Supplementary Information

A metal-, solvent-, halogen-, and additive-free catalysis for CO2 fixation by carbon dots

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1. Experimental Procedures

1.1 Materials

All chemicals were purchased from commercial sources and used without further purification, unless otherwise noted. Syringic acid (SA, Aladdin, 98.0%), triethylamine (TEA, Aladdin, 99.0%), benzyl glycidy ether (TCI, 97.0%), (*R*)-benzyl glycidyl ether (Adamas, 98%), glycidyl phenyl ether (TCI, 99.0%), styrene oxide (Aladdin, 98.0%), (R)-Styrene oxide (Adamas, 99%), furfuryl glycidyl ether (Aladdin, 96.0%), 1,2-Epoxyhexane (TCI, 96.0%), Epibromohydrin (TCI, 97.0%), Epichlorohydrin (TCI, 99.0%), allyl glycidyl ether (TCI, 99%), glycidyl propargyl ether (Aladdin, 90.0%), 1,4-Butanediol diglycidyl ether (TCI, 93.0%), chloroform-d ($CDCl_3$, Adamas), 2,2,2-Trifluoro-N,N-dimethylacetamide (Bidepharm, 98%). CO_2 was supplied from Ha Qinghua Gas Technology Co, Ltd with a purity of >99.5%.

1.2 Methods

Reactions were monitored by thin-layer chromatography (TLC) carried out on 25 mm silica gel plates. Visualization was performed with a UV-lamp (254 nm) or $KMnO_4$ solution. Flash column chromatography was performed on silica gel (particle size 230-400 mesh, purchased from Canada) and eluted with petroleum ether/ethyl acetate. ^1H NMR spectra were recorded on Bruker-500 MHz spectrometer. The chemical shifts (δ) are given in parts per million relative to $CDCl_3$ (7.26 ppm for ^1H) or TMS (0 ppm for ^1H). The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were acquired on JEOL JEM-2100 instrument. X-ray diffraction (XRD) patterns were collected on the Shimadzu XRD-6100 powder diffractometer. Raman spectra were recorded using a LabRAM HR Evolution confocal Raman microscope (Horiba, ltd., Kyoto, Japan). Fourier Transform Infrared Spectrometric (FT-IR) analysis of samples were recorded with a PerkinElmer Frontier FT-IR spectrometer. The chemical composition, content and state of the samples were determined by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi). High performance liquid chromatography was performed on Agilent Series HPLC, using OD-H chiral column eluted with a mixture of hexane and isopropyl alcohol.

Table S1. Epoxide substrates.

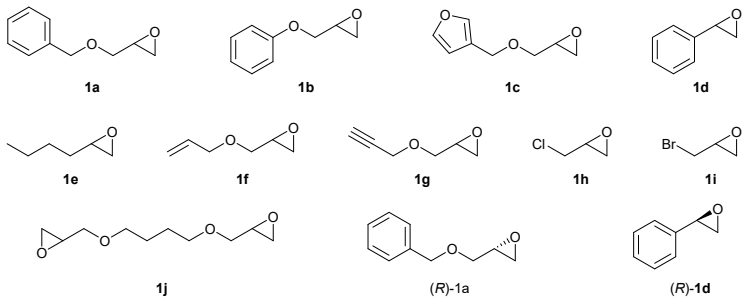
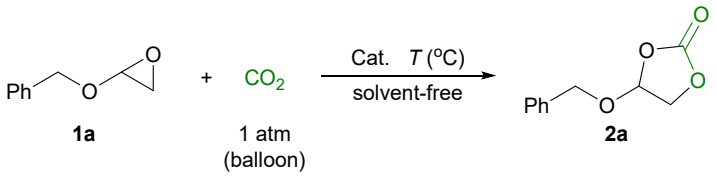


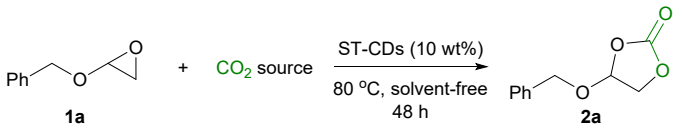
Table S2. The optimization of the reaction conditions.



Entry	Catalyst	T (**°C**)	Yield (%)[b]	Sel. (%)[b]
1	ST-CDs (10 wt%)	120	96	99
2	ST-CDs (10 wt%)	100	96	99
3	ST-CDs (10 wt%)	80	95	99
4	ST-CDs (10 wt%)	60	36	99
5	ST-CDs (10 wt%)	40	10	99
6	ST-CDs (12.5 wt%)	80	95	99
7	ST-CDs (7.5 wt%)	80	88	99
8	ST-CDs (5.0 wt%)	80	83	99
9	ST-CDs (2.5 wt%)	80	66	99
10	SA (10 wt%)	80	0	-
11	NEt_3 (10 wt%)	80	5	-[c]
12	none	80	0	-
13	4-ST-CDs (10 wt%)	80	52	99
14	1-ST-CDs (10 wt%)	80	82	99

[a]Conditions: **1a** (5 mmol), CO_2 (1 atm, ballon), the reaction was performed as neat. [b]Yield and selectivity were measured by ^{1}H NMR spectroscopy ($CDCl_3$) of the crude mixture using 2,2,2-trifluoro-*N,N*-dimethylacetamide (CF_3-DMA) as internal standard. [c]Not detected.

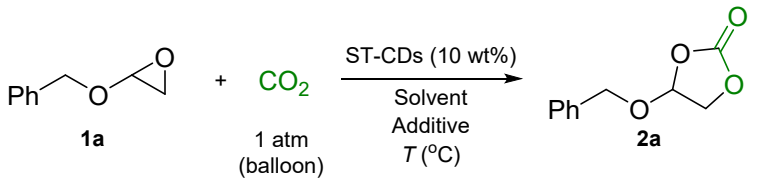
Table S3. The effect of CO_2 source.[a]



Entry	CO_2 source	**2a** yield
1	CO_2/air (1/1)	16% (16% conversion)
2	CO_2/air (1/9)	9% (10% conversion)
3	air	2% (2% conversion)

[a]Yield and conversion were measured by ^{1}H NMR spectroscopy ($CDCl_3$) of the crude mixture using 2,2,2-trifluoro-*N,N*-dimethylacetamide (CF_3-DMA) as internal standard.

Table S4. The effect of additive.[a]



Entry	Catalyst	Additive	Temperature (°C)	Solvent	Reaction time (h)	Yield of **2a** (%)
1	ST-CDs	-	80	-	48	96
2	-	TBAI (5 mol%)	80	-	48	8
3	ST-CDs	TBAI (5 mol%)	80	-	12	98
4	ST-CDs	TBAI (5 mol%)	60	-	24	94
5	-	-	80	DMF (1 mL)	48	0
6	ST-CDs	-	80	DMF (1 mL)	36	91

[a]Yield and conversion were measured by ^{1}H NMR spectroscopy ($CDCl_3$) of the crude mixture using 2,2,2-trifluoro-*N,N*-dimethylacetamide (CF_3-DMA) as internal standard.

1.3 Preparation of ST Carbon Dots Catalysts

The ST carbon dots (ST-CDs) catalysts were prepared by hydrothermal synthesis. Specifically, SA (2 mmol) and TEA (8 mmol) were dissolved in 30 mL ultrapure water and mixed uniformly. Then the mixed solution was transferred to a poly(tetrafluoroethylene) (Teflon)-lined reactor and carbonized at 180 °C for 10 h.

After the reaction, the reactor allowed to cool to room temperature naturally. Finally, the mixture was filtered through a 0.22 μm syringe filter and dialyzed against ultrapure water through a 200 Da dialysis membrane for 2 days. The purified solution was dried in an oven to give the CDs (210 mg, 17.0 wt% yield). The same procedure was conducted for the preparation of CDs with ratios of SA and TEA in 4:1 and 1:1, which were name as 4-ST-CDs and 1-ST-CDs, respectively.

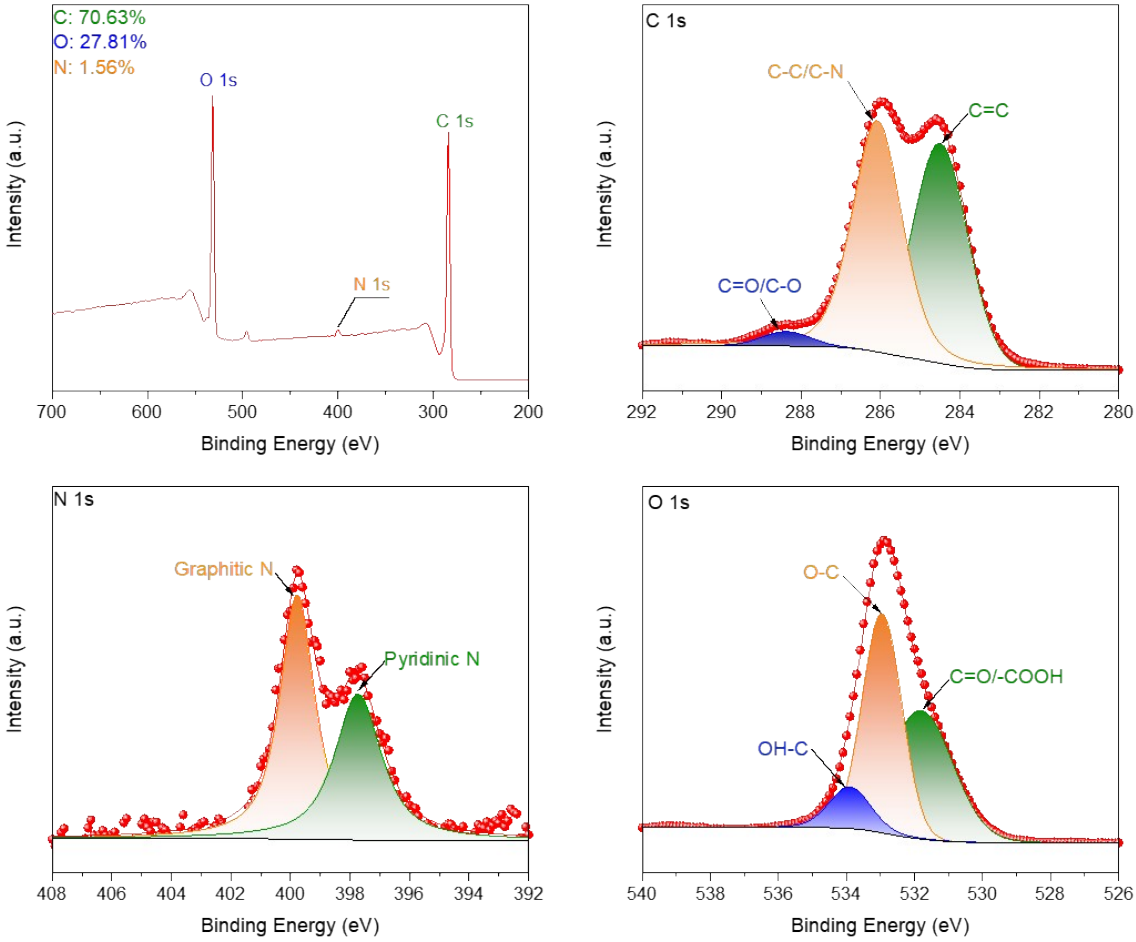


Figure S1. XPS of 4-ST-CDs including high resolution on C1s scan, O1s scan, and N1s scan.

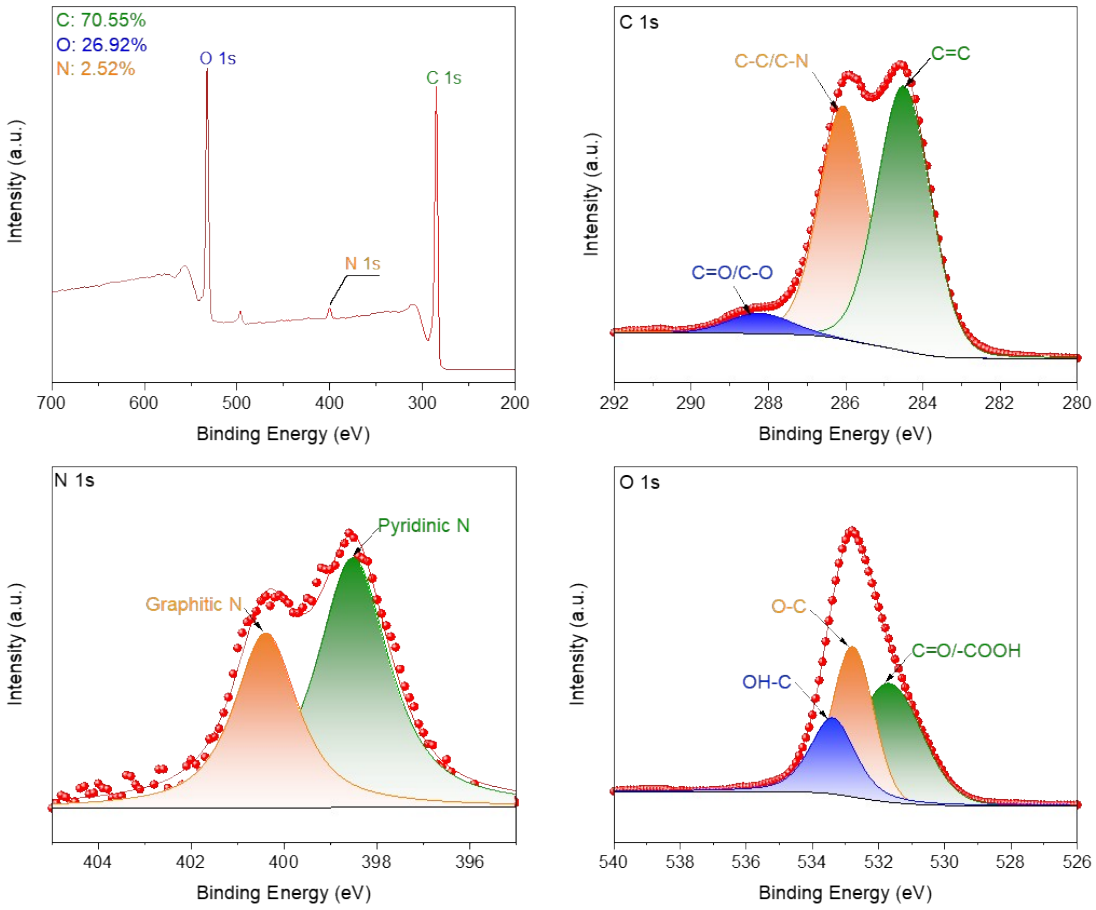


Figure S2. XPS of 1-ST-CDs including high resolution on C1s scan, O1s scan, and N1s scan.

