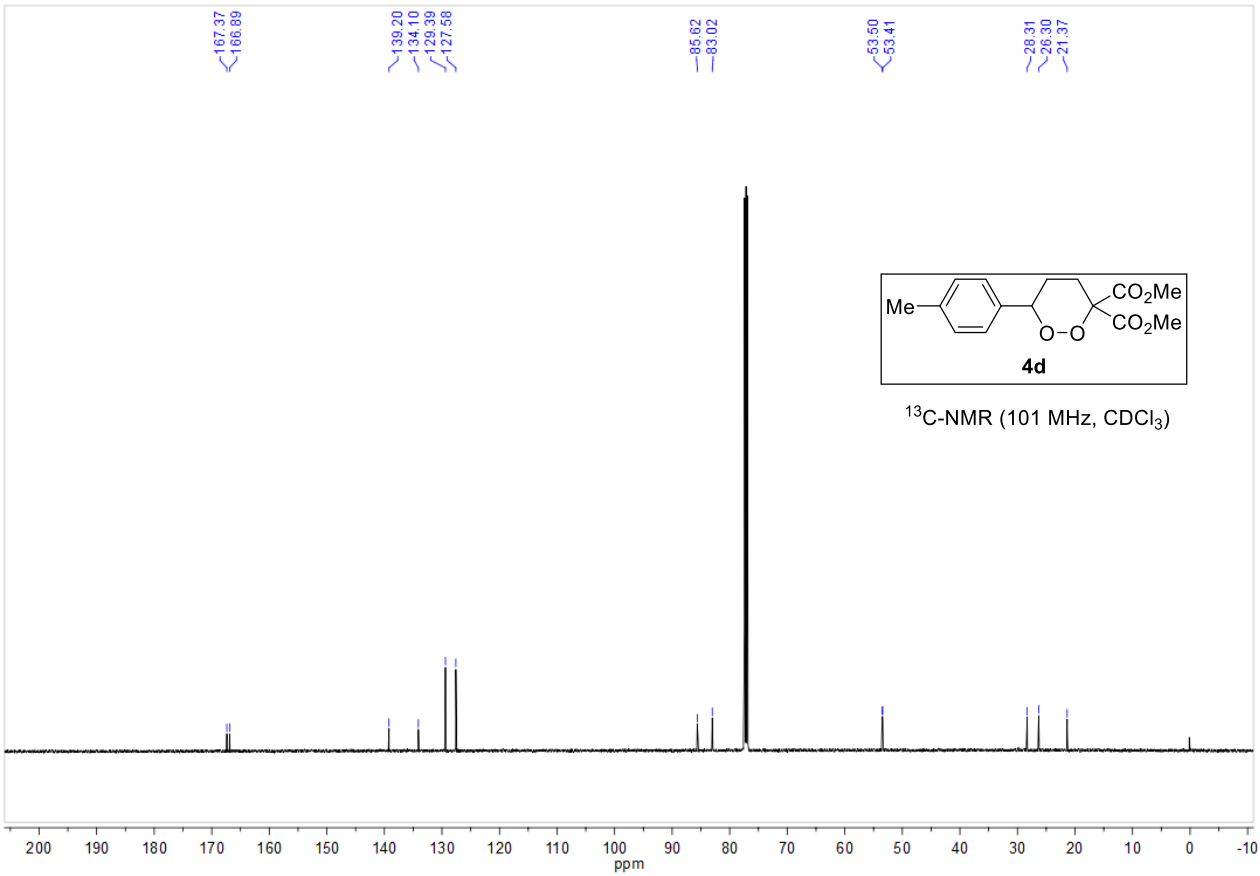
^{1}H-NMR (400 MHz, $CDCl_3$)



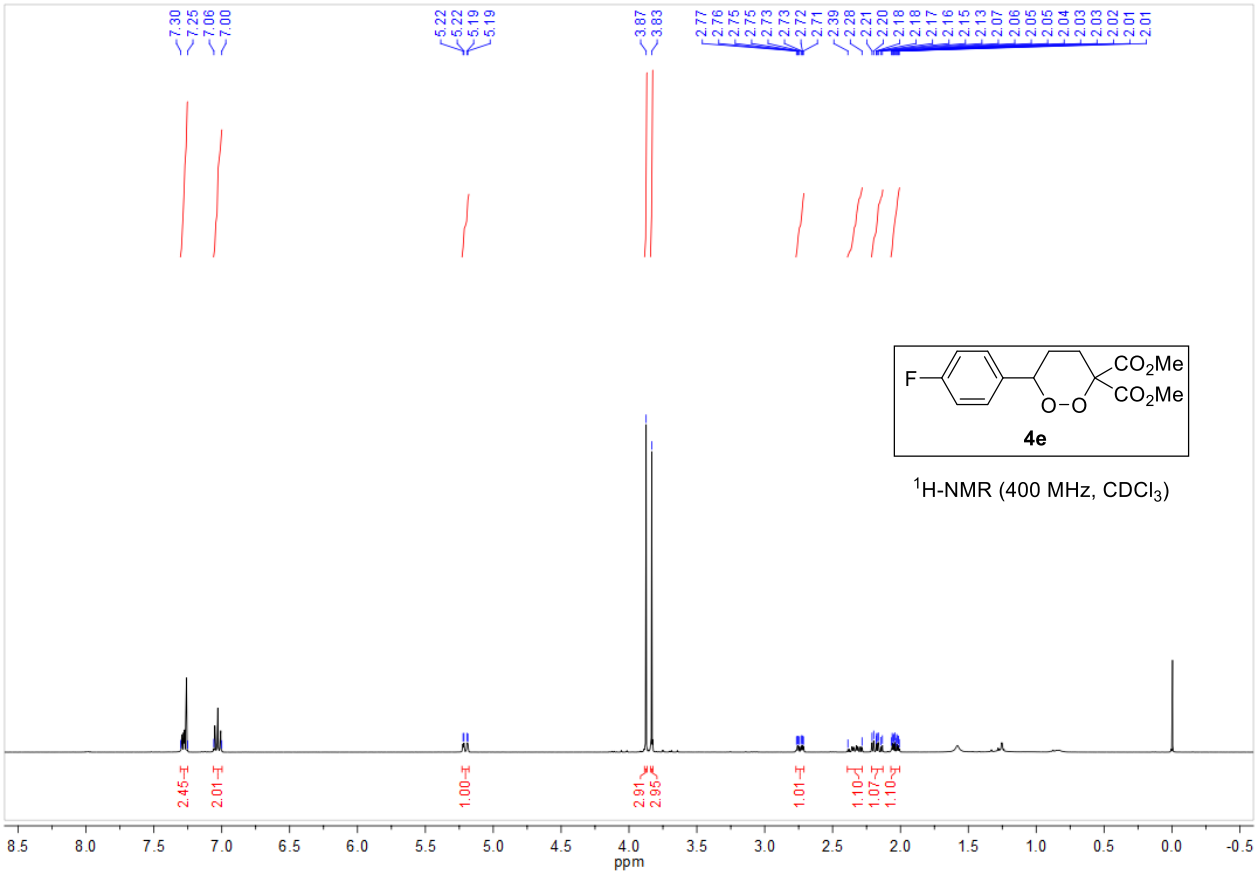
^{13}C-NMR (101 MHz, $CDCl_3$)



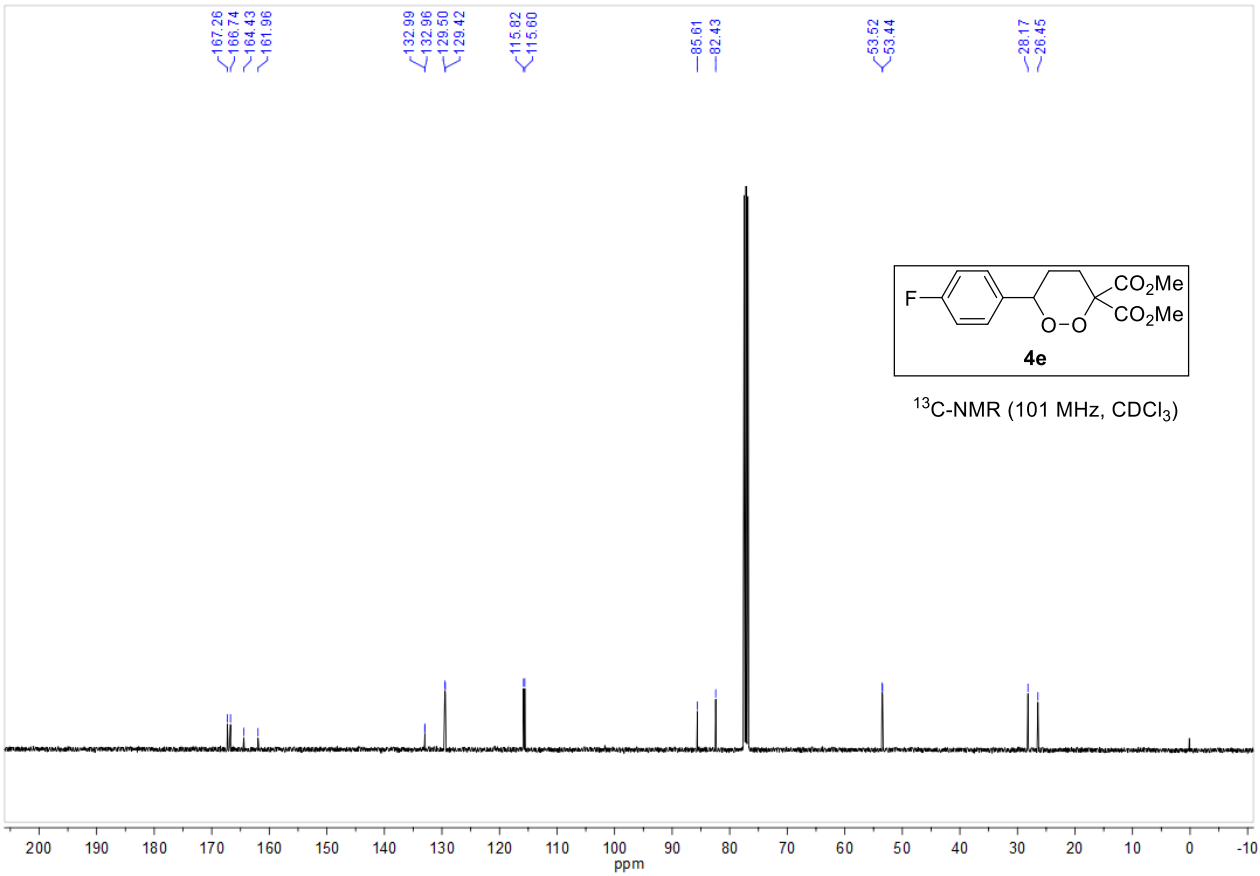
^{1}H-NMR (400 MHz, $CDCl_3$)



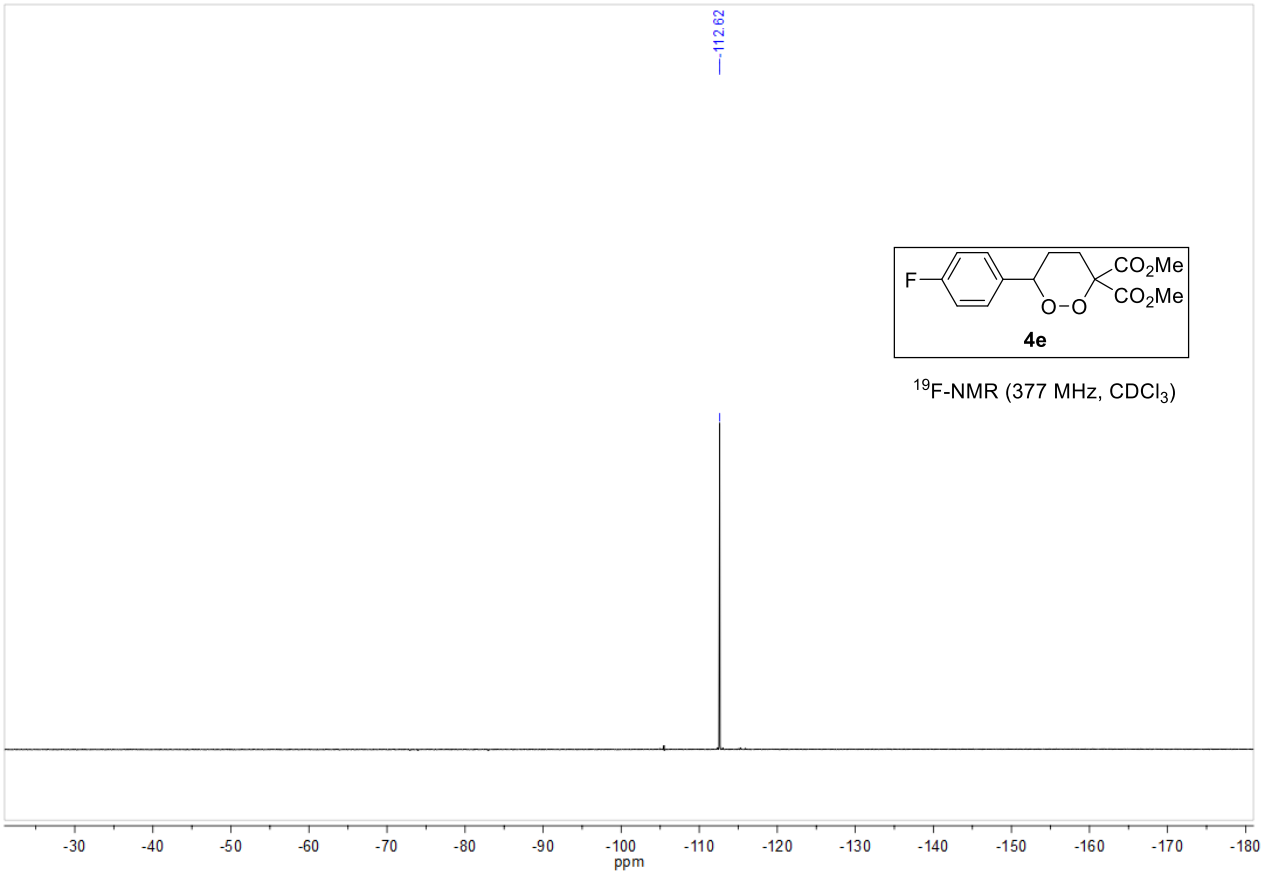
^{13}C-NMR (101 MHz, $CDCl_3$)



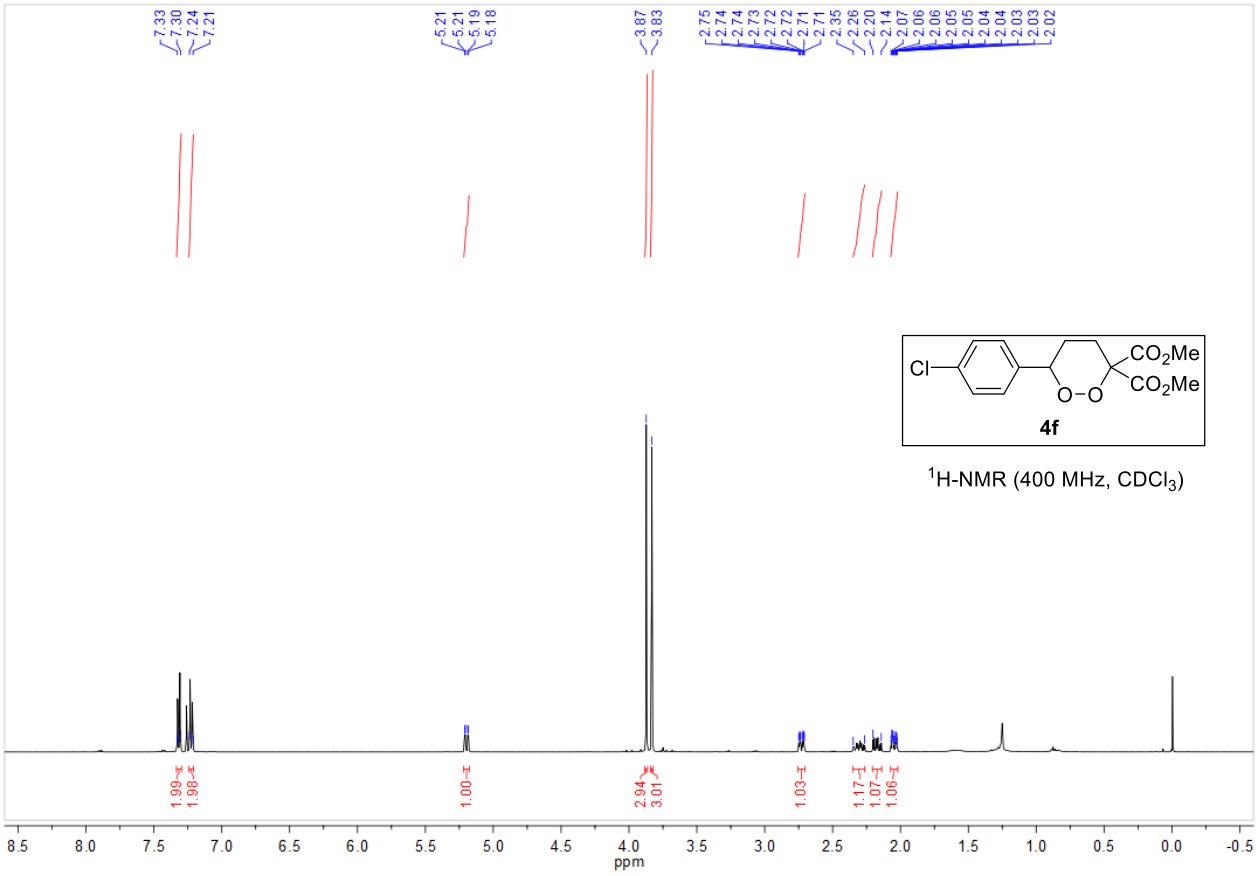
^{1}H-NMR (400 MHz, $CDCl_3$)



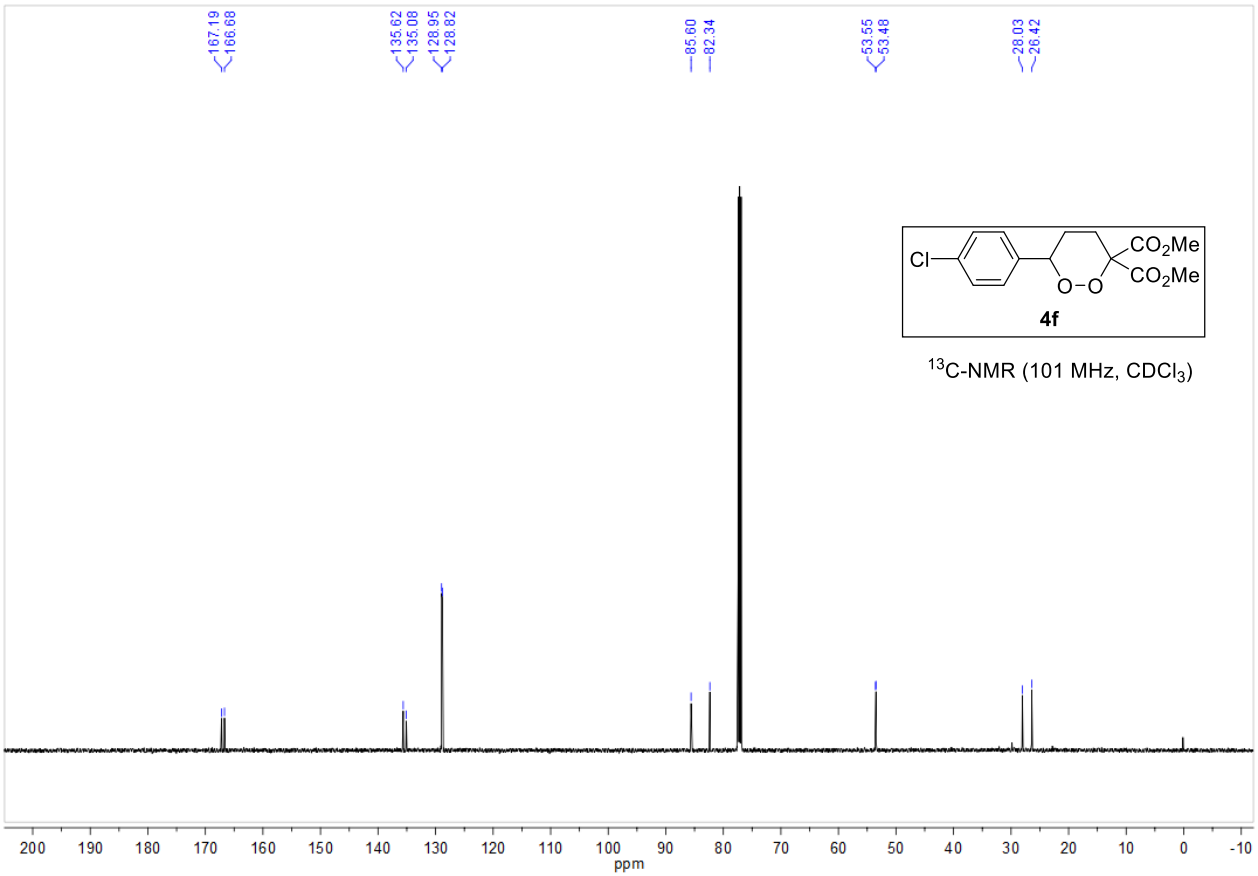
^{13}C-NMR (101 MHz, $CDCl_3$)



