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Polystyrene-supported bifunctional resorcinarenes as cheap, metal-free and recyclable catalysts for epoxide/CO₂ coupling reactions†

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We here report the synthesis of bifunctional catalysts that can be assembled using simple, cheap and accessible building blocks based on resorcinarenes, and their application as efficient, one-component homogeneous catalysts in the coupling of both terminal and internal epoxides with carbon dioxide affording their cyclic carbonate products. Furthermore, a heterogeneous version was also prepared that combines the activity of these bifunctional systems with excellent stability and recycling potential, allowing for a turnover of >1250. This newly prepared organocatalyst obviates the use of any metal, solvent or additives marking it as an attractive catalyst for CO₂ valorization.

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Introduction

Carbon dioxide (CO₂) is an abundant waste material that may be recycled using effective catalysis technologies.¹ Key to CO₂ conversion is the use of high-energy reactants that provide a thermodynamic driving force, and historically epoxides have been popular coupling partners to afford cyclic organic carbonates (COCs).² These heterocyclic structures find many useful applications representing precursors for polymeric carbonates,³ being green solvents⁴ and offering new opportunities in synthetic chemistry.⁵ The “fixation” of CO₂ into COCs has advanced tremendously over the years with a prominent role for (transition) metal-based catalysts.⁶ The use of efficient metal catalysis has allowed, *inter alia*, the resolution of challenging conversions of CO₂ with oxetanes,⁷ and disubstituted⁸ and even trisubstituted oxiranes.⁹

In contrast, organocatalysts have only recently emerged as potential sustainable alternatives to metal-based catalyst systems,¹⁰ though the vast majority of the cases still require the assistance of co-catalysts, solvents and/or elevated temperatures (>100 °C). Exceptions to these harsher temperature requirements were only recently reported, and showed that

proper catalyst design and using conceptually new and powerful substrate activation strategies are crucial to be able to bridge the gap between metal- and organo-catalysis.¹¹ In this context, particularly the system from Detrembleur, Tassaing and Jérôme (a fluorinated bis-alcohol derivative) stands out as it represents one of the most active homogeneous, hydrogen-bond donor catalysts reported to date for cyclic carbonate synthesis.¹² We have recently set out to develop conceptually new and efficient organocatalysts for the coupling of more challenging internal epoxides and CO₂. In order to achieve more powerful catalysts, we used the unique oxo-anion stabilization potential of squaramide based catalysts¹³ and cooperative hydrogen-bonding catalysis based on polyphenols¹⁴ including resorcinarene- and pyrogallene-based structures (Fig. 1a).¹⁵

These latter catalysts represent cheap and readily accessible materials comprising of four well-positioned resorcinol or pyrogallol subunits, respectively. These polyphenolic compounds in combination with external (halide-based) nucleophiles showed improved activity for terminal epoxide/CO₂ couplings at temperatures as low as 45 °C, and a record-high initial TOF of 488 h⁻¹ at 80 °C.

We previously reported the successful immobilization of pyrogallol onto a bifunctional polystyrene support and application as a recyclable catalyst for cyclic carbonate synthesis.¹⁶ Inspired by our former results, we imagined that the immobilization of amine-functionalized resorcinarenes would offer powerful bifunctional catalysts (Fig. 1c) thus amplifying their potential towards metal-free, recyclable systems for COC formation. In this work, we present a simple and effective approach towards the preparation of modular bifunctional catalysts for COC synthesis, the immobilization onto a polystyrene support and the recycling features of this hetero-

