Supplementary Information

For

Halide-free deep eutectic solvents constructed from natural compounds for converting carbon dioxide to cyclic carbonate

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Experimental section

Materials and Chemicals

Betaine (Bet), glycerol (Gly), L-carnitine (Lca), citric acid (CA), glycolic acid (Ga), styrene oxide (SO), propylene oxide (PO), epichlorohydrin, epibromohydrin, 1,2-epoxybutane, (2,3-epoxypropyl)-benzene, isobutylene oxide, 2-(chloromethyl)-2-methyloxirane, tert-butyl glycidyl ether, butyl glycidyl ether, glycidyl phenyl ether, allyl glycidyl ether, furfuryl glycidyl ether, glycidyl methacrylate and cyclohexene oxide were purchased from Aladdin Reagent and used without further purification. CO_2 (99.999%) is supplied by

Sichuan Chengdu Qiaoyuan Gas Company.

Instrumentations

^1H NMR spectra were recorded at ambient temperature using a Bruker Avance III 400 spectrometer (^1H NMR 400 MHz, ^{13}C NMR 126 MHz). Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Bruker Alpha spectrometer. Thermogravimetric analyses (TGA) were carried out with a PerkinElmer Pyris 1 TGA under N_2 atmosphere with the 20 °C/min heating rate ranging from 30 °C to 600 °C.

Synthesis of DESs

All DESs in this article were prepared according to the methods described in the literature.[1] Betaine (Bet) and glycerol (Gly) are added in a molar ratio of one to two to a round bottom flask, stirred magnetically at 80 °C for one hour until a uniform transparent liquid was formed, then cooled to room temperature and dried under vacuum at 60 °C for 24 hours to obtain Bet/Gly natural deep eutectic solvent. Other DESs including Bet/Ga, Bet/CA, Lca/Ga, Lca/Gly and Lca/CA were prepared using the same steps as above.

Cycloaddition reaction of CO_2 catalyzed by DESs

The cycloaddition reaction between CO_2 and styrene oxide (SO) was taken as the model reaction. Typically, 37.5 mmol SO and 0.6 mol% DESs catalyst were put into stainless steel high-pressure autoclave equipped with stirring. The reactor was purged three times with CO_2, filled with 1.0 MPa CO_2 and sealed. The reaction solution was heated to 120 °C and stirred at 310 $r \cdot min^{-1}$ for 6 h. After the reaction was completed, the high-pressure autoclave was cooled to room temperature and the remaining CO_2 was slowly discharged from the reactor. 20 μL of the reaction solution was taken out and dissolved in $CDCl_3$. The yield and selectivity of styrene carbonate (SC) was assessed by ^1H NMR spectroscopy of the crude mixture. For other epoxides, the cycloaddition reaction proceeds in a similar manner. The reaction products were separated by column chromatography. Spectra of ^{1}H NMR and ^{13}C NMR of cyclic carbonates were shown in the Figures S12-S49 in the supplementary information.

Calculation details

To study the mechanism of the cycloaddition reaction between CO_2 and epoxide catalyzed by Bet/Gly DESs, the density functional theory (DFT) calculations at the M06-2X/Def2-TZVPP level employing propylene oxide (PO) as the substrate was carried out with the Gaussian 09 program package. For transition state geometries, intrinsic reaction coordinate (IRC) calculations were carried out to confirm whether it is connected to reactants and products. Cartesian Coordinates of the Optimized Geometries can be found in the supplementary material. The natural bond orbital (NBO) analysis was calculated at the M06-2X/Def2-TZVPP level by using Gaussian 09 program package.

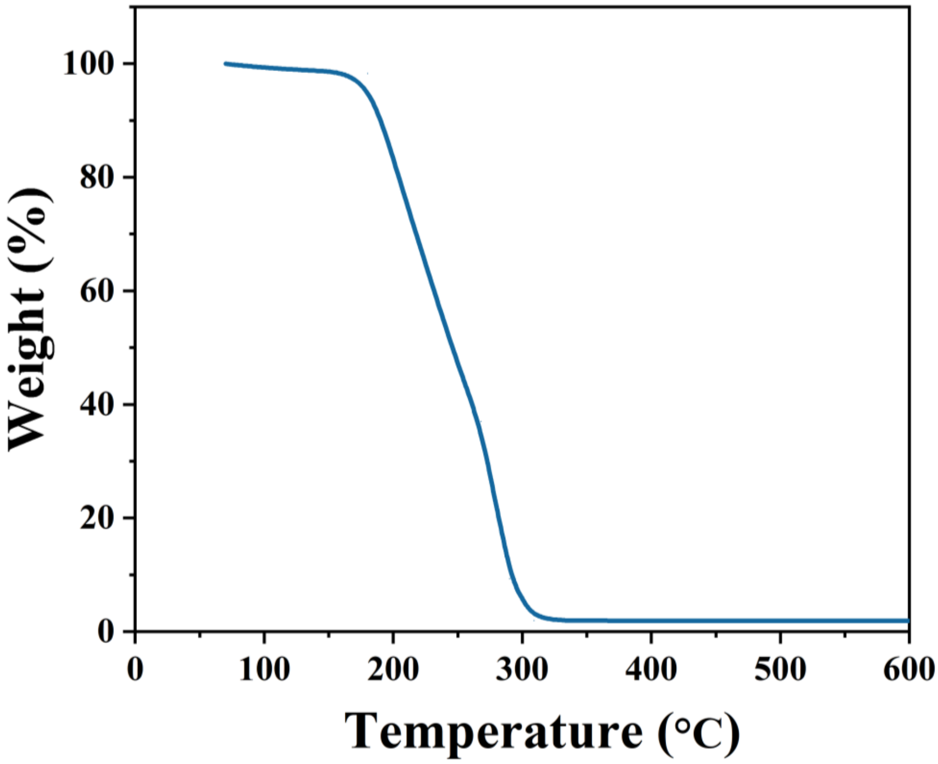


Fig. S1. TG curve of **Bet/Gly** DESs.

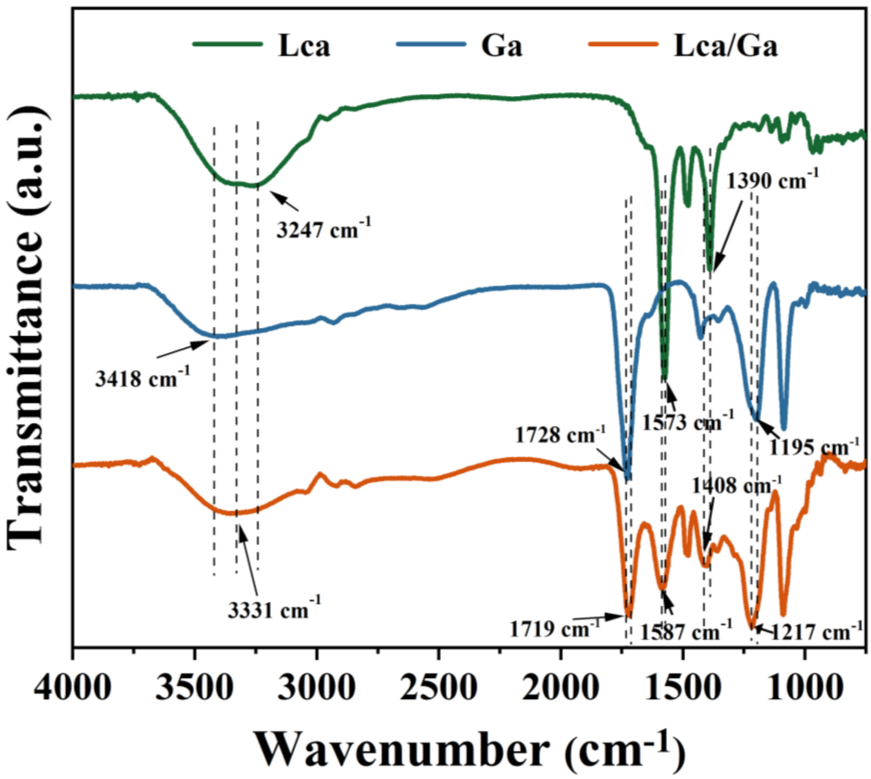


Fig. S2. FT-IR spectra of Lca, Ga and Lca/Ga.

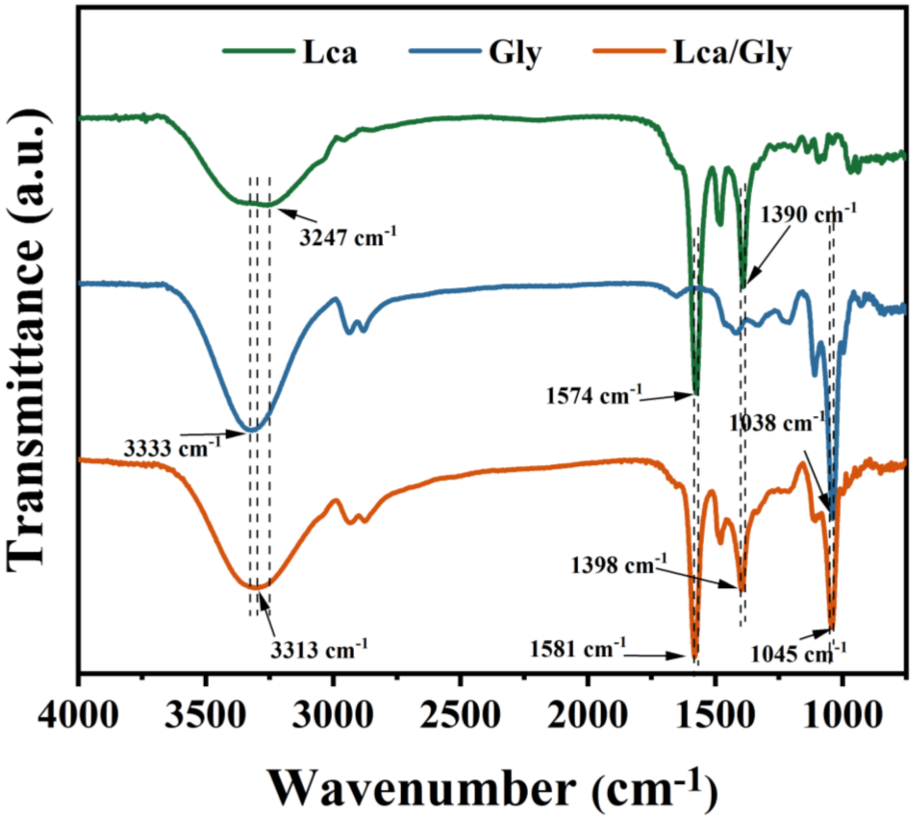


Fig. S3. FT-IR spectra of Lca, Gly and Lca/Gly.

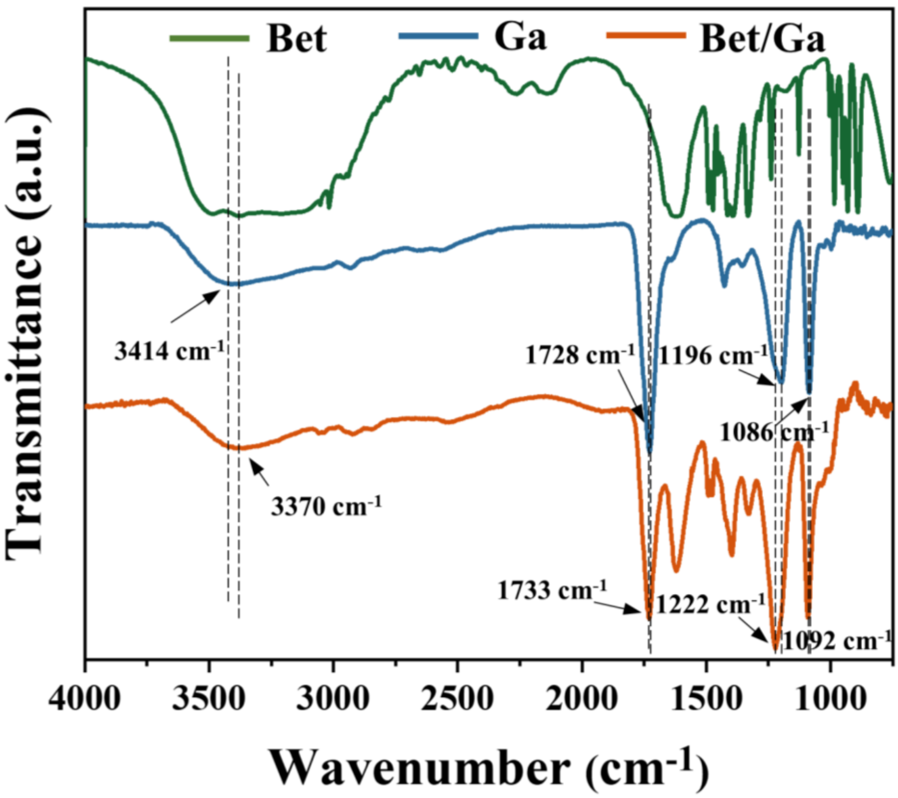


Fig. S4. FT-IR spectra of Bet, Ga and Bet/Ga.

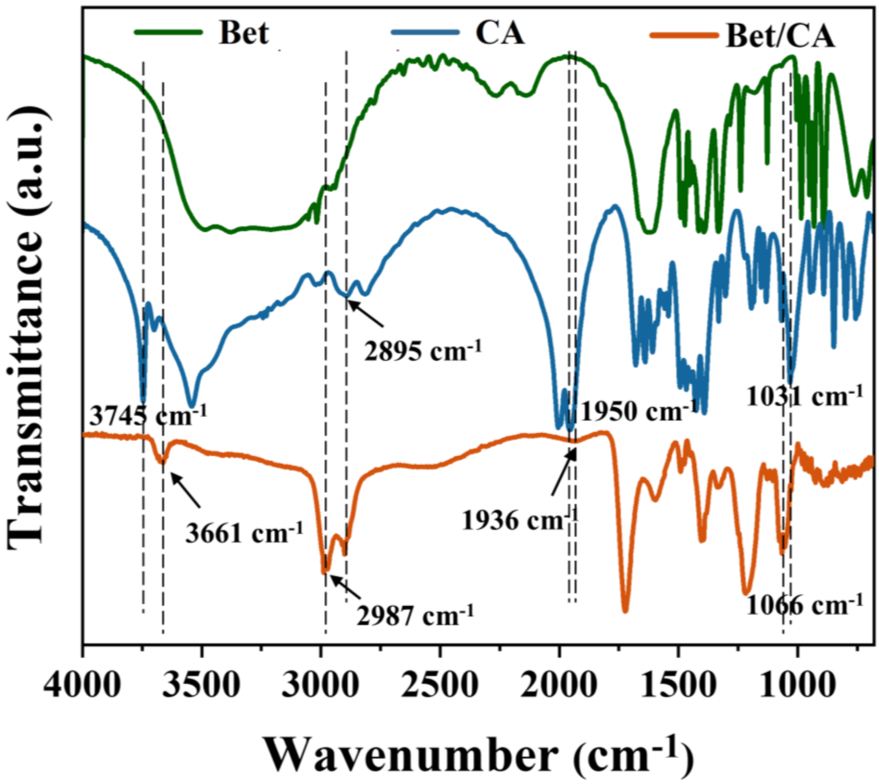


Fig. S5. FT-IR spectra of Bet, CA and Bet/CA.

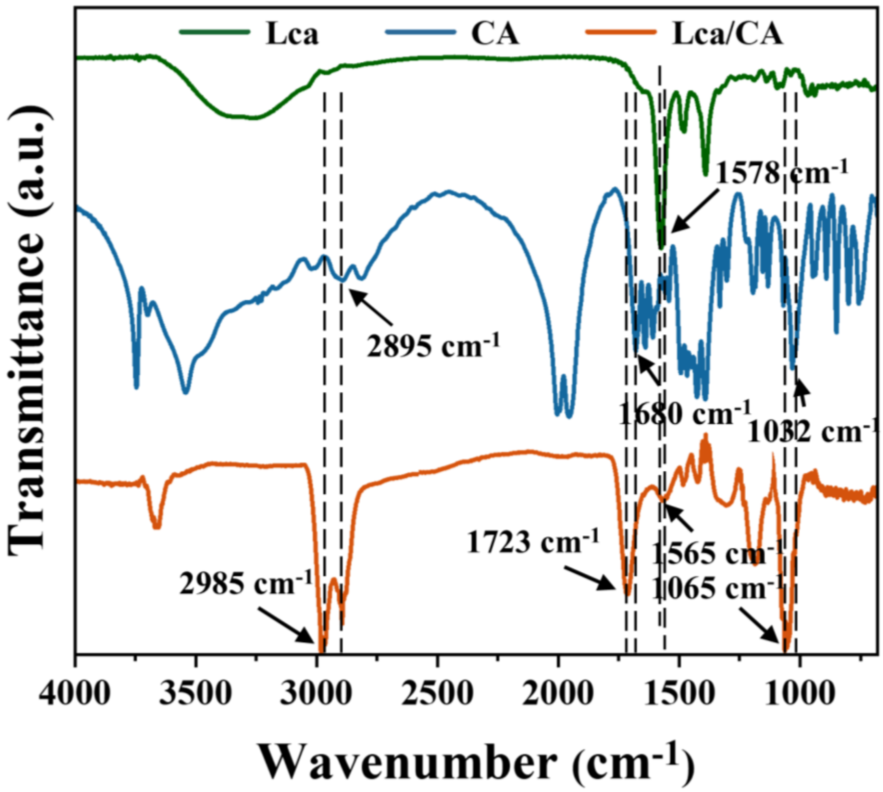


Fig. S6. FT-IR spectra of Lca, CA and Lca/CA.

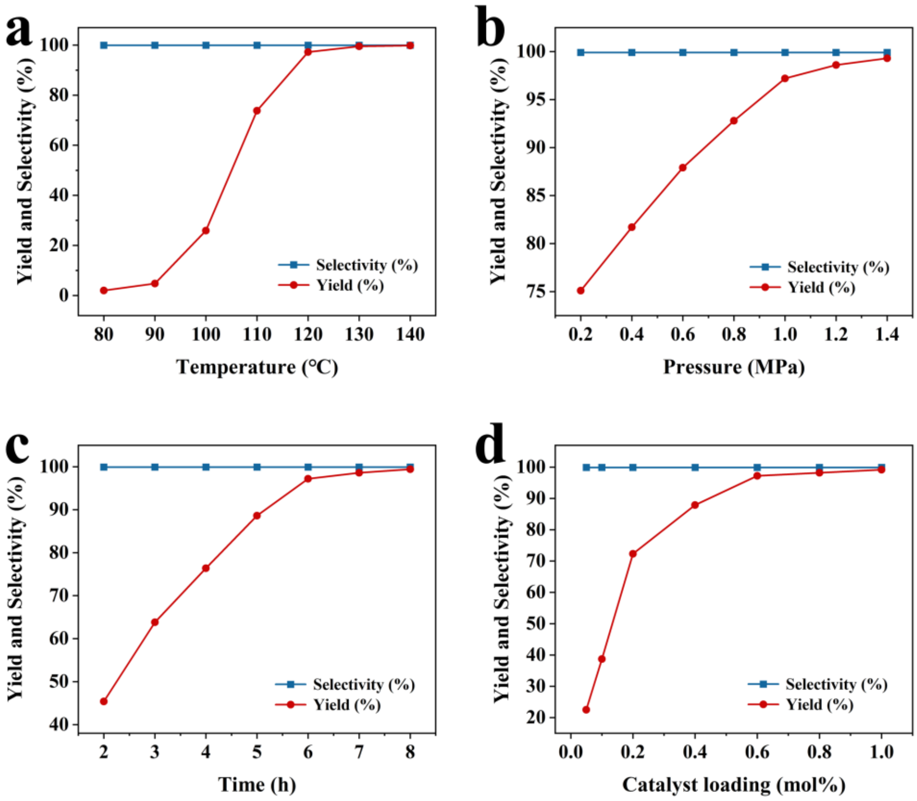


Fig. S7 Effects of (a) reaction temperature, (b) CO_2 pressure, (c) time and (d) catalyst loading on the yield and selectivity of SC. Reaction conditions: 37.5 mmol SO, 120 °C, 1 Mpa CO_2,6 h, 0.6 mol% Bet/Gly.

