Supporting information

Chemical CO_2 fixation using a green biocatalytic system based on Ugi conjugated cobalt phthalocyanine on cellulose

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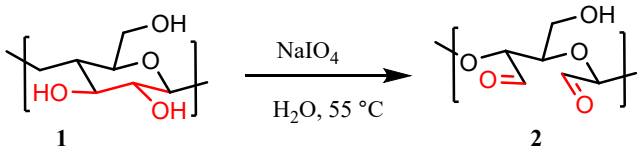
1. Experimental section

1.1. Oxidation of cellulose via periodate (OCell)

Cellulose (1.00 g, 6.16 mmol) was added to 40 mL of deionized water. $NaIO_4$ (1.58 g, 7.38 mmol) was suspended on 10 mL into deionized water that vessel was covered with aluminum foil. Then slowly add the $NaIO_4$ solution to the suspension and the flask was covered with aluminum foil to stop periodate decomposition induced by light. The reaction was conducted for 15 h at 55 °C. Then, ethylene glycol (4.1 mL, 73.8 mmol) was added to the dull red mixture to silence the unreacted $NaIO_4$. Subsequently, the reaction mixture was poured dropwise into 300 mL of ethanol and afterward filtered. The resulting white precipitate was then washed several times with ice water to remove the rest of the periodontium and by-products to obtain a pure product with a yield of 74% (Scheme S1).[1]

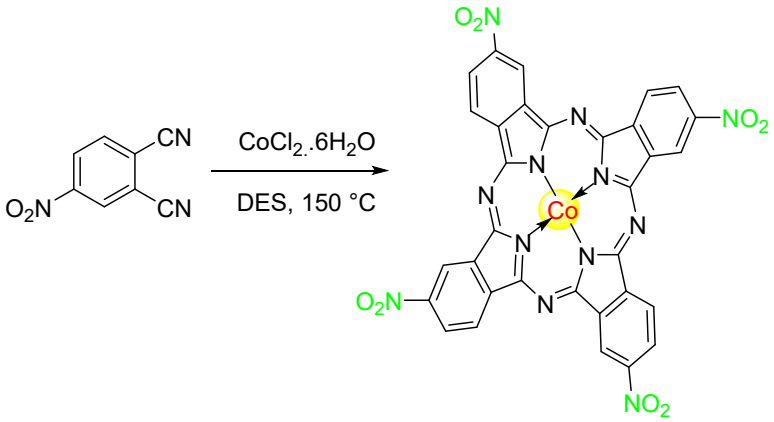


Scheme S1. Preparation of *Ocell*

1.2. Preparation of cobalt (II)-4,9,16,23-tetranitrophthalocyanine *(Co-PcTN)*

Deep eutectic solvent (DES) based on urea (360 mg, 6 mmol) and choline chloride (420 mg, 3 mmol) at 70 °C was generated and used without further purification. Afterward, a mixture of $CoCl_2.6H_2O$ (165 mg, 0.70 mmol) and 4-nitro-phthalonitrile (520 mg, 3.00 mmol) in DES was heated at 150 °C for 1 h. After ensuring the completion of the reaction, 10 ml of water was added to the mixture of the reaction. The insolvable crude product was filtered under a vacuum and washed sequentially with water and hot methanol and then dried. Subsequent, the product was

