

Supporting Information

Synthesis of Cyclic Carbonates from CO₂ and Epoxides Catalyzed by Low Loadings of Benzyl Bromide/DMF at Ambient Pressure

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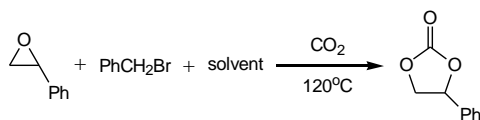
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Table S1. Screening of Solvents.^a

Entry	Solvent	Yield (%) ^b
1	DMF	86
2	DMAc	83
3	<i>N</i> -Formylpiperidine	68
4	<i>N</i> -methylpyrrolidone	51
5	<i>N</i> -Formylmorpholine	47
6	<i>N,N,N',N'</i> -Tetramethylurea	71

^a Reaction conditions: catalyst (1 mol%), epoxide (5 mmol), DMF (5 equiv.), CO₂ (99.999%, balloon), temperature 120 °C, total reaction time 24h. ^b Isolated yield.

Table S2. Screening of Catalysts.^a

Entry	Catalyst	Yield (%) ^b
1		86
2		92
3		80
4		88
5		89
6		85
7		86
8		72
9		82
10		88
11		0

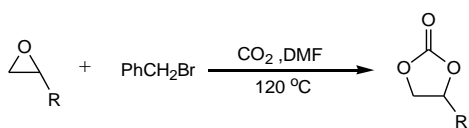
^aReaction conditions: catalyst (1 mol%), epoxide (5 mmol), DMF (5 equiv.), CO₂ (99.999%, balloon), temperature 120 °C, total reaction time 24h. ^bIsolated yield.

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. ^1H (500 MHz) and ^{13}C (125 MHz) NMR spectra were obtained using a Bruker 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 DMF, the DMF–BnBr mixture, and the reaction mixture, while the outer cell contained DMSO-d_6 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 or 205 nm.

Representative procedure for the Cyclic Carbonate Formation



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

In a 20 mL two-neck flask, styrene oxide **8a** (5 mmol, 0.601 g) and DMF (5 equiv., 25 mmol, 1.827 g, flushed with CO₂ for 10 min) were stirred at 120 °C for 4 h under an atmosphere of CO₂ (99.999%, balloon), and then PhCH₂Br (0.05mmol, 0.0086 g) was added. The reaction mixture was stirred for 20 h at the same temperature and DMF was removed under reduced pressure. The residue was dissolved in ethyl acetate (50 mL) and washed with water (15 ml) and brine (15 mL × 2), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane : ethyl acetate = 3 : 1) to afford the desired cyclic carbonate 0.705 g (yield: 86.0%).

¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 155.0, 135.9, 129.7, 129.2, 126.0, 78.0, 71.2.

Propylene carbonate (1b)

Propylene oxide (**1a**, 10 mmol, 0.581g), DMF (5 equiv., 50 mmol, 3.655 g), benzyl bromide (0.1 mmol, 0.0171 g) 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 0.766 g (yield: 75.0%).

¹H NMR (500 MHz, CDCl₃): 4.92–4.80 (m, 1H), 4.62–4.51 (m, 1H), 4.10–3.95 (m, 1H), 1.55–1.40 (m, 3H). ¹³C NMR (125 MHz, CDCl₃): 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), DMF (5 equiv., 30 mmol, 2.193 g), benzyl bromide (0.06 mmol, 0.0103 g) 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 0.618 g (yield: 78.6%).

¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 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**, 5 mmol, 0.641 g), DMF (5 equiv., 25 mmol, 1.827 g), benzyl bromide (0.05 mmol, 0.0086 g) 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 0.666 g (yield: 81.5%).

¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 155.2, 77.2, 69.4, 33.7, 31.5, 28.7, 24.3, 22.4, 13.9.

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

Epichlorohydrin (**4a**, 6 mmol, 0.556 g), DMF (5 equiv., 30 mmol, 2.193 g), benzyl bromide (0.06 mmol, 0.0103 g) 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 0.602 g (yield: 73.5%).

¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 154.8, 74.7, 67.0, 44.6.

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

1,2-Epoxy-5-hexene (**5a**, 6 mmol, 0.589 g), DMF (5 equiv., 30 mmol, 2.193 g), benzyl bromide (0.06 mmol, 0.0103 g) 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 0.490 g (yield: 57.4%).

¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (125 MHz, CDCl₃): 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**, 5 mmol, 0.571 g), DMF (5 equiv., 25 mmol, 1.827 g), benzyl

bromide (0.05 mmol, 0.0086 g) 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 0.648 g (yield: 81.9%).

¹H NMR (CDCl₃, 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). ¹³C NMR (125 MHz, CDCl₃): 155.2, 133.9, 117.3, 75.4, 72.3, 68.9, 66.2.

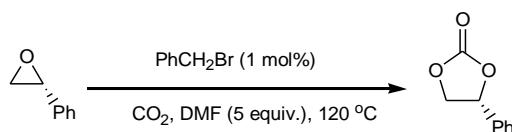
4-(Phenoxymethyl)-1,3-dioxolan-2-one (7b)

1,2-Epoxy-3-phenoxy propane (**7a**, 5 mmol, 0.750 g), DMF (5 equiv., 25 mmol, 1.827 g), benzyl bromide (0.05 mmol, 0.0086 g) 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 0.870 g (yield: 89.6%).

