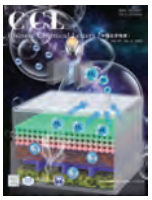
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Cycloaddition of epoxides and atmospheric CO_2 in aqueous catalyzed by an upper-rim functionalized calix[4]arene organocatalyst

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ABSTRACT

The cycloaddition of epoxides and CO_2 has been achieved by using the designed upper-rim functionalized calix[4]arene organocatalyst in aqueous at a mild temperature under normal pressure. The upper rim of this novel calix[4]arene organocatalyst contains two hemisquaramides at the 1,4-positions. A variety of cyclic carbonate derivatives were obtained in good yields, demonstrating excellent compatibility with various functional groups. The $\pi\cdots\pi$ supramolecular interaction between the calixarene cavity and epoxide substrate may also play a significant role in facilitating this cycloaddition process. Additionally, this novel reaction offers a valuable complementary approach to synthesizing cyclic carbonates from epoxides and CO_2.

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Carbon dioxide (CO_2) is one of the most significant greenhouse gases in the Earth's atmosphere [1,2]. Despite being a greenhouse gas implicated in global warming, CO_2 is also a plentiful and renewable C1 resource that undergoes chemical transformations to yield high-value compounds [3–6]. In this field, the cycloaddition of epoxides with CO_2 to construct cyclic carbonates has been regarded as one of the most promising CO_2 conversion routes [7,8]. Furthermore, cyclic carbonates are also high-value organic compounds serving as electrolytes for lithium-ion secondary batteries, monomers for polymers, and intermediates in pharmaceuticals [9–16]. Although extensive efforts have been attempted for the synthesis of cyclic carbonates from epoxides and CO_2, the development of a novel green and efficient strategy would be of great significance.

Recently, upper- or lower-rim functionalized calix[4]arenes have been recognized as ideal catalysts in organic chemistry due to their exceptional selectivity and efficient phase transfer catalytic function [17–21]. However, only a few reports focused on the cycloaddition of epoxides with CO_2 [22–24]. In 2016, the Kleij group used the resorcin[4]arene catalyst for the cycloaddition of epoxides with CO_2 in the presence of TBAI at a high pressure (Fig. 1a) [22]. Furthermore, they also designed a bifunctional resorcin[4]arene catalyst to achieve the same reaction without TBAI (Fig. 1b) [23]. In 2020, Yuan and co-workers modified the upper rim of calix[4]arene to obtain a cationic calix[4]arene polymer catalyst, which can synthesize cyclic carbonates from CO_2 and epoxides at elevated temperature (100 °C) under atmospheric pressure (Fig. 1c) [24]. In addition, both metal-based catalysts and ionic liquids also serve as typical catalysts for the synthesis of cyclic carbonates from CO_2 [25–30]. Despite their potential, these approaches are predominantly limited by requirements for high reaction pressures and temperatures, as well as a restricted substrate scope. Consequently, the development of novel functionalized calix[4]arene organocatalysts to address these issues would represent a significant advancement in synthetic chemistry.

In our continuing efforts for developing novel supramolecular catalysis reactions [31–34], the designed upper-rim functionalized calix[4]arenes bearing hemisquaramides (**cat-1**, **cat-2** and **cat-3**), squaramides (**cat-4**) and salophens (**cat-5**) have been used as organocatalysts for the cycloaddition of epoxides and CO_2 in aqueous at a mild temperature under normal pressure (Fig. 2).

Our investigation began with the reaction of styrene oxide (**1a**), TBAI (tetrabutylammonium iodide) and CO_2 (1.0 atm) in H_2O solvent at room temperature for 24 h using the upper-rim functionalized calix[4]arene bearing mono-hemisquaramide **cat-1** as the organocatalyst. The desired cyclic carbonate **2a** was isolated with 22 % yield (Table 1, entry 1). To our delight, the yield of **2a** was increased to 90 % by using 1,3-bis-hemisquaramides calix[4]arene catalyst **cat-2**. This observation suggests that the synergistic effect between two hemisquaramide groups can significantly contribute to improved catalytic performance (Table 1, entry 2). However, the use of 1,2-bis-hemisquaramides calix[4]arene catalyst **cat-3** only afforded 13 % yield indicating that the positioning of hemisquaramide groups is also crucial for this process (Table 1, entry 3). Additionally, the utilization of 1,3-bis-squaramides

