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FULL PAPER

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Cobalt-based catalytic system for the chemical fixation of CO_2 under solvent-free conditions

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Abstract

We have described a novel and efficient method for synthesizing cyclic carbonates with 'Co $(NO_3)_2{\cdot}6H_2O$/**L6**'-catalyzed coupling of epoxides and CO_2 under solvent-free conditions. We proposed a possible reaction mechanism based on some control experiments. Phenylpropiolic acid could be provided by using the same method.

KEYWORDS

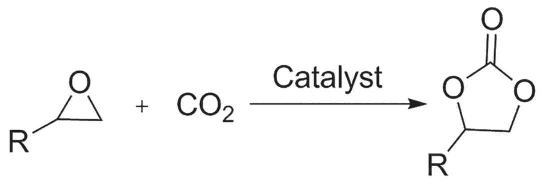
carbon dioxide, chemical fixation, cobalt, cyclic carbonates, epoxide

1 | INTRODUCTION

The chemical conversion of CO_2 into value-added bulk and fine chemicals has attracted considerable attention in recent years,[1] because CO_2 is an abundant inexpensive, nonflammable, and renewable C1 synthon.[2] This C1 feedstock could be utilized for the synthesis of carbamate derivatives, cyclic urethanes, N,N′-disubstituted urea compounds, formic acid, poly (carbonates), carboxylic acids, carbon monoxide and others.[3] Among them, cyclic carbonates are an important compound, due to its high atom efficiency and the widespread application of products such as degrease in medicine, electrolytes in lithium ion batteries, and eco-friendly non-protic solvents.[4]

One of the most successful method for preparing five-membered cyclic carbonates is the cycloaddition of CO_2 and epoxides (Scheme 1).[5] Cyclic carbonates have been synthesized in industries, but high pressure, high temperature, and large catalyst loading amount are indispensable in the process. These conditions require energy consumption, and may thus cause serious environmental problems.[6] In hence, great efforts have been made for the development of effective catalytic systems such as, imidazolium salts,[7] quaternary ammonium salt,[8] quaternary phosphonium salt,[9] dipyridine salt,[10] phenolic resin,[11] organic polymer based on organosilicone and urea,[12] MOFs,[13] Zn@Salen-typle porous material,[14] **hypercrosslinked porous polymer materials,**[15] ionic liquid,[16] metal complex,[17] and proton donor,[18] for the coupling of epoxides and CO_2. Although numerous catalysts promote the reaction to form the corresponding cyclic carbonates in excellent yields, in many case, harsh reaction conditions, the large loading amount of catalyst, metal halide or halide salt as co-catalyst are required. To circumvent these disadvantages, new types of active and efficient catalysts are desirable to be developed.

As a continuation of our study on using ligands for enhancing the coupling reaction,[19] and encouraged by



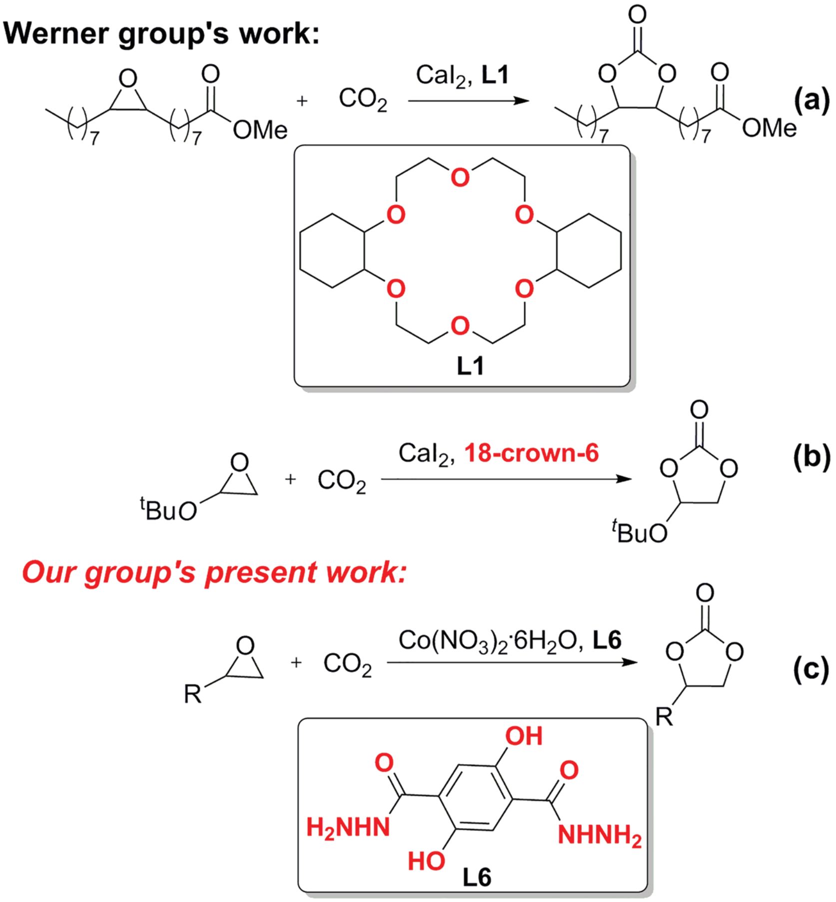
SCHEME 1 The reaction of epoxides and CO2

