Conversion of Oxiranes and CO₂ to Organic Cyclic Carbonates using a Recyclable, Bifunctional Polystyrene-Supported Organocatalyst

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The development of a heterogeneous one-component bifunctional catalyst system able to catalyse the conversion of carbon dioxide and oxiranes to organic cyclic carbonates at low temperature (45 ºC) is reported. The bifunctional system can be easily recycled and reactivated when required. When compared with other heterogeneous organocatalysts for the same transformation, the reported catalyst is active at 10 much milder temperatures, thus emphasising the optimal sustainability profile of the new catalyst system.

Introduction

The use of carbon dioxide (CO_2) in chemical synthesis is attracting significant interest as a result of growing concerns about the 15 environmental impact of this greenhouse gas, but also because CO_2 as a potential carbon source is inexpensive, widely available and non-toxic.[1-4] The principal limitation to the use of CO_2 as a carbon source is its high kinetic stability and therefore chemical processes utilising CO_2 as feedstock usually require elevated operating 20 temperatures limiting overall sustainability. An ideal CO_2 utilising process should emit less CO_2 than it uses, hence there is a desire for the use of lower reaction temperatures as energy generation required for heating results in emissions of CO_2. To date the development of CO_2 utilising processes which are operative at 25 ambient conditions is and continues to be a huge challenge. The combination of CO_2 and a reagent with high intrinsic energy can facilitate the conversion of CO_2 and indeed, one of the most developed reactions for the conversion of CO_2 into value-added organic matter is the ring-expansion addition reaction of CO_2 to 30 oxiranes (Scheme 1).
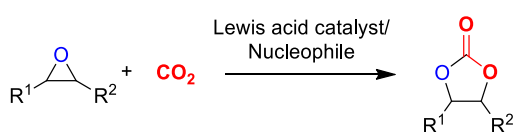
Scheme 1 Ring-expansion addition reaction of CO_2 to oxiranes.

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In the simplest case, this reaction proceeds in the presence of only a catalytic amount of a tetrabutylammonium halide salt at 120 ºC to yield the desired cyclic organic carbonates.[5] In addition to 40 utilising a reagent with high intrinsic energy, efficient catalytic systems can be employed to further enhance the reaction kinetics and for the aforementioned ring-expansion addition reaction of CO_2 to oxiranes there have been extensive reports of catalytic systems able to mediate this conversion.[6,7] The use of a Lewis acid 45 catalyst in addition to a nucleophilic co-catalyst permits the use of more sustainable reaction conditions and over recent years several Lewis acidic catalysts have been reported to be active at ambient temperatures based on Al,[8] Zn[9] and Fe.[10]

In contrast to the number of metal-based catalyst systems 50 reported, the number of organocatalyst systems reported is relatively scarce and this is most probably due to their reduced substrate activation potential. As a result, most of the reported examples typically require the use of unfavourable elevated temperatures (>100 ºC) challenging the sustainability and hence 55 applicability of these catalysts. Previously, in our laboratory we have developed an organocatalyst system active at more favourable temperatures (25–45 ºC). We reported that commercially available 1,2,3-tris-hydroxybenzene (pyrogallol) in combination with tetrabuylammonium iodide (TBAI) is able to 60 convert CO_2 and a variety of oxiranes into the corresponding organic cyclic carbonates at ambient temperature and $pCO_2 = 1.0$ MPa.[11] The mode of action of this catalyst system was elucidated through DFT calculations and it was found that an extended hydrogen-bonding network is responsible for more efficient 65 stabilisation of reaction intermediates, making the oxiranes more susceptible towards ring opening by the co-catalytic halide nucleophile. This binary catalyst system showed non-optimal recycling potential and in order to further increase the sustainability of this catalyst system we decided to pursue the 70 possibility to develop a heterogenised system by anchoring the pyrogallol unit onto a suitable support.

Immobilisation of catalysts allows facile separation from the reaction mixture by simple filtration, avoiding tedious isolation/purification steps and as a result allows for catalyst 75 recycling. The main benefits of polystyrene (PS) as supporting material include its high chemical, thermal, and mechanical stability and the fact that the support allows for facile chemical modification. Furthermore, heterogenised catalysts combine the properties of their homogeneous analogues with the key features 80 of heterogeneous catalysts and are suitable for continuous flow processes avoiding co-elution of the catalyst.[12-14] Recently, part of us had considerable success in realising polystyrene supported organocatalyst systems for a variety of catalytic applications [15-18] and thus we decided to use these favourable support features to 85 develop a heterogenised and more sustainable catalyst based on the aforementioned pyrogallol.