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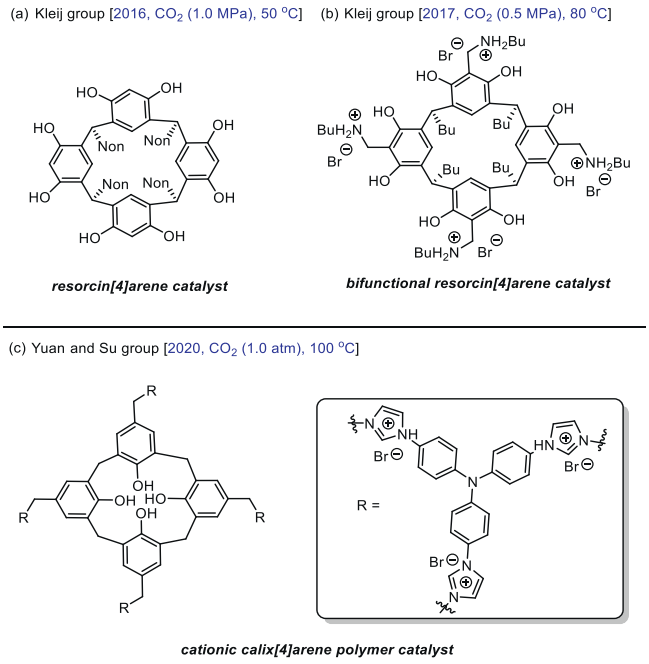


Fig. 1. Previous strategies for the synthesis of cyclic carbonates *via* CO_2 and epoxides based on the calix[4]arene-derived catalysts.

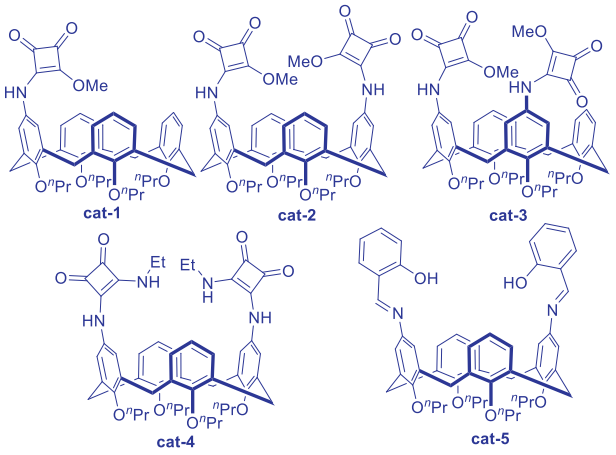
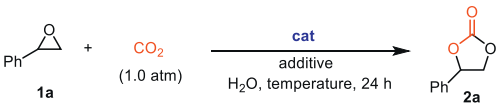


Fig. 2. Designed upper-rim functionalized calix[4]arene organocatalysts.

calix[4]arene catalyst **cat-4** resulted in an 81% isolated yield, whereas the employment of the 1,3-bis-salophens calix[4]arene catalyst **cat-5** failed to generate product **2a**. This implies that the hemisquaramide group exhibits optimal performance within our strategy (Table 1, entries 4 and 5). Next, the examination on iodide additive revealed that other iodide additives including KI or NH_4I failed to provide the desired product **2a** (Table 1, entries 6 and 7). Furthermore, the use of TBAB (tetrabutylammonium bromide) afforded the desired product **2a** in 65% yield (Table 1, entry 8). The subsequent investigation on the amounts of **cat-2** and TBAI revealed that 5 mol% of **cat-2** and 10 mol% of TBAI are optimal (Table 1, entries 9–12). It is worth noting that the yield of **2a** was increased to 99% by improving the reaction temperature to 40 °C (Table 1, entry 13). Finally, the yield of **2a** decreased to 23% in the absence of **cat-2**, while only a trace amount of product was detected in the absence of TBAI (Table 1, entries 14 and 15).