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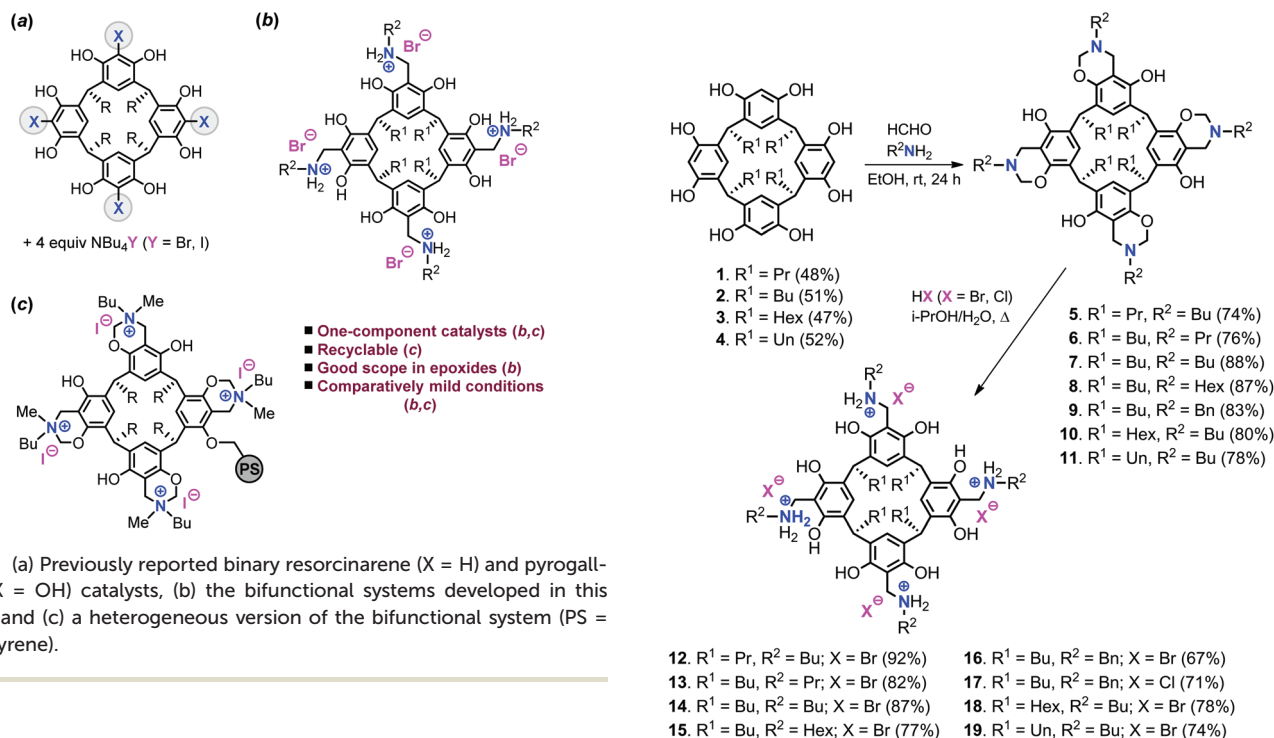


Fig. 1 (a) Previously reported binary resorcinarene ($\text{X} = \text{H}$) and pyrogallene ($\text{X} = \text{OH}$) catalysts, (b) the bifunctional systems developed in this work, and (c) a heterogeneous version of the bifunctional system ($\text{PS} = \text{polystyrene}$).

geneous catalyst. These bifunctional, one-component metal-free catalysts show promise towards the coupling of various terminal and internal epoxides, and thus unite favourable activity, good recycling potential and sustainability features.

Results and discussion

Bifunctional catalyst synthesis

Various resorcin[4]arene precursors (1–4) with different alkyl chain lengths at the lower rim (R^1), the tetrabenzoxazine derivatives 5–11 and the bifunctional resorcinarene salts 12–19 were prepared according to previous reported procedures (Scheme 1).^{15,17}

From these precursors 1–4, the bifunctional resorcinarene structures 12–19 were obtained in two steps. First, various tetrabenzoxazines (5–11) were prepared by the condensation reaction of readily available resorcinarenes with various aliphatic primary amines and formaldehyde under ambient conditions. The intermediates 5–11 were then treated with strong aqueous acids (HCl , HBr) to afford the ring-opened benzyl ammonium functionalized resorcinarenes 12–19. The latter compounds were fully characterized by $^1\text{H}/^{13}\text{C}$ NMR, IR and elemental analysis prior to their use in the catalytic studies (see ESI† for details). Importantly, high-pressure NMR analysis (80 °C, 0.5 MPa of CO_2 , 18 h) of the bifunctional system 14 did not show any decomposition, a feature of high importance in catalytic applications (*vide infra*).

