



Cutting-edge research for a greener sustainable future

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Y. Li, D. Cui, J. Zhu, P. Huang, Z. Tian, Y. Jia and P. Wang, Green Chem., 2019, DOI: 10.1039/C9GC02058F.



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.



rsc.li/greenchem

ARTICLE

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

DOI: 10.1039/x0xx00000x

www.rsc.org/



Yue-Dan Li,^{a,†} Dong-Xiao Cui,^{a,b,†} Jun-Chao Zhu,^a Ping Huang,^a Zhuang Tian,^a Yan-Yan Jia,^b and Ping-An Wang^{a,‡}

A series of achiral and chiral bifunctional phase-transfer catalysts with a quaternary onium center and hydrogen-bonding donor group were prepared for fixation of CO₂ with commercially available epoxides under mild conditions by using a CO₂ balloon (1 atm). In the presence of 2.5 mol% of achiral bifunctional phase-transfer catalysts, cyclic carbonates were obtained in good to excellent yields (up to 95%). Additionally, optical carbonates and epoxides were obtained through the kinetic resolution of *rac*-epoxides by 1 mol% chiral bifunctional phase-transfer catalysts with low enantioselectivities. These catalysts featured simple synthetic route, good modularity and high efficiency.

Introduction

Published on 09 July 2019. Downloaded by University of Iowa on 7/9/2019 1:27:56 PM

The activation and fixation of carbon dioxide (CO₂) to result in valuable chemicals such as carbonates, carboxylic acids, oxazolidinones as synthetic blocks play an important role both in industries and academies.¹ Novel manufactured materials including polycarbonates, poly(ether)carbonates and polyurethanes are also based on the direct utilization of CO₂.² In the past four decades, the field of catalytic CO_2 conversion has been dominated by the use of metal-based catalysts being either heterogeneous or homogeneous in nature, even harsh conditions such as high temperature and pressure are necessary to most cases. Therefore, the fixation of CO₂ at low temperature (< 100 °C) and atmospheric pressure is still a challenge.³

The advent of organocatalysis provides an alternative for activation and fixation of CO_2 by using small organic molecules as catalysts.⁴ N-Heterocyclic Carbenes (NHCs),⁵ N-heterocyclic bases (NHCBs),⁶ frustrated Lewis pairs (FLPs),⁷ quaternary onium hydroxide⁸/quaternary onium salts (PTCs),⁹ polyphenols, fluroalcohols, silanediols with co-catalysts¹⁰ and lonic liquids (ILs)¹¹ are used as catalysts for catalytic CO₂ activation and fixation in recent years. Among them, phase-transfer catalysed CO₂ fixation is very attractive to chemists due to the easy availability, simple handling and high efficiency of catalysts. A

group of structurally variable chiral quaternary onium salts containing multiple hydrogen-bonding donors, also called bifunctional phase-transfer catalysts,¹² have been developed and successfully applied to many asymmetric transformations to achieve good to excellent performances both in yields and enantioselectivities. In recent years, Werner¹³ and colleagues have developed a series of bifunctional ammonium and phosphonium salts (**A** and **B**) for the addition of CO₂ to epoxides (**Figure 1**). Toda^{14a} and Shirakawa's groups^{14b} have independently reported bifunctional quaternary phosphonium salts **C** and **D** as catalysts for CO₂ fixation reaction with

Previous works



Werner¹³ *et. al.* with 2 mol% **A** or **B**, neat, 90 °C, 10 bar CO₂, 2 h, 90~99% yields Toda^{14a} *et. al.* with 15 mol% **C**, PhCl, 120 °C, 1 atm CO₂, 12 h, 72~96% yields Shirakawa^{14b} *et. al.* with 1 mol% **D**, neat, 60 °C, 1 atm CO₂, 24 h, 72~93% yields Kleij¹⁵ *et. al.* with 3 mol% **E**, neat, 80 °C, 10 bar CO₂, 18 h, 63~90% yields

This work



Figure 1. Bifunctional phase-transfer catalysts for CO_2 fixation.

^{a.} Department of Medicinal Chemistry, School of Pharmacy, Fourth Military Medical University, Changle West Road 169, Xi'an, 710032, P. R. China.