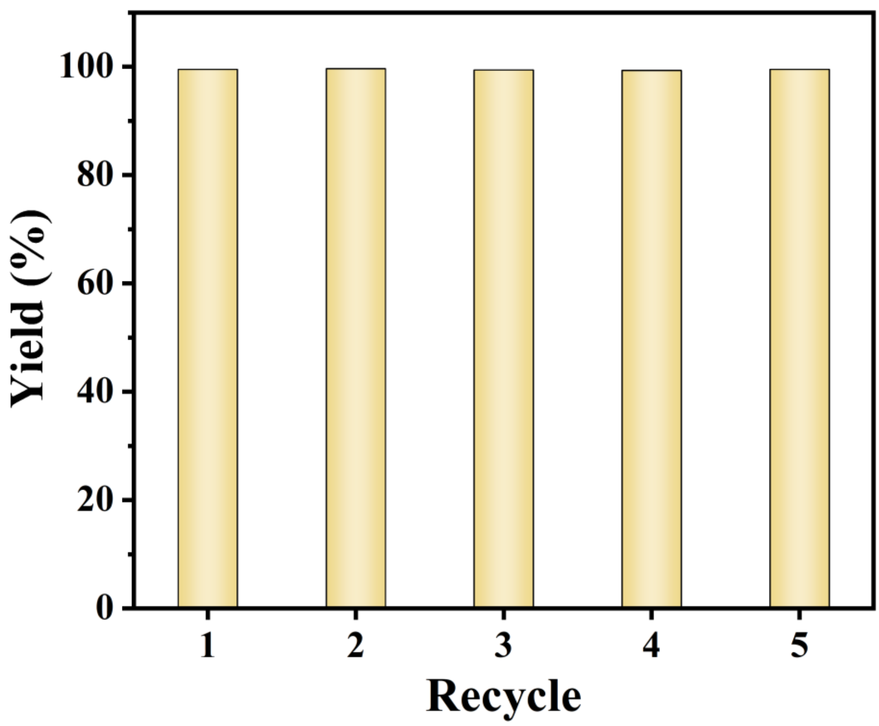


Fig. S8 Cyclic performance of the Bet/Gly catalyst.

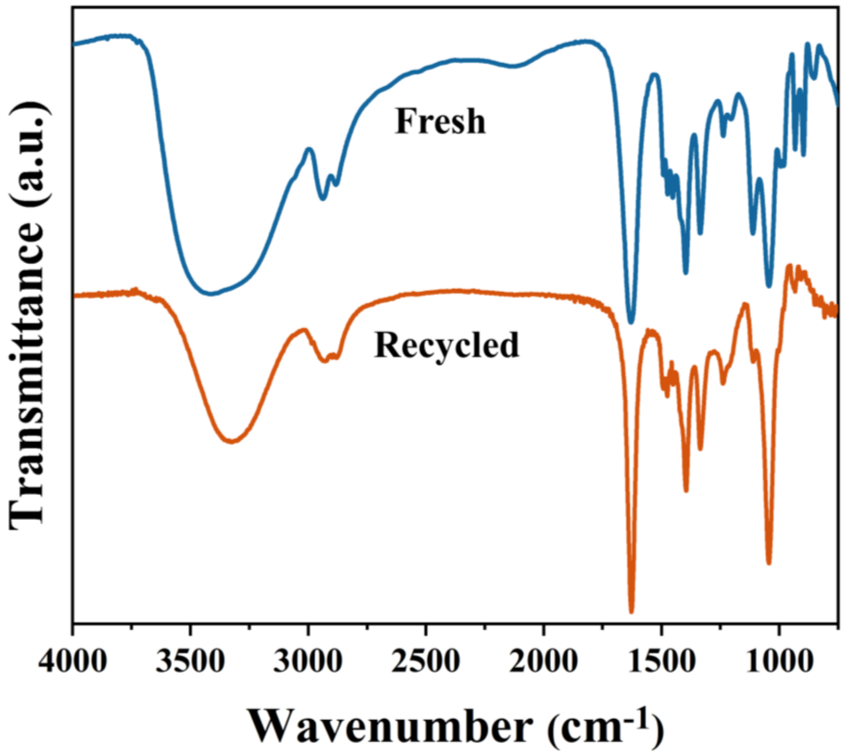
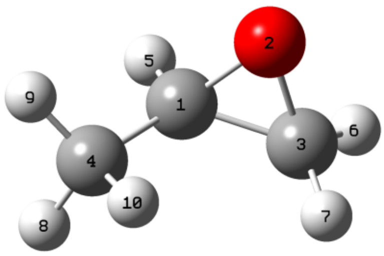


Fig. S9 FT-IR spectra of fresh and recycled Bet/Gly DESs.

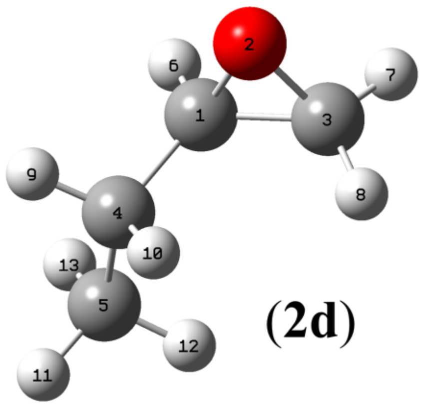


(2c)

Summary of Natural Population Analysis:

Atom	No	Natural Charge	Natural Population Core	Valence	Rydberg	Total
C	1	0.01427	1.99915	3.96274	0.02384	5.98573
O	2	-0.49664	1.99992	6.48820	0.00852	8.49664
C	3	-0.14101	1.99910	4.12009	0.02183	6.14101
C	4	-0.61957	1.99950	4.60778	0.01229	6.61957
H	5	0.20176	0.00000	0.79627	0.00196	0.79824
H	6	0.19625	0.00000	0.80203	0.00172	0.80375
H	7	0.19508	0.00000	0.80312	0.00180	0.80492
H	8	0.20884	0.00000	0.78973	0.00144	0.79116
H	9	0.22355	0.00000	0.77504	0.00141	0.77645
H	10	0.21748	0.00000	0.78103	0.00149	0.78252
* Total *		-0.00000	7.99766	23.92603	0.07631	32.00000

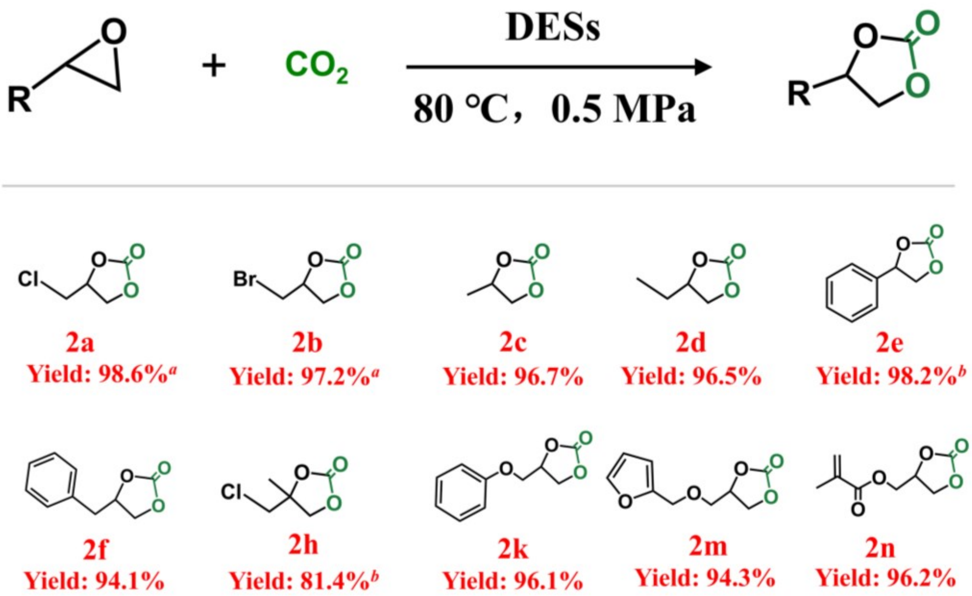
Fig. S10 The NBO charge distribution of **2c** calculated at the M06-2X/Def2-TZVPP level with Gaussian 09.



Summary of Natural Population Analysis:

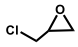
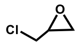
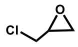
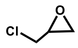
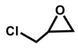
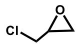
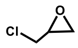
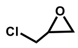
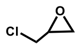
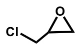
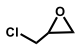
Atom	No	Natural Charge	Natural Population: Core	Valence	Rydberg	Total
C	1	0.02023	1.99908	3.95666	0.02403	5.97977
O	2	-0.49369	1.99992	6.48542	0.00836	8.49369
C	3	-0.14180	1.99909	4.12142	0.02129	6.14180
C	4	-0.41070	1.99948	4.39553	0.01570	6.41070
C	5	-0.60590	1.99951	4.60064	0.00575	6.60590
H	6	0.19766	0.00000	0.80019	0.00215	0.80234
H	7	0.19646	0.00000	0.80182	0.00171	0.80354
H	8	0.19525	0.00000	0.80292	0.00183	0.80475
H	9	0.21409	0.00000	0.78394	0.00197	0.78591
H	10	0.21084	0.00000	0.78721	0.00195	0.78916
H	11	0.21401	0.00000	0.78453	0.00146	0.78599
H	12	0.20133	0.00000	0.79680	0.00188	0.79867
H	13	0.20222	0.00000	0.79605	0.00172	0.79778
* Total *		-0.00000	9.99709	29.91313	0.08978	40.00000

Fig. S11 The NBO charge distribution of **2d** calculated at the M06-2X/Def2-TZVPP level with Gaussian 09.



Scheme S1 The cycloaddition of CO_2 with various epoxides at 80 °C and 0.5 MPa. Isolated yield of purified cyclic carbonate by column chromatography. Reaction conditions: 37.5 mmol epoxide, 80 °C, 0.5 MPa CO_2, 6 h, 4 mol% Bet/Gly. [a]4 h. [b]12 h, 6 mol% Bet/Gly.

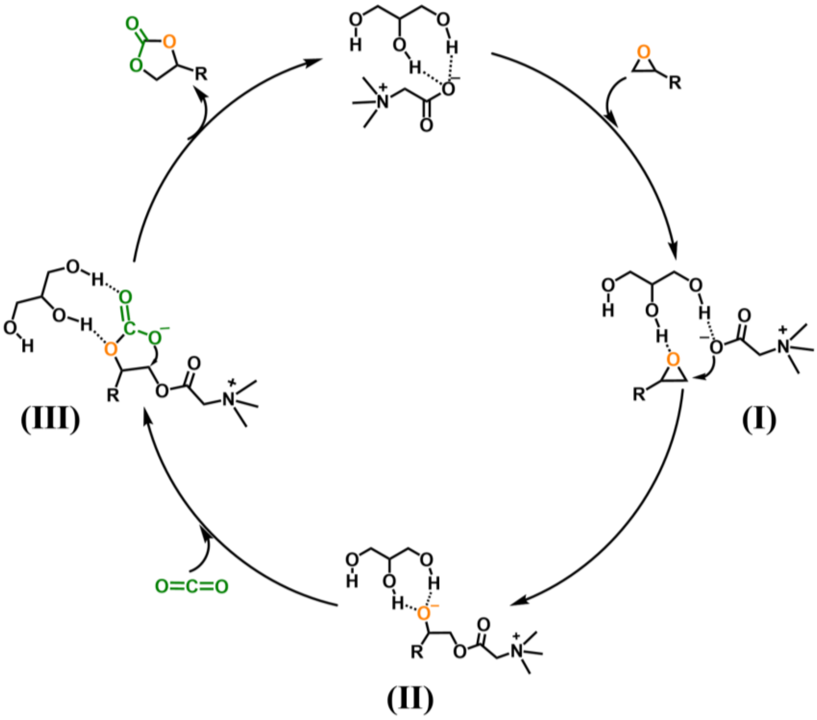
Table S1. The comparison of various halide-free catalytic systems for the cycloaddition of CO_2 and epoxides.

Entry	Catalyst	Epoxide	Temp. [°C]	Catalyst loading [mol%]	Pressure [MPa]	Time [h]	Carbonate yield [%]	**TOF**[a]	Ref.
1	Sq–PhOH-p/t-BuP_2		120	2.5	0.1	8	80.1	4.0	2
2	[P_{4444}] [IsoNic]		120	2	2	12	96.9	4.0	3
3	N,N′-Phenylenebis(5-tert-butylsalicylideneimine)		120	1	1	3.5	76	21.7	4
4	[TEEDA]		120	0.1	1	10	97	97.0	5
5	[N_{1888}][HYD]		120	10	2	6	88	1.5	6
6	Carbodicarbene		100	5	2	12	92	1.5	7
7	[*n* $Bu_4N]_2[MoO_4$]		120	2.5	3	9	99	4.4	8
8	PPy · Sac		60	10	0.1	24	90	0.4	9
9	$(DBUH)_3NbO_5$		130	3	3	5	90	6.1	10
10	1-a-60/b-SBA-15		120	0.2	1.5	18	89	24.7	11
11	Bet/Gly		120	0.3	1	0.5	99.1	**645**	**This work**

[a]Turnover frequency (TOF) = moles of product/ (moles of catalyst × time).

Table S2. The apparent first-order rate constants k_{obs} for the cycloaddition at 1 MPa and different temperature.

T (°C)	90	100	110	120	130
$10^5 \cdot k_{obs}$ (s^{-1})	0.32	2.04	8.08	20.82	52.65



Scheme S2 The possible catalysis mechanism for the cycloaddition of CO_2 with epoxides catalyzed by Bet/Gly.

Cartesian Coordinates of the Optimized Geometries

R

N	0.64994	-2.34997	0.11434
C	0.3616	-0.87579	0.06591
C	0.4928	-2.86088	-1.27696
C	2.03822	-2.61699	0.58969
C	-0.34685	-3.01599	1.00503
C	0.30558	-0.14117	1.42157
O	0.84132	-0.63227	2.40955
O	-0.31572	0.95754	1.32361
H	-0.61762	-0.79319	-0.41307
H	1.13852	-0.4174	-0.56302
H	0.67627	-3.94247	-1.27873
H	-0.5253	-2.62596	-1.61624
H	1.22947	-2.34886	-1.90834
H	2.12633	-2.20161	1.59843
H	2.72881	-2.11666	-0.10022

H	2.19988	-3.70245	0.5829
H	-1.3475	-2.67931	0.70393
H	-0.23387	-4.10212	0.901
H	-0.14725	-2.68983	2.03068
C	-3.01375	1.34128	-0.25699
C	-3.57747	-0.96623	-1.15631
O	-1.72433	1.34299	-0.82133
O	-2.65871	-0.69934	1.01932
O	-2.34351	-1.1161	-1.81921
H	-1.94056	-0.22919	-1.84802
H	-2.16479	-0.02851	1.51741
H	-1.09532	1.18377	-0.05333
H	-3.0314	1.9607	0.65935
H	-3.71397	1.79974	-0.97402
H	-3.9103	-1.96787	-0.84314
H	-4.34904	-0.55901	-1.83713
O	3.18892	-0.20491	-1.30499
C	3.91723	0.6789	-0.462
C	3.42275	1.11213	-1.77537
C	3.25083	1.11117	0.81317
H	4.98033	0.41709	-0.39131
H	3.19022	0.28834	1.53989
H	2.23129	1.47349	0.62074
H	3.82081	1.93043	1.27394
H	2.53903	1.75883	-1.80533
H	4.10868	1.1855	-2.62488
C	-3.49847	-0.07062	0.07643
H	-4.52745	0.02058	0.47855
C	-0.18563	3.41022	0.13309
O	0.74073	3.09125	-0.48645
O	-1.0932	3.7858	0.74027

Int1

N	-2.08399	1.82582	-0.07369
C	-2.49404	0.49488	0.48151
C	-2.14049	2.80584	1.04853
C	-0.67058	1.78928	-0.59207
C	-3.00741	2.26099	-1.1614
C	-2.36237	-0.66122	-0.498
O	-2.50918	-1.80823	0.15898
O	-2.25568	-0.54122	-1.68776
H	-3.53411	0.58071	0.83074
H	-1.82911	0.27294	1.32174

H	-1.85799	3.79204	0.66288
H	-3.16186	2.83424	1.44665
H	-1.4343	2.48016	1.8201
H	-0.41812	2.81212	-0.89827
H	-0.60016	1.09774	-1.43935
H	-0.00746	1.44408	0.21105
H	-4.02669	2.3069	-0.75798
H	-2.69177	3.25518	-1.49886
H	-2.94286	1.53424	-1.97583
C	3.96444	1.04189	-0.82999
C	2.17929	-0.3218	-1.99588
O	4.20703	1.88027	0.26557
O	2.06197	0.33167	0.34917
O	0.81116	-0.50122	-2.2298
H	0.39571	-0.79148	-1.37591
H	1.27966	-0.31928	0.29737
H	3.66729	1.50534	0.97598
H	4.31757	1.55122	-1.73992
H	4.51742	0.08484	-0.73931
H	2.64828	-0.01159	-2.9449
H	2.66914	-1.26653	-1.68162
O	-0.04817	-1.04917	0.22632
C	-0.22525	-2.40226	0.43832
C	-1.55535	-2.81519	-0.2138
C	0.92201	-3.24325	-0.1158
H	-0.32228	-2.62583	1.5253
H	0.75955	-4.32192	0.03431
H	1.85511	-2.95829	0.391
H	1.03781	-3.04613	-1.19363
H	-1.94475	-3.7726	0.15371
H	-1.46973	-2.83797	-1.31112
C	2.47754	0.73016	-0.93557
H	1.95461	1.66648	-1.23101
C	0.68917	-0.1268	2.65382
O	0.00177	0.81039	2.58251
O	1.36427	-1.0428	2.82933

TS1

N	-3.84884	-0.09014	0.27215
C	-3.46865	-1.15799	-0.72578
C	-5.17251	-0.44778	0.84762
C	-2.82335	-0.0303	1.36525
C	-3.94119	1.25709	-0.37913