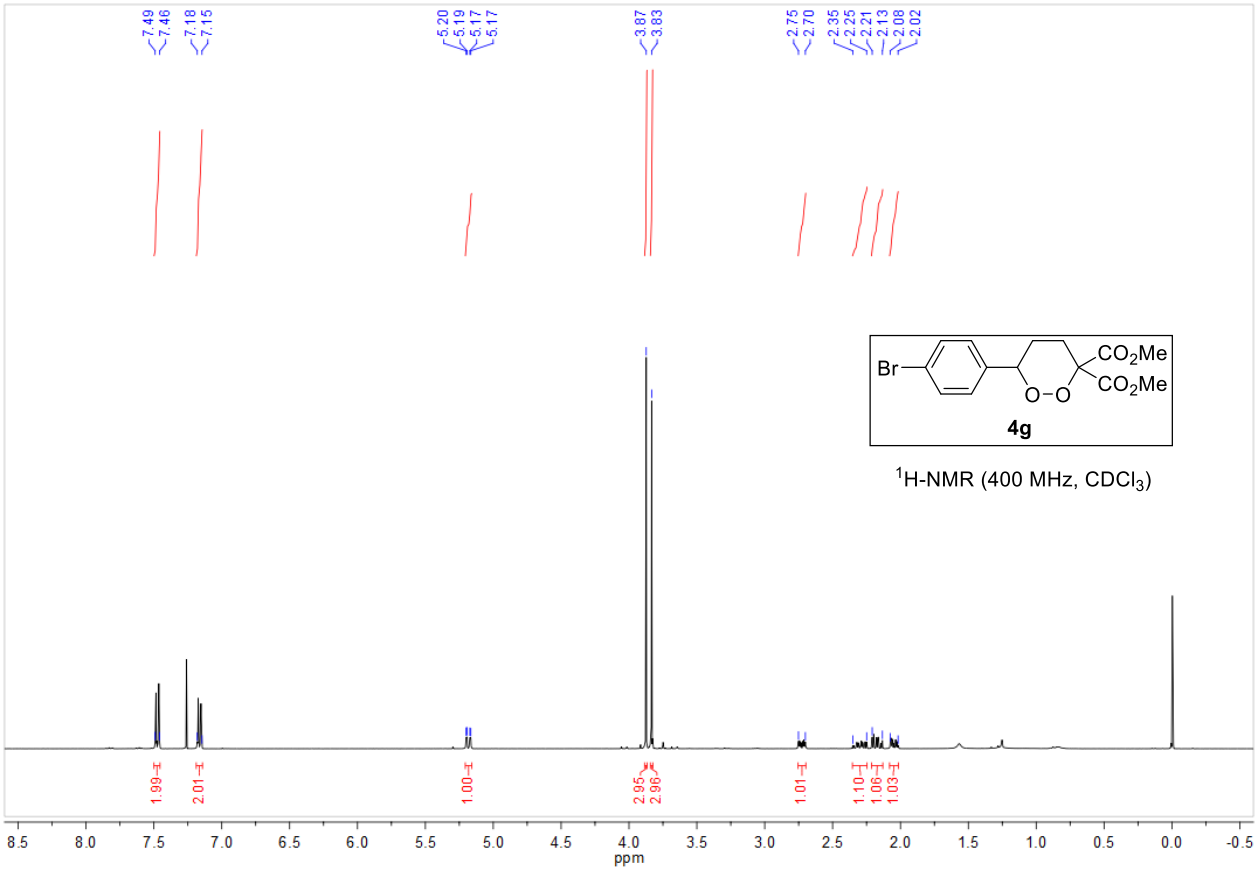
^{19}F-NMR (377 MHz, $CDCl_3$)

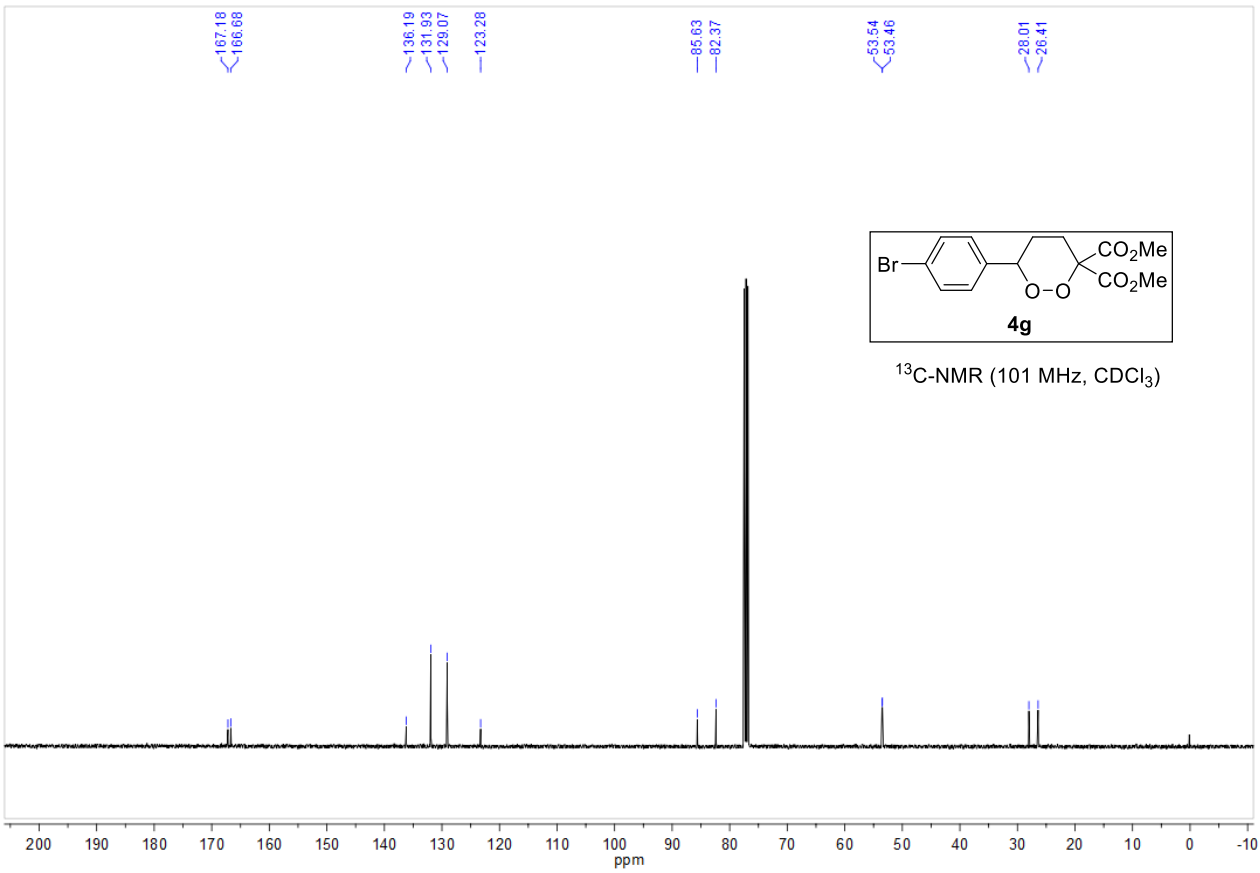


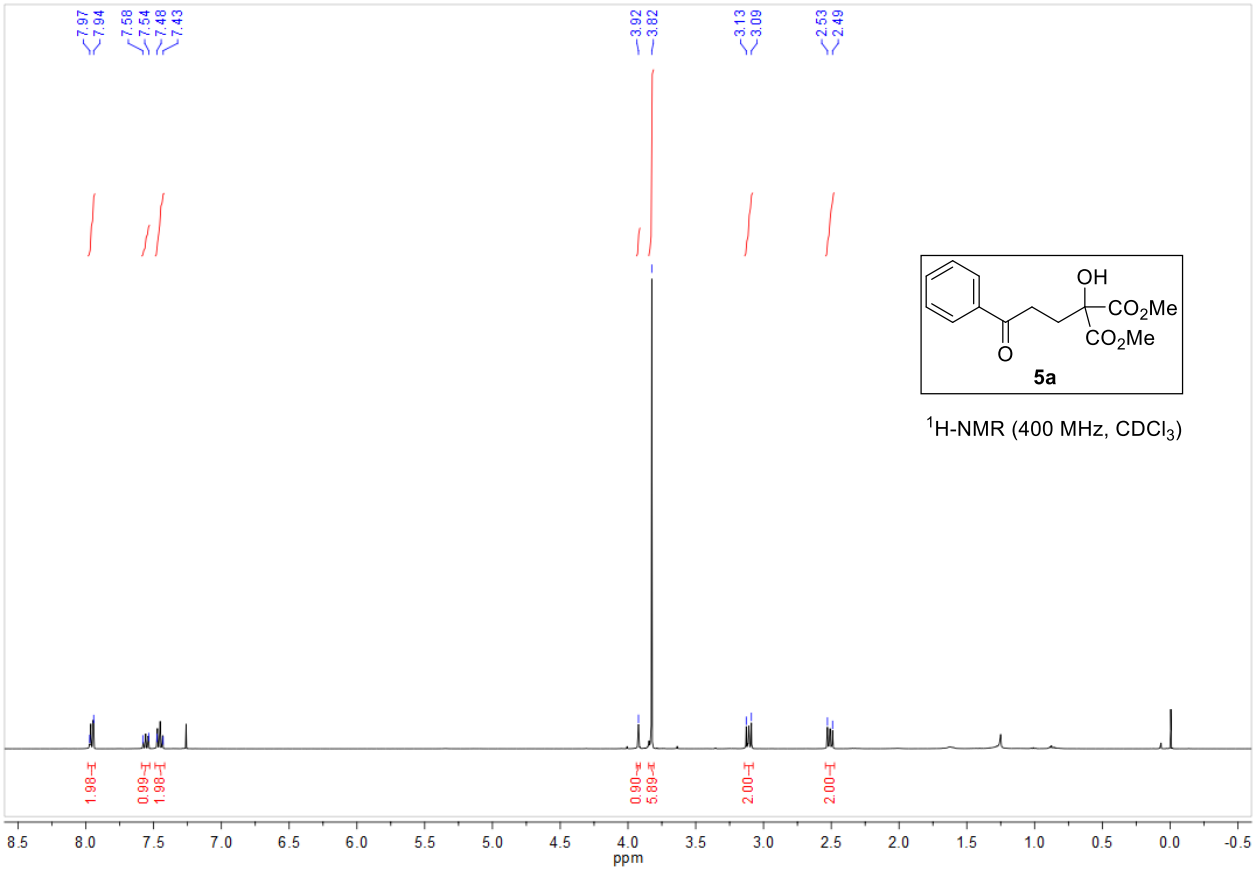
^{1}H-NMR (400 MHz, $CDCl_3$)



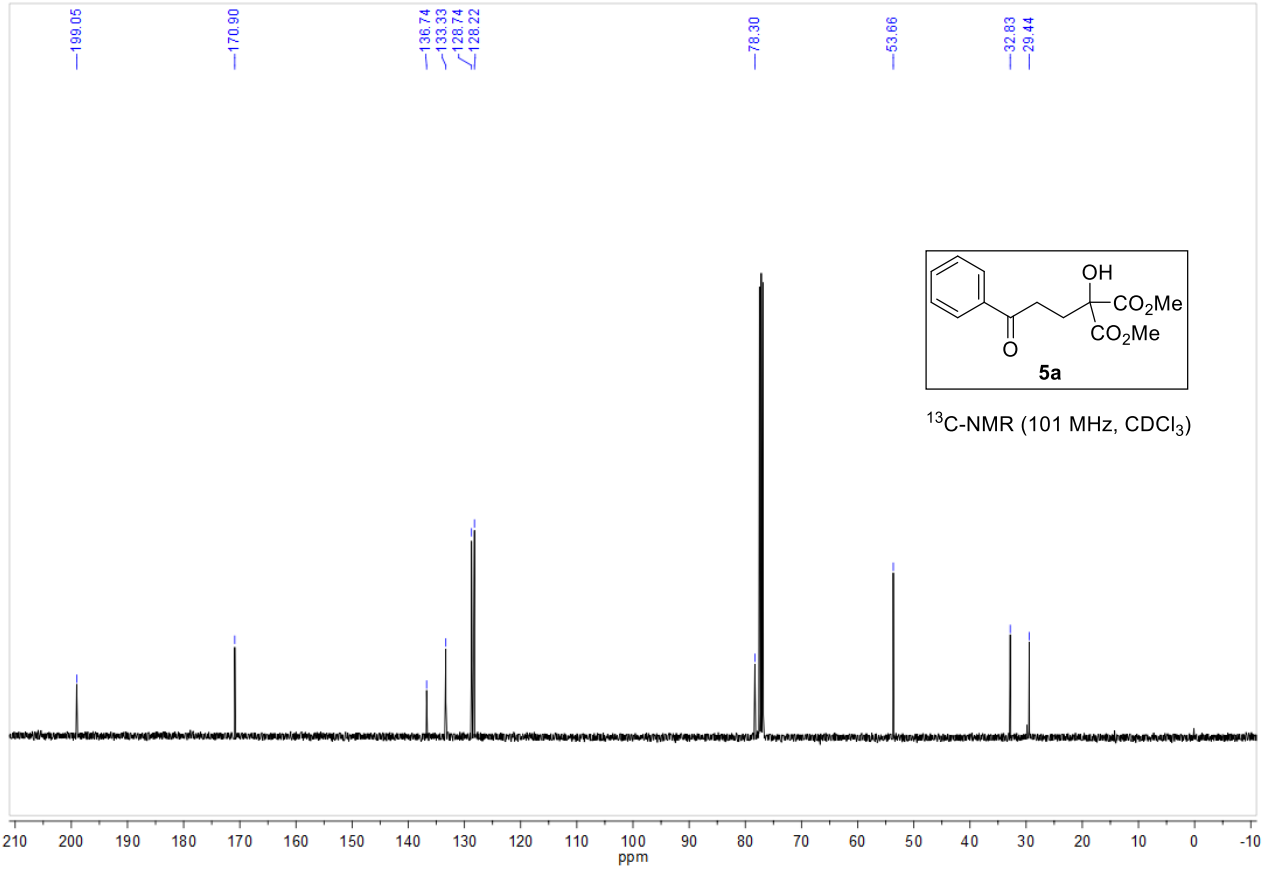
^{13}C-NMR (101 MHz, $CDCl_3$)


7.49
7.46
7.18
7.15
5.20
5.19
5.17
5.17
3.87
3.83
2.75
2.70
2.35
2.25
2.21
2.13
2.08
2.02
Br
CO2Me
CO2Me
O–O
4g
1H-NMR (400 MHz, CDCl3)
1.99
2.01
1.00
2.95
2.96
1.01
1.10
1.06
1.03
ppm

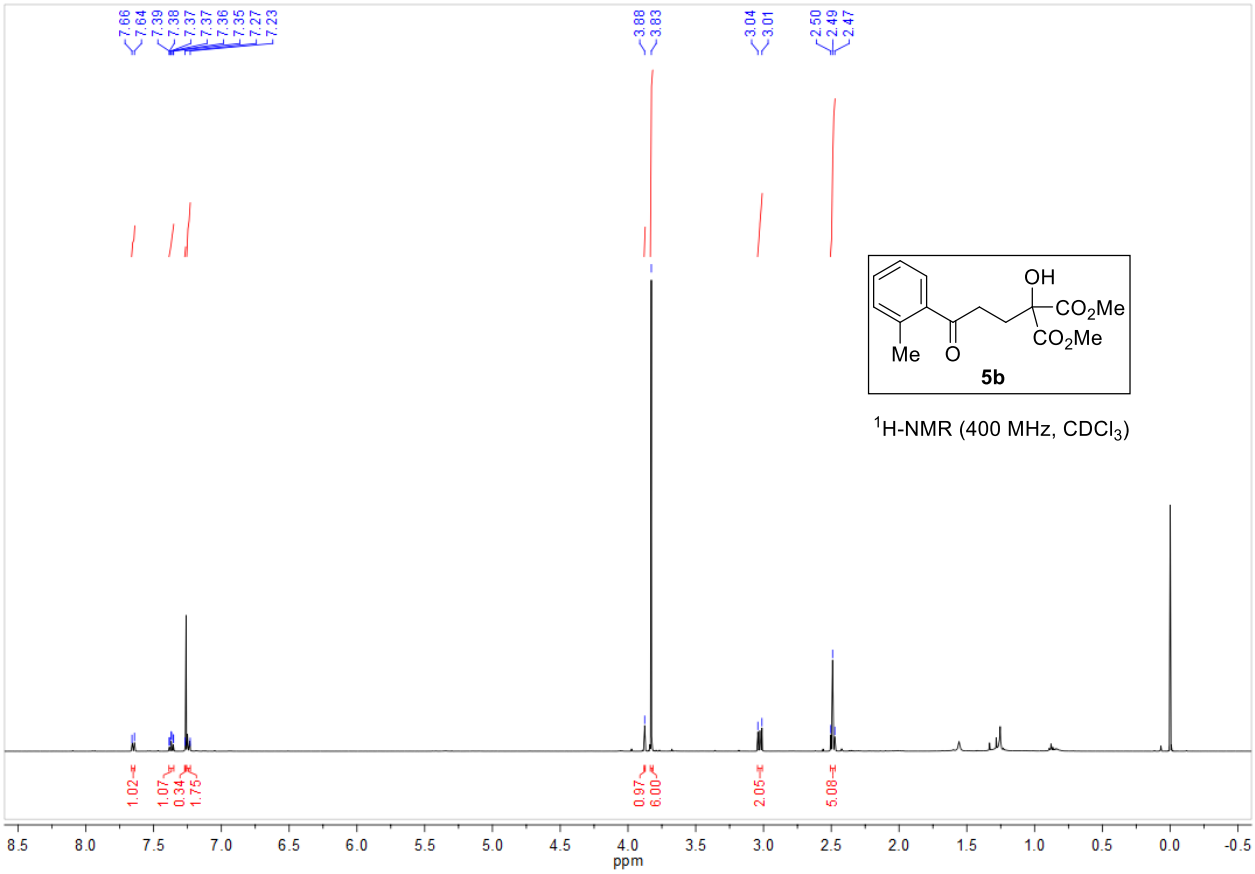

167.18
166.68
136.19
131.93
129.07
123.28
85.63
82.37
53.54
53.46
28.01
26.41
Br
CO2Me
CO2Me
O–O
4g
13C-NMR (101 MHz, CDCl3)
ppm



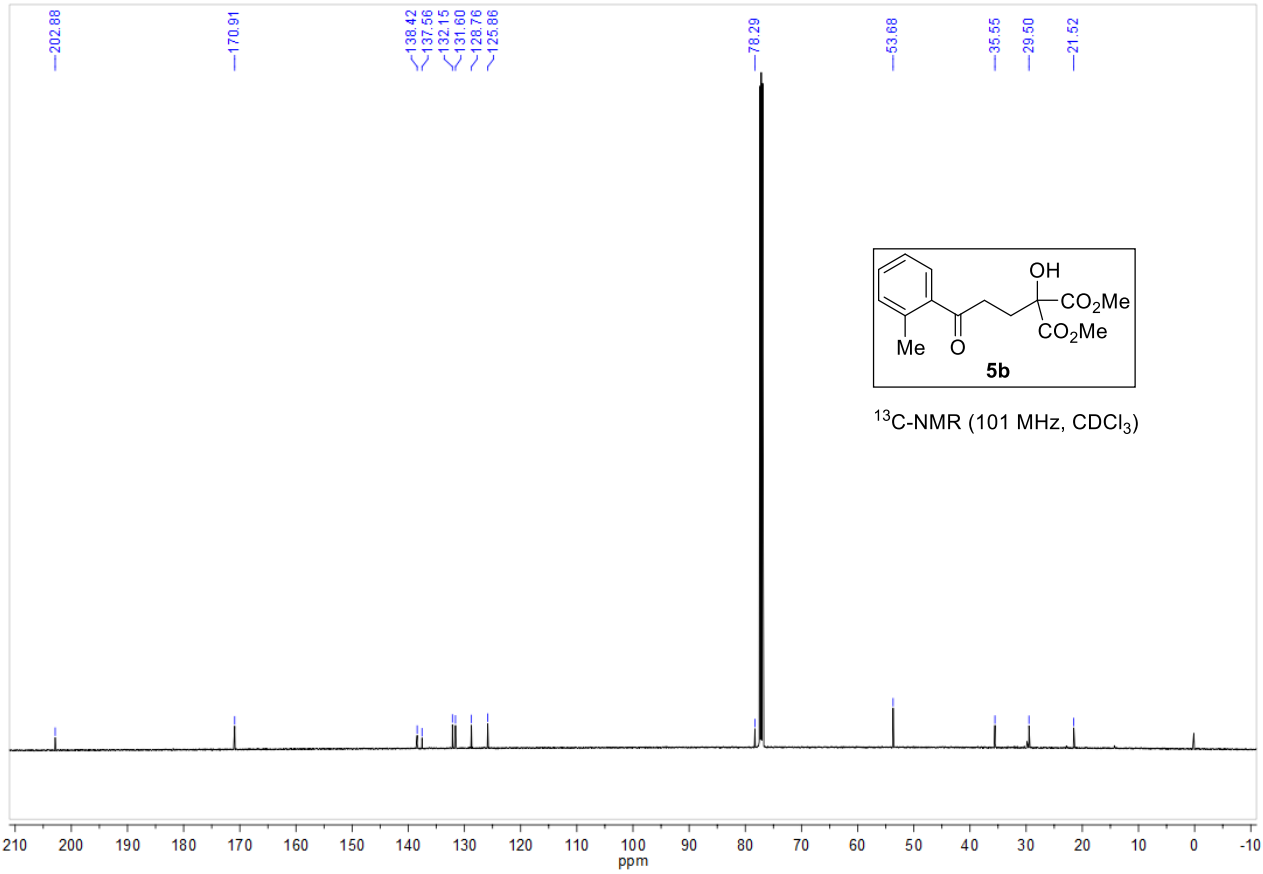
^{1}H-NMR (400 MHz, $CDCl_3$)