1.4 General Procedure for CDs-Catalyzed Reaction of CO_2 with Epoxides

For reaction conditions screening, epoxide **1** (5 mmol, 1 equiv.) and CDs (82.1 mg, 10 wt%) were weighted into a 25 mL reaction tube. The air in the tube was firstly replaced with CO_2, and the CO_2 of the balloon was then allowed to flow into the tube. The reaction was stirred at 80 °C for 48 h under 1 atm of CO_2 atmosphere (balloon, ~ 3 L). The reaction was monitored by TLC. After the reaction was completed, the residue was purified by column chromatography on silica gel with a gradient eluent of petroleum ether/ethyl acetate to afford the desired product. For substrate screening, all procedures were conducted at 80 °C for 48 h under 1 atm of CO_2 atmosphere (balloon).

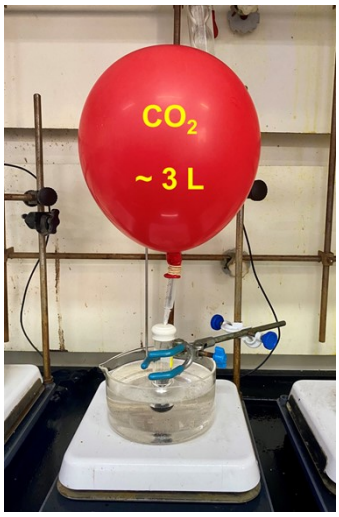


Figure S3. CDs-catalyzed CO_2 with epoxide reaction device

1.5 Procedure for Large-scale Reaction of Epoxides with CO_2

Epoxide **1** (8.21 g, 50 mmol) and CDs (821 mg, 10 wt%) were weighted into a 50 mL flask, followed by charging with CO_2. The reaction mixture was conducted at 80 °C for 96 h under 1 atm of CO_2 atmosphere (CO_2 bag, 42 L). After the reaction was completed, a certain amount of ethyl acetate (EA) was added and the mixture filtrated through a short pad of silica gel. The residue was purified by column chromatography on silica gel with a gradient eluent of petroleum ether/ethyl acetate (4/1) to afford the desired product **1** (9.786 g, 94% yield).

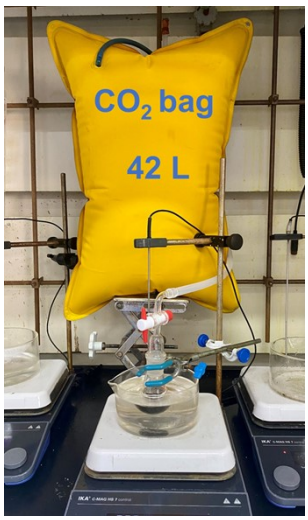


Figure S4. Large scale reaction device of epoxide and CO_2

1.6 Procedure for Recycling Experiments of CDs for CO_2 Conversion

Epoxide **1** (5 mmol, 1 equiv.) and CDs (82.1 mg) were weighted into a 25 mL reaction tube, followed by charging with CO_2. The reaction was stirred at 80 °C for 48 h under 1 atm of CO_2 atmosphere (balloon). At the end of the reaction, a certain amount of EA was added into the flask, the CDs sediment was formed after a 30 min standing. The supernate was removed by a dropper after centrifugation. The solid residue was washed with EA for 3 times followed by centrifugation. Finally, the solid residue was dried in oven at 105°C to remove the solvent in residue and readied for the recycling experiment. The EA solution was collected and concentrated under vacuum to afford the cyclic carbonate.

1.7 DFT Studies

The geometries of coronene with hydroxyl and carboxyl groups, nitrogen-doped coronene and their complexes with phenyl ethylene oxide(PEO) and CO_2 were all optimized under the framework of density of functional theory (DFT) with B3LYP functional[3-5] and 6-31g(d,p)[6,7] basis set. The binding energy is calculated according to the formular: E(binding) = E(complex) - E(coronene) - E(mol) where E(complex), E(coronene) and E(mol) are energies of complex, coronene and adsorbed molecule. The thermodynamic correction terms of the structures at 353.15K were then obtained using Shermo program.[8] All these DFT calculations were performed using Gaussian 16 program suite [Gaussian, Inc., Wallingford CT, 2016].

To simplify the calculation process, coronene was used as the backbone model of the carbon dots in the calculations. According to the XPS analysis for surface of CDs, 4 models of the carbon dots with -OH, and -CO_2H groups on the surface, pyridinic N and graphitic N which could interact with epoxides and CO_2 were simulated for calculation. The models are displayed as below:

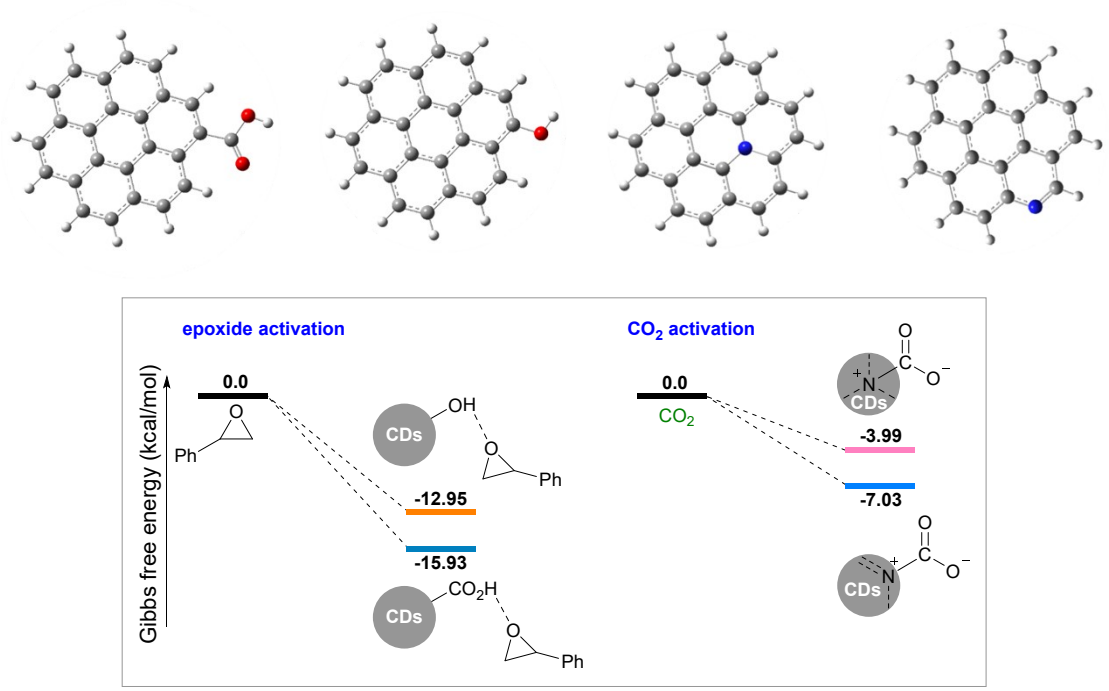
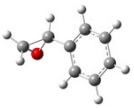


Figure S5. Free-energy profiles for the activation of epoxide 1d (left) and CO_2 (right) by ST-CDs using different activation sites (hydroxyl, carboxylic acid, graphitic N and pyridinic N) at 80 °C.

The cartesian coordinates of the optimized geometries of the transition states and intermediates

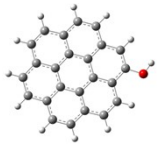


Styrene oxide (SO)

C	7.31960000	-0.56250000	-2.24270000
C	7.94350000	-0.59200000	-0.90990000
H	7.98350000	-0.63970000	-3.10280000
H	7.36860000	-0.96770000	-0.07120000
H	9.01950000	-0.69160000	-0.82200000
O	7.48390000	0.59590000	-1.47600000
C	5.95110000	-1.09960000	-2.45310000
C	4.88500000	-0.64770000	-1.68500000
C	5.73360000	-2.07860000	-3.41540000
C	3.61900000	-1.17040000	-1.87520000
H	5.05580000	0.12690000	-0.95220000
C	4.46700000	-2.60270000	-3.59980000
H	6.55970000	-2.42910000	-4.01750000
C	3.40810000	-2.15070000	-2.83000000
H	2.79440000	-0.81070000	-1.27740000
H	4.30480000	-3.36440000	-4.34810000
H	2.41950000	-2.55970000	-2.97720000

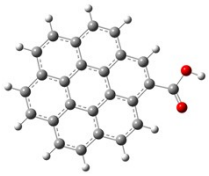
CO_2

O	-4.23800204	-0.62102762	0.00000000
C	-5.49640204	-0.62102762	0.00000000
O	-6.75480204	-0.62102762	0.00000000



CDs-OH

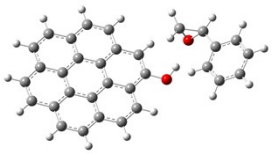
C	-1.59310000	-5.02960000	-0.00070000
C	-0.17900000	-5.03440000	-0.00060000
C	0.50480000	-3.80060000	-0.00030000
C	-0.22370000	-2.58540000	-0.00010000
C	-1.63430000	-2.61040000	-0.00030000
C	-2.29440000	-3.86100000	-0.00050000
C	1.92150000	-3.77630000	-0.00010000
C	0.46330000	-1.34570000	0.00030000
C	1.88040000	-1.32190000	0.00060000
C	2.60740000	-2.53810000	0.00040000
C	2.55530000	-0.08510000	0.00120000
C	1.80680000	1.11270000	0.00140000
C	0.44390000	1.08640000	0.00100000
C	-0.26440000	-0.13680000	0.00050000
C	-1.67820000	-0.19180000	0.00020000
C	-2.33820000	-1.38360000	-0.00020000
H	-3.41900000	-1.41040000	-0.00040000
H	-2.22880000	0.73850000	0.00020000
H	-2.11130000	-5.97840000	-0.00090000
H	-3.37550000	-3.87220000	-0.00060000
H	2.34440000	2.04830000	0.00180000
H	-0.11970000	2.00870000	0.00110000
C	0.57410000	-6.23190000	-0.00090000
C	1.93650000	-6.20830000	-0.00080000
C	2.64780000	-4.98590000	-0.00050000
H	0.04330000	-7.17370000	-0.00110000
H	2.49940000	-7.13130000	-0.00110000
C	4.06040000	-4.93050000	-0.00040000
C	4.72100000	-3.73820000	0.00020000
C	4.01710000	-2.51170000	0.00060000
H	4.61250000	-5.86000000	-0.00070000
H	5.80190000	-3.71320000	0.00030000
C	3.98010000	-0.08610000	0.00160000
C	4.67740000	-1.26400000	0.00130000
H	5.76070000	-1.24950000	0.00150000
O	4.60400000	1.12360000	0.00230000
H	5.56010000	0.99420000	0.00250000



CDs-COOH

C	-1.58570000	-5.03680000	-0.00070000
C	-0.17170000	-5.03030000	-0.00060000
C	0.50340000	-3.79130000	-0.00030000
C	-0.23030000	-2.58020000	-0.00010000
C	-1.64120000	-2.61740000	-0.00030000
C	-2.29330000	-3.87250000	-0.00050000
C	1.91890000	-3.75510000	-0.00010000
C	0.44950000	-1.33550000	0.00030000
C	1.86880000	-1.29240000	0.00070000
C	2.59550000	-2.51030000	0.00040000
C	2.54300000	-0.04680000	0.00140000
C	1.76470000	1.13430000	0.00140000
C	0.40200000	1.08890000	0.00090000
C	-0.29520000	-0.13800000	0.00040000
C	-1.70840000	-0.20240000	0.00010000
C	-2.35880000	-1.39890000	-0.00020000
H	-3.43910000	-1.43670000	-0.00040000
H	-2.26430000	0.72450000	0.00010000
H	-2.09710000	-5.98910000	-0.00080000
H	-3.37420000	-3.88950000	-0.00060000
H	2.26840000	2.08580000	0.00180000
H	-0.16870000	2.00680000	0.00090000
C	0.58960000	-6.22150000	-0.00090000
C	1.95230000	-6.18760000	-0.00090000
C	2.65380000	-4.96040000	-0.00050000
H	0.06610000	-7.16730000	-0.00110000
H	2.52220000	-7.10610000	-0.00110000
C	4.06760000	-4.90220000	-0.00040000
C	4.72090000	-3.70790000	0.00020000
C	4.00620000	-2.48550000	0.00060000
H	4.62130000	-5.83050000	-0.00080000
H	5.80090000	-3.67150000	0.00030000
C	3.97470000	-0.04840000	0.00200000
C	4.66110000	-1.24230000	0.00150000
H	5.74040000	-1.23220000	0.00190000
C	4.76780000	1.19950000	0.00290000
O	4.35260000	2.33440000	0.00380000
O	6.09790000	0.97260000	0.00370000

