Supporting Information

Auto-Relay Catalysis for the Oxidative Carboxylation of Alkenes into Cyclic Carbonates by a MOF Catalyst

Ha Phan,[a] Pol de la Cruz-Sánchez,[a] María Jesús Cabrera-Afonso,[a,b] Belén Martín-Matute[a*]

[a] *Department of Organic Chemistry, Stockholm University, 106 91 Stockholm, Sweden.*

[b] *Organic Chemistry Department, Universidad Autónoma de Madrid (UAM), Avda. Francisco Tomás y Valiente 7, Cantoblanco 28049, Madrid (Spain).*

[*]To whom correspondence should be addressed.

E-mail: belen.martin.matute@su.se

Number of pages: 108

Number of figures: 136

Number of tables: 10

Number of schemes: 3

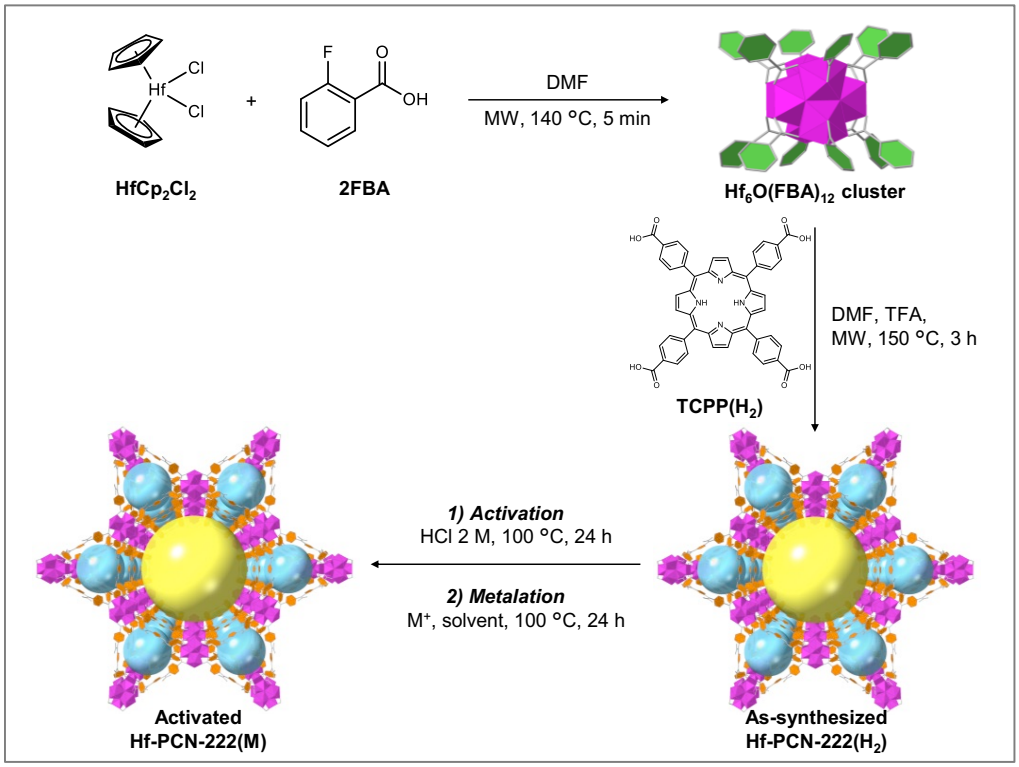
TABLE OF CONTENT

1. General Considerations

General. The CO_2 cycloaddition reactions and the tandem reactions were performed using point-tipped vials, 5 – 10 mL, Biotage®, 20mm flange top, cs/100, capped with a rubber septum. NMR spectra (^1H, ^{13}C, ^{19}F) were acquired on a Bruker Avance 400 MHz spectrometer. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$, δ_H = 7.26 ppm, δ_C = 77.16 ppm; or CD_3OD, δ_H = 3.31 ppm, δ_C = 49.00 ppm). ^{13}C NMR and ^{19}F spectra were acquired on a broad band decoupled mode. The following abbreviations are used to describe peak patterns when appropriate: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), br (broad). Reactions were monitored by ^1H NMR, and/or TLC on silica gel plates (60 Å porosity, 250 μm thickness). Analytical thin layer chromatography (TLC) was performed using pre-coated aluminum-backed plates (Merck Kieselgel 60 F_{254}) and visualized using potassium permanganate stain, and/or UV light with wavelength of 254 nm. Flash column chromatography was performed using silica gel Merck-60 from Aldrich. Elemental analysis was performed by duplicate on a Carlo Erba Flash 1112 elemental analyzer and the metal content was determined by inductively coupled plasma-optical emission spectrometry (ICP–OES) on a Varian Vista MPX ICP–OES at Medac Ltd, Chobham, UK. High Resolution Mass Spectrometry (HRMS) analyses were conducted on Bruker MicrOTOF using electrospray ionization (ESI). The utilized software calibrates the instruments and reports measurements by use of neutral atomic masses. UV-Vis studies and fluorescence measurements were measured in a 1 cm plastic cuvette using a Agilent Cary 5000 UV-Vis-NIR Spectrophotometer. SEM images were acquired using a JEOL-7401F, JEOL-7000F and JEOL-IT800 field-emission scanning electron microscope at 0.5 kV, 5.0 kV, and 15 kV. The samples were loaded on carbon ink or on a TEM grid by drop-casting using EtOH solvent prior to SEM analysis. Thermalgravimetric analysis (TGA) was performed under a nitrogen flow with the temperature range between 25 °C and 600 °C and heating rate of 4 °C.min^{-1} using TA Instruments Discovery thermogravimetric analyzer in an aluminum cup loaded with approx. 7 mg of samples. Nitrogen adsorption analysis data were obtained at 77 K on a Micromeritics ASAP2020 analyzer with the pressure range p/p^0 = 0.001–0.98. Carbon dioxide adsorption analysis data were obtained at 273 K and 298 K on a Micromeritics ASAP2020 analyzer with the absolute pressure range of 2 – 780 mmHg. The gas adsorption analysis samples were degassed at 150 °C for 10 h under 10 μmHg vacuum prior to analysis. Attenuated Total Reflectance – Fourier Transform Infrared (ATR-FTIR) measurements were performed in a Varian 610 IR FT-IR spectrometer equipped with a Specac Golden Gate single reflaction attenuated total reflection (ATR). Powder X-ray Diffraction (PXRD) data of the MOF samples were acquired using a Panalytical X'pert Pro diffractometer (Cu $K\alpha_{1,2}$, λ_1 = 1.5406 Å, λ_2 = 1.5444 Å). Centrifugation was performed in a Centurion Scientific K3 series centrifuge. Microwave reactions were performed in an Initiator Classic microwave reactor from Biotage®.

Chemicals. Deuterated NMR solvents, all the reagents (diacetoxyiodo)benzene, TBAB, 5,10,15,20-(tetra-4-carboxyphenyl)porphyrin, 2-fluorobenzoic acid, hafnocene dichloride, trifluoroacetic acid, manganese(II) chloride cobalt(II) chloride, the corresponding alkenes, epoxides or aldehydes, and solvents (DMF, THF, EtOH and MeCN) were purchased and used as received. Iodosobenzene (PhIO)[1], alkenes **1r**,[2] **1aj**,[3] **1ak**,[4] **1al**[4] and epoxide **2l**[5] were synthesized from the corresponding commercially available compounds, according to the literature.

2. Synthesis of Hf-PCN-222 MOF series



Scheme S1. Synthesis of Hf-PCN-222(H_2) and Hf-PCN-222(M).

2.1. Synthesis of Hf-PCN-222(H_2)

To a 20-mL Biotage® microwave reaction vial, $HfCp_2Cl_2$ (137 mg, 0.36 mmol), 2-fluorobenzoic acid (2FBA, 760 mg, 5.42 mmol) and DMF (5 mL) were added. The reagents were dissolved in an ultrasonic bath before irradiated in a microwave oven at 140 °C for 5 min. After reaction, 12-connected Hf_6-oxo clusters by 2FBA were formed and used directly for the next step without isolation. To another flask, tetrakis(4-carboxyphenyl)porphyrin (H_2TCPP, 56 mg, 0.07 mmol) had been pre-dissolved in hot DMF (5 mL) before the solution was transferred to the vial containing Hf_6-oxo clusters. The above-mentioned vial was further charged trifluoroacetic acid (280 μL) and sealed before irradiated at 175 °C for 3 h (Scheme S1). After reaction, the purple crystals were harvested by centrifugation (10000 rpm, 10 min) and washed with DMF (30 mL × 3 times) and EtOH (30 mL × 3 times). Afterwards, the solid was transferred to a scintillation vial and dried at 100 °C overnight. One synthesis batch yields ca. 84 mg of the as-synthesized Hf-PCN-222(H_2) which corresponds to 81% reaction yield.

2.2. Activation of Hf-PCN-222(H_2)

Hf-PCN-222(H_2) activation optimization was done at 100 °C for 24 h with different HCl:DMF concentration. To a 50-mL round-bottom flask was added 60 mg as-synthesized Hf-PCN-222(H_2) and HCl:DMF solution (20 mL, 0.5 – 8.0 M). The solid quickly turned green due to the protonation of porphyrin linkers. The mixture was then heated up at 100 °C for 24 h. Afterwards, the solid was collected by centrifugation and washed with DMF (30 mL × 3 times), then EtOH (30 mL × 3 times), followed by drying at 100 °C overnight. The resulting solid has a bright purple color.

The crystallinity of the MOF treated with HCl:DMF solution up to 4 M was reserved. At 8.0 M HCl in DMF, the original structure was destroyed (Figure S1A). Samples treated with HCl:DMF solutions showed an increase in surface area (Figure S1B–C). The two characteristic pore sizes remain unchanged (Figure S1D).

PCN-222(H_2) activation with HCl 2.0 M in DMF was selected for the next step (Scheme S1).

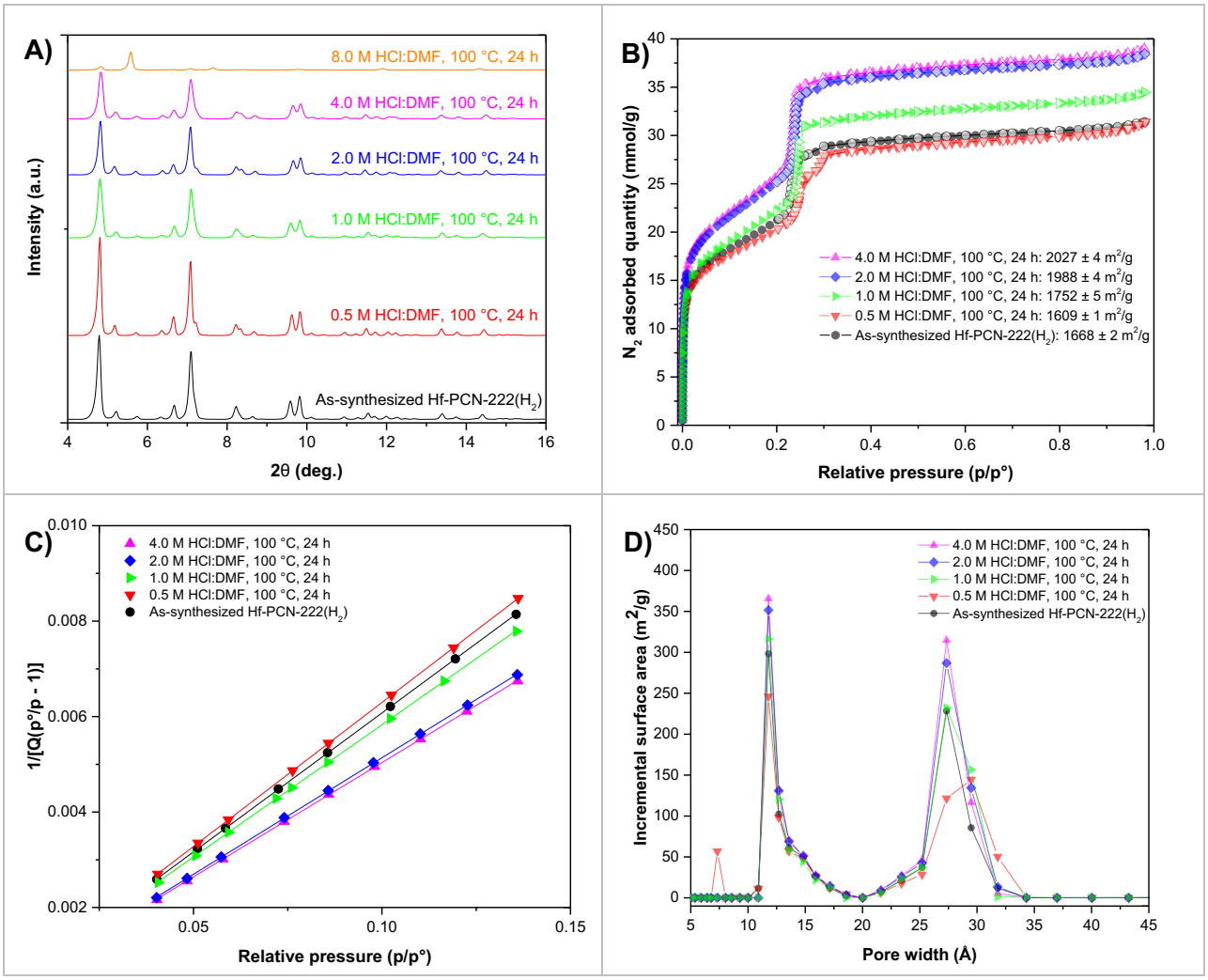


Figure S1. Characterizations of PCN-222(H_2) samples treated with HCl:DMF solution at different concentrations. A) PXRD patterns. B) N_2 adsorption–desorption isotherms at 77 K. C) Plot of the linear region of the adsorption N_2 isotherm used for the BET equation. D) Pore size distribution.

2.3. Synthesis of Hf-PCN-222(Mn) and Hf-PCN-222(Co)

Hf-PCN-222(Mn) was prepared by post-synthetic metalation of activated Hf-PCN-222(H_2) (Scheme S1). Anhydrous $MnCl_2$ (63 mg, 0.5 mmol) was dissolved in D.I. water (10 mL) in a 20-mL Pyrex^{TM} pressure tube. Then activated Hf-PCN-222(H_2) (73 mg, 0.05 mmol based on porphyrin linker) was added to the solution. The tube was then sealed with an O-ring PTFE screw cap and the post-synthesis metalation was carried out at 100 °C for 24 h. After reaction, the metalated MOF was collected by centrifugation and washed with H_2O (30 mL × 3 times) then EtOH (30 mL × 3 times) before being dried at 100 °C overnight. The resulting solid has a green color. Likewise, Hf-PCN-222(Co) was prepared using anhydrous $CoCl_2$ (65 mg, 0.5 mmol) instead of $MnCl_2$ (Scheme S1). The resulting solid has a brown color. Metalation efficiency was confirmed by FT-IR, UV-Vis, SEM–EDS, and ICP–OES.

2.4. Comparison of synthetic methods for the preparation of Hf-PCN-222(M) structures

Table S1. Comparison of non-green chemicals used for similar Hf/PCN-222 MOFs.

	mmol of Hf-precursor	mmol of Metal precursor	Total hazardous solvent used	mL DMF /mmol of Hf	Total non-hazardous solvent used	Total acid used	Yield	Reference
1	0.3	0.056	523 mL of DMF[a]	1743 ml/mmol	315 mL[b]	2.7 g BA	49%	J. Am. Chem. Soc. 2015, 137, 42, 13624–13631.[6]
2	0.031	0.06	103 mL of DMF and unspecified DMF amount for the washing.[c]	3322 ml/mmol	Unspecified	0.15 mL TFA	95%	Chem. Sci., 2019, 10, 10577–10585.[7]
3	0.36	0.5	217 mL of DMF [c]	602 mL/mmol	280 mL[d,e]	769 mg 2FBA, 0.3mL TFA 3 mL HCl	77%	This study.

[a]8 mL of DEF and 515 ml DMF. [b]Acetone. [c]DMF. [d]EtOH. [e]Water. BA = Benzoic acid; TFA = trifluoroacetic acid. 2FBA: 2-Fluorobenzoic acid.

3. Characterization of Hf-PCN-222 MOF series

3.1. Thermogravimetric analysis

Thermalgravimetric analysis of Hf-PCN-222(H_2), Hf-PCN-222(Co), and Hf-PCN-222(Mn) showed the thermal stability of the MOFs up to 450 °C (Figure S2).

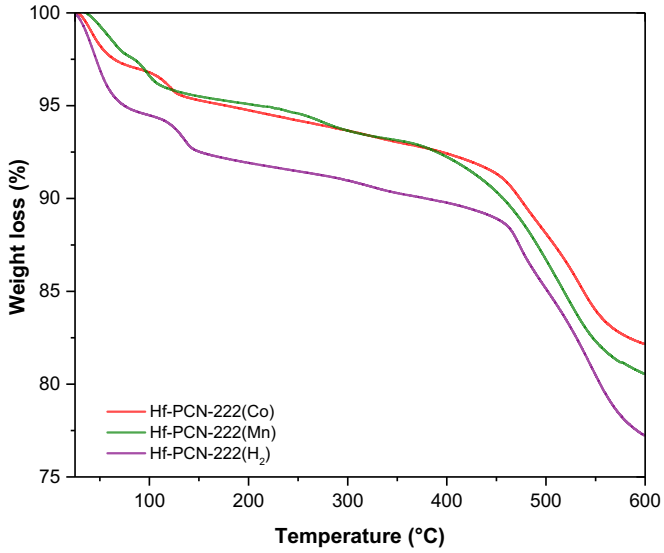


Figure S2. Thermogravimetric analysis of Hf-PCN-222(H_2), Hf-PCN-222(Mn) and Hf-PCN-222(Co).

3.2. Powder X-ray diffraction

PXRD patterns of Hf-PCN-222(H_2), Hf-PCN-222(Mn) and Hf-PCN-222(Co) matches with the simulated patterns confirming the success of the microwave-assisted Hf-PCN-222 synthesis and metalation of the linker doesn't affect the structure (Figure S3).

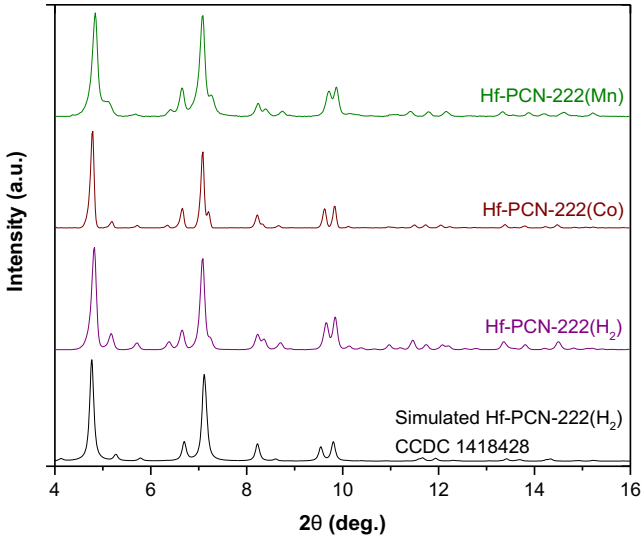


Figure S3. PXRD patterns of Hf-PCN-222(H_2), Hf-PCN-222(Mn) and Hf-PCN-222(Co).

3.3. Gas adsorption analysis and porosity analysis

Hf-PCN-222(H_2), Hf-PCN-222(Mn) and Hf-PCN-222(Co) possesses type IV isotherm. Surface area of Hf-PCN-222(Mn) and Hf-PCN-222(Co) is slightly lower than surface area of Hf-PCN-222(H_2) (Figure S4A–B). All three samples have two characteristic pore sizes of 12 Å and 28 Å (Figure S4C–D).

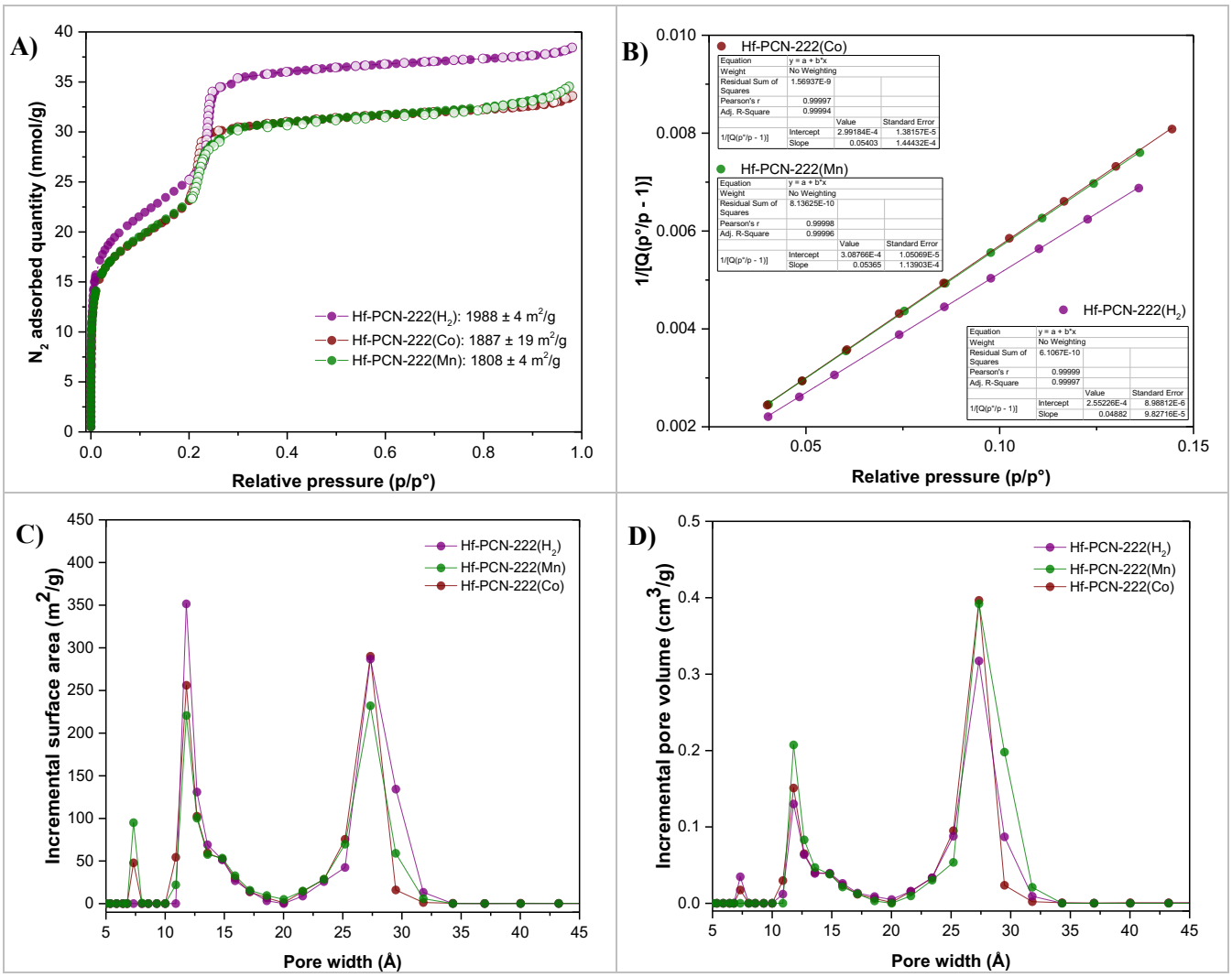


Figure S4. Porosity analysis of Hf-PCN-222(M), M = H_2, Co, Mn. A) N_2 adsorption – desorption isotherms at 77

K. B) Plot of the linear region of the adsorption N_2 isotherm used for the BET equation. C-D) DFT pore size distribution.

Carbon dioxide adsorption analysis was carried out at 273 K and 298 K (Figure S5). The experimental CO_2 adsorbed values are shown in Table S2.

Table S2. Pore volume and CO2 adsorbed value at 1 bar of Hf-PCN-222(M), M = H_2, Co, Mn.

Sample	**Pore volume** ($cm^3.g^{-1}$)	**CO_2 adsorbed value at 1 bar** ($mmol.g^{-1}$)	
		273 K	**298 K**
Hf-PCN-222(H_2)	1.1750	2.9887	1.7594
Hf-PCN-222(Co)	1.0209	2.6965	1.6118
Hf-PCN-222(Mn)	1.0157	2.4719	1.6171

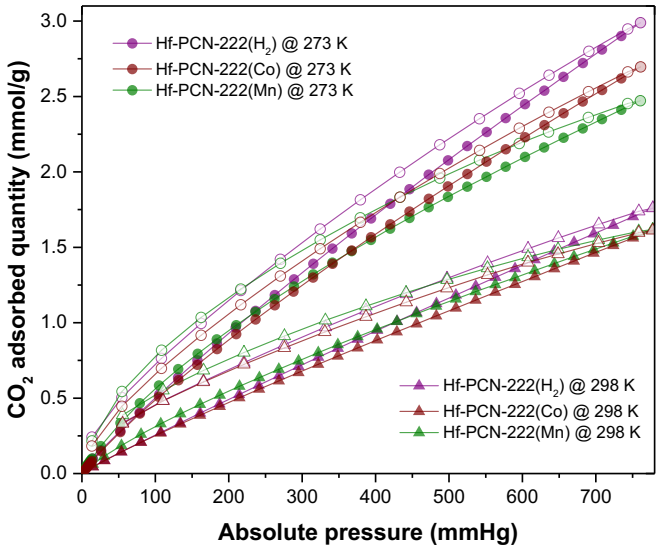


Figure S5. Carbon dioxide adsorption analysis of Hf-PCN-222(H_2), Hf-PCN-222(Mn) and Hf-PCN-222(Co) at 273 K and 298 K.

3.4. Fourier-transform infrared spectroscopy

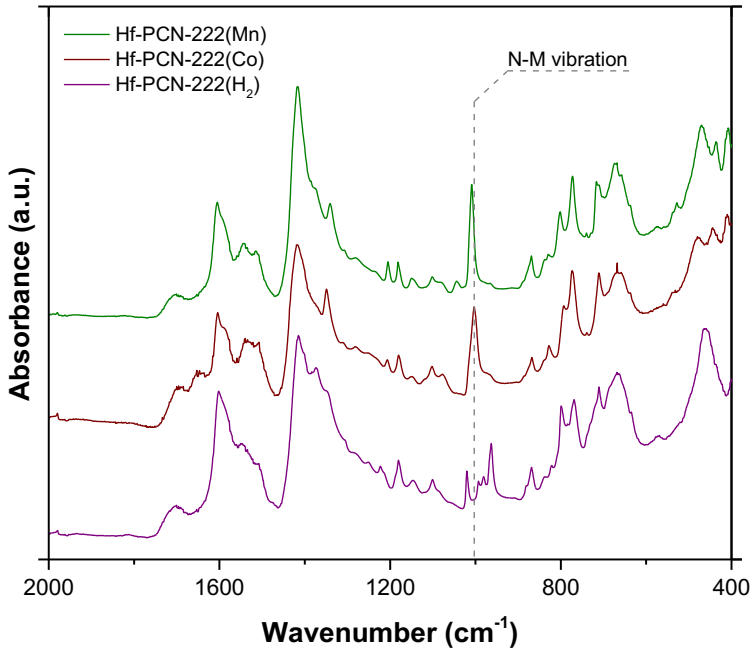


Figure S6. Fourier-transform infrared spectroscopy. N–M vibration indicates the success of metalation.

3.5. Ultraviolet-visible spectroscopy

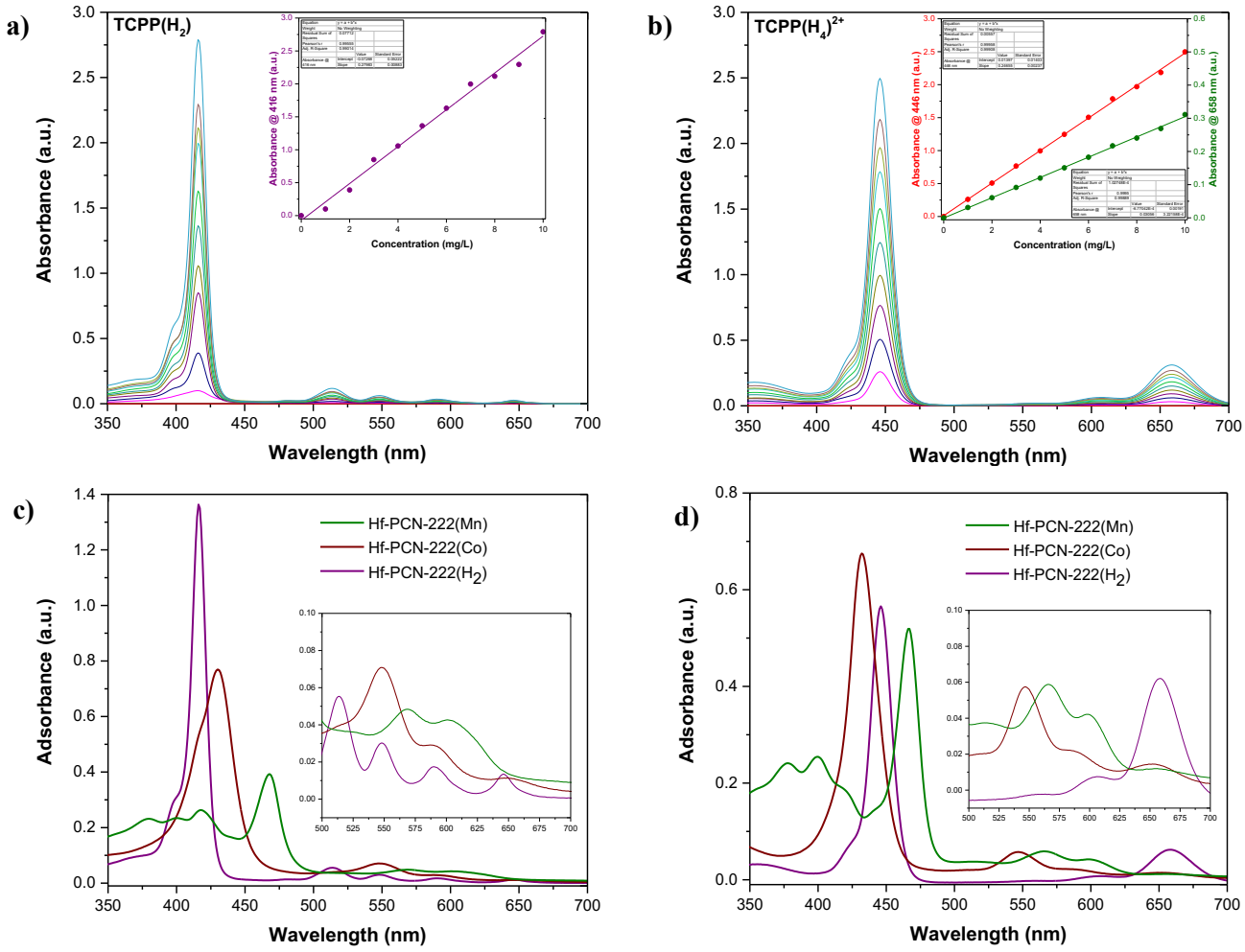


Figure S7. UV-Vis spectra of Hf-PCN-222(H_2), Hf-PCN-222(Mn) and Hf-PCN-222(Co).

3.6. Scanning electron microscopy – energy dispersive X-ray spectroscopy

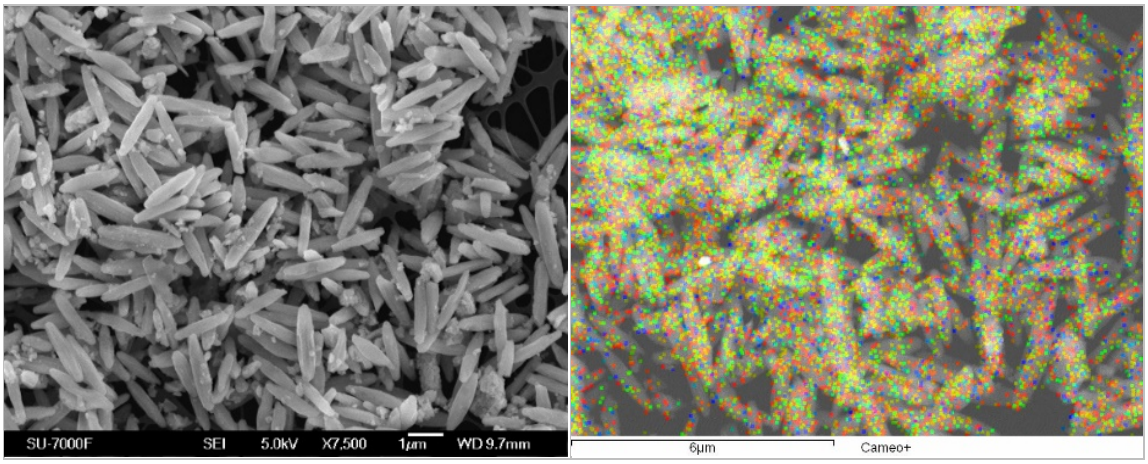
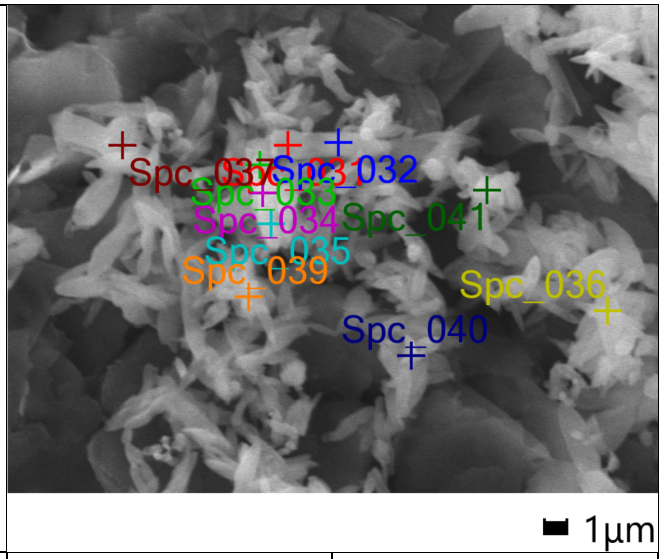


Figure S8. SEM image and overlapped EDS mapping image of Hf-PCN-222(Mn).

SEM–EDS was used to confirm the full metalation efficiency of Hf-PCN-222(Co) (Table S3).

Table S3. EDS results of Hf-PCN-222(Co).

Hf-PCN-222(Co)		
	Co atom%	Hf atom%
Point 1	0.34	1.00
Point 2	0.34	0.97
Point 3	0.35	0.99
Point 4	0.43	1.30
Point 5	0.50	1.22
Point 6	0.65	1.97
Point 7	0.30	0.80
Point 8	0.55	1.61
Point 9	0.36	0.98
Point 10	0.40	1.24
Average Co/Hf	0.3521	
%Metalation	106%	

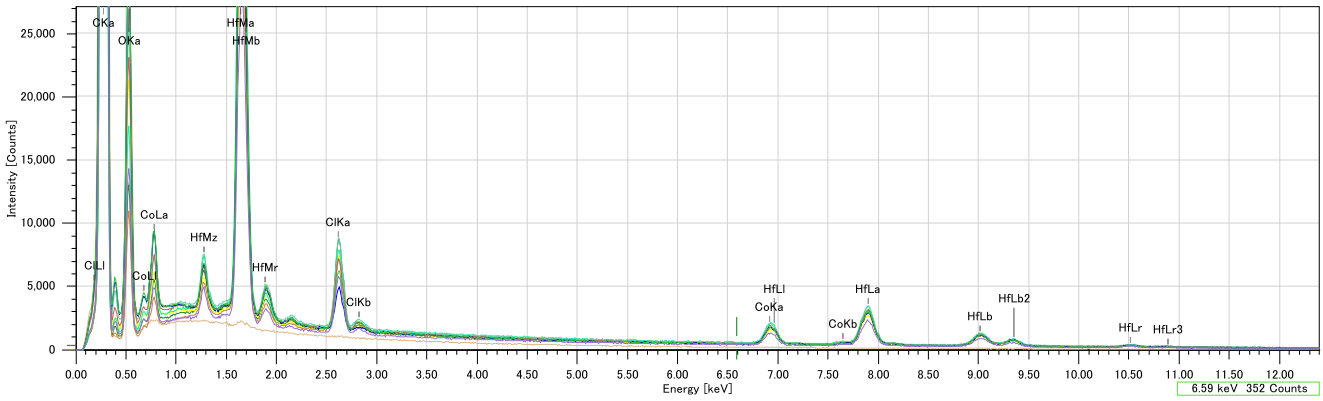


Figure S9. EDS spectra of 10 different points on Hf-PCN-222(Co).

3.7. Inductively coupled plasma optical emission spectroscopy

ICP–OES was used to confirm the metalation efficiency of Hf-PCN-222(Mn) (Table S4). The experimental Mn/Hf = 0.3144 compared to the theoretical (100% metalation) Mn/Hf = 0.3333 indicates the metalation efficiency of 95%.

Table S4. ICP-OES report and metalation efficiency of Hf-PCN-222(Mn).

Element ratio	N	Cl	Hf	Mn	Mn/Hf	Mn/Cl
wt%	3.23	1.57	27.65	2.68	-	-
mol%	0.2302	0.0441	0.1559	0.0487	0.3144	1.1030
Theoretical mol%	0.2584	0.0646	0.1940	0.0646	0.3333	1.0000
%Metalation			**95%**			

3.8. Chemical stability test

The aim of this test is to confirm the high stability of Hf-PCN-222(H_2) in various types of solvent at high temperature in comparison with its counterpart, Zr-PCN-222(H_2). Zr-PCN-222(H_2) was synthesized following a reported procedure.[8]

To an 8-mL scintillation vial was added 15 mg as-synthesized Hf-PCN-222(H_2) or Zr-PCN-222(H_2), following by addition of 4 mL solvent. The mixture was sealed and heated up at 100 °C for 24 h. Afterwards, the solid was collected by centrifugation at 14000 rpm and washed with the solvent used (3 times × 4 mL each time) then EtOH (3 times × 4 mL each time). The final solid was dried at 100 °C overnight and checked with PXRD analysis.

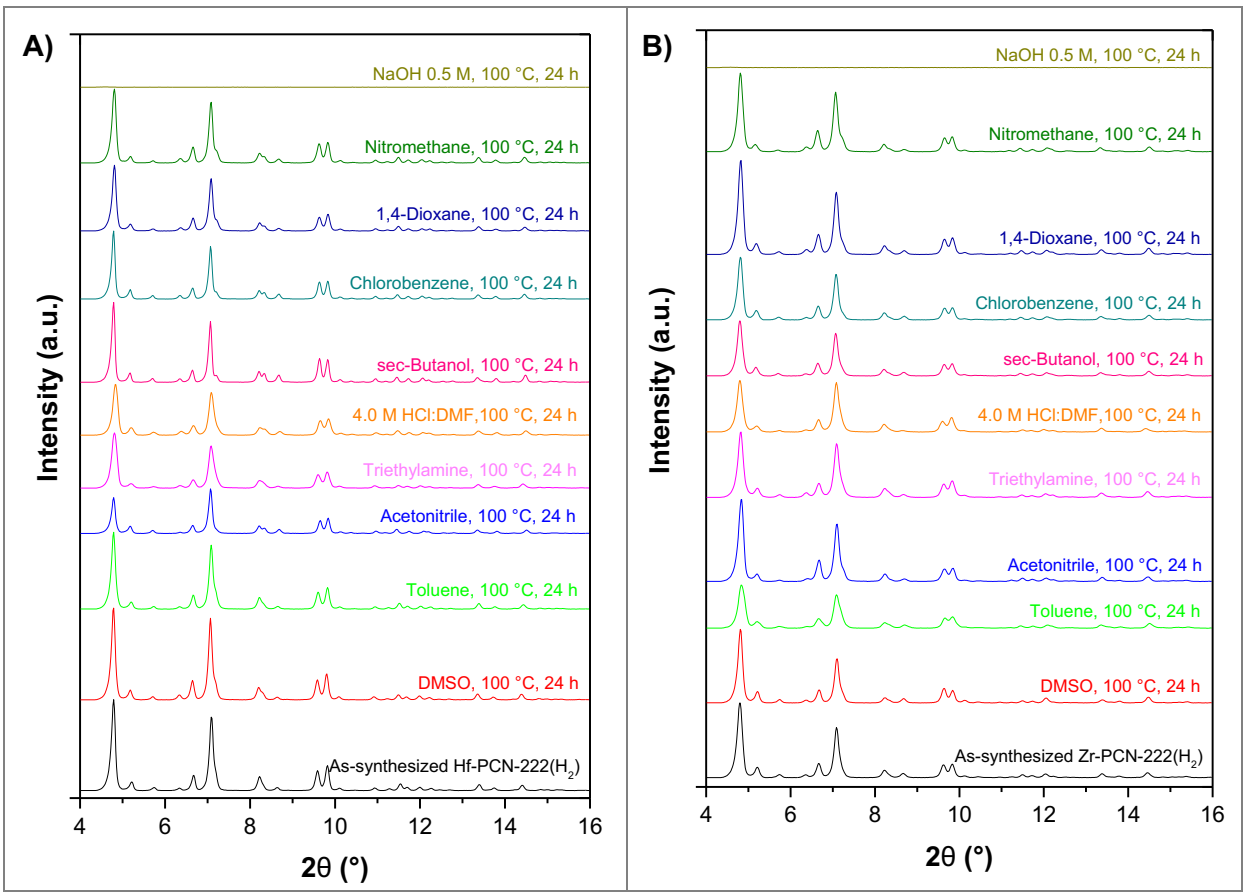
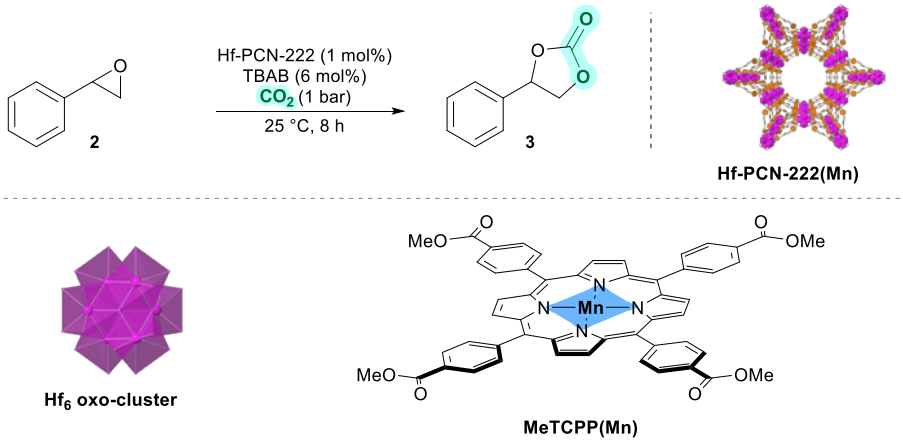


Figure S10. PXRD patterns of as-synthesized MOF treated with different solvents at 100 °C for 24 h. a) Hf-PCN-222(H_2). b) Zr-PCN-222(H_2).

4. Synthesis of cyclic carbonates from epoxides

4.1. Reaction optimization

Table S5. Optimization and control experiments for the insertion of CO_2 into epoxides.



Entry	Deviation from standard conditions[a]	3a yield (%)[b]
1	None	85 (85)[c]
2	Hf-PCN-222(H_2) 2 mol %	27
3	as-synthesized Hf-PCN-222(H2) 2 mol %	16
4	MeTCPP(Mn) 2 mol %	n.d.
5	Hf_6 oxo-cluster 2 mol %	n.d.
6	Hf_6 oxo-cluster and MeTCPP(Mn) 2 mol %	n.d.
7	24 h	93
8	No CO_2	n.d.
9	No TBAB	6
10	No Hf-PCN-222(Mn)	n.d.

[a]Reaction conditions: **2a** (0.20 mmol), PhIO (1.5 equiv), TBAB (12 mol %), and **Hf-PCN-222(Mn)** (6.2 mg, 2 mol % based on Mn) for 24 h at 40 ºC. [b]Yields were calculated by ^{1}H NMR analysis using trimethoxybenzene as internal standard from the crude mixture. [c]Isolated yield on 0.20 mmol scale. Abbreviations: n.d., not detected.

4.2. Synthesis of epoxides

Epoxides **2a**-**2k**, **2m, 2o**-**2u** are commercially available. Epoxide **2l** was synthesized from the corresponding commercially available compounds, according to the literature procedure.[5] Diepoxide **2n** was synthesized from **1aj** by epoxidation using *m*CPBA.

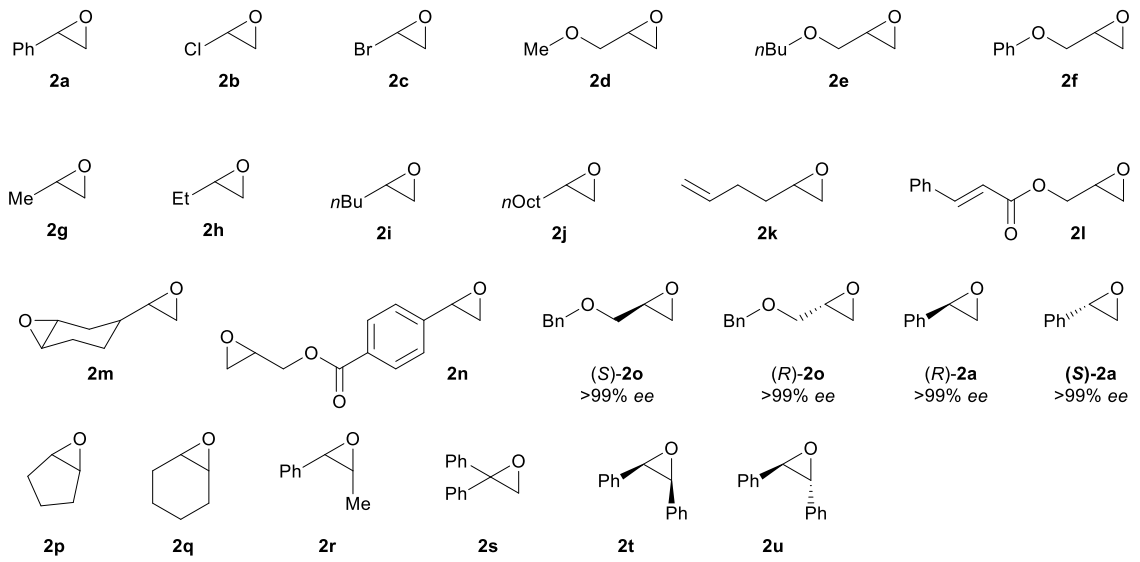
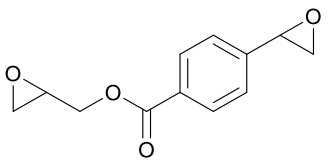


Figure S11. List of epoxides used in this project.

Oxiran-2-ylmethyl 4-(oxiran-2-yl)benzoate (2n)



To a stirred solution of allyl 4-vinylbenzoate **1aj** (110 mg, 0.58 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (9 mL) at 0 °C, *m*-chloroperoxybenzoic acid (70-75% balance 3-chlorobenzoic acid and water**,** 293.6 mg, 1.28 mmol, 2.2 equiv.) was added and stirred for 24 h at room temperature. After that, another equivalent of *m*-chloroperoxybenzoic acid (70-75% balance 3-chlorobenzoic acid and water, 133.4 mg, 0.58 mmol, 1.0 equiv.) was added to the reaction mixture at 0 °C and stirred for an additional 24 h at room temperature. When no starting material or monoepoxide product was observed the reaction mixture was filtrated through celite and washed with Et_2O (5 mL x 2). The solvent in the filtrate solution was removed under vacuum and resulted crude mixture was purified by flash column chromatography on silica gel using n-pentane:EtOAc:NEt_3 90:10:0.1 as eluents. The desired diepoxide product **2n** was isolated as a colorless oil (85 mg, 0.39 mmol, 67%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 8.00 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 4.62 (dd, *J* = 12.3, 3.0 Hz, 1H), 4.12 (dd, *J* = 12.3, 6.3 Hz, 1H), 3.86 (dd, *J* = 4.1, 2.5 Hz, 1H), 3.30 (m, 1H), 3.14 (dd, *J* = 5.6, 4.1 Hz, 1H), 2.85 (t, *J* = 4.5 Hz, 1H), 2.74 (dd, *J* = 5.6, 2.5 Hz, 1H), 2.69 (dd, *J* = 4.9, 2.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 165.8, 143.3, 129.9 (2C), 129.4, 125.4 (2C), 65.5, 51.8, 51.4, 49.4, 44.6.

HRMS (ESI) *m/z*: 243.0572 [M+Na^+], $C_{12}H_{12}O_4Na$+ requires 243.0628.

4.3. General Procedure A

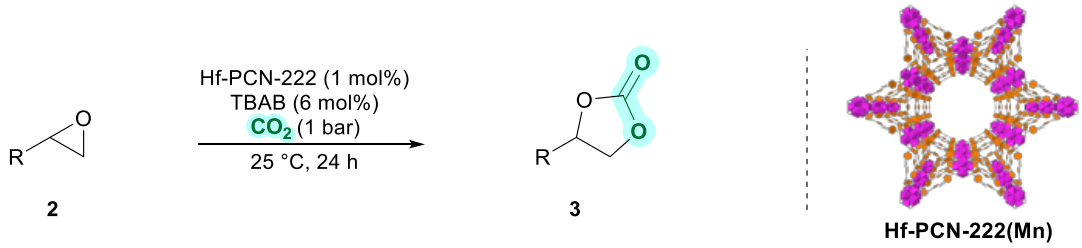
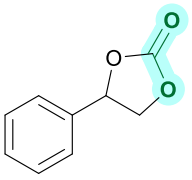


Figure S12. CO_2 cycloaddition to epoxides.

To a 2 mL conical bottom microwave vial equipped with a triangle shape magnetic stir bar was added epoxide **2** (0.20 mmol, 1.0 equiv., if it is solid), TBAB (4.0 mg, 6.0 mol%) and Hf-PCN-222(Mn) (3.1 mg, 1 mol%, calculated based on porphyrin linker). The vial was capped with a rubber septum and the inside atmosphere was purged with CO_2. At this point, epoxide **2** (0.20 mmol, 1.0 equiv.) was added via syringe if it is a liquid, and the mixture was stirred at 25 °C for 24 hours under CO_2 atmosphere. To ensure the CO_2 atmosphere, a balloon of CO_2 was used. The reaction was monitored by TLC analysis and quenched once the epoxide **2** was totally consumed. Upon completion, the solid was washed with CH_2Cl_2 (2 mL), and the suspension was centrifuged, keeping the solution. The remain solid was washed 3 times with CH_2Cl_2 (2 mL), and all the organic solutions were combined. The volatiles were removed under reduced pressure. The crude mixture was subjected to purification by flash column chromatography.

4.4. Characterization Data

4-Phenyl-1,3-dioxolan-2-one (3a)



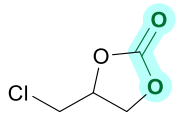
Prepared according to *General Procedure A* using 2-phenyloxirane (**2a**, 24 mg, 0.20 mmol, 1.0 equiv.). After chromatographic purification (10 – 40% EtOAc in *n*-pentane), the title compound **3a** was obtained as a white solid (28 mg, 0.17 mmol, 85%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.49 – 7.41 (m, 3H), 7.39 – 7.33 (m, 2H), 5.67 (t, J = 8.0 Hz, 1H), 4.80 (t, J = 8.4 Hz, 1H), 4.34 (t, J = 8.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 155.0, 135.9, 129.8, 129.3 (2C), 126.0, (2C) 78.1, 71.3.

Spectroscopic data are in agreement with those in the literature.[9]

4-(Chloromethyl)-1,3-dioxolan-2-one (3b)



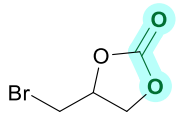
Prepared according to *General Procedure A* using 2-(chloromethyl)oxirane (**2b**, 19 mg, 0.20 mmol, 1.0 equiv.). After chromatographic purification (10 – 40% EtOAc in *n*-pentane), the title compound **3b** was obtained as a colorless oil (22 mg, 0.16 mmol, 80%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 5.02 – 4.89 (m, 1H), 4.59 (dd, *J* = 8.8, 8.2 Hz, 1H), 4.41 (dd, *J* = 8.9, 5.7 Hz, 1H), 3.78 (dd, *J* = 12.0, 5.6 Hz, 1H), 3.73 (dd, *J* = 12.1, 3.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 154.2, 74.4, 67.1, 43.7.

Spectroscopic data are in agreement with those in the literature.[10]

4-(Bromomethyl)-1,3-dioxolan-2-one (3c)



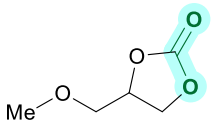
Prepared according to *General Procedure A* using 2-(bromomethyl)oxirane (**2c**, 27 mg, 0.20 mmol, 1.0 equiv). After chromatographic purification (10 – 40% EtOAc in *n*-pentane), the title compound **3c** was obtained as a colorless oil (23 mg, 0.13 mmol, 64%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 5.01 – 4.89 (m, 1H), 4.64 – 4.55 (m, 1H), 4.38 – 4.33 (m, 1H), 3.62 – 3.52 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 154.2, 74.1, 68.3, 31.3.

Spectroscopic data are in agreement with those in the literature.[11]

4-(Methoxymethyl)-1,3-dioxolan-2-one (3d)



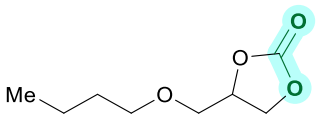
Prepared according to *General Procedure A* using 2-(methoxymethyl)oxirane (**2d**, 18 mg, 0.20 mmol, 1.0 equiv.). After chromatographic purification (10 – 40% EtOAc in *n*-pentane), the title compound **3d** was obtained as a colorless oil (21 mg, 0.16 mmol, 78%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 4.85 – 4.75 (m, 1H), 4.49 (t, *J* = 8.4 Hz, 1H), 4.37 (dd, *J* = 8.3, 6.1 Hz, 1H), 3.64 (dd, *J* = 11.0, 3.8 Hz, 1H), 3.56 (dd, *J* = 11.0, 3.8 Hz, 1H), 3.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 155.0, 75.1, 71.6, 66.3, 59.8.

Spectroscopic data are in agreement with those in the literature.[12]

4-(Butoxymethyl)-1,3-dioxolan-2-one (3e)



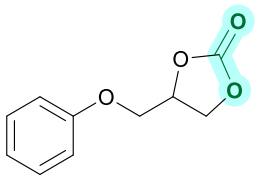
Prepared according to *General Procedure A* using 2-(butoxymethyl)oxirane (**2e**, 26 mg, 0.20 mmol, 1.0 equiv.). After chromatographic purification (10 – 40% EtOAc in *n*-pentane), the title compound **3e** was obtained as a yellow oil (27 mg, 0.16 mmol, 84%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 4.84 – 4.74 (m, 1H), 4.48 (t, *J* = 8.3 Hz, 1H), 4.38 (dd, *J* = 8.3, 6.1 Hz, 1H), 3.66 (dd, *J* = 11.0, 4.0 Hz, 1H), 3.59 (dd, *J* = 11.0, 3.7 Hz, 1H), 3.50 (t, *J* = 6.5 Hz, 2H), 1.59 – 1.50 (m, 2H), 1.42 – 1.28 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 155.1, 75.2, 72.0, 69.8, 66.4, 31.6, 19.3, 13.9.

Spectroscopic data are in agreement with those in the literature.[13]

4-(Phenoxymethyl)-1,3-dioxolan-2-one (3f)



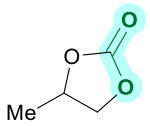
Prepared according to *General Procedure A* using 2-(phenoxymethyl)oxirane (**2f**, 30 mg, 0.20 mmol, 1.0 equiv). After chromatographic purification (10 – 40% EtOAc in pentane), the title compound **3f** was obtained as a white solid (30 mg, 0.16 mmol, 89%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.31 (t, *J* = 8.0 Hz, 1H, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 2H), 5.07 – 4.97 (m, 1H), 4.60 (t, *J* = 8.5 Hz, 1H), 4.52 (dd, *J* = 8.6, 5.9 Hz, 1H), 4.23 (dd, *J* = 10.6, 4.1 Hz, 1H), 4.13 (dd, *J* = 10.6, 3.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 157.9, 154.8, 129.8 (2C), 122.1, 114.7 (2C), 74.3, 67.0, 66.3.

Spectroscopic data are in agreement with those in the literature.[10]

4-Methyl-1,3-dioxolan-2-one (3g)



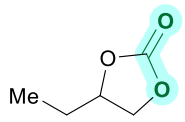
Prepared according to *General Procedure A* from propylene oxide (**2g**, 12 mg, 0.20 mmol, 1.0 equiv.). After chromatographic purification (10 – 40% EtOAc in pentane), the title compound **3g** was obtained as a colorless oil (15 mg, 0.15 mmol, 74%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 4.92 – 4.79 (m, 1H), 4.55 (dd, *J* = 8.4, 7.6 Hz, 1H), 4.02 (dd, *J* = 8.4, 7.2 Hz, 1H), 1.50 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 155.1, 73.6, 70.8, 19.6.

Spectroscopic data are in agreement with those in the literature.[9]

4-Ethyl-1,3-dioxolan-2-one (2h)



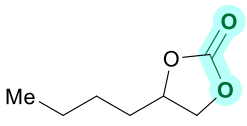
Prepared according to *General Procedure A* using 2-ethyloxirane (**2h**, 14 mg, 0.20 mmol, 1.0 equiv.). After chromatographic purification (10 – 40% EtOAc in pentane), the title compound **3h** was obtained as a colorless oil (18 mg, 0.15 mmol, 76%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 4.74 – 4.64 (m, 1H), 4.54 (t, *J* = 8.1 Hz, 1H), 4.10 (dd, *J* = 8.4, 7.0 Hz, 1H), 1.92 – 1.72 (m, 2H), 1.06 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 155.2, 78.1, 69.1, 27.1, 8.7.

Spectroscopic data are in agreement with those in the literature.[9]

4-Butyl-1,3-dioxolan-2-one (3i)



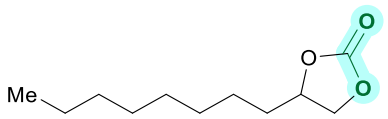
Prepared according to *General Procedure A* using 2-butyloxirane (**2i**, 20 mg, 0.20 mmol, 1.0 equiv.). After chromatographic purification (10 – 40% EtOAc in *n*-pentane), the title compound **3i** was obtained as a white foam (19 mg, 0.13 mmol, 66%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 4.70 (qd, *J* = 7.5, 5.5 Hz, 1H), 4.56 – 4.49 (m, 1H), 4.06 (dd, *J* = 8.4, 7.2 Hz, 1H), 1.88 – 1.74 (m, 1H), 1.73 – 1.63 (m, 1H), 1.51 – 1.32 (m, 4H), 0.92 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 155.2, 77.2, 69.5, 33.7, 26.6, 22.4, 13.9.

Spectroscopic data are in agreement with those in the literature.[9]

4-Octyl-1,3-dioxolan-2-one (3j)



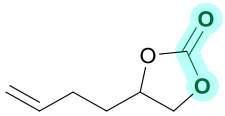
Prepared according to *General Procedure A* using 2-octyloxirane (**2j**, 31 mg, 0.20 mmol, 1.0 equiv.). After chromatographic purification (10 – 40% EtOAc in *n*-pentane), the title compound **3j** was obtained as a colorless oil (30 mg, 0.15 mmol, 75%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 4.74 – 4.63 (m, 1H), 4.51 (t, *J* = 8.1 Hz, 1H), 4.05 (t, *J* = 7.8 Hz, 1H), 1.84 – 1.74 (m, 1H), 1.70 – 1.63 (m, 1H), 1.52 – 1.40 (m, 1H), 1.39 – 1.20 (m, 11H), 0.87 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 155.2, 77.2, 69.5, 34.0, 31.9, 29.4, 29.2 (2C), 24.5, 22.7, 14.2.

Spectroscopic data are in agreement with those in the literature.[14]

4-(But-3-en-1-yl)-1,3-ioxolan-2-one (3k)



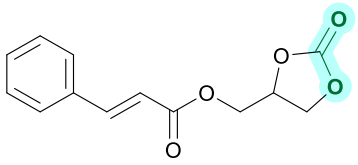
Prepared according to *General Procedure A* using 2-(but-3-en-1-yl)oxirane (**2k**, 20 mg, 0.20 mmol, 1.0 equiv.). After chromatographic purification (10 – 40% EtOAc in *n*-pentane), the title compound **3k** was obtained as a colorless oil (24 mg, 0.17 mmol, 84%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 5.85 – 5.71 (m, 1H), 5.14 – 5.01 (m, 2H), 4.78 – 4.66 (m, 1H), 4.52 (t, *J* = 8.1 Hz, 1H), 4.08 (dd, *J* = 8.5, 7.2 Hz, 1H), 2.32 – 2.11 (m, 2H), 1.99 – 1.86 (m, 1H), 1.82 – 1.72 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 155.1, 136.2, 116.6, 76.4, 69.4, 33.2, 28.8.

Spectroscopic data are in agreement with those in the literature.[10]

(2-Oxo-1,3-dioxolan-4-yl)methyl cinnamate (3l)



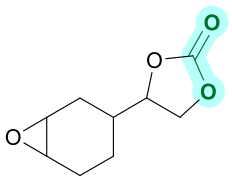
Prepared according to *General Procedure A* using oxiran-2-ylmethyl cinnamate (**2l**, 41 mg, 0.20 mmol, 1.0 equiv.). After chromatographic purification (10 – 40% EtOAc in *n*-pentane), the title compound **3l** was obtained as a colorless oil (20 mg, 0.08 mmol, 40%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.74 (d, *J* = 16.0 Hz, 1H), 7.58 – 7.49 (m, 2H), 7.44 – 7.36 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 5.04 – 4.96 (m, 1H), 4.60 (t, *J* = 8.6 Hz, 1H), 4.48 (dd, *J* = 12.6, 3.4 Hz, 1H), 4.41 (dd, *J* = 12.3, 4.2 Hz, 1H), 4.37 (dd, *J* = 8.7, 5.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 166.4, 154.6, 146.9, 134.0, 131.0, 129.1 (2C), 128.5 (2C), 116.5, 74.0, 66.2, 63.2.

Spectroscopic data are in agreement with those in the literature.[15]

4-(7-Oxabicyclo[4.1.0]heptan-3-yl)-1,3-dioxolan-2-one (3m)

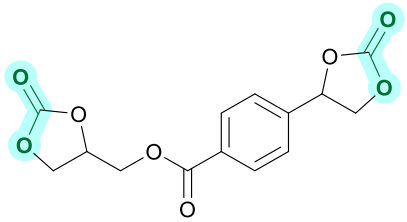


Prepared according to *General Procedure A* using 3-(oxiran-2-yl)-7-oxabicyclo[4.1.0]heptane (**2m**, 28.0 mg, 0.2 mmol, 1.0 equiv.) in 24 h. After chromatographic purification (10 – 40% EtOAc in *n*-pentane), the title compound **3m** was obtained as a colorless oil (24.7 mg, 0.13 mmol, 67%)

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 4.53 – 4.33 (m, 2H), 4.21 – 4.08 (m, 1H), 3.30 – 3.12 (m, 2H), 2.41 – 2.00 (m, 2H), 1.97 – 1.81 (m, 1H), 1.73 – 1.51 (m, 2H), 1.43 – 1.01 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 154.91 (d, *J* = 5.0 Hz), 80.43 – 79.16 (m), 68.44 – 66.93 (m), 53.13 – 49.51 (m), 36.39 (d, *J* = 37.2 Hz), 34.10 (d, *J* = 23.0 Hz), 27.35 – 23.62 (m), 23.16 – 21.24 (m), 19.09 (d, *J* = 84.9 Hz).

(2-Oxo-1,3-dioxolan-4-yl)methyl 4-(2-oxo-1,3-dioxolan-4-yl)benzoate (3n)



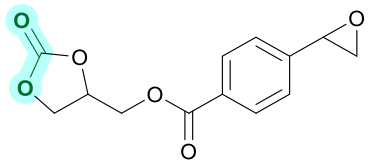
Prepared according to *General Procedure B* using oxiran-2-ylmethyl 4-(oxiran-2-yl)benzoate (**2n**, 44.0 mg, 0.2 mmol, 1.0 equiv.) in 24 h. After chromatographic purification (50% EtOAc in n-pentane), the title compound **3n** was obtained as a colorless oil (28.3 mg, 0.09 mmol, 46%)

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 8.08 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 5.75 (t, *J* = 8.0 Hz, 1H), 5.08 (ddt, *J* = 8.5, 5.3, 3.6 Hz, 1H), 4.85 (t, *J* = 8.5 Hz, 1H), 4.68 – 4.58 (m, 2H), 4.52 (dd, *J* = 12.7, 4.0 Hz, 1H), 4.42 (dd, *J* = 8.8, 5.5 Hz, 1H), 4.30 (t, *J* = 8.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 165.1, 154.4, 154.4, 141.5, 130.7 (2C), 130.0, 125.9 (2C), 77.0, 73.8, 70.8, 66.1, 64.0.

HRMS (ESI) *m/z*: 331.0451 [M+Na^+], $C_{14}H_{12}O_8Na$+ requires 331.0424.

(2-Oxo-1,3-dioxolan-4-yl)methyl 4-(oxiran-2-yl)benzoate (3n')



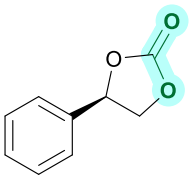
Prepared according to General Procedure A using oxiran-2-ylmethyl 4-(oxiran-2-yl)benzoate (**2n**, 44 mg, 0.2 mmol, 1.0 equiv.) in 24 h. After chromatographic purification (50% EtOAc in n-pentane), the title compound **3n'** was obtained as a colorless oil (27.5 mg, 0.10 mmol, 52%)

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 8.01 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 5.08 (dddd, *J* = 8.6, 5.7, 4.0, 3.1 Hz, 1H), 4.71 – 4.58 (m, 2H), 4.52 (ddd, *J* = 12.6, 5.2, 4.0 Hz, 1H), 4.43 (ddd, *J* = 8.8, 5.6, 2.4 Hz, 1H), 3.93 (dd, *J* = 4.1, 2.5 Hz, 1H), 3.21 (dd, *J* = 5.6, 4.1 Hz, 1H), 2.80 (dd, *J* = 5.6, 2.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 165.6, 154.4, 143.9, 130.0, 128.6 (2C), 128.4, 125.7 (2C), 73.9, 66.1, 63.7, 51.6.

HRMS (ESI) *m/z*: 287.0540 [M+Na^+], $C_{13}H_{12}O_6Na$+ requires 287.0526.

(*R*)-4-Phenyl-1,3-dioxolan-2-one ((*R*)-3a)



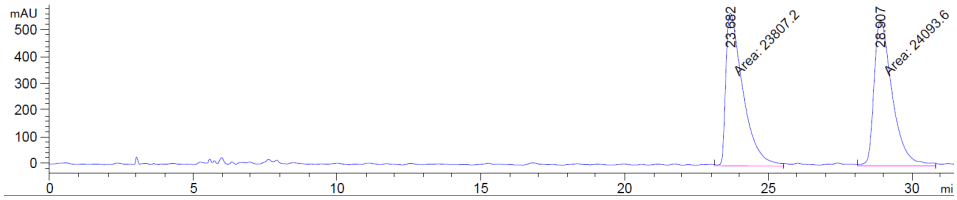
Prepared according to *General Procedure B* using (*R*)-2-phenyloxirane ((*R*)-**2a**, 24 mg, 0.20 mmol, 1.0 equiv.). After chromatographic purification (10 – 40% EtOAc in *n*-pentane), the title compound (*R*)-**3a** was obtained as a white solid (28 mg, 0.17 mmol, 84%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.49 – 7.41 (m, 3H), 7.39 – 7.33 (m, 2H), 5.67 (t, *J* = 8.0 Hz, 1H), 4.80 (t, *J* = 8.4 Hz, 1H), 4.34 (t, *J* = 8.2 Hz, 1H).

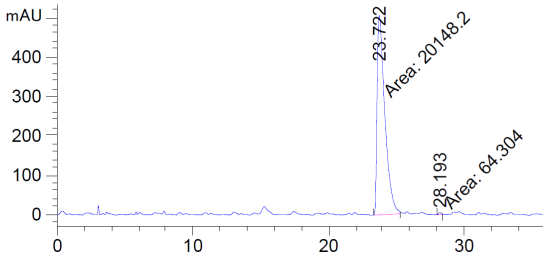
^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 155.0, 135.9, 129.8, 129.3 (2C), 126.0, (2C) 78.1, 71.3.

Spectroscopic data are in agreement with those in the literature.[16]

Chiral HPLC: *Daicel Chiralpack OD-H*, *n*-hexane/isopropanol, 90/10, flow rate 1 mL/min, λ = 210 nm, t_R = 23.72 min, temperature = 20 ºC, ee > 99%.



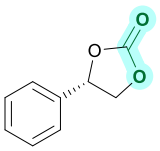
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.682	MM	0.6926	2.38072e4	572.86377	49.7010
2	28.907	MM	0.7366	2.40936e4	545.15942	50.2990



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.722	MM	0.6622	2.01482e4	507.12271	99.6819
2	28.193	MM	0.2241	64.30399	4.78211	0.3181

Figure S13. HPLC diagrams of (*R*)-**3a** and **3a**.

(*S*)-4-Phenyl-1,3-dioxolan-2-one ((*S*)-3a)



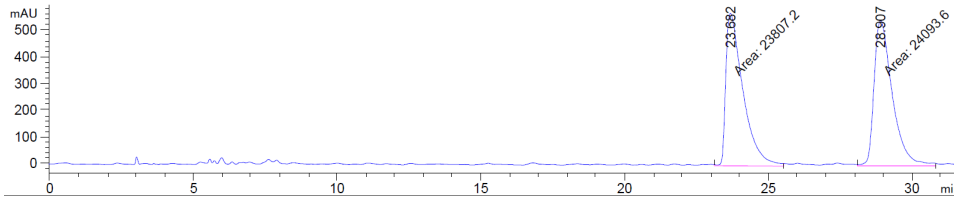
Prepared according to *General Procedure A* using (*S*)-2-phenyloxirane ((*S*)-**2a**, 24 mg, 0.20 mmol, 1.0 equiv.). After chromatographic purification (10 – 40% EtOAc in *n*-pentane), the title compound (*S*)-**3a** was obtained as a white solid (30.8 mg, 0.19 mmol, 94%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.49 – 7.41 (m, 3H), 7.39 – 7.33 (m, 2H), 5.67 (t, *J* = 8.0 Hz, 1H), 4.80 (t, *J* = 8.4 Hz, 1H), 4.34 (t, *J* = 8.2 Hz, 1H).

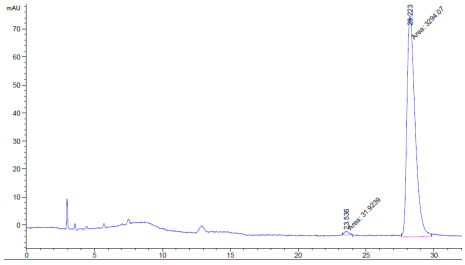
^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 155.0, 135.9, 129.8, 129.3 (2C), 126.0, (2C) 78.1, 71.3.

Spectroscopic data are in agreement with those in the literature.[16]

Chiral HPLC: *Daicel Chiralpack OD-H*, *n*-hexane/isopropanol, 90/10, flow rate 1 mL/min, λ = 210 nm, t_R = 28.22 min, temperature = 20 ºC, ee > 99%.



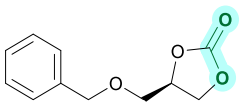
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.682	MM	0.6926	2.38072e4	572.86377	49.7010
2	28.907	MM	0.7366	2.40936e4	545.15942	50.2990



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.536	MM	0.4093	31.92395	1.29979	0.9598
2	28.223	MM	0.6955	3294.06689	78.94324	99.0402

Figure S14. HPLC diagrams of (*S*)-**3a** and **3a**.

(*R*)-4-((Benzyloxy)methyl)-1,3-dioxolan-2-one ((*R*)-3o)

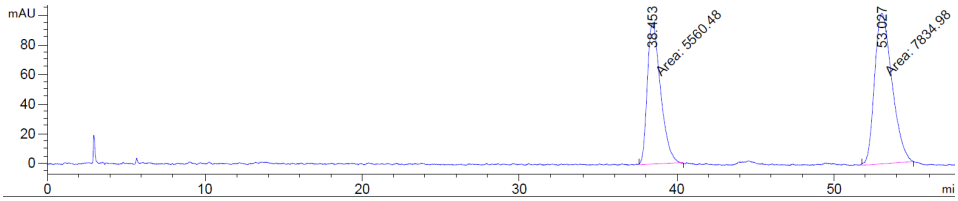


Prepared according to *General Procedure B* using (*S*)-2-((benzyloxy)methyl)oxirane ((*S*)-**2o**, 33 mg, 0.20 mmol, 1.0 equiv.). After chromatographic purification (10 – 40% EtOAc in *n*-pentane), the title compound (*R*)-**3o** was obtained as a white solid (39 mg, 0.19 mmol, 94%).