There have been several reports of immobilised organocatalyst systems for the conversion of oxiranes and CO_2 to organic cyclic carbonates including immobilised ionic liquids,[19] bio-polymers[20] 90 and immobilised amino acids[21] amongst others. Unfortunately though, as mentioned earlier, most of these catalyst systems require operating temperatures above 100 ºC which challenges their

overall sustainability. Herein, we report the synthesis and application of more sustainable and recyclable catalyst systems based on polystyrene supported pyrogallol for the conversion of CO_2 and oxiranes into cyclic organic carbonates under attractive conditions.
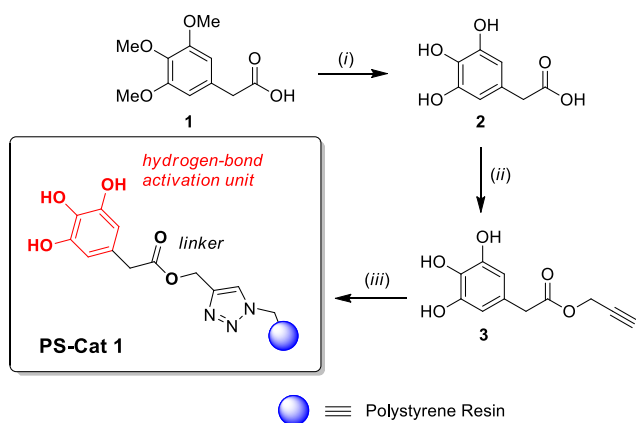
Scheme 2 Synthesis of the **PS-Cat 1**. Reagents and conditions: (*i*) HBr, AcOH, 16 h, reflux, 76%; (*ii*) NaHCO$_3$ (2.4 eq.), propargyl bromide (2.0 eq.), DMF, 14 h, rt, 64%; (*iii*) azidomethyl polystyrene, Cu-cat (3 mol%), DMF/THF (1:1), 1.5 h, 80 °C, 200 W.

Results and discussion

The synthesis of the initial **PS-Cat 1** could be achieved in three simple steps from commercially available starting materials and is shown in Scheme 2. Demethylation of 3,4,5-trimethoxyphenylacetic acid **1** with hydrobromic acid afforded 3,4,5-trihydroxyacetic acid **2**, which was subsequently converted into the corresponding propargylated product **3** by reaction with propargyl bromide. **PS-Cat 1** (f = 1.0 mmol·g^{-1}) was then obtained from the reaction of azidomethyl polystyrene and **3** *via* a copper-catalysed alkyne azide cycloaddition (CuAAC) reaction (See ESI† for full procedures and details).[22,23]

When **PS-Cat 1** was used as catalyst for the conversion of 1,2-epoxyhexane, our benchmark substrate, at a loading of 2 mol% in the presence of TBAI (2 mol%) at 45 °C and a CO_2 pressure of 1.0 MPa, we observed a conversion of 78% after 18 hours (Table 1, entry 2). The binary catalyst system could be easily separated from the product by the addition of diethyl ether (with NBu$_4$I being rather insoluble in this solvent) and subsequent filtration. After removal of the solvent and unreacted substrate from the filtrate under reduced pressure, pure organic cyclic carbonate was obtained. In comparison, under these conditions TBAI alone at a loading of 2 mol% allows for a much lower isolated yield of 24% (Table 1, entry 1). The recovered catalyst system was then used in a second run. Unfortunately, the activity of the catalyst system was reduced in the second run, whereby only 48% product yield was obtained (Table 1, entry 3). The catalyst system was recovered and used again in a third run in which a further reduction in isolated product was observed (30%, Table 1, entry 4).

Table 1 Conversion of 1,2-epoxyhexane **4** into its corresponding cyclic carbonate **4a** using **PS-Cat 1**.[a]
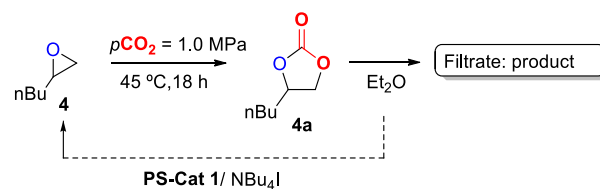
Entry	PS-Cat	Run	Yield (%)[b]	TON[c]
1	–	–	24	–
2	**1**	1	78	39
3	**1**	2	48	24
4	**1**	3	30	15

[a] reaction conditions: 1,2-epoxyhexane (1.0 g, 9.98 mmol), **PS-Cat 1** (2.0 mol%), TBAI (2.0 mol%), 45 °C, pCO_2 = 1.0 MPa, 18 h. [b] Isolated yield. [c] TON is defined as turnover per pyrogallol unit.