Catalysis studies

The catalyst screening phase was carried out using 1,2-epoxyhexane as benchmark substrate (**S1**) and bifunctional catalysts 12–19 under various reaction conditions. Based on previous

Scheme 1 Synthesis of bifunctional resorcinarene derivatives and their isolated yields.

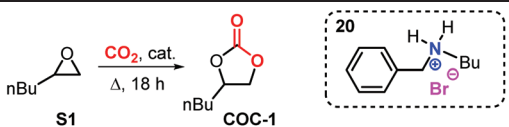
use of bifunctional Zn-based catalysts for the same reaction,¹⁸ we chose to start the screening at 80 °C for 18 h using a mild pressure of 0.5 MPa (5 bar) under solvent-free conditions, see Table 1 (entries 1–11).

As expected no conversion was noted in the absence of any (catalytic) additive (entry 1), while the catalytic performance of the parent resorcinarene 2 and the tetrabenzoxazine derivative 7 was poor (entries 2 and 3) leading only to very low yields of product **COC-1**. We then turned our focus on the bifunctional catalysts 12–19 (entries 4–11) and examined their potential to mediate the formation of **COC-1** from **S1** and CO_2 . As can be judged from the catalytic data, bifunctional 14, 15 and 18 gave quantitative yield of **COC-1** under these conditions whereas the other systems showed inferior activities. The lowest activity was noted for 17 that has chloride anions incorporated, and therefore the low potential of this catalyst to mediate **COC** formation is not surprising as chloride is a weaker nucleophile/poorer leaving group than bromide. Since compound 14 displays the highest comparative overall yield in the two-step preparation, we decided to use 14 (with two butyl-substituents) to further investigate the influence of catalyst loading, reaction temperature and pressure on the yield of **COC-1** (entries 12–21).¹⁹

First, the amount of 14 was varied from 0.8 to 1.2 mol% (*cf.*, entries 6 *versus* 12 and 13) showing that a loading of 0.8 mol% of 14 still gave an appreciable yield (80%) of **CC-1**, whereas higher loadings than 1.0 mol% do not represent any advantage. Lower reaction temperatures were then evaluated



Table 1 Screening and optimization of the coupling between 1,2-epoxyhexane and CO₂ under various reaction conditions using bifunctional resorcinarene based catalysts **12**–**19**^a



Entry	Cat.	Amount (mol%)	Temp. (°C)	t (h)	P (MPa)	Yield ^b (%)
1	—	—	80	18	0.5	0
2	2	1.0	80	18	0.5	6
3	7	1.0	80	18	0.5	21
4	12	1.0	80	18	0.5	86
5	13	1.0	80	18	0.5	92
6	14	1.0	80	18	0.5	>99
7	15	1.0	80	18	0.5	>99
8	16	1.0	80	18	0.5	81
9	17	1.0	80	18	0.5	19
10	18	1.0	80	18	0.5	>99
11	19	1.0	80	18	0.5	82
12	14	0.8	80	18	0.5	80
13	14	1.2	80	18	0.5	>99
14	14	1.0	40	18	0.5	57
15	14	1.0	40	6	0.5	21
16	14	1.0	60	18	0.5	86
17	14	1.0	60	6	0.5	42
18	14	1.0	80	18	0.1	84
19	14	1.0	80	6	0.5	53
20	14	1.0	80	12	0.5	85
21	14	1.0	80	15	0.5	91
22	20	4.0	80	18	0.5	34
23	2 + 20	1.0, 4.0	80	18	0.5	94

^a General conditions: 8.3 mmol 1,2-epoxyhexane, 80 °C, 18 h, $p(\text{CO}_2)^\circ = 5$ bar, neat. Note that the amount of catalyst is on a molar basis. ^b Yield and selectivity of epoxide were determined by ¹H NMR (CDCl₃) using mesitylene as an internal standard, selectivity towards the cyclic carbonate was >99% in all cases.

