Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Organic base/benzyl bromide: an efficient catalytic system for chemical fixation of CO_2 into cyclic carbonates under metal- and solvent-free conditions

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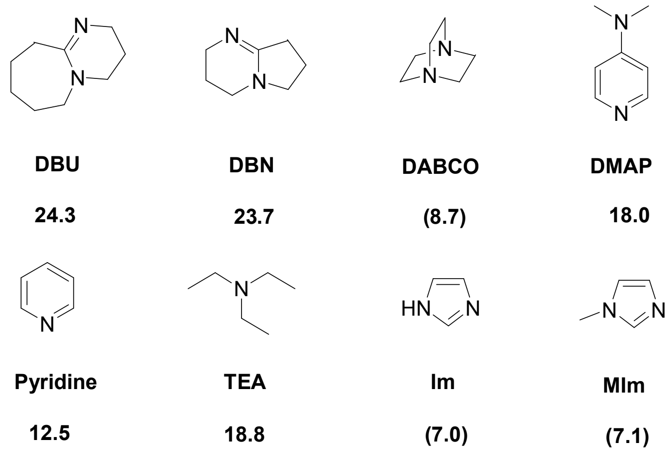
Experimental Section



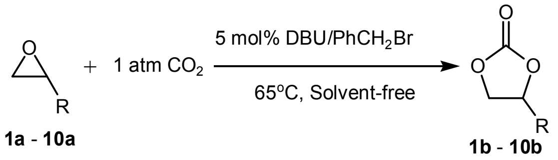
Scheme S1 Chemical structures and designations of the organic bases used in this work.

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. 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. Enantiomeric excesses of the carbonates were determined by HPLC analyses with a Daicel Chiralcel OD-3 with detection at 254 nm.

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), DBU (5 mol%, 0.046g) and $PhCH_2Br$ (5 mol%, 0.051g) were added and stirred at 65 °C for 22 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 0.778g (yield: 95.0%).

^{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), DBU (5 mol%, 0.046g) and $PhCH_2Br$ (5 mol%, 0.051g) 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 0.502 g (yield: 82.0%).

^{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), DBU (5 mol%, 0.046g) and $PhCH_2Br$ (5 mol%, 0.051g) 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 0.735 g (yield: 85%).

^1H 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), DBU (5 mol%, 0.046g) and $PhCH_2Br$ (5 mol%, 0.051g) 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 0.568 g (yield: 55%).

^1H 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), DBU (5 mol%, 0.046g) and $PhCH_2Br$ (5 mol%, 0.051g) 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 0.691 g (yield: 81%).

^{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), DBU (5 mol%, 0.046g) and $PhCH_2Br$ (5 mol%, 0.051g) 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 0.807 g (yield: 85%).

^{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**, 6 mmol, 0.900 g), DBU (5 mol%, 0.046g) and $PhCH_2Br$ (5 mol%, 0.051g) 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 1.09 g (yield: 94%).

^{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), DBU (5 mol%, 0.046g) and $PhCH_2Br$ (5 mol%, 0.051g) were added and stirred at 65 °C for 22 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 0.806 g (yield: 82.0%).

^{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), DBU (5 mol%, 0.046g) and $PhCH_2Br$ (5 mol%, 0.051g) were added and stirred at 95 °C for 22 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 0.251 g (yield: 31.0%).

^{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.

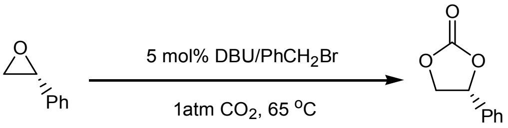
(*R*)-4-Benzyloxymethyl-1,3-dioxolan-2-one ((*R*)-10b)

(*R*)-Glycidyl benzyl ether (**10a**, 6 mmol, 0.985 g), DBU (5 mol%, 0.046g) and $PhCH_2Br$ (5 mol%, 0.051g) 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 1.10g (yield: 89%).

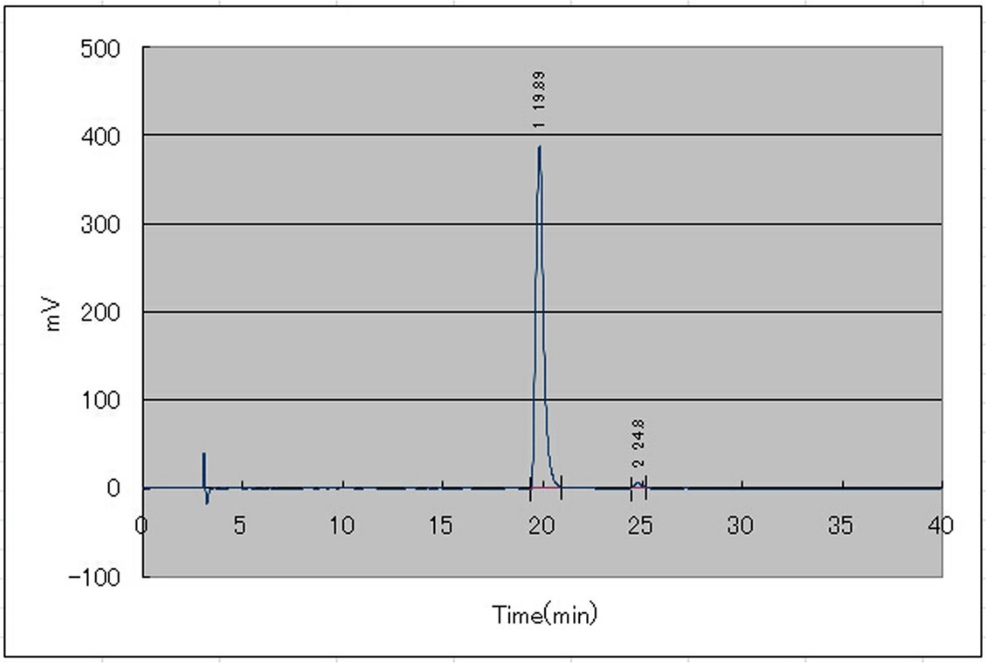
^{1}H NMR (500 MHz, $CDCl_3$): 7.40-7.27 (m, 5H), 4.88-4.75 (m, 1H), 4.55 (q, J = 12.0 Hz, 2H), 4.47 (t, J = 8.5 Hz, 1H), 4.37 (dd, J = 8.5 Hz, 6.5 Hz, 1H), 3.71 (dd, J = 10.5 Hz, 3.5 Hz, 1H), 3.61 (dd, J = 11.0 Hz, 3.5 Hz, 1H) ^{13}C NMR (125 MHz, $CDCl_3$): 154.91, 137.06, 128.59, 128.1, 127.77, 74.98, 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=19.89 min, t_S=24.8 min, 254 nm. Minimal racemization of the product (98% *ee*) relative to the starting material (99% *ee*) was observed.



