

***In-situ* copper nanoparticles immobilization on the indigo carmine-functionalized chitosan: A versatile biocatalyst towards CO₂ fixation and click reactions in water**

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1. The optimization conditions for the click reaction

1-1. Catalytic activity of Cu₂O/IC-CS bio-nanocomposite

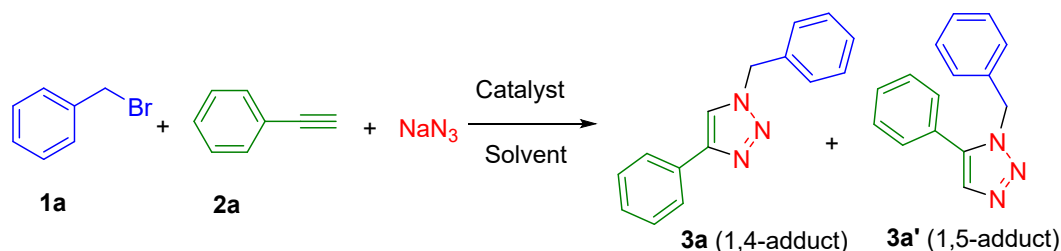
In the beginning, the catalytic activity of the newly synthesized Cu₂O/IC-CS bio-nanocomposite was evaluated in the click reaction. A model reaction of benzyl bromide **1a**,

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phenylacetylene **2a** and sodium azide was examined under different conditions (Table S1). Initially, water was chosen as a reaction medium and the model reaction was explored in various amounts of catalyst. In the absence of catalyst at 60 °C after 1 h no desired product was obtained (Table, Entry 1). The reaction was repeated in the presence of different amounts of catalyst at different times and temperatures, where the desired product was obtained by using 5 mg of catalyst at 60 °C for 40 minutes with a yield of 97% (Table S1, Entries 2-8). After realizing the time, temperature, and optimal amount of the catalyst, the reaction was investigated in solvents such as MeOH, CH₂Cl₂, MeCN, and DMF (Table S1, Entries 9-12). The results show that water is the most optimal solvent for this reaction (Table S1, Entry 6). To determine the effect of temperature, the reaction was repeated under optimal conditions at room temperature, the result shows that no product was observed (Table S1, Entry 13). For the efficiency of the synthesized catalyst, the reaction was designed under optimal conditions, using CuO/CS and Cu₂O/IC instead of the synthesized catalyst, and products with acceptable efficiencies were not obtained (Table S1, Entries 14-15).

Table S1. Optimization of the click reaction conditions for the synthesis of 1,2,3-triazole^a



Entry	Catalyst	Amount of catalyst (mg)	Time (min)	Solvent	T (°C)	Yield (%)
1	-	-	60	H ₂ O	60	13 (both regioisomers)
2	Cu ₂ O/IC-CS	5	20	H ₂ O	60	22 (only 1,4-adduct)
3	Cu ₂ O/IC-CS	5	30	H ₂ O	60	53 (only 1,4-adduct)
4	Cu ₂ O/IC-CS	10	40	H ₂ O	40	49 (only 1,4-adduct)
5	Cu ₂ O/IC-CS	20	40	H ₂ O	50	26 (only 1,4-adduct)
6	Cu₂O/IC-CS	5	40	H₂O	60	97 (only 1,4-adduct)
7	Cu ₂ O/IC-CS	5	40	H ₂ O	40	49 (only 1,4-adduct)
8	Cu ₂ O/IC-CS	5	40	H ₂ O	50	35 (only 1,4-adduct)
9	Cu ₂ O/IC-CS	5	40	MeOH	60	45 (only 1,4-adduct)
10	Cu ₂ O/IC-CS	5	40	CH ₂ Cl ₂	60	Trace
11	Cu ₂ O/IC-CS	5	40	MeCN	60	Trace
12	Cu ₂ O/IC-CS	5	40	DMF	60	66 (only 1,4-adduct)

13	Cu ₂ O/IC-CS	5	40	H ₂ O	-	0
14	Cu ₂ O/CS	5	40	H ₂ O	60	43 (only 1,4-adduct)
15	Cu ₂ O/IC	5	40	H ₂ O	60	62 (only 1,4-adduct)

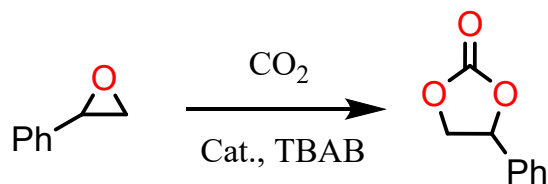
^aReaction conditions: benzyl bromide (1.00 mmol), sodium azide (1.00 mmol), phenylacetylene (1.00 mmol), and catalyst in a solvent.

