Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Electrosynthesis of cyclic carbonates from CO_2 and epoxides on reusable copper nanoparticles cathode

Laxia Wu [a, b], Hengpan Yang [b], Huan Wang [b], Jiaxing Lu [*b]

[a] *School of Chemistry and Chemical Engineering, Anqing Normal University, Anqing 246011, China*
[b] *Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, China*

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1. Materials and Instruments

All reagents were used as received except for products in Table 2, entries 2-8.

Galvanostatic electrosynthesis was performed using a direct current-regulated power supply (HY3002D, HYelec®, China).

^{1}H-NMR spectra were recorded on an AVANCE 500 (500 MHz, Bruker, Germany) or Ascend 400 (400 MHz, Bruker, Germany) spectrometer in $CDCl_3$ with Me_4Si as an internal standard.

The product yield was determined by Gas Chromatography-Flame Ionization Detector (GC-FID) (SHIMADZU, GC-2014).

Microstructure and morphology of Cu NPs were analyzed using Hitachi S-4800 field emission Scanning Electron Microscope (FE-SEM) and TECNAI G^{2}F30 Transmission Electron Microscope (TEM).

X-ray diffraction (XRD) patterns were recorded by a Ultima IV X-ray powder diffractometer using Cu Kα radiation (k= 1.5406 Å).

N_2 adsorption was carried out at 77 K on a BELSORP-MAX instrument after outgassing the samples for 10 h under vacuum at 573 K.

2. General procedure

2.1 Prepare compacted Cu NPs electrode

100 nm: 5 g $CuSO_4 \cdot 5H_2O$ was dissolved in 100 mL deionized water. After 10 min stirring, 50 mL hydrazine hydrate solution (10%) was added, and the mixture was stirred at 25 ^oC for 4 h. Cu was precipitated immediately. The precipitate was filtered, washed with 10 mL water and 10 mL anhydrous ethanol for 4 times respectively, and dried for 12 h at 35 ^oC under vacuum. Cu NPs powder was pressed into coin and used as cathode for electrosynthesis of cyclic carbonates from CO_2 and epoxide.

300 nm: The same method except that 25 mL hydrazine hydrate solution (20%) was added.

50 nm: 10 mL 0.25 M copper acetate and urea aqueous solution were mixed and transferred to a Teflon-lined reactor. The reactor was kept in an oven at 130 ^oC for 1 h. The reaction solution was centrifuged. Dark precipitate was obtained after being washed three times with distilled water and drying at 60 ^oC for 12 h. The dark precipitate was reduced in H_2 atmosphere at 130 ^oC for 3 h.

10 nm: The method was the same as 50 nm except for 0.025 M copper acetate and urea aqueous

solution.

Fig. S1 Cu NPs before (left) and after (right) press.

2.2 General electrosynthesis

A typical galvanostatic electrolysis was carried out in a mixture of propylene oxide (100 mM), supporting electrolyte TEAI (0.1 M) and 10 mL MeCN saturated with CO_2 (1 atm) in an undivided glass cell equipped with a sacrificial magnesium (Mg) rod anode and Cu NPs cathode (d = 2 cm). Continuous CO_2 flow was maintained throughout the duration of the whole electrolysis process. The pure products were isolated by column chromatography using petroleum ether/ethyl acetate mixture as an eluent.