No.	Rt	Area	Area (%)	Height	NTP	Tf
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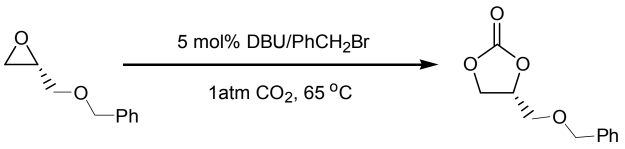
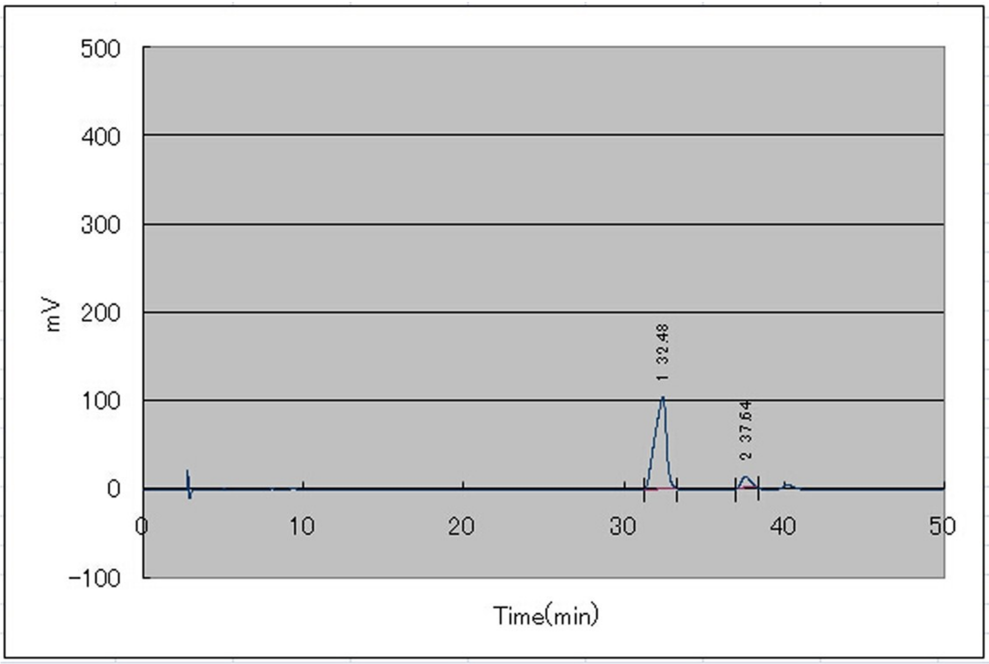
2	24.8	121119.3	1.0555	5258	27084.8	1.089

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

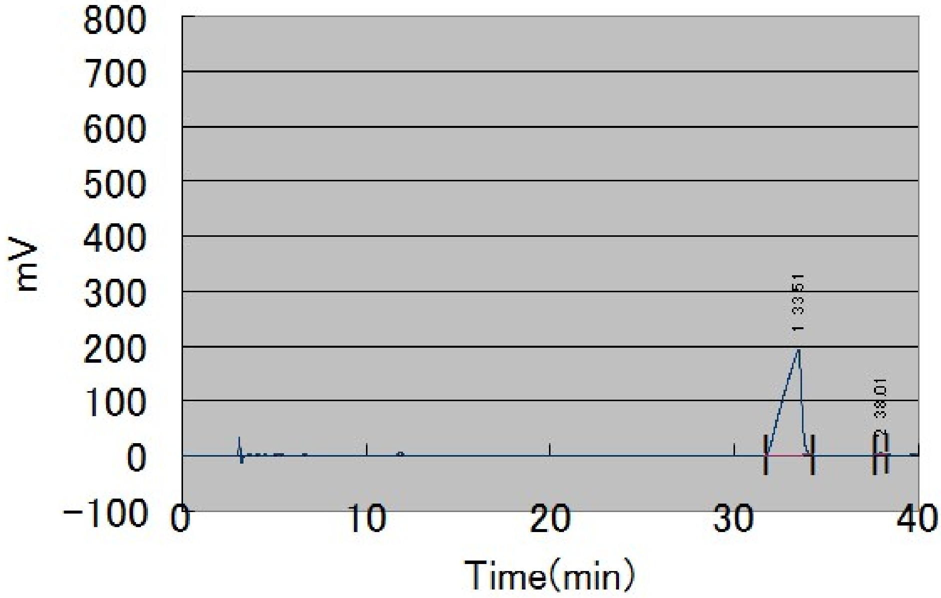


Reaction of (*R*)-Glycidyl benzyl ether was conducted according to the representative procedure, and the *ee* of the product was determined by chiral HPLC measurement using Chiralcel OD-3, 10% IPA/hexanes, 1 mL/min, t_R=32.48 min, t_S=37.64 min, 254 nm. Some racemization of the product (84% *ee*) relative to the starting material (99% *ee*) was observed.



No.	Rt	Area	Area (%)	Height	NTP	Tf
1	32.48	5129703.029	91.9748	103839	9651.7	0.782
2	37.64	447591.732	8.0252	12465	25039	1.181

When only DBU was used as catalyst, (*R*)-**10b** was obtained in 35% yield with retention of stereochemistry (>99% *ee*), and the *ee* of the product was determined under the same condition.



No.	Rt	Area	Area (%)	Height	NTP	Tf
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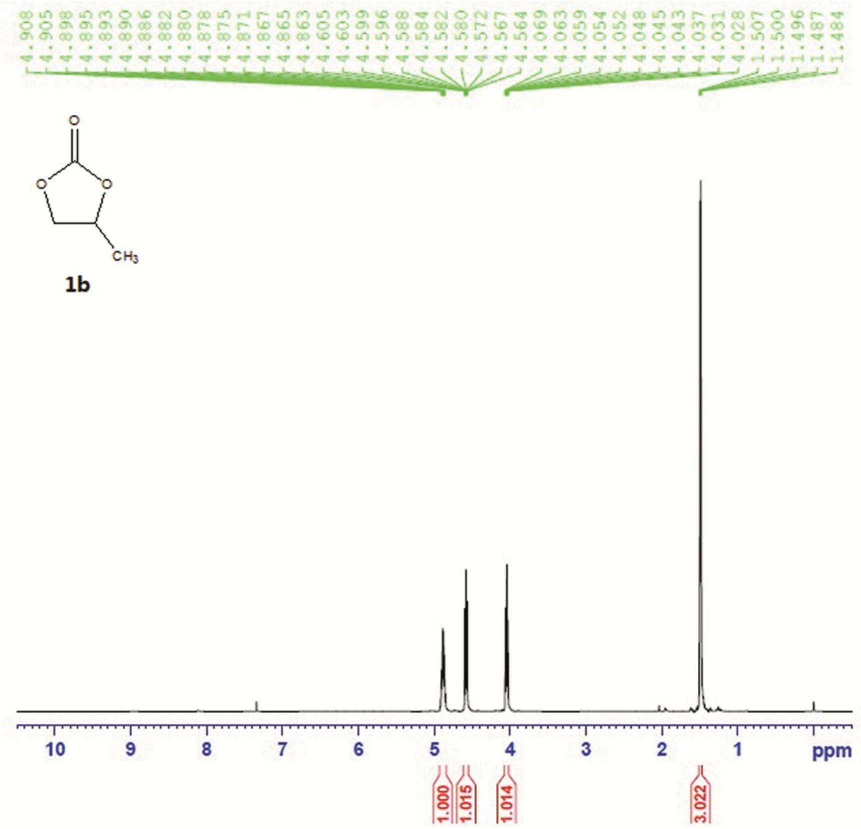
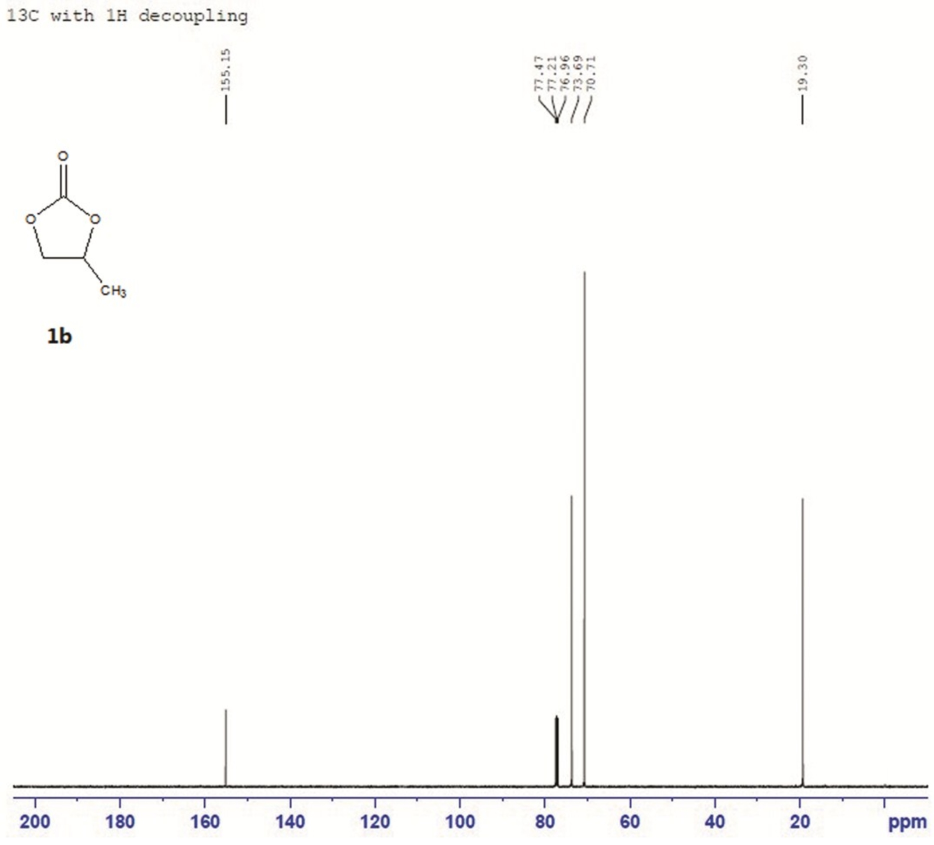
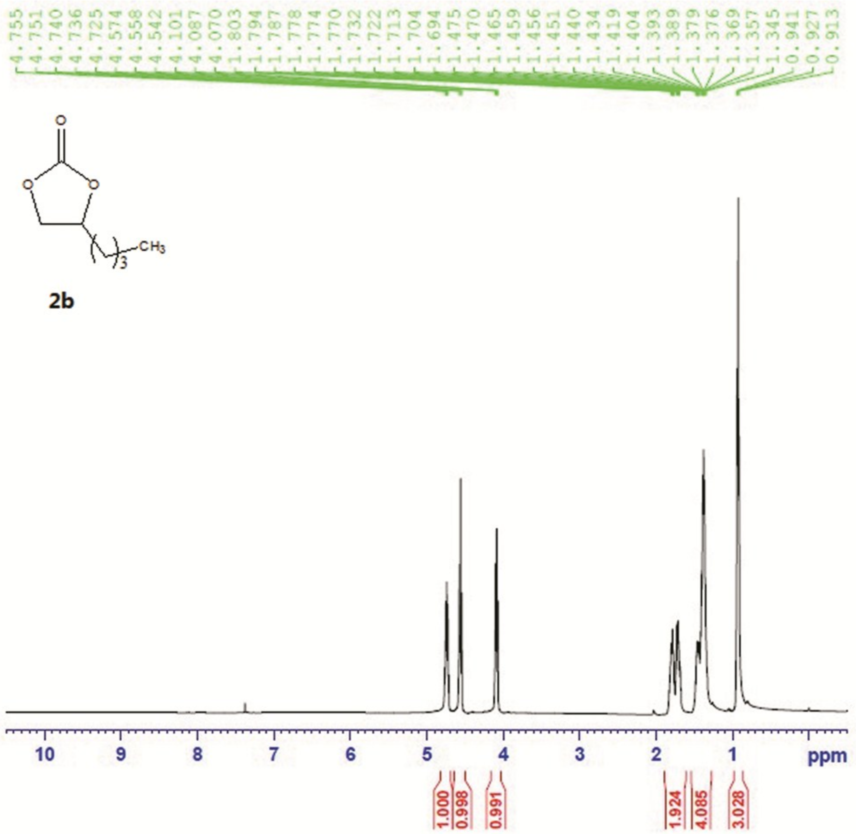
2	38.01	52386.3	0.4126	2211	25032	1.091