(entries 14–17) and we were pleased to find that at 40 °C still a moderately high yield of 57% could be attained after 18 h, while at 60 °C the yield of **COC-1** was already high (86%).

Further lowering the pressure from 0.5 MPa to 0.1 MPa (*i.e.*, 1 bar) showed only a small decrease in the yield of the COC product to 84% (entry 18). When following the kinetics in time (entries 19–21 *versus* 6), it can be observed that catalyst **14** produces already a high yield of **COC-1** (85%) after 12 h. These combined observations (*vide infra*) help to establish that the bifunctionality of **14** allows for the coupling of 1,2-epoxyhexane (**S1**) and CO₂ under comparatively mild reaction conditions. To show the advantage of having the resorcinarene and nucleophile merged into one structure, we also compared bifunctional catalyst **14** with a binary analogue (**2** + **20**) and with the onium salt itself; the results (entries 6, 22 and 23) indeed show a much higher efficiency for the bifunctional system compared to the use of **20** only. While both bifunctional and binary catalysts **14** and **2** + **20** show similar yields for **COC-1**, the former obviously has better recycling potential (*vide infra*).

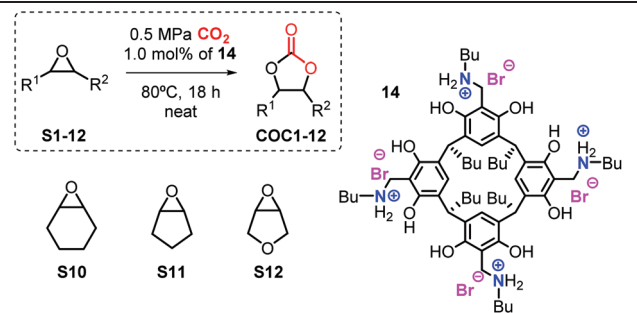
When considering the kinetic data from entries 14–21 it seems that low temperatures of 40 °C provide relatively slow

conversions after 6 and 18 h with molecular turnover frequencies of 3 to 4 h⁻¹. This implies that the activation barrier for the carbonate synthesis mediated by bifunctional catalyst **14** should be at least 24 kcal mol⁻¹, in line with previous data reported for other homogeneous catalysts used for cyclic carbonate synthesis and conversions.²⁰

Substrate scope phase

After having determined the optimized conditions for high substrate conversion of terminal epoxides (Table 1, entry 6: 80 °C, 1.0 mol% of **14**, 0.5 MPa, 18 h), we decided to investigate the scope and limitations of the epoxide/CO₂ coupling process and the results of these investigations are summarized in Table 2.

Table 2 Development of the product scope using epoxides **S1**–**S12** and bifunctional catalyst **14** to afford **COC1**–**12**^a



Entry	Sub.	COC	R ¹	R ²	Conv. ^b (%)	Yield ^c (%)
1	S1	1		H	>99	93
2	S2	2		H	>99	97
3	S3	3		H	>99	81
4	S4	4		H	>99	88
5	S5	5		H	>99	95
6	S6	6		H	>99	91
7	S7	7		H	>99	85
8	S8	8		H	>99	94
9	S9	9		H	>99	80
10 ^d	S10	10			54 (69)	29
11 ^d	S11	11			63 (76)	41
12 ^d	S12	12			39 (86)	30
13 ^e	S10	10			65 (68)	41
14 ^e	S11	11			95 (76)	69
15 ^e	S12	12			71 (86)	59

^a Typical conditions: 8.3 mmol of epoxide, 1.0 mol% of **14**, 80 °C, 18 h, $p(\text{CO}_2)^\circ = 5$ bar, neat. Note that the amount of catalyst is on a molar basis. ^b Conversion determined by ¹H NMR (CDCl₃); selectivity towards the COC > 99% unless stated otherwise in brackets. ^c Isolated yield after chromatographic purification. ^d Reactions carried out at 100 °C for 64 h. ^e Reactions carried out 100 °C for 64 h with 3.0 mol% of **14**.