3. Characterization of Cu nanoparticles

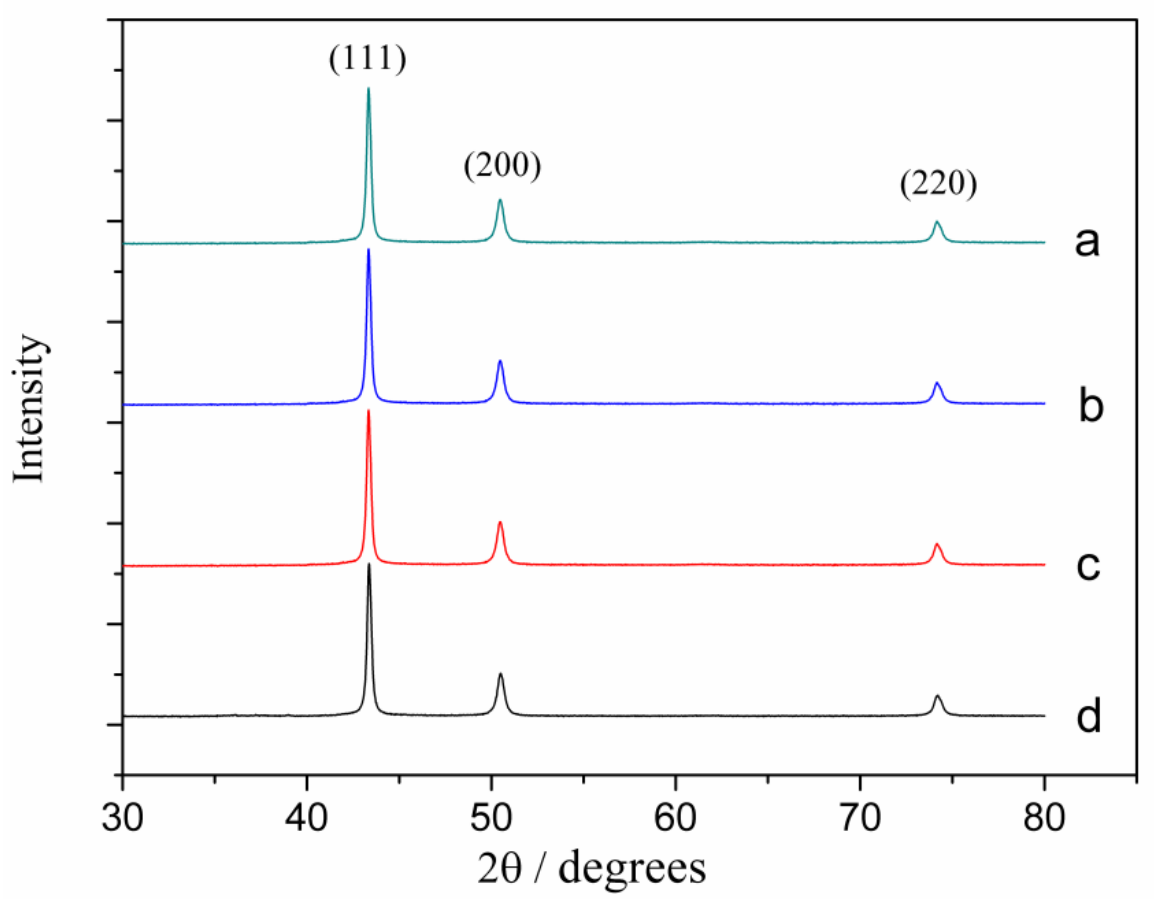

Fig. S2 X-ray diffraction (XRD) patterns of Cu NPs in the size range of ~300 nm (a), 100 nm (b), 50 nm (c) and 10 nm (d).

4. Characterization Data for All Products

4-(Chloromethyl)-1,3-dioxolan-2-one 2b[1] GC-MS (m/z, %) 132 (M^+, 1), 87 (100), 64 (5), 43 (29), 28 (16) ; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.72-3.78 (m, 2H), 4.43 (q, J = 8 Hz, 1H), 4.61(t, J = 8 Hz, 1H), 4.97-5.01 (m, 1H).

4-Ethyl-1,3-dioxolan-2-one 2c[2] GC-MS (m/z, %) 116 (M^+, 4), 87 (64), 71 (4), 57 (15), 43 (100); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.04 (t, J = 8 Hz, 3H), 1.73-1.86 (m, 2H), 4.10 (t, J = 8 Hz, 1H), 4.54 (t, J = 8 Hz, 1H), 4.67 (q, J = 7 Hz, 1H).

4-Popyl-1,3-dioxolan-2-one 2d GC-MS (m/z, %) 129 (1), 102 (1), 87 (67), 71 (20), 57 (40), 43 (100); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.99 (t, J = 7 Hz, 3H), 1.42-1.44 (m, 1H), 1.50-1.53 (m, 1H), 1.66-1.69 (m, 1H), 1.80-1.82 (m, 1H), 4.08 (t, J = 8 Hz, 1H), 4.54 (t, J = 8 Hz, 1H), 4.70-4.76 (m, 1H).

