Green Chemistry

PAPER

View Article Online
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Cite this: *Green Chem.*, 2019, **21**, 6335

Highly regio- and stereoselective synthesis of cyclic carbonates from biomass-derived polyols *via* organocatalytic cascade reaction†

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Received 27th August 2019,
Accepted 28th October 2019

DOI: 10.1039/c9gc03013a

rsc.li/greenchem

The cascade reaction of CO_2, vicinal diols, and propargylic alcohol, was firstly achieved by dual Lewis base (LB) organocatalytic systems involving LB–CO_2 adducts and commercially available organic amines. This methodology could overcome the chemical inertness of CO_2, providing an alternative route to various functionalized five-membered cyclic carbonates in moderate to high yields under mild reaction conditions (25 °C, 1.0 atm of CO_2). More importantly, this method could also be applied for facile and efficient synthesis of chiral polycyclic carbonates from biomass-derived polyols with complete configuration retention of chiral centers. This study provides an environment-friendly, scalable and cost effective protocol to construct value-added cyclic carbonates with multi-functional groups and chiral centers.

Introduction

Cyclic carbonates have extensive applications, such as aprotic polar solvents,[1] electrolytes in lithium-ion secondary batteries,[2] raw materials for the synthesis of polycarbonates and polyurethanes,[3] and more recently as key intermediates in organic synthesis.[4] Enantiopure cyclic carbonates are important chiral intermediates in producing a variety of pharmaceutically compounds and fine chemicals.[5] Their preparation mainly involves three routes: metal-complexes catalyzed insertion of carbon dioxide (CO_2) into chiral epoxides, the cyclization of chiral diols with triphosgene, and enzyme-mediated enantioselective hydrolysis of racemic cyclic carbonates.[6] Although many efforts were paid to develop chiral catalyst systems for the catalytic kinetic resolution of racemic epoxides and CO_2,[7] the progress is very limited, and the highest kinetic resolution coefficient to date of 75.8 obtained at −25 °C using a multichiral catalyst system.[8]

On the other hand, polyhydroxy compounds, as a class of cheap and readily available chemicals, which can be easily obtained through organic synthesis, natural product separation and biomass conversion, are ideal reaction substrates for the synthesis of cyclic carbonates in the presence of carbonylation reagents.[1] As a consequence, the chemical transformations of polyhydroxy compounds, especially vicinal diols, with plentiful carbonylation reagents, including phosgene,[1a] carbon monoxide (CO),[9] CO_2,[10] dimethyl carbonate,[11] and urea[12] have been extensively exploited, as shown in Fig. 1. Among them, phosgenation of alcohols is the first to be used for the industrial production of organic carbonates; however, high toxicity and strong causticity of raw materials restricted the wide use of phosgenation method (Fig. 1. **I**).[1a] In addition, CO-involved oxidative carbonylation of alcohols is a well-known route (Fig. 1. **II**). However, owing to the presence of CO and O_2, the poisoning of catalyst significantly hampers the process.[9] In viewpoints of environmental and green chemistry, CO_2-involved direct condensation with vicinal diols is one of the most promising method, and H_2O is the sole byproduct simultaneously with CO_2 sequestration (Fig. 1. **III**). Unfortunately, the reactivity is unsatisfactory because of a severe thermodynamic limitation. In order to overcome the equilibrium limitation, a slow H_2O remove protocol by introducing the dehydrating agents has to be adopted under high pressure conditions.[10] Alternatively, a safe and easily accessible process is the alcoholysis reaction of diols with carbonates or urea (Fig. 1. **IV** and **V**). The reactions usually carry out under vacuum distillation conditions to remove the by-product, and thereby displace chemical equilibrium toward cyclic carbonate formation.[11,12]

α-Alkylidene cyclic carbonates(***a*CC**) is a new class of carbonylation reagent,[3a,13] which could be directly obtained by the carboxylative cyclization of CO_2 with propargylic alcohols.[14] Recently, a silver carbonate/phosphines-promoted catalytic system for the synthesis of cyclic carbonates by the

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†Electronic supplementary information (ESI) available. CCDC 1946539, 1940555 and 1937066–1937068. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9gc03013a