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



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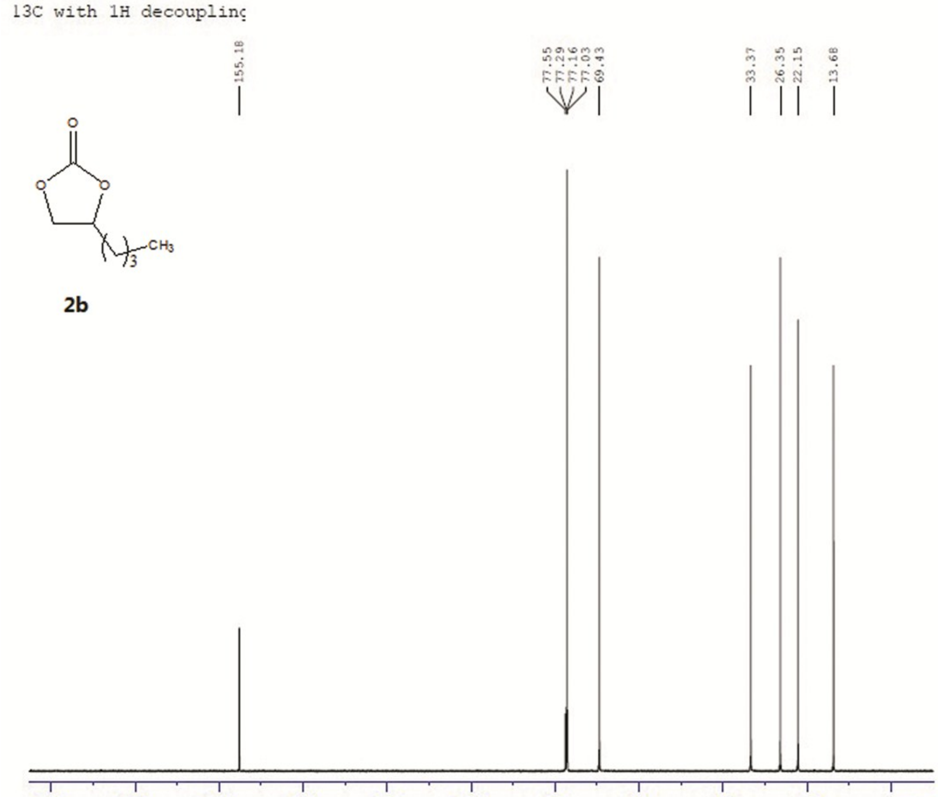
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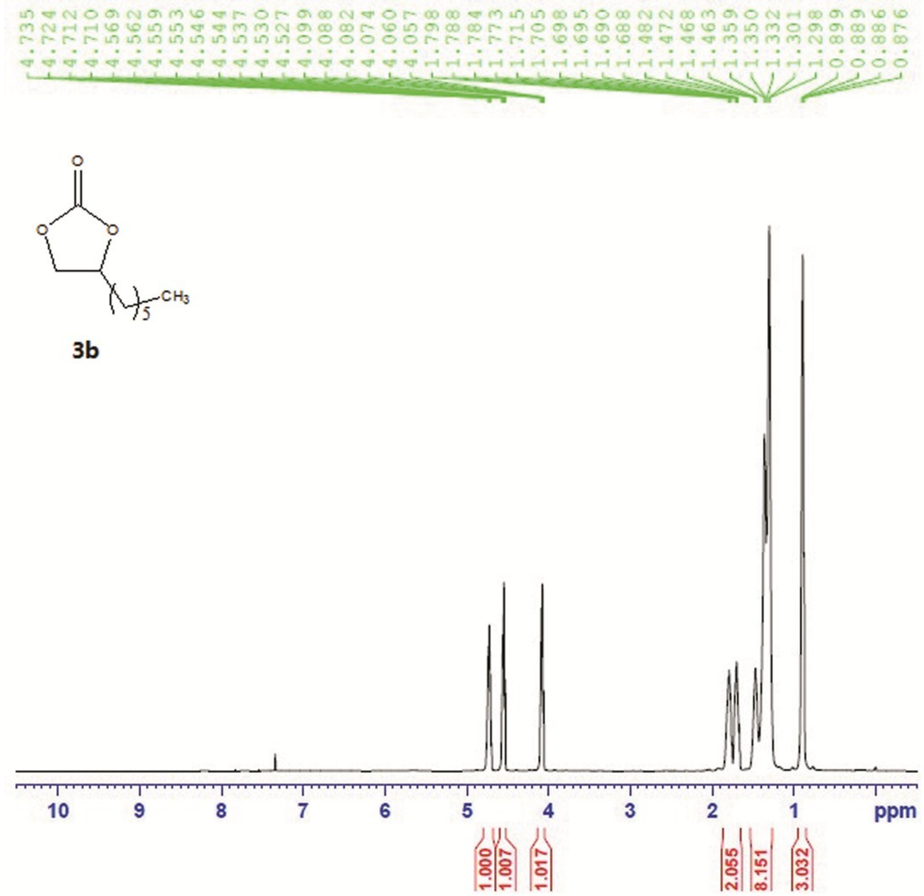
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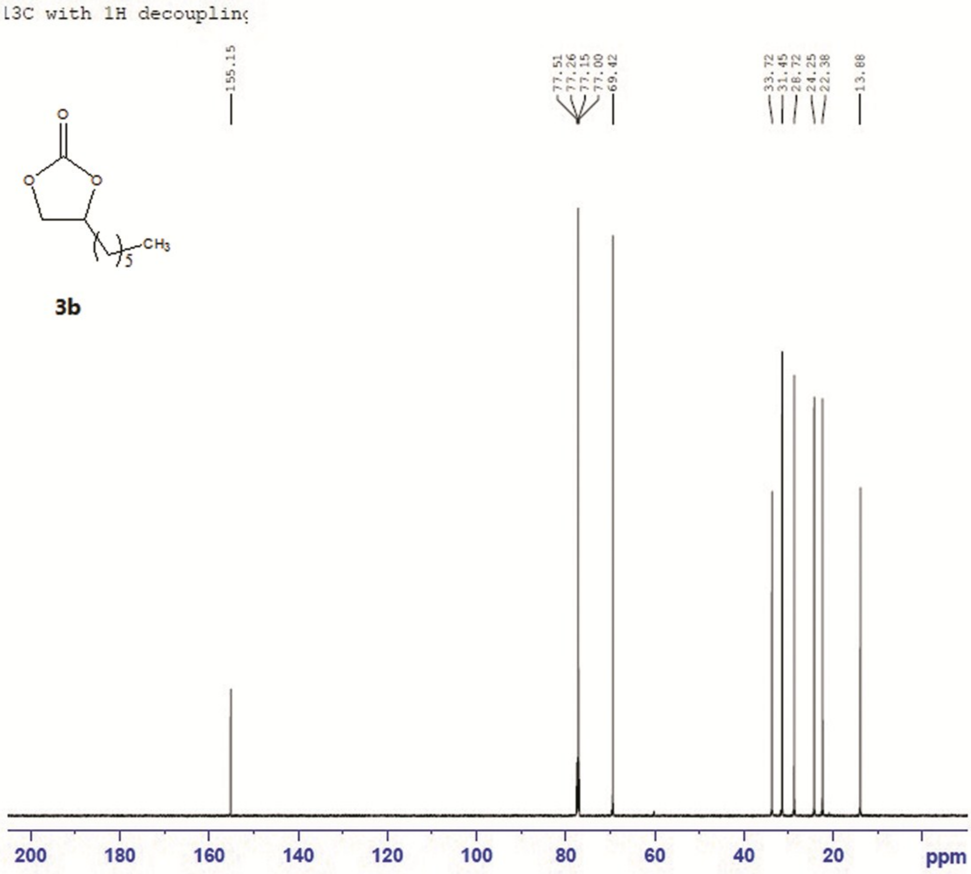