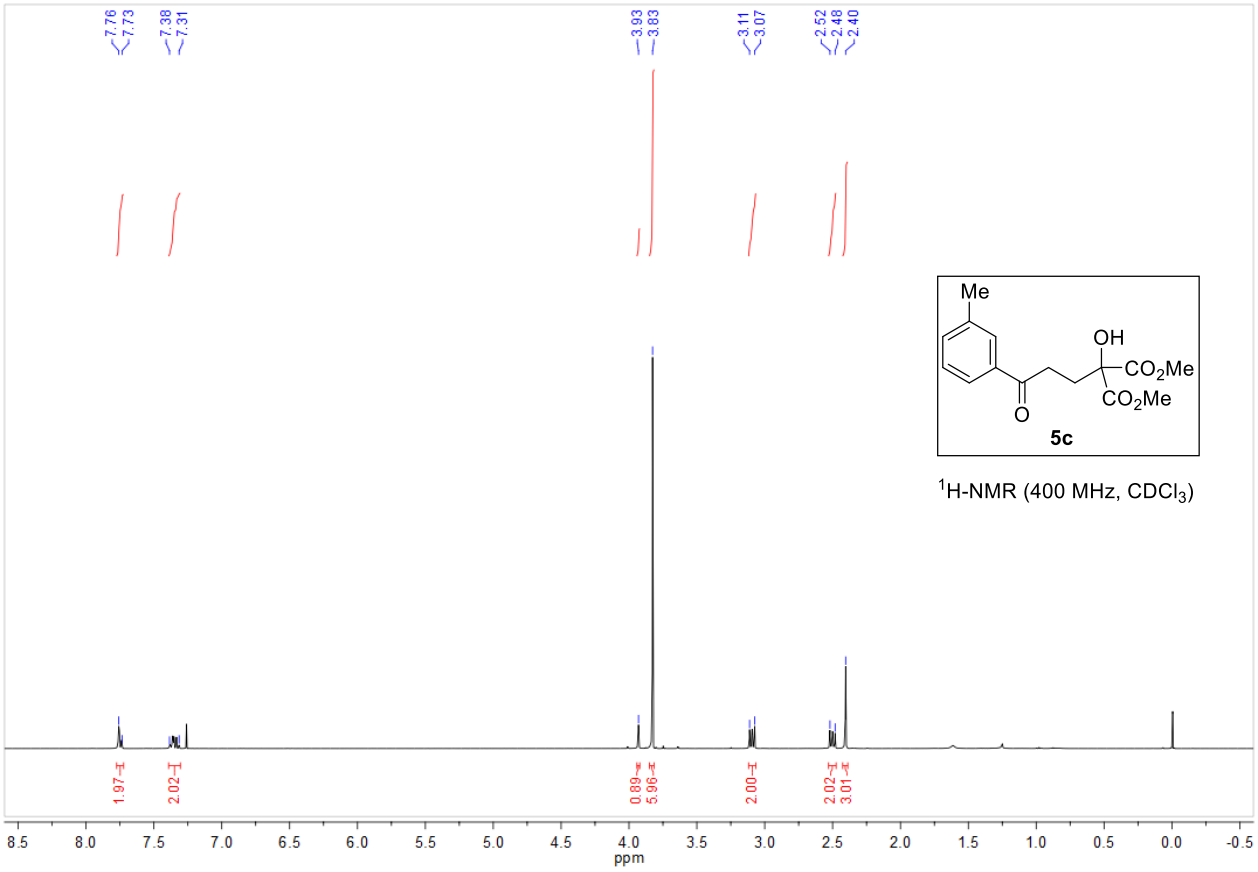
^{13}C-NMR (101 MHz, $CDCl_3$)



^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (101 MHz, $CDCl_3$)



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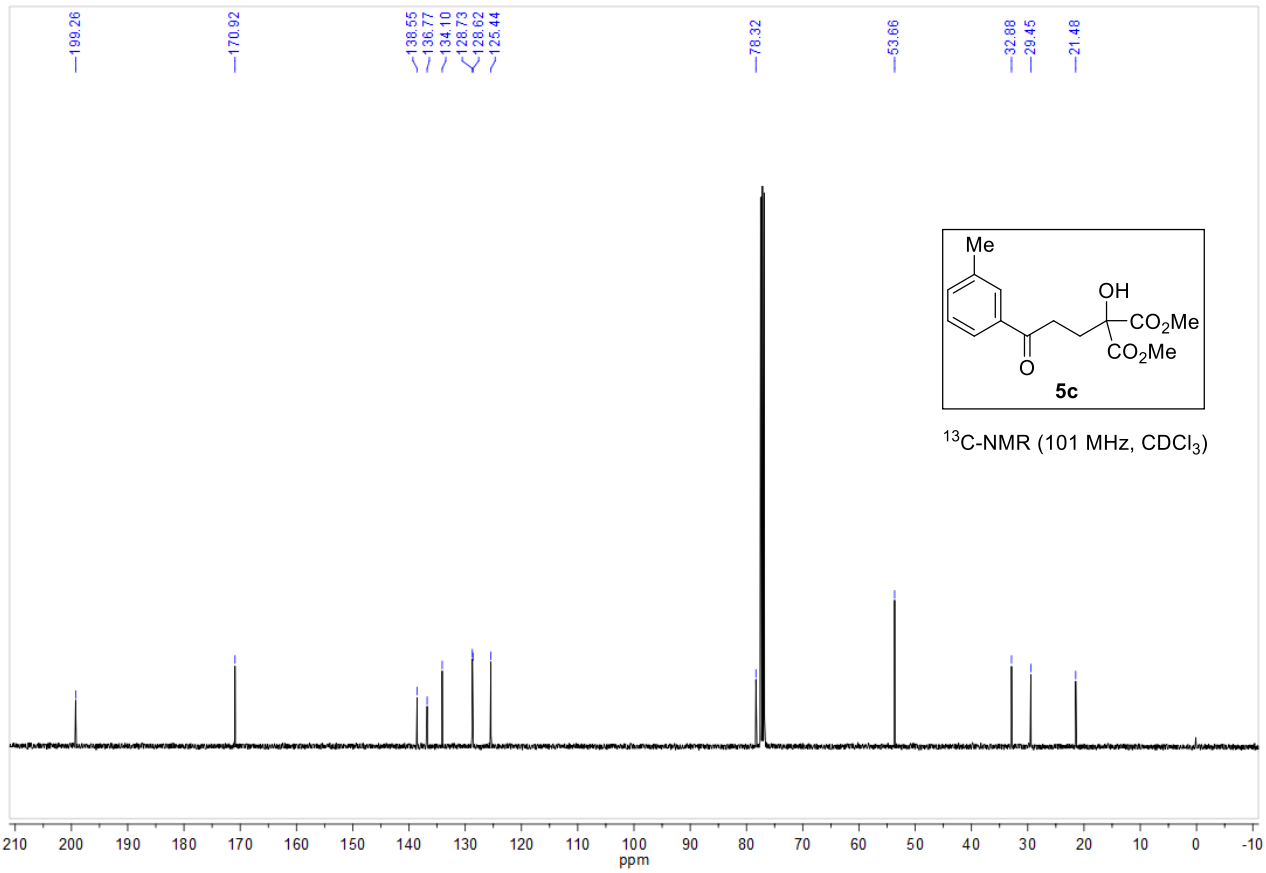
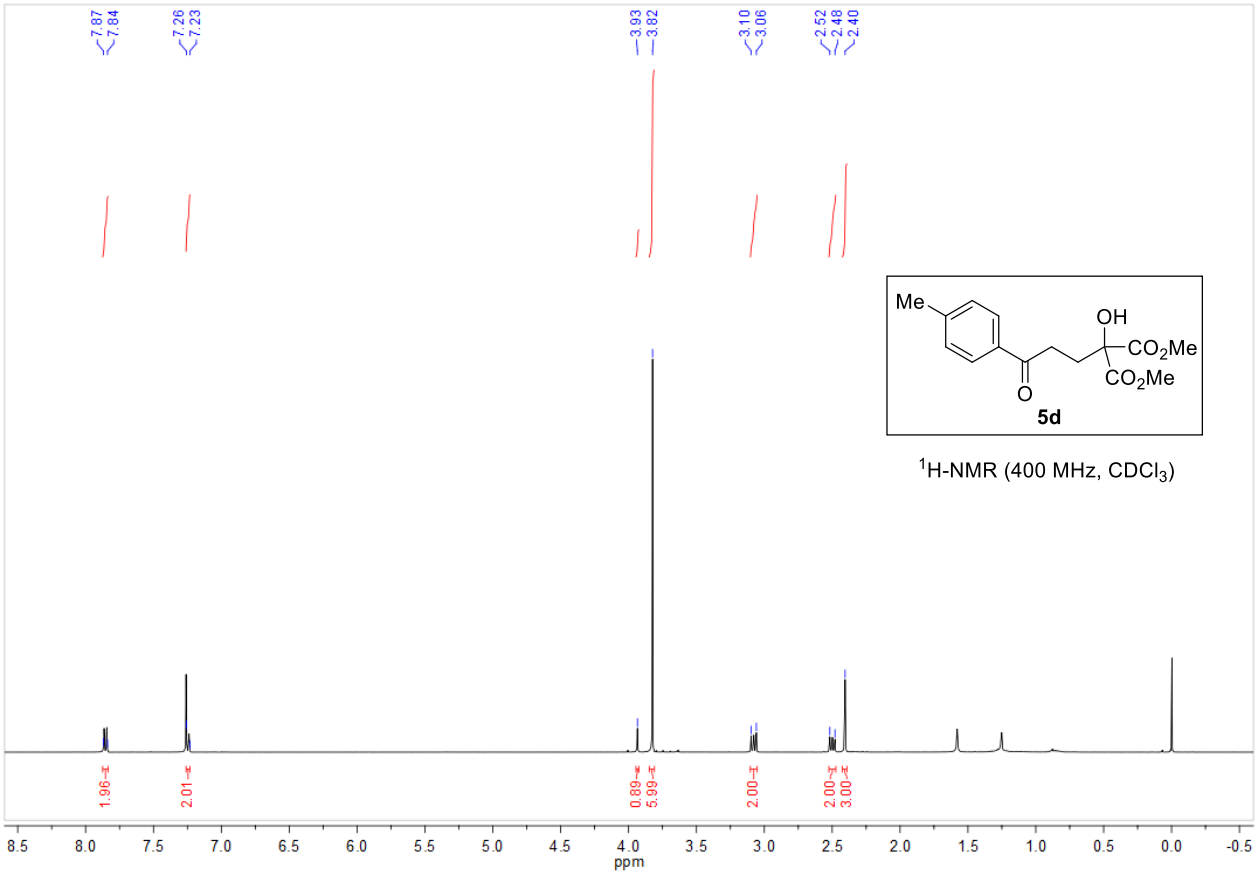


^{13}C-NMR (101 MHz, $CDCl_3$)



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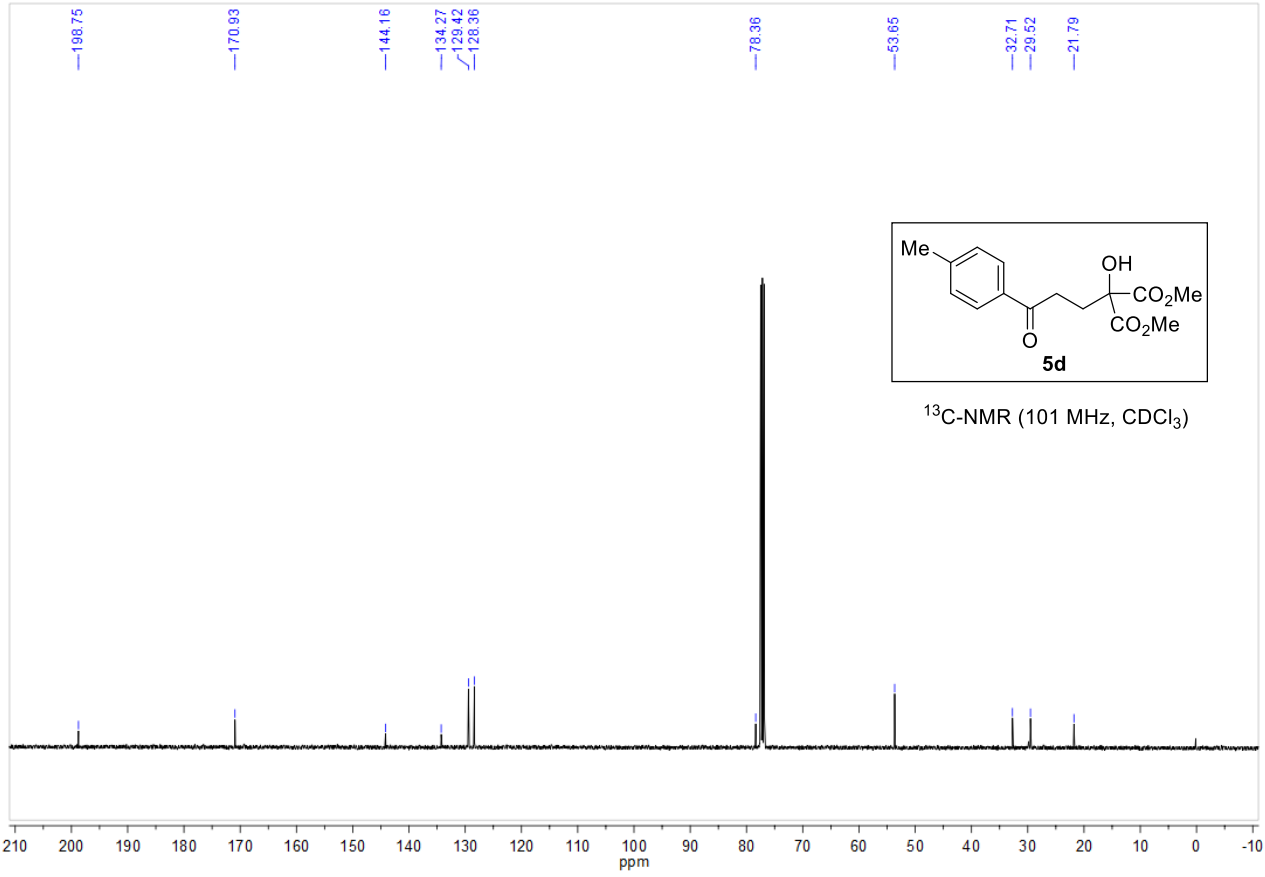
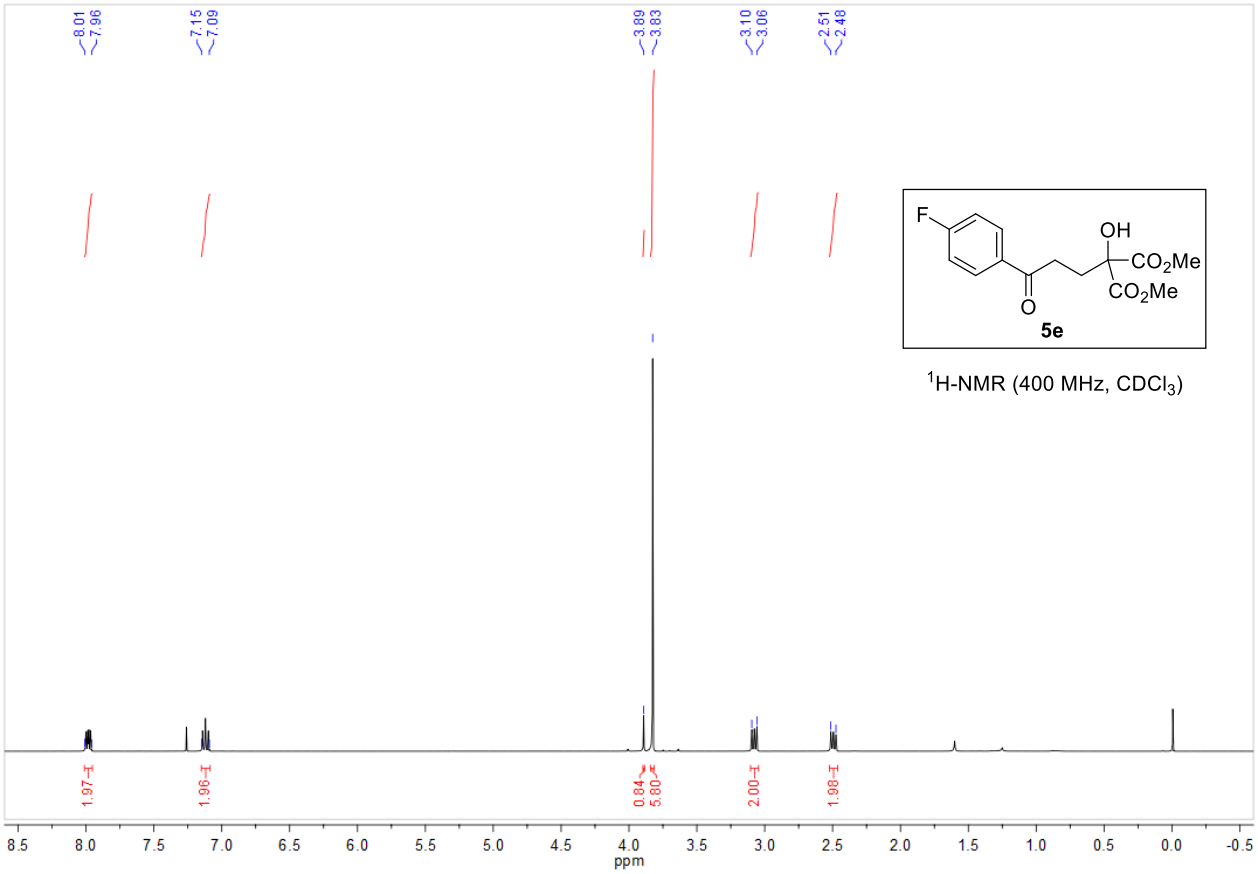
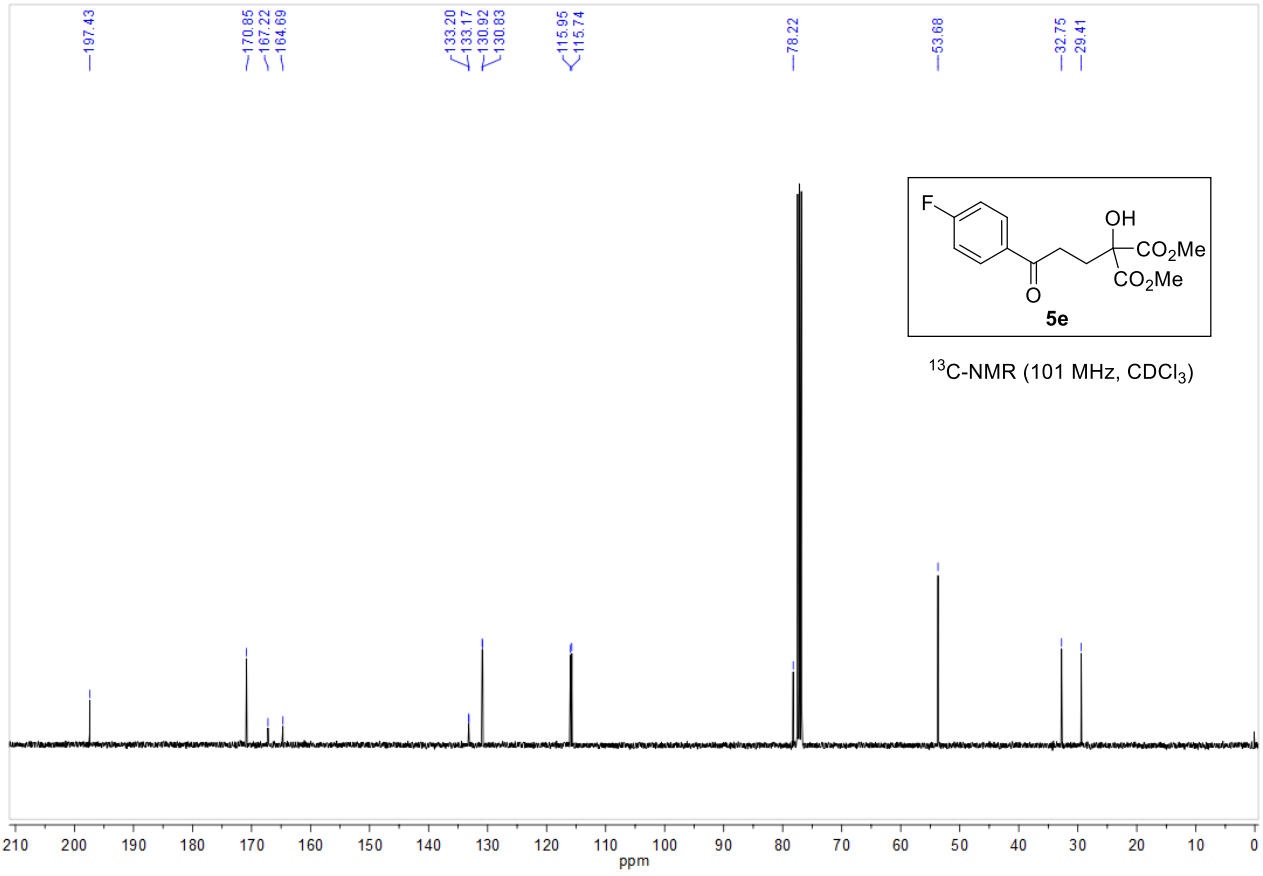


