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General Methods.

^{1}H-NMR spectra were recorded on Varian 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterochloroform: 7.24 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd= doublet-doublet, t = triplet, td = triple doublet, dt = double triplet, q = quartet, sext = sextet, sept = septet, p = pseudo, b = broad, m = multiplet), coupling constants (Hz). ^{13}C-NMR spectra were recorded on a Varian 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuterochloroform: 77.0 ppm).

HRMS spectra were obtained with a G2XS QTof mass spectrometer using APCI ionization techniques, as specified case by case.

Chromatographic purification was done with 240-400 mesh silica gel. Other anhydrous solvents were supplied by Sigma Aldrich in Sureseal® bottles and used without any further purification. Commercially available chemicals were purchased from Sigma Aldrich, Stream and TCI and used without any further purification.

Anhydrous DMF was purchased from Merck and used as received. All other commercially available starting materials and (non-anhydrous) solvents were purchased from Merck, TCI chemicals, Fluorochem or Alfa Aesar and were used as such without further purification.

CO2 ≥ 99.5% purity, purchased from SIAD, was used in the Arg-GO CO_2 fixation.

Starting materials **1a**, **1g**, **1h**, **1l**, and **1m** are commercially available: these were purchased from Merck and used as received.

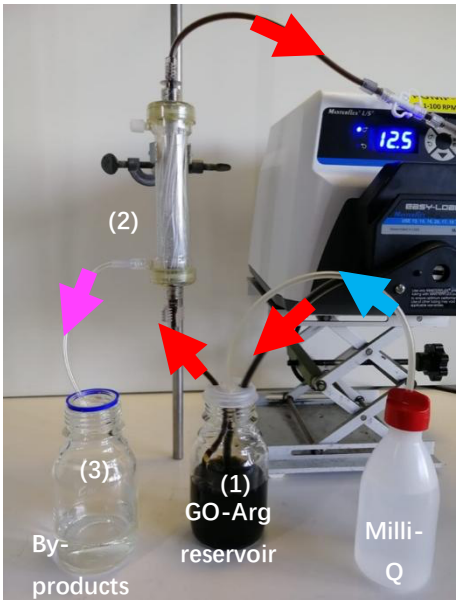
Starting materials **1b**,[1] **1c**,[2] **1d**,[1] **1e**,[2] **1f**,[3] **1i**,[4] **1j**,[1] and **1k**[1] were synthesized through Corey-Chaykovsky epoxidation starting from the respective benzaldehydes, following an unmodified literature procedure.[5] Spectral data match with the ones reported.

Starting materials **1n**[6] and **1o**[6] were synthesized through *m*-CPBA epoxidation of the corresponding olefins following an unmodified literature procedure.[7] Spectral data match with the ones reported.

X-Ray Photoelectron spectroscopy (XPS): High-resolution XPS by using a Phoibos 100 hemispherical energy analyser (Specs GmbH, Berlin, Germany), using Mg Kα radiation (ħω = 1253.6 eV; X-Ray power = 125W) in constant analyser energy (CAE) mode, with analyser pass energies of 10 eV. Base pressure in the analysis chamber during analysis was 4.2×10^{-8} mbar. Spectra were fitted by using CasaXPS (www.casaxps.com) after Tougaard background subtraction and all spectra were calibrated to the C_{1s} binding energy (285.0 eV). XPS samples were prepared as tablet from the dry powder of each material and fixing it on the sample holder by conductive carbon tape.

Attenuated Total Reflectance Fourier Transform (ATR FT-IR) measurements were performed with a N2 purged Bruker Vertex 70 interferometer using a single reflection Platinum-ATR accessory (diamond crystal), a DLaTGS detector and a KBr beamsplitter.

Synthesis and purification of GO-Arg. A basic solution of *L*-Arginine (*i.e. L*-Arg) was prepared by adding 6.0 g of *L*-Arg (34.4 mmol) and 1.05 g of NaOH (26.3 mmol) in MilliQ water (50 mL). The solution was then added to 400 mL of GO suspension (5 mg/mL in MilliQ water, sonicated for 2 h). The mixture was kept under stirring and at 80 °C for 24 h then 5 mL of EtOH were added. The crude product was purified by MF (Plasmart 100, Medica SpA) in loop filtration modality by using a peristaltic pump at 100 mL/min. Pure water was progressively added to the feed solution (tot. volume= 3.2 L). The process was stopped when a neutral pH was measured in the permeated water. 2.3 g of GO-Arg were obtained after freeze drying.



Synthesis and purification of GO-5a. Graphene oxide (Abalonyx (S-126/36)), was homogeneously dispersed in 40 mL of distilled water through sonication for 2 h to prepare GO aqueous suspensions (5 mg/mL). Then 60 mg of *n*-pentylguanidine and 210 mg of NaOH were dissolved in 10 mL (6 mg/mL for *n*-pentylguanidine; 21 mg/mL for NaOH) of mQ water. These two dispersions were mixed, and the solution was kept under stirring at 80 °C for 24 h. Once the reaction was completed the crude was purified by centrifugation and dried by freeze drying.

XPS-analyses

The pristine GO presents C 1s (285.0 eV), O 1s (532.6 eV), N 1s (401.5 eV), Cl 2p (200.2 eV) and S 2p (168.6 eV) signals. GO-Arg present a significantly higher amount of N respect to the pristine GO. The overall oxidation (O 1s / C 1s) was lower than GO due to the presence of aliphatic chains of Arginine. The presence of Ca 2p (347.5 eV) in the Arg-GO and GO-**5a** can be ascribed to the presence of Ca ions in the washing water used during purification. The parameters used for the fitting of C1s and N1s signal are reported in more details in our previous work.[8] Pure *L*-Arginine presents roughly the expected atomic composition (C:N:O = 6:4:2), moreover, the C 1s deconvolution is in good agreement with the data reported in literature, along with the main position of N 1s signal at 400.0 eV. The deconvolution of N 1s core level signal reported in Figure 2 of *L*-Arginine (and GO-Arg) is based on literature results (the Artemenko et al. work cited in main text) that associated to *L*-Arginine two components at 399.3 (NH_2 and C=NH) and 400.0 eV (C-NH-C and $C=NH_2^+$). The binding energies of *L*-Arginine obtained in our fit was found slightly shifted to higher binding energies respect to the literature (c.a. +0.5 eV), such mismatch is compatible with C=C sp^2 and C-C sp^3 relative shift, as a matter of fact, these two carbons are the main one in GO and *L*-Arginine respectively, thus it is probably due to the selection of C 1s calibration value: we have chosen 285.0 eV for GO, that is a compromise between 284.6 eV of C=C sp2 and 285.4 eV for C-C sp3 (red and green peak in Figure S3a), than we calibrated GO-Arg in the same way, given the similar sp^2-sp^3 amounts. The calibration of *L*-Arginine was chosen as 285.4 eV in accordance with C-C sp3 peaks in GO and GO-Arg calibration but was slightly different from the one reported in literature (285.0 eV). N 1s – C1s (400-285.4=114.6eV) and O 1s - N 1s (531.4-400=131.4 eV)) relative shifts are the same of those reported in literature (399.5-285=114.6 eV and 530.8-399.5=131.3eV) and it is above the aim of these paper to provide an absolute XPS reference values for pristine *L*-Arginine.

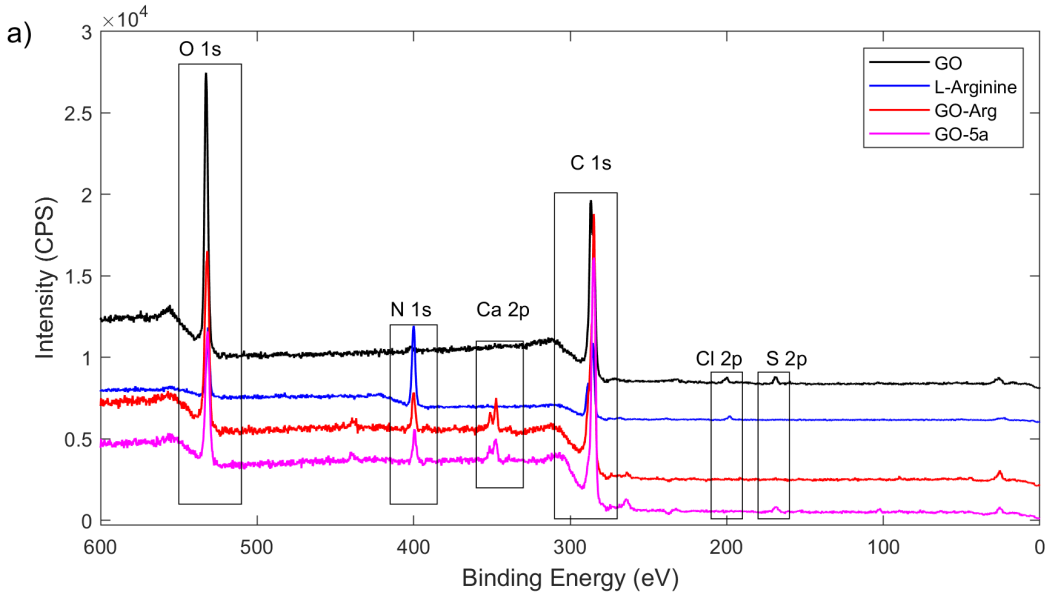


Figure S1: Survey spectra of graphene oxide (black line), L-Arginine (blue line), GO-Arg (red line) and GO-**5a** (magenta line).

Material	C	O	N	Cl	S	Ca
GO	70.4	27	0.7	0.8	1	-
Arginine	58.4	13.7	27.0	0.9	\\	\\
GO-Arg	73.6	19.6	4.9	< 0.2	< 0.2	1.8
GO-5a	79.1	14.7	3.5	< 0.2	0.9	1.7

Table S1: XPS Atomic composition.

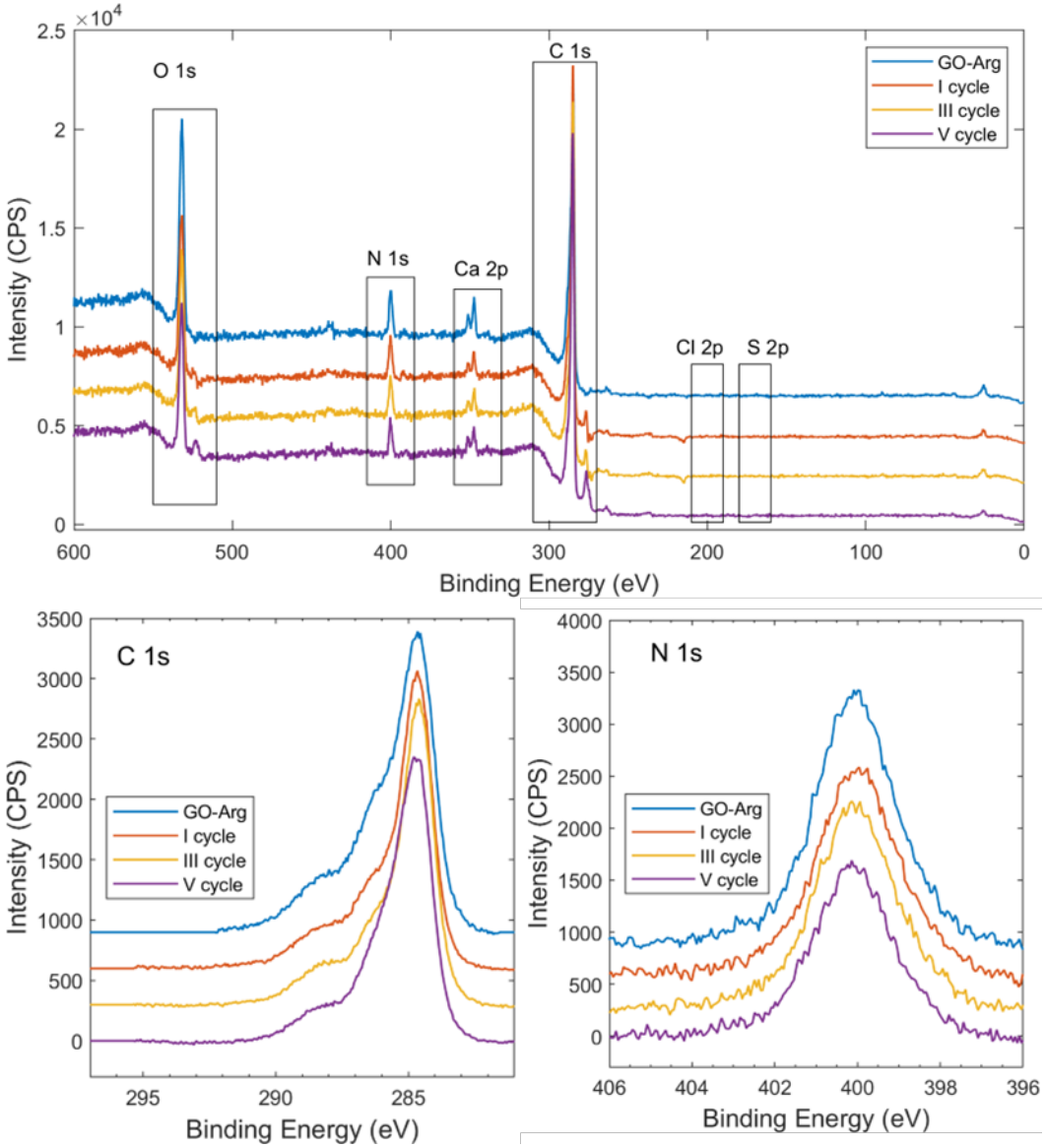


Figure S2: Top: Survey spectra of pristine GO-Arg and GO-Arg after 1, 3 and 5 cycle of catalysis. Bottom: C1s and N1s.

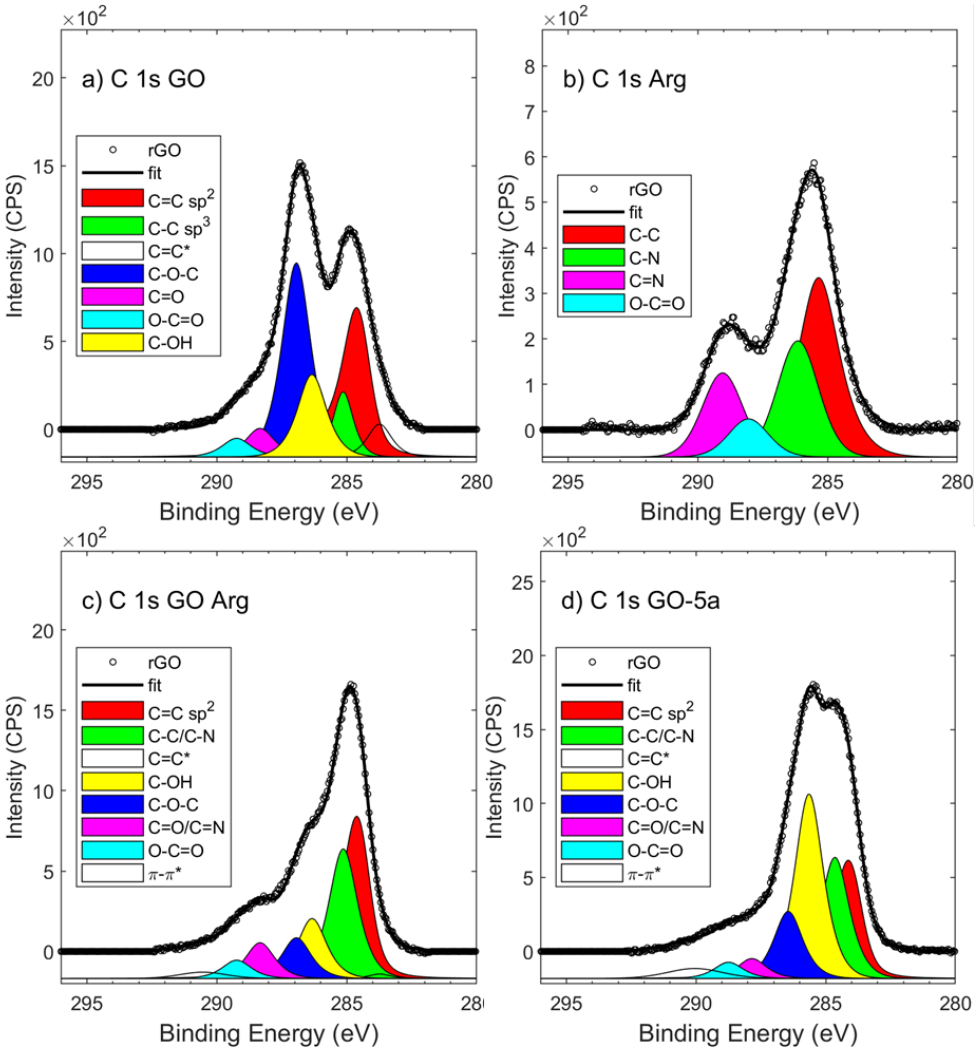


Figure S3: C1s deconvolution of a) graphene oxide, b) Arginine, c) GO-Arg and d) GO-**5a**.