^{b.} Department of Pharmacy, Xijing Hospital, Fourth Military Medical University, Changle West Road 15, Xi'an 710032, P. R. China.

⁺ Co-first authors. These two authors have the same contribution to this work.

[‡] Corresponding author: ping_an1718@outlook.com. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

ARTICLE

Vanu

een Chemistry Accepted

epoxides at atmospheric pressure to provide cyclic carbonates in high yields. Very recently, Kleij¹⁵ and colleagues have used the combination of TEAB($Et_4N^+Br^-$) and squaramide **E** as a binary catalytic system for fixation of CO₂ in cyclic addition of various epoxides under neat condition and 10~30 bar pressure to give cyclic carbonates in good yields. In fact, commercially available phase-transfer catalysts (such as TBAC, TBAB and TBAI) are usually used as co-catalysts with other organocatalysts or metal catalysts for CO2 fixation. Inspired by these above mentioned elegant works on fixation of CO₂, we have envisioned that quaternary onium salts with a urea, thiourea or squaramide motif as hydrogen-bonding donors could be served as good bifunctional phase-transfer catalysts for fixation CO₂ into epoxides. We have developed a class of chiral bifunctional phase-transfer catalysts for asymmetric amination of nitrooleins under neutral and water-rich conditions with high yields and enantioselectivities.¹⁶ In order to test the validity of our hypothesis, herein, we have synthesized a series of bifunctional phase-transfer catalysts containing one urea, thiourea or squaramide group and demonstrated their catalytic activities in fixation CO2 with epoxides to afford cyclic carbonates in good to excellent yields under very mild conditions (low temperature and ambient pressure of CO₂). Furthermore, the kinetic resolution of monosubstituted epoxides through CO₂ fixation by using chiral quaternary onium salts as bifunctional phase-transfer catalysts is also investigated.

Results and discussion

A. Synthesis of achiral bifunctional phase-transfer catalysts and catalytic fixation CO_2 by them

As illustrated in Figure 2, ten achiral phase-transfer catalysts (**APTC-1**~**APTC-10**) were prepared from commercially available 1-(2-aminoethyl)pyrrolidine and 4-(2-aminoethyl)morpholine in two or three steps with high modularity, and one urea, thiourea or squaramide group was introduced to these phase-

transfer catalysts (see Supplementary Materialse of for preparation of APTCs), respectively. In the 1976/9741677567 thiourea-containing catalysts APTC-2 and APTC-5, S-benzylation was found in the reaction of thioureas with benzyl bromide. In order to avoid S-benzylation, the primary amine was firstly protected by Boc₂O following quarterization with benzyl bromide, after deprotection of Boc group and coupling with aryl isothiocyanate to provide APTC-2 and APTC-5 in good yields.¹⁷

With these above-prepared phase-transfer catalysts in hand, the fixation of CO₂ with epoxide **1a** to form cyclic carbonate **2a** was investigated. Under neat conditions with a CO₂ balloon (1 atm), epoxide 1a was converted into cyclic carbonate 2a after 24 h of heating in the presence of 2.5 mol% of APTC-1~APTC-10, and the results are listed in Table 1. From Table 1, we found that APTC-1 with a urea group is a good catalyst for this transformation to provide cyclic carbonate 2a in 87% yield. Catalyst APTC-2 with a thiourea group produced 2a in 52% yield, and APTC-3 with a squaramide group demonstrated poor performance in this transformation (Table 1, entries 2 and 3) to afford trace of 2a. APTC-4 and APTC-5 containing a morpholine ring and a urea group or thiourea group gave 57% and 42% yield of 2a, respectively. Instead of 3,5bistrifluoromethylphenyl group in APTC-1 by 4-methylphenyl or 3,5-dimethylphenyl generated APTC-6 and APTC-7, these two catalysts produced inferior results comparing with APTC-1 (Table 1, entries 6 and 7). This indicated that the modification of electronic properties of catalyst lead to dramatic change of catalytic activity. APTC-8 with a more electron-withdrawing group (from 4-trifluromethylbenzyl bromide) at quaternary ammonium center produced a similar catalytic activity to APTC-4 (Table 1, entry 8 vs entry 4). Catalysts APTC-9 and APTC-10 afforded cyclic carbonate 2a in moderate yields under the same conditions (Table 1, entries 9 and 10). Under the same conditions, 2a was obtained in 49% yield in the presence of TBAB (Table 1, entry 11). The increase of catalyst-loading from 2.5 mol% to 5 mol% furnished increased yield of cyclic (Table 1, entry 12 vs entry 1, 92% carbonate 2a



Figure 2. The chemical structures of APTC-1~10.