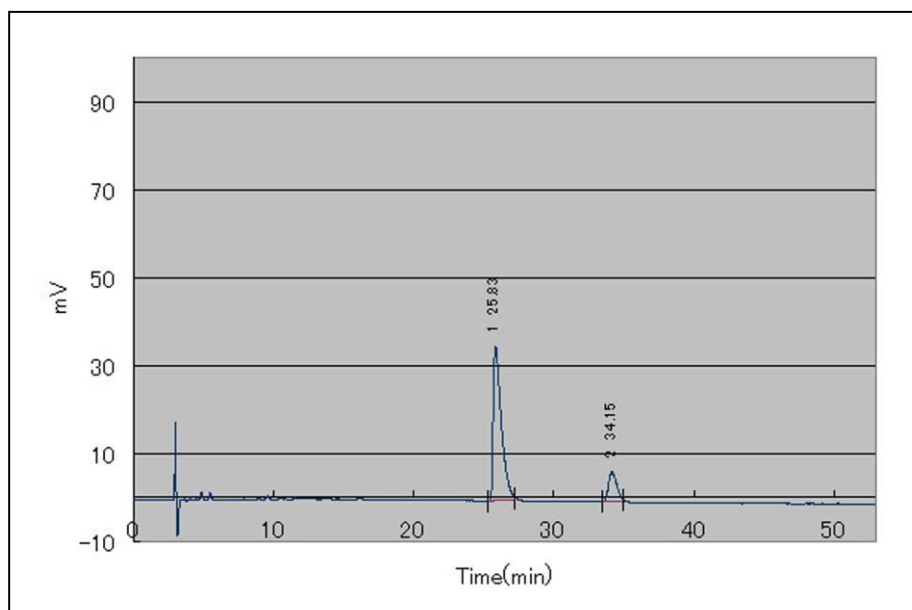
¹H NMR (500 MHz, CDCl₃): 7.36–7.22 (m, 2H), 7.06–6.92 (m, 1H), 6.91–6.85 (m, 2H), 5.06–4.95 (m, 1H), 4.65–4.56 (m, 1H), 4.55–4.46 (m, 1H), 4.22 (dd, *J* = 10.5, 4.0 Hz, 1H), 4.12 (dd, *J* = 10.5, 3.5 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): 157.8, 154.8, 129.7, 122.0, 114.7, 74.2, 66.9, 66.2.

Reaction of chiral epoxide

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

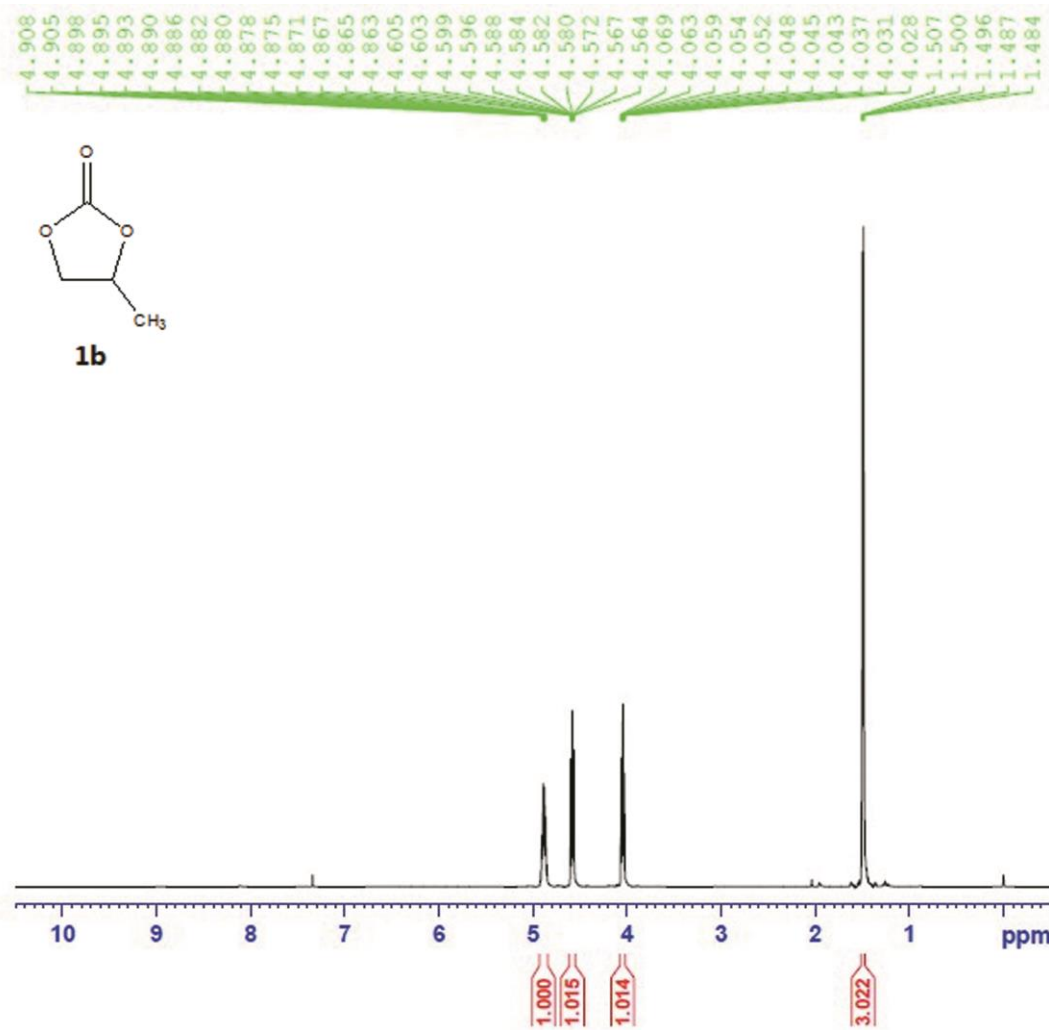


Reaction of (*R*)-styrene oxide was conducted according to the representative procedure, and the *ee* of the product was determined by chiral HPLC measurement using Chiralcel OD-3, 10% IPA/hexanes, 1 mL/min, $t_R=25.83$ min, $t_S=34.15$ min, 254 nm. Partial racemization of the product relative to the starting material was observed (68.6% *ee*). The DMF solution of the isolated product was kept for 24 h at 120 °C and negligible change of optical purity was observed (66.6 %*ee*).