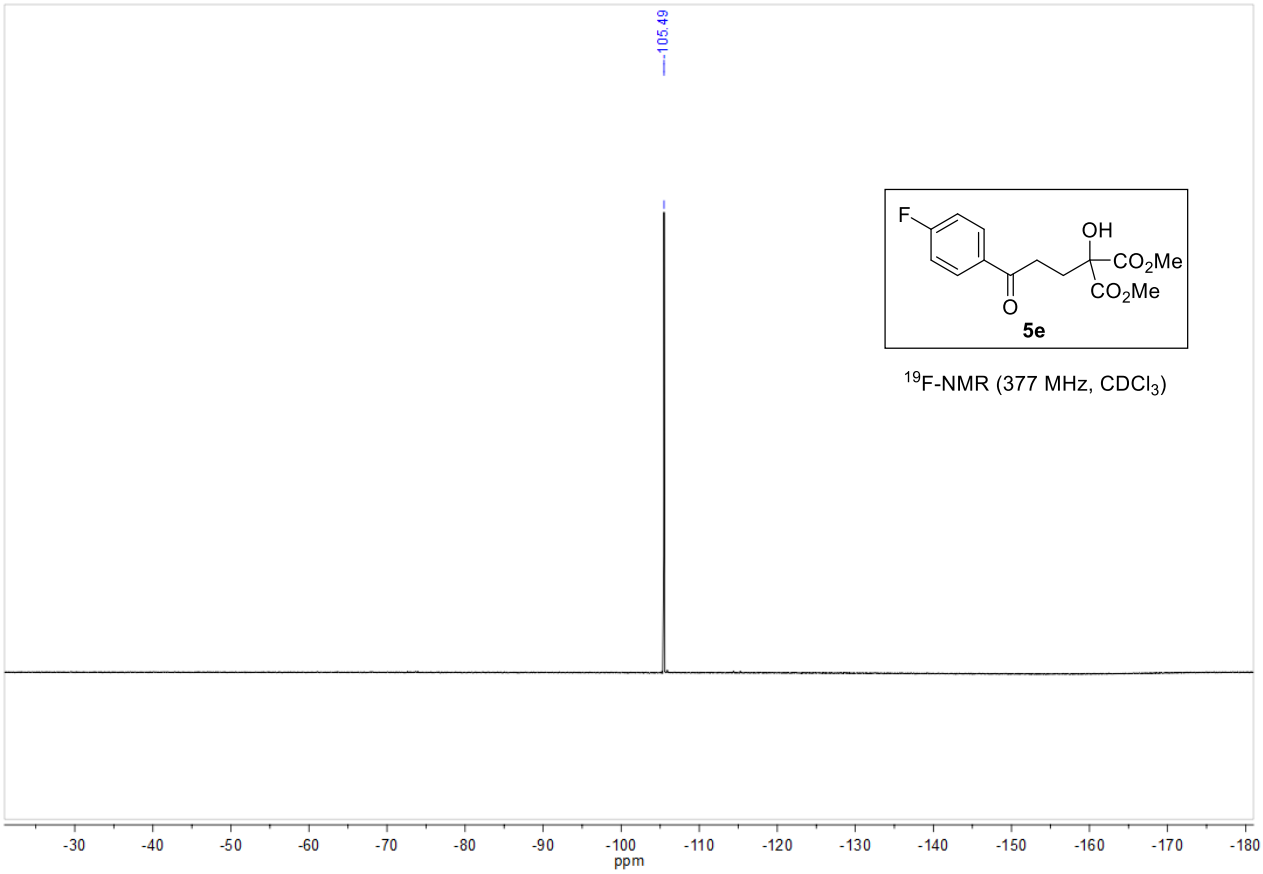
^{13}C-NMR (101 MHz, $CDCl_3$)



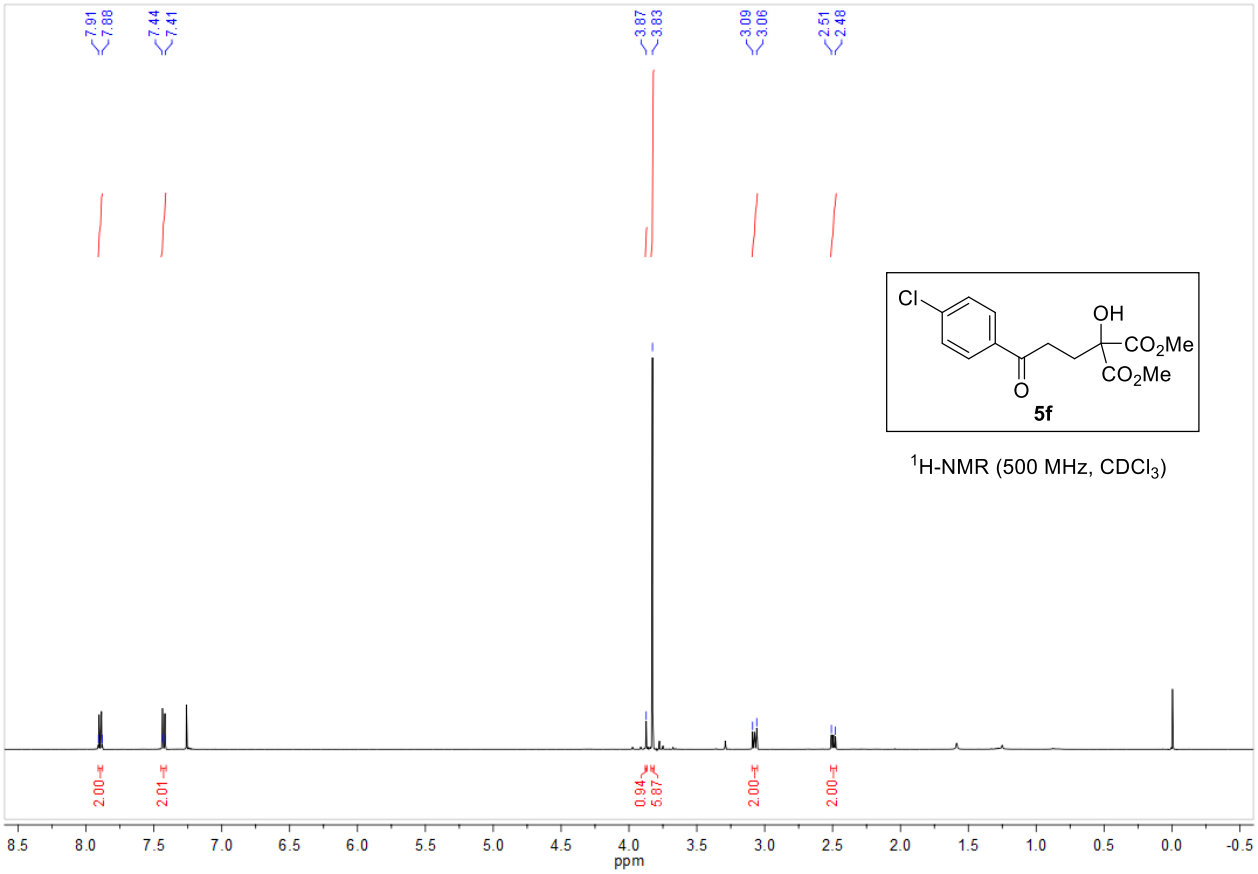
^{1}H-NMR (400 MHz, $CDCl_3$)



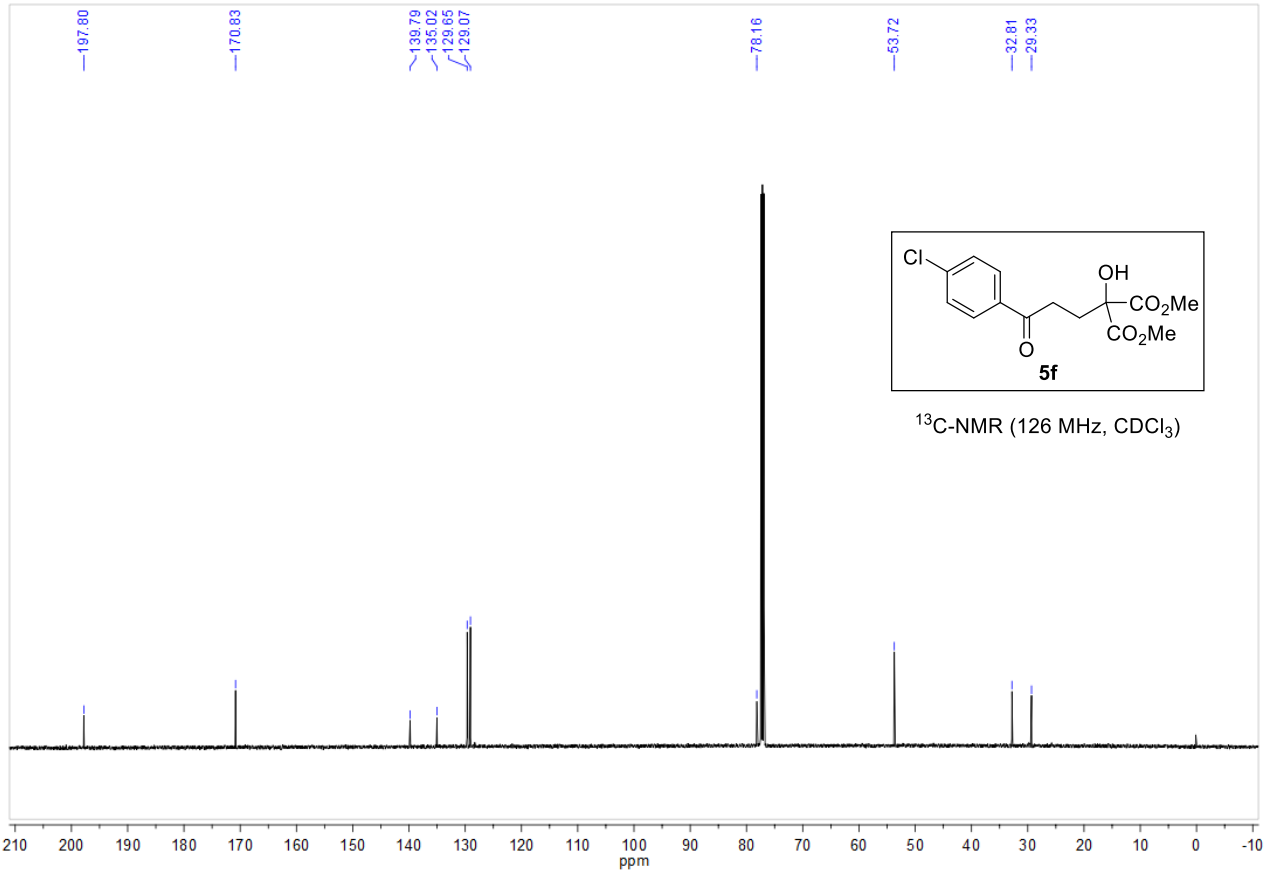
^{13}C-NMR (101 MHz, $CDCl_3$)



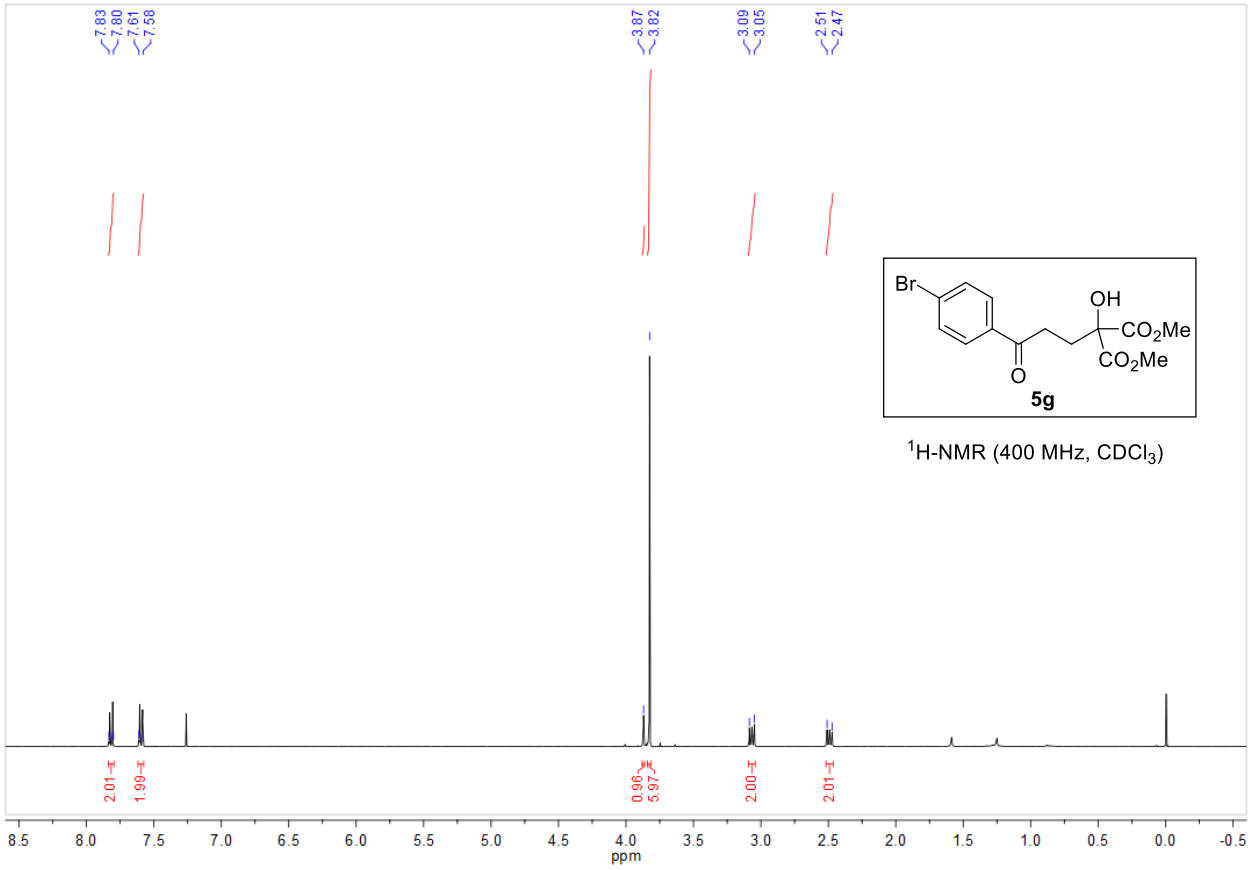
^{19}F-NMR (377 MHz, $CDCl_3$)



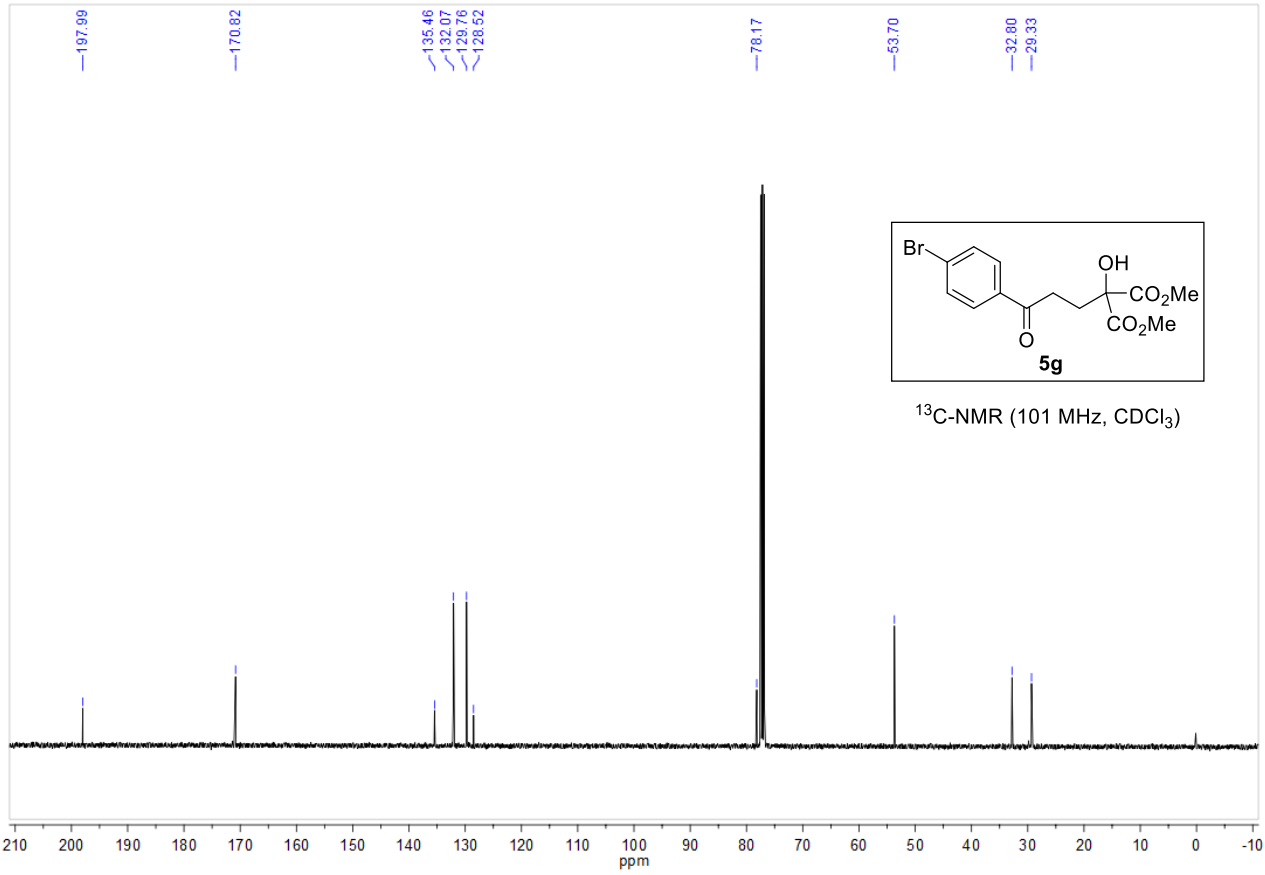
^{1}H-NMR (500 MHz, $CDCl_3$)



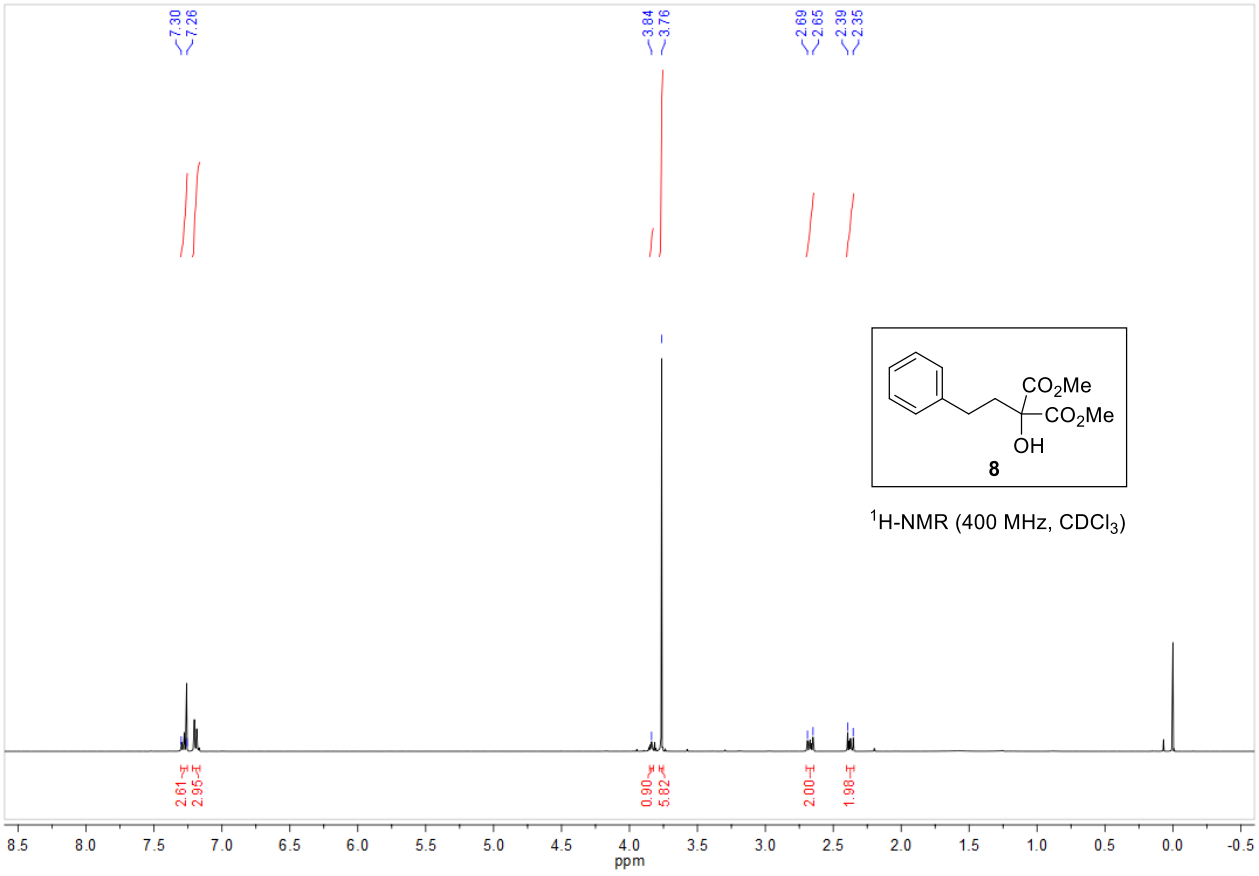
^{13}C-NMR (126 MHz, $CDCl_3$)