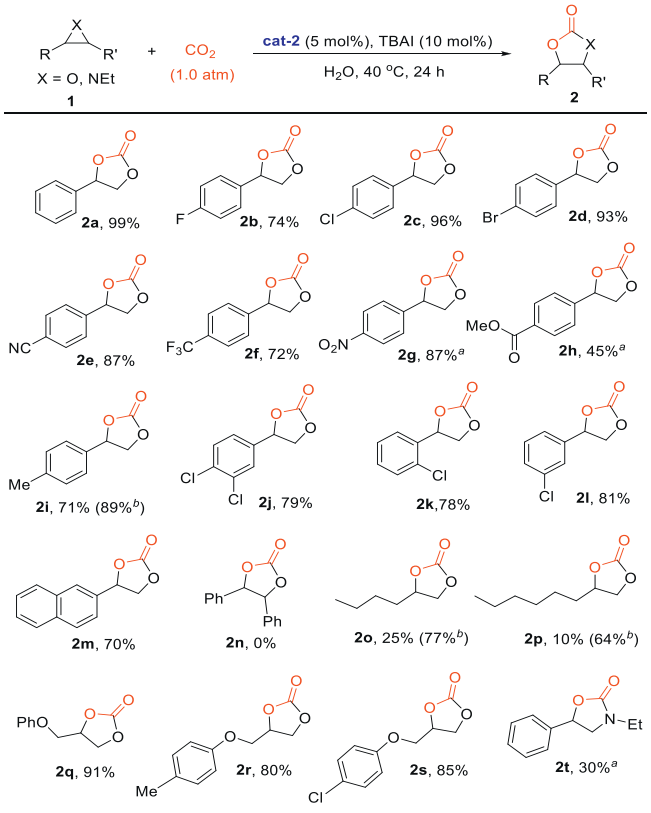
With the optimized reaction conditions in hand, the substrate scope study of epoxides was carried out in Scheme 1. A variety of 2-aryl oxiranes generated the corresponding cyclic carbonates **2a-2m** in good to excellent yields. Both electron-withdrawing and electron-donating groups at the *para*-, *meta*- or *ortho*-position on the aryl group were suitable in this catalytic system. Unfortunately, the use of 2,3-diphenyloxirane failed to provide the desired product **2n** due to the steric hindrance effect. Additionally, this catalytic system was compatible with 2-alkyl oxiranes such as 2-butyloxirane and 2-hexyloxirane, resulting in moderate to good yields of the desired products **2o-p**. Furthermore, 2-alkyl oxiranes

Table 1
Optimization of reaction conditions.[a]

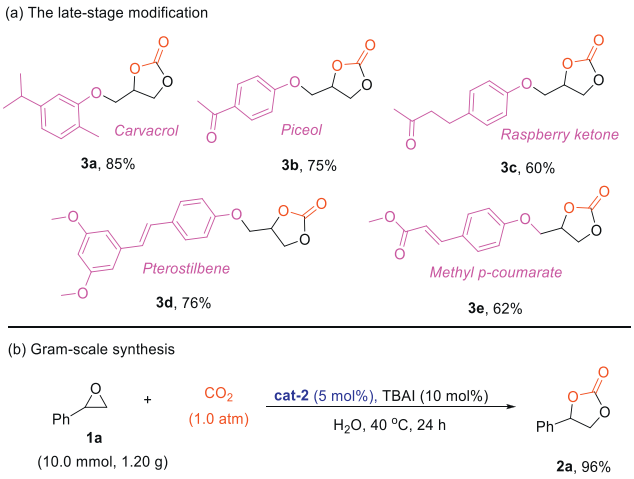


Entry	**cat** (mol%)	Additive (mol%)	Temp (°C)	Yield (%)[b]
1	**cat-1** (5)	TBAI (10)	25	22
2	**cat-2** (5)	TBAI (10)	25	90
3	**cat-3** (5)	TBAI (10)	25	13
4	**cat-4** (5)	TBAI (10)	25	81
5	**cat-5** (5)	TBAI (10)	25	trace
6	**cat-2** (5)	KI (10)	25	trace
7	**cat-2** (5)	NH_4I (10)	25	trace
8	**cat-2** (5)	TBAB (10)	25	65
9	**cat-2** (3)	TBAI (10)	25	83
10	**cat-2** (10)	TBAI (10)	25	81
11	**cat-2** (5)	TBAI (5)	25	76
12	**cat-2** (5)	TBAI (20)	25	87
13	**cat-2** (5)	TBAI (10)	40	99
14	–	TBAI (10)	40	23
15	**cat-2** (5)	–	40	trace