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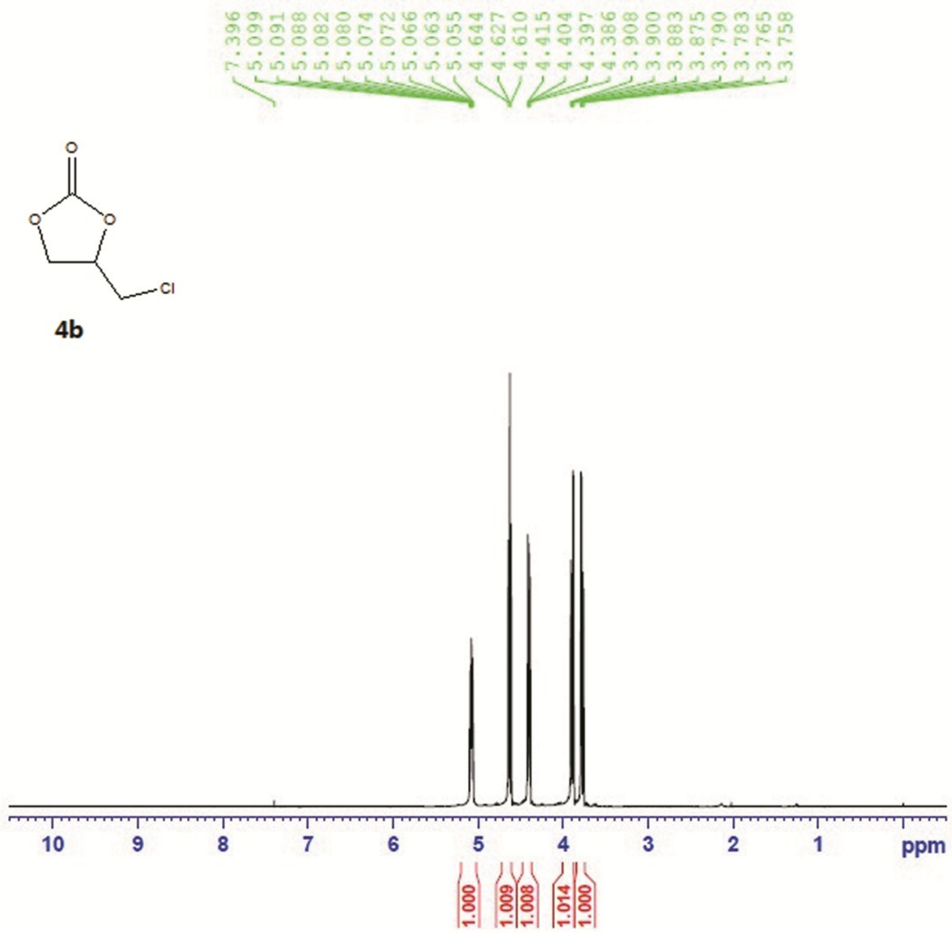
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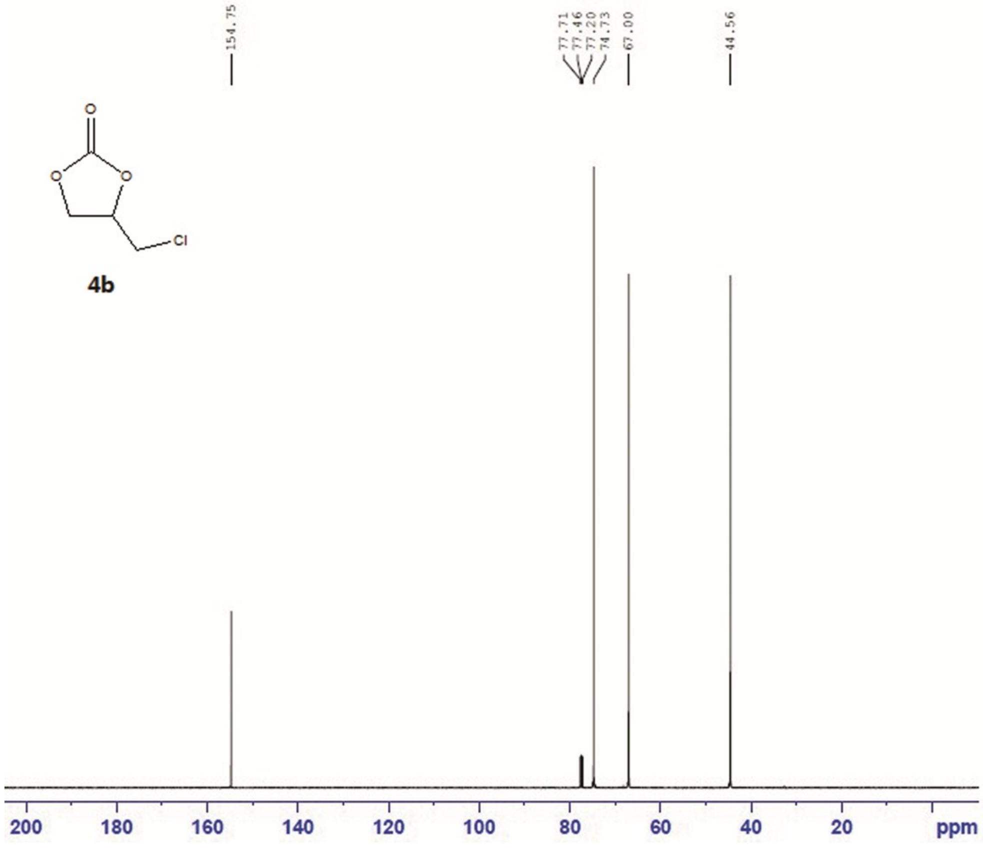
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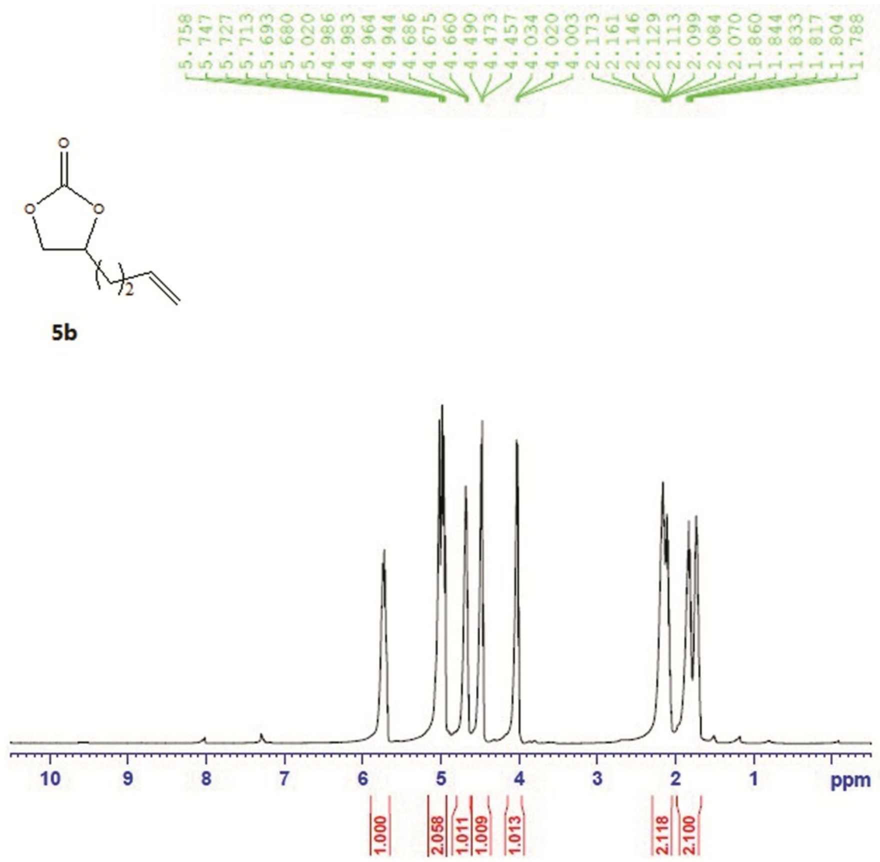
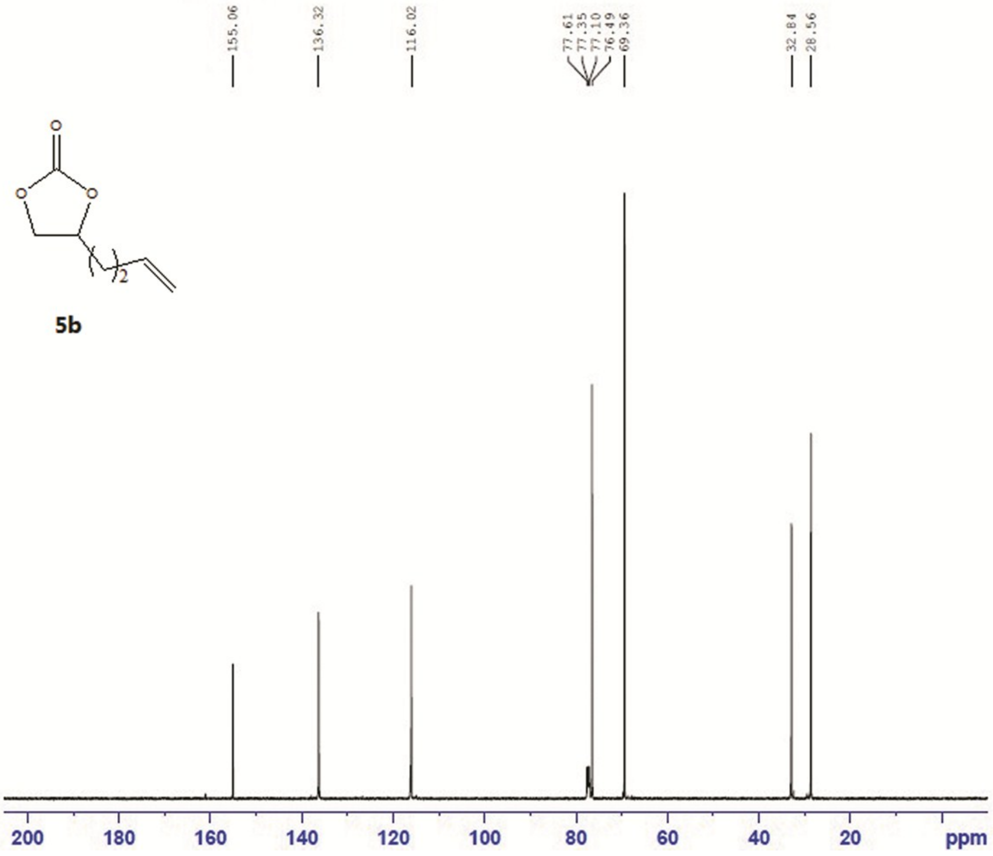
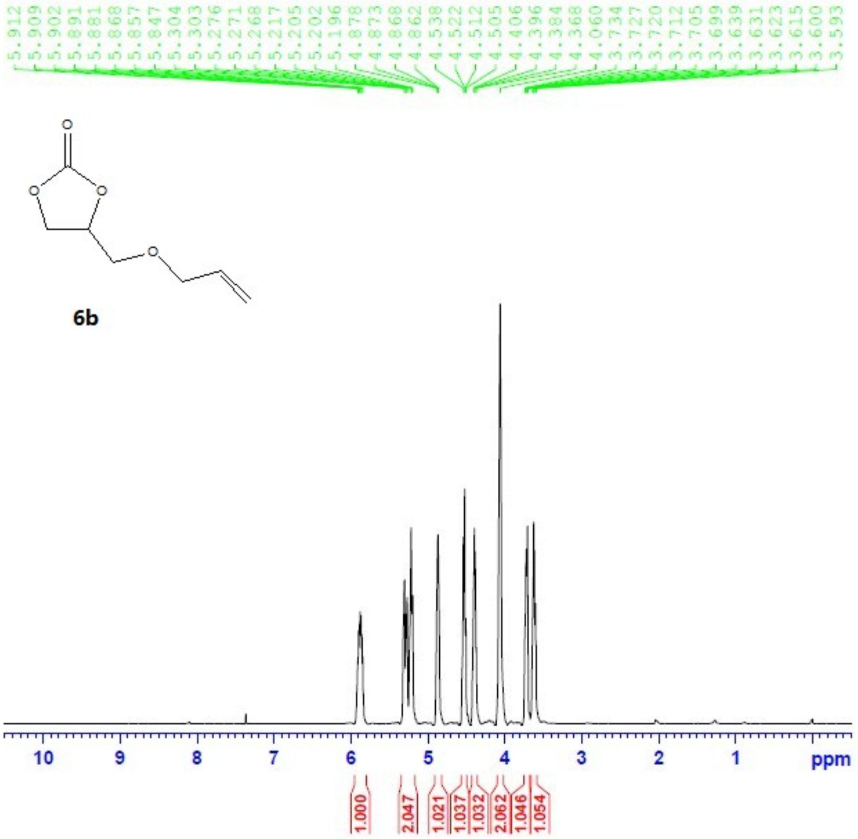