C	-1.97998	-1.02386	-1.12366
O	-1.2604	-1.96499	-0.68949
O	-1.66023	-0.02163	-1.7539
H	-4.12012	-1.03243	-1.60032
H	-3.64374	-2.12659	-0.24364
H	-5.49033	0.34853	1.53077
H	-5.89673	-0.55276	0.03122
H	-5.07881	-1.3956	1.39014
H	-3.24052	0.55967	2.18996
H	-1.92786	0.46994	0.96988
H	-2.59671	-1.05325	1.68839
H	-4.68322	1.19747	-1.18384
H	-4.26316	1.97231	0.38739
H	-2.95365	1.53012	-0.76643
C	2.66313	3.36634	0.22034
C	0.1627	2.98446	0.12642
O	3.90832	2.73554	0.28719
O	1.70512	1.46424	-0.84693
O	-0.83911	2.01101	-0.06086
H	-0.53243	1.43001	-0.7821
H	1.98272	0.5528	-0.47784
H	3.8613	1.9965	-0.33582
H	2.5807	4.04799	1.08251
H	2.56182	3.97449	-0.70175
H	-0.07689	3.54893	1.04045
H	0.16787	3.69545	-0.72122
O	2.1134	-0.78777	0.19541
C	0.84845	-1.00783	0.7268
C	0.57126	-1.50824	-0.61781
C	0.7972	-1.99057	1.87581
H	0.30423	-0.07228	0.9698
H	-0.24187	-2.25199	2.12895
H	1.28202	-1.55352	2.76062
H	1.33824	-2.90657	1.60145
H	0.92894	-2.51198	-0.84349
H	0.50005	-0.77494	-1.4179
C	1.53924	2.33843	0.23466
H	1.60765	1.77451	1.18636
C	3.95263	-2.44205	-0.17903
O	4.73713	-1.60419	-0.30803
O	3.25561	-3.36496	-0.0756

Int2

N	-2.9069	-0.57083	-0.1253
C	-1.81658	-1.59304	-0.22368
C	-3.78661	-0.9972	1.00026
C	-2.37465	0.80702	0.20113
C	-3.68233	-0.51554	-1.39464
C	-0.66822	-1.22756	-1.15264
O	0.25569	-2.15565	-1.02844
O	-0.62628	-0.26285	-1.86929
H	-2.26556	-2.53728	-0.56545
H	-1.38835	-1.77512	0.77766
H	-4.63933	-0.31128	1.05694
H	-4.13125	-2.02244	0.81958
H	-3.19581	-0.95333	1.92335
H	-3.22157	1.43102	0.50616
H	-1.90346	1.21715	-0.69273
H	-1.63257	0.70015	1.00469
H	-4.14806	-1.49305	-1.57138
H	-4.45284	0.25823	-1.2971
H	-2.99035	-0.26192	-2.20492
C	-0.19179	3.44278	-0.35507
C	2.03376	2.38612	-1.00406
O	-1.2129	3.37628	0.61129
O	1.1488	2.25839	1.2105
O	2.81095	1.22613	-0.86321
H	2.67678	0.91337	0.04699
H	0.81826	1.39776	1.58602
H	-0.73708	3.17455	1.43341
H	-0.65512	3.38516	-1.35313
H	0.3517	4.40535	-0.29097
H	1.76071	2.49177	-2.06694
H	2.60002	3.28894	-0.70371
O	1.79673	-0.80314	0.87431
C	2.3322	-1.86645	0.10681
C	1.64323	-1.84673	-1.25357
C	3.83198	-1.67559	-0.03098
H	2.09543	-2.81442	0.61202
H	4.27963	-2.51955	-0.57476
H	4.2843	-1.62758	0.96804
H	4.05805	-0.74372	-0.56823
H	2.04239	-2.61858	-1.92422
H	1.73802	-0.84807	-1.70395
C	0.78577	2.29121	-0.14603
H	0.28345	1.34533	-0.41151
C	0.64068	-1.04798	1.63404

O	0.03434	0.01245	1.91746
O	0.32218	-2.20523	1.87011

TS2

N	-2.77298	-0.17525	-0.14384
C	-1.89646	-1.34872	-0.45205
C	-3.58684	-0.54336	1.05089
C	-1.96024	1.04933	0.20124
C	-3.66338	0.12798	-1.29714
C	-0.82441	-1.10552	-1.50015
O	-0.13771	-2.22948	-1.65468
O	-0.68645	-0.09104	-2.12679
H	-2.53681	-2.18939	-0.75559
H	-1.35153	-1.60033	0.46524
H	-4.29452	0.26861	1.25346
H	-4.1275	-1.47422	0.84101
H	-2.89899	-0.67843	1.89376
H	-2.59862	1.73166	0.77274
H	-1.6362	1.5243	-0.72459
H	-1.08337	0.73865	0.78411
H	-4.31664	-0.73434	-1.47911
H	-4.26383	1.01092	-1.04745
H	-3.03286	0.33051	-2.16934
C	0.55326	3.65032	0.10363
C	2.4293	2.2507	-0.92485
O	-0.58436	3.53364	0.92492
O	1.13351	1.55869	0.98434
O	2.73364	0.95228	-1.36852
H	2.30339	0.33584	-0.75635
H	1.17075	0.57188	0.78748
H	-0.31688	2.87081	1.58122
H	0.26852	4.19296	-0.80973
H	1.34978	4.22965	0.60991
H	2.41863	2.9196	-1.80153
H	3.19116	2.62514	-0.21504
O	0.94421	-0.90935	0.38635
C	1.65669	-1.97972	-0.1266
C	1.2982	-2.10964	-1.61108
C	3.1716	-1.9061	0.07796
H	1.31643	-2.93044	0.34667
H	3.66169	-2.82647	-0.27525
H	3.37505	-1.79604	1.151

H	3.62027	-1.05384	-0.45249
H	1.69829	-3.01743	-2.07971
H	1.60662	-1.21685	-2.17769
C	1.07868	2.26234	-0.23312
H	0.37931	1.76502	-0.93281
C	0.43892	-1.28861	2.47984
O	-0.65067	-0.84687	2.47003
O	1.41491	-1.8085	2.83255

Int3

N	3.00006	-0.91118	-0.25955
C	2.72257	0.5619	-0.18255
C	3.56557	-1.29412	1.07153
C	1.75571	-1.74444	-0.46519
C	3.96238	-1.18915	-1.35716
C	1.66647	1.06111	-1.15539
O	1.24579	2.24318	-0.74262
O	1.29243	0.47689	-2.13481
H	3.6674	1.09599	-0.36241
H	2.39116	0.82122	0.83441
H	3.89194	-2.33921	1.02263
H	4.41352	-0.63745	1.30146
H	2.75835	-1.16606	1.8085
H	1.99816	-2.77218	-0.17369
H	1.4555	-1.68802	-1.512
H	0.97517	-1.35945	0.19737
H	4.91383	-0.68863	-1.13932
H	4.1123	-2.27303	-1.42475
H	3.52894	-0.80857	-2.28976
C	-2.03539	-2.73813	0.06702
C	-3.82194	-1.34161	-1.07158
O	-0.76328	-2.73332	0.65324
O	-2.78567	-0.63211	0.93116
O	-4.36004	-0.04847	-1.12502
H	-4.28814	0.27367	-0.21397
H	-2.04217	-0.01774	1.06439
H	-0.6914	-1.98742	1.27955
H	-1.97938	-3.34398	-0.85332
H	-2.78641	-3.2081	0.7313
H	-3.62945	-1.67989	-2.10063
H	-4.53577	-2.05439	-0.61185
O	-0.67948	1.0473	0.74802
C	-0.87717	2.38636	0.33577

C	-0.11979	2.60486	-0.97286
C	-2.36552	2.62259	0.14558
H	-0.45041	3.04985	1.10187
H	-2.55637	3.64096	-0.22263
H	-2.88614	2.5006	1.10507
H	-2.78545	1.90087	-0.57192
H	-0.1362	3.66049	-1.27179
H	-0.52959	1.98206	-1.78124
C	-2.529	-1.34055	-0.2625
H	-1.74556	-0.81289	-0.84122
C	0.31583	0.74112	1.73478
O	0.38945	-0.48546	1.922
O	0.97298	1.67073	2.17504

TS3

N	-3.71682	0.17882	0.18578
C	-3.21221	-1.16949	-0.25722
C	-5.10643	-0.00985	0.68722
C	-2.86043	0.71755	1.29426
C	-3.73974	1.17369	-0.9383
C	-1.71195	-1.19891	-0.61619
O	-1.18884	-2.33065	-0.3976
O	-1.18446	-0.18918	-1.05474
H	-3.80561	-1.47333	-1.13129
H	-3.39833	-1.87596	0.56065
H	-5.50877	0.96383	0.9889
H	-5.71918	-0.4374	-0.11504
H	-5.08678	-0.69092	1.54587
H	-3.386	1.56952	1.74146
H	-1.90888	1.06357	0.87029
H	-2.72052	-0.07555	2.03932
H	-4.30444	0.73829	-1.7713
H	-4.23837	2.07734	-0.56861
H	-2.71069	1.40243	-1.22663
C	2.87542	2.86644	0.33226
C	0.35589	3.24169	-0.06567
O	3.81173	1.93965	0.78845
O	1.44088	1.33003	-0.82562
O	-0.82092	2.50516	-0.32698
H	-0.50173	1.71691	-0.80963
H	1.72253	0.48088	-0.4498

H	3.85328	1.16142	0.20268
H	2.86764	3.70437	1.05024
H	3.1342	3.28039	-0.66301
H	0.17522	3.91239	0.78755
H	0.62907	3.86216	-0.93978
O	2.11702	-0.89455	0.54761
C	0.99154	-1.72519	0.71311
C	0.6434	-2.3531	-0.63236
C	1.22536	-2.77897	1.78071
H	0.18388	-1.04437	1.01492
H	0.30916	-3.36529	1.93996
H	1.51965	-2.3004	2.72361
H	2.03067	-3.45035	1.45273
H	0.61628	-3.43008	-0.76054
H	0.60809	-1.71953	-1.51509
C	1.48398	2.26284	0.22951
H	1.27194	1.75319	1.19057
C	3.03911	-1.41105	-0.40056
O	2.60891	-2.47103	-0.92664
O	4.02591	-0.73559	-0.58186

Int4

N	-4.04125	0.2749	-0.02345
C	-3.53233	-1.13756	0.16847
C	-5.52724	0.2248	-0.09424
C	-3.64648	1.15714	1.12029
C	-3.5167	0.84797	-1.30291
C	-1.98507	-1.34279	0.16788
O	-1.67047	-2.52758	0.09612
O	-1.27639	-0.32086	0.2542
H	-3.96217	-1.7367	-0.63176
H	-3.92963	-1.48809	1.12209
H	-5.91079	1.2372	-0.2043
H	-5.82153	-0.37793	-0.95114
H	-5.90739	-0.22153	0.82235
H	-4.08748	2.13898	0.95455
H	-2.56423	1.21976	1.1483
H	-4.03946	0.71859	2.0365
H	-3.78216	0.16867	-2.11086
H	-3.98444	1.81951	-1.45461
H	-2.4395	0.95268	-1.21532

C	2.93466	2.934	0.00286
C	0.4296	3.00356	-0.41057
O	3.95217	2.28316	0.72512
O	1.50424	1.0117	0.20309
O	-0.79721	2.37979	-0.0914
H	-0.62473	1.42338	-0.01091
H	1.88526	0.56279	0.96391
H	4.11286	1.41213	0.33552
H	3.00611	4.00357	0.22967
H	3.06508	2.80299	-1.08009
H	0.32862	4.07169	-0.20245
H	0.65925	2.88271	-1.47837
O	2.62739	-1.44986	0.74591
C	1.42279	-2.19847	0.46107
C	1.217	-1.91276	-1.02705
C	1.63086	-3.65796	0.79097
H	0.61875	-1.75645	1.04315
H	0.70174	-4.19127	0.59334
H	1.89898	-3.78343	1.83909
H	2.42522	-4.08327	0.1735
H	0.95254	-2.79838	-1.59705
H	0.4945	-1.1131	-1.18365
C	1.5634	2.41647	0.40967
H	1.39144	2.63049	1.47175
C	3.21143	-1.05608	-0.39915
O	2.5116	-1.46322	-1.45806
O	4.22247	-0.42429	-0.44659

P

N	-2.64218	-1.02366	-0.26273
C	-1.42821	-0.52844	0.47527
C	-3.29063	0.11145	-0.99195
C	-2.16699	-2.0223	-1.26236
C	-3.61509	-1.65409	0.67145
C	-1.65523	0.64989	1.46069
O	-2.79058	0.9161	1.83533
O	-0.56385	1.20336	1.77656
H	-0.71008	-0.23589	-0.29844
H	-1.00443	-1.38609	1.0173
H	-3.62661	0.8388	-0.24658
H	-2.53526	0.5385	-1.66429
H	-4.13574	-0.29238	-1.56315

H	-1.66632	-2.84022	-0.73065
H	-1.44114	-1.53067	-1.92116
H	-3.03111	-2.39742	-1.82451
H	-4.47778	-2.00378	0.09094
H	-3.12138	-2.50322	1.15962
H	-3.90132	-0.89808	1.40964
C	-0.05212	2.05361	-1.60512
C	1.51668	3.24661	-0.05298
O	-0.43201	0.8552	-2.2467
O	1.27853	0.83555	0.02898
O	0.42436	3.66337	0.71329
H	0.11428	2.94076	1.28756
H	0.59037	0.9676	0.75029
H	0.33098	0.26815	-2.36221
H	0.03696	2.87687	-2.33694
H	-0.85306	2.33397	-0.90096
H	2.42461	3.08499	0.56034
H	1.74118	4.05963	-0.76206
O	1.33888	-2.05802	0.1847
C	2.38285	-1.94617	1.16123
C	3.41453	-1.06623	0.43415
C	1.84093	-1.36619	2.44733
H	2.77872	-2.96117	1.32357
H	1.32572	-0.4141	2.25583
H	2.66482	-1.19212	3.15432
H	1.13389	-2.06314	2.9176
H	3.35832	-0.02385	0.77217
H	4.43757	-1.45349	0.50317
C	1.2593	1.95271	-0.82848
H	2.08787	1.80386	-1.54613
C	1.73136	-1.53925	-0.98392
O	2.99348	-1.12126	-0.92275
O	1.04493	-1.50699	-1.96415

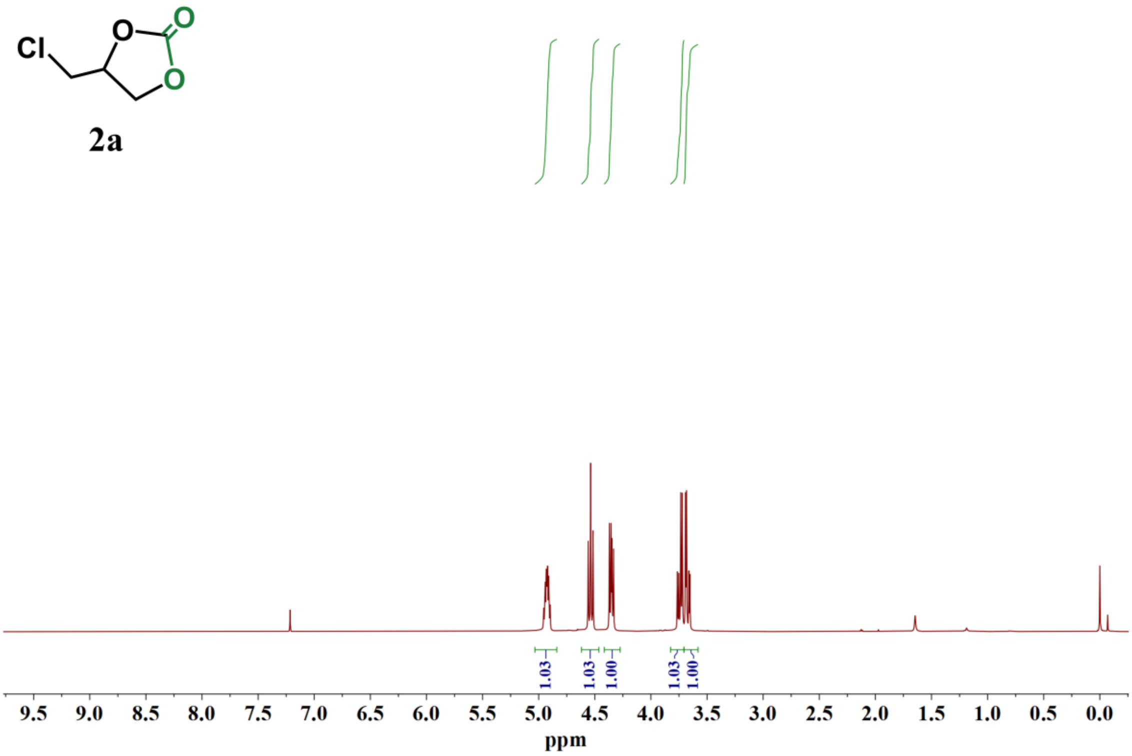


Fig. S12. ^{1}H NMR spectrum of **2a** (400 MHz, $CDCl_3$, 298 K).

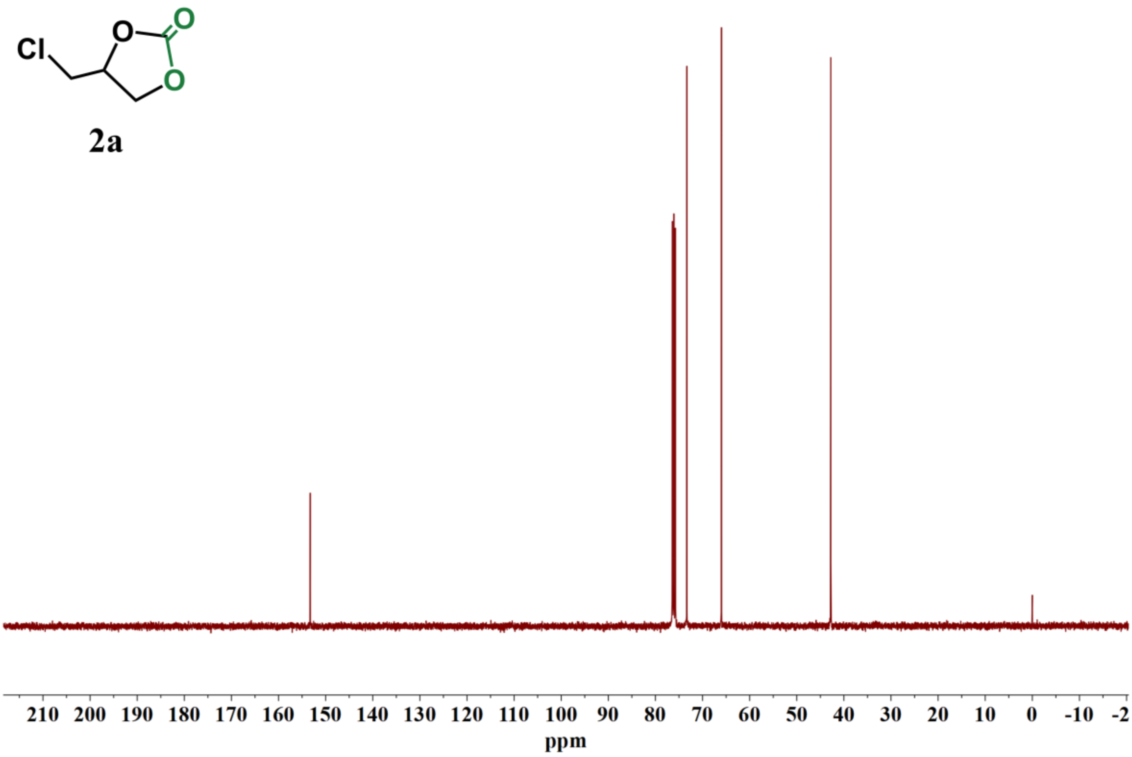


Fig. S13. ^{13}C NMR spectrum of **2a** (126 MHz, $CDCl_3$, 298 K).