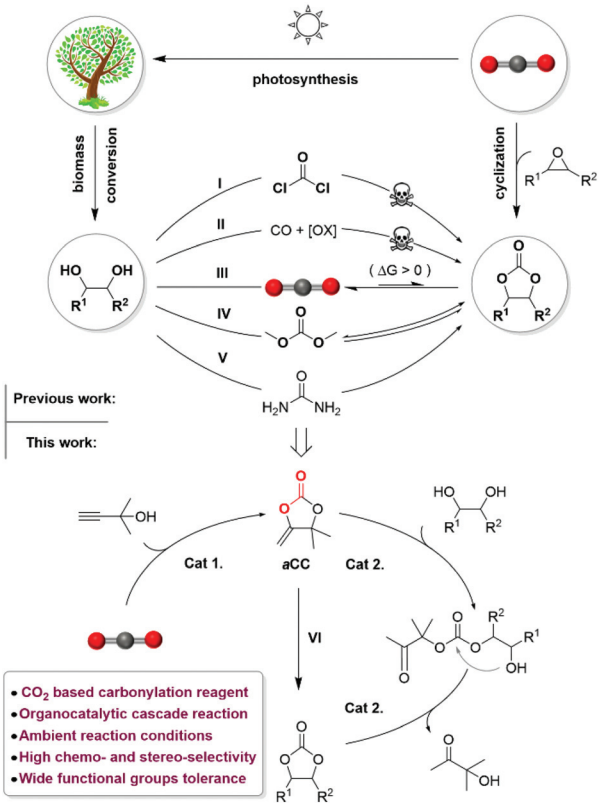


Fig. 1 Different carbonylation reagents involved chemical transformation of vicinal diols for the synthesis of cyclic carbonates.

cascade reaction of CO_2, vicinal diols and propargylic alcohols has been pioneered by He group,[15] and subsequently extended by Zhang and coworkers.[16] In these cases, ***a*CC** prepared *in situ* as carbonylation reagent, further reacted with vicinal diols by transesterification, thus forming the corresponding cyclic carbonates (Fig. 1. **VI**). Compared with traditional carbonates (Fig. 1. **IV**), ***a*CC** featuring an exocyclic C=C double bond, behaves many remarkable advantages: green synthesis from CO_2, high regio- and chemo-selectivity *via* transesterification process, and high yields through completely suppressing the reversible transesterification due to the low nucleophilicity of the resulting α-hydroxyl ketone.

Organocatalyzed CO_2 transformation into heterocycles has become a subject of interest in recent years because the use of a substoichiometric amount of an organic compound to accelerate the reactions is more environmentally friendly compared to organometallic catalysis.[14d,17] For the carboxylative cyclization of CO_2 with propargylic alcohols, although organic amines as organocatalysts were early reported by Li *et al.*, with low catalytic activity and chemoselectivity,[18] a series of novel organocatalytic systems have been successfully developed.[19] Of note is that CO_2 adducts of Lewis base (LB) were recently designed in our laboratory, and these LB–CO_2 adducts,[17e] especially N-heterocyclic carbene–CO_2 adducts (NHC–CO_2)[20] and N-heterocyclic olefins–CO_2 adducts (NHO–CO_2)[21] exhibit superior efficiency for this transformation at mild conditions. Furthermore, organic amine-catalyzed transesterification of ***a*CC** with primary alcohol were also developed by Detrembleur *et al.* for selectively synthesizing linear cyclic carbonate under ambient temperature.[13]

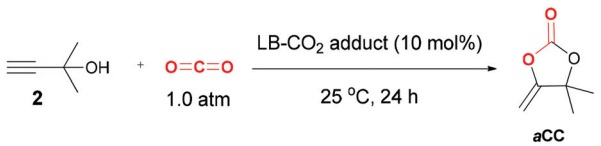
Based on the above research work and our ongoing interest in CO_2 chemical transformations, we reasoned that a suitable organocatalytic system might display satisfying catalytic activity toward this cascade reaction. In this paper, we reported the NHO–CO_2/MTBD organocatalyzed cascade reaction of CO_2, vicinal diols and propargylic alcohol to construct functionalized five-membered cyclic carbonates under ambient conditions in one pot. Of importance, this transformation displayed high activity and excellent **c**hemoselectivity. Moreover, a series of biorenewable sugar alcohols as renewable feedstocks are also tolerated in this process. Notably, chiral polycyclic carbonates from biomass-derived polyols are effectively synthesized with complete retention of stereochemistry. The operational simplicity and mild reaction condition involved in this process make it particularly promising for large-scale applications.

