Supporting Information

Efficient Metal- and Solvent-Free Organocatalytic System for Chemical Fixation of CO_2 into Cyclic Carbonates under Mild Conditions

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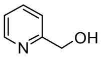
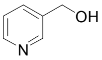
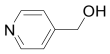
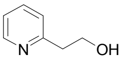
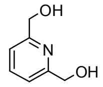
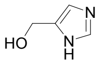
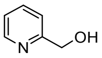
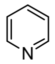
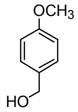
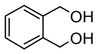
Table, Figure and Experimental Section:

Experimental Section

Table S1 Model reaction and screening results for various co-catalysts[a]

Entry	Co-catalyst 1	Co-catalyst 2	Yield[b] %
1		$n\mathrm{Bu_4NI}$	97 (71)
2		$n\mathrm{Bu_4NI}$	90 (62)
3		$n\mathrm{Bu_4NI}$	89 (57)
4		$n\mathrm{Bu_4NI}$	87 (51)
5		$n\mathrm{Bu_4NI}$	97 (68)
6		$n\mathrm{Bu_4NI}$	78 (50)
7[c]		NaI	89 (54)
8		$n\mathrm{Bu_4NI}$	65
9		$n\mathrm{Bu_4NI}$	77
10		$n\mathrm{Bu_4NI}$	82 (47)

[a] Reaction conditions: epichlorohydrin (6 mmol), catalyst (0.48 mmol, 8 mol%), CO_2 (99.999%, balloon), 20 h. [b] Isolated yield, reaction time: 8 h (in parentheses). [c] KI was used as co-catalyst 2, yield: 90%, 20h.

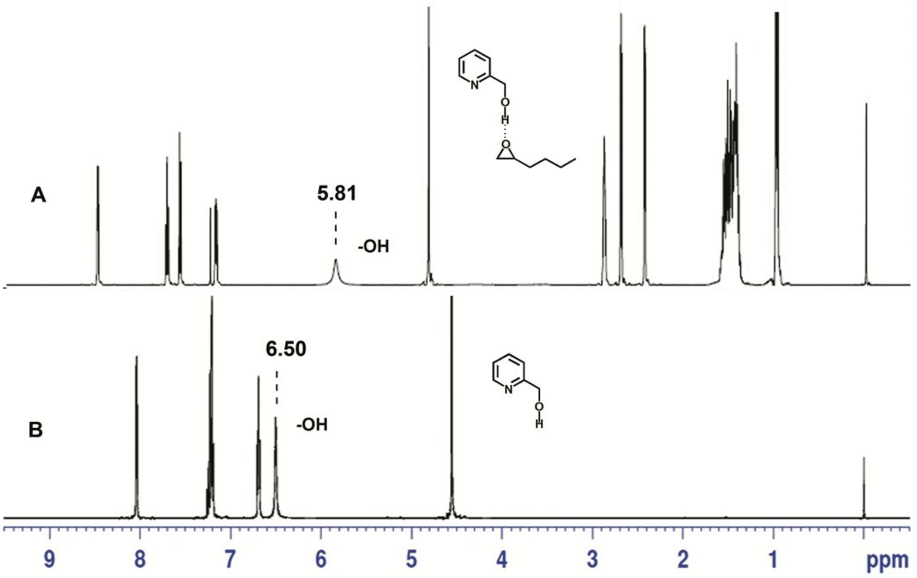


Fig. S1 ^{1}H NMR spectra of a mixture of 2-pyridinemethanol and 1,2-epoxyhexane (molar ratio = 1 : 2) (A) and 2-pyridinemethanol (B) at 298 K, Dual NMR tube. The samples were placed in the inner tube, whereas $CDCl_3$ was placed in the outer tube as the external standard.

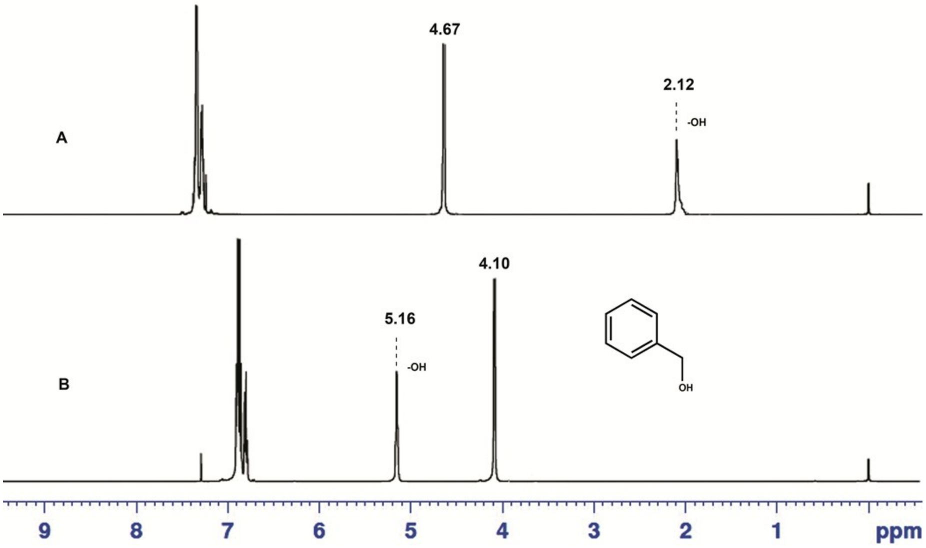


Fig. S2 ^{1}H NMR spectra of benzyl alcohol in $CDCl_3$ at 298 K, in a normal NMR tube (A) and benzyl alcohol at 298 K, in a dual NMR tube, where only benzyl alcohol was placed in the inner tube, whereas $CDCl_3$ was placed in the outer tube as the external standard (B).

Experimental Section

General information

All starting materials and solvents commercially available were purchased at the highest quality from Sigma-Aldrich or Wako and used as received unless otherwise indicated. Reactions were monitored by thin layer chromatography using 0.25-mm E. Merck silica gel coated on aluminum plates (60F-254) with UV light to visualize the course of the reaction. Chemical yields refer to the pure isolated substances. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were obtained using a Brucker AV-500 (500 MHz) spectrometer. The chemical shifts of the products were reported in ppm with reference to Me_4Si as the internal standard in $CDCl_3$ solution. The data were reported in the following order: chemical shift, multiplicity, coupling constants in Hz and integration. On the other hand, the spectra of the reaction system materials were taken using a coaxial dual NMR cell. The inner cell contained 2-pyridinemethanol, and the 2-pyridinemethanol−epichlorohydrin mixture, while the outer cell contained $CDCl_3$ as the external standard. Enantiomeric excesses of the carbonates were determined by HPLC analyses with a Daicel Chiralcel OD-3 with detection at 254 nm.

Catalyst recycling studies:

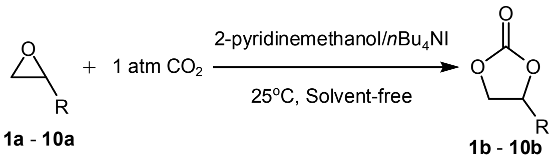
Catalyst recycling experiments of the binary catalytic system, 2,6-pyridinedimethanol/*n*Bu_4NI, were investigated. The reaction of CO_2 with epichlorohydrin was carried out under the optimal reaction conditions (25 °C, 1 atm CO_2, 20 h). After completion, the unreacted sbustrate was removed under vacuum, and then added dry diethyl ether. After the extraction of cyclic carbonate with diethyl ether, the precipitated catalysts were filtered, dried in vacuum and used for the next run under the same reaction conditions. Note: The 2,6-pyridinedimethanol was easily recycled from the reaction system, but some amount of TBAI may be dissolved in the crude carbonate, but after 4 times of recrystallization from the concentrated crude product by dry diethyl ether, the catalysts can be recycled without no significant loss.

Table S2 The amount of the recovered catalysts[a]

Catalytic system	Total amount
2,6-pyridinedimethanol/ (8 mmol%) 0.052 g TBAI/(8 mmol%) 0.177 g	0.229 g
1st Recovered catalysts	0.210 g
2nd Recovered catalysts	0.196 g

[a] Notes: The catalysts were filtered and washed by dry diethyl ether, then 3mL diethyl ether was added in the concentrated crude product, all the catalysts were collected after 4 times of recrystallization.

Representative procedure for the Cyclic Carbonate Formation



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

In a 20 mL two-neck flask, epichlorohydrin **4a** (6 mmol, 0.555 g), 2-pyridinemethanol (8% mmol, 0.052g) and *n*Bu_4NI (8% mmol, 0.177g) were added under N_2 gas with a magnetic stirring bar, then the flask was flushed with CO_2 for 30 seconds. The reaction mixture was stirred at 25 °C for 20 h under an atmosphere of CO_2 (99.999%, balloon). After completion, the reaction mixture was purified by column chromatography (hexane : ethyl acetate = 1 : 1) to afford the desired cyclic carbonate 0.794 g (yield: 97.0%).

^{1}H NMR (500 MHz, $CDCl_3$): 5.12−5.01 (m, 1H), 4.69−4.55 (m, 1H), 4.48−4.35 (m, 1H), 3.89 (dd, J = 12.5, 4.0 Hz, 1H), 3.77 (dd, J = 12.5, 3.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 154.8, 74.7, 67.0, 44.6.

Propylene carbonate (1b)

Propylene oxide (**1a**, 6 mmol, 0.349 g), 2-pyridinemethanol (8% mmol, 0.052g) and nBu$_4$NI (8% mmol, 0.177g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 1 : 1) to afford the desired cyclic carbonate 0.527 g (yield: 86.0%).