2. The optimization conditions for the CO₂ fixation

2-1. Catalytic activity of the synthesized CuO/IC-CS

The CO₂ fixation reaction with styrene epoxide as a model reaction was studied in the presence of CuO/IC-CS biocatalyst and TBAB under the net condition at 80 °C and 1 bar for 4 h, which product was obtained with a yield of 48% (Table S2, Entry 1). In the first step to improving the reaction yield, the effect of CO₂ pressure was investigated, and by increasing the CO₂ to 3 bar the reaction yield was improved to 94% (Table S2, Entries 2-5). In the second step, this reaction was investigated in solvents such as DMF, EtOH, H₂O, CH₂Cl₂, and CH₃CN at different temperatures, pressure 1 bar, and catalysts amount of 30 mg and showed that the desired product was obtained in water with higher efficiency (Table S2, Entries 6-10). After identifying the optimal solvent, in the next steps, the reaction was investigated in different amounts of catalyst and co-catalyst. The best results were obtained with 30 mg of catalyst and 12 mg of cocatalyst (Table S2, Entries 11-14). Finally, to find out the effect of temperature, the reaction was investigated at 25 °C and no products were obtained (Table S2, Entry 16). Also, at 100 °C, no increase in product yield was observed (Table S2, Entry 15). This shows that in addition to the temperature catalyst, it is also a factor influencing the reaction. For the efficiency of the synthesized catalyst, the reaction under optimal conditions was designed using CuO/CS and CuO/IC in water and solvent-free conditions instead of the synthesized catalyst, and products with acceptable efficiencies were not obtained (Table S2, Entries 17-20). All these documents discussed in Table S2 indicate the activeness and efficiency of the catalyst.

Table 3. Screening the reaction conditions for the consecutive CO₂ cycloaddition with styrene oxide^a.



Entry	Catalyst	Amount of catalyst (mg)	TBAB (mg)	Time (h)	T (°C)	Solvent	P (bar)	Yield (%)
1	CuO/IC-CS	30	12	4	80	-	1 (CO ₂ balloon)	48
2	CuO/IC-CS	30	12	4	80	-	2	74
3	CuO/IC-CS	30	12	2	80	-	2	74
4	CuO/IC-CS	30	12	2	80	-	3	92
5	CuO/IC-CS	30	12	2	90	-	3	94
6	CuO/IC-CS	30	12	2	80	CH ₃ CN	1 (CO ₂ balloon)	45
7	CuO/IC-CS	30	12	2	40	CH ₂ Cl ₂	1 (CO ₂ balloon)	trace
8	CuO/IC-CS	30	12	2	80	DMF	1 (CO ₂ balloon)	30
9	CuO/IC-CS	30	12	2	78	EtOH	1 (CO ₂ balloon)	37
10	CuO/IC-CS	30	12	2	80	H₂O	1 (CO₂ balloon)	96
11	CuO/IC-CS	30	8	2	80	H ₂ O	1 (CO ₂ balloon)	71
12	CuO/IC-CS	30	16	2	80	H ₂ O	1 (CO ₂ balloon)	96
13	CuO/IC-CS	20	12	2	80	H ₂ O	1 (CO ₂ balloon)	88
14	CuO/IC-CS	10	12	2	80	H ₂ O	1 (CO ₂ balloon)	76
15	CuO/IC-CS	30	12	2	100	H ₂ O	1 (CO ₂ balloon)	96
16	CuO/IC-CS	30	12	2	25	H ₂ O	1 (CO ₂ balloon)	0
17	CuO/CS	30	12	4	80	-	1 (CO ₂ balloon)	27
18	CuO/CS	30	12	4	80	H ₂ O	1 (CO ₂ balloon)	42
19	CuO/IC	30	12	4	80	-	1 (CO ₂ balloon)	36
20	CuO/IC	30	12	4	80	H ₂ O	1 (CO ₂ balloon)	33

^aConditions of reaction: Epoxide (3 mmol), CO₂, TBAB, catalyst.

^bIsolated yield.

3. ¹H NMR data of isolated pure product triazoles

1-Benzyl-4-phenyl-1*H*-1,2,3-triazole (3a)

White solid: mp 127-128°C. ¹H-NMR (300.13 MHz, CDCl₃) δ: 5.61 (2H, s, CH₂_{benzylic}), 7.32-7.85 (11H, m, H_{arom}).

