Electronic Supplementary Information

Zinc Iodide-Metal Chloride-Organic Base: An Efficient Catalytic System for Synthesis of Cyclic Carbonates from Carbon Dioxide and Epoxides under Ambient Conditions

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Characterization of Compounds 2a-i

^{1}H and ^{13}C NMR spectra were obtained on a JEOL JNM-ECA600 (600 MHz, 151MHz) instrument. Chemical shifts were reported in ppm relative to tetramethylsilane (δ-units). Mass spectra were recorded on a SHIMADZU GCMS-QP2010 Ultra. 5-Membered cyclic carbonates **2a-i** were identified by comparison of their spectroscopic data (^{1}H and ^{13}C NMR) with those in the literature.

Styrene carbonate (2a) [34]

Yield: 95% (white solid);

^{1}H NMR (600 MHz, $CDCl_3$): δ 4.35 (dd, J = 9.0, 7.8 Hz, 1H), 4.80 (t-like, J = 8.4 Hz, 1H), 5.67-5.69 (m, 1H), 7.36-7.47 (m, 5H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 71.14, 77.97, 125.85, 129.19, 129.69, 135.76, 154.84;

MS (EI), *m/z* (%) = 164 (M^+, 50), 91 (71), 90 (100), 78 (74).

Propylene carbonate (2b) [34]

Yield: 90% (colorless liquid);

^{1}H NMR (600 MHz, $CDCl_3$): δ 1.50 (d, J = 6.0 Hz, 3H), 4.04 (dd, J = 7.8, 7.2 Hz, 1H), 4.57 (t-like, J = 8.4 Hz, 1H), 4.84-4.90 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 19.36, 70.59, 73.49, 154.98;

MS (EI), *m/z* (%) = 102 (M^+, 4), 87 (20), 58 (15), 57 (100).

4-Phenoxymethyl-1,3-dioxolan-2-one (2c) [67]

Yield: 92% (white solid);

^{1}H NMR (600 MHz, $CDCl_3$): δ 4.16 (dd, J = 10.2, 3.6 Hz, 1H), 4.24 (dd, J = 10.2, 4.2 Hz, 1H), 4.55 (dd, J = 8.4, 6.0 Hz, 1H), 4.62 (t-like, J = 8.4 Hz, 1H), 5.01-5.05 (m, 1H), 6.90-6.92 (m, 2H), 7.01-7.03 (m, 1H), 7.30-7.33 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 66.23, 66.83, 74.06, 114.57, 121.99, 129.69, 154.62, 157.72;

MS (EI), *m/z* (%) = 194 (M^+, 54), 107 (100), 94 (83), 77 (100).

4-Chloromethyl-1,3-dioxolan-2-one (2d) [34]

Yield: 85% (colorless liquid);

^{1}H NMR (600 MHz, $CDCl_3$): δ 3.73-3.79 (m, 2H), 4.42 (dd, J = 9.0, 6.0 Hz, 1H), 4.60 (t-like, J = 8.4 Hz, 1H), 4.94-4.98 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 43.56, 66.94, 74.19, 154.08;

MS (EI), *m/z* (%) = 136 (M^+, 0.4), 87 (100), 57 (8).

4-Octyl-1,3-dioxolan-2-one (2e) [68]

Yield: 89% (colorless liquid);

^{1}H NMR (600 MHz, $CDCl_3$): δ 0.89 (t, J = 6.6 Hz, 3H), 1.22-1.51 (m, 12H), 1.65-1.71 (m, 1H), 1.78-1.84 (m, 1H), 4.07 (t-like, J = 8.4 Hz, 1H), 4.53 (t-like, J = 8.4 Hz, 1H), 4.68-4.73 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 14.03, 22.57, 24.31, 29.05, 29.09, 29.25, 31.72, 33.84, 69.36, 77.03, 155.06;

MS (EI), *m/z* (%) = 200 (M^+, 0.01), 110 (21), 96 (50), 81 (73), 67 (88), 55 (100).

4-Allyloxymethyl-1,3-dioxolan-2-one (2f) [34]

Yield: 89% (colorless liquid);

^{1}H NMR (600 MHz, $CDCl_3$): δ 3.63 (dd, J = 10.8, 4.2 Hz, 1H), 3.69 (dd, J = 10.8, 4.2 Hz, 1H), 4.04-4.10 (m, 2H), 4.41 (dd, J = 8.4, 6.0 Hz, 1H), 4.51 (t-like, J = 8.4 Hz, 1H), 4.80-4.84 (m, 1H), 5.23-5.31 (m, 2H), 5.84-5.91 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 66.23, 68.78, 72.55, 74.96, 117.90, 133.60, 154.90;

MS (EI), *m/z* (%) = 158 (M^+, 0.06), 102 (36), 71 (55), 57 (100).

4,4'-(Butane-1,4-diyl)-bis-1,3-dioxolan-2-one (2g) [67]

Yield: 95% (colorless liquid);

^{1}H NMR (600 MHz, $CDCl_3$): δ 1.46-1.64 (m, 4H), 1.71-1.85 (m, 4H), 4.08 (t-like, J = 8.4 Hz, 2H), 4.55 (t-like, J = 8.4 Hz, 2H), 4.70-4.75 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 24.17, 24.23, 33.67, 33.75, 69.24, 76.60, 154.83;

MS (EI), *m/z* (%) = 230 (M^+, 0.02), 129 (19), 82 (47), 67 (100), 54 (78).