^{1}H NMR (500 MHz, $CDCl_3$): 4.92−4.80 (m, 1H), 4.62−4.51 (m, 1H), 4.10−3.95 (m, 1H), 1.55−1.40 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 155.2, 73.7, 70.7, 19.3.

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

1,2-Epoxyhexane (**2a**, 6 mmol, 0.601 g), 2-pyridinemethanol (8% mmol, 0.052g) and nBu$_4$NI (8% mmol, 0.177g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.769 g (45 ^{o}C, yield: 88.6%).

^{1}H NMR (500 MHz, $CDCl_3$): 4.80−4.65 (m, 1H), 4.60−4.50 (m, 1H), 4.18−4.01 (m, 1H), 1.85−1.62 (m, 2H), 1.55−1.22 (m, 4H), 0.93 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125

MHz, $CDCl_3$): 155.2, 77.2, 69.4, 33.4, 26.4, 22.2, 13.7.

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

1,2-Epoxyoctane (**3a**, 6 mmol, 0.769 g), 2-pyridinemethanol (8% mmol, 0.052g) and *n*Bu_4NI (8% mmol, 0.177g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 3 : 1) to afford the desired cyclic carbonate 0.898 g (reaction temperature 45 °C, yield: 87%).

^{1}H NMR (500 MHz, $CDCl_3$): 4.79−4.68 (m, 1H), 4.61−4.50 (m, 1H), 4.15−4.02 (m, 1H), 1.85−1.62 (m, 2H), 1.55−1.21 (m, 8H), 0.89 (t, J = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 155.2, 77.2, 69.4, 33.7, 31.5, 28.7, 24.3, 22.4, 13.9.

4-(But-3-en-1-yl)-1,3-dioxolan-2-one (5b)

1,2-Epoxy-5-hexene (**5a**, 6 mmol, 0.589 g), 2-pyridinemethanol (8% mmol, 0.052g) and *n*Bu_4NI (8% mmol, 0.177g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.725 g (yield: 85%).

^{1}H NMR (500 MHz, $CDCl_3$): 5.89−5.63 (m, 1H), 5.18−4.90 (m, 2H), 4.79−4.60 (m, 1H), 4.59−4.42 (m, 1H), 4.15−3.95 (m, 1H), 2.30−2.01 (m, 2H), 1.95−1.65 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): 155.1, 136.3, 116.0, 76.5, 69.4, 32.8, 28.6.

4-Allyloxymethyl-1,3-dioxolan-2-one (6b)

Allyl glycidyl ether (**6a**, 6 mmol, 0.685 g), 2-pyridinemethanol (8% mmol, 0.052g) and *n*Bu_4NI (8% mmol, 0.177g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 1 : 1) to afford the desired cyclic carbonate 0.835 g (yield: 88%).

^{1}H NMR (CDCl$_3$, 500 MHz): 5.95−5.80 (m, 1H), 5.35−5.12 (m, 2H), 4.93−4.80 (m, 1H), 4.60−4.45 (m, 1H), 4.44−4.30 (m, 1H), 4.11−3.99 (m, 2H), 3.75−3.65 (m, 1H), 3.64−3.52 (m, 1H). ^{13}C NMR (125 MHz, CDCl$_3$): 155.2, 133.9, 117.3, 75.4, 72.3, 68.9, 66.2.

4-(Phenoxymethyl)-1,3-dioxolan-2-one (7b)

1,2-Epoxy-3-phenoxy propane (**7a**, 5 mmol, 0.900 g), 2-pyridinemethanol (8% mmol, 0.052g) and *n*Bu$_4$NI (8% mmol, 0.177g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 1.06 g (yield: 91%).

^{1}H NMR (500 MHz, CDCl$_3$): 7.36−7.22 (m, 2H), 7.06−6.92 (m, 1H), 6.91−6.85 (m, 2H), 5.06−4.95 (m, 1H), 4.65−4.56 (m, 1H), 4.55−4.46 (m, 1H), 4.22 (dd, *J* = 10.5, 4.0 Hz, 1H), 4.12 (dd, *J* = 10.5, 3.5 Hz, 1H). ^{13}C NMR (125 MHz, CDCl$_3$): 157.8, 154.8, 129.7, 122.0, 114.7, 74.2, 66.9, 66.2.

4-Phenyl-1,3-dioxolan-2-one (8b)

In a 20 mL two-neck flask, styrene oxide **8a** (6 mmol, 0.721 g), 2-pyridinemethanol (8% mmol, 0.052g) and *n*Bu$_4$NI (8% mmol, 0.177g) were added and stirred at 25 ^{o}C for 20 h under an atmosphere of CO$_2$ (99.999%, balloon). After completion, the reaction mixture was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.718 g (yield: 73.0%).

^{1}H NMR (500 MHz, CDCl$_3$): 7.42−7.37 (m, 2H), 7.37−7.30 (m, 3H), 5.70−5.60 (m, 1H), 4.81–4.70 (m, 1H), 4.31–4.20 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 155.0, 135.9, 129.7, 129.2, 126.0, 78.0, 71.2.

Hexahydro-benzo[1,3]dioxol-2-one (9b)

In a 20 mL two-neck flask, styrene oxide **9a** (6 mmol, 0.589 g), 2-pyridinemethanol (8% mmol, 0.052g) and *n*Bu_4NI (8% mmol, 0.177g) were added and stirred at 45 ^oC for 20 h under an atmosphere of CO_2 (99.999%, balloon). After completion, the reaction mixture was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.128 g (yield: 15.0%).

^{1}H NMR (300 MHz, $CDCl_3$): 4.76-4.59 (m, 2H), 2.0-1.79 (m, 4H), 1.72-1.53 (m, 2H), 1.51-1.31 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 155.35 , 75.73, 26.78, 19.17.

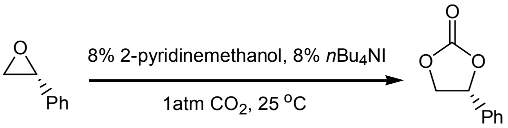
(*R*)-4-Benzyloxymethyl-1,3-dioxolan-2-one ((*R*)-10b)

(*R*)-Glycidyl benzyl ether (**10a**, 6 mmol, 0.985 g), 2-pyridinemethanol (8% mmol, 0.052g) and *n*Bu_4NI (8% mmol, 0.177g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 1.08 g (yield: 87%).

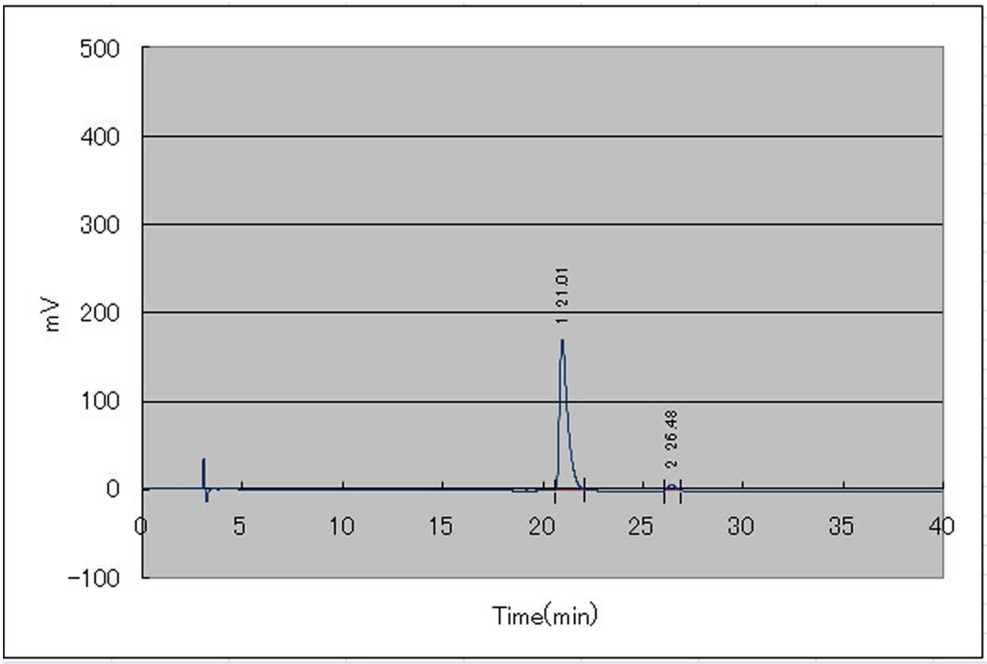
^{1}H NMR (500 MHz, $CDCl_3$): 7.40-7.27 (m, 5H), 4.88-4.75 (m, 1H), 4.55 (q, J = 12.0 Hz, 2H), 4.47 (t, J = 8.5 Hz, 1H), 4.37 (dd, J = 8.5 Hz, 6.5 Hz, 1H), 3.71 (dd, J = 10.5 Hz, 3.5 Hz, 1H), 3.61 (dd, J = 11.0 Hz, 3.5 Hz, 1H) ^{13}C NMR (125 MHz, $CDCl_3$): 154.91, 137.06, 128.59, 128.1, 127.77, 74.98, 73.73, 68.84, 66.31

Reaction of chiral epoxide

(*R*)-4-Phenyl-1,3-dioxolan-2-one ((*R*)-8b)

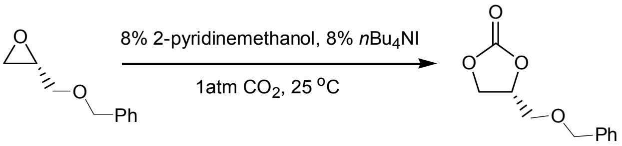


Reaction of (*R*)-styrene oxide was conducted according to the representative procedure, and the *ee* of the product was determined by chiral HPLC measurement using Chiralcel OD-3, 10% IPA/hexanes, 1 mL/min, t_R=21.01 min, t_S=26.48 min, 254 nm. Minimal racemization of the product (94% ee) relative to the starting material (99% ee) was observed.