Material	C 1s Deconvolution						
	C sp2	C sp3	C=C*	C-OH	C-O-C	C=O	O-C=O
GO	31.2	7.9	4.8	14.3	33.7	5.0	3.2
GO-Arg pristine	39.8	27.1	0.7	12.6	8.5	7.5	3.8
GO-Arg I Cycle	68.4	8.7	0.6	7.8	5.3	6.4	2.8
GO-Arg III Cycle	67.6	10.5	0.6	7.6	4.5	6.4	2.8
GO-Arg V Cycle	50.8	24.0	0.4	12.9	3.0	6.2	2.8

Table S2: C1s deconvolution of GO, GO-Arg and GO-Arg after several cycle.

ATR-IR spectra

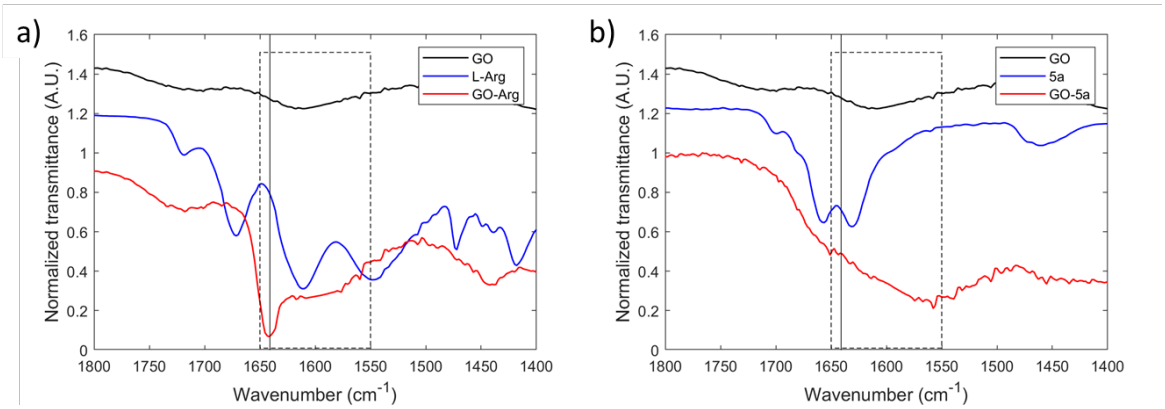
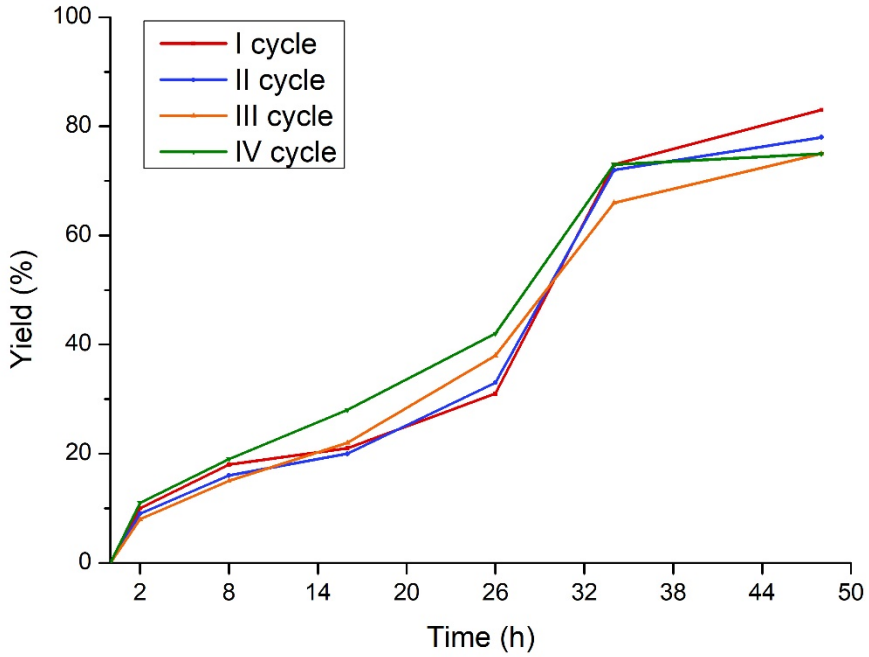


Figure S4: Detailed IR of Fig 2b and 4b.

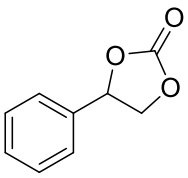
Kinetic Profile



General procedure for the Arg-GO catalyzed CO_2 fixation.

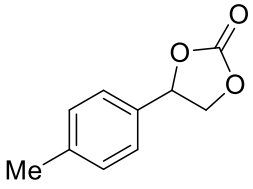
In a heat-gun dried screw-capped Schlenk flask, equipped with a magnetic stirring bar and under N_2 atmosphere, **Arg-GO** (5.0 mg) was added. The tube was evacuated and backfilled with CO_2 (three times). Anhydrous DMF (1.0 mL) was then added and bubbled for 1 minute under a flow of CO_2. Then, **1** (0.2 mmol, 1 equiv.) and TBAI (22.0 mg, 0.06 mmol, 30 mol%) were added. The tube was then sealed and placed in an oil bath at 100 °C where it was vigorously stirred for 48 h. After cooling to room temperature, the reaction mixture was filtered through a Celite pad to remove **Arg-GO**, washing with EtOAc (3 x 5 mL). The solvents were removed under reduced pressure (rotary evaporator then high-vacuum pump to remove DMF) and the residue was purified by flash column chromatography (FC) on silica gel (*n*-hexane/EtOAc mixtures) to afford pure products **2**.

NOTE: Products **2l** and **2m** were found to be somewhat volatile and loss of material was observed during evaporation of DMF under high vacuum. Thus, the work-up was adjusted by DMF removal through aqueous extraction (3 x 20 mL) followed by careful evaporation of EtOAc under reduced pressure and flash chromatography.



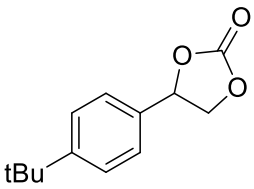
2a. White solid. FC eluent: *n*Hex/EtOAc: 2:1. Yield = 83%, (0.166 mmol, 26.9 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.46 – 7.39 (m, 3H), 7.37 – 7.32 (m, 2H), 5.66 (t, *J* = 8.0 Hz, 1H), 4.78 (t, *J* = 8.4 Hz, 1H), 4.32 (dd, *J* = 8.6, 7.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.8, 135.8, 129.7, 129.2, 125.9, 78.0, 71.2.

2a is a known compound and the reported spectroscopic data match with the ones reported in the literature.[9]



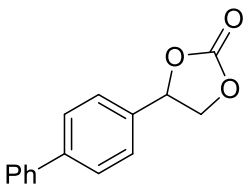
2b. Pale yellow solid. FC eluent: *n*Hex/EtOAc: 2:1. Yield = 80%, (0.160 mmol, 28.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.23 (*pseudo*-s, 4H), 5.62 (t, *J* = 8.0 Hz, 1H), 4.75 (t, *J* = 8.4 Hz, 1H), 4.32 (dd, *J* = 8.6, 7.9 Hz, 1H), 2.36 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.9, 139.9, 132.7, 129.9 (2C), 126.0 (2C), 78.1, 71.2, 21.2.

2b is a known compound and the reported spectroscopic data match with the ones reported in the literature.[10]



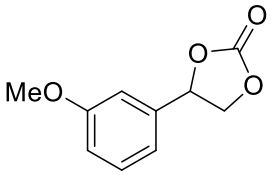
2c. Pale yellow oil. FC eluent: *n*Hex/EtOAc: 2:1. Yield = 57%, (0.114 mmol, 25.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.49 – 7.38 (m, 2H), 7.32 – 7.26 (m, 2H), 5.64 (t, *J* = 8.0 Hz, 1H), 4.76 (t, *J* = 8.4 Hz, 1H), 4.34 (t, *J* = 8.3 Hz, 1H), 1.31 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.9, 153.1, 132.6, 126.2 (2C), 125.8 (2C), 78.0, 71.1, 34.7, 31.2 (3C).

2c is a known compound and the reported spectroscopic data match with the ones reported in the literature.[11]



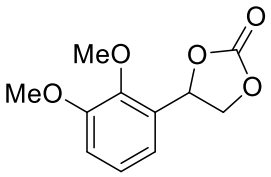
2d. Pale yellow solid. FC eluent: *n*Hex/EtOAc: 2:1. Yield = 56%, (0.112 mmol, 26.8 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.60 – 7.53 (m, 2H), 7.53 – 7.46 (m, 2H), 7.41 – 7.25 (m, 5H), 5.62 (t, *J* = 8.0 Hz, 1H), 4.73 (t, *J* = 8.4 Hz, 1H), 4.29 (t, *J* = 8.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.7, 142.7, 139.9, 134.5, 128.8 (2C), 127.8 (2C), 127.8, 127.0 (2C), 126.3 (2C), 77.8, 71.0.

2d is a known compound and the reported spectroscopic data match with the ones reported in the literature.[12]

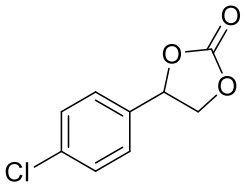


2e. Colourless oil. FC eluent: *n*Hex/EtOAc: 2:1. Yield = 51%, (0.102 mmol, 19.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.34 (t, *J* = 7.9 Hz, 1H), 6.95 – 6.85 (m, 3H), 5.63 (t, *J* = 8.0 Hz, 1H), 4.77 (t, *J* = 8.4 Hz, 1H), 4.31 (dd, *J* = 8.6, 7.9 Hz, 1H), 3.81 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 160.2, 154.7, 137.3, 130.4, 117.8, 115.1, 111.2, 77.8, 71.1, 55.4.[10]

2e is a known compound and the reported spectroscopic data match with the ones reported in the literature.

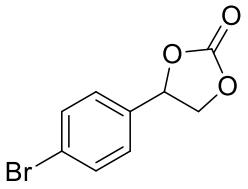


2f. Colourless oil. FC eluent: *n*Hex/EtOAc: 2:1. Yield = 60%, (0.120 mmol, 26.9 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.08 (dd, *J* = 8.3, 7.6 Hz, 1H), 6.98 – 6.92 (m, 2H), 5.81 (t, *J* = 8.1 Hz, 1H), 4.80 (t, *J* = 8.5 Hz, 1H), 4.28 (dd, *J* = 8.4, 7.5 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 155.1, 152.6, 146.2, 130.0, 124.4, 118.0, 113.6, 74.9, 70.8, 60.9, 55.8. **HRMS (APCI)** m/z: $[M+H]^+$ calcd. for $C_{11}H_{13}O_5$ 225.0757; found 225.0749.



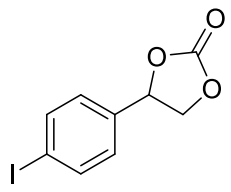
2g. White solid. FC eluent: *n*Hex/EtOAc: 2:1. Yield = 62%, (0.124 mmol, 24.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.44 – 7.38 (m, 2H), 7.32 – 7.26 (m, 2H), 5.64 (t, *J* = 8.0 Hz, 1H), 4.78 (t, *J* = 8.4 Hz, 1H), 4.29 (dd, *J* = 8.7, 7.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.5, 135.8, 134.3, 129.5 (2C), 127.2 (2C), 77.2, 71.0.

2g is a known compound and the reported spectroscopic data match with the ones reported in the literature.[8]

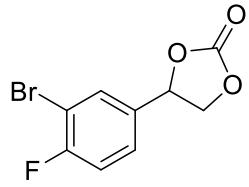


2h. White solid. FC eluent: *n*Hex/EtOAc: 2:1. Yield = 80%, (0.160 mmol, 38.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.62 – 7.54 (m, 2H), 7.24 – 7.20 (m, 2H), 5.62 (t, *J* = 7.9 Hz, 1H), 4.78 (t, *J* = 8.4 Hz, 1H), 4.28 (dd, *J* = 8.7, 7.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.5, 134.8, 132.5 (2C), 127.4 (2C), 123.9, 77.2, 70.9.

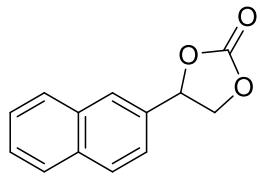
2h is a known compound and the reported spectroscopic data match with the ones reported in the literature.[8]



2i. Pale yellow solid. FC eluent: *n*Hex/EtOAc: 2:1. Yield = 78%, (0.156 mmol, 45.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.73 – 7.65 (m, 2H), 7.05 – 6.97 (m, 2H), 5.53 (t, *J* = 8.0 Hz, 1H), 4.71 (t, *J* = 8.4 Hz, 1H), 4.20 (dd, *J* = 8.7, 7.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.4, 138.3 (2C), 135.4, 127.5 (2C), 95.5, 77.2, 70.8. **HRMS (APCI)** m/z: $[M+H]^+$ calcd. for $C_9H_8IO_3$ 290.9513; found 290.9524.

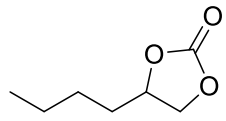


2j. Pale yellow oil. FC eluent: *n*Hex/EtOAc: 2:1. Yield = 81%, (0.162 mmol, 42.3 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.57 (dd, *J* = 6.2, 2.3 Hz, 1H), 7.29 (ddd, *J* = 8.6, 4.5, 2.3 Hz, 1H), 7.18 (t, *J* = 8.3 Hz, 1H), 5.63 (t, *J* = 7.9 Hz, 1H), 4.79 (t, *J* = 8.5 Hz, 1H), 4.29 (dd, *J* = 8.8, 7.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 159.7 (d, *J* = 250.6 Hz), 154.3, 133.3 (d, *J* = 3.8 Hz), 131.3 (d, *J* = 1.2 Hz), 126.6 (d, *J* = 7.8 Hz), 117.3 (d, *J* = 22.9 Hz), 110.1 (d, *J* = 21.6 Hz), 76.5, 70.9 (d, *J* = 1.1 Hz). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -105.03 (dt, *J* = 8.0, 5.3 Hz); **HRMS (APCI)** m/z: $[M+H]^+$ calcd. for $C_9H_7{}^{79}BrFO_3$ 260.9558; found 260.9569; calcd. for $C_9H_7{}^{81}BrFO_3$ 262.9537; found 262.9525.



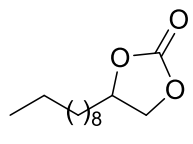
2k. Pale yellow solid. FC eluent: *n*Hex/EtOAc: 2:1. Yield = 82%, (0.164 mmol, 35.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 8.6 Hz, 1H), 7.80 – 7.71 (m, 3H), 7.49 – 7.39 (m, 2H), 7.32 (dd, *J* = 8.6, 1.9 Hz, 1H), 5.73 (t, *J* = 8.0 Hz, 1H), 4.75 (t, *J* = 8.4 Hz, 1H), 4.32 (dd, *J* = 8.7, 7.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.8, 136.8, 133.6, 132.9, 129.5, 128.0, 127.8, 127.1, 126.9, 125.7, 122.3, 78.1, 71.0.

2k is a known compound and the reported spectroscopic data match with the ones reported in the literature.[13]



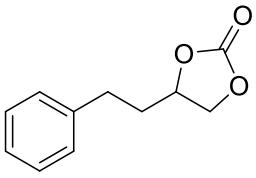
2l. Pale yellow oil. FC eluent: *n*Hex/EtOAc: 2:1. Yield = 79%, (0.158 mmol, 22.8 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 4.65 (qd, *J* = 7.5, 5.4 Hz, 1H), 4.47 (t, *J* = 8.1 Hz, 1H), 4.02 (dd, *J* = 8.4 7.2 Hz, 1H), 1.83 – 1.71 (m, 1H), 1.68 – 1.58 (m, 1H), 1.47 – 1.24 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 155.0, 76.9, 69.3, 33.5, 26.4, 22.2, 13.7.

2l is a known compound and the reported spectroscopic data match with the ones reported in the literature.[8]



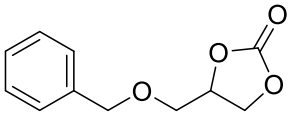
2m. Pale yellow oil. FC eluent: *n*Hex/EtOAc: 2:1. Yield = 78%, (0.156 mmol, 35.9 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 4.63 (qd, *J* = 7.5, 5.4 Hz, 1H), 4.45 (t, *J* = 8.1 Hz, 1H), 3.99 (t, *J* = 7.8 Hz, 1H), 1.80 – 1.67 (m, 1H), 1.66 – 1.55 (m, 1H), 1.48 – 1.11 (m, 16H), 0.81 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 155.0, 77.0, 69.3, 33.8, 31.8, 29.5, 29.4, 29.3, 29.2, 29.1, 24.3, 22.6, 14.0.