Published on 09 July 2019. Downloaded by University of Iowa on 7/9/2019 1:27:56 PM

Journal Name

ARTICLE

Table 1. The optimization of reaction conditions.

PhO CO_2 (balloon) O									
		1a			2a				
entry ^a	cat.(mol%)	solvent	T(°C)	yield(%) ^b	entry ^a	cat.(mol%)	solvent	T(°C)	yield(%) ^b
1	APTC-1 (2.5)	neat	80	87	11	TBAB ^c (2.5)	neat	80	49
2	APTC-2 (2.5)	neat	80	52	12	APTC-1 (5.0)	neat	80	92
3	APTC-3 (2.5)	neat	80	trace	13	APTC-1 (1.0)	neat	80	64
4	APTC-4 (2.5)	neat	80	57	14	APTC-1 (2.5)	neat	60	61
5	APTC-5 (2.5)	neat	80	42	15	APTC-1 (2.5)	neat	25	32
6	APTC-6 (2.5)	neat	80	50	16	APTC-1 (2.5)	PhCl	80	59
7	APTC-7 (2.5)	neat	80	trace	17	APTC-1 (2.5)	dioxane	80	40
8	APTC-8 (2.5)	neat	80	64	18	APTC-1 (2.5)	toluene	80	33
9	APTC-9 (2.5)	neat	80	45	19	APTC-1 (2.5)	DMF	80	82
10	APTC-10 (2.5)	neat	80	54	20	none	neat	80	0

^aReaction was performed in a 0.5 mmol scale; ^bIsolated yield based on **1a**; ^cTBAB = Tetra-n-butyl ammonium bromide.

vs 87%). **2a** was obtained in 64% yield in the presence of 1.0 mol% of **APTC-1** (Table 1, entry 13). When the reaction temperature was decreased from 80 °C to 60 °C, the yield of cyclic carbonate **2a** was slightly dropped to 61% (Table 1, entry 14 vs entry 1). When the reaction was performed at room temperature, the yield of **2a** is 32% (Table 1, entry 15 vs entry 1). The solvent effect of this model reaction was also investigated. It was found that only DMF was used as solvent

to give the comparative yield of **2a** to neat conditions (Table 1, entries 16^{19} vs entry 1). No cyclic carbonate **2a** was furnished without catalyst (Table 1, entry 20). When the reaction was performed in 5 mmol scale under optimal conditions, **2a** was obtained in 95% yield. Therefore, the optimal reaction conditions were established as follows: 2.5 mol% **APTC-1**, neat, 1.0 atm CO₂ (balloon), 80 °C and 24 h.

Figure 3. The substrates scope for APTC-1 catalyzed cycloaddition of CO₂.



J. Name., 2013, 00, 1-3 | 3

View Article Online

DOI: 10.1039/C9GC02058F

Journal Name

ARTICLE

Published on 09 July 2019. Downloaded by University of Iowa on 7/9/2019 1:27:56 PM

After then, various epoxides (or oxetanes) were used as substrates for this type of cycloaddition under optimal conditions. The reaction results are listed in Figure 3. It was found that glycidyl ethers 1a-f were converted to their corresponding cyclic carbonates 2a-f in high to excellent yields, however, styrene oxides 1g-i provided carbonates 2g-i in moderate yields. When enantiopure styrene oxides 1j and 1k were used as substrates, the corresponding cyclic carbonates 2j and 2k were obtained in good yields and moderate enantioselectivities (78.3% and 66.7% ee), the reason to the inversion of stereochemistry of cyclic carbonates is due to the electron-withdrawing nature of benzene ring, which makes nucleophilic ring-opening of styrene oxide both at the methine bond and the methylene bond. Fortunately, the enantiopure glycidyl ethers 11-n retained their chirality under the optimal conditions to produce 21-n in excellent ee values (> 99% ee, see SI for details). 2,2-Disubstitued epoxide 10 is not a good substrate for this transformation, and no reaction was found when oxetanes 1p and 1q were used in this type of cycloaddition even with a prolongation of reaction time.