All terminal epoxides (**S1–S9**) were conveniently coupled with CO₂ to afford the cyclic carbonates **COC1–9** in excellent chemo-selectivity (>99%) and isolated yields of 80–97% (entries 1–9). Several substitutions and functional groups such as ethers, free alcohols, halogens and double bonds were unaffected by the catalytic procedure. In order to further challenge the catalytic protocol, we chose three internal epoxides (*viz.*, cyclohexene oxide, cyclopentene oxide, and a related tetrahydrofuran oxide; entries 10–15). In these latter conversions, a higher reaction temperature (100 °C) and longer reaction time (64 h) were required to achieve sufficient turnover. The analysis of the crude reaction mixtures in these cases revealed, however, that the overall chemo-selectivity towards the COC targets was negatively affected, and significant amount of diol by-product was observed in all three cases (entries 10–12). We therefore attempted to dry the catalysts and reagents prior to use, though this had no observable effect on the outcome of these transformations. By further increasing the catalyst loading of **14** to 3 mol% (entries 13–15) we finally achieved improved yields for cyclic carbonates **COC10–12** (41–69%). All isolated carbonates were characterized by ¹H/¹³C NMR and IR spectroscopy, and these data are summarized in the ESI†

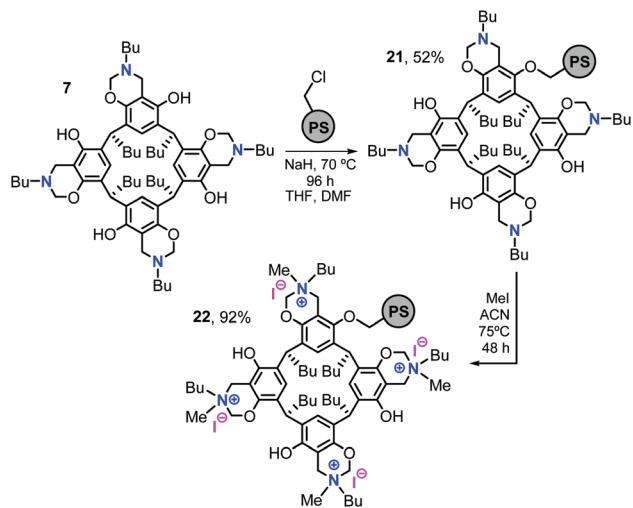
Immobilization onto a polystyrene support and recycling studies

In order to extend the potential of these cavitand-based systems such as **14** and to be able to recycle such compounds after formation of the COC product, we decided to support tetrabenzoxazine **7** on a Merrifield resin by simple etherification chemistry (Scheme 2).²¹ The polystyrene-supported tetrabenzoxazine derivative **21** was obtained in 52% yield after treatment with the polystyrene resin (degree of functionalization: $f = 1.09 \text{ mmol g}^{-1}$) and **21** ($f = 0.26 \text{ mmol g}^{-1}$; $f_{\text{max}} = 0.50 \text{ mmol g}^{-1}$) was analysed by elemental analysis and IR

spectroscopy (ESI†). Then **21** was reacted with MeI in CH₃CN to obtain the tetra-butylmethyl ammonium iodide supported catalyst **22** ($f = 0.23 \text{ mmol g}^{-1}$; $f_{\text{max}} = 0.25 \text{ mmol g}^{-1}$, ESI† for details) in 92% yield. The reasoning for choosing **21** as starting point to prepare a supported catalyst is two-fold. First, the benzoxazines are rather stable compounds and the *N*-alkylation process is known. Second, the introduction of methylammonium iodide groups was thought to be not only practical but this would also add a higher stability to the final catalyst structure **22** while preserving the presence of a nucleophilic halide.²²