2l is a known compound and the reported spectroscopic data match with the ones reported in the literature.[11]



2n. Pale yellow solid. FC eluent: *n*Hex/EtOAc: 2:1. Yield = 77%, (0.154 mmol, 29.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.34 – 7.26 (m, 2H), 7.24 – 7.19 (m, 1H), 7.19 – 7.14 (m, 2H), 4.66 (tdd, *J* = 8.2, 7.2, 4.8 Hz, 1H), 4.45 (dd, *J* = 8.5, 7.8 Hz, 1H), 4.02 (dd, *J* = 8.5, 7.2 Hz, 1H), 2.84 (ddd, *J* = 14.1, 8.9, 5.3 Hz, 1H), 2.72 (dt, *J* = 13.9, 8.1 Hz, 1H), 2.20 – 2.07 (m, 1H), 2.03 – 1.90 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.9, 139.7, 128.7 (2C), 128.4 (2C), 126.6, 76.0, 69.3, 35.6, 30.8.

2n is a known compound and the reported spectroscopic data match with the ones reported in the literature.[14]



2o. Pale yellow solid. FC eluent: *n*Hex/EtOAc: 2:1. Yield = 57%, (0.114 mmol, 24.4 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.38 – 7.27 (m, 5H), 4.83 – 4.75 (m, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 12.1 Hz, 1H), 4.46 (t, *J* = 8.3 Hz, 1H), 4.36 (dd, *J* = 8.3, 6.0 Hz, 1H), 3.69 (dd, *J* = 10.9, 4.0 Hz, 1H), 3.60 (dd, *J* = 10.9, 3.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.9, 137.0, 128.6 (2C), 128.1, 127.7 (2C), 75.0, 73.7, 68.8, 66.3.

2o is a known compound and the reported spectroscopic data match with the ones reported in the literature.[9]

General procedure for the GO-5a catalyzed CO_2 fixation

In a heat-gun dried screw-capped Schlenk flask, equipped with a magnetic stirring bar and under N_2 atmosphere, **5a-GO** (5.0 mg) was added. The tube was evacuated and backfilled with CO_2 (three times). Anhydrous DMF (1.0 mL) was then added and bubbled for 1 minute under a flow of CO_2. Then, **1** (0.2 mmol, 1 equiv.) and TBAI (22.0 mg, 0.06 mmol, 30 mol%) were added. The tube was then sealed and placed in an oil bath at 100 °C where it was vigorously stirred for 48 h. After cooling to room temperature, the reaction mixture was filtered through a Celite pad to remove **5a-GO**, washing with EtOAc (3 x 5 mL). The solvents were removed under reduced pressure (rotary evaporator then high-vacuum pump to remove DMF) and the residue was purified by flash column chromatography (FC) on silica gel (*n*-hexane/EtOAc mixtures) to afford pure product **2a**

General procedure for the recovering/reuse test

Recycling experiments were conducted similarly to the previously mentioned reactions. After the completion of each reaction cycle, the mixture was centrifuged with EtOAc, to separate the product from the catalyst. Then, **GO-Arg** was washed through reiterative centrifugation with DMF (removal of TBAI), and freeze dried, after which it was ready to be re-utilized. A total of 5 consecutive recycling runs were conducted.

GO-Arg catalyzed CO_2 fixation on enantiopure 1a

In a heat-gun dried screw-capped Schlenk flask, equipped with a magnetic stirring bar and under N_2 atmosphere, **GO-Arg** (15.0 mg) was added. The tube was evacuated and backfilled with CO_2 (three times). Anhydrous DMF (1.0 mL) was then added and bubbled for 1 minute under a flow of CO_2. Then, **1a** (0.6 mmol, 1 equiv.) and TBAI (66.0 mg, 0.18 mmol, 30 mol%) were added. The tube was then sealed and placed in an oil bath at 100 °C where it was vigorously stirred for 48 h. After cooling to room temperature, the reaction mixture was filtered through a Celite pad to remove the catalyst and the enantiomeric excess of **2a** was determined by chiral HPLC measurement using HPLC with chiral column (ChiralCel OD, 10% IPA/*n*Hex, 1 mL/min, 25 °C).

Racemization tests were carried out by stirring enantiopure (*S*)-**1a** in DMF at 100 °C with the desired additive (*i.e.* TBAI, GO-Arg and TBAI/GO-Arg). The enantiomeric excess of the resulting **1a** was determined via chiral HPLC on one aliquot of solution upon cooling at rt. (ChiralPak AD, 2% IPA/*n*Hex, 1 mL/min, 25 °C).

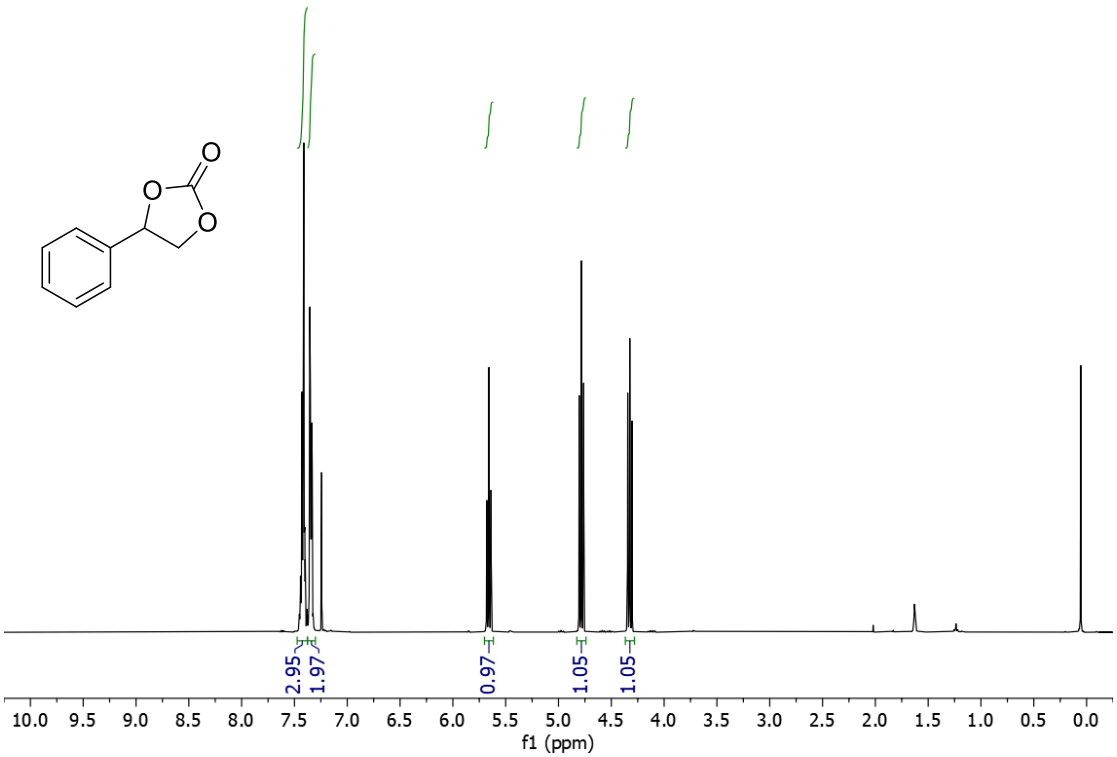
General procedure for the hot filtration test

In a heat-gun dried screw-capped Schlenk flask, equipped with a magnetic stirring bar and under N_2 atmosphere, **Arg-GO** (5.0 mg) was added. The tube was evacuated and backfilled with CO_2 (three times). Anhydrous DMF (1.0 mL) was then added and bubbled for 1 minute under a flow of CO_2. Then, **1** (0.2 mmol, 1 equiv.) and TBAI (22.0 mg, 0.06 mmol, 30 mol%) were added. The tube was then sealed and placed in an oil bath at 100 °C where it was vigorously stirred for 16 h. Then the reaction mixture was filtered, without cooling, through a Celite pad to remove the catalyst. A small amount of the filtered solution was analysed by ^{1}H-NMR, observing a conversion of 37%, while the remaining was placed again in the oil bath at 100 °C in a new heat-gun dried screw-capped Schlenk flask for further 16h. After cooling to room temperature, the DMF was removed with a high-vacuum pump and the residue was analysed with ^{1}H NMR using an internal standard, observing a conversion of 36%, so no progressing formation of carbonate occurred,

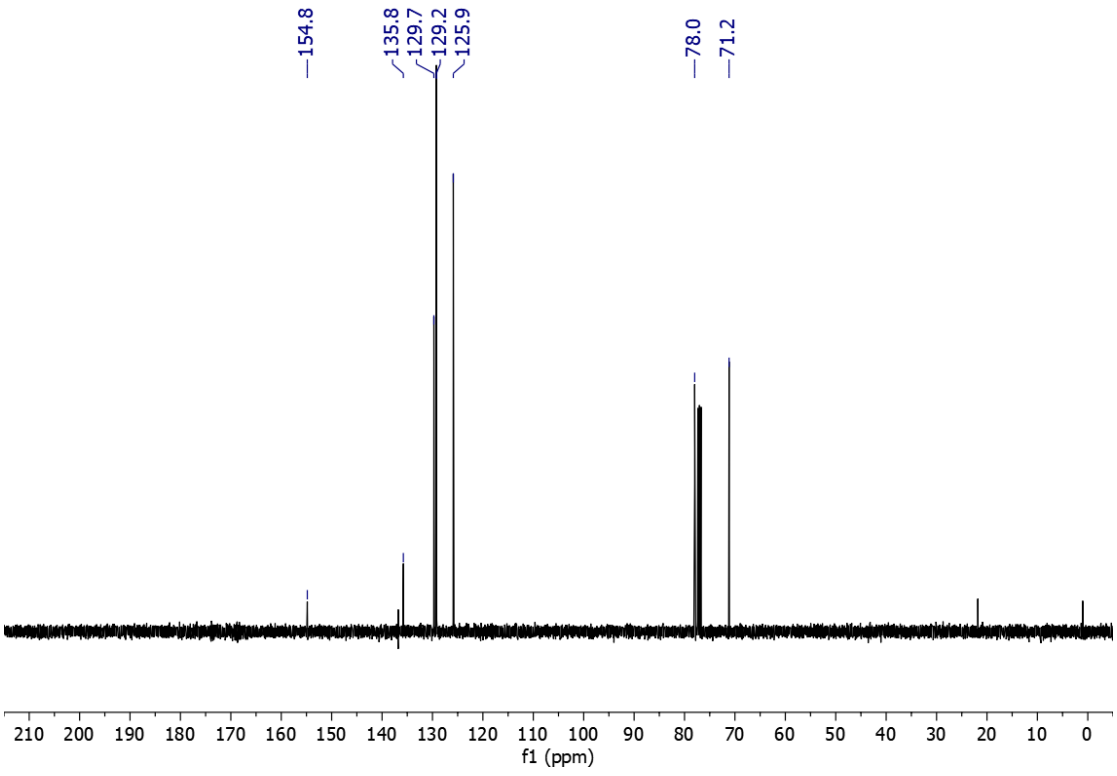
the

^{1}H and ^{13}C NMR spectra

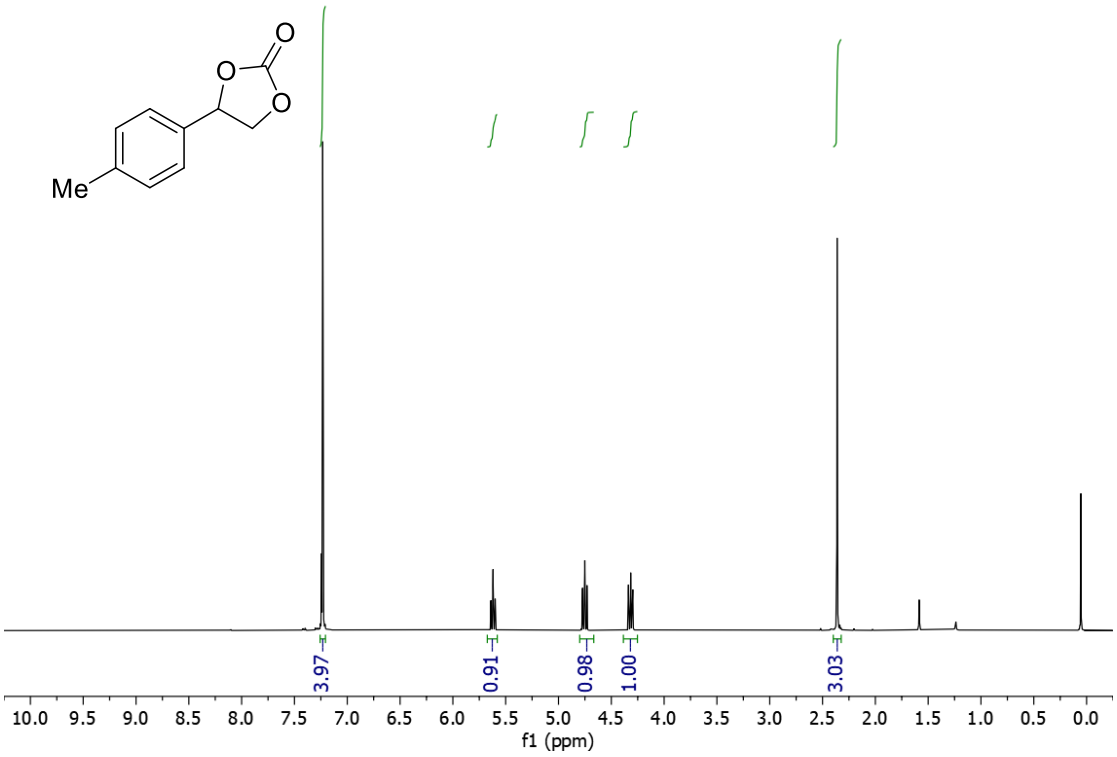
2a ^{1}H NMR (400 MHz, $CDCl_3$)



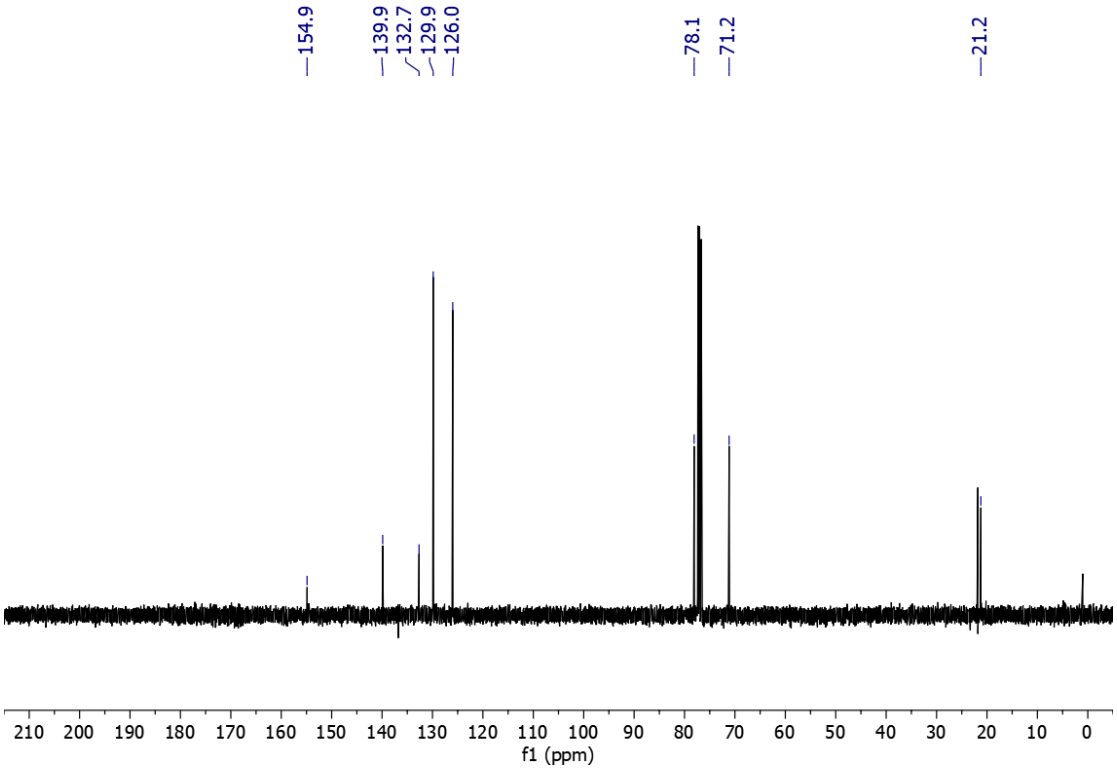
2a ^{13}C NMR (100 MHz, $CDCl_3$)