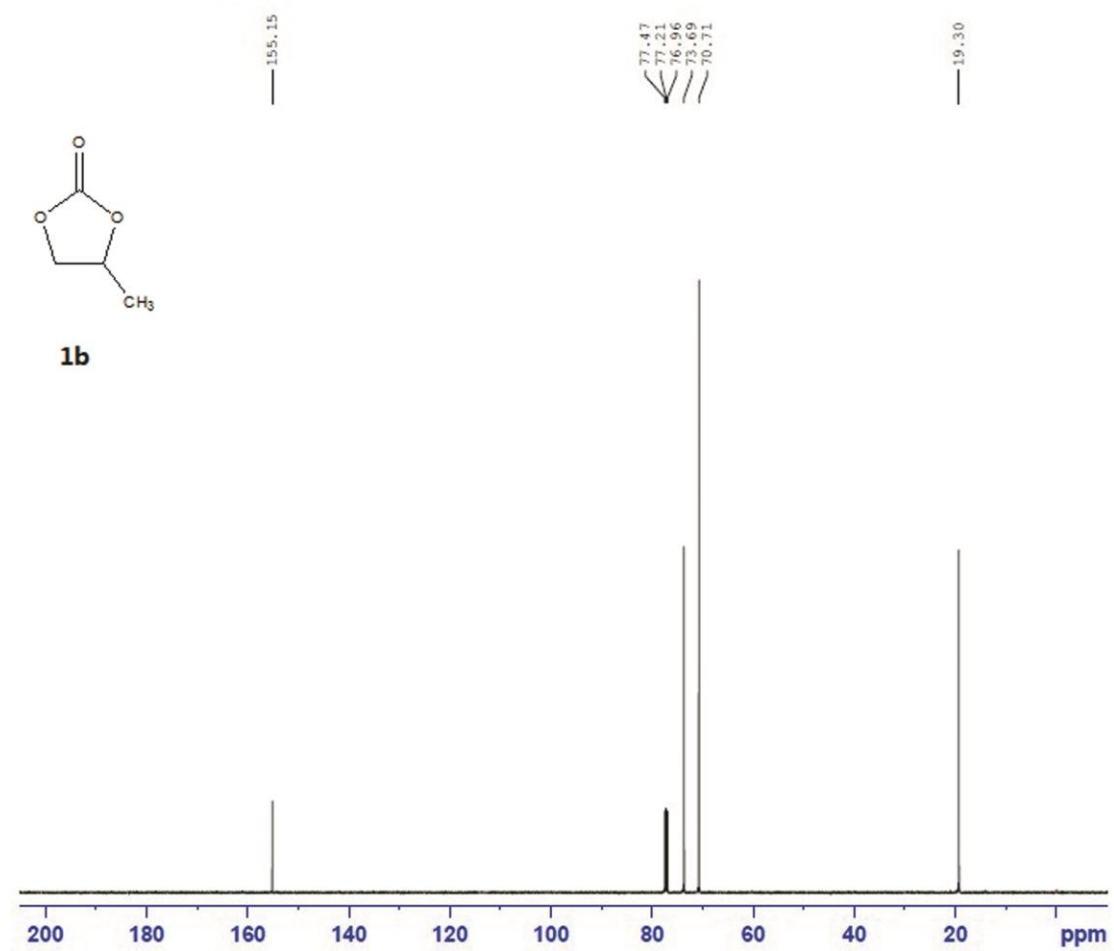


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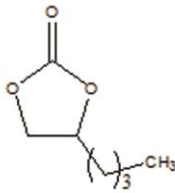
^1H and ^{13}C NMR Spectra:



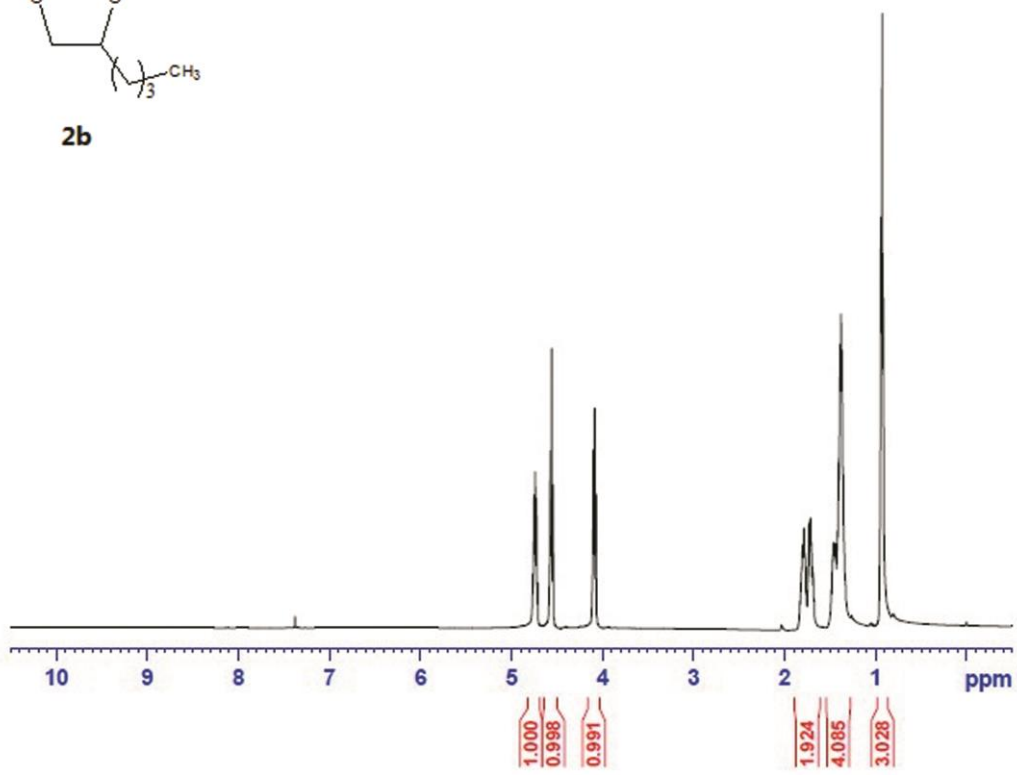
^{13}C with ^1H decoupling



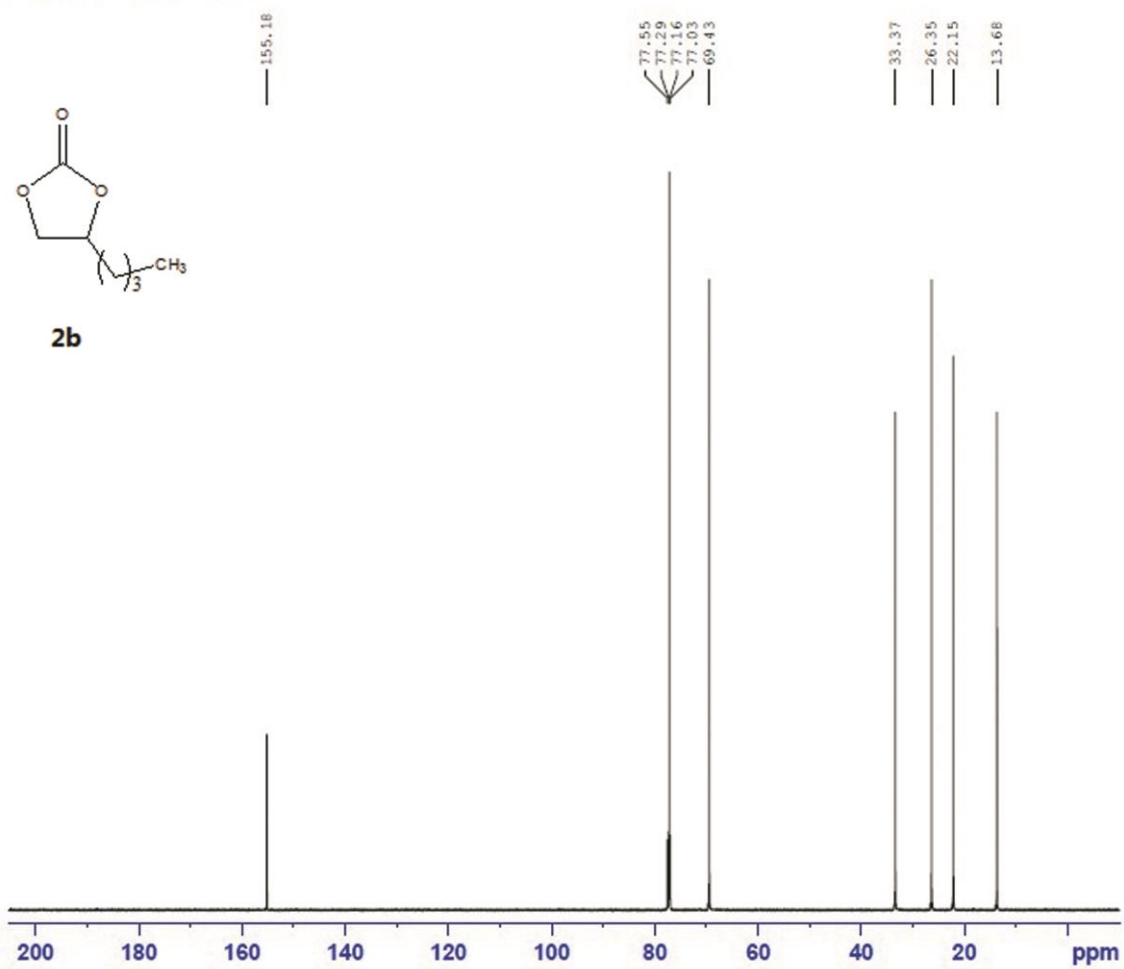
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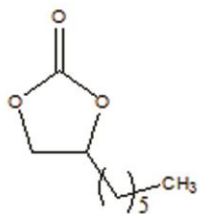
2b