Heterogeneous bifunctional catalyst **22** was then applied in the coupling of **S1** and CO₂ under the same optimized conditions as reported for **14** (80 °C, 0.5 MPa CO₂ pressure, 18 h) using 0.89 mol% of **22** (Table S3† and Fig. 2). All the starting materials (Merrifield resin with chloromethyl functionalities, polystyrene-supported tetrabenzoxazine derivative **21** and MeI) were first tested under the same conditions to determine any background conversion. As expected, no to low catalytic activity was observed (see Table S1 of the ESI†) with the use of **21** giving only a relatively low yield (25%) of **COC-1**.

Contrary to the starting materials required for the synthesis of **22**, the latter was significantly more active. Fig. 2 demonstrates that the bifunctional catalyst shows a quantitative yield (>99%, selectivity towards **COC-1** was >99%) in the first four runs for the cyclic carbonate product. After each run, the catalyst was recycled and washed thoroughly with diethyl ether, then dried, weighed and subsequently applied in a subsequent run. During this catalyst isolation process, we noted a slight loss of material with the amount of **22** in the fourth run (third recycle) being reduced to 0.80 mol%. Since in the fourth run still a quantitative yield of **COC-1** was achieved, the results give the impression that 0.80 mol% is the minimal amount required for quantitative conversion of **S1**/CO₂ into **COC-1** under these experimental conditions.



Scheme 2 Synthesis of the bifunctional polystyrene-supported catalyst **22**.

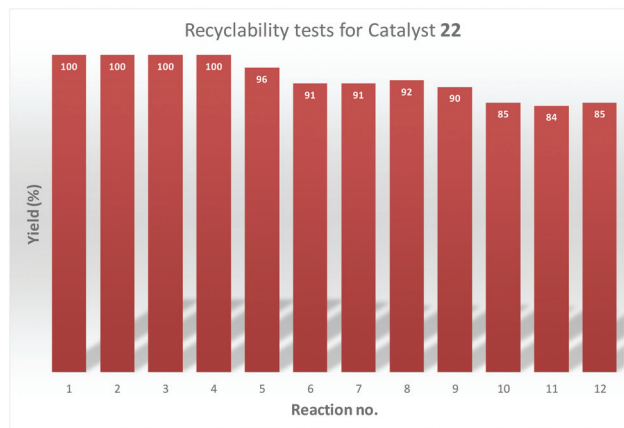


Fig. 2 Recycling studies performed with supported catalyst **22** in the coupling of 1,2-epoxyhexane (**S1**) and CO₂ to afford cyclic carbonate **COC-1**. Yields were determined by ¹H NMR (CDCl₃) using mesitylene as internal standard after collecting an aliquot of the crude reaction mixture.



Upon further recycling of **22**, the activity decreased slightly as shown in the Fig. 2 and the catalyst was used in 12 runs without a dramatic loss in catalytic efficiency. To get further insight into the loss of the activity we compared the mass of catalyst obtained after the ninth run (expressed in 0.69 mol% relative to the epoxide substrate) with the required amount for quantitative conversion of **S1** under the experimental conditions (0.80 mol%) which is a mass loss of 14%. Interestingly, about 15% loss in conversion was noted between the fourth and the ninth run, which seem to corroborate well with the idea that most of the loss in activity is caused by the washing and isolation of **22** prior to the next run and not be any decomposition process of the resorcinarene backbone. After the twelfth run, we isolated the catalyst and subjected it to elemental analysis: both the N- and I-content had decreased throughout the entire recycling campaign from 1.26 → 0.91% and 12.28 → 3.86%, respectively (ESI† for more details). This seems to suggest that some degree of retro-Mentschutkin reactions had taken place as observed previously with other bifunctional catalysts in cyclic carbonate synthesis.²³ These analytical data clearly show that the catalyst structure is affected in due course with significant loss of the nucleophile. Nonetheless, the overall activity of the original catalyst **22** is not dramatically influenced, and after 12 runs, an appreciable total turnover of 1252 could be achieved, which is comparatively a very good result for an organocatalyst in the area of cyclic carbonate synthesis.