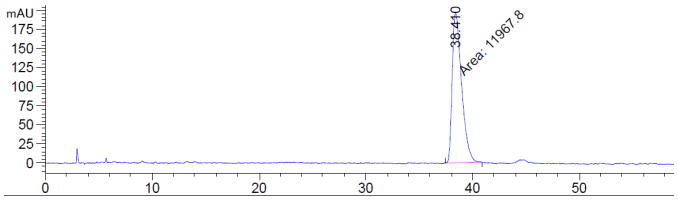
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.40 – 7.27 (m, 5H), 4.86 – 4.76 (m, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.47 (t, *J* = 8.4 Hz, 1H), 4.38 (dd, *J* = 8.4, 6.1 Hz, 1H), 3.71 (dd, *J* = 10.9, 3.9 Hz, 1H), 3.62 (dd, *J* = 10.9, 3.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 155.1, 137.2, 128.7 (2C), 128.2, 127.9 (2C), 75.1, 73.8, 68.9, 66.4. Spectroscopic data are in agreement with those in the literature.[16]

Chiral HPLC: *Daicel Chiralpack OD-H*, *n*-hexane/isopropanol, 90/10, flow rate 1 mL/min, λ = 210 nm, t_R = 38.41 min, temperature = 20 ºC, ee > 99%.



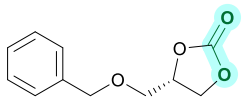
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.453	MM	0.9753	5560.48438	95.02431	41.5102
2	53.027	MM	1.2846	7834.97803	101.65276	58.4898



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.410	MM	1.0213	1.19678e4	195.30992	100.0000

Figure S15. HPLC diagrams of (*R*)-**3o** and **3o**.

(*S*)-4-((Benzyloxy)methyl)-1,3-dioxolan-2-one ((*S*)-3o)

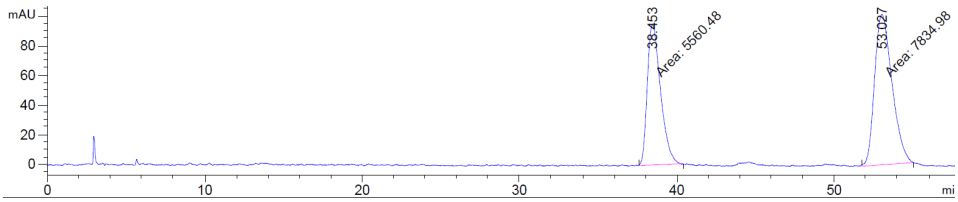


Prepared according to *General Procedure B* using (*R*)-2-((benzyloxy)methyl)oxirane ((*R*)-**2o**, 33 mg, 0.20 mmol, 1.0 equiv.). After chromatographic purification (10 – 40% EtOAc in *n*-pentane), the title compound (*S*)-**3o** was obtained as a white solid (40 mg, 0.19 mmol, 96%).

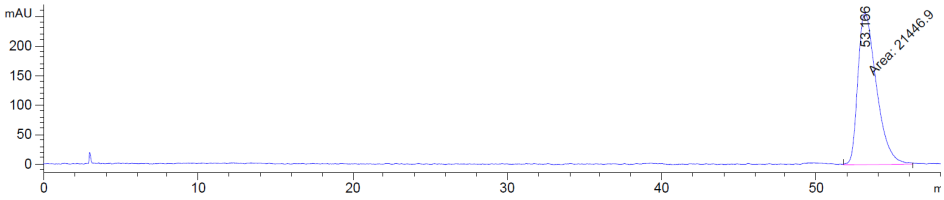
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.40 – 7.27 (m, 5H), 4.86 – 4.76 (m, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.47 (t, *J* = 8.4 Hz, 1H), 4.38 (dd, *J* = 8.4, 6.1 Hz, 1H), 3.71 (dd, *J* = 10.9, 3.9 Hz, 1H), 3.62 (dd, *J* = 10.9, 3.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 155.1, 137.2, 128.7 (2C), 128.2, 127.9 (2C), 75.1, 73.8, 68.9, 66.4. Spectroscopic data are in agreement with those in the literature.[16]

Chiral HPLC: *Daicel Chiralpack OD-H*, *n*-hexane/isopropanol, 90/10, flow rate 1 mL/min, λ = 210 nm, t_R = 53.17 min, temperature = 20 ºC, ee > 99%.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.453	MM	0.9753	5560.48438	95.02431	41.5102
2	53.027	MM	1.2846	7834.97803	101.65276	58.4898



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	53.166	MM	1.3903	2.14469e4	257.10675	100.0000

Figure S16. HPLC diagrams of (*S*)-**3o** and **3o**.

4.5. Recyclability

The recyclability test was performed using styrene oxide, as model substrate, and following *General Procedure A*. The resulted crude mixture was analyzed by ^{1}H-HMR using 1,3,5-trimethoxybenzenee as internal standard. Hf-PCN-222(Mn) was washed with CH_2Cl_2 (4 mL × 3 times), collected by centrifugation (14000 rpm, 2 min), dried under high vacuum, and reused for the next cycle.

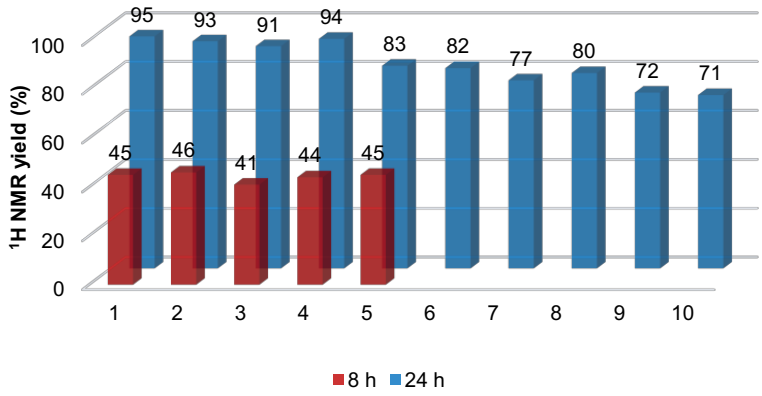
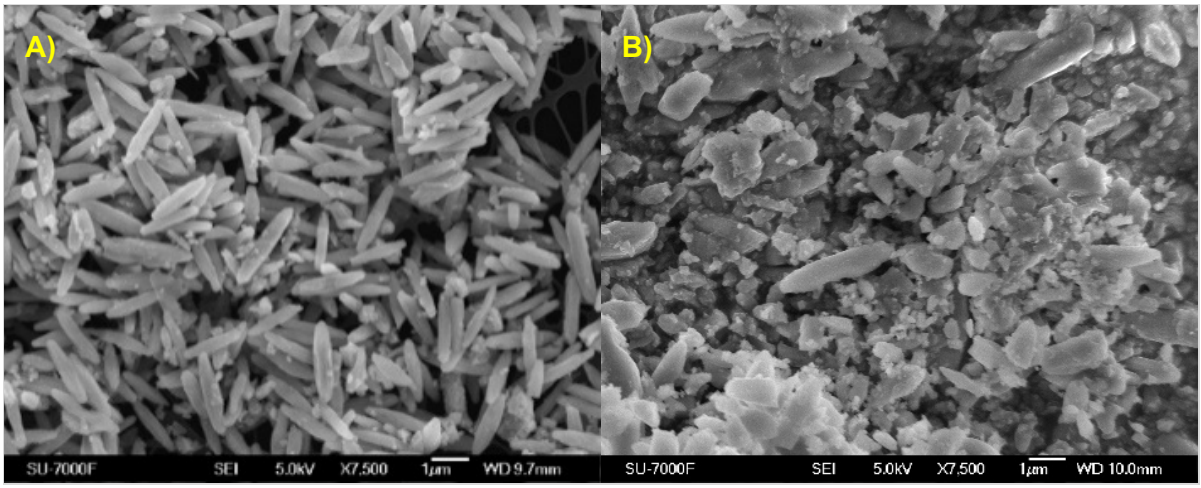


Figure S17. Study of recyclability of Hf-PCN-222(Mn) for the cycloaddition of CO_2 using styrene oxide



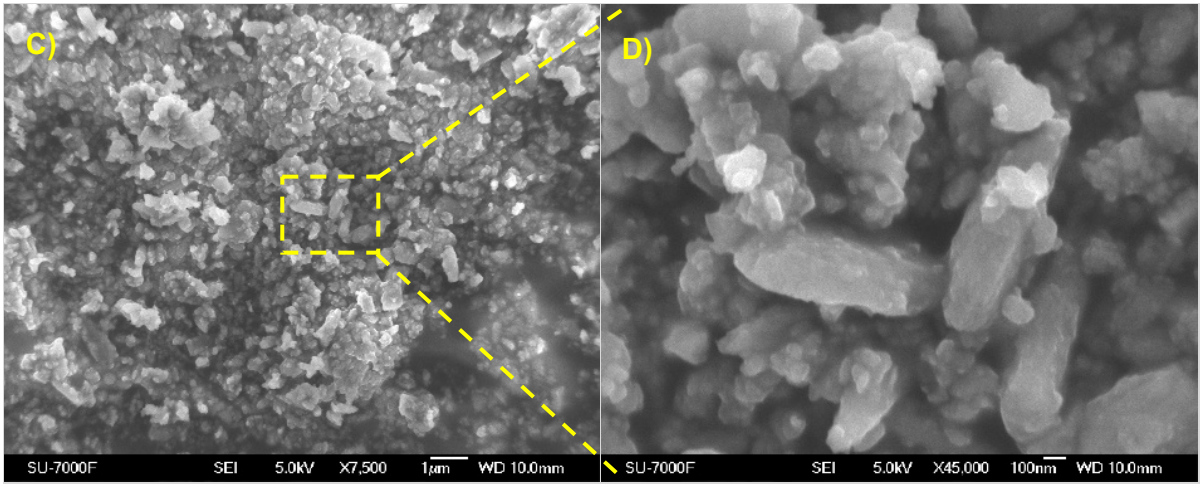
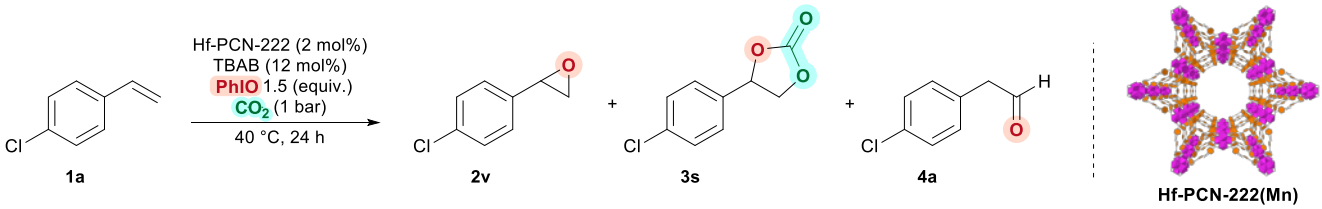


Figure S18. SEM images of fresh (A) and recycled Hf-PCN-222(Mn) after 5 runs (B) and 10 runs (C and D). The reaction time for each run is 24 h.

5. Synthesis of cyclic carbonates from alkenes

5.1. Reaction optimization:

Table S6. Optimization and control experiments for oxidative carboxylation of alkenes.



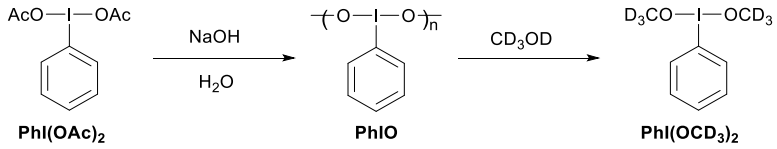
Entry	Deviation from standard conditions[a]	Yield 2v (%)[b]	Yield 3s (%)[b]	Yield 4a (%)[b]
1	None	2	75 (75)[c]	n.d.
2	CO_2 (1 bar, 2 equiv.)	n.d.	39	<1
3	No TBAB	3	n.d.	15
4	TBAB (6 mol %)	10	37	n.d.
5	No Hf-PCN-222(Mn)	7	2	4
6	Hf-PCN-222(Mn) (1 mol %)	6	57	n.d.
7	$PhI(OAc)_2$ (1.5 equiv.), H_2O (1.5 equiv.)	n.d.	n.d.	n.d.
8	No PhIO	n.d.	n.d.	n.d.
9	PhIO 1.0 equiv	n.d.	54	n.d.
10	Hf-PCN-222(Co) (2 mol %)	n.d.	8	1

[a]Reaction conditions: **1a** (0.20 mmol), PhIO (1.5 equiv), TBAB (12 mol %), and Hf-PCN-222(Mn) (2 mol % based on Mn) for 24 h at 40 ºC.

[b]Yields were calculated by ^{1}H NMR analysis using trimethoxybenzene as internal standard from the crude mixture.

[c]Isolated yield on 0.20 mmol scale. Abbreviations: std, standard; n.d., not detected.

5.2. Synthesis of iodosobenzene



Scheme S2. Synthesis of PhIO and reaction of PhIO with CD_3OD.

Iodosobenzene (PhIO) was synthesized from commercially available (diacetoxyiodo)benzene following a reported procedure.[1] To a 250-mL round-bottom flask containing (diacetoxyiodo)benzene (16.1 g, 0.05 mol) was slowly added 3 M aqueous NaOH solution (150 mL), and stirred at room temperature 1 h. The solid formed was collected by filtration on a Büchner funnel, re-dispersed in deionized H_2O (200 mL), and re-collected by filtration. This process was repeated 5 times to remove the excess amount of NaOH. Finally, the white solid was washed uith chloroform (100 mL) and dried under reduced pressure overnight at room temperature. The resulting solid was ground to obtain a fine white powder (PhIO). The resulting PhIO was kept in freezer at –20 °C and used up within 2 months from the date of synthesis. The NMR analysis of the polymer was done in CD_3OD, after complete reaction of PhIO with the CD_3OD to form $PhI(OCD_3)_2$.

^{1}H NMR (400 MHz, CD_3OD), δ (ppm) = 8.09 – 7.98 (m, 2H), 7.62 – 7.52 (m, 3H).

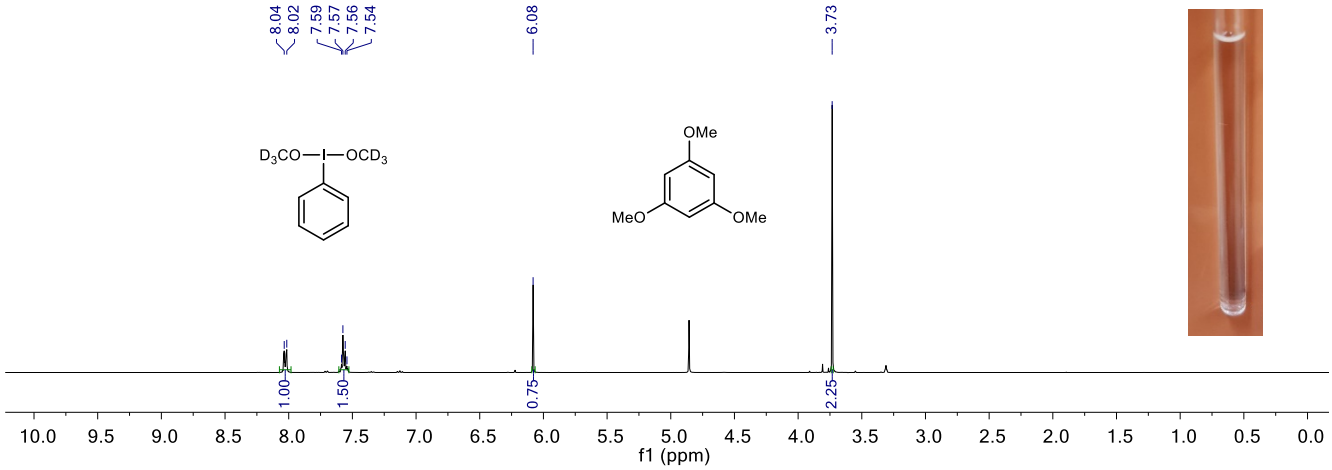
^{13}C NMR (101 MHz, CD_3OD), δ (ppm) = 133.3 (2C), 132.2, 132.0 (2C).

Spectroscopic data are in agreement with those in the literature.[1]

Caution! This compound explodes if heated to 210°.

Note: PhIO is unstable and tend to decompose slowly at room temperature. Hence, storing PhIO in a freezer could slow down this process. To check the actual amount of PhIO in the resulting solid, PhIO (44 mg, 0.2 mmol), 1,3,5-trimethoxybenzene (internal standard, 16.8 mg, 0.1 mmol), and CD_3OD (1 mL) were added to a small vial. The mixture is sonicated for 15 min and the ^{1}H NMR spectrum of the above mixture was obtained.

Freshly made PhIO reacts with CD_3OD within 5 min giving a transparent solution. ^{1}H NMR spectrum showed that the actual PhIO is 100%. On the contrary, PhIO sample which has been stored at room temperature for 1 month is not fully soluble in CD_3OD even after 1 week and the actual PhIO is 86% (Figure S19). The spoiled PhIO gave very bad yields when used for the epoxidation – cycloaddition of CO_2.



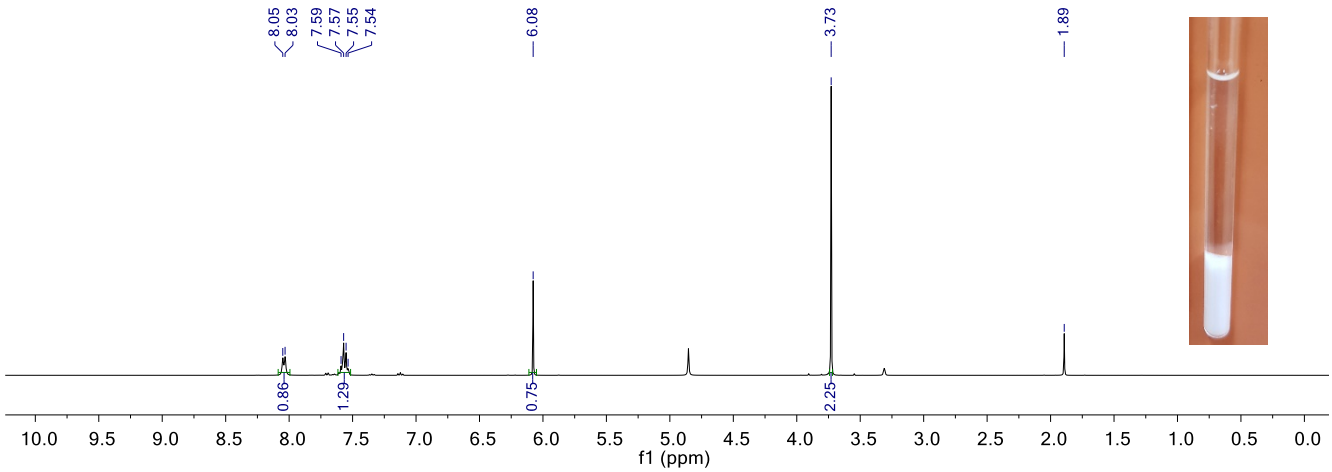


Figure S19. NMR spectra of PhIO and internal standard in CD_3OD with freshly-made PhIO (top, 100% actual PhIO) and PhIO stored at room temperature for 1 month (bottom, 86% actual PhIO).

5.3. Synthesis of alkenes

Alkenes **1a-1q**, **1s-1ai** are commercially available. Alkenes **1r**[2] and **1aj-1al**[3-4] were synthesized from the corresponding commercially available compounds, according to the literature procedure.

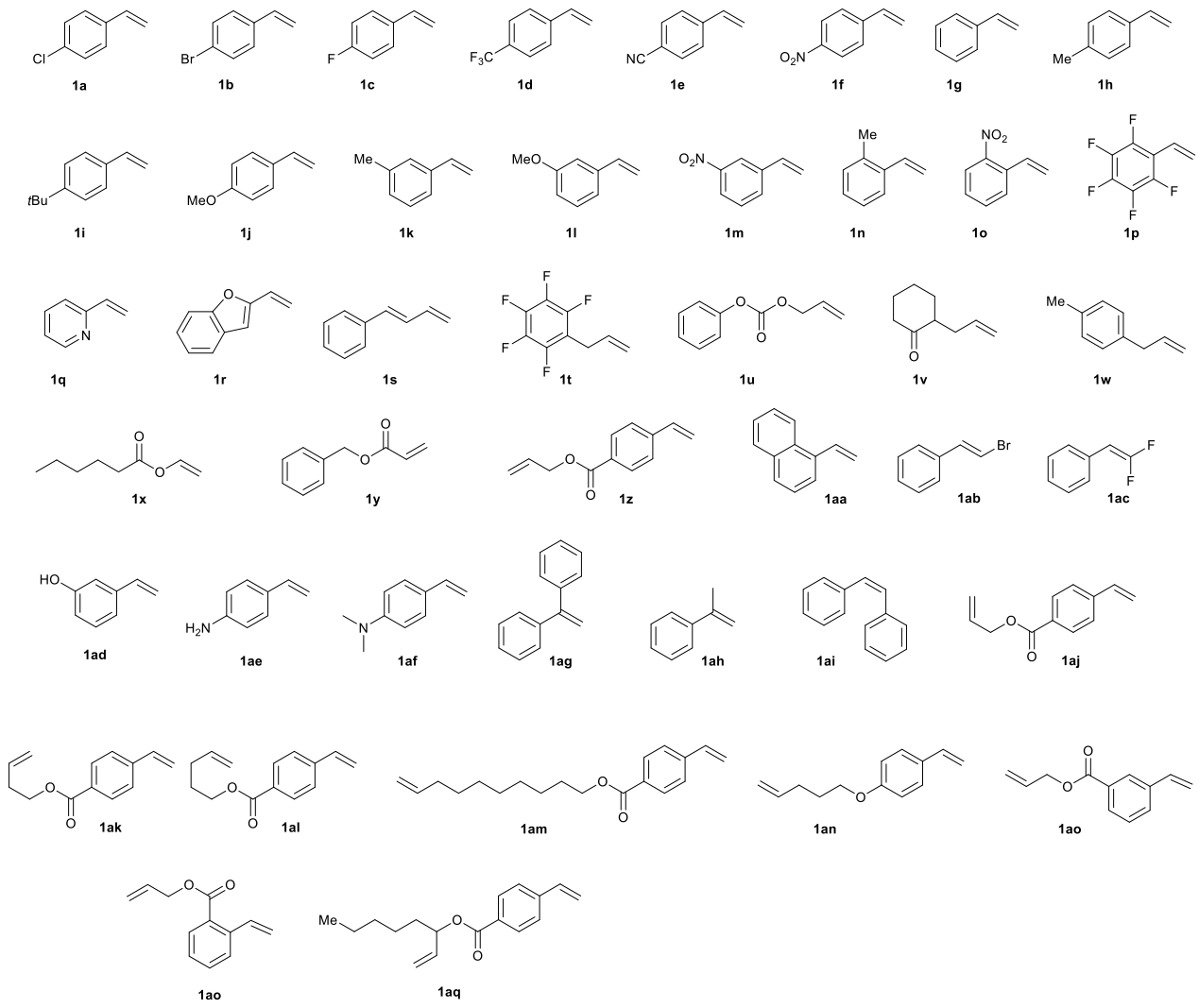
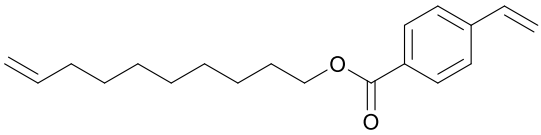


Figure S20. List of alkenes used in this project.

Dec-9-en-1-yl 4-vinylbenzoate (1am)



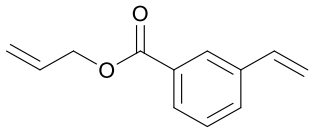
To a stirred solution of 4-vinylbenzoic acid (444 mg, 3.0 mmol, 1.0 equiv.) in anhydrous DMF (4 mL) was added 4-dimethylaminepyridine (DMAP, 20 mg, 0.16 mmol, 5 mol%) and 9-decen-1-ol (1070 µL, 6.0 mmol, 2.0 equiv.). Then, dicyclohexylcarbodiimide (DCC, 680 mg, 3.3 mmol, 1.1 equiv.) was added to the reaction mixture at 0 °C, which was then stirred for 5 min at 0 °C and overnight at 25 °C. Afterwards, the precipitated urea was filtered off and the filtrate was concentrated in vacuo. The residue is taken up in CH_2Cl_2 and CH_2Cl_2 solution was washed twice with 0.5 N HCl and with saturated $NaHCO_3$ solution, and then dried over $MgSO_4$. Purification by flash column chromatography (n-pentane: EtOAc = 100:0 to 95:5, v/v) afforded the desired ester product **1am** as a colorless oil (720 mg, 2.52 mmol, 84%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 8.00 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.85 (d, *J* = 17.6 Hz, 1H), 5.86 – 5.74 (m, 1H), 5.37 (d, *J* = 10.9 Hz, 1H), 5.05 – 4.94 (m, 1H), 4.97 – 4.89 (m, 1H), 4.31 (t, *J* = 6.7 Hz, 2H), 2.04 (q, *J* = 6.8 Hz, 2H), 1.80 – 1.73 (m, 2H), 1.47 – 1.30 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 166.5, 141.9, 139.2, 136.2, 129.9 (2C), 129.8, 126.2 (2C), 116.4, 114.3, 65.2, 33.9, 29.5, 29.3, 29.1, 29.0, 28.8, 26.1.

HRMS (ESI) *m/z*: 309.1778 [M+Na^+], $C_{19}H_{26}O_2Na$+ requires 309.1825.

Allyl 3-vinylbenzoate (1ao)



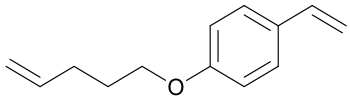
A solution of 3-vinylbenzoic acid (445 mg, 3.0 mmol, 1.0 equiv.) and K_2CO_3 (830 g, 6 mmol, 2.0 equiv.) in DMF (6.0 mL) was added allyl bromide (312 µL, 3.6 mmol, 1.2 equiv.) slowly at room temperature. Then, the resulting solution was stirred for 12 h at 60 °C. H_2O (20 mL) was added to the reaction and the solution was extracted with EtOAc (20 mL × 3 times). The combined EtOAc layer was washed with brine (20 mL × 3 times), dried over Na_2SO_4 and concentrated in vacuo. Purification by flash column chromatography (n-pentane: EtOAc = 100:0 to 95:5, v/v) afforded the desired ester product **1ao** as a colorless oil (536 mg, 2.85 mmol, 95%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 8.10 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 6.76 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.12 – 5.98 (m, 1H), 5.83 (d, *J* = 17.6 Hz, 1H), 5.42 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.35 – 5.28 (m, 2H), 4.84 (dt, *J* = 5.7, 1.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 166.3, 138.0, 136.1, 132.4, 130.7, 130.6, 129.0, 128.7, 127.6, 118.5, 115.3, 65.8.

HRMS (ESI) *m/z*: 211.0666 [M+Na^+], $C_{12}H_{12}O_2Na$+ requires 211.0730.

1-(Pent-4-en-1-yloxy)-4-vinylbenzene (1an)



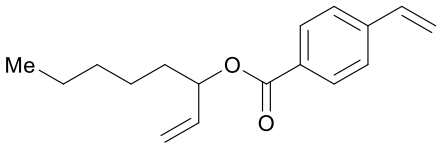
Compound **1an** was synthesized following a reported procedure.[7] 4-Vinylphenol 10 wt% in propylene glycol (2400 mg, 2.0 mmol, 1.0 equiv.), MeCN (10 mL), K_2CO_3 (829 mg, 6 mmol, 3.0 equiv) and 5-bromo-1-pentene (355 µL, 3.0 mmol, 1.5 equiv.) were added to a 20-mL Biotage® vial and the vial was sealed. The reaction mixture was heated at 90 °C for 10 h. After cooling to room temperature, the solution was filtered, washed with acetone, and the volatiles were removed under reduced pressure. After chromatographic purification (10% EtOAc in *n*-pentane), the title compound **1an** was obtained as colorless oil (282 mg, 1.5 mmol, 75%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.34 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 8.3 Hz, 2H), 6.66 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.93 – 5.79 (m, 1H), 5.61 (d, *J* = 17.6 Hz, 1H), 5.12 (d, *J* = 10.9 Hz, 1H), 5.04 (dd, *J* = 24.4, 13.7 Hz, 2H), 3.98 (t, *J* = 6.4 Hz, 2H), 2.25 (q, *J* = 7.0 Hz, 2H), 1.95 – 1.83 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 159.0, 137.9, 136.4, 130.5, 127.5 (2C), 115.3, 114.6 (2C), 111.6, 67.3, 30.2, 28.6.

HRMS (ESI) *m/z*: 211.0687 [M+Na^+], $C_{13}H_{16}ONa$+ requires 211.0730.

Oct-1-en-3-yl 4-vinylbenzoate (1aq)



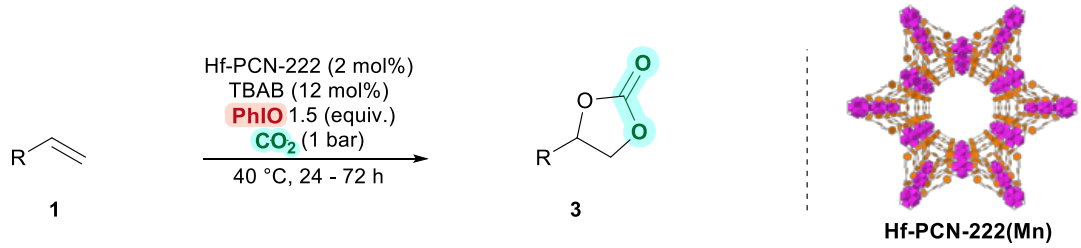
To a stirred solution of 4-vinylbenzoic acid (444 mg, 3.0 mmol, 1.0 equiv.) in anhydrous DMF (4 mL) was added 4-dimethylaminepyridine (DMAP, 20 mg, 0.16 mmol, 5 mol%) and oct-1-en-3-ol (mushroom alcohol, 927 µL, 6.0 mmol, 2.0 equiv.). Then, dicyclohexylcarbodiimide (DCC, 680 mg, 3.3 mmol, 1.1 equiv.) was added to the reaction mixture at 0 °C, which is then stirred for 5 min at 0 °C and overnight at 25 °C. Afterwards, the precipitated urea was filtered off and the filtrate was concentrated in vacuo. The residue is taken up in CH_2Cl_2 and CH_2Cl_2 solution was washed twice with 0.5 N HCl and with saturated $NaHCO_3$ solution, and then dried over $MgSO_4$. Purification by flash column chromatography (n-pentane: EtOAc = 100:0 to 95:5, v/v) afforded the desired ester product **1aq** as a colorless oil (419 mg, 1.62 mmol, 54%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 8.02 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 6.76 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.96 – 5.83 (m, 1H), 5.86 (dd, *J* = 17.6, 0.6 Hz, 1H), 5.53 – 5.43 (m, 1H), 5.38 (dd, *J* = 10.9, 0.7 Hz, 1H), 5.32 (dt, *J* = 17.3, 1.3 Hz, 1H), 5.20 (dt, *J* = 10.5, 1.3 Hz, 1H), 1.81 – 1.66 (m, 2H), 1.45 – 1.37 (m, 2H), 1.34 – 1.30 (m, 4H), 0.92 – 0.84 (t, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 165.8, 142.0, 136.8, 136.2, 130.0 (2C), 129.9, 126.2 (2C), 116.7, 116.6, 75.5, 34.4, 31.7, 24.9, 22.7, 14.1.

HRMS (ESI) *m/z*: 281.1512 [M+Na^+], $C_{17}H_{22}O_2Na$+ requires 281.1512.

5.4. General Procedure B



Scheme S3. Oxidative carboxylation of alkenes

PhIO is taken out from freezer and allowed to warm up slowly to room temperature. To a 2 mL conical-bottom microwave vial equipped with a triangle-shape magnetic stir bar was added alkene **1** (0.20 mmol, 1.0 equiv., if it is solid), PhIO (66.0 mg, 0.30 mmol, 1.5 equiv.), tetrabutylammonium bromide (TBAB, 8.0 mg, 12.0 mol%) and Hf-PCN-222(Mn) (6.2 mg, 2 mol%, calculated based on porphyrin linker). The vial was capped with a rubber septum and the vial was purged with CO_2. The solid mixture is mixed well on a magnetic stirrer at 0 °C. At this point, alkene **1** (0.20 mmol, 1.0 equiv.) was added via syringe if it is a liquid, and the mixture was stirred at 40 ºC for 24 – 72 hours under CO_2 atmosphere. To ensure the CO_2 atmosphere, a balloon of CO_2 was used. The reaction was monitored by TLC analysis and quenched once the alkene **1** or/and the corresponding intermediate epoxide were totally consumed. Upon completion, the solid was washed with CH_2Cl_2 (2 mL), and the suspension was centrifuged, keeping the solution. The remaining solid was washed 3 times with CH_2Cl_2 (2 mL), and all the organic solutions were combined. The volatiles were removed under reduced pressure, and the crude mixture was subjected to purification by flash column chromatography on silica gel using n-pentane:EtOAc (90:10 to 50:50, v/v) as eluents.

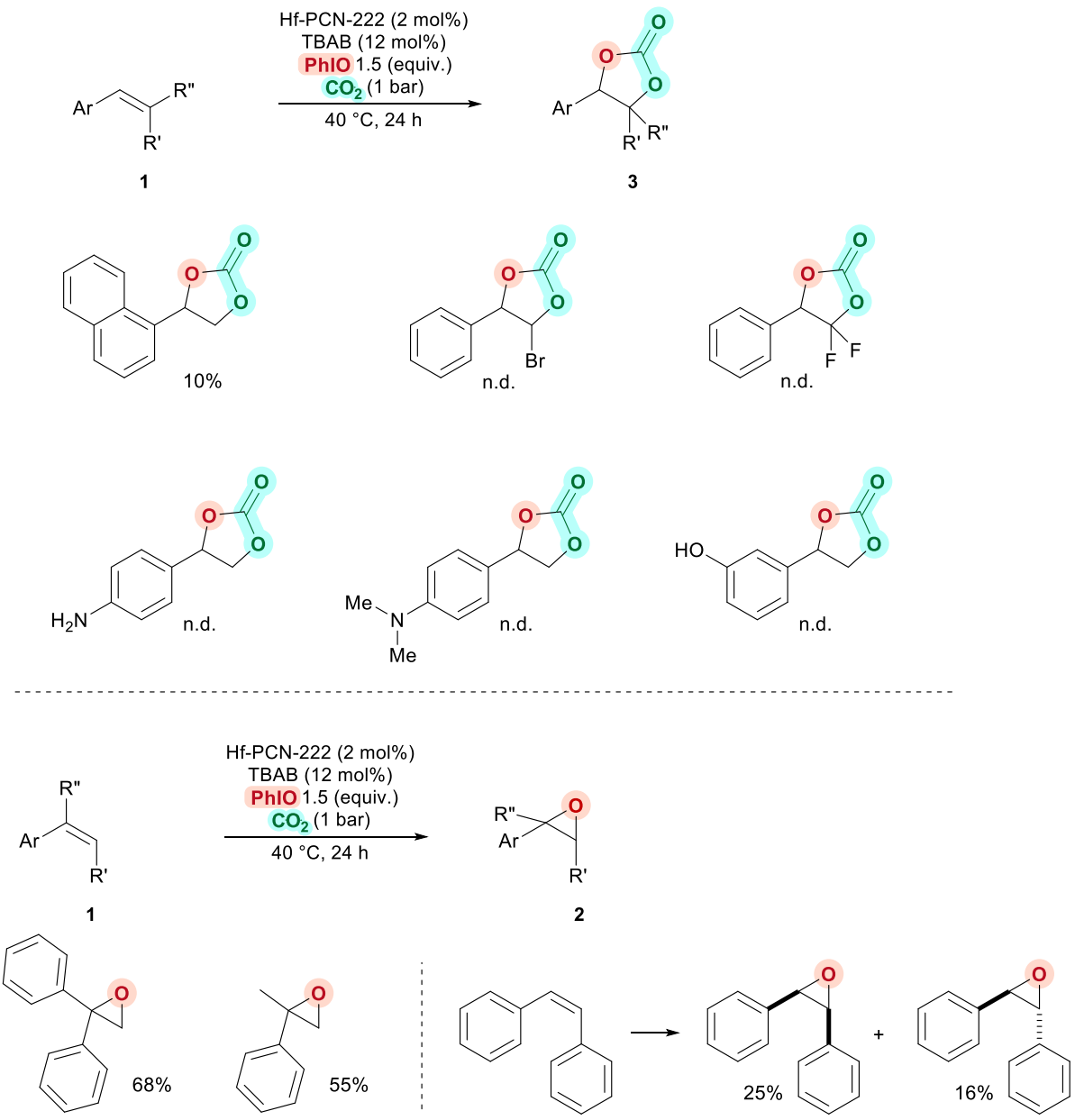
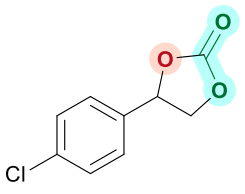


Figure S21. Unsuccessful substrates. Abbreviations: n.d., not detected. ^{1}H NMR yields are given.

5.5. Characterization data

4-(4-Chlorophenyl)-1,3-dioxolan-2-one (3s)



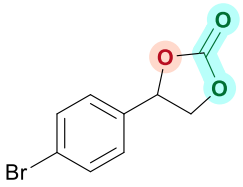
Prepared according to *General Procedure B* using 4-chlorostyrene (**1a**, 28 mg, 0.20 mmol, 1.0 equiv.) in 24 h. After chromatographic purification (10 – 50% EtOAc in *n*-pentane), the title compound **3s** was obtained as a white solid (24 mg, 0.12 mmol, 60%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.42 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 5.66 (t, *J* = 8.0 Hz, 1H), 4.80 (t, *J* = 8.4 Hz, 1H), 4.30 (dd, *J* = 8.7, 7.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 154.6, 135.9, 134.4, 129.6 (2C), 127.4 (2C), 77.4, 71.1.

Spectroscopic data are in agreement with those in the literature.[9]

4-(4-Bromophenyl)-1,3-dioxolan-2-one (3t)



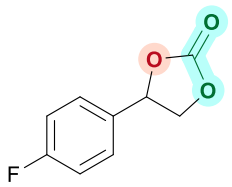
Prepared according to *General Procedure B* using 4-bromostyrene (**1b**, 37 mg, 0.20 mmol, 1.0 equiv.) in 24 h. After chromatographic purification (10 – 50% EtOAc in *n*-pentane), the title compound **3t** was obtained as a brown solid (32 mg, 0.13 mmol, 65%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.58 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 5.64 (t, *J* = 8.0 Hz, 1H), 4.80 (t, *J* = 8.4 Hz, 1H), 4.30 (dd, *J* = 8.7, 7.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 154.6, 134.9, 132.6 (2C), 127.6 (2C), 124.0, 77.4, 71.0.

Spectroscopic data are in agreement with those in the literature.[17]

4-(4-Fluorophenyl)-1,3-dioxolan-2-one (3u)



Prepared according to *General Procedure B* using 4-fluorostyrene (**1c**, 24 mg, 0.20 mmol, 1.0 equiv.) in 24 h. After chromatographic purification (10 – 50% EtOAc in *n*-pentane), the title compound **3u** was obtained as a white solid (23 mg, 0.13 mmol, 63%).

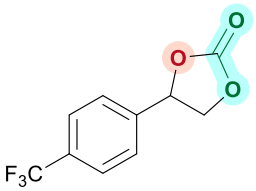
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.39 – 7.32 (m, 2H), 7.13 (t, *J* = 8.6 Hz, 2H), 5.66 (t, *J* = 8.0 Hz, 1H), 4.80 (t, *J* = 8.4 Hz, 1H), 4.32 (dd, *J* = 8.7, 7.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 163.5 (d, $J_{C\text{-}F}$ = 249.5 Hz), 154.7, 131.7 (d, $J_{C\text{-}F}$ = 3.3 Hz), 128.1 (d, $J_{C\text{-}F}$ = 8.6 Hz, 2C), 116.5 (d, $J_{C\text{-}F}$ = 22.1 Hz, 2C), 77.5, 71.2.

^{19}F NMR (377 MHz, $CDCl_3$), δ (ppm) = –110.93.

Spectroscopic data are in agreement with those in the literature.[9]

4-(4-(Trifluoromethyl)phenyl)-1,3-dioxolan-2-one (3v)



Prepared according to *General Procedure B* using 1-(trifluoromethyl)-4-vinylbenzene (**1d**, 34 mg, 0.20 mmol, 1.0 equiv.) in 48 h. After chromatographic purification (10 – 50% EtOAc in *n*-pentane), the title compound **3v** was obtained as a pale-yellow oil (29 mg, 0.13 mmol, 66%).

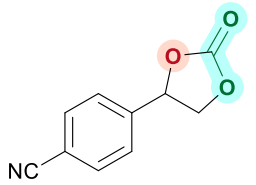
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.72 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.1 Hz, 2H), 5.75 (t, J = 7.9 Hz, 1H), 4.86 (t, J = 8.5 Hz, 1H), 4.32 (dd, J = 8.6, 7.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 154.5, 140.0, 132.0 (q, $J_{C\text{-}F}$ = 32.8 Hz), 126.5 (q, $J_{C\text{-}F}$ = 3.8 Hz, 2C), 126.2 (2C), 123.8 (q, $J_{C\text{-}F}$ = 272.3 Hz), 77.0, 71.0.

^{19}F NMR (377 MHz, $CDCl_3$), δ (ppm) = –62.88.

Spectroscopic data are in agreement with those in the literature.[9]

4-(4-Isocyanophenyl)-1,3-dioxolan-2-one (3w)



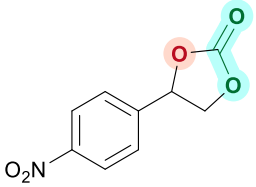
Prepared according to *General Procedure B* using 1-isocyano-4-vinylbenzene (**1e**, 26 mg, 0.20 mmol, 1.0 equiv.) in 48 h. After chromatographic purification (10 – 20% EtOAc in *n*-pentane), the title compound 3**w** was obtained as a colorless oil (20 mg, 0.11 mmol, 53%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.75 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 5.75 (t, J = 7.9 Hz, 1H), 4.87 (t, J = 8.5 Hz, 1H), 4.29 (dd, J = 8.7, 7.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 154.3, 141.1, 133.2 (2C), 126.4 (2C), 118.0, 113.7, 76.7, 70.8.

Spectroscopic data are in agreement with those in the literature.[18]

4-(4-Nitrophenyl)-1,3-dioxolan-2-one (3x)



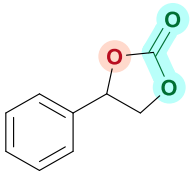
Prepared according to *General Procedure B* using 4-nitrostyrene (**1f**, 30 mg, 0.20 mmol, 1.0 equiv.) in 48 h. After chromatographic purification (10 – 20% EtOAc in *n*-pentane), the title compound **3x** was obtained yellow solid (23 mg, 0.11 mmol, 54%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 8.31 (d, *J* = 8.7 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 5.81 (t, *J* = 7.9 Hz, 1H), 4.90 (t, *J* = 8.5 Hz, 1H), 4.32 (dd, *J* = 8.7, 7.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 154.2, 148.7, 142.9, 126.7 (2C), 124.7 (2C), 76.5, 70.8.

Spectroscopic data are in agreement with those in the literature.[10]

4-Phenyl-1,3-dioxolan-2-one (3a)



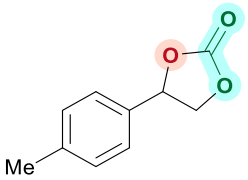
Prepared according to *General Procedure B* using styrene (**1g**, 21 mg, 0.20 mmol, 1.0 equiv.) in 24 h. After chromatographic purification (10 – 40% EtOAc in *n*-pentane), the title compound **3a** was obtained as a white solid (19 mg, 0.11 mmol, 57%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.49 – 7.41 (m, 3H), 7.39 – 7.33 (m, 2H), 5.67 (t, *J* = 8.0 Hz, 1H), 4.80 (t, *J* = 8.4 Hz, 1H), 4.34 (t, *J* = 8.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 155.0, 135.9, 129.8, 129.3 (2C), 126.0, (2C) 78.1, 71.3.

Spectroscopic data are in agreement with those in the literature.[9]

4-(*p*-Tolyl)-1,3-dioxolan-2-one (3y)

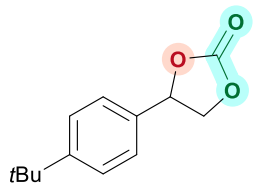


Prepared according to *General Procedure B* using 4-methylstyrene (**1h**, 24 mg, 0.20 mmol, 1.0 equiv.) in 24 h. After chromatographic purification (10 – 40% EtOAc in *n*-pentane), the title compound **3y** was obtained as a white solid (20 mg, 0.11 mmol, 55%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.26 – 7.22 (m, 4H), 5.64 (t, *J* = 8.0 Hz, 1H), 4.77 (t, *J* = 8.4 Hz, 1H), 4.33 (dd, *J* = 8.7, 7.9 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 155.0, 140.0, 132.8, 130.0 (2C), 126.1 (2C), 78.2, 71.3, 21.4. Spectroscopic data are in agreement with those in the literature.[17]

4-(4-(*tert*-Butyl)phenyl)-1,3-dioxolan-2-one (3z)



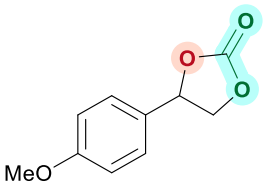
Prepared according to *General Procedure B* using 1-(*tert*-butyl)-4-vinylbenzene (**1i**, 32 mg, 0.20 mmol, 1.0 equiv.) in 24 h. After chromatographic purification (10 – 40% EtOAc in *n*-pentane), the title compound **3z** was obtained as a white solid (20 mg, 0.09 mmol, 46%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.46 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 5.65 (t, *J* = 8.0 Hz, 1H), 4.77 (t, *J* = 8.4 Hz, 1H), 4.36 (dd, *J* = 8.7, 8.0 Hz, 1H), 1.33 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 155.0, 153.2, 132.8, 126.3 (2C), 126.0 (2C), 78.2, 71.2, 34.9, 31.3 (3C).

Spectroscopic data are in agreement with those in the literature.[17]

4-(4-Methoxyphenyl)-1,3-dioxolan-2-one (3aa)



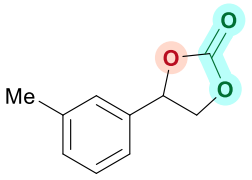
Prepared according to *General Procedure B* using 1-methoxy-4-vinylbenzene (**1j**, 27 mg, 0.20 mmol, 1.0 equiv.) in 24 h. After chromatographic purification (10 – 50% EtOAc in *n*-pentane), the title compound **3aa** was obtained as a yellow solid (12 mg, 0.06 mmol, 31%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.30 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 5.62 (t, *J* = 8.1 Hz, 1H), 4.75 (t, *J* = 8.4 Hz, 1H), 4.35 (t, *J* = 8.4 Hz, 1H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 160.9, 155.0, 127.9 (2C), 127.5, 114.7 (2C), 78.3, 71.2, 55.5.

Spectroscopic data are in agreement with those in the literature.[17]

4-(*m*-Tolyl)-1,3-dioxolan-2-one (3ab)



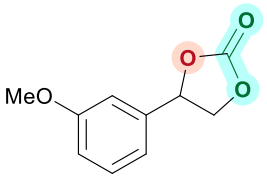
Prepared according to *General Procedure B* using 1-methyl-3-vinylbenzene (**1k**, 24 mg, 0.20 mmol, 1.0 equiv.). After chromatographic purification (10 – 40% EtOAc in *n*-pentane), the title compound **3ab** was obtained as a pale-yellow oil (17 mg, 0.09 mmol, 47%) in 24 h.

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.33 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.19 – 7.13 (m, 2H), 5.64 (t, *J* = 8.0 Hz, 1H), 4.78 (t, *J* = 8.4 Hz, 1H), 4.34 (t, *J* = 8.2 Hz, 1H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 155.0, 139.3, 135.9, 130.6, 129.2, 126.6, 123.1, 78.2, 71.3, 21.5.

Spectroscopic data are in agreement with those in the literature.[17]

4-(3-Methoxyphenyl)-1,3-dioxolan-2-one (3l)



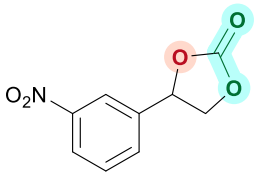
Prepared according to *General Procedure B* using 1-methoxy-3-vinylbenzene (**1l**, 27 mg, 0.20 mmol, 1.0 equiv) in 24 h. After chromatographic purification (10 – 50% EtOAc in *n*-pentane), the title compound **3ac** was obtained as a yellow oil (15 mg, 0.08 mmol, 39%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.35 (t, *J* = 7.9 Hz, 1H), 6.96 – 6.87 (m, 3H), 5.64 (t, *J* = 8.0 Hz, 1H), 4.79 (t, *J* = 8.4 Hz, 1H), 4.33 (dd, *J* = 8.6, 7.9 Hz, 1H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 160.4, 154.9, 137.5, 130.6, 117.9, 115.3, 111.4, 77.9, 71.3, 55.5.

Spectroscopic data are in agreement with those in the literature.[17]

4-(3-Nitrophenyl)-1,3-dioxolan-2-one (3ad)



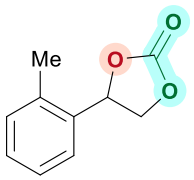
Prepared according to *General Procedure B* using 1-nitro-3-vinylbenzene (**1m**, 30 mg, 0.20 mmol, 1.0 equiv) in 24 h. After chromatographic purification (10 – 50% EtOAc in *n*-pentane), the title compound **3ad** was obtained as a yellow solid (20.5 mg, 0.10 mmol, 49%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 8.29 (d, *J* = 8.1 Hz, 1H), 8.24 (s, 1H), 7.75 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.68 (t, *J* = 7.9 Hz, 1H), 5.82 (t, *J* = 7.9 Hz, 1H), 4.91 (t, *J* = 8.5 Hz, 1H), 4.36 (dd, *J* = 8.8, 7.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 154.20, 148.75, 138.19, 131.68, 130.76, 124.70, 121.08, 76.58, 70.87.

Spectroscopic data are in agreement with those in the literature.[9]

4-(*o*-Tolyl)-1,3-dioxolan-2-one (3ae)



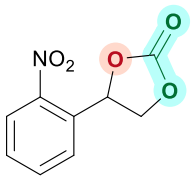
Prepared according to *General Procedure B* using 1-methyl-2-vinylbenzene (**1n**, 24 mg, 0.20 mmol, 1.0 equiv.) in 24 h. After chromatographic purification (10 – 40% EtOAc in *n*-pentane), the title compound **3ae** was obtained as a colorless oil (18 mg, 0.10 mmol, 51%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.45 – 7.40 (m, 1H), 7.33 – 7.27 (m, 2H), 7.24 – 7.20 (m, 1H), 5.90 (t, *J* = 8.0 Hz, 1H), 4.83 (t, *J* = 8.3 Hz, 1H), 4.28 (dd, *J* = 8.4, 7.8 Hz, 1H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 155.0, 134.7, 134.2, 131.1, 129.4, 127.0, 124.8, 75.7, 70.5, 19.1.

Spectroscopic data are in agreement with those in the literature.[17]

4-(2-Nitrophenyl)-1,3-dioxolan-2-one (3af)



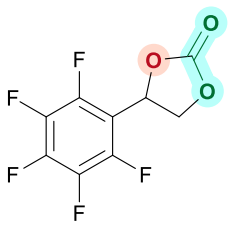
Prepared according to *General Procedure B* using 1-nitro-2-vinylbenzene (**1o**, 28 mg, 0.20 mmol, 1.0 equiv.) in 24 h. After chromatographic purification (10 – 20% EtOAc in *n*-pentane), the title compound **3af** was obtained as a yellow solid (13 mg, 0.06 mmol, 31%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 8.28 (d, *J* = 8.3 Hz, 1H), 7.87 – 7.78 (m, 2H), 7.68 – 7.57 (m, 1H), 6.28 (dd, *J* = 8.6, 6.1 Hz, 1H), 5.17 (t, *J* = 8.9 Hz, 1H), 4.28 (dd, *J* = 9.1, 6.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 154.6, 146.0, 135.4, 134.2, 130.2, 126.4, 125.9, 74.6, 71.5.

Spectroscopic data are in agreement with those in the literature.[9]

4-(Perfluorophenyl)-1,3-dioxolan-2-one (3ag)



Prepared according to *General Procedure B* using 1,2,3,4,5-pentafluoro-6-vinylbenzene (**1p**, 39 mg, 0.20 mmol, 1.0 equiv.) in 24 h. After chromatographic purification (10 – 50% EtOAc in *n*-pentane), the title compound **3ag** was obtained as a white solid (19 mg, 0.07 mmol, 36%).

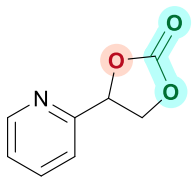
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 6.02 (dd, *J* = 9.2, 6.8 Hz, 1H), 4.86 (t, *J* = 9.0 Hz, 1H), 4.53 (dd, *J* = 8.8, 6.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 153.7, 148.8 – 145.5 (m), 144.9 – 143.5 (m), 142.3 – 140.9 (m), 140.1 – 138.8 (m), 137.8 – 136.0 (m), 111.7 – 108.6 (m), 68.4, 67.8.

^{19}F NMR (377 MHz, $CDCl_3$), δ (ppm) = -142.06 – -142.30 (m, 2F), -148.96 – -149.28 (m, 1F), -159.34 – -159.63 (m, 2F).

HRMS (ESI) *m/z*: 276.9795 [M+Na^+], $C_9H_3F_5O_3Na$+ requires 276.9895.

4-(Pyridin-2-yl)-1,3-dioxolan-2-one (3ah)



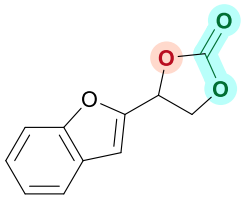
Prepared according to *General Procedure B* using 2-vinylpyridine (**1q**, 21 mg, 0.20 mmol, 1.0 equiv.) in 72 h. After chromatographic purification (10 – 50% EtOAc in *n*-pentane), the title compound **3ah** was obtained was a yellow oil (17 mg, 0.10 mmol, 51%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 8.68 – 8.57 (m, 1H), 7.79 (td, *J* = 7.7, 1.8 Hz, 1H), 7.50 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.33 (ddd, *J* = 7.7, 4.8, 1.1 Hz, 1H), 5.74 (dd, *J* = 8.4, 6.5 Hz, 1H), 4.87 (t, *J* = 8.5 Hz, 1H), 4.69 (dd, *J* = 8.6, 6.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 155.7, 154.9, 150.1, 137.5, 124.2, 120.8, 77.0, 69.8.

HRMS (ESI) *m/z*: 188.0266 [M+Na^+], $C_8H_7NO_3Na$+ requires 188.0318.

4-(Benzofuran-2-yl)-1,3-dioxolan-2-one (3ai)



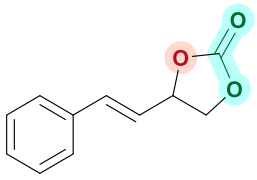
Prepared according to *General Procedure B* using 2-vinylbenzofuran (**1r**, 29 mg, 0.20 mmol, 1.0 equiv.) in 48 h. After chromatographic purification (10 – 50% EtOAc in *n*-pentane), the title compound **3ai** was obtained as a white solid (14 mg, 0.07 mmol, 35%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.61 (d, *J* = 7.7 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.40 – 7.35 (m, 1H), 7.31 – 7.26 (m, 1H), 6.94 (s, 1H), 5.81 (t, *J* = 7.7 Hz, 1H), 4.82 – 4.71 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 155.6, 154.3, 149.6, 127.2, 126.1, 123.7, 122.0, 111.9, 108.3, 71.5, 67.6.

HRMS (ESI) *m/z*: 227.0177 [M+Na^+], $C_{11}H_8O_4Na$+ requires 227.0315.

(*E*)-4-Styryl-1,3-dioxolan-2-one (3aj)



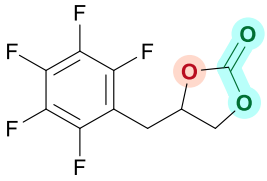
Prepared according to *General Procedure B* using (*E*)-buta-1,3-dien-1-ylbenzene (**1s**, 26 mg, 0.20 mmol, 1.0 equiv.) in 48 h. After chromatographic purification (10 – 50% EtOAc in *n*-pentane), the title compound **3aj** was obtained as a white solid (16 mg, 0.08 mmol, 41%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.43 – 7.33 (m, 5H), 6.79 (d, *J* = 15.8 Hz, 1H), 6.18 (dd, *J* = 15.8, 7.8 Hz, 1H), 5.33 – 5.27 (m, 1H), 4.65 (t, *J* = 8.3 Hz, 1H), 4.24 (dd, *J* = 8.7, 7.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 154.9, 137.0, 134.9, 129.3, 129.0 (2C), 127.1 (2C), 122.5, 77.9, 69.5.

Spectroscopic data are in agreement with those in the literature.[9]

4-((Perfluorophenyl)methyl)-1,3-dioxolan-2-one (3ak)



Prepared according to *General Procedure B* using 1-allyl-2,3,4,5,6-pentafluorobenzene (**1t**, 42 mg, 0.20 mmol, 1.0 equiv.) in 72 h. After chromatographic purification (10 – 40% EtOAc in *n*-pentane), the title compound **3ak** was obtained as a white solid (14 mg, 0.05 mmol, 26%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 4.98 – 4.87 (m, 1H), 4.63 – 4.56 (m, 1H), 4.22 (dd, J = 8.8, 6.3 Hz, 1H), 3.26 – 3.08 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 154.0, 147.3 – 146.1 (m), 144.8 – 143.9 (m), 140.2 – 139.5 (m), 139.5 – 138.7 (m), 136.9 – 136.3 (m), 108.4 – 107.6 (m), 74.6, 68.7, 27.0.

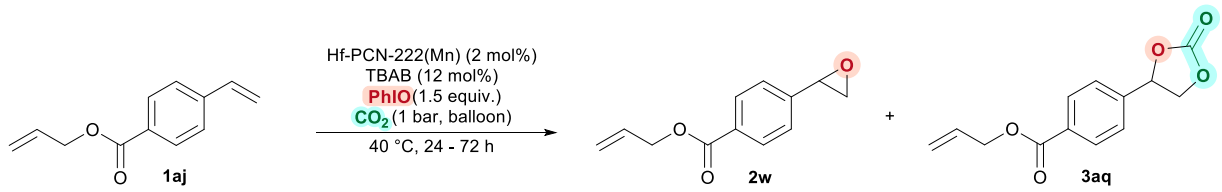
^{19}F NMR (377 MHz, $CDCl_3$), δ (ppm) = -141.88 – -142.01 (m, 2F), -153.62 (t, *J* = 20.8 Hz, 1F), -160.72 – -160.94 (m, 2F).

Spectroscopic data are in agreement with those in the literature.[19]

6. Chemoselective synthesis of en-cyclic-carbonates from dienes

Reaction optimization

Table S7. Optimization of chemoselective oxidative carboxylation reaction.



Entry	Time (h)	Yield 2w (%)	Yield 3aq (%)
1	24	41	26
2	48	21	46
3	72	4	68

To a 2 mL conical bottom microwave vial equipped with a triangle shape magnetic stir bar was added allyl 4-vinylbenzoate (**1aj**, 38 mg, 0.20 mmol, 1.0 equiv.), PhIO (66.0 mg, 0.30 mmol, 1.5 equiv.), tetrabutylammonium bromide (TBAB, 8.0 mg, 12.0 mol%) and Hf-PCN-222(Mn) (6.2 mg, 2 mol%, calculated based on porphyrin linker). The vial was capped with a rubber septum and vial was purged with CO_2, and the mixture was stirred at 40 ºC under CO_2 atmosphere for the time indicated in the table above. To ensure the CO_2 atmosphere, a balloon of CO_2 was used. The solid was washed with CH_2Cl_2 (2 mL), and the suspension was centrifuged (14000 rpm, 2 min), keeping the solution. The remaining solid was washed 3 times with CH_2Cl_2 (2 mL), and all the organic solutions were combined. The volatiles were removed under reduced pressure, and the crude mixture was subjected to purification by flash column chromatography (0 – 10% EtOAc in *n*-pentane), obtaining the cyclic organic carbonate **3aq** and/or epoxide **2w**. Data for cyclic organic carbonate **3aq**:

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 8.13 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 6.10 – 5.98 (m, 1H), 5.74 (t, *J* = 8.0 Hz, 1H), 5.41 (d, *J* = 16.9 Hz, 1H), 5.30 (d, *J* = 10.4 Hz, 1H), 4.87 – 4.81 (m, 3H), 4.31 (t, *J* = 8.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 165.5, 154.6, 140.8, 132.0, 131.5, 130.7 (2C), 125.7 (2C), 118.7, 77.3, 71.0, 66.0.

HRMS (ESI) *m/z*: 271.0622 [M+Na^+], $C_{13}H_{12}O_5Na$+ requires 271.0577.

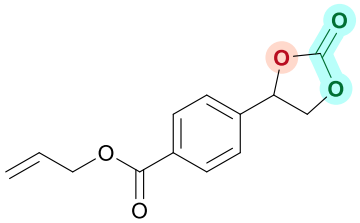
Data for epoxide **2w**:

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 8.04 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.11 – 5.97 (m, 1H), 5.41 (d, *J* = 17.2 Hz, 1H), 5.29 (d, *J* = 10.4 Hz, 1H), 4.82 (d, *J* = 5.6 Hz, 2H), 3.91 (t, *J* = 3.2 Hz, 1H), 3.19 (dd, *J* = 5.6, 4.2 Hz, 1H), 2.79 (dd, *J* = 5.7, 2.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 166.0, 143.1, 132.3, 130.1, 130.0 (2C), 125.5 (2C), 118.5, 65.8, 52.1, 51.6.

HRMS (ESI) *m/z*: 226.9409 [M+Na^+], $C_{12}H_{12}O_3Na$+ requires 227.0679.

Allyl 4-(2-oxo-1,3-dioxolan-4-yl)benzoate (3aq)



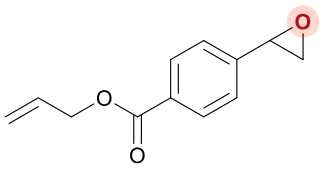
Prepared according to *General Procedure B*using allyl 4-vinylbenzoate (**1aj**, 38 mg, 0.20 mmol, 1.0 equiv.) in 72 h. After chromatographic purification (10 – 30% EtOAc in *n*-pentane), the title compound **3aq** was obtained as a colorless oil (30 mg, 0.12 mmol, 61%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 8.13 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 6.10 – 5.98 (m, 1H), 5.74 (t, *J* = 8.0 Hz, 1H), 5.41 (d, *J* = 16.9 Hz, 1H), 5.30 (d, *J* = 10.4 Hz, 1H), 4.87 – 4.81 (m, 3H), 4.31 (t, *J* = 8.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 165.5, 154.6, 140.8, 132.0, 131.5, 130.7 (2C), 125.7 (2C), 118.7, 77.3, 71.0, 66.0.

HRMS (ESI) *m/z*: 271.0622 [M+Na^+], $C_{13}H_{12}O_5Na$+ requires 271.0577.

Allyl 4-(oxiran-2-yl)benzoate (2w)



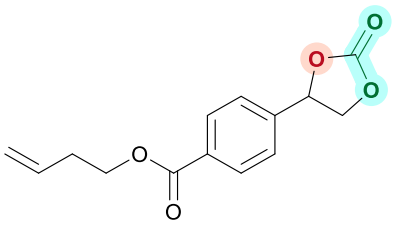
Prepared according to *General Procedure B* using allyl 4-vinylbenzoate (**1aj**, 38 mg, 0.20 mmol, 1.0 equiv.) in 48 h. After chromatographic purification (10 – 30% EtOAc in *n*-pentane), the title compound **2w** was obtained as a colorless oil (5.7 mg, 0.03 mmol, 14%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 8.04 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.04 (ddt, *J* = 16.4, 10.8, 5.5 Hz, 1H), 5.41 (dt, *J* = 17.2, 1.5 Hz, 1H), 5.29 (dd, *J* = 10.5, 1.8 Hz, 1H), 4.82 (dd, *J* = 5.7, 1.5 Hz, 2H), 3.91 (t, *J* = 3.2 Hz, 1H), 3.19 (dd, *J* = 5.6, 4.2 Hz, 1H), 2.79 (dd, *J* = 5.7, 2.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 166.0, 143.1, 132.3, 130.1, 130.0 (2C), 125.5 (2C), 118.5, 65.8, 52.1, 51.6.

HRMS (ESI) *m/z*: 226.9409 [M+Na^+], $C_{12}H_{12}O_3Na$+ requires 227.0679.

But-3-en-1-yl 4-(2-oxo-1,3-dioxolan-4-yl)benzoate (3ar)



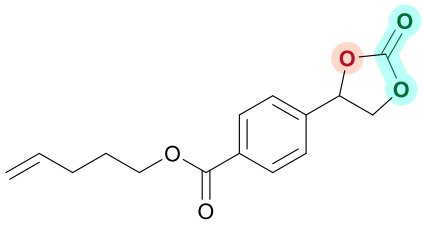
Prepared according to *General Procedure B* using but-3-en-1-yl 4-vinylbenzoate (**1ak**, 41 mg, 0.20 mmol, 1.0 equiv.) in 72 h. After chromatographic purification (10 – 30% EtOAc in *n*-pentane), the title compound **3ar** was obtained as a colorless oil (27 mg, 0.10 mmol, 52%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 8.10 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 5.93 – 5.80 (m, 1H), 5.74 (t, *J* = 8.0 Hz, 1H), 5.14 (dd, *J* = 23.5, 13.7 Hz, 2H), 4.84 (t, *J* = 8.4 Hz, 1H), 4.39 (t, *J* = 6.7 Hz, 2H), 4.31 (t, *J* = 8.2 Hz, 1H), 2.53 (q, *J* = 6.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 165.8, 154.6, 140.7, 134.0, 131.8, 130.6 (2C), 125.7 (2C), 117.6, 77.3, 71.0, 64.4, 33.2.

HRMS (ESI) *m/z*: 285.0715 [M+Na^+], $C_{14}H_{14}O_5Na$+ requires 285.0733.

Pent-4-en-1-yl 4-(2-oxo-1,3-dioxolan-4-yl)benzoate (3as)



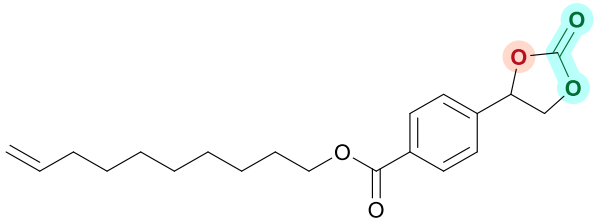
Prepared according to *General Procedure B* using pent-4-en-1-yl 4-vinylbenzoate (**1al**, 43 mg, 0.20 mmol, 1.0 equiv.) in 72 h. After chromatographic purification (10 – 30% EtOAc in *n*-pentane), the title compound **3as** was obtained as a colorless oil (20 mg, 0.07 mmol, 36%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 8.11 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 7.9 Hz, 2H), 5.92 – 5.77 (m, 1H), 5.74 (t, *J* = 8.0 Hz, 1H), 5.11 – 4.98 (m, 2H), 4.84 (t, *J* = 8.4 Hz, 1H), 4.39 – 4.27 (m, 3H), 2.22 (q, *J* = 7.2 Hz, 2H), 1.94 – 1.83 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 165.8, 154.6, 140.7, 137.5, 131.9, 130.6 (2C), 125.7 (2C), 115.6, 77.3, 71.1, 64.9, 30.3, 28.0.

HRMS (ESI) *m/z*: 299.0853 [M+Na^+], $C_{15}H_{16}O_5Na$+ requires 299.0890.

Dec-9-en-1-yl 4-(2-oxo-1,3-dioxolan-4-yl)benzoate (3at)



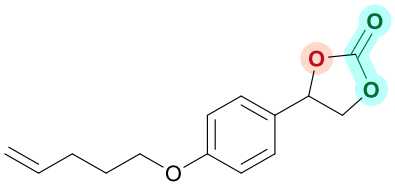
Prepared according to *General Procedure B* using dec-9-en-1-yl 4-vinylbenzoate (**1am**, 57 mg, 0.20 mmol, 1.0 equiv.) in 72 h. After chromatographic purification (10 – 30% EtOAc in *n*-pentane), the title compound **3at** was obtained as a colorless oil (6.0 mg, 0.02 mmol, 9%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 8.12 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 5.87 – 5.77 (m, 1H), 5.74 (t, *J* = 7.9 Hz, 1H), 5.04 – 4.90 (m, 2H), 4.84 (t, *J* = 8.4 Hz, 1H), 4.37 – 4.27 (m, 3H), 2.04 (q, *J* = 6.9 Hz, 2H), 1.83 – 1.71 (m, 2H), 1.50 – 1.32 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 165.9, 154.6, 140.6, 139.3, 132.0, 130.6 (2C), 125.7 (2C), 114.3, 77.3, 71.1, 65.7, 33.9, 29.5, 29.4, 29.2, 29.0, 28.8, 26.1.

HRMS (ESI) *m/z*: 369.1594 [M+Na^+], $C_{20}H_{26}O_5Na$+ requires 369.1672.

4-(4-(Pent-4-en-1-yloxy)phenyl)-1,3-dioxolan-2-one (3au)



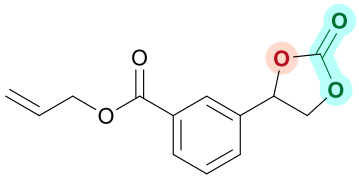
Prepared according to *General Procedure B* using 1-(hex-5-en-1-yloxy)-4-vinylbenzene (**1an**, 38 mg, 0.20 mmol, 1.0 equiv.) in 72 h. After chromatographic purification (10 – 30% EtOAc in *n*-pentane), the title compound **3au** was obtained as a colorless oil (20 mg, 0.08 mmol, 40%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.29 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 5.90 – 5.80 (m, 1H), 5.61 (t, *J* = 8.1 Hz, 1H), 5.06 (dq, *J* = 17.1, 1.7 Hz, 1H), 5.03 – 4.99 (m, 1H), 4.74 (dd, *J* = 8.7, 8.1 Hz, 1H), 4.35 (dd, *J* = 8.7, 8.1 Hz, 1H), 3.99 (t, *J* = 6.4 Hz, 2H), 2.29 – 2.19 (m, 2H), 1.95 – 1.85 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 160.4, 155.0, 137.8, 127.9 (2C), 127.4, 115.5, 115.3 (2C), 78.3, 71.2, 67.5, 30.2, 28.4.

HRMS (ESI) *m/z*: 271.0921 [M+Na^+], $C_{14}H_{16}O_4Na$+ requires 271.0941.

Allyl 3-(2-oxo-1,3-dioxolan-4-yl)benzoate (3av)



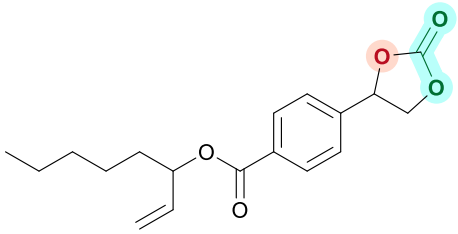
Prepared according to *General Procedure B* using allyl 3-vinylbenzoate (**1ao**, 38 mg, 0.20 mmol, 1.0 equiv) in 72 h. After chromatographic purification (10 – 30% EtOAc in *n*-pentane), the title compound **3av** was obtained as a colorless oil (22 mg, 0.09 mmol, 44%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 8.11 (d, *J* = 7.5 Hz, 1H), 8.04 (s, 1H), 7.62 – 7.50 (m, 2H), 6.11 – 5.97 (m, 1H), 5.74 (t, *J* = 8.0 Hz, 1H), 5.41 (dd, *J* = 17.2, 1.5 Hz, 1H), 5.31 (dd, *J* = 10.4, 1.3 Hz, 1H), 4.88 – 4.80 (m, 3H), 4.39 – 4.30 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 165.5, 154.6, 136.5, 132.0, 131.4, 131.0, 130.3, 129.7, 127.2, 118.9, 77.5, 71.1, 66.1.

HRMS (ESI) *m/z*: 271.0243 [M+Na^+], $C_{13}H_{12}O_5Na$+ requires 271.0755.

Oct-1-en-3-yl 4-(2-oxo-1,3-dioxolan-4-yl)benzoate (3ax)



Prepared according to *General Procedure B* using oct-1-en-3-yl 4-vinylbenzoate (**1aq**, 52 mg, 0.20 mmol, 1.0 equiv.) in 72 h. After chromatographic purification (10 – 30% EtOAc in *n*-pentane), the title compound **3ax** was obtained as a colorless oil (8 mg, 0.03 mmol, 13%).

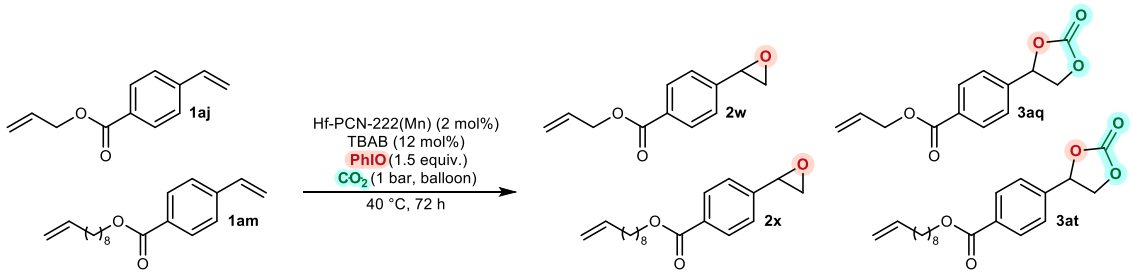
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 8.13 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 5.95 – 5.82 (m, 1H), 5.74 (t, *J* = 8.0 Hz, 1H), 5.52 – 5.45 (m, 1H), 5.31 (dt, *J* = 17.2, 1.3 Hz, 1H), 5.21 (dt, *J* = 10.5, 1.2 Hz, 1H), 4.84 (t, *J* = 8.4 Hz, 1H), 4.31 (dd, *J* = 8.6, 7.7 Hz, 1H), 1.83 – 1.68 (m, 2H), 1.44 – 1.36 (m, 2H), 1.35 – 1.26 (m, 4H), 0.91 – 0.84 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) = 165.1, 154.6, 140.7, 136.5, 132.1, 130.6 (2C), 125.7 (2C), 117.1, 77.3, 76.1, 71.1, 34.4, 31.7, 24.9, 22.6, 14.1.