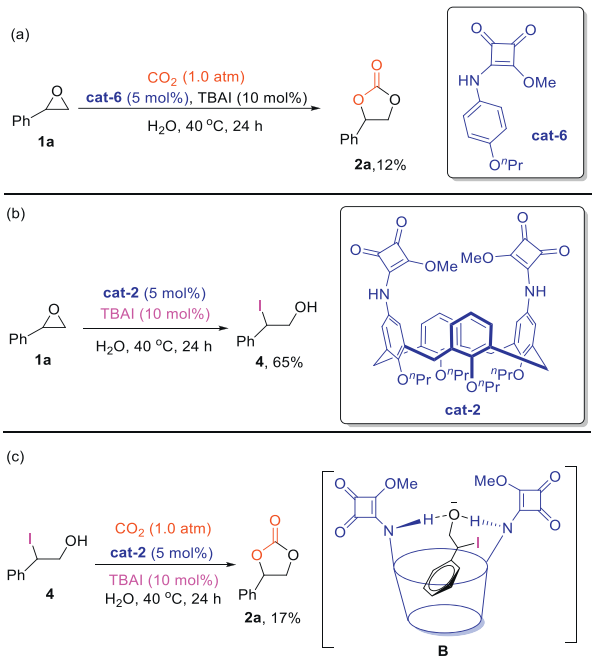
[a] Reaction conditions: **1a** (2.0 mmol), CO_2 (1.0 atm), calix[4]arene (**cat**), additive, H_2O (5 mL), temperature, 24 h.
[b] Isolated yields.



Scheme 1. Scope of epoxides. Reaction conditions: **1** (2.0 mmol), CO_2 (1.0 atm), **cat-2** (5 mol%), TBAI (10 mol%), H_2O (5 mL), 40 °C, 24 h. Isolated yield. [a] 48 h. [b] TBAI (5 mol%), EtOH (5 mL).



Scheme 2. The late-stage modification and gram-scale synthesis.

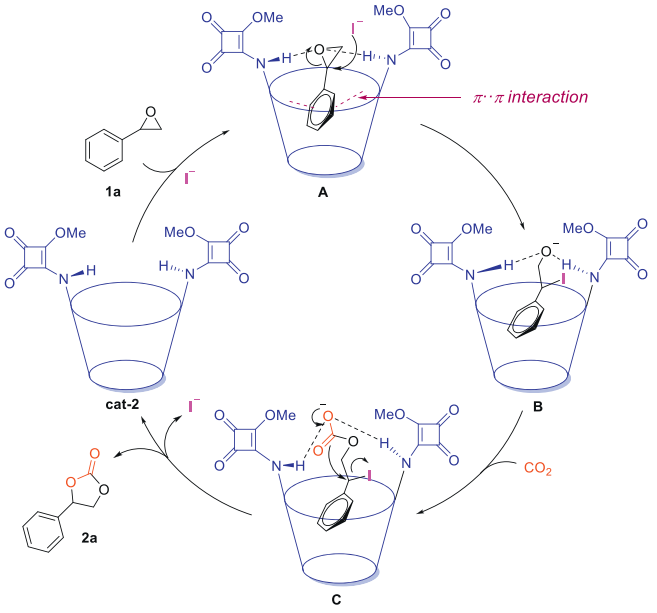


Scheme 3. Mechanistic studies.

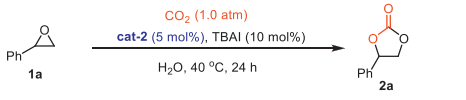
bearing an ether group also provided the desired products **2q-2s** in good yield. Finally, 1-ethyl-2-phenylaziridine was also utilized in our protocol to form the desired product **2t** with a moderate yield.

To illustrate the synthetic utility of this novel catalytic approach, the late-stage modification of natural products was first performed in Scheme 2a. As expected, natural products containing epoxides derived from complex organic skeletons, such as carvacrol, piceol, raspberry ketone, pterostilbene and methyl *p*-coumarate, have also been easily converted into the desired products **3a-e** with good yields. In addition, a gram-scale reaction of styrene oxide (**1a**) and CO_2 was also conducted under standard conditions. To our delight, 4-phenyl-1,3-dioxolan-2-one (**2a**) was obtained with a yield of 96% (Scheme 2b).

To gain some insights into the reaction mechanism, several control experiments have been performed (Scheme 3). The utilization of **cat-6** led to the isolation of only a 12% yield of the desired product **2a** in the model reaction. This comparative experiment suggests the possible existence of $\pi\cdots\pi$ supramolecular interaction



Scheme 4. The proposed mechanism.