the Werner group's work,[20] which depicted that catalyst system 'CaI$_2$/L1' (or 'CaI$_2$/18-crown-6') could be used for the synthesis of cyclic carbonates from epoxides and CO_2 (Scheme 2, a and b), we tried the reaction in the presence of different ligands, and found that the combination of 'CoNO$_3$·6H$_2$O/L2' could efficiently promote the coupling reaction of CO_2 and epoxides in solvent-free reactions (Scheme 2, c).

2 | RESULT AND DISCUSSION

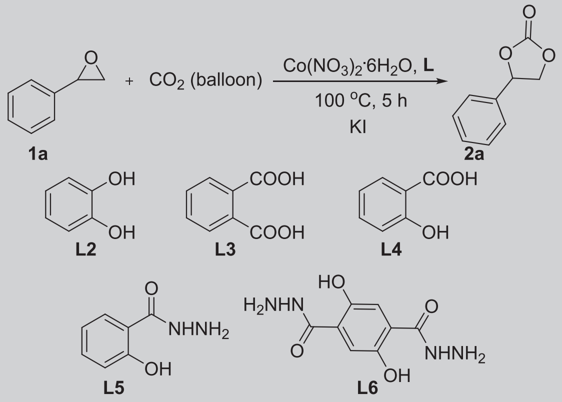
Our attempt was commenced with the transformation of styrene oxide **1a** and CO_2 at 100 °C in 5 hr. As shown in Table 1, only 17% **2a** yield was obtained in the absence of ligand (entry 1). Then, O,O-type ligands **L2**, **L3**, and **L4** were investigated, the yields were slightly increased (entries 2, 3, and 4). When N,O-type ligand **L5** was used, 48% yield was provided (entry 5). When quadridentate O,N-ligand **L6** was employed, 63% **2a** yield was obtained, may due to its strong coordination ability to cobalt (entry 6).

To further increase the reaction efficiency, we examined other reaction conditions (Table 2). More starting material was recovered without metal and co-catalyst (entry 1). Co (NO$_3$)$_2$·6H$_2$O was crucial for the successful reaction, and KI also played important role in this transformation (entries 2 and 3). Next, other metal catalysts were investigated, the results indicated that Co (NO$_3$)$_2$·6H$_2$O was the superior choice over others (entries 4, 5, and 6). Moreover, evaluation of co-catalysts such as KBr, KCl, NaI, and NaCl were underwent, KBr was better in promoting the transformation (entries 7, 8, 9, and 10). Switching the CO_2 pressure to 0.3 and 0.6 MPa, the yields of **2a** were obtained in 71% and 82%, respectively (entries 11 and 12). In addition, the effects of reaction time were scrutinized, the results showed that 5 hr was optimal



SCHEME 2 The ligand-promoted cobalt-catalyzed reaction of epoxides and CO2

TABLE 1 Screening ligands for the reaction[a]



[a] Reaction conditions: **1a** (5 mmol), CO_2 atmospheric pressure, $Co(NO_3)_2·6H_2O$ (0.1 mmol), **L2-L5** (0.2 mmol), **L6** (0.1 mmol), KI (0.1 mmol), 100 °C, 5 h;

[b] Yields were determined by ^1H NMR spectroscopy using 1,1,2,2-tetrachloroethane as the internal standard.