H	6.55860000	1.82600000	0.00480000



CDs-OH-SO

C	4.68345574284692	-0.15436842027487	0.84326760148889
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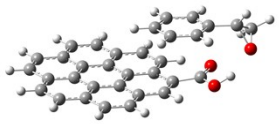
C	2.47763590177653	-0.68268797178981	-0.03227802453321
C	2.24612881207598	0.69915698020459	-0.24301115966345
C	3.24307175789954	1.63903296616471	0.09321933199093
C	4.46108822251279	1.17495068697192	0.64148593642322
C	1.47646573009915	-1.62704592494699	-0.36888050738980
C	1.01434957793686	1.13726143161918	-0.79054476756315
C	0.01114703193279	0.19244810346089	-1.12192932840498
C	0.24439556951842	-1.18870948221149	-0.91009396146890
C	-1.21341950437752	0.63651176623509	-1.65925667811205
C	-1.41633307112193	2.01879935191998	-1.86631443289606
C	-0.44847629224447	2.92520267944099	-1.55061134991655
C	0.78797955249476	2.51361519221129	-1.00328913134488
C	1.80665562320869	3.43347034664985	-0.66006276680478
C	2.98901233393152	3.01230674626973	-0.13028762766554
H	3.75806583533687	3.72684137160028	0.12868491006087
H	1.62642428923986	4.48634260668616	-0.82726421538509
H	5.61989928560494	-0.49472092921910	1.26306838361968
H	5.21911859906522	1.90138931280140	0.89972998939997
H	-2.35948669529307	2.33667126976134	-2.28380856437632
H	-0.61406731402836	3.98078255781321	-1.71457459257614
C	3.90898197849287	-2.50460304744867	0.70754332719883
C	2.94699819766596	-3.41292357084689	0.38073914288904
C	1.70767717432969	-3.00365553559286	-0.16309876937627
H	4.85160969543545	-2.83176630192504	1.12382242700205
H	3.11796554667784	-4.46947149928081	0.53447085173451
C	0.69004676370722	-3.92272789407590	-0.50848002851154
C	-0.49745457279246	-3.50027846754793	-1.02660358734065
C	-0.75635619859506	-2.12608768143645	-1.24079443809666
H	0.87345809093586	-4.97674981637469	-0.35175313085507
H	-1.26611950683328	-4.21492197647073	-1.28599406705254
C	-2.21228356855849	-0.33030401455776	-1.97578075962263
C	-1.97923191862541	-1.66493281488286	-1.77018357969595
H	-2.74947525237801	-2.38298102174348	-2.01942269580119
O	-3.38741825663339	0.12177071905353	-2.47652689386296
H	-3.98875075418533	-0.63423321536598	-2.60812764288858
C	-6.68182442997857	-1.96276232222403	-2.13521014974197
C	-5.83085980796947	-1.85025790031877	-0.94125600431949
H	-7.13279659890500	-2.93389019238720	-2.32858954681098
H	-5.71611973006483	-0.88402072585211	-0.46464544011289
H	-5.69247644451472	-2.71046655301486	-0.29725699729733
O	-5.28015314713059	-1.96004587584062	-2.22282821277145
C	-7.45086927958157	-0.80672529989401	-2.66114999661899
C	-6.87896093060975	0.45410871768861	-2.79070711126277
C	-8.78061487558809	-0.99295418681879	-3.02275705231827
C	-7.62933579667681	1.50911270951041	-3.27812246040230
H	-5.84513842030627	0.61329945451909	-2.52478949389018
C	-9.52824082871029	0.06599837123942	-3.50397393911538
H	-9.22898489586057	-1.97123078305493	-2.92422038639826
C	-8.95341016980618	1.31939356626282	-3.63438548796589
H	-7.17481392865373	2.48339876024633	-3.38072643816408
H	-10.56008185161605	-0.08840064539790	-3.78134162903459
H	-9.53589684629191	2.14477932516687	-4.01554018660967



CDs-COOH-SO

C	5.33505117823089	-0.37938249917927	0.46330797374858
C	4.34687794213561	0.61717391694093	0.28975381350555
C	3.03114836497323	0.22239142814061	-0.03159842631122
C	2.71598669156348	-1.15103484449604	-0.17481288875830
C	3.72176032610627	-2.12401019108085	0.00699620979384
C	5.03271982578863	-1.70101532064657	0.32739128851774
C	2.02150992244383	1.19940229980238	-0.21111636290427
C	1.39509652461999	-1.54678757974315	-0.50427866999775
C	0.38305590387294	-0.57065040025697	-0.69449303355033
C	0.70146721344980	0.80239465121873	-0.53928815488349
C	-0.92763050102523	-0.96961482916293	-1.04365201436875
C	-1.20261890615134	-2.35050080527400	-1.17376918164939

C	-0.23082010390882	-3.28597388916454	-0.97851686196336
C	1.09113670212411	-2.91681759712528	-0.64556876725331
C	2.11661247320281	-3.87181418659805	-0.45244646530780
C	3.38600715676514	-3.48997394641896	-0.13895440021630
H	4.16184879571219	-4.22923257532359	0.00283326983062
H	1.87103339203640	-4.91869596519715	-0.56282736395031
H	6.34154017872166	-0.07014868838062	0.70788419985032
H	5.79697682470954	-2.45343713476886	0.46289058113216
H	-2.20030133359800	-2.65726203213256	-1.44044137242180
H	-0.46236577205451	-4.33668013105551	-1.08180399148403
C	4.63094113871157	1.99559456818058	0.42677148260914
C	3.65926326613564	2.93605200052459	0.25719224897252
C	2.33231652018126	2.56817179870550	-0.06408802531687
H	5.64159650894488	2.29127337208374	0.67113245070722
H	3.89005427270609	3.98646857735337	0.36592314811245
C	1.30695003744524	3.52621735628165	-0.24357793189662
C	0.03674677217708	3.14678055737184	-0.55559488794493
C	-0.29972581277743	1.78111911298414	-0.71310149536496
H	1.55395176211158	4.57216076708223	-0.12809374139614
H	-0.73991092523031	3.88586494163943	-0.69047853231381
C	-1.91895462377075	0.04082752241277	-1.22088648032491
C	-1.60382129178965	1.36519058240969	-1.04535770512485
H	-2.36949171025905	2.11458457959935	-1.18190784921805
C	-3.30653843316930	-0.29767820083482	-1.62531775841728
O	-3.61730914353994	-1.21920166944052	-2.34708232998406
O	-4.20195723848219	0.54912846968775	-1.12704839707456
H	-5.12027078035380	0.27914581920596	-1.38289631742625
C	-6.88860710012639	-1.78494416417539	-1.31392705975774
C	-6.71624315173685	-1.42969547681610	-2.72374068405426
H	-7.89589893673190	-2.01336231383502	-0.96622477900372
H	-5.75147650820321	-1.60398589359454	-3.18570903293641
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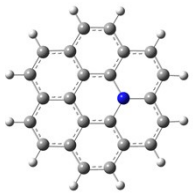
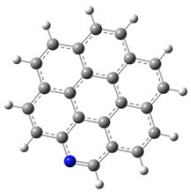
C	-5.25671035861817	-1.80951358015413	0.57983410016869
C	-5.27072490165004	-3.65232188886971	-0.96019333785795
C	-4.20999871358068	-2.39544811320123	1.26937790100543
H	-5.65667089680294	-0.85847327242382	0.90027462407075
C	-4.23232760090304	-4.24023085956938	-0.26090621847107
H	-5.67881302464043	-4.13134693860885	-1.83793088903605
C	-3.69625289791648	-3.61026894411347	0.85004385177348
H	-3.79151218056333	-1.89860046524062	2.13202872698449
H	-3.83125738904186	-5.18678172525242	-0.59205653088764
H	-2.87345843576807	-4.06195118519697	1.38410248798922



CDs- graphitic N

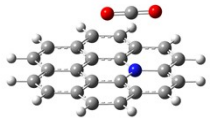
C	-1.59970000	-5.03100000	-0.00070000
C	-0.18210000	-5.03700000	-0.00060000
C	0.49900000	-3.80820000	-0.00020000
C	-0.21500000	-2.58500000	0.00000000
C	-1.63350000	-2.60590000	-0.00030000
C	-2.29520000	-3.86520000	-0.00050000
C	1.91470000	-3.76540000	-0.00010000
C	0.48230000	-1.35730000	0.00040000
C	2.58630000	-2.52350000	0.00040000
C	2.54710000	-0.11320000	0.00130000
C	1.81080000	1.08080000	0.00140000
C	0.45060000	1.08980000	0.00090000
C	-0.25150000	-0.15510000	0.00050000
C	-1.65240000	-0.20130000	0.00010000
C	-2.33370000	-1.39480000	-0.00020000
H	-3.41340000	-1.40850000	-0.00040000
H	-2.19190000	0.73420000	0.00020000
H	-2.11680000	-5.98020000	-0.00080000
H	-3.37570000	-3.86810000	-0.00060000
H	2.37080000	2.00360000	0.00180000
H	-0.11120000	2.00930000	0.00100000
C	0.57430000	-6.23600000	-0.00090000
C	1.93150000	-6.20800000	-0.00090000
C	2.64870000	-4.97950000	-0.00050000
H	0.04340000	-7.17750000	-0.00110000
H	2.50170000	-7.12580000	-0.00110000
C	4.04690000	-4.93140000	-0.00040000
C	4.69790000	-3.72110000	0.00020000
C	3.99470000	-2.50860000	0.00060000
H	4.60740000	-5.85430000	-0.00080000
H	5.77720000	-3.68280000	0.00030000

C	4.67820000	-1.25350000	0.00140000
H	5.75570000	-1.24240000	0.00170000
C	3.94960000	-0.10470000	0.00170000
H	4.43560000	0.85900000	0.00230000
N	1.86480000	-1.34400000	0.00070000



CDs- pyridinic N

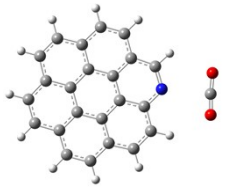
C	-1.60370000	-5.03680000	-0.00070000
C	-0.18870000	-5.04690000	-0.00060000
C	0.49410000	-3.81340000	-0.00030000
C	-0.23250000	-2.59650000	-0.00010000
C	-1.64210000	-2.61450000	-0.00030000
C	-2.30290000	-3.86580000	-0.00050000
C	1.90950000	-3.79490000	-0.00020000
C	0.45500000	-1.35860000	0.00030000
C	1.86720000	-1.34530000	0.00060000
C	2.59150000	-2.55710000	0.00030000
C	2.57940000	-0.12790000	0.00110000
C	1.84570000	1.08200000	0.00130000
C	0.48100000	1.07000000	0.00100000
C	-0.25380000	-0.14070000	0.00050000
C	-1.66790000	-0.18940000	0.00020000
C	-2.33430000	-1.37990000	-0.00020000
H	-3.41520000	-1.39800000	-0.00040000
H	-2.21640000	0.74210000	0.00020000
H	-2.12560000	-5.98340000	-0.00090000
H	-3.38400000	-3.87680000	-0.00060000
H	2.39970000	2.00790000	0.00170000
H	-0.06840000	2.00120000	0.00110000
C	0.57170000	-6.24040000	-0.00090000
C	1.93600000	-6.21790000	-0.00080000
C	2.64760000	-4.99510000	-0.00050000
H	0.04440000	-7.18430000	-0.00110000
H	2.49650000	-7.14220000	-0.00110000
C	4.06280000	-4.92230000	-0.00030000
C	4.71830000	-3.72540000	0.00020000
C	3.99900000	-2.50800000	0.00060000
H	4.62210000	-5.84760000	-0.00070000
H	5.79850000	-3.68980000	0.00030000
C	4.59190000	-1.21920000	0.00120000
H	5.67240000	-1.13050000	0.00150000
N	3.93290000	-0.09830000	0.00150000



CDs- graphitic N-CO_2

C	-1.58840000	-5.01100000	0.00290000
C	-0.17100000	-5.01670000	-0.01580000
C	0.50960000	-3.78890000	-0.05220000
C	-0.20460000	-2.56610000	-0.06830000
C	-1.62260000	-2.58690000	-0.04200000
C	-2.28420000	-3.84540000	-0.00870000
C	1.92510000	-3.74650000	-0.06810000
C	0.49130000	-1.33880000	-0.10600000
C	2.59700000	-2.50590000	-0.10580000
C	2.55750000	-0.09400000	-0.16840000
C	1.82090000	1.09890000	-0.17930000
C	0.46090000	1.10780000	-0.15000000
C	-0.24120000	-0.13640000	-0.11230000
C	-1.64210000	-0.18240000	-0.08190000
C	-2.32280000	-1.37540000	-0.04860000
H	-3.40220000	-1.38880000	-0.02720000
H	-2.18140000	0.75310000	-0.08630000
H	-2.10520000	-5.95980000	0.02870000
H	-3.36450000	-3.84800000	0.00790000
H	2.38010000	2.02130000	-0.20780000
H	-0.10110000	2.02710000	-0.15510000
C	0.58510000	-6.21570000	0.00310000
C	1.94230000	-6.18800000	-0.00820000
C	2.65890000	-4.95990000	-0.04150000
H	0.05440000	-7.15680000	0.02900000

