

# Green Chemistry

Cutting-edge research for a greener sustainable future

Accepted Manuscript

View Article Online  
View Journal

This article can be cited before page numbers have been issued, to do this please use: G. Shi, R. Zhai, H. Li and C. Wang, *Green Chem.*, 2021, DOI: 10.1039/D0GC03510F.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

## ARTICLE

# Highly Efficient Synthesis of Alkylidene Cyclic Carbonates from Low Concentration CO<sub>2</sub> using Hydroxyl and Azolate Dual Functionalized Ionic Liquids

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Guiling Shi,<sup>a</sup> Ran Zhai,<sup>a</sup> Haoran Li,<sup>a</sup> and Congmin Wang<sup>\*,a</sup>

A highly efficient catalytic system was developed for the reaction between CO<sub>2</sub> and propargylic alcohols for alkylidene cyclic carbonates. Ionic liquids (ILs) with different anions and cations were designed as cocatalysts, in order to find out the effect of the cation and the anion on this reaction. The results indicated that the effect of the cation was significant, especially, hydroxyl group on the cation played an important role due to the presence of hydrogen bond. It was also found that the basicity of anion was important to its catalytic activity, where the anion with moderate basicity gave the best activity. Moreover, this hydroxyl and azolate dual functionalized catalytic system showed excellent reusability and generality. It was worth mentioning that under low concentration of CO<sub>2</sub>, this dual functionalized catalytic system showed excellent catalytic activity even on a gram-scale reaction, which indicating the potential in carbon capture and utilization process.

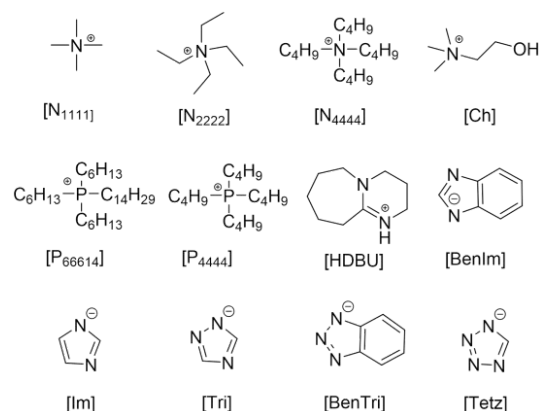
## Introduction

CO<sub>2</sub> capture and utilization (CCU) has evoked great interest in the past decades, because CO<sub>2</sub> can be regarded as an abundant, cheap, environmentally friendly C1 synthon, which was widely used for the synthesis of many fine chemicals.<sup>1–6</sup> Unfortunately, because of its inherent thermodynamic stability and kinetic inertness, CCU processes usually require high energy input (including high temperature, high pressure) and the addition of metal catalysts or excessive strong base.<sup>7,8</sup> In addition, compared with other CO<sub>2</sub> sources, fixation CO<sub>2</sub> from flue gas, one of the major CO<sub>2</sub> sources, is still a severe challenge due to its low CO<sub>2</sub> concentration (~10 vol.%).<sup>9–11</sup> Thus, effective catalysts are still urgently desired for CO<sub>2</sub> upgrading under low concentration.

Ionic liquid (IL) is a promising and eco-friendly candidate as CO<sub>2</sub> absorbent, because of their unique properties, such as high thermal stability, negligible vapor pressure, and tunable structures. By finely tuning of ILs structures and properties, significant achievements could be achieved in designing ILs with impressive CO<sub>2</sub> capacity.<sup>12–25</sup> At the same time, thanks to their tunable structures and superior CO<sub>2</sub> absorption ability, ILs have the ability to realize CCU processes even under mild conditions.<sup>26–33</sup> There have been many systematical reports focusing on the influence of anions in ILs, where the anion played a key role on CCU processes due to its dual roles as absorbent and catalyst.<sup>34–38</sup> However, few work could be realized the important role of the cation in CCU processes such as the synthesis of alkylidene cyclic carbonates.

