

Supporting Information

Cu(I)/Ionic liquids Promoted the Conversion of Carbon Dioxide into Oxazolidinones at Room Temperature

Jikuan Qiu¹, Yue Zhao¹, Yuling Zhao^{1,}, Huiyong Wang¹, Zhiyong Li¹, Jianji Wang^{1,*}
and Tiantian Jiao²*

1, Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007 (P. R. China)

E-mail: jwang@htu.cn; ylzhao@htu.cn

2, College of Chemical and Environmental Engineering, Shandong University of Science and Technology, Qingdao 266590, Shandong, China

Table of Contents

Section 1. Synthetic Procedures of the ILs	2
Section 2. Figures and Tables	3
Section 3. References	4
Section 4. NMR Spectra	6

Section 1: Synthetic Procedures of the ILs

[P₄₄₄₄][Im], [P₄₄₄₄][Triz] and [P₄₄₄₄][Ind] were synthesized and purified by the following procedures[1-2]. As an example, the procedure for the preparation of [P₄₄₄₄][Im] was described. First, [P₄₄₄₄]OH (tetrabutylphosphonium hydroxide) was obtained from the raw material [P₄₄₄₄]Br through the anion-cation exchange resin (water : ethanol=1:1). Equimolar Im was added, and the mixture was then stirred for 12 h at room temperature. After that, the solvent was distilled off at 45 °C by rotary evaporation. The obtained products were dried for at least 24 h under reduced pressure. The chemical structures of these ILs were confirmed by ¹H NMR and ¹³C NMR spectroscopy. The data of products is consistent with the previously reported experimental results [3].

[P₄₄₄₄][Im]. orange oil; ¹H NMR (CDCl₃, 400 MHz) δ : 7.56 (s, 1 H), 6.95 (s, 2 H), 2.30-2.14 (m, 8 H), 1.51-1.34 (m, 16 H), 0.88 (t, $J = 8.0$ Hz, 12 H) ppm; ¹³C NMR (CDCl₃, 150 MHz) δ : 135.04, 23.68, 18.79, 18.48, 13.02 ppm.

[P₄₄₄₄][Triz]. orange oil; ¹H NMR (DMSO-d₆, 400 MHz) δ : 17.67 (s, 2H), 2.22–2.12 (m, 8H), 1.51–1.34 (m, 16H), 0.92 (t, $J=7.2$ Hz, 12H) ppm; ¹³C NMR (CDCl₃, 150 MHz) δ : 146.63, 145.89, 23.72, 23.62, 23.24, 18.50, 18.19, 13.17 ppm.

[P₄₄₄₄][Ind]. orange oil; ¹H NMR (CDCl₃, 400 MHz) δ : 7.89 (s, 1H), 7.57 (d, $J=8.0$ Hz, 1H), 7.06–6.75 (m, 3H), 2.22–2.11 (m, 8H), 1.52–1.34 (m, 16H), 0.92 (t, $J=6.8$ Hz, 12H) ppm; ¹³C NMR (CDCl₃, 150 MHz) δ : 158.86, 140.33, 133.76, 126.08, 123.06, 120.37, 110.58, 23.89, 23.54, 18.88, 18.58, 13.40 ppm.

Section 2: Figures

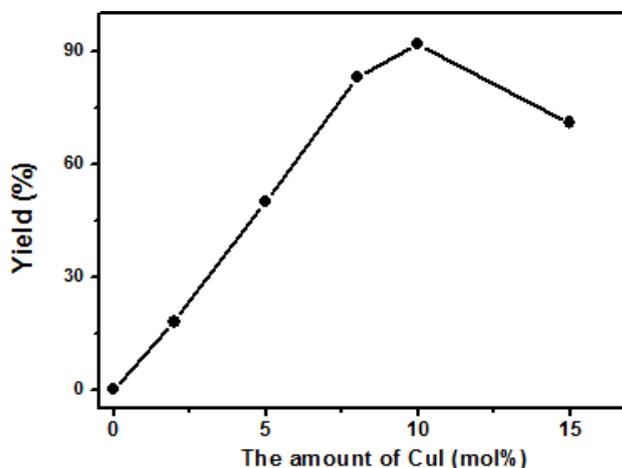


Figure S1. Influence of CuI amount on the yield of oxazolidinones. Reaction conditions: 1a (1 mmol), 2a (1mmol), [P₄₄₄₄][Im] (10 mol%), CO₂ (1atm), 30 °C, 24 h. The yields were determined by ¹H NMR spectroscopy.