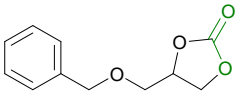
H	2.51260000	-7.10550000	0.00860000
C	4.05730000	-4.91160000	-0.04790000
C	4.70820000	-3.70210000	-0.08120000
C	4.00480000	-2.48980000	-0.11180000
H	4.61800000	-5.83410000	-0.02630000
H	5.78740000	-3.66370000	-0.08540000
C	4.68780000	-1.23500000	-0.14950000
H	5.76520000	-1.22430000	-0.15440000
C	3.95950000	-0.08640000	-0.17910000
H	4.44530000	0.87660000	-0.20750000
N	1.87500000	-1.32540000	-0.13000000
C	1.80550000	-1.45090000	2.84800000
O	1.25380000	-2.45290000	2.87020000
O	2.35840000	-0.44930000	2.83300000



CDs- pyridinic N-CO_2

C	-1.63080000	-5.09390000	-0.00120000
C	-0.21580000	-5.08770000	-0.00090000
C	0.45270000	-3.84640000	-0.00030000
C	-0.28730000	-2.63770000	-0.00010000
C	-1.69660000	-2.67220000	-0.00050000
C	-2.34320000	-3.93110000	-0.00100000
C	1.86760000	-3.81150000	0.00000000
C	0.38600000	-1.39180000	0.00040000
C	1.79850000	-1.36130000	0.00080000
C	2.53500000	-2.56570000	0.00050000
C	2.49560000	-0.13470000	0.00130000
C	1.74730000	1.06670000	0.00160000
C	0.38280000	1.03610000	0.00120000
C	-0.33770000	-0.18300000	0.00060000
C	-1.75120000	-0.24800000	0.00020000
C	-2.40350000	-1.44610000	-0.00030000
H	-3.48410000	-1.47700000	-0.00060000
H	-2.31040000	0.67700000	0.00040000
H	-2.14150000	-6.04660000	-0.00160000
H	-3.42390000	-3.95440000	-0.00130000
H	2.28540000	2.00080000	0.00210000
H	-0.17780000	1.96040000	0.00140000
C	0.55820000	-6.27240000	-0.00100000
C	1.92220000	-6.23400000	-0.00070000
C	2.61950000	-5.00320000	-0.00020000
H	0.04200000	-7.22230000	-0.00140000
H	2.49360000	-7.15150000	-0.00090000
C	4.03410000	-4.91510000	0.00010000
C	4.67610000	-3.71130000	0.00060000
C	3.94180000	-2.50230000	0.00080000
H	4.60320000	-5.83420000	0.00000000
H	5.75550000	-3.66170000	0.00090000
C	4.52200000	-1.21030000	0.00130000
H	5.60120000	-1.10960000	0.00150000
N	3.85060000	-0.09480000	0.00160000
C	5.44810000	1.90840000	0.00310000
O	6.36130000	1.21590000	-0.00080000
O	4.61270000	2.69290000	0.00680000

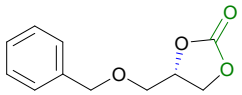
2. Characterization of Compounds



2a

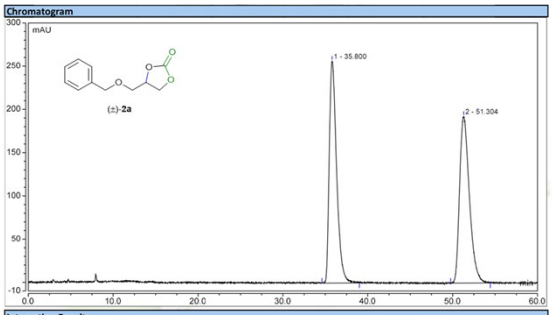
The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4/1) to afford the product **1** as light-yellow oil. (989.0 mg, 95% yield). Known compound[1]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.29 (m, 5H), 4.84-4.79 (m, 1H), 4.60 (dd, *J* = 12.0, 27.0 Hz, 2H), 4.48 (t, *J* = 8.0 Hz, 1H), 4.39 (dd, *J* = 6.0,

8.5 Hz, 1H), 3.71 (dd, *J* = 4.0, 11.0 Hz, 1H), 3.62 (dd, *J* = 3.5, 11.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.05, 137.14, 128.69, 128.20, 127.87, 75.09, 73.80, 68.91, 66.40.



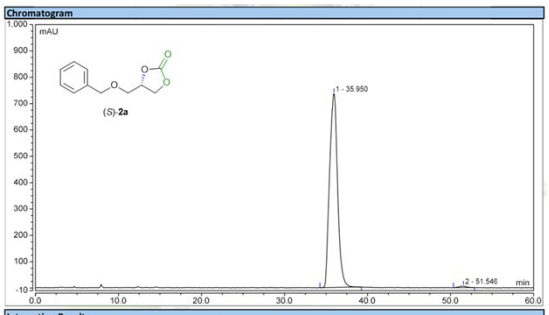
(*S*)-**2a**

The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4/1) to afford the product **2** as light-yellow oil. (926.5 mg, 89% yield, 99% e.e.). Known compound[1]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.29 (m, 5H), 4.84-4.79 (m, 1H), 4.60 (dd, *J* = 12.0, 27.0 Hz, 2H), 4.48 (t, *J* = 8.0 Hz, 1H), 4.39 (dd, *J* = 6.0, 8.5 Hz, 1H), 3.71 (dd, *J* = 4.0, 11.0 Hz, 1H), 3.62 (dd, *J* = 3.5, 11.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.05, 137.14, 128.70, 128.21, 127.88, 75.09, 73.81, 68.91, 66.41. HPLC: (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow 1.0 mL/min, detection at 214 nm) retention time = 35.95 min (major) and 51.55 min (minor).



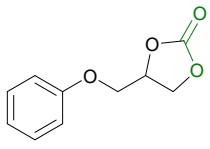
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		35.800	256.986	256.691	49.92	57.11	n.a.
2		51.304	257.803	192.814	50.08	42.89	n.a.
Total:			514.789	449.505	100.00	100.00	



Integration Results

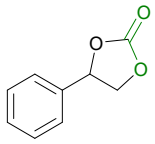
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		35.950	818.781	735.880	99.36	99.17	n.a.
2		51.546	5.260	6.140	0.64	0.83	n.a.
Total:			824.041	742.020	100.00	100.00	



2b

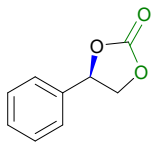
The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4/1) to afford the product **3** as white solid. (893.3 mg, 92% yield). Known compound[1]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.28 (m, 2H), 7.02 (t, *J* = 15.0

Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 5.06-5.01 (m, 1H), 4.62 (t, *J* = 8.5 Hz, 1H), 4.55 (dd, *J* = 5.5, 8.5 Hz, 1H), 4.24 (dd, *J* = 4.5, 11.0 Hz, 1H), 4.15 (dd, *J* = 4.0, 10.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ157.85, 154.76, 129.84, 122.15, 114.72, 74.19, 66.97, 66.39.



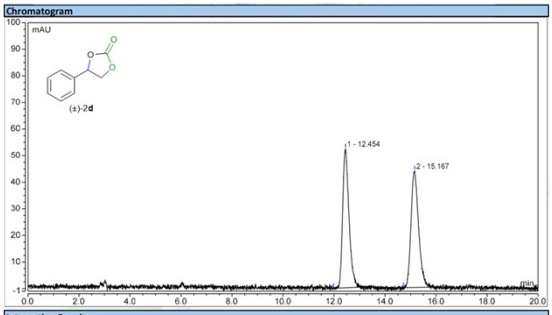
2d

The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3/1) to afford the product **4** as white solid. (722.3 mg, 88% yield). Known compound[1]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.40 (m, 3H), 7.38-7.35 (m, 2H), 5.68 (t, *J* = 8.0 Hz, 1H), 4.81 (t, *J* = 8.5 Hz, 1H), 4.36 (dd, *J* = 8.0, 8.5 Hz, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 154.94, 135.90, 129.89, 129.39, 126.00, 78.13, 71.31.

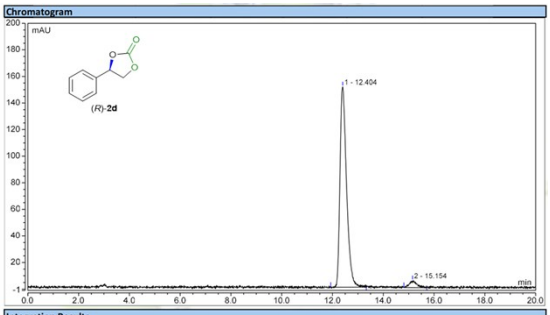


(*R*)-**2d**

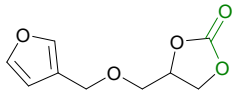
The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3/1) to afford the product **4** as white solid. (574.6 mg, 70% yield, 94% e.e.). Known compound[1]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.41 (m, 3H), 7.38-7.35 (m, 2H), 5.68 (t, *J* = 8.0 Hz, 1H), 4.81 (t, *J* = 8.5 Hz, 1H), 4.35 (dd, *J* = 8.0, 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.93, 135.90, 129.90, 129.39, 126.00, 78.13, 71.31. HPLC: (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow 1.0 mL/min, detection at 214 nm) retention time = 12.40 min (major) and 15.15 min (minor).



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.454	15.061	52.303	49.93	54.40	n.a.
2		15.167	15.105	43.835	50.07	45.60	n.a.
Total:			30.165	96.139	100.00	100.00	

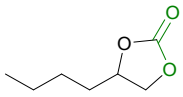


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.404	45.304	150.801	96.21	96.62	n.a.
2		15.154	1.783	5.278	3.79	3.38	n.a.
Total:			47.087	156.080	100.00	100.00	



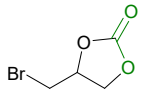
2c

The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3/1) to afford the product **6** as yellow oil. (832.3 mg, 84% yield). Known compound[1]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.41 (m, 3H), 7.38-7.35 (m, 2H), 5.68 (t, *J* = 8.0 Hz, 1H), 4.81 (t, *J* = 8.5 Hz, 1H), 4.35 (dd, *J* = 8.0, 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.98, 150.76, 143.31, 110.35, 110.26, 74.97, 68.58, 66.39, 65.41.



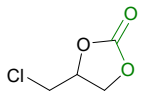
2e

The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4/1) to afford the product **7** as colorless oil. (605.5 mg, 84% yield). Known compound[1]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.73-4.66 (m, 1H), 4.52 (t, *J* = 8.0 Hz, 1H), 4.06 (dd, *J* = 7.5, 8.5 Hz, 1H), 1.84-1.76 (m, 1H), 1.72-1.64 (m, 1H), 1.48-1.41 (m, 1H), 1.40-1.31 (m, 3H), 0.91 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.24, 77.19, 69.52, 33.68, 26.55, 22.37, 13.93.



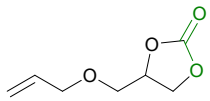
2i

The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3/1) to afford the product **8** as colorless oil. (696.8 mg, 77% yield). Known compound[1]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.98-4.93 (m, 1H), 4.58 (t, *J* = 8.5 Hz, 1H), 4.33 (dd, *J* = 6.0, 9.0 Hz, 1H), 3.62-3.54 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.33, 74.09, 68.16, 31.76.



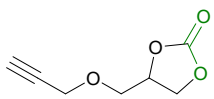
2h

The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1/1) to afford the product **9** as colorless oil. (580.3 mg, 85% yield). Known compound[1]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.99-4.94 (m, 1H), 4.61-4.57 (m, 1H), 4.43-4.40 (m, 1H), 3.78 (dd, *J* = 5.5, 12.0 Hz, 1H), 3.73 (dd, *J* = 3.5, 12.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.25, 74.34, 67.09, 43.74.



2f

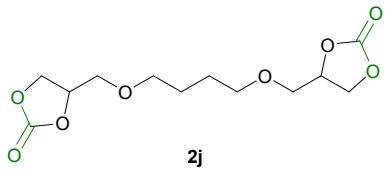
The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3/1) to afford the product **10** as colorless oil. (664.2 mg, 84% yield). Known compound[1]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.84-5.76 (m, 1H), 5.23-5.12 (m, 2H), 4.81-4.76 (m, 1H), 4.45 (t, *J* = 8.0 Hz, 1H), 4.32 (dd, *J* = 6.5, 8.5 Hz, 1H), 4.02-3.94 (m, 2H), 3.64 (dd, *J* = 3.5, 11.0 Hz, 1H), 3.54 (dd, *J* = 3.5, 11.0 Hz, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 155.05, 133.69, 117.57, 128.20, 75.19, 72.33, 68.80, 66.16.



2g

The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1/2) to afford the product **11** as colorless oil. (663.6 mg, 85% yield). Known compound[1]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.86-4.81 (m, 1H), 4.48 (t, *J* = 8.5

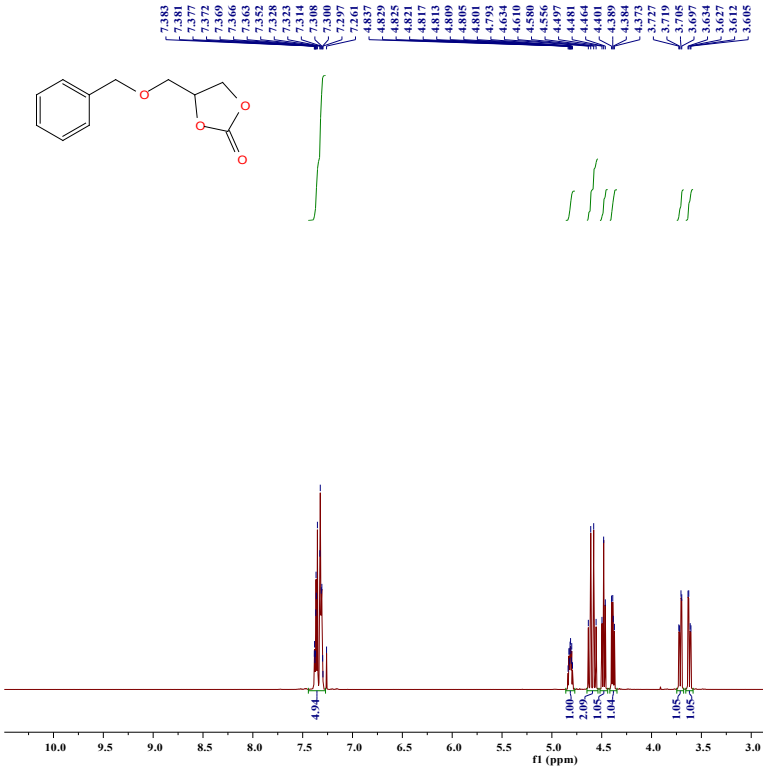
Hz, 1H), 4.35 (dd, *J* = 6.0, 8.5 Hz, 1H), 4.24-4.13 (m, 2H), 3.75 (dd, *J* = 3.5, 11.0 Hz, 1H), 3.67 (dd, *J* = 3.5, 11.0 Hz, 1H), 2.48 (t, *J* = 2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.97, 78.61, 75.61, 74.87, 68.45, 66.16, 58.75.