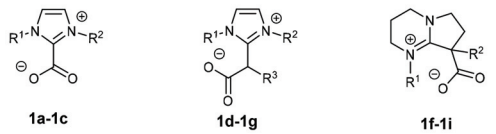
Results and discussion

Since two elementary reactions are involved in the cascade process of CO_2, propargylic alcohols and vicinal diols, they were investigated independently (Fig. 1). Previously, LB–CO_2 adducts have been proven to be highly effective organocatalysts for catalyzing the carboxylative cyclization of CO_2 with propargylic alcohols.[20,21] Considering the operability and universality of the catalytic systems, we tested the catalytic activities of LB–CO_2 adducts (**1a–1k**) for the coupling of CO_2 and 2-methyl-3-butyn-2-ol (**2**) as model substrate to synthesize 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (***a*CC**) under solvent-free and ambient conditions, as shown in Table 1. The reaction was first evaluated in the presence of 10 mol% of organocatalyst at 25 °C for 24 h, and CO_2 was introduced with a balloon. Interestingly, in comparison to NHC–CO_2 adducts **1a–1c** (entries 1–3), NHO–CO_2 adducts **1e–1k** (entries 5–11) displayed much higher reactivity toward the formation of ***a*CC**. The most satisfactory result was obtained with 1 h. Lowering the amount of 1 h to 5.0 mol% or shortening the reaction time to 12 h led to the obvious decrease in yield (entries 12 and 13).

Encouraged by the initial results, the subsequent transesterification of ***a*CC** with 1,2-propanediol **3a** was further selected as a model reaction using a series of commercial available organic amines as catalysts, as shown in Table 2. When using DMAP as organocatalyst, the corresponding cyclic carbonate **4a** was obtained in 33% yield (entry 1), along with the formation of α-hydroxyl ketone (**5**). Enhancing the basicity of organic amines significantly improved the catalytic activity, and MTBD showed the highest yield of 98% (Table 2, entries 2, 3 and 5). Whereas, employing TBD as organocatalyst, the yield only reached 47%, probably due to the presence of intramolecular hydrogen bonding (entry 4). When changing the solvent to $CHCl_3$, DMF or DMSO, the yield was slightly

Table 1 Cyclic addition of propargylic alcohol with CO_2 catalyzed by LB–CO_2 adducts[a]



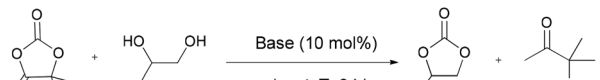


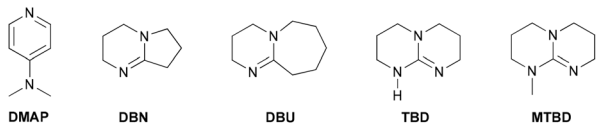
1a: $R^1 = R^2 =$ -^{i}Pr
1b: $R^1 = R^2 =$ **-IPr**
1c: $R^1 = R^2 =$ **-IMes**
IPr = 2,6-diisopropylphenyl
IMes= 2,4,6-trimethylphenyl
1d: $R^1 = R^2 = R^3 =$ -Me
1e: $R^1 = R^2 =$ **IPr**, $R^3 =$ -H
1f: $R^1 =$ **-IPr**, $R^2 = R^3 =$ -Me
1g: $R^1 =$ -Et, $R^2 =$ **-IPr**, $R^3 =$ -Me
1h: $R^1 =$ -Bn, $R^2 =$ -H
1i : $R^1 =$ -Me, $R^2 =$ -H
1j : $R^1 = R^2 =$ -Me
1k: $R^1 =$ -^{n}Bu, $R^2 =$ -H

Entry	LB–CO_2 adduct **1**	Yield of ***a*CC**[b] (%)
1	**1a**	24
2	**1b**	<1
3	**1c**	<1
4	**1d**	5
5	**1e**	33
6	**1f**	34
7	**1g**	51
8	**1h**	92
9	**1i**	91
10	**1j**	75
11	**1k**	50
12	**1h**	52[c]
13	**1h**	46[d]

[a] Reaction conditions: **2** (84 mg, 1.0 mmol), **LB–CO_2 adduct**. **1** (0.1 mmol, 10 mol%), CO_2 = 1.0 atm, 25 °C, 24 h. [b] Yields of ***a*CC** were determined by ^{1}H-NMR analysis using 1,2,4,5-tetramethyl-benzen as an internal standard. [c] 5.0 mol% of **1h**. [d] 12 h.