This reduction in catalytic activity was coupled with a visible darkening of the PS-support as more runs were carried out. In order to investigate this darkening we reacted pyrogallol, TBAI and 1,2-epoxyhexane stoichiometrically using a minimal amount of dichloromethane as solvent. After 18 hours the darkened reaction mixture was analysed by ^{1}H NMR spectroscopy, where it was observed that the spectrum had changed from that of the initial one. Isolation of the reaction products indicated that the pyrogallol had reacted with TBAI to yield an ammonium phenolate salt and iodide had reacted with the 1,2-epoxyhexane resulting in the formation of a halohydrin species (see Scheme 3).
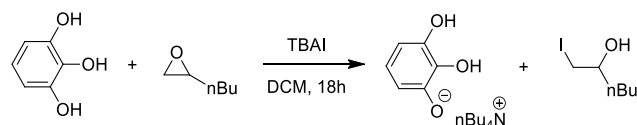
Scheme 3 Products arising from the reaction of pyrogallol, 1,2-epoxyhexane and TBAI.

We propose that this reaction may be a catalyst deactivation route as the hydrogen-bonding network decreases and halide nucleophile concentration becomes depleted over successive runs as a result. **PS-Cat 1** contains a triazole linker as a result of the CuAAC reaction involved in the PS functionalisation step. It was envisaged that reaction of this triazole linker with methyl iodide could result in a one-component bifunctional catalyst system (*cf.*, **PS-Cat 2**, Scheme 4) with a higher stability than that of the binary catalyst system described above.
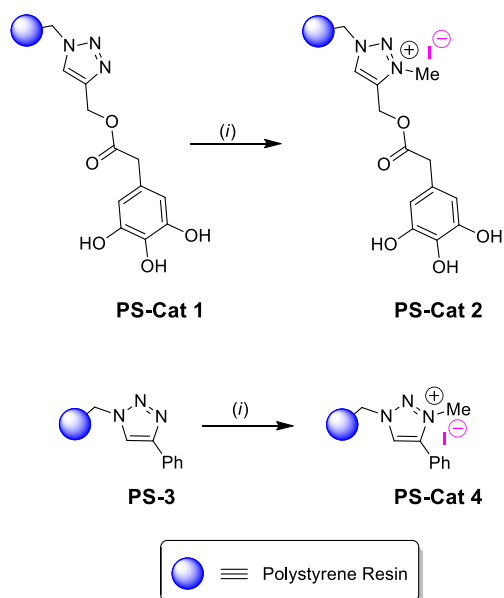
Scheme 4 Synthesis of **PS-Cat 2** and **PS-Cat 4**. Reagents and conditions: (*i*) MeI (5.0 eq.), CH₃CN, 48 h, 75 °C.

Table 2 Conversion of 1,2-epoxyhexane **4** into its corresponding cyclic carbonate **4a** using **PS-Cat 2** and **PS-Cat 4**.[a]
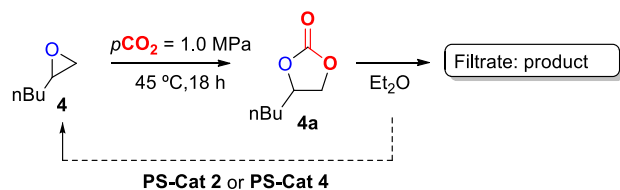

Entry	PS-Cat	Run	Yield (%)[b]	TON[c]
1	**4**	–	20	5
2	**2**	1	84	21
3	**2**	2	76	19
4	**2**	3	62	16
5	**2**	4	48	12

[a] Reaction conditions: 1,2-epoxyhexane (1.0 g, 9.98 mmol), **PS-Cat 2** or **PS-Cat 4** (4.0 mol%), 45 °C, pCO_2 = 1.0 MPa, 18 h. [b] Isolated yield. [c] TON is defined as turnover per pyrogallol unit.

The remote position of a potential triazolium ion from the 1,2-trihydroxybenzene site is likely to make a one-component bifunctional catalyst more stable toward the aforementioned decomposition compared with the binary catalyst system. Reaction of **PS-Cat 1** with methyl iodide in acetonitrile resulted in the formation of **PS-Cat 2** (Scheme 4). A support material terminated in a phenyl-triazole unit, **PS-3**, was also prepared for comparison and reacted with methyl iodide in the same manner to realise **PS-Cat 4** which was used to ensure that any activity observed is not the result of catalysis involving the co-catalyst only.