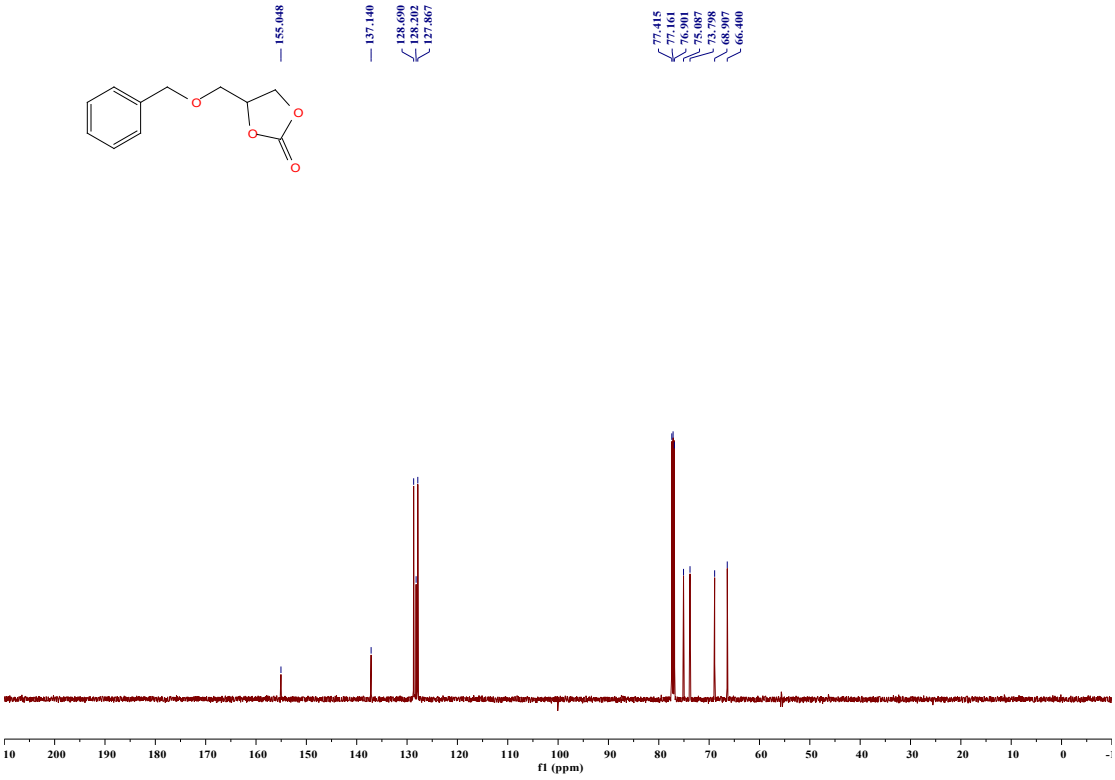


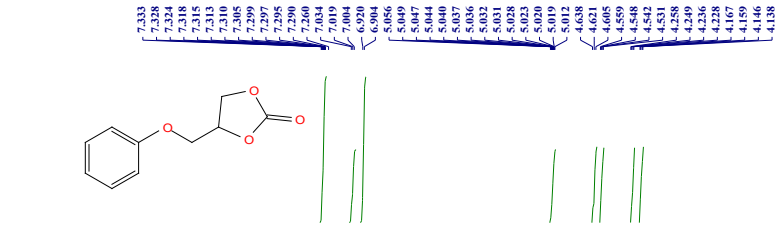
2j

The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1/1) to afford the product **12** as colorless oil. (1132.1 mg, 78% yield). Known compound[2]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.83-4.78 (m, 1H), 4.49 (t, *J* = 8.5 Hz, 1H), 4.40-4.36 (m, 1H), 3.68 (dd, *J* = 3.5, 11.0 Hz, 1H), 3.59-3.55 (m, 1H), 3.52(t, *J* = 6 Hz, 2H), 1.64-1.62 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.19, 75.31, 71.67, 69.72, 66.31, 26.12.