HRMS (ESI) *m/z*: 341.1345 [M+Na^+], $C_{18}H_{22}O_5Na$+ requires 341.1359.

7. Substrate-size selectivity

Table S8. Control experiment on size-selective oxidative carboxylation.



Entry	Conditions[a]		Diene (%)		Epoxide (%)		Cyclic carbonate (%)	
	PhIO	CO_2	1aj	1am	2w	2x	3aq	3al
1	Yes	No	17	38	32	17	n.d.	n.d.
2	Yes	Yes	22	44	9	8	36	9

[a]Conditions: **11a** (0.2 mmol), **11d** (0.2 mmol), TBAB (12 mol%), Hf-PCN-222(Mn) (4 mol%), CO_2 (1 bar, balloon, 100 equiv.) or in N_2 atmosphere, neat, 40 °C, 72 h. ^{1}H NMR yields were obtained using 1,3,5-trimethoxybenzene as an internal standard combined with GC-FID using calibration curve.

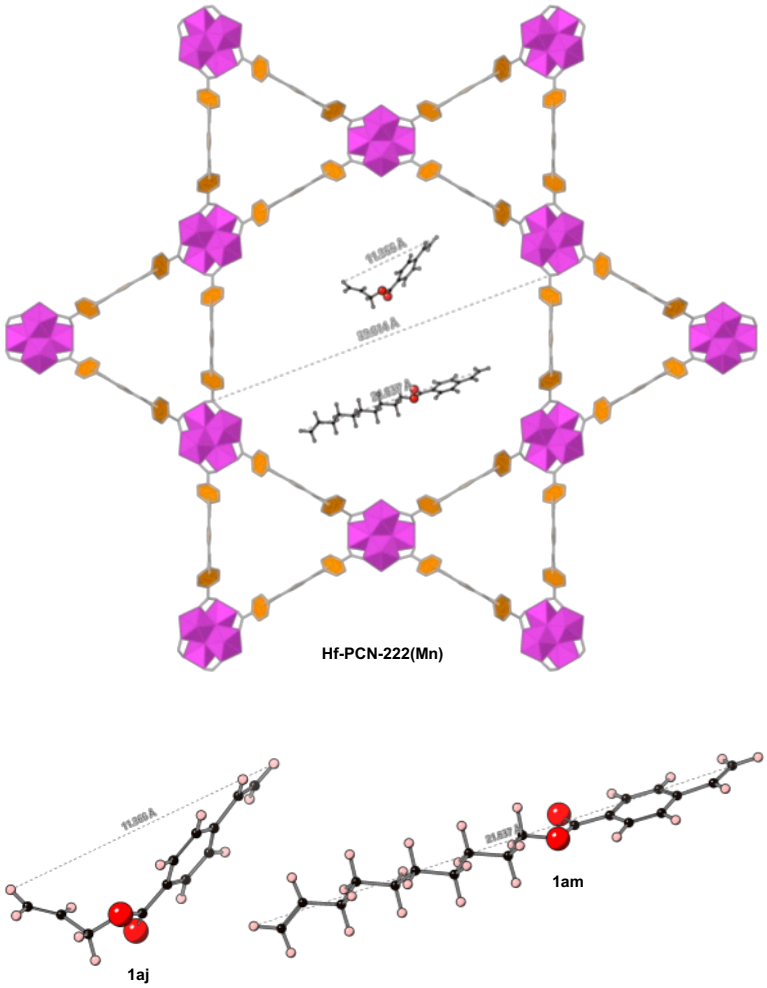


Figure 22. Relative size of dienes **1aj** and **1am** in comparison to the pore size of Hf-PCN-222(Mn).

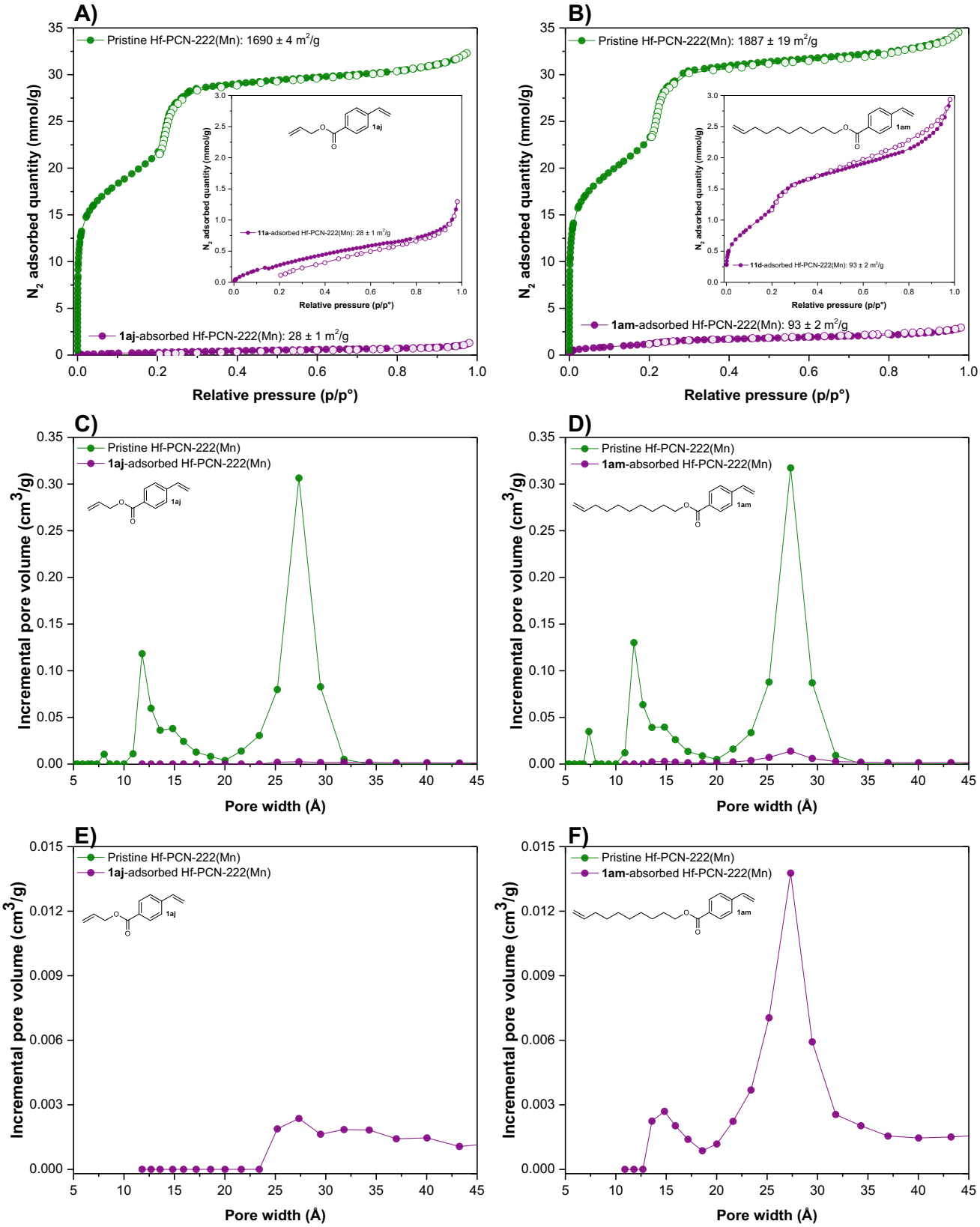


Figure S23. Isotherm curves (A–B) and pore size distribution (C–F) of Hf-PCN-222(Mn) and **1aj** or **1am** adsorbed Hf-PCN-222(Mn).

8. Recyclability

The recyclability test was performed using 4-chlorostyrene, as model substrate, and following *General Procedure B*. Internal standard 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol) was added to the reaction mixture at the end, following by addition of $CDCl_3$ (1 mL). The mixture was mixed well and then transferred to a 2-mL Eppendorf tube. The solid catalyst was separated from the liquid phase by centrifugation at 14000 rpm for 2 min. The liquid phase was taken for ^1H NMR analysis. The solid Hf-PCN-222(Mn) was re-dispersed in EtOAc (1.5 mL) and collected by centrifugation, this process was repeated 3 times to wash the solid Hf-PCN-222(Mn) thoroughly. Then, the collected catalyst was washed with MeOH (1.5 mL × 3 times) before being dried under high vacuum at room temperature and reused for the next cycle without any further treatment.

The reused catalyst was examined with PXRD showing the MOF crystallinity is maintained

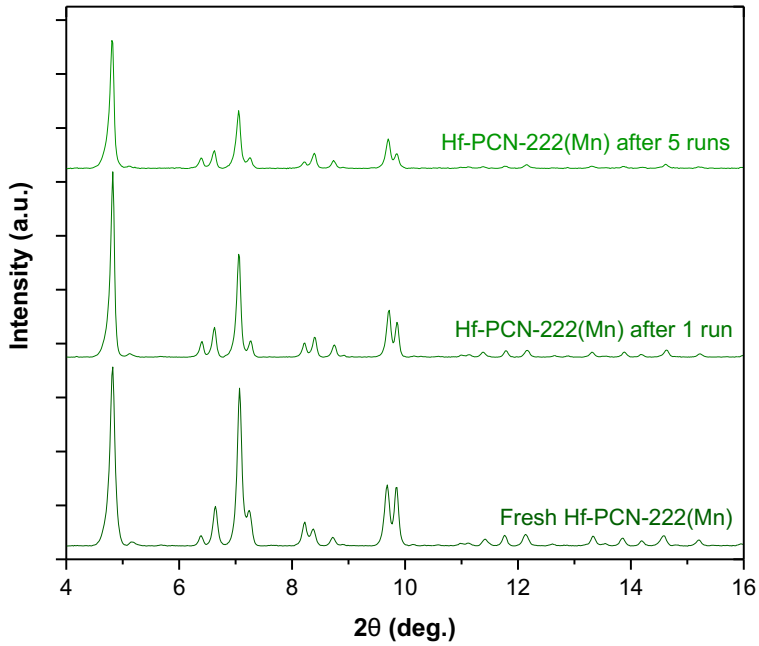
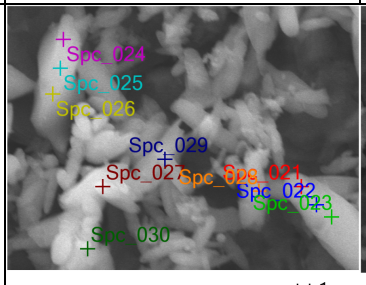
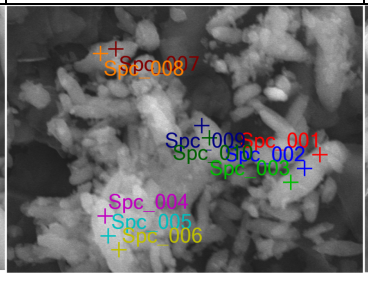
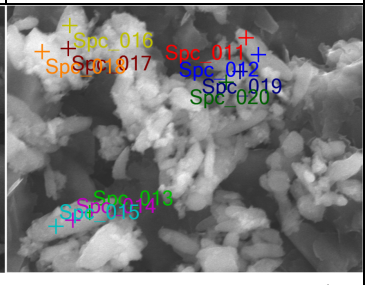


Figure S24. PXRD pattern of Hf-PCN-222(Mn) fresh, after 1 run and after 5 runs.

SEM–EDS analysis shows that the Mn/Hf ratio remains unchanged, indicating now significant leaching of the metal during catalysis.

Table S9. EDS results of Hf-PCN-222(Mn) fresh, after 1 run and after 5 runs.

	Fresh Hf-PCN-222(Mn)		**Hf-PCN-222(Mn) After 1 run**		**Hf-PCN-222(Mn) After 5 runs**	
						
	Mn atom%	Hf atom%	Mn atom%	Hf atom%	Mn atom%	Hf atom%
Point 1	0.44	1.62	0.31	1.03	0.04	0.18

Point 2	0.48	1.80	0.34	1.14	0.11	0.40
Point 3	0.62	2.30	0.43	1.44	0.35	1.25
Point 4	0.39	1.52	0.39	1.51	0.50	1.75
Point 5	0.41	1.71	0.46	1.65	0.41	1.39
Point 6	0.46	1.72	0.6	1.89	0.22	0.79
Point 7	0.26	1.04	0.13	0.44	0.30	1.10
Point 8	0.63	2.30	0.21	0.68	0.06	0.22
Point 9	0.27	0.94	0.18	0.73	0.29	1.03
Point 10	0.77	2.93	0.37	1.32	0.37	1.38
Average Mn/Hf	0.2646		0.2884		0.2732	
%Metalation	79%		86%		82%	

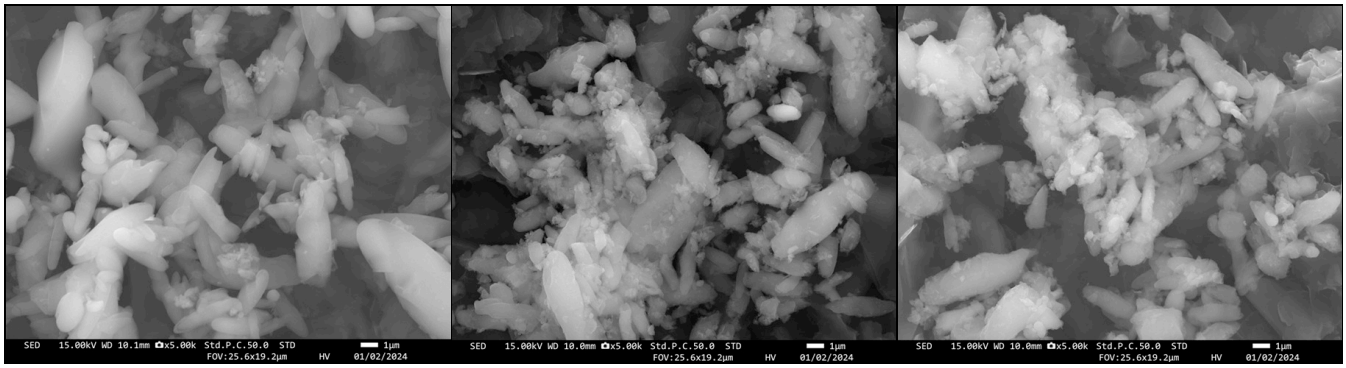
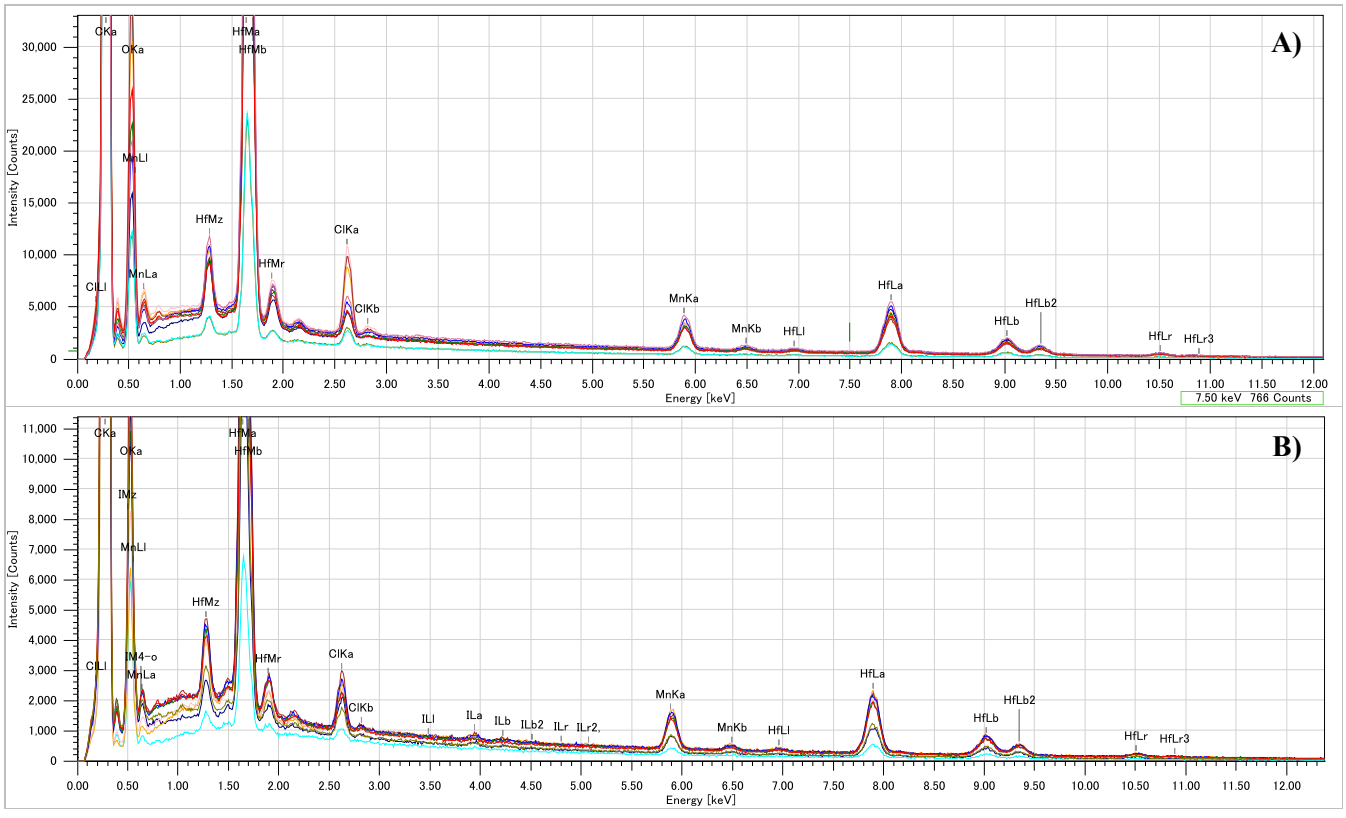


Figure S25. Hf-PCN-222(Mn) fresh (left), after 1 run (middle) and after 5 runs (right).



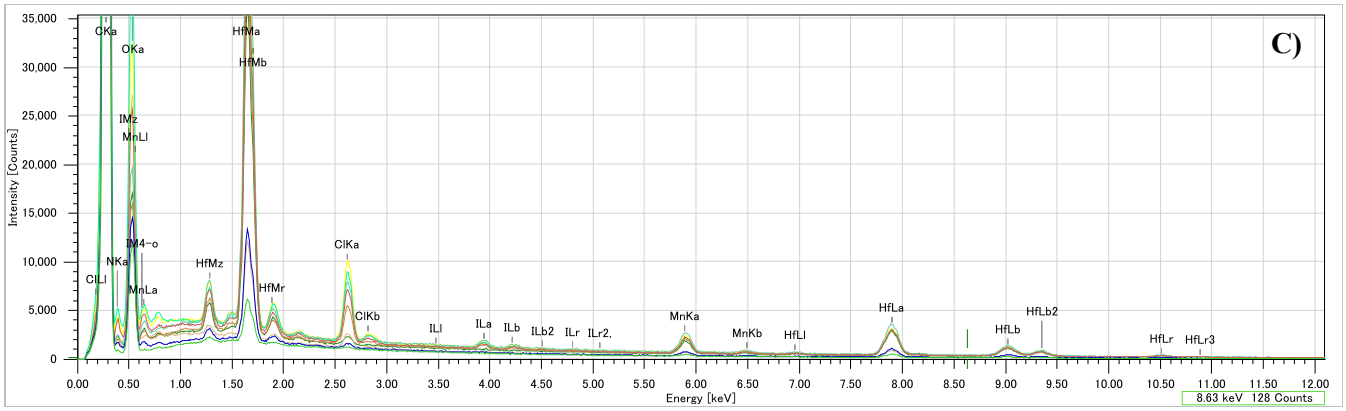


Figure S26. EDS spectra of Hf-PCN-222(Mn) before catalysis (A), after 1 run (B) and after 5 runs (C)

9. Comparison of MOF systems for the auto-tandem oxidative cycloaddition

Table S10. Comparison table of MOF-catalyzed oxidative carboxylation of alkenes to cyclic organic carbonates.

	Catalyst	Co-catalyst	Oxidant	Solvent	Pressure (bar)	Temperature (°C)	COC yield (%)	Alkene scope	Reference
1	Cr-MIL-101	TBAB	TBHP[a]	none	8	25	19	Styrene	J. Energy Chem. 2013, 22, 1, 130–135.[20]
2	ZnW-PYI2	TBAB	TBHP[b]	none	50	50	90	4 alkenes	Nat. Commun. 2015, 6, 10007.[21]
3	MOF-590	TBAB	TBHP[b]	none	1	80	87	Styrene	Inorg. Chem. 2018, 57, 21, 13772–13782.[22]
4	MOF-892	TBAB	TBHP[b]	none	1	80	80	Styrene	ACS Appl. Mater. Interfaces 2018, 10, 1, 733–744.[23]
5	ImBr-MOF-545(Mn)	none	O_2/IBA[c]	none	5	70	98	7 alkenes	Appl. Catal. B: Environ. 2020, 273, 119059.[24]
6	Co-NDPhTZ	TBAB	TBHP[b]	none	3	110	78	Styrene	J. CO2 Util. 2023, 67, 102298.[25]
7	NiBDC NS	TBAB	TBHP[b]	none	1	80	87	6 alkenes	Chem. Eng. Sci. 2023, 278, 118898.[26]
8	Zr-BTB/PA-Co	none	THBP[b]	none	1	80	93	8 alkenes	AIChE J. 2024, 70, 2 e18290.[27]
9	IL-Au@UiO-66-NH_2/CMC	TBAB	TBHP[b]	none	1	80	80	8 alkenes	ACS Appl. Mater. Interfaces 2024, 16, 6, 7364–7373.[28]
10	Fe@MOF1	TBAB	PhIO	DCM	8	50	90	3 alkenes	Chem. Eur. J. 2018, 24, 16662.[29]
11	Ti-MMM-E	TBAB	TBHP[b]	none	8	70	70	6 alkenes	Appl. Catal. B: Environ. 2016, 181, 363–370.[30]
12	Fe-IPOP1	None	PhIO	DCM	1	80	96	10 alkenes	Inorg. Chem. Front., 2023,10, 2088-2099.[31]
13	Zr-CPB-Cu	TBAB	TBHP[b]	none	1	80	92	8 alkenes	New J. Chem., 2024,48, 5300-5310[32]
14	Mn@Hf-PCN222	TBAB	PhIO	none	1	40	Up to 75% Isolated yield	27 alkenes	This study

[a]Aqueous solution. [b]In decane. [c]5 bar of O_2.

10. References

[1] H. Saltzman, J. G. Sharefkin, *Org. Synth.* **1963**, 60.

[2] H. Seo, A. Liu, T. F. Jamison, *J. Am. Chem. Soc.* **2017**, *139*, 13969-13972.

[3] A. Deb, S. Manna, A. Modak, T. Patra, S. Maity, D. Maiti, *Angew. Chem. Int. Ed.* **2013**, *52*, 9747-9750.

[4] Y.-Y. Cheng, J.-X. Yu, T. Lei, H.-Y. Hou, B. Chen, C.-H. Tung, L.-Z. Wu, *Angew. Chem. Int. Ed.* **2021**, *60*, 26822-26828.

[5] C. Giordano, C. Gallina, V. Consalvi, R. Scandurra, *Eur. J. Med. Chem.* **1990**, *25*, 479-487.

[6] H. Beyzavi, N. A. Vermeulen, A. J. Howarth, S. Tussupbayev, A. B. League, N. M. Schweitzer, J. R. Gallagher, A. E. Platero-Prats, N. Hafezi, A. A. Sarjeant, J. T. Miller, K. W. Chapman, J. F. Stoddart, C. J. Cramer, J. T. Hupp, O. K. Farha, *J. Am. Chem. Soc.* **2015**, *137*, 13624-13631.

[7] S. Li, H.-M. Mei, S.-L. Yao, Z.-Y. Chen, Y.-L. Lu, L. Zhang, C.-Y. Su, *Chem. Sci.* **2019**, *10*, 10577-10585.

[8] S. Carrasco, A. Sanz-Marco, B. Martín-Matute, *Organometallics* **2019**, *38*, 3429-3435.

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

[10] Y. Fan, M. Tiffner, J. Schörgenhumer, R. Robiette, M. Waser, S. R. Kass, *J. Org. Chem.* **2018**, *83*, 9991-10000.

[11] Bhaskaran, M. Trivedi, A. K. Yadav, G. Singh, A. Kumar, G. Kumar, A. Husain, N. P. Rath, *Dalton Trans.* **2019**, *48*, 10078-10088.

[12] L. Poletti, C. Rovegno, G. Di Carmine, F. Vacchi, D. Ragno, A. Brandolese, A. Massi, P. Dambruoso, in *Molecules, Vol. 28*, **2023**.

[13] H. Ma, S. Liu, H. Wang, G. Li, K. Zhao, X. Cui, F. Shi, *Green Chem.* **2023**, *25*, 2293-2298.

[14] M. Navarro, A. Garcés, L. F. Sánchez-Barba, D. González-Lizana, A. Lara-Sánchez, *Dalton Trans.* **2023**, *52*, 6105-6116.

[15] A. Axelsson, A. Antoine-Michard, H. Sundén, *Green Chem.* **2017**, *19*, 2477-2481.

[16] Y.-D. Li, D.-X. Cui, J.-C. Zhu, P. Huang, Z. Tian, Y.-Y. Jia, P.-A. Wang, *Green Chem.* **2019**, *21*, 5231-5237.

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

[18] T. Iwasaki, N. Kihara, T. Endo, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 713-719.

[19] S. E. Lyubimov, M. V. Sokolovskaya, B. Chowdhury, A. V. Arzumanyan, R. S. Tukhvatshin, L. F. Ibragimova, A. A. Tyutyunov, V. A. Davankov, A. M. Muzafarov, *Russ. Chem. Bull.* **2019**, *68*, 1866-1868.

[20] O. V. Zalomaeva, N. V. Maksimchuk, A. M. Chibiryaev, K. A. Kovalenko, V. P. Fedin, B. S. Balzhinimaev, *J. Energy Chem.* **2013**, *22*, 130-135.

[21] Q. Han, B. Qi, W. Ren, C. He, J. Niu, C. Duan, *Nat. Commun.* **2015**, *6*, 10007.

[22] H. T. D. Nguyen, Y. B. N. Tran, H. N. Nguyen, T. C. Nguyen, F. Gándara, P. T. K. Nguyen, *Inorg. Chem.* **2018**, *57*, 13772-13782.

[23] P. T. K. Nguyen, H. T. D. Nguyen, H. N. Nguyen, C. A. Trickett, Q. T. Ton, E. Gutiérrez-Puebla, M. A. Monge, K. E. Cordova, F. Gándara, *ACS Appl. Mater. Interfaces* **2018**, *10*, 733-744.

[24] K. Yu, P. Puthiaraj, W.-S. Ahn, *Appl. Catal. B* **2020**, *273*, 119059.

[25] A. Valverde-González, M. C. Borrallo-Aniceto, U. Díaz, E. M. Maya, F. Gándara, F. Sánchez, M. Iglesias, *J. CO2 Util.* **2023**, *67*, 102298.

[26] Y. Yu, X. Chen, X. Wang, X. Feng, S. Liu, C. Duan, Y. Wu, H. Xi, *Chem. Eng. Sci.* **2023**, *278*, 118898.

[27] Y. Yu, X. Feng, Z. Xie, Y. Wu, H. Xi, *AlChE J.* **2024**, *70*, e18290.

[28] X. Zhao, G. Chang, H. Xu, Y. Yao, D. Dong, S. Yang, G. Tian, X. Yang, *ACS Appl. Mater. Interfaces* **2024**, *16*, 7364-7373.

[29] N. Sharma, S. S. Dhankhar, S. Kumar, T. J. D. Kumar, C. M. Nagaraja, *Chem. Eur. J.* **2018**, *24*, 16662-16669.

[30] N. V. Maksimchuk, I. D. Ivanchikova, A. B. Ayupov, O. A. Kholdeeva, *Appl. Catal. B* **2016**, *181*, 363-370.

[31] R. Das, S. Kamra, C. M. Nagaraja, *Inorganic Chemistry Frontiers* **2023**, *10*, 2088-2099.

[32] Y. B. N. Tran, P. T. K. Nguyen, V.-A. Dao, V.-D. Le, *New J. Chem.* **2024**, *48*, 5300-5310.

11. NMR spectra

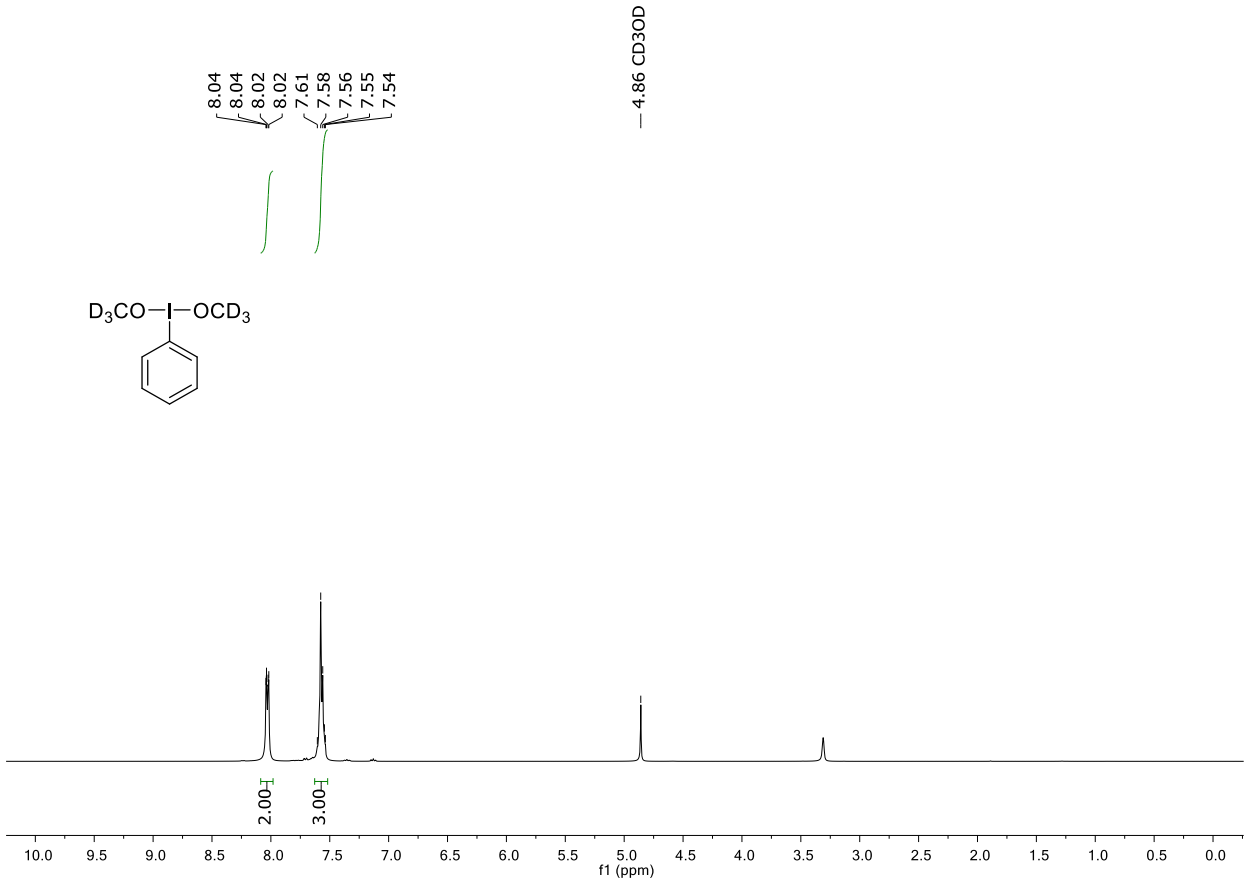


Figure S27. ^{1}H NMR (400 MHz, Methanol-d_4) spectrum of bis(methyl-d3)(phenyl)- λ^3-iodane.

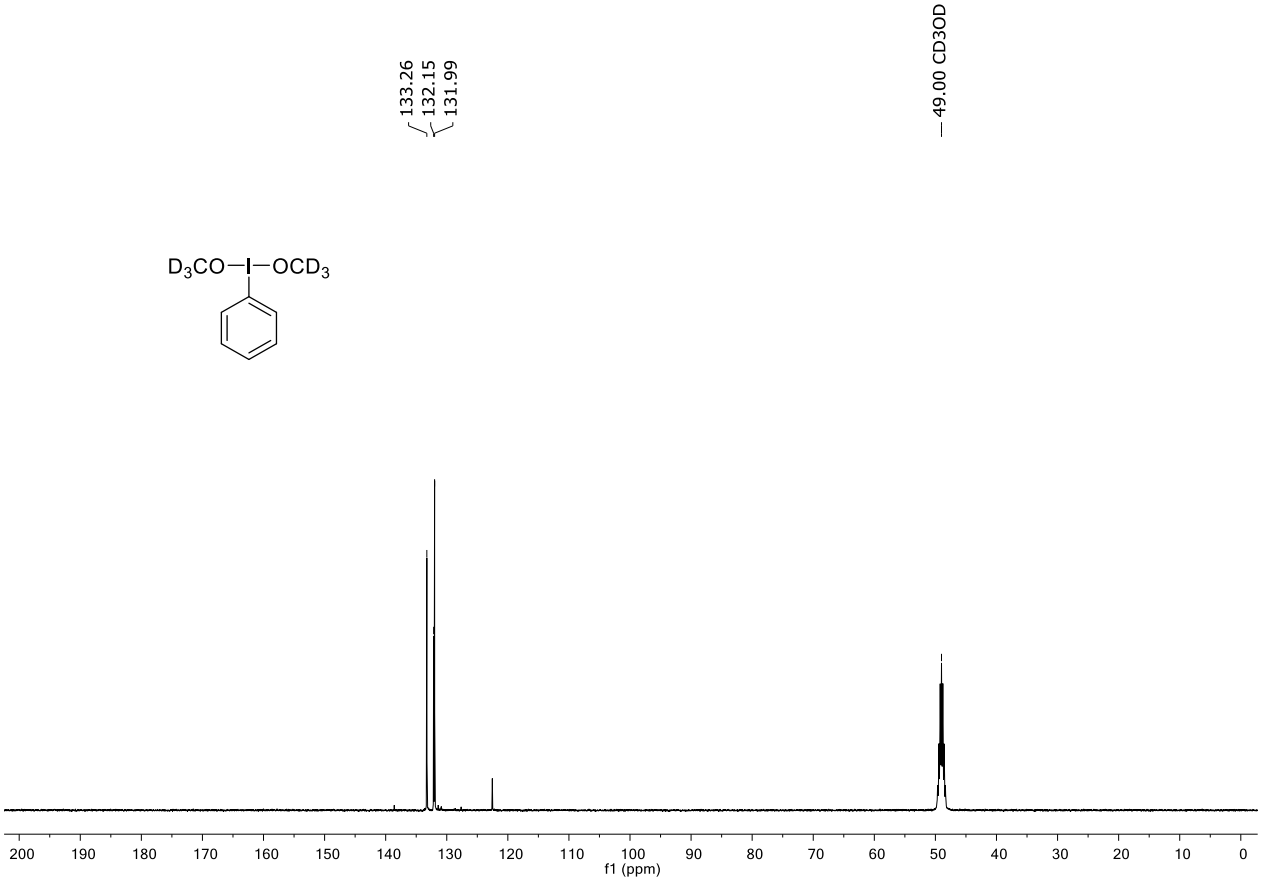


Figure S28. ^{13}C NMR (101 MHz, Methanol-d_4) spectrum of bis(methyl-d3)(phenyl)- λ^3-iodane.

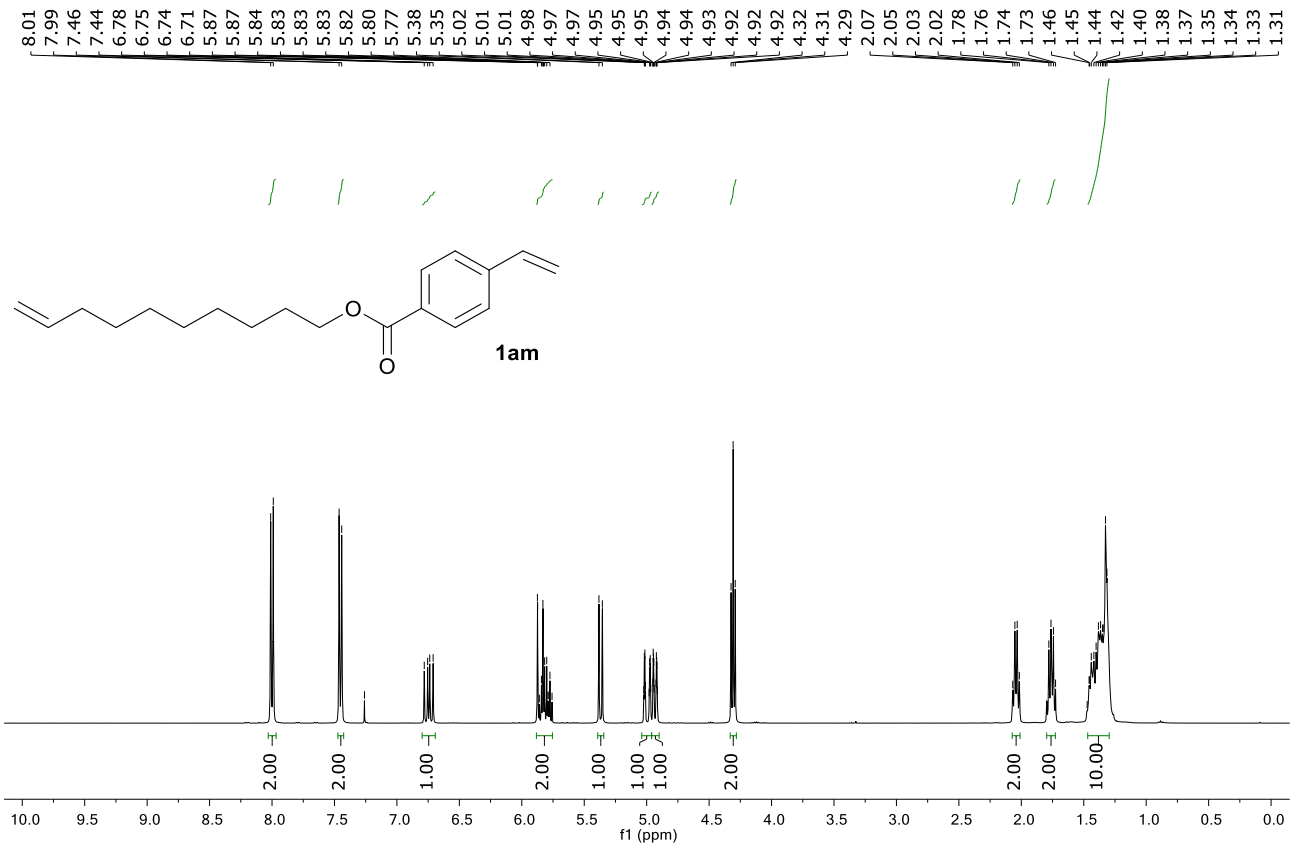


Figure S29. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of dec-9-en-1-yl 4-vinylbenzoate (**1am**).

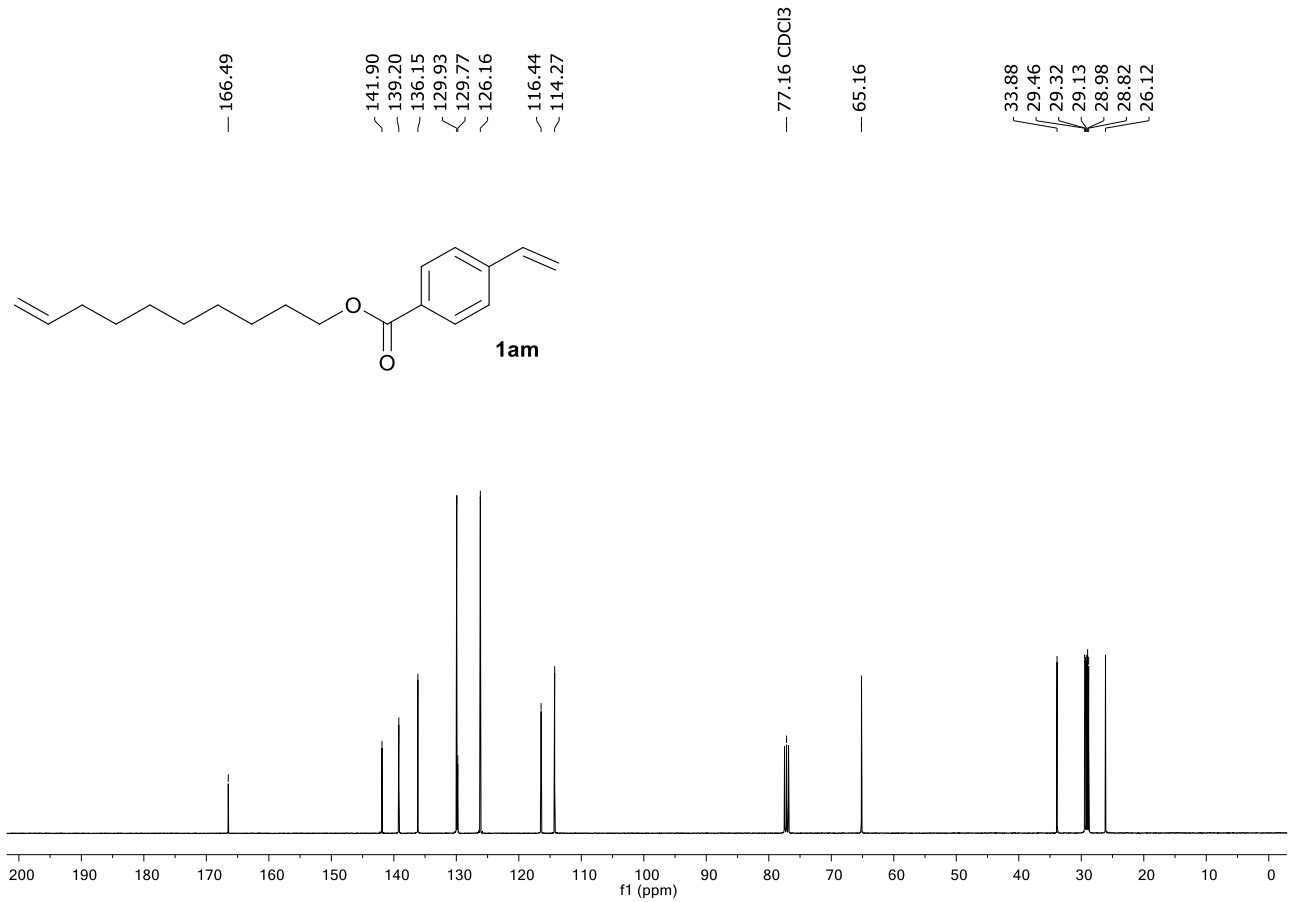


Figure S30. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of dec-9-en-1-yl 4-vinylbenzoate (**1am**).

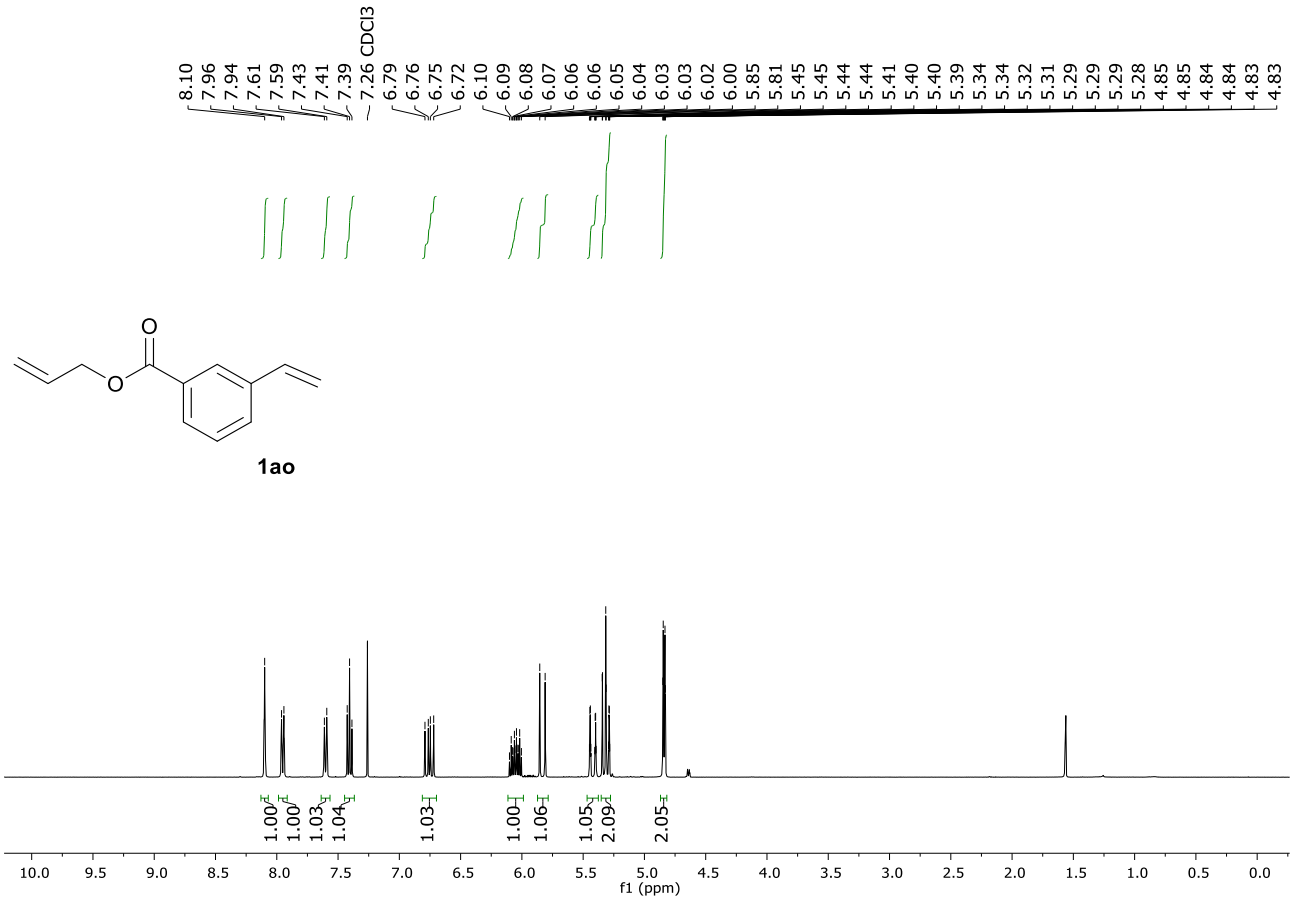


Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of allyl 3-vinylbenzoate (**1ao**).

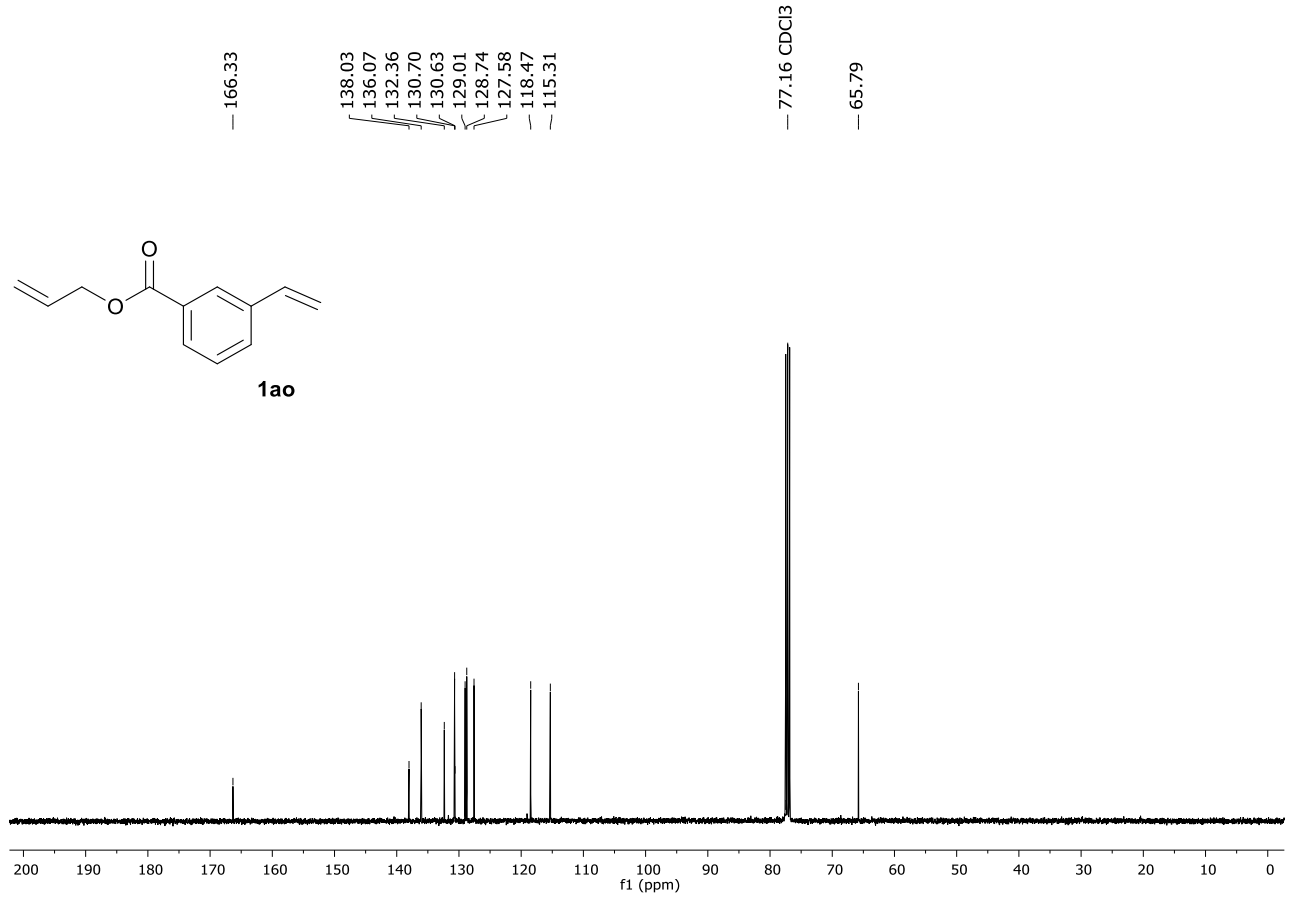


Figure S32. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of allyl 3-vinylbenzoate (**1ao**).

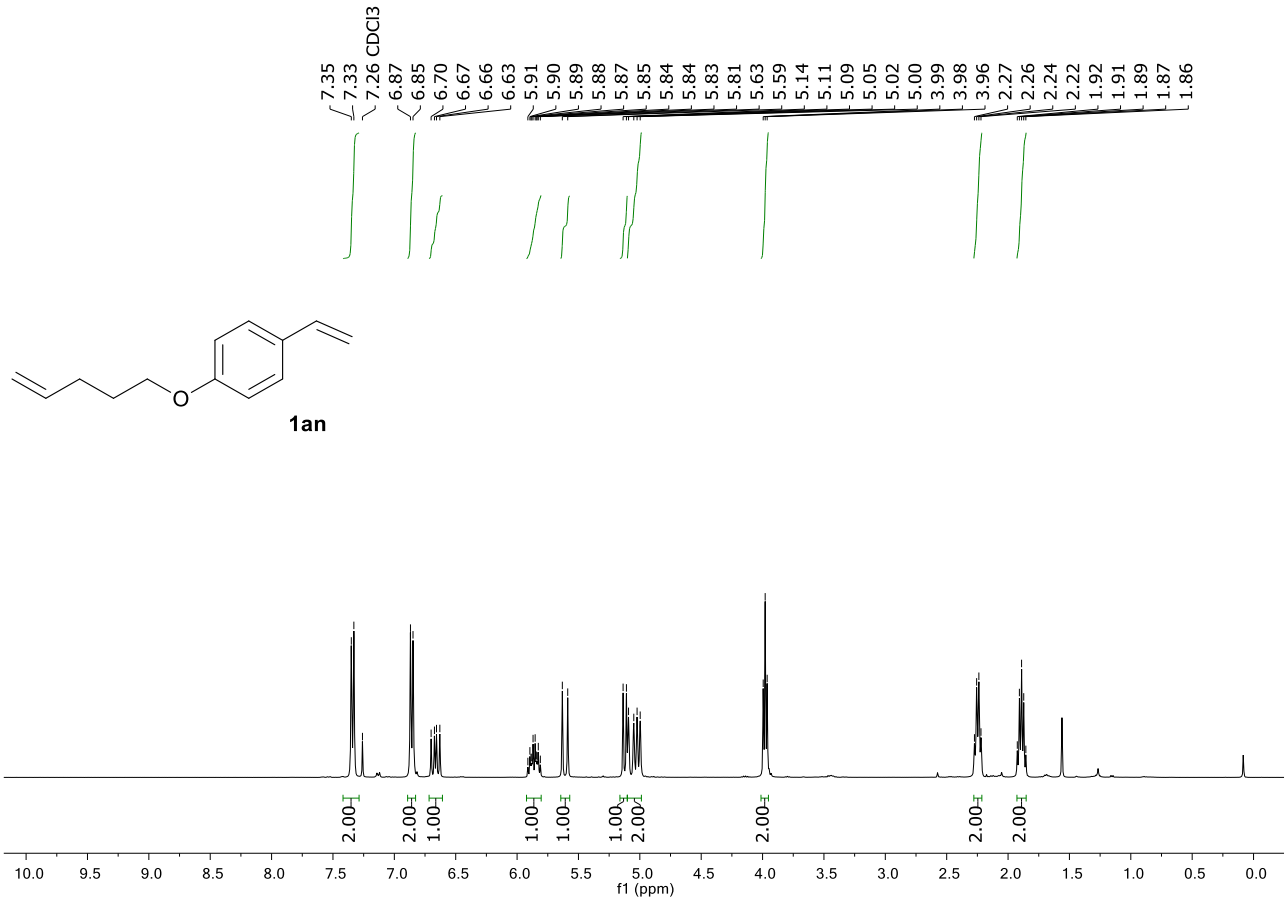


Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-(pent-4-en-1-yloxy)-4-vinylbenzene (**1an**).

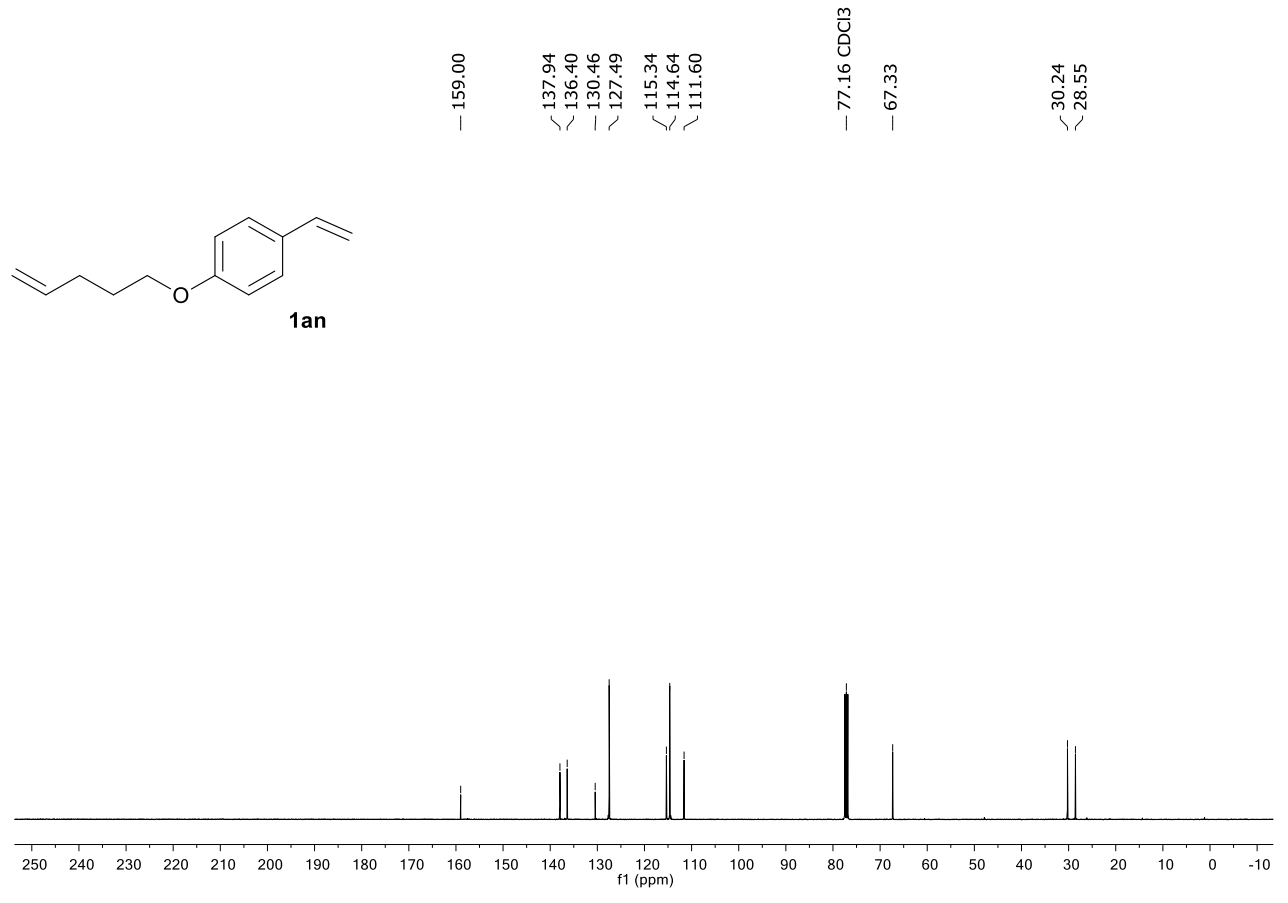


Figure S34. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1-(pent-4-en-1-yloxy)-4-vinylbenzene (**1an**).

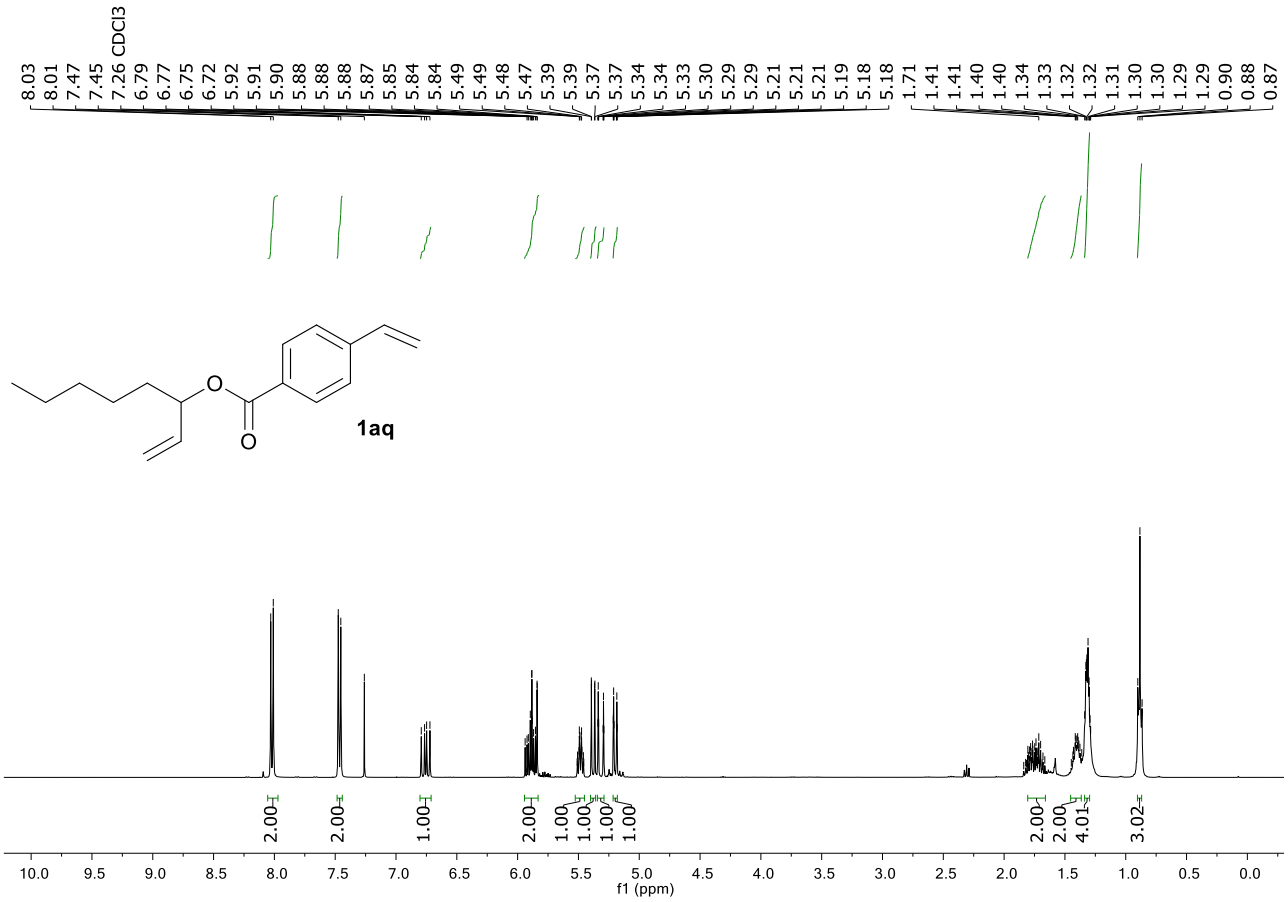


Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of oct-1-en-3-yl 4-vinylbenzoate (**1aq**).

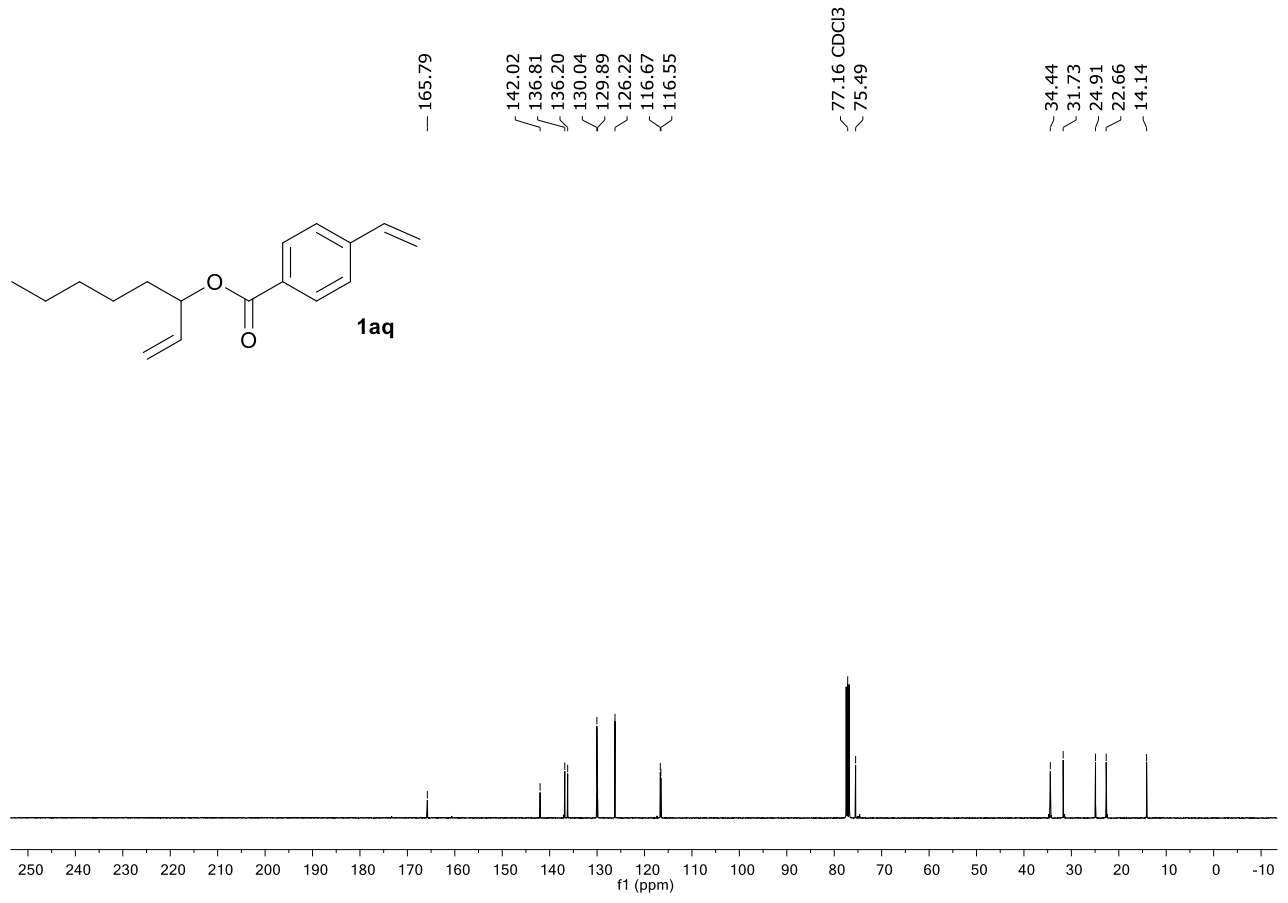


Figure S36. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of oct-1-en-3-yl 4-vinylbenzoate (**1aq**).

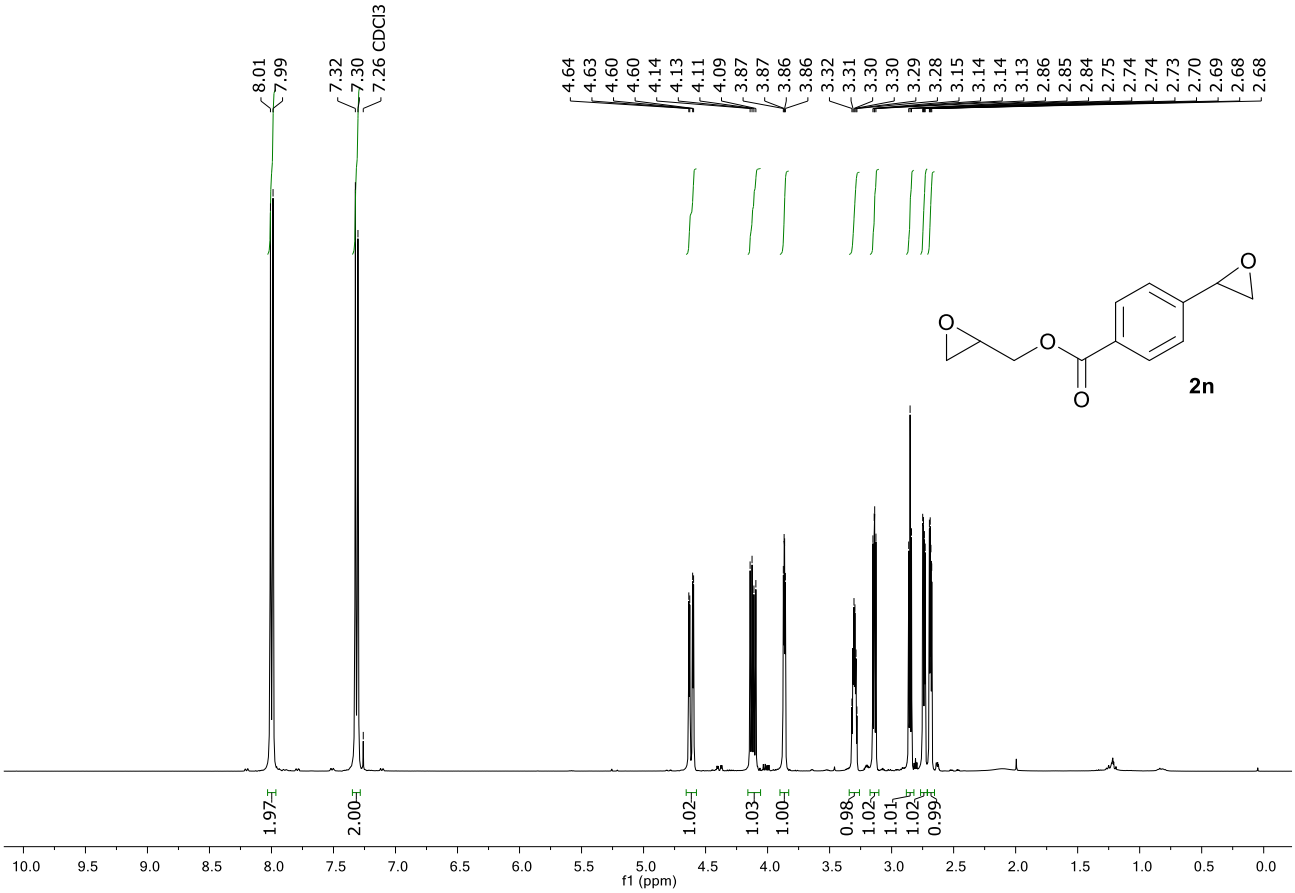


Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of oxiran-2-ylmethyl 4-(oxiran-2-yl)benzoate (**2n**).

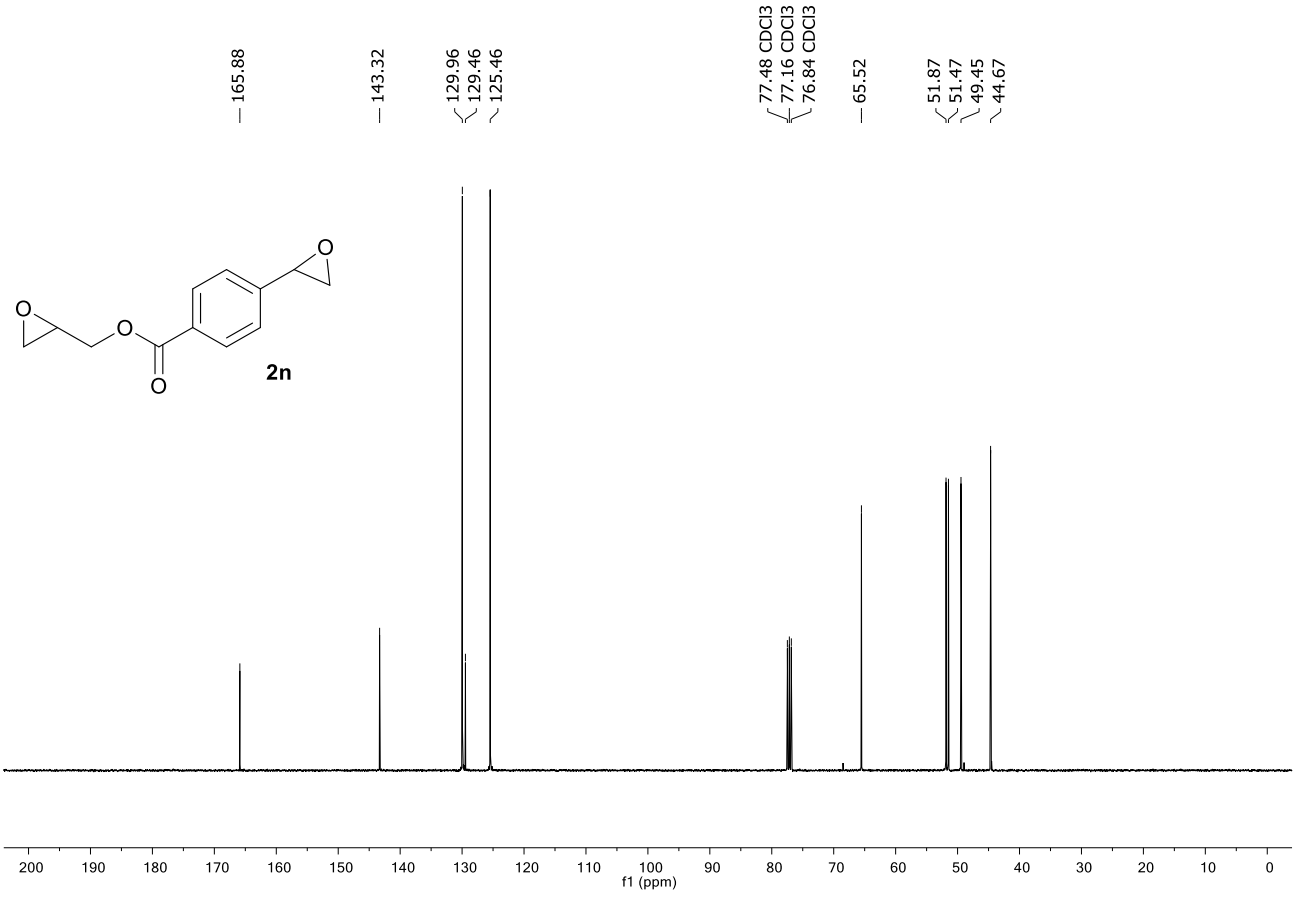


Figure S38. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of oxiran-2-ylmethyl 4-(oxiran-2-yl)benzoate (**2n**).