Table 2 Organic base catalyzed carbonylation of 1,2-propanediol with ***a*CC**[a]





Entry	Base	solvent	*T* (°C)	**4a**/**5** Yield[b] (%)
1	DMAP	CH_3CN	80	33/31
2	DBN	CH_3CN	80	89/88
3	DBU	CH_3CN	80	94/90
4	TBD	CH_3CN	80	47/47
5	MTBD	CH_3CN	80	98/92
6	MTBD	$CHCl_3$	80	83/75
7	MTBD	DMF	80	81/80
8	MTBD	DMSO	80	79/78
9	MTBD	CH_3CN	25	93/84
10[c]	MTBD	CH_3CN	25	89/86

[a] Reaction conditions: ***a*CC** (50 mg, 0.39 mmol), **3a** (30 mg, 0.39 mmol), organic base (0.039 mmol, 10 mol%), solvent (0.5 mL), 24 h. [b] Yield determined by ^{1}H NMR using 1,2,4,5-tetramethyl-benzen as an internal standard. [c] 5.0 mol% of MTBD was employed. DMAP = 4-dimethylaminopyridine, DBN = 1,5-diazabicyclo[4.3.0]non-5-ene, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, TBD = 1,5,7-triazabicyclo [4.4.0]dec-5-ene, MTBD = 1-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene.

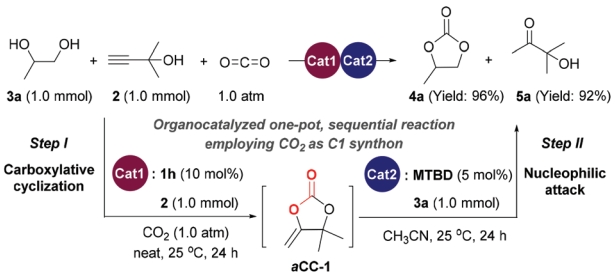


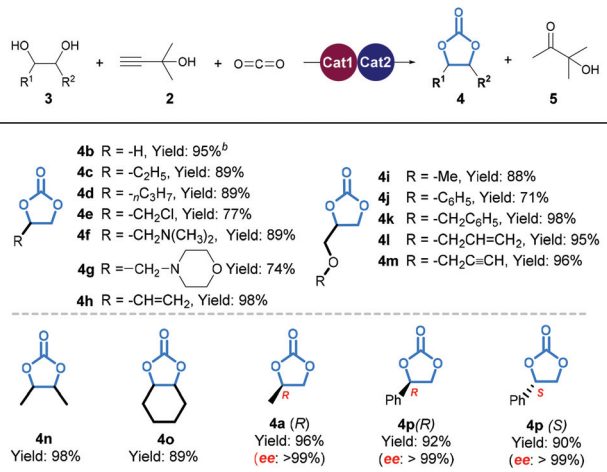
Fig. 2 Organocatalyzed one-pot reaction of CO_2, **2** and **3a**.

decreased (entries 6–8). Notably, reducing the reaction temperature to 25 °C or the catalyst loading to 5.0 mol% still provided appreciable yield of **4a** (entries 9 and 10).

Having established the optimal conditions for the two distinct catalytic reactions, we next tried combining both into a one-pot cascade synthesis, as shown in Fig. 2. The initial LB–CO_2 adducts (**1h**)-catalyzed carboxylative cyclization was run under ambient conditions until the full conversion of propargylic alcohol (**2**) in 24 h, and then MTBD, 1,2-propanediol (**3a**) and solvent were added successively for the subsequent transesterification. As expected, this one-pot cascade reaction could carry out smoothly under ambient conditions and the corresponding propylene carbonate **4a** was obtained in 96% yield (see Experimental section for details).