As may be expected, the one-component **PS-Cat 2** requires a higher catalyst loading in order to attain a similar activity to that of the binary system containing both but separate **PS-Cat 1** and TBAI (Table 1, entry 2 *vs.* Table 2, entry 2). The bifunctional **PS-Cat 2** shows a fourfold higher yield under these conditions than **PS-Cat**

4 suggesting the involvement of the 1,2,3-trihydroxybenzene moiety in the catalysis reaction (Table 2, entries 1 and 2). It can also be seen that the decrease in activity for bifunctional **PS-Cat 2** is slower than that observed for the binary catalyst system **PS-Cat 1**. A reduction in the isolated product yield to 48% already occurs in run 2 using the **PS-Cat 1**/TBAI binary catalyst system, while in the case of the bifunctional **PS-Cat 2** a similar decrease in product yield is noted in the fourth run and thus **PS-Cat 2** retains activity for a longer period of time. Elemental analysis obtained for the **PS-Cat 2** system before use (11.73% I) and after 4 runs (2.45% I) indicates that the loss of activity should be ascribed to the reduction in the halide nucleophile that is required for the ring opening of the oxirane during the conversion into its carbonate. A similar iodine elemental analysis performed on **PS-Cat 4** showed that in this case no decrease in the halide occurs with reuse, and this suggests that the adjacent pyrogallol unit facilitates this process in **PS-Cat 2** (*e.g.*, through a hydrogen-bond assisted Herzig-Meyer demethylation).
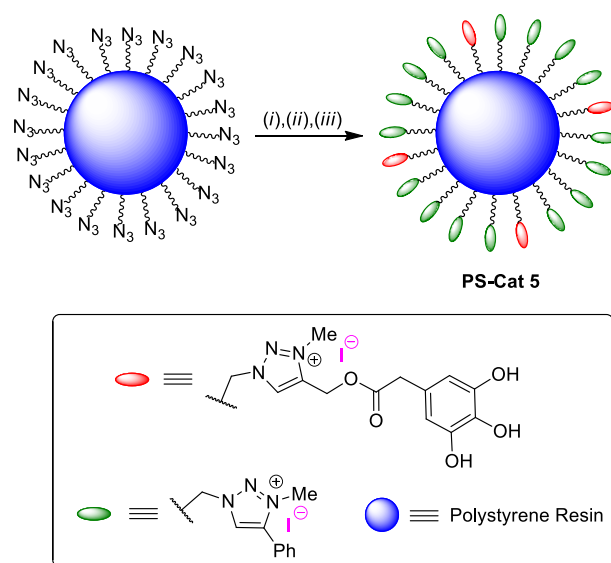
Scheme 5 Synthesis of **PS-Cat 5**. Reagents and conditions: (*i*) **3** (0.2 eq.), Cu-cat (3 mol%), DMF/THF (1:1), 1.5 h, 80 °C, 200 W; (*ii*) Phenylacetylene (1.2 eq.), Cu-cat (3 mol%), DMF/THF (1:1), 1.5 h, 80 °C, 200 W; (*iii*) MeI (5 eq.), CH₃CN, 48 h, 75 °C.

In an attempt to realise a PS-supported catalyst system that does not suffer from deactivation problems, we planned to prepare a bifunctional resin where the triazolium and pyrogallol units could be linked to distinct positions along the polymer backbone. This could be easily brought into practice as a result of the non-discriminating nature of CuAAC reactions. Thus, even the relative proportions of the two desired functional units could be in principle controlled by performing on the same azido-functionalized polymer two sequential CuAAC reactions with the minor, limiting unit being introduced first. We accordingly devised a straightforward synthetic protocol for the preparation of a resin where the PS-supported 1,2,3-trihydroxybenzene containing moieties and the other units (*cf.*, red and green parts in Scheme 5) existed in an optimal 1:4 ratio. This could be brought into practice through the sequence shown in Scheme 5, where a final treatment