Recently, carbonates have drawn much attention because of their potential bioactivities and widespread applications in Li ion batteries and pharmaceutical industry.<sup>39–40</sup> Based on the principles of green and sustainable chemistry, the carboxylative cyclization of propargylic alcohols and CO<sub>2</sub> is a promising route to reach α-alkylidene cyclic carbonates.<sup>41–42</sup> Up to now, although numerous heterogeneous catalysts have been reported for this reaction,<sup>43–57</sup> most of them were suffered from harsh reaction conditions including high CO<sub>2</sub> pressure, excessive catalysts loading and poor reusability of catalysts, which can be ascribed to the poor activity or low stability of catalysts. How to realise this processes efficiently under low concentration of CO<sub>2</sub> (such as 10%) is still a puzzle for researchers.

Herein, we developed a highly efficient catalytic system used for the reaction between CO<sub>2</sub> and propargylic alcohols. ILs with different anions and cations were used as cocatalysts (Figure 1), in order to



**Figure 1.** Structures of the cation and anion of the IL used in this work

<sup>a</sup> Department of Chemistry, State Key Laboratory of Chemical Engineering, Zhejiang University, Hangzhou 310027, China.

Electronic Supplementary Information (ESI) available: NMR, Table S1, Table S2. See DOI:10.1039/D0GC03510F

find out the effect of ILs on this reaction. The results indicated that both the cation and anion played a key role. Therefore, dual functionalized IL with hydroxyl and azolate group [Ch][Triz] was designed, which exhibited excellent activity and good reversibility in this reaction. It was worth mentioning that under 10% of CO<sub>2</sub>, the catalytic system (AgNO<sub>3</sub>/[Ch][Tri]) showed excellent catalytic activity even on a gram-scale reaction.

## Experimental

### Materials and methods

All chemicals used in this work were purchased from commercial and used without further purification unless otherwise stated. 3-Methyl-1-pentyn-3-ol, 2-Phenyl-3-butyn-2-ol and 1-Ethynylcyclopentanol were purchased from J&K Scientific Ltd. 2-Methyl-3-butyn-2-ol were purchased from Aladdin Ind. Co., Ltd. 1H-Tetrazole (Tetz), 1H-Benzotriazole (Bentri), 1,2,4-Triazole (Triz), Benzimidazole (BenIm), Tetrabutylammonium hydroxide ([N<sub>4444</sub>][OH]), Imidazole (Im), Tetraethylammonium hydroxide ([N<sub>2222</sub>][OH]), Tetramethylammonium hydroxide ([N<sub>1111</sub>][OH]), choline (Ch) and 1-Ethynyl-1-cyclohexanol were purchased from Energy-Chemistry Co., Ltd. CO<sub>2</sub> (99.99%), CO<sub>2</sub> (10%) and N<sub>2</sub> (99.99%) were purchased from Hangzhou Jingong Special Gas Co., Ltd. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker spectrometer (400 MHz) in DMSO-d<sub>6</sub>, which was obtained from Adamas-beta, with DMSO as the standard.

### The synthesis of functionalized ILs

These functionalized ILs were easily prepared by the neutralization of superbases or the solution of [N<sub>1111</sub>][OH], [N<sub>2222</sub>][OH], [N<sub>4444</sub>][OH], [P<sub>4444</sub>][OH] or choline with azole compound. In a typical example, the reaction mixture was stirred at 50 °C for 6 h and then applying the vacuum-rotary evaporation procedure to remove most of water. After that, ILs were dried under vacuum at 80 °C for more than 24 hours to reduce possible traces of water. Before use, the water content of ILs was determined with a Karl Fisher titration and found to be less than 0.1 wt%.