***cis*-Cyclohexene carbonate (*cis*-2h)** [69]

Yield: 32% (white solid);

^{1}H NMR (600 MHz, $CDCl_3$): δ 1.40-1.46 (m, 2H), 1.60-1.66 (m, 2H), 1.89-1.92 (m, 4H), 4.67-4.70 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 19.13, 26.74, 75.70, 155.32;

MS (EI), *m/z* (%) = 142 (M^+, 0.2), 88 (33), 69 (98), 55 (100).

***trans*-Cyclohexene carbonate (*trans*-2h)** [69]

Yield: 6% (white solid);

^{1}H NMR (600 MHz, $CDCl_3$): δ 1.37-1.46 (m, 2H), 1.65-1.72 (m, 2H), 1.91-1.96 (m, 2H), 2.26-2.29 (m, 2H), 4.00-4.05 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 23.17, 28.21, 83.49, 155.06;

MS (EI), *m/z* (%) = 142 (M^+, 0.2), 69 (100), 57 (55).

***trans*-4,5 Diphenyl-1,3-dioxolan-2-one (2i)** [34]

Yield: 53% (white solid);

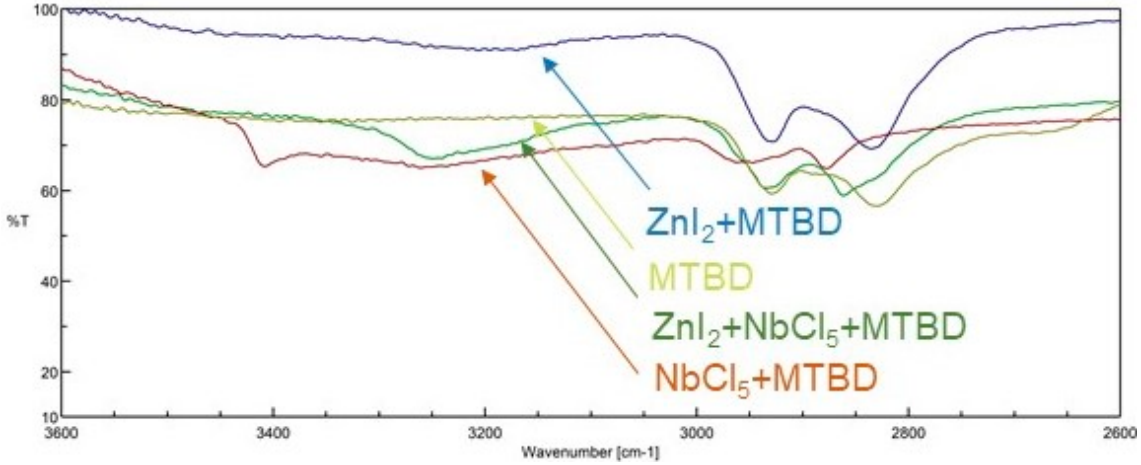
^{1}H NMR (600 MHz, $CDCl_3$): δ 5.44 (s, 2H), 7.31-7.33 (m, 4H), 7.43-7.45 (m, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 85.36, 126.02, 129.21, 129.78, 134.76, 154.08;

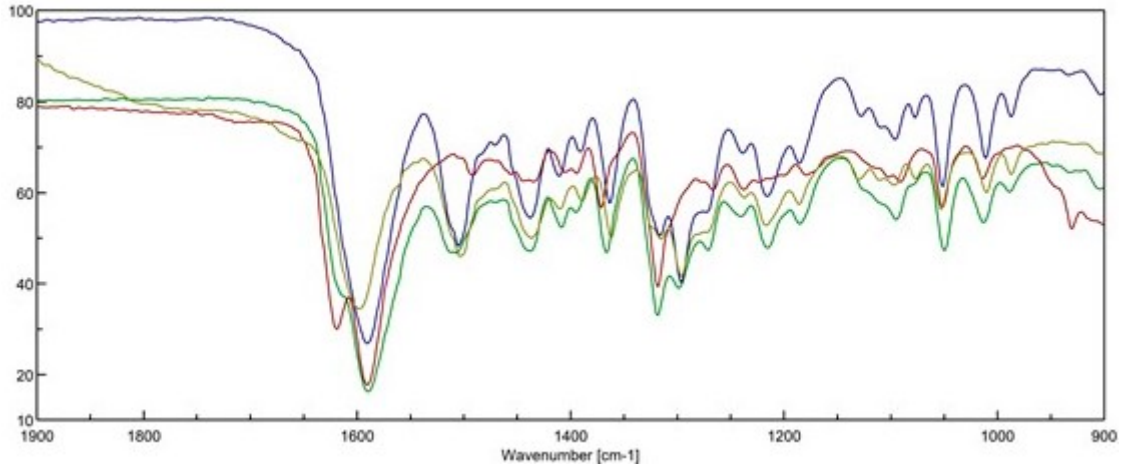
MS (EI), *m/z* (%) = 240 (M^+, 24), 195 (25), 167 (50), 90 (100).

IR spectra of ZnI_2, $NbCl_5$, or/and MTBD

After ZnI_2 (012 mmol), MTBD (0.3 mmol), or/and $NbCl_5$ (0.03 mmol) were mixed by a spatula, IR spectra were recorded on a JASCO FT-IR-4100/Smiths Detection DuraScope instrument.



(a)



(b)

Figure S1. IR spectra of MTBD, ZnI_2+MTBD, $NbCl_5$+MTBD, and ZnI_2+$NbCl_5$+MTBD (a: 3600-2600 cm^{-1}, b: 1900-900 cm^{-1}).