Scheme 1. Comparison of APTCs catalyzed cycloaddition of CO2.

In order to know the importance of the hydrogen-bonding interaction between catalyst and substrate in this cycloaddition, we have prepared the mono-N-Me substituted catalyst APTC-1' and its catalytic activity was investigated under the optimal conditions. To our surprise, the yield of cyclic carbonate was only decreased slightly from 87% to 84%, which is much more higher than n-Bu₄N⁺Br⁻(TBAB) as catalyst under the same conditions (Table 1, entry 11, 87% vs 49%). We have also prepared APTC-11 which containing two hydroxyl groups to catalyze the cycloaddition of CO2 with epoxide 1a, cyclic carbonate 2a was obtained in 90% yield, however, when these two hydroxyl groups were blocked by Ms (APTC-11'), the yield of 2a was decreased dramatically to 33% under the same conditions (Scheme 1). All above-mentioned facts indicated that APTCs with H-bonding donor group have shown more effective catalytic activities than without H-bonding group in the cycloaddition of CO₂ to epoxides.

Based on experimental facts, the mechanism of the bifunctional phase-transfer catalyst APTC-1 for fixation of CO_2 by epoxides was



Figure 4. Proposed catalytic cycle of fixaition CO₂ by epoxides.

proposed in Figure 4. At the beginning, the epoxide **1** is activated by **APTC-1** through hydrogen-bonding interaction between N-H and O atom to form intermediate **A**, which undergoes nucleophilic attack from Br to give intermediate **B**, intermediate **B** attacks CO_2 to yield intermediate **C**, the intramolecular ring-closing of intermediate **C** provides cyclic carbonate **2** with a release of **APTC-1** to take apart in the next catalytic cycle.

B. Synthesis of chiral bifunctional phase-transfer catalysts and kinetic resolution of epoxides with CO_2 by them

Shirakawa^{14b} and colleagues have demonstrated binol-derived bifunctional quaternary phosphonium salt catalysts for kinetic resolution of epoxides to produce chiral cyclic carbonatesand epoxides in low *ee* values. Very recently, Meggers^{14c} and colleagues have developed a facile kinetic resolution of epoxides with CO₂ by 1 mol% of chiral-at-iridium complex catalyst in the presence of 1.5 mol% co-catalyst Et₄NBr to give chiral cyclic carbonates in high ee values and selectivity factors (up to 86% ee and 16.6). However, the kinetic resolution of epoxides solely by chiral organocatalysts to achieve good ee values and selectivity factors is still a challenge.14d,e We have deduced that chiral bifunctional quaternary ammonium salt catalysts may also accomplish this transformation. Recently, we have developed a class of chiral bifunctional phase-transfer catalysts for asymmetric amination of nitrooleins under neutral and water-rich conditions with high yields and enantioselectivities.¹⁶ For our continuous interest on the utility of these bifunctional phase-transfer catalysts, the kinetic resolution of epoxides by CO₂ was performed to form chiral cyclic carbonates and epoxides. Fourteen CPTCs (Figure 5) based on various chiral scaffolds including 3-aminopyrrolidine, amino acids, ferrocene and

ARTICLE

View Article Online



cinchona alkaloids were investigated for kinetic resolution of racemic epoxides.

At first, (+/-)-styrene oxide 1g was chosen as model substrate for kinetic resolution by these above-mentioned CPTCs. The preliminary results are shown in Scheme 2. Among them, only CPTC-2 with a urea group has provided chiral cyclic carbonate 2g' in 26% isolated yield and 21.7% ee. The increase of catalyst-loading of CPTC-2 from 1 mol% to 10 mol%, the yield of the cyclic carbonate 2g' was increased to 57% but with the decrease of enantioselectivity (13% ee vs 21.7% ee). CPTCs with a urea group based on L-valine scaffold including CPTC-3~5 furnished rac- cyclic carbonate respectively. Ferrocene-based chiral bifunctional phasetransfer catalysts CPTC-6 and CPTC-7 have also demonstrated dissatisfactory results. Switched hydrogen bonding donor (urea or thiourea) group to squaramide (such as CPTC-11~14), there is no significant improvement for kinetic resolution of (+/-)-styrene oxide **1g** by CO₂, all of them afforded *rac*-cyclic carbonate. When glycidyl phenylether 1a and glycidyl benzylether 1b were used as substrates, all catalysts failed to give chiral cyclic carbonates under the same conditions (see Supplementary Information for details).