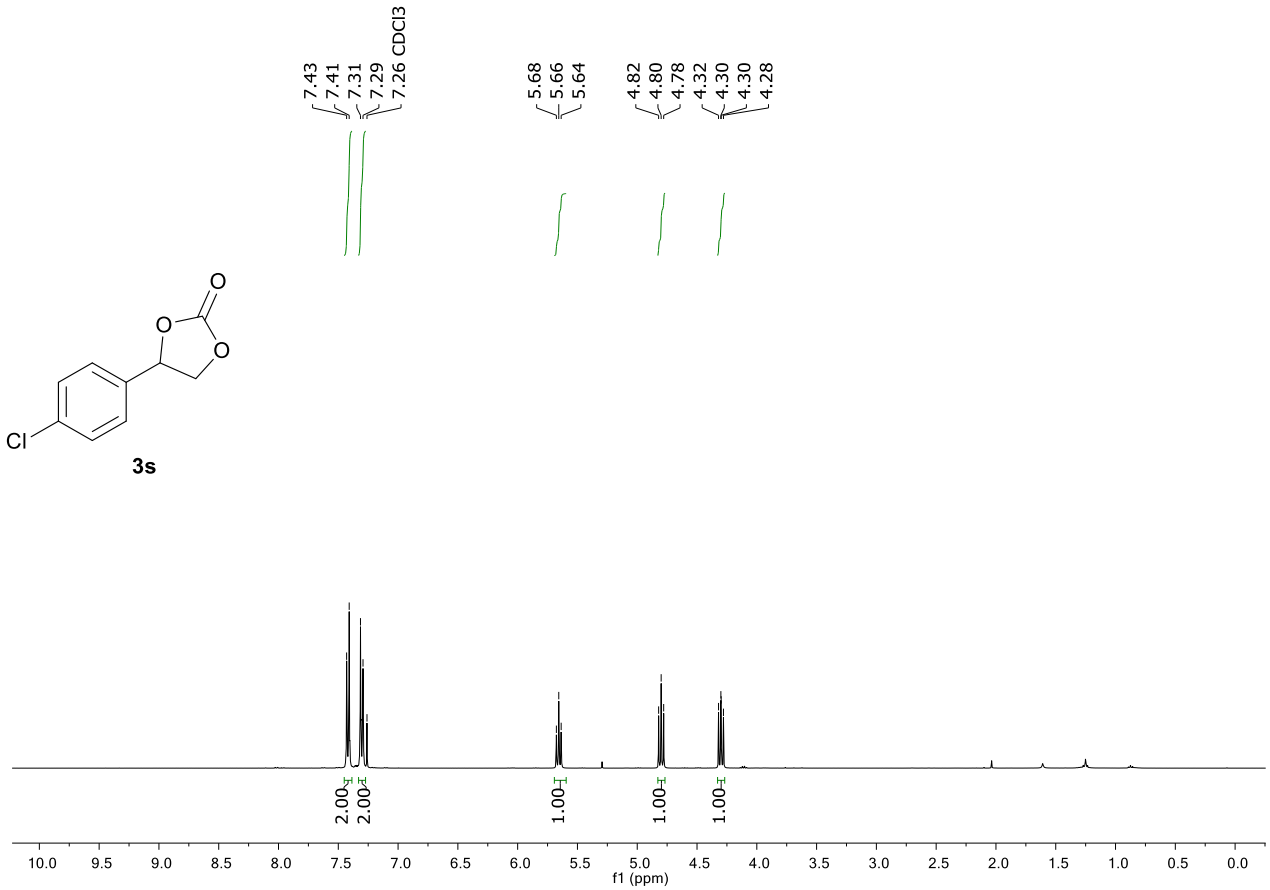


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(4-chlorophenyl)-1,3-dioxolan-2-one (**3s**).

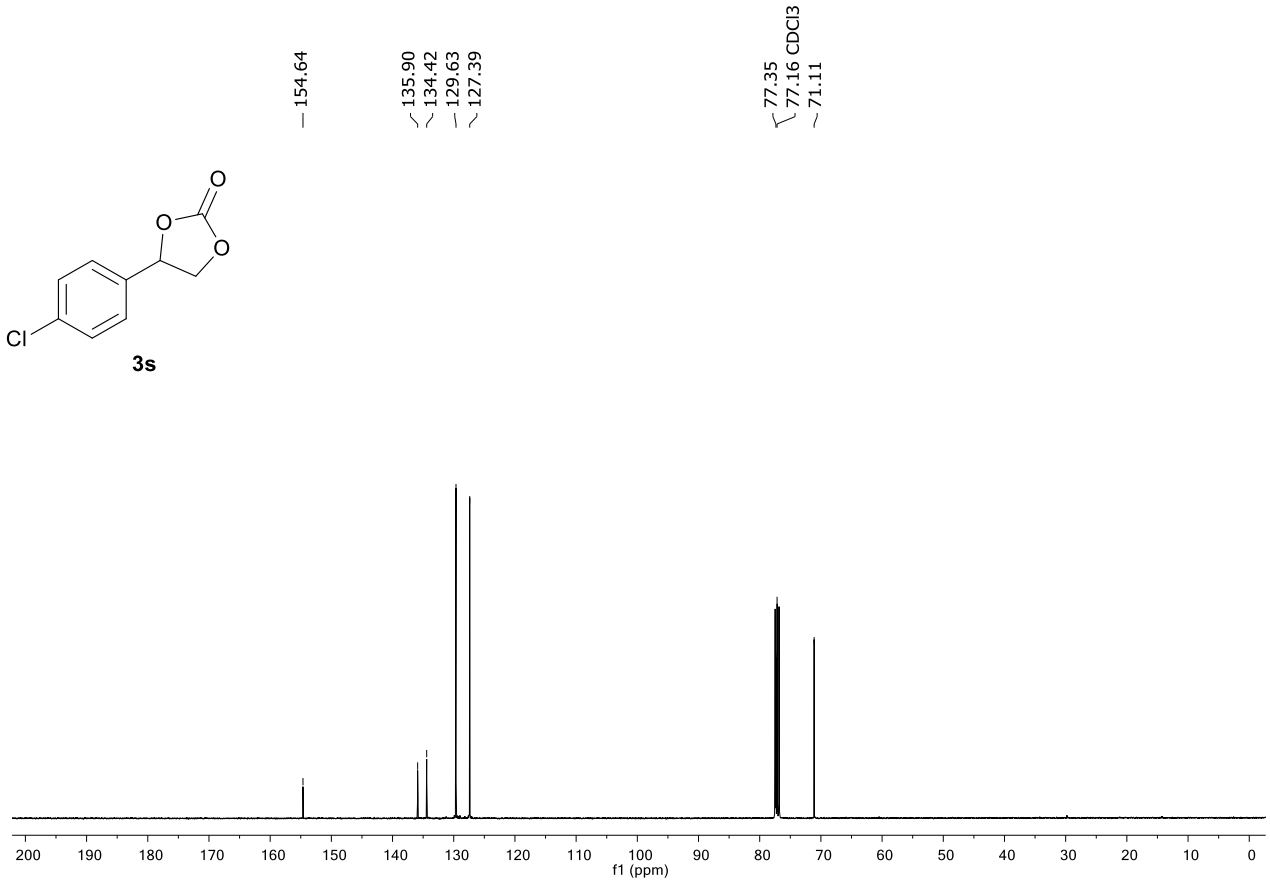


Figure S40. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(4-chlorophenyl)-1,3-dioxolan-2-one (**3s**).

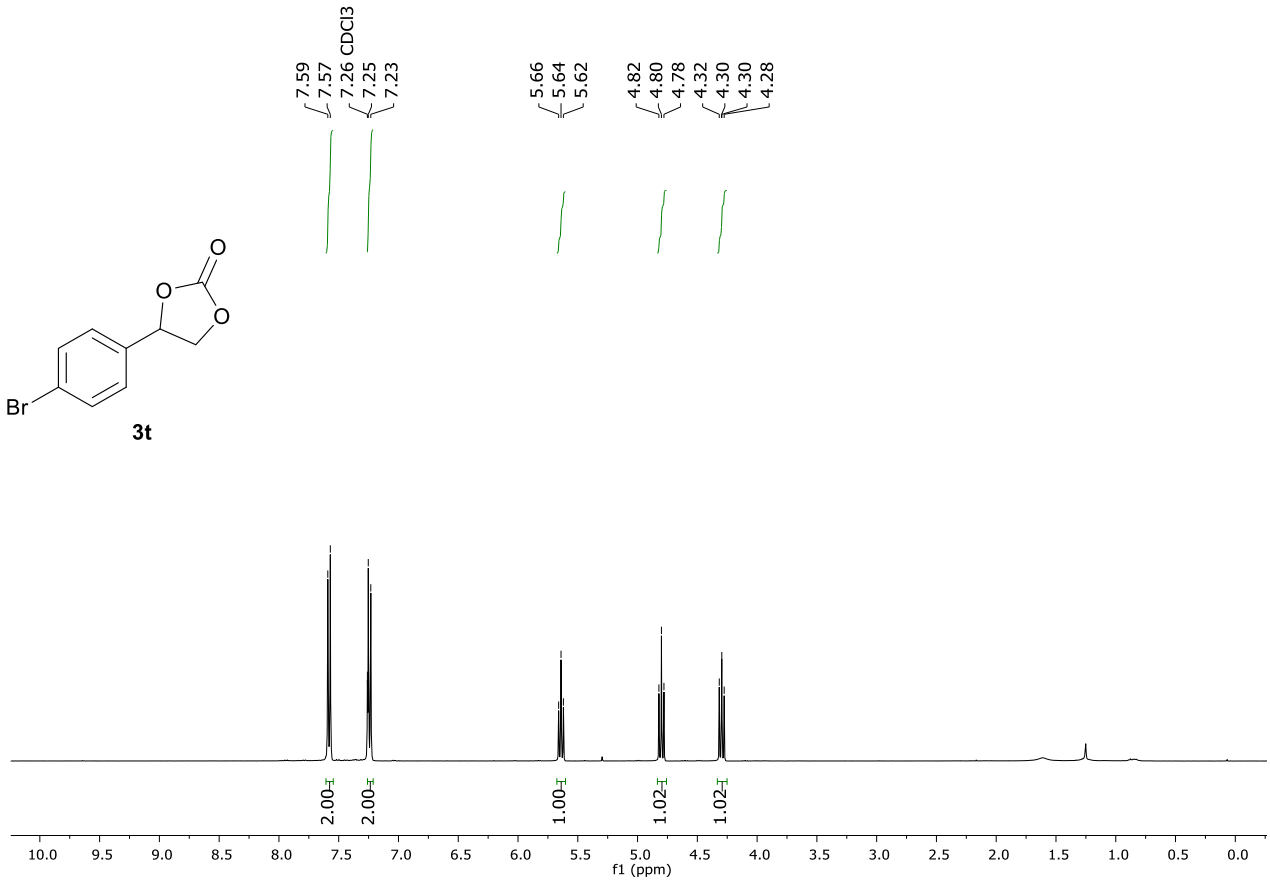


Figure S41. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(4-bromophenyl)-1,3-dioxolan-2-one (**3t**).

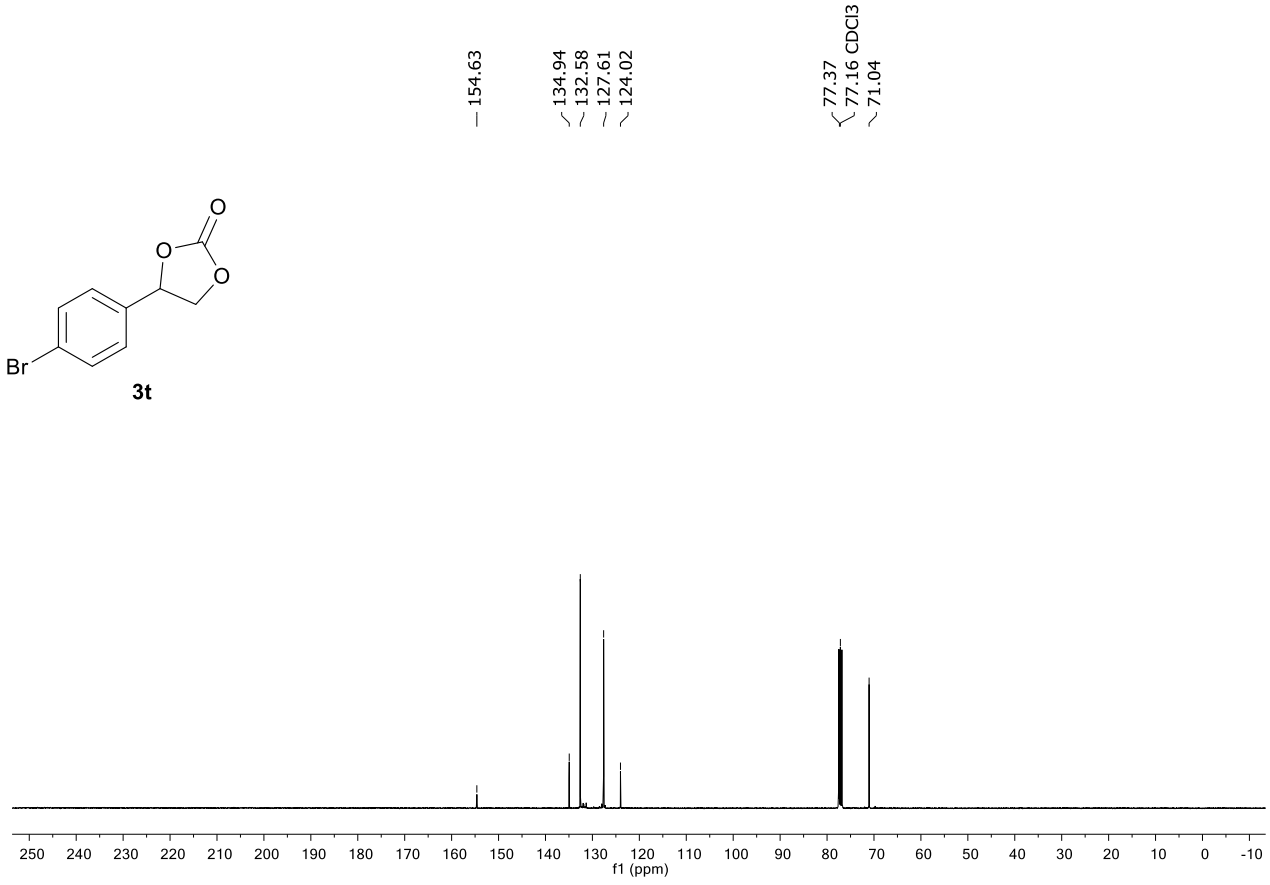


Figure S42. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(4-bromophenyl)-1,3-dioxolan-2-one (**3t**).

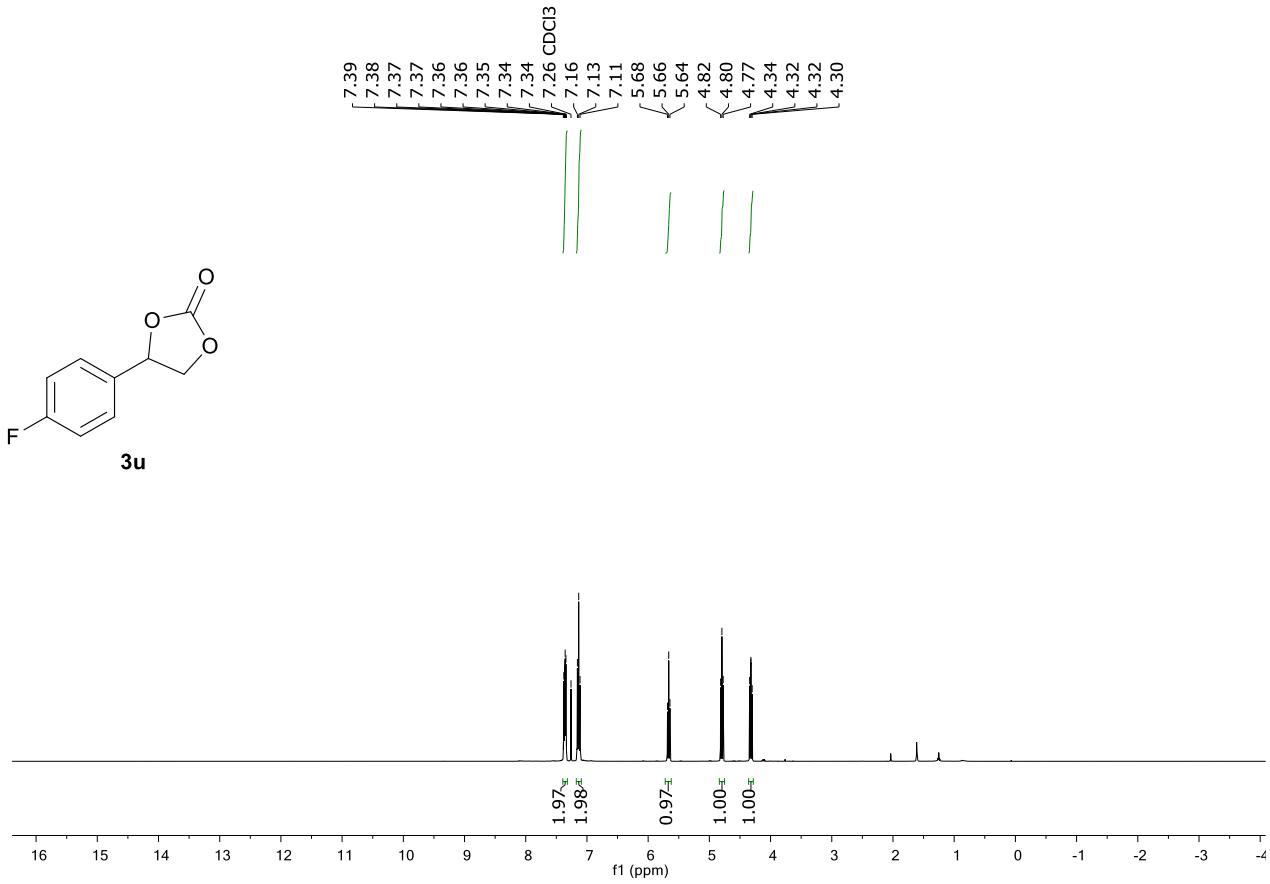


Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(4-fluorophenyl)-1,3-dioxolan-2-one (**3u**).

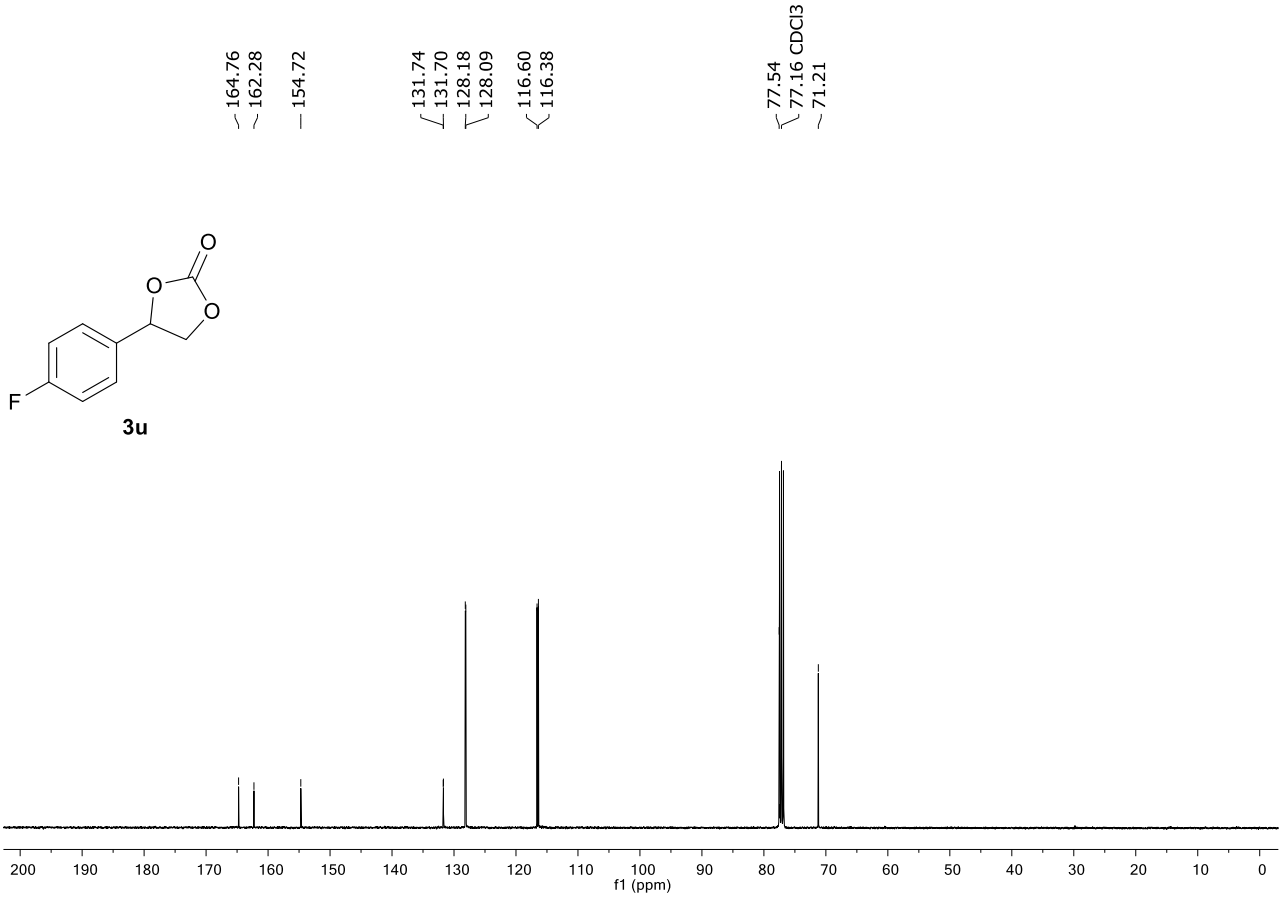


Figure S44. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(4-fluorophenyl)-1,3-dioxolan-2-one (**3u**).

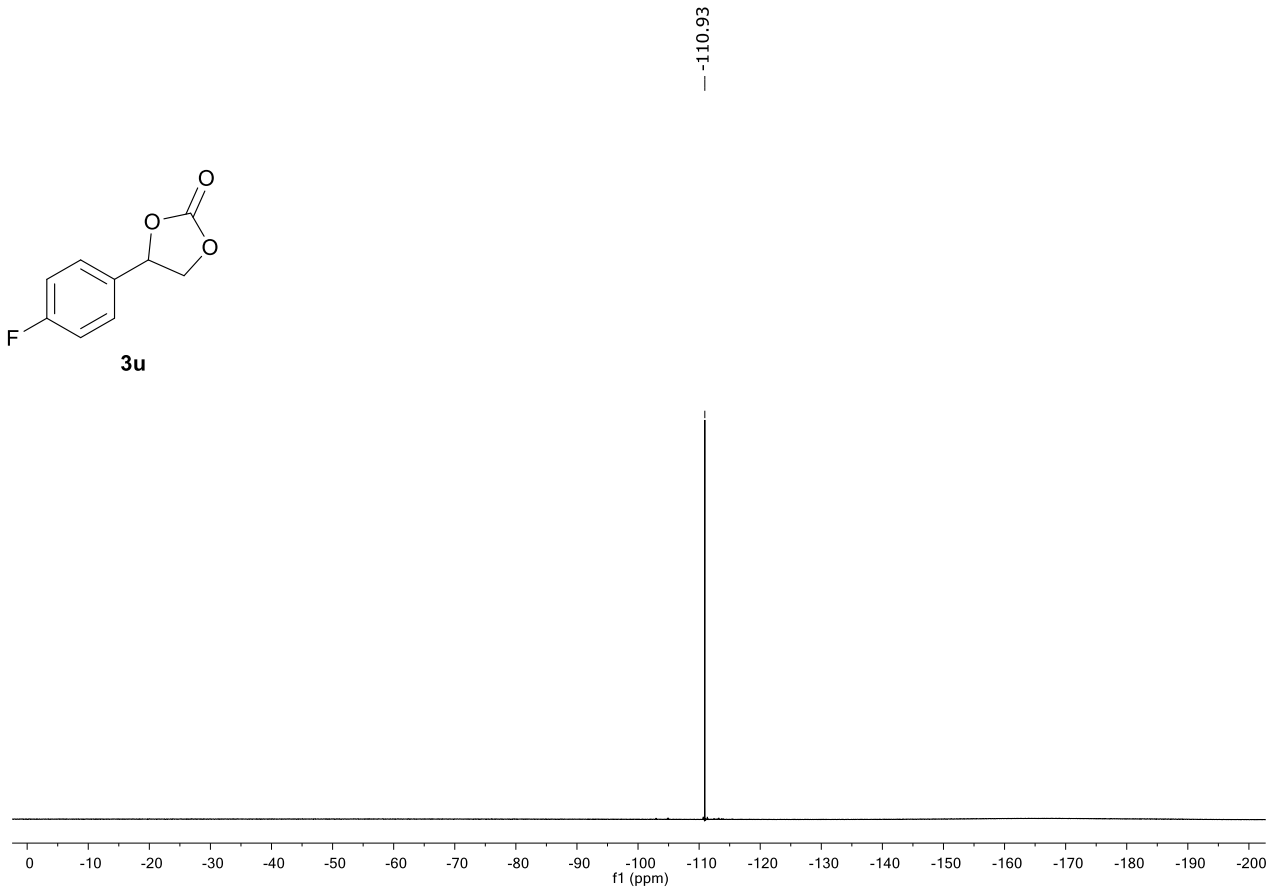


Figure S45. ^{19}F NMR (377 MHz, $CDCl_3$) spectrum of 4-(4-fluorophenyl)-1,3-dioxolan-2-one (**3u**).

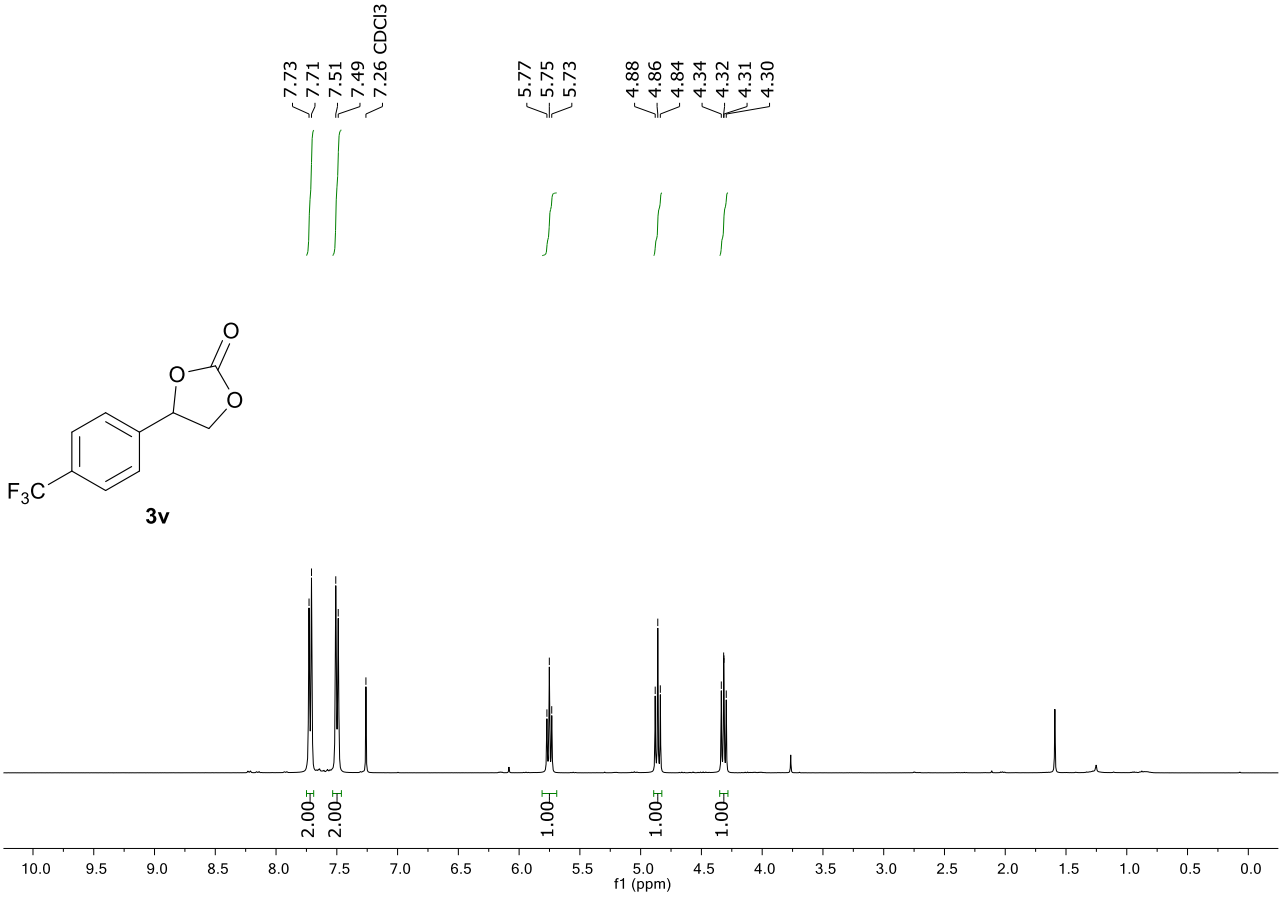


Figure S46. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(4-(trifluoromethyl)phenyl)-1,3-dioxolan-2-one (**3v**).

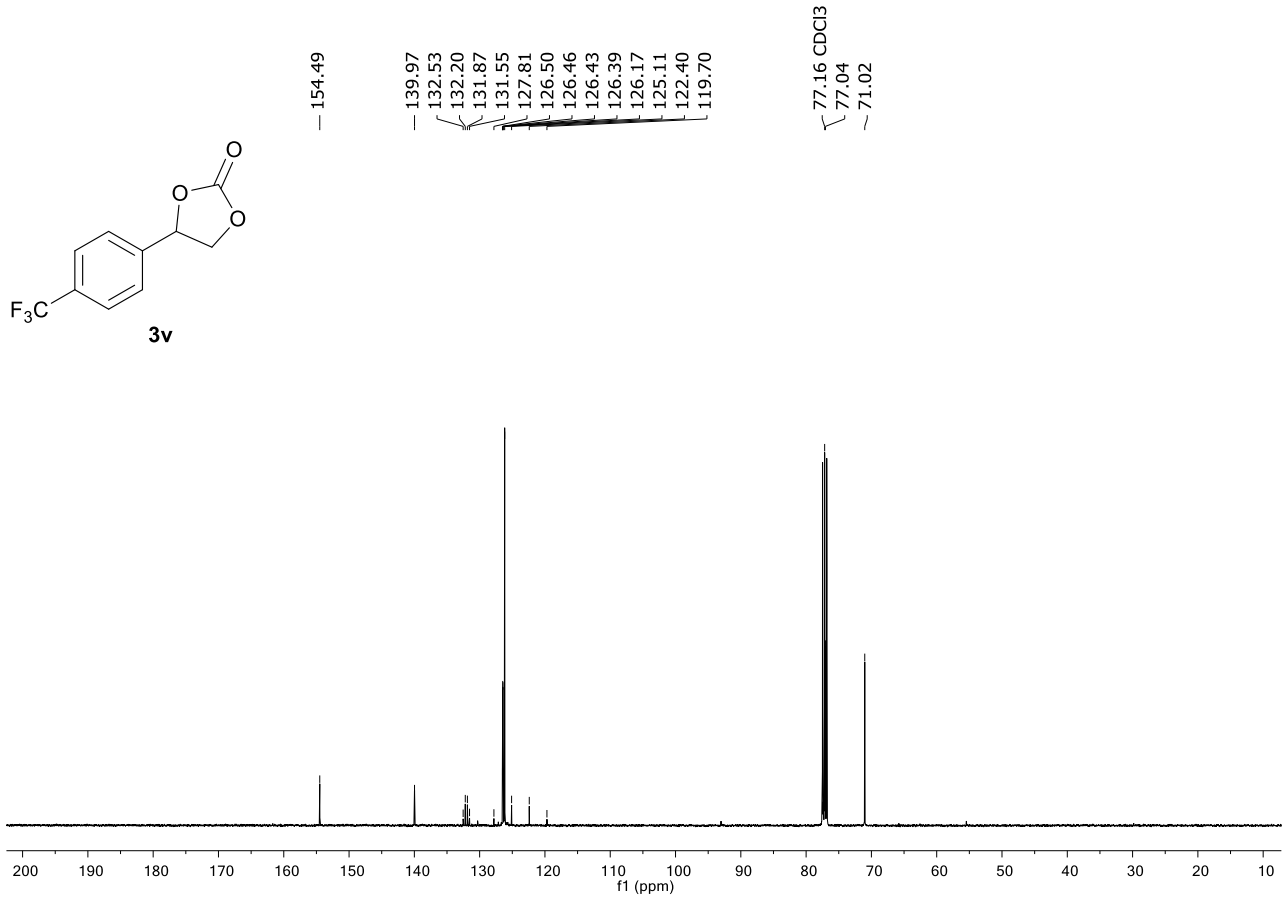


Figure S47. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(4-(trifluoromethyl)phenyl)-1,3-dioxolan-2-one (**3v**).

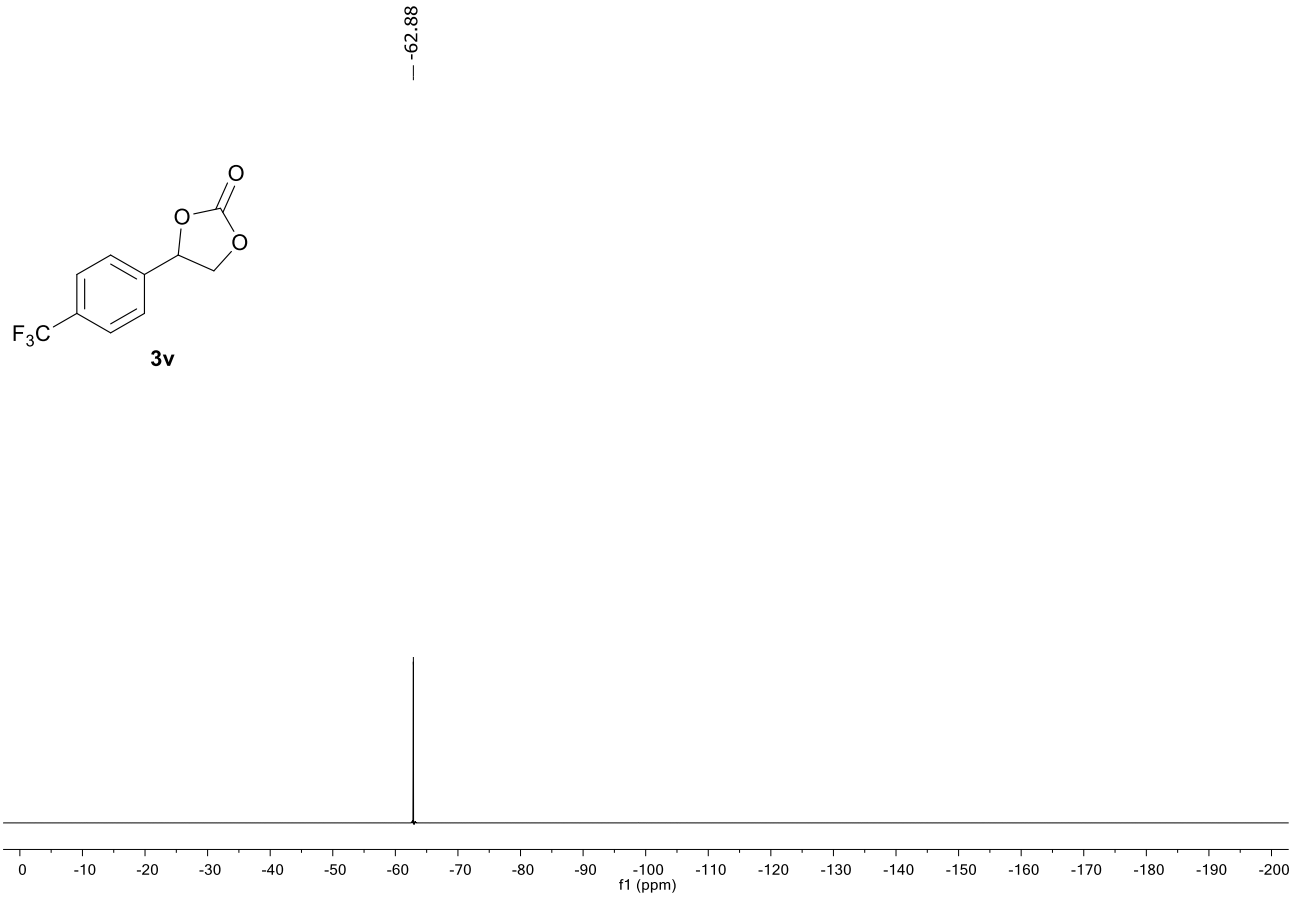


Figure S48. ^{19}F NMR (377 MHz, $CDCl_3$) spectrum of 4-(4-(trifluoromethyl)phenyl)-1,3-dioxolan-2-one (**3v**).

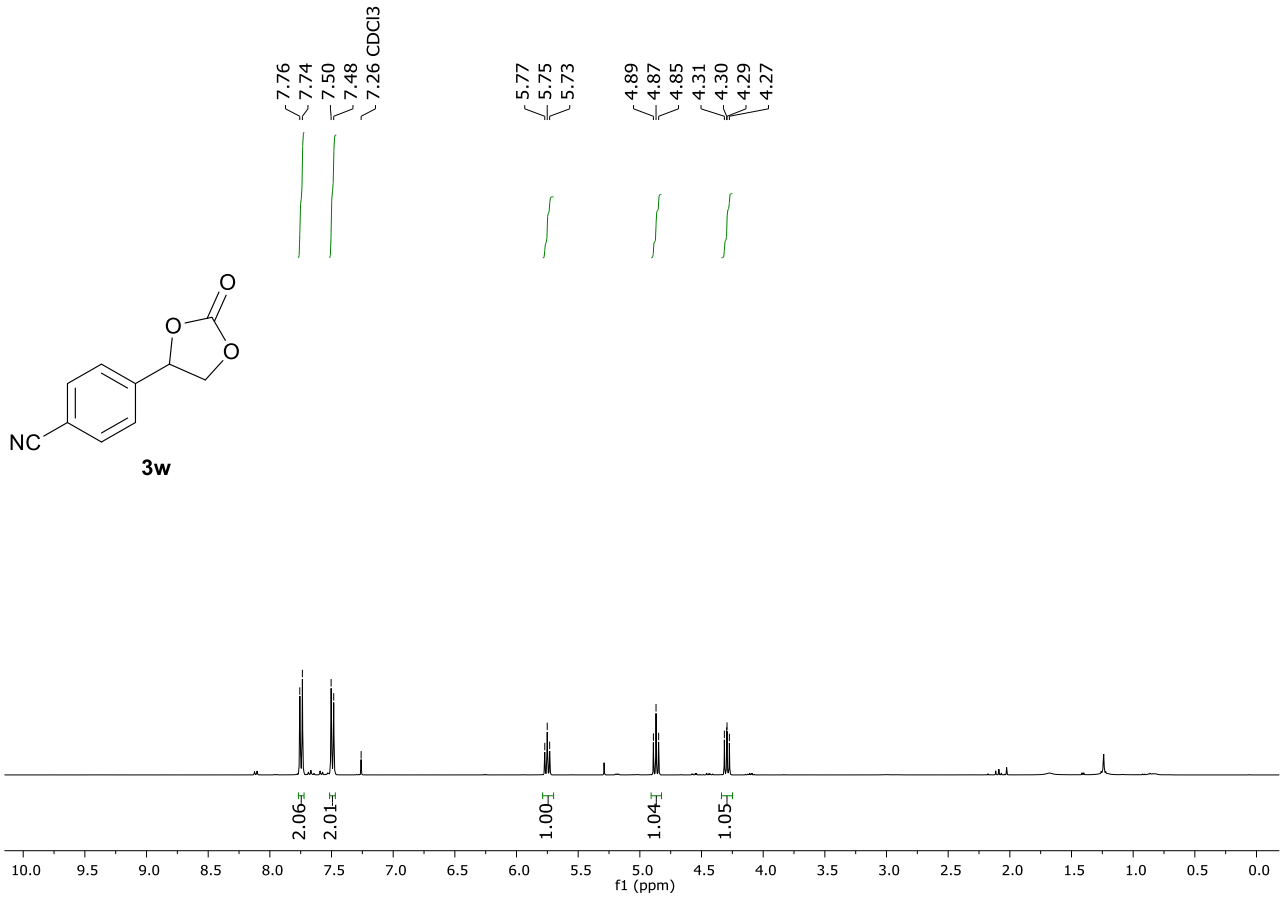


Figure S49. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(2-oxo-1,3-dioxolan-4-yl)benzonitrile (**3w**).

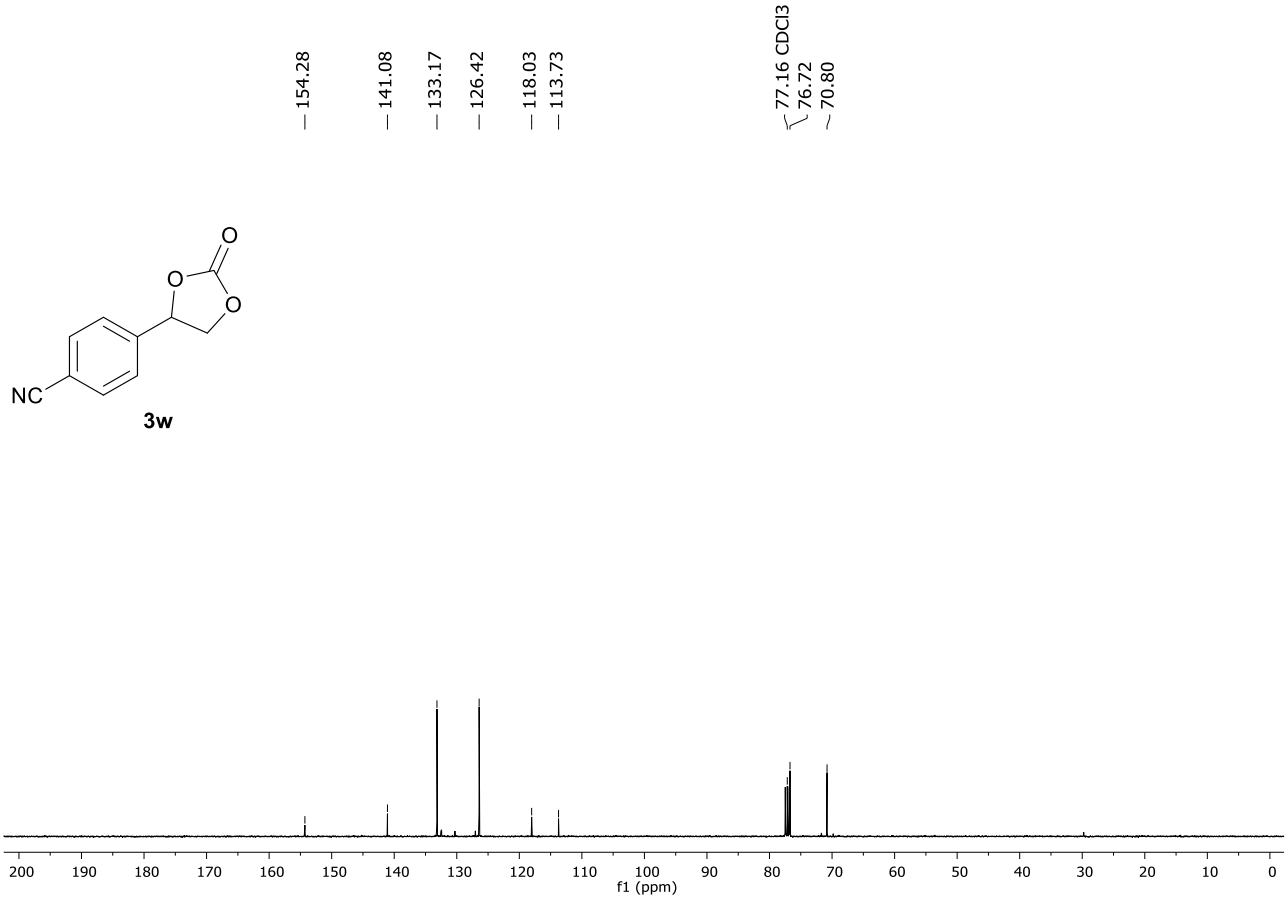


Figure S50. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(2-oxo-1,3-dioxolan-4-yl)benzonitrile (**3w**).

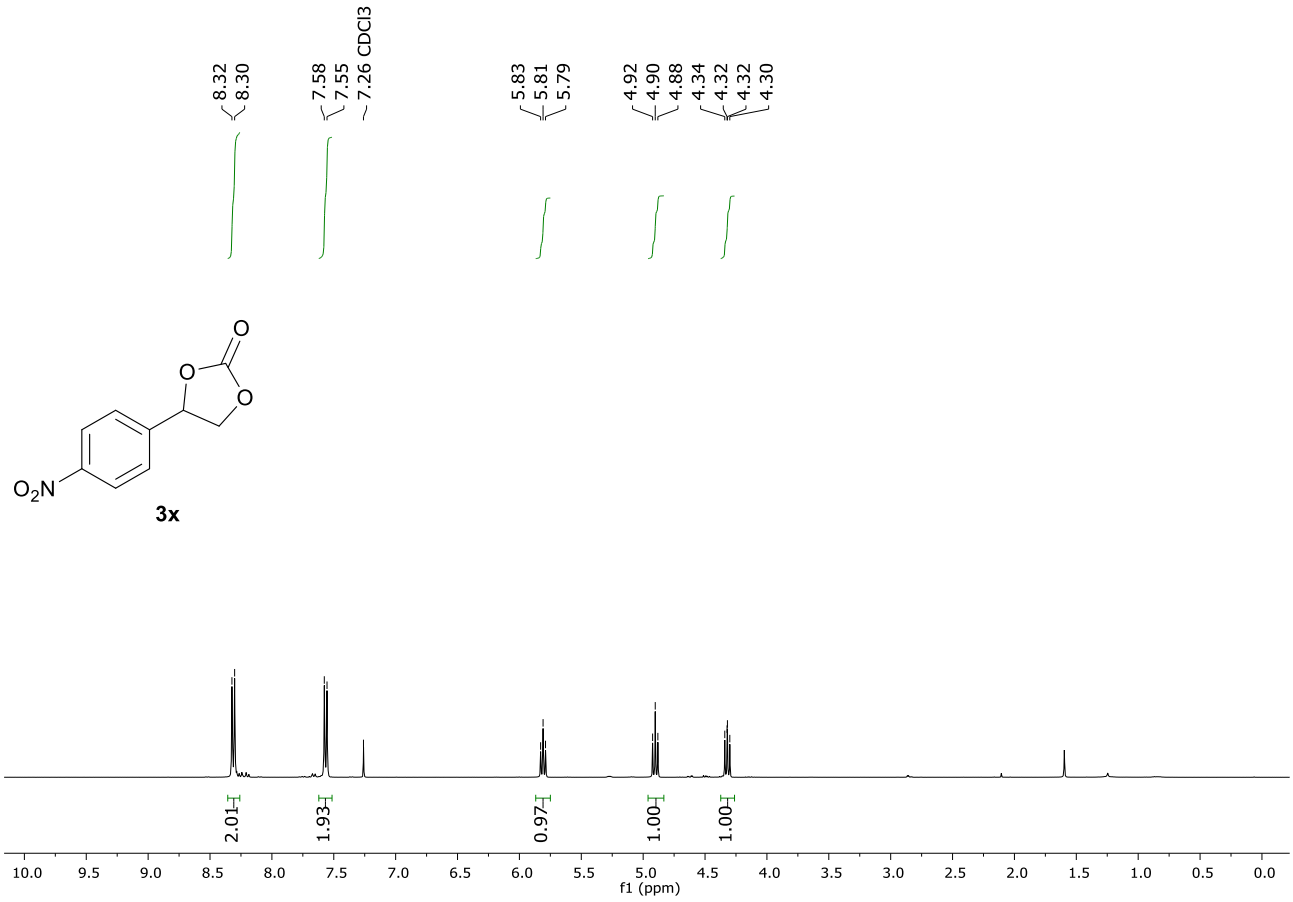


Figure S51. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(4-nitrophenyl)-1,3-dioxolan-2-one (**3x**).

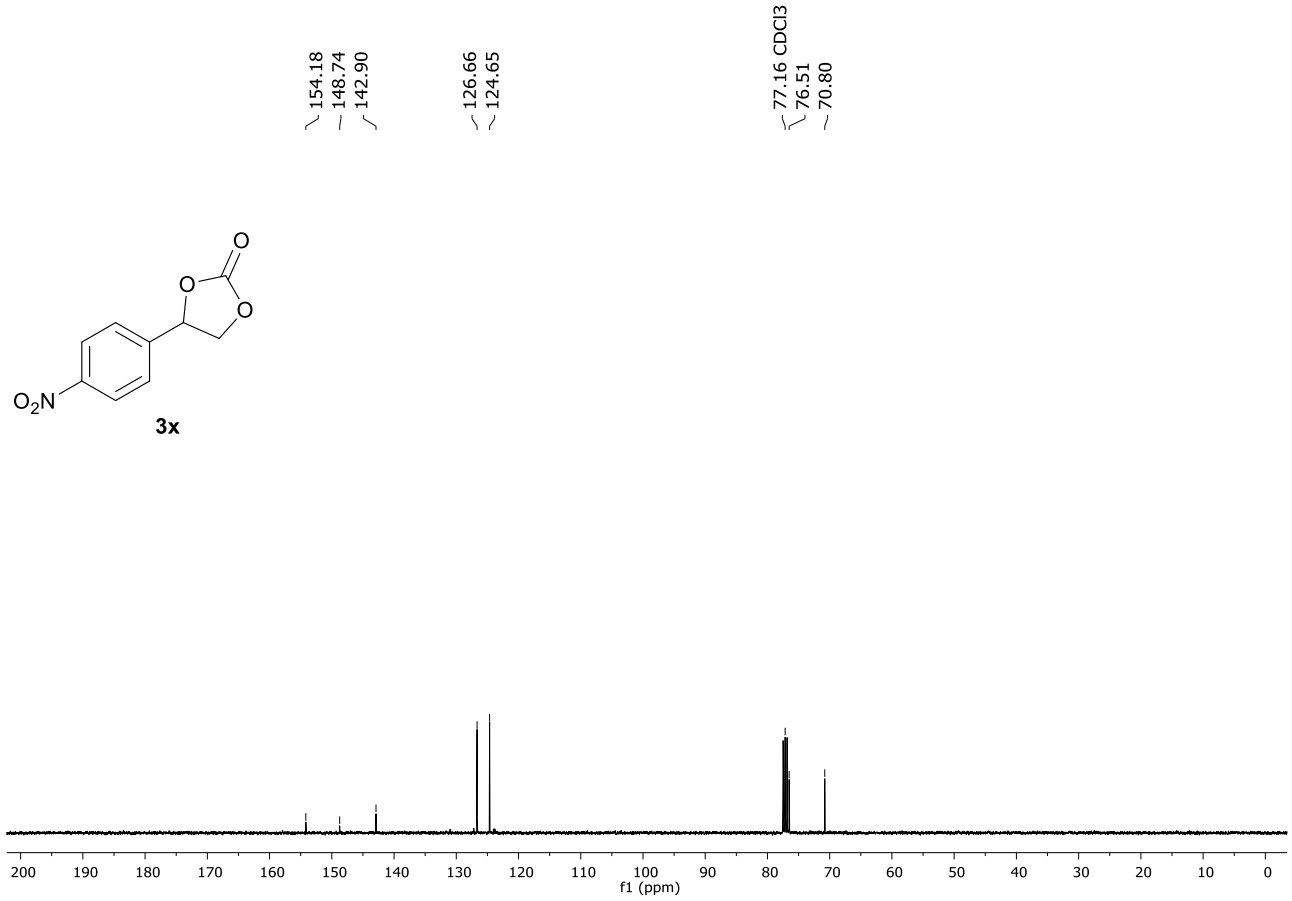


Figure S52. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(4-nitrophenyl)-1,3-dioxolan-2-one (**3x**).

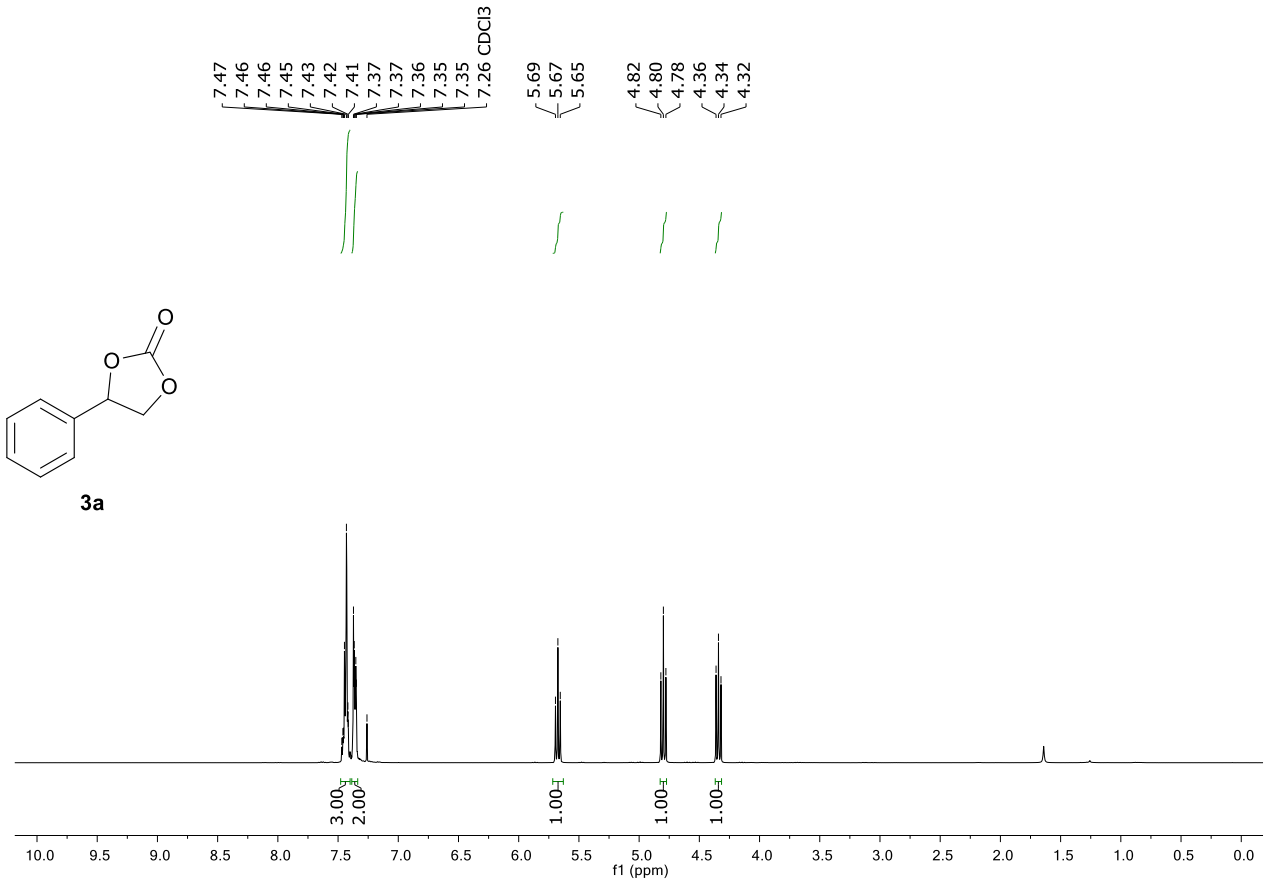
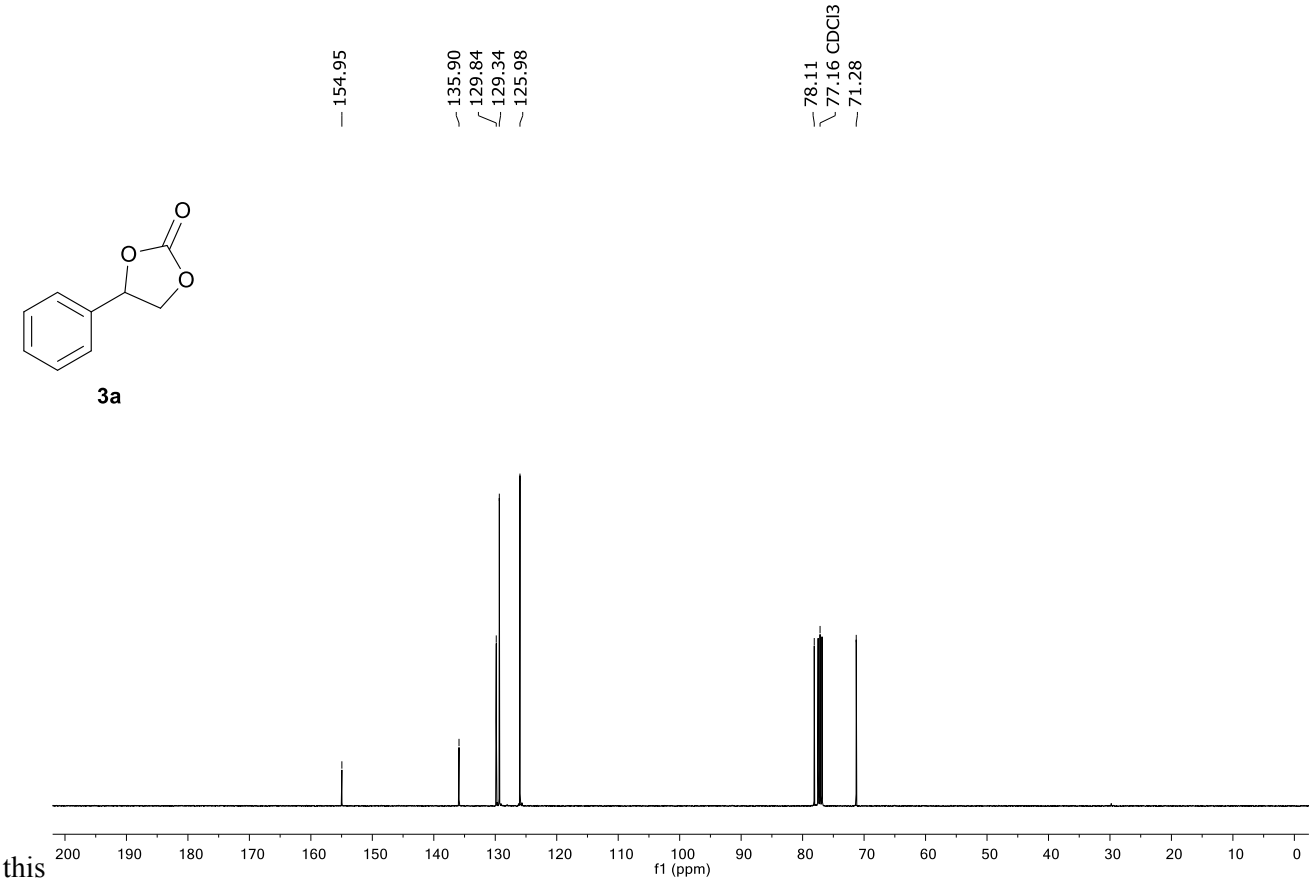


Figure S53. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-phenyl-1,3-dioxolan-2-one (**3a**).



this

Figure S54. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-phenyl-1,3-dioxolan-2-one (**3a**).

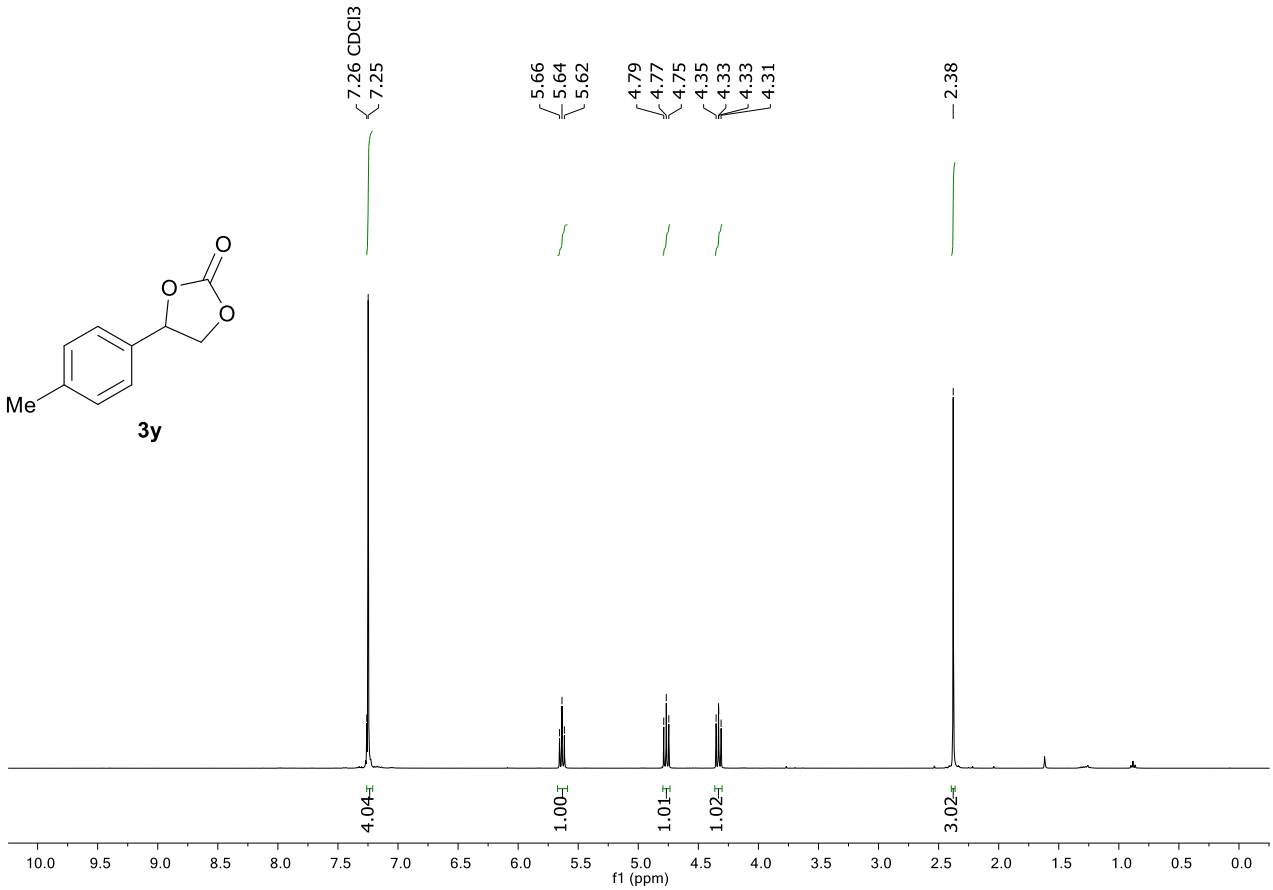


Figure S55. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(*p*-tolyl)-1,3-dioxolan-2-one (**3y**).

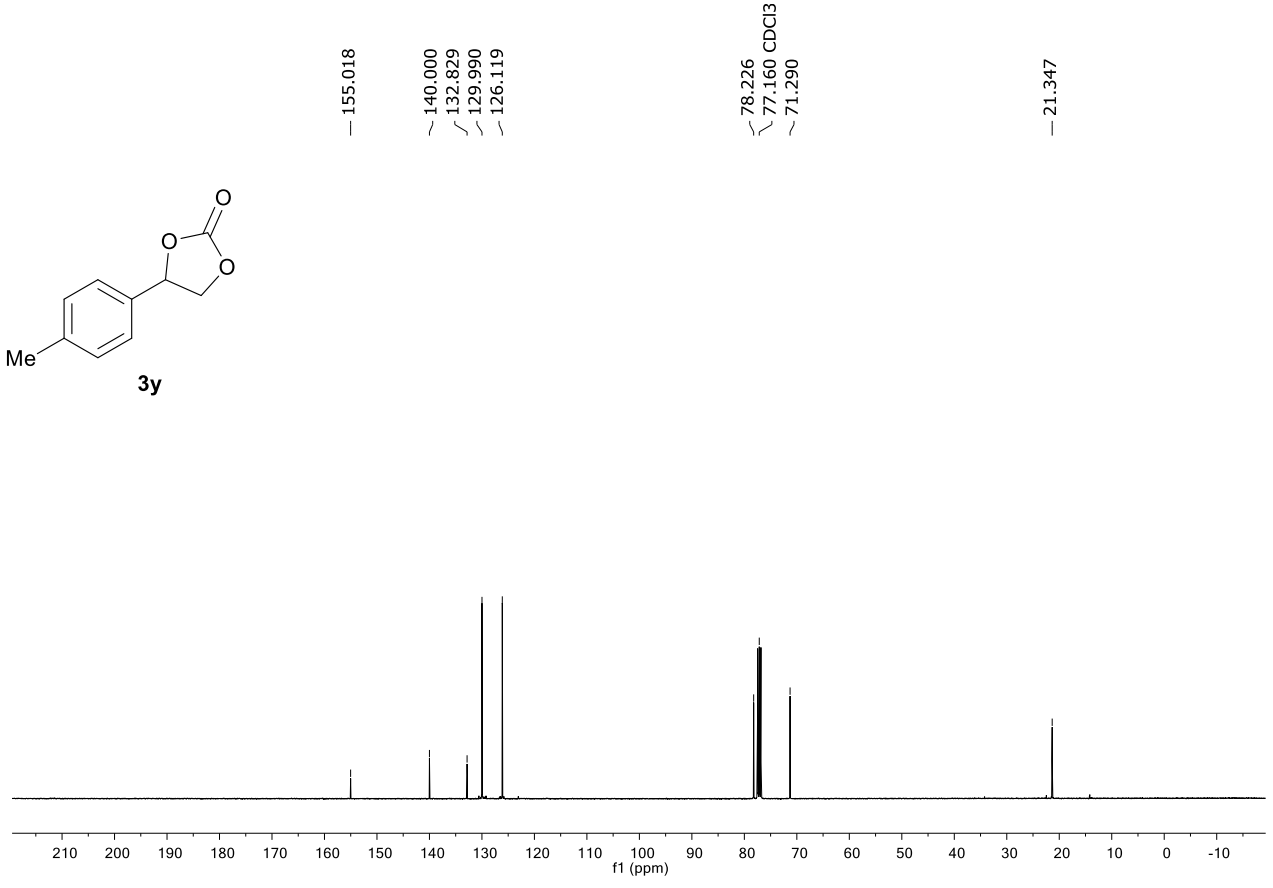


Figure S56. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(*p*-tolyl)-1,3-dioxolan-2-one (**3y**).

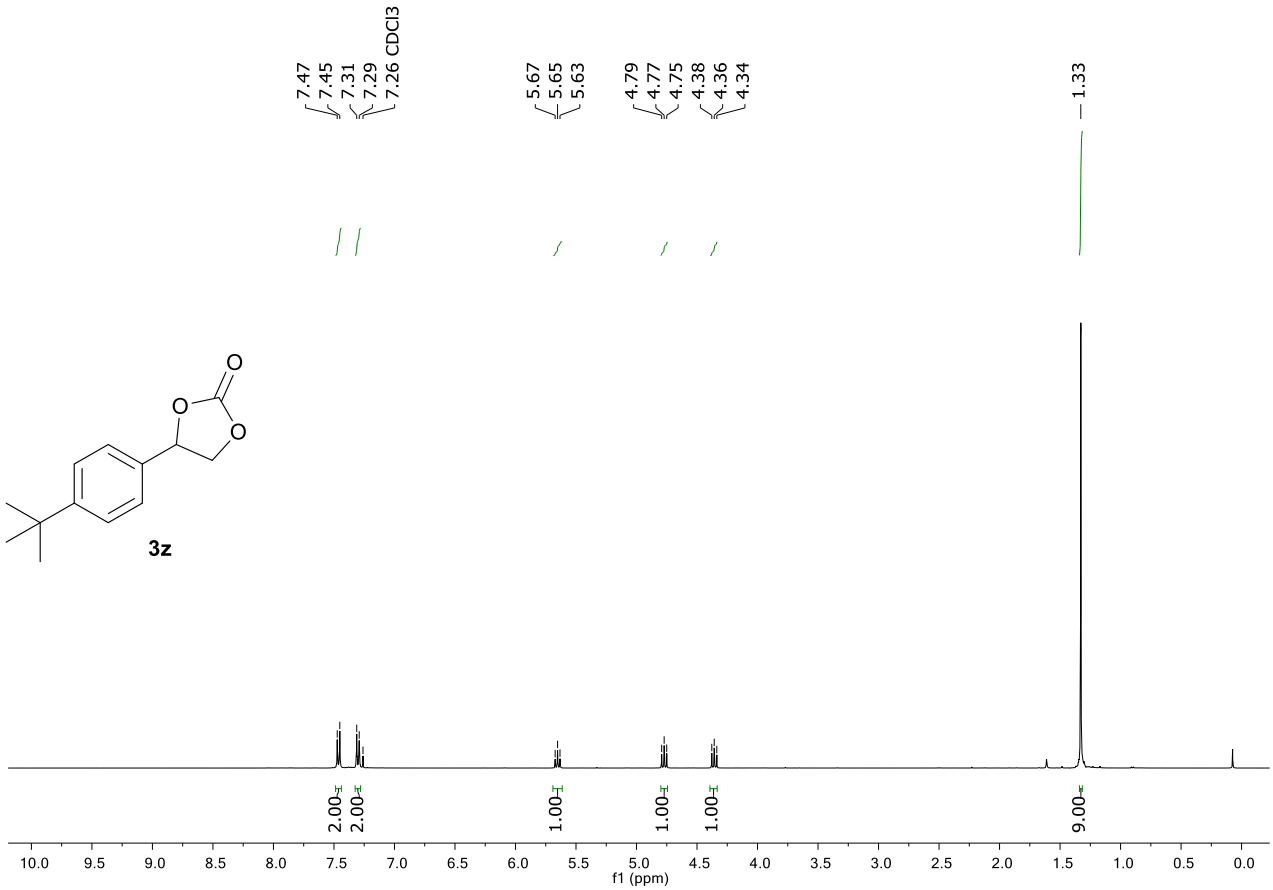


Figure S57. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(4-(*tert*-butyl)phenyl)-1,3-dioxolan-2-one (**3z**).

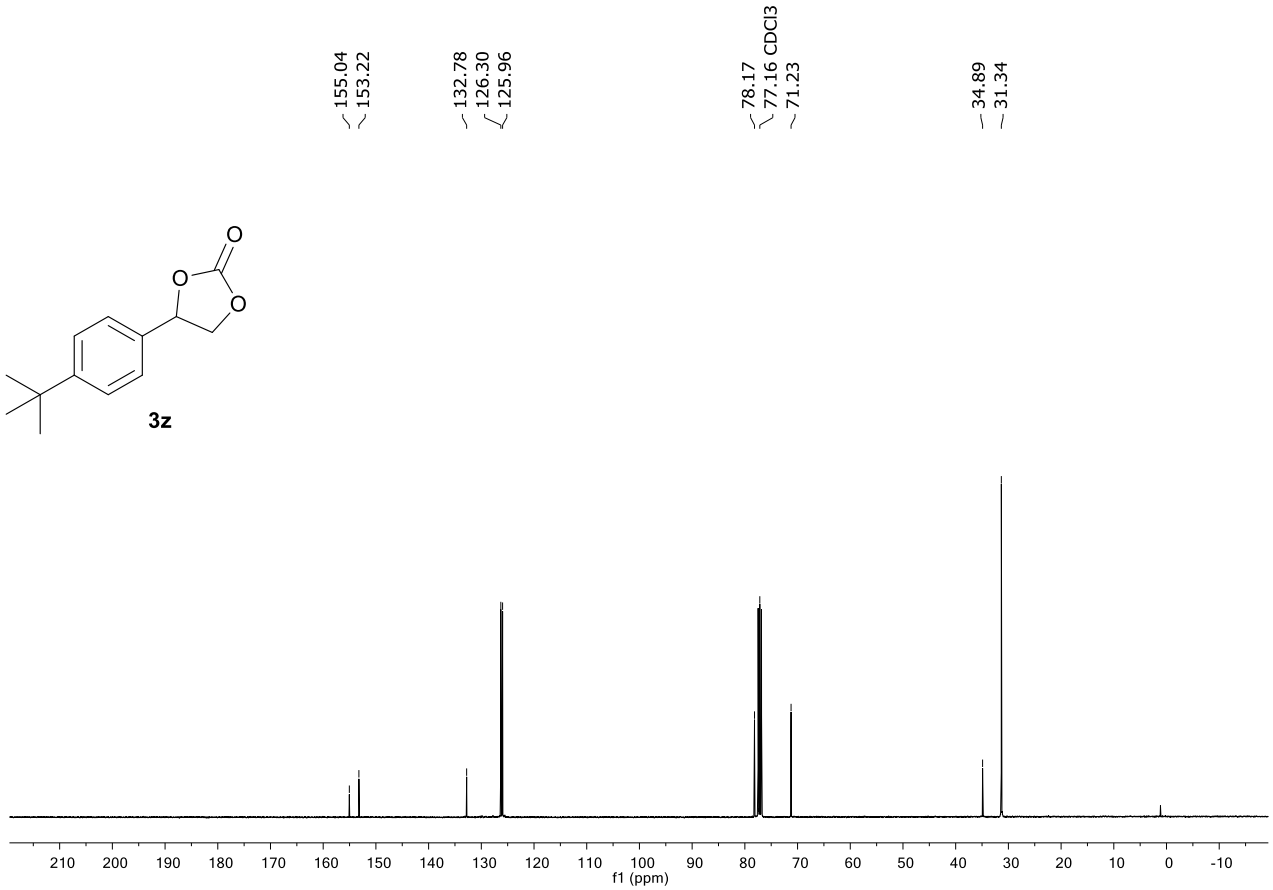


Figure S58. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(4-(*tert*-butyl)phenyl)-1,3-dioxolan-2-one (**3z**).