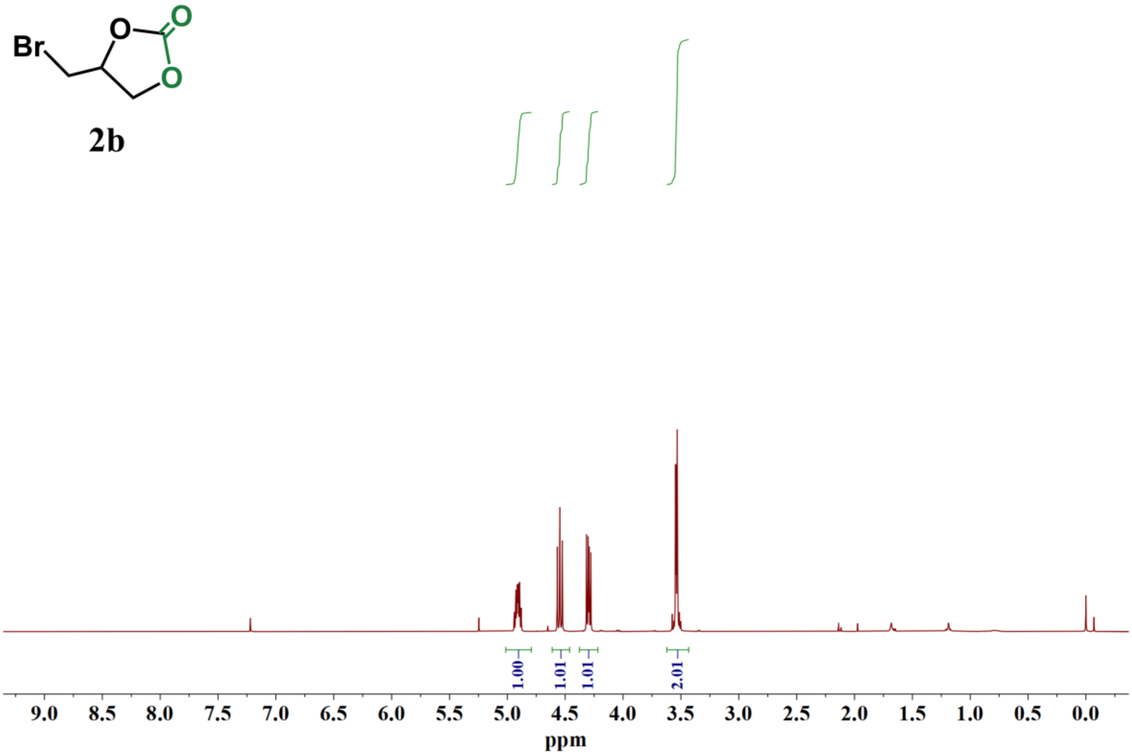


Fig. S14. [1]H NMR spectrum of **2b** (400 MHz, $CDCl_3$, 298 K).

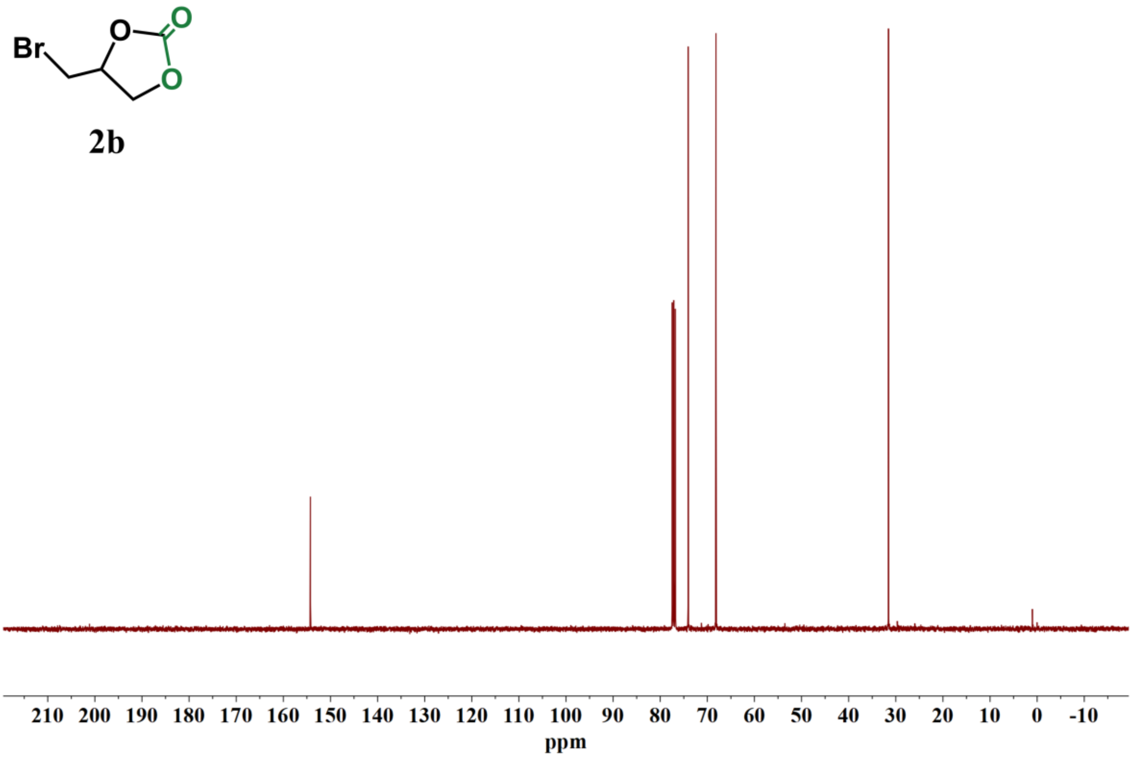
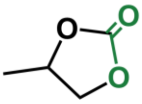


Fig. S15. [13]C NMR spectrum of **2b** (126 MHz, $CDCl_3$, 298 K).



2c

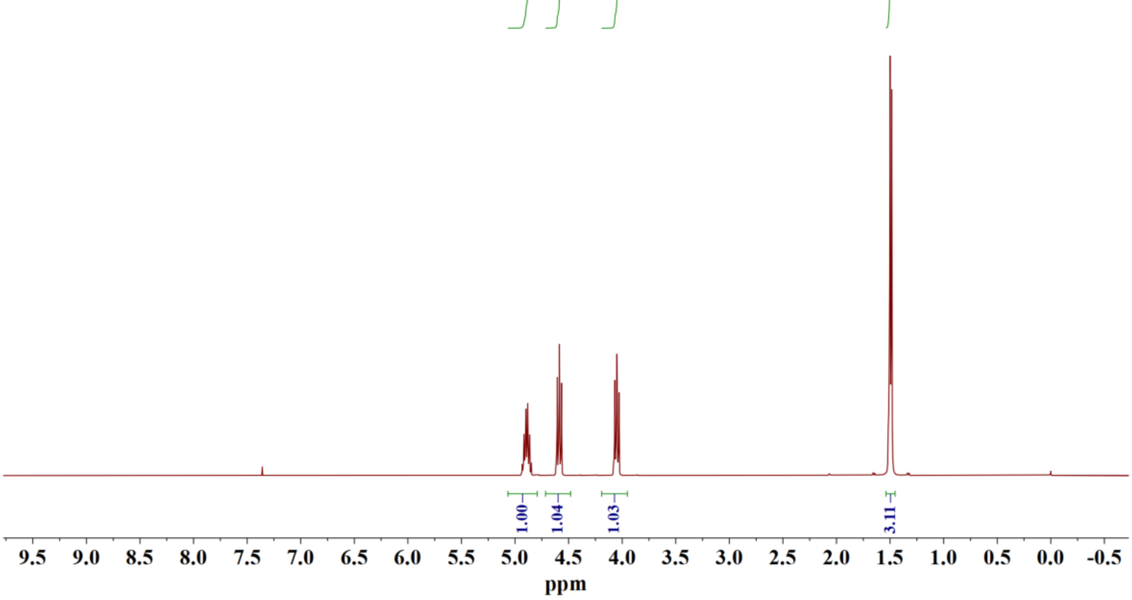
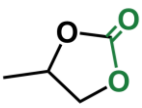


Fig. S16. ^{1}H NMR spectrum of **2c** (400 MHz, $CDCl_3$, 298 K).



2c

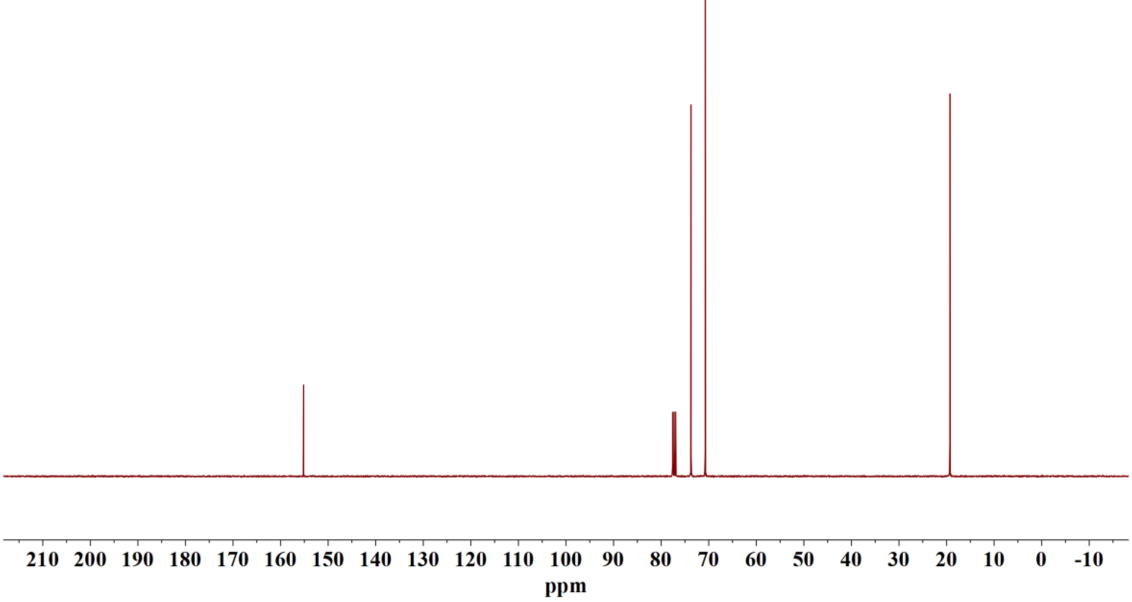


Fig. S17. ^{13}C NMR spectrum of **2c** (126 MHz, $CDCl_3$, 298 K).

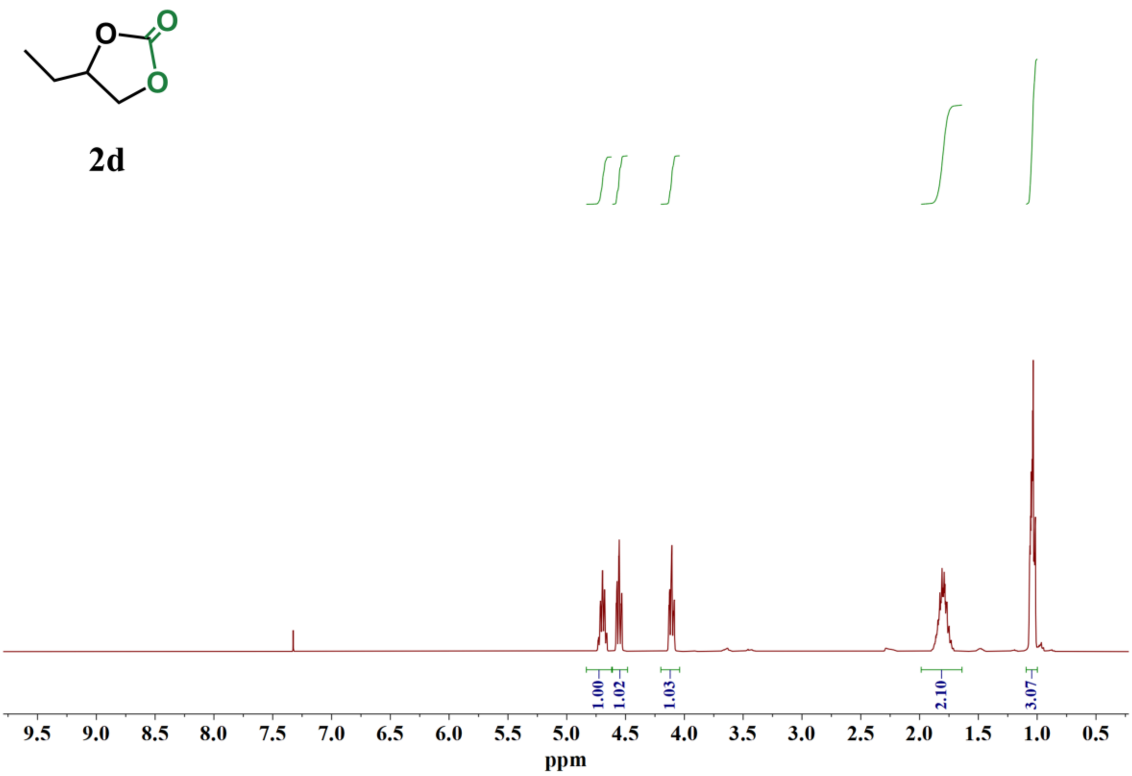


Fig. S18. ^{1}H NMR spectrum of **2d** (400 MHz, $CDCl_3$, 298 K).

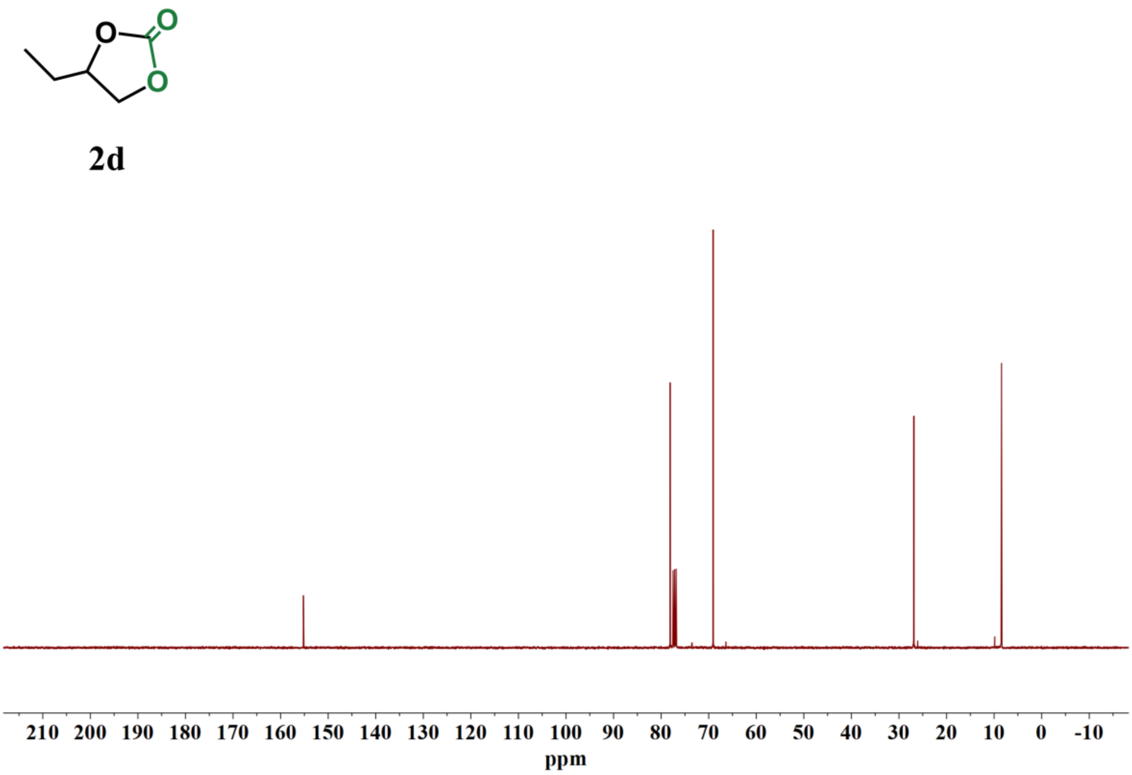


Fig. S19. ^{13}C NMR spectrum of **2d** (126 MHz, $CDCl_3$, 298 K).

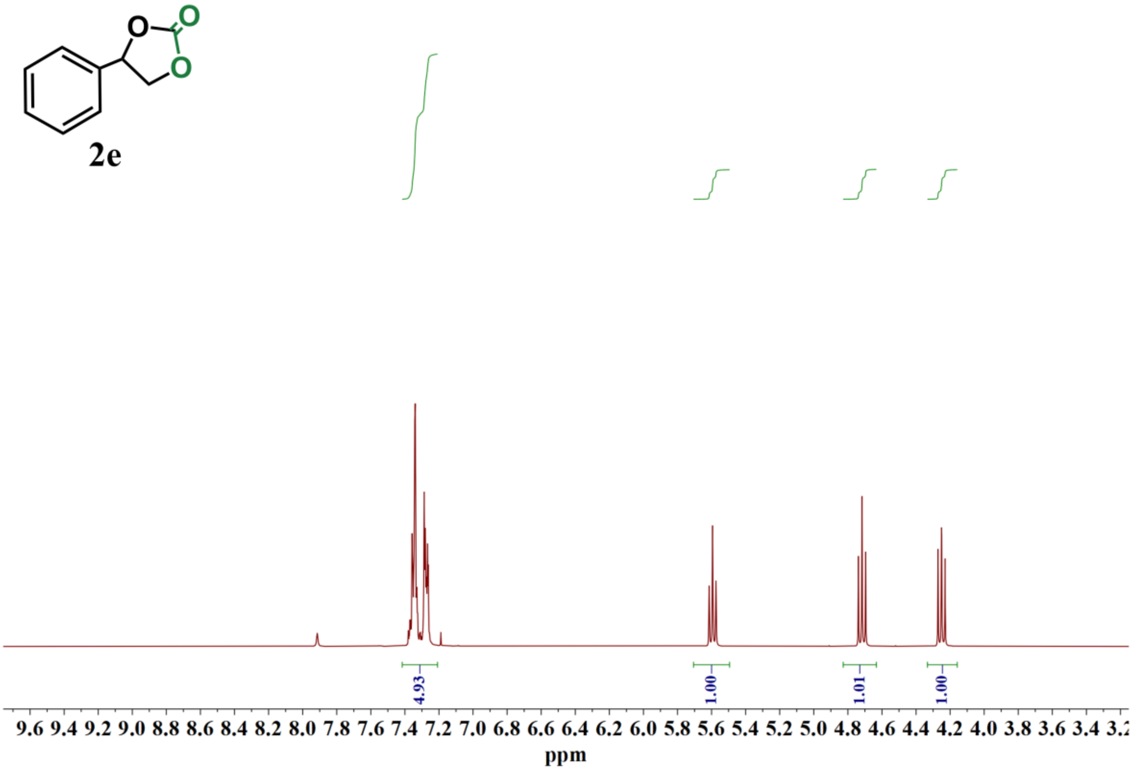


Fig. S20. [1]H NMR spectrum of **2e** (400 MHz, $CDCl_3$, 298 K).