^alsolated yield. ^bDetermined by HPLC on chiral stationary phase. ^cCalculated as $(\ln[1 - c(1 + ee)])/(\ln[1 - c(1 - ee)])$ where c is the conversion and ee is the enantiomeric excess of the cyclic carbonate product.

Scheme 2. CPTCs catalyzed kinetic resolution of rac-styrene oxide by CO₂.

Experimental

Typical procedure for cycloaddition of epoxide with CO₂

A mixture of 0.5 mmol of epoxide 1a and 2.5 mol% of APTC-1 (6.8 mg) was heated at 80 °C for 24 h under CO₂ atmosphere (1atm, using a balloon). After cooled to room temperature, a small amount of CH_2Cl_2 was added to the mixture and it was purified by a flash column chromatography (petroether/ethyl acetate = 10/1 to 3/1, v/v) to give cyclic carbonate **2a** as offwhite solid.

Typical procedure for kinetic resolution of epoxide by CO₂

A mixture of 0.25 mmol of epoxide 1g and 1.0 mol% of CPTC-2 (1.5 mg) was heated at 60 °C for 24 h under CO₂ atmosphere

(1atm, using a balloon). After cooled to room temperature, a small amount of CH_2Cl_2 was added to the mixture and it was purified by a flash column chromatography (petroether/ethyl acetate = 10/1 to 3/1, v/v) to give cyclic carbonate and epoxide respectively. The *ee* of products were determined by HPLC using a chiral column (Daicel Chiralpak AD-H or OD-H), and the absolute configurations of products were assigned according to literature report.¹⁴

Conclusions

ARTICLE

In summary, we have demonstrated a series of bifunctional quaternary ammonium salts as phase-transfer catalysts for fixation of CO_2 with epoxides to afford cyclic carbonates in good to excellent yields under mild conditions. These bifunctional catalysts are structure-tuneable and easily prepared, they also demonstrated high efficiency for fixation of CO_2 under ambient pressure. Additionally, a number of chiral bifunctional quaternary onium salts based on privileged scaffolds were synthesized for kinetic resolution of *rac*epoxides by CO_2 to produce chiral cyclic carbonate up to 21.7% *ee*. The endeavour to improve the enantioselectivity of kinetic resolution of epoxide by CO_2 with chiral quaternary onium salts was underway in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the National Science Foundation of China (no. 21372259 and 81503028) for financial support of this work.

Notes and references

- For reviews of CO₂ fixation, see: (a) E. S. Sanz-Pérez, C. R. Murdock, S. A. Didas, C. W. Jones, Chem. Rev., 2016, 116, 11840; (b) M. Aresta, A. Dibenedeto, A. Angelini, Chem. Rev., 2014, 114, 1709; (c) C. Martín, G. Fiorani, A. W. Kleij, ACS Catal., 2015, 5, 1353; (d) S. Wang, C.-J. Xi, Chem. Soc. Rev., 2019, 48, 382; (e) K. Huang, C.-L. Sun, Z.-J. Shi, Chem. Soc. Rev., 2011, 40, 2435; (f) F. M. Mota, D. H. Kim, Chem. Soc. Rev., 2019, 48, 205; (g) A. Tortajada, F. Juliá-Hernández, M. Börjesson, T. Moragas, R. Martin, Angew. Chem. Int. Ed., 2018, 57, 15948; (h) Yeung, C., Angew. Chem. Int. Ed., 2019, 58, 5492; (i) N. A. Tappe, R. M. Reich, V. D'Elia, F. E. Kühn, Dalton Trans., 2018, 47, 13281; (j) X. Chang, T. Wang, P. Yang, G. Zhang, J. L. Gong, Adv. Mater., 2018, 1804710; (k) F. Della Monica, A. Buonerba, C. Capacchione, Adv. Synth. Catal., 2019, 361, 265. (I) A. Cherubini-Celli, J. Mateos, M. Bonchio, L. Dell'Amico, X. Companyó, ChemSusChem, 2018, 11, 3056; (m) J. Luo, I. Larrosa, ChemSusChem, 2017, 10, 3317; (n) D.-H. Lan, N. Fan, Y. Wang, X. Gao, P. Zhang, L. Chen, C.-T. Au, S.-F. Yin, Chin. J. Catal., 2016, 37, 826.
- For reviews of CO₂ conversion to polymers, see: (a) A. Darabi,
 P. G. Jessop, M. F. Cunningham, *Chem. Soc. Rev.*, 2016, 45, 4391; (b) J. Artz, T. E. Müller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow, W. Leitner, *Chem. Rev.*, 2018, 118, 434; (c) Q. Liu, L.-P. Wu, R. Jackstell, M. Beller, *Nature*