with methyl iodide leads to **PS-Cat 5**. It is interesting to note that this versatile methodology may have wider applicability as it can be applied to the preparation of other types of bifunctional heterogeneous catalyst systems whereby the inclusion of different catalytic moieties on the same PS support is required. Even in the case that the triazolium moieties linking the 1,2,3-trihydroxybenzene units to the polystyrene backbone suffered a decomposition similar to the one observed in **PS-Cat 2**,[24] the more abundant phenyltriazolium units should remain stable with time (as observed with **PS-Cat 4**) and preserve better the catalytic activity of **PS-Cat 5**. Indeed, **PS-Cat 5** (4 mol%) maintains its activity levels for a longer period of time than **PS-Cat 2**, whilst the reduction in the number of pyrogallol units in **PS-Cat 5** (from 4.0 to 0.8 mol%) only leads to a modest reduction in the overall activity, suggesting that the amount of halide nucleophile present in **PS-Cat 2** is indeed limiting the overall activity. An appreciable reduction in activity of **PS-Cat 5** only started to occur after five runs (Fig. 1).
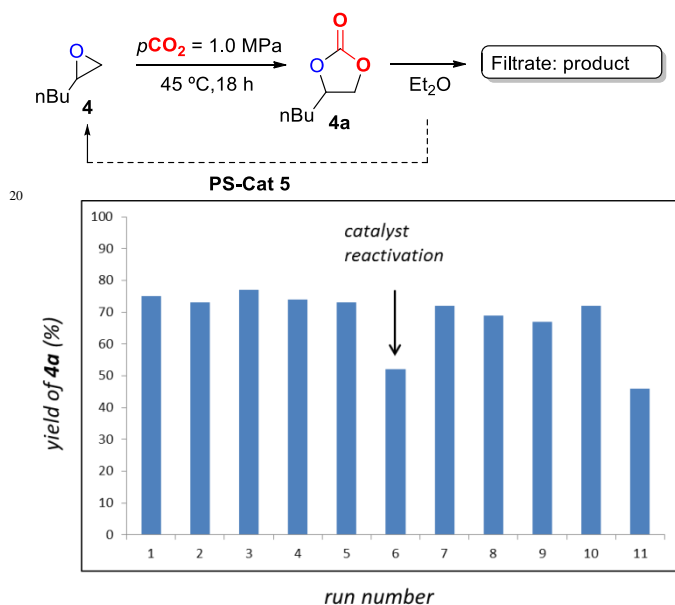

Fig. 1 Recycling of bifunctional **PS-Cat 5** in the synthesis of **4a**. Conditions: 1,2-epoxyhexane (1.0 g, 9.98 mmol), **PS-Cat 5** (4.0 mol%), 45 ℃, pCO_2 = 1.0 MPa, 18 h. Note that 4 mol% of "iodide" based PS supported catalyst only gives 20% yield, cf. Table 2, entry 1. The catalyst was reactivated after run 6.

At this point, the support had slightly darkened in colour, but less significantly than observed in the case of the binary couple **PS-Cat 2**/TBAI. Importantly, after a regenerative treatment of **PS-Cat 5** with methyl iodide, the initial activity was virtually recovered (Fig. 1, run 7) and the supported catalyst regained a pale brown colour. The same sample of **PS-Cat 5** was used in 11 consecutive runs giving a total of 938 turnovers/1,2,3-trihydroxybenzene unit which is significantly higher than those that may be obtained with **PS-Cat 1** or **PS-Cat 2**.
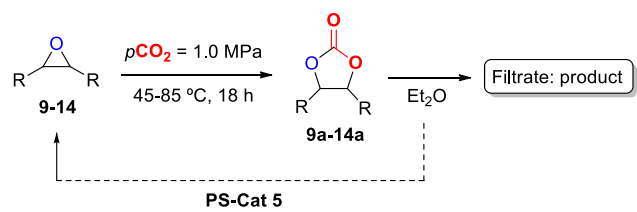
The bifunctional **PS-Cat 5** was also studied for the conversion of other substrates.[25] In these experiments the supported catalyst was used to convert one sub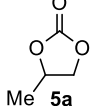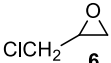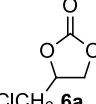strate and then recycled in order to convert further substrates. Table 3 summarises the results obtained from this study. Propylene oxide (**5**), epichlorohydrin (**6**) and 1,2-epoxy-5-hexene (**7**) could be successively converted (Table 3, entries 1−3) into their respective organic carbonates **5a-7a** with excellent isolated yields. The catalyst system was then further challenged by using styrene oxide **8** (Table 3, entry 4). This substrate was found to be more sluggish using the homogeneous version of the pyrogallol-based catalyst system reported previously.[11] The isolated yield of the carbonate product **8a** (53%) was lower in this case but in the same order of magnitude as for the homogeneously catalysed reaction. To check if this reduced yield was a result of deactivation of the catalyst system **PS-Cat 5**, propylene oxide (**5**) was then again tested as substrate and the isolated yield proved to be only slightly lower (89%) than at the beginning of the recycling experiment (Table 3, entry 1 versus entry 5).
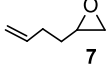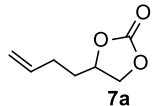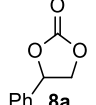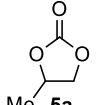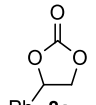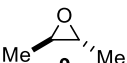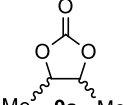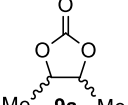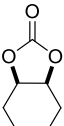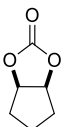
As there was a small reduction in the yield it was decided to reactivate the support by reaction with methyl iodide before further use (after run 5, Table 3). With the intention of increasing the obtained yield of the organic cyclic carbonate from styrene oxide we decided to increase the operating temperature to 65 ℃ (entry 6), which is still significantly lower than the temperatures reported for other heterogeneous organocatalyst systems. At this higher temperature an almost quantitative yield of the organic cyclic carbonate product was obtained. This result prompted us to challenge the catalyst system still further, by attempting to convert an internal oxirane (entries 7 and 8). Internal oxiranes have been shown to be difficult substrates to convert and we chose the simplest example for our study, *trans*-2,3-epoxybutane. At 65 ℃ a low yield of only 8% was achieved, but upon increasing the temperature and time of the reaction we were able to obtain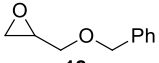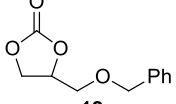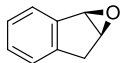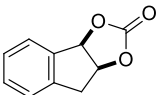 up to 18% yield. Although this yield may not appear significant, it should be noted that most metal−based catalyst systems are unable to mediate efficient conversion of this substrate. We also noted that although the starting material was 100% pure *trans*-2,3-epoxybutane, at the higher temperature there was a significant loss of configuration in the product (up to 18% *cis*-carbonate was obtained). This behaviour has been studied before using an iron(III) amino-triphenolate based catalyst system and was suggested to arise from different ring-closure mechanisms.[26]