With the optimized conditions in hand, the scope in vicinal diols substrates was investigated to further evaluate the generality and efficiency of dual organocatalytic systems, and the results are summarized in Table 3. Gratifyingly, a wide range of vicinal diols, including halide, ether, ester, protected amino groups, are tolerant in one-pot system, giving the corresponding terminal cyclic carbonates in good to excellent yields (**4b–4g**, **4i–4k**). It is interesting to note that that the C=C and C≡C bond moiety in the substrates remained intact under this reaction conditions. Notably, the synthetically useful vinyl and alkynyl substituted cyclic carbonates (**4h**, **4l** and **4m**) were smoothly obtained in 95–98% yields. Moreover, this process was also used in the synthesis of sterically congested cyclic carbonates such as **4n** and **4o**. Another important feature of the process was that the chiral **3a**(*R*), **3p**(*R*) and **3p**(*S*) as substrates were smoothly converted to **4a**(*R*), **4p**(*R*) and **4p**(*S*), respectively, with retention of stereochemistry (see ESI† for details). Noting that previous approaches towards asymmetric cycloaddition of CO_2 and styrene oxide only afforded styrene carbonate **4p** with a relatively low ee values, due to the remarkable electron-withdrawing effect.[22]

Table 3 Substrate scope of the one-pot cascade reaction[a]



[a] Reaction conditions: (Step **I**) Sub. **2** (84.1 mg, 1.0 mmol), **Cat.1**: **1h** (0.1 mmol, 10 mol%), $P(CO_2)$ = 1.0 atm, 25 °C, 24 h; (Step **II**) Sub. **3** (1.0 mmol), **Cat.2**: **MTBD** (0.05 mmol, 5.0 mol%), CH_3CN (0.5 mL), 25 °C, 24 h. [b] Yield determined by ^1H NMR using 1,2,4,5-tetramethylbenzen as an internal standard.

Biomass-derived polyols as new bio-platform molecules have been unanimously identified as the practical source for sustainable production of fuels and chemicals.[23] With the above results in hand, we began to investigate the precise synthesis of bio-based cyclic carbonates by controlling more complex polyhydroxyl carbohydrate derivatives as substrates for this one-pot process, and several useful bio-transformations have been devised, as shown in Fig. 3. Worth noting here is that the catalytic transformation of polyols is not as easy as it looks due to the presence of multiple reactive sites, so the reaction conditions need be further optimized to struggle with selectivity or side reactions.

Glycerol **3q** was firstly conducted with equimolar amount of **2** in one-pot process, and 4-hydroxymethyl-2-oxo-1,3-dioxolane **4q** was selectively formed in 85% isolated yield (Fig. 3. **I**). Under an excess amount of **2** (2.0 equivalents), **4q** as intermediate further reacted with excess ***a*CC-1** generated *in situ* to form 2-methyl-3-oxobutan-2-yl(2-oxo-1,3-dioxolan-4-yl)methyl carbonate **4q′** in 80% isolated yield (Fig. 3. **II**). Interestingly, when using more complex alpha-chloralose **3t** as triol substrate, **4r** containing two cyclic carbonate rings, was selectively synthesized in 60% yield (Fig. 3. **III**). Meanwhile, the molecular structure of **4r** has also been determined by single crystal X-ray diffraction (Fig. 4. **4r**), which demonstrates that the dimensional configuration of all chiral carbon atoms has been fully maintained during this process.

Very recently, meso-erythritol **3s** containing four hydroxyl groups, has been employed to react with carbonylation reagents, including dimethyl carbonate and diphenyl carbonate, *via* transesterification to successively achieve 2,4,7-trioxa-3-oxy-bicyclo[3.3.0]octane **4s** and [4,4′-bi(1,3-dioxolane)]-2,2′ dione **4s′** at 120 °C under a reduced pressure of 30 mbar.[11b,24] More delightfully, **3s** was also tolerant in this one-pot process,