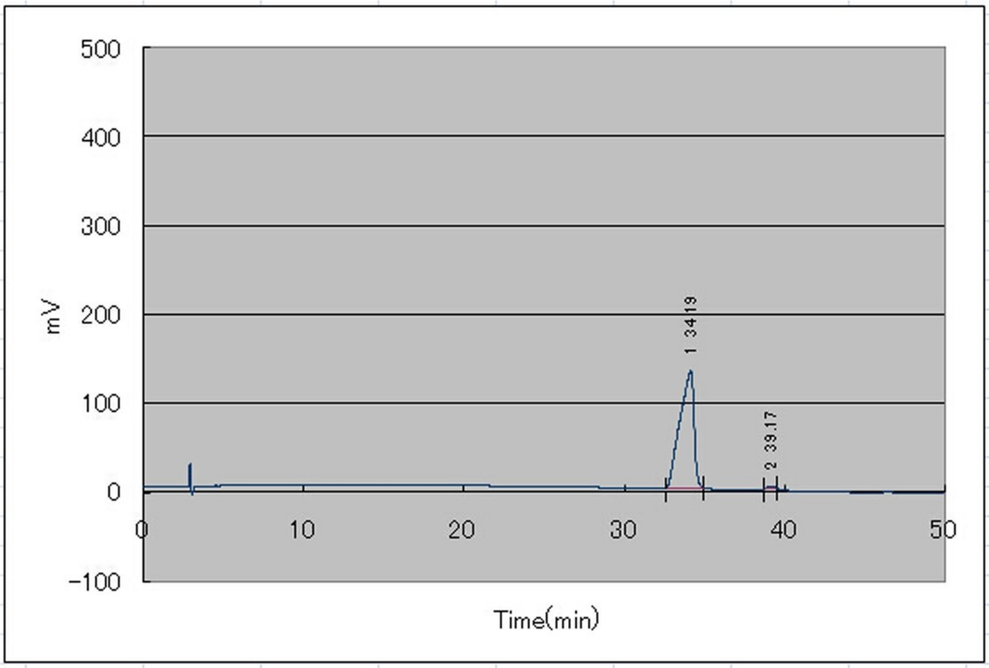


No.	Rt	Area	Area (%)	Height	NTP	Tf
1	21.01	4791051.4	97.0125	169453	11147	1.959
2	26.48	152976.259	2.9875	6412	29075.3	1.147

(*R*)-4-Benzyloxymethyl-1,3-dioxolan-2-one ((*R*)-10b)

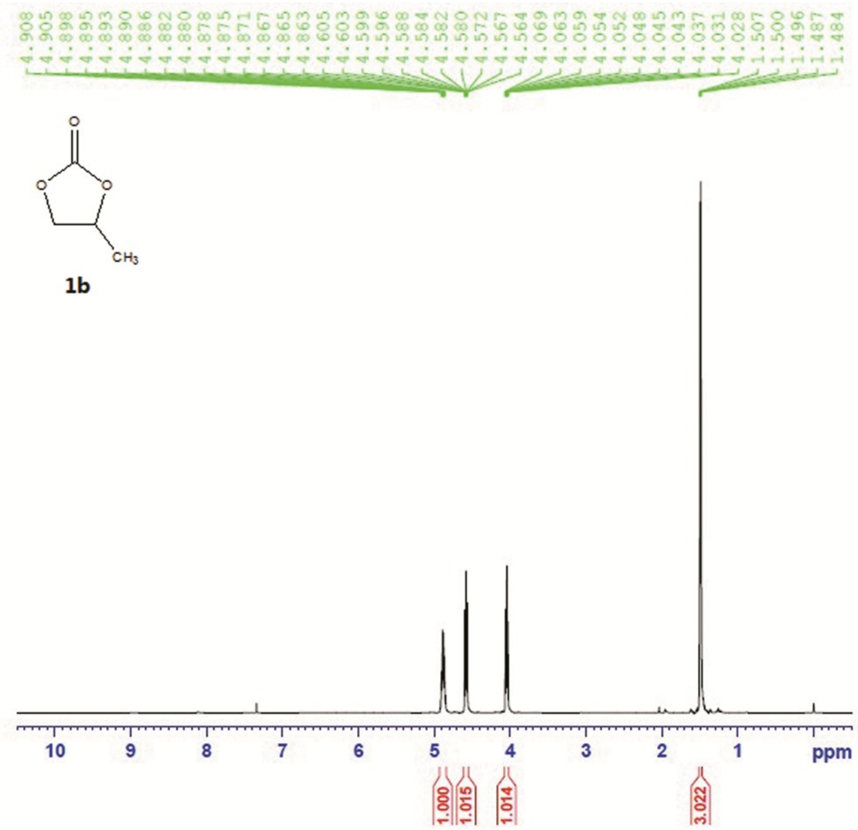


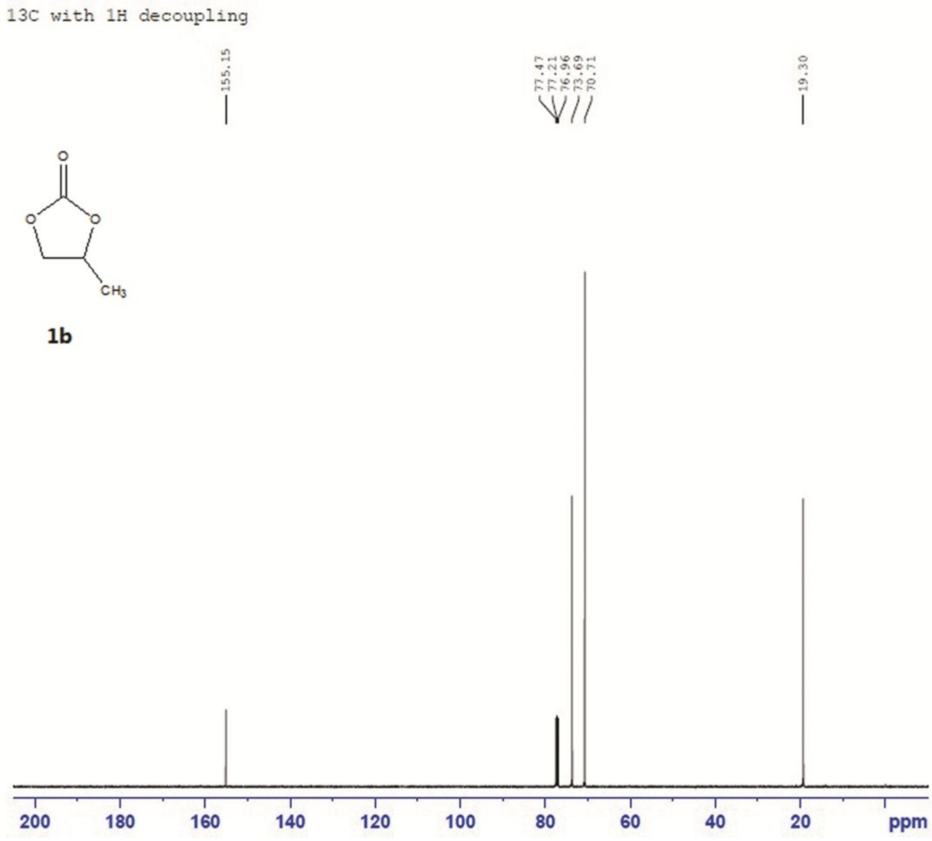
Reaction of (*R*)-Glycidyl benzyl ether was conducted according to the representative procedure, and the *ee* of the product was determined by chiral HPLC measurement using Chiralcel OD-3, 10% IPA/hexanes, 1 mL/min, t_R=34.19 min, t_S=39.17 min, 254 nm. Only minimal racemization of the product (98.3% ee) relative to the starting material (99% ee) was observed.



No.	Rt	Area	Area (%)	Height	NTP	Tf
1	34.19	8025074.8	99.1712	132345	7119.1	0.69
2	39.17	67065.382	0.8288	2601	60546.5	0.943

^{1}H and ^{13}C NMR Spectra:

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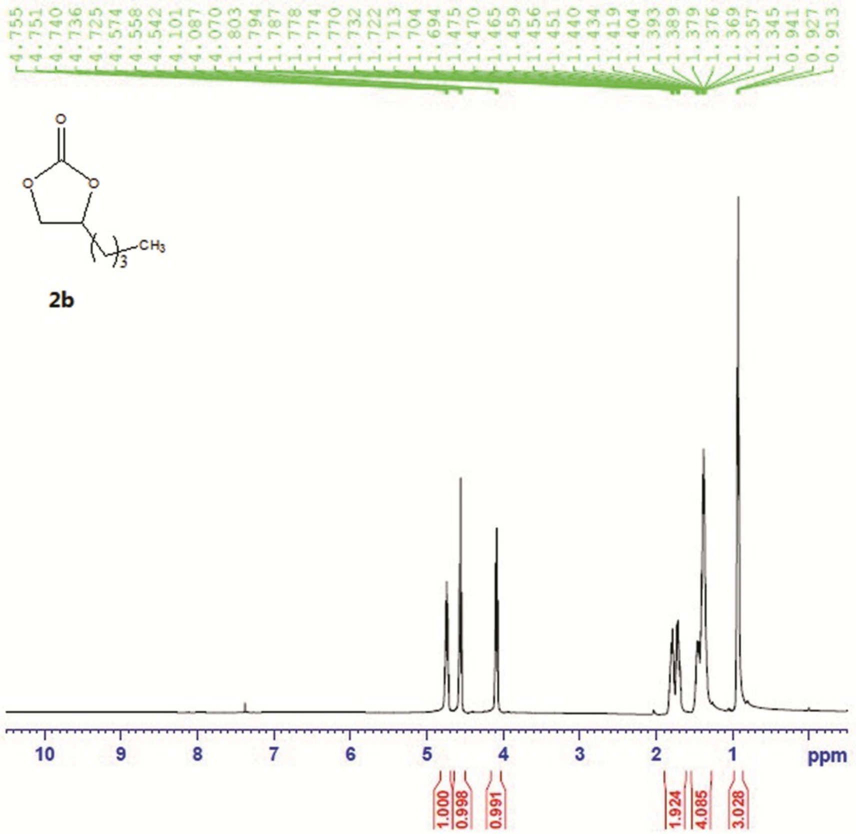
ppm