### General procedure for the synthesis of alkylidene carbonates

As a typical example, the procedure using 2-Methyl-3-butyn-2-ol (1a) as a typical substrate was described. AgNO<sub>3</sub> (0.066 g, 0.4 mmol), [Ch][Triz] (0.138 g, 0.8 mmol), and 1a (0.336 g, 8 mmol) was added into a Schlenk flask, connecting with a CO<sub>2</sub> balloon filled with CO<sub>2</sub> (99.99%). Then the reaction mixture was stirred at 30 °C for 24 h. The conversion and yield of product 1b were quantitatively analyzed by gas chromatography (GC) with biphenyl as the internal standard. When the reusability of the catalyst system was investigated, the reaction mixture was extracted with *n*-hexane (4 × 15 mL). The upper layer was collected and removed the solvent to obtain the product, and the lower layer, composed of AgNO<sub>3</sub> and [Ch][Triz], can be dried in the vacuum at 60 °C for next cycle.

## Results and discussion

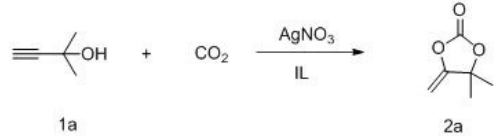
At first, various catalysts were applied to the reaction, the results were listed in Table S1. It was seen that the effect of different metal catalysts on this reaction was obvious, where AgNO<sub>3</sub> and AgOAc catalyst displayed better catalytic reactivity. Considering the basicity of AgOAc may affect the catalytic reactivity of ILs, we chose AgNO<sub>3</sub> for further research.

The effect of the cation on catalytic activity was investigated, which was seen in Table 1. At first, the reaction could not take place with no IL as cocatalyst (entry 1). When a protic IL ([DBU][Tri]) was used as the cocatalyst, the reaction did not occur. It was clear that the type of IL made a big difference. Then, a series of aprotic ILs with different kinds of cation were designed and prepared for the reaction. It was illustrated that the chain length of the cation affected its catalyst activity significantly. When aprotic ILs, [N<sub>1111</sub>][Tri], [N<sub>2222</sub>][Tri] and [N<sub>4444</sub>][Tri], were used as the cocatalyst, the yields of 81%, 69% and 67% were obtained (Table 1, entry 3-5), respectively. In other word, the cation with shorter chain length gave higher yield of 2a in this reaction. We could come to a similar conclusion by comparing entry 5 and entry 6. Besides, [N<sub>4444</sub>][Tri] and [P<sub>4444</sub>][Tri] resulted in comparable yields of 67% and 64% (Table 1, entry 4 and 5), which indicated that the impact of central atom of the cation was weak.

Considering that hydrogen bond played an important role in some CCU processes, a hydroxyl functionalized aprotic IL [Ch][Tri] was designed, prepared, and used in this reaction. To be excited, the conversion and yield could be improved to 99% and 93% (Table 1, entry 8), respectively. These results indicated that hydroxyl group of the cation could promote this reaction well. As a controlled experiment, no reaction was proceeded without AgNO<sub>3</sub> (Table 1, entry 9). Clearly, both of AgNO<sub>3</sub> and base (also called co-catalyst) were indispensable for this reaction.

To investigate the influence of the basicity of the anion, the reaction was carried out using the ILs with various basic anions, and the results were listed in Table 2. When [Ch][Cl] was used, only a 4% yield of the product was obtained, which implied that the basicity was also significant for this reaction. By tuning the basicity of the anion, it was obvious that this reaction was affected by the strength of the base, where higher conversion was achieved when stronger basic IL was used. As for the anion with weak basicity, like [Tetz] and [BenTri], the reaction was not complete within 24 hours, implying for poor catalytic activity (entry 2, 3). To our delight, [Tri], whose pK<sub>a</sub> was 18.6, could improve the conversion and yield to 99%

**Table 1.** The effect of the cation on catalytic activity<sup>[a]</sup>

			
Entry	Ionic liquid	Conversion [%] <sup>[b]</sup>	Yield [%] <sup>[b]</sup>
1	-	-	<1
2	[DBU][Tri]	4	<1
3	[N <sub>1111</sub> ][Tri]	90	81
4	[N <sub>2222</sub> ][Tri]	82	69
5	[N <sub>4444</sub> ][Tri]	77	67
6	[P <sub>4444</sub> ][Tri]	75	64
7	[P <sub>66614</sub> ][Tri]	70	59
8	[P <sub>66614</sub> ][Tri]	70	59
9 <sup>[c]</sup>	[Ch][Tri]	<1	<1

