Supporting Information

Ionic liquid post-modified carboxylate-rich MOFs for efficiently catalytic CO₂ cycloaddition under solvent-free conditions

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Products characterization

4-phenyl-1,3-dioxolan-2-one (1b)

¹**H NMR** (300 MHz, CDCl₃) δ 7.57 – 7.15 (m, 5H), 5.95 – 5.41 (td, J = 8.0, 1.8 Hz, 1H), 4.97 – 4.61 (td, J = 8.5, 2.2 Hz, 1H), 4.42 – 4.15 (td, J = 8.2, 2.6 Hz, 1H).

¹³C NMR (75MHz, CDCl₃) δ 155.08 (d, J = 1.5 Hz), 135.94 (d, J = 1.7 Hz), 129.68, 129.20, 126.05, 78.10, 71.24.



4-methyl-1,3-dioxolan-2-one (2b)

¹**H** NMR (300 MHz, CDCl₃) δ 4.83 (h, J = 6.7 Hz, 1H), 4.65 – 4.32 (m, 1H), 4.20 – 3.76 (m, 1H), 1.44 (d, J = 6.3, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 151.46, 69.97, 67.01, 15.66.



4-ethyl-1,3-dioxolan-2-one (3b)

¹**H NMR** (300 MHz, CDCl₃) δ 4.68 – 4.59 (m, 1H), 4.49 (t, *J* = 8.2 Hz, 1H), 4.04 (ddd, *J* = 8.3, 7.0, 1.0 Hz, 1H), 1.73 (dddd, *J* = 16.0, 14.7, 7.3, 5.9 Hz, 2H), 0.97 (tt, *J* = 7.4, 1.4 Hz, 3H). ¹³**C NMR** (75 MHz, CDCl₃) δ 151.46, 74.33, 65.30, 23.04, 4.63.



4-butyl-1,3-dioxolan-2-one (4b)

¹H NMR (300 MHz, CDCl₃) δ 4.33 (qd, J = 7.5, 5.5 Hz, 1H), 4.15 (t, J = 8.1 Hz, 1H), 3.73 – 3.64 (m, 1H), 1.48 – 1.25 (m, 2H), 1.09 – 0.90 (m, 4H), 0.52 (t, J = 7.0 Hz, 3H).
¹³C NMR (75 MHz, CDCl₃) δ 151.58, 73.53, 65.82, 29.84, 22.77, 18.58, 10.14.

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

¹**H NMR** (300 MHz, CDCl₃) δ 4.81 – 4.57 (m, 1H), 4.24 (t, *J* = 8.6 Hz, 1H), 4.05 (dd, *J* = 8.9, 5.7 Hz, 1H), 3.54 – 3.30 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 151.49, 71.45, 63.97, 41.07.

Br₁

4-(bromomethyl)-1,3-dioxolan-2-one (6b)

¹H NMR (300 MHz, CDCl₃) δ 4.84 – 4.60 (m, 1H), 4.32 (t, *J* = 8.6 Hz, 1H), 4.06 (t, *J* = 8.9, 5.9 Hz, 1H), 3.47 – 3.18 (m, 2H).
¹³C NMR (75 MHz, CDCl₃) δ 151.42, 71.09, 65.10, 29.15.

4,4-dimethyl-1,3-dioxolan-2-one (7b)

¹**H** NMR (300 MHz, CDCl₃) δ 4.02 (s, *J* = 8.4, 7.1 Hz, 2H), 1.57 (s, *J* = 1.1 Hz, 6H). ¹³**C** NMR (75 MHz, CDCl₃) δ 155.31, 82.10, 75.55, 25.89.



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

¹H NMR (300 MHz, CDCl₃) δ 7.30 - 7.19 (q, 2H), 6.99 - 6.79 (m, 3H), 4.95 (dq, *J* = 9.5, 6.0, 3.6 Hz, 1H), 4.69 - 4.35 (m, 2H), 4.10 (m, *J* = 35.9, 10.7, 3.6 Hz, 2H).
¹³C NMR (75 MHz, CDCl₃) δ 153.40, 150.52, 125.32, 117.53, 110.21, 69.94, 62.46, 61.82.



4-((benzyloxy)methyl)-1,3-dioxolan-2-one (9b)

 $\label{eq:hardenergy} {}^{1}\textbf{H} \ \textbf{NMR} \ (300 \ \text{MHz}, \ \text{CDCl}_3) \ \delta \ 7.27 - \ 7.15 \ (m, \ 5\text{H}), \ 4.64 \ (ddt, \ J=9.1, \ 6.6, \ 3.4 \ \text{Hz}, \ 1\text{H}), \ 4.42 \ (d, \ J=3.5 \ \text{Hz}, \ 2\text{H}), \ 4.32 - 4.12 \ (m, \ 2\text{H}), \ 3.62 - 3.32 \ (m, \ 2\text{H}).$

¹³C NMR (75 MHz, CDCl₃) δ 152.76, 134.89, 125.40, 125.13, 72.82, 70.84, 66.45, 63.69.



Figure S2 ¹³C NMR of 4-phenyl-1,3-dioxolan-2-one (1b)





Figure S4 ¹³C NMR of 4-methyl-1,3-dioxolan-2-one (2b)



Figure S6 ¹³C NMR of 4-ethyl-1,3-dioxolan-2-one (3b)



Figure S8 ¹³C NMR of 4-butyl-1,3-dioxolan-2-one (4b)



210 200 190 180 170 160 150 140 130 120 110 $\frac{100}{5}$ 90 80 70 60 50 40 30 20 10 0 -10 Figure S10 ¹³C NMR of 4-(chloromethyl)-1,3-dioxolan-2-one (5b)



210 200 190 180 170 160 150 140 130 120 110 $\frac{100}{5}$ 90 80 70 60 50 40 30 20 10 0 -10 Figure S12 ¹³C NMR of 4-(bromomethyl)-1,3-dioxolan-2-one (6b)









Figure S18 ¹³C NMR of 4-((benzyloxy)methyl)-1,3-dioxolan-2-one (9b)