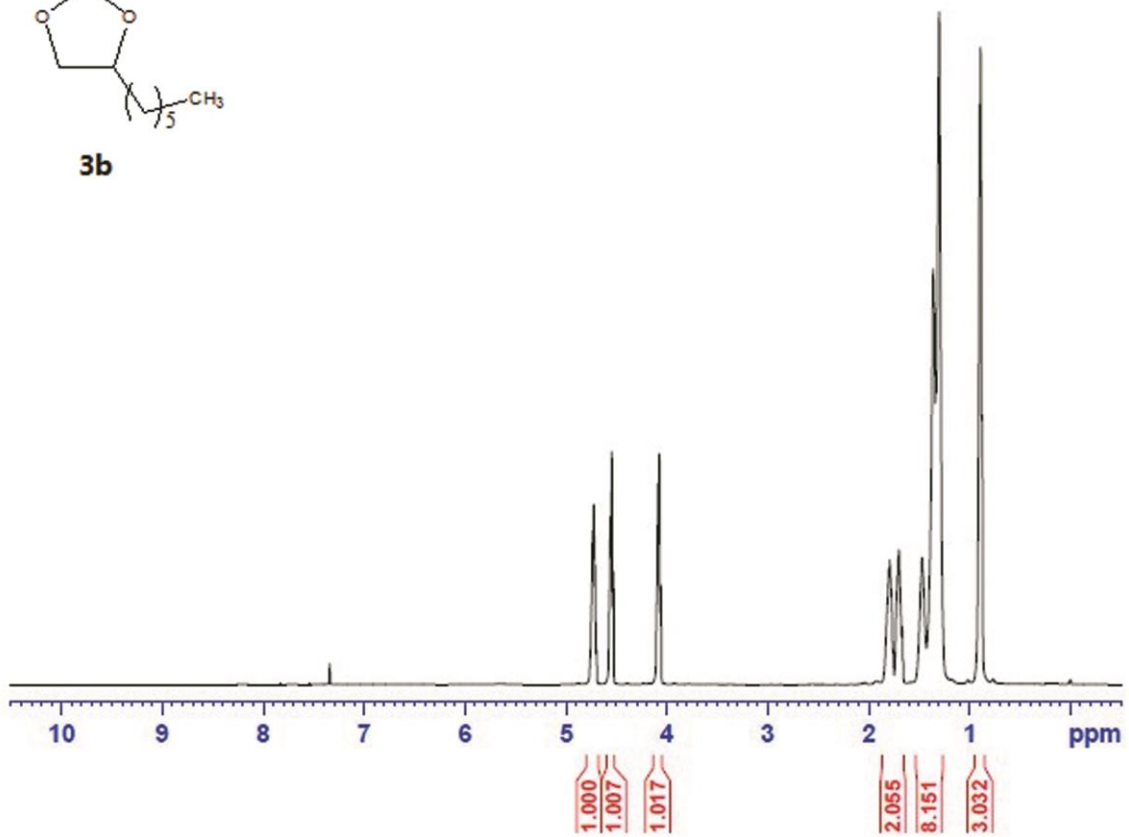
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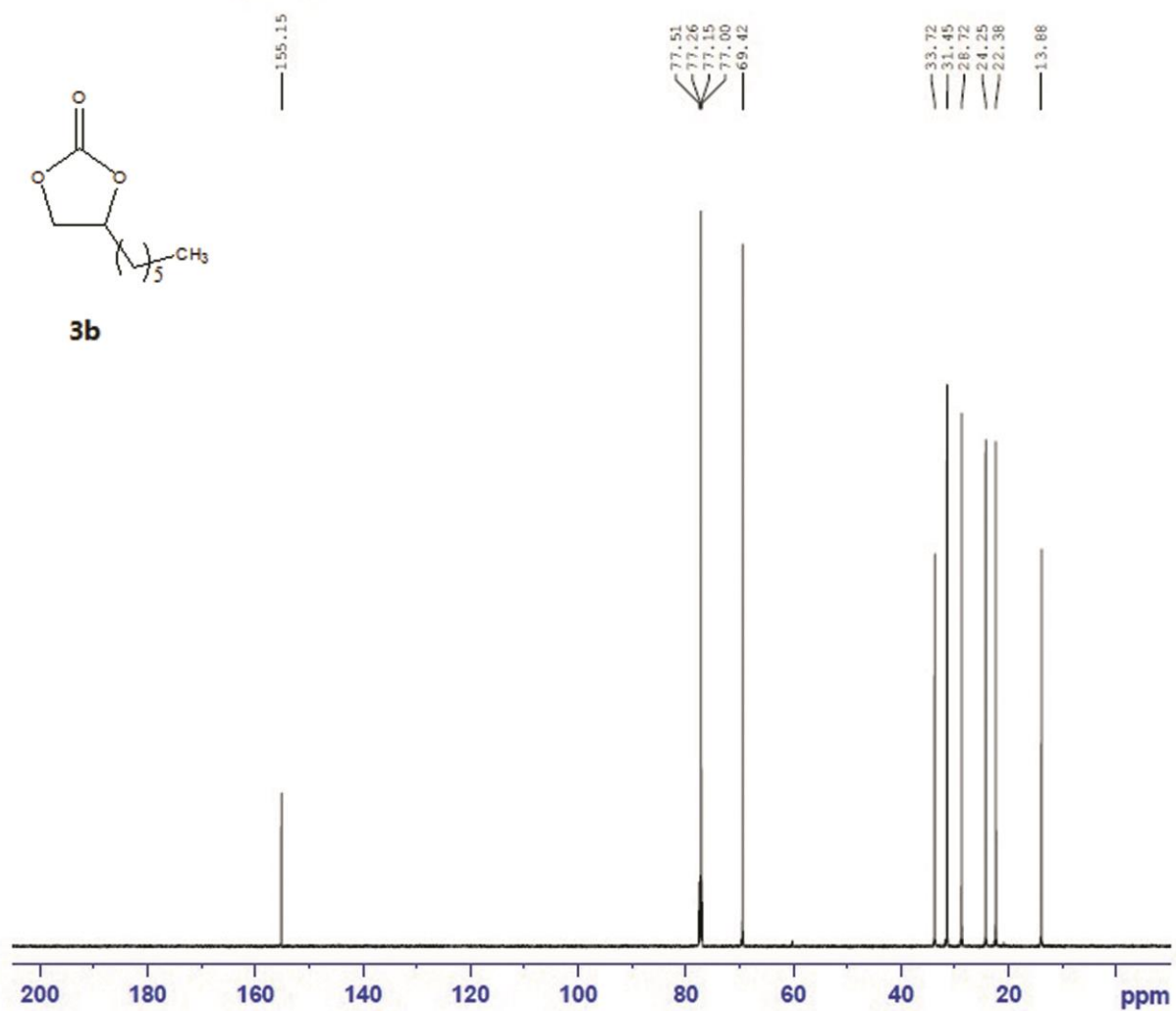
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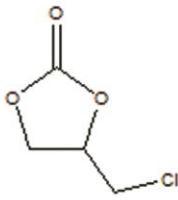