4,5-Dimethyl-1,3-dioxolan-2-one 2e[3] GC-MS (m/z, %) 116 (M^+, 3), 101 (4), 86 (1), 73 (3), 57 (7), 43 (100), 38 (6), 28 (78); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.46 (q, J = 6 Hz, 6H), 4.32-4.35 (m, 2H).

Tetrahydro-3a*H*-cyclopenta[*d*]-1,3-**dioxol-2-one 2f** GC-MS (m/z, %) 113 (2), 97 (12), 83 (37), 69 (100), 55 (77), 41 (89), 28 (40); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.41-1.47 (m, 2H), 1.59-1.66 (m, 2H), 1.88 (q, J = 4 Hz, 4H), 4.67-4.72 (m, 2H).

Hexahydrobenzo[*d*]-1,3- **dioxol-2-one 2g**[4] GC-MS (m/z, %) 128 (M^+, 7), 99 (4), 83 (14), 69 (3), 55 (100), 41 (20), 28 (19); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.68-1.82 (m, 4H), 2.15-2.18 (m, 2H), 5.10 (d, J = 4 Hz, 2H)

4-Phenyl-1,3-dioxolan-2-one 2h[5] GC-MS (m/z, %) 164 (M^+, 66), 131 (1), 119 (15), 105 (32), 90 (100), 78 (71), 65 (19), 51 (25), 39 (13); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 4.36 (t, J = 9 Hz, 1H), 4.83 (t, J = 9 Hz, 1H), 5.69 (t, J = 8 Hz, 1H), 7.27-7.48 (m, 5H).

^{1}H-NMR Spectra

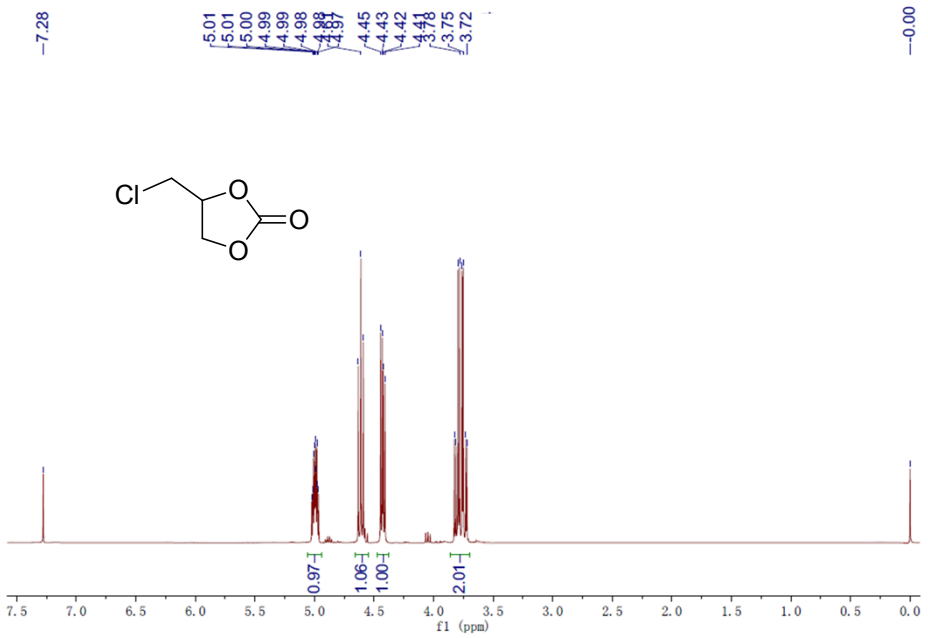

Fig. S3. ^{1}H-NMR spectrum of **2b**.