[a] Reaction conditions: 1a (4 mmol), AgNO<sub>3</sub> (0.4 mmol), base (0.8 mmol) and CO<sub>2</sub> (1 bar) for 24 h at 30 °C. [b] Determined by GC using internal standard method. [c] Without AgNO<sub>3</sub>

**Table 2.** The effect of different basic anion on catalytic activity<sup>[a]</sup>

Entry	Ionic liquid	pK <sub>a</sub> of anions <sup>[b]</sup>	Conversion [%] <sup>[c]</sup>	Yield[%] <sup>[c]</sup>
1	[Ch][Cl]	1.8	15	4
2	[Ch][Tetz]	8.2	23	17
3	[Ch][BenTri]	11.9	67	64
4	[Ch][Tri]	13.9	99	93
5	[Ch][BenIm]	18.2	97	67
6	[Ch][Im]	18.9	99	64

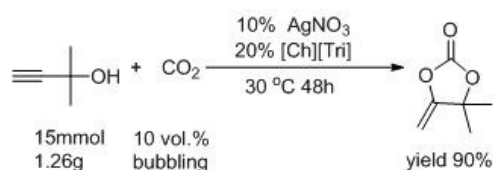
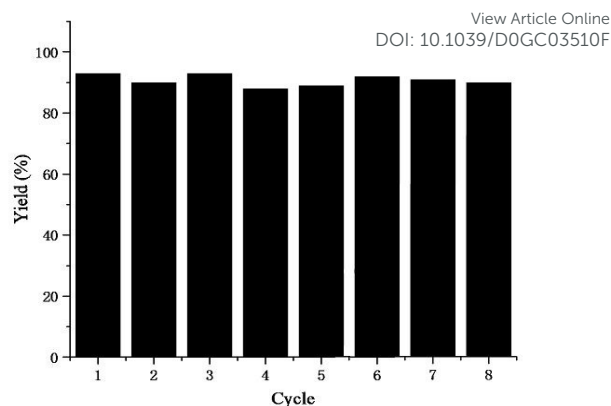
[a] Reaction conditions: **1a** (4 mmol), AgNO<sub>3</sub> (0.4 mmol), base (0.8 mmol) and CO<sub>2</sub> (1 bar) for 24 h at 30 °C. [b] Values in DMSO. [c] Determined by GC using internal standard method.

and 93% (entry 4), respectively. However, strongly basic ILs, [Ch][BenIm] and [Ch][Im], resulted in much lower yields of product than [Ch][Tri], due to the decreased selectivity (entry 5,6). Therefore, dual functionalized IL with hydroxyl group and moderately basicity [Ch][Tri] exhibited the best catalytic activity. Besides, compared with other AgNO<sub>3</sub>-based systems, AgNO<sub>3</sub>/[Ch][Tri] exhibited excellent performance for CO<sub>2</sub> utilization (Table S4).

Compared with other CO<sub>2</sub> sources, capturing CO<sub>2</sub> from flue gas was a severe challenge due to its low concentration (~10 vol.%). Therefore, to further evaluate its practicability, the reaction was also carried out under low concentration CO<sub>2</sub> of 10%. To our delight, after extending the reaction time to 48 hours, this catalytic system composed of AgNO<sub>3</sub> and [Ch][Tri] gave **2a** in a yield of 90% after bubbling CO<sub>2</sub> at 0.1 bar under 30 °C, even at a gram-scale (Figure 2).

The reusability of the catalytic system was a critical property for CO<sub>2</sub> utilization, which had a direct impact on the cost because it determined the frequency of the replacement of catalyst. Therefore, we investigated the recycling performance of AgNO<sub>3</sub> and [Ch][Tri] catalytic system under the optimized reaction conditions. The results for 8 cycles were shown in Figure 3. It was found that good catalytic activity was well-maintained during the 8 cycles.