3. NMR Spectra



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7.019
7.004
6.920
6.904
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5.049
5.047
5.044
5.040
5.037
5.036
5.032
5.031
5.028
5.023
5.020
5.019
5.012
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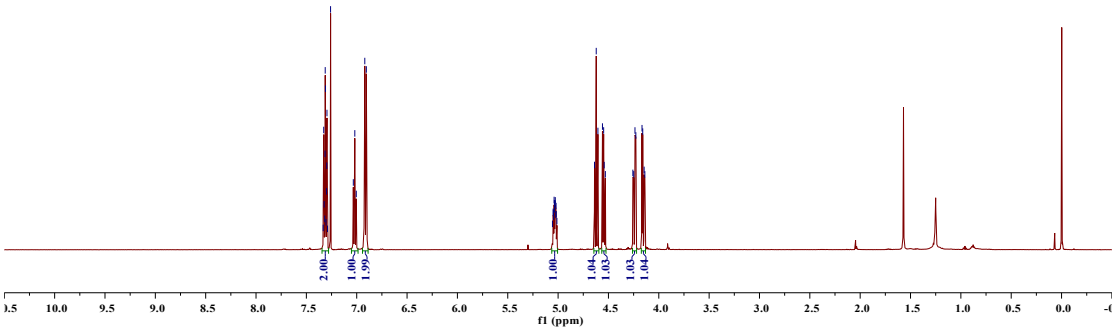
4.138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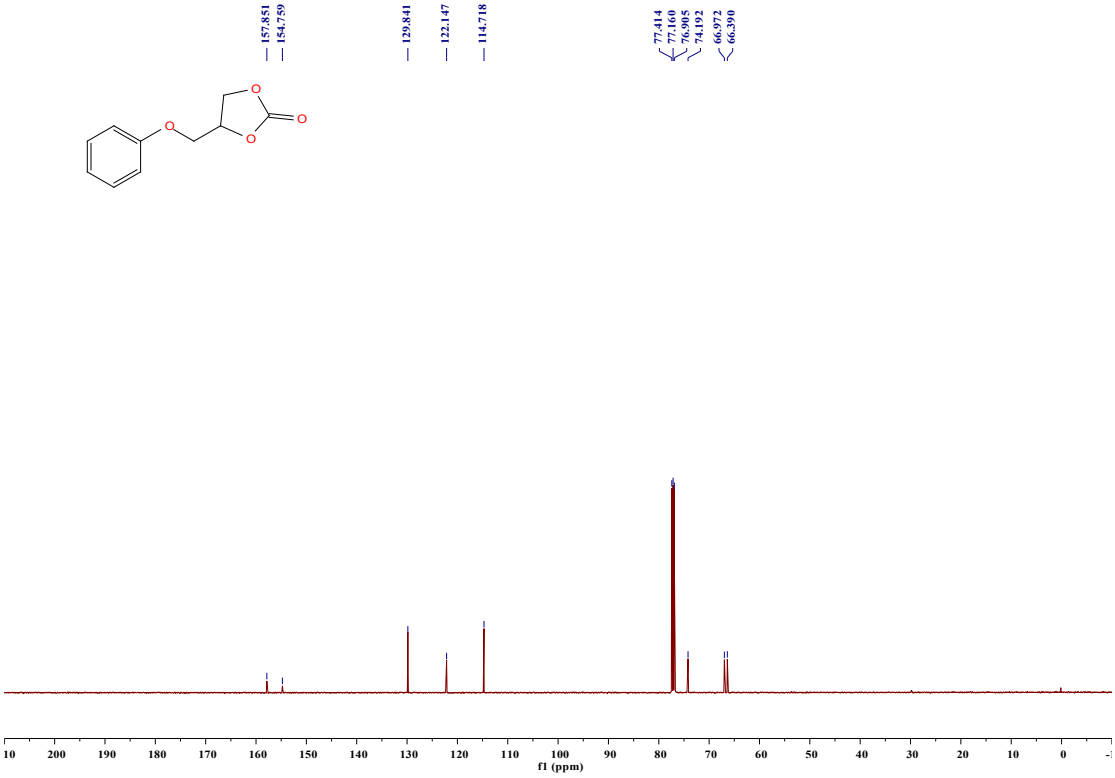
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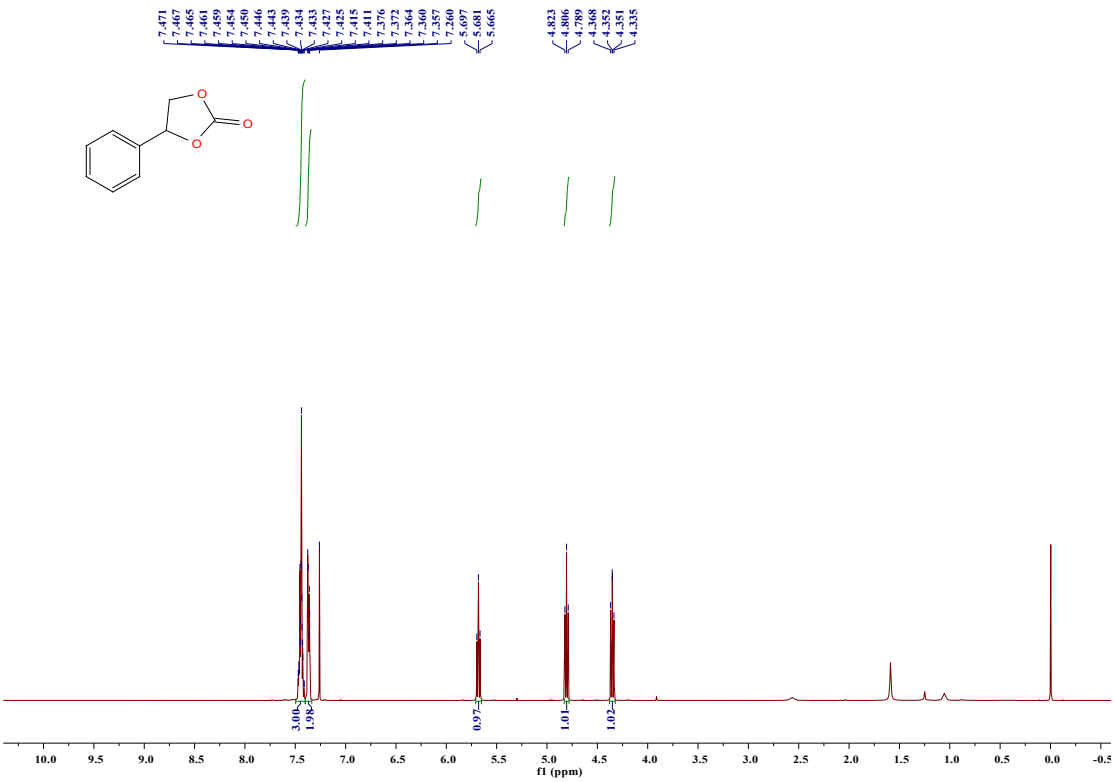
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4.789
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4.335
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1.02
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8.0
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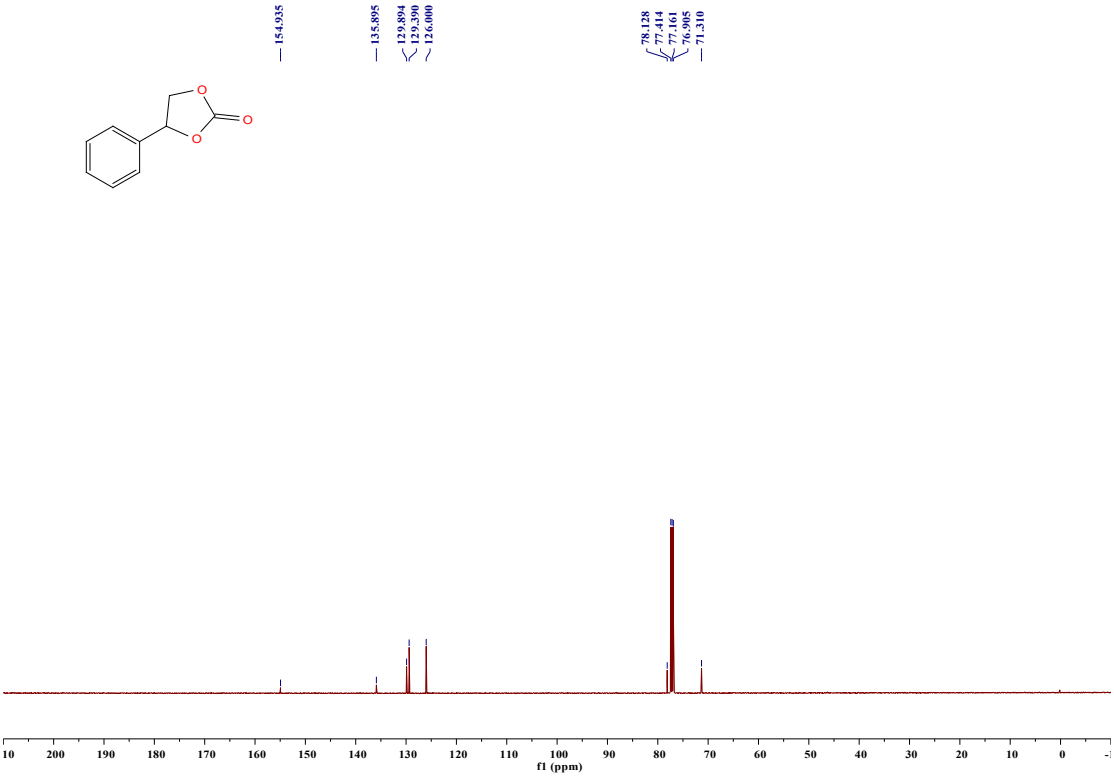
f1 (ppm)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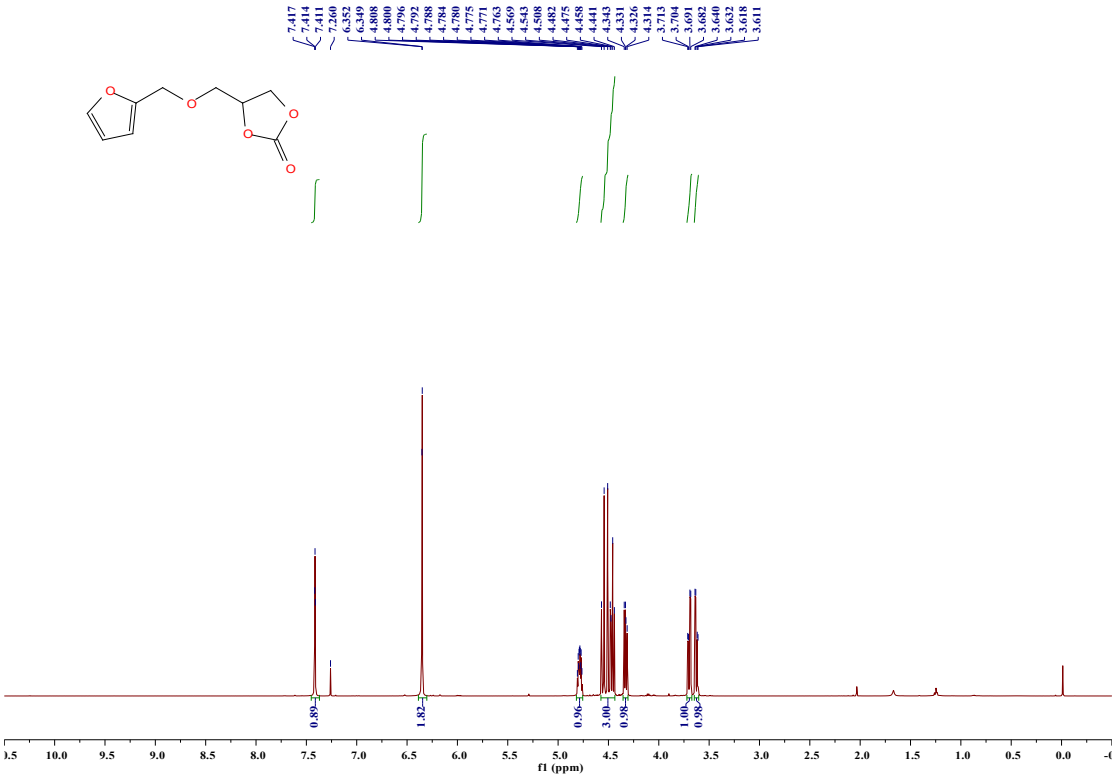
f1 (ppm)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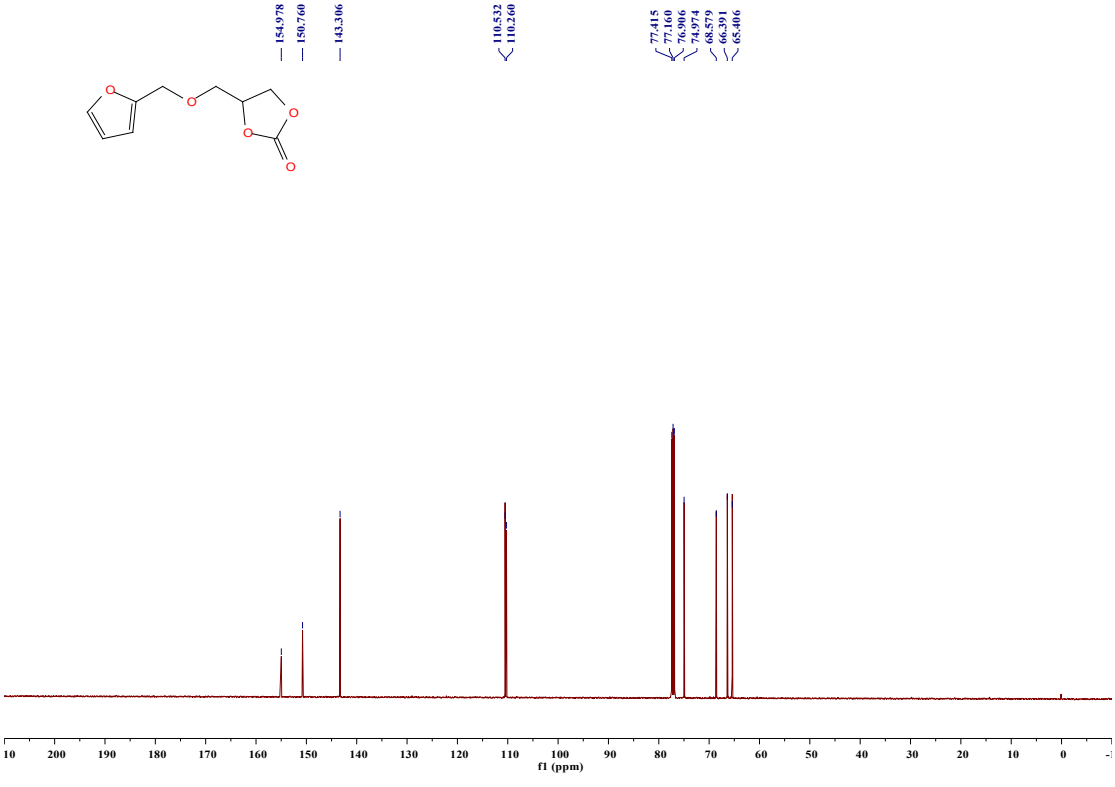