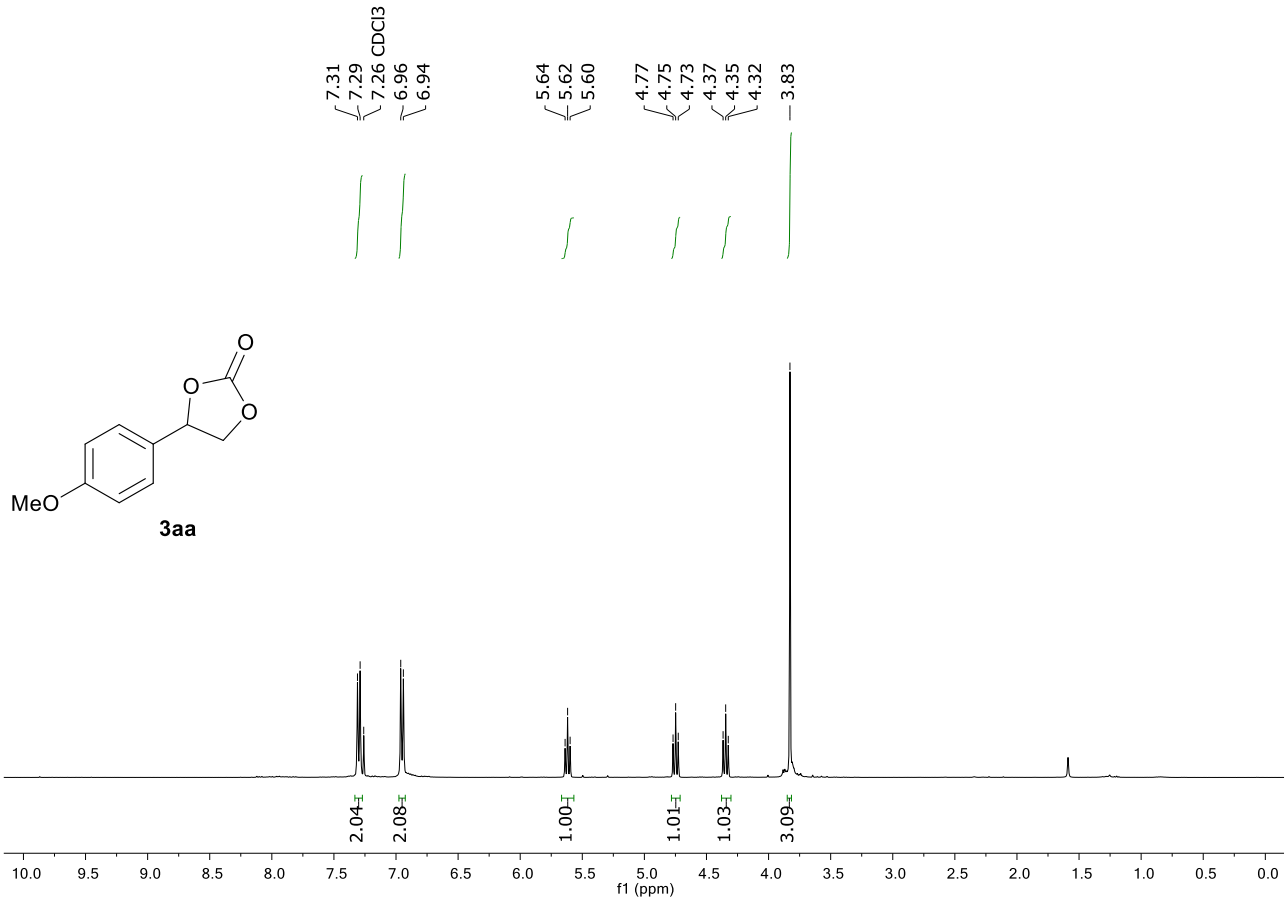


Figure S59. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(4-methoxyphenyl)-1,3-dioxolan-2-one (**3aa**).

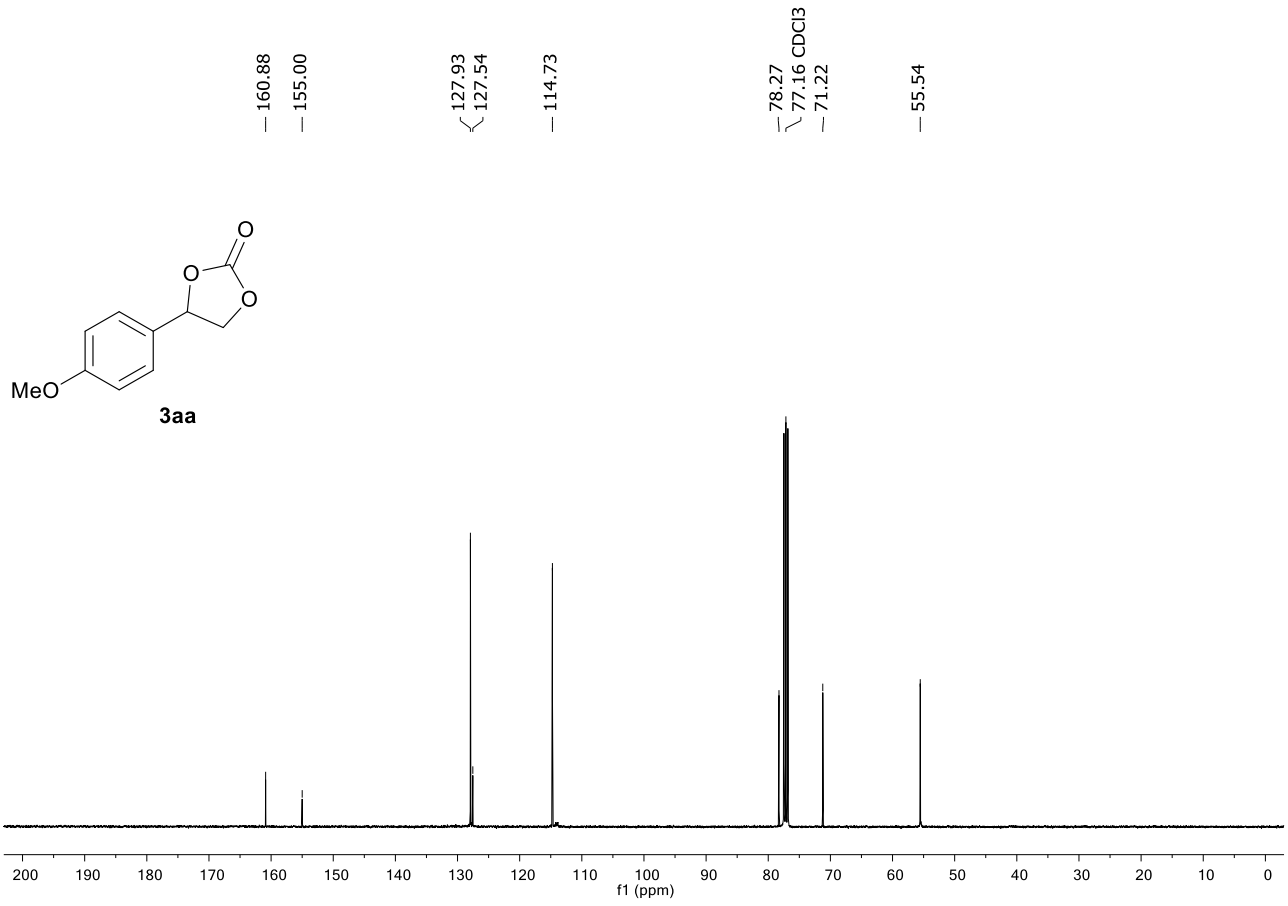


Figure S60. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(4-methoxyphenyl)-1,3-dioxolan-2-one (**3aa**).

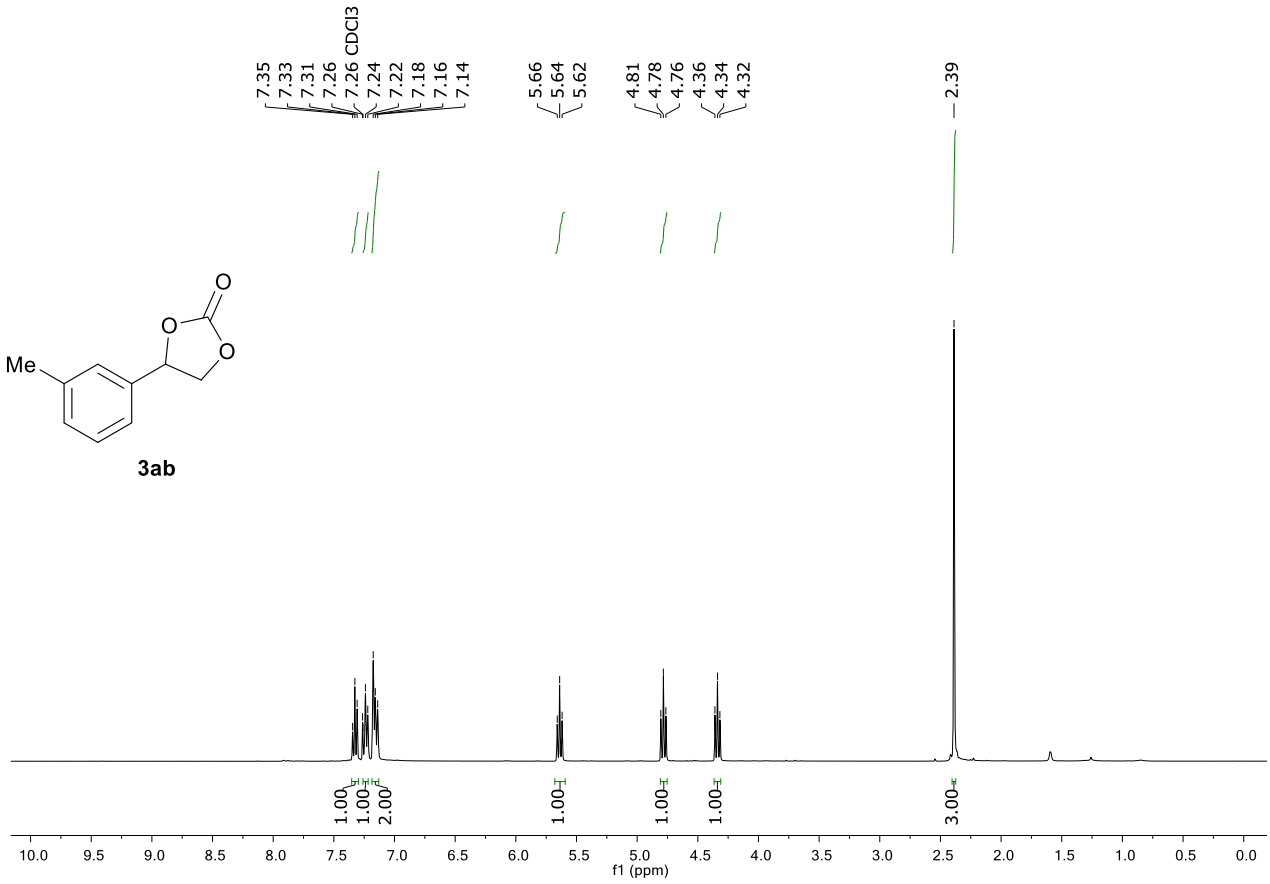


Figure S61. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(*m*-tolyl)-1,3-dioxolan-2-one (**3ab**).

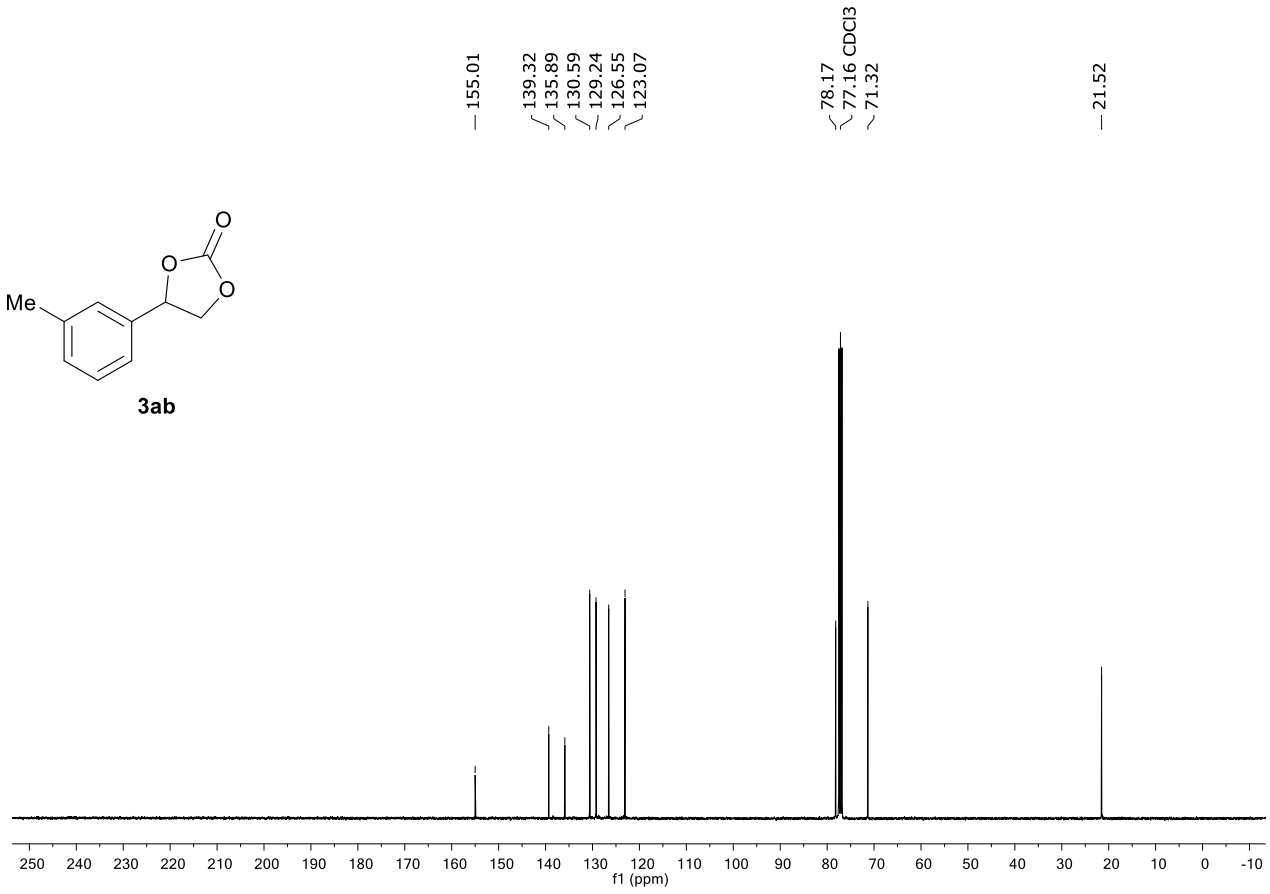


Figure S62. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(*m*-tolyl)-1,3-dioxolan-2-one (**3ab**).

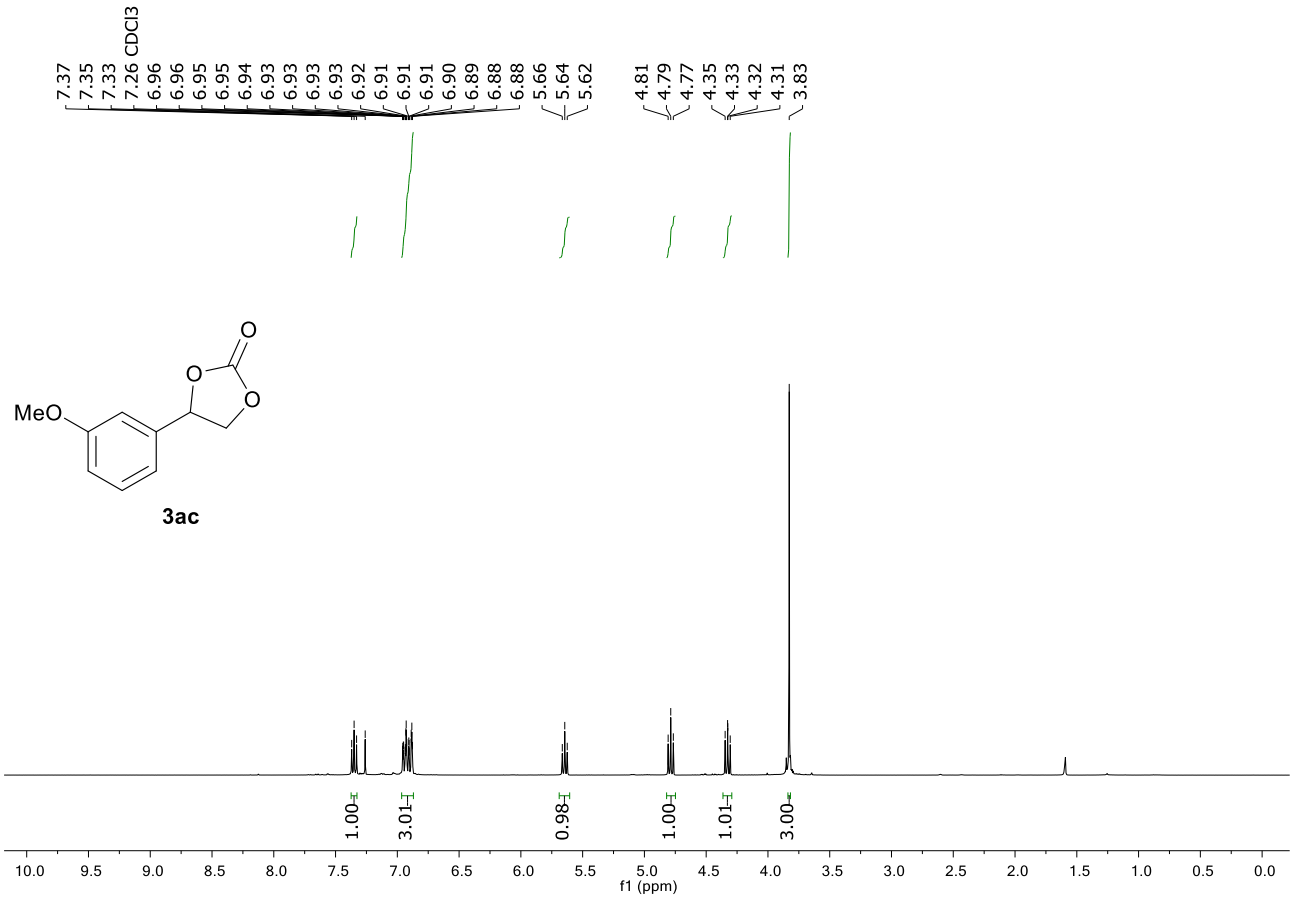


Figure S63. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(3-methoxyphenyl)-1,3-dioxolan-2-one (**3ac**).

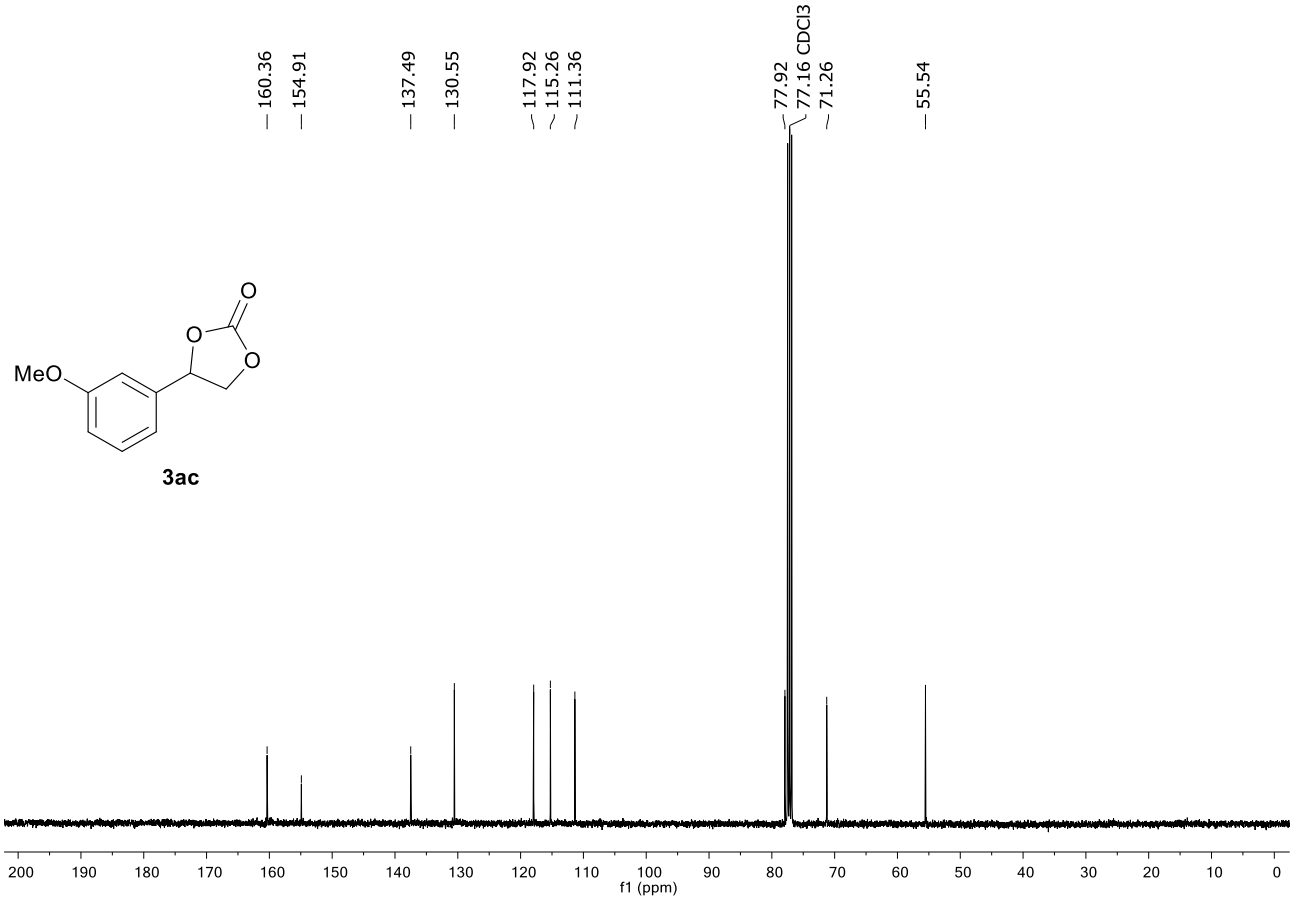


Figure S64. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(3-methoxyphenyl)-1,3-dioxolan-2-one (**3ac**).

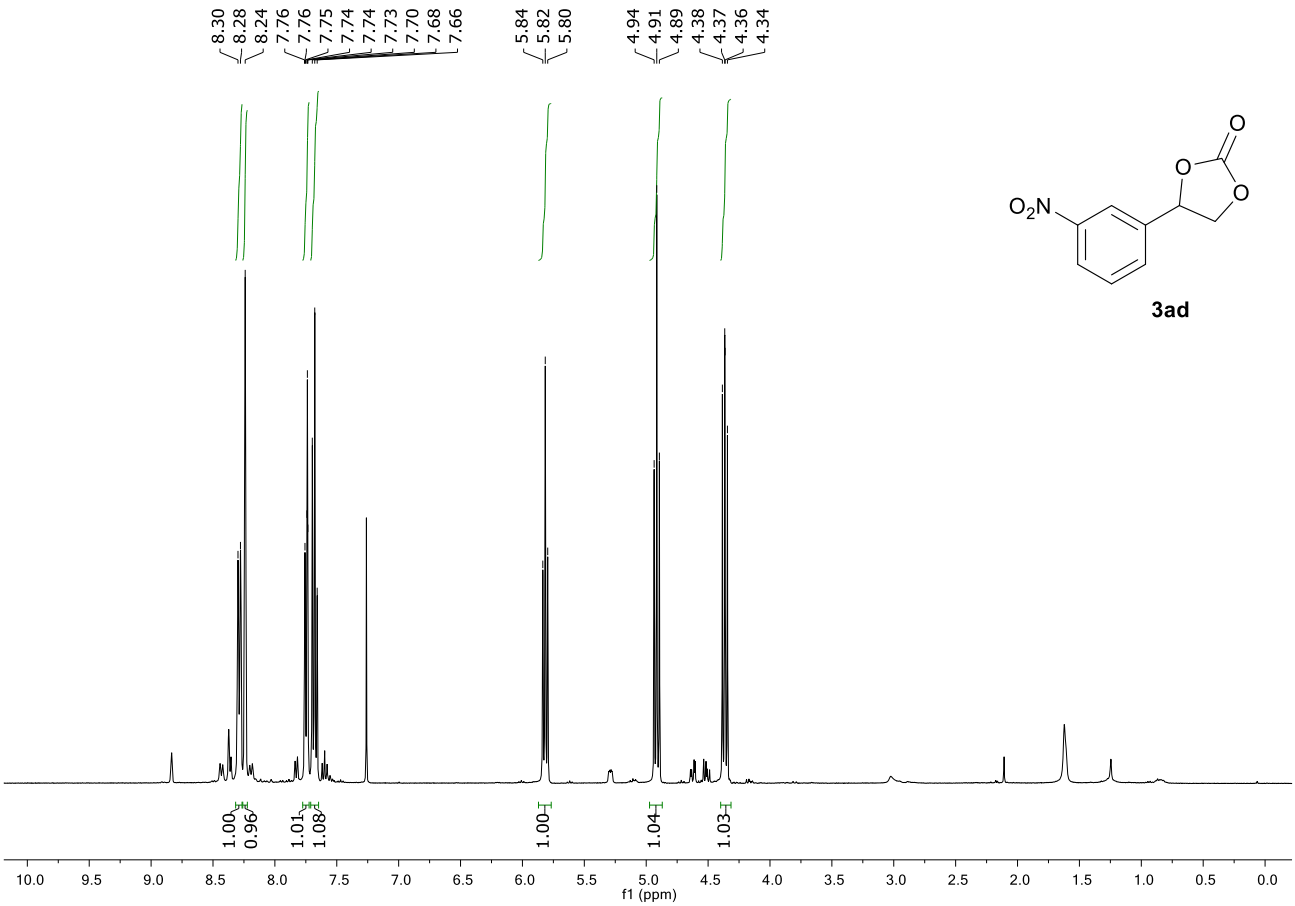


Figure S65. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(3-nitrophenyl)-1,3-dioxolan-2-one (**3ad**).

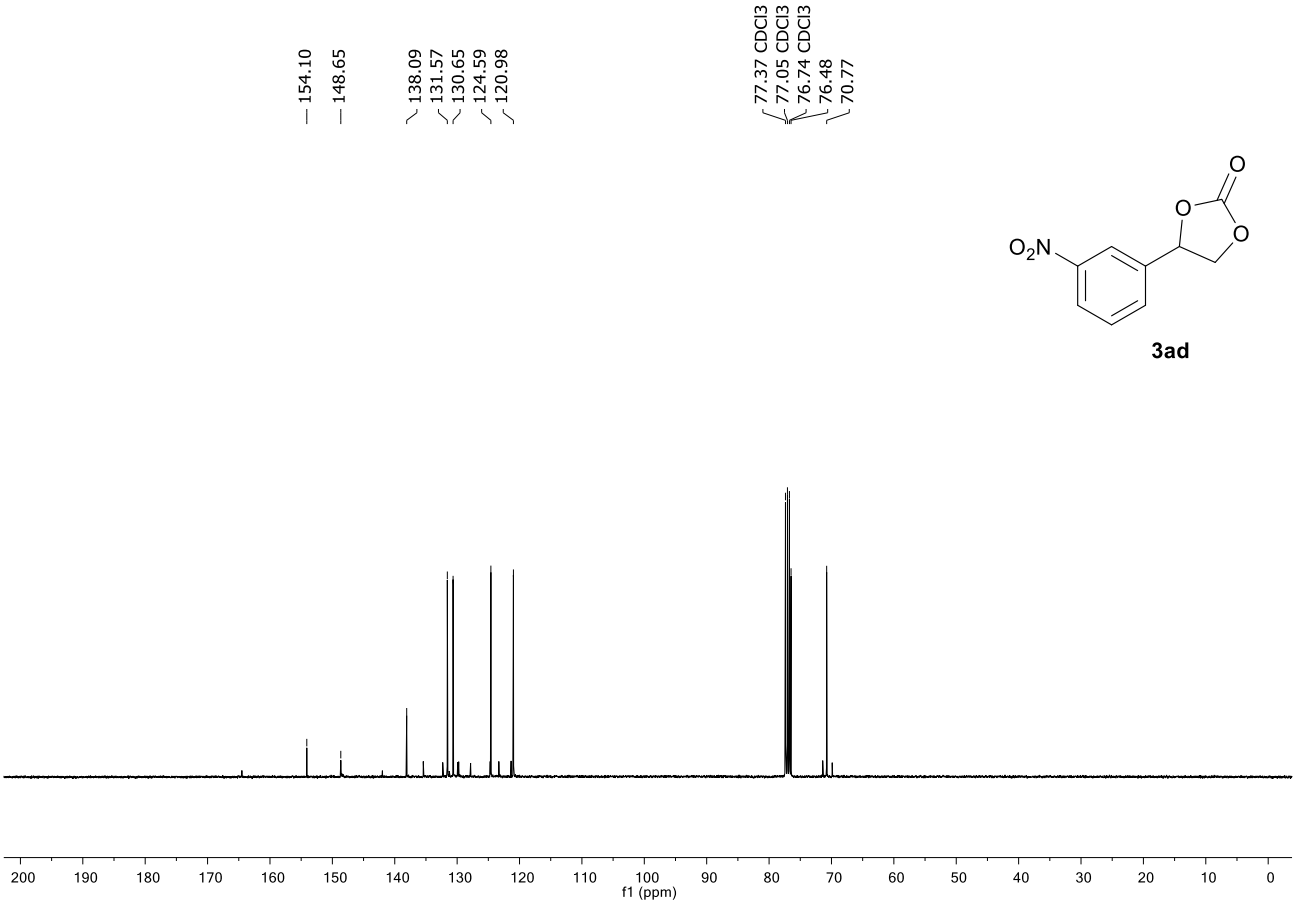


Figure S66. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(3-nitrophenyl)-1,3-dioxolan-2-one (**3ad**).

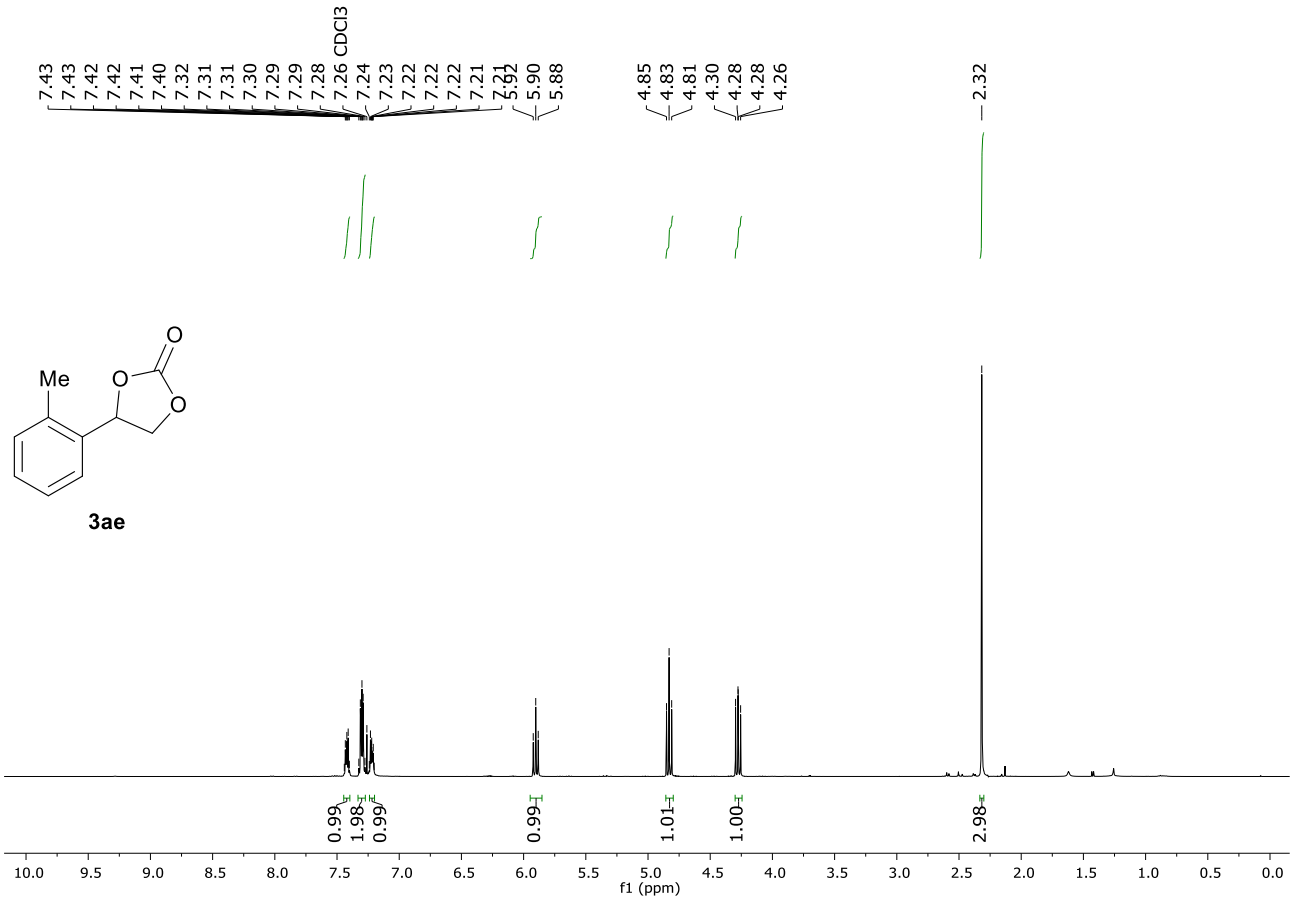


Figure S67. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(*o*-tolyl)-1,3-dioxolan-2-one (**3ae**).

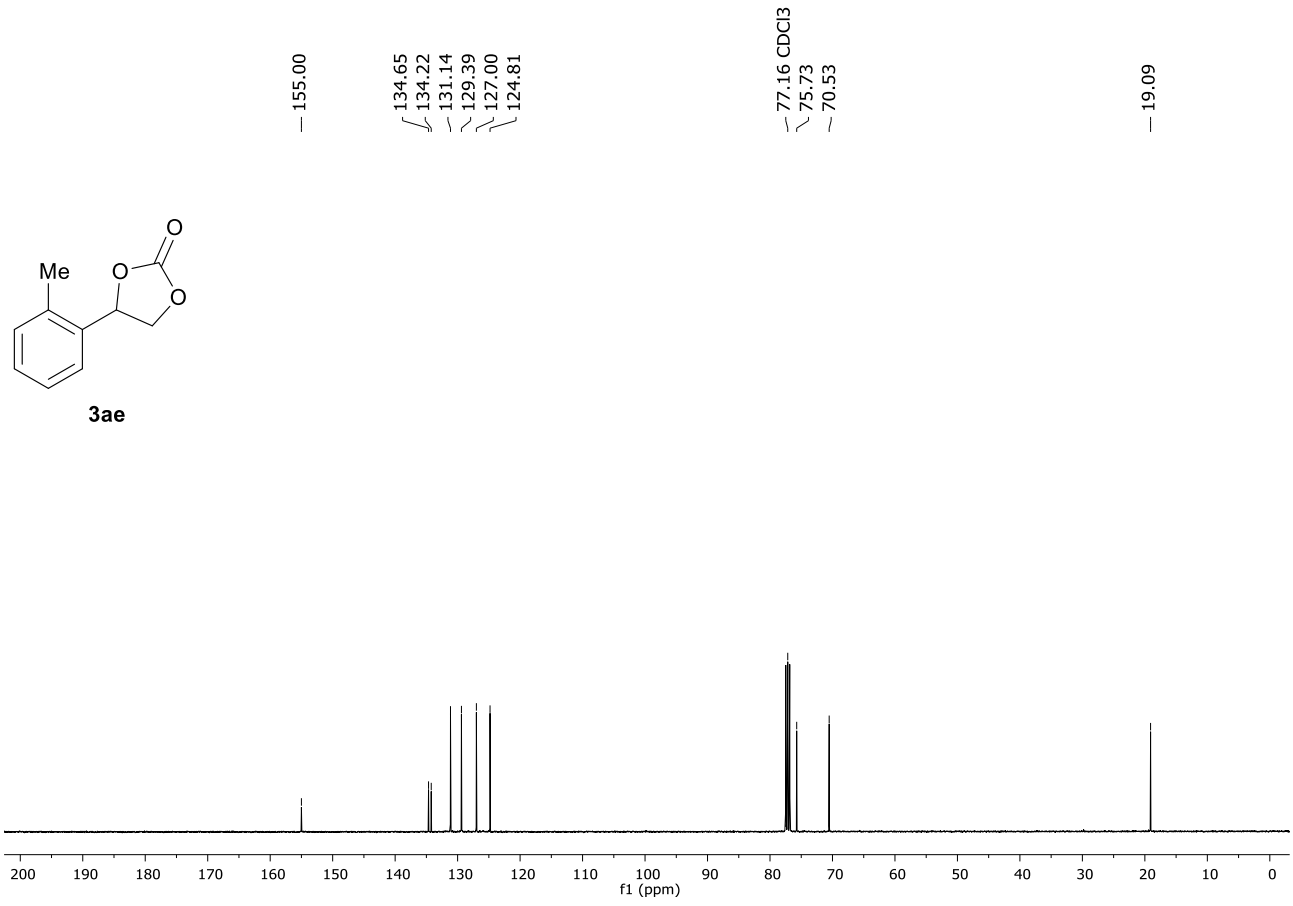


Figure S68. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(*o*-tolyl)-1,3-dioxolan-2-one (**3ae**).

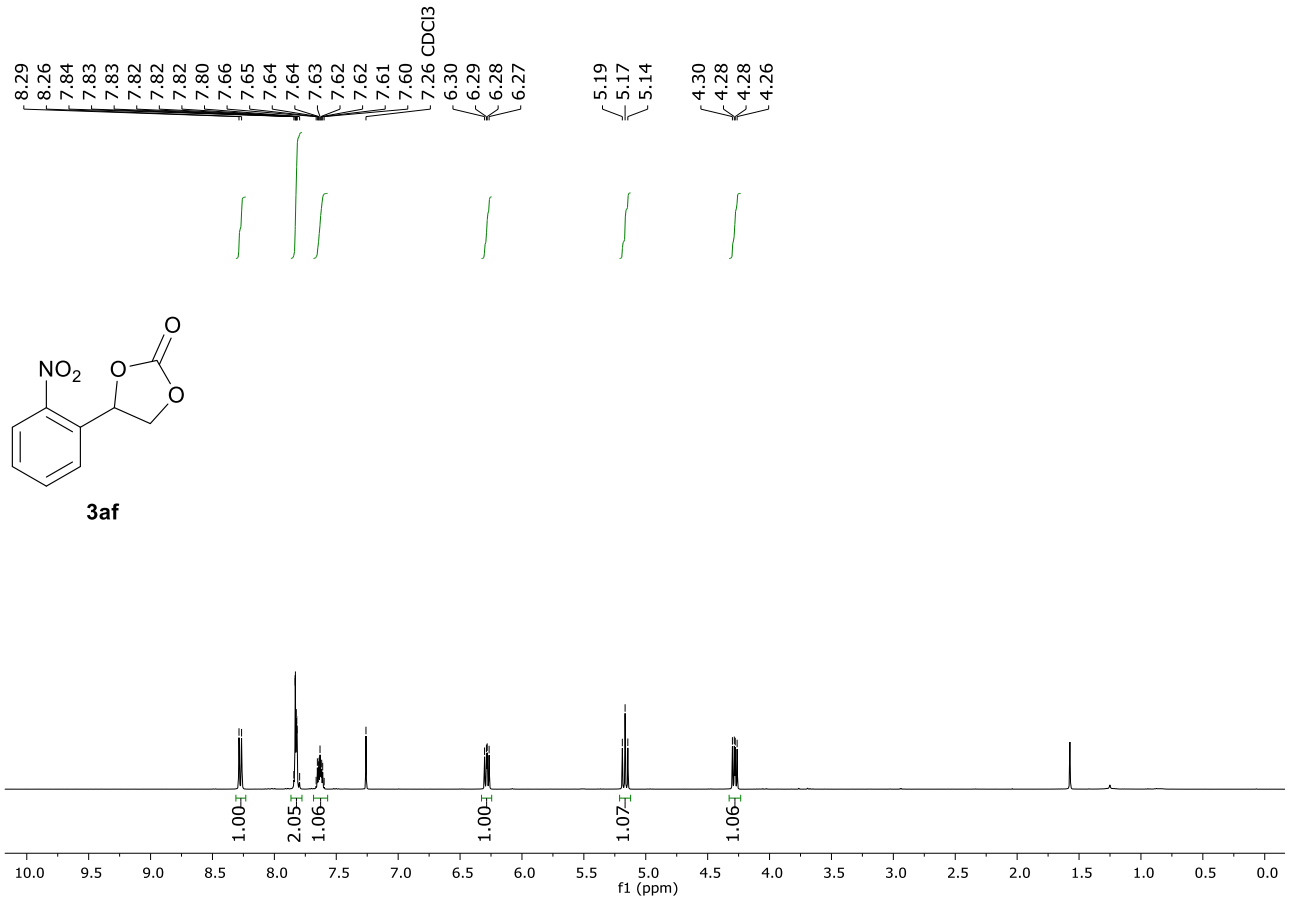


Figure S69. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(2-nitrophenyl)-1,3-dioxolan-2-one (**3af**).

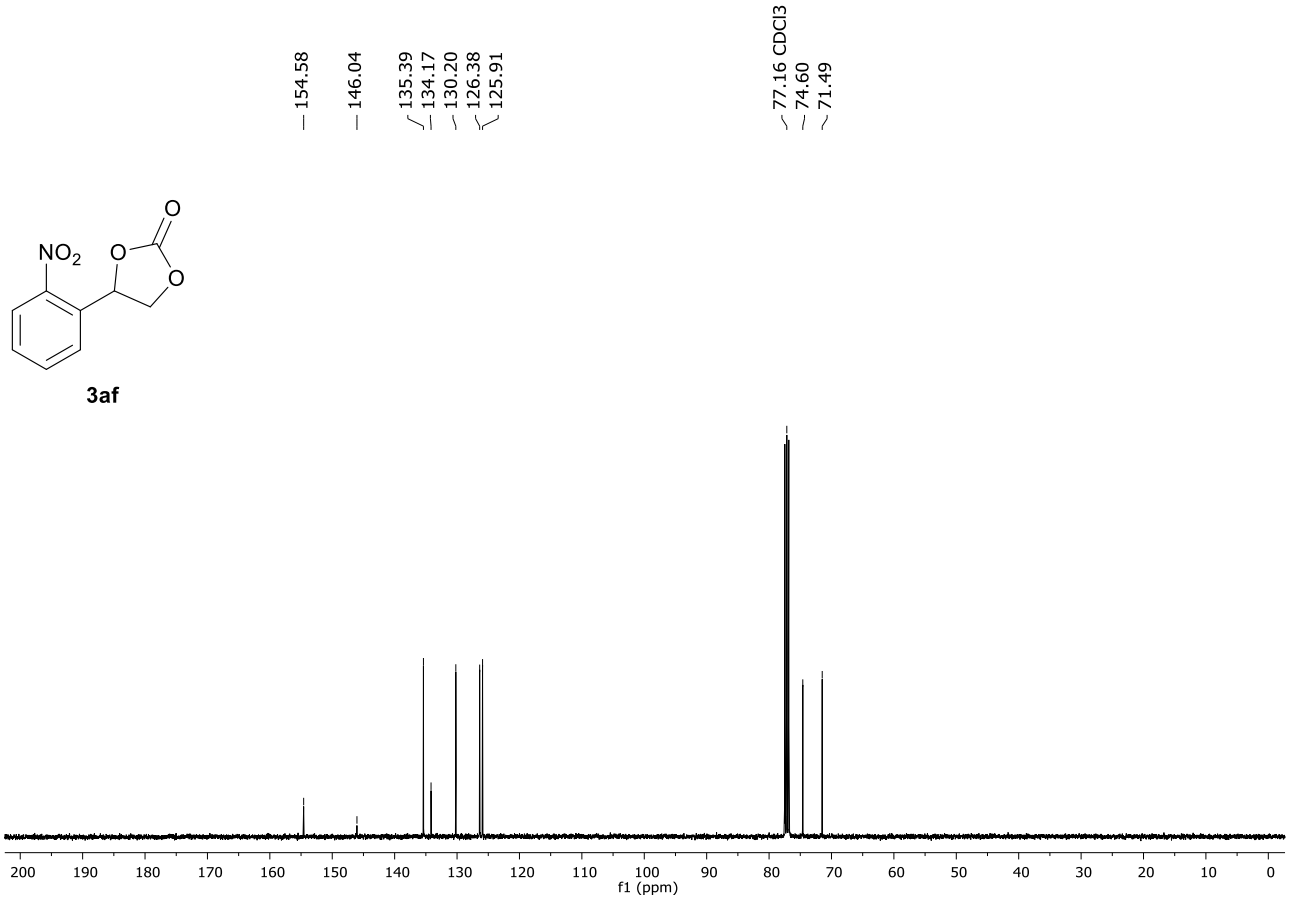


Figure S70. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(2-nitrophenyl)-1,3-dioxolan-2-one (**3af**).

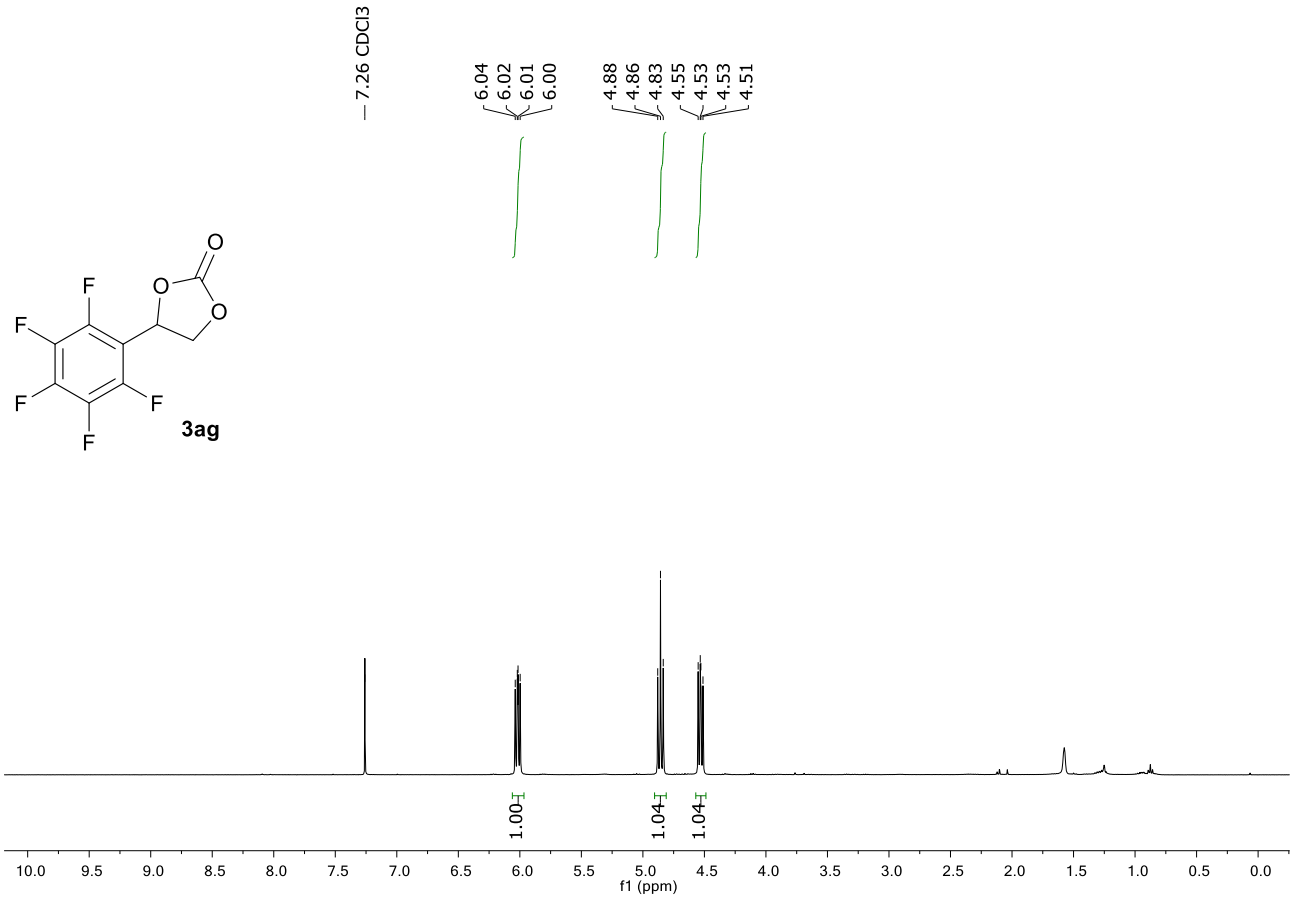


Figure S71. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(perfluorophenyl)-1,3-dioxolan-2-one (**3ag**).

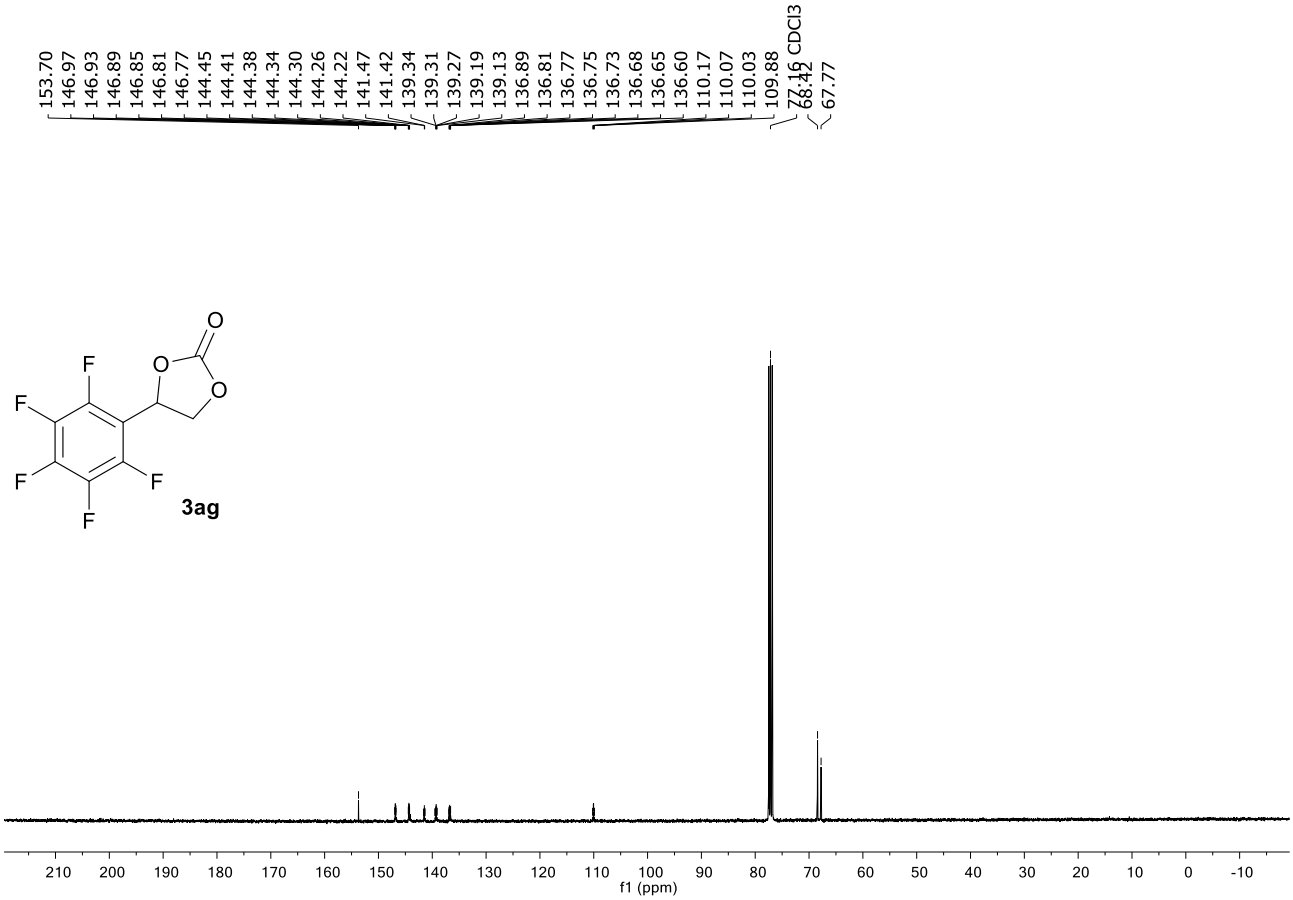


Figure S72. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(perfluorophenyl)-1,3-dioxolan-2-one (**3ag**).

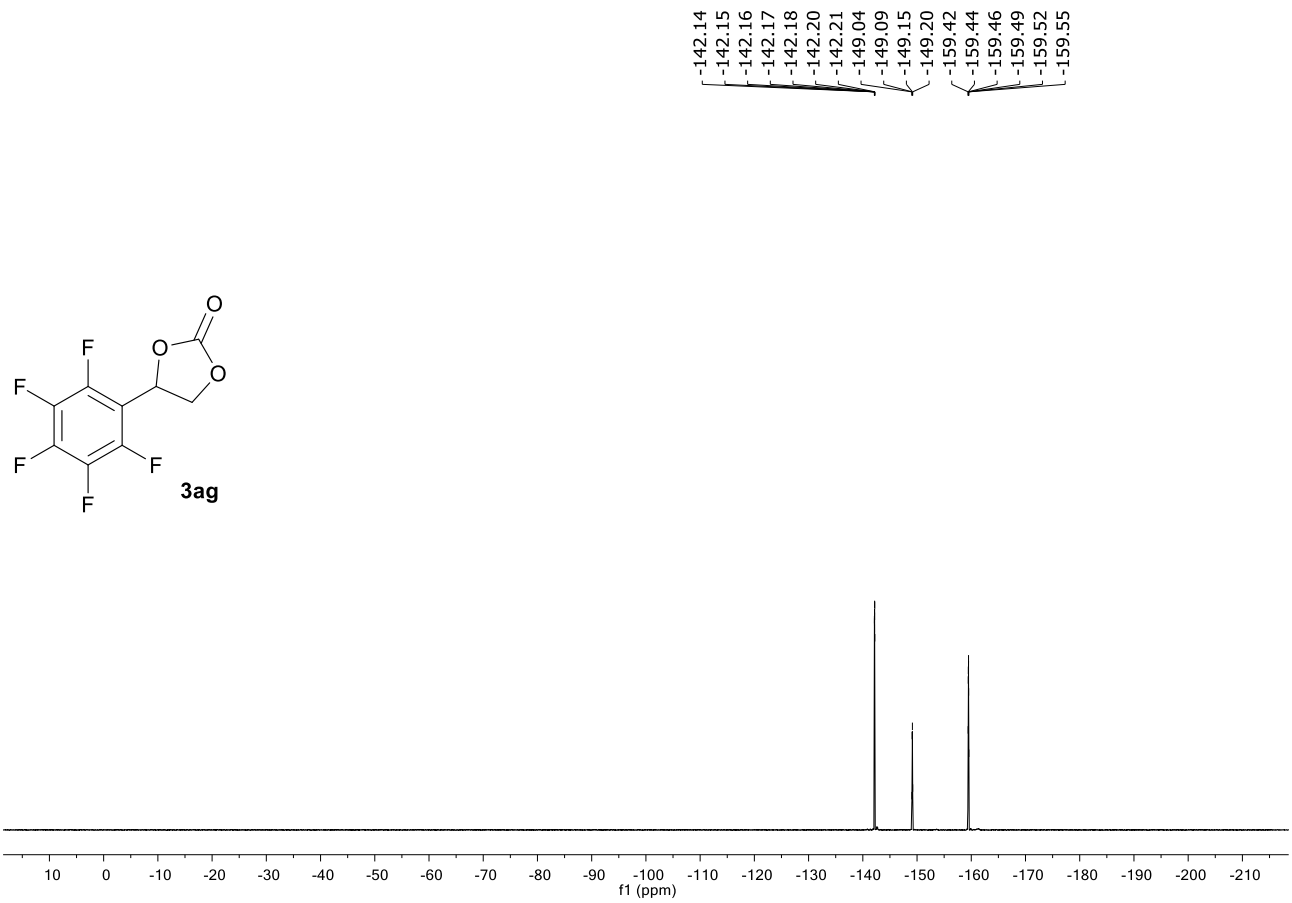


Figure S73. ^{19}F NMR (377 MHz, $CDCl_3$) spectrum of 4-(perfluorophenyl)-1,3-dioxolan-2-one (**3ag**).

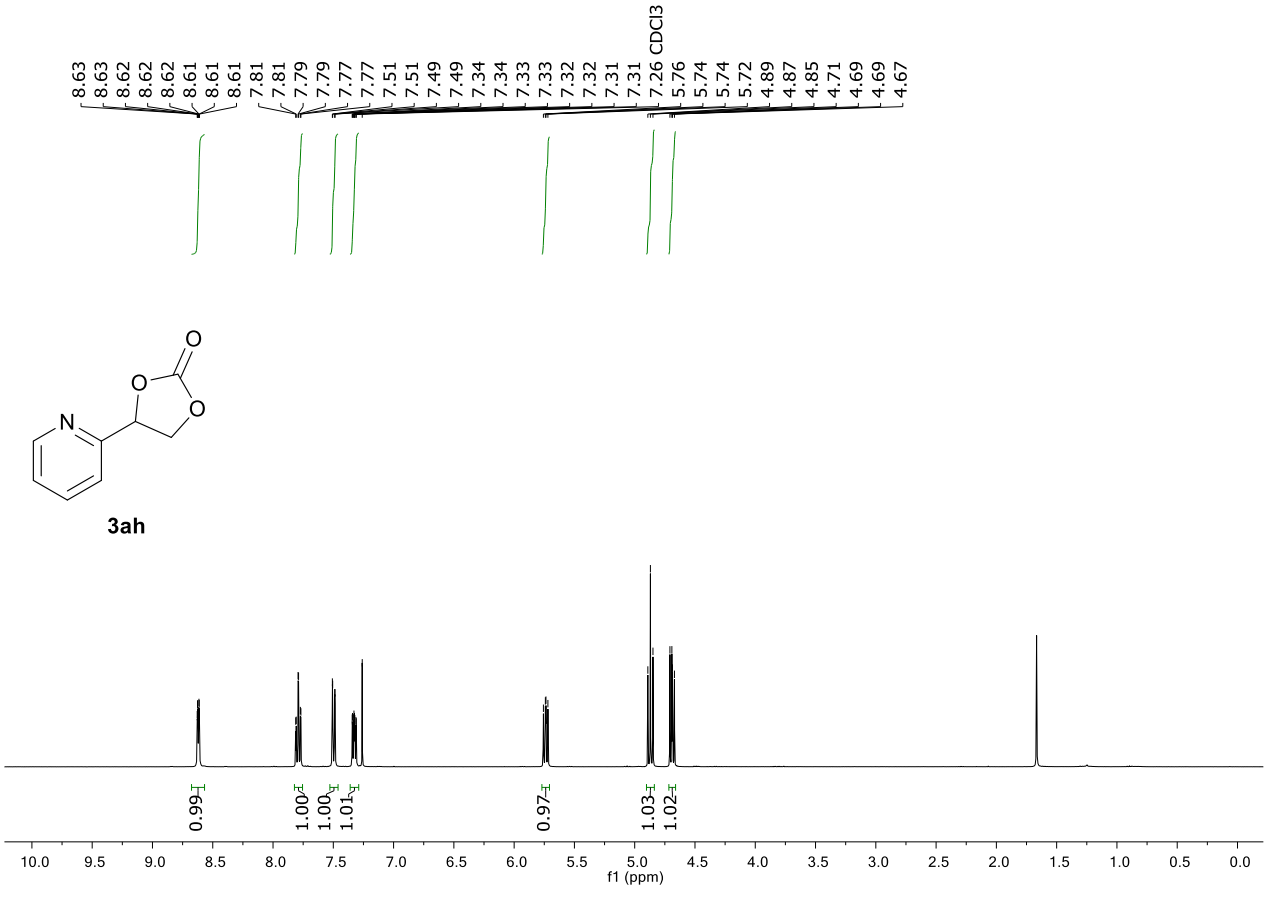


Figure S74. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(pyridin-2-yl)-1,3-dioxolan-2-one (**3ah**).

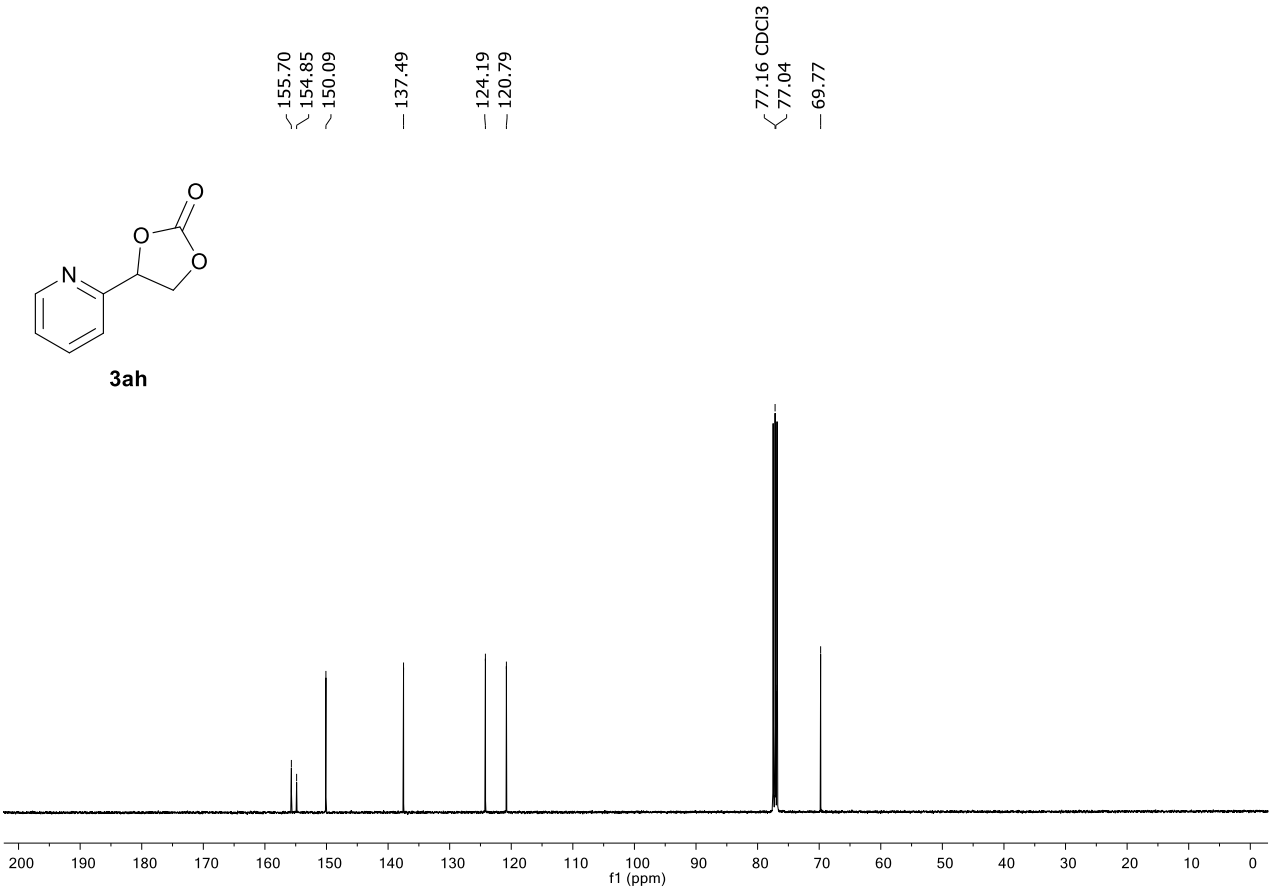


Figure S75. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(pyridin-2-yl)-1,3-dioxolan-2-one (**3ah**).

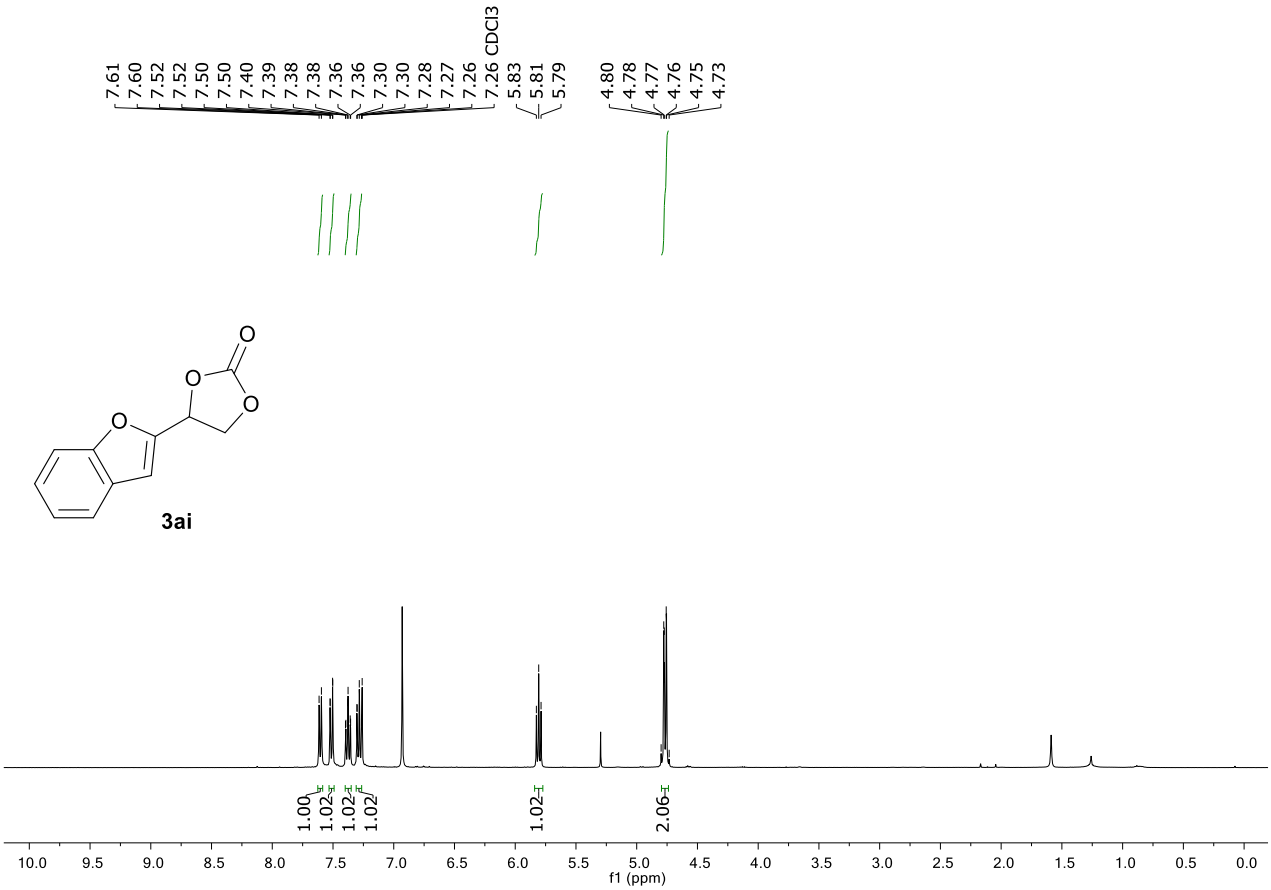


Figure S76. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(benzofuran-2-yl)-1,3-dioxolan-2-one (**3ai**).

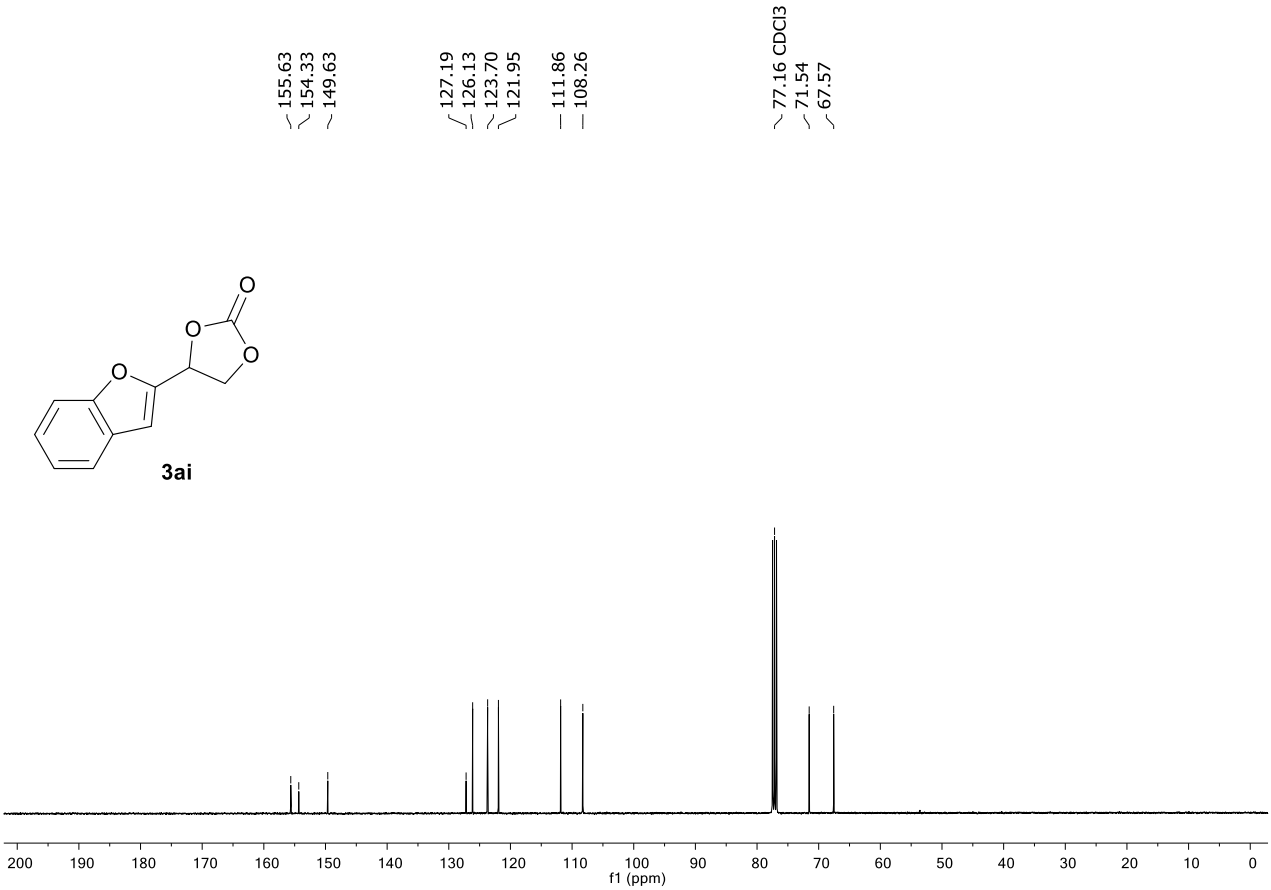


Figure S77. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(benzofuran-2-yl)-1,3-dioxolan-2-one (**3ai**).