Commun., 2015, **6**, 5933; (d) X.-Y. Zhang, M. View Article Online Jones, R. M. Waymouth, *Chem. Rev.*, 2018, **118**, 3299; (e) Mode Childers, J. M. Longo, N. J. V. Zee, A. M. LaPointe, G. W. Coates, *Chem. Rev.*, 2014, **114**, 8129; (f) B. Yu, L.-N. He, *ChemSusChem*, 2015, **8**, 52; (g) X.-B. Lu, W.-M. Ren, G.-P. Wu, *Acc. Chem. Res.*, 2012, **45**, 1721; (h) P. P. Pescarmona, M. Taherimehr, *Catal. Sci. Technol.*, 2012, **2**, 2169.

- 3 For recent examples of utilization of CO₂ under atmospheric pressure and mild temperature, see: (a) J.-Y. Hu, J. Ma, H.-Z. Liu, Q.-L. Qian, C. Xie, B.-X. Han, Green Chem., 2018, 20, 2990; (b) J. Hou, A. Ee, W.Feng, J.-H. Xu, Y. Zhao, J. Wu, J. Am. Chem. Soc., 2018, 140, 5257; (c) G. Bresciani, M. Bortoluzzi, F. Marchetti, G. Pampaloni, ChemSusChem, 2018, 11, 2737; (d) F. D. Bobbink, F. Menoud, P. J. Dyson, ACS Sustainable Chem. Eng., 2018, 6, 12119; (e) S. Zhang, F. Han, S.-R. Yan, M.-Y. He, C.-X. Miao, L.-N. He, Eur. J. Org. Chem., 2019, 1311; (f) F. Yang, M. Tiffner, J. Schörgenhumer, R. Robiette, M. Waser, S. R. Kass, J. Org. Chem., 2018, 83, 9991; (g) Wang, G. Zhang, K. Kodama, T. Hirose, Green Chem., 2016, 18, 1229; (h) J. A. Castro-Osma, K. J. Lamb, M. North, ACS Catal., 2016, 6, 5012; (i) J. A. Castro-Osma, M. North, X. Wu, Chem.-Eur. J., 2016, 22, 2100 (j) H. Zhou, G.-X. Wang, W.-Z. Zhang, X.-B. Lu, ACS Catal., 2015, 5, 6773.
- 4 For reviews of CO₂ fixation with organocatalysts, see: (a) R. A. Pramudita, K. Motokura, *Green Chem.*, 2018, **20**, 4834; (b) A. Cherubini-Celli, J. Mateos, M. Bonchio, L. Dell'Amico, X. Companyó, *ChemSusChem*, 2018, **11**, 3056; (c) Z. Zhang, J.-H. Ye, D.-S. Wu, Y.-Q. Zhou, D.-G. Yu, *Chem. Asian J.*, 2018, **13**, 2292; (d) M. Alves, B. Grignard, R. Mereau, C. Jerome, T. Tassaing, C. Detrembleur, *Catal. Sci. Technol.*, 2017, **7**, 2651; (e) Q.-W. Song, Z.-H. Zhou, L.-N. He, *Green Chem.*, 2017, **19**, 3707; (f) M. Cokoja, M. E. Wilhelm, M.H. Anthofer, W. A. Herrmann, F. E. Kühn, *ChemSusChem*, 2015, **8**, 2436; (g) G. Fiorani, W.-S. Guo, A. W. Kleij, *Green Chem.*, 2015, **17**, 1375; (h) F.-G. Fontaine, M.-A. Courtemanche, M.-A. Légaré, *Chem. Eur. J.*, 2014, **20**, 2990.