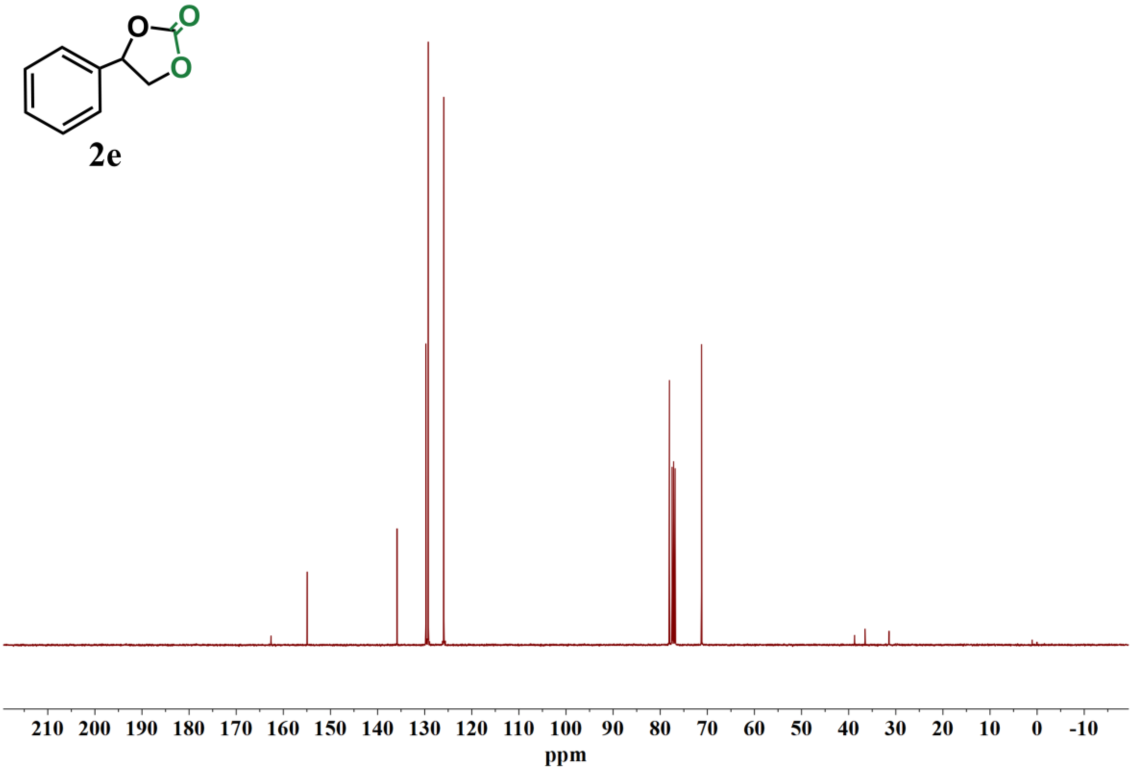
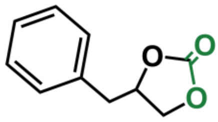


Fig. S21. [13]C NMR spectrum of **2e** (126 MHz, $CDCl_3$, 298 K).



2f

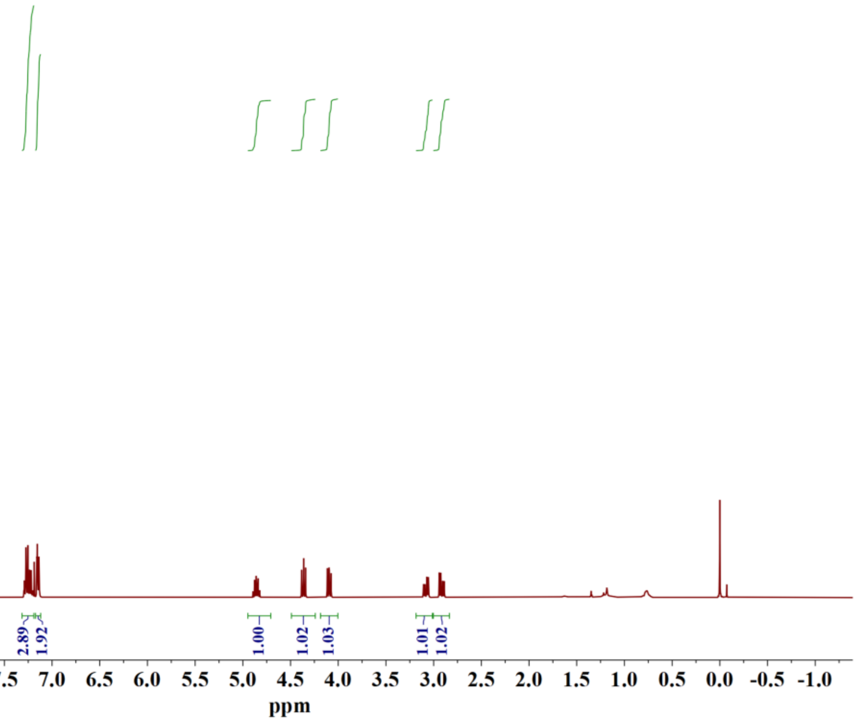
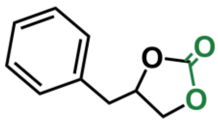


Fig. S22. ^{1}H NMR spectrum of **2f** (400 MHz, $CDCl_3$, 298 K).



2f

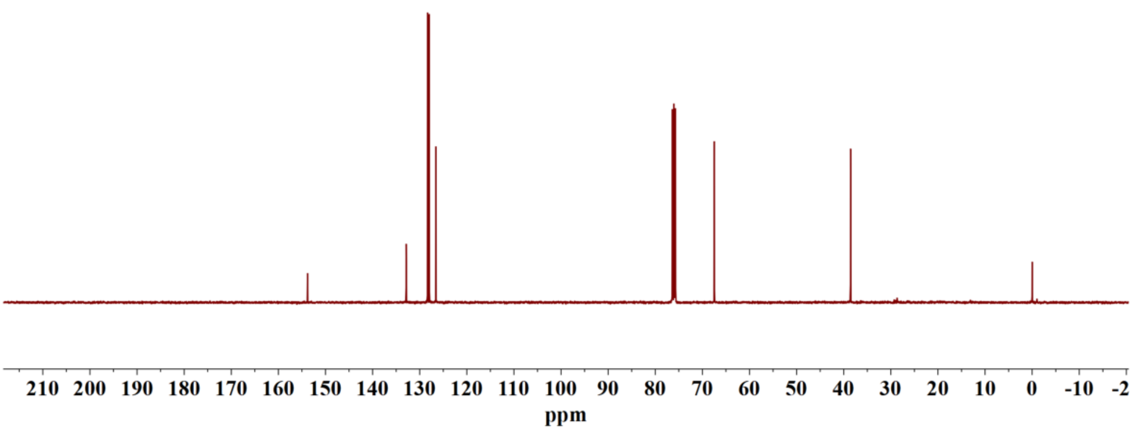


Fig. S23. ^{13}C NMR spectrum of **2f** (126 MHz, $CDCl_3$, 298 K).

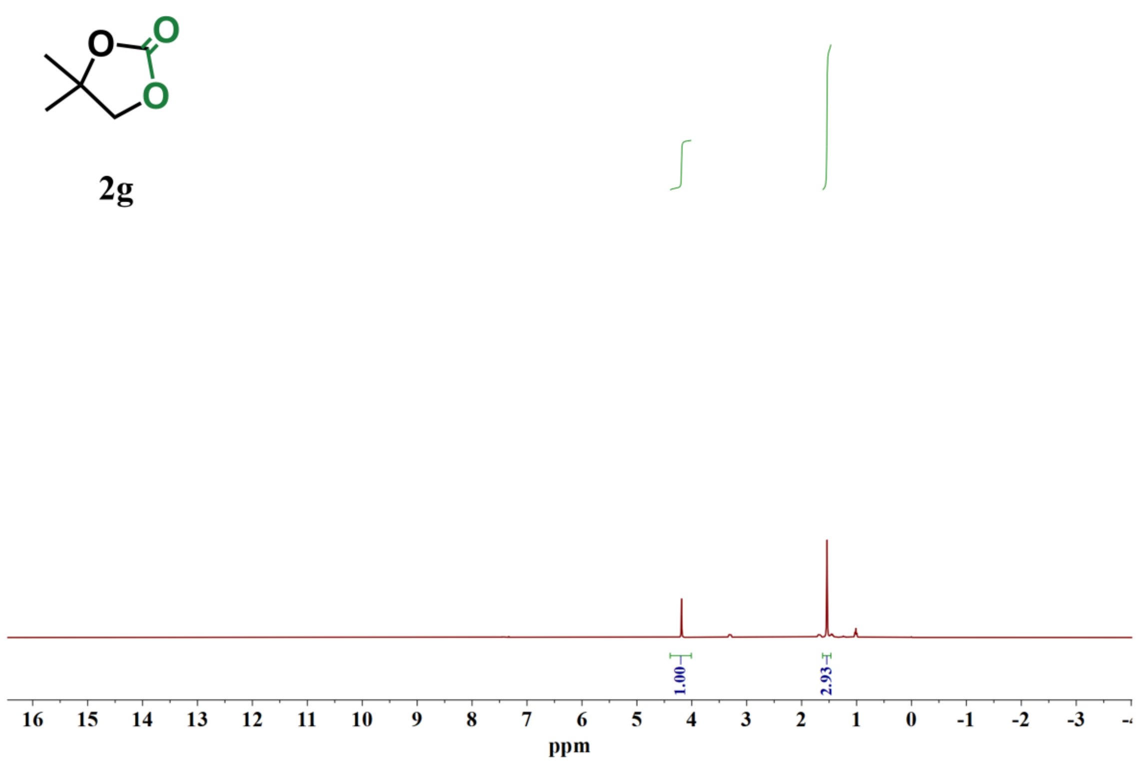


Fig. S24. ^{1}H NMR spectrum of **2g** (400 MHz, $CDCl_3$, 298 K).

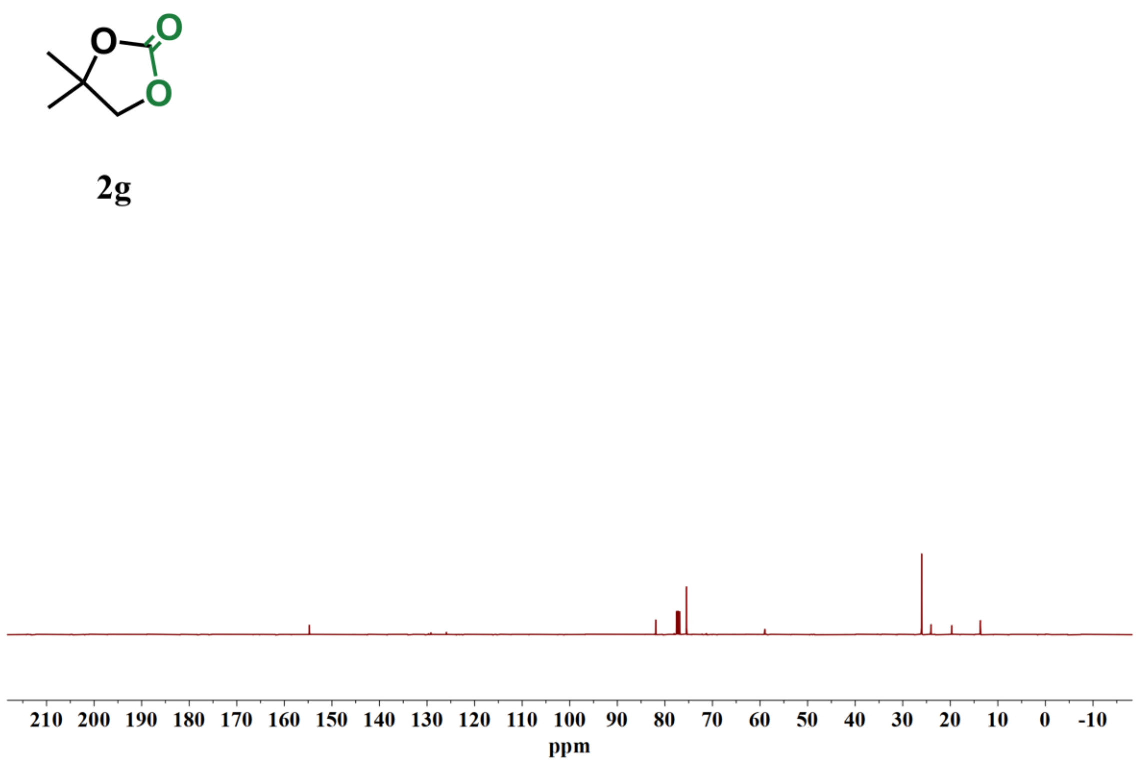


Fig. S25. ^{13}C NMR spectrum of **2g** (126 MHz, $CDCl_3$, 298 K).

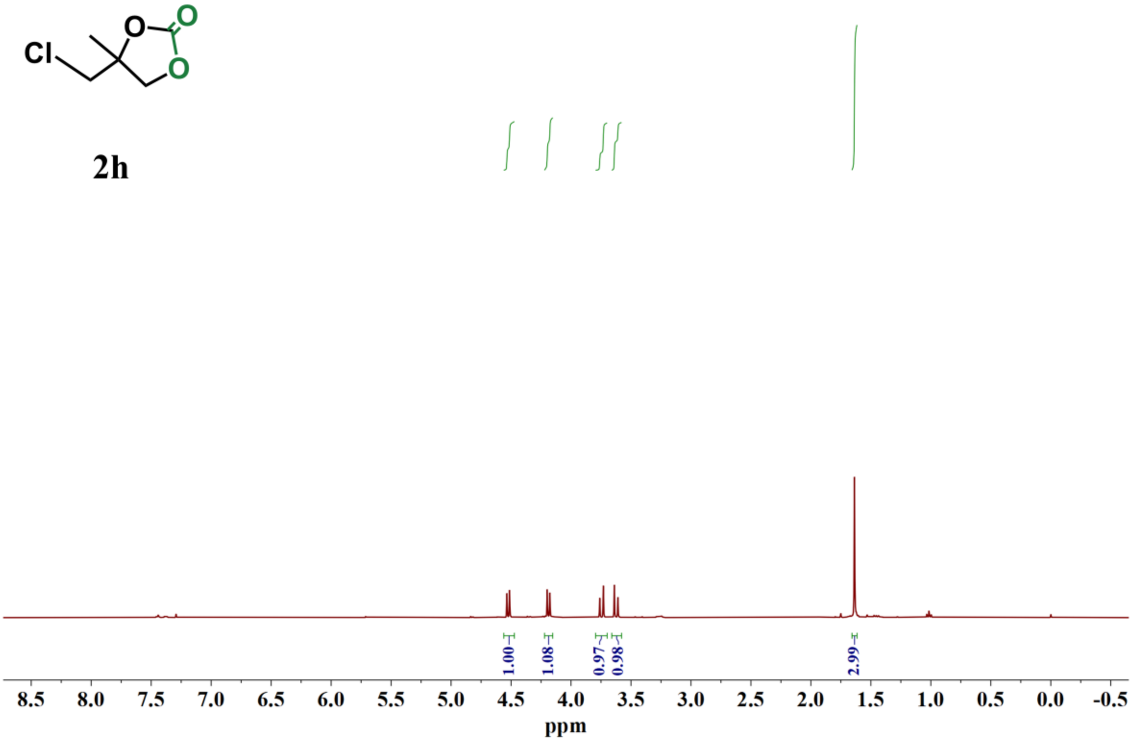


Fig. S26. ^{1}H NMR spectrum of **2h** (400 MHz, $CDCl_3$, 298 K).

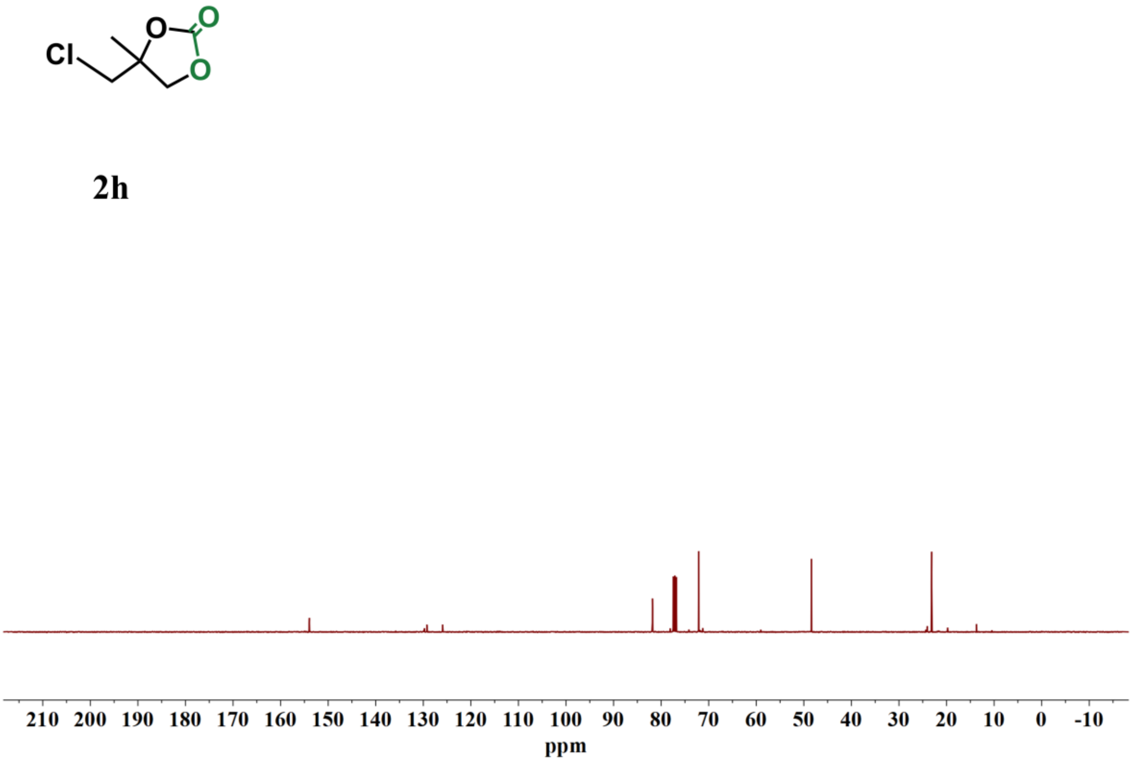
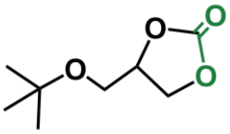


Fig. S27. ^{13}C NMR spectrum of **2h** (126 MHz, $CDCl_3$, 298 K).



