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Auto-relay catalysis for the oxidative carboxylation of alkenes into cyclic carbonates by a MOF catalyst†

Ha Phan, ^a Pol de la Cruz-Sánchez, ^a María Jesús Cabrera-Afonso ^{a,b} and Belén Martín-Matute ^{*a}

In this study, we present the preparation and application of a new manganoporphyrin Hf-MOF catalyst, Hf-PCN-222(Mn) for the direct oxidative carboxylation of alkenes with CO₂, leading to the effective formation of cyclic organic carbonates (COCs). In contrast to the conventional two-step process, this one-step methodology eliminates the need for the preparation, purification, and handling of epoxides. Hf-PCN-222(Mn) operates under very mild conditions, enabling the synthesis of a wide variety of COCs from alkenes (23 examples, up to 75% yield), as well as the chemoselective and size-selective carboxylation of dienes (7 examples, up to 61% yield). Additionally, we observed that Hf-PCN-222(Mn) could be recycled multiple times without significant loss of activity, providing insight into the sustainability of this approach.

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1. In this study, we introduce Hf-PCN-222(Mn), a new MOF-based catalyst for the direct oxidative carboxylation of alkenes with CO₂. This methodology advances in the application of CO₂ as a C1 synthon for the preparation of high-value compounds, contributing to the circularity CO₂ and to the reduction of the carbon footprint. For the first time we show that the methodology can be applied to a broad range of substrates. The catalyst shows size and chemoselectivity.
2. Preparing Hf-PCN-222(H₂) with microwave-assisted techniques lowers preparation time significantly (from days to hours) and minimizes “non-green” or hazardous solvent/reagents use. The MOF-catalyst efficiently yields cyclic organic carbonates from alkenes using CO₂ as feedstock, eliminating toxic epoxide preparation and handling. The reaction runs solvent-free at low temperatures and atmospheric CO₂. That allows the exploration of a wide range of alkenes (30 examples) with diverse functional groups. Additionally, this heterogeneous catalyst is reusable up to five times without yield loss.
3. Future efforts should focus on (1) replacing hazardous solvents in MOF synthesis and (2) substituting PhIO with a more environmentally friendly oxidant.

Introduction

Carbon dioxide is an abundant, inexpensive, non-flammable, and non-toxic carbon source that can be used as a C1-synthon for the preparation of organic compounds.^{1–12} Recycling carbon from CO₂ as a precursor contributes to the circularity of CO₂, and to the reduction of the carbon footprint.

One of the ways to use CO₂ as a carbon feedstock for the synthesis of organic molecules is the preparation of cyclic

organic carbonates (COCs). These species are rather stable compounds that present low toxicity, low flammability, and high boiling point. Due to these properties, COCs are broadly used as polar aprotic solvents, lithium battery electrolytes, and as monomers for the synthesis of cyclic carbonate functional polymers.^{4,13–19} They also serve as synthons or intermediates for the preparation of a variety of functionalized organic compounds, such as 1,2-diols,²⁰ β-hydroxycarbamates,²¹ and other functionalized intermediates²² by replacing other toxic and difficult to handle reagents, such as phosgene or cyanates.

Currently, one of the most widely used process for the synthesis of COCs is the cycloaddition reaction of CO₂ with epoxides (Fig. 1A, right).^{23,24} In this well-known process, a Lewis acid species activates the epoxide through the oxygen atom while, at the same time, a nucleophile facilitates the ring opening of the epoxide enabling the insertion of CO₂ (Fig. 1A, left).^{17,25}

^aDepartment of Organic Chemistry, Stockholm University, 106 91 Stockholm, Sweden. E-mail: belen.martin.matute@su.se

^bOrganic Chemistry Department, Universidad Autónoma de Madrid (UAM), Avda. Francisco Tomás y Valiente 7, Cantoblanco 28049, Madrid, Spain

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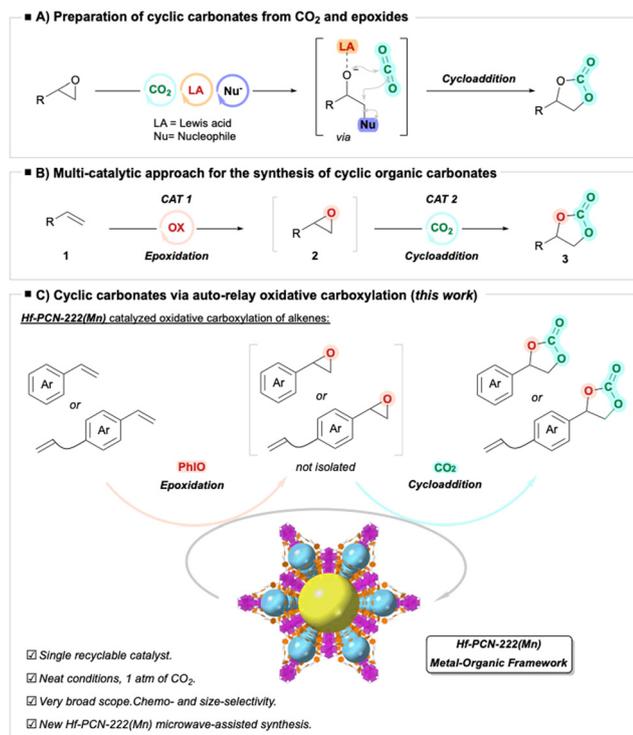


Fig. 1 Strategies to synthesize COCs from CO₂ and this work.