5b

13C with 1H decoupling



5b



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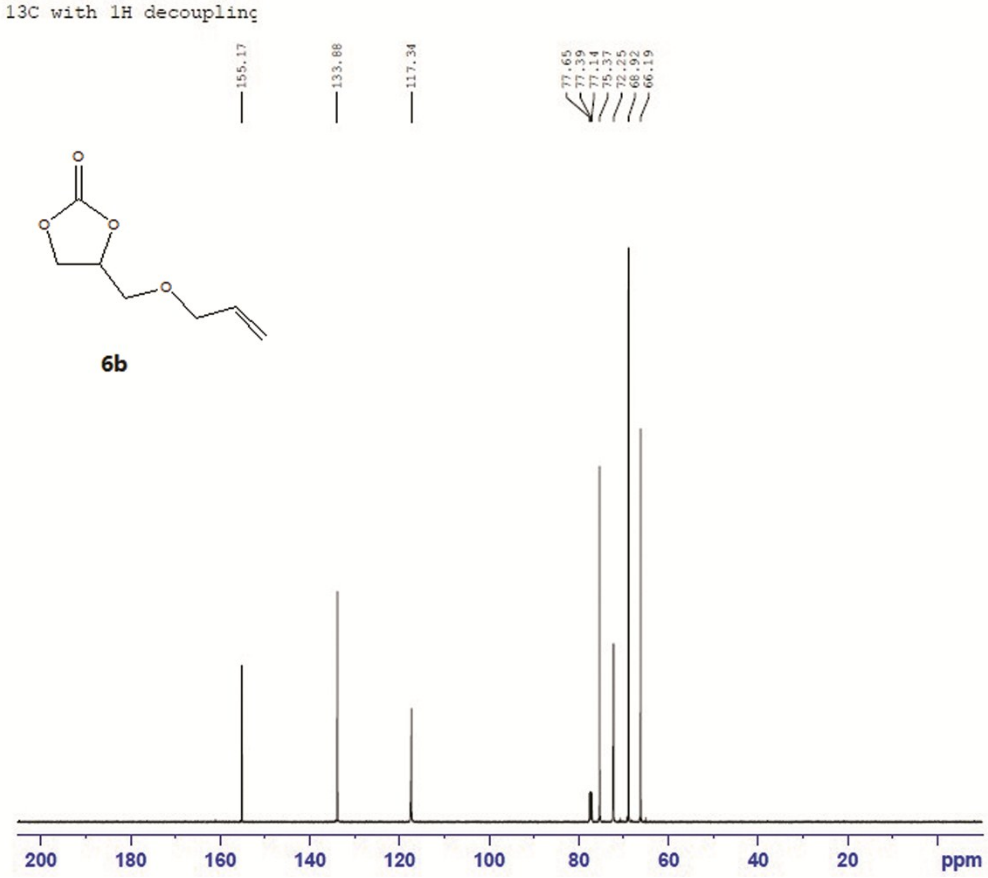
6b