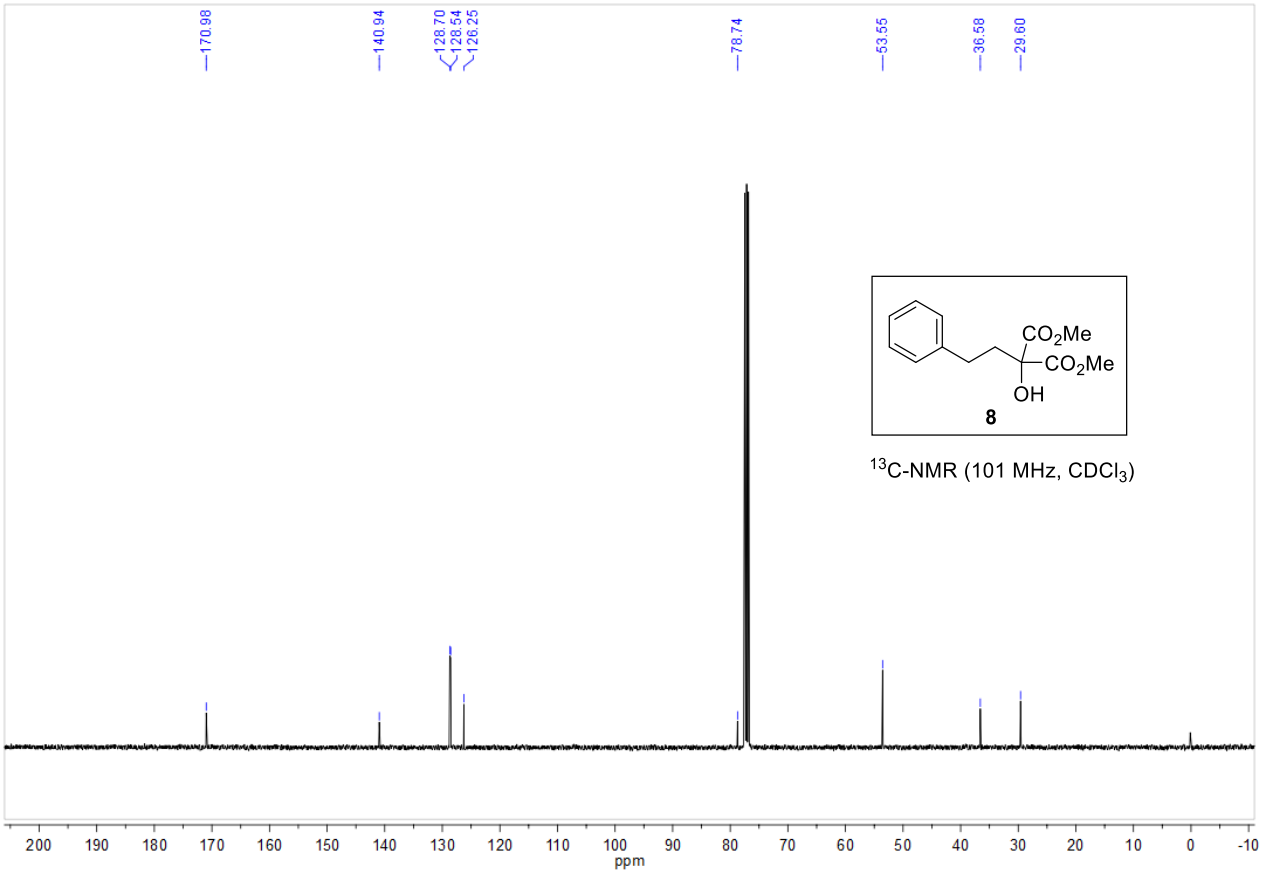
^{1}H-NMR (400 MHz, $CDCl_3$)



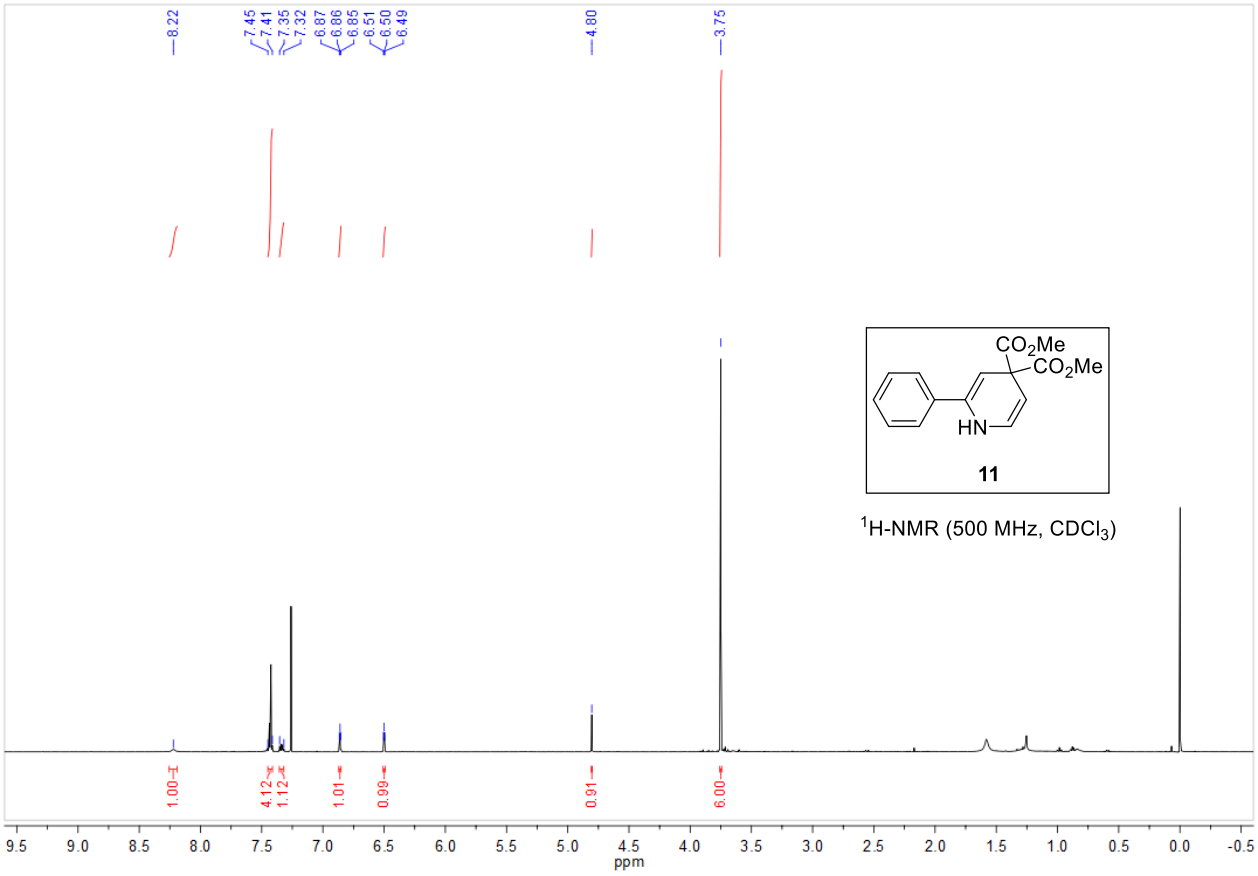
^{13}C-NMR (101 MHz, $CDCl_3$)



^{1}H-NMR (400 MHz, $CDCl_3$)



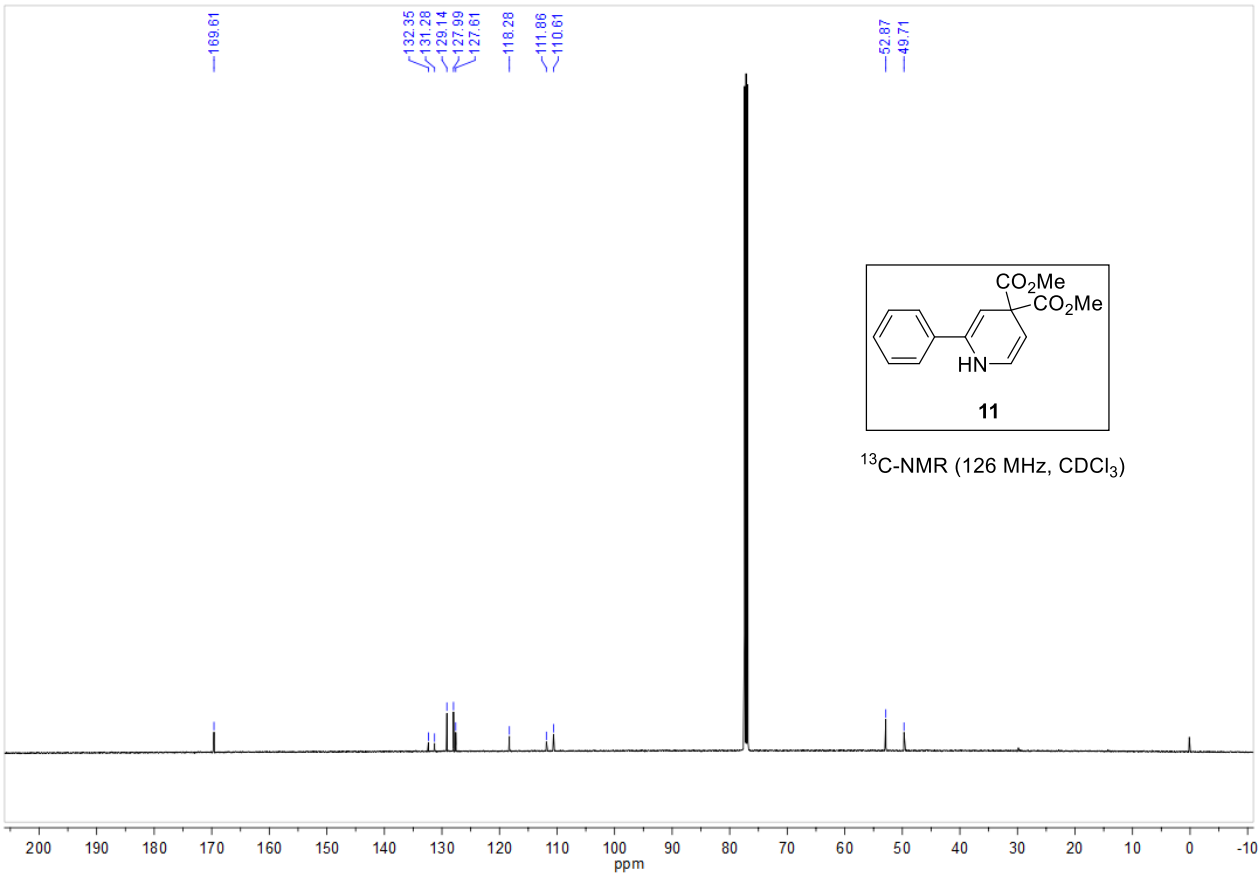
^{13}C-NMR (101 MHz, $CDCl_3$)



CO_2Me
CO_2Me
HN

11

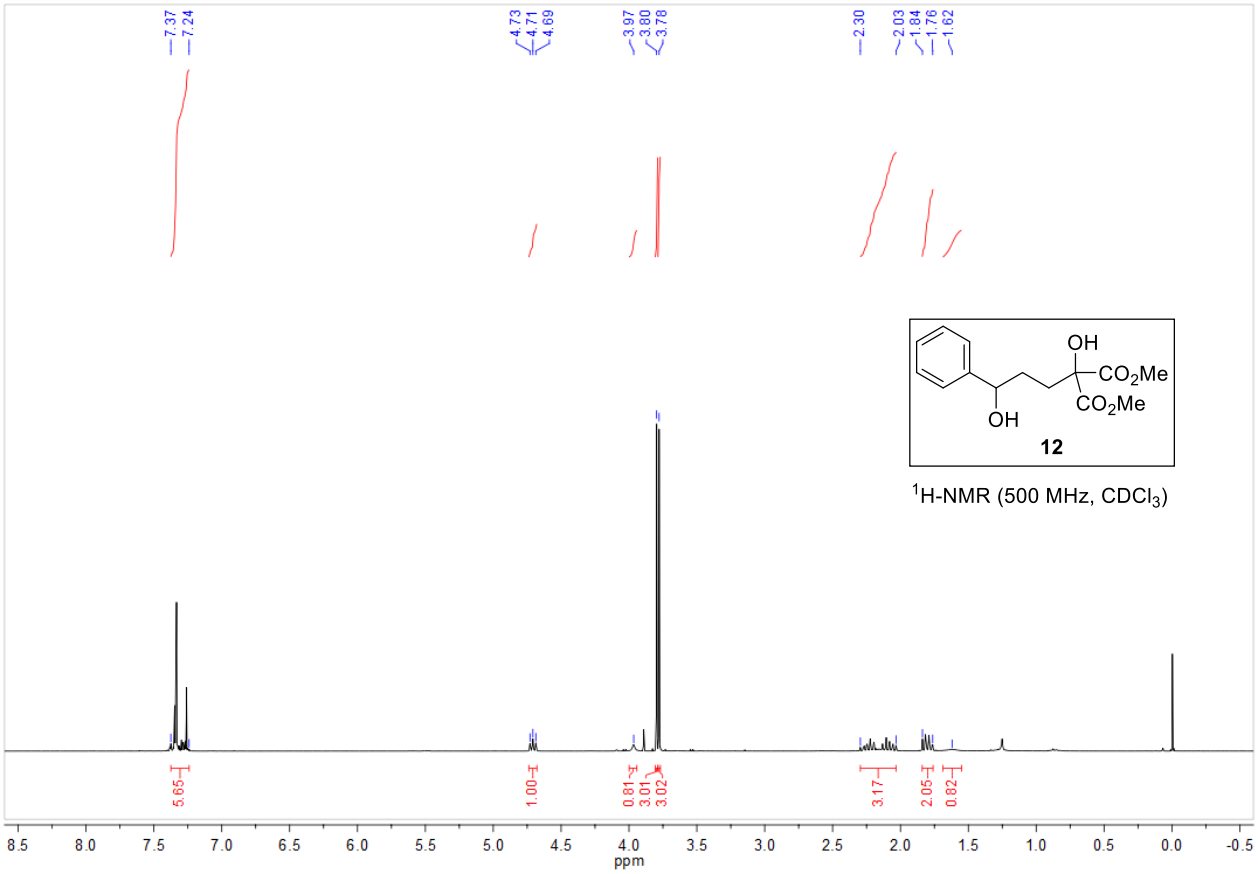
^{1}H-NMR (500 MHz, $CDCl_3$)



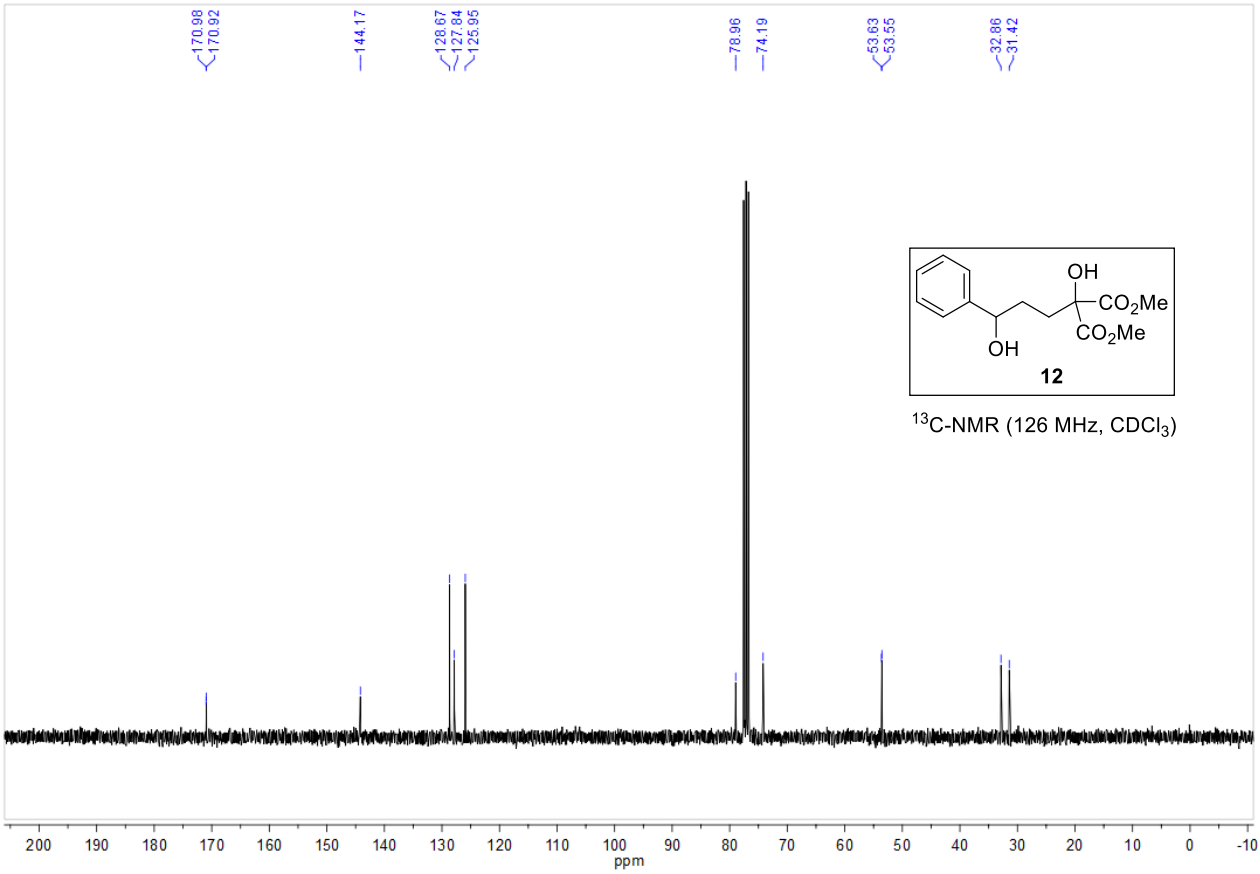
CO_2Me
CO_2Me
HN

11

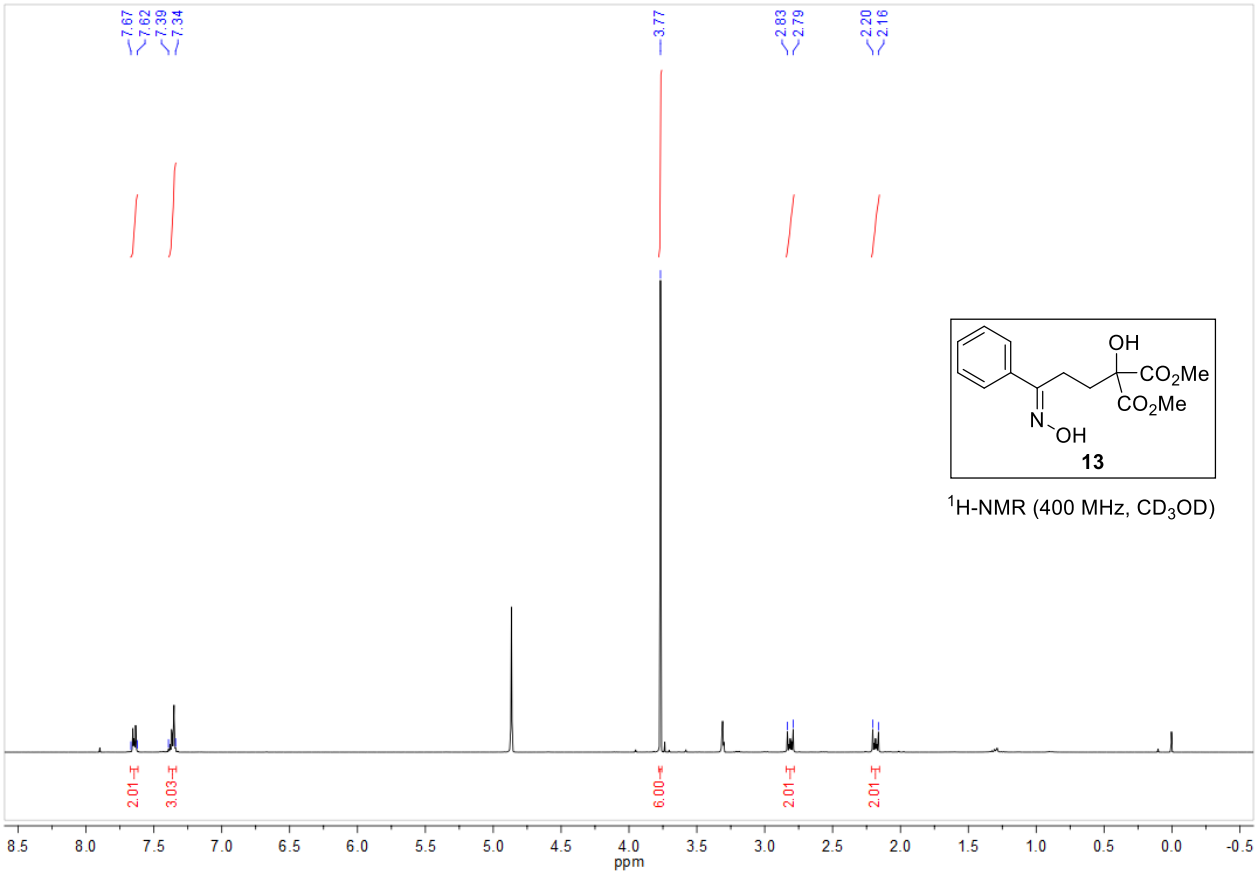
^{13}C-NMR (126 MHz, $CDCl_3$)