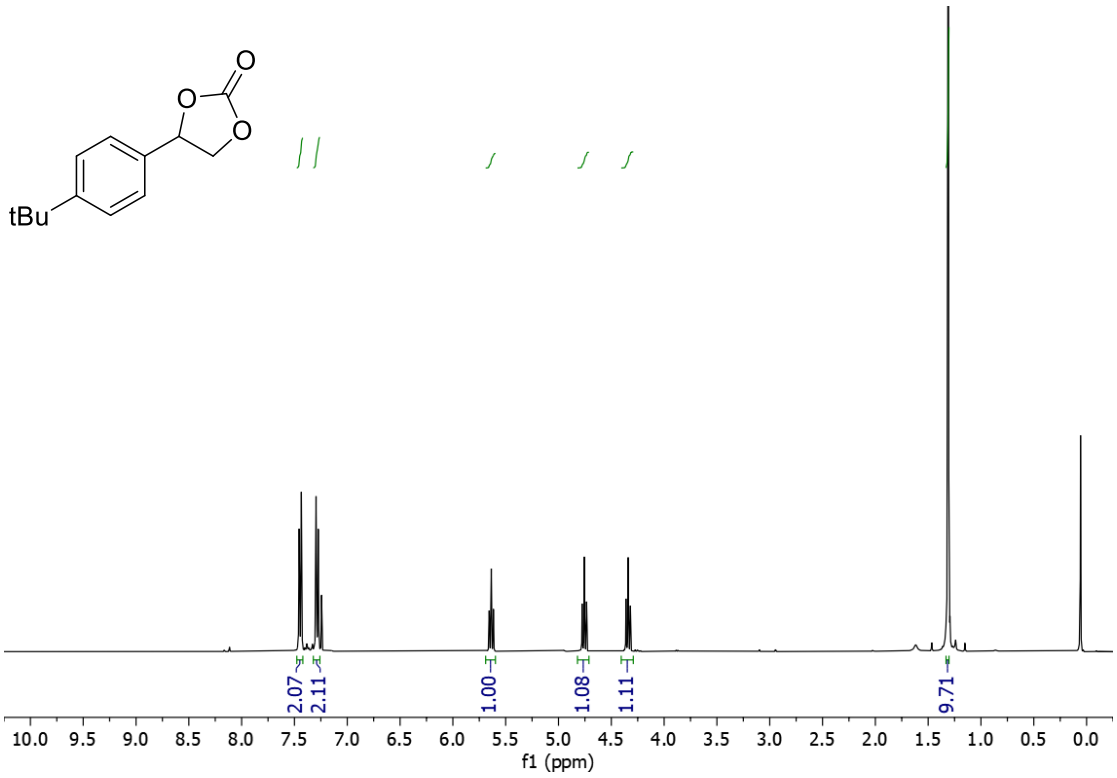
2b ^{1}H NMR (400 MHz, $CDCl_3$)



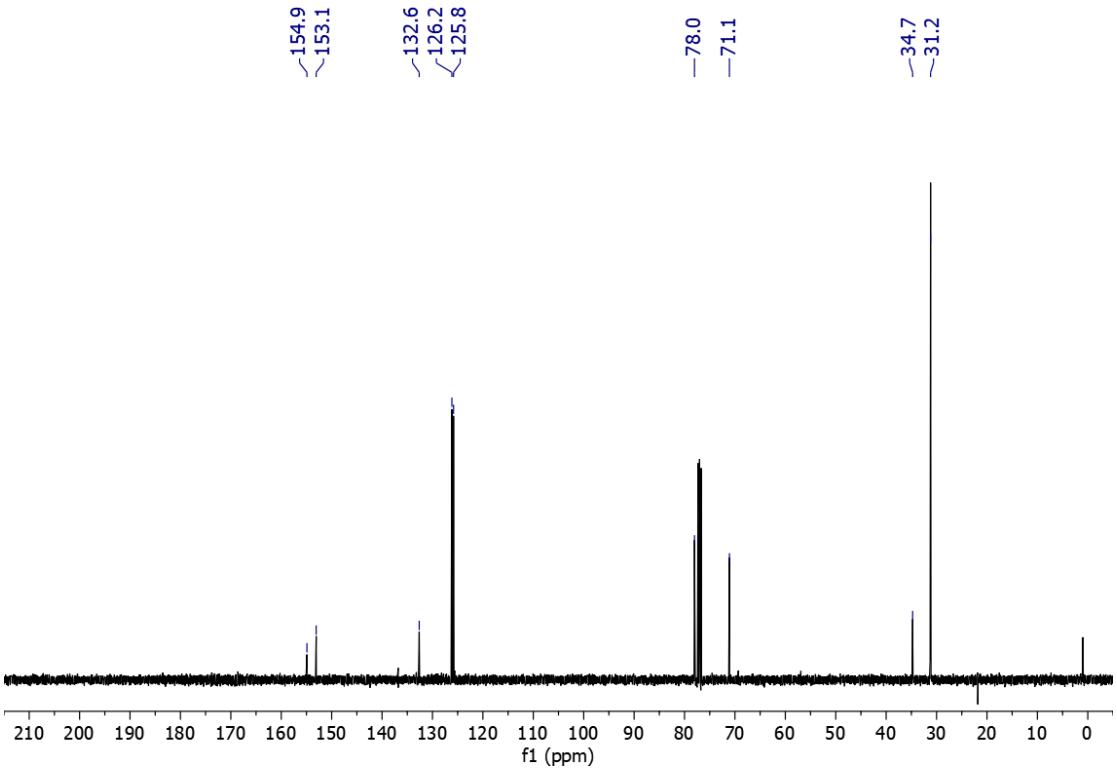
2b ^{13}C NMR (100 MHz, $CDCl_3$)



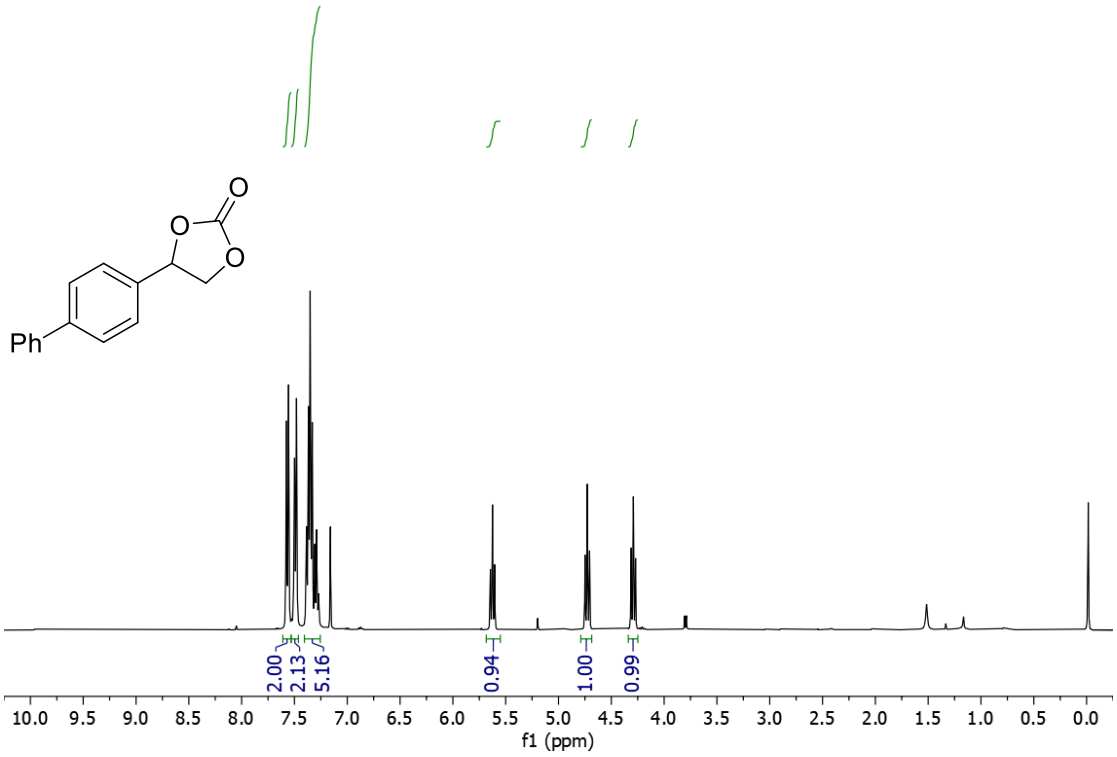
2c ^{1}H NMR (400 MHz, $CDCl_3$)



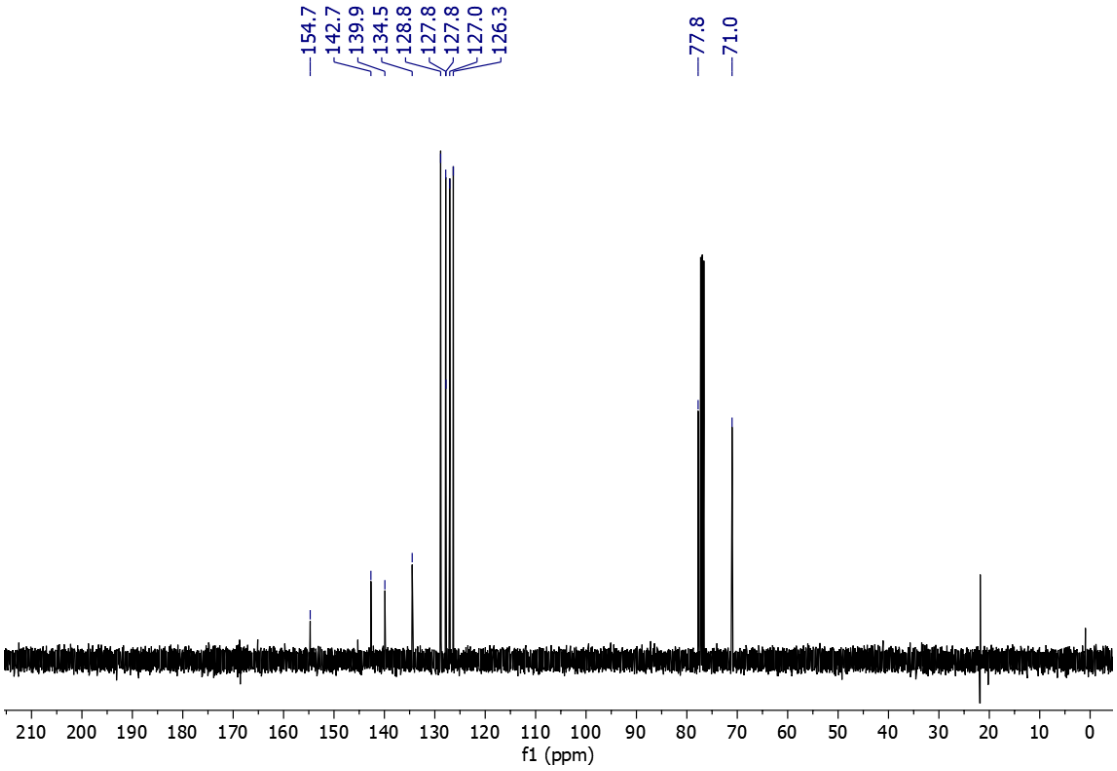
2c ^{13}C NMR (100 MHz, $CDCl_3$)



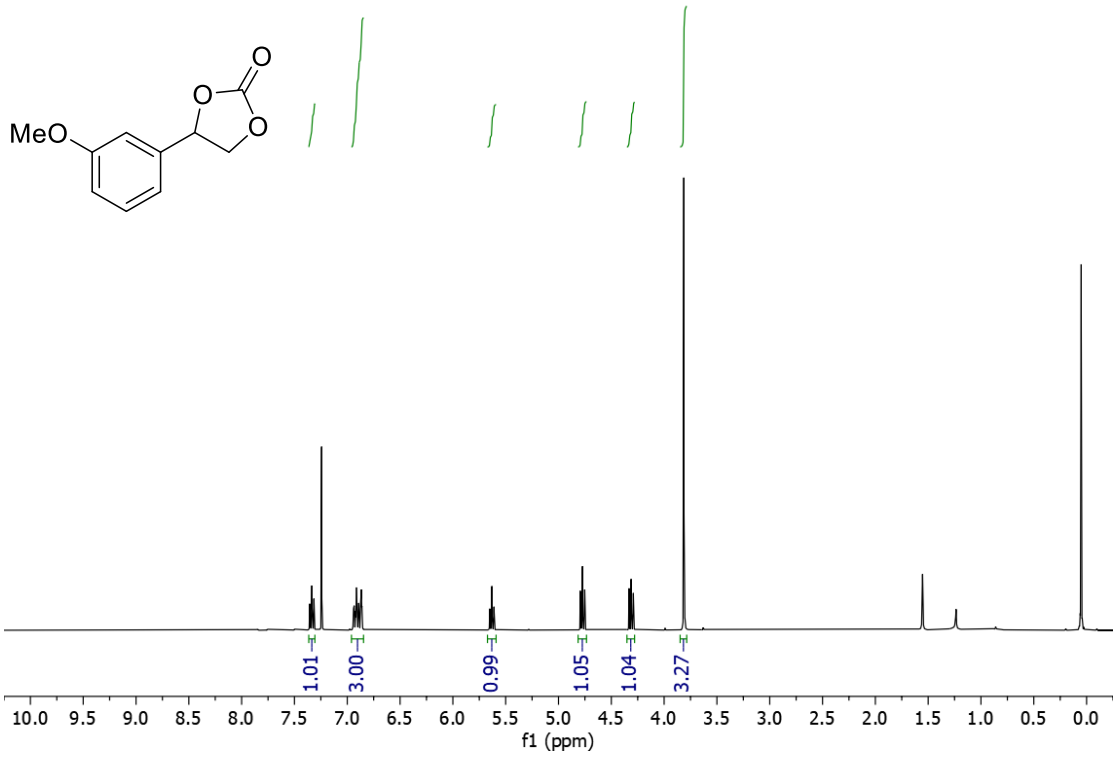
2d ^{1}H NMR (400 MHz, $CDCl_3$)



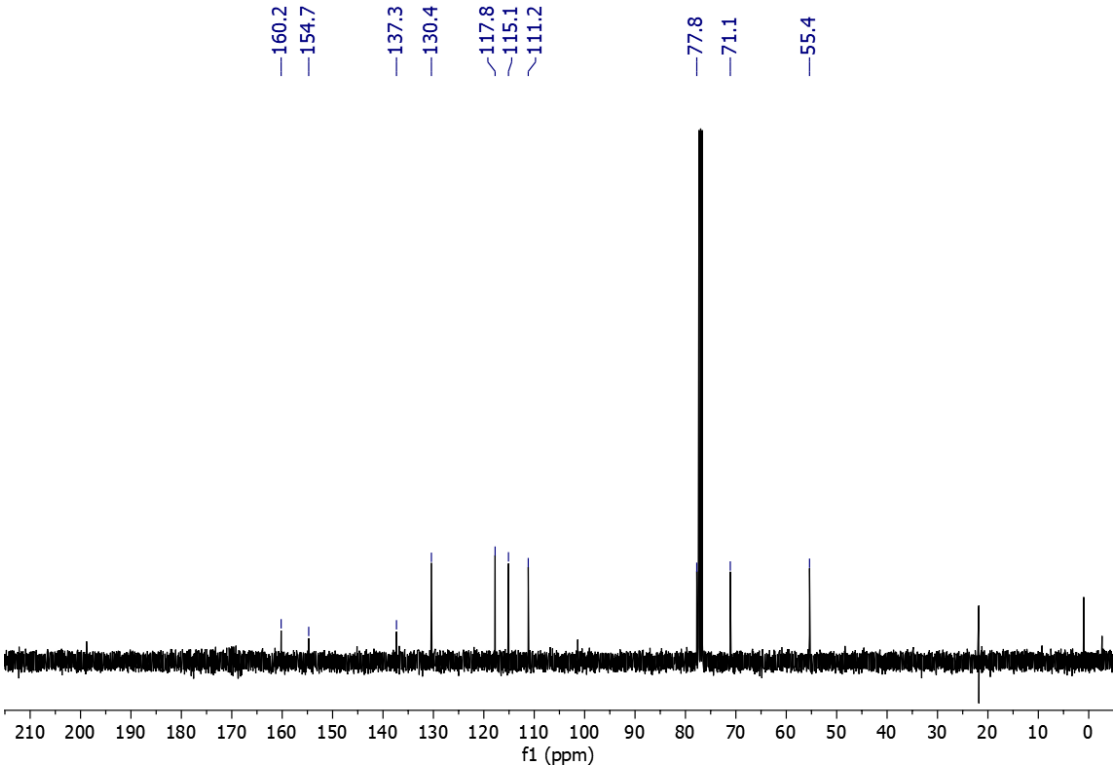
2d ^{13}C NMR (100 MHz, $CDCl_3$)