1b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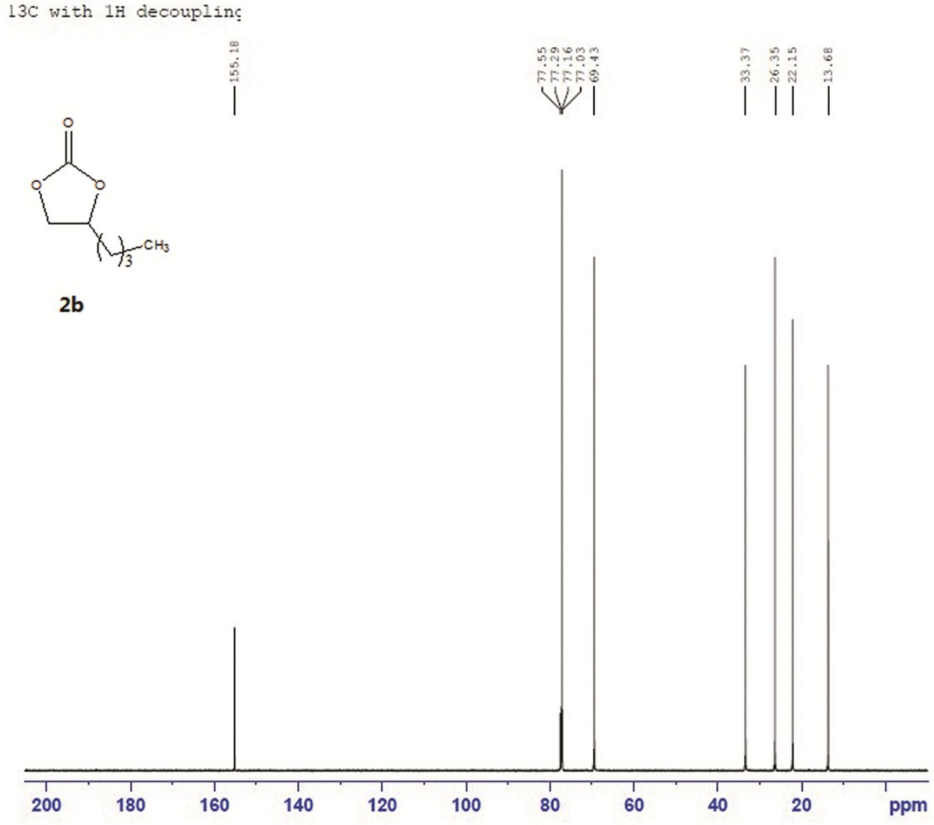
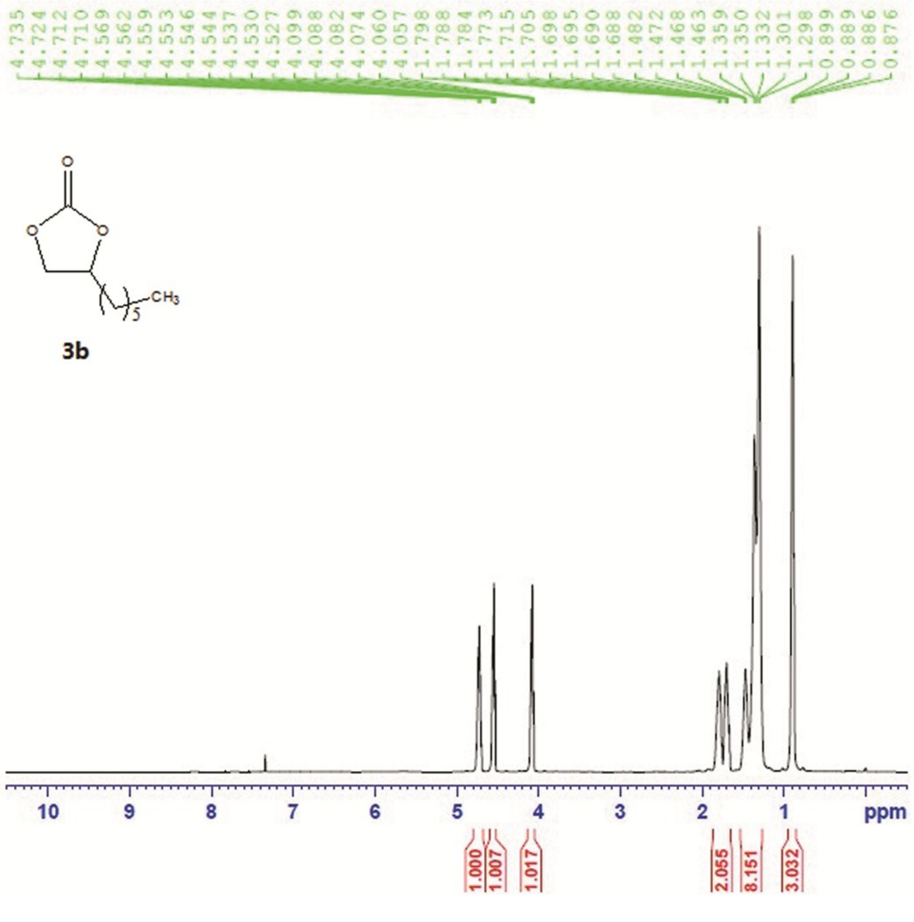
2b