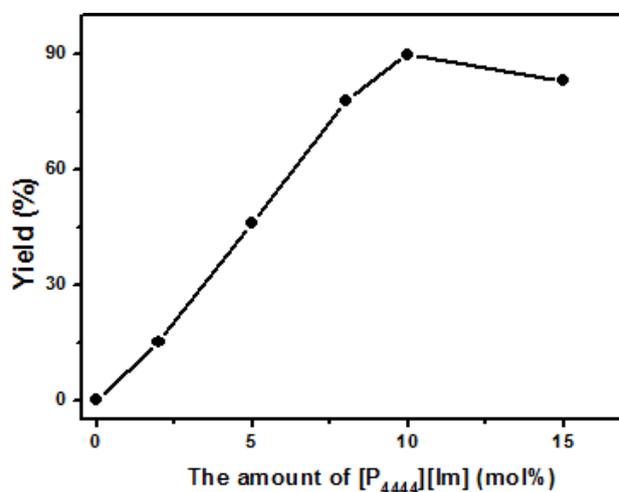


Figure S2. Influence of [P₄₄₄₄][Im] amount on the yield of oxazolidinones. Reaction conditions: 1a (1 mmol), 2a (1mmol), CuI (10 mol%), CO₂ (1atm), 30 °C, 24 h. The yields were determined by ¹H NMR spectroscopy.

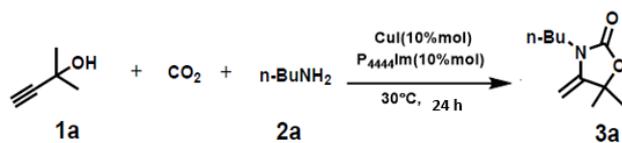
Table S1. The effect pKa of different ionic liquids on the synthesis of 3-butyl-5,5-dimethyl-4-methyleneoxazolidin-2-one (3a) from atmospheric CO₂^a

Reaction scheme: 2-methylbut-3-yn-2-ol (1a) + CO₂ + n-BuNH₂ (2a) $\xrightarrow[30^\circ\text{C}, 1\text{atm}]{\text{CuI}(10\%\text{mol}), \text{IL}(10\%\text{mol})}$ 3-butyl-5,5-dimethyl-4-methyleneoxazolidin-2-one (3a)

Entry	IL	pKa of IL in DMSO ^[4]	Yield/ % ^b
4	[P4444][Im]	18.6	91
5	[P4444][Triz]	13.9	70
6	[P4444][Ind]	--	41
7	[P4444][CF ₃ COO]	3.45	35
8	P4444]NO ₃	0.9	30
9	[P4444]Br	--	28

^a Reaction condition: 2-methylbut-3-yn-2-ol (1a, 1.2 mmol), n-Butylamine (2a, 1.2mmol), CuI (0.10 mol), IL (0.10 mol), CO₂ (0.1 MPa, 99.999%), 24 h, 30 °C; ^b The isolated yield.

Table S2. Effect of CO₂ pressure on the isolated yield of 3a.



Entry	CO ₂ pressure	Yield (%) ^b
1	0	0
2	0.3	33
3	0.5	52
4	0.7	63
5	1.0	90

Reaction conditions: 1a (1 mmol), 2a (1 mmol), CuI (0.1 mmol), [P₄₄₄₄][Im] (0.1 mmol), 30 °C, 24 h

Section 3: References

- [1] Pei, X.; Xiong, D.; Pei, Y.; Wang, H.; Wang, J. Switchable oil–water phase separation of ionic liquid-based microemulsions by CO₂. *Green Chem.* **2018**, *20*, 4236-4244.
- [2] Shi, Y.; Xiong, D.; Wang, H.; Zhao, Y.; Wang, J. Reversible switching of amphiphilic self- assemblies of ionic liquids between micelle and vesicle by CO₂. *Langmuir*, **2016**, *32*, 6895-6901.
- [3] Zhao, Y.; Yang, Z.; Yu, B.; Zhang, H.; Xu, H.; Hao, L.; Han, B.; Liu, Z. Task specific ionic liquid and CO₂-cocatalysed efficient hydration of propargylic alcohols to a-hydroxy ketones. *Chem. Sci.* **2015**, *6*, 2297-2301.
- [4] Bordwell, F. G. Equilibrium acidities in dimethyl sulfoxide solution. *Acc. Chem. Res.* **1988**, *21*, 456-463.

Section 4: NMR Spectra