1-(4-Bromobenzyl)-4-phenyl-1*H*-1,2,3-triazole (3b)

White solid: mp 148-150°C. ¹H-NMR (300.13 MHz, CDCl₃) δ: 5.55 (2H, s, CH₂_{benzylic}), 7.18-7.86 (10H, m, H_{arom}).

2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-ol (3c)

White solid: mp 79-80°C. ¹H-NMR (300.13 MHz, CDCl₃) δ: 1.66 (6H, s, 2CH₃), 2.90 (1H, br s, OH), 5.60 (2H, s, CH₂_{benzylic}), 7.26-7.42 (6H, m, H_{arom}).

1-Benzyl-4-*p*-tolyl-1*H*-[1,2,3]triazole (3d)

White solid: $^1\text{H-NMR}$ (300.13 MHz, CDCl_3) δ : 2.39 (3H, s, CH_3), 5.60 (2H, s, $\text{CH}_{2\text{benzylic}}$), 7.22-7.73 (10H, m, H_{arom}).

(1-Benzyl-1*H*-[1,2,3]triazol-4-yl)-dimethyl-amine (3e)

White solid: $^1\text{H-NMR}$ (300.13 MHz, CDCl_3) δ : 2.60-3.22 (6H, s, 2CH_3), 5.10 (2H, s, CH_2), 5.59 (2H, s, $\text{CH}_{2\text{benzylic}}$), 7.06-7.74 (10H, m, H_{arom}).

1-(4-Bromo-benzyl)-4-*p*-tolyl-1*H*-[1,2,3]triazole (3f)

White solid: $^1\text{H-NMR}$ (300.13 MHz, CDCl_3) δ : 2.39-2.40 (3H, s, CH_3), 5.55-5.56 (2H, s, $\text{CH}_{2\text{benzylic}}$), 7.20-7.73 (9H, m, H_{arom}).

4. ^1H NMR data of isolated pure product cyclic carbonates

4-Phenyl-1,3-dioxolan-2-one (5a)

White solid: $^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 4.35-4.39 (t, $J = 6$ Hz, 1H), 4.79-4.89 (t, $J = 9$ Hz, 1H), 5.67-5.72 (t, $J = 6$ Hz, 1H), 7.37-7.48 (m, 5HAr).

4-(Phenoxymethyl)-1,3-dioxolan-2-one (5b)

White solid: $^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 4.15-4.29 (m, 2H), 4.54-4.67 (m, 2H), 5.02-5.09 (m, 1H), 6.92-7.06 (m, 3HAr), 7.31-7.61 (m, 5HAr).

Tetrahydro-4*H*-cyclopenta[*d*][1,3]dioxol-2-one (5c)

Colorless oil: $^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 1.42-1.50 (m, 2H), 1.76-1.85 (m, 2H), 2.13-2.19 (m, 2H), 5.12-5.15 (m, 1H).