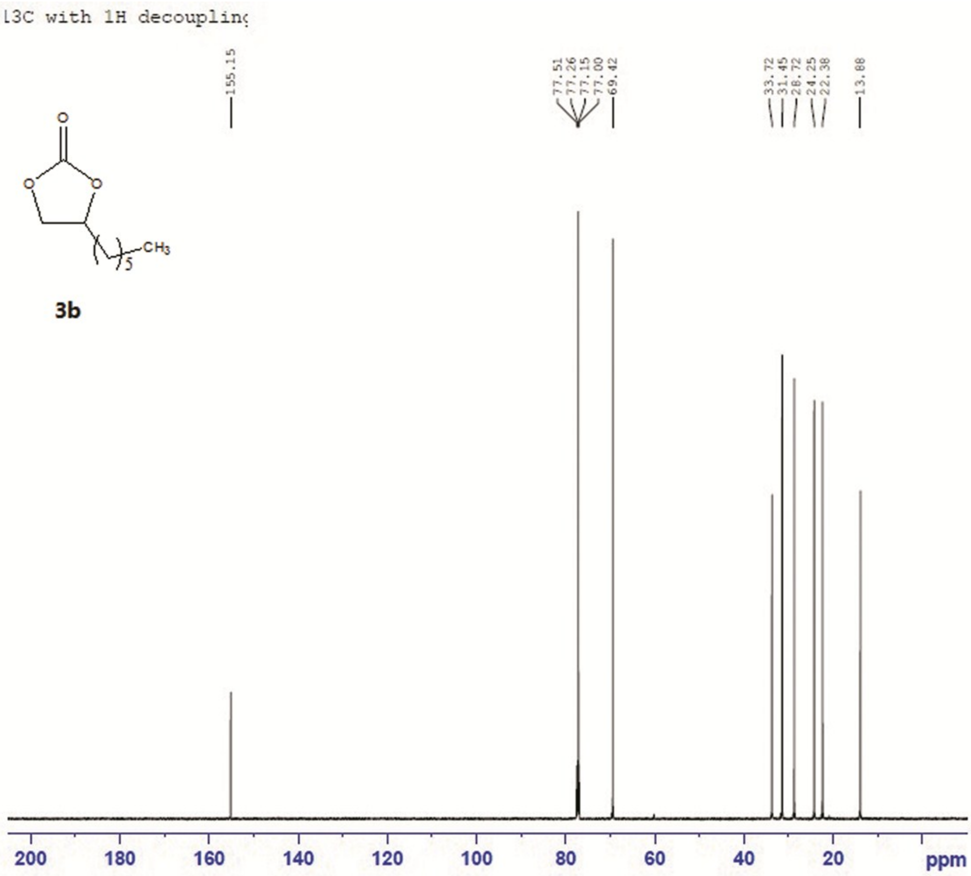
13C with 1H decoupling



2b



3b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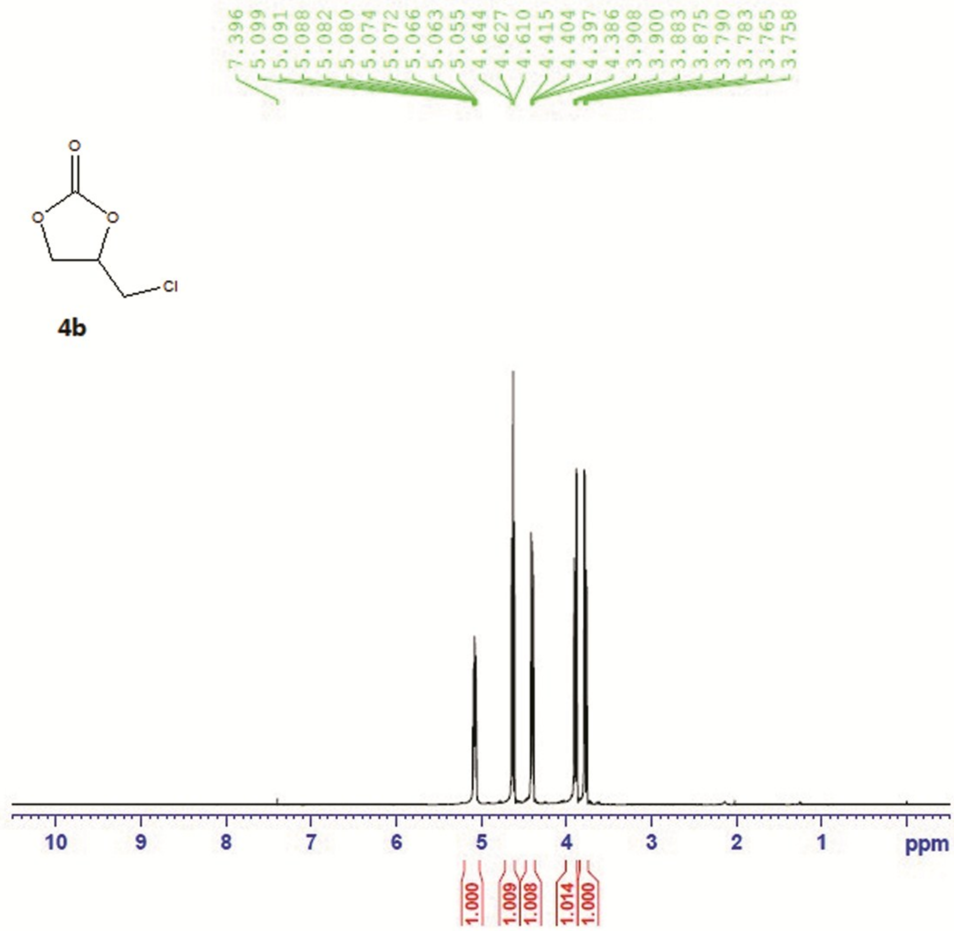
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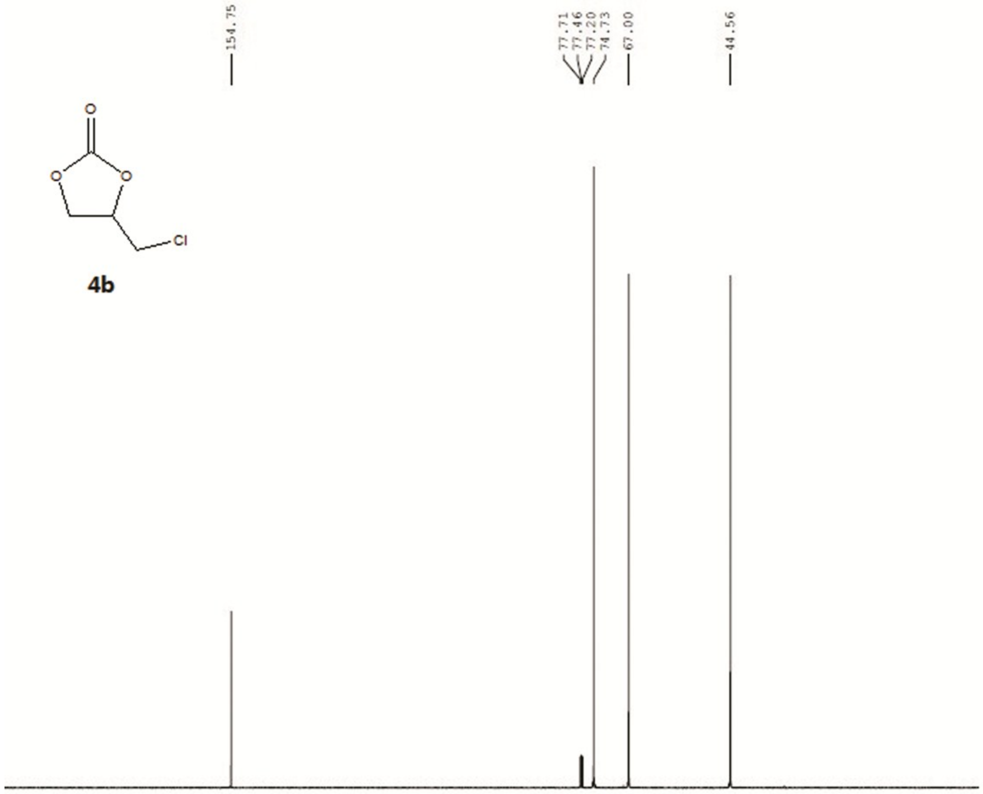