- For examples of CO₂ fixation by N-Heterocyclic Carbenes (NHCs), see: (a) L.-H. Yang, H.-M. Wang, *ChemSusChem*, 2014, **7**, 962; (b) A.-H. Liu, Y.-L. Dang, H. Zhou, J.-J. Zhang, X.-B. Lu, *ChemCatChem*, 2018, **10**, 2686; (c) W. Desens, T. Werner, *Adv. Synth. Catal.*, 2016, **358**, 622; (d) Y.-B. Wang, D.-S. Sun, H. Zhou, W.-Z. Zhang, X.-B. Lu, *Green Chem.*, 2015, **17**, 4009; (e) Y.-Q. Xiao, X.-Q. Kong, Z.-C. Xu, C.-S. Cao, G.-S. Pang, Y.-H. Shi, *RSC Adv.*, 2015, **5**, 5032; (f) H. Zhou, Y.-M. Wang, W.-Z. Zhang, J.-P. Qu, X.-B. Lu, *Green Chem.*, 2011, **13**, 644; (g) S. Riduan, Y.-G. Zhang, J. Y. Ying, *Angew. Chem. Int. Ed.*, 2009, **48**, 3322.
- 6 For examples of CO₂ fixation by N-heterocyclic bases (NHCBs), see: (a) T. Niemi, J. E. Perea-Bucet, I. Fernández, O.-M. Hiltunen, V. Salo, S. Rautiainen, M. T. Räisänen, T. Repo, *Chem. Eur. J.*, 2016, **22**, 10355; (b) Z. Xin, C. Lescot, S. D. Friis, K. Daasbjerg, T. Skrydstrup, *Angew. Chem. Int. Ed.*, 2015, **54**, 6862; (c) W.-Z. Zhang, S, Liu, X.-B. Lu, *Beilstein J. Org. Chem.*, 2015, **11**, 906.
- For examples of CO₂ fixation by frustrated Lewis pairs (FLPs), see: (a) M.-A. Courtemanche, M.-A. Legaré, L. Maron,. F.-G. Fontaine, *J. Am. Chem. Soc.*, 2013, **135**, 9326; (b) M.-A. Courtemanche, A. P. Pulis, E. Rochette, M.-A. Légaré, D. W. Stephan, F.-G. Fontaine, *Chem. Commun.*, 2015, **51**, 9797.
- 8 T. Ema, K. Fukuhara, T. Sakai, M. Ohbo, F.-Q. Bai, J. Hasegawa, *Catal. Sci. Technol.*, 2015, **5**, 2314.
- 9 For recent examples of CO₂ fixation by bifunctional quaternary onium salts (PTCs), see: (a) A. Rostami, M. Mahmoodabadi, A. H. Ebrahimi, H. Khosravi, A. Al-Harrasi, *ChemSusChem*, 2018, 11, 4262; (b) H. Büttner, J. Steinbauer, C. Wulf, M. Dindaroglu, H.-G. Schmalz, T. Werner, *ChemSusChem*, 2017, **10**, 1076; (c) B. A. Vara, T. J.

View Article Online DOI: 10.1039/C9GC02058F

Struble, W. Wang, M. C. Dobish, J. N. Johnston, *J. Am. Chem. Soc.*, 2015, **137**, 7302; (d) A. R. Hajipour, Y. Heydari, G. Kozehgary, *RSC Adv.*, 2015, **5**, 61179.