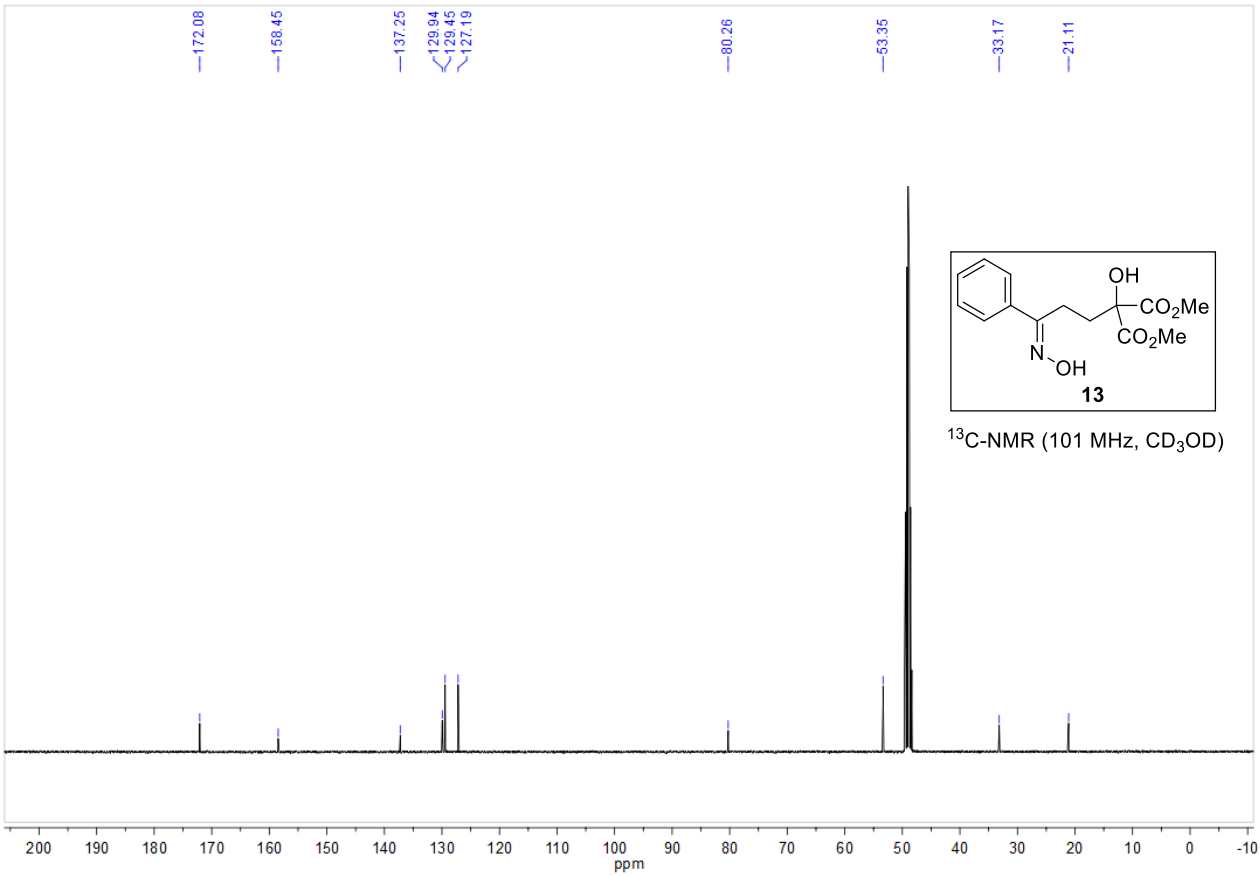
^{1}H-NMR (500 MHz, $CDCl_3$)



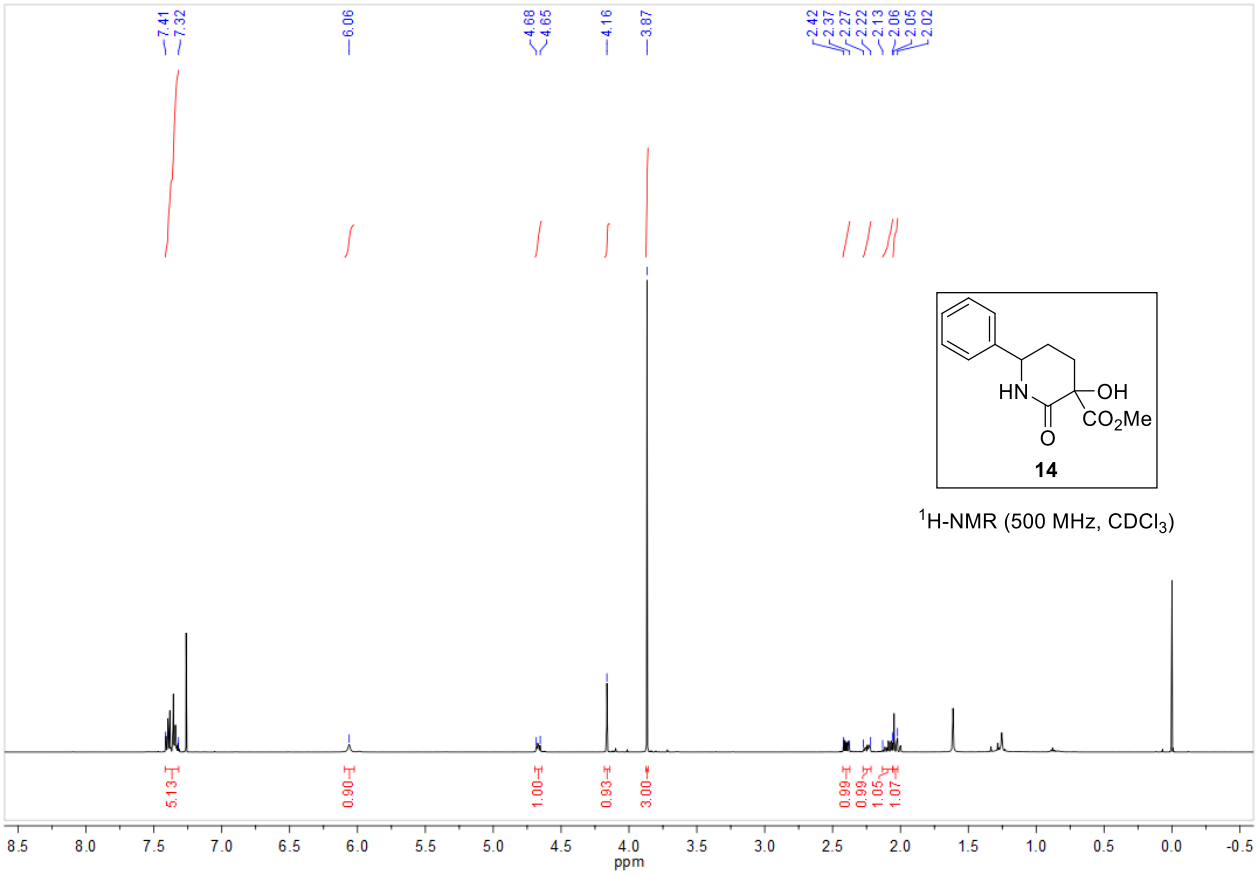
^{13}C-NMR (126 MHz, $CDCl_3$)



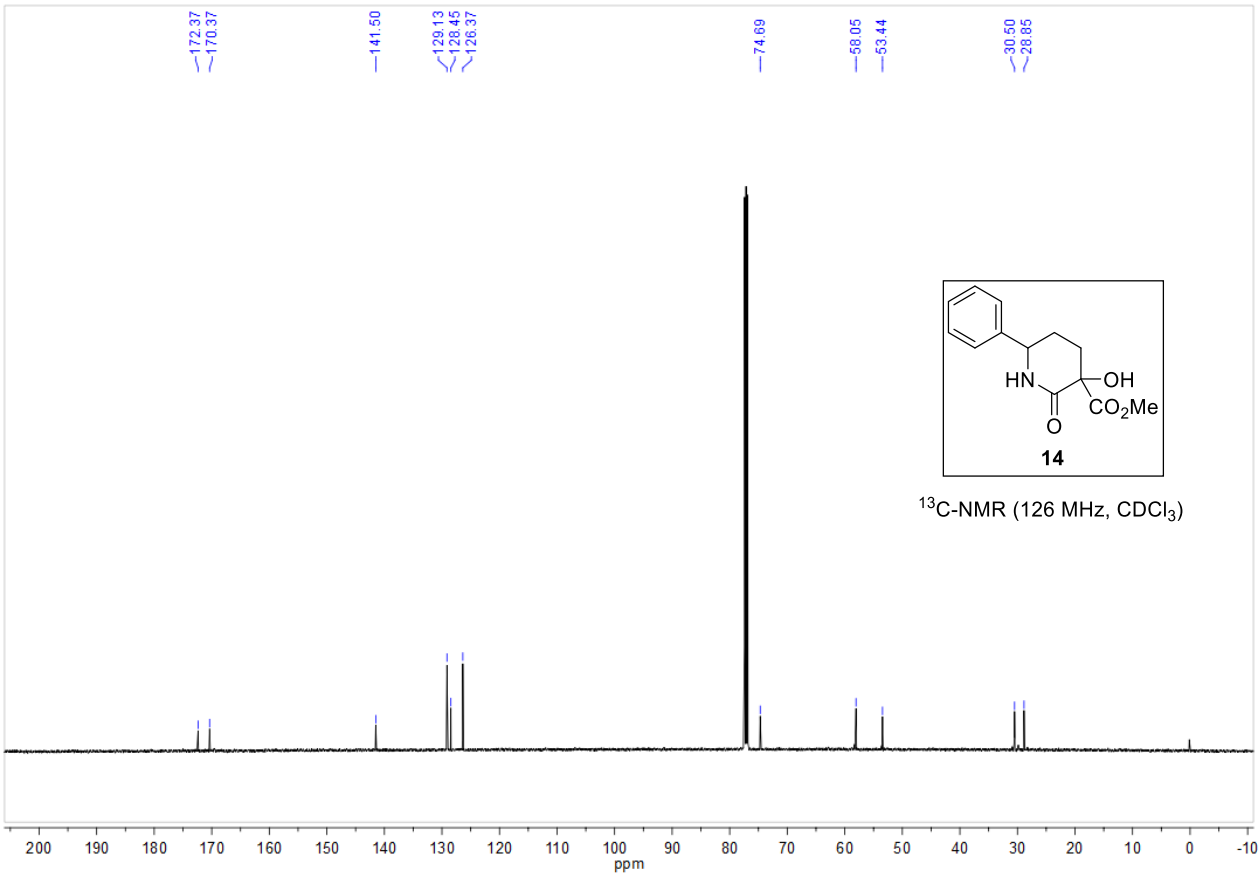
^{1}H-NMR (400 MHz, CD_3OD)



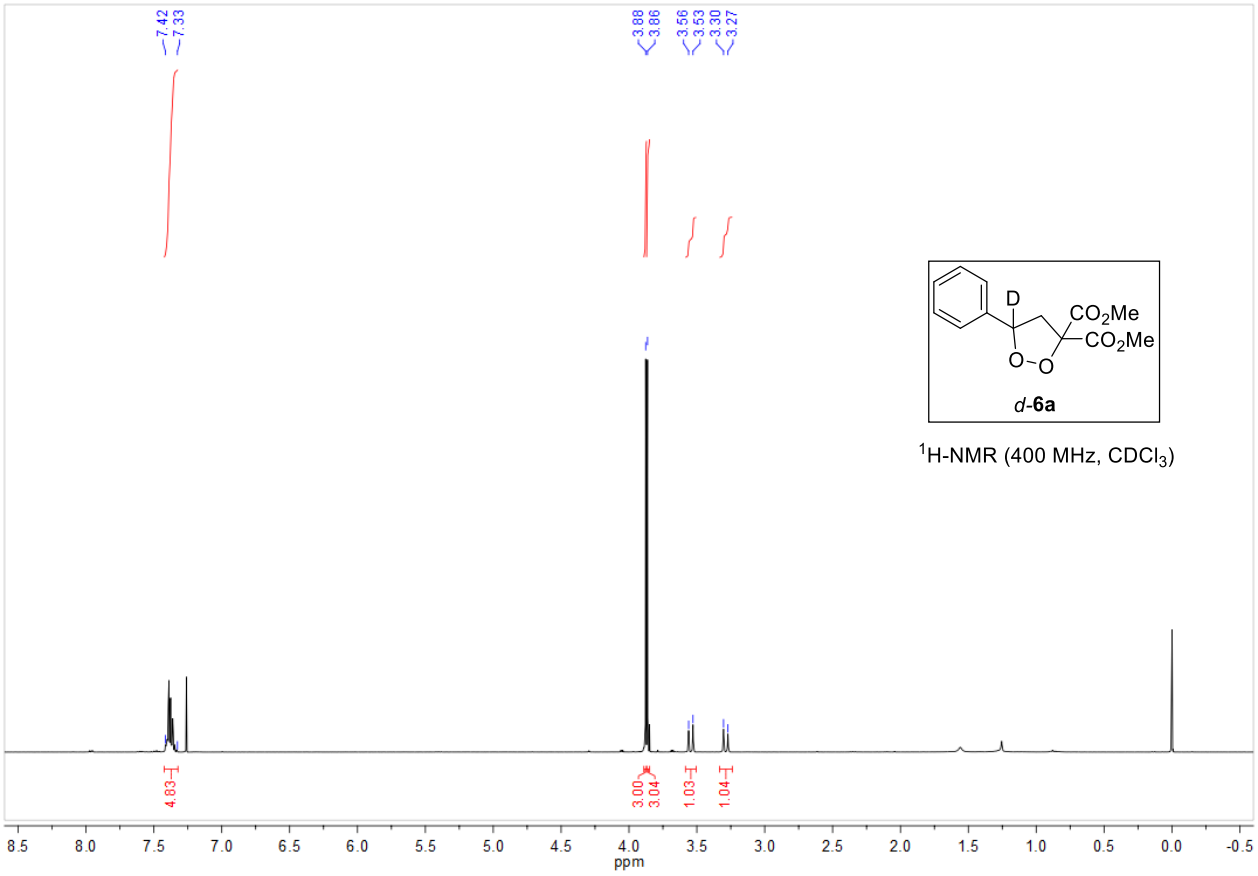
^{13}C-NMR (101 MHz, CD_3OD)



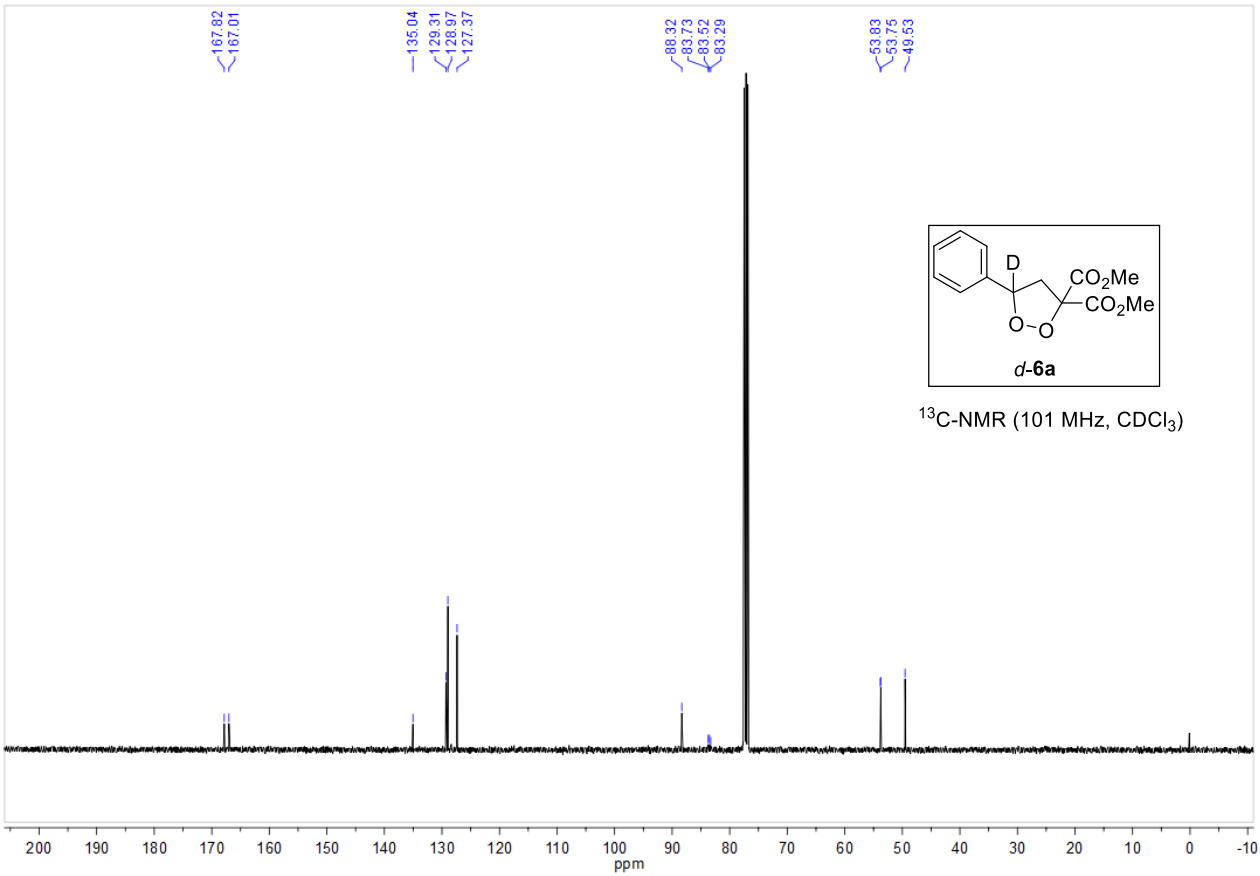
^{1}H-NMR (500 MHz, $CDCl_3$)