The advantages and the enhancement of the catalytic activity in these bifunctional systems (both homogeneous and heterogeneous) is believed to be the result of a high local concentration of phenol sites (*cf.*, hydrogen bond activation of the epoxide) and the presence of ammonium halide groups (providing the nucleophilic sites for epoxide ring opening). The presence of all these groups and their synergistic involvement in the conversion of CO₂ and epoxides towards cyclic carbonate formation are aspects that were studied in detail in our previous work.^{13–16} However, the current work represents a unique bifunctional one-component homogenous catalyst that is able to perform well without the addition of any co-catalyst or solvent. The system is also easily immobilized onto polystyrene supports through simple transformations affording higher substrate turnover numbers.

Conclusions

Here we report on easily accessible, cheap and efficient bifunctional catalysts for the formation of cyclic carbonates from various epoxides and CO₂ in excellent yields and solvent-free conditions. The starting materials are modular in nature allowing for the optimization of the catalytic activity, and providing an easy entry towards heterogeneous versions of bifunctional catalysts for carbonate synthesis. The presented recycling studies help to establish that also a heterogenized bifunctional catalyst can display attractive activity under comparatively mild reaction conditions with a high substrate turnover number.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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- 18 C. Martín, C. J. Whiteoak, E. Martin, M. Martínez Belmonte, E. C. Escudero-Adán and A. W. Kleij, *Catal. Sci. Technol.*, 2014, **4**, 1615.
- 19 Note that we did try to prepare iodide based bifunctional catalyst systems derived from 5–11; however, during purification of these compounds we found by elemental analyses that the iodide content was consistently significantly higher than expected, and we therefore continued with the bromide-based bifunctional catalysts.
- 20 For illustrative examples please refer to: (a) W. Guo, J. González-Fabra, N. A. G. Bandeira, C. Bo and A. W. Kleij, *Angew. Chem., Int. Ed.*, 2015, **54**, 11686; (b) M. Alves, R. Méreau, B. Grignard, C. Detrembleur, C. Jérôme and T. Tassaing, *RSC Adv.*, 2017, **7**, 18993–19001; (c) C. J. Whiteoak, A. Nova, F. Maseras and A. W. Kleij, *ChemSusChem*, 2012, **5**, 2032. Note that bifunctional catalyst 14 contains four active sites though it may be difficult to assess whether all sites are involved simultaneously. As the heterogeneous system 22 shows comparable conversion kinetics, it may be assumed that the activation barrier for the homogeneous and heterogeneous catalyzed formation of COC-1 is rather similar.
- 21 Part of us have reported the immobilization of various organocatalysts onto similar supports using comparable approaches, see: (a) S. Cañellas, C. Ayats, A. H. Henseler and M. A. Pericàs, *ACS Catal.*, 2017, **7**, 1383; (b) L. Clot-Almenara, C. Rodríguez-Esrich, L. Osorio-Planes and M. A. Pericàs, *ACS Catal.*, 2016, **6**, 7647; (c) P. Llanes, S. Sayalero, C. Rodríguez-Esrich and M. A. Pericàs, *Green Chem.*, 2016, **18**, 3507; (d) J. Izquierdo and M. A. Pericàs, *ACS Catal.*, 2016, **6**, 348.
- 22 Note that the presence of bromide or iodide likely does not bear too much difference in overall activity, as they are known for other systems to mediate the coupling of epoxides and CO₂ with similar efficiencies.
- 23 (a) M. North, B. Wang and C. Young, *Energy Environ. Sci.*, 2011, **4**, 4163; (b) See also ref. 16; in this particular case we were able to re-alkylate the catalyst structure with MeI to regenerate the required ammonium iodide groups.