- b) To be recamples of CO₂ fixation by polyphenols or silanediol, with co-catalysts TBAB or TBAI, see: (a) C. J. Whiteoak, A. Nova, F. Maseras, A. W. Kleij, *ChemSusChem*, 2012, **5**, 2032 (b) A. M. Hardman-Baldwin, A. E. Mattson, *ChemSusChem*, 2014, **7**, 3275.
- 11 For reviews and examples of CO₂ fixation by ionic liquids (ILs), see: (a) J.-M. Zhang, J. Sun, X.-C. Zhang, Y.-S. Zhao, S.-J. Zhang, *Greenhouse Gas Sci. Technol.*, 2011, 1, 142; (b) B.-H. Xu, J.-Q. Wang, J. Sun, Y. Huang, J.-P. Zhang, X.-P. Zhang, S.-J. Zhang, *Green Chem.*, 2015, 17, 108; (c) Q. He, J. W. O'Brien, K. A. Kitselman, L. E. Tompkins, G. C. T. Curtis, F. M. Kerton, *Catal. Sci. Technol.*, 2014, 4, 1513; (d) R. Babu, J. F. Kurisingal, J.-S. Chang, D.-W. Park, *ChemSusChem*, 2018, 11, 924; (e) D.-N. Zheng, T.-F. Wang, X.-R. Zhu, C. Chen, T.-G. Ren, L. Wang, J.-L Zhang, *Mol. Syst. Des. Eng.*, 2018, 3, 348.
- 12 For reviews and examples of bifunctional phase-transfer catalysts, see: (a) A. Golandaj, A. Ahmad, D. Ramjugernath, Adv. Synth. Catal., 2017, 359, 3676; (b) S.-Y. Liu, Y. Kumatabara, S. Shirakawa, Green Chem., 2016, 18, 331; (c) S. Kaneko, Y. Kumatabara, S. Shirakawa, Org. Biomol. Chem., 2016, 14, 5367; (d) J. Novacek, M. Waser, Eur. J. Org. Chem., 2013, 637; (e) S. Paria, Q.-K. Kang, M. Hatanaka, K. Maruoka, ACS Catal., 2019, 9, 78; (f) V. Capaccio, K. Zielke, A. Eitzinger, A. Massa, L. Palombi, K. Faust, M. Waser, Org. Chem. Front., 2018, 5, 3336; (g) W.-H. Liu, Y.-F. Wang, D.-Q. Xu, Org. Biomol. Chem., 2018, 16, 8704; (h) A. Jakhar, M. Nazish, N. Gupta, N.-u. H. Khan, R. I. Kureshy, ChemistrySelect, 2018, 3, 4838; (i) B. Hu, L. Deng, Angew. Chem. Int. Ed., 2018, 57, 2233; (j) N. Lu, R.-X. Li, Z.-L. Wei, J.-G. Cao, D.-P. Liang, Y.-J. Lin, H.-F. Duan, J. Org. Chem., 2017, 82, 4668.
- 13 (a) H. Büttner, K. Lau, A. Spannenberg, T. Werner, *ChemCatChem*, 2015, **7**, 459; (b) T. Werner, Büttner, ChemSusChem, 2014, **7**, 3268.
- 14 (a) Y. Toda, Y. Komiyama, A. Kikuchi, H. Suga, ACS Catal., 2016, 6, 6906; (b) S.-Y. Liu, N. Suematsu, K. Maruoka, S. Shirakawa, Green Chem., 2016, 18, 4611; (c) J. Qin, V. A. Larionov, K. Harms, E. Meggers, ChemSusChem, 2019, 12, 320; (d) T. Ema, M. Yokoyama, S. Watanabe, S. Sasaki, H. Ota, K. Takaishi, Org. Lett., 2017, 19, 4070; (e) K. Takaishi, T. Okuyama, S. Kadosaki, M. Uchiyama, T. Ema, Org. Lett. 2019, 21, 1397.
- 15 S. Sopeña, E. Martin, E. C. Escudero-Adán, A. W. Kleij, *ACS Catal.*, 2017, **7**, 3532.
- 16 J.-C. Zhu, D.-X. Cui, Y.-D. Li, J.-X. He, W.-P. Chen, P.-A. Wang, Org. Biomol. Chem., 2018, 16, 3012.
- 17 J. Novacek, M. Waser, Eur. J. Org. Chem., 2014, 802.

Green Chemistry Accepted Manuscript

Bifunctional phase-transfer catalysts for fixation of CO₂ with epoxides under 9/C9GC02058F ambient pressure

Yue-Dan Li,^{a,†} Dong-Xiao Cui,^{a,b,†} Jun-Chao Zhu,^a Ping Huang,^a Zhuang Tian,^a Yan-Yan Jia,^b and Ping-An Wang^{a,‡}

A series of achiral and chiral bifunctional phase-transfer catalysts with a quaternary onium center and hydrogen-bonding donor group were prepared for fixation of CO_2 with epoxides under mild conditions by using a CO_2 balloon (1 atm) to produce cyclic carbonates up to 95% yields.