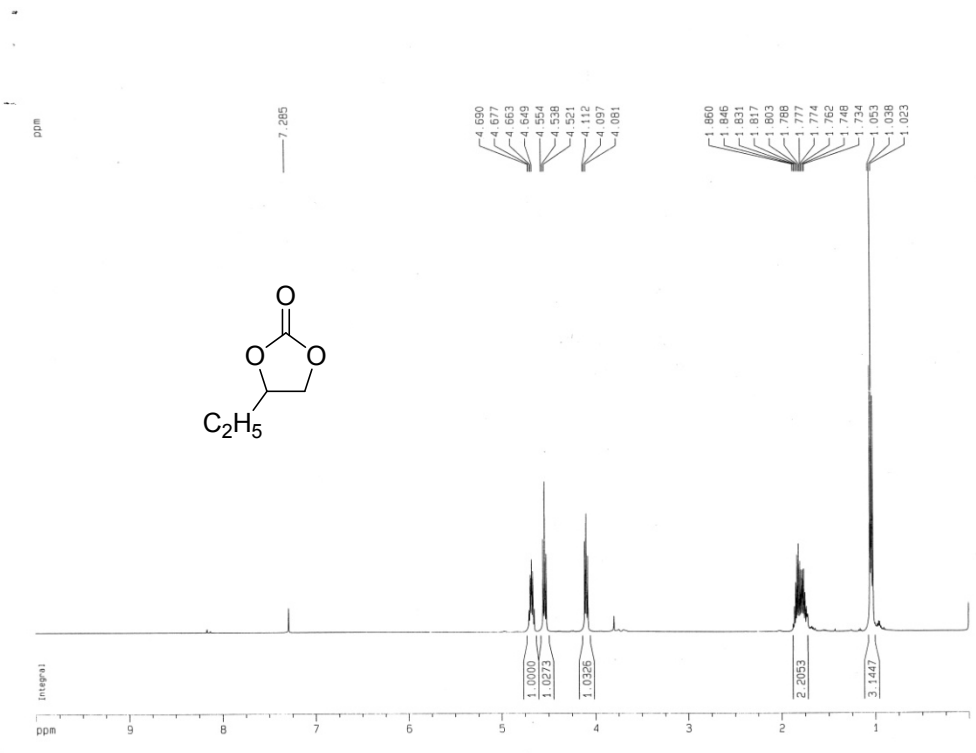

Fig. S4. ^{1}H-NMR spectrum of **2c**.

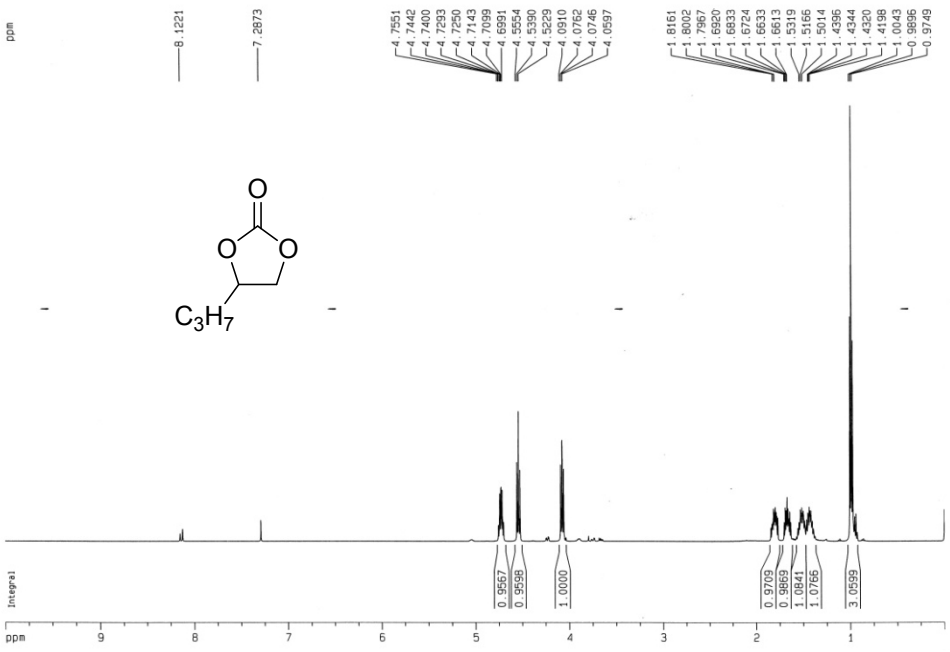

Fig. S5. ^{1}H-NMR spectrum of **2d**.