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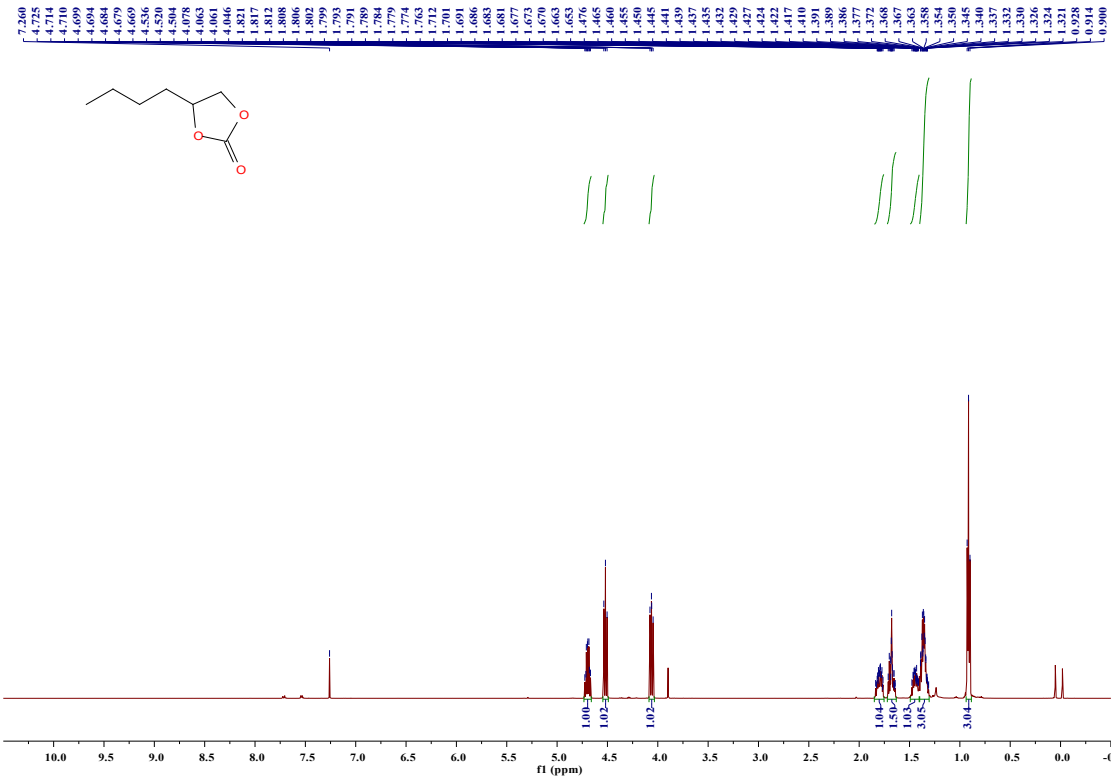
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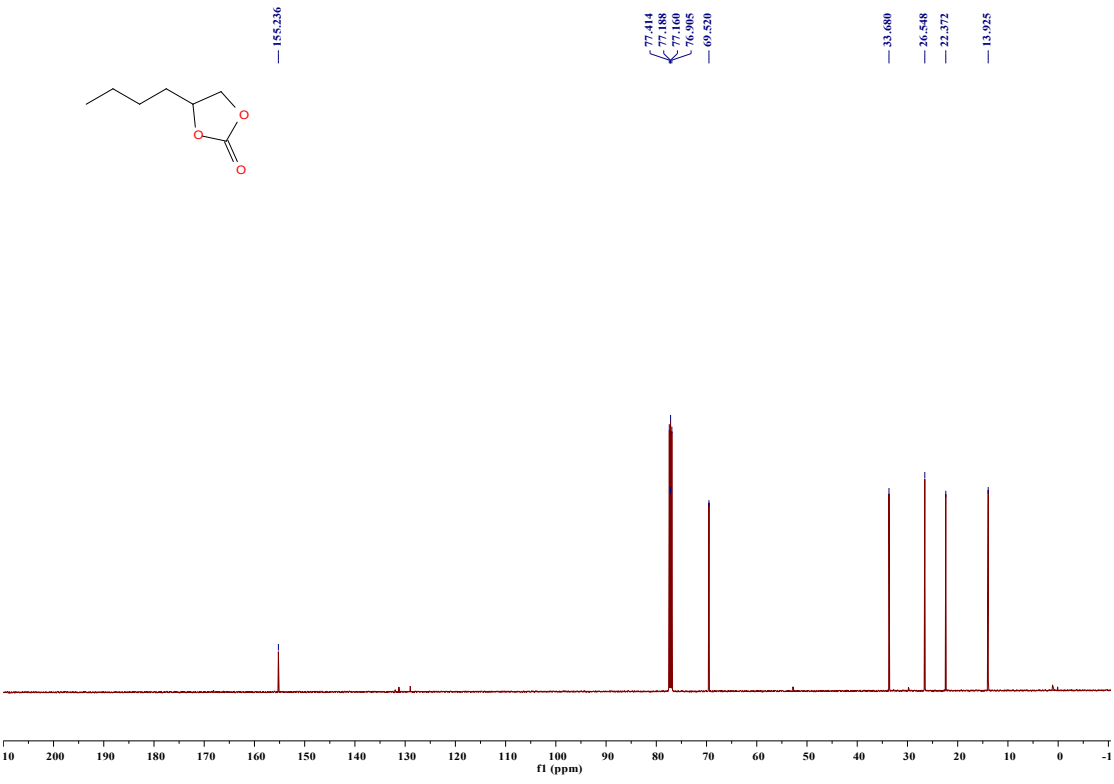
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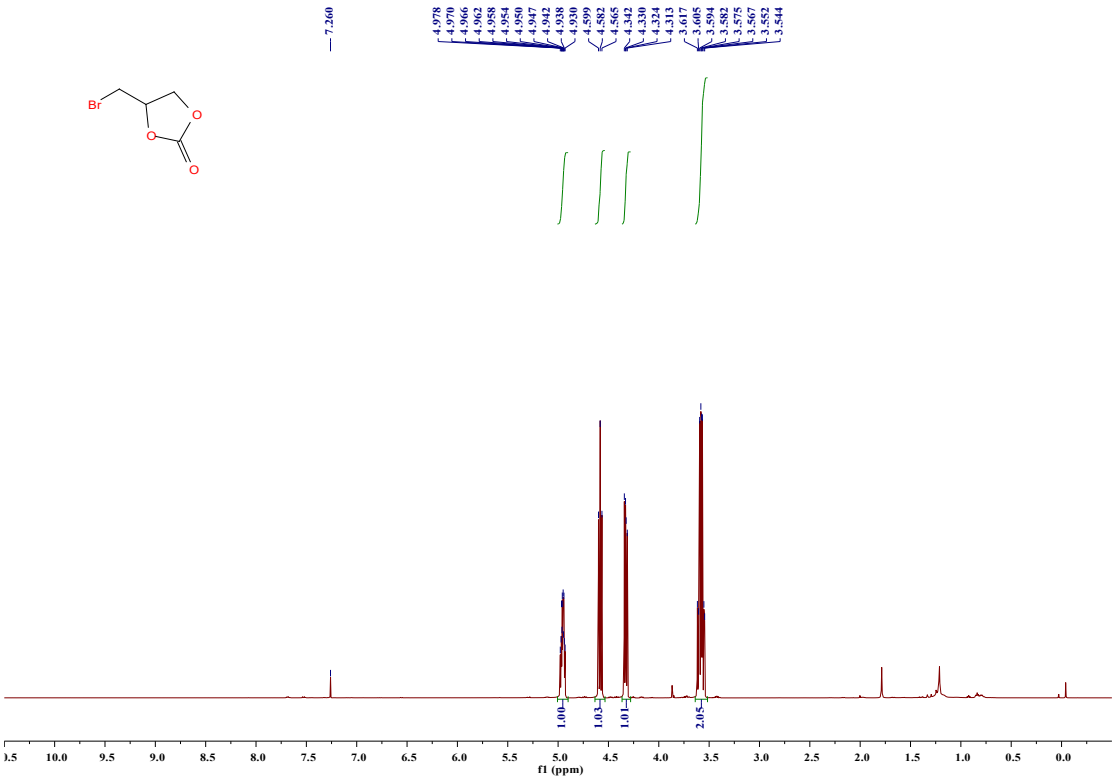
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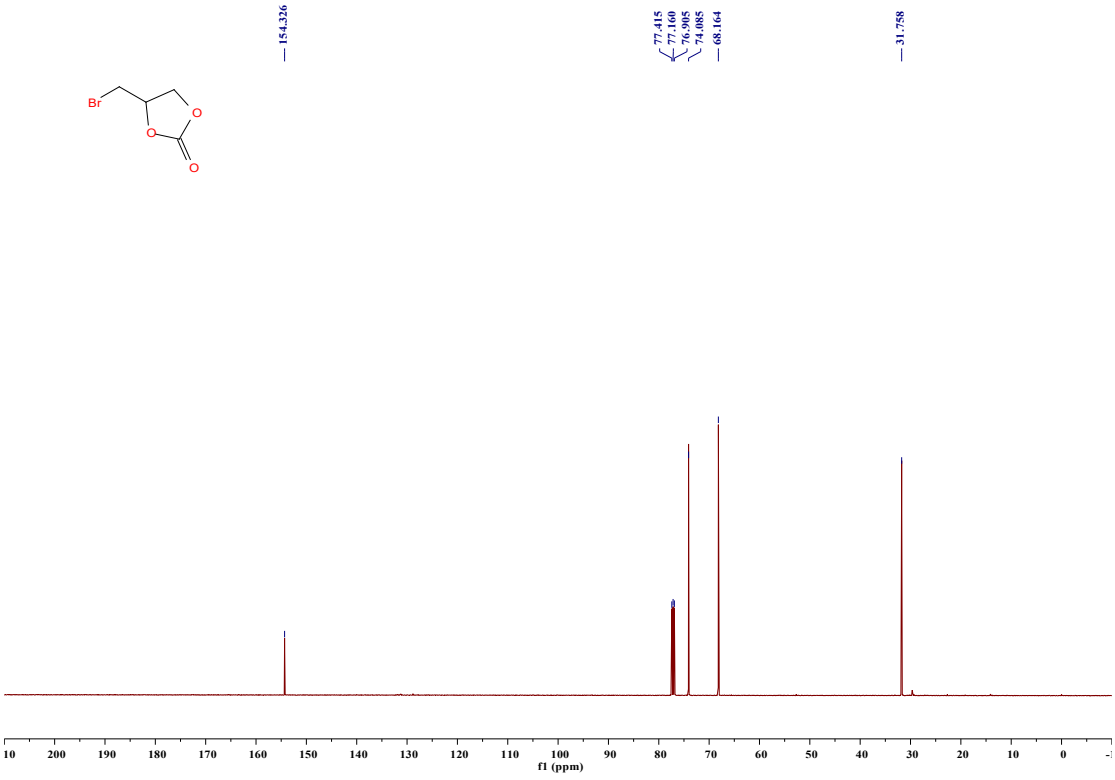
f1 (ppm)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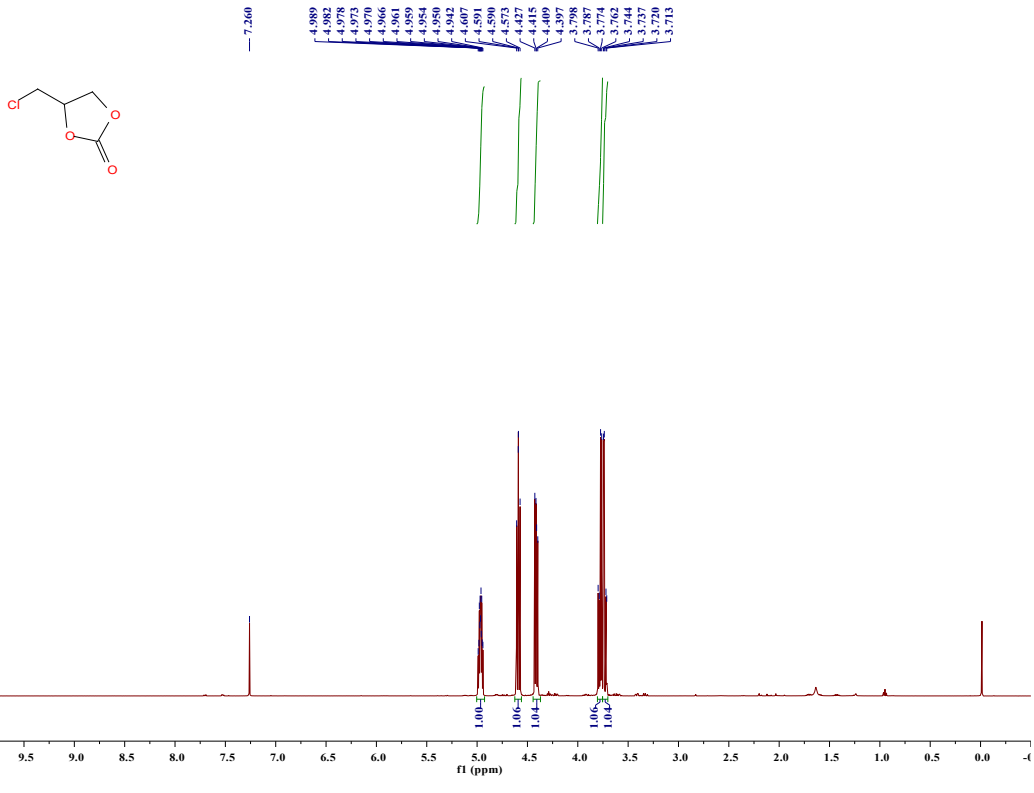
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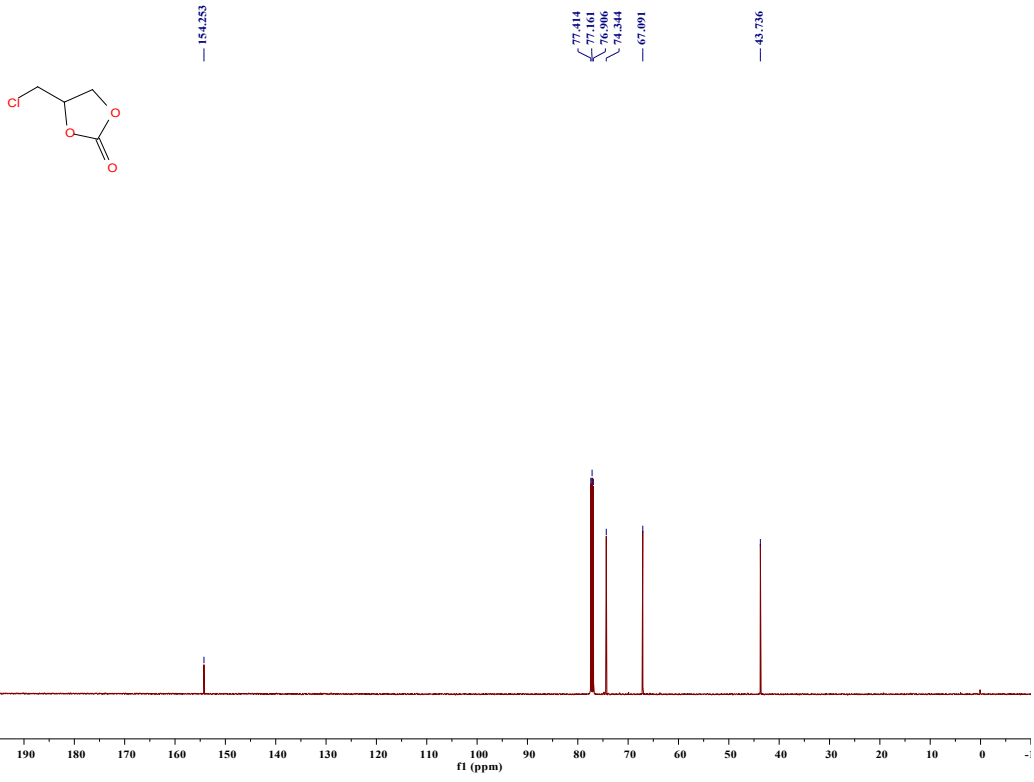
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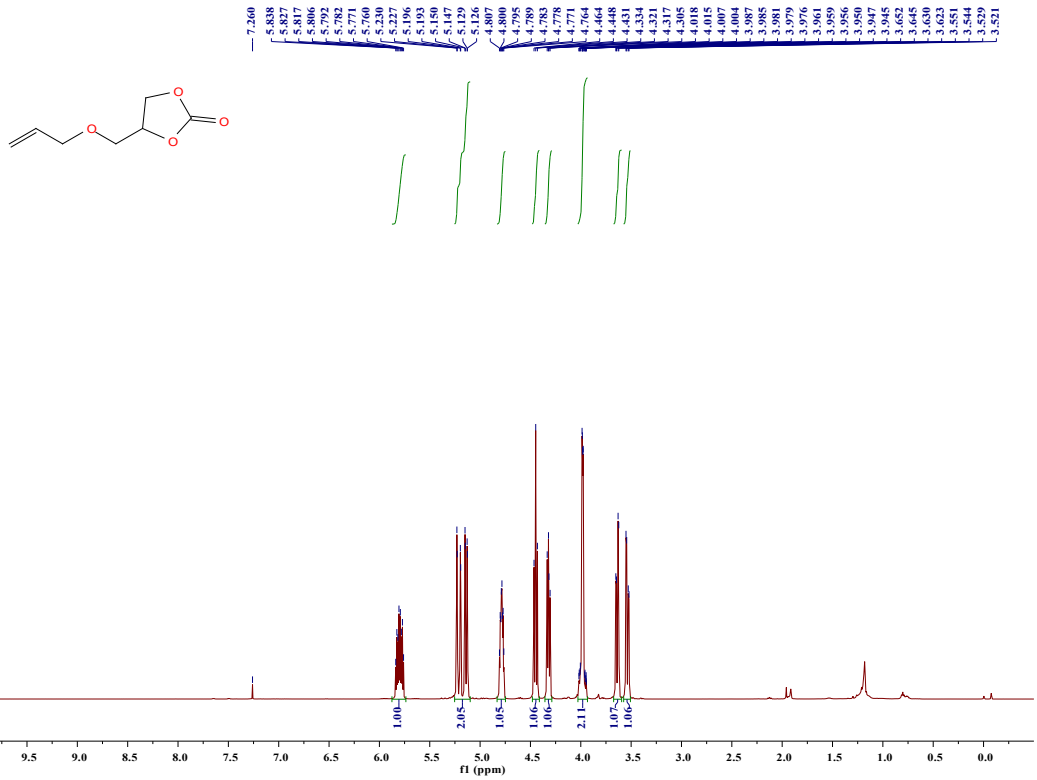
f1 (ppm)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4.778
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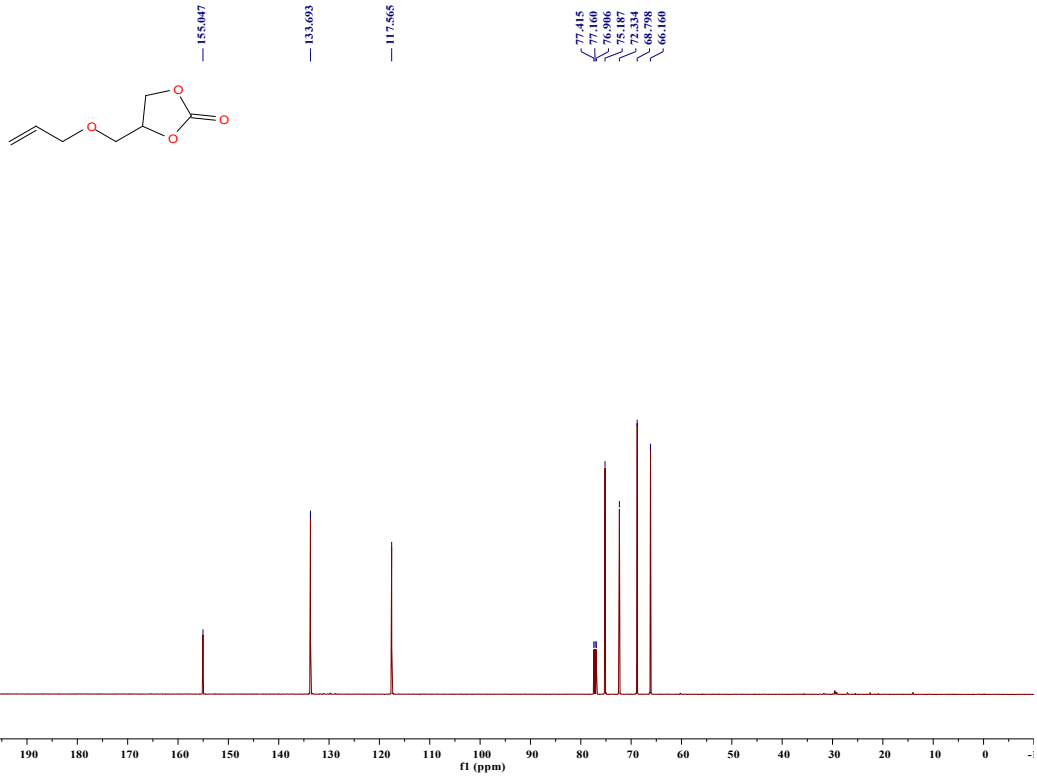
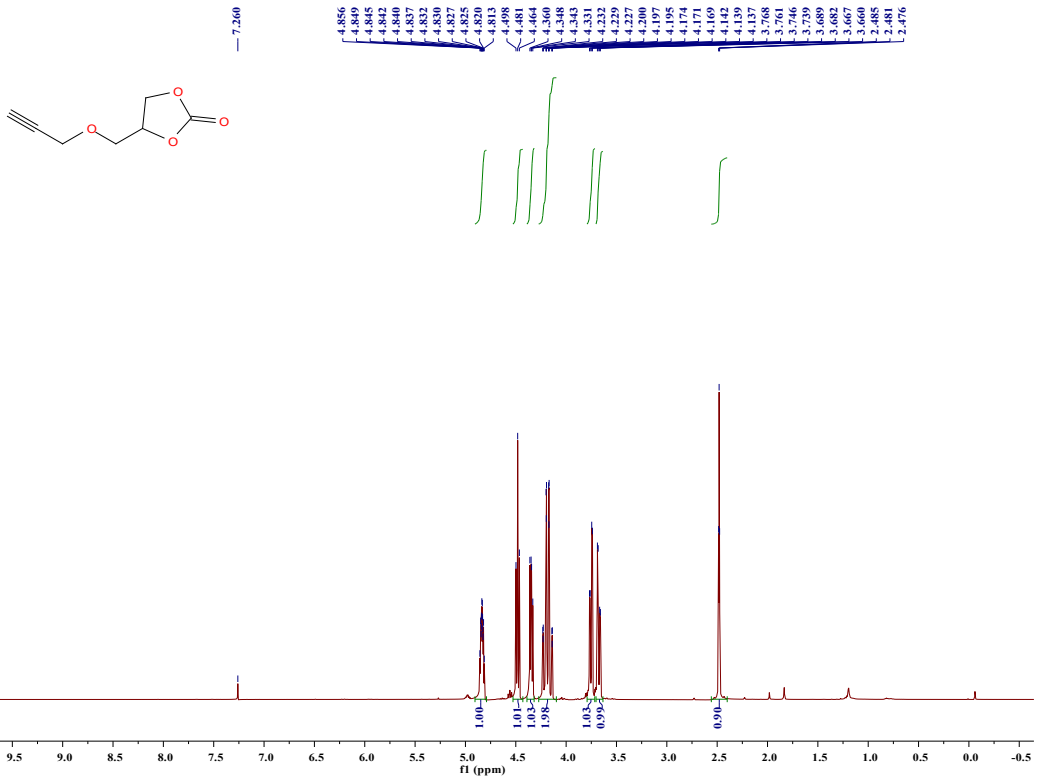
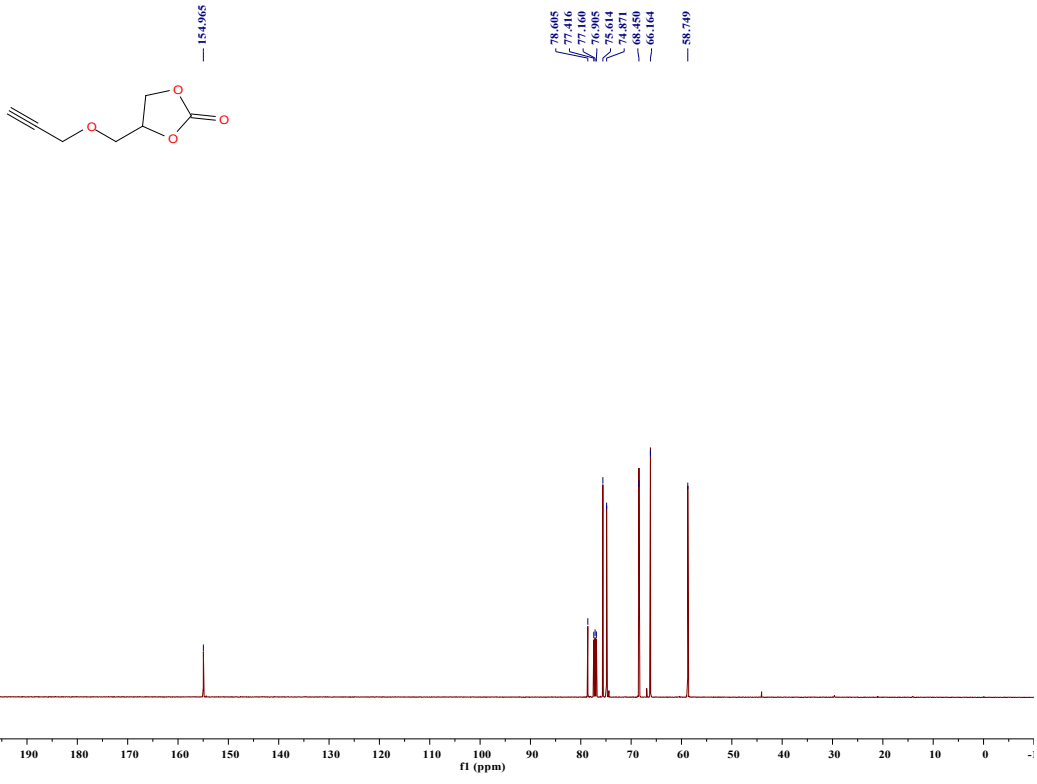
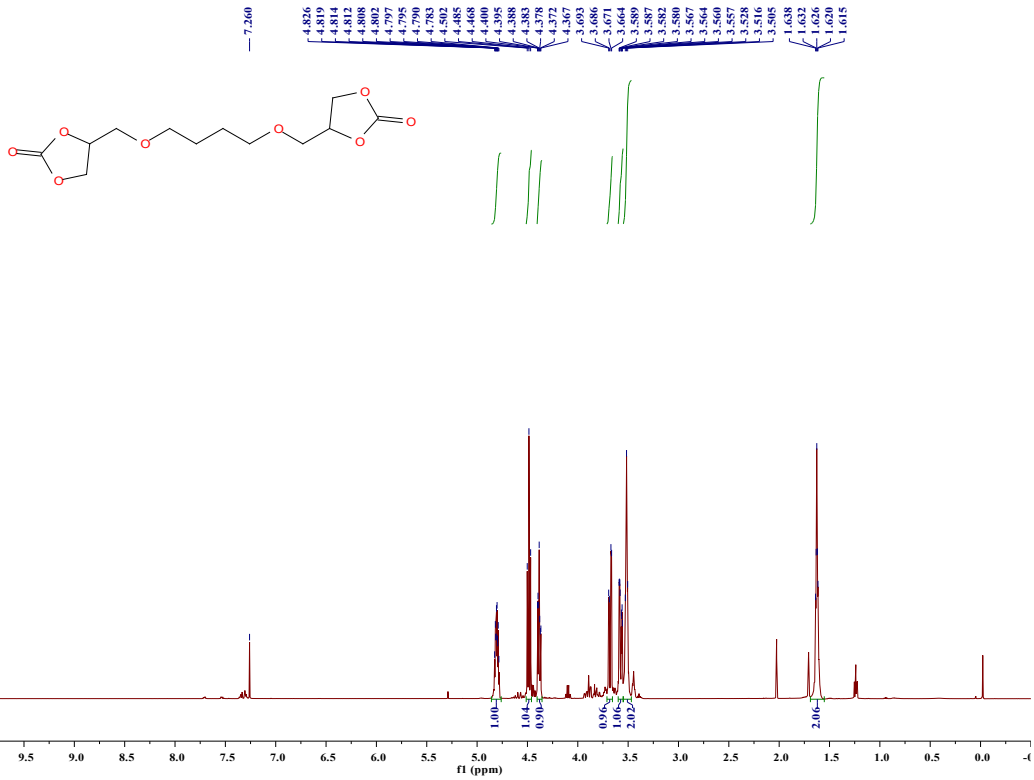
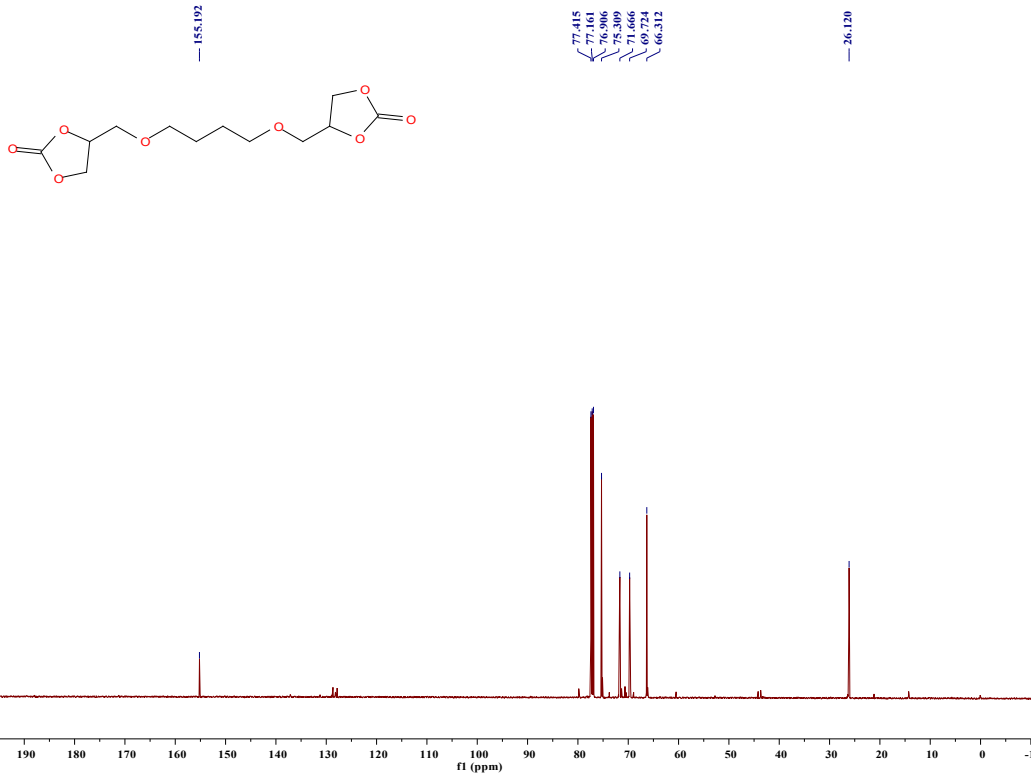
3.645
3.630
3.623
3.551
3.544
3.529
3.521
O
O
O
O
1.00
2.05
1.05
1.06
1.06
2.11
1.07
1.06
fl (ppm)