2i

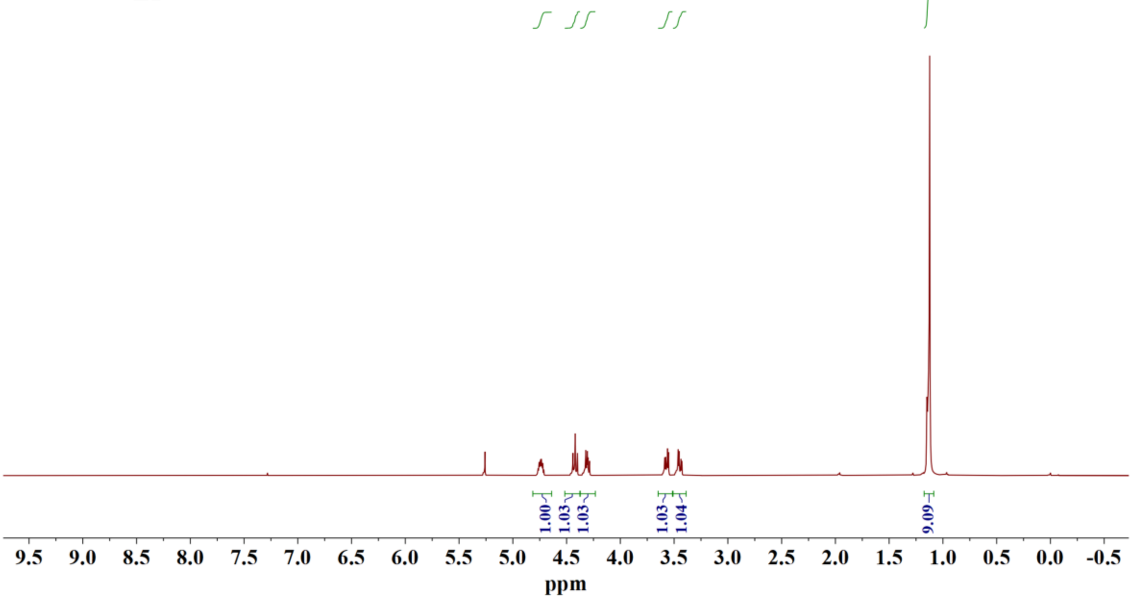
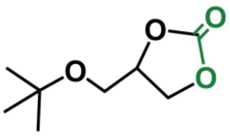


Fig. S28. [1]H NMR spectrum of **2i** (400 MHz, $CDCl_3$, 298 K).



2i

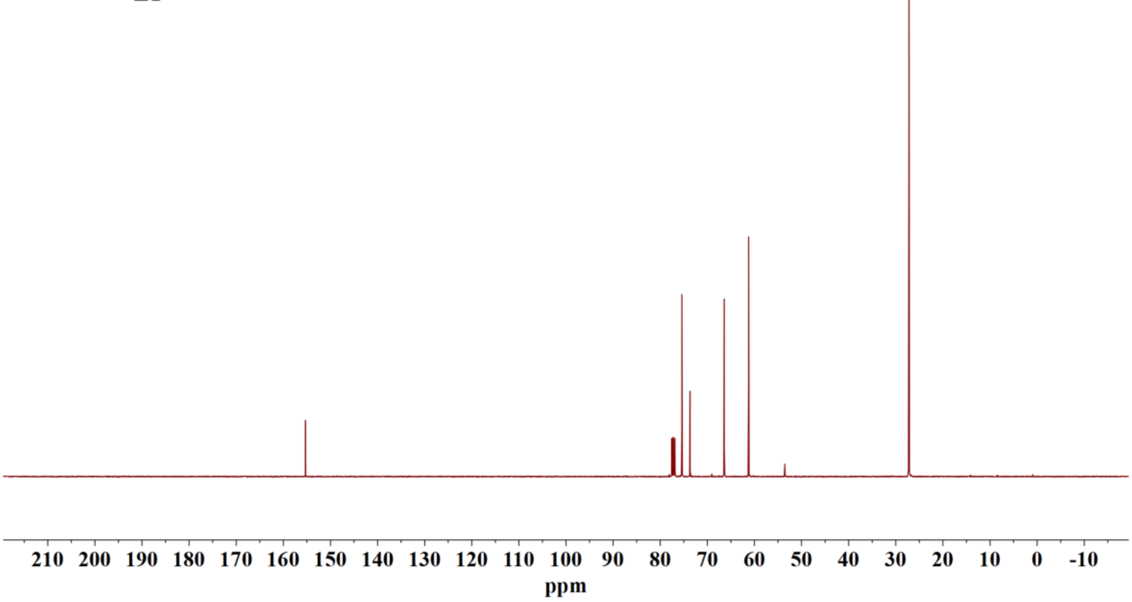


Fig. S29. [13]C NMR spectrum of **2i** (126 MHz, $CDCl_3$, 298 K).

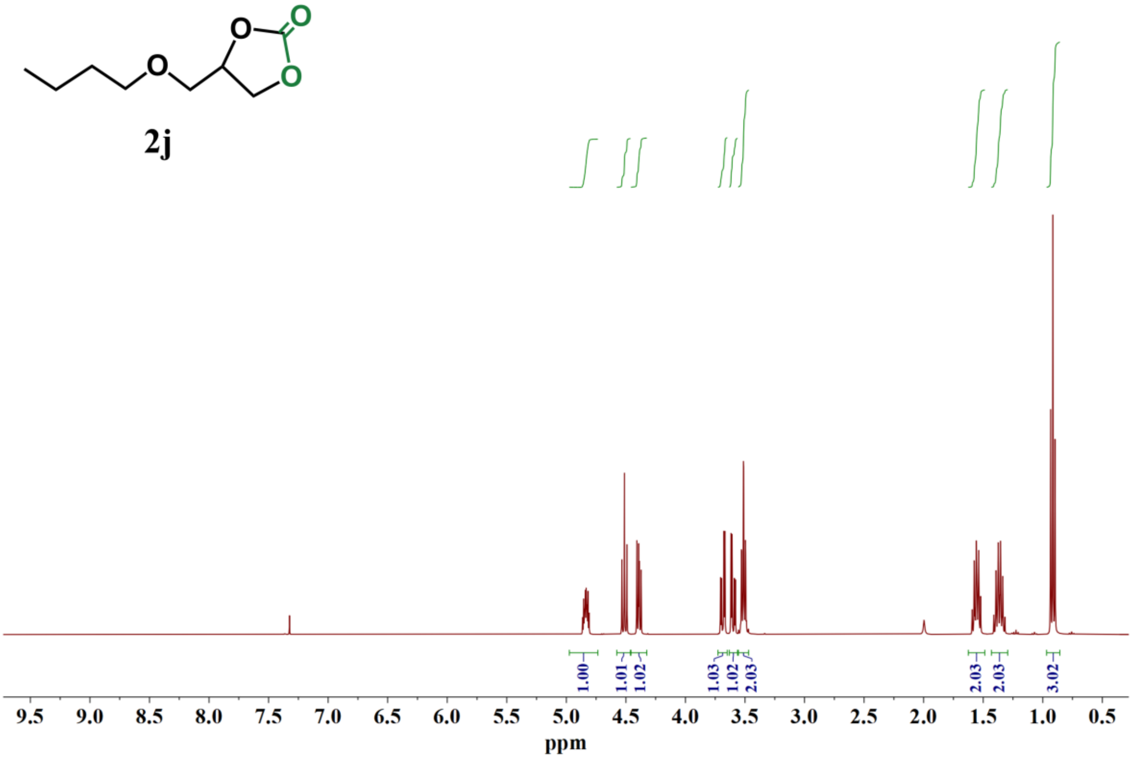


Fig. S30. ^{1}H NMR spectrum of **2j** (400 MHz, $CDCl_3$, 298 K).

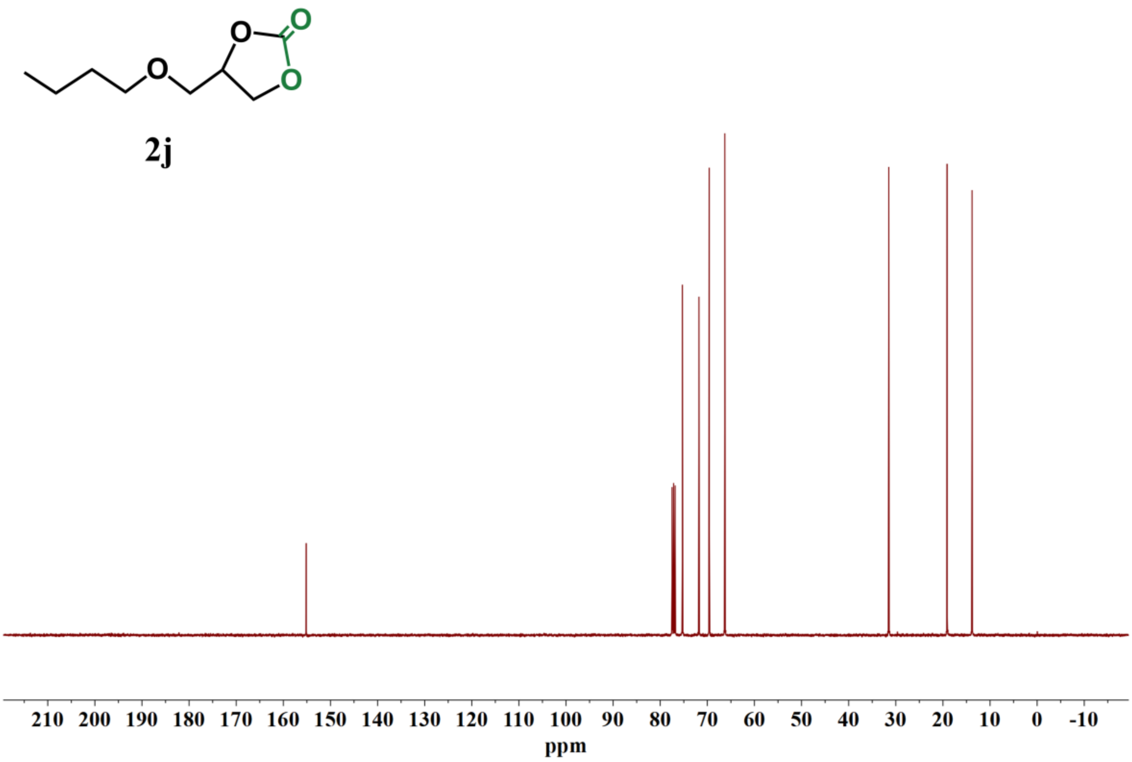


Fig. S31. ^{13}C NMR spectrum of **2j** (126 MHz, $CDCl_3$, 298 K).

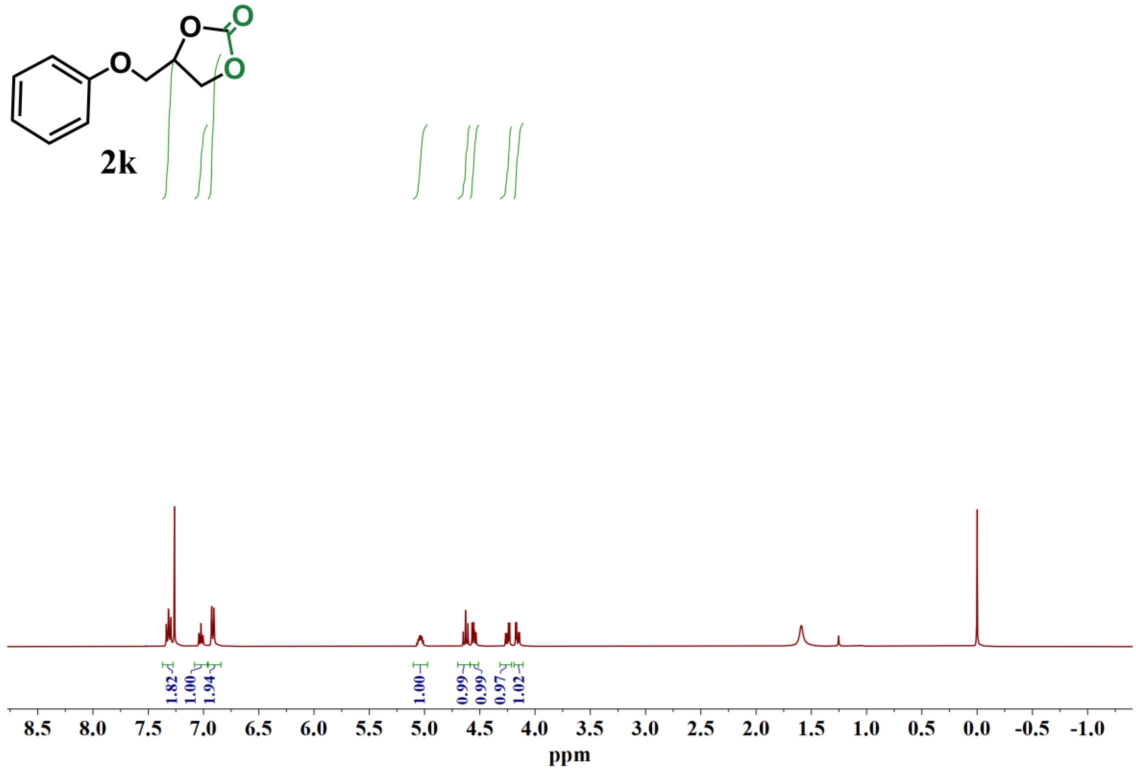


Fig. S32. ^{1}H NMR spectrum of **2k** (400 MHz, $CDCl_3$, 298 K).

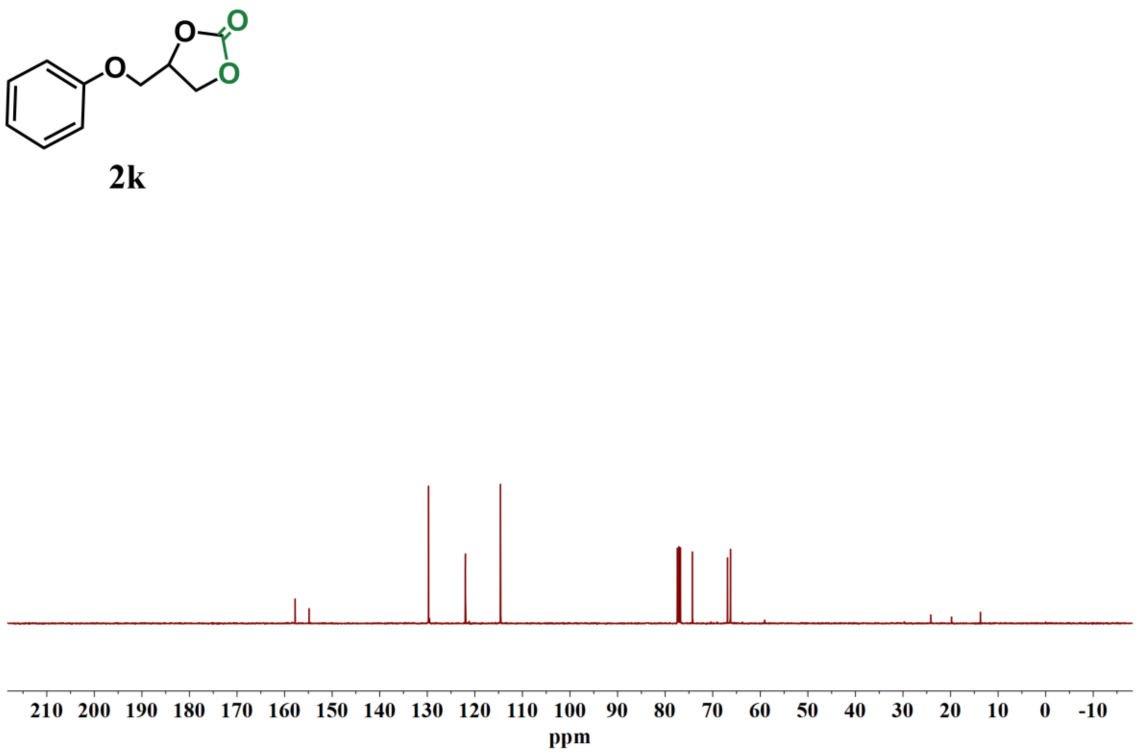


Fig. S33. ^{13}C NMR spectrum of **2k** (126 MHz, $CDCl_3$, 298 K).

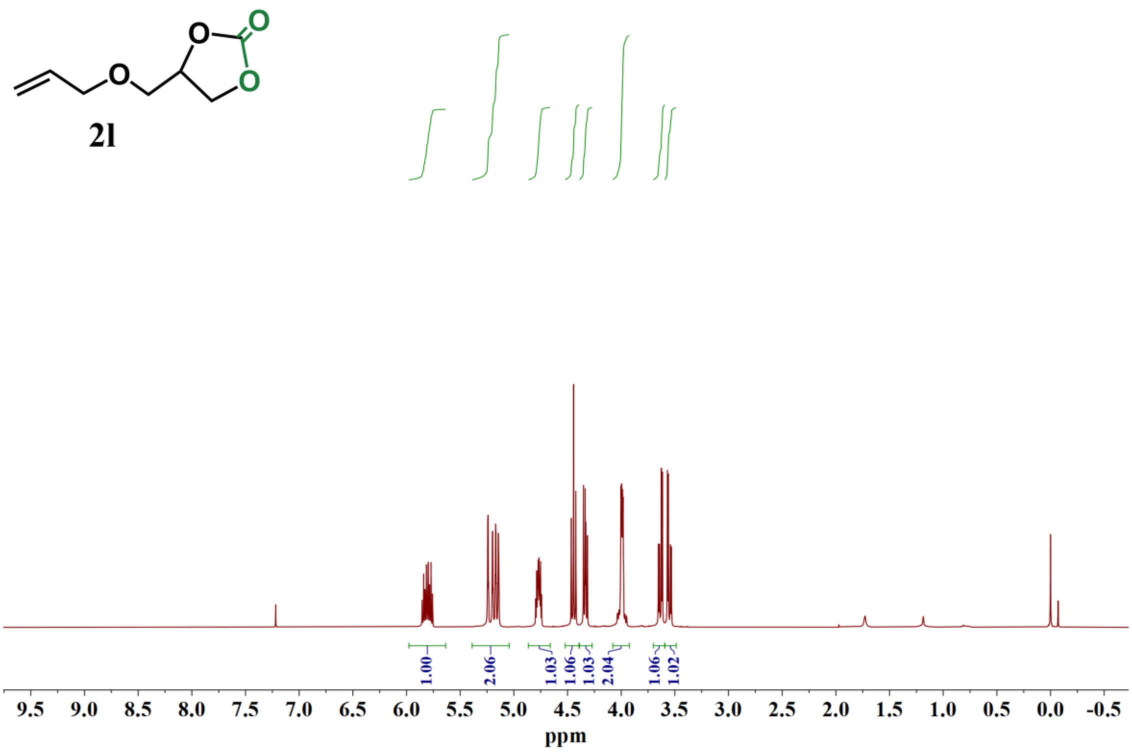


Fig. S34. [1]H NMR spectrum of **2l** (400 MHz, $CDCl_3$, 298 K).