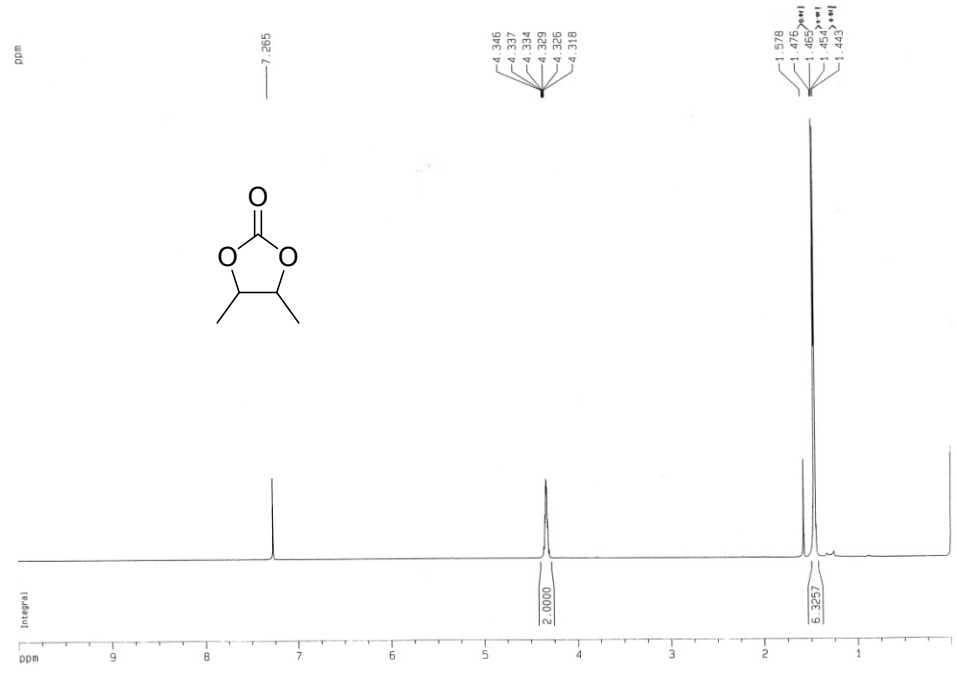

Fig. S6. ^{1}H-NMR spectrum of **2e**.

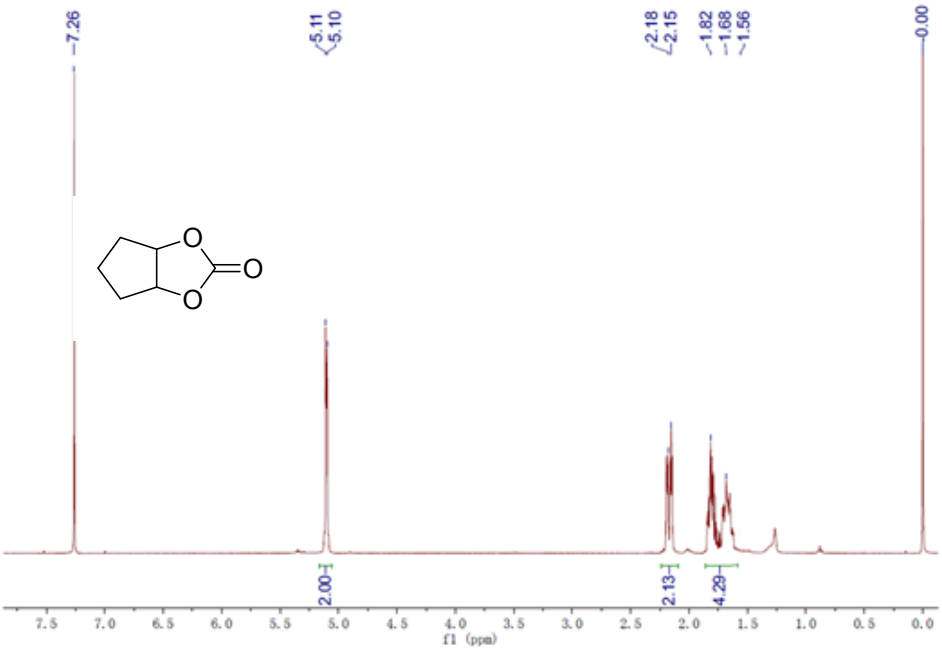

Fig. S7. ^{1}H-NMR spectrum of **2f**.