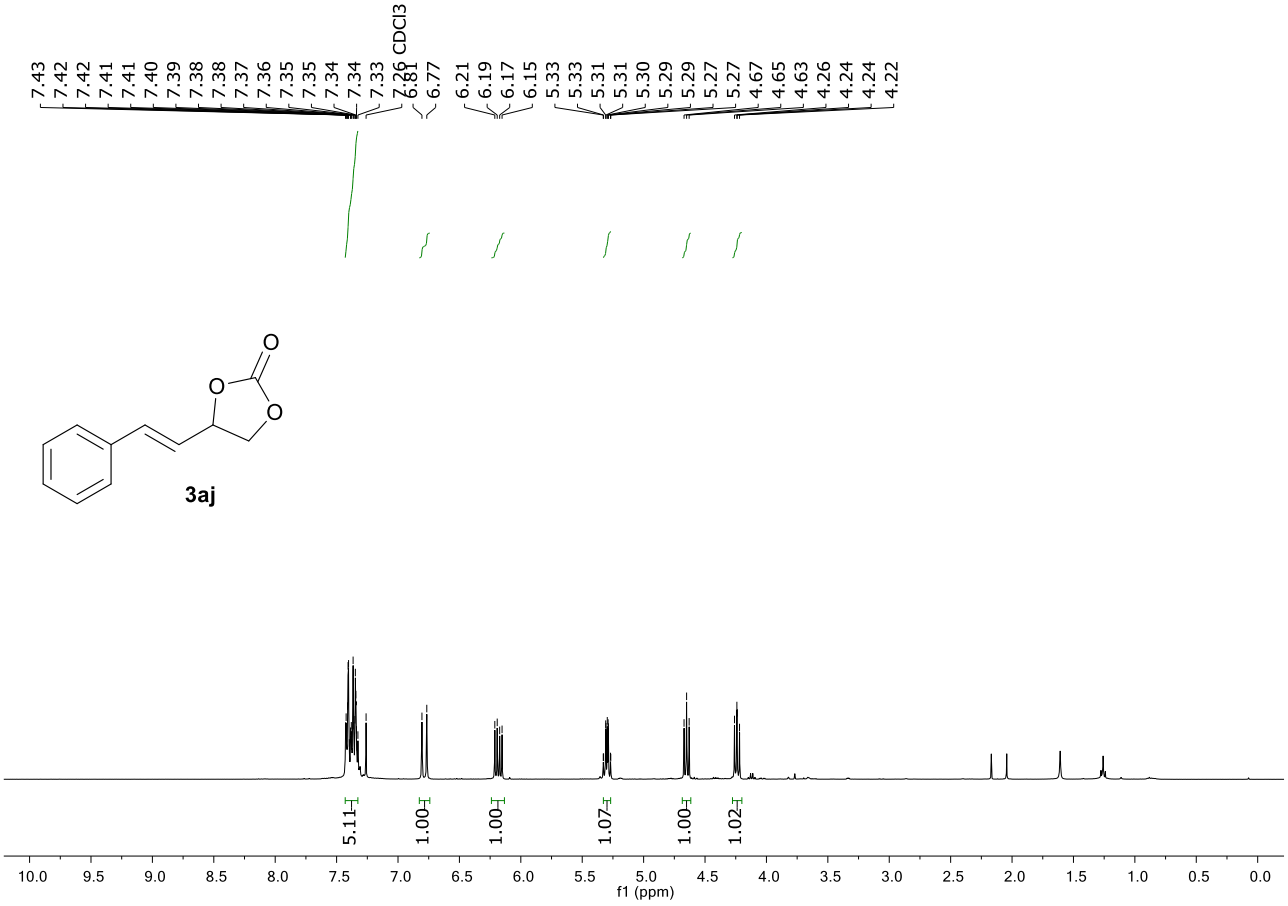


Figure S78. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-4-styryl-1,3-dioxolan-2-one (**3aj**).

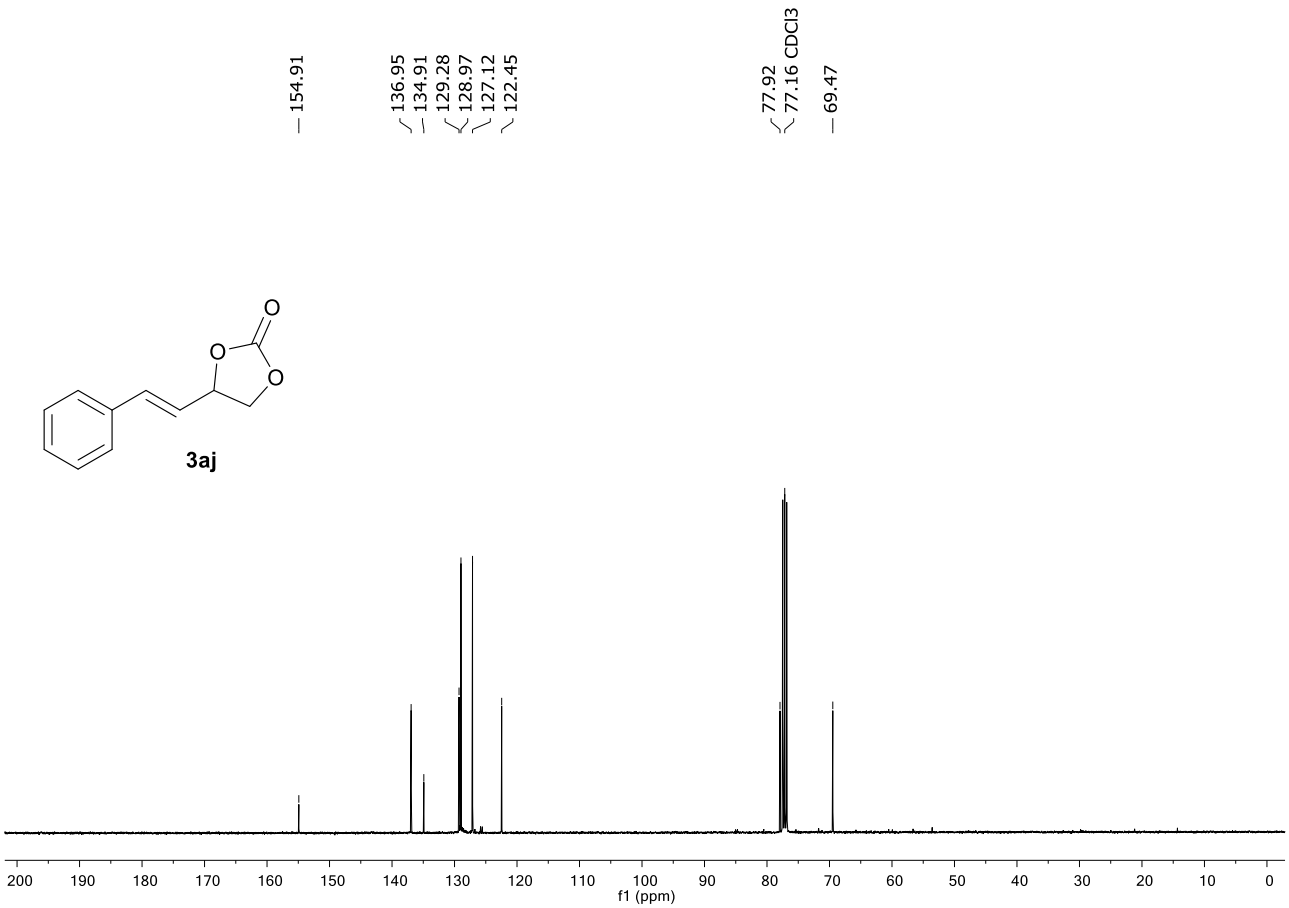


Figure S79. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (*E*)-4-styryl-1,3-dioxolan-2-one (**3aj**).

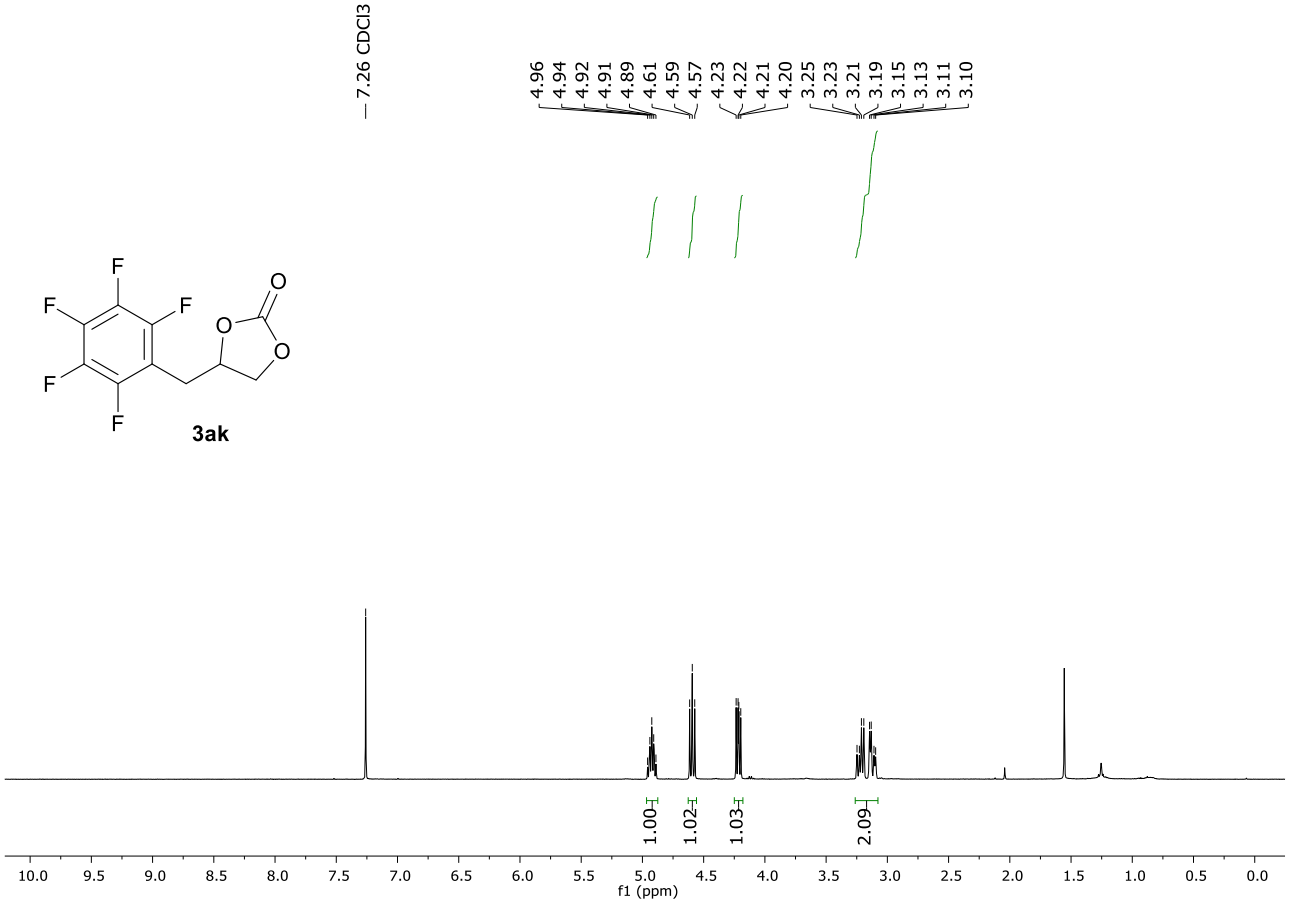


Figure S80. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-((perfluorophenyl)methyl)-1,3-dioxolan-2-one (**3ak**).

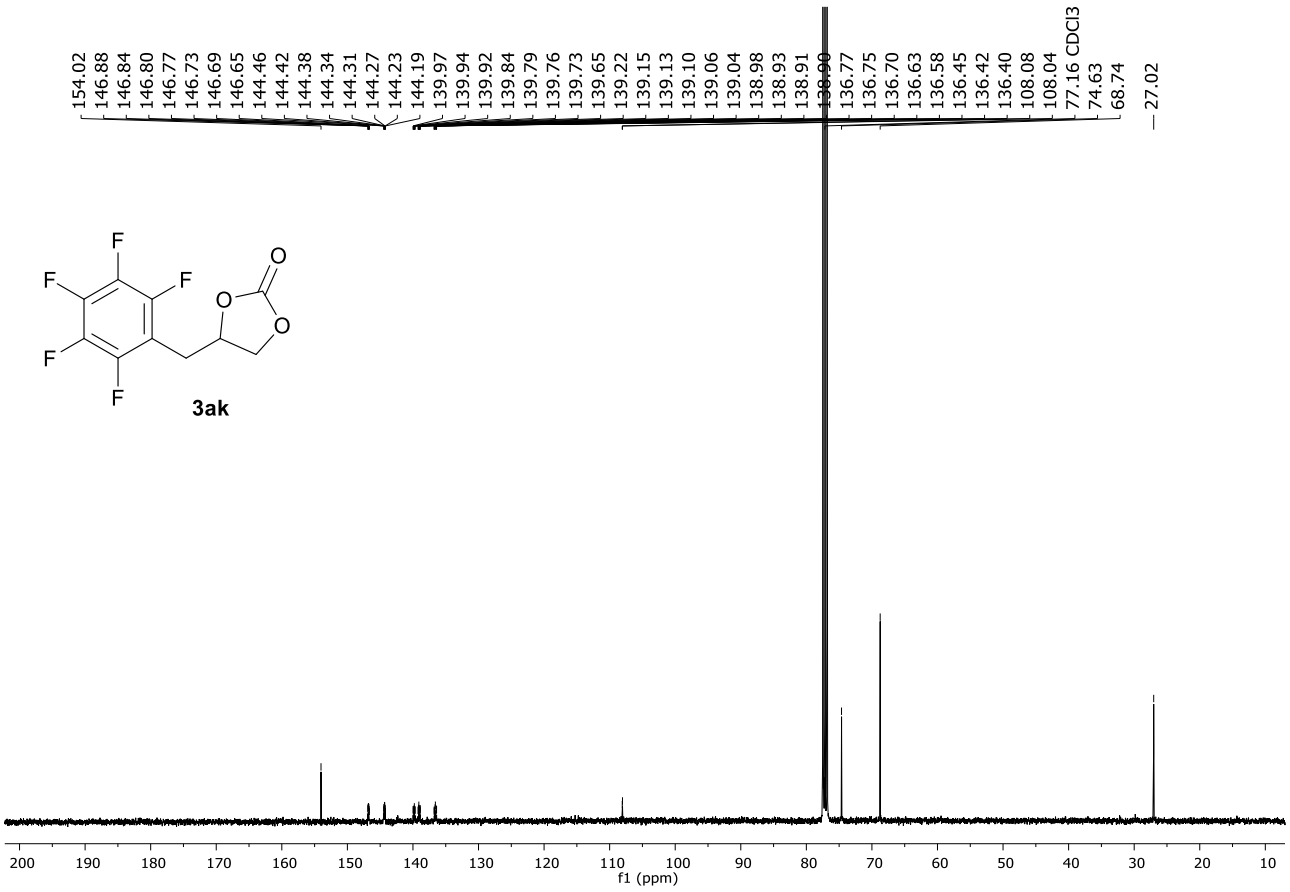


Figure S81. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-((perfluorophenyl)methyl)-1,3-dioxolan-2-one (**3ak**).

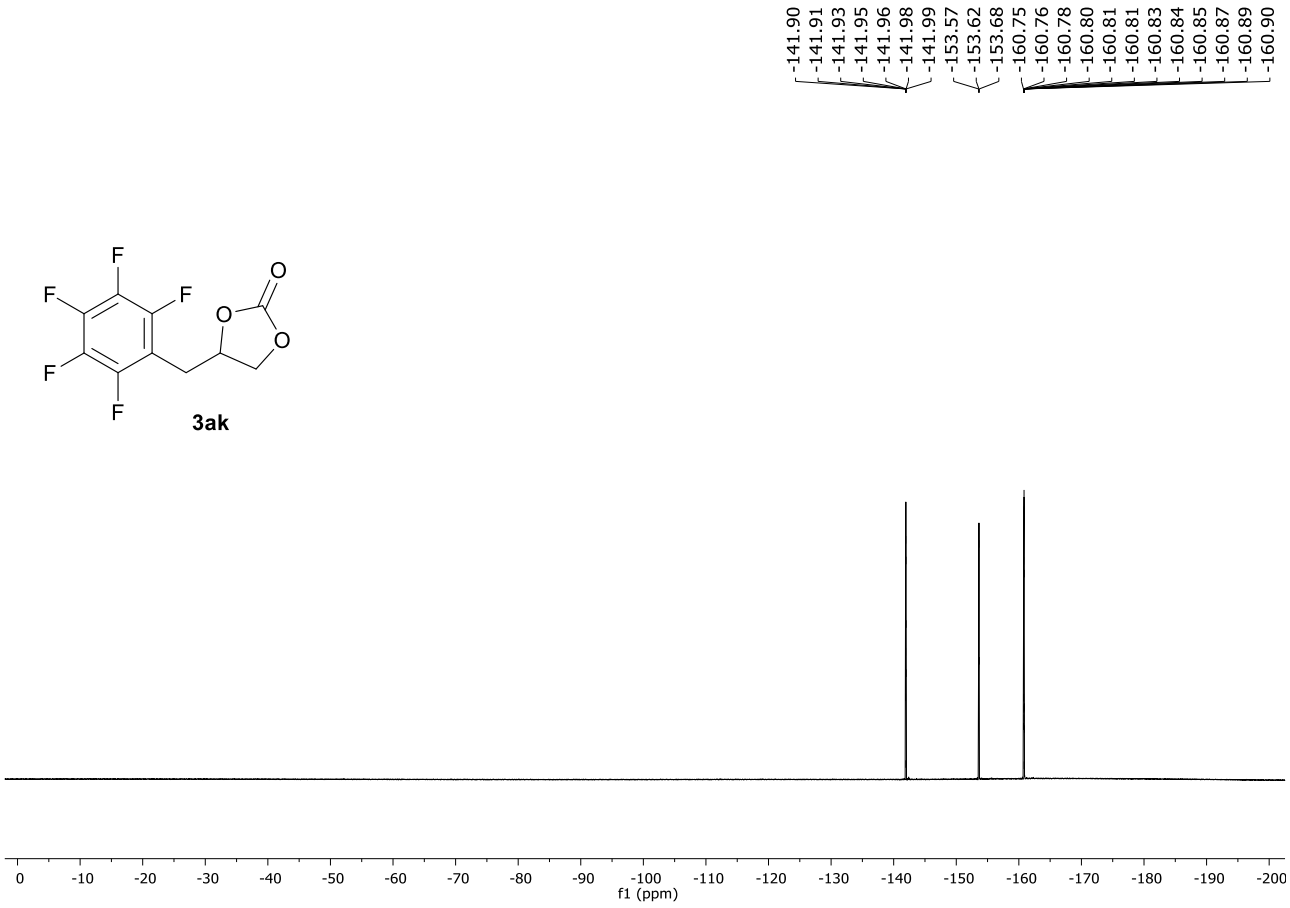


Figure S82. ^{19}F NMR (377 MHz, $CDCl_3$) spectrum of 4-((perfluorophenyl)methyl)-1,3-dioxolan-2-one (**3ak**).

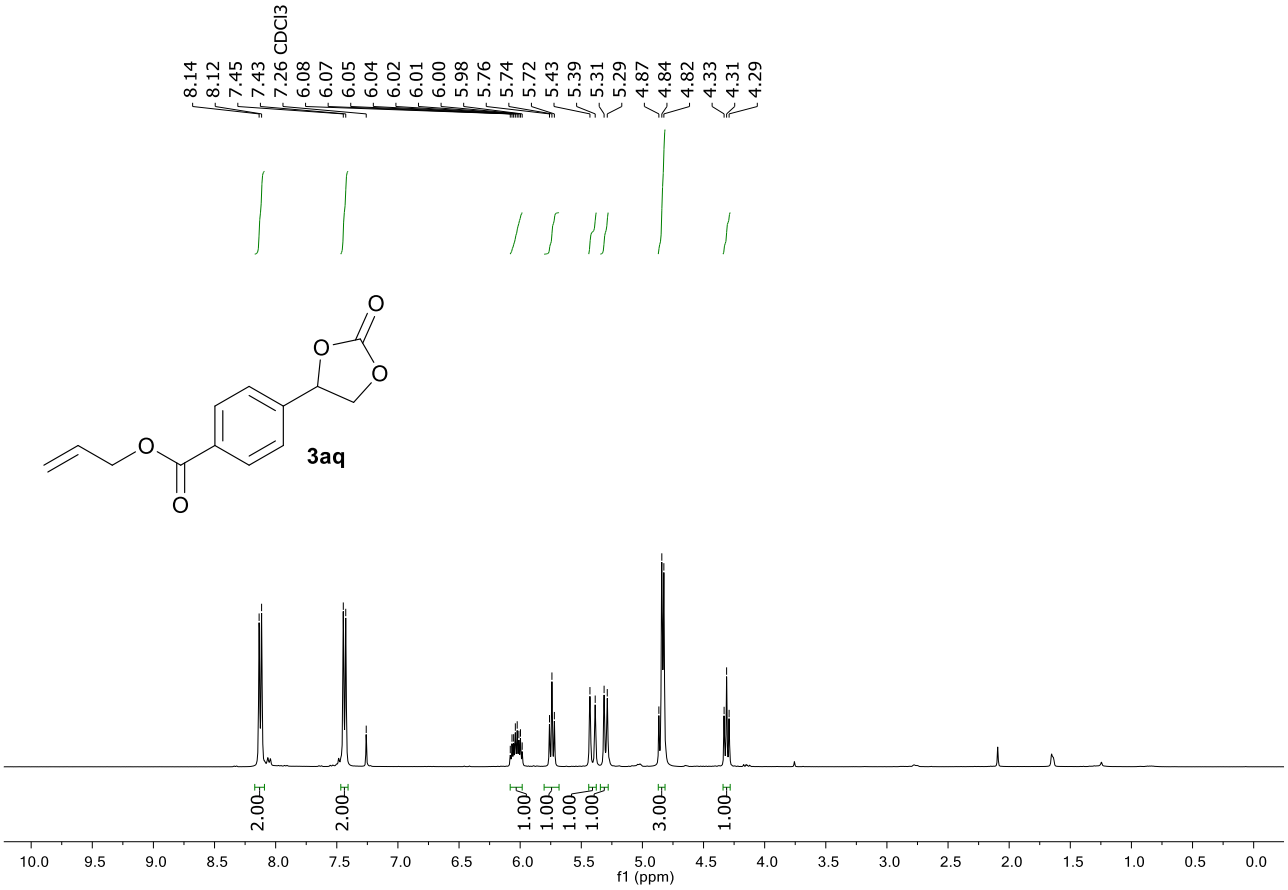


Figure S83. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of allyl 4-(2-oxo-1,3-dioxolan-4-yl)benzoate (**3aq**).

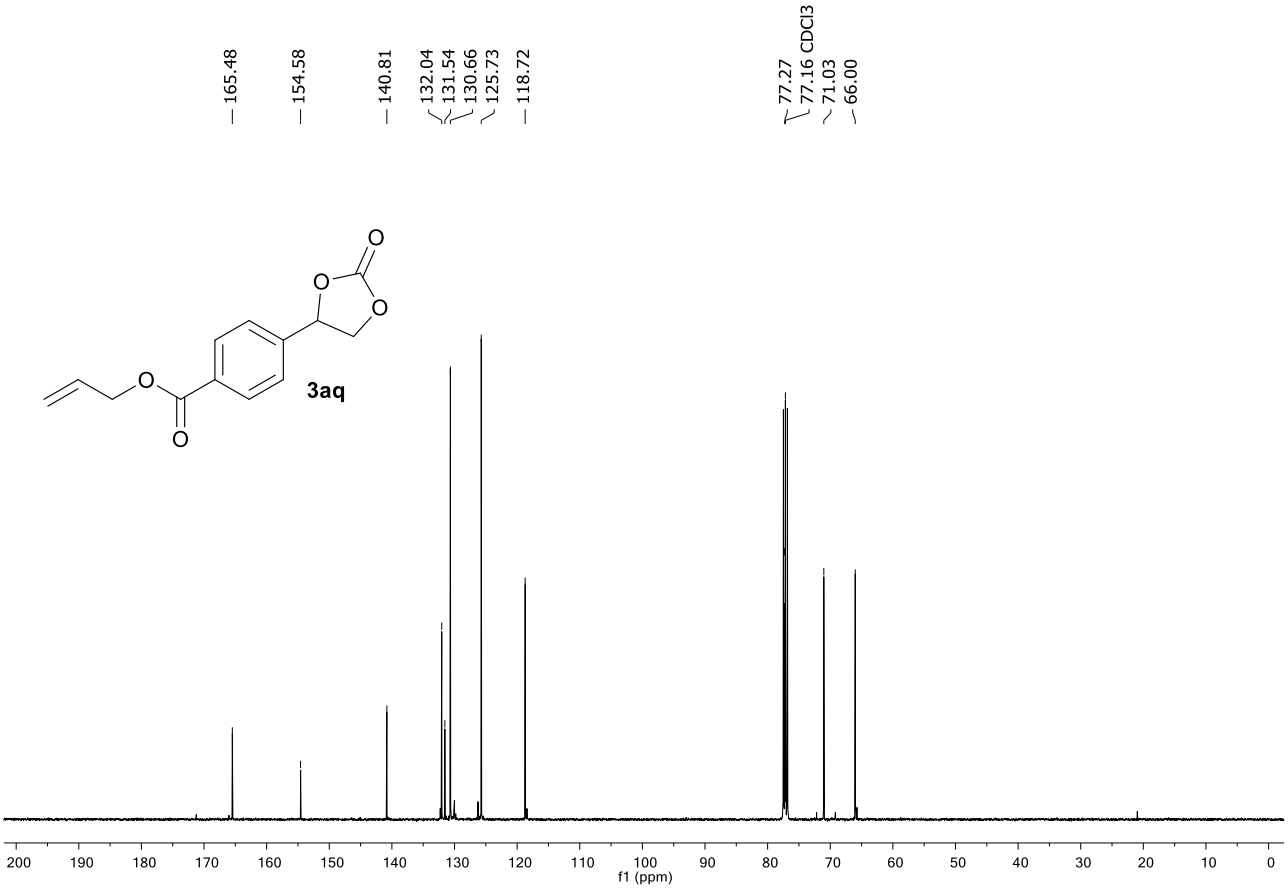


Figure S84. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of allyl 4-(2-oxo-1,3-dioxolan-4-yl)benzoate (**3aq**).

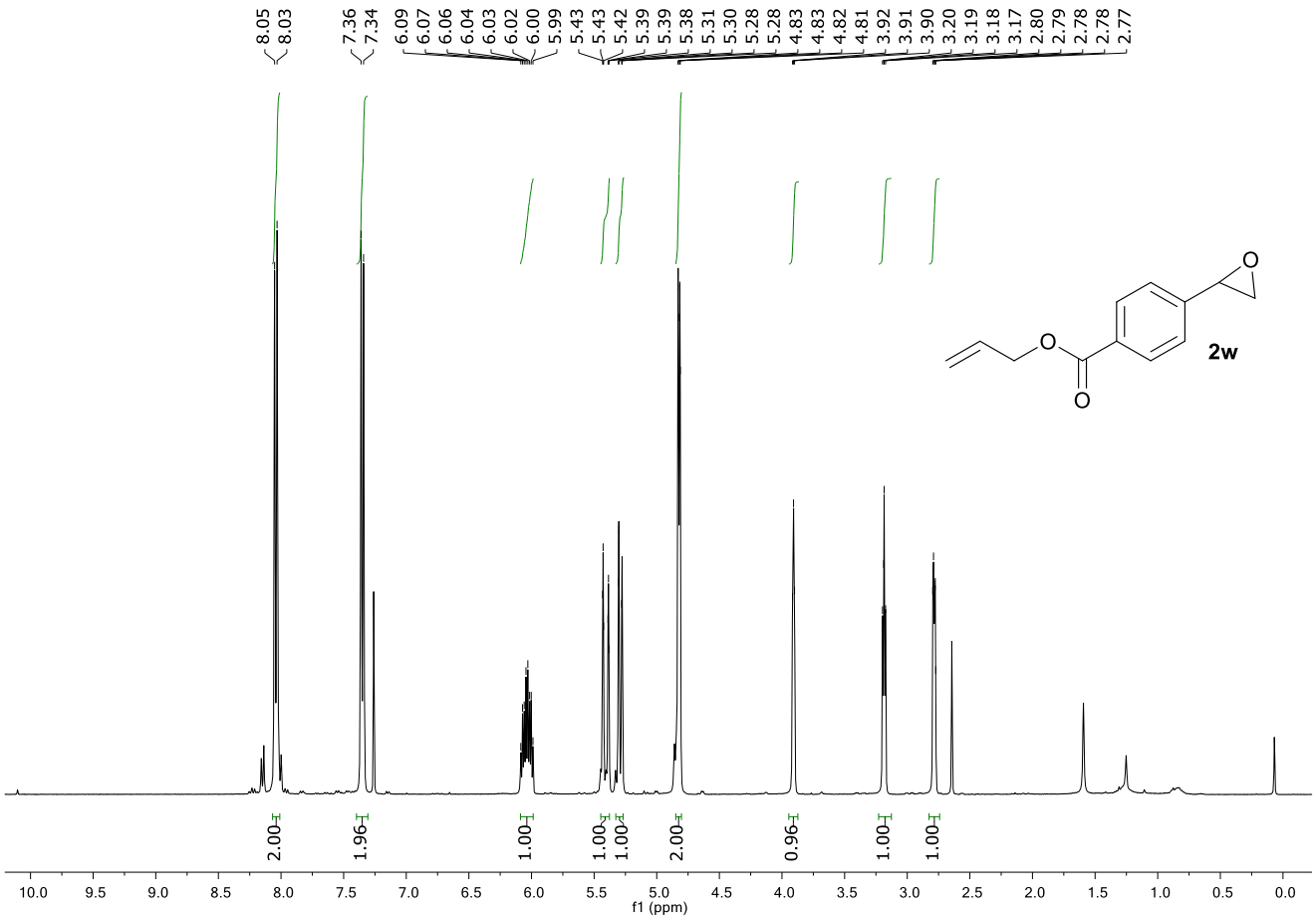


Figure S85. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of allyl 4-(oxiran-2-yl)benzoate (**2w**).

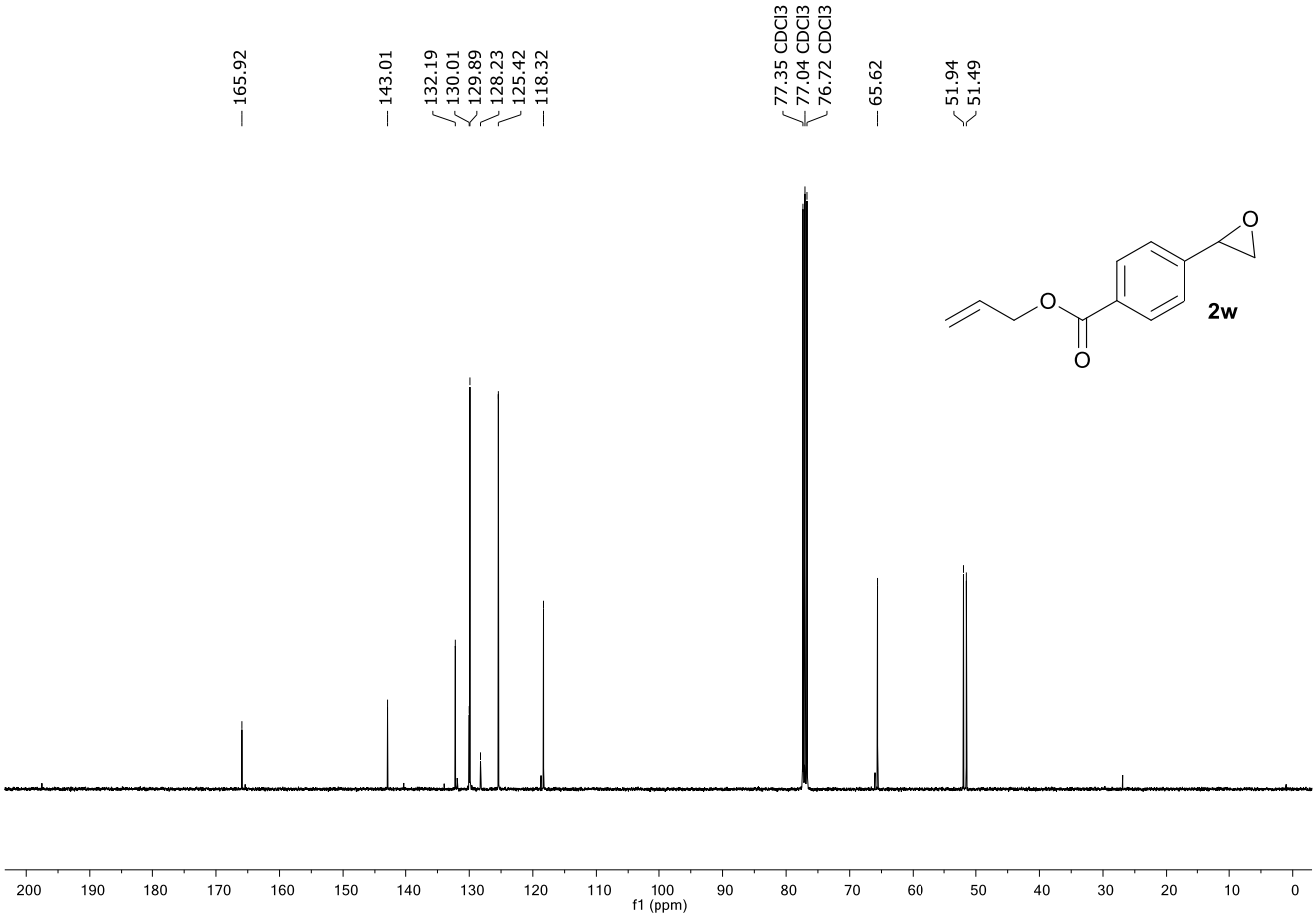


Figure S86. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of allyl 4-(oxiran-2-yl)benzoate (**2w**).

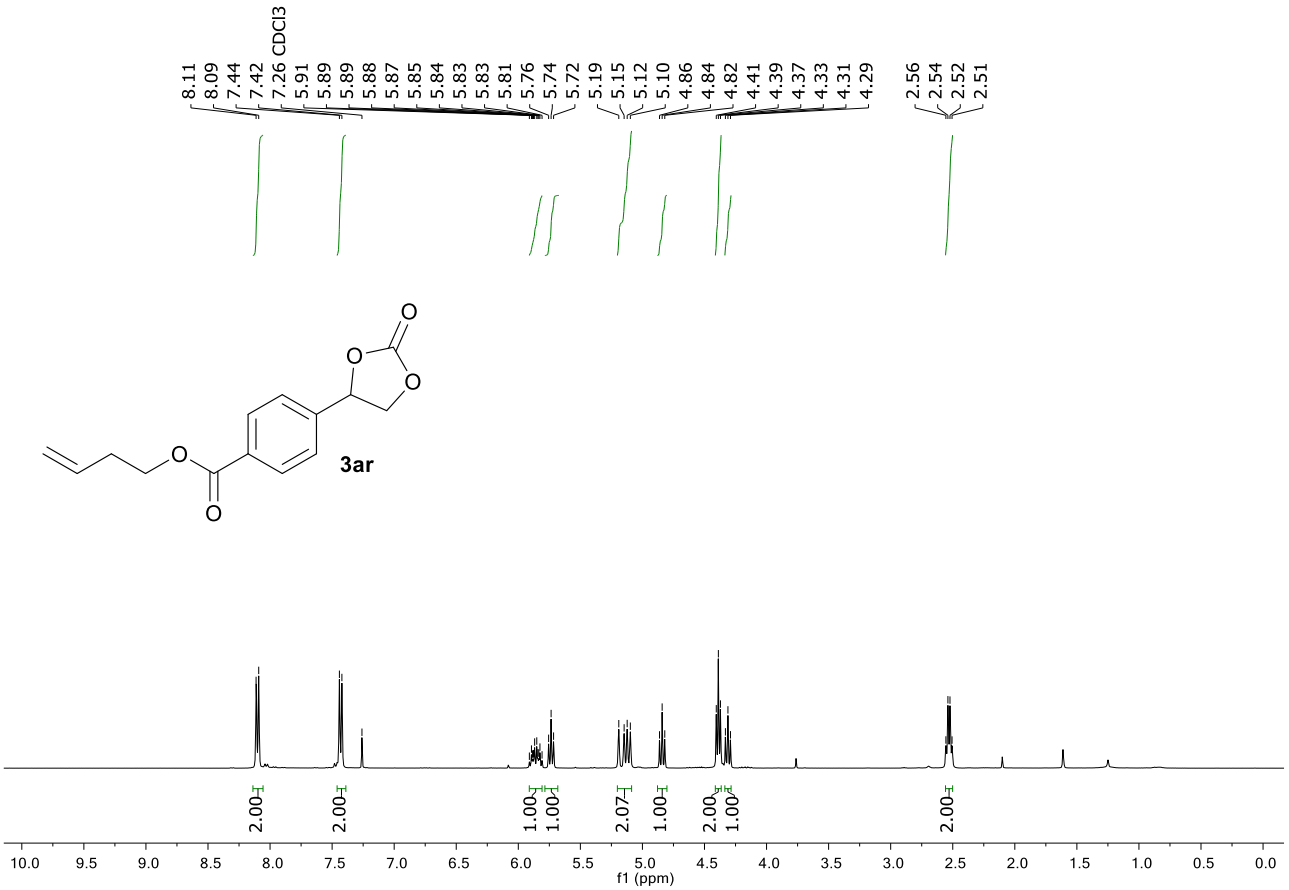


Figure S87. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of but-3-en-1-yl 4-(2-oxo-1,3-dioxolan-4-yl)benzoate (**3ar**).

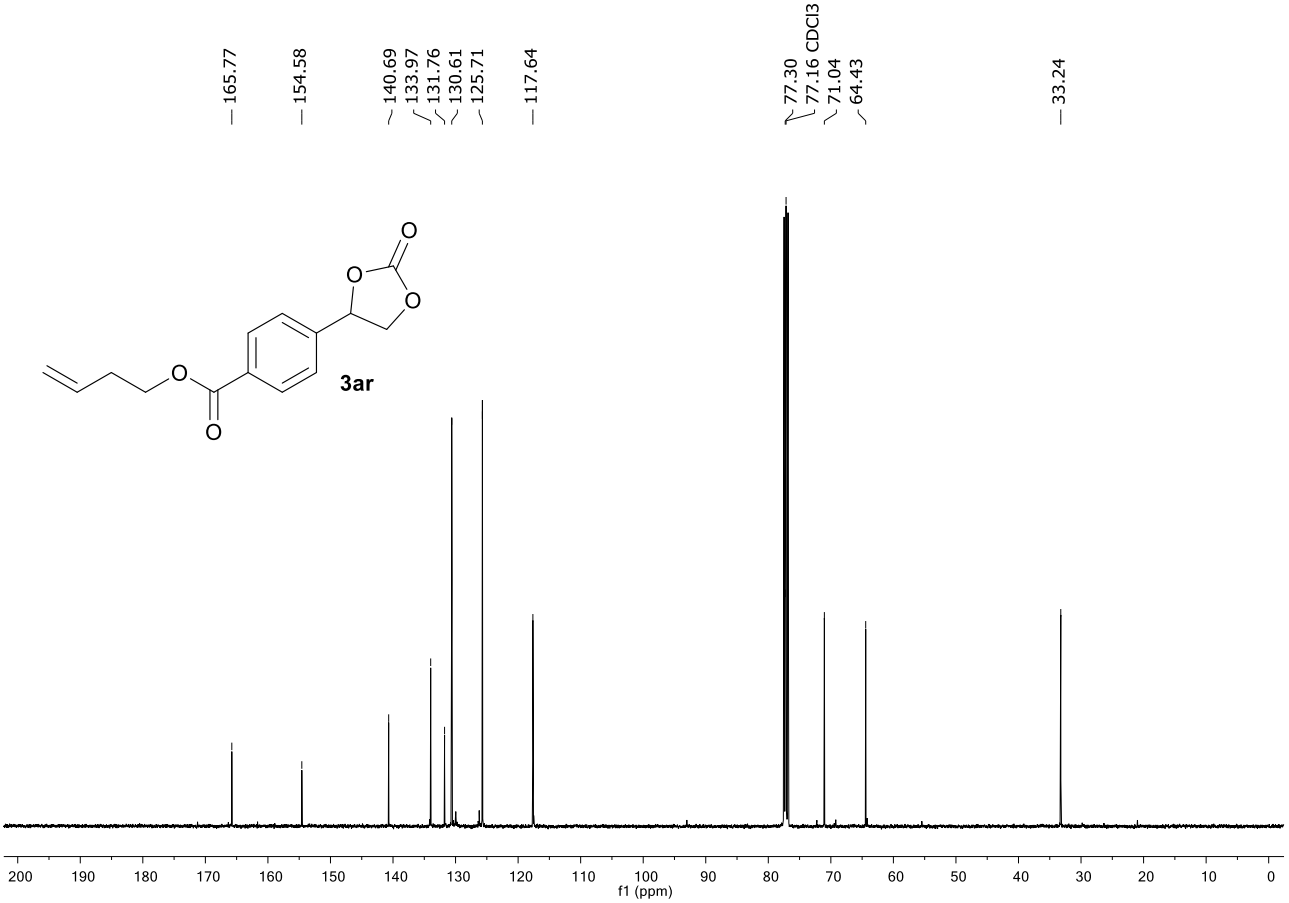


Figure S88. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of but-3-en-1-yl 4-(2-oxo-1,3-dioxolan-4-yl)benzoate (**3ar**).

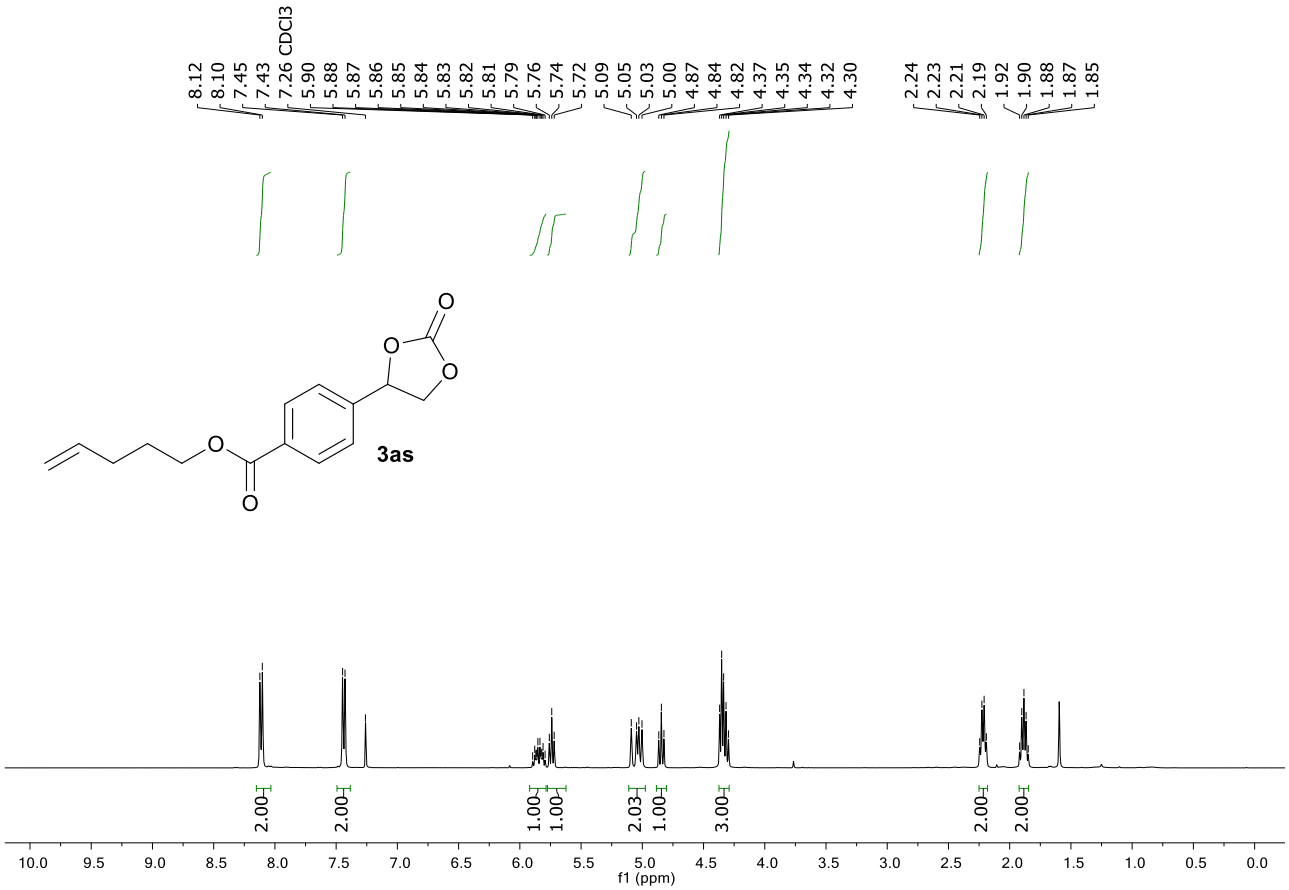


Figure S89. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of pent-4-en-1-yl 4-(2-oxo-1,3-dioxolan-4-yl)benzoate (**3as**).

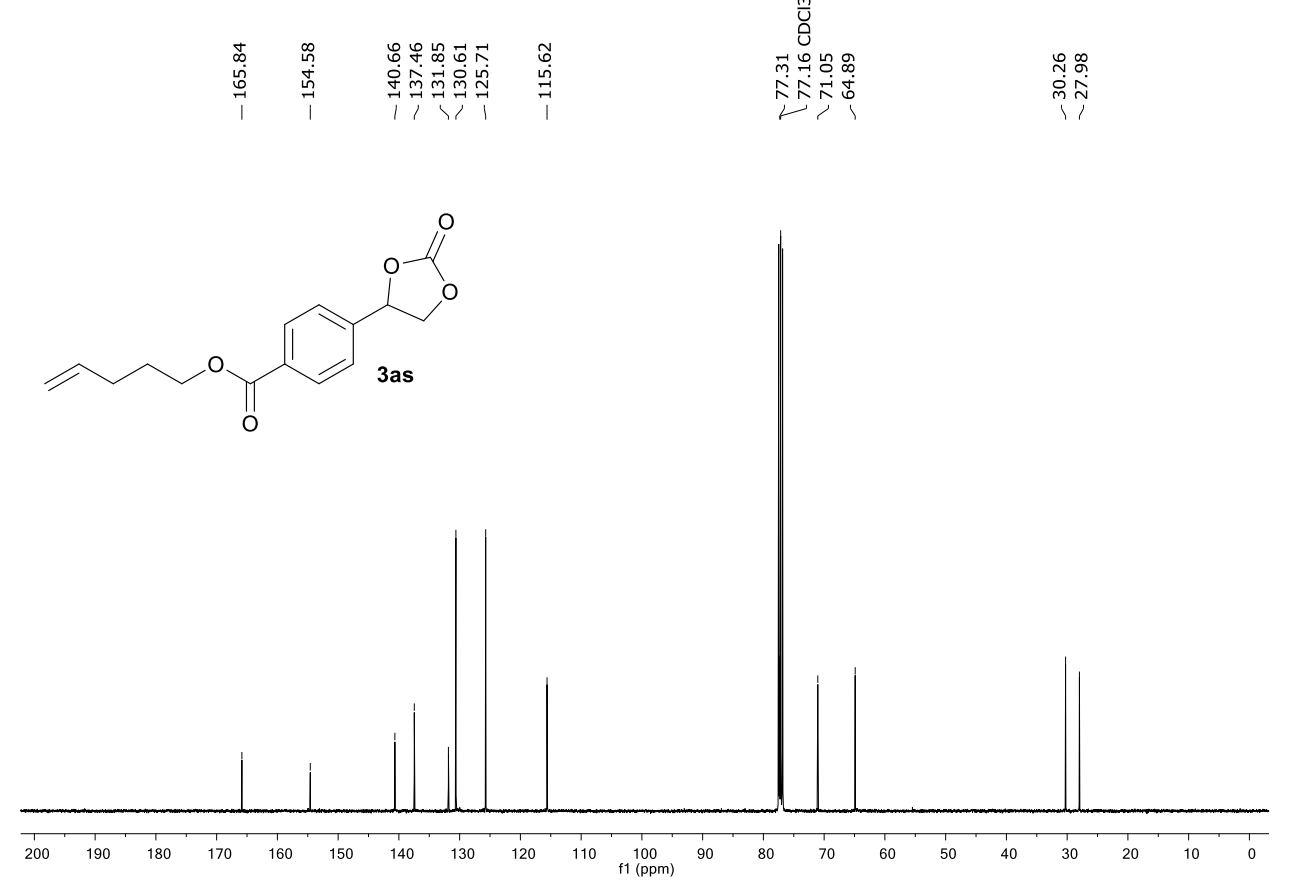


Figure S90. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of pent-4-en-1-yl 4-(2-oxo-1,3-dioxolan-4-yl)benzoate (**3as**).

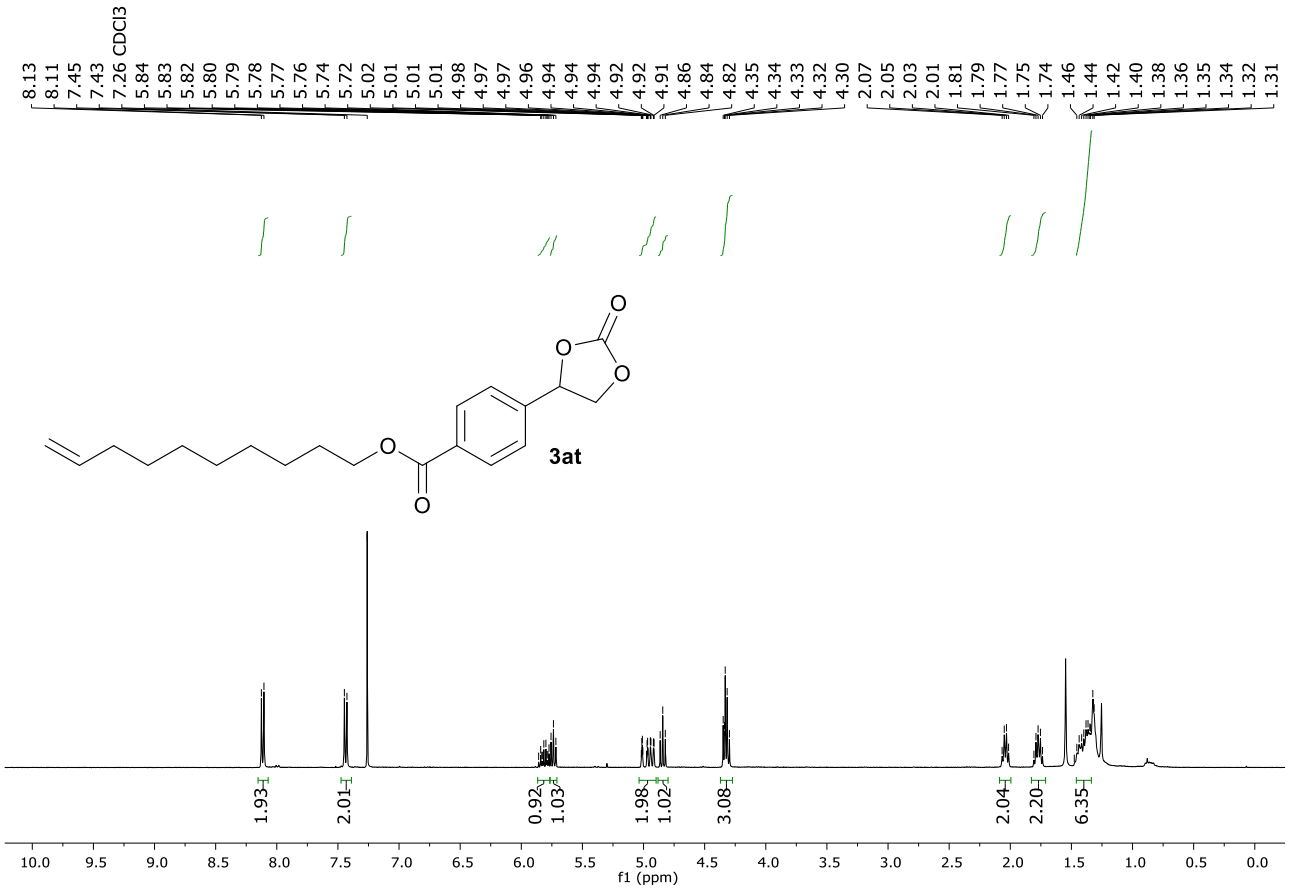


Figure S91. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of dec-9-en-1-yl 4-(2-oxo-1,3-dioxolan-4-yl)benzoate (**3at**).

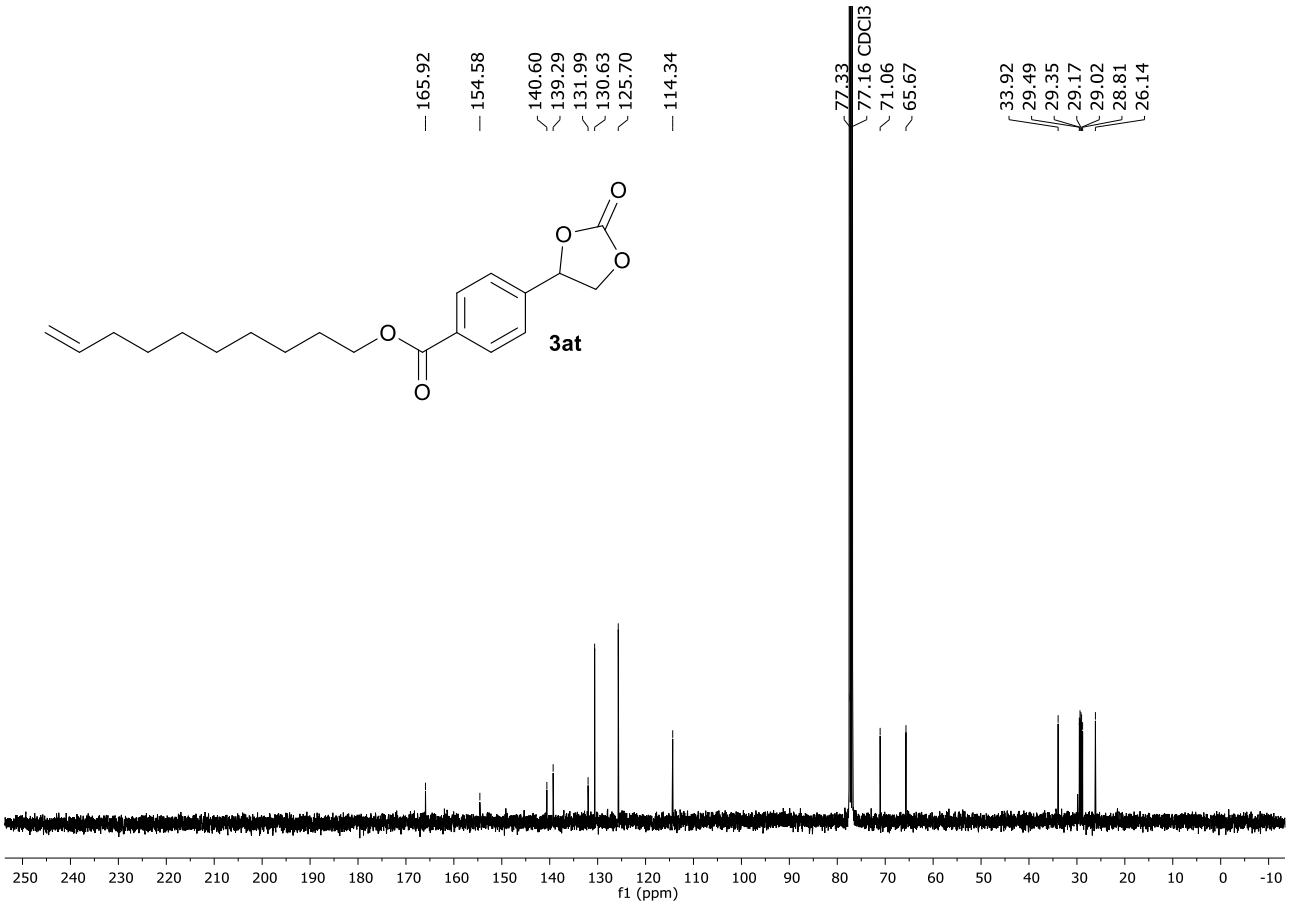


Figure S92. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of dec-9-en-1-yl 4-(2-oxo-1,3-dioxolan-4-yl)benzoate (**3at**).

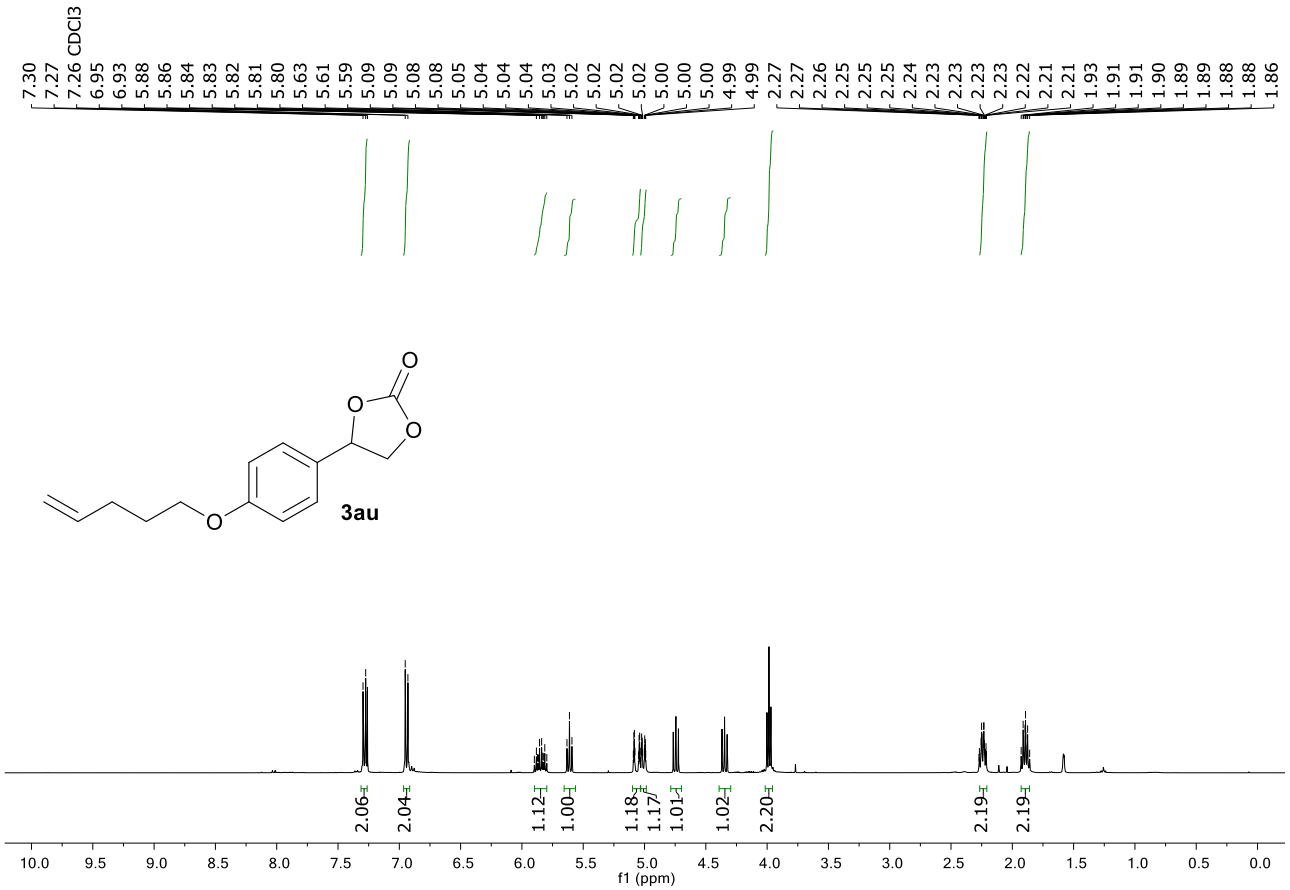


Figure S93. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(4-(pent-4-en-1-yloxy)phenyl)-1,3-dioxolan-2-one (**3au**).

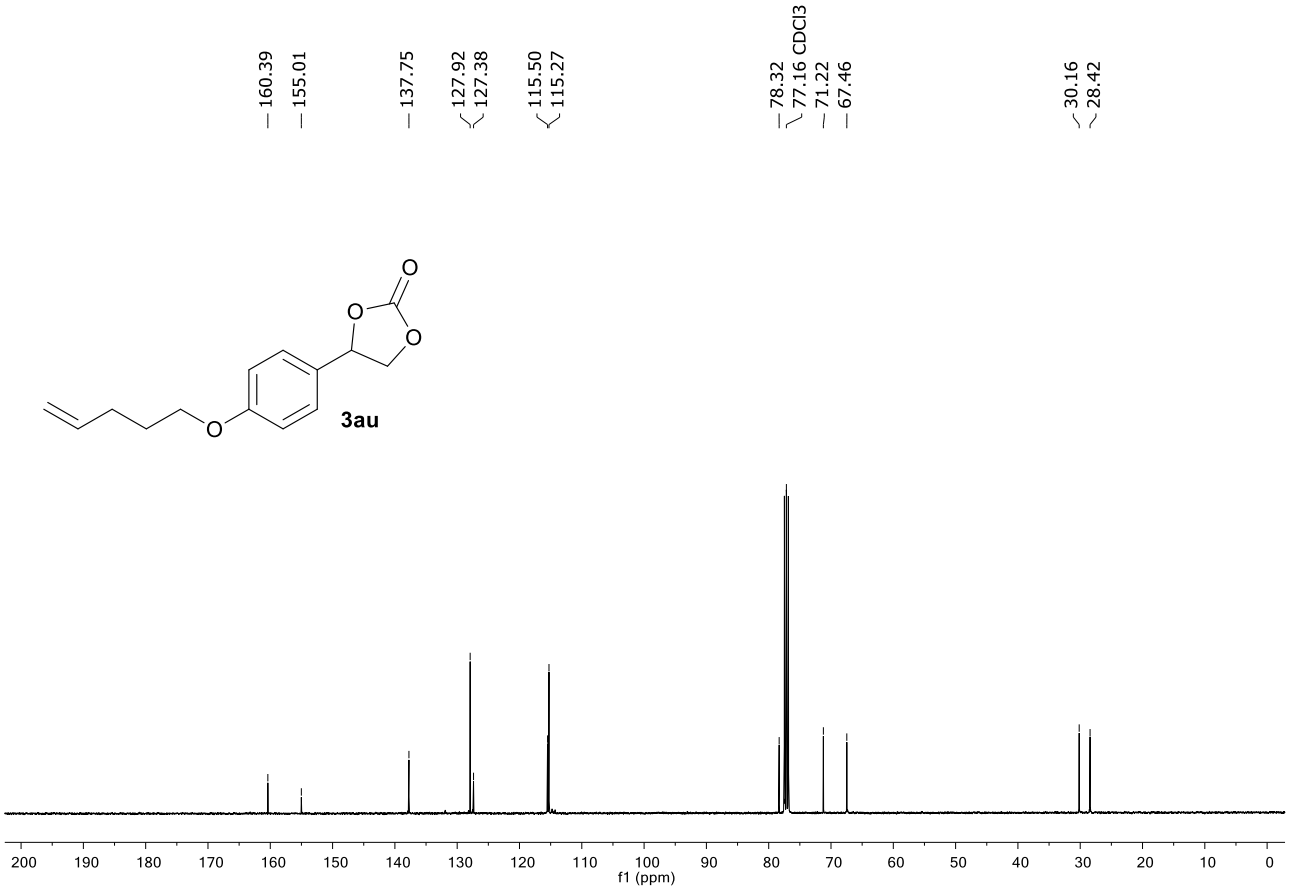


Figure S94. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(4-(pent-4-en-1-yloxy)phenyl)-1,3-dioxolan-2-one (**3au**).

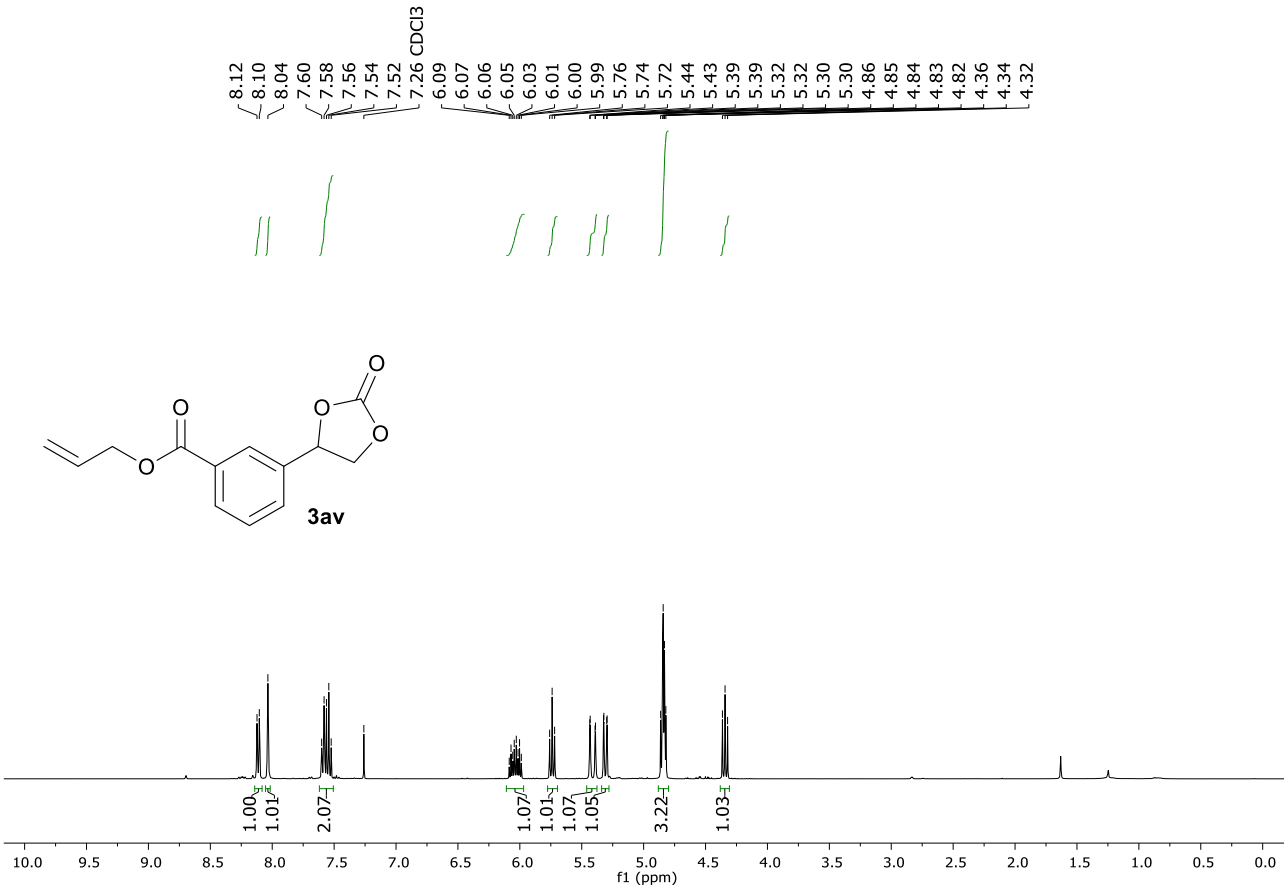


Figure S95. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of allyl 3-(2-oxo-1,3-dioxolan-4-yl)benzoate (**3av**).

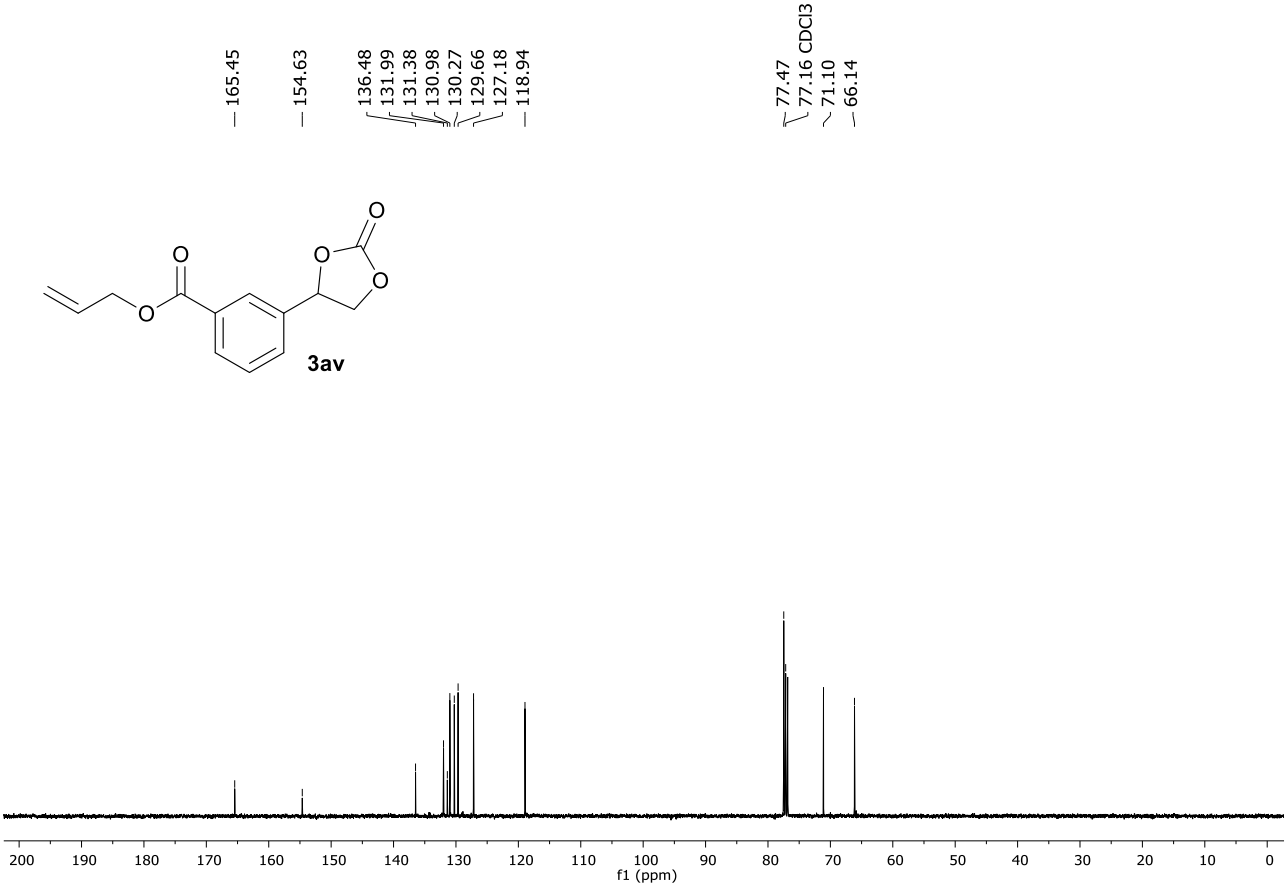


Figure S96. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of allyl 3-(2-oxo-1,3-dioxolan-4-yl)benzoate (**3av**).

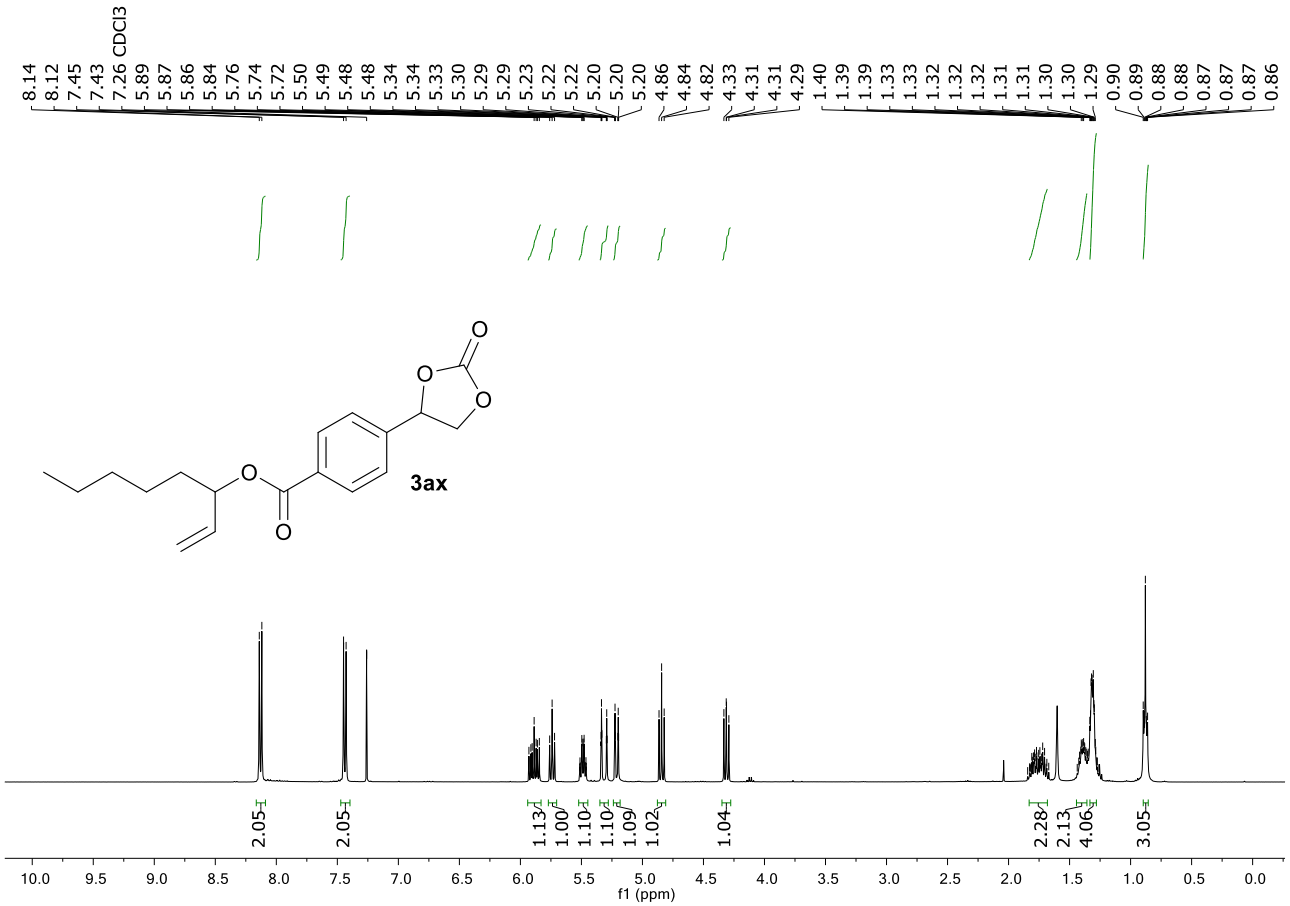


Figure S97. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of oct-1-en-3-yl 4-(2-oxo-1,3-dioxolan-4-yl)benzoate (**3ax**).