The substrate scope and generality of this reaction were investigated by using this dual functionalized catalytic system. As illustrated in Table 3, all of these substrates could react with CO<sub>2</sub> under mild conditions, and good to excellent yields were

**Figure 2.** A gram-scale reaction under low concentration of CO<sub>2</sub> using AgNO<sub>3</sub> as the catalyst and [Ch][Tri] as the cocatalyst.**Figure 3.** Recycling experiments using AgNO<sub>3</sub> as the catalyst and [Ch][Tri] as the cocatalyst.**Table 3.** The synthesis of alkylidene carbonates from CO<sub>2</sub> using [Ch][Tri].<sup>[a]</sup>

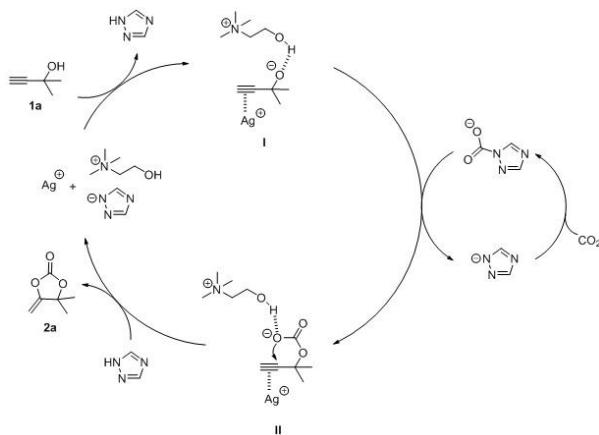
Entry	substrate	R <sub>1</sub>	R <sub>2</sub>	T [h]	Yield [%] <sup>[b]</sup>
1	<b>1a</b>	Me	Me	24	93
2	<b>1a</b> <sup>[c]</sup>	Me	Me	48	85
3	<b>1a</b> <sup>[d]</sup>	Me	Me	48	87
4	<b>1b</b>	Me	Et	24	92
5	<b>1c</b>	Me	Ph	36	95 (87) <sup>[e]</sup>
6	<b>1d</b>	-(CH <sub>2</sub> ) <sub>5</sub> -		36	92
7	<b>1f</b>	-(CH <sub>2</sub> ) <sub>4</sub> -		30	89

[a] Reaction conditions: substrate (4 mmol), AgNO<sub>3</sub> (0.4 mmol), [Ch][Tri] (0.8mmol) and CO<sub>2</sub> (1 bar) at 30 °C. [b] Determined by NMR using internal standard method. [c] 10 vol.% of CO<sub>2</sub>. [d] 15 vol.% of CO<sub>2</sub>. [e] Isolated yield.

obtained. With an ethyl group, **2b** was given in a yield of 92% (entry 4). By extending the reaction time, substrate with a large substituent group could also convert totally. The reactivity of phenyl substituted propargylic alcohol was investigated, and a 95% yield of **2c** was provided (entry 5). In addition, the reaction of **1d** and **1f** was found to occur smoothly with yields of 92% and 89%, respectively, which means this dual functionalized IL also has a good catalytic activity on propargylic alcohol with a cycloalkane group.

On the basis of experimental results and previous literature reports, we proposed a plausible mechanism for this reaction (Figure 4). Firstly, the carbon-carbon triple bond on the substrate **1a** could be activated by silver ions (AgNO<sub>3</sub>). Meanwhile, [Tri] had a sufficiently basicity to extract the proton from hydroxyl group on **1a** to form intermediate **I**, and the hydroxyl group on [Ch] could stabilize the intermediate **I** through intermolecular hydrogen bonding. Subsequently, intermediate **II** was obtained by intermediate **I** nucleophilic attacked CO<sub>2</sub>, which was captured by [Tri]. Finally, **2a** was generated through an intramolecular ring-

closing reaction in **II**, and silver ions and [Ch][Tri] were regenerated. With this proposed mechanism, ILs acted as a CO<sub>2</sub> absorbent and a base at the same time. As a CO<sub>2</sub> absorbent, it can be seen that ILs with higher basicity could capture more CO<sub>2</sub>, while the strong interaction between ILs and CO<sub>2</sub> would impede the reaction of CO<sub>2</sub> and propargylic alcohols. On the other hand, as a base, ILs with weak basicity were hard to initiate the reaction by abstracting hydrogen from propargylic alcohols.