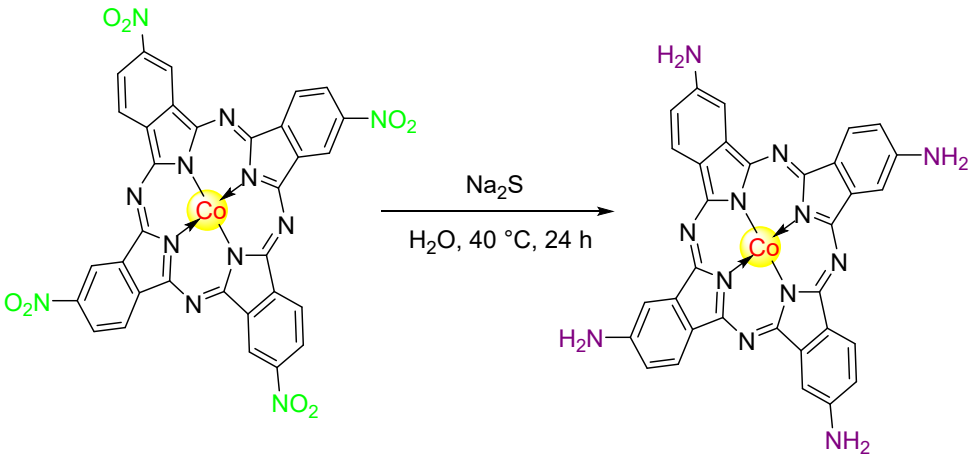
dissolved in the concentrated H_2SO_4 (7 ml), precipitated from water (250 ml), filtrated off, washed with water, and dried in an oven (70 °C) to give the Co-PcTN (422 mg, 75%) (Scheme S2), and to be utilized in the continuation of the procedure.[2]



Scheme S2. Preparation of Co-PcTN

1.3. Preparation of cobalt *(II) 2,9,16,23-tetra-amino phthalocyanine (Co-PcTA)*

Working on the previous reports,[3] sodium sulfide (Na_2S) (224 mg, 3.5 mmol) and Co-PcTN (376 mg, 0.5 mmol) were added to a 40 mL flask containing distilled water (6 mL), and the reaction vessel was covered and held for stirring at 40 °C for 24 h. Afterward, the Co-PcTA was filtered under a vacuum and washed with hot water several times to extract unreacted Na_2S. Then, it was granted a 0.1 N HCl wash several times followed by washing repeatedly with 0.1 N NaOH. Eventually, the remnants were washed with hot water, filtered and the Co-PcTA dried under a vacuum at 70 °C. The Co-PcTA isolated yield of this reaction was 85 % (267 mg) (Scheme ES3).



Scheme S3. Preparation of Co-PcTA

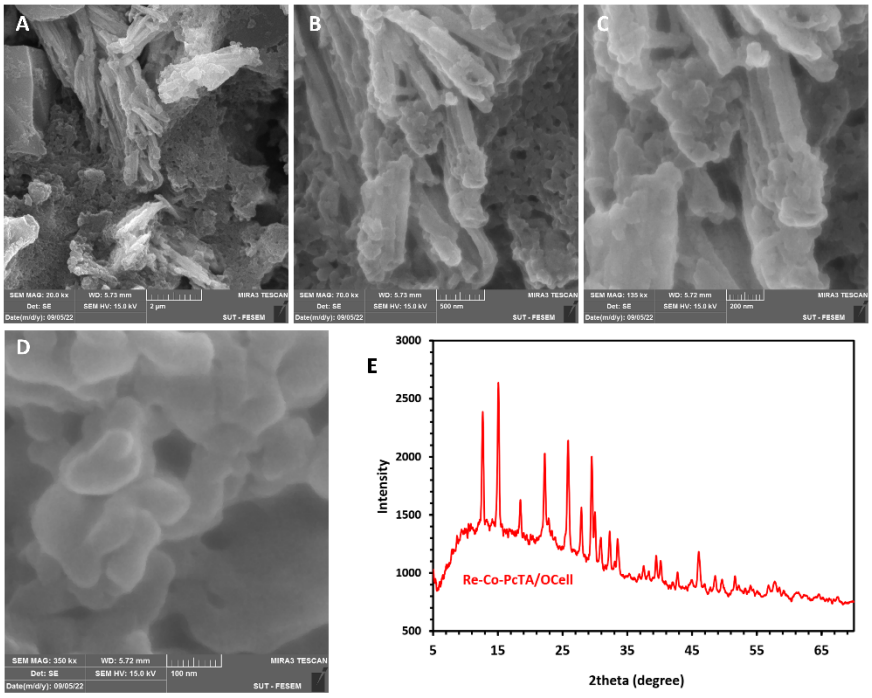


Figure S1. FE-SEM image and XRD of the reused biocatalyst (Re-Co-PcTA/OCell).