3b

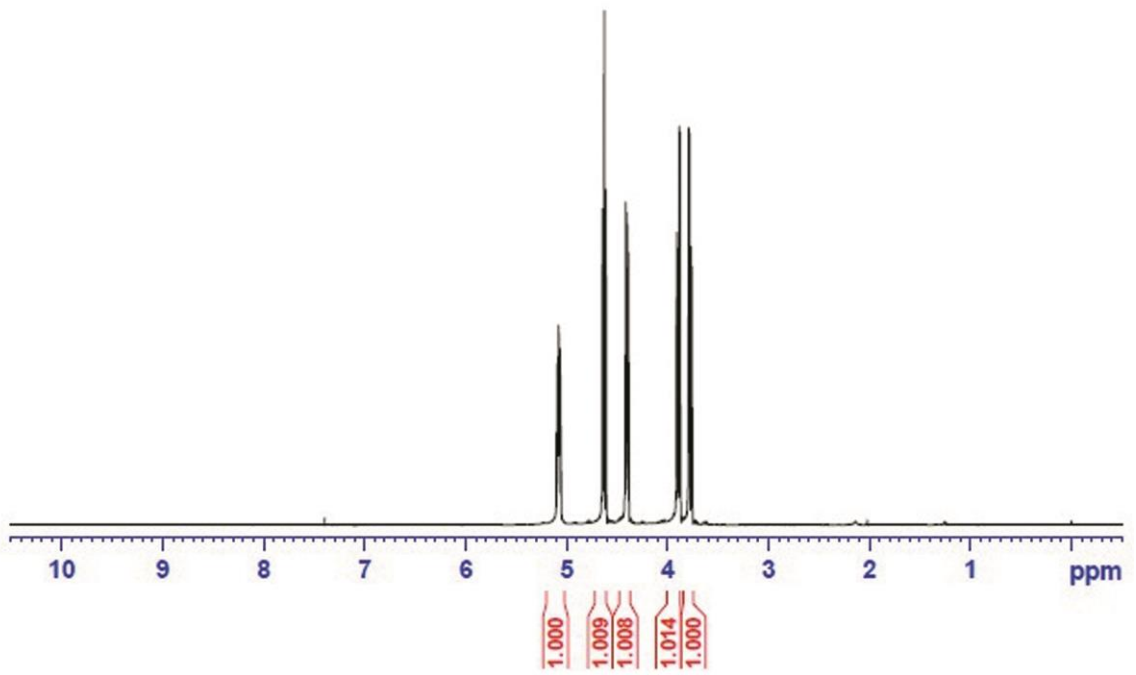


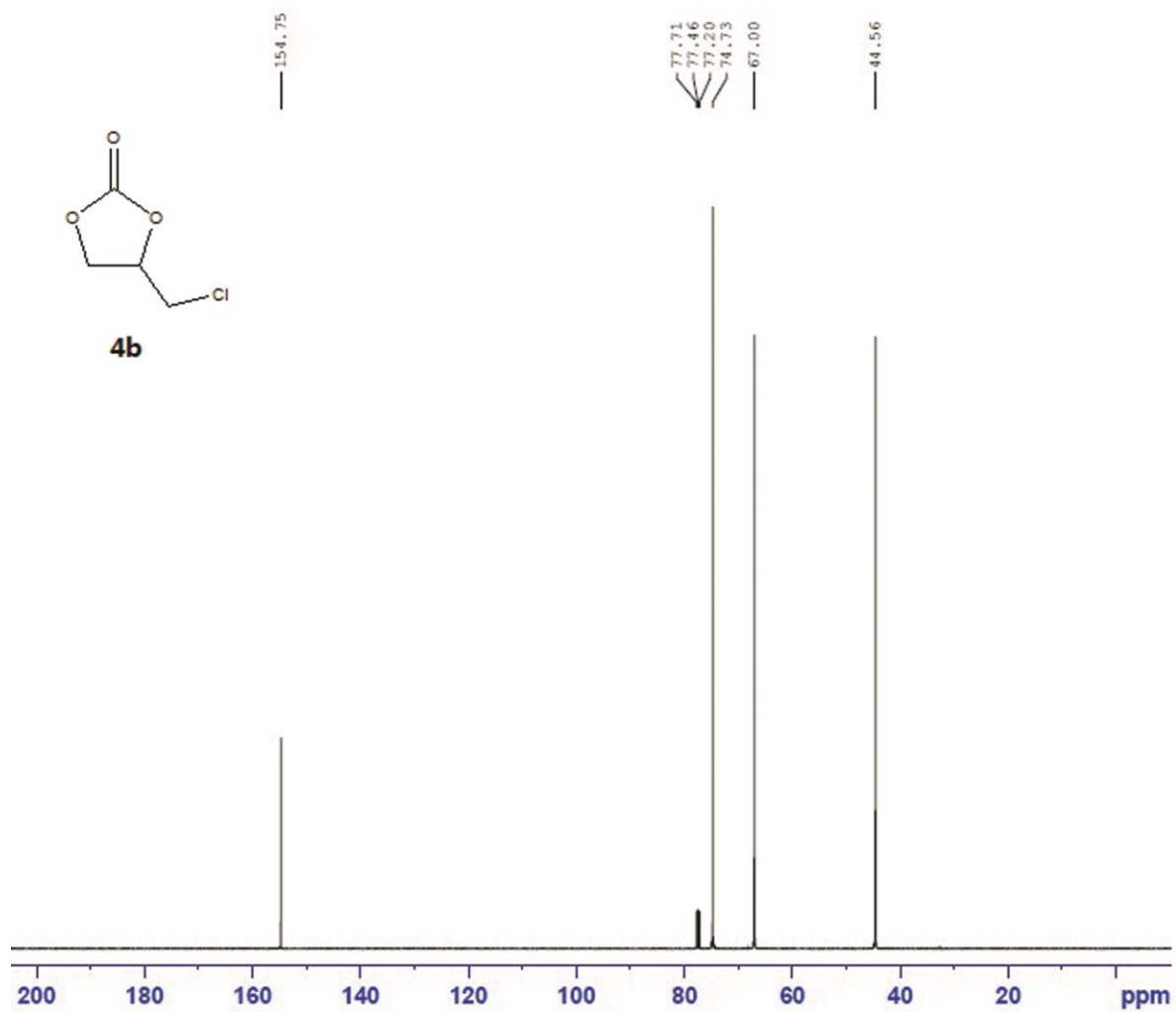
¹³C with ¹H decoupling

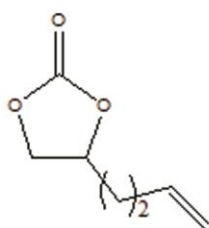