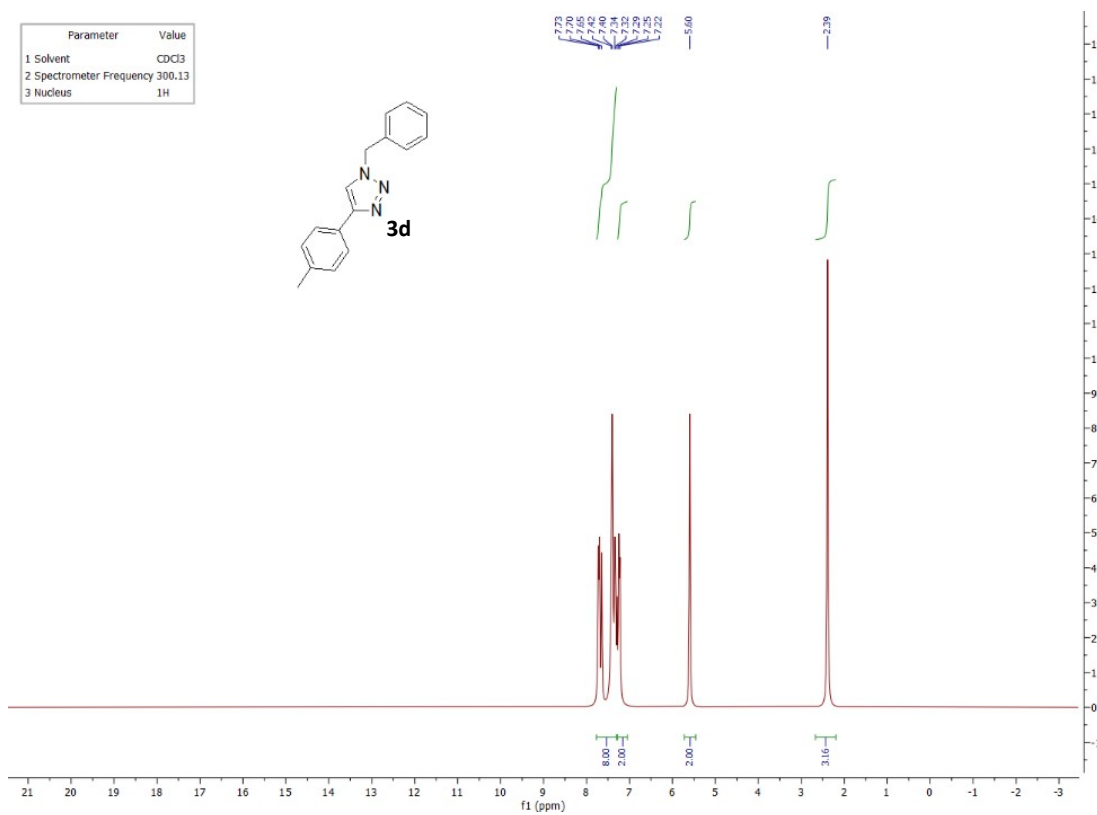
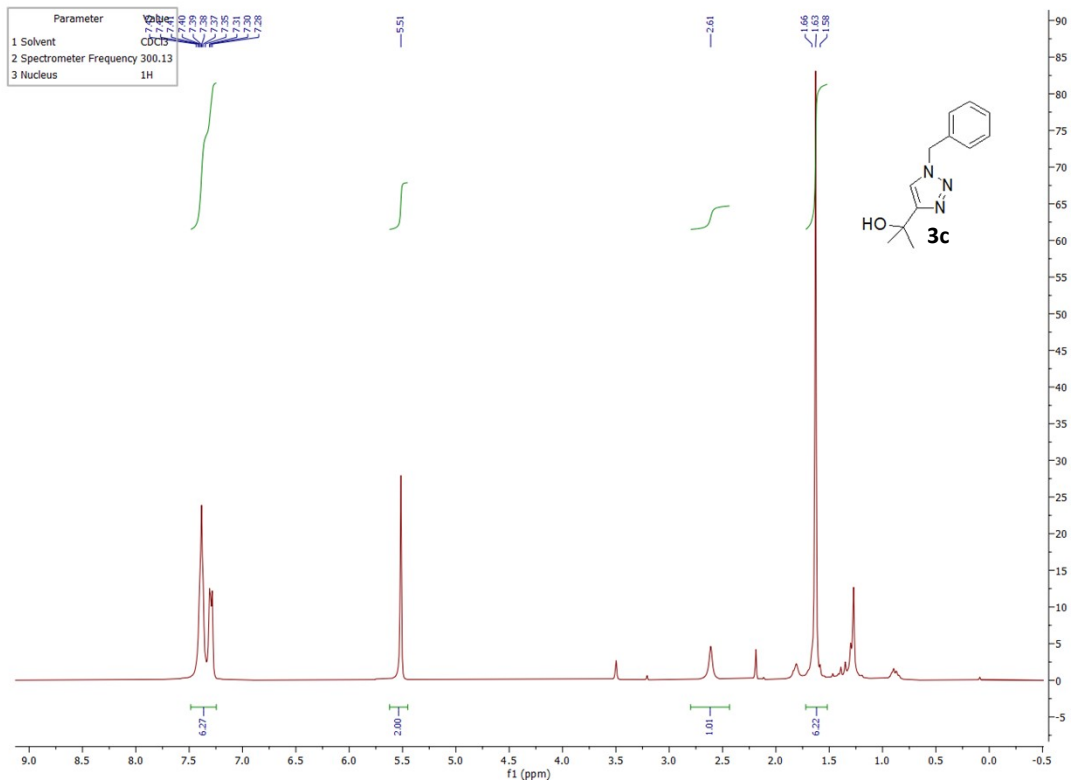
4-Butyl-1,3-dioxolan-2-one (5d)

