Supporting information for

Cycloaddition of CO₂ to Epoxides Catalyzed by N-heterocyclic Carbene (NHC)/ZnBr₂ System under Mild Conditions

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Experimental Section

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General procedure: Imidazol(in)ium chlorides were prepared using literature procedures. All other chemicals were commercially available and used as received unless otherwise stated. THF and toluene were distilled from sodium benzenephone ketyl prior to use. DMF was stirred over MgSO₄ overnight, filtered, and then distilled over 4Å molecular sieves. DMSO was distilled over calcium hydride and stored with 4Å molecular sieves. CO₂ (purity ≥ 95%) was dried by going through concentrated sulfuric acid or more pure CO₂ (purity ≥ 99.95%) was used directly. ¹H and ¹³C NMR spectra were recorded on Bruker AV400 spectrometers. Chemical shift values are expressed in ppm relative to solvent residue. GC-MS was performed on an Agilent 6890-5973N system with electron ionization (EI) mass spectrometry. IR spectra were recorded on KBr pellets on a FTIR-Tensor 27 spectrometer.

General procedure for the cycloaddition reaction of epoxides with CO₂: An oven-dried 50 mL of round-bottom flask containing 2 mol% of catalyst c (0.149 g, 0.35 mmol), 2 mol% of K₂CO₃ (0.048 g, 0.35 mmol) and 2 mol% of ZnBr₂ (0.079 g, 0.35 mmol) was purged with CO₂ under atmosphere pressure for three times. Then 17.5 mmol of epoxide and 10 mL of DMSO were injected into the flask by syringe and CO₂ was provided by a balloon. The reaction was stirred at 80°C for 24 hours. After the reaction was cooled down, 200 mL of water was added in the reaction mixture. The organic layer was extracted with DCM (3 x 20 mL), and filtered through silica plug. The products were collected by evaporating volatiles and dried under vacuum. Using high pure CO₂ or low grade of CO₂ gave no difference on the results.

For the reaction under less than 1atm of CO₂, the mixture of argon and CO₂ with different ratio was used for purging and reaction.

Preparation of 1,3-bis(2,6-diisopropylphenyl)imidazolinium-2-carboxylate (c-CO₂): The imidazolium chloride (0.214 g, 0.5 mmol) and potassium tert-butoxide (0.067 g, 0.6 mmol) were added into an oven-dried 50 mL of round-bottom flask equipped with a magnetic stir bar. The flask was purged with CO₂ for three times and 15 mL of THF was added. CO₂ was provided by a balloon and the...
The collected precipitation was redissolved in 10 mL of DCM, and the resulting suspension was filtered. The filtrate was concentrated and dried. Subsequent washing with 10 mL of ether afforded the imidazolinium carboxylate (c-CO$_2$). Yield: 55%. 1H NMR (400 MHz, CDCl$_3$): δ 7.48 (t, $J$ = 8.0 Hz, 2H), 7.28 (d, $J$ = 7.6 Hz, 4H), 4.88 (s, 4H), 3.02 (sextet, $J$ = 6.8 Hz, 4H), 1.40 (d, $J$ = 6.8 Hz, 12H), 1.25 (d, $J$ = 6.8 Hz, 12H). IR: 1681 cm$^{-1}$ ν(CO$_2$).

Preparation of Zn-NHC complex (c-ZnCl$_2$): 15 mL of THF was added into an oven-dried 50 mL of round-bottom flask with imidazolinium chloride c (0.214 g, 0.5 mmol) and potassium tert-butoxide (0.067 g, 0.6 mmol) under Ar atmosphere. The solution was allowed to stir at 50 °C for 2 h before being filtered through cotton. The formed carbene solution was then transferred slowly into another 50 mL of round-bottom flask with ZnCl$_2$ (0.068 g, 0.5 mmol). The mixture was stirred at room temperature for 12 h, and was concentrated to 3 mL. 20 mL of petroleum ether was added. The collected precipitation was redissolved in 10 mL of DCM, and the resulting suspension was filtered. The filtrate was concentrated and dried in vacuo. Yield: 80%. 1H NMR (400 MHz, CDCl$_3$): δ 7.28 (t, $J$ = 8.0 Hz, 2H), 7.08 (d, $J$ = 8.0 Hz, 4H), 4.81 (s, 4H), 2.95 (sextet, $J$ = 6.8 Hz, 4H), 1.21 (d, $J$ = 6.8 Hz, 12H), 1.02 (d, $J$ = 6.8 Hz, 12H). 13C NMR (100 MHz, CDCl$_3$): δ 156.6, 146.5, 131.3, 129.4, 124.9, 55.7, 28.9, 25.4, 23.8. Anal. Calcd for C$_{27}$H$_{38}$Cl$_2$N$_2$Zn (526.9 g/mol): C, 61.55; H, 7.27; N, 5.32. Found: C, 61.41; H, 7.57; N, 5.27%.

The reaction of c-ZnCl$_2$ complex with CO$_2$: An oven-dried 5 mL of round-bottom flask equipped with a magnetic stir bar was purged 3 times with CO$_2$. A solution of the c-ZnCl$_2$ complex in 2 mL of CDCl$_3$ was injected into the flask. The reaction was stirred at 50 °C for 3 h with a CO$_2$ balloon. The solution was transferred to a NMR tube for measuring NMR spectrum.

**Data for cyclic carbonates**

**4-ethyl-1,3-dioxolan-2-one.**

4 yellow oil. 1H NMR (400 MHz, CDCl$_3$): δ 4.69-4.62 (m, 1H), 4.52 (t, $J$ = 8.0 Hz, 1H), 4.08 (t, $J$ = 7.6 Hz, 1H), 1.87-1.68 (m, 2H), 1.02 (t, $J$ = 7.6 Hz, 3H). IR: 1799 cm$^{-1}$ (νCO).