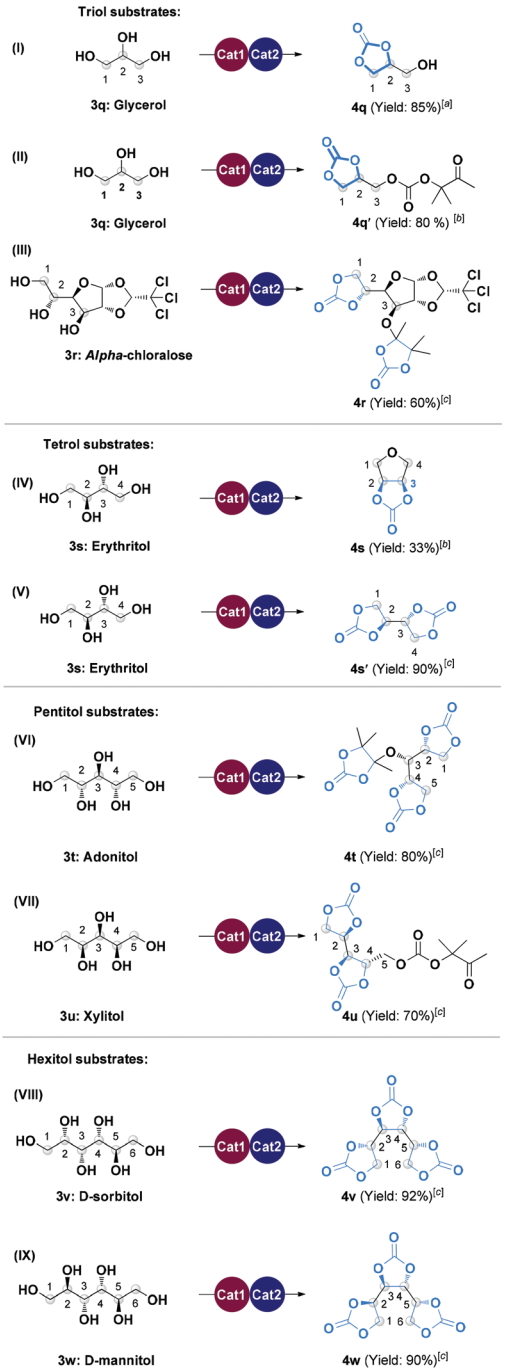


Fig. 3 General reaction conditions: (Step **I**) Sub. **2** (1.0–4.0 mmol), **Cat.1** (10 mol%), $P(CO_2)$ = 1.0 atm, 25 °C, 24 h; (Step **II**) Sub. **3** (1.0 mmol), **Cat.2** (10 mol%), solvent (1.0 mL), 25 °C, 24 h. [a] Sub. **2** (1.0 mmol), CH_3CN as solvent. [b] Sub. **2** (2.0 mmol), CH_3CN as solvent. [c] Sub. **2** (4.0 mmol), DMF as solvent.

and the corresponding **4s** and **4s′** could be selectively obtained by simply controlling the proportion between **2** and **3s** under milder reaction conditions (Fig. 3. **IV** and **V**). Moreover, the molecular structure of **4s′** was also determined by single crystal X-ray crystallography (Fig. 4. **4s′**).

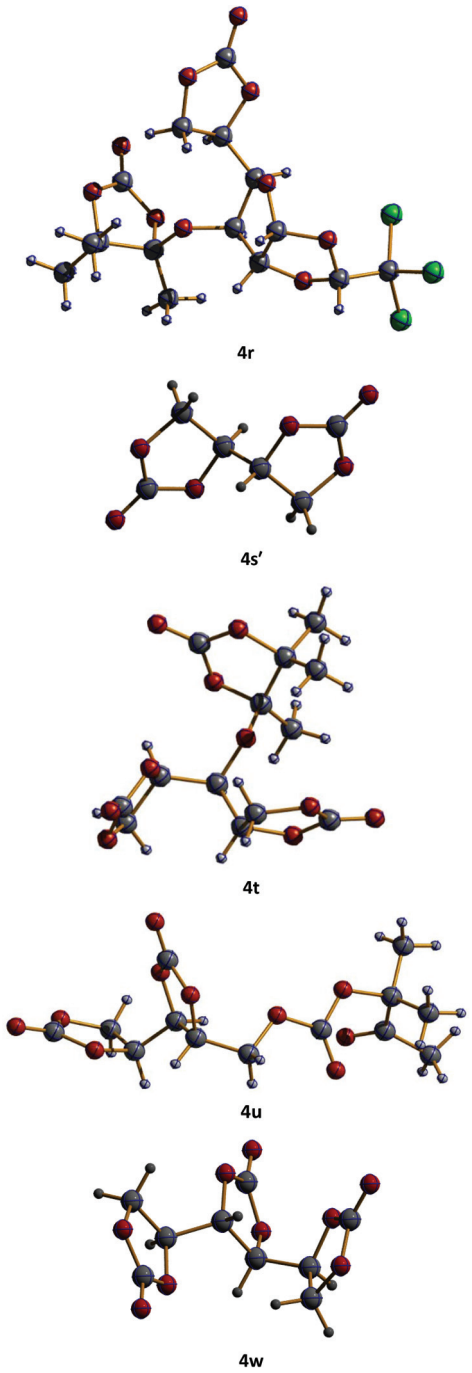


Fig. 4 Molecular structures of **4r**, **4s′**, **4t**, **4u** and **4w** as determined by single crystal X-ray diffraction. See ESI† for complete details.