We then also investigated the use of some more challenging internal epoxides (Table 3, entries 9-14). The cyclic epoxides of entries 9 and 10 were, as expected, only converted to a minor extent (12 and 15% yields, respectively) in line with previous reports that internal epoxides generally require highly potent (metal) catalysts and more harsh reaction conditions.[10,26,27] Hereafter, the benzyl glycidyl ether substrate (entry 11) could be cleanly converted in high yield (89%) and also the rarely reported conversion of indene oxide[28] proceeded smoothly (entry 12, >99% yield).

Table 3 Reuse of bifunctional **PS-Cat 5** with different substrates.[a]

Run	T (°C)	Substrate	Product	Yield (%)[b]
1	45	Me **5**	Me **5a**	96
2	45	ClCH₂ **6**	ClCH₂ **6a**	94
3	45	**7**	**7a**	91
4	45	Ph **8**	Ph **8a**	53
5[c]	45	Me **5**	Me **5a**	89
6	65	Ph **8**	Ph **8a**	98
7[d]	65	Me **9** Me	Me **9a** Me	8[e]
8[f]	85	Me **9** Me	Me **9a** Me	18[g]
9	85	**10**	**10a**	12
10	85	**11**	**11a**	15
11	45	**12** O Ph	**12a** O Ph	89
12	85	**13**	**13a**	>99

| 13 | 45 | | 72 | |

| 14[h] | 85 | | | i |
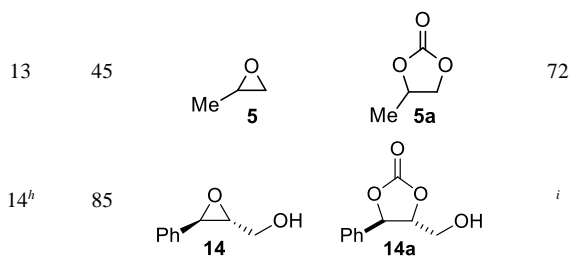
[a] Reaction conditions: substrate (10.0 mmol), **PS-Cat 5** (8.0 mol%), pCO_2 = 1.0 MPa, 18 h. [b] Isolated yield. [c] Reactivation of **PS-Cat 5** with methyl iodide done after this run. [d] 42 h. [e] Traces of *cis*-product present. [f] 66 h. [g] Product mixture contained 82% *trans*- and 18% *cis*-carbonate by ^{1}H NMR analysis. [h] The catalyst was reactivated with MeI before this run was carried out. [i] A mixture of products was obtained, for details see the ESI†.

In order to test whether the catalyst had lost some of its activity, propylene oxide was then used as substrate (entry 13) and this afforded a 72% yield of the carbonate product being lower than those reported in entries 1 and 5. Therefore, before further use the **PS-Cat 5** was first reactivated again using MeI.[29] As a final substrate in the series, phenyl glycidol (entry 14) was evaluated; unlike in the case of glycidol[25] the product of this experiment could be isolated (see ESI for details). However, ^{1}H NMR analysis and by comparison with authentic samples prepared individually it is clear that the reaction proceeds with much lower selectivity, and indications were found for the formation of polyols, i.e. ring-opening of this epoxide substrate by adventitious water had occurred.