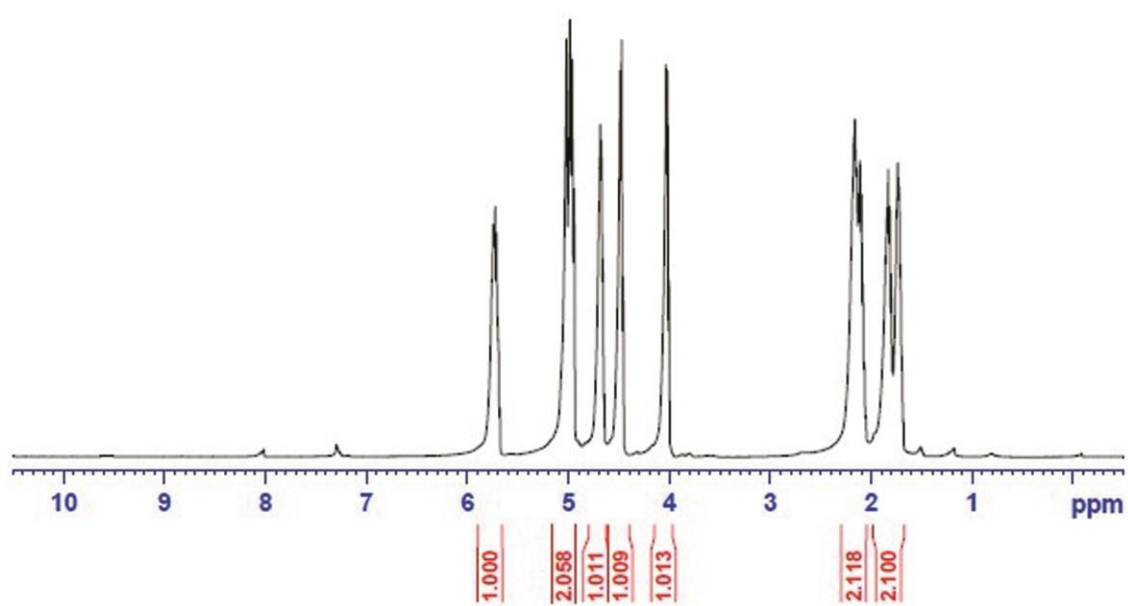
4b



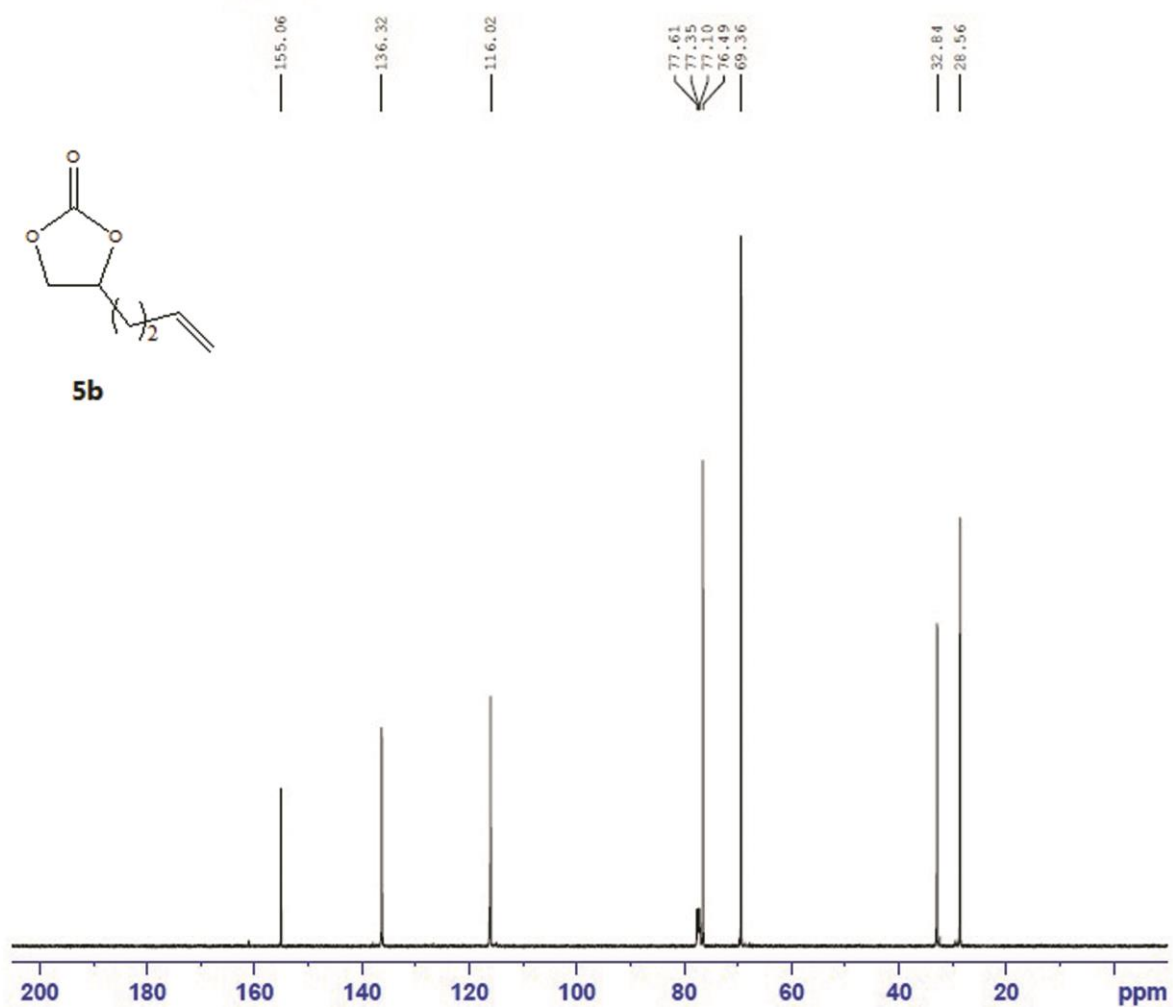


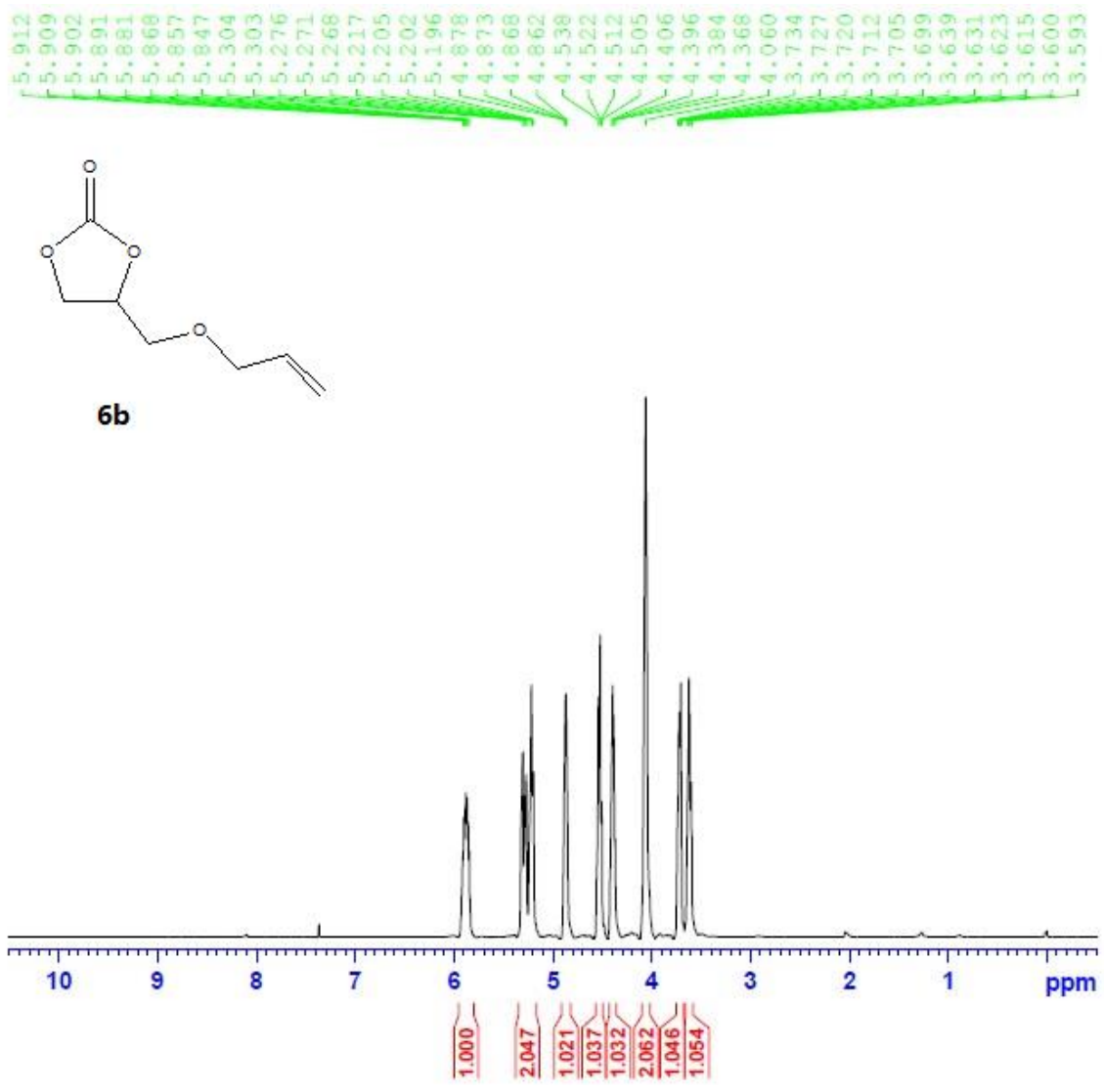


5b

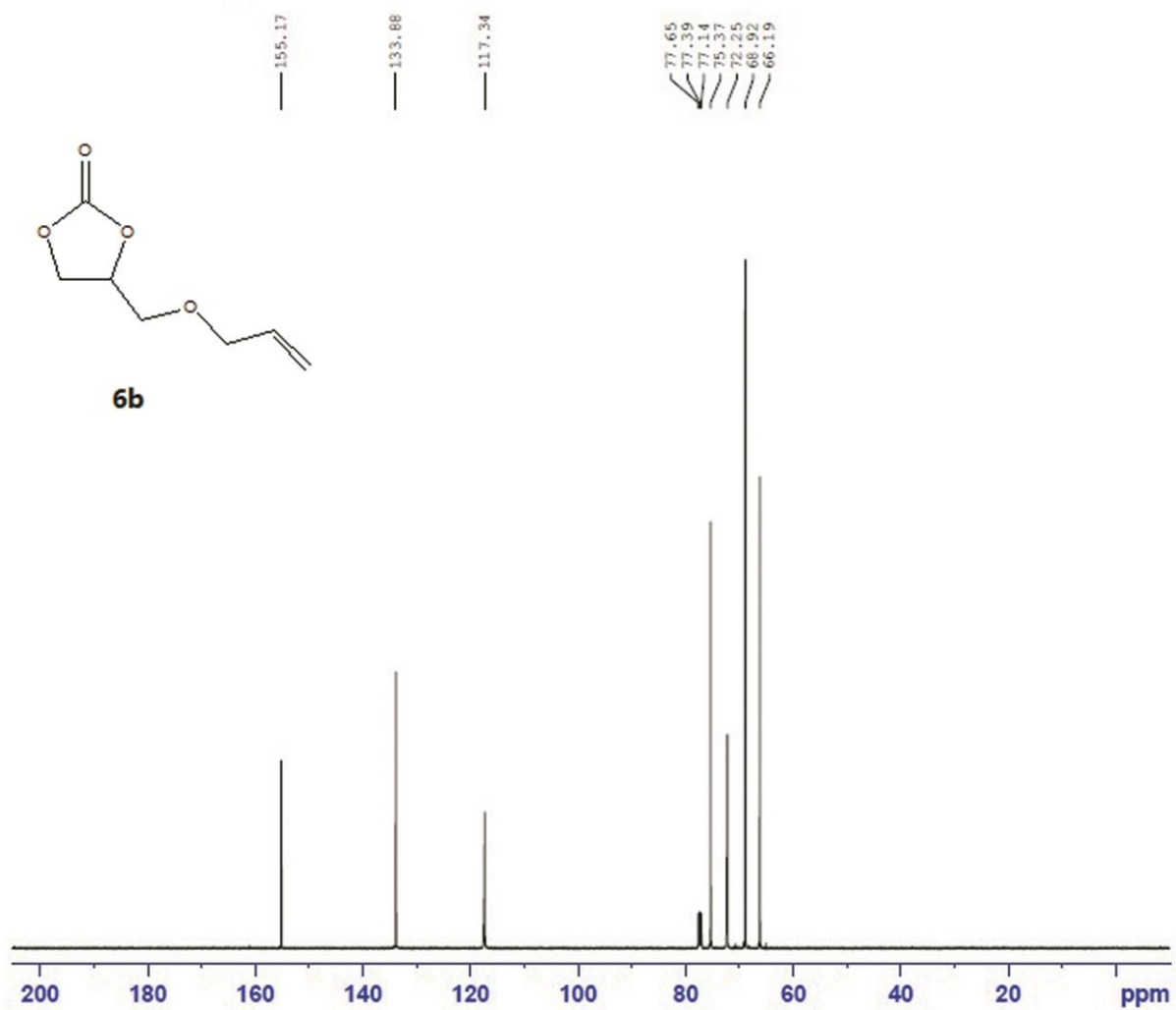


¹³C with ¹H decoupling





^{13}C with ^1H decoupling



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7.022
7.020
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