Entry	Ligand	Yield (%)[b]
1	-	22
2	**L2**	26
3	**L3**	32
4	**L4**	39
5	**L5**	48
6	**L6**	63

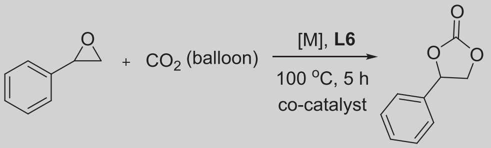
[a]Reaction conditions: **1a** (5 mmol), CO_2 atmospheric pressure, Co $(NO_3)_2·6H_2O$ (0.1 mmol), **L2-L5** (0.2 mmol), **L6** (0.1 mmol), KI (0.1 mmol), 100 °C, 5 hr;
[b]Yields were determined by ^1H NMR spectroscopy using 1,1,2,2-tetrachloroethane as the internal standard.

(entries 13 and 14). From the above, the best reaction conditions were **1a** (5 mmol), CO_2 pressure (0.6 MPa), Co $(NO_3)_2·6H_2O$ (0.1 mmol), **L6** (0.1 mmol), KBr (0.1 mmol), 100 °C, 5 hr.

Having optimized the reaction conditions, we started to expand the substrate scope of the reaction. As summarized in Scheme 3, epoxides containing phenyl group were successfully converted into corresponding products in good yields (**2a-2f**). Epoxide with weak electron-withdrawing group in phenyl was superior to the one with electron-donating group (**2a-2c** *vs* **2d**). Ester group was tolerant under the optimal reaction conditions (**2e-2 g** and **2i**). The length of alkyl group had a little negative effect on the reaction (**2j-2 l**). The carbon–carbon double bond was compatible under these reaction conditions, producing the target compounds **2 g** and **2 h** in 85% and 89% ^1H NMR yields. Epibromohydrin and epichlorohydrin was tested and found to be tolerant in the transformation (**2 m** and **2n**). The reaction of glycidol (or cyclohexene oxide) and CO_2 offered the corresponding products in poor yield (**2o** and **2p**).

To elucidate the reaction mechanism, we performed some control experiments shown in Scheme 4. In the presence of Co $(NO_3)_2·6H_2O$, the model reaction was hardly occurred (Scheme 4, a). We treated the reaction under the KBr, 12% **2a** yield was observed (Scheme 4, b). In combination of and KBr, the yield was increased to 25% (Scheme 4, c). These experiments suggested that KBr addition may affect **2a** to become more active intermediate to complete the reaction, and Co $(NO_3)_2·6H_2O$ could promote the reaction in the presence of KBr. Then we attempted to carry out the reaction between **3a** and CO_2, which 73% **2a** yield was obtained (Scheme 4, d). This result demonstrated that **3a** may be transformed into an active bromine intermediate. When we carried the reaction under different amount of **L6** (0.1 mol, 0.2 mol, 0.3 mol), the product

TABLE 2 The other optimization of reaction conditions[a]



[a] Reaction conditions: **1a** (5 mmol), CO_2 atmospheric pressure, $Co(NO_3)_2{\cdot}6H_2O$ (0.1 mmol), **L6** (0.1 mmol), co-catalyst (0.1 mmol), 100 °C, 5 h;

[b] Yields were determined by ^1H NMR spectroscopy using 1,1,2,2-tetrachloroethane as the internal standard;

[c] CO_2 (0.3 MPa);

[d] CO_2 (0.6 MPa);

[e] Isolated yield;