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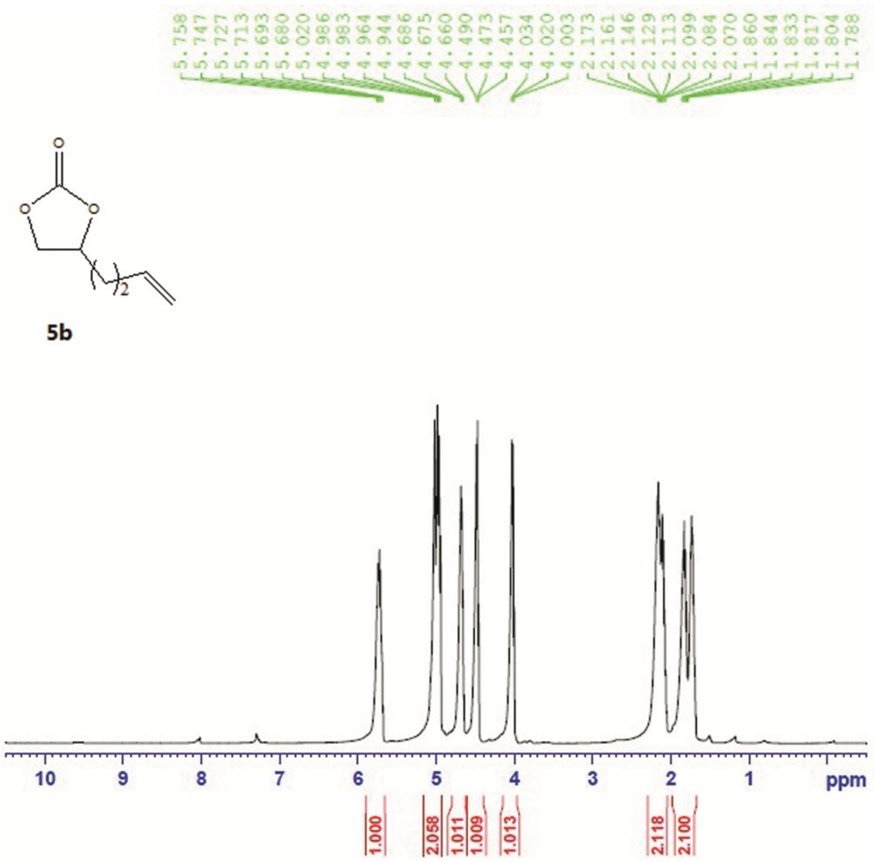
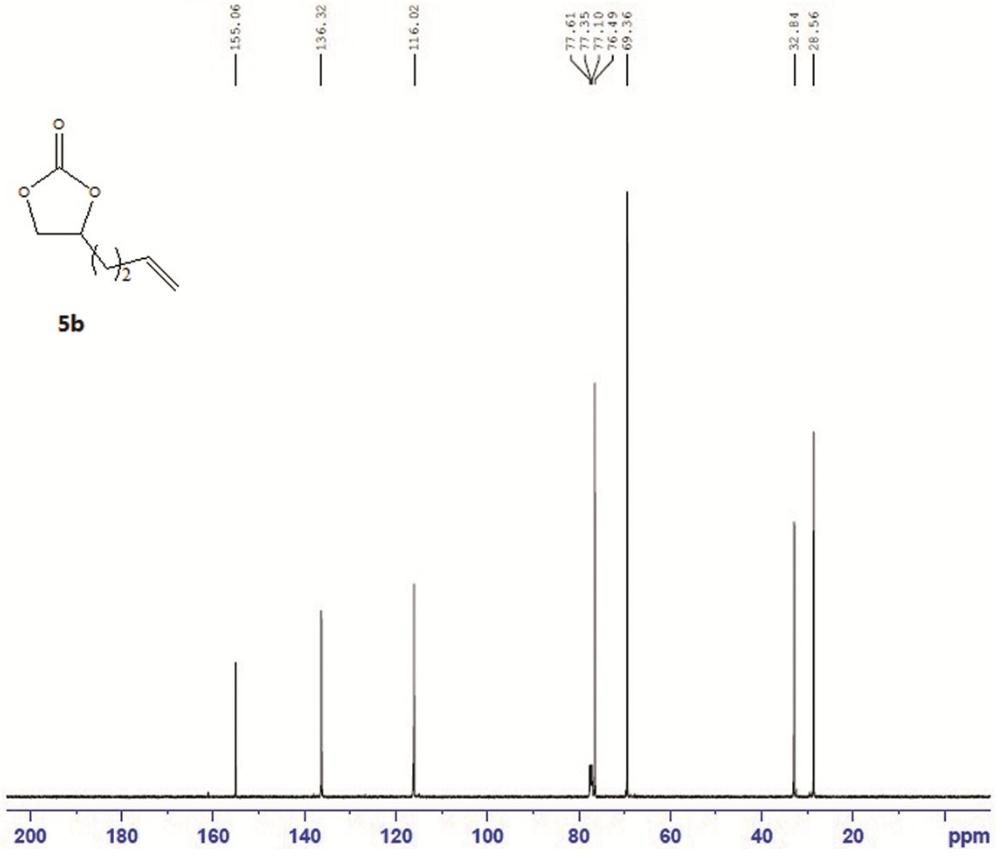
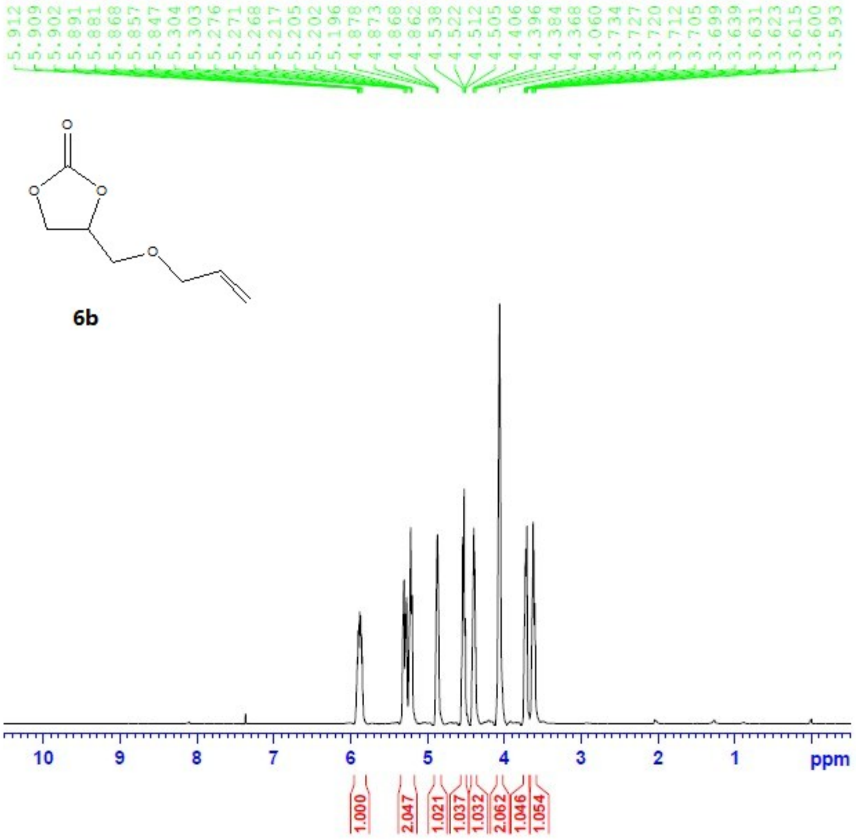
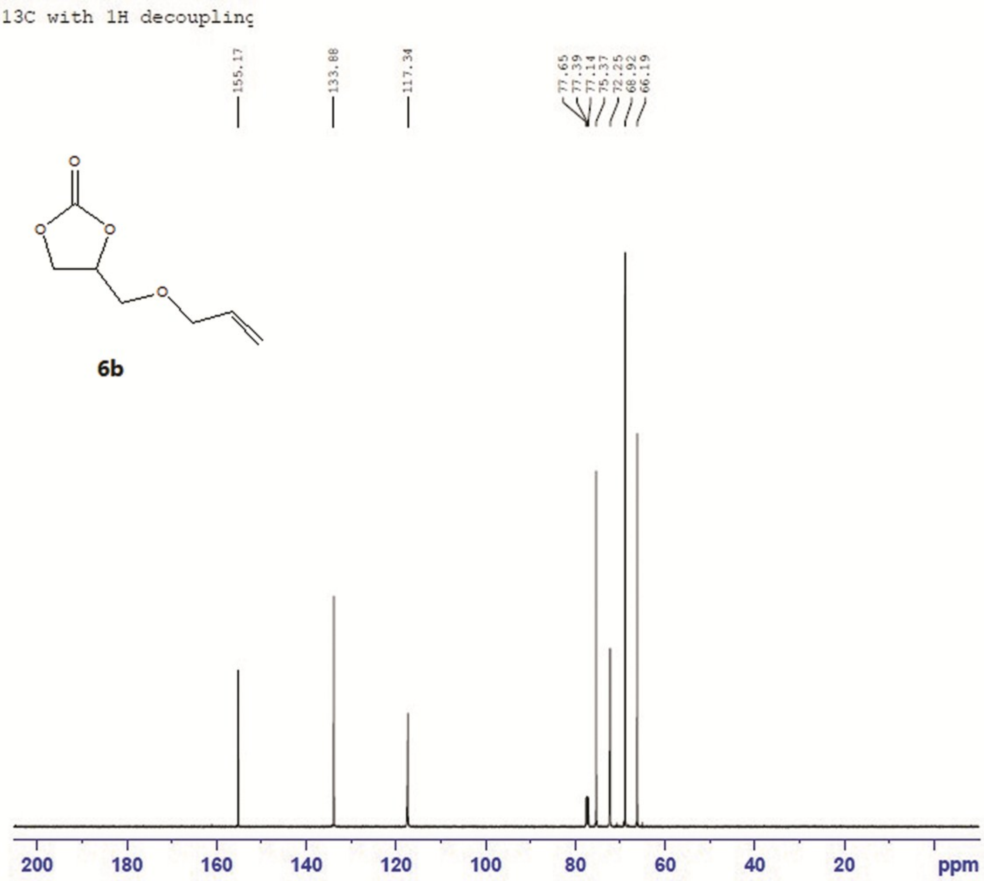
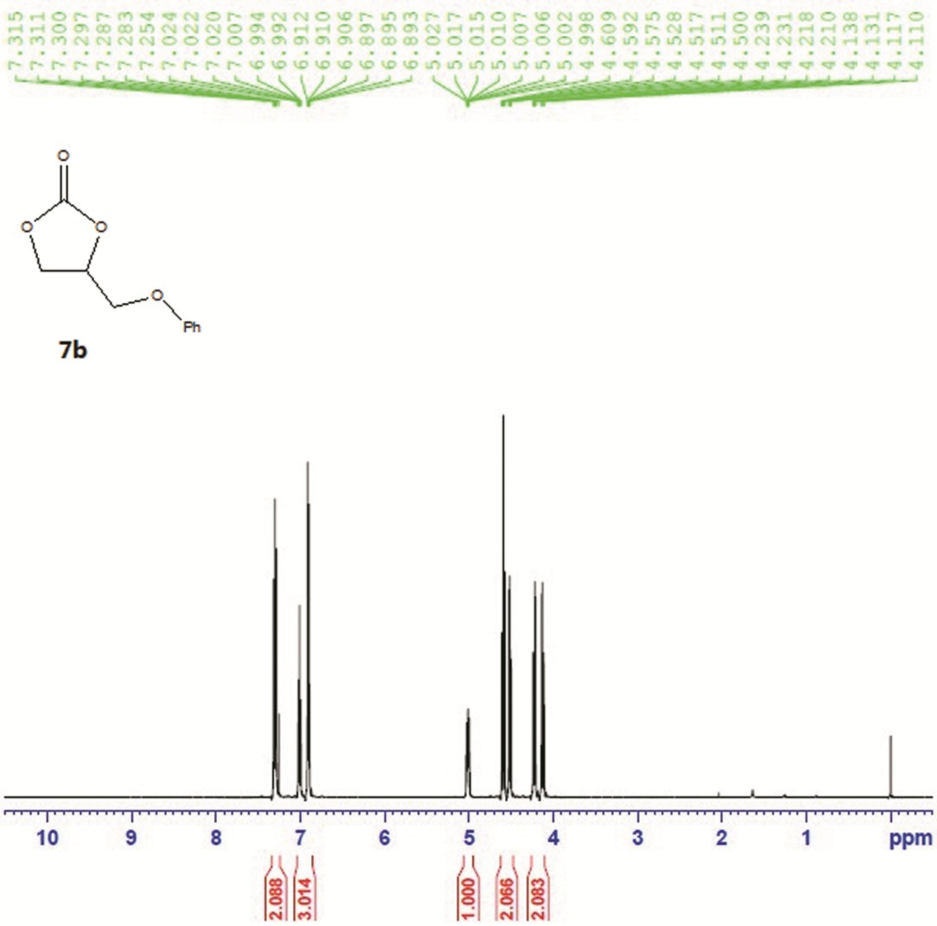