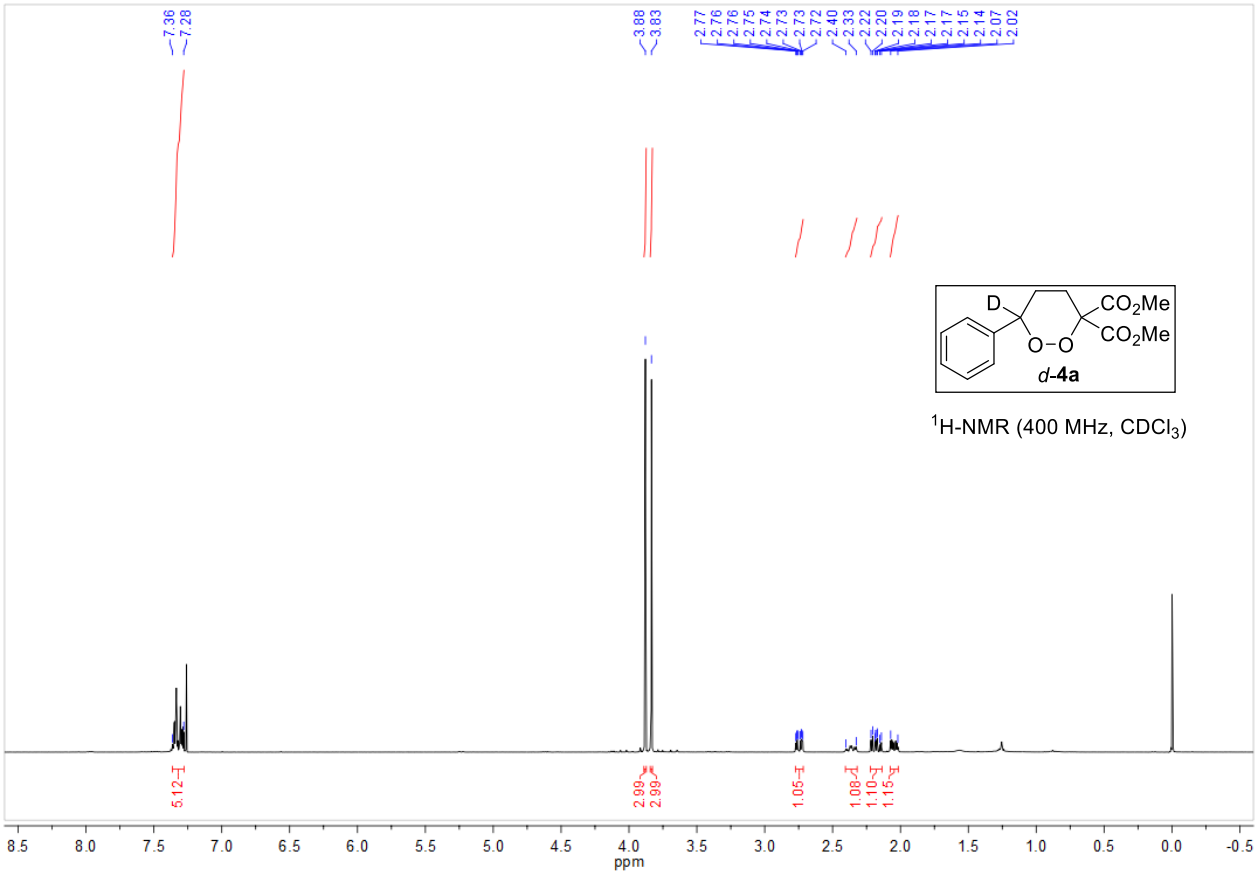
^{13}C-NMR (126 MHz, $CDCl_3$)



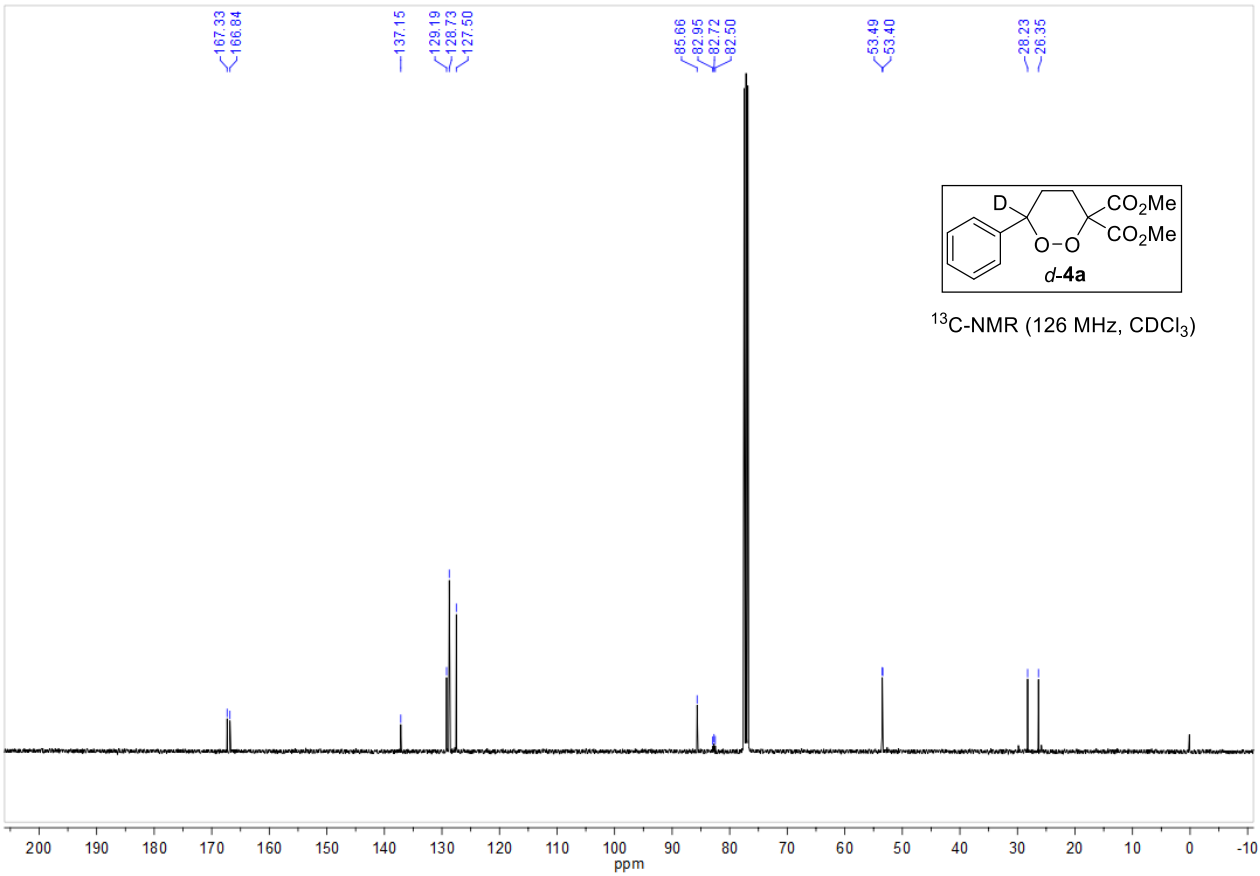
^{1}H-NMR (400 MHz, $CDCl_3$)



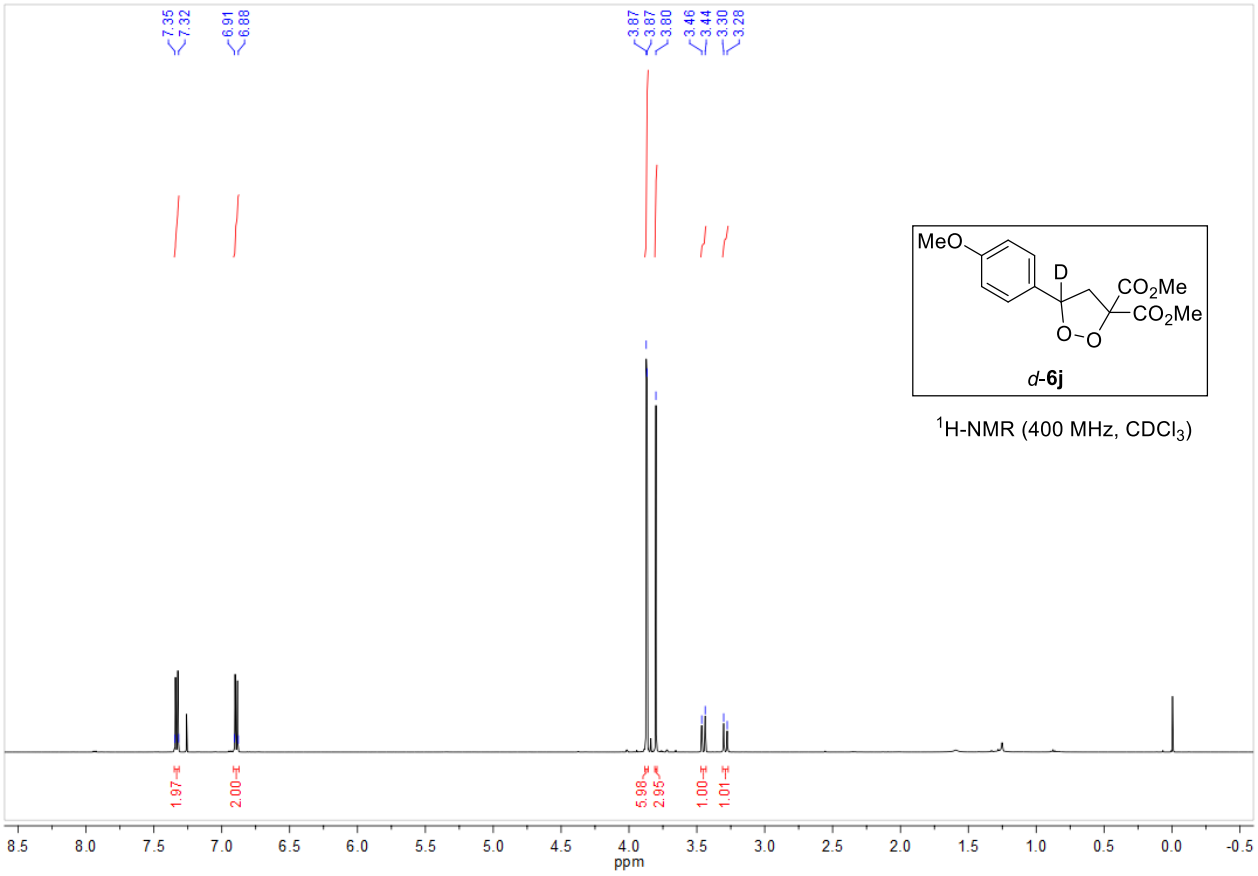
^{13}C-NMR (101 MHz, $CDCl_3$)



^{1}H-NMR (400 MHz, $CDCl_3$)

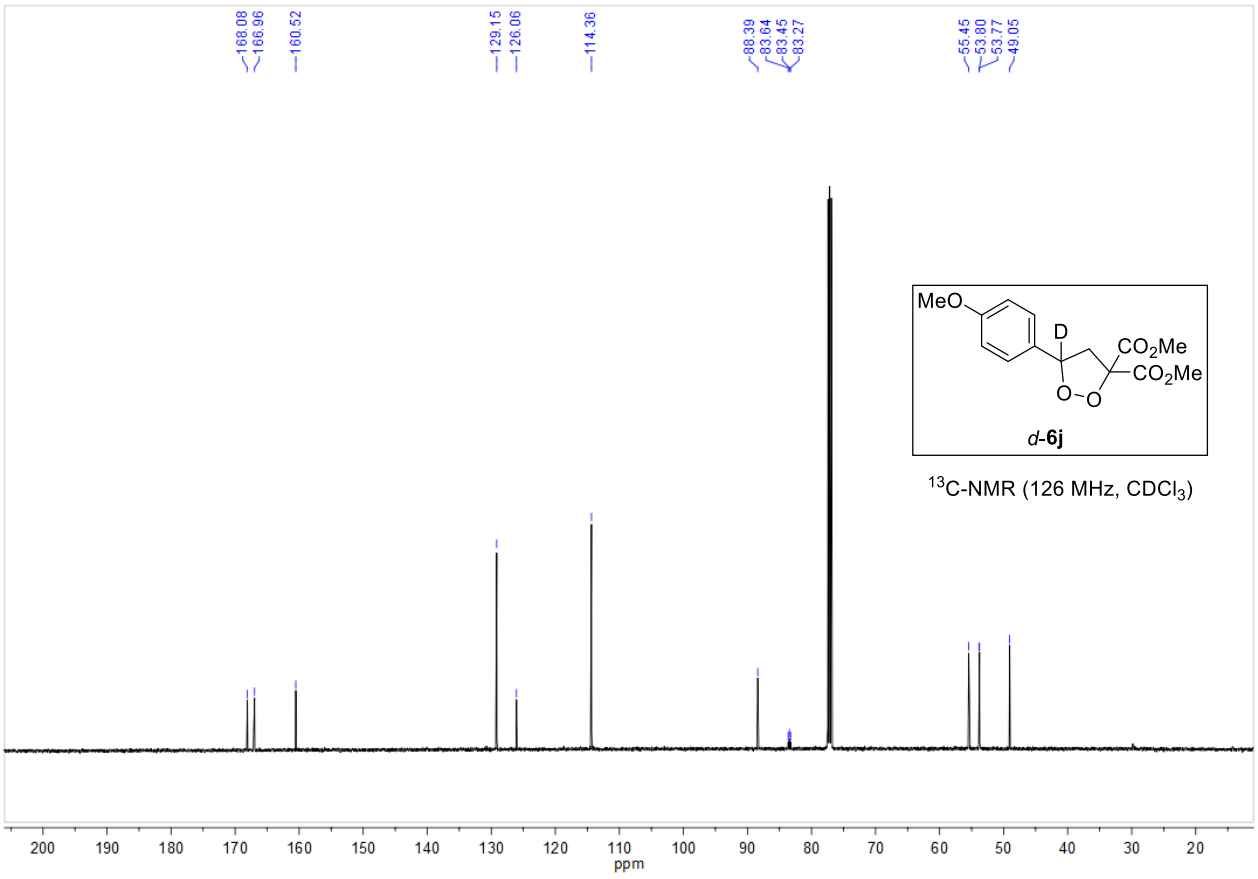


^{13}C-NMR (126 MHz, $CDCl_3$)



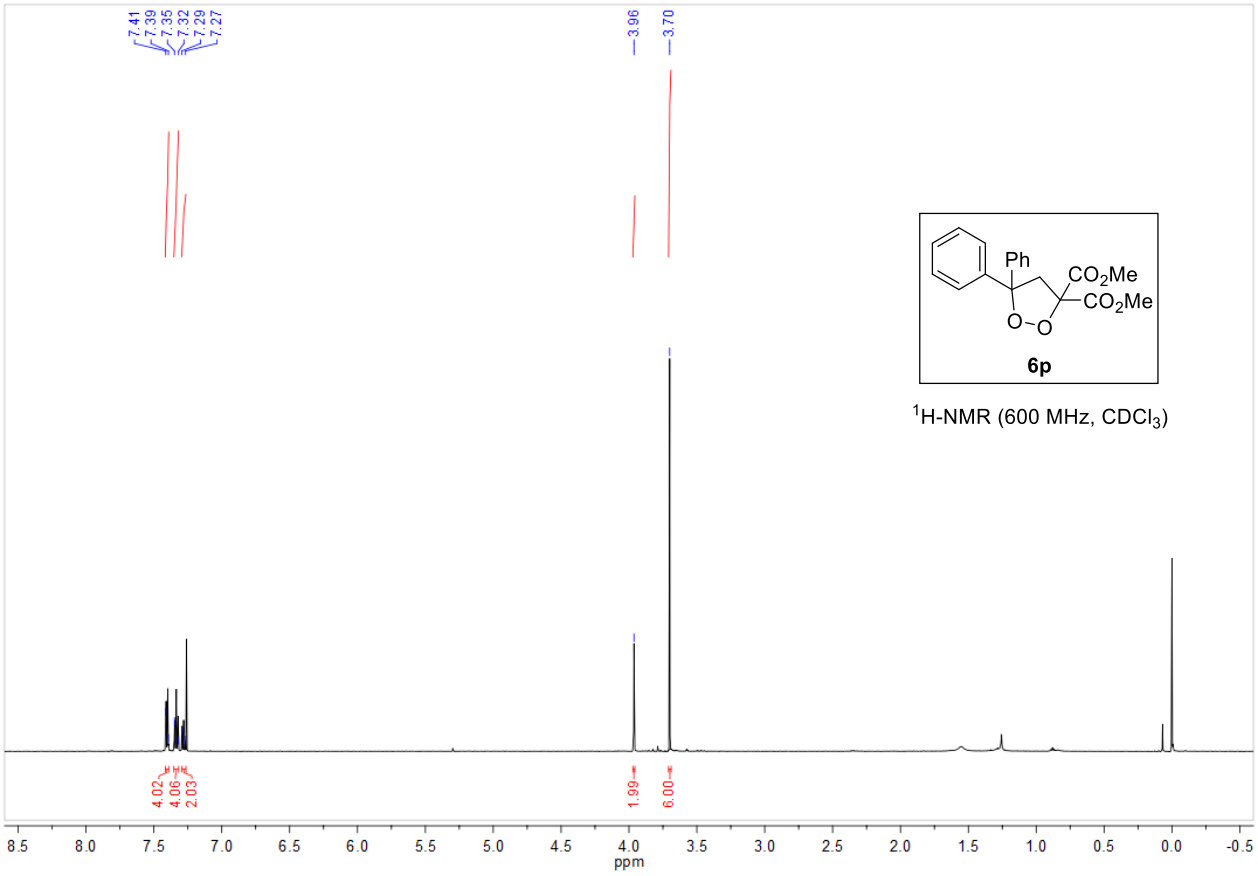
d-**6j**

^{1}H-NMR (400 MHz, $CDCl_3$)

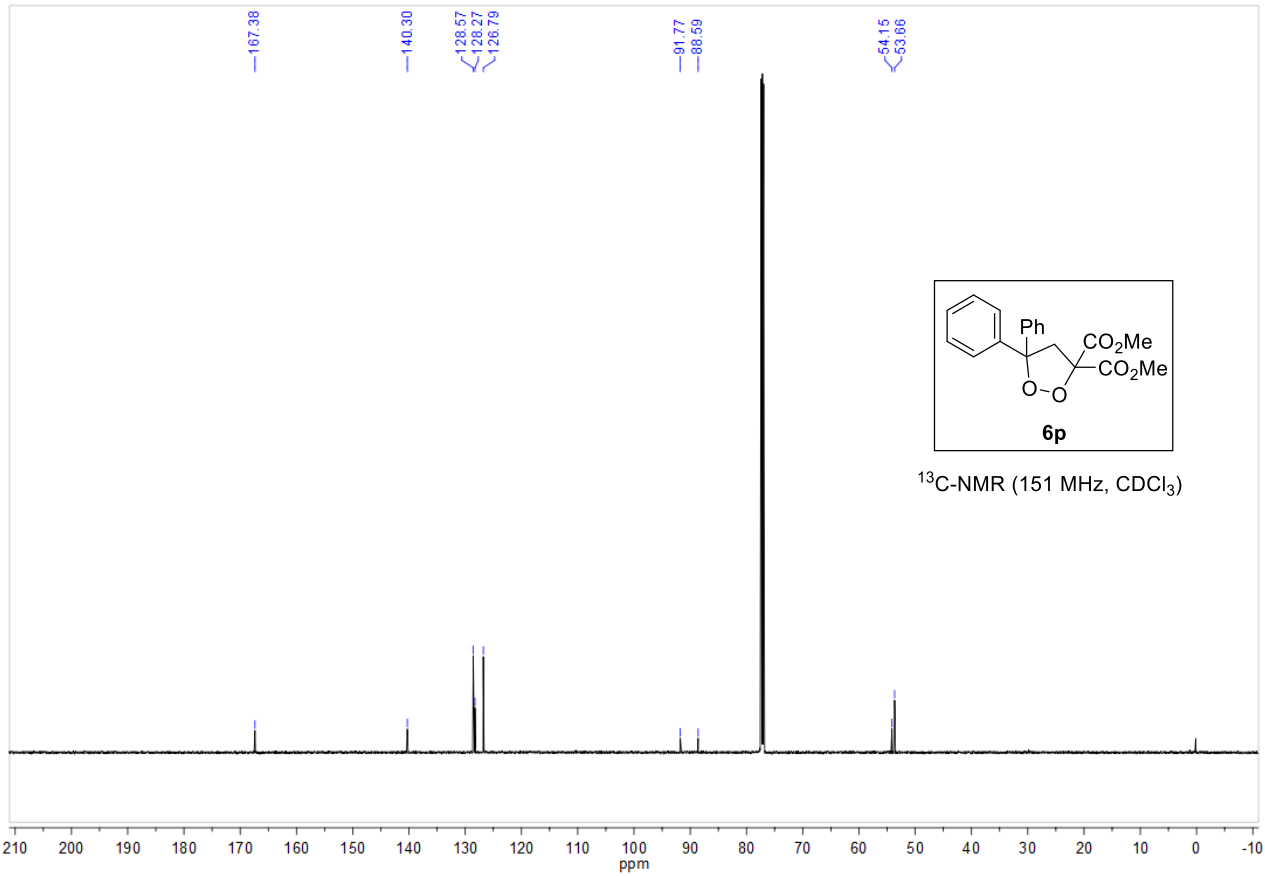


d-**6j**

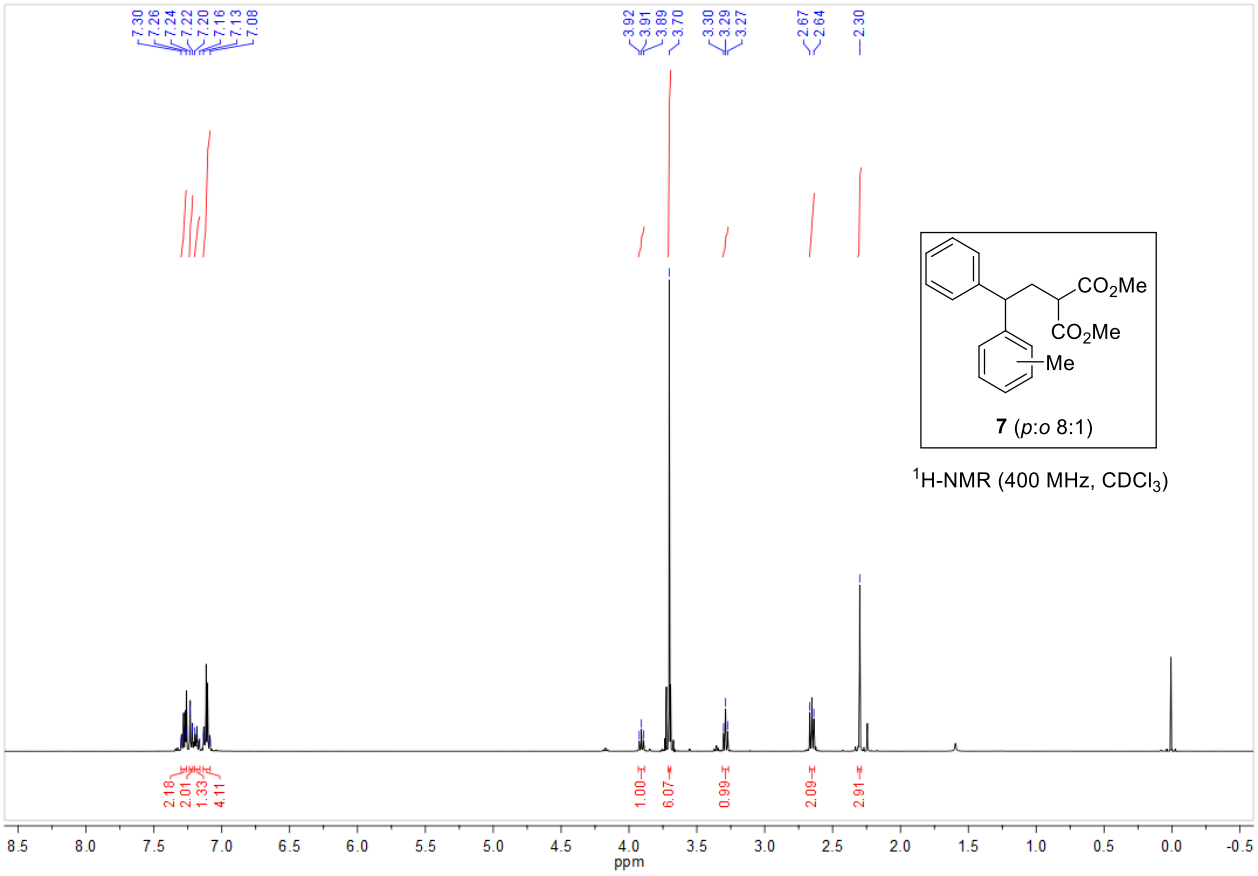
^{13}C-NMR (126 MHz, $CDCl_3$)