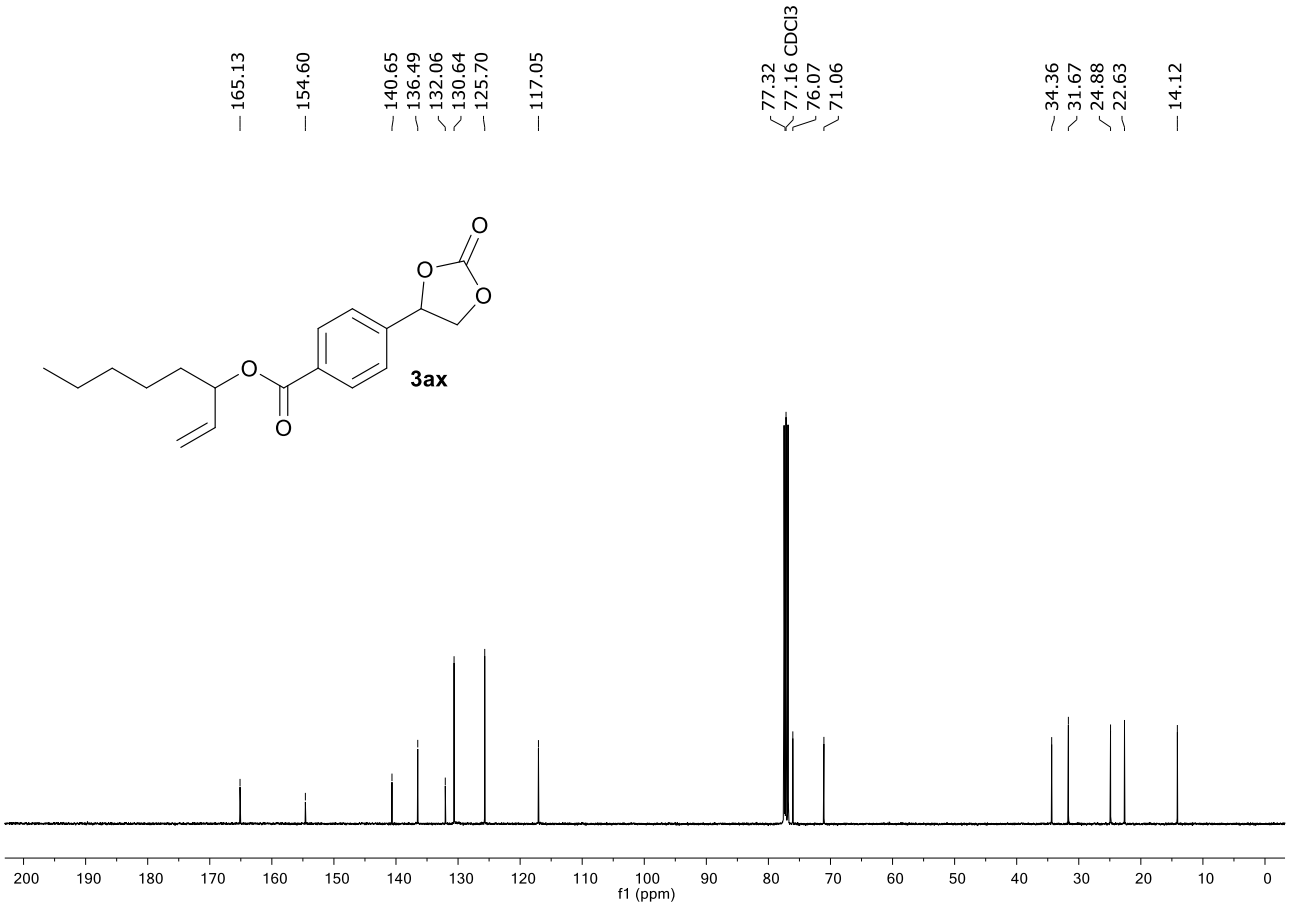


Figure S98. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of oct-1-en-3-yl 4-(2-oxo-1,3-dioxolan-4-yl)benzoate (**3ax**).

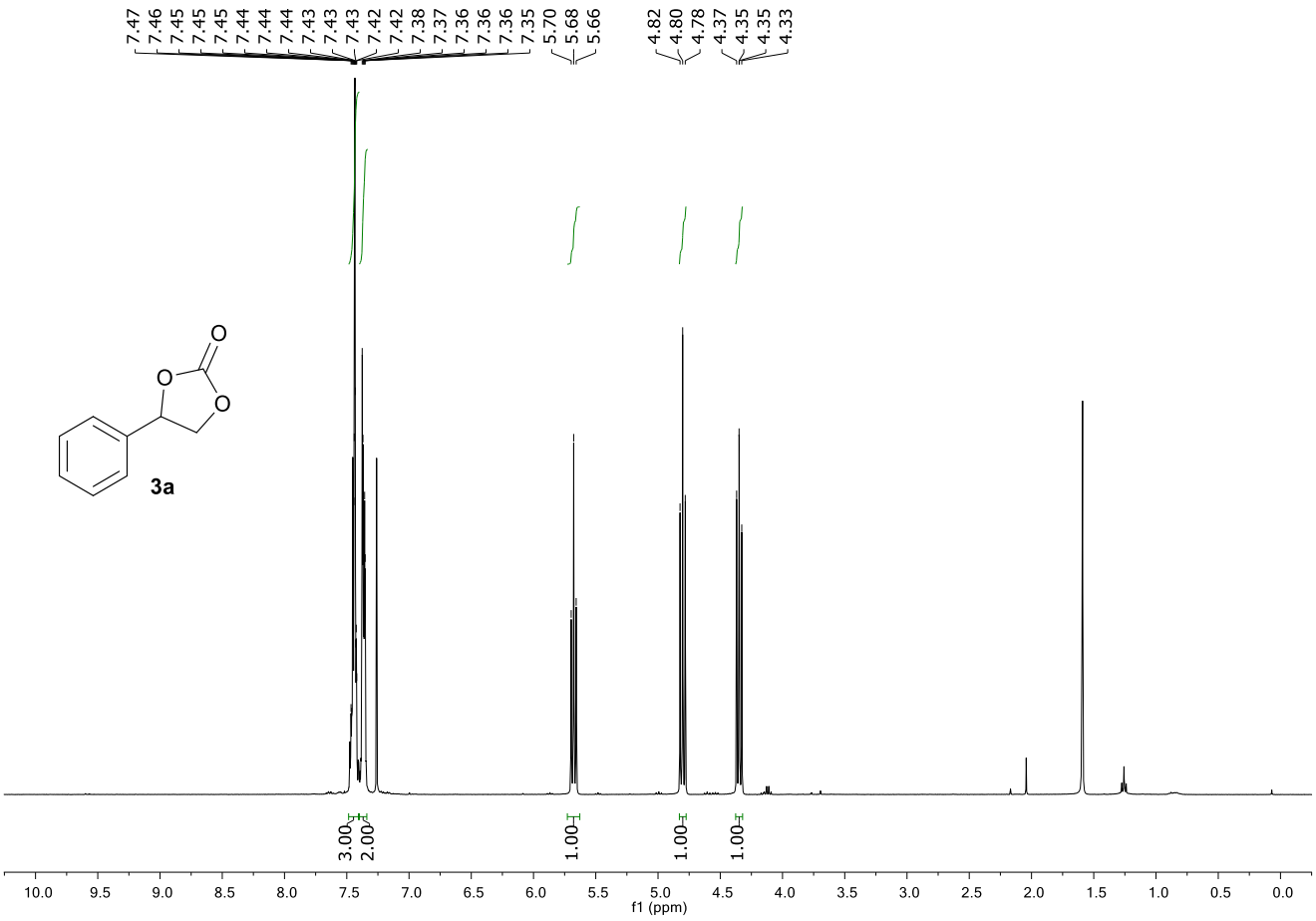


Figure S99. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-phenyl-1,3-dioxolan-2-one (**3a**).

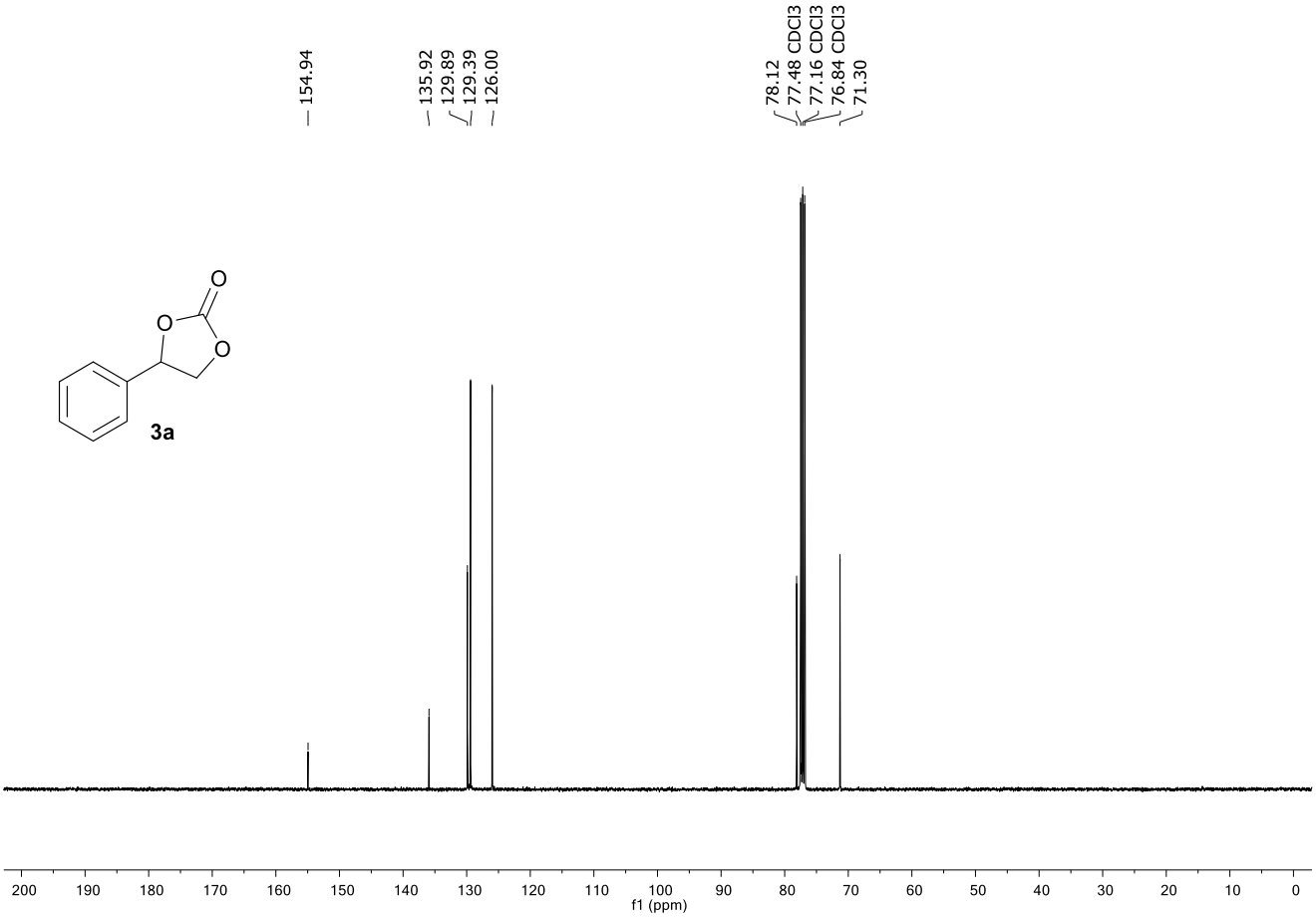


Figure S100. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-phenyl-1,3-dioxolan-2-one (**3a**).

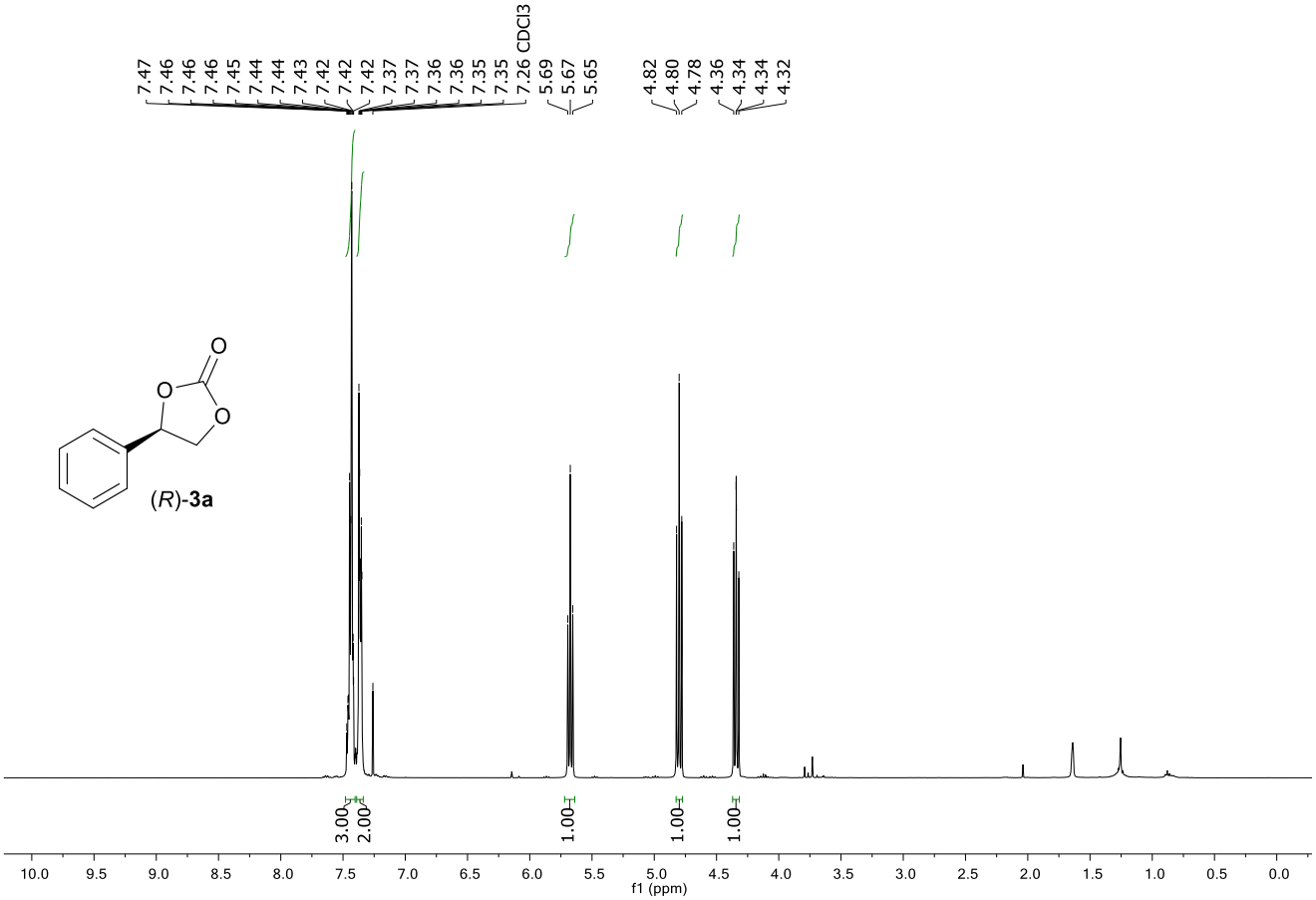


Figure S101. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-4-phenyl-1,3-dioxolan-2-one ((*R*)-**3a**).

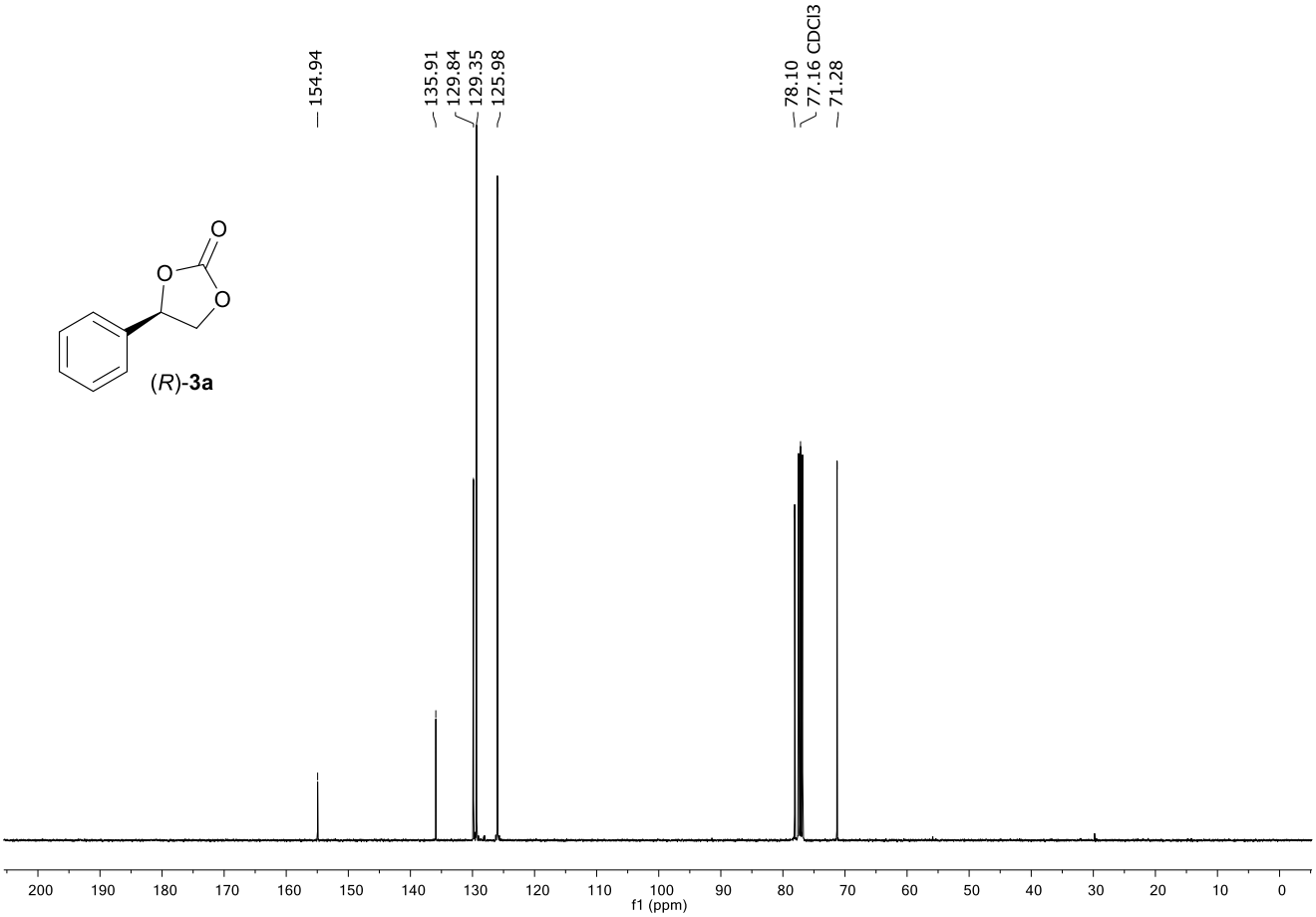


Figure S102. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (*R*)-4-phenyl-1,3-dioxolan-2-one ((*R*)-**3a**).

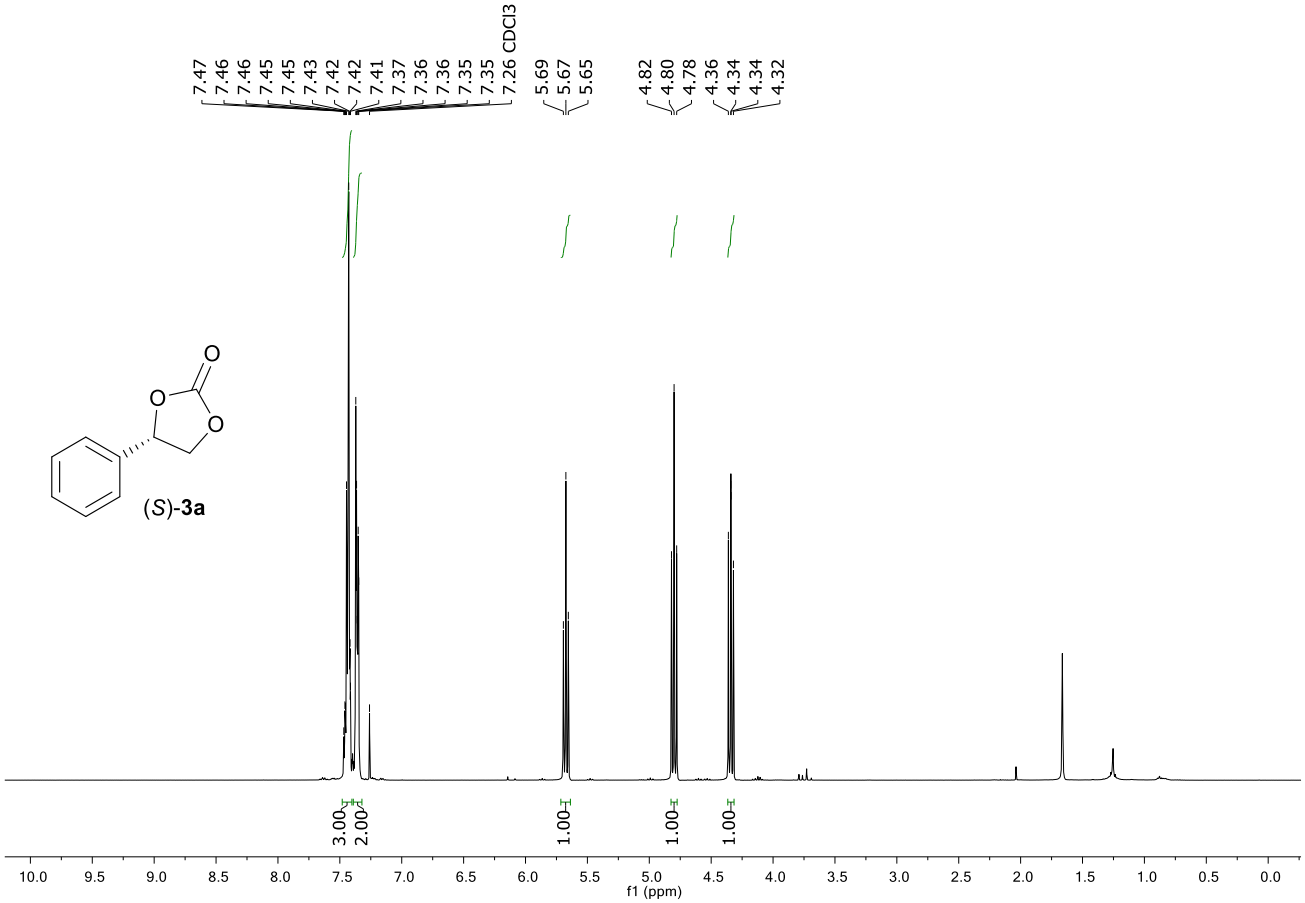


Figure S103. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-4-phenyl-1,3-dioxolan-2-one ((*S*)-**3a**).

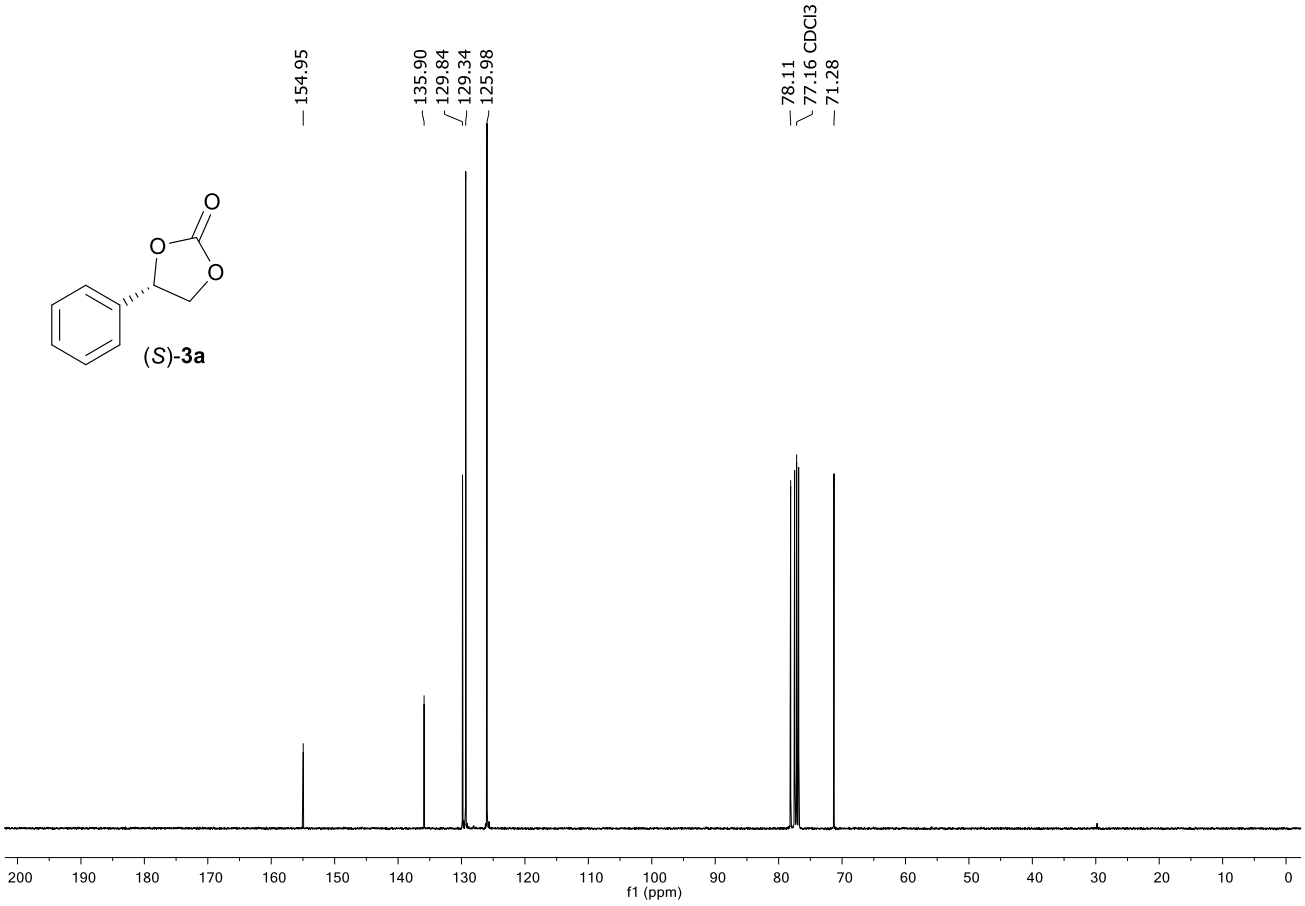


Figure S104. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (*S*)-4-phenyl-1,3-dioxolan-2-one ((*S*)-**3a**).

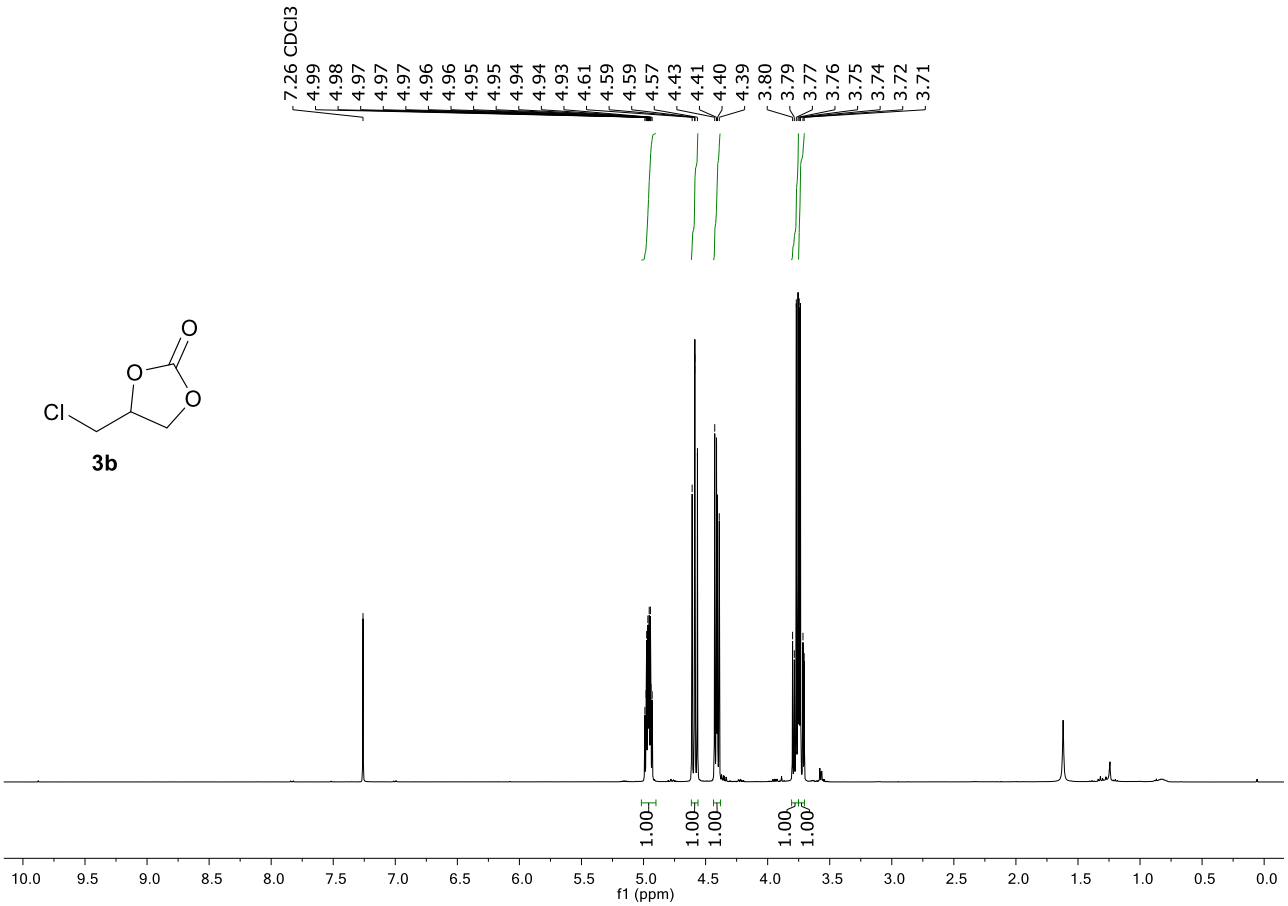


Figure S105. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(chloromethyl)-1,3-dioxolan-2-one (**3b**).

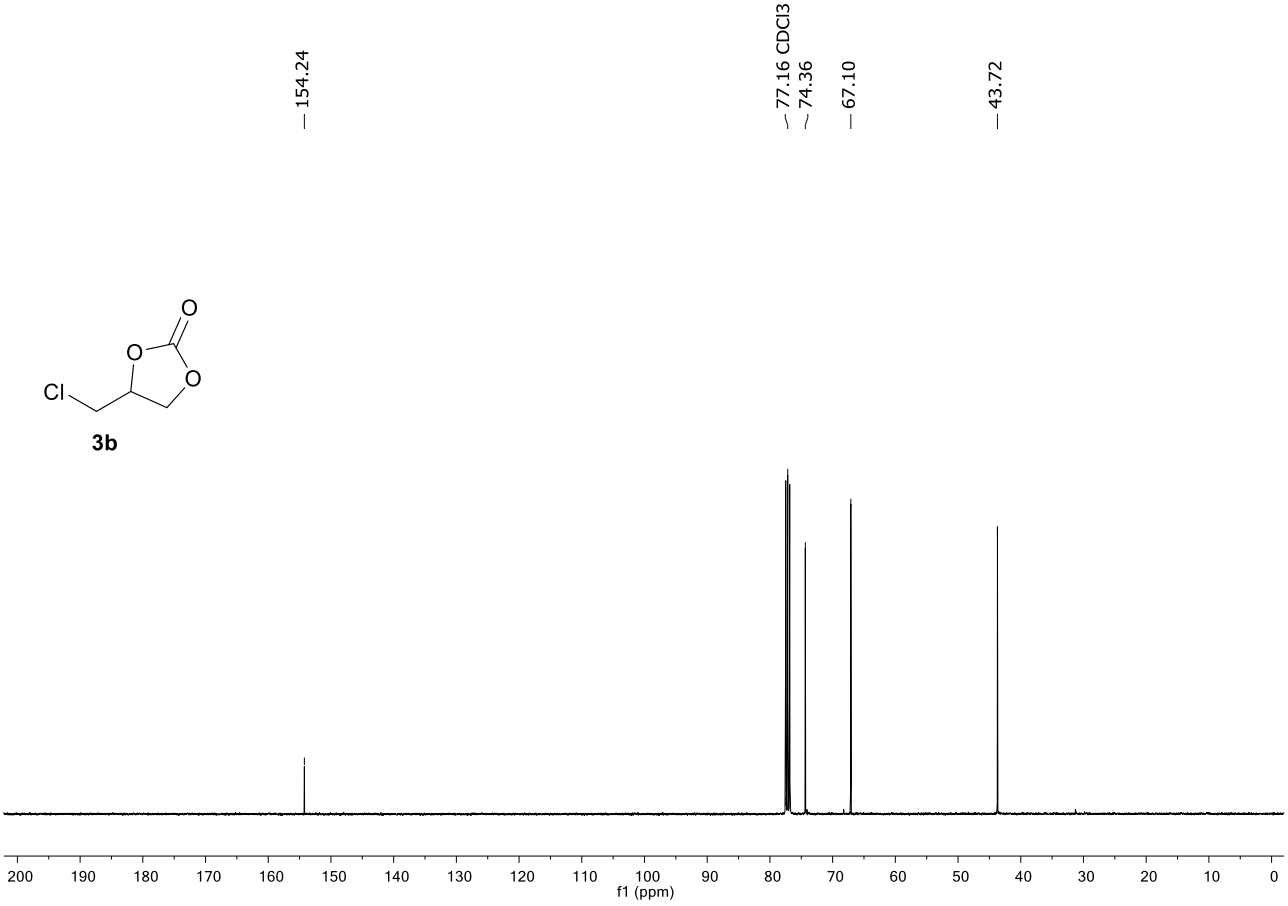


Figure S106. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(chloromethyl)-1,3-dioxolan-2-one (**3b**).

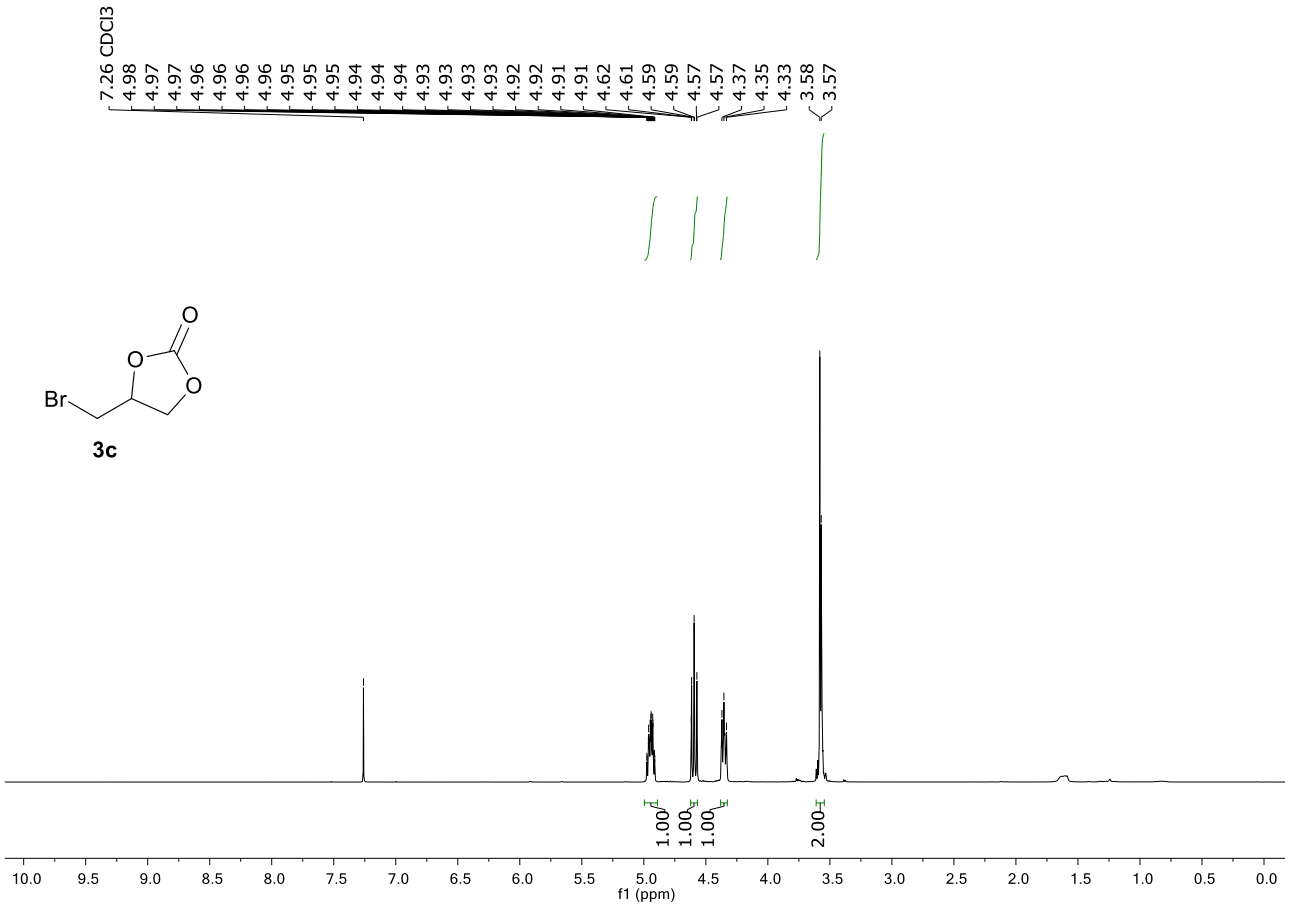


Figure S107. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(bromomethyl)-1,3-dioxolan-2-one (**3c**).

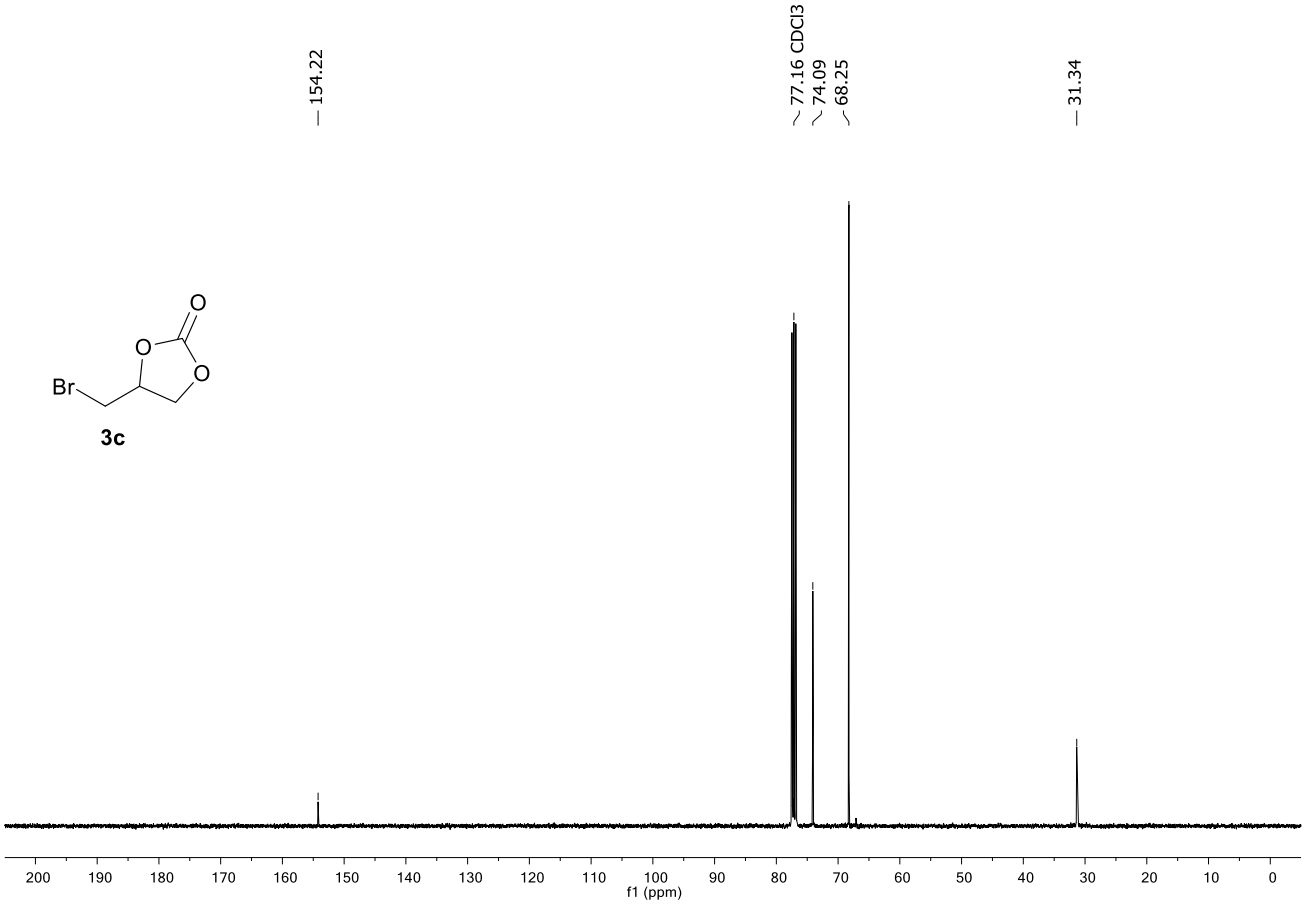


Figure S108. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(bromomethyl)-1,3-dioxolan-2-one (**3c**).

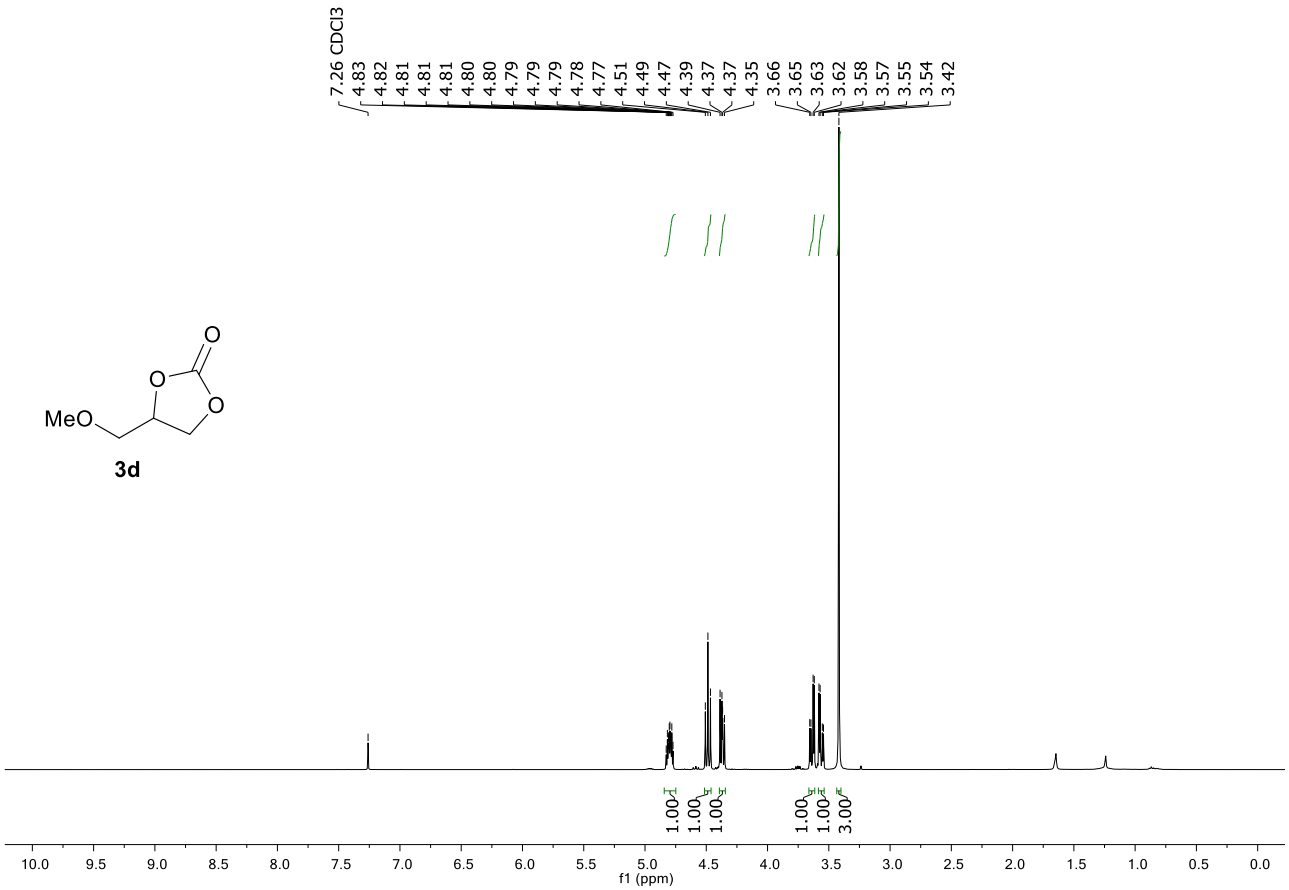


Figure S109. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(methoxymethyl)-1,3-dioxolan-2-one (**3d**).

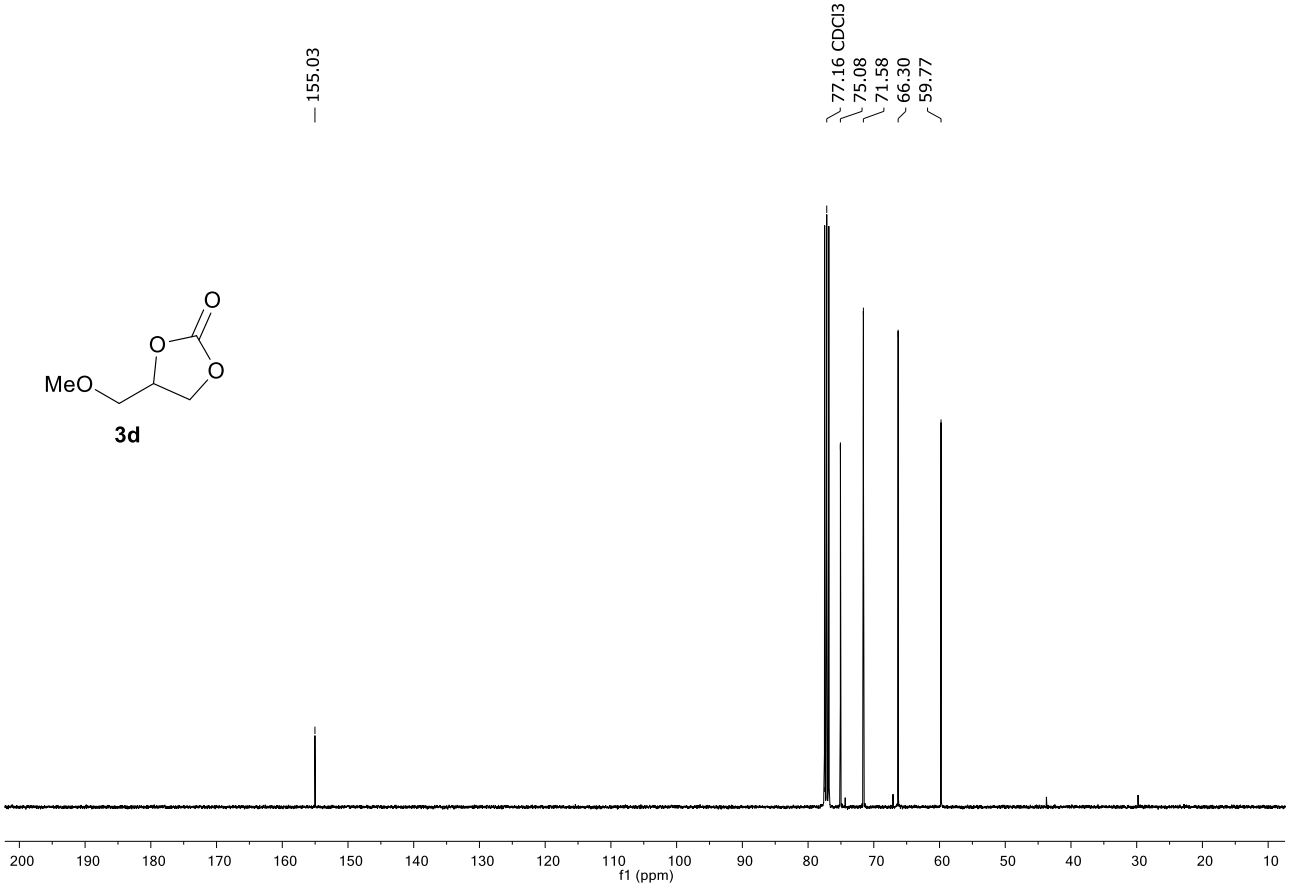


Figure S110. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of 4-(methoxymethyl)-1,3-dioxolan-2-one (**3d**).

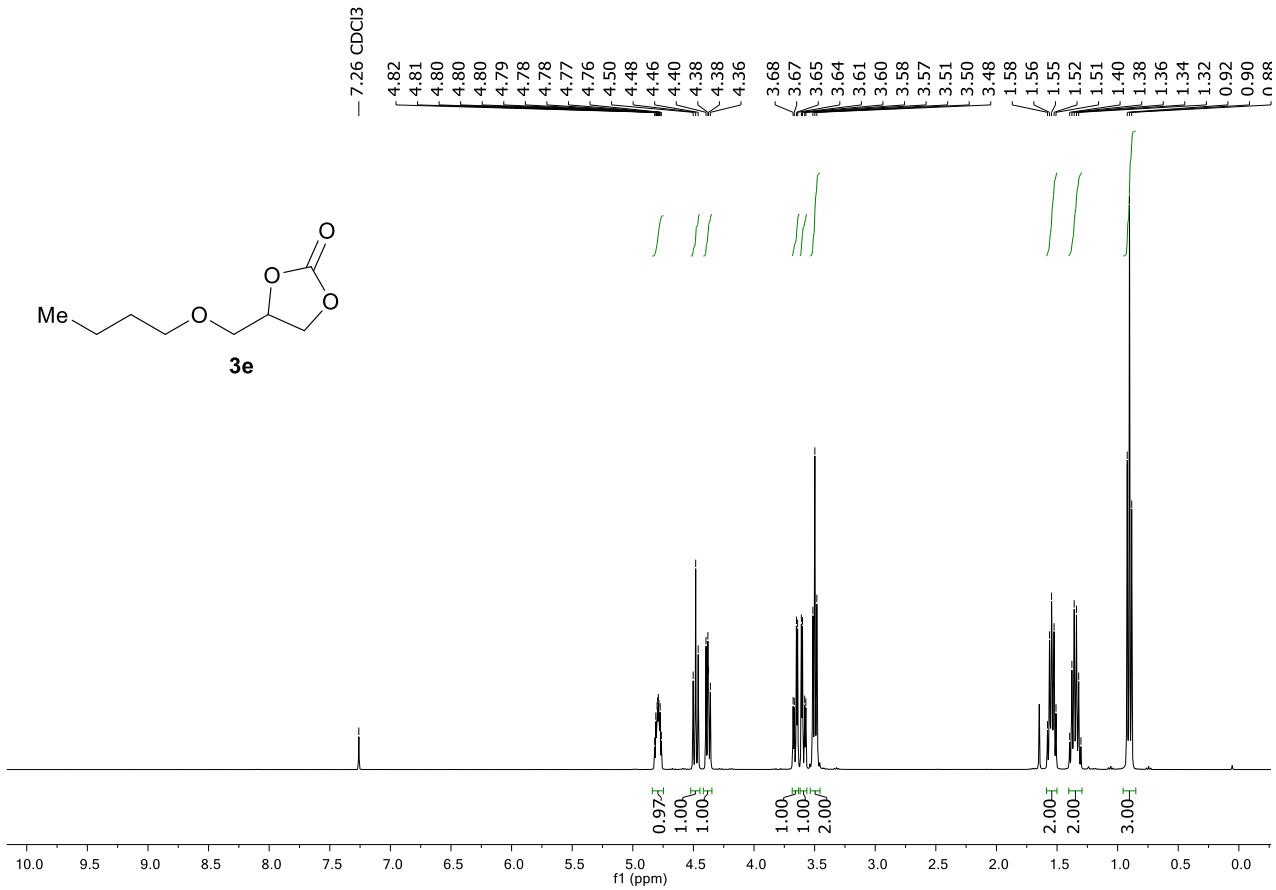


Figure S111. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(butoxymethyl)-1,3-dioxolan-2-one (**3e**).

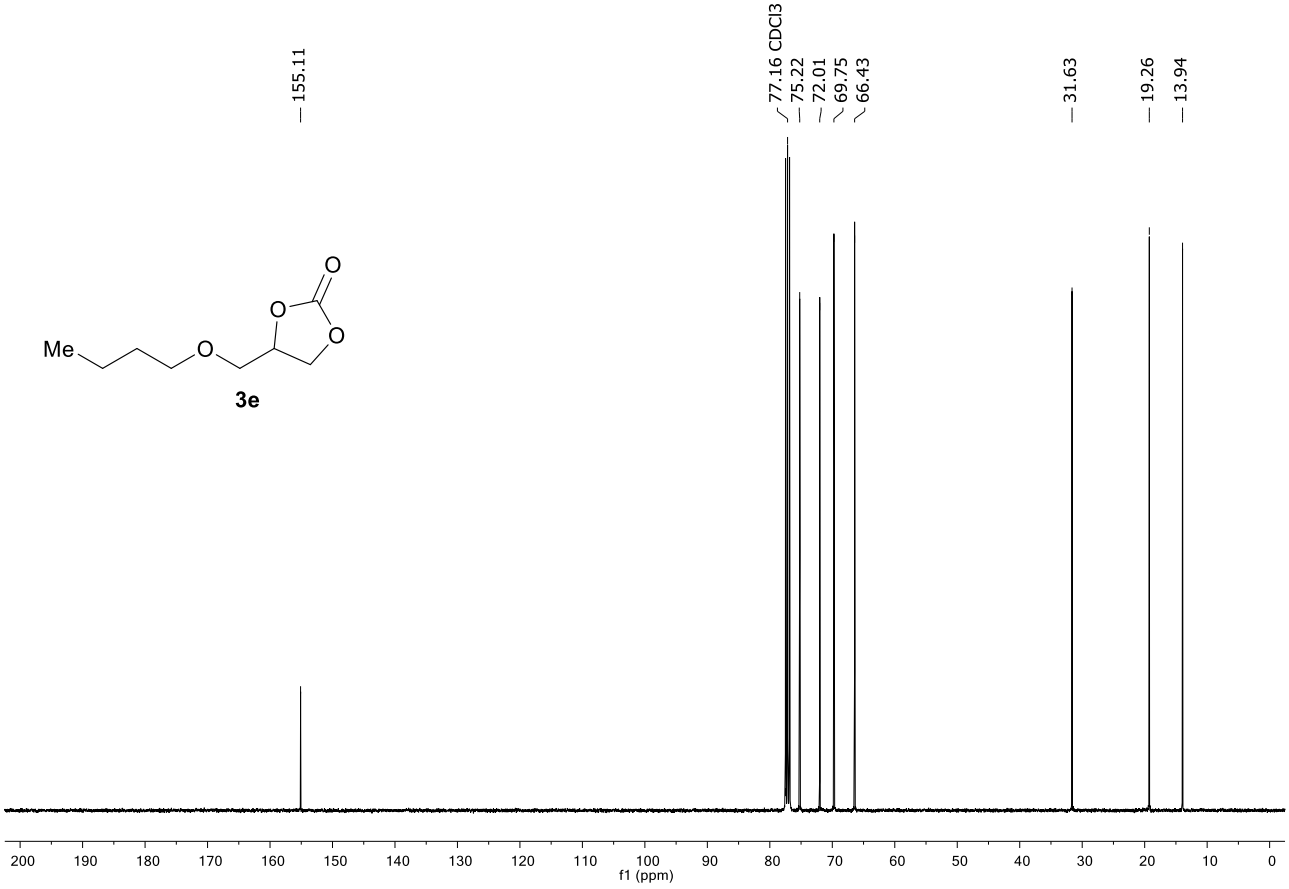


Figure S112. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(butoxymethyl)-1,3-dioxolan-2-one (**3e**).

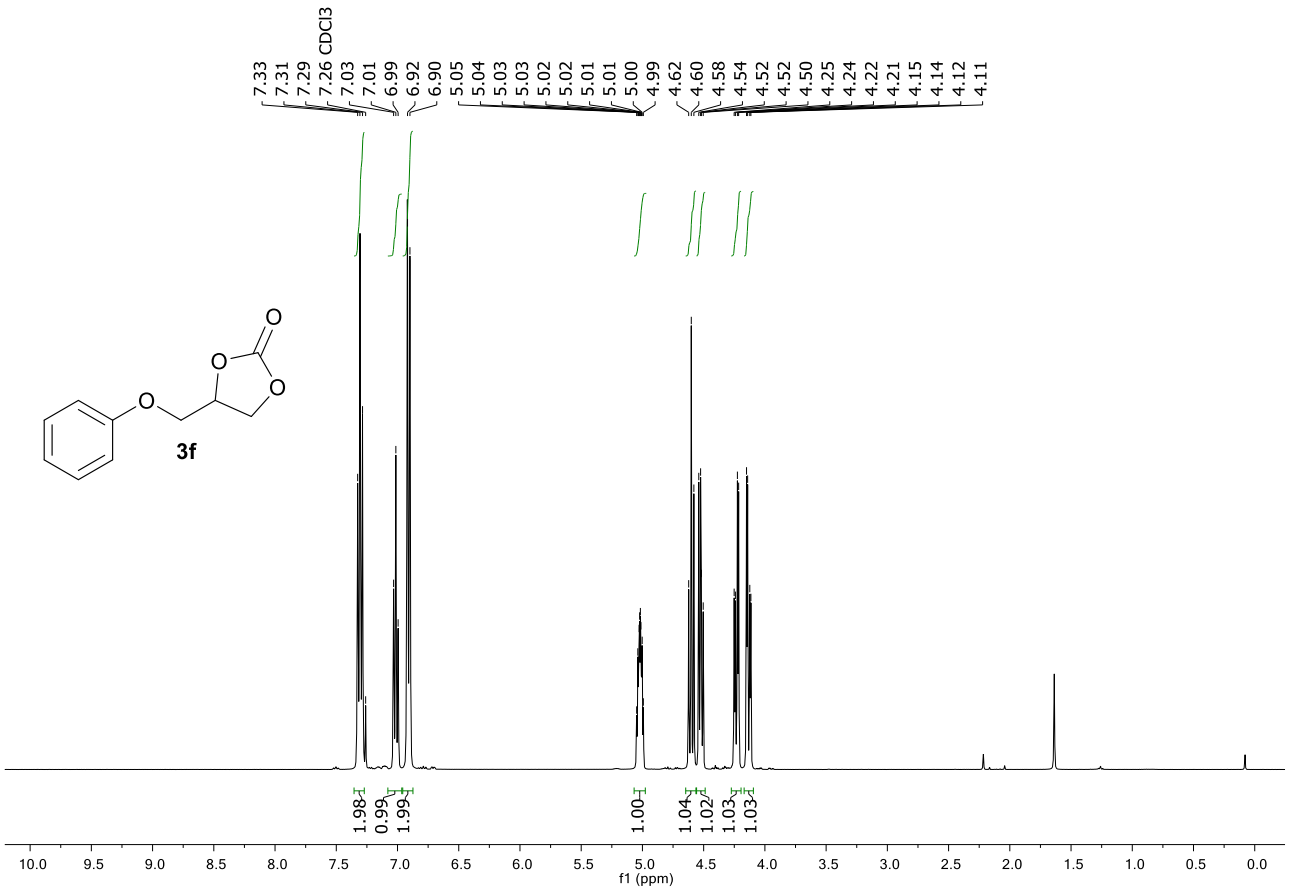


Figure S113. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(phenoxymethyl)-1,3-dioxolan-2-one (**3f**).

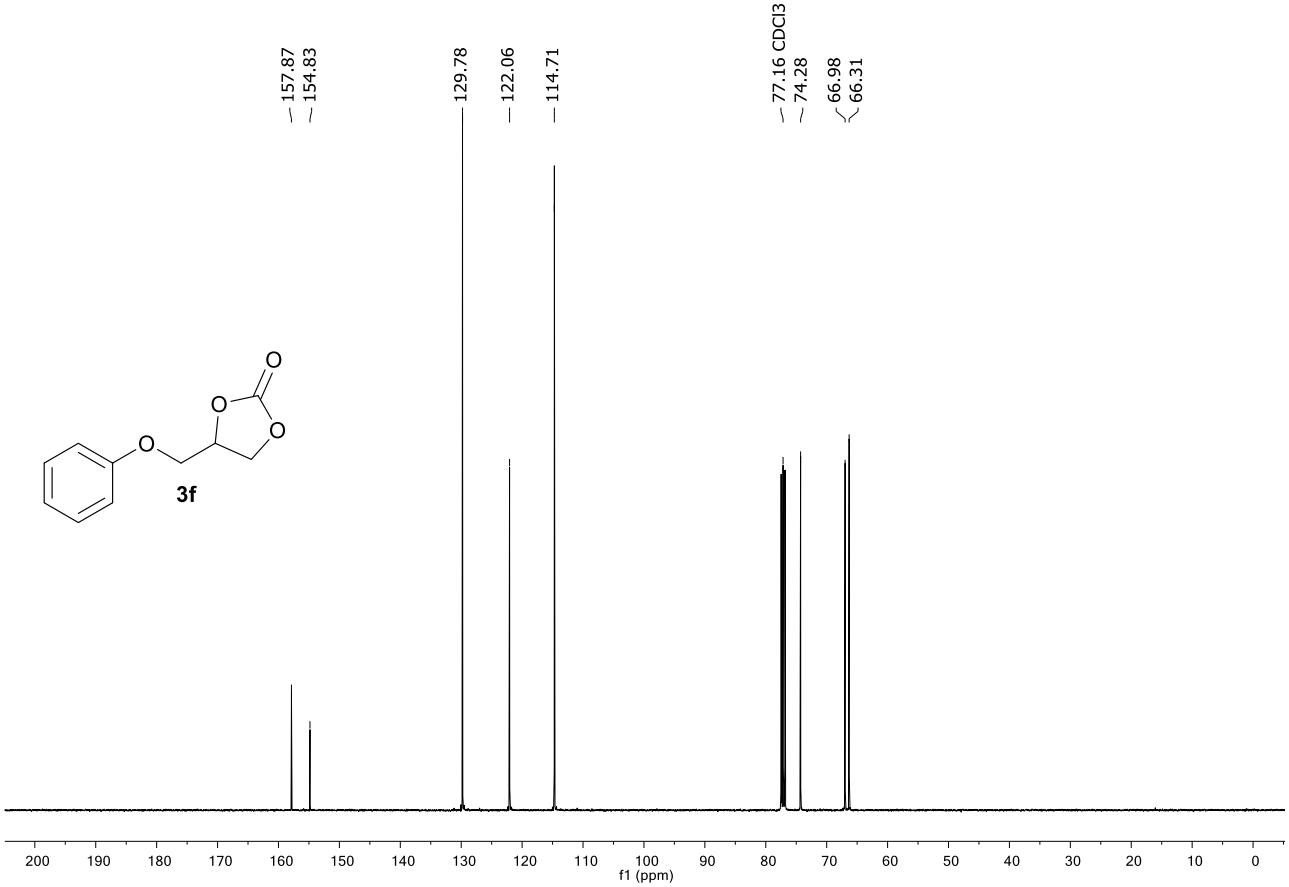


Figure S114. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(phenoxymethyl)-1,3-dioxolan-2-one (**3f**).

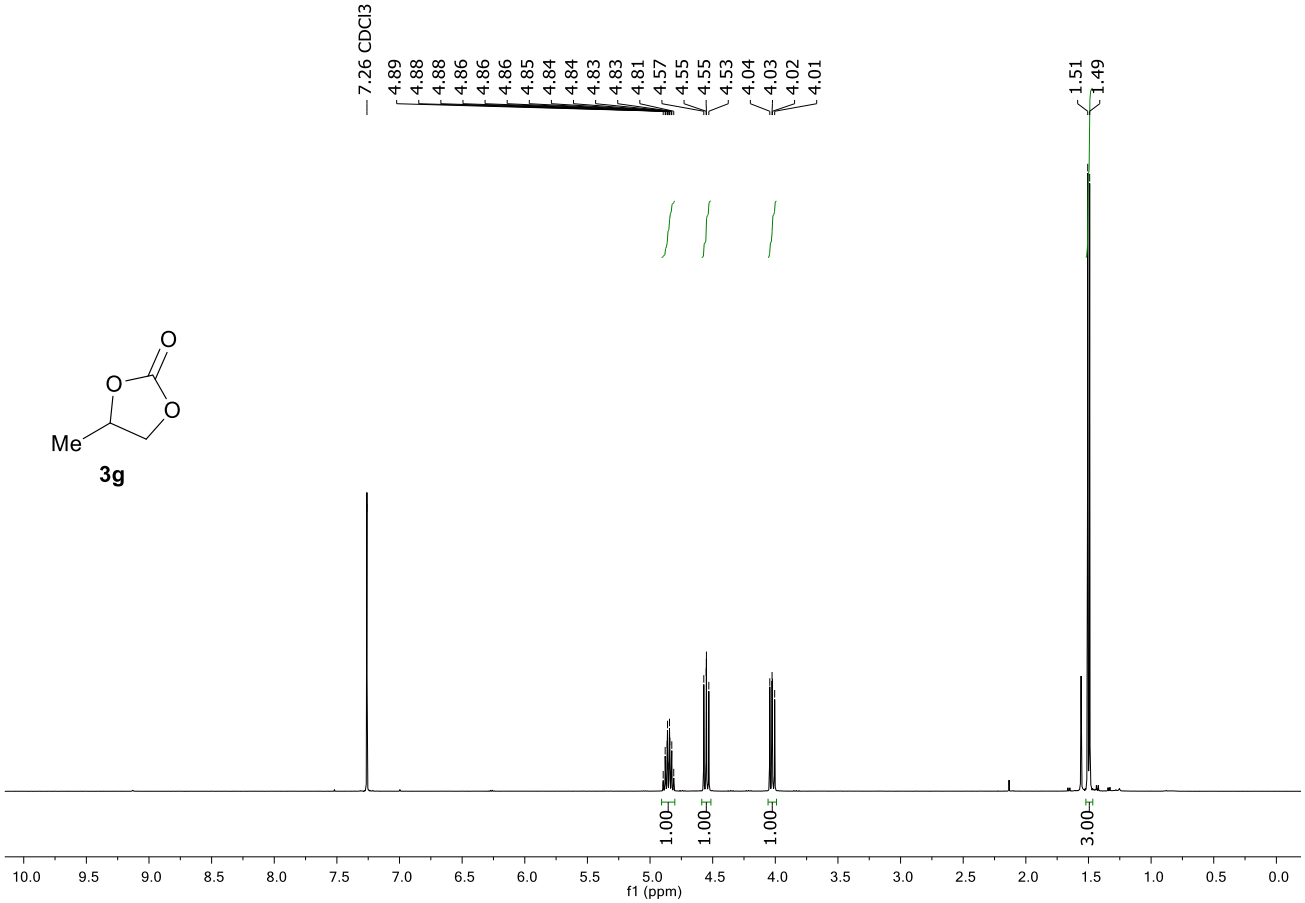


Figure S115. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-methyl-1,3-dioxolan-2-one (**3g**).

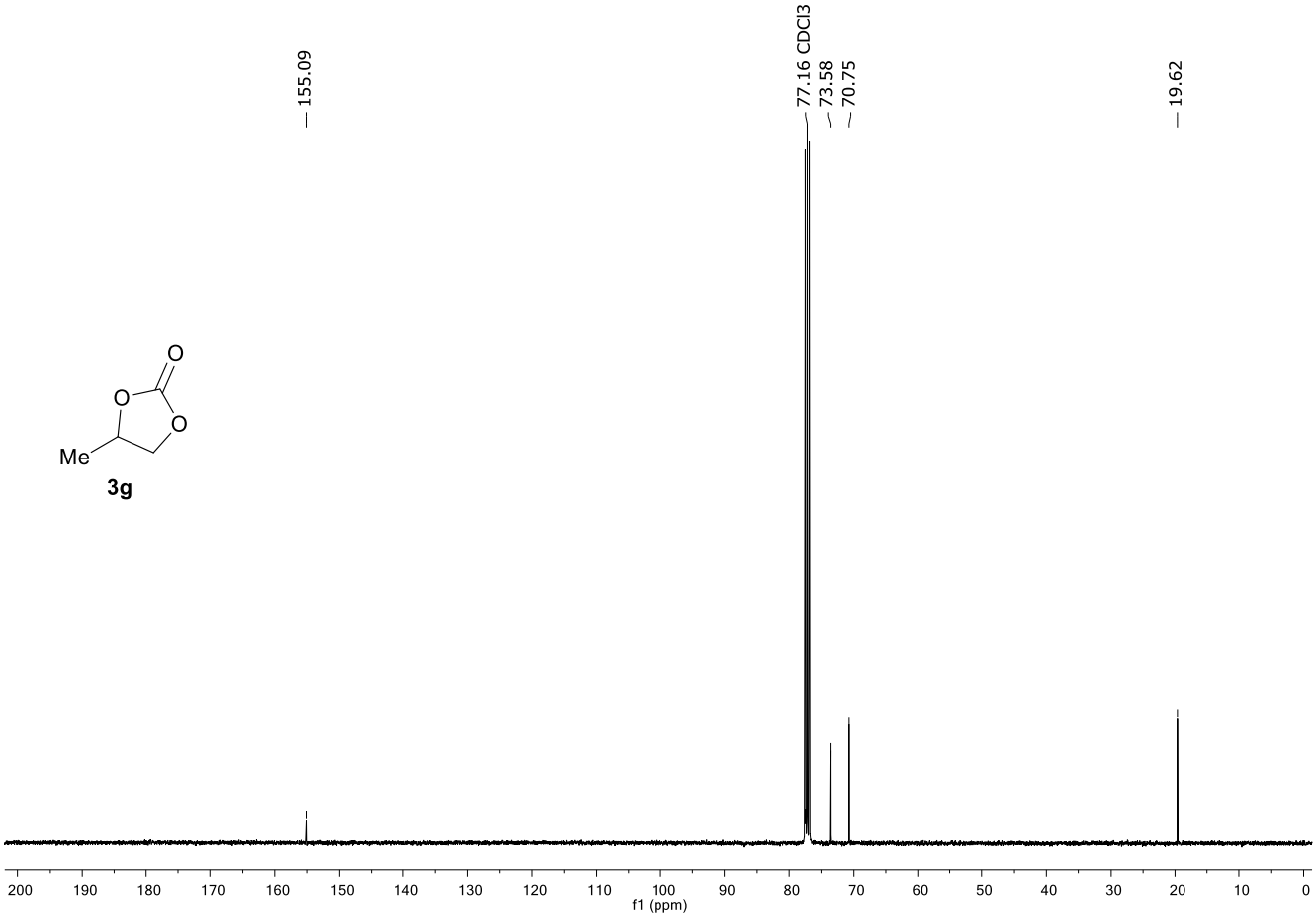


Figure S116. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-methyl-1,3-dioxolan-2-one (**3g**).