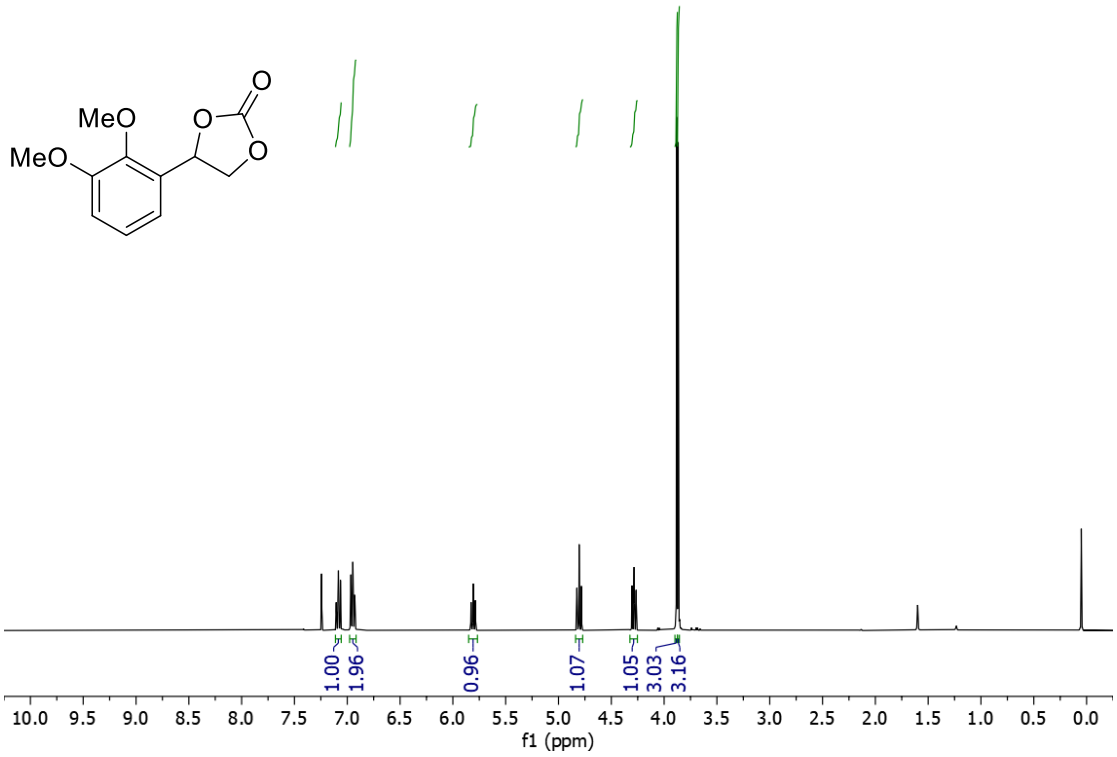
2e ^{1}H NMR (400 MHz, $CDCl_3$)



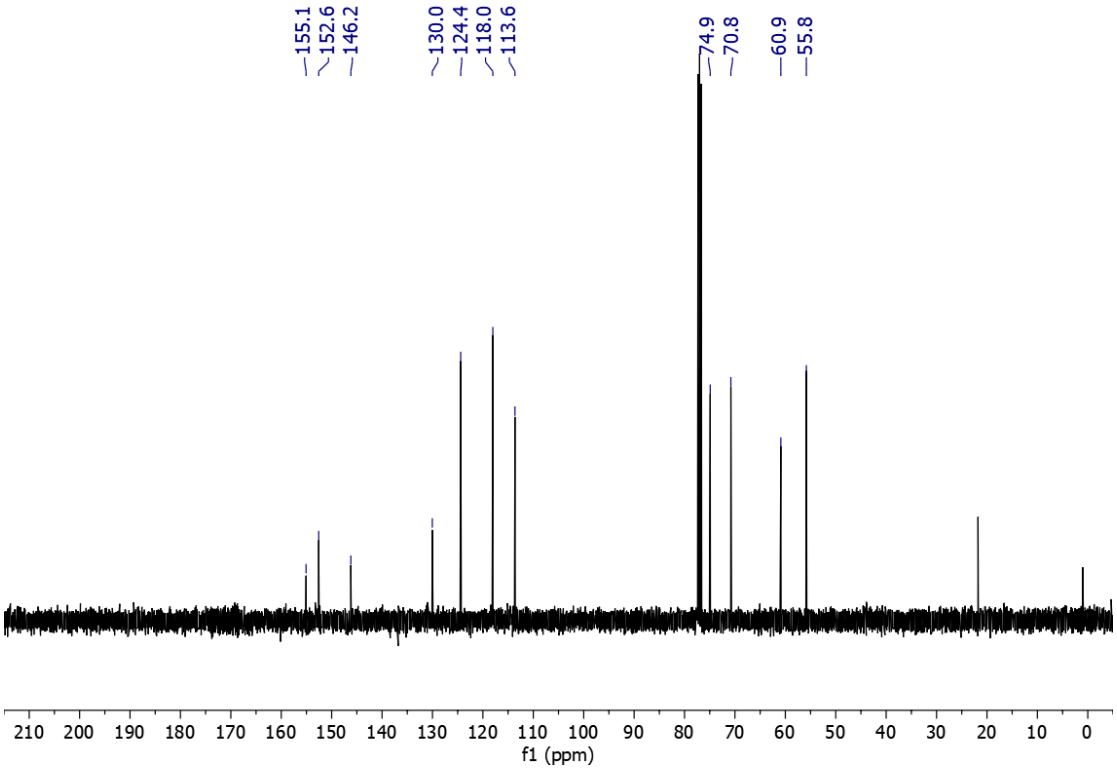
2e ^{13}C NMR (100 MHz, $CDCl_3$)



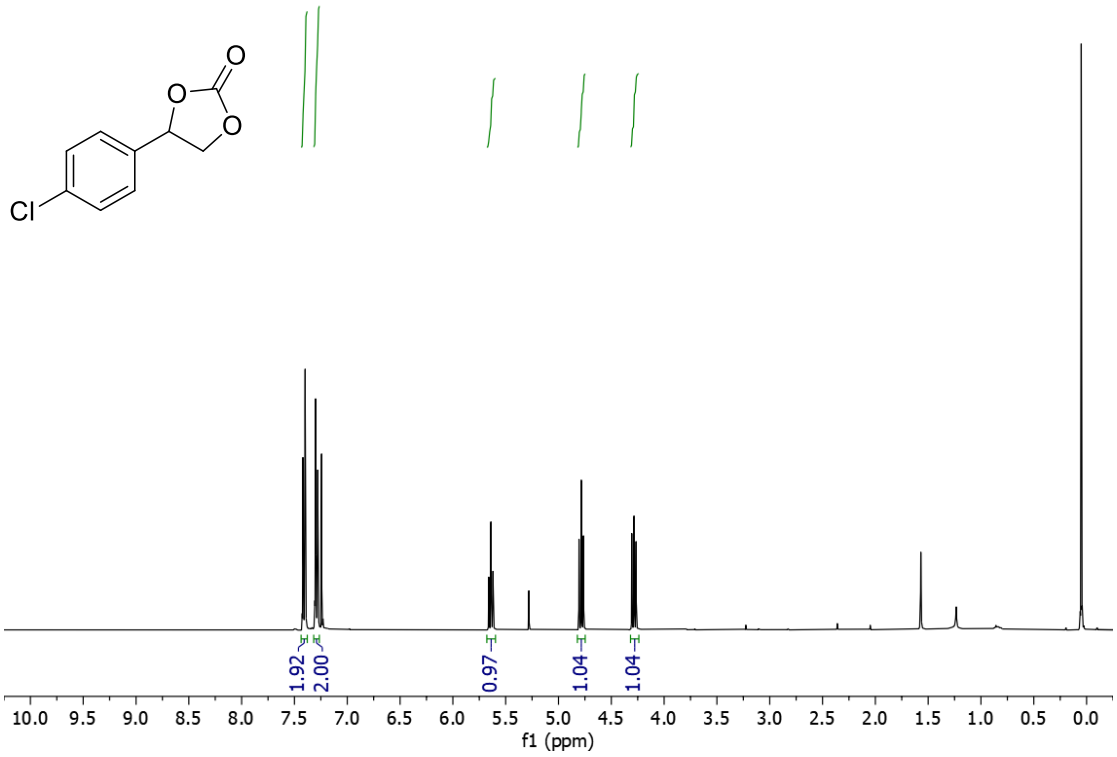
2f ^{1}H NMR (400 MHz, $CDCl_3$)



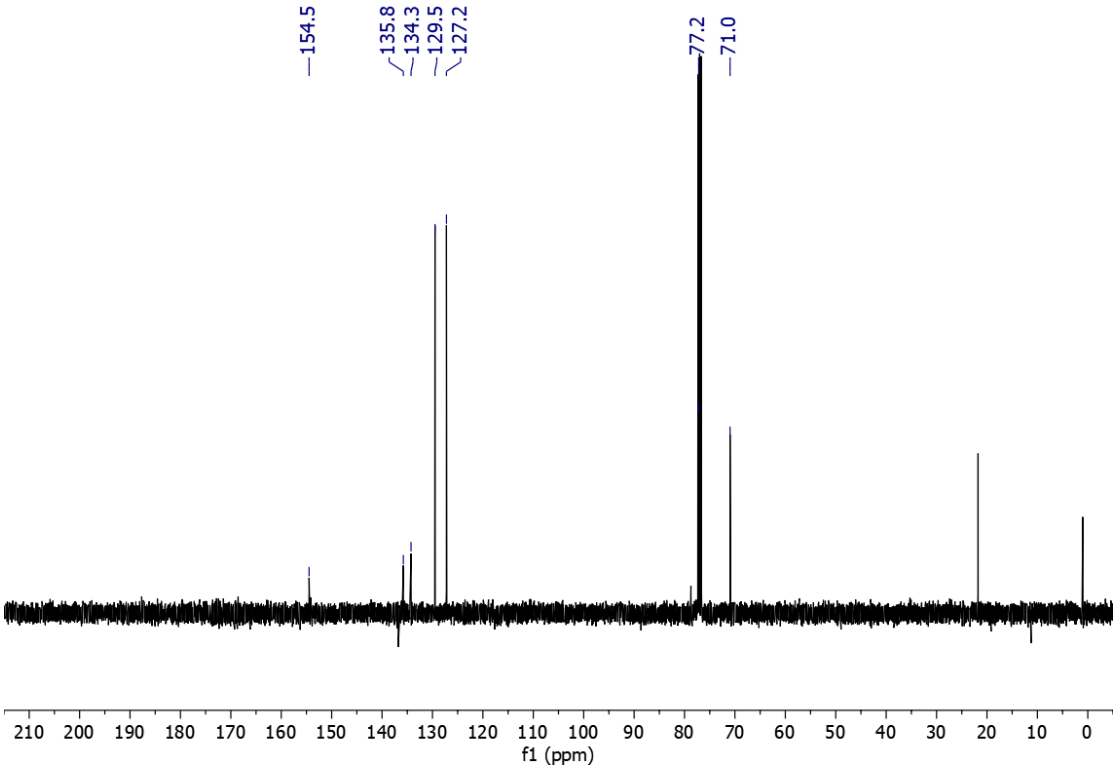
2f ^{13}C NMR (100 MHz, $CDCl_3$)



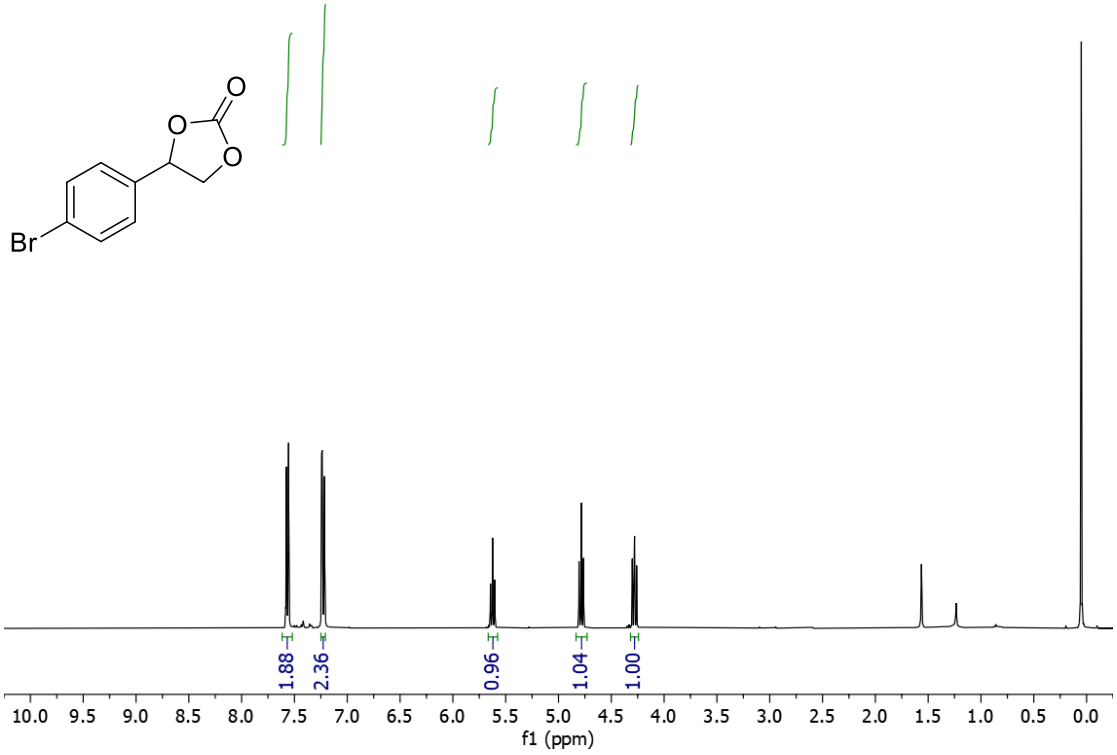
2g ^{1}H NMR (400 MHz, $CDCl_3$)



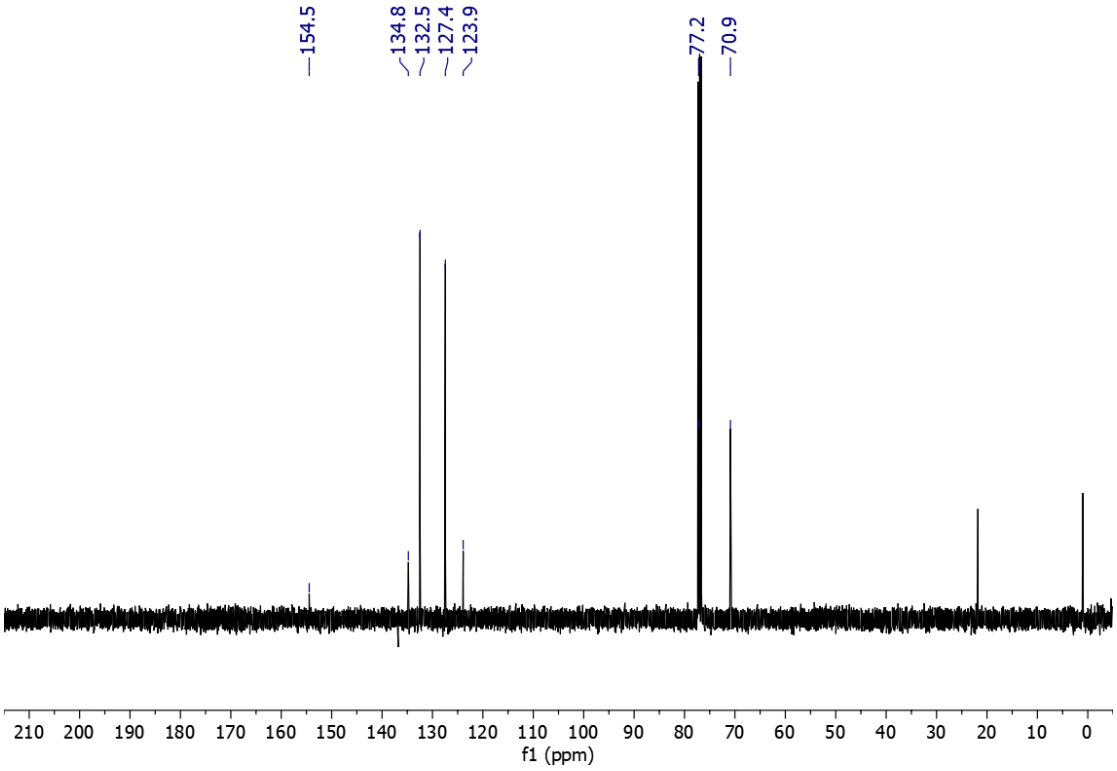
2g ^{13}C NMR (100 MHz, $CDCl_3$)