155.047
133.693
117.565
77.415
77.160
76.906
75.187
72.334
68.798
66.160
O
O
O
O
fl (ppm)


7.260
4.856
4.849
4.845
4.842
4.840
4.837
4.832
4.830
4.827
4.825
4.820
4.813
4.498
4.481
4.464
4.360
4.348
4.343
4.331
4.232
4.229
4.227
4.200
4.197
4.195
4.174
4.171
4.169
4.142
4.139
4.137
3.768
3.761
3.746
3.739
3.689
3.682
3.667
3.660
2.485
2.481
2.476
1.00
1.01
1.03
1.98
1.03
0.99
0.90
f1 (ppm)


154.965
78.605
77.416
77.166
76.905
75.614
74.871
68.450
66.164
58.749
f1 (ppm)


7.260
4.826
4.819
4.814
4.812
4.808
4.802
4.797
4.795
4.790
4.783
4.502
4.485
4.468
4.400
4.395
4.388
4.383
4.378
4.372
4.367
3.693
3.686
3.671
3.664
3.589
3.587
3.582
3.580
3.567
3.564
3.560
3.557
3.528
3.516
3.505
1.638
1.632
1.626
1.620
1.615
1.00
1.04
0.90
0.96
1.06
2.02
2.06
f1 (ppm)


155.192
77.415
77.161
76.906
75.309
71.666
69.724
66.312
26.120
f1 (ppm)

4. Supplementary References

1. R. Wang, J. Wan, H. Guo, B. Tian, S. Li, J. Li, S. Liu, T.D. James, Z. Chen, *Carbon* **2023**, *211*, 118118.

2. X. Meng, Z. Ju, S. Zhang, X. Liang, N. von Solms, X. Zhang, X. Zhang, *Green Chem.* **2019**, *21*, 3456-3463.

3. A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098-3100.

4. C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785-789.

5. A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652.

6. G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley, J. Mantzaris, *J. Chem. Phys*. **1988**, *89*, 2193-2218.

7. G. Petersson, M. A. Al-Laham, *J. Chem. Phys.* **1991**, *94*, 6081-6090.

8. T. Lu, Q. Chen, *Comput. Theor. Chem*. **2021**, *1200*, 113249.