13C with 1H decoupling
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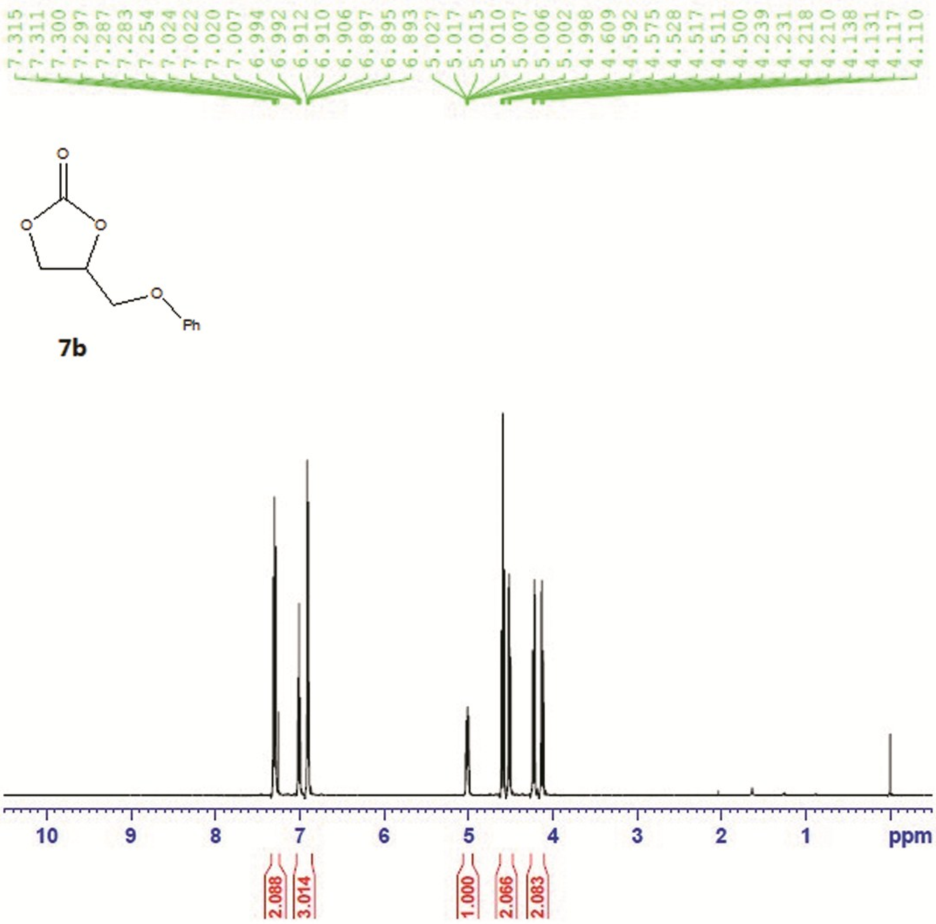
6b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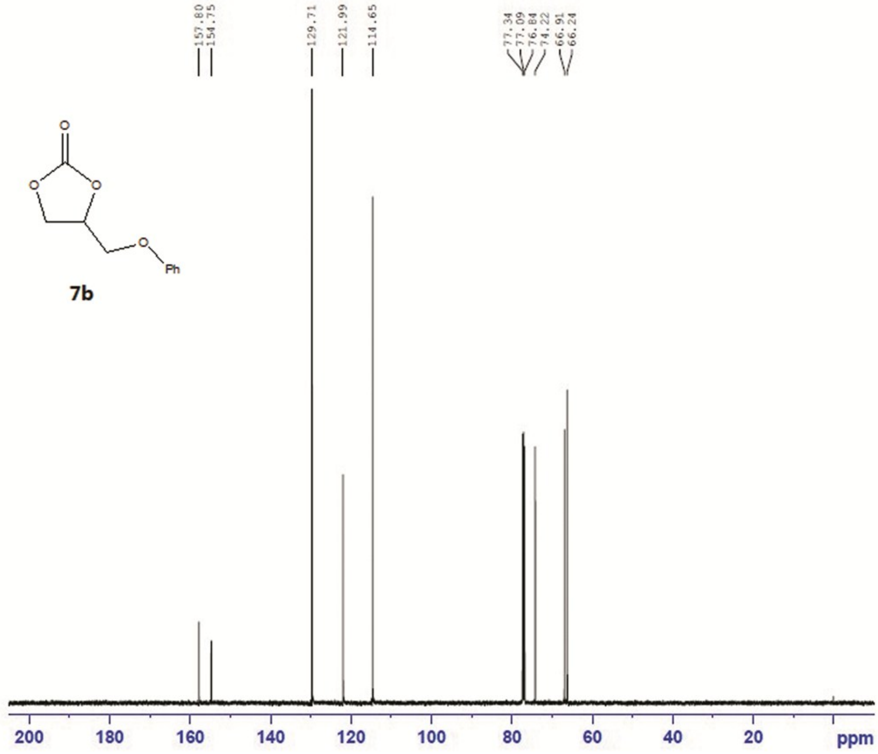
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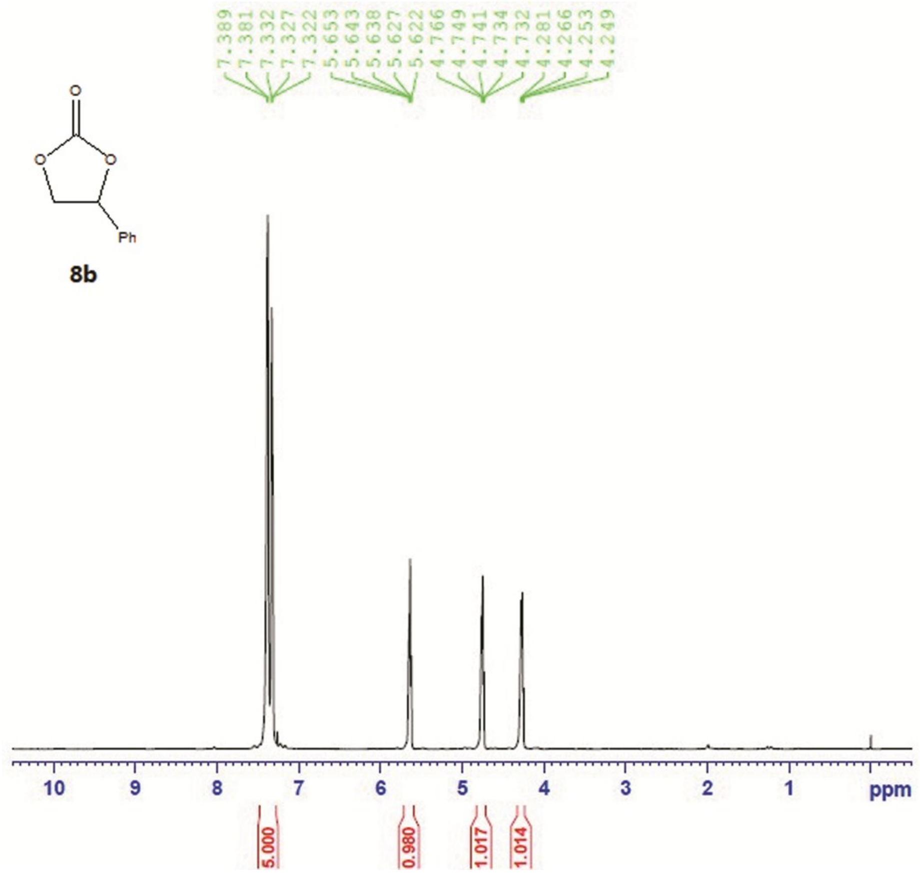
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O