**Figure 4.** Possible mechanisms for this reaction.

## Conclusions

In summary, an efficient catalytic system was developed for the reaction between CO<sub>2</sub> and propargylic alcohols under mild conditions. We found the effect of the cation on the reaction was significant, where hydroxyl group on the cation could promote this reaction well. It was also found that the basicity of anion was important to its activity, where the anion with moderate basicity gave the best activity. Therefore, the catalytic system comprising of dual functionalized IL [Ch][Tri] and AgNO<sub>3</sub> exhibited excellent reusability and generality. To be specialized, this catalytic system showed excellent performance on a gram-scale reaction even under low concentration of CO<sub>2</sub>. We believed that this method developed by this work through tuning both the cation and the anion was not only important for CCU processes, but also for gas separation.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

We acknowledge the support of the National Natural Science Foundation of China (21776239), the Zhejiang Provincial Natural Science Foundation of China (LZ17B060001), and the State Key Laboratory of Chemical Engineering (No. SKL-ChE-20T05).

## Notes and references

1. J. Y. Hu, J. Ma, Q. G. Zhu, Z. F. Zhang, C. Y. Wu and B. X. Han,

*Angew Chem Int Edit*, 2015, **54**, 5399-5403.

View Article Online

2. M. D. Porosoff, B. H. Yan and J. G. G. Chen, *Energy Environ Sci*, 2016, **9**, 62-73.
3. T. Sakakura, J. C. Choi and H. Yasuda, *Chem Rev*, 2007, **107**, 2365-2387.
4. Z. Z. Yang, Y. N. Zhao and L. N. He, *Rsc Adv*, 2011, **1**, 545-567.
5. Y. F. Zhao, Z. Z. Yang, B. Yu, H. Y. Zhang, H. J. Xu, L. D. Hao, B. X. Han and Z. M. Liu, *Chem Sci*, 2015, **6**, 2297-2301.
6. Y. F. Zhao, B. Yu, Z. Z. Yang, H. Y. Zhang, L. D. Hao, X. Gao and Z. M. Liu, *Angew Chem Int Edit*, 2014, **53**, 5922-5925.
7. J. P. Hallett and T. Welton, *Chem Rev*, 2011, **111**, 3508-3576.
8. F. Maier, *Angew Chem Int Edit*, 2011, **50**, 10133-10134.
9. W. Clegg, R. W. Harrington, M. North and R. Pasquale, *Chem-Eur J*, 2010, **16**, 6828-6843.
10. K. Motokura, S. Itagaki, Y. Iwasawa, A. Miyaji and T. Baba, *Green Chem*, 2009, **11**, 1876-1880.