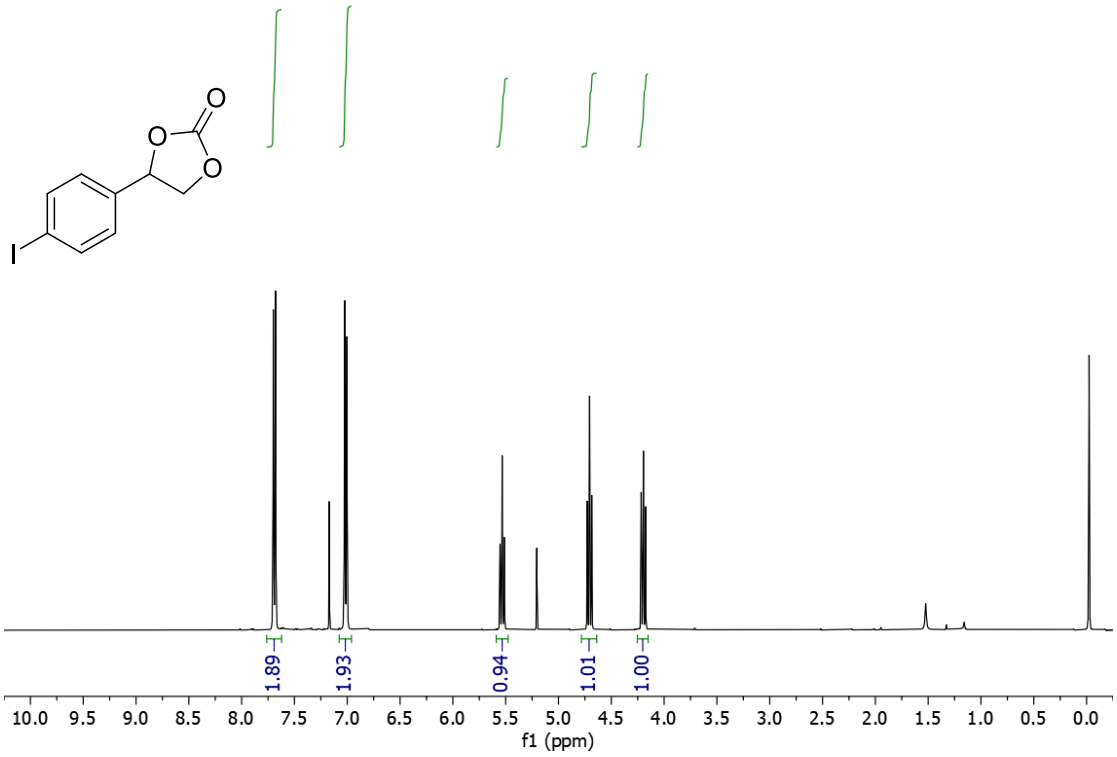
2h ^{1}H NMR (400 MHz, $CDCl_3$)



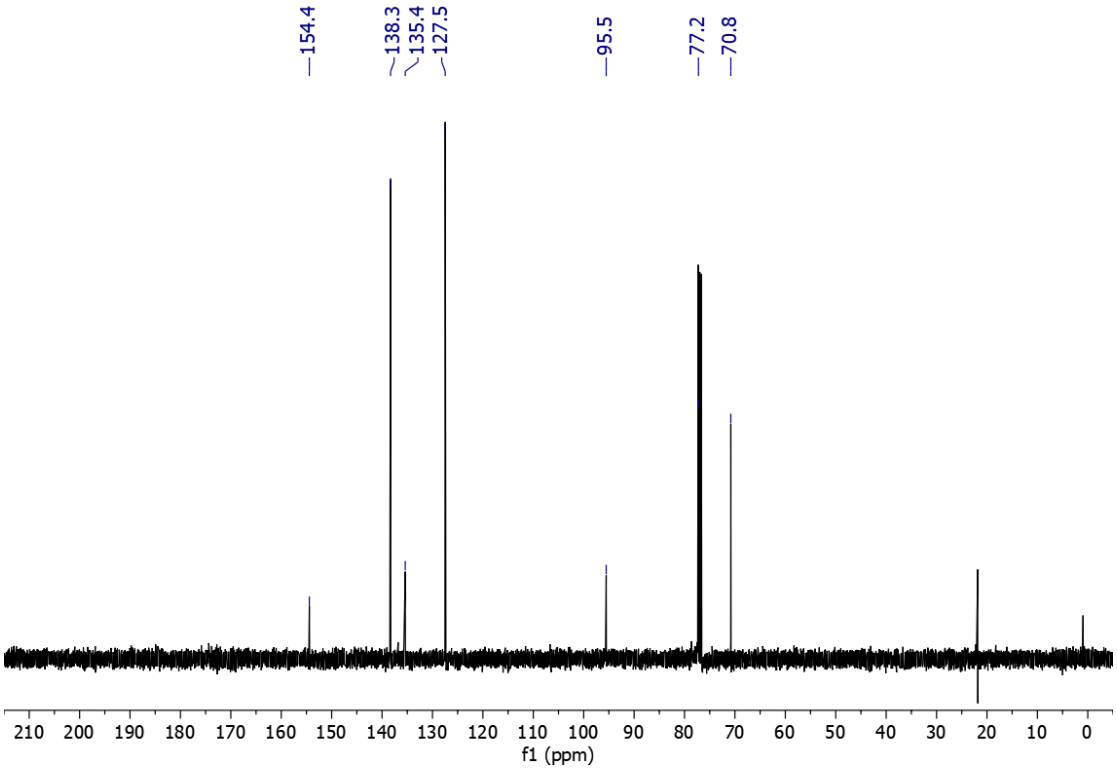
2h ^{13}C NMR (100 MHz, $CDCl_3$)



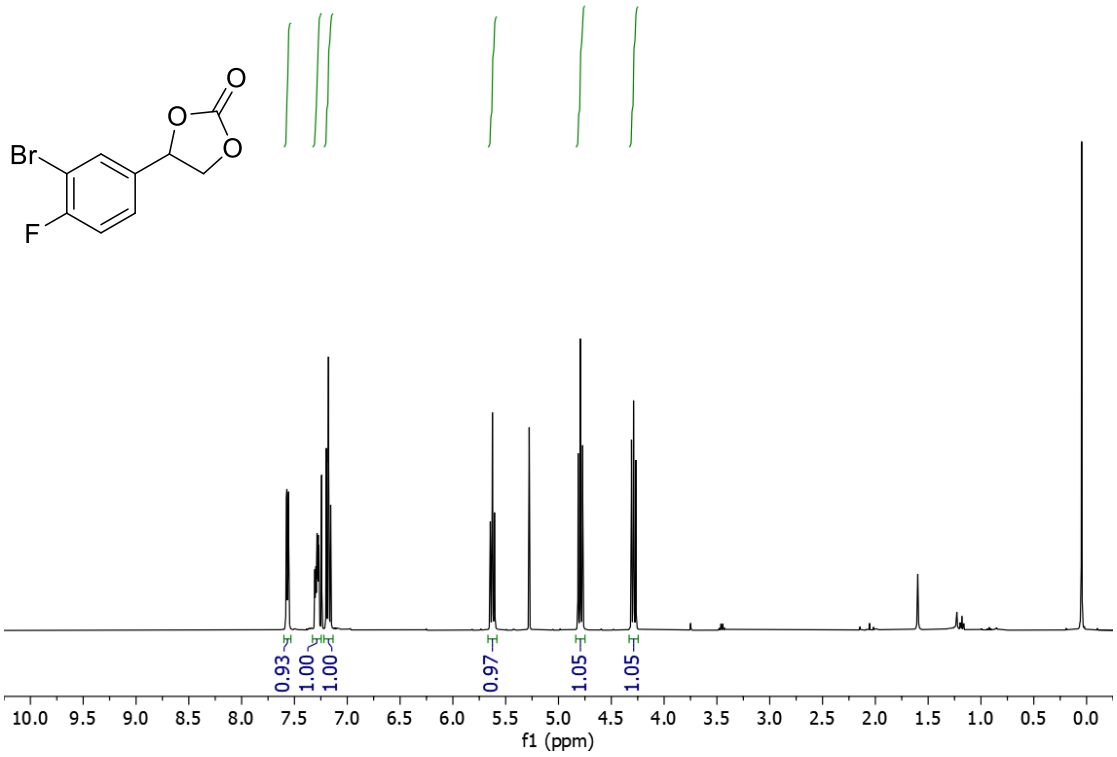
2i ^{1}H NMR (400 MHz, $CDCl_3$)



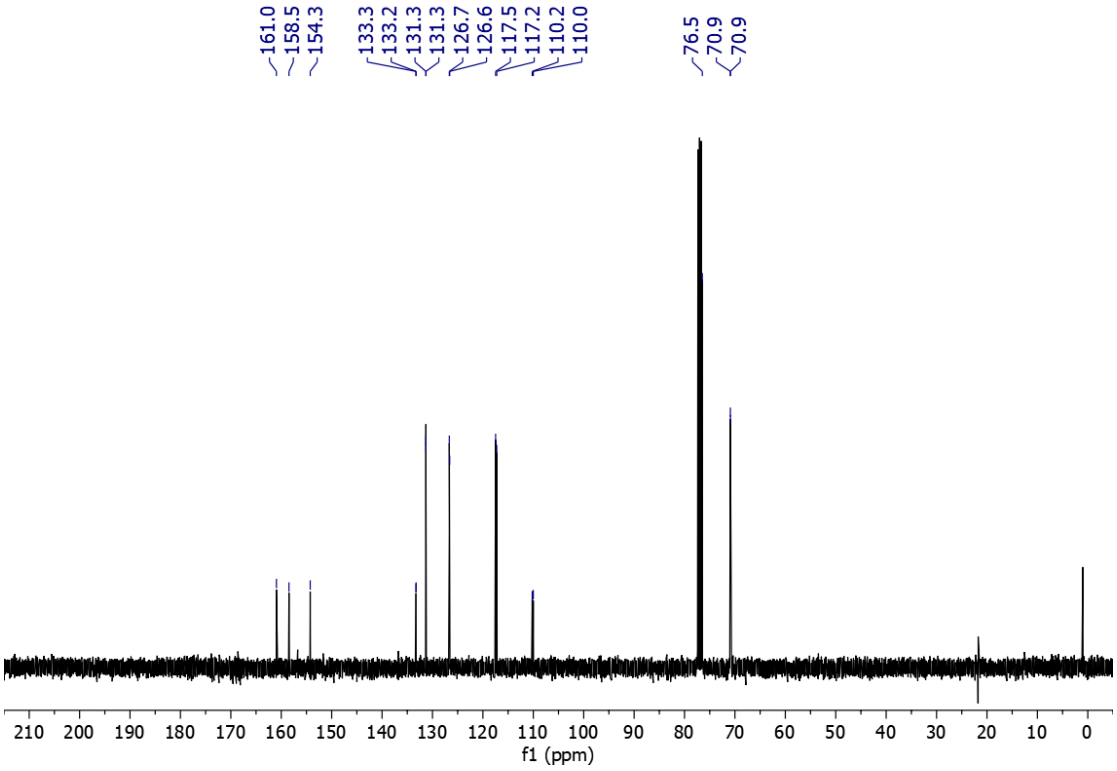
2i ^{13}C NMR (100 MHz, $CDCl_3$)



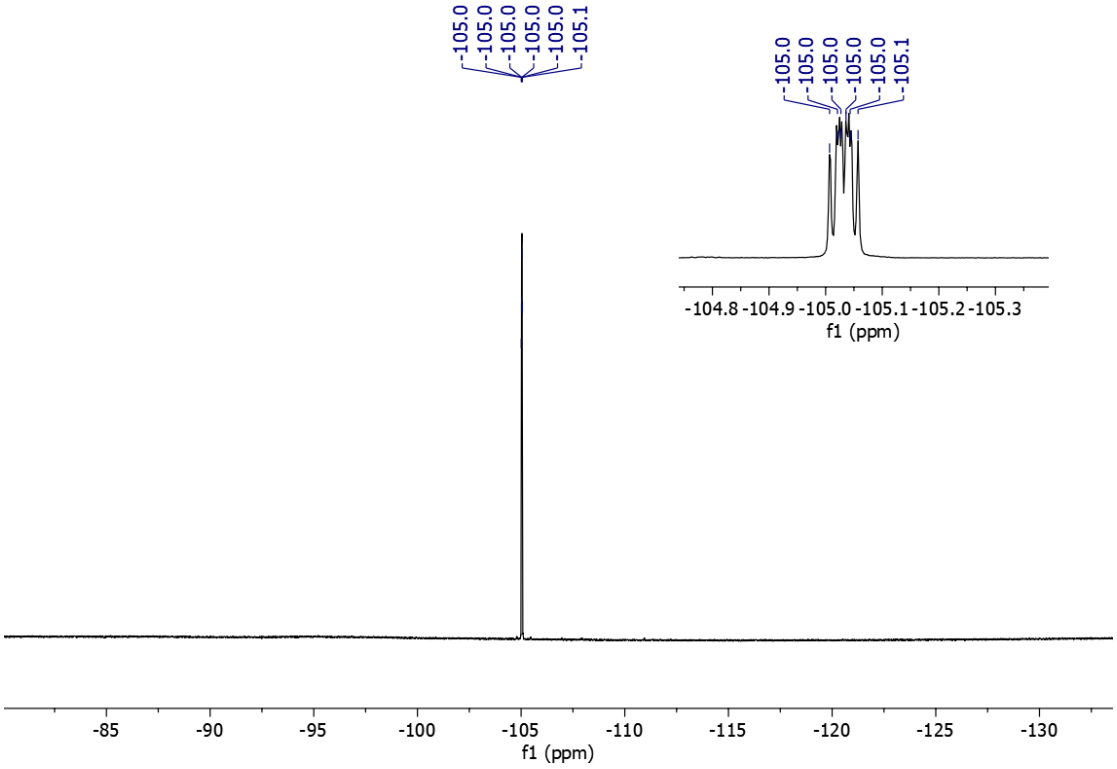
2j ^{1}H NMR (400 MHz, $CDCl_3$)



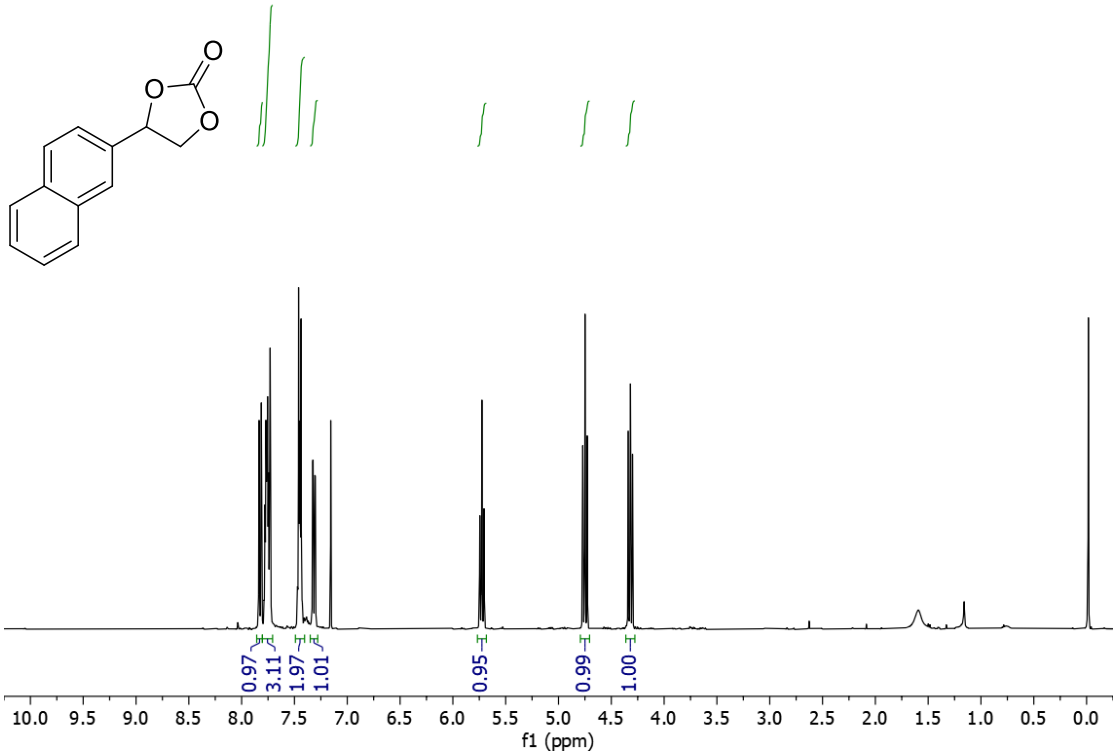
2j ^{13}C NMR (100 MHz, $CDCl_3$)