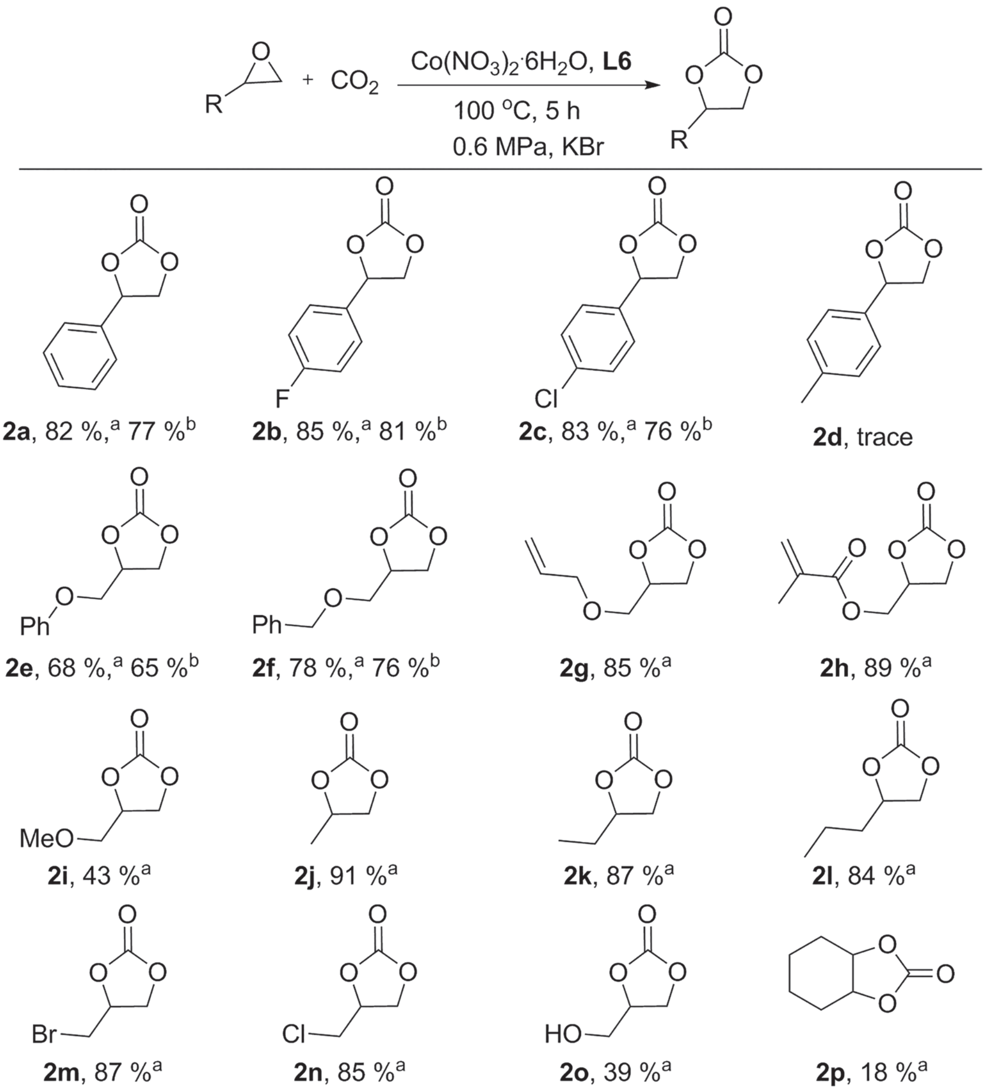
[f] 3 h;

[g] 8 h;

Entry	[M]	Co-catalyst	Yield (%)[b]
1	-	-	17
2	-	KI	15
3	$Co\ (NO_3)_2{\cdot}6H_2O$	-	14
4	$Zn\ (NO_3)_2$	KI	51
5	$Fe\ (NO_3)_3$	KI	48
6	$Cu\ (NO_3)_2{\cdot}6H_2O$	KI	42
7	$Co\ (NO_3)_2{\cdot}6H_2O$	KBr	65
8	$Co\ (NO_3)_2{\cdot}6H_2O$	KCl	54
9	$Co\ (NO_3)_2{\cdot}6H_2O$	NaI	57
10	$Co\ (NO_3)_2{\cdot}6H_2O$	NaCl	46
11[c]	$Co\ (NO_3)_2{\cdot}6H_2O$	KBr	71
12[d]	$Co\ (NO_3)_2{\cdot}6H_2O$	KBr	82, 77[e]
13[f]	$Co\ (NO_3)_2{\cdot}6H_2O$	KBr	52
14[g]	$Co\ (NO_3)_2{\cdot}6H_2O$	KBr	85