2. ^{1}H NMR data of isolated pure products

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

White solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.37 (t, J = 6 Hz, 1H), 4.80-4.85 (m, 1H), 5.70 (t, J = 6 Hz, 1H), 7.34-7.48 (m, $5H_{Ar}$).

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

White solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.22 (dd, J = 3 Hz, J = 12 Hz, 2H), 4.54-4.67 (m, 2H), 5.03-5.06 (m, 1H), 6.93 (d, J = 6 Hz, $2H_{Ar}$), 7.04 (t, J = 6 Hz, $2H_{Ar}$), 7.33 (t, J = 9 Hz, $2H_{Ar}$).

4-((Allyloxy)methyl)-1,3-dioxolan-2-one (8c)

White solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.26 (t, J = 9 Hz, 1H, 2H), 3.58-3.74 (m, 3H), 3.94-4.01 (m, 1H), 4.18-4.21 (m, 2H), 5.56-5.58 (bs, 1H), 6.13-6.15 (bs, 1H).

Octahydrocycloocta[*d*][1,3]dioxol-2-one (8d)

Colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.99-1.11 (m, 4H), 1.30-1.37 (m, 4H), 1.92 (d, J = 15 Hz, 4H), 3.18 (t, J = 15 Hz, 2H).

4-Butyl-1,3-dioxolan-2-one (8e)

Orange oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.73 (t, J = 6 Hz, 3H), 1.18-1.29 (m, 4H), 1.47-1.57 (m, 2H), 3.91 (t, J = 9 Hz, 3H), 4.43 (t, J = 9 Hz, 1H), 4.59 (t, J = 9 Hz, 1H).

4-(Chloromethyl)-1,3-dioxolan-2-one (8f) White solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.78–3.70 (ddd, J = 3 Hz, J = 15 Hz, J = 27 Hz, 2 H, CH_2Cl), 4.60 (m, 1 H, OCH_2), 4.57-4.66 (m, 1 H, OCH_2), 4.97-5.04 (m, 1 H, OCH_2).