Cycle	1st	2nd	3rd	4th	5th
Yield	99%	96%	96%	94%	90%

Scheme 5. The recyclability experiments of calix[4]arene organocatalyst **cat-2**.

between the calixarene cavity and substrate **1a**. Furthermore, the model reaction without CO_2 was also examined, and the product **4** was isolated with a yield of 65%. This result demonstrates that the acid ring-opening of **1a** occurs in our catalytic system. Additionally, under standard conditions, product **4** only yielded 17% of the desired product **2a**, suggesting that our system may proceed through an anionic intermediate **B**.

Based on our control experiments and the previous reports, a plausible catalytic cycle is proposed (Scheme 4) [7,8,31–39]. Initially, 2-phenyloxirane **1a** interacts with **cat-2** to form the intermediate **A** through both hydrogen bonding and $\pi\cdots\pi$ interactions [32,33,39]. Notably, the solvent water may also facilitate the transfer of substrate **1a** into the hydrophobic cavity of calix[4]arene. In this case, the C–O bond of **1a** is activated by a hydrogen bonding interaction with two hemisquaramide groups, while its aryl group is stabilized by $\pi\cdots\pi$ interaction with the calix[4]arene cavity. Subsequently, the sterically hindered carbon of **1a** is attacked by an iodide ion to form the anionic intermediate **B**. Next, CO_2 reacts with the anionic intermediate **B** to afford the carbonate anion intermediate **C**. Finally, the desired product **2a** is formed through an intramolecular cyclization process, accompanied by the regeneration of **cat-2** and iodide ion.

To evaluate the recyclability of calix[4]arene organocatalyst **cat-2** within this process, five consecutive reaction cycles between **1a** and CO_2 were carried out under the same catalyst. The results indicated that the catalytic activity of **cat-2** showed only a minor decrease after five cycles, maintaining a yield of 90% (Scheme 5).

In summary, the cycloaddition of epoxides and CO_2 in aqueous has been developed by using an upper-rim functionalized calix[4]arene organocatalyst bearing two hemisquaramides at the 1,4-positions. Compared with previous catalytic systems, our cat-

alytic protocol operates at a mild temperature under normal pressure, demonstrating excellent functional group compatibility and good isolated yields. The mechanism studies demonstrate the essential role of the calixarene cavity, and suggest that the reaction may involve a $\pi\cdots\pi$ supramolecular interaction between the calixarene cavity and epoxide. The late-stage modification of natural products, gram-scale synthesis, and catalyst recyclability experiments further demonstrated the synthetic utility of this innovative methodology. The mild strategy presented here offers an important complementary approach for the synthesis of cyclic carbonates from epoxides and CO_2 in the field of organic chemistry.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Zheng-Yi Li: Writing – review & editing, Supervision, Funding acquisition, Formal analysis, Conceptualization. **Tao Li:** Formal analysis, Data curation. **Zuquan Wang:** Formal analysis, Data curation. **Yi Zhao:** Data curation. **Jing Shi:** Writing – review & editing. **Xiaoqiang Sun:** Writing – review & editing. **Ke Yang:** Writing – review & editing, Writing – original draft, Supervision, Data curation.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2025.111352.