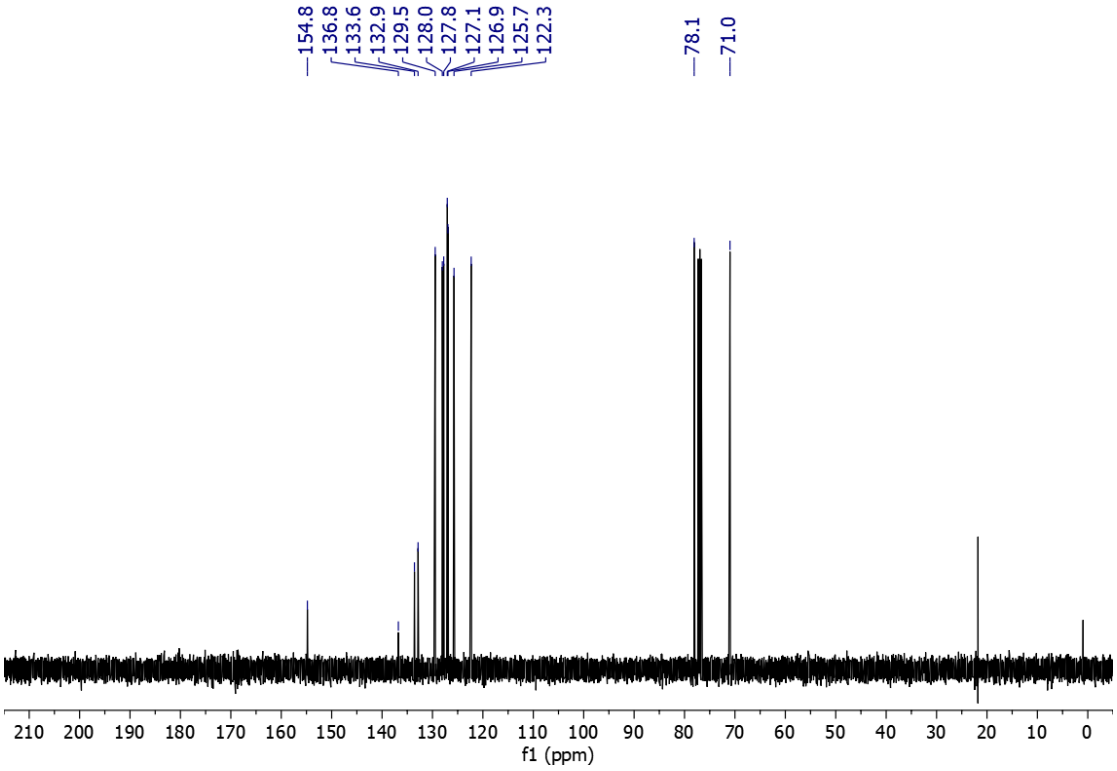
2j ^{19}F NMR (377 MHz, $CDCl_3$)



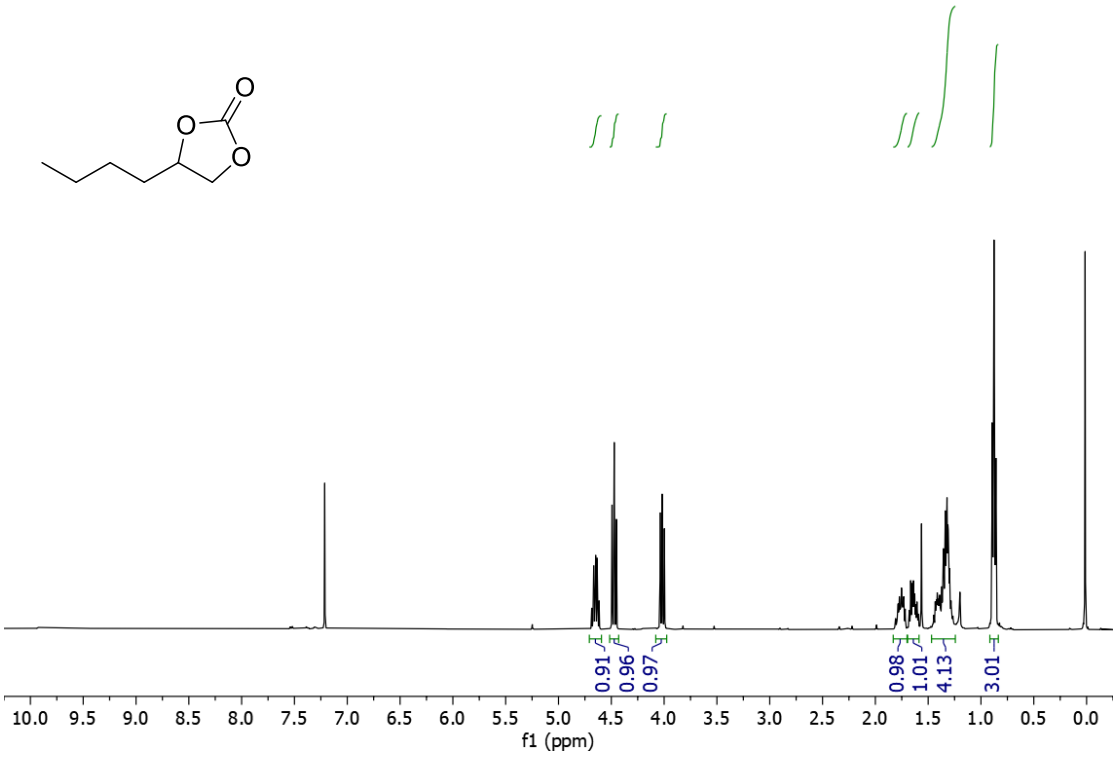
2k ^{1}H NMR (400 MHz, $CDCl_3$)



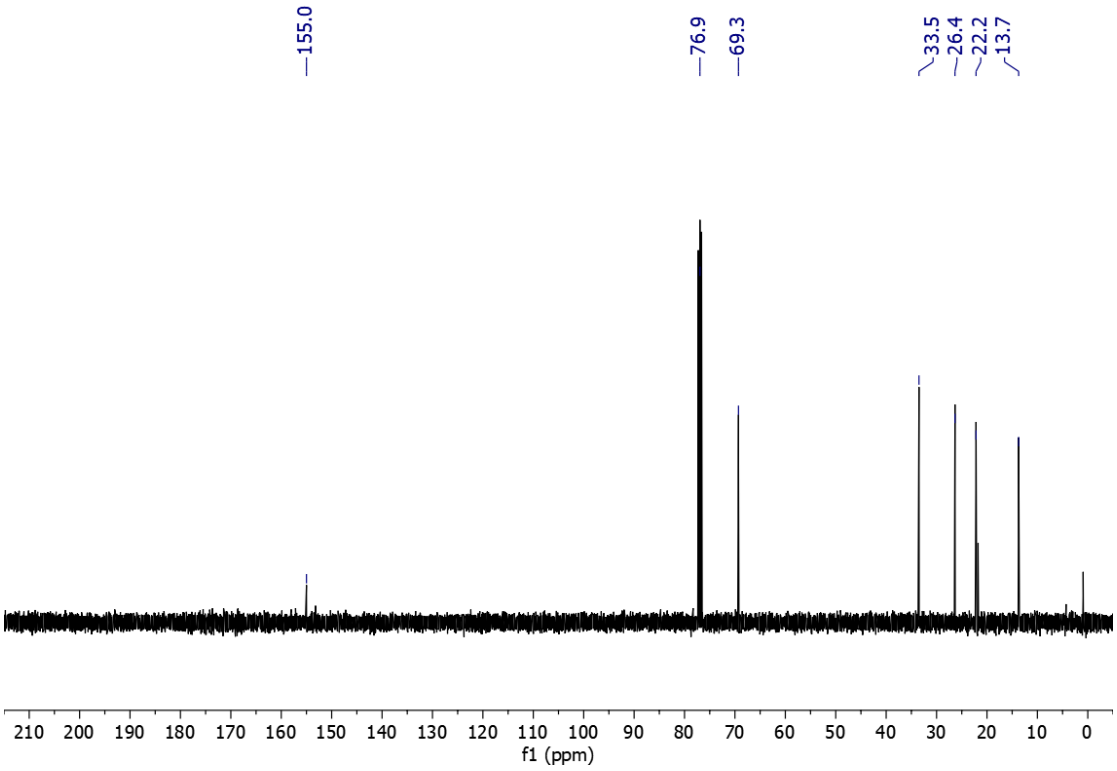
2k ^{13}C NMR (100 MHz, $CDCl_3$)



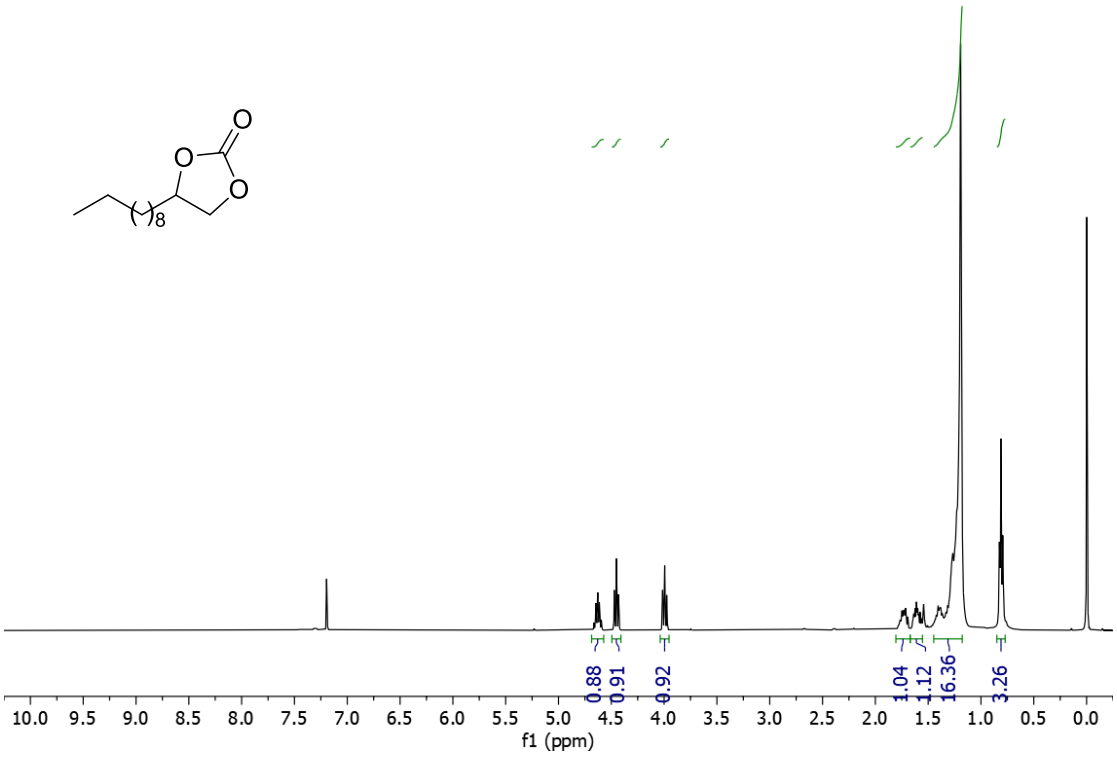
2l ^{1}H NMR (400 MHz, $CDCl_3$)



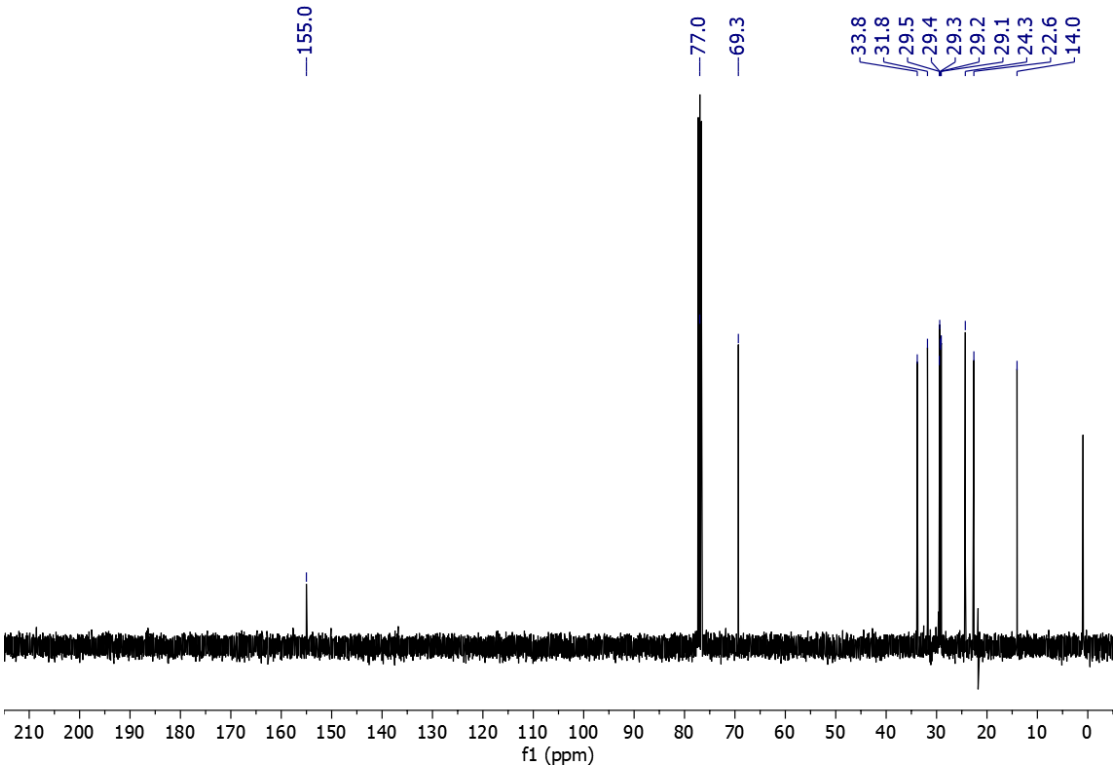
2l ^{13}C NMR (100 MHz, $CDCl_3$)



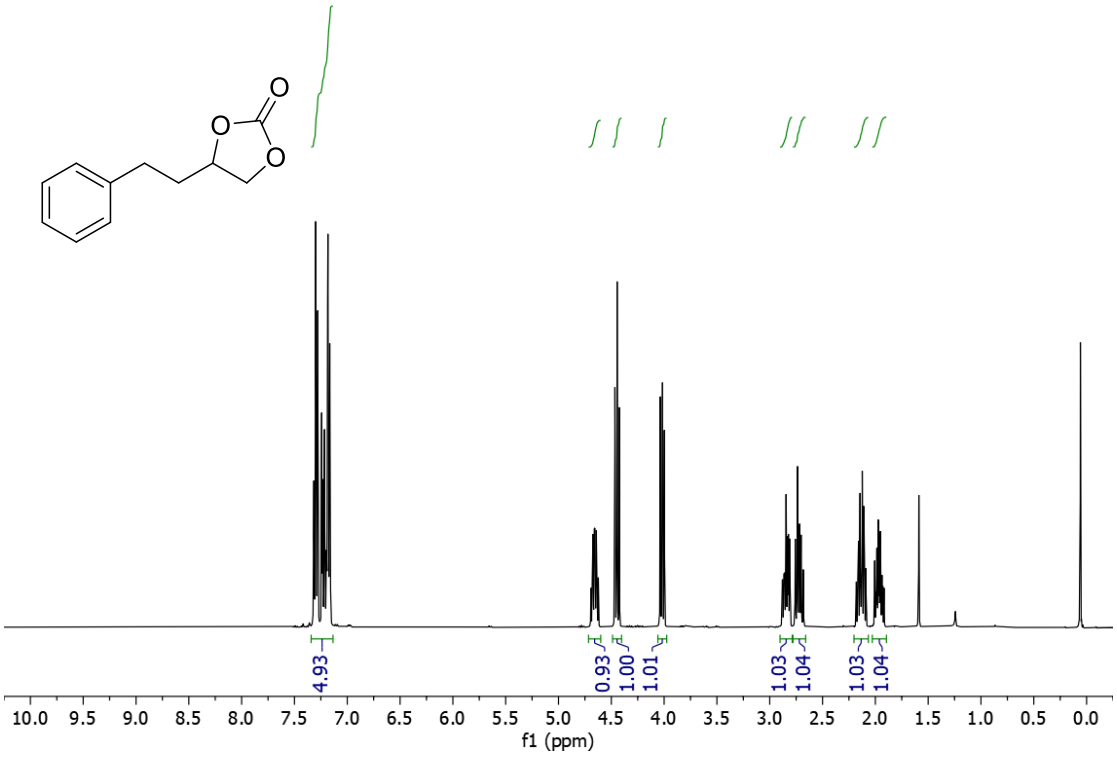
2m ^{1}H NMR (400 MHz, $CDCl_3$)