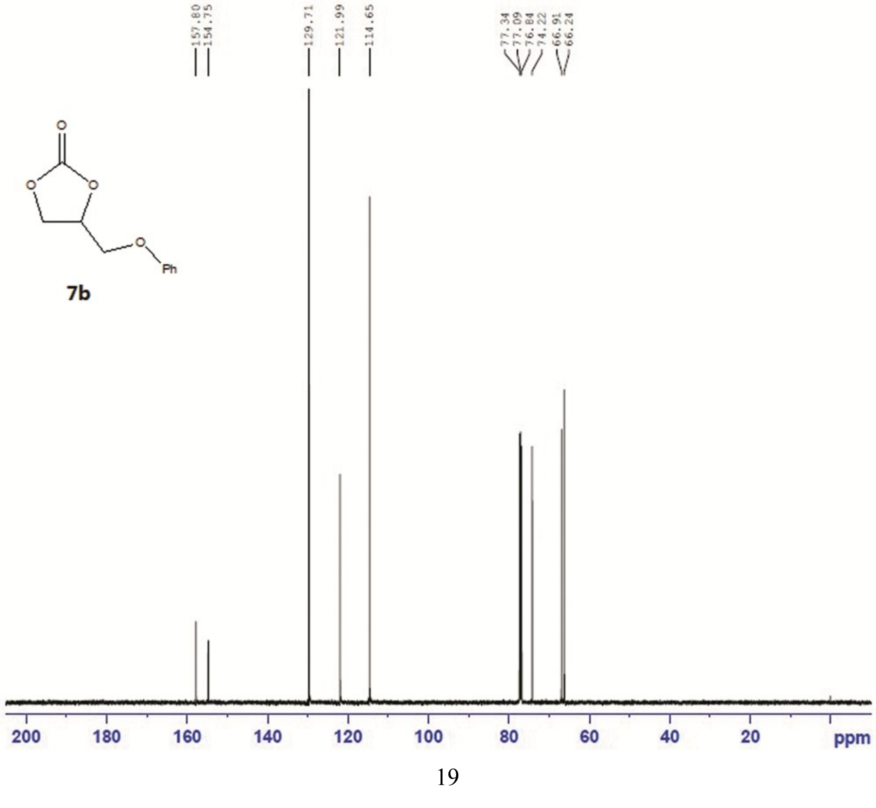
13C with 1H decoupling

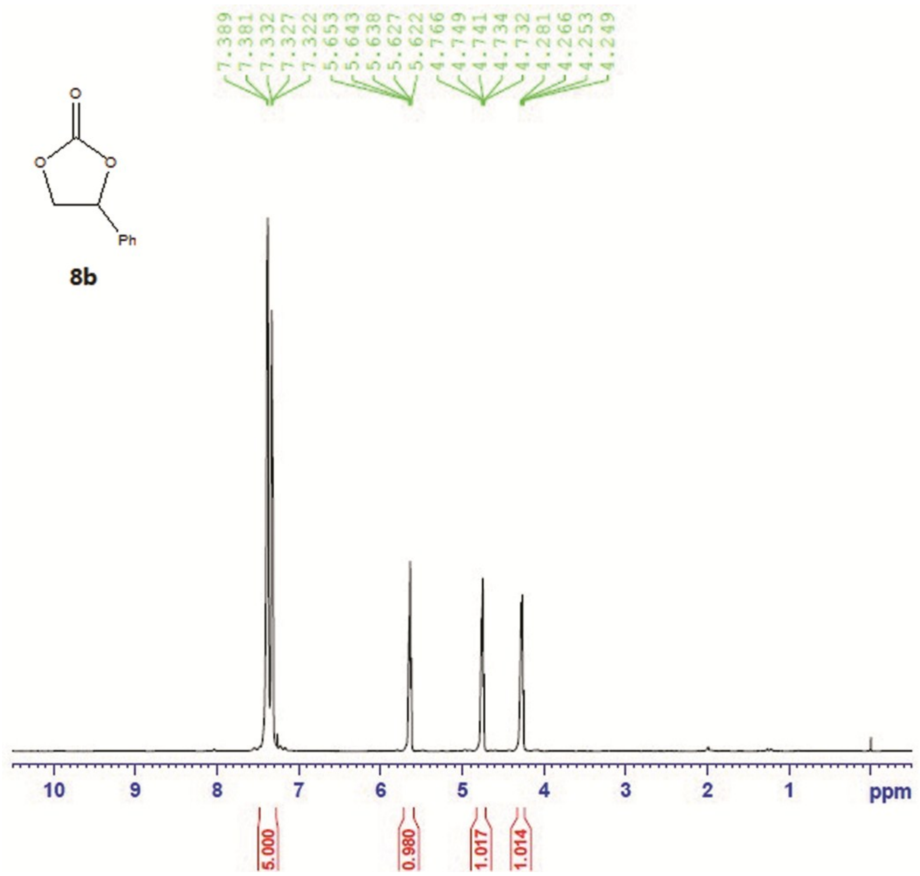


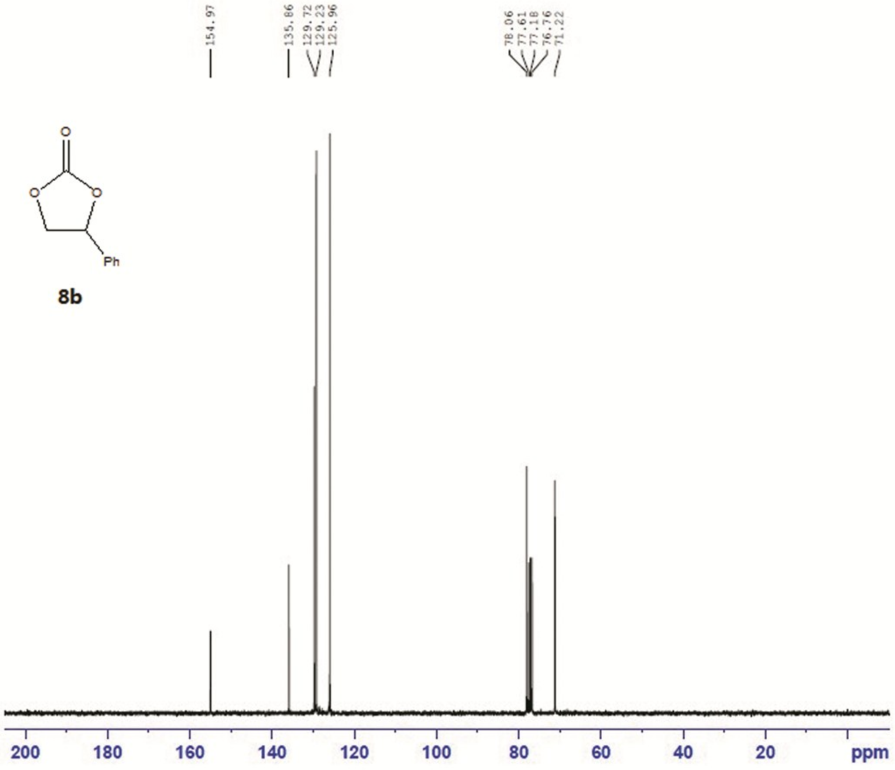

5.912
5.909
5.902
5.891
5.881
5.868
5.857
5.847
5.304
5.303
5.276
5.271
5.268
5.217
5.205
5.202
5.196
4.878
4.873
4.868
4.862
4.538
4.522
4.512
4.505
4.406
4.396
4.384
4.368
4.060
3.734
3.727
3.720
3.712
3.705
3.699
3.639
3.631
3.623
3.615
3.600
3.593
6b
10
9
8
7
6
5
4
3
2
1
ppm
1.000
2.047
1.021
1.037
1.032
2.062
1.046
1.054

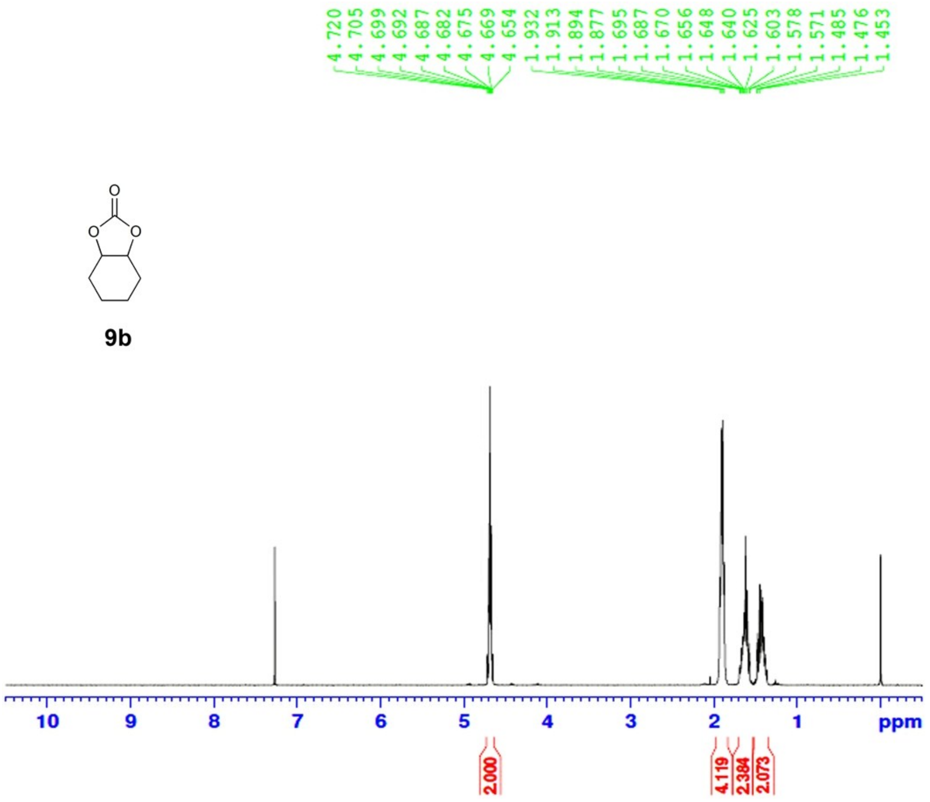

13C with 1H decoupling
155.17
133.88
117.34
77.65
77.39
77.14
75.37
72.25
68.92
66.19
6b
200
180
160
140
120
100
80
60
40
20
ppm