3. ^{1}H NMR spectrum of products 8a-e

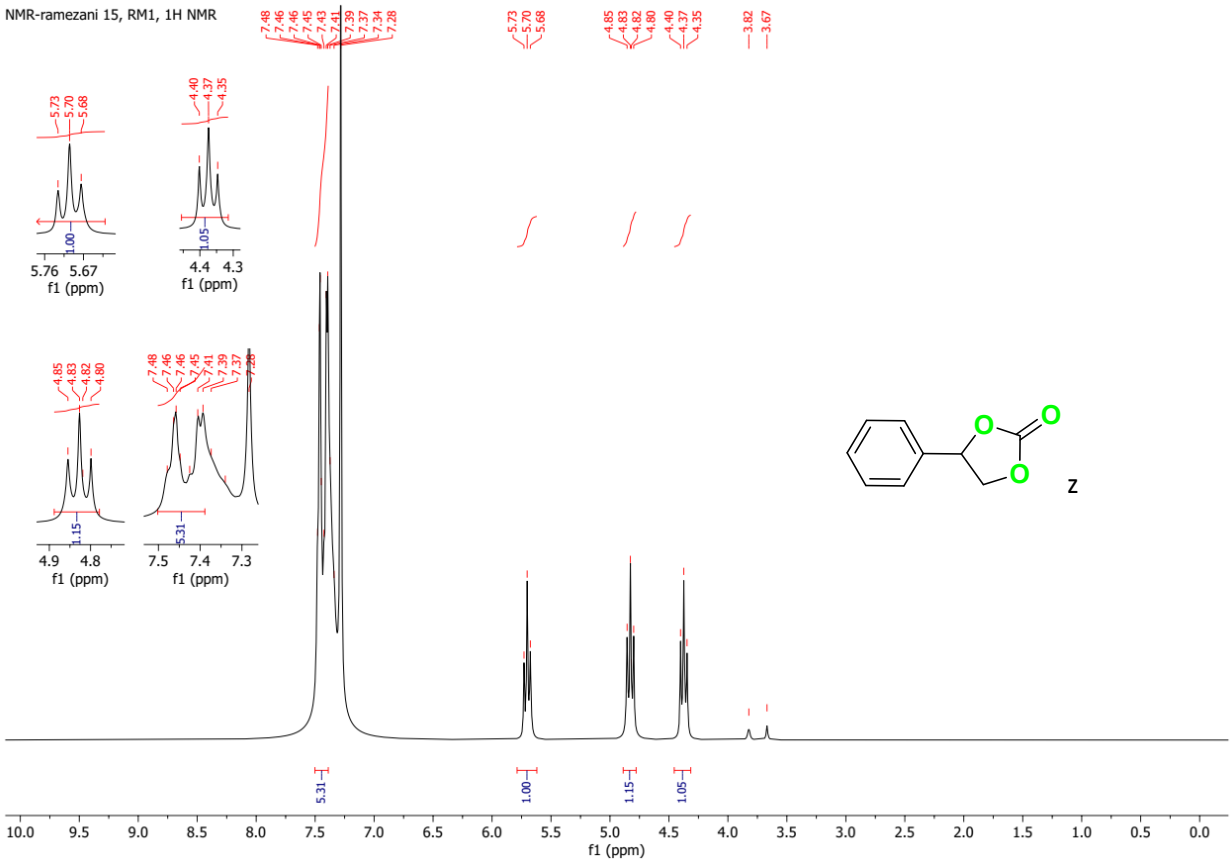


Figure S2. ^{1}H NMR spectrum of 4-phenyl-1,3-dioxolan-2-one (**8a**).