[a] Reaction conditions: **1a** (5 mmol), CO_2 atmospheric pressure, $Co\ (NO_3)_2{\cdot}6H_2O$ (0.1 mmol), **L6** (0.1 mmol), co-catalyst (0.1 mmol), 100 °C, 5 hr;
[b] Yields were determined by ^1H NMR spectroscopy using 1,1,2,2-tetrachloroethane as the internal standard;
[c] CO_2 (0.3 MPa);
[d] CO_2 (0.6 MPa);
[e] Isolated yield;
[f] 3 hr;
[g] 8 hr;

yields were 18%, 28%, and 31%, suggesting that **L6** could promote the reaction in some extend (Scheme 4, e), which may be attributed to the hydrogen bond donor catalysis.[21] However, with the aid of Co $(NO_3)_2{\cdot}6H_2O$ and **L6**, no increasing yield was provided (Scheme 4, f????????). Under the standard reaction conditions, the yield was 82% (Scheme 4, g), may due to that the complex compound from Co $(NO_3)_2{\cdot}6H_2O$ and **L6** could obviously expedite the reaction with the assistance of KBr, and hydrogen bond donor catalysis.

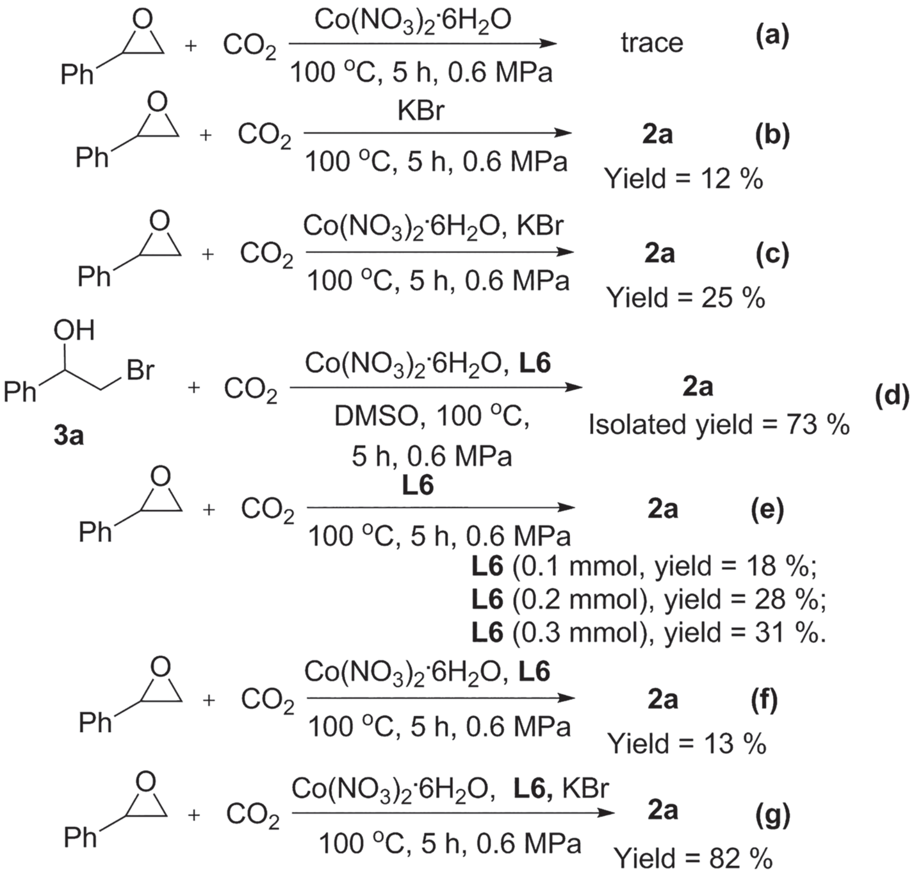


Reaction conditions: epoxides (5 mmol), CO_2 (0.6 MPa), $Co(NO_3)_2·6H_2O$ (0.1 mmol), **L6** (0.1 mmol), KBr (0.1 mmol), 100 °C, 5 h.
[a] Yields were determined by ^1H NMR spectroscopy;
[b] Isolated yield.