Nonetheless, the results reported in Table 3 clearly demonstrate the unique potential of this supported, bifunctional catalyst **PS-CAT 5** for the conversion of a variety of different epoxides into their cyclic carbonates using a single catalyst batch.

Conclusions

In summary, we have reported an efficient PS supported organocatalyst system based on a pyrogallol (i.e., 1,2,3-trihydroxybenzene) scaffold for the conversion of CO_2 and oxiranes into organic cyclic carbonates which is active at significantly lower temperatures (45 °C) than those previously reported for other heterogeneous organocatalyst systems (>100 °C). This catalyst system represents an improvement of our previously reported pyrogallol catalyst and is an example of how click-chemistry can be utilised for the immobilisation of an organocatalyst onto functionalised-PS. The reported catalyst system (**PS-Cat 5**) can also be recycled and upon loss of activity can be easily regenerated by reaction with methyl iodide. In addition, we have exemplified the potential for inclusion of different catalytic moieties on the same PS support, which may have wider applicability for the realisation of other heterogeneous catalysts which require multiple catalytic sites. It therefore marks this versatile catalyst preparation procedure as highly attractive for optimising structure-reactivity features of new catalyst systems with an improved sustainability footprint.

Experimental

All substrates and reagents are commercially available and were used as received. Carbon dioxide (purchased from PRAXAIR) was used without further purification or drying prior to use. Procedures for the synthesis of the PS supported catalyst systems can be found in the Electronic Supplementary Information (ESI†). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 or AV-500 spectrometer and referenced to the residual deuterated solvent signals. IR spectra were obtained using a Bruker Alpha FT-IR. Elemental analysis was performed by MEDAC Ltd, United Kingdom.

Typical procedure for organic cyclic carbonate synthesis from oxiranes and CO_2

1,2-epoxyhexane (1.0 g, 10.1 mmol) was placed in a 30 mL stainless steel autoclave with a **PS-Cat** (2.0 mol%) and TBAI (2.0 mol%) (i.e., binary catalyst system) or **PS-Cat 5** (4.0 mol%) (i.e., the bifunctional catalyst system). The autoclave was then subjected to three cycles of pressurisation and depressurisation with carbon dioxide (5 MPa), before final stabilisation of the pressure to 10 MPa. The autoclave was sealed and heated to 45 °C and left stirring. After 18 hours the reaction mixture was suspended in diethyl ether (20 mL) and filtered. The catalyst system was further washed with diethyl ether (3 × 10 mL) and the solvent removed from the combined organic filtrates under reduced pressure to yield the organic cyclic carbonate product. The identity of the organic cyclic carbonate product was confirmed by comparison to literature data. The collected catalyst system was used again in subsequent catalytic runs. ^{1}H and ^{13}C NMR and IR spectra of the organic cyclic carbonate products can be found in the Electronic Supplementary Information (ESI). Below a listing of analytical data is presented of the obtained cyclic carbonates **4a–13a**.

4-Butyl-1,3-dioxolan-2-one (4a).[30] ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.79 – 4.62 (m, 1H), 4.52 (dd, $^2J_{HH}$ = 8.1 and $^3J_{HH}$ = 8.1 Hz, 1H), 4.08 (dd, $^2J_{HH}$ = 8.1 and $^3J_{HH}$ = 7.3 Hz, 1H), 1.90 – 1.58 (m, 2H), 1.53 – 1.25 (m, 4H), 0.92 (t, $^3J_{HH}$ = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 155.2 (C=O), 77.2, 69.5, 33.4, 26.4, 22.2, 13.7. IR (neat): ν = 1786 cm^{-1} (C=O).

4-Methyl-1,3-dioxolan-2-one (5a).[30] ^{1}H NMR (400 MHz, CDCl$_3$) δ 93 – 4.79 (m, 1H), 4.56 (dd, $^2J_{HH}$ = 8.5 and $^3J_{HH}$ = 7.6 Hz, 1H), 4.03 (dd, $^2J_{HH}$ = 8.5 and $^3J_{HH}$ = 7.2 Hz, 1H), 1.48 (d, $^3J_{HH}$ = 6.3 Hz, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 155.1 (C=O), 73.6, 70.7, 19.4. IR (neat): ν = 1781 cm^{-1} (C=O).