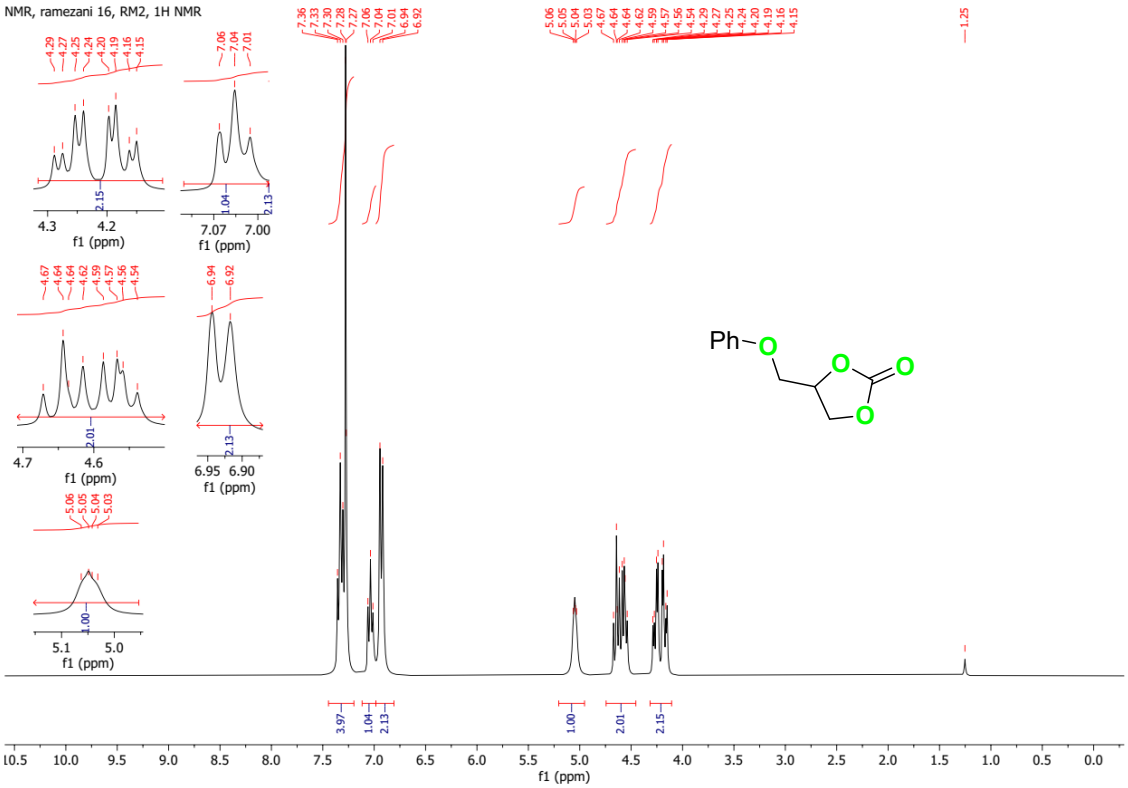


Figure S3. ^{1}H NMR spectrum of 4-(phenoxymethyl)-1,3-dioxolan-2-one (**8b**).

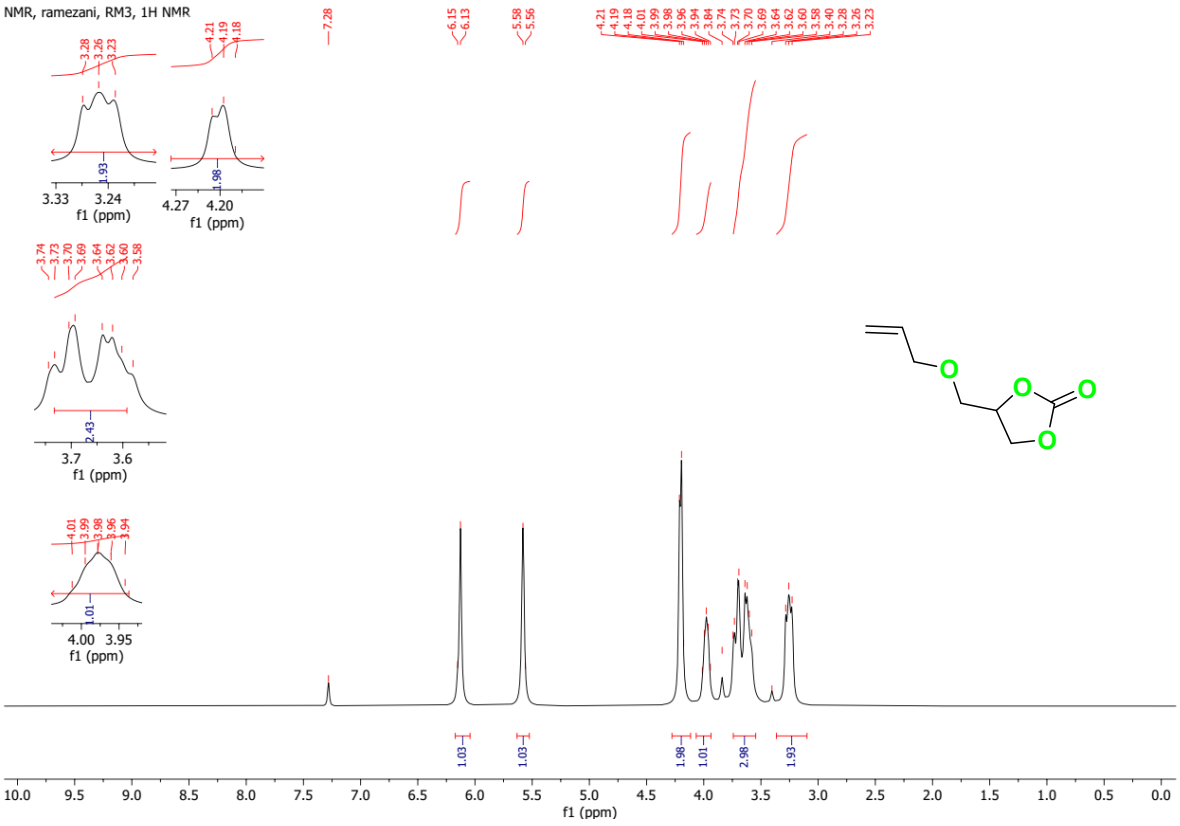


Figure S4. ^{1}H NMR spectrum of 4-((allyloxy)methyl)-1,3-dioxolan-2-one (**8c**).