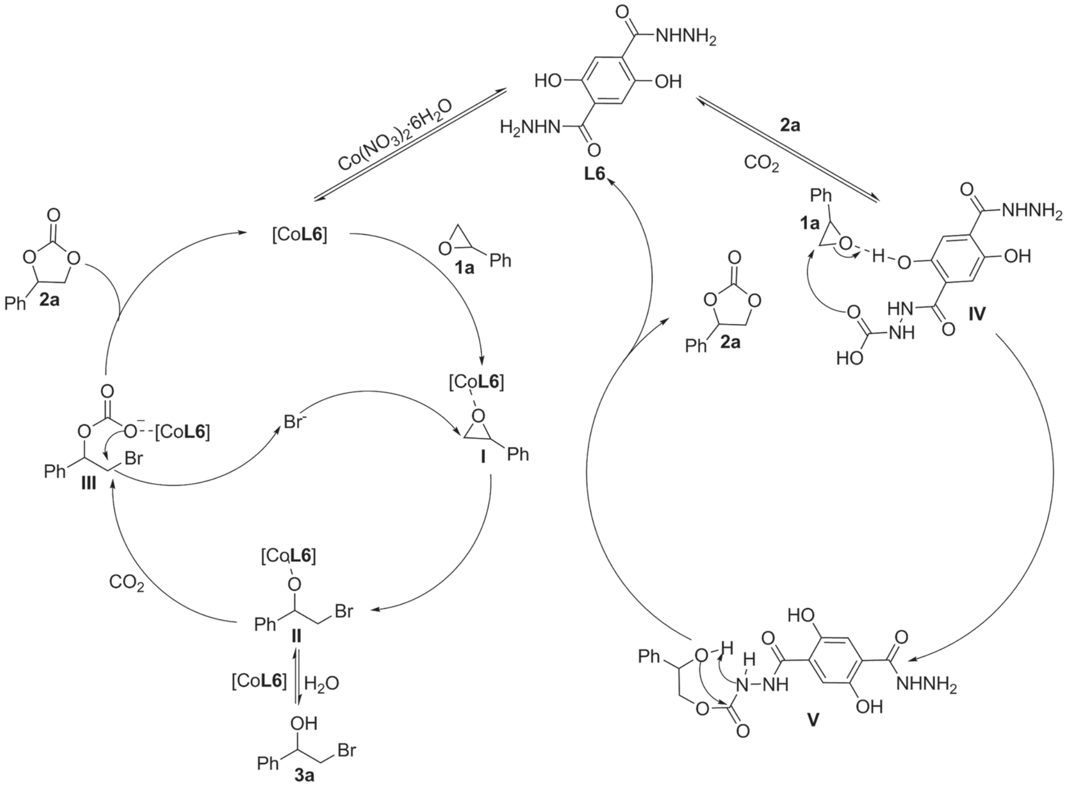
SCHEME 3 The substrate scope of the reaction

Based on control experiments and previous reports,[21,22] we proposed a possible mechanism for model transformation. As depicted in Scheme 5, there were two pathways for the cyclization: (a) Initially, **1a** was activated in the presence of [Co**L6**], which was *in situ* generated from Co $(NO_3)_2·6H_2O$ and **L6**, to produce an intermediate **I**, followed by ring-opening reaction to form more active bromine intermediate **II**. By hydrolyzation, **3a** can be generated. Then, **II** was interacted with CO_2 to provide intermediate **III**, which finally produced the product **2a** *via* a intramolecular nucleophile reaction; (b) The phenol group from **L6** was used as a Brønsted acid to activate the epoxide, and diazanyl activated carbon dioxide, forming the intermediate **IV**. And then, **IV** was quickly transferred to **V** by intramolecular nucleophilic addition, followed to produce the target compound **2a**.