11. Y. Yang, Y. Hayashi, Y. Fujii, T. Nagano, Y. Kita, T. Ohshima, J. Okuda and K. Mashima, *Catal Sci Technol*, 2012, **2**, 509-513.
12. E. D. Bates, R. D. Mayton, I. Ntai and J. H. Davis, *J Am Chem Soc*, 2002, **124**, 926-927.
13. F. F. Chen, K. Huang, Y. Zhou, Z. Q. Tian, X. Zhu, D. J. Tao, D. E. Jiang and S. Dai, *Angew Chem Int Edit*, 2016, **55**, 7166-7170.
14. G. K. Cui, J. J. Wang and S. J. Zhang, *Chem Soc Rev*, 2016, **45**, 4307-4339.
15. B. E. Gurkan, J. C. de la Fuente, E. M. Mindrup, L. E. Ficke, B. F. Goodrich, E. A. Price, W. F. Schneider and J. F. Brennecke, *J Am Chem Soc*, 2010, **132**, 2116-+.
16. Y. J. Huang, G. K. Cui, Y. L. Zhao, H. Y. Wang, Z. Y. Li, S. Dai and J. J. Wang, *Angew Chem Int Edit*, 2017, **56**, 13293-13297.
17. M. D. Soutullo, C. I. Odom, B. F. Wicker, C. N. Henderson, A. C. Stenson and J. H. Davis, *Chem Mater*, 2007, **19**, 3581-3583.
18. C. M. Wang, X. Y. Luo, H. M. Luo, D. E. Jiang, H. R. Li and S. Dai, *Angew Chem Int Edit*, 2011, **50**, 4918-4922.
19. W. Z. Wu, B. X. Han, H. X. Gao, Z. M. Liu, T. Jiang and J. Huang, *Angew Chem Int Edit*, 2004, **43**, 2415-2417.
20. Y. S. Zhao, R. Gani, R. M. Afzal, X. P. Zhang and S. J. Zhang, *Aiche J*, 2017, **63**, 1353-1367.
21. K. H. Chen, W. J. Lin, X. N. Yu, X. Y. Luo, F. Ding, X. He, H. R. Li and C. M. Wang, *Aiche J*, 2015, **61**, 2028-2034.
22. K. H. Chen, G. L. Shi, X. Y. Zhou, H. R. Li and C. M. Wang, *Angew Chem Int Edit*, 2016, **55**, 14362-14366.
23. K. Huang, Y. L. Chen, X. M. Zhang, S. Xia, Y. T. Wu and X. B. Hu, *Chem Eng J*, 2014, **237**, 478-486.
24. C. M. Wang, G. K. Cui, X. Y. Luo, Y. J. Xu, H. R. Li and S. Dai, *J Am Chem Soc*, 2011, **133**, 11916-11919.
25. K. Zhang, S. H. Ren, L. Y. Meng, Y. C. Hou, W. Z. Wu and Y. Y. Bao, *Energy Fuel*, 2017, **31**, 1786-1792.
26. Z. Z. Yang, L. N. He, J. Gao, A. H. Liu, B. Yu, *Energy Environ. Sci.* 2012, **5**, 6602-6639.
27. P. G. Jessop, S. M. Mercer, D. J. Heldebrant, *Energy Environ. Sci.* 2012, **5**, 7240-7253.
28. X. B. Lu, L. Shi, Y. M. Wang, R. Zhang, Y. J. Zhang, X. J. Peng, Z. C. Zhang, B. Li, *J. Am. Chem. Soc.* 2006, **128**, 1664-1674.
29. J. Liu, W. M. Ren, Y. Liu, X. B. Lu, *Macromolecules* 2013, **46**, 1343-1349.
30. W. M. Ren, G. P. Wu, F. Lin, J. Y. Jiang, C. Liu, Y. Luo, X. B. Lu, *Chem. Sci.* 2012, **3**, 2094-2102.