References

[1] C. Song, Catal. Today 115 (2006) 2–32.
[2] N. von der Assen, P. Voll, M. Peters, A. Bardow, Chem. Soc. Rev. 43 (2014) 7982–7994.
[3] J. Hong, M. Li, J. Zhang, B. Sun, F. Mo, ChemSusChem 12 (2019) 6–39.
[4] M.D. Burkart, N. Hazari, C.L. Tway, E.L. Zeitler, ACS Catal. 9 (2019) 7937–7956.
[5] E.S. Sanz-Perez, C.R. Murdock, S.A. Didas, C.W. Jones, Chem. Rev. 116 (2016) 11840–11876.
[6] K. Beydoun, J. Klankermayer, Top. Organomet. Chem. 63 (2018) 39.
[7] T. Yan, H. Liu, Z.X. Zeng, W.G. Pan, J. CO_2 Util. 68 (2023) 102355.
[8] P.P. Pescarmona, Curr. Opin. Green Sustain. Chem. 29 (2021) 100457.
[9] X. Wei, W. Xu, M. Vijayakumar, et al., Adv. Mater. 26 (2014) 7649–7653.
[10] B. Schaffner, F. Schaffner, S.P. Verevkin, A. Borner, Chem. Rev. 110 (2010) 4554–4581.
[11] V. Besse, F. Camara, C. Voirin, et al., Polym. Chem. 4 (2013) 4545–4561.
[12] M. Fleischer, H. Blattmann, R. Mülhaupt, Green Chem. 15 (2013) 934–942.
[13] M. Bahr, R. Mulhaupt, Green Chem. 14 (2012) 483–489.
[14] A.J. Kamphuis, F. Picchioni, P.P. Pescarmona, Green Chem. 21 (2019) 406–448.
[15] R.R. Shaikh, S. Pornpraprom, V. D' Elia, ACS Catal. 8 (2018) 419–450.
[16] N.S. Suveges, A.A. Rodriguez, C.C. Diederichs, et al., Eur. J. Org. Chem. 2018 (2018) 2931–2938.
[17] S. Sayin, M. Yilmaz, Tetrahedron 72 (2016) 6528–6535.
[18] M. Durmaz, E. Halay, S. Bozkurt, Beilstein J. Org. Chem. 14 (2018) 1389–1412.
[19] H. Zhao, X.H. Yang, Y.C. Pan, et al., Chin. Chem. Lett. 31 (2020) 1873–1876.
[20] Z. Ma, Y. Li, X.Q. Sun, K. Yang, Z.Y. Li, Chin. J. Org. Chem. 41 (2021) 2188–2201.
[21] B. Banerjee, G. Kaur, N. Kaur, Curr. Org. Chem. 25 (2021) 209–222.
[22] L. Martinez-Rodriguez, J.O. Garmilla, A.W. Kleij, ChemSusChem 9 (2016) 749–755.
[23] T. Jose, S. Canellas, M.A. Pericas, A.W. Kleij, Green Chem. 19 (2017) 1–3.
[24] Y. Zhang, K. Su, Z. Hong, Z. Han, D. Yuan, Ind. Eng. Chem. Res. 59 (2020) 7247–7254.
[25] H. Büttner, L. Longwitz, J. Steinbauer, C. Wulf, T. Werner, Top. Curr. Chem. 375 (2017) 1–56.
[26] J. Kiriratnikom, N. Laiwattanapaisarn, K. Vongnam, et al., Inorg. Chem. 60 (2021) 6147–6151.
[27] Y.Y. Kang, Y. Kim, J. Lee, H. Park, Bull. Korean Chem. Soc. 36 (2015) 1296–1299.
[28] S. Lian, C. Song, Q. Liu, et al., J. Environ. Sci. 99 (2021) 281–295.
[29] M. Liu, L. Liang, X. Li, X. Gao, J. Sun, Green Chem. 18 (2016) 2851–2863.
[30] X. Zhang, D. Su, L. Xiao, W. Wu, J. CO_2 Util. 17 (2017) 37–42.
[31] Y. Wu, Z. Ma, J. Shi, et al., Chin. Chem. Lett. 33 (2022) 5116–5119.
[32] K. Yang, Z.Y. Ma, H.X. Tong, X.Y. Hu, Z.Y. Li, Chin. Chem. Lett. 31 (2020) 3259–3262.
[33] Z.Y. Li, H.X. Tong, Y. Chen, et al., Beilstein J. Org. Chem. 14 (2018) 1901–1907.
[34] Z.Y. Li, Y. Chen, C.Q. Zheng, et al., Tetrahedron 73 (2017) 78–85.
[35] C. Wei, Y. He, X. Shi, Z. Song, Coordin. Chem. Rev. 385 (2019) 1–19.
[36] M. Delbianco, P. Bharate, S. Varela-Aramburu, P.H. Seeberger, Chem. Rev. 116 (2016) 1693–1752.
[37] K. Takaishi, T. Okuyama, S. Kadosaki, M. Uchiyama, T. Ema, Org. Lett. 21 (2019) 1397–1401.
[38] S. Sopena, E. Martin, E.C. Escudero-Adan, A.W. Kleij, ACS Catal. 7 (2017) 3532–3539.
[39] H. Huang, D.M. Li, W. Wang, et al., Org. Biomol. Chem. 10 (2012) 729–735.