Furthermore, we investigated other reaction by using 'Co $(NO_3)_2·6H_2O$/**L6**' to extend the utility of the proposed method. Through this method, phenylpropiolic acid **5a**, an important synthetic intermediates in medical chemistry and organic synthesis,[23] could be formed from **4a** and CO_2 in 67% yield (Scheme 6).

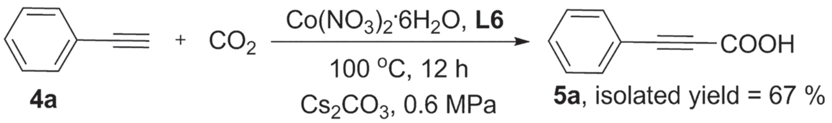


SCHEME 4 Some control experiments



SCHEME 5 The proposed reaction mechanism

SCHEME 6 The reaction of 4a and CO2



Reaction conditions: **4a** (5 mmol), CO_2 (0.6 MPa), $Co(NO_3)_2 \cdot 6H_2O$ (0.1 mmol), **L6** (0.1 mmol), Cs_2CO_3 (1 mmol), 100 °C, 12 h.

3 | CONCLUSION

In summary, we have developed a efficient protocol to synthesize cyclic carbonates *via* 'Co $(NO_3)_2 \cdot 6H_2O$/**L6**'-catalyzed the coupling of CO_2 and epoxides under mild reaction conditions without any solvents. On the basis of some control experiments, we proposed the possible reaction mechanism. In addition, phenylpropiolic acid could be obtained with this method.

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REFERENCES

[1] See some selected reviews:a)C. Maeda, Y. Miyazaki, T. Ema, *Catal. Sci. Technol.* **2014**, *4*, 1482. b)S. Kawi, Y. Kathiraser, J. Ni, U. Oemar, Z. Li, E. T. Saw, *ChemSusChem* **2015**, *8*, 3556. c)X.-L. Du, Z. Jiang, D. S. Su, J.-Q. Wang, *ChemSusChem* **2016**, *9*, 322. d)D. J. Darensbourg, *Chem. Rev.* **2007**, *107*, 2388.

[2] a)M. Yoshida, M. Ihara, *Chem.– Eur. J.* **2004**, *10*, 2886. b) M. Taherimehr, A. Decortes, S. M. Al-Amsyar, W. Lueangchaichaweng, C. J. Whiteoak, E. C. Escudero-Adan, A. W. Kleij, P. P. Pescarmona, *Catal. Sci. Technol.* **2012**, *2*, 2231. c)C. Song, *Catal. Today* **2006**, *115*, 2. d)L. Zhang, Z. M. Hou, *Chem. Sci.* **2013**, *4*, 3395.

[3] a)S. N. Riduan, Y.-G. Zhang, *Dalton Trans.* **2010**, *39*, 3347. b) H. S. Kim, J. J. Kim, B. G. Lee, O. S. Jung, H. G. Jang, S. O. Kang, *Angew. Chem. Int. Ed.* **2000**, *39*, 4096. c)Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nat. Commun.* **2015**, *6*, 5933.

[4] a)K. C. Nicolaou, Z. Yang, J. J. Liu, H. Ueno, P. G. Nantermet, R. K. Guy, C. F. Claiborne, J. Renaud, E. A. Couladouros, K. Paulvannan, E. J. Soresen, *Nature* **1994**, *367*, 630. 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.

[5] a)A. A. G. Shaikh, S. Sivaram, *Chem. Rev.* **1996**, *96*, 951. b) Y. Yuan, Y. Xie, D. Song, C. Zeng, S. Chaemchuen, C. Chen, F. Verpoort, *Appl. Organomet. Chem.* **2017**, *31*, 3867.

[6] M. Mikkelsen, M. Jørgensen, F. C. Krebs, *Energy Environ. Sci.* **2010**, *3*, 43.

[7] a)J. Wang, W. Song, G. Yi, Y. Zhang, *Chem. Commun.* **2015**, *51*, 12076. b)Y. Xie, J. Liang, Y. Fu, M. Huang, X. Xu, H. Wang, S. Tu, J. Li, *J. Mater. Chem. A* **2018**, *6*, 6660. c) M. Liu, L. Liang, X. Li, X. Gao, J. Sun, *Green Chem.* **2016**, *18*, 2851.