4-Chloro-1,3-dioxolan-2-one (6a).[31] ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.09 – 4.83 (m, 1H), 4.60 (dd, $^2J_{HH}$ = 8.5 and $^3J_{HH}$ = 8.5 Hz, 1H), 4.42 (dd, $^2J_{HH}$ = 8.5 and $^3J_{HH}$ = 5.8 Hz, 1H), 3.81 (dd, $^2J_{HH}$ = 12.2 and $^3J_{HH}$ = 5.8 Hz, 1H), 3.75 (dd, $^2J_{HH}$ = 12.2 and $^3J_{HH}$ = 3.6 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 154.4 (C=O), 74.4, 67.0, 43.90. IR (neat): ν = 1779 cm^{-1} (C=O).

4-(But-3-en-1-yl)-1,3-dioxolan-2-one (7a).[32] ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.87 – 5.67 (m, 1H), 5.11 – 5.06 (m, 1H), 5.06 – 5.01 (m, 1H), 4.78 – 4.66 (m, 1H), 4.52 (dd, $^2J_{HH}$ = 8.6 and $^3J_{HH}$ = 8.6 Hz, 1H), 4.06 (dd, $^2J_{HH}$ = 8.6 and $^3J_{HH}$ = 7.2 Hz, 1H), 2.32 – 2.12 (m, 2H), 1.99 – 1.86 (m, 1H), 1.84 – 1.69 (m, 1H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 155.0 (C=O), 136.2, 116.3, 76.4, 69.4, 33.0, 28.6. IR (neat): ν = 1783 cm^{-1} (C=O).

4-Phenyl-1,3-dioxolan-2-one (8a).[30] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.52 – 7.40 (m, 3H), 7.40 – 7.32 (m, 2H), 5.69 (dd, $^3J_{HH}$ = 8.5 and 8.0 Hz, 1H), 4.81 (dd, $^2J_{HH}$ = 8.5 and $^3J_{HH}$ = 8.5 Hz, 1H), 4.35 (dd, $^2J_{HH}$ = 8.5 and $^3J_{HH}$ = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 154.8 (C=O), 135.8, 129.7, 129.2, 125.9, 78.0, 71.2. IR (neat): ν = 1774 cm^{-1} (C=O).

4,5-Dimethyl-1,3-dioxolan-2-one (9a).[33] *trans*-carbonate: ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.39 – 4.27 (m, 2H), 1.44 (d, $^3J_{HH}$ = 5.9 Hz, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 154.33 (C=O), 79.9, 18.3. IR Neat: 1774 cm^{-1} (C=O). *cis*-carbonate: ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.91 – 4.78 (m, 2H), 1.34 (d, $^3J_{HH}$ = 5.9 Hz, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 154.3 (C=O), 76.1, 14.3. IR (neat): ν = 1774 cm^{-1} (C=O).

Hexahydrobenzo[*d*][1,3]dioxol-2-one (10a).[34] ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.71 – 4.66 (m, 2H), 1.94 – 1.82 (m, 4H), 1.66 – 1.55 (m, 2H), 1.46 – 1.37 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 155.4 (C=O), 75.8, 26.7, 19.1. IR (neat): ν = 1784 cm^{-1} (C=O).

Tetrahydro-3a*H*-cyclopenta[*d*][1,3]dioxol-2-one (11a).[35] ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.12 – 5.08 (m, 2H), 2.15 – 2.06 (m, 2H), 1.83 – 1.61 (m, 4H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 155.5 (C=O), 81.9, 33.1, 21.6. IR (neat): ν = 1780 cm-1 (C=O).

4-(phenoxymethyl)-1,3-dioxolan-2-one (12a).[36] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37 – 7.29 (m, 2H), 7.07 – 7.02 (m, 1H), 6.96 – 6.91 (m, 2H), 5.08 – 5.01 (m, 1H), 4.63 (dd, $^2J_{HH}$ = 8.3, $^3J_{HH}$ = 8.3 Hz, 1H), 4.56 (dd, $^2J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 5.9 Hz, 1H), 4.25 (dd, $^2J_{HH}$ = 10.6, $^3J_{HH}$ = 4.2 Hz, 1H), 4.17 (dd, $^2J_{HH}$ = 10.6, $^3J_{HH}$ = 3.6 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 157.8 (C=O), 129.7, 122.0, 114.6, 74.1, 66.9, 66.3. IR (neat): ν = 1784 cm^{-1} (C=O).

8,8a-dihydro-3a*H*-indeno[1,2-*d*][1,3]dioxol-2-one (13a).[34] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.55 – 7.29 (m, 4H), 6.02 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 5.49 – 5.43 (m, 1H), 3.43 – 3.39 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 155.8 (C=O), 140.1, 136.5, 131.1, 128.3, 126.5, 125.7, 83.6, 79.8, 38.0. IR (neat): ν = 1786 cm^{-1} (C=O).

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Notes and references

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