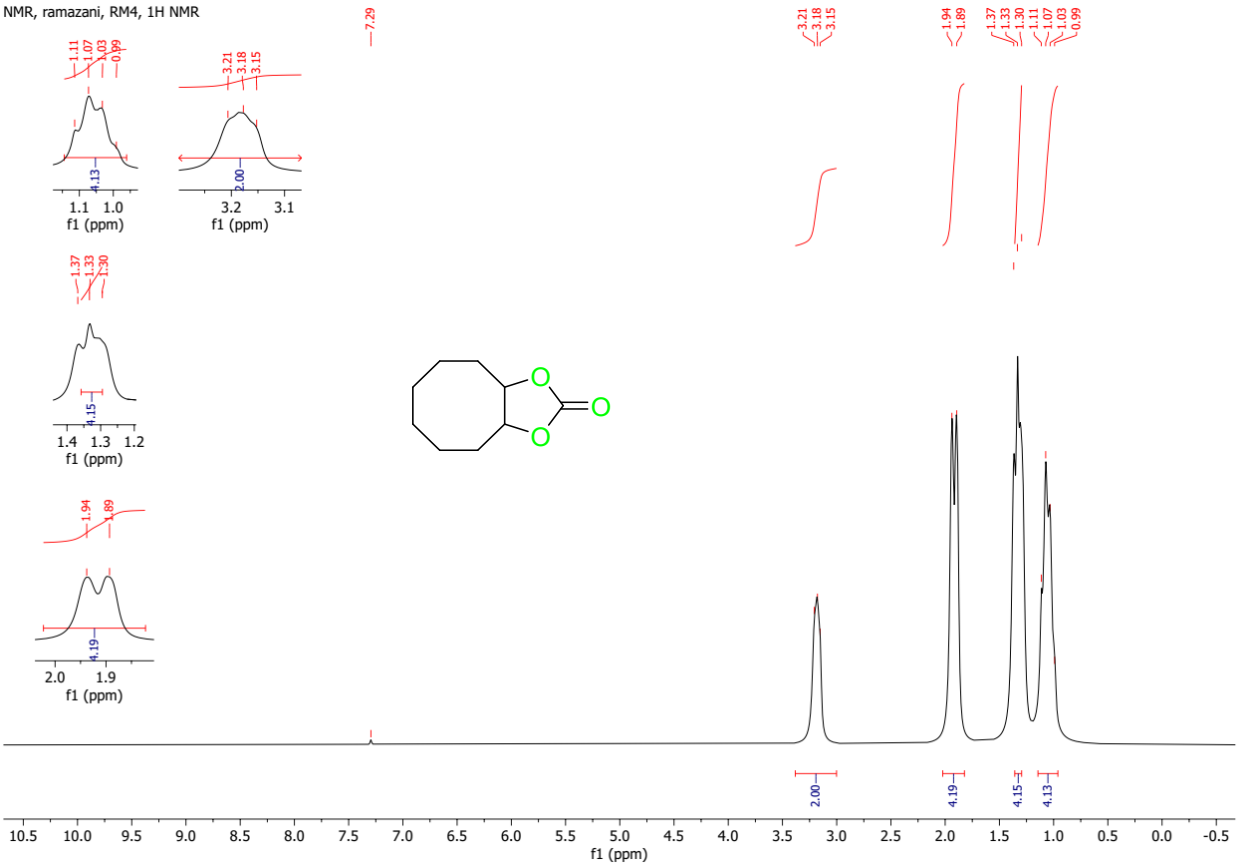


Figure S5. ^{1}H NMR spectrum of octahydrocycloocta[*d*][1,3]dioxol-2-one (**8d**).