**4-butyl-1,3-dioxolan-2-one.**

4 yellow oil. 1H NMR (400 MHz, CDCl$_3$): δ 4.72-4.65 (m, 1H), 4.51 (t, $J$ = 8.0 Hz, 1H), 4.05 (t, $J$ = 8.0 Hz, 1H), 1.82-1.61 (m, 2H), 1.46-1.27 (m, 4H), 0.89 (t, $J$ = 6.8 Hz, 3H). 13C NMR (100 MHz, CDCl$_3$): δ 155.0 (C=O), 69.3, 53.4, 33.4, 26.3, 22.1, 13.7. IR: 1790 cm$^{-1}$ (νCO).

**4-(chloromethyl)-1,3-dioxolan-2-one.**

4 yellow oil. 1H NMR (400 MHz, CDCl$_3$): δ 4.99-4.93 (m, 1H), 4.59 (app. t, $J$ = 8.4 Hz, 1H), 4.41 (dd, $J$ = 6.0 Hz, $J$ = 8.8 Hz, 1H), 3.78 (dd, $J$ = 12.0 Hz, $J$ = 5.6 Hz, 1H), 3.73 (dd, $J$ = 12.0 Hz, $J$ = 4.0 Hz, 1H). 13C NMR (100 MHz, CDCl$_3$): δ 154.0 (C=O), 74.2, 66.9, 43.5. IR: 1790 cm$^{-1}$ (νCO).
4-(bromomethyl)-1,3-dioxolan-2-one. Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.97-4.90 (m, 1H), 4.60 (app. t, $J = 8.4$ Hz, 1H), 4.36 (dd, $J = 6.0$ Hz, $J = 9.0$ Hz, 1H), 3.61-3.52 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 154.2 (C=O), 73.9, 68.0, 31.7. IR: 1794 cm$^{-1}$ (vCO).

4-phenyl-1,3-dioxolan-2-one. White solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.47-7.35 (m, 5H), 5.68 (t, $J = 8.0$ Hz, 1H), 4.80 (t, $J = 8.4$ Hz, 1H), 4.35 (t, $J = 8.4$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 154.8 (C=O), 135.8, 129.7, 129.2, 125.8, 77.9, 71.1. IR: 1775 cm$^{-1}$ (vCO).

4-benzyl-1,3-dioxolan-2-one. Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.36-7.21 (m, 5H), 4.96-4.89 (m, 1H), 4.44 (t, $J = 8.0$ Hz, 1H), 4.17 (t, $J = 7.2$ Hz, 1H), 3.15 (dd, $J = 14.0$ Hz, $J = 6.4$ Hz, 1H), 2.99 (dd, $J = 14.2$ Hz, $J = 6.4$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 154.8 (C=O), 133.8, 129.3, 128.9, 127.5, 76.7, 68.4, 39.5. IR: 1791 cm$^{-1}$ (vCO).

4-(phenoxymethyl)-1,3-dioxolan-2-one. White solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.31 (t, $J = 7.6$ Hz, 2H), 7.02 (t, $J = 7.2$ Hz, 1H), 6.91 (d, $J = 8.4$ Hz, 2H), 5.06-5.00 (m, 1H), 4.62 (t, $J = 8.8$ Hz, 1H), 4.54 (dd, $J = 8.4$ Hz, $J = 6.0$ Hz, 1H), 4.24 (dd, $J = 10.0$ Hz, $J = 4.0$ Hz, 1H), 4.15 (dd, $J = 10.4$ Hz, $J = 3.2$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 157.7, 154.6 (C=O), 129.7, 121.9, 114.5, 74.1, 66.8, 66.2. IR: 1803 cm$^{-1}$ (vCO).

(2-oxo-1,3-dioxolan-4-yl)methyl benzoate. Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.02 (d, $J = 8.0$ Hz, 2H), 7.60 (t, $J = 7.2$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 2H), 5.09-5.03 (m, 1H), 4.65-4.57 (m, 2H), 4.51 (dd, $J = 12.8$ Hz, $J = 4.0$ Hz, 1H), 4.43 (dd, $J = 8.4$ Hz, $J = 5.6$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.9 (C=O), 154.4 (C=O), 133.7, 129.8, 128.6, 128.4, 73.8, 66.0, 63.6. IR: 1793 cm$^{-1}$ (vCO).
References:

NMR Spectra:

c-ZnCl₂
$^1$H NMR spectra in CDCl$_3$. aa) c-CO$_2$ adduct, bb) c-ZnCl$_2$ complex, cc) treatment of c-ZnCl$_2$ complex with CO$_2$

4-ethyl-1,3-dioxolan-2-one (Table 3, entry 1)
4-butyl-1,3-dioxolan-2-one (Table 3, entry 2)
4-(chloromethyl)-1,3-dioxolan-2-one (Table 3, entry 3)
4-(bromomethyl)-1,3-dioxolan-2-one (Table 3, entry 4)
4-phenyl-1,3-dioxolan-2-one (Table 3, entry 5)
4-benzyl-1,3-dioxolan-2-one (Table 3, entry 6)
4-(phenoxymethyl)-1,3-dioxolan-2-one (Table 3, entry 7)
4-(benzyloxymethyl)-1,3-dioxolan-2-one (Table 3, entry 8)
(2-oxo-1,3-dioxolan-4-yl)methyl benzoate (Table 3, entry 9)