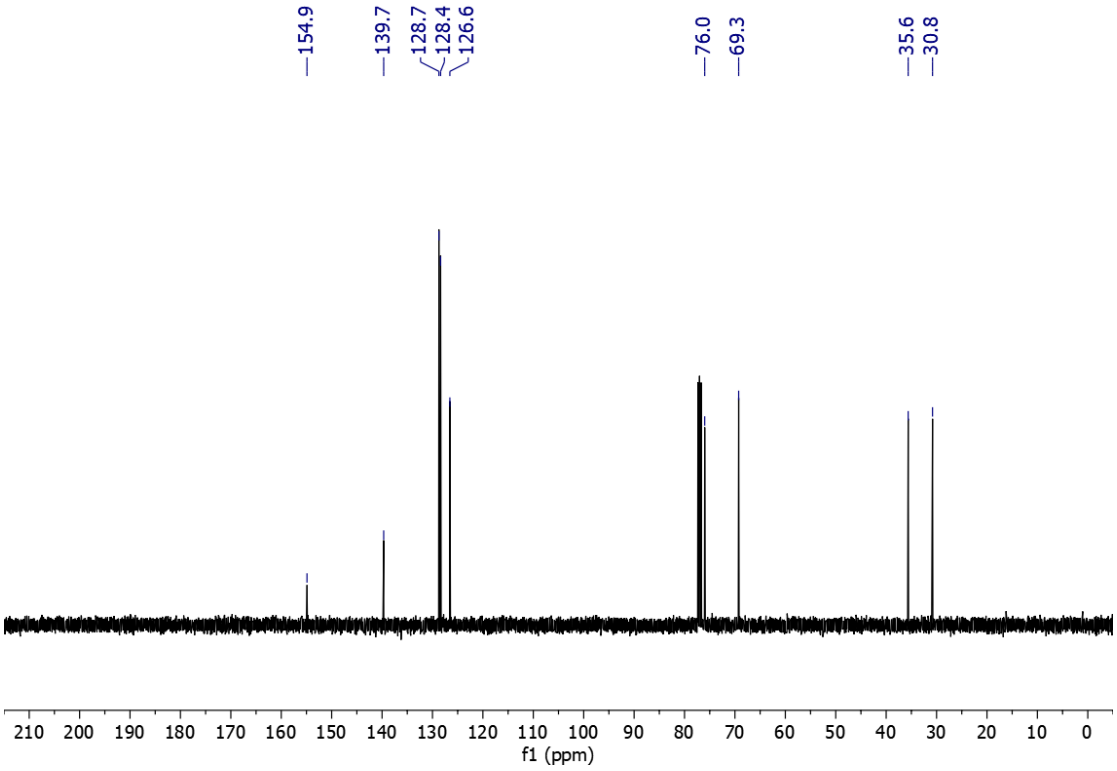
2m ^{13}C NMR (100 MHz, $CDCl_3$)



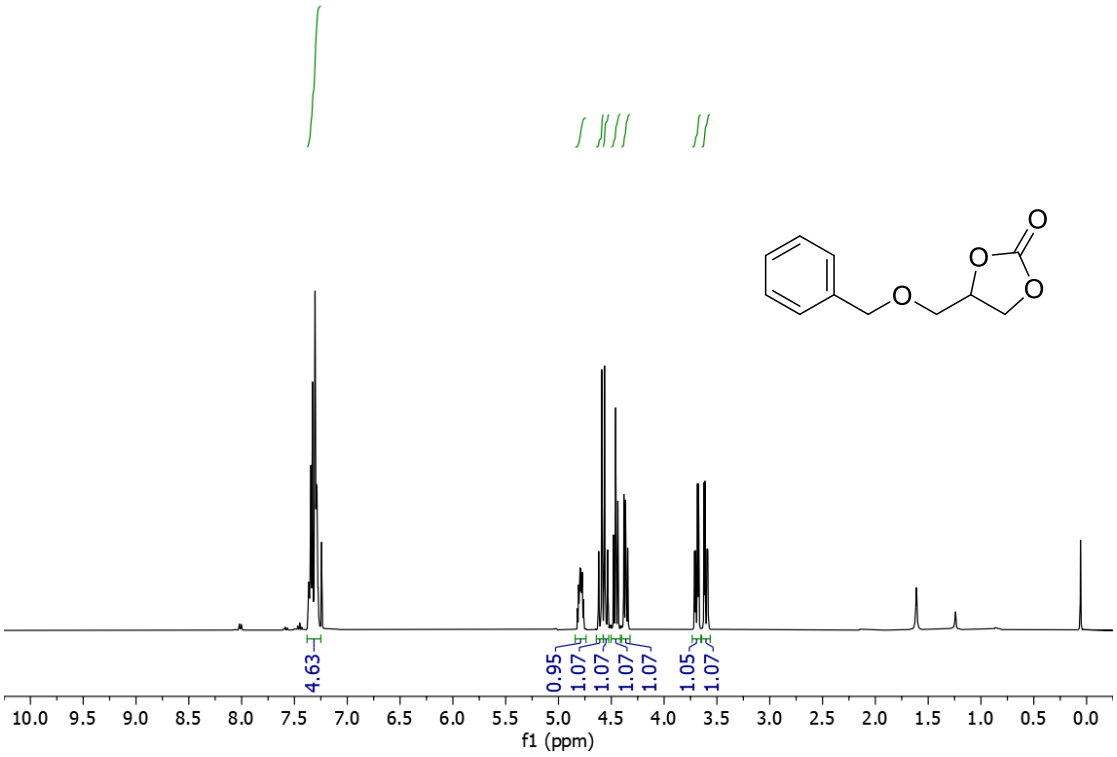
2n ^{1}H NMR (400 MHz, $CDCl_3$)



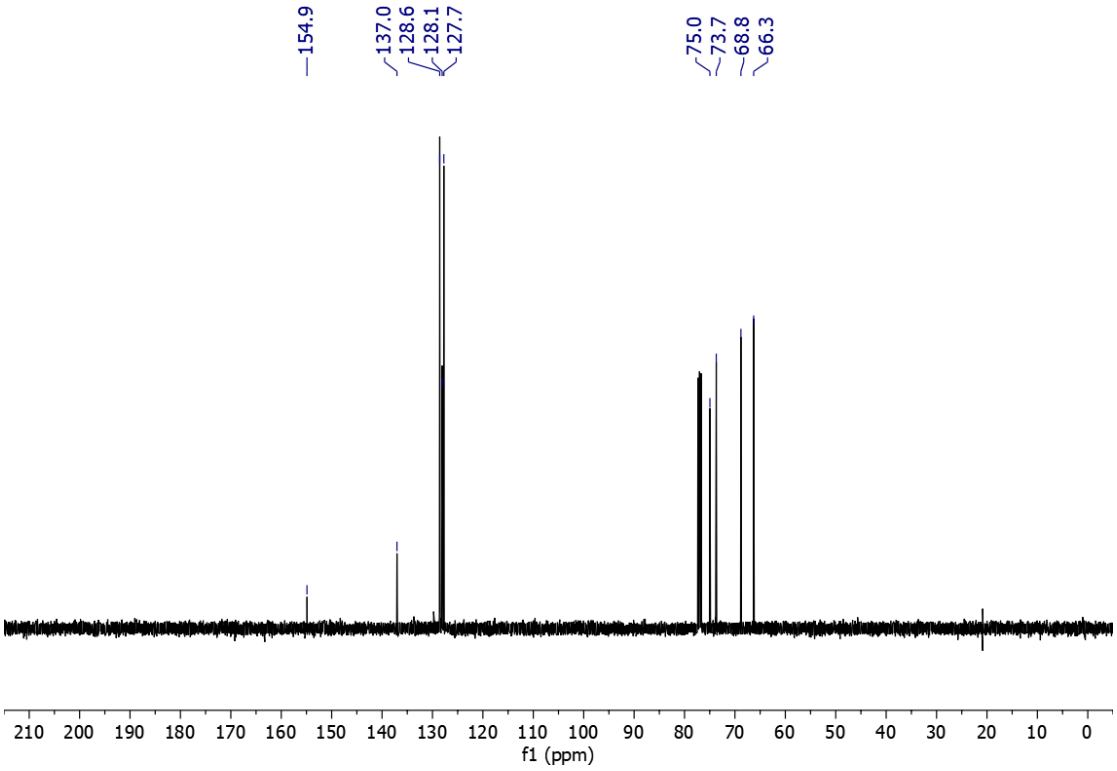
2n ^{13}C NMR (100 MHz, $CDCl_3$)



2o ^{1}H NMR (400 MHz, $CDCl_3$)

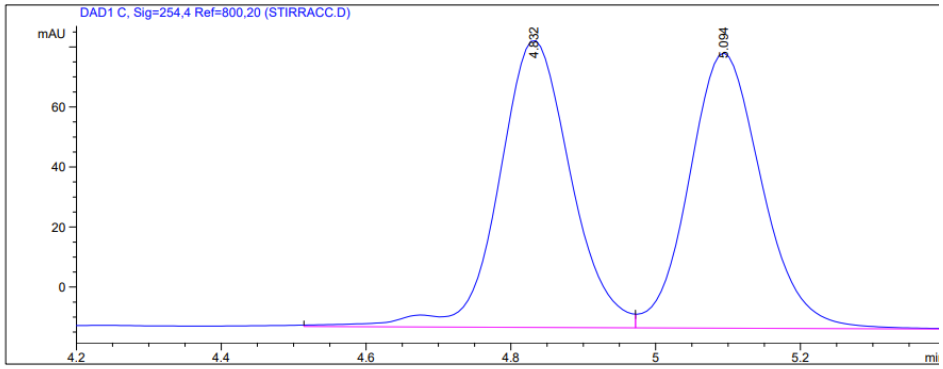


2o ^{13}C NMR (100 MHz, $CDCl_3$)



Chiral HPLC traces

Racemic 2a

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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


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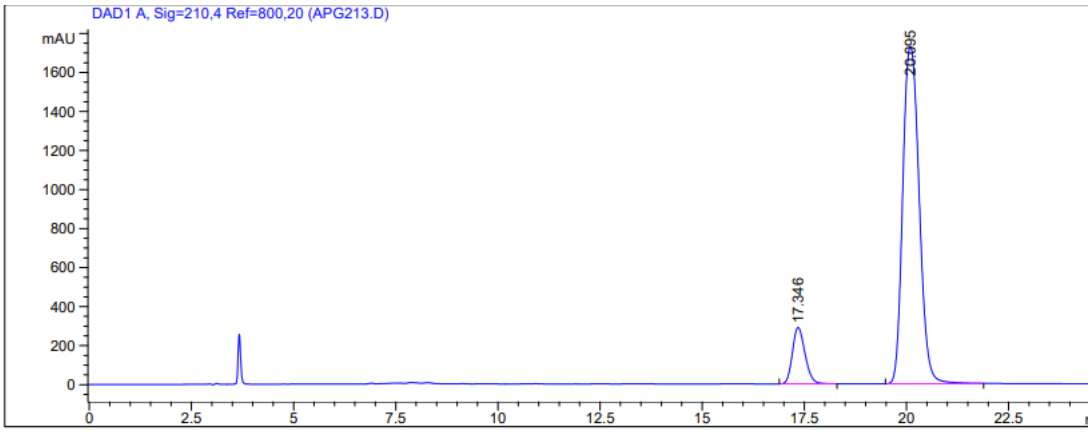
Enantioenriched 2a, Scheme 4 i)

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Use Multiplier & Dilution Factor with ISTDs


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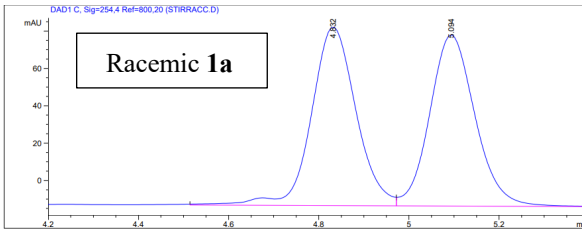


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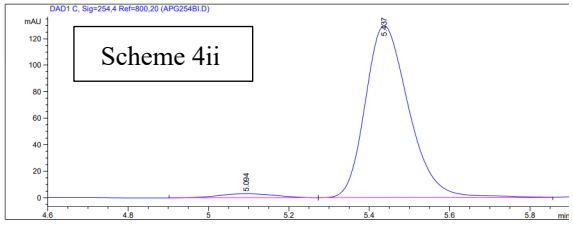
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=254,4 Ref=800,20

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.832 BV    0.1063  658.80634   95.66039  50.7593
   2   5.094 VB    0.1073  639.09595   91.69160  49.2407

Totals :                   1297.90228  187.35199
```



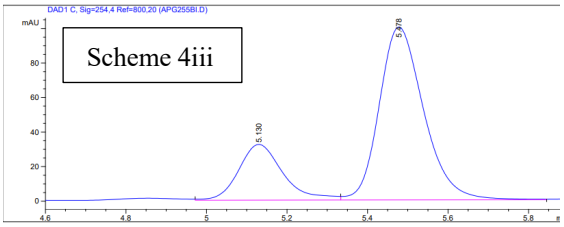

```
================================================================================
                            Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=254,4 Ref=800,20

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.094 PV    0.1541   30.20074   3.08923   3.0056
   2   5.437 VV    0.1154  974.61938  130.12402  96.9944

Totals :                   1004.82012  133.21325
```



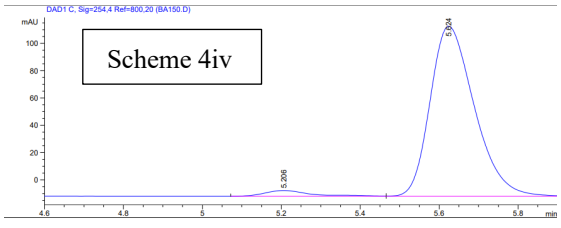

```
================================================================================
                            Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=254,4 Ref=800,20

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.130 VV    0.1172  246.81845   32.29513  24.3188
   2   5.478 VB    0.1194  768.10828  100.24619  75.6812

Totals :                   1014.92673  132.54131
```




```
================================================================================
                            Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=254,4 Ref=800,20

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.206 BV    0.1234   35.79642   4.28899   3.5488
   2   5.624 VV    0.1189  972.88727  124.83141  96.4512

Totals :                   1008.68369  129.12040
```

Small inconsistencies in the retention time of **1a** are due to the preparation of the HPLC sample in the case of reactions exemplified in Scheme 4, where traces of DMF are present.

References

[1] S. Song, X. Huang, Y.-F. Liang, C. Tang, X. Li, N. Jiao, *Green Chem.* **2017**, *17*, 2727-2731.

[2] M. R. Monaco, D. Fazzi, N. Tsuji, M. Leutzsch, S. Liao, W. Thiel, B. List, *J. Am. Chem. Soc.* **2016**, *138*, 14740-14749.

[3] A. Guy, J. Doussot, C. Ferroud, R. Garreau, A. Godefroy-Falguieres, *Synthesis* **1992**, *9*, 821-822.

[4] H. Jin, Z.-y. Li, X.-W. Dong, *Org. Biomol. Chem.* **2004**, *2*, 408-414.

[5] S. Li, Y. Shi, P. Li, J. Xu, *J. Org. Chem.* **2019**, *84*, 4443-4450.

[6] T. Yamazaki, M. Iida, T. Kawaski-Takasuka, T. Agou, *J. Fluor. Chem.* **2022**, *257-258*, 109971.

[7] M. Muehlbacher, C. D. Poulter, *J. Org. Chem.* **1988**, *53*, 1026-1030.

[8] A. Kovtun, D. Jones, S. Dell'Elce, E. Tresso, A. Liscio, V. Palermo, *Carbon*, **2019**, *143*, 268-275.

[9] J. A. Castro-Osma, K. J. Lamb, M. North *ACS Catal*. **2016**, *6*, 5012-5025.

[10] F. Zhou, S.-L. Xie, X.-T. Gao, R. Zhang, C.-H. Wang, G.-Q. Yin, J. Zhou, *Green Chem.* **2017**, *19*, 3908-3915.

[11] D. Zhao, X.-H. Liu, Z.-Z. Shi, C.-D. Zhu, Y. Zhao, P. Wang, W.-Y. Sun, *Dalton Trans.* **2016**, *45*, 14184-14190.

[12] L. Martìnez-Rodrìguez, J. Otalora Garmilla, A. W. Kleij, *ChemSusChem* **2016**, *9*, 749-755.

[13] X. Yiang, J. Wu, X. Mao, T. F. Jamison, T. A. Hatton, *Chem. Commun.* **2014**, *50*, 3245-3248.

[14] R. D. Aher, B. S. Kumar, A. Sudalai, *Synlett* **2014**, *25*, 97-101.