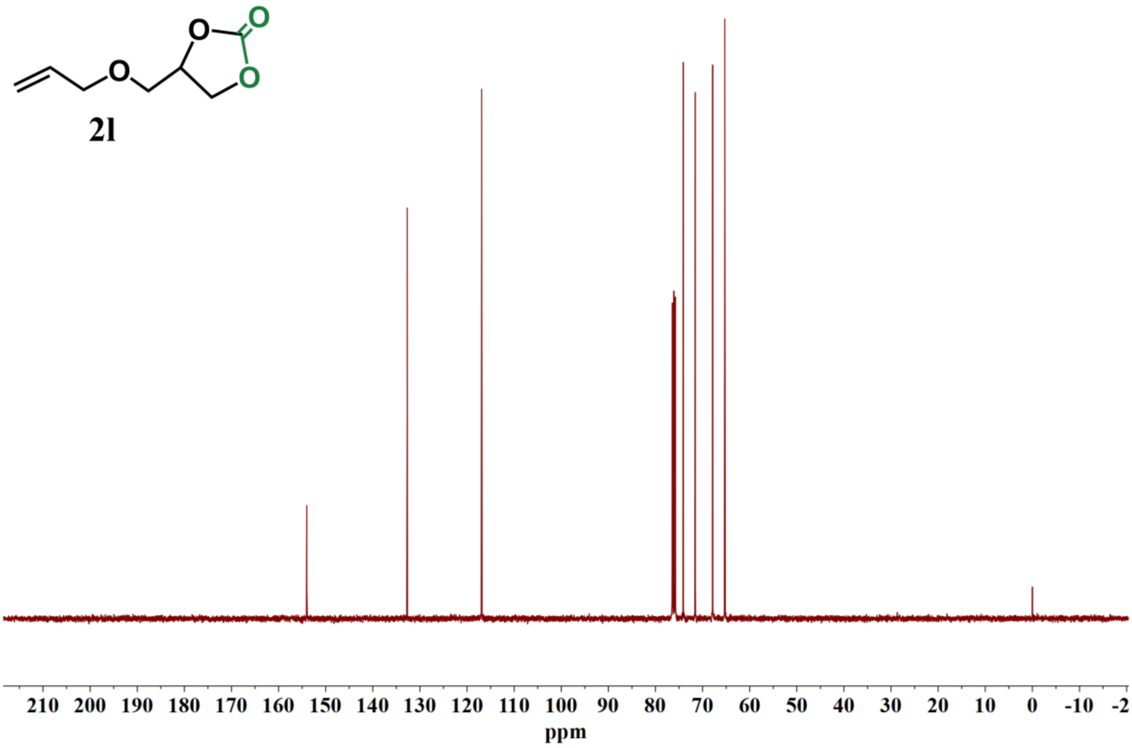


Fig. S35. [13]C NMR spectrum of **2l** (126 MHz, $CDCl_3$, 298 K).

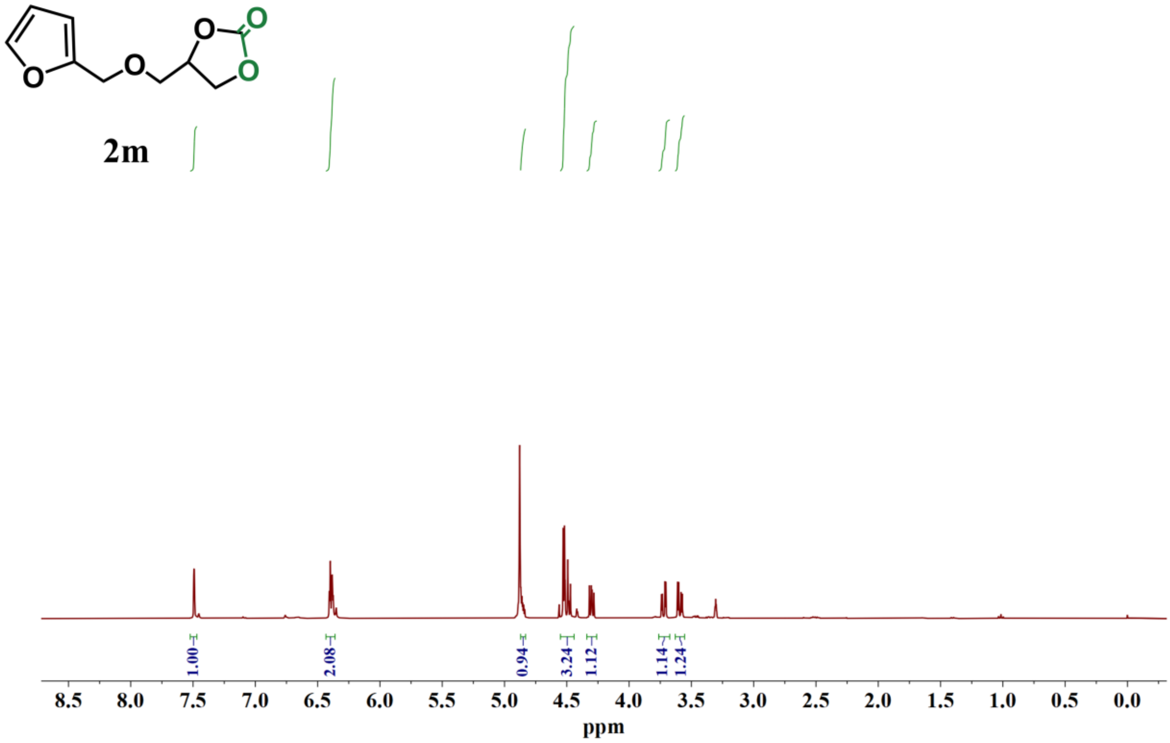


Fig. S36. ^{1}H NMR spectrum of **2m** (400 MHz, $CDCl_3$, 298 K).

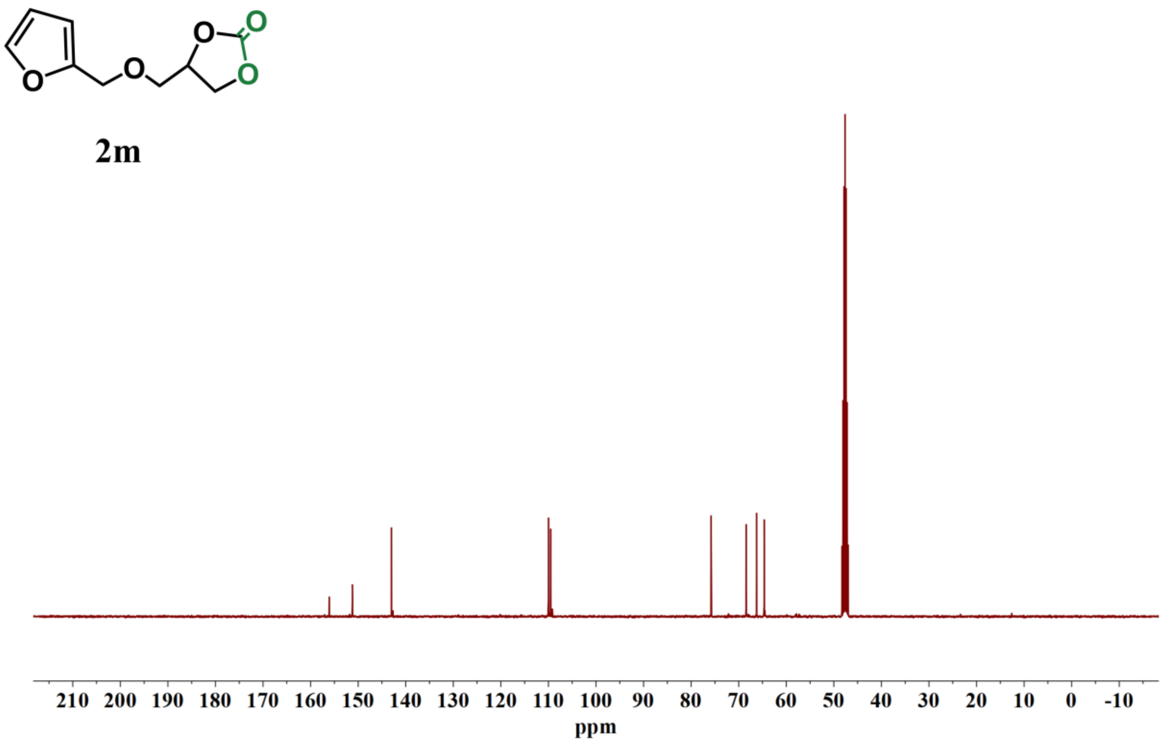
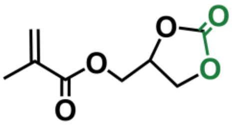


Fig. S37. ^{13}C NMR spectrum of **2m** (126 MHz, $CDCl_3$, 298 K).



2n

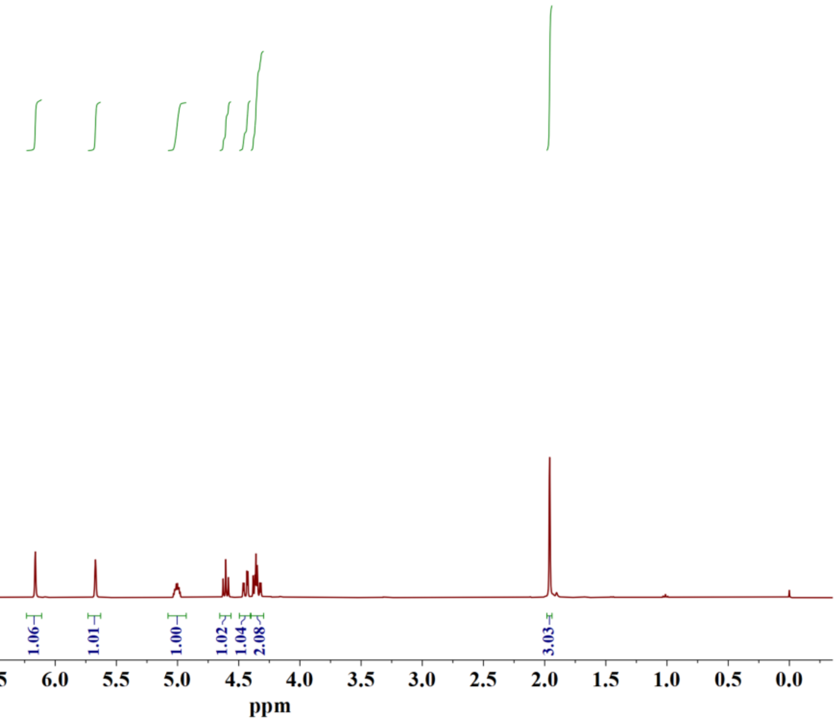
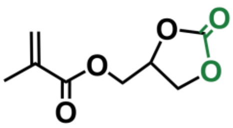


Fig. S38. ^{1}H NMR spectrum of **2n** (400 MHz, $CDCl_3$, 298 K).



2n

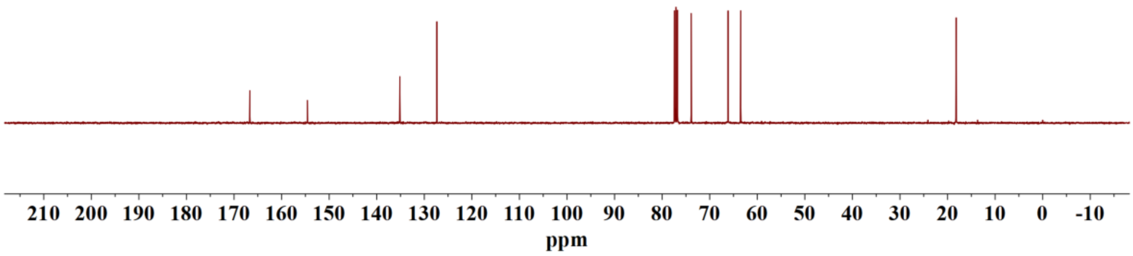
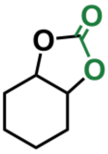


Fig. S39. ^{13}C NMR spectrum of **2n** (126 MHz, $CDCl_3$, 298 K).



2o

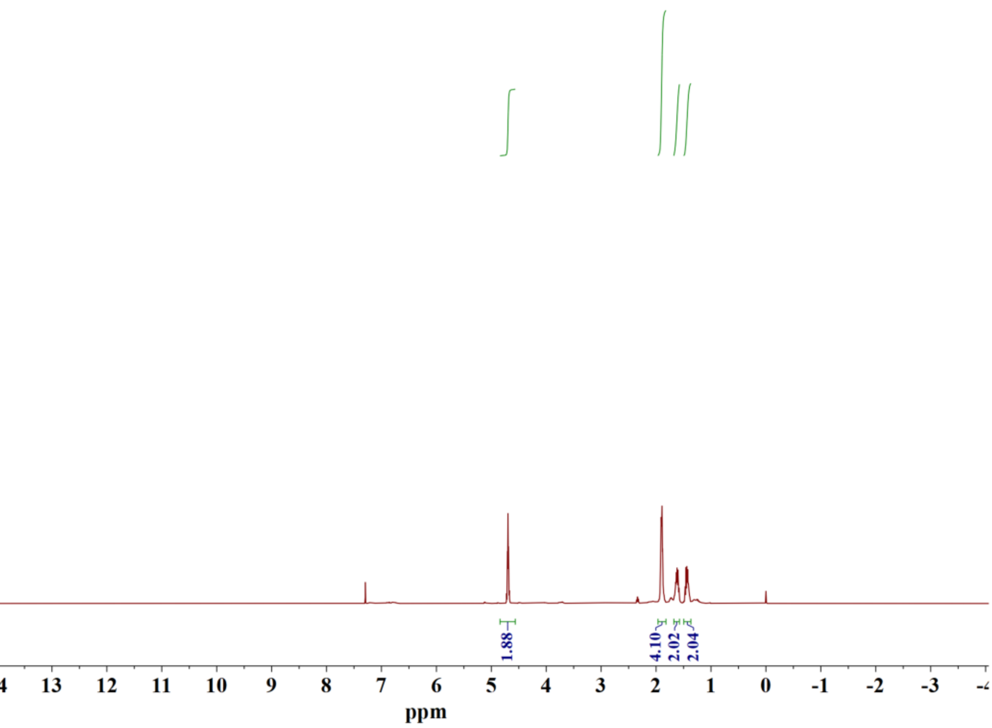
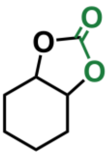


Fig. S40. ^{1}H NMR spectrum of **2o** (400 MHz, $CDCl_3$, 298 K).



2o

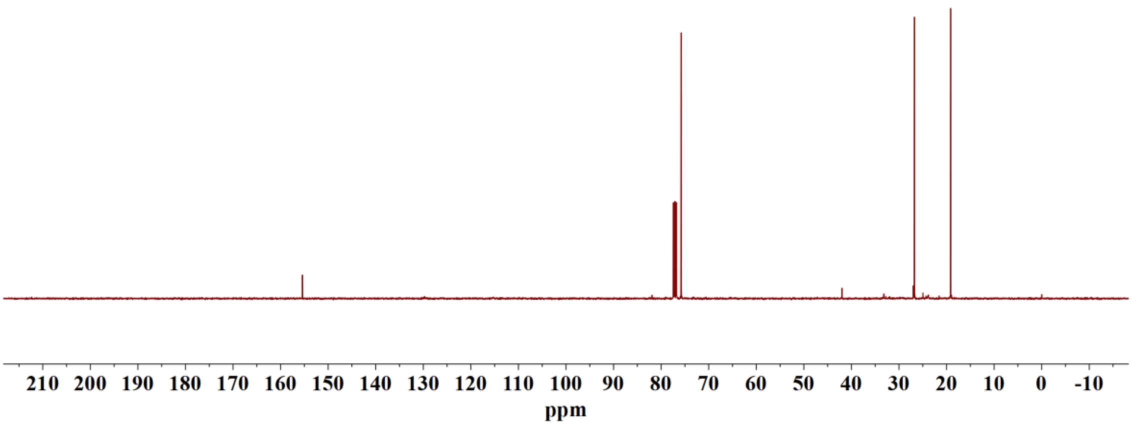
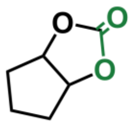


Fig. S41. ^{13}C NMR spectrum of **2o** (126 MHz, $CDCl_3$, 298 K).



2p

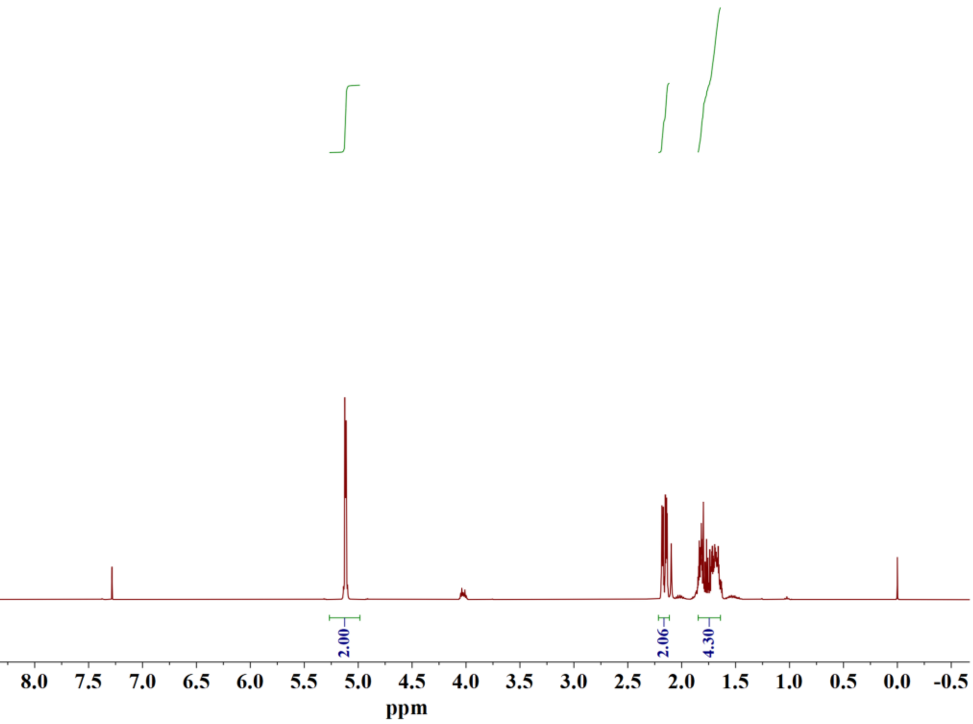
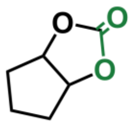


Fig. S42. ^{1}H NMR spectrum of **2p** (400 MHz, $CDCl_3$, 298 K).