31. D. Z. Xiong, G. K. Cui, J. J. Wang, H. Y. Wang, Z. Y. Li, K. S. Yao, S. J. Zhang, *Angew. Chem., Int. Ed.* 2015, **54**, 7265–7269.
32. W. H. Yao, H. Y. Wang, G. K. Cui, Z. Y. Li, A. L. Zhu, S. J. Zhang, J. J. Wang, *Angew. Chem., Int. Ed.* 2016, **55**, 7934–7938.
33. Z. J. Guo, Q. W. Jiang, Y. M. Shi, J. Li, X. N. Yang, W. Hou, Y. Zhou, J. Wang, *ACS Catal.* 2017, **7**, 6770–6780.
34. X. F. Liu, X. Y. Li, C. Qiao, H. C. Fu, L. N. He, *Angew. Chem., Int. Ed.* 2017, **56**, 7425–7429.
35. Y. F. Zhao, B. Yu, Z. Z. Yang, H. Y. Zhang, L. D. Hao, X. Gao, Z. M. Liu, *Angew. Chem., Int. Ed.* 2014, **53**, 5922–5925.
36. M. Hulla, S. Chamam, M. A. G. Laurenczy, S. Das, P. J. Dyson, *Angew. Chem., Int. Ed.* 2017, **56**, 10559–10563.
37. K. H. Chen, G. L. Shi, W. D. Zhang, H. R. Li, C. M. Wang, *J. Am. Chem. Soc.* 2016, **138**, 14198–14201.
38. K. H. Chen, G. L. Shi, R. N. Dao, K. Mei, X. Y. Zhou, H. R. Li and C. M. Wang, *Chem Commun*, 2016, **52**, 7830–7833.
39. A. A. Shaikh and S. Sivaram, *Chem Rev*, 1996, **96**, 951–976.
40. T. Sakakura and K. Kohno, *Chem. Commun.*, 2009, 1312–1330.
41. X. B. Lu, R. He and C. X. Bai, *J. Mol. Catal. A: Chem.*, 2002, **186**, 1–11.
42. Y. Du, F. Cai, D. L. Kong and L. N. He, *GreenChem.*, 2005, **7**, 518–523.
43. Y. Sugawara, W. Yamada, S. Yoshida, T. Ikeno and T. Yamada, *J. Am. Chem. Soc.*, 2007, **129**, 12902–12903.
44. W. Yamada, Y. Sugawara, H. M. Cheng, T. Ikeno and T. Yamada, *Eur. J. Org. Chem.*, 2007, 2604–2607.
45. Z. Z. Yang, Y. F. Zhao, H. Y. Zhang, B. Yu, Z. S. Ma, G. P. Ji and Z. M. Liu, *Chem. Commun.*, 2014, **50**, 13910–13913.
46. Y. L. Gu, F. Shi and Y. Q. Deng, *J. Org. Chem.*, 2004, **69**, 391–394.
47. Y. Kayaki, M. Yamamoto and T. Ikariya, *Angew. Chem., Int. Ed.*, 2009, **48**, 4194–4197.
48. Y. B. Wang, Y. M. Wang, W. Z. Zhang and X. B. Lu, *J. Am. Chem. Soc.*, 2013, **135**, 11996–12003.
49. Y. B. Wang, D. S. Sun, H. Zhou, W. Z. Zhang and X. B. Lu, *Green Chem.*, 2014, **16**, 2266–2272.
50. Y. Kayaki, M. Yamamoto and T. Ikariya, *J. Org. Chem.*, 2007, **72**, 647–649.
51. T. Kimura, K. Kamata and N. Mizuno, *Angew. Chem., Int. Ed.*, 2012, **51**, 6700–6703.
52. Q. W. Song, W. Q. Chen, R. Ma, A. Yu, Q. Y. Li, Y. Chang and L. N. He, *ChemSusChem*, 2015, **8**, 821–827.
53. Q. W. Song, B. Yu, X. D. Li, R. Ma, Z. F. Diao, R. G. Li, W. Li and L. N. He, *GreenChem.*, 2014, **16**, 1633–1638.
54. Q. W. Song and L. N. He, *Adv. Synth. Catal.*, 2016, **358**, 1251–1258.
55. Y. Yuan, Y. Xie, C. Zeng, D. D. Song, S. Chaemchuen, C. Chen, F. Verpoort, *Green Chem.*, 2017, **19**, 2936–2940.
56. Y. Yuan, Y. Xie, C. Zeng, D. D. Song, S. Chaemchuen, C. Chen, F. Verpoort, *Appl. Organometal. Chem.*, 2017, **31**, e3867.
57. Y. Yuan, Y. Xie, C. Zeng, D. D. Song, S. Chaemchuen, C. Chen, F. Verpoort, *Catal. Sci. Technol.*, 2017, **7**, 2935–2939.

View Article Online  
DOI: 10.1039/D0GC03510F