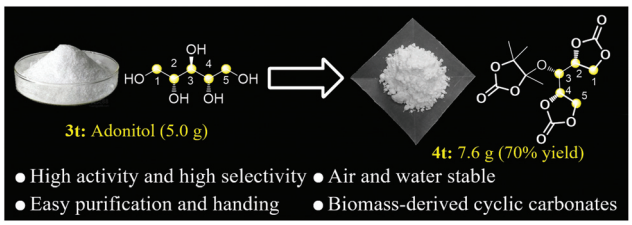


Fig. 5 Gram-scale cascade reaction of **3t** to construct adonitol-based tricyclic carbonate **4t**.

Up to now, the preparation of adonitol- and xylitol-based cyclic carbonates has never been reported. Further study found that the steric configuration of pentitol substrates directed the reaction chemoselectivity toward the formation of multiple cyclic carbonates. Under our standard conditions, (2*R*,3*s*,4*S*)-pentane-1,2,3,4,5-pentaol **3t** mostly converted to **4t** containing tricyclic carbonate rings with 80% isolated yield (Fig. 3. **VI**), while for (2*R*,3*r*,4*S*)-pentane-1,2,3,4,5-pentol **3u** as substrate, **4u** was selectively obtained through a distinct pathway (Fig. 3. **VII**). To get better insight into the proposed mechanism, the geometries of reaction intermediates were optimized by density functional theory (DFT) calculation, which point out that intramolecular hydrogen bonding is partly responsible for such chemo-selectivity (see ESI† for details). Furthermore, the unique molecular structures of **4t** and **4u** have also been clearly proved by single-crystal X-ray crystallography (Fig. 4. **4t** and **4u**).

In addition, in the presence of excess amount of **2** (4.0 equivalents), D-sorbitol **3v** being the most commonly used sugar alcohol (it is the least costly), was also tolerated equally well, thus providing tricyclic carbonate **4v** in 92% yields. To the best of our knowledge, this is only the second example of such a transformation. The other one was reported recently by Mülhaupt *et al.*, in which **4v** was synthesized from diphenyl carbonate as carbonylation reagent in DMSO solution and catalyzed by potassium carbonate under harsh conditions (120 °C, 30 mbar).[11a] It is worth noting that when employing another hexitol (D-mannitol **3w**) as substrate, the steric configuration has no significant effect on the catalytic activity and chemo-selectivity, and the corresponding tricyclic carbonate **4w** was smoothly obtained in 90% yields under the same conditions. Moreover, the molecular structure of **4w** was also established using single-crystal X-ray crystallography (Fig. 4. **4w**).

The low biodegradability of petroleum-based polymers and the exhaustible nature of the oil reserves have intensified interest in natural renewing resources for the chemical synthesis of polymers.[25] Very recently, polycyclic carbonates, especially **4s'** and **4v** derived from bio-mass, have been developed to react with polyamines to successfully construct non-isocyanate based polyurethanes.[11a,b] Given these facts, developing novel bio-monomer is an important research direction for this area. To illustrate the practicability and scalability of this strategy, a gram-scale cascade reaction of **3t** (5 g, 32.8 mmol) was firstly conducted under optimal reaction conditions, which still afford the adonitol-based tricyclic carbonate **4t** (7.6 g, 23.0 mmol) in 70% yield by a simple recrystallization process (Fig. 5).

Conclusions

In conclusion, we have developed a dual LB–CO_2/MTBD organocatalytic system to realize a cascade reaction of propargylic alcohol, CO_2, and vicinal diols under ambient conditions. This

process constitutes a wide range of substituted cyclic carbonates in moderate to high yields using CO_2 as a C1 synthon. More importantly, this eco-friendly method can also expand to a variety of sugar alcohols that are widely available and low-cost bio-feedstock, thus effectively obtaining structurally diverse polycyclic carbonates with high chemo- and stereoselectivity. Further investigation towards the practical application of functionalized cyclic carbonates, especially bio-based polycyclic carbonates, is currently underway in our laboratories.

Conflicts of interest

We declare that we have no conflicts of interest.

Acknowledgements

This work is supported by National Natural Science Foundation of China (Grant No. 91856108), the Program for Changjiang Scholars and Innovative Research Team in University (IRT-17R14), and the Fundamental Research Funds for the Central Universities (DUT18LK55).

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