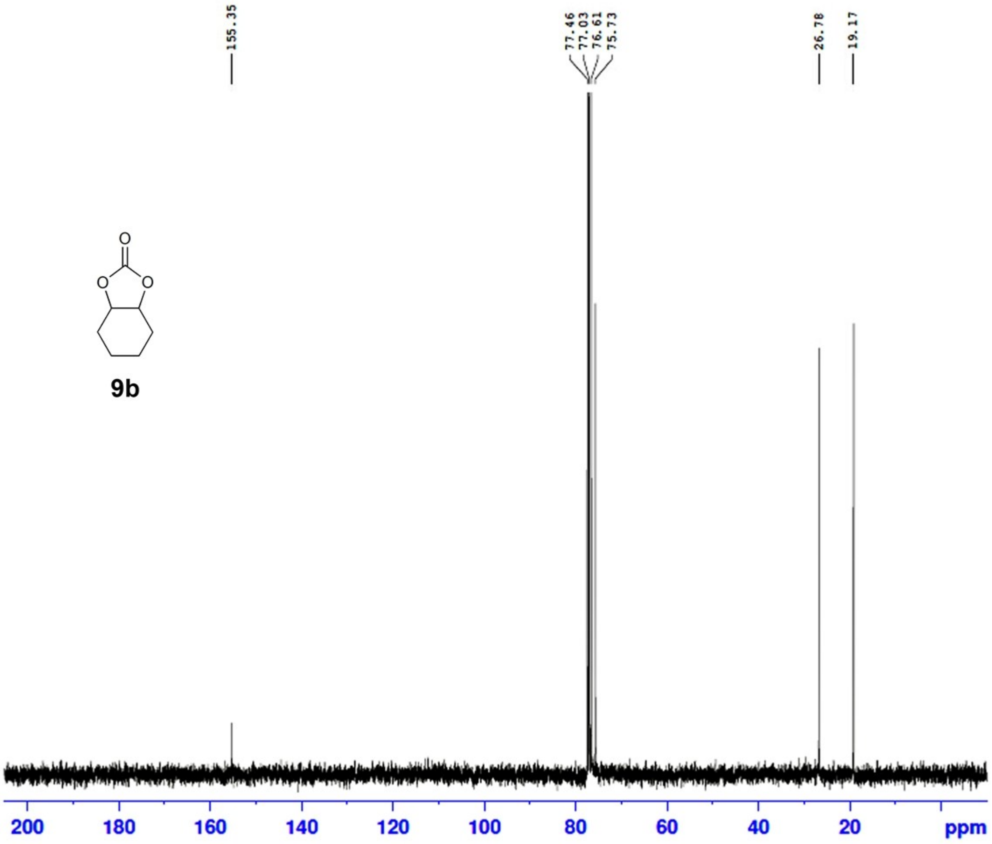

7.315
7.311
7.300
7.297
7.287
7.283
7.254
7.024
7.022
7.020
7.007
6.994
6.992
6.912
6.910
6.906
6.897
6.895
6.893
5.027
5.017
5.015
5.010
5.007
5.006
5.002
4.998
4.609
4.592
4.575
4.528
4.517
4.511
4.500
4.239
4.231
4.218
4.210
4.138
4.131
4.117
4.110
O
O
O
O
Ph
7b
10
9
8
7
6
5
4
3
2
1
ppm
2.088
3.014
1.000
2.066
2.083

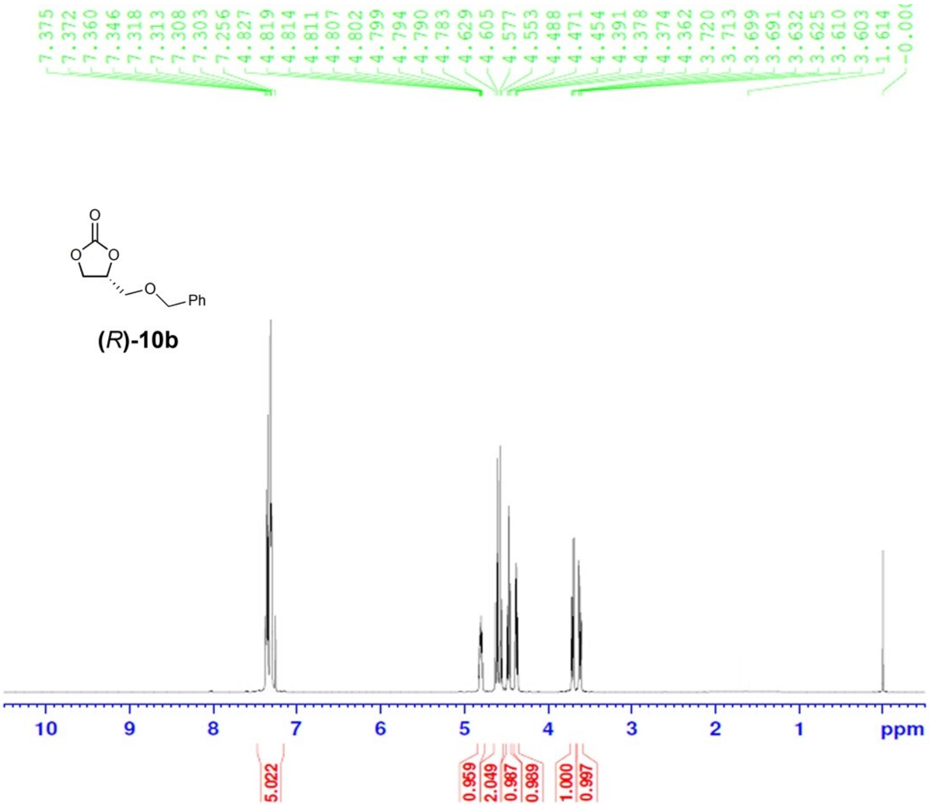

157.80
154.75
129.71
121.99
114.65
77.34
77.09
76.84
74.22
66.91
66.24
O
O
O
O
Ph
7b
200
180
160
140
120
100
80
60
40
20
ppm


7.389
7.381
7.332
7.327
7.322
5.653
5.643
5.638
5.627
5.622
4.766
4.749
4.741
4.734
4.732
4.281
4.266
4.253
4.249
O
O
O
Ph
8b
10
9
8
7
6
5
4
3
2
1
ppm
5.000
0.980
1.017
1.014

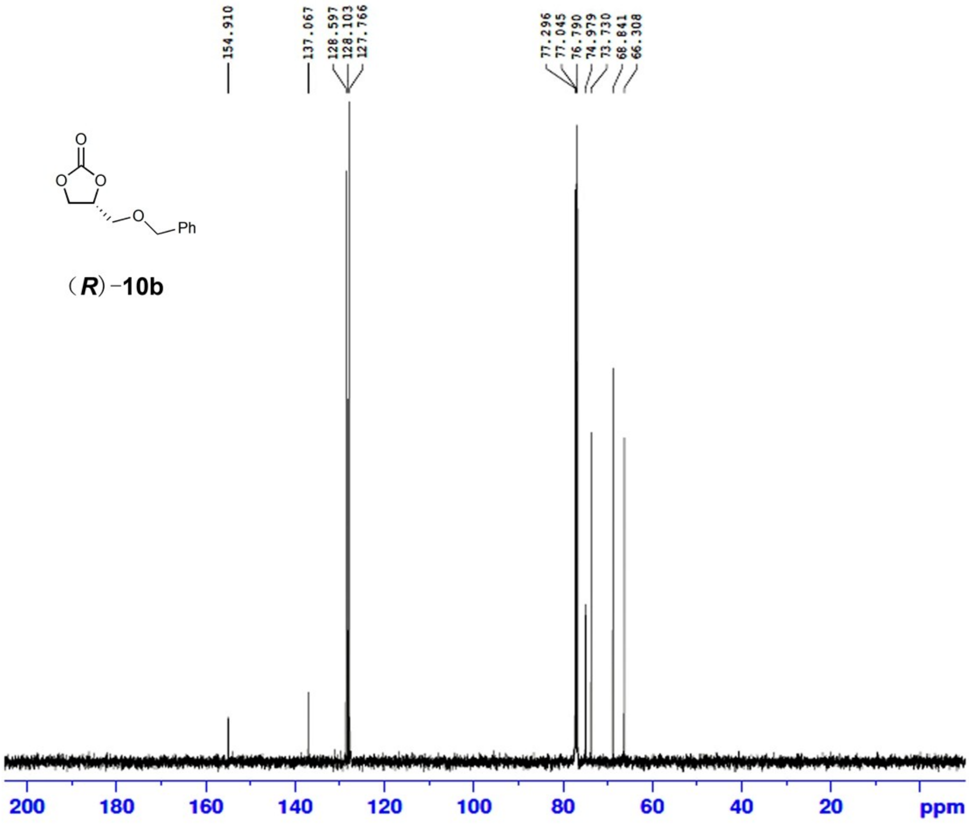

154.97
135.86
129.72
129.23
125.96
78.06
77.61
77.18
76.76
71.22
O
O
O
Ph
8b
200
180
160
140
120
100
80
60
40
20
ppm


4.720
4.705
4.699
4.692
4.687
4.682
4.675
4.669
4.654
1.932
1.913
1.894
1.877
1.695
1.687
1.670
1.656
1.648
1.640
1.625
1.603
1.578
1.571
1.485
1.476
1.453
9b
10
9
8
7
6
5
4
3
2
1
ppm
2.000
4.119
2.384
2.073


155.35
77.46
77.03
76.61
75.73
26.78
19.17
9b
200
180
160
140
120
100
80
60
40
20
ppm


7.375
7.372
7.360
7.346
7.318
7.313
7.308
7.303
7.256
4.827
4.819
4.814
4.811
4.807
4.802
4.799
4.794
4.790
4.783
4.629
4.605
4.577
4.553
4.488
4.471
4.454
4.391
4.378
4.374
4.362
3.720
3.713
3.699
3.691
3.632
3.625
3.610
3.603
1.614
-0.00
O
O
O
O
Ph
10
9
8
7
6
5
4
3
2
1
ppm
5.022
0.959
2.049
0.987
0.989
1.000
0.997

(*R*)-**10b**


154.910
137.067
128.597
128.103
127.766
77.296
77.045
76.790
74.979
73.730
68.841
66.308
O
O
O
O
Ph
200
180
160
140
120
100
80
60
40
20
ppm

（***R***）-**10b**