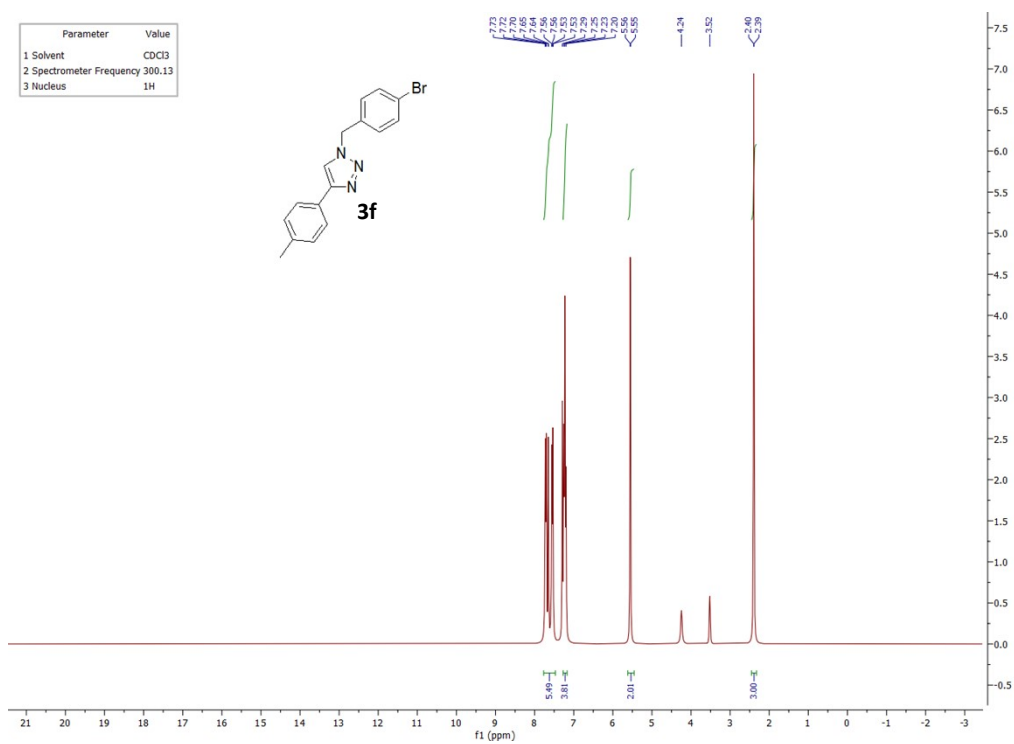
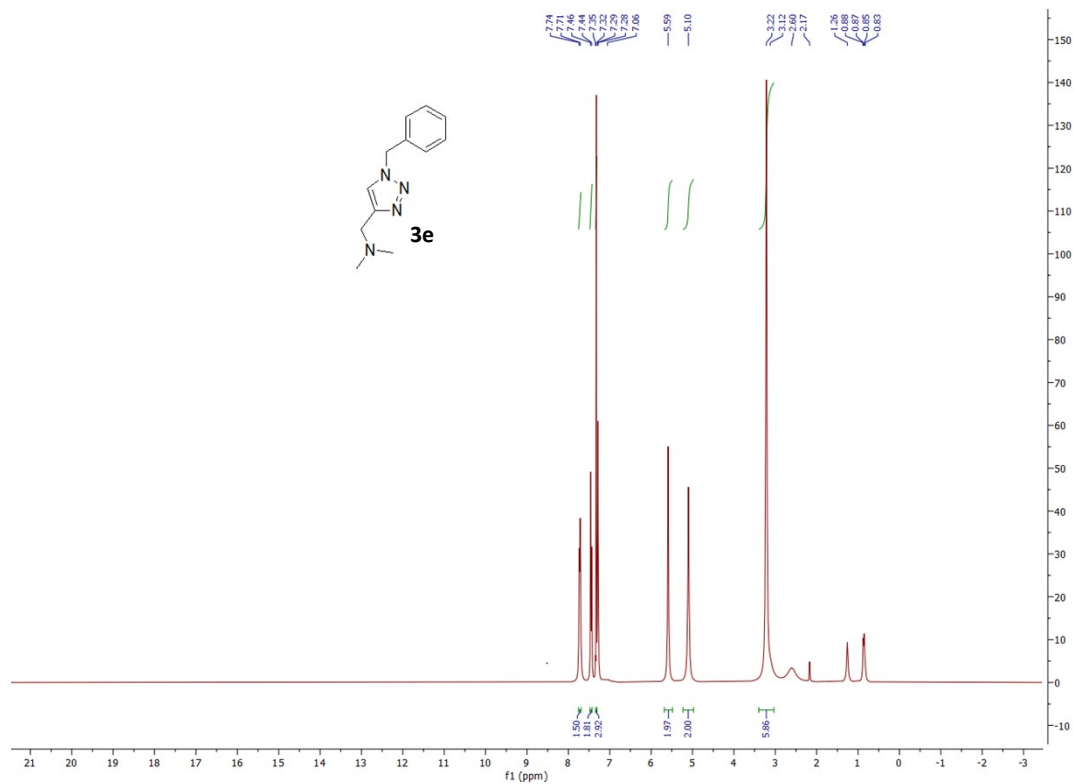
Orange oil: $^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 0.89-0.94 (t, $J = 9$ Hz, 3H), 1.16-1.43 (m, 4H), 1.54-1.97 (m, 2H), 3.98-4.03 (t, $J = 6$ Hz, 1H), 4.48-4.54 (t, $J = 6$ Hz, 1H), 4.63-4.72 (t, $J = 6$ Hz, 1H).