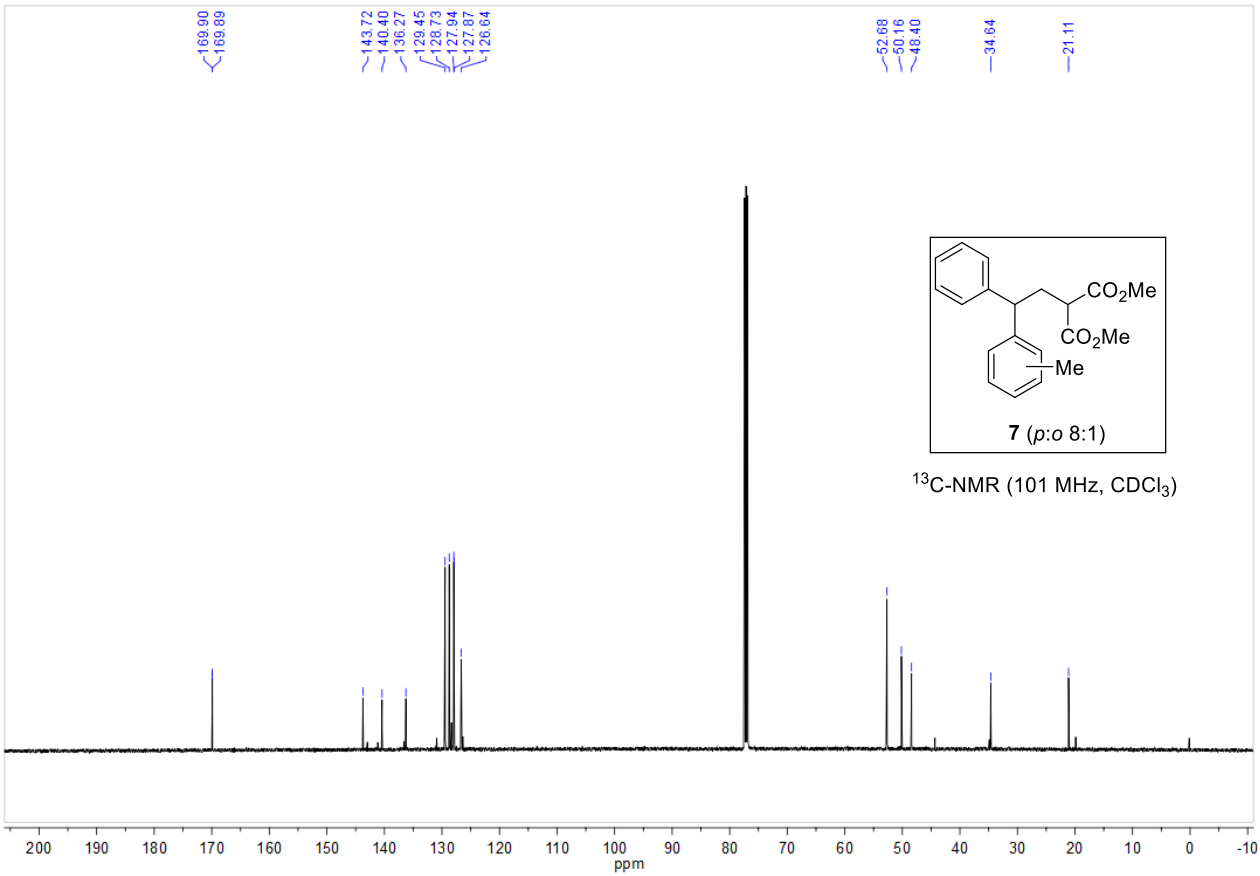
^{1}H-NMR (600 MHz, $CDCl_3$)



^{13}C-NMR (151 MHz, $CDCl_3$)



^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (101 MHz, $CDCl_3$)

12. Crystal Structure Determinations

Crystals were mounted in inert oil on nylon loops and transferred to the cold gas stream of a Rigaku/Oxford XtaLAB Synergy diffractometer. Measurements were performed using mirror-focussed Mo-*K*a radiation. Absorption corrections were implemented on the basis of multi-scans. The structures were refined anisotropically on F^2 using the program SHELXL-2018.[27] Hydrogen atoms of NH or OH groups were refined freely. Other hydrogen atoms were included using rigid methyl groups or a riding model starting from calculated positions. *Special features for compound* ***9***: The structure was refined as a pseudomerohedral twin. The twinning is associated with a twofold rotation of a pseudo-*C*-centred orthorhomic cell. The twin matrix is [-1 0 0 / 0 -1 0 / 1 0 1] and the fraction of the smaller twin component refined to 0.0164(5). Despite this small value, the refinement was significantly improved. The compound is achiral and crystallizes only by chance in a chiral (Sohncke) space group. The absolute structure was established with reasonable certainty by the Parsons method, with a Flack parameter of –0.01(19), despite the limited extent of anomalous scattering for a light-atom structure.

Crystallographic data are summarized in Table S4. Additionally, complete data have been deposited with the Cambridge Crystallographic Data Centre under the numbers CCDC 2058833–2058836. Copies of the data can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif.

Table S4. Crystallographic data and structure refinement details for compounds **2a**, **4f**, **5a**, and **9**.

Compound	**2a**	**4f**	**5a**	**9**
CCDC number	2058833	2058834	2058835	2058836
Formula	$C_{13}H_{14}O_6$	$C_{14}H_{15}ClO_6$	$C_{14}H_{16}O_6$	$C_{13}H_{12}N_2O_3$
M_r	266.24	314.71	280.27	244.25
Cryst. size (mm)	0.25 x 0.25 x 0.2	0.2 x 0.2 x 0.1	0.25 x 0.2 x 0.15	0.25 x 0.2 x 0.2
Crystal system	orthorhombic	Triclinic	monoclinic	monoclinic
Space group	*Pbca*	*P*(-1)	$P2_1/c$	$P2_1$
Temperature (°C)	-173	-173	-173	-173
a (Å)	7.86328(17)	5.9522(2)	10.7792(2)	8.3598(3)
b (Å)	10.7192(2)	10.5680(4)	32.3527(7)	5.59576(14)
c (Å)	29.3301(6)	11.8459(6)	7.64904(16)	13.4683(4)
α (°)	90	74.745(3)	90	90
β (°)	90	78.003(3)	92.689(2)	108.000(3)
γ (°)	90	88.810(3)	90	90
V (Å^3)	2472.2	702.73	2664.6	599.20
Z	8	2	8	2
D_x (Mg m^{-3})	1.431	1.487	1.397	1.354
λ (Å)	0.71073	0.71073	0.71073	0.71073
μ (mm^{-1})	0.11	0.30	0.11	0.10
Transmissions	0.843 – 1.000	0.791 – 1.000	0.855 – 1.000	0.837 – 1.000
F(000)	1120	328	1184	256
$2\theta_{max}$	71.8	68.4	68.3	72
Refl. measured	108765	45370	168597	47675
Refl. indep.	5553	5275	10296	5251
R_{int}	0.032	0.038	0.033	0.040
Parameters	178	192	373	169
Restraints	0	0	0	1
wR(F^2, all refl.)	0.097	0.093	0.103	0.104
R(*F*, >4σ(*F*))	0.033	0.032	0.037	0.036
S	1.03	1.06	1.03	1.04
Max. Δ*p* (e Å^{-3})	0.52, –0.25	0.55, –0.25	0.47, –0.23	0.42, –0.22

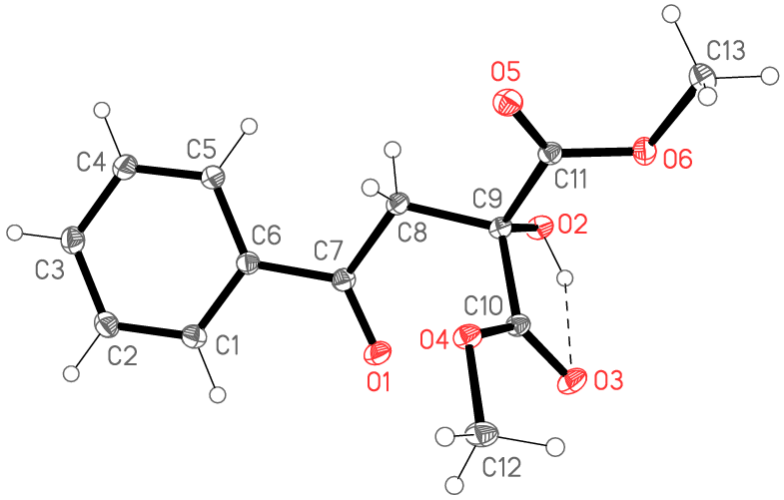


Fig. S6. Structure of compound **2a** in the crystal.

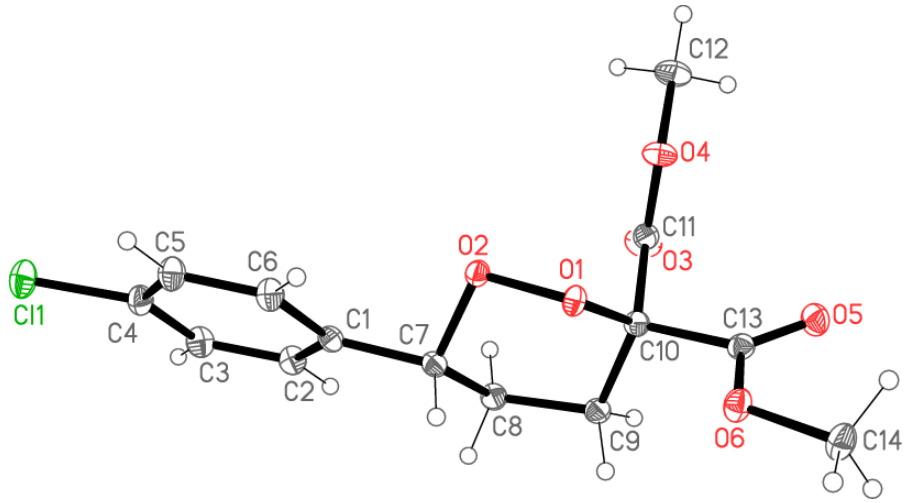


Fig. S7. Structure of compound **4f** in the crystal.

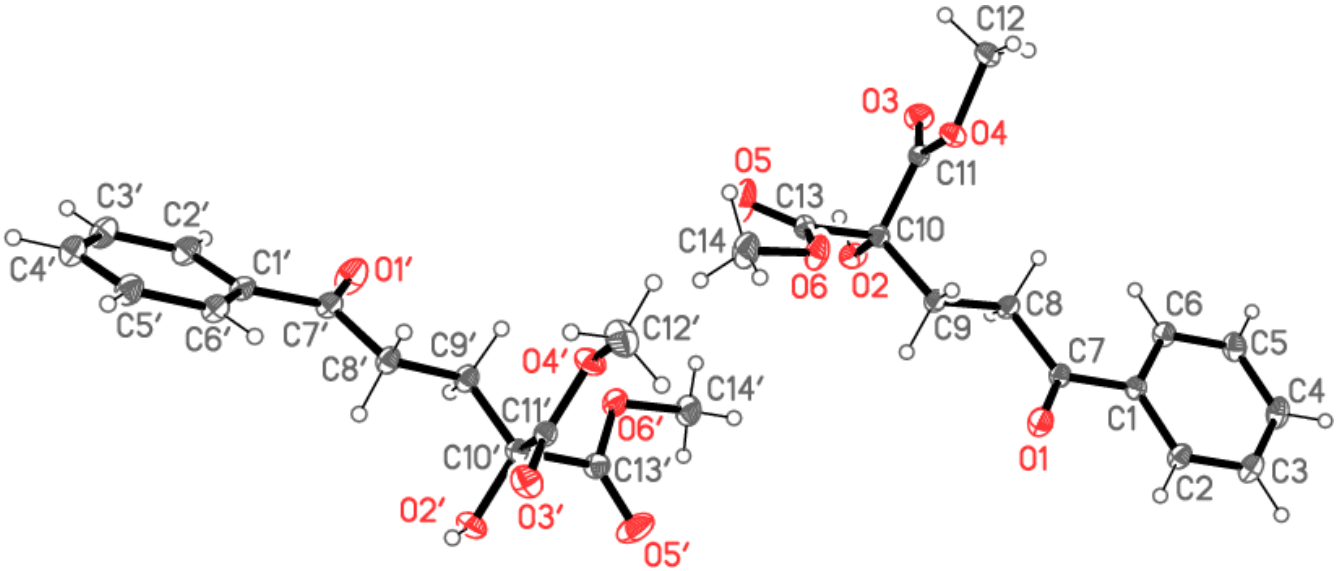


Fig. S8. Structure of compound **5a** in the crystal. The asymmetric unit consists of two independent molecules, which are closely similar (r.m.s. deviation 0.2 Å).

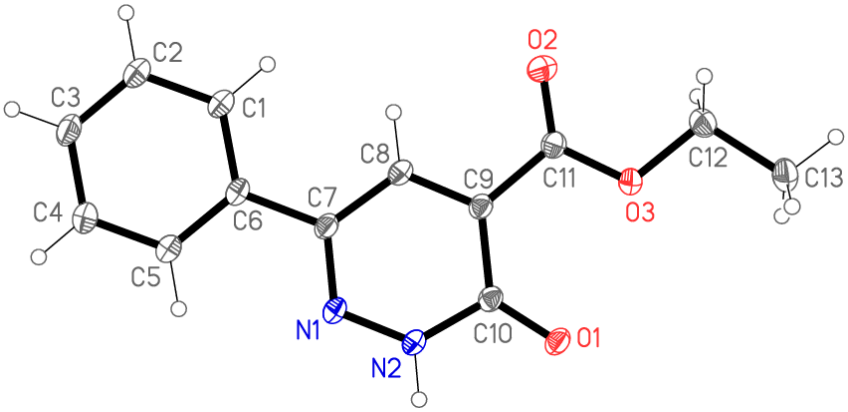


Fig. S9. Structure of compound **9** in the crystal.

Packing diagrams

Numerical details of hydrogen bonds are given in the deposited CIF files. Hydrogen atoms not involved in hydrogen bonds are omitted for clarity. Compound **4f** does not display any unusually short contacts.

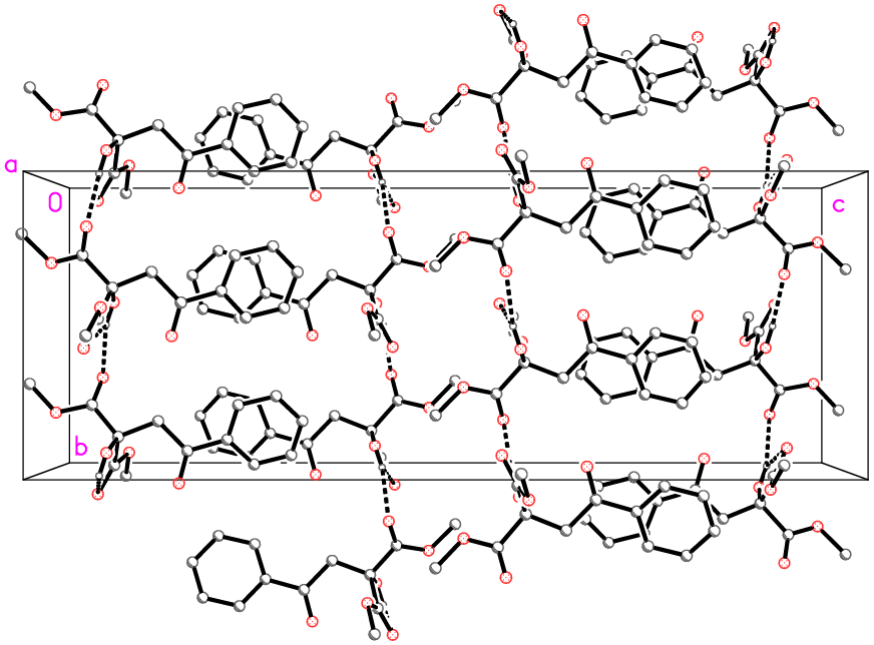


Fig. S10. Packing diagram of compound **2a**.

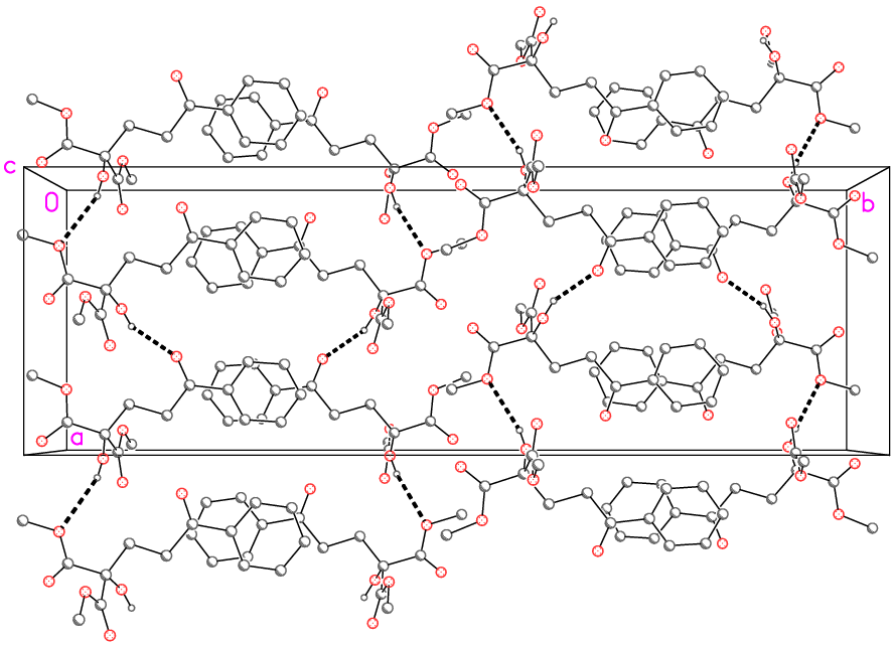


Fig. S11. Packing diagram of compound **5a**.

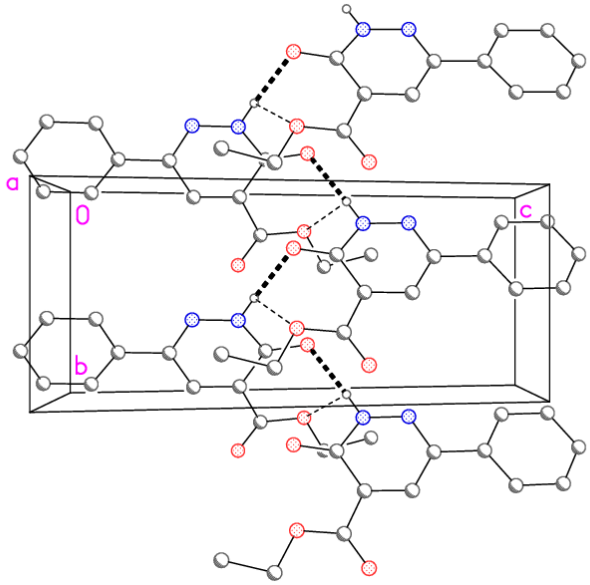


Fig. S12. Packing diagram of compound **9**. The three-centre hydrogen bonds are markedly asymmetric.

13. References

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