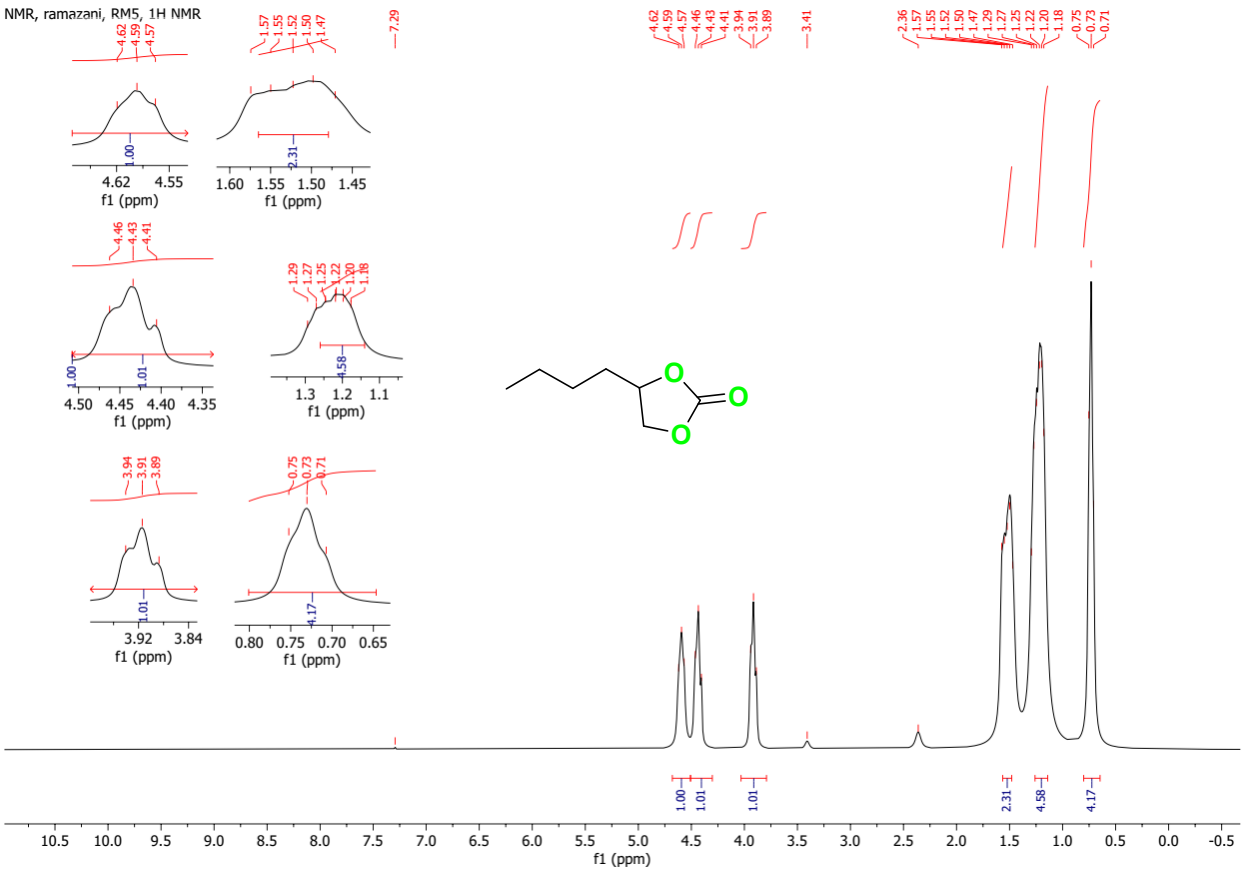


Figure S6. ^{1}H NMR spectrum of 4-butyl-1,3-dioxolan-2-one (**8e**).