2p

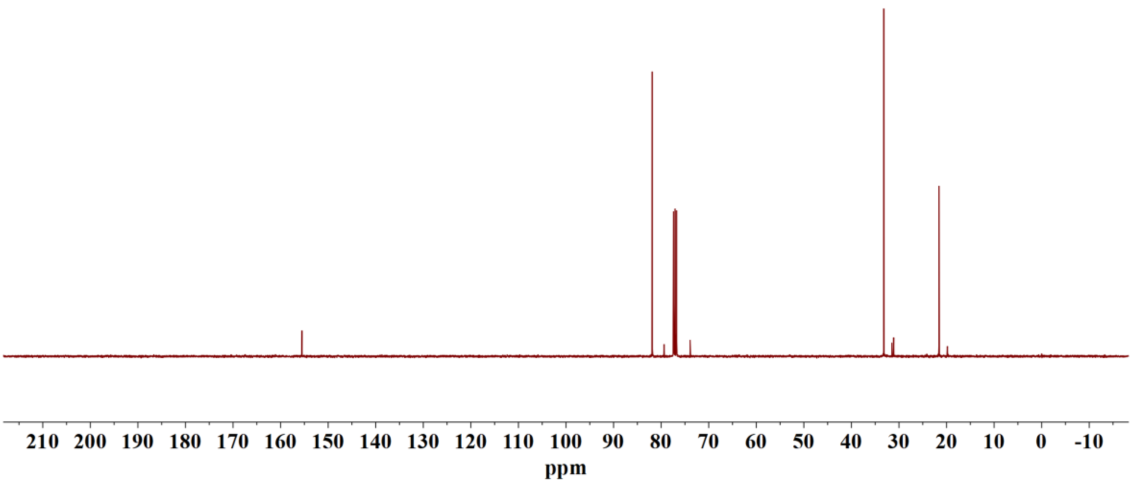


Fig. S43. ^{13}C NMR spectrum of **2p** (126 MHz, $CDCl_3$, 298 K).

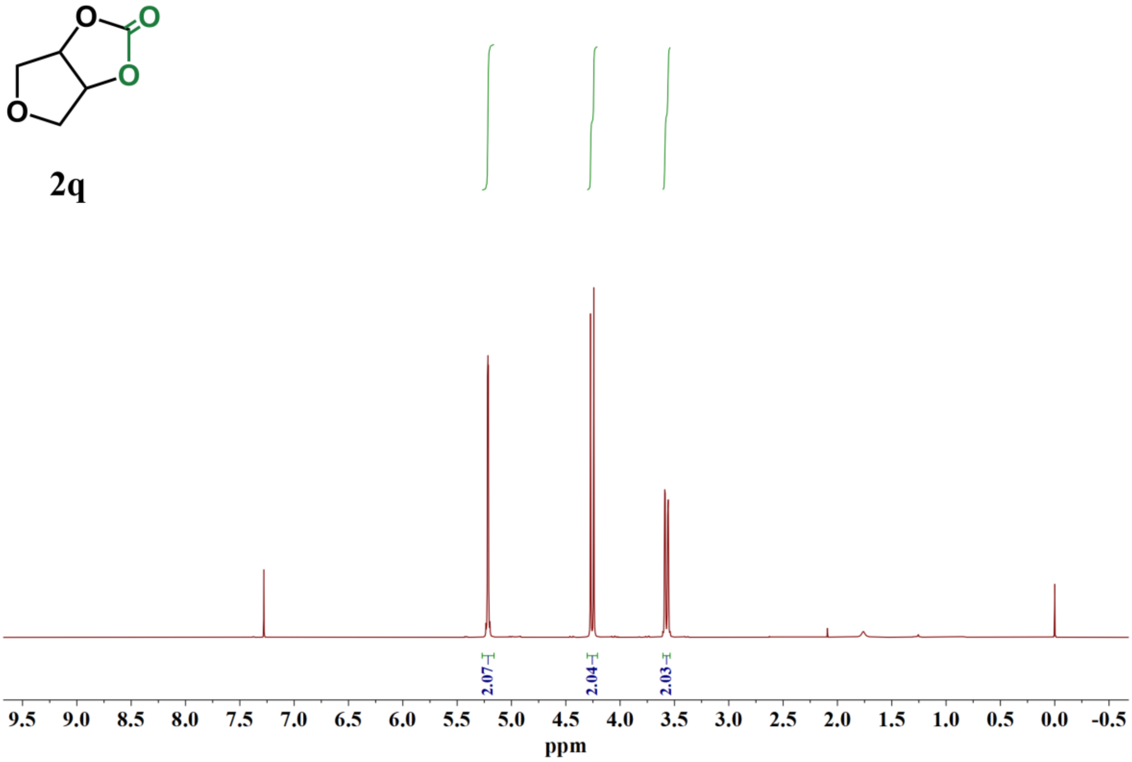


Fig. S44. [1]H NMR spectrum of **2q** (400 MHz, $CDCl_3$, 298 K).

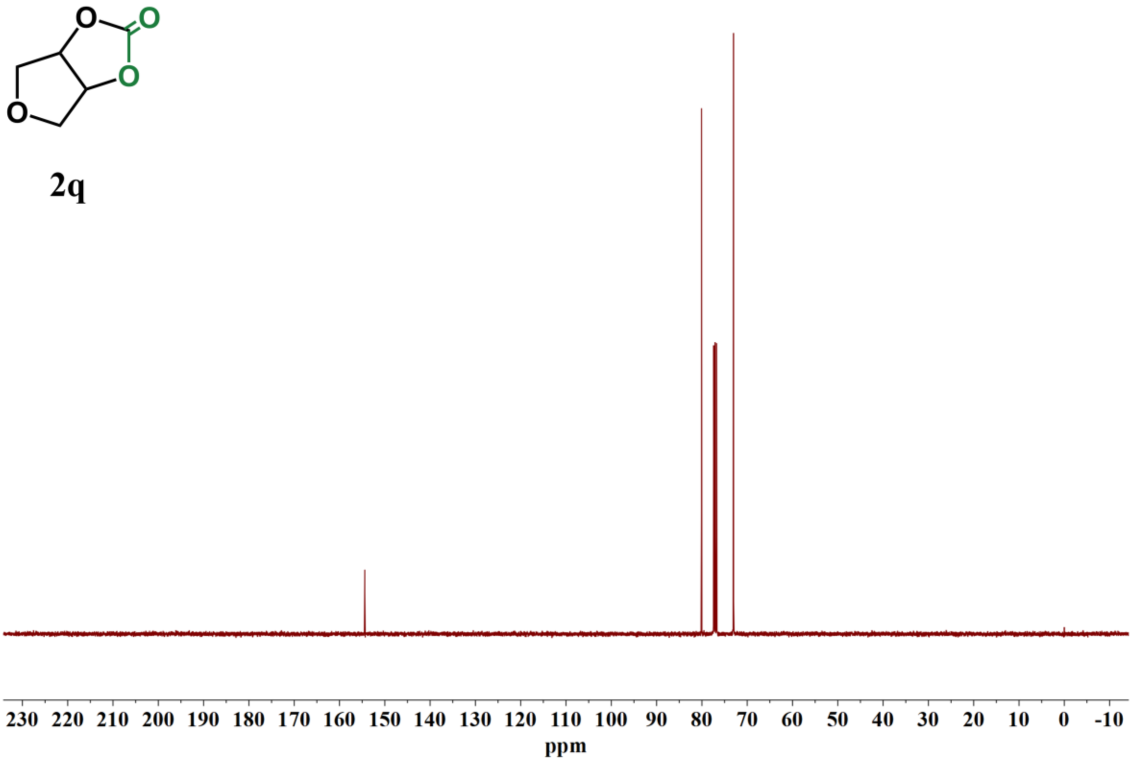
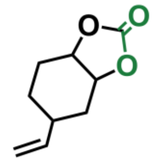


Fig. S45. [13]C NMR spectrum of **2q** (126 MHz, $CDCl_3$, 298 K).



2r

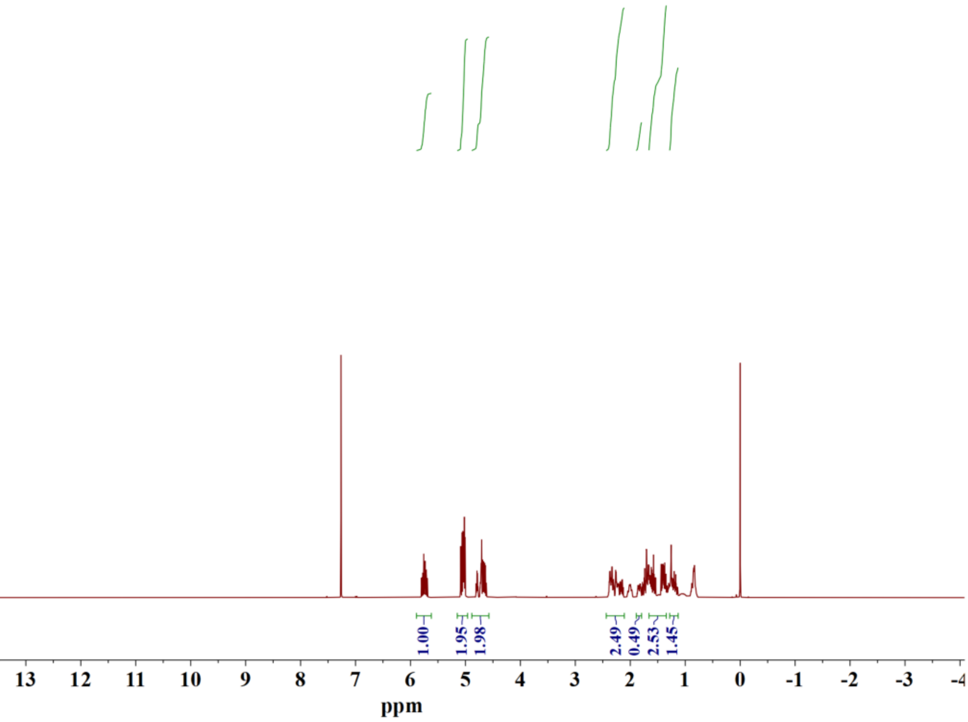
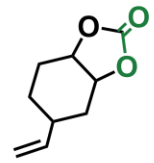


Fig. S46. ^{1}H NMR spectrum of **2r** (400 MHz, $CDCl_3$, 298 K).



2r

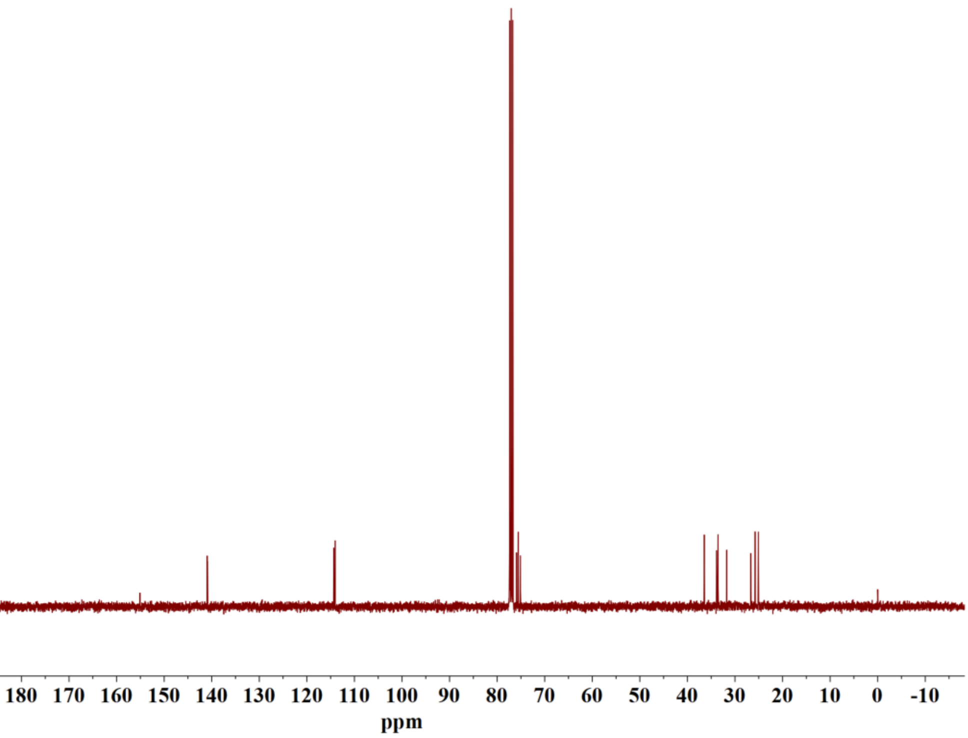


Fig. S47. ^{13}C NMR spectrum of **2r** (126 MHz, $CDCl_3$, 298 K).

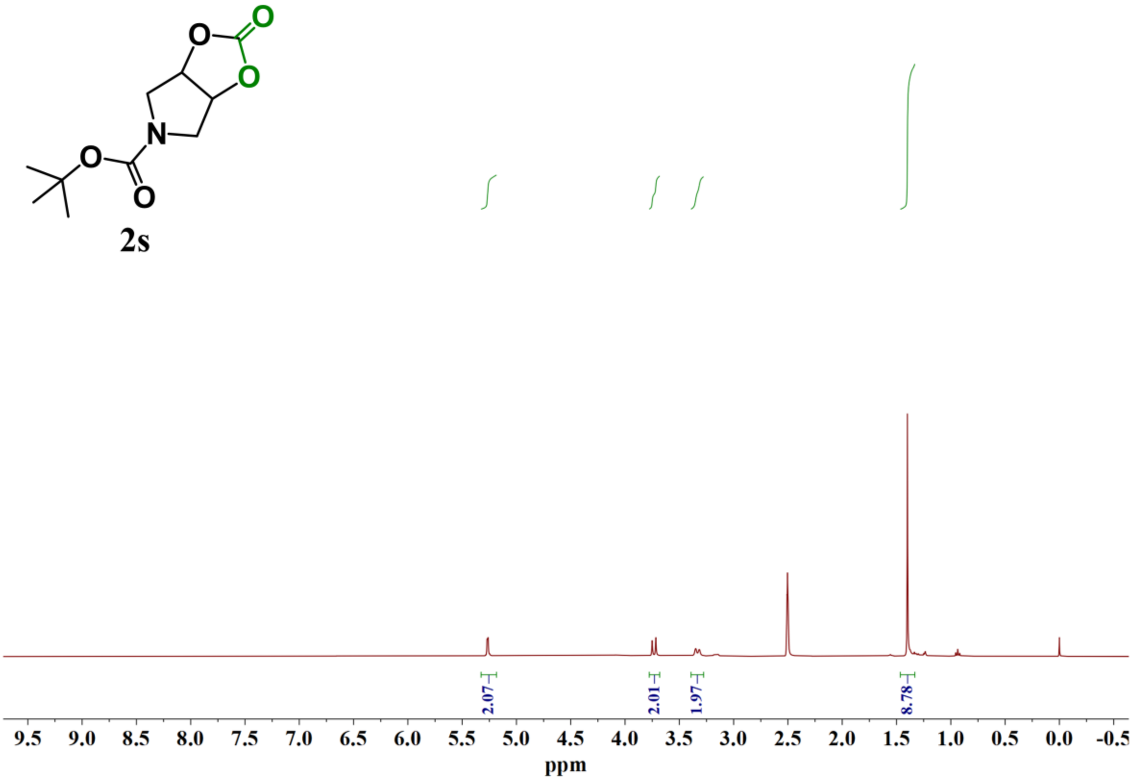


Fig. S48. ^{1}H NMR spectrum of **2s** (400 MHz, $CDCl_3$, 298 K).

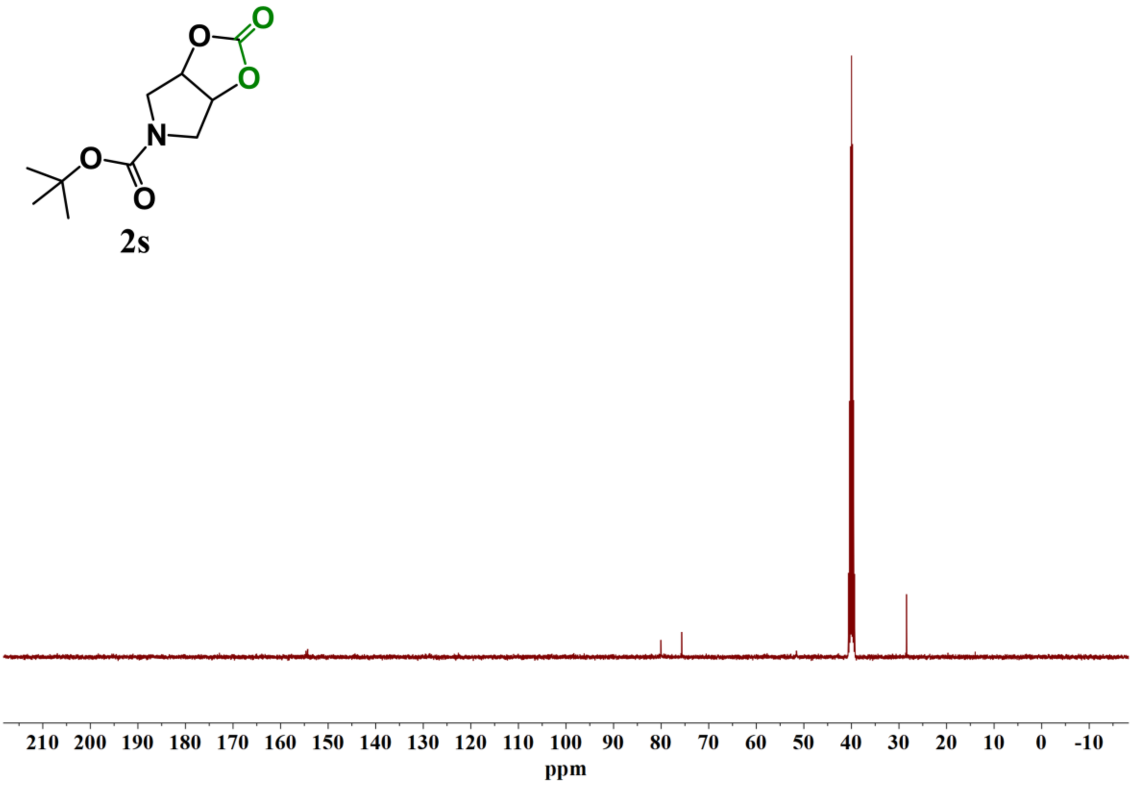


Fig. S49. ^{13}C NMR spectrum of **2s** (126 MHz, $CDCl_3$, 298 K).

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