Octahydrocycloocta[*d*][1,3]dioxol-2-one (5e)

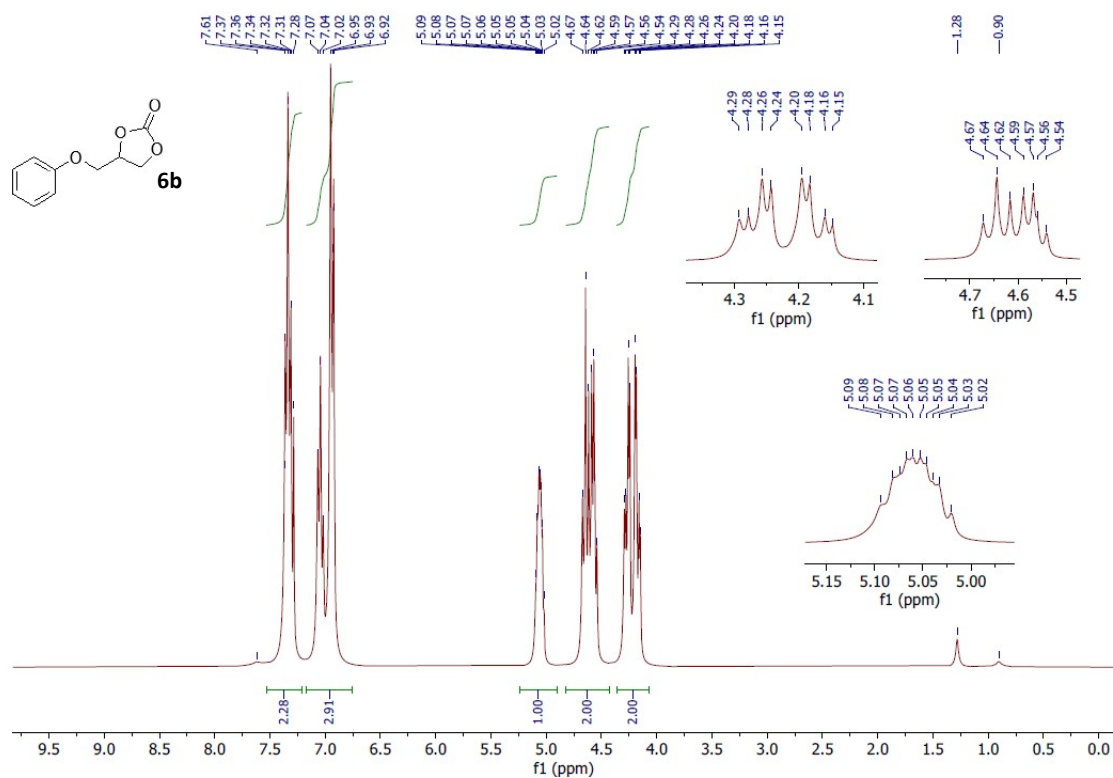
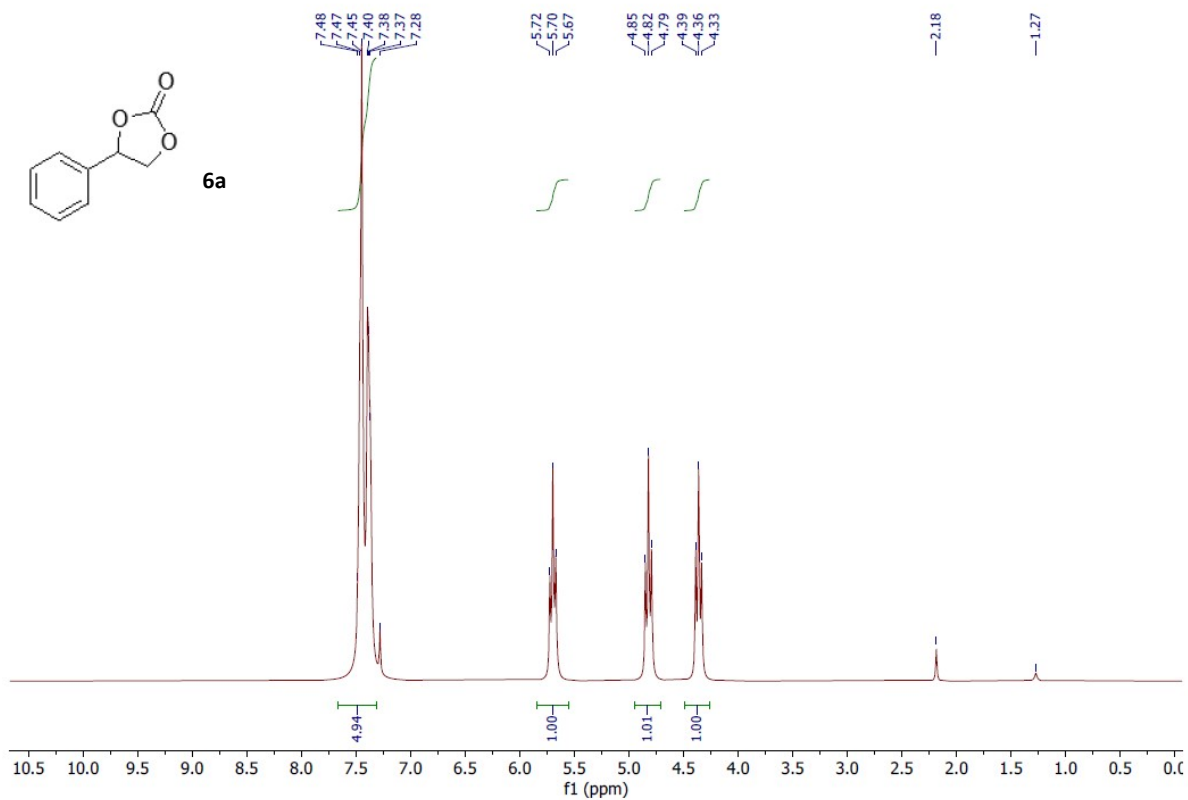
Colorless oil: $^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 1.06-1.14 (m, 4H), 1.40-1.46 (m, 4H), 1.96-2.24 (m, 4H), 3.16-3.27 (m, 2H).