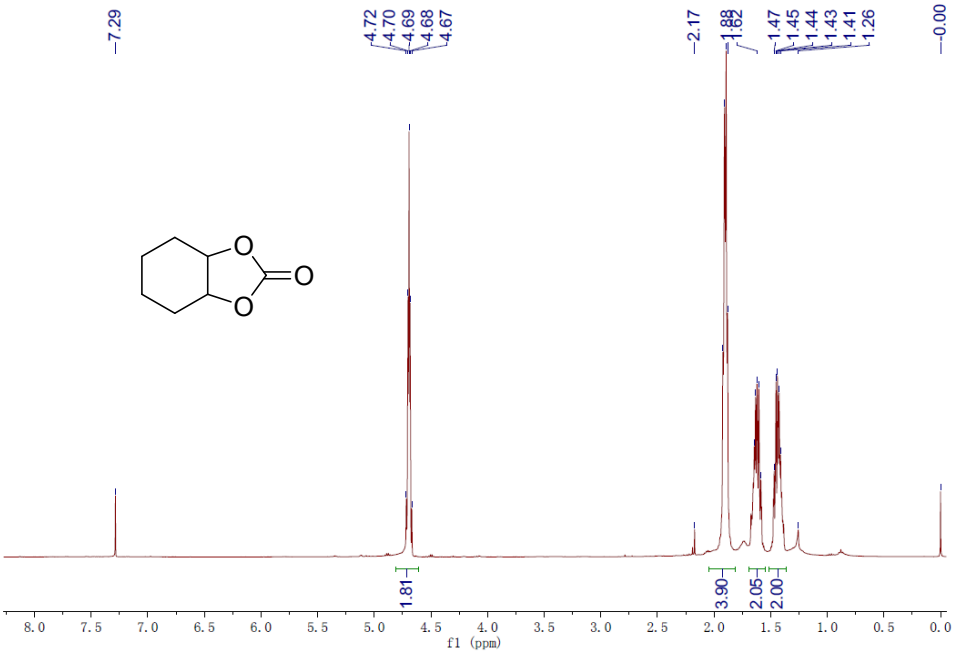

Fig. S8. ^{1}H-NMR spectrum of **2g**.

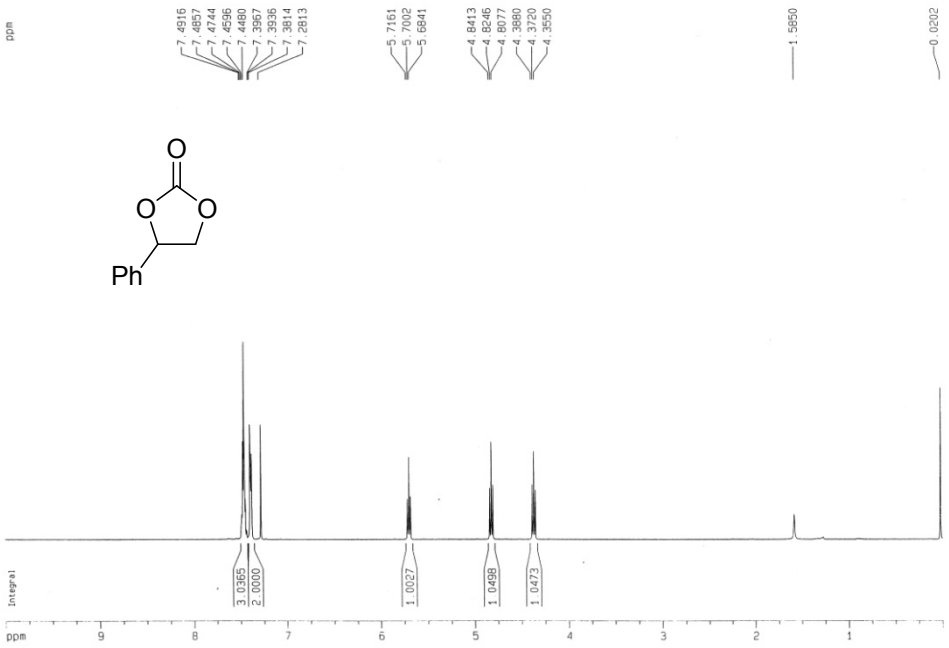

Fig. S9. ^{1}H-NMR spectrum of **2h**.

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