[8] a)Y. Xie, Q. Sun, Y. Fu, L. Song, J. Liang, X. Xu, H. Wang, J. Li, S. Tu, X. Lu, J. Li, *J. Mater. Chem. A* **2017**, *5*, 25594. *b)* F. Chen, D. Chen, L. Shi, N. Liu, B. Dai, *J. CO2 Util.* **2016**, *16*, 391.

[9] Q. Sun, Y. Jin, B. Aguila, X. Meng, S. Ma, F.-S. Xiao, *ChemSusChem* **2017**, *10*, 1160.

[10] O. Buyukcakir, S.-H. Je, D. S. Choi, S. N. Talapaneni, Y. Seo, Y. Jung, K. Polychronopoulou, A. Coskun, *Chem. Commun.* **2016**, *52*, 934.

[11] M. Ding, H.-L. Jiang, *Chem. Commun.* **2016**, *52*, 12294.

[12] M. Liu, X. Lu, L. Shi, F. Wang, J. Sun, *ChemSusChem* **2017**, *10*, 1110.

[13] a)G. Zhang, G. Wei, Z. Liu, S. R. J. Oliver, H. Fei, *Chem. Mater.* **2016**, *28*, 6276. b)H.-F. Zhou, B. Liu, L. Hou, W.-Y. Zhang, Y.-Y. Wang, *Chem. Commun.* **2018**, *54*, 456. c)G. Zhang, H. Yang, H. Fei, *ACS Catal.* **2018**, *8*, 2519.

[14] S. Bhunia, R. A. Molla, V. Kumari, S. M. Islamb, A. Bhaumik, *Chem. Commun.* **2015**, *51*, 15732.

[15] S. Wang, K. Song, C. Zhang, Y. Shu, T. Li, B. Tan, *J. Mater. Chem. A* **2017**, *5*, 1509.

[16] W. Dai, W. Yang, Y. Zhang, D. Wang, X. Luo, X. Tu, *J. CO2 Util.* **2017**, *17*, 256.

[17] F. Chen, N. Liu, B. Dai, *ACS Sustainable Chem. Eng.* **2017**, *5*, 9065.

[18] N. Liu, Y.-F. Xie, C. Wang, S.-J. Li, D. Wei, M. Li, B. Dai, *ACS Catal.* **2018**, *8*, 9945.

[19] a)F. Wu, C. Nan, M. Ma, H. Li, J. Xie, *Appl. Organomet. Chem.* **2019**, *33*, e5195. b)F. Wu, J. Zhang, Q. Wei, P. Liu, J. Xie, H. Jiang, B. Dai, *Org. Biomol. Chem.* **2014**, *12*, 9696.

[20] a)L. Longwitz, J. Steinbauer, A. Spannenberg, T. Werner, *ACS Catal.* **2018**, *8*, 665. b) J. Steinbauer, A. Spannenberg, T. Werner, *Green Chem.* **2017**, *19*, 3769.

[21] a)X. Wu, C. Chen, Z. Guo, M. North, A. C. Whitwood, *ACS Catal.* **2019**, *9*, 1895. b)S. Arayachukiat, C. Kongtes, A. Barthel, S. V. C. Vummaleti, A. Poater, S. Wannakao, L. Cavallob, V. DElia, *ACS Sustainable Chem. Eng.* **2017**, *5*, 6392. c) S. Sopeña, E. Martin, E. C. Escudero-Adán, A. W. Kleij, *ACS Catal.* **2017**, *7*, 3532.

[22] a)H. Ullah, B. Mousavi, H. A. Younus, Z. A. K. Khattak, S. Suleman, M. T. Jan, B. Yu, S. Chaemchuen, F. Verpoort, *J. Catal.* **2019**, *377*, 190. b)F. Zhou, S.-L. Xie, X.-T. Gao, R. Zhang, C.-H. Wang, G.-Q. Yin, J. Zhou, *Green Chem.* **2017**, *19*, 3908.

[23] X.-H. Liu, J.-G. Ma, Z. Niu, G.-M. Yang, P. Cheng, *Angew. Chem. Int. Ed.* **2014**, *53*, 1.

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