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8b
10
9
8
7
6
5
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3
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ppm
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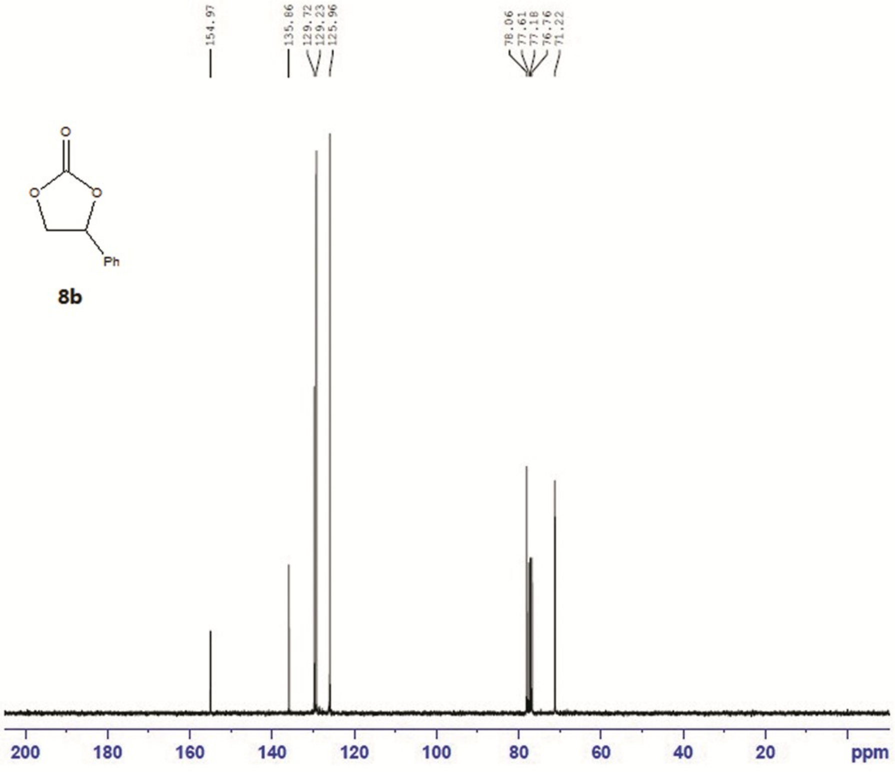
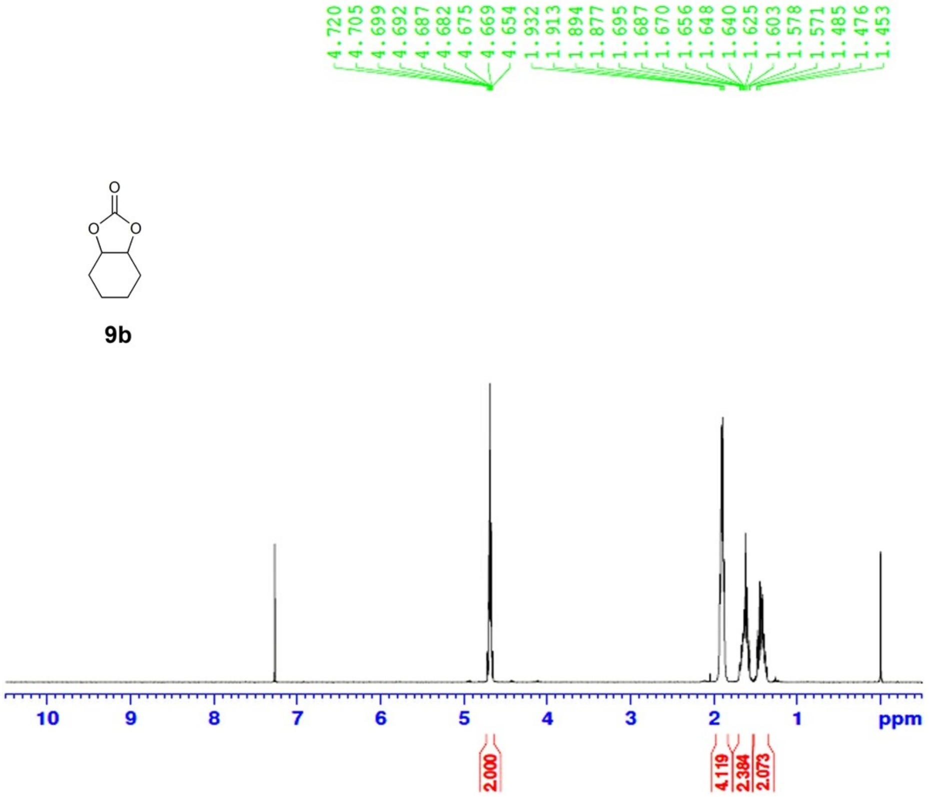
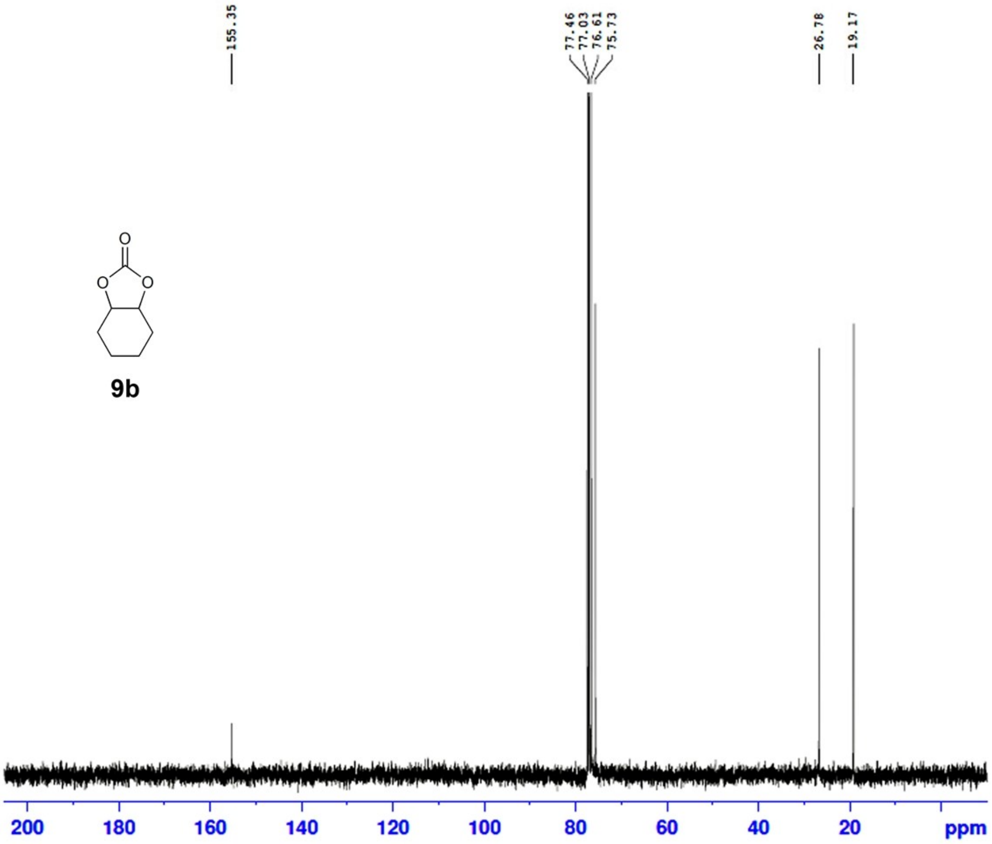
1.017
1.014