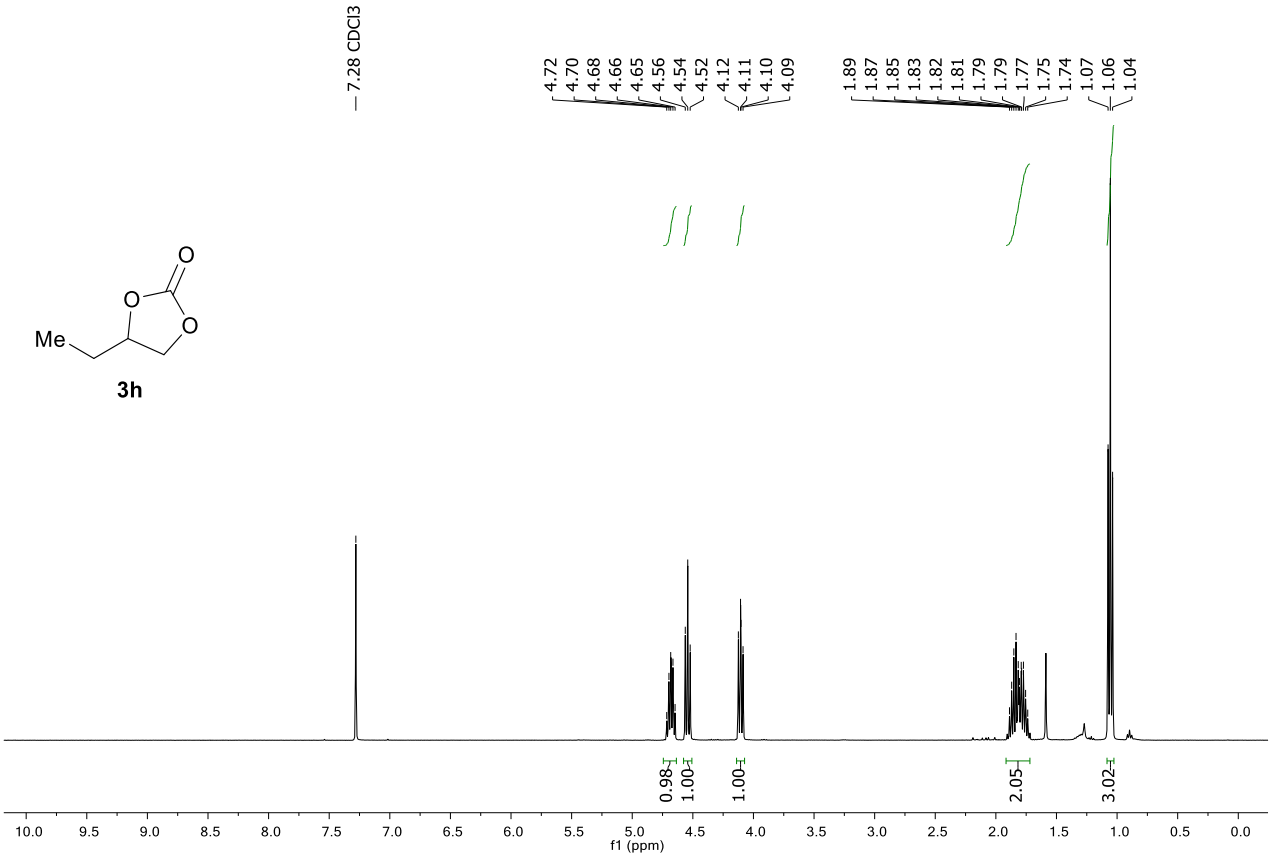


Figure S117. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-ethyl-1,3-dioxolan-2-one (**3h**).

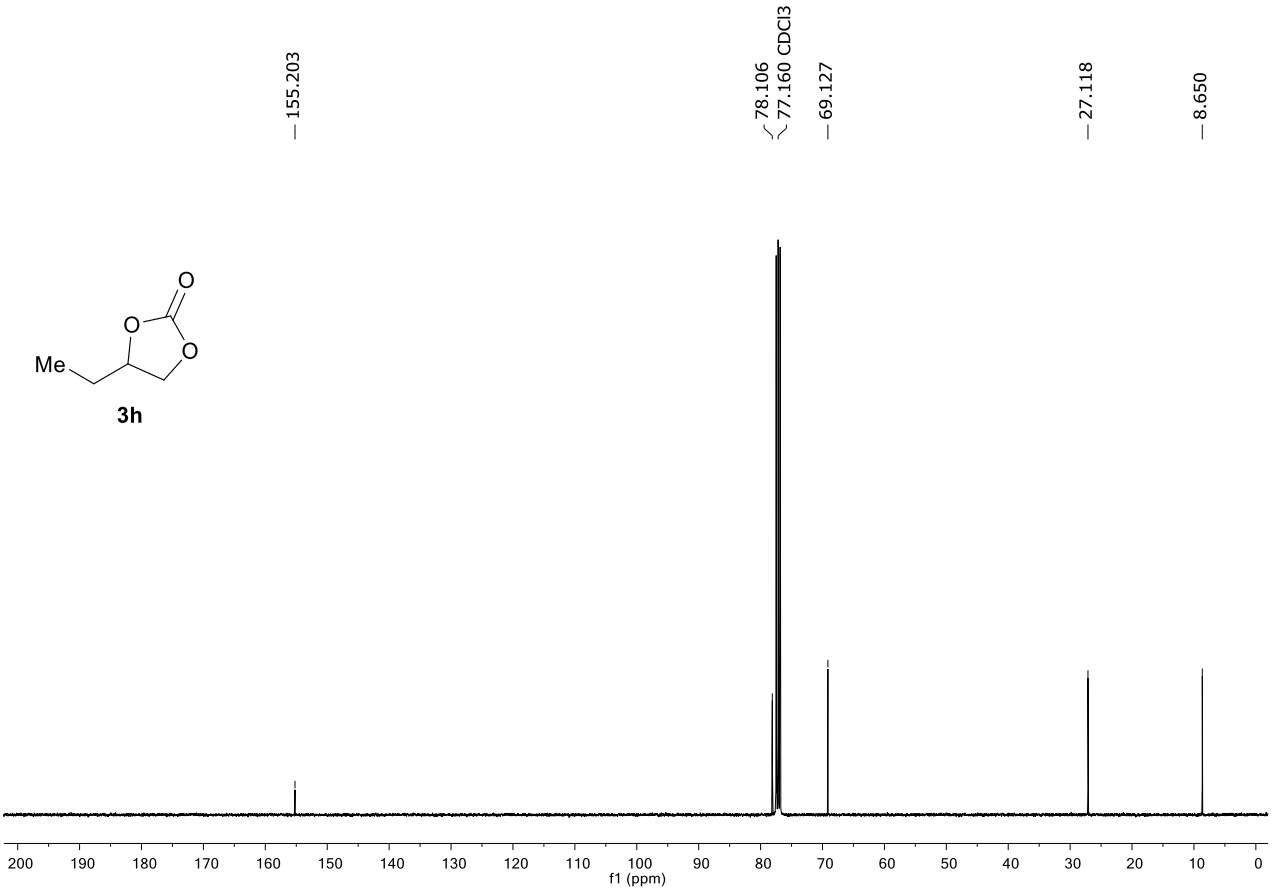


Figure S118. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-ethyl-1,3-dioxolan-2-one (**3h**).

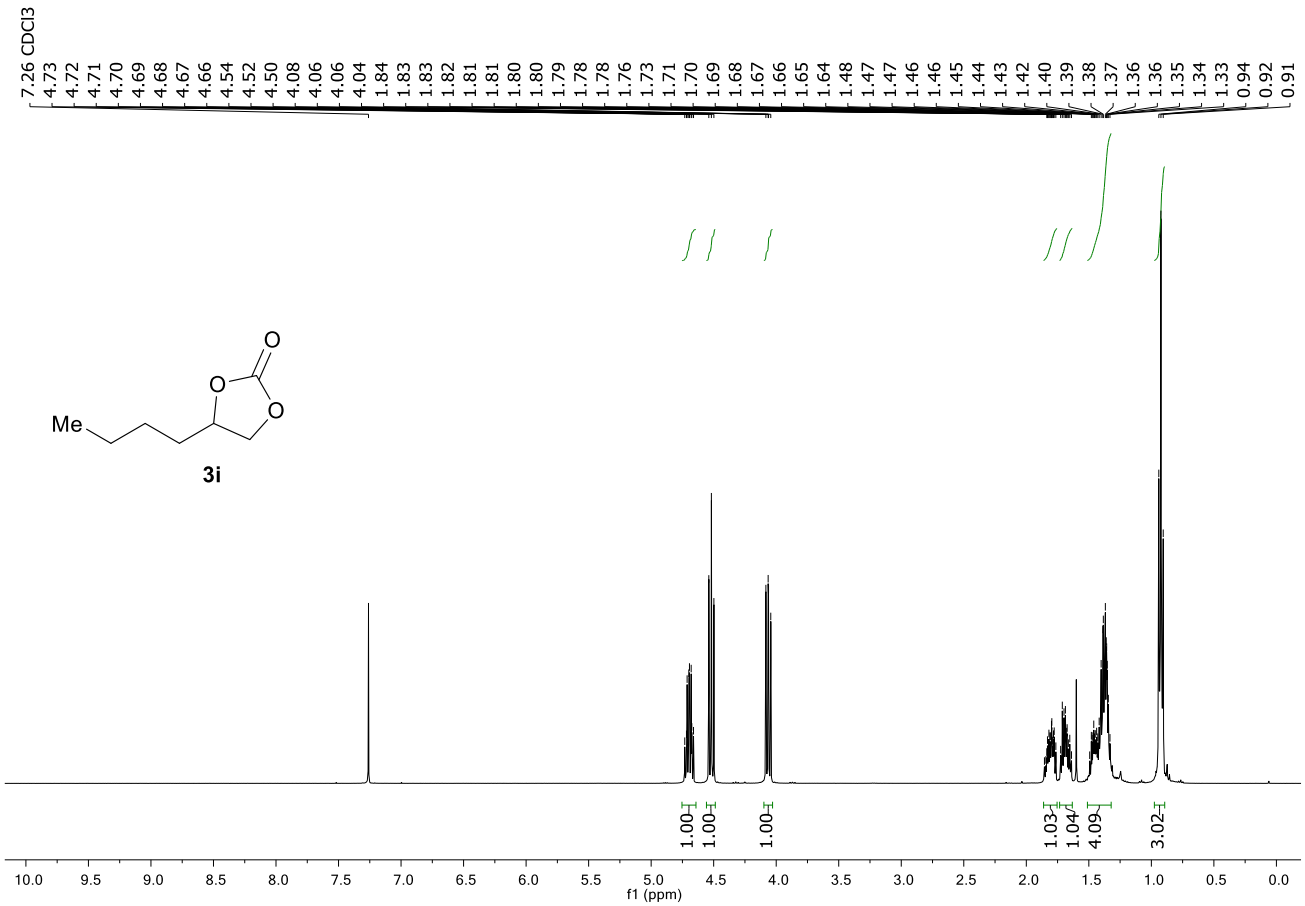


Figure S119. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-butyl-1,3-dioxolan-2-one (**3i**).

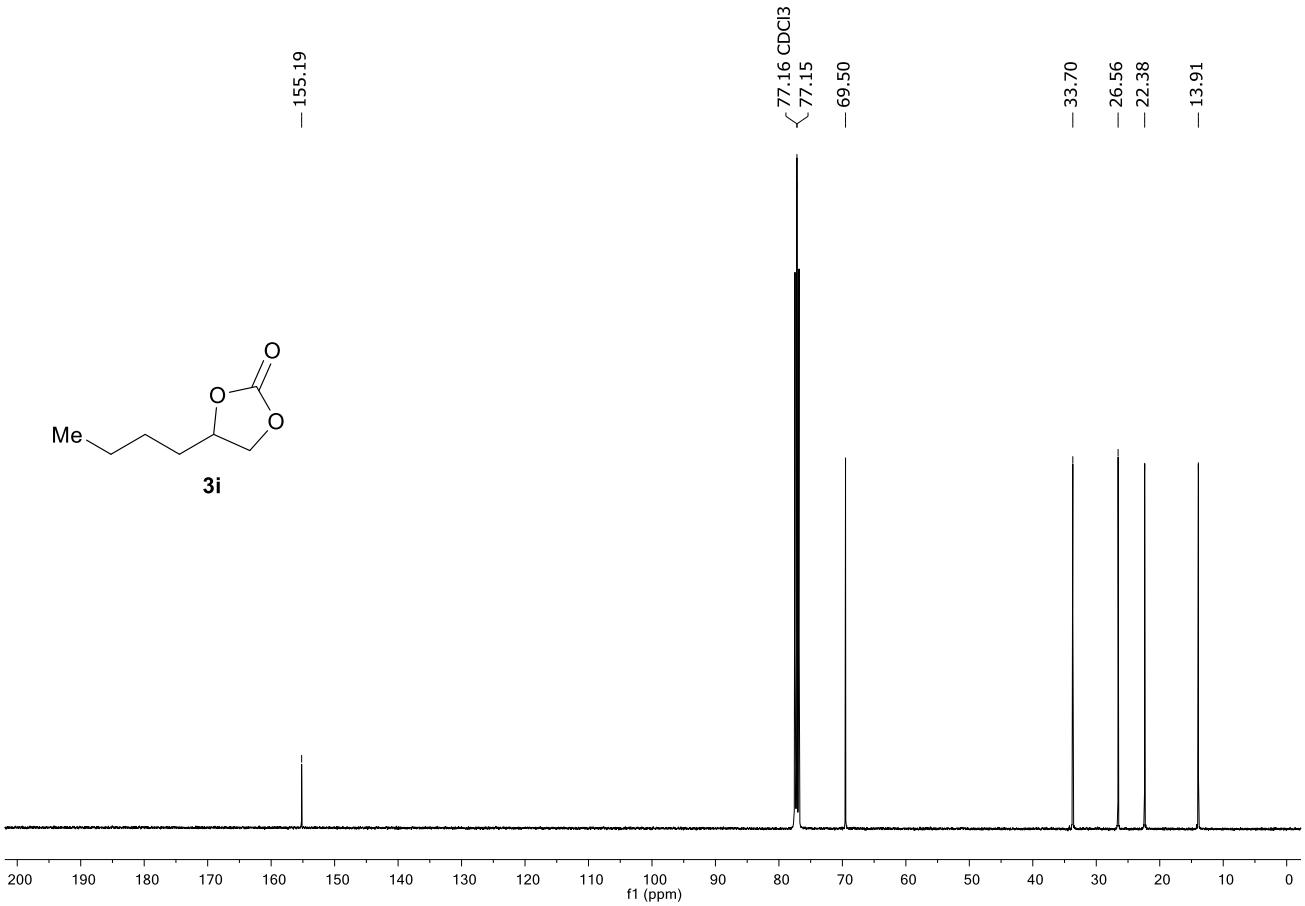


Figure S120. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-butyl-1,3-dioxolan-2-one (**3i**).

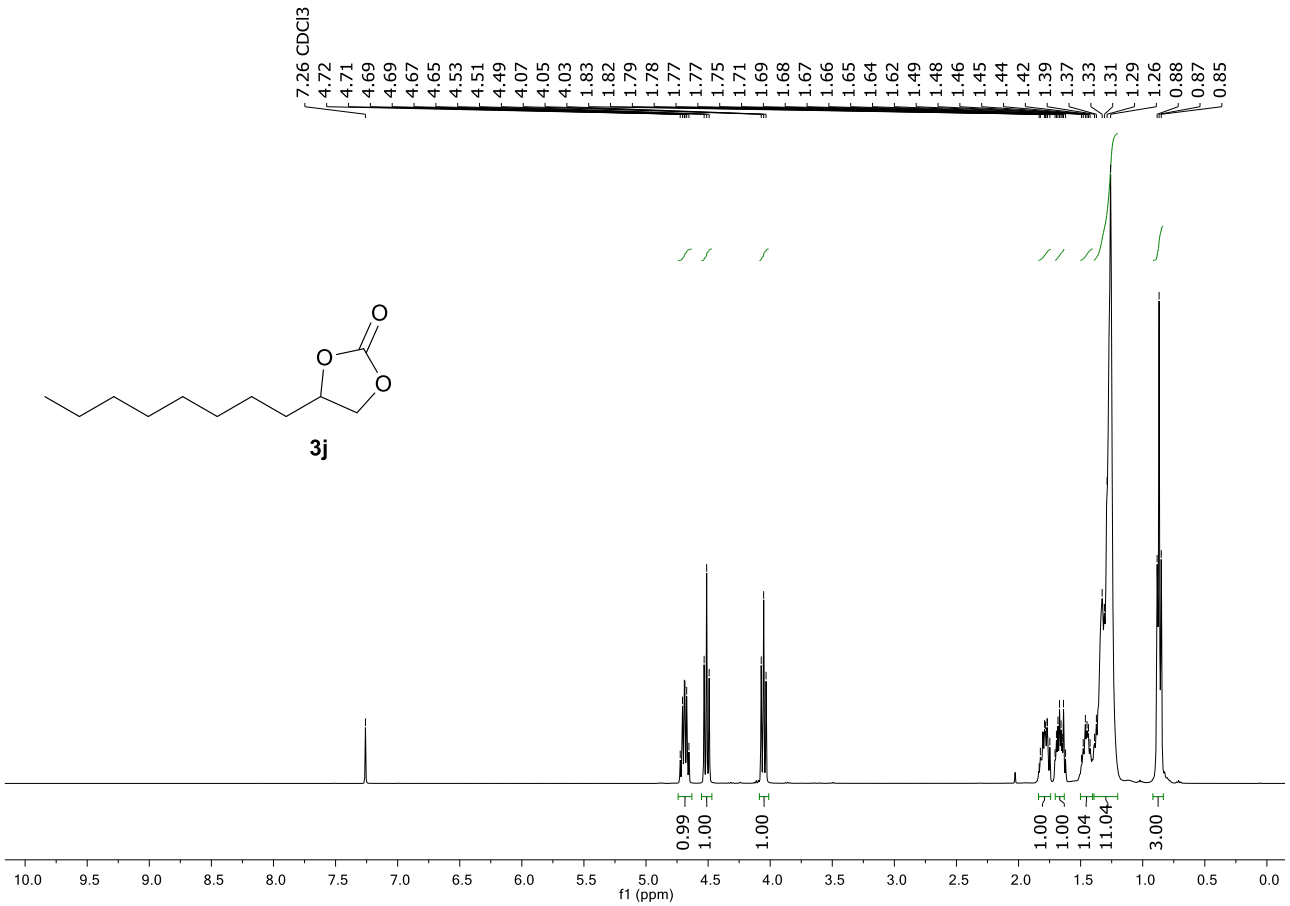


Figure S121. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-octyl-1,3-dioxolan-2-one (**3j**).

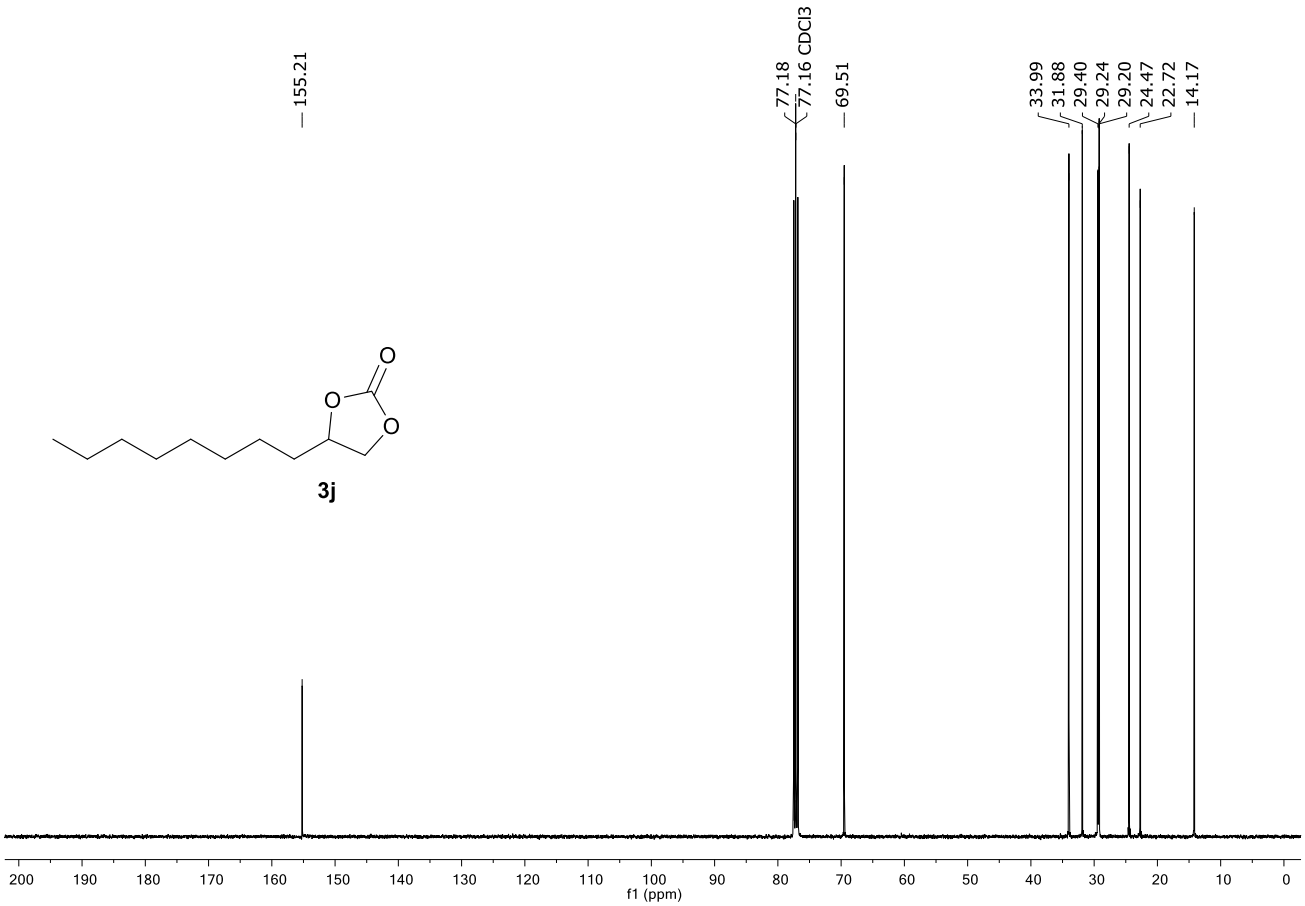


Figure S122. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-octyl-1,3-dioxolan-2-one (**3j**).

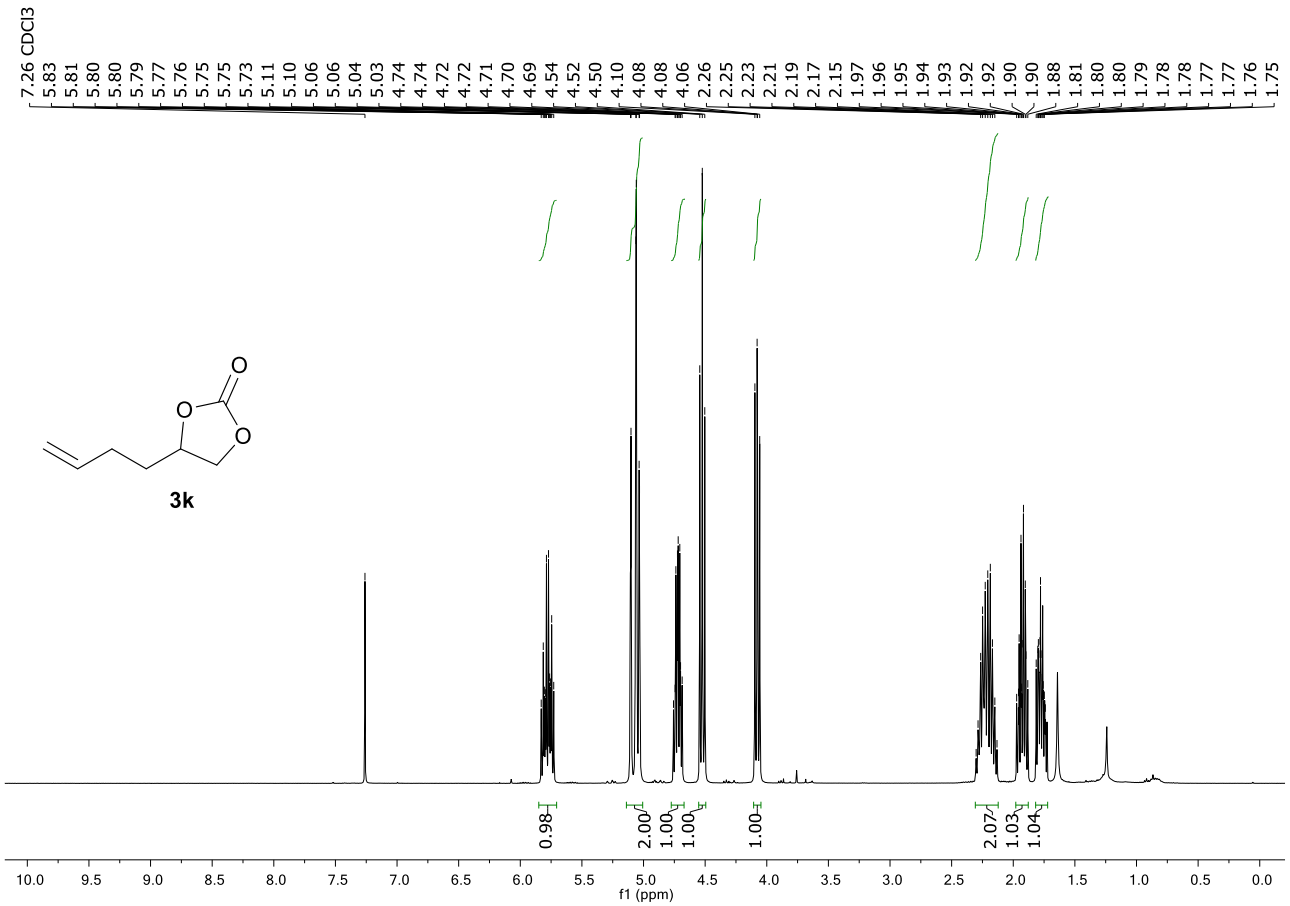


Figure S123. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(but-3-en-1-yl)-1,3-dioxolan-2-one (**3k**).

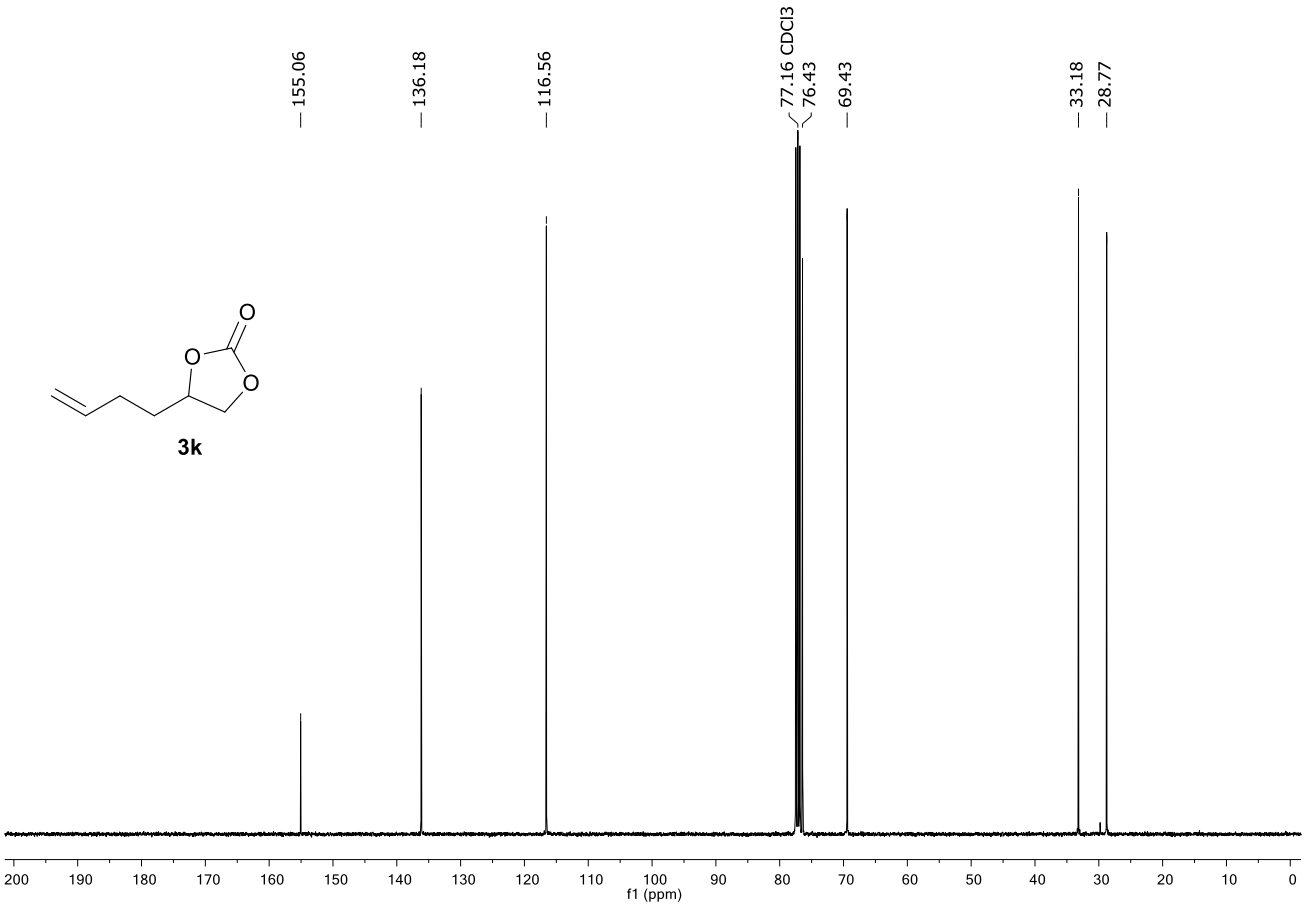


Figure S124. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(but-3-en-1-yl)-1,3-dioxolan-2-one (**3k**).

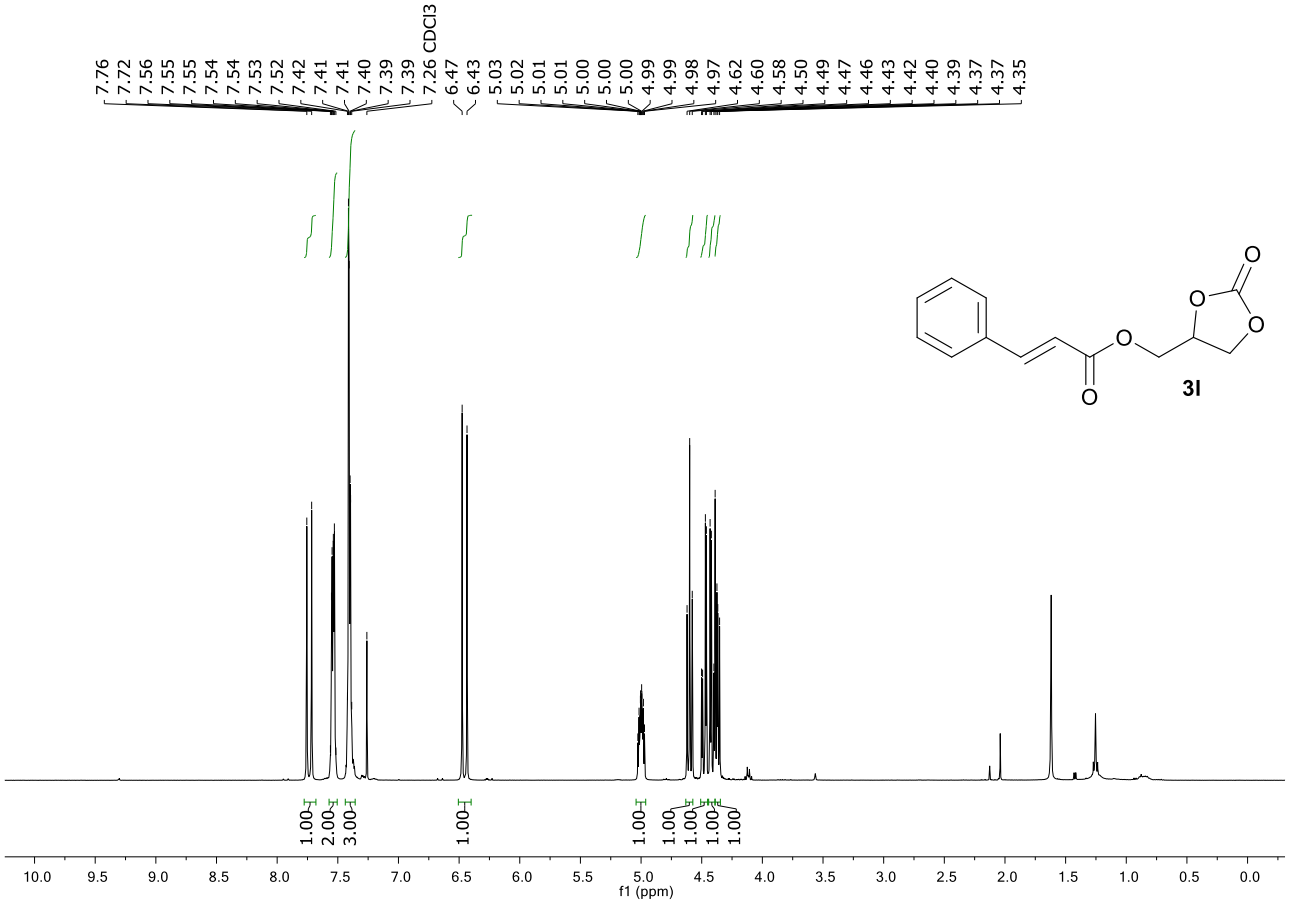


Figure S125. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-oxo-1,3-dioxolan-4-yl)methyl cinnamate (**3l**).

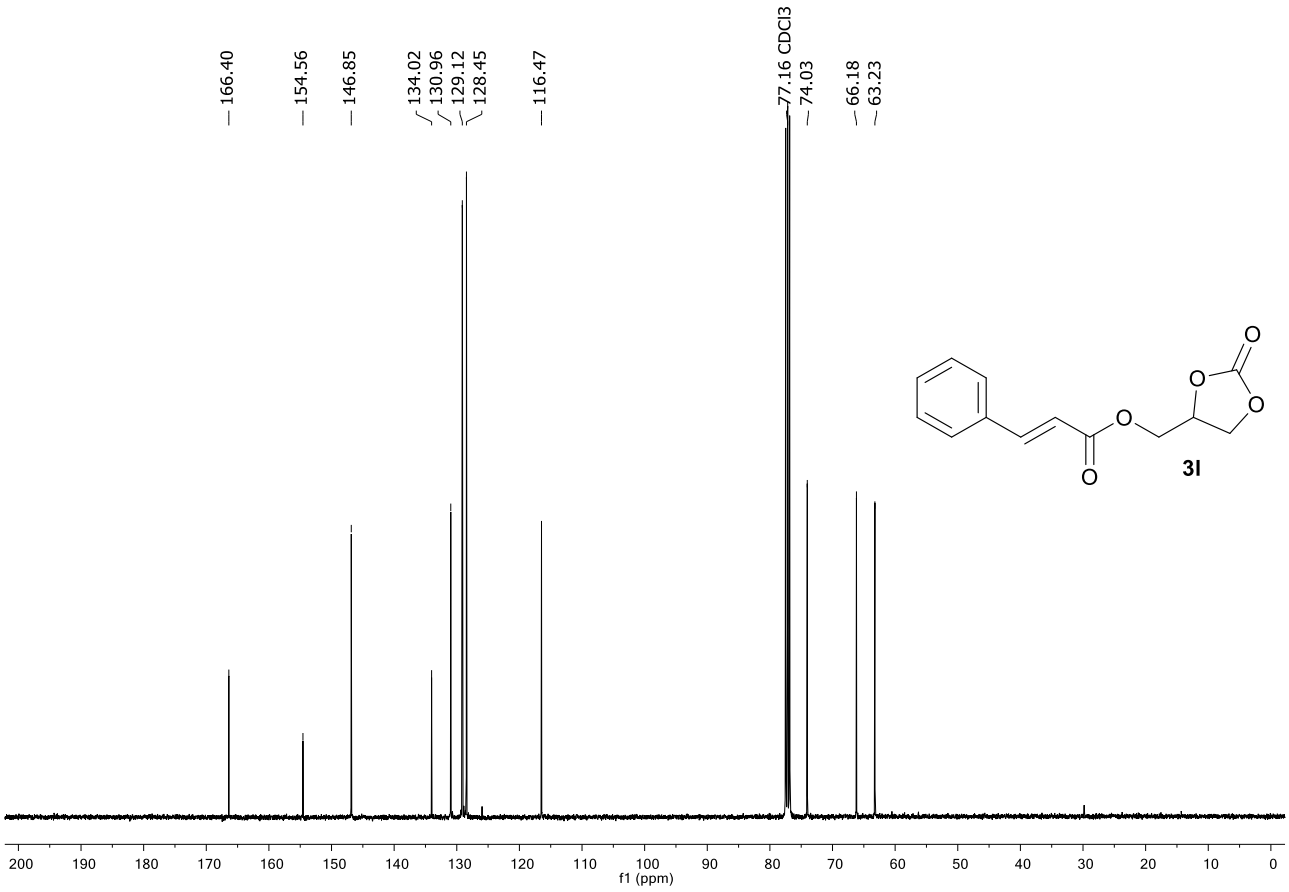


Figure S126. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2-oxo-1,3-dioxolan-4-yl)methyl cinnamate (**3l**).

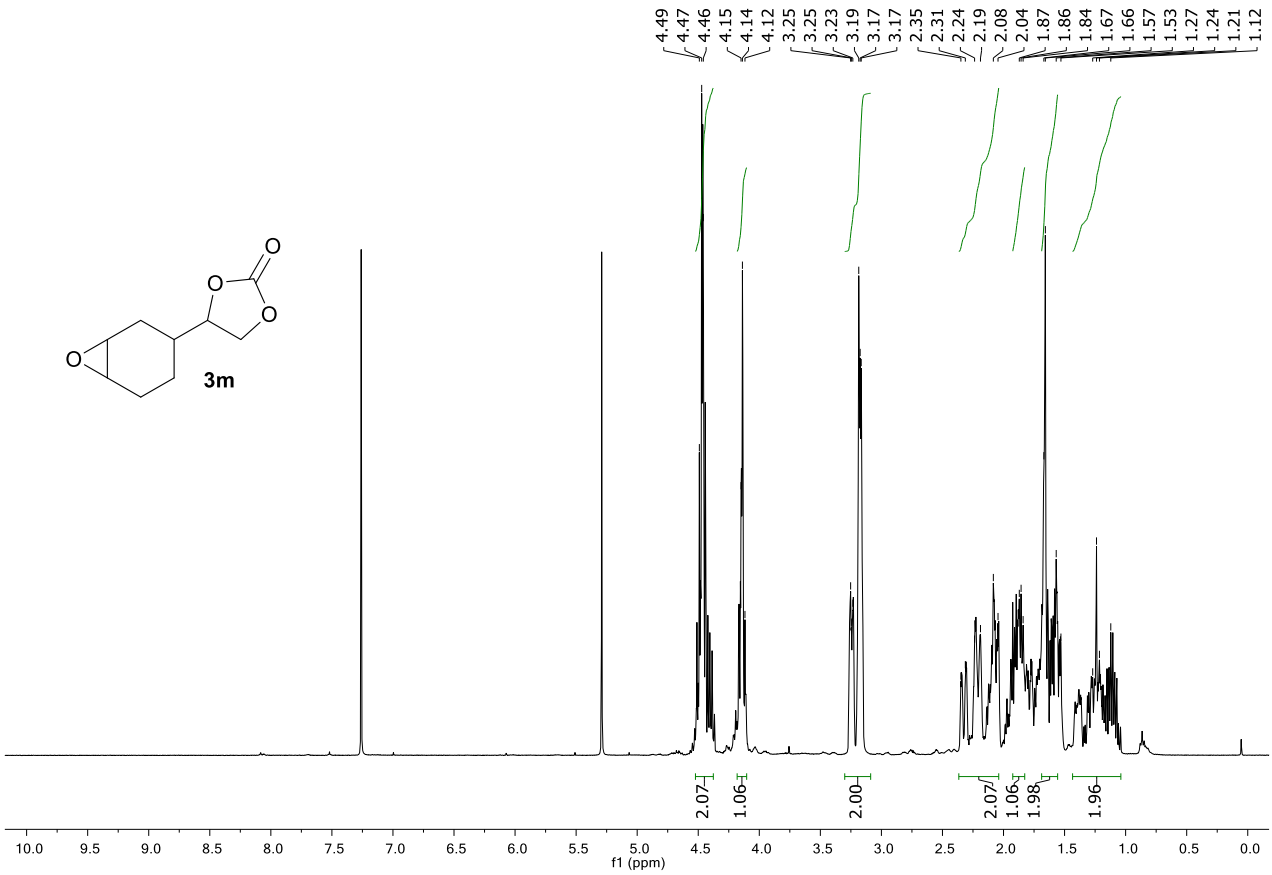


Figure S127. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(7-oxabicyclo[4.1.0]heptan-3-yl)-1,3-dioxolan-2-one (**3m**).

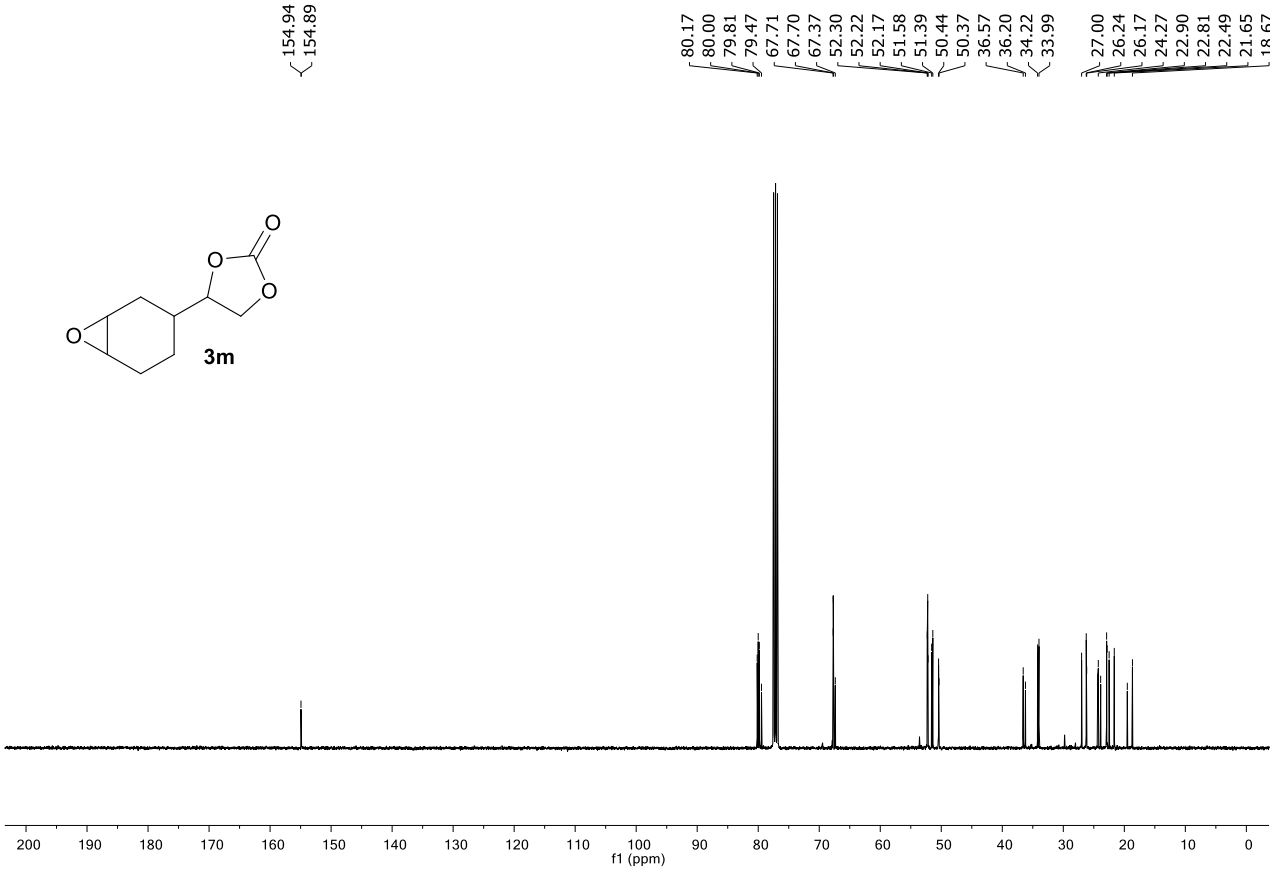


Figure S128. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(7-oxabicyclo[4.1.0]heptan-3-yl)-1,3-dioxolan-2-one (**3m**).

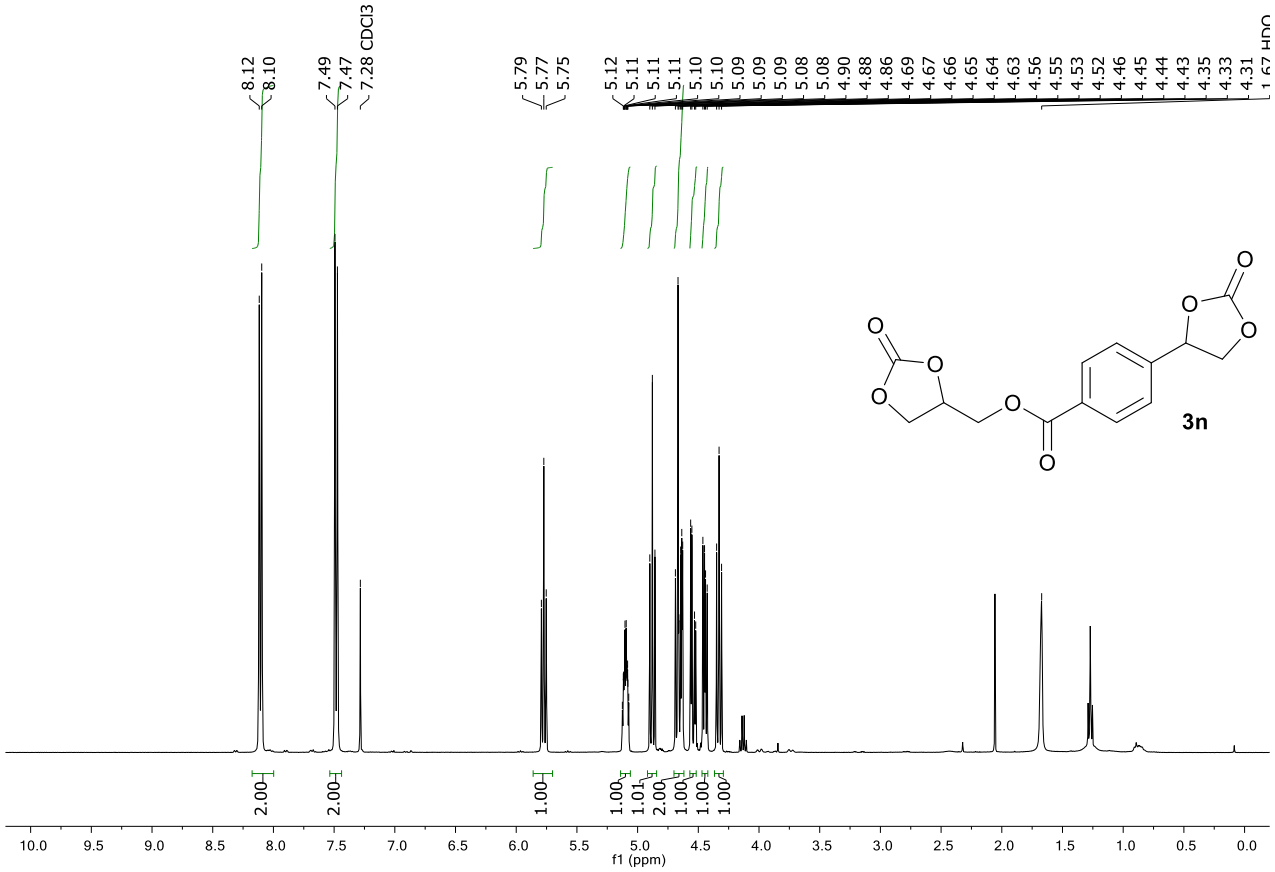


Figure S129. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (2-oxo-1,3-dioxolan-4-yl)methyl 4-(2-oxo-1,3-dioxolan-4-yl)benzoate (**3n**).

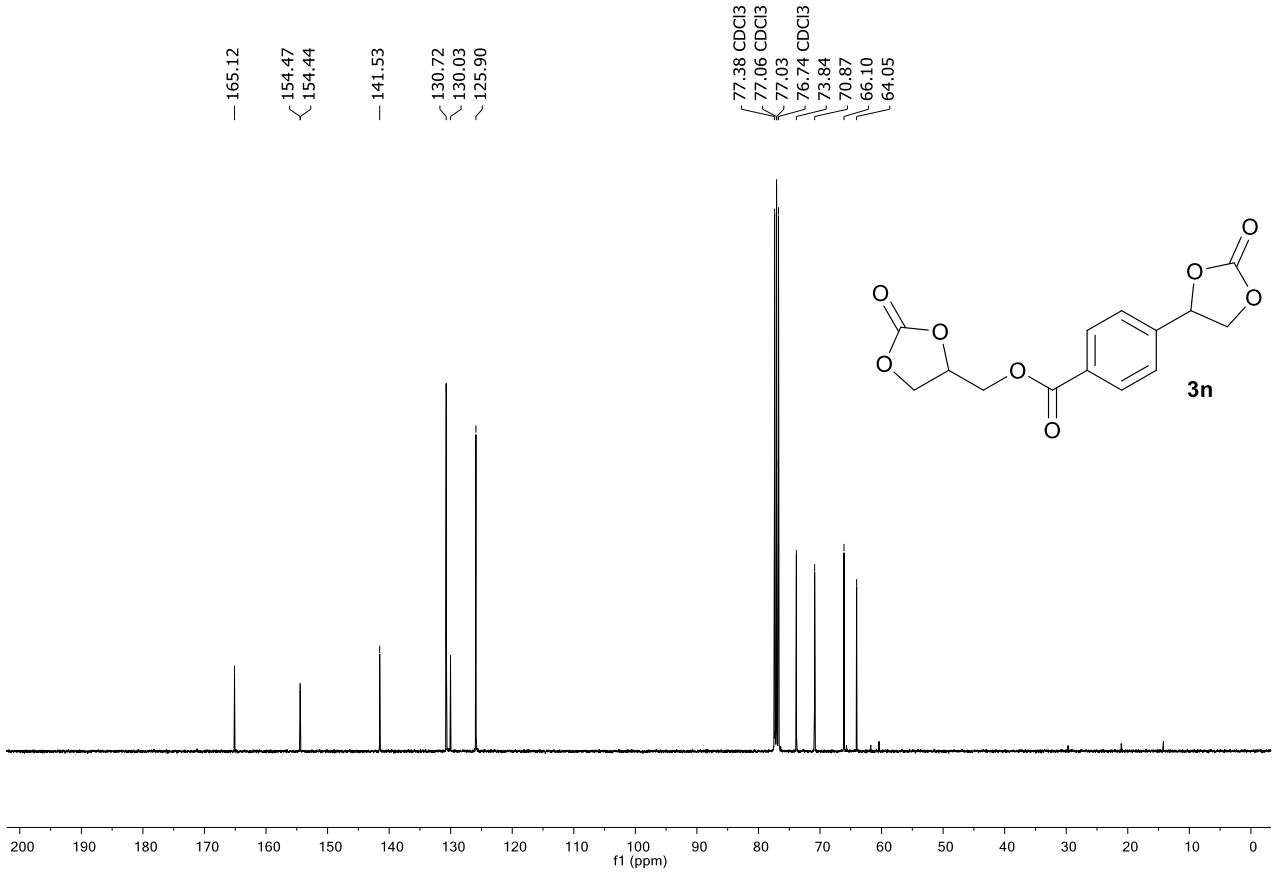


Figure S130. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (2-oxo-1,3-dioxolan-4-yl)methyl 4-(2-oxo-1,3-dioxolan-4-yl)benzoate (**3n**).

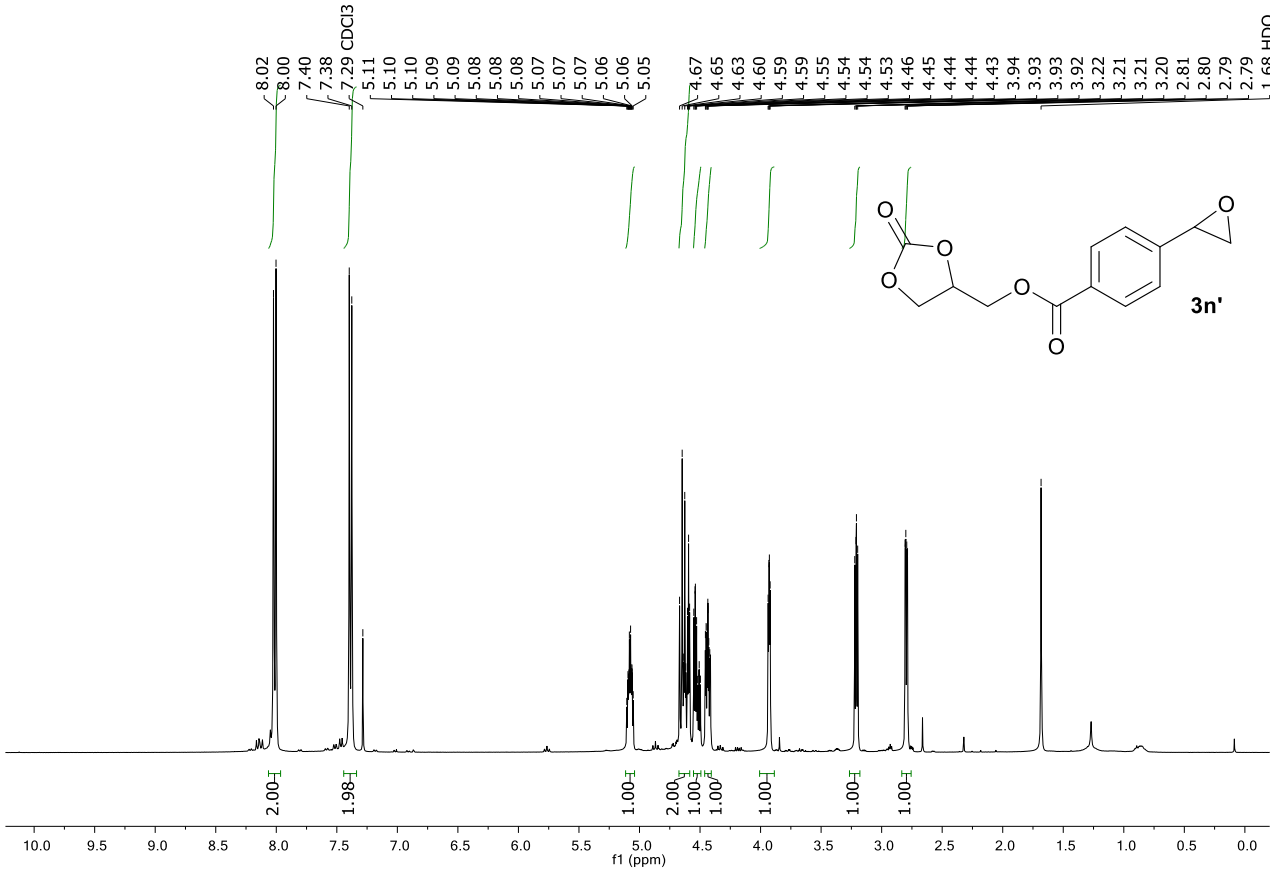


Figure S131. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (2-oxo-1,3-dioxolan-4-yl)methyl 4-(oxiran-2-yl)benzoate (**3n'**).

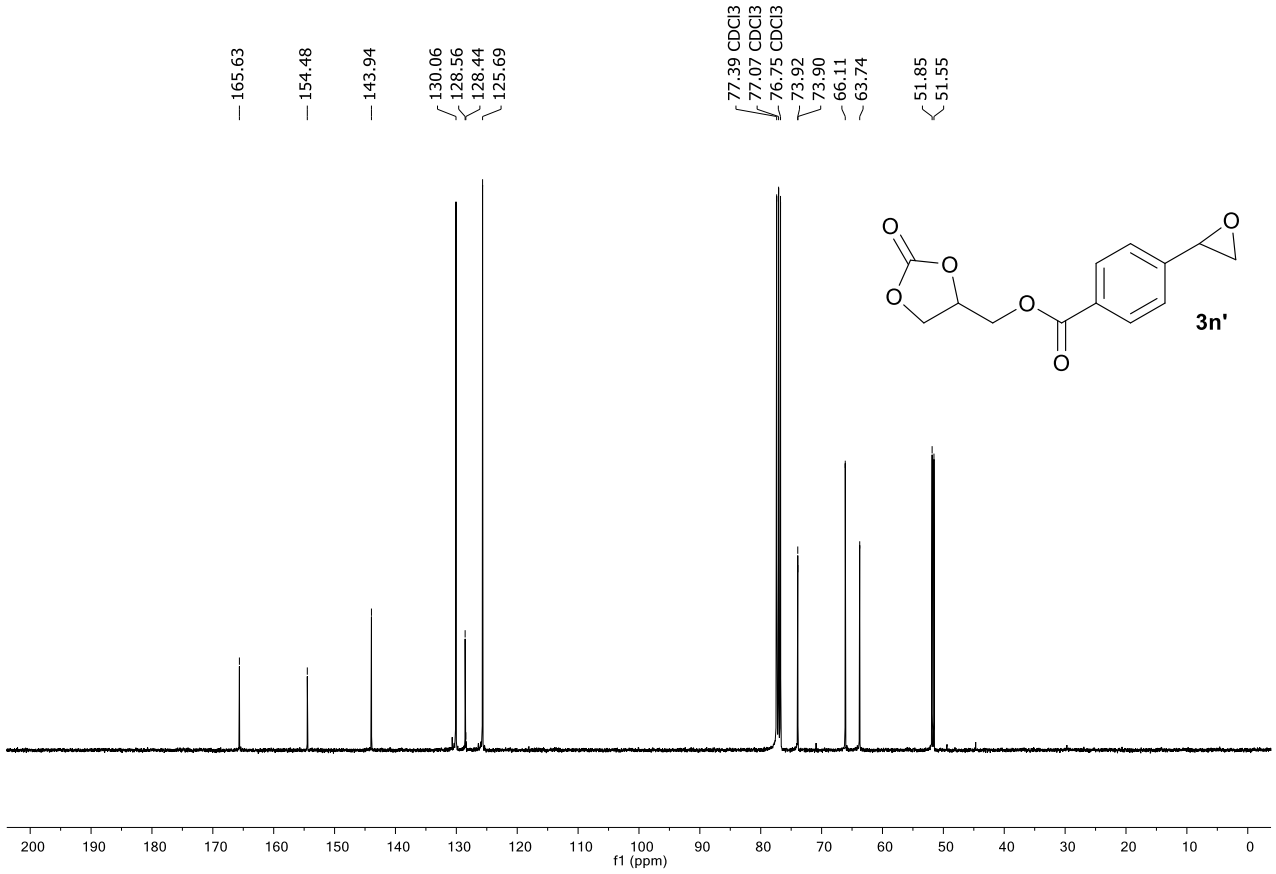


Figure S132. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (2-oxo-1,3-dioxolan-4-yl)methyl 4-(oxiran-2-yl)benzoate (**3n'**).

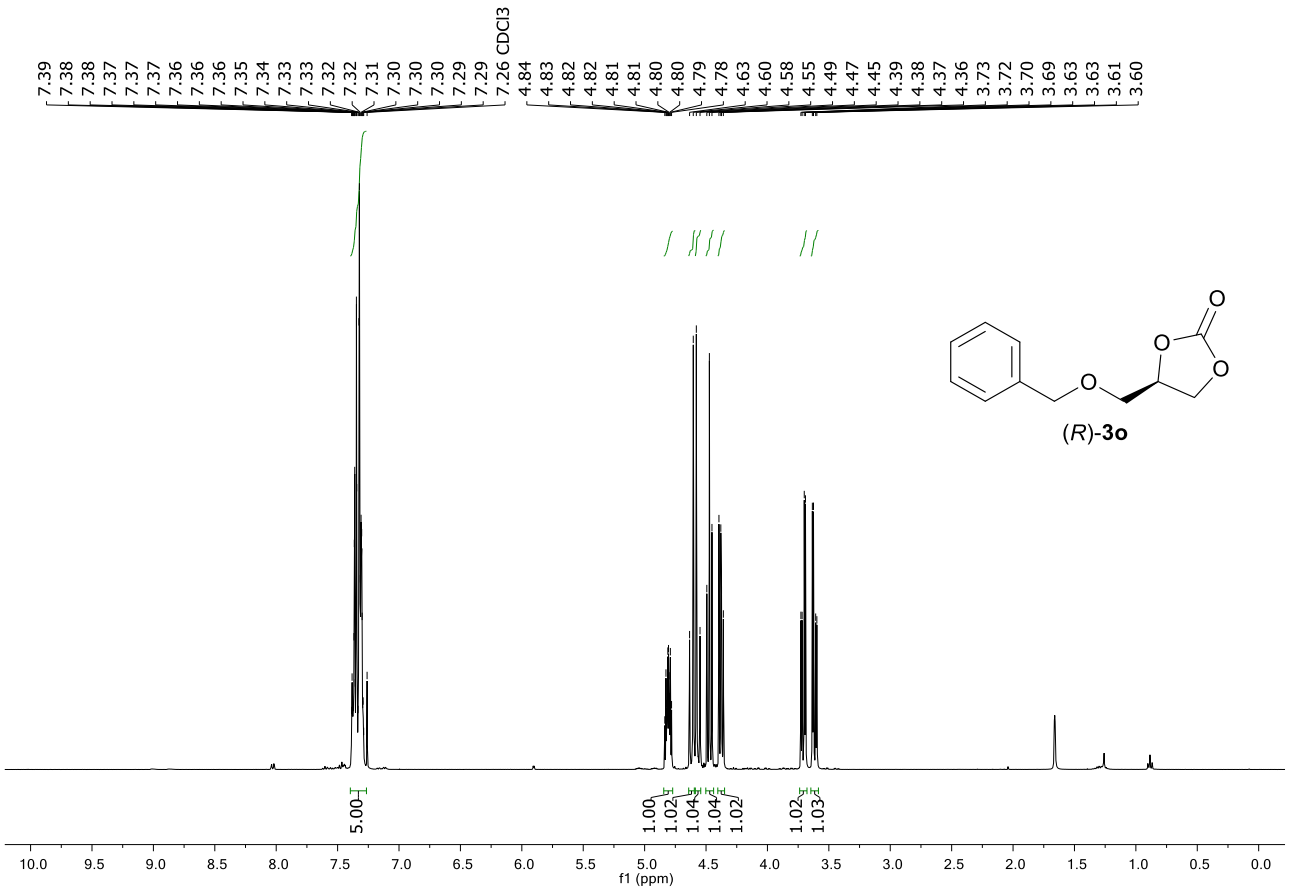


Figure S133. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-4-((benzyloxy)methyl)-1,3-dioxolan-2-one ((*R*)-**3o**).

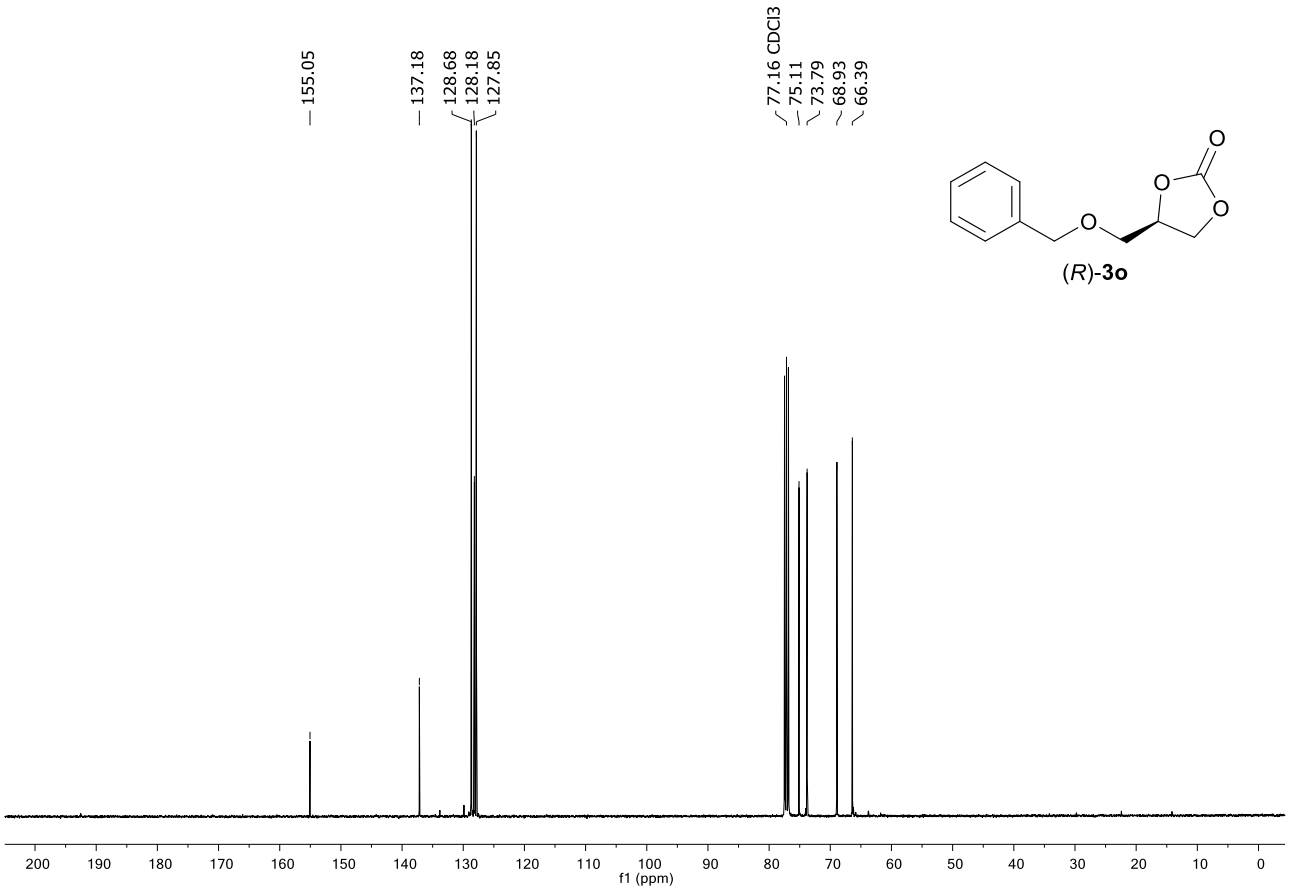


Figure S134. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (*R*)-4-((benzyloxy)methyl)-1,3-dioxolan-2-one ((*R*)-**3o**).

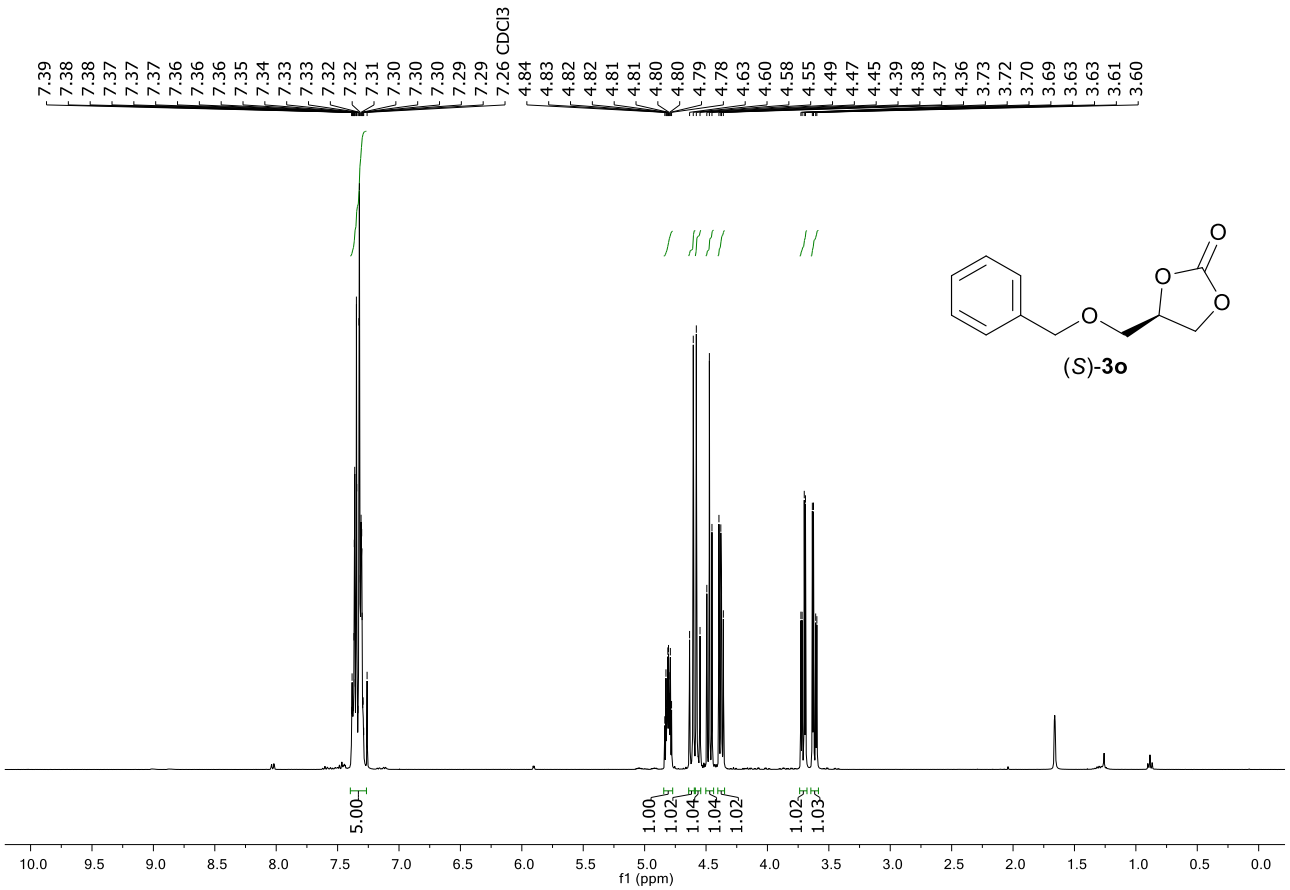


Figure S135. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-4-((benzyloxy)methyl)-1,3-dioxolan-2-one ((*S*)-**3o**).

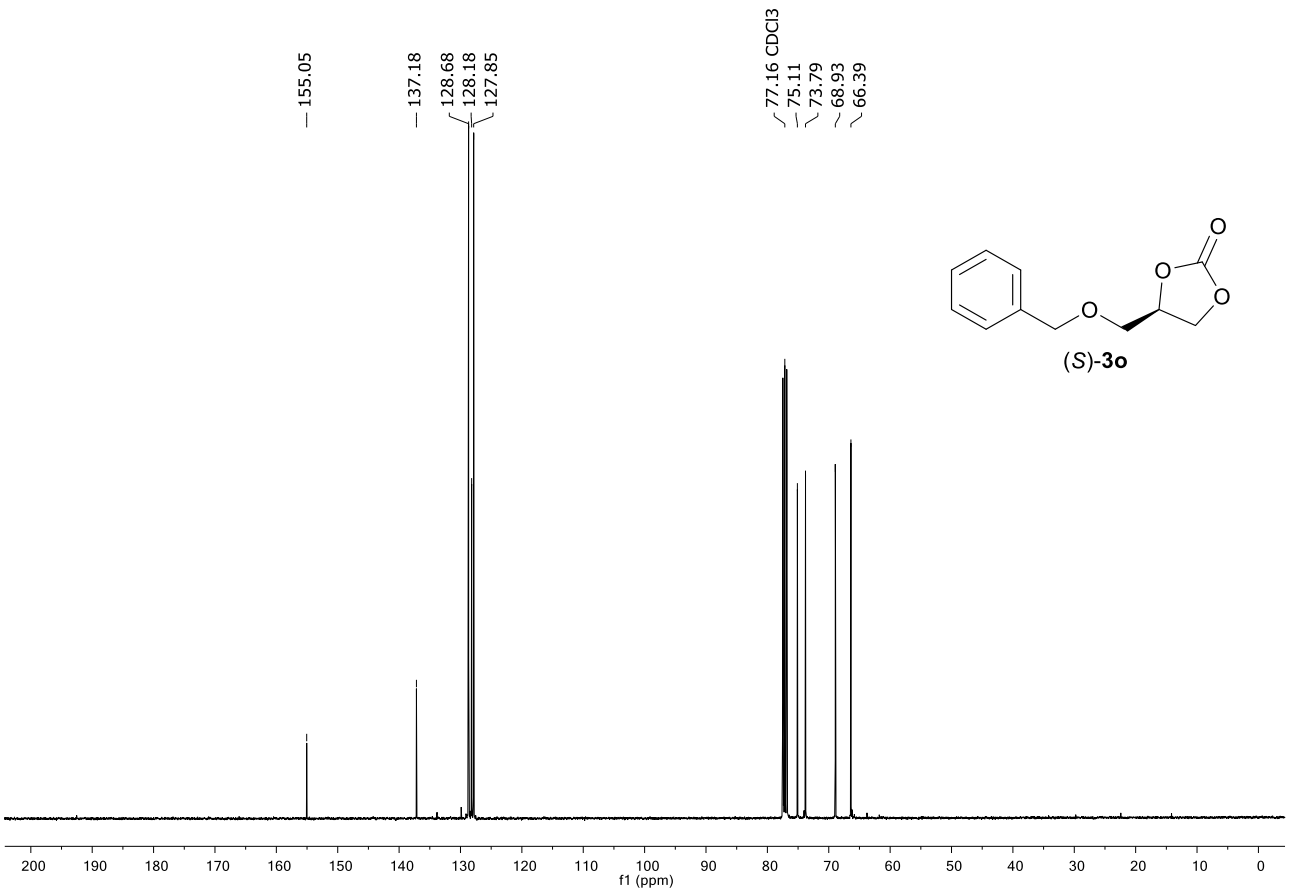


Figure S136. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (*S*)-4-((benzyloxy)methyl)-1,3-dioxolan-2-one ((*S*)-**3o**).