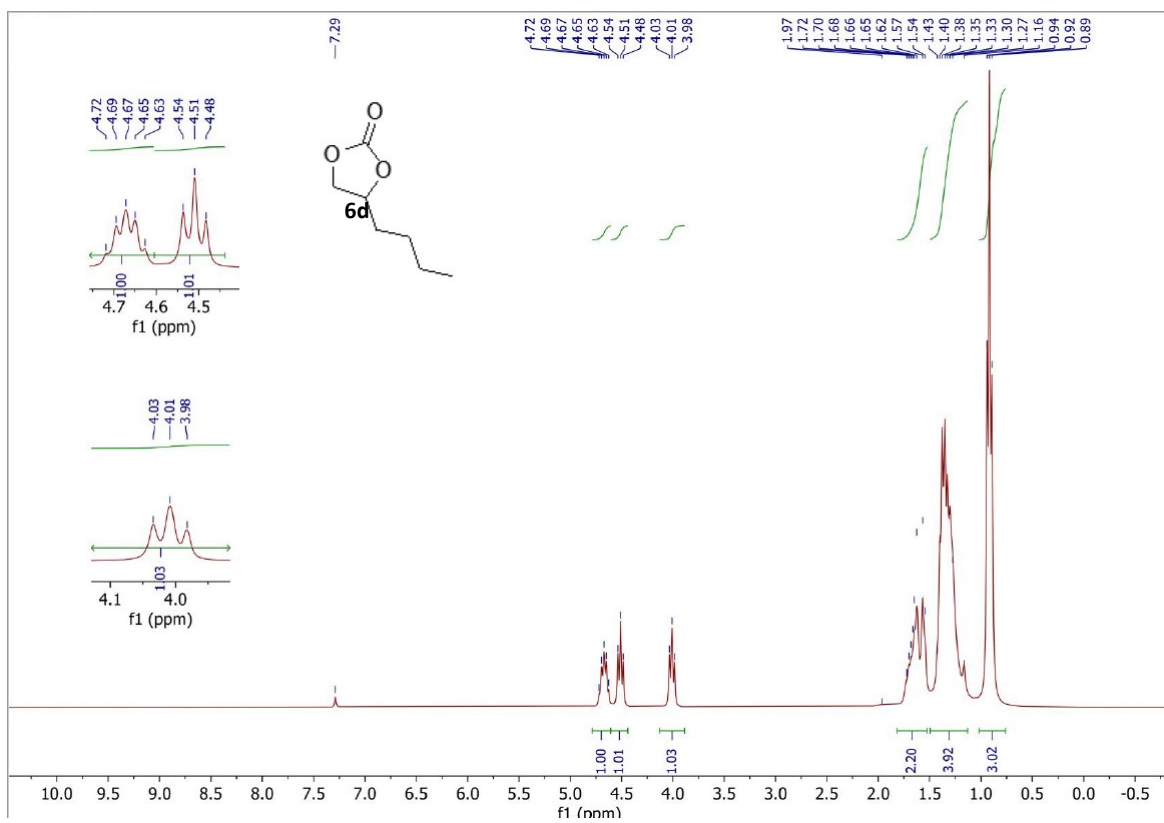
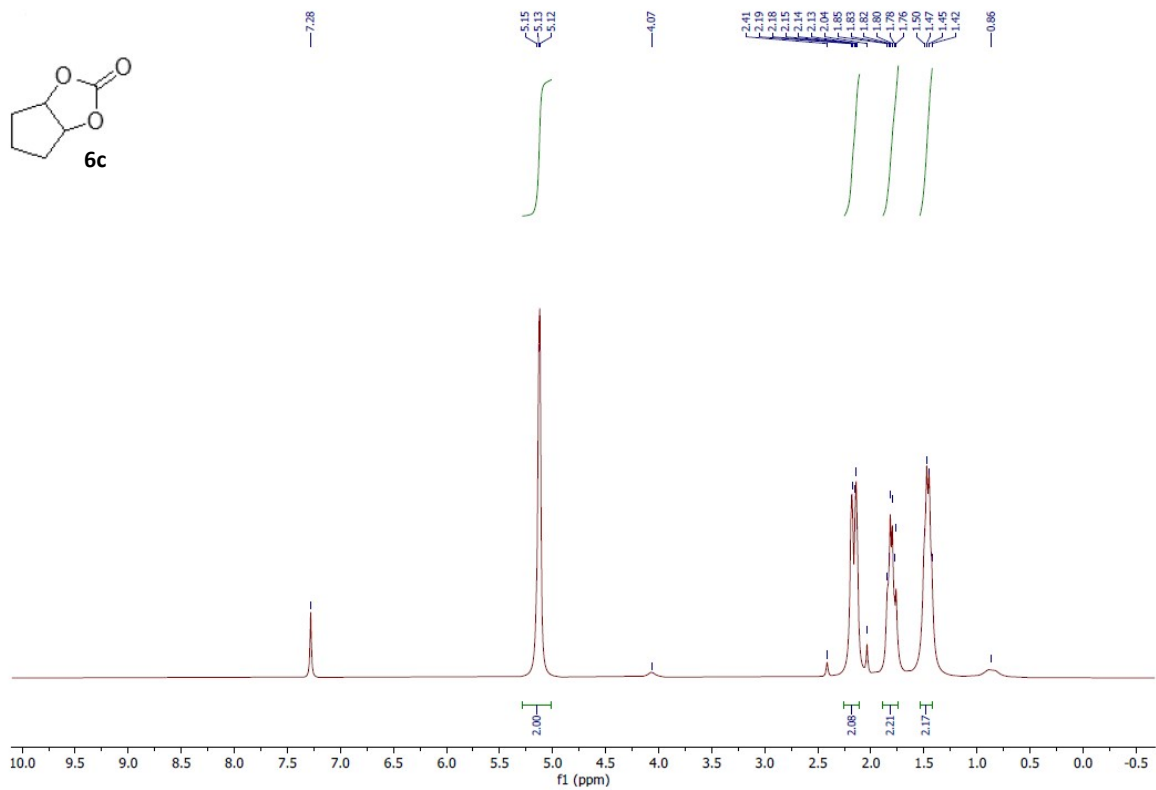
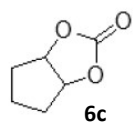
5. ^1H NMR spectra of products 3a-f

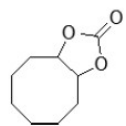




6. ¹H NMR spectrum of products 6a-e







6e