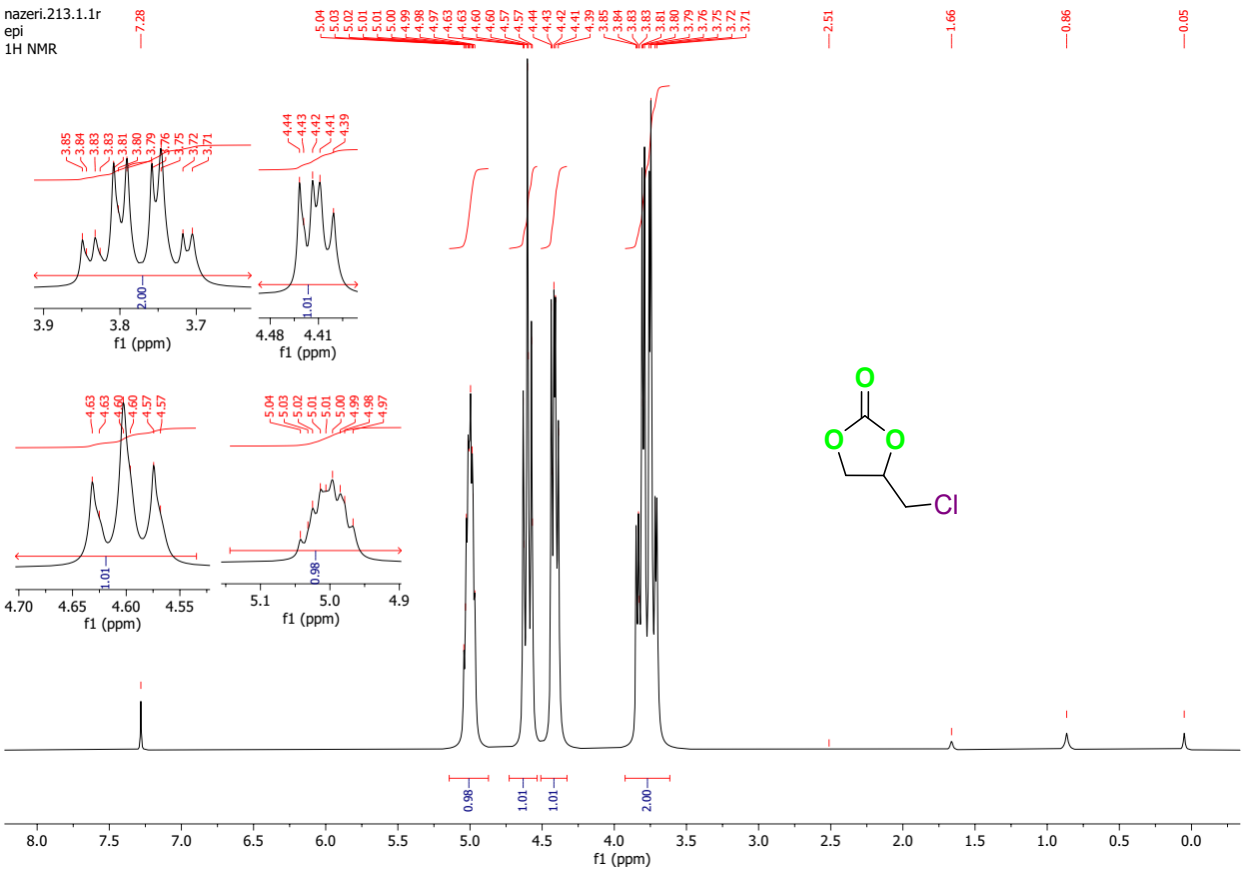


Figure S7. ^{1}H NMR spectrum of 4-(chloromethyl)-1,3-dioxolan-2-one (**8f**).

References

(1) Esen, E.; Meier, M. A. Sustainable Functionalization of 2, 3-Dialdehyde Cellulose via the Passerini Three-Component Reaction. *ACS Sustain. Chem. Eng.* **2020**, *8* (41), 15755-15760.

(2) Shaabani, A.; Hooshmand, S. E.; Afshari, R.; Shaabani, S.; Ghasemi, V.; Atharnezhad, M.; Akbari, M. Direct construction of diverse metallophthalocyanines by manifold substrates in a deep eutectic solvent. *J. Solid State Chem.* **2018**, *258*, 536-542.

(3) Guo, D.; Zhang, J.; Liu, G.; Luo, X.; Wu, F. Cobalt phthalocyanine-based nanodots as efficient catalysts for chemical conversion of CO_2 under ambient conditions. *J. Mater. Sci.* **2021**, *56* (18), 10990-10999.