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
O
O
O
9b
10
9
8
7
6
5
4
3
2
1
ppm
2.000
4.119
2.384
2.073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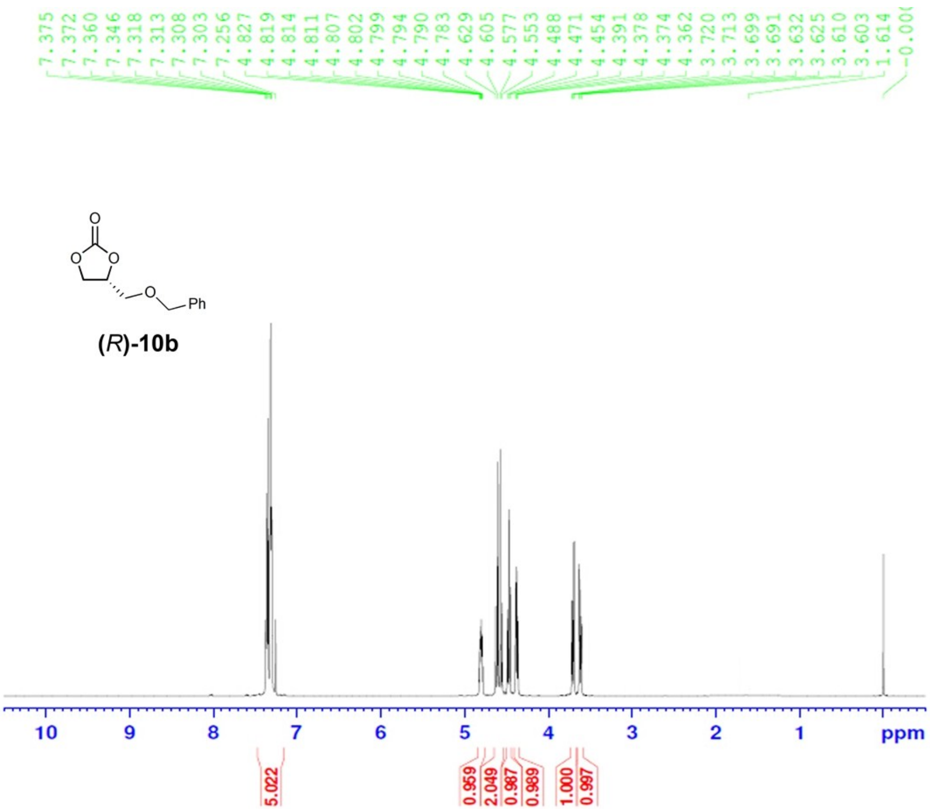
77.46
77.03
76.61
75.73
26.78
19.17
O
O
O
9b
200
180
160
140
120
100
80
60
40
20
ppm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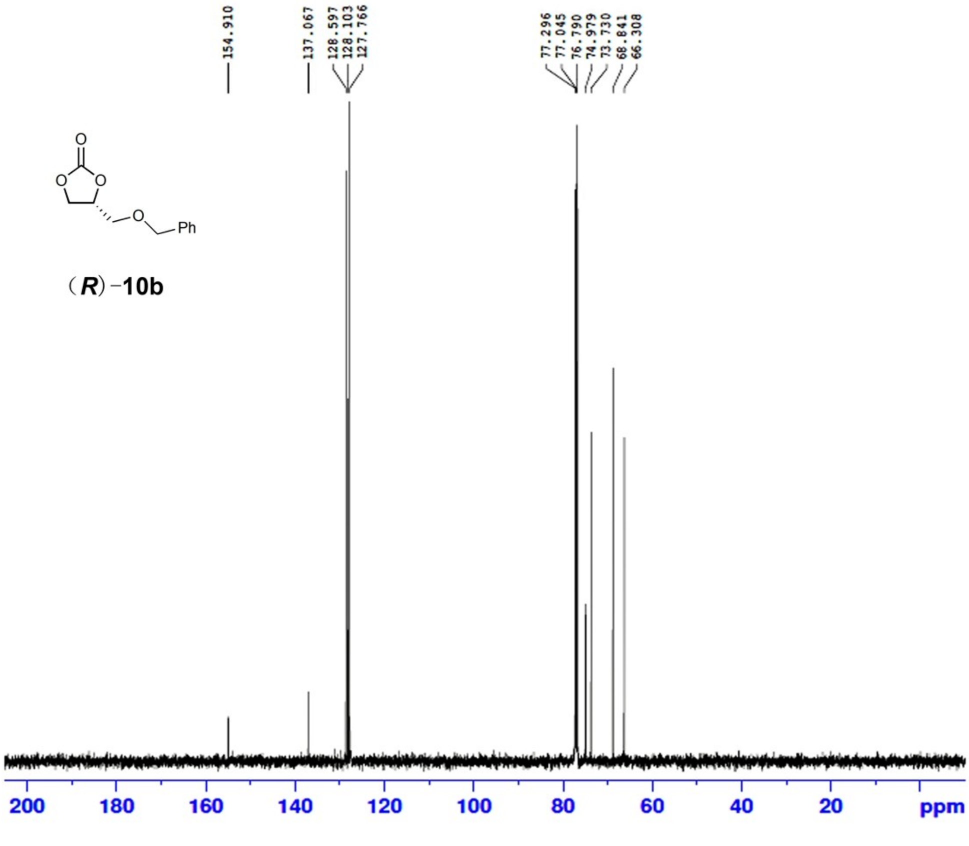
7.372
7.360
7.346
7.318
7.313
7.308
7.303
7.256
4.827
4.819
4.814
4.811
4.807
4.802
4.799
4.794
4.790
4.783
4.629
4.605
4.577
4.553
4.488
4.471
4.454
4.391
4.378
4.374
4.362
3.720
3.713
3.699
3.691
3.632
3.625
3.610
3.603
1.614
-0.00
O
O
O
O
Ph
(*R*)-10b
10
9
8
7
6
5
4
3
2
1
ppm
5.022
0.959
2.049
0.987
0.989
1.000
0.997


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
（***R***）-10b
200
180
160
140
120
100
80
60
40
20
ppm