However, the major drawbacks for this methodology, especially in the metal-free examples, have been the limited selectivity, and the need to use high temperatures and very high pressures.^{26–33} However, recent advances in catalyst design have enabled the cycloaddition reaction under milder conditions, and using atmospheric CO₂ pressure.^{6,34–44} Furthermore, the sustainability of metal-based catalysts for the synthesis of COCs has been reviewed by North and co-workers.⁴⁵

Although epoxides are readily available substrates, accessible *via* oxidation of alkenes,^{46–48} they are highly toxic (potentially mutagenic)^{49,50} and unstable, requiring special conditions for transportation, handling, and storage. To address the challenges associated with the inherent properties of epoxides, recent research has focused on the *in situ* generation of epoxides from alkenes and their subsequent conversion into cyclic carbonates. Therefore, the direct conversion of alkenes to COCs *via* oxidative carboxylation using readily available alkenes avoids the direct handling of epoxides, being a less toxic, safer and more sustainable alternative (Fig. 1B).^{51–62} Ideally, a single catalyst is used for both steps under the same reaction conditions, a process referred to as auto-relay catalysis.^{63,64} However, this approach remains challenging since it requires a catalyst that would mediate two catalytic reactions of rather different nature, namely, alkene epoxidation using an oxidant, and a cycloaddition reaction of CO₂, a gas reagent, to the epoxide.^{51–62} In this context, metal-organic frameworks (MOFs) with their high affinities towards CO₂,^{65–70} and their structural and chemical tunability, have the potential to catalyze tandem or auto-relay reactions that involve the use

of CO₂ as a C1 feedstock.^{51–53} The use of MOFs as catalysts in CO₂ cycloadditions to epoxides has been previously demonstrated.^{71–75} For example, we reported that Zr-PCN-222 (Co) catalyzes the CO₂ cycloaddition to epoxides under very mild conditions (atmospheric pressure and at room temperature).⁷⁶ These advances have prompted several research groups to develop MOF-based systems as sole catalysts for the tandem oxidative carboxylation of alkenes.^{54,58,77–87} However, the application of MOFs for the oxidative cycloaddition of alkenes with CO₂ suffer limitations due to the need of high temperatures^{58,79–83,86,87} and high pressures.^{54,77,79,80,84,85} They often require the use of chlorinated solvents (CH₂Cl₂),^{84,86} or other solvents such as decane, classified as a volatile organic compound (VOC).^{57,78–83,85,87} A major common drawback that is also encountered is the lack of selectivity^{88–91} when the reaction is applied to styrene structures, due to formation of styrene diols, phenyl acetaldehydes (*e.g.* **4a**, *vide infra*), benzaldehydes and polystyrene during the epoxidation step, as well as due to unconsumed styrene oxide intermediate.⁸⁴ Further, the scope has been limited to primarily styrene as the substrate. Therefore, a catalyst for the selective and high-yielding oxidative carboxylation of a large scope alkenes remains elusive.

Towards achieving this goal, an alkene oxidation method reported by Nam and co-workers caught our attention.⁹² The authors reported the stoichiometric use of Mn(III)-iodosylarene porphyrin adducts to mediate the epoxidation of alkenes at low temperatures. However, catalytic loading of Mn was only tolerated when 20 equiv. of alkene were used with respect to the oxidant, PhIO. This opened the possibility for the development of a manganese-based catalytic system able to conduct simultaneously the oxidation of the alkene and the cycloaddition step in a two-step one-pot manner without the use of solvent.

Therefore, with these antecedents, herein we present a new and straightforward method to rapidly synthesize, for the first time, manganoporphyrinic Hf-based MOF catalyst Hf-PCN-222 (Mn), as well as its application in the auto-relay catalytic oxidative carboxylation of alkenes, affording a wide range of cyclic organic carbonates (COCs, Fig. 1C). This catalyst overcomes limitations of previous systems: the reaction is solventless, runs at mild temperature (40 °C), and under 1 atm of CO₂. It does not suffer from lack of selectivity, and it mediates the chemoselective oxidative carboxylation of dienes. Its catalytic efficiency is demonstrated in the oxidative carboxylation of a large variety of alkenes, giving access to COCs, important intermediates in synthetic organic chemistry. Taking advantage of its porous nature, size-selectivity is also demonstrated. Furthermore, recyclability test showed that Hf-PCN-222(Mn) could be reused multiple times for the oxidative carboxylation of alkenes without loss of activity or crystalline structure, giving insights on the sustainability of the process.

Results and discussion

Regarding the preparation of our MOF catalytic system, in 2015, Farha's group reported the first synthesis of Hf-PCN-222(Fe),⁹³



a three-dimensional Hf₆-oxo cluster nodes connected by Fe-porphyrin linkers with alternate hexagonal and triangular 1D channels. In their approach, the MOF-catalyst was prepared by using the pre-metallated linker under solvothermal conditions. More recently, the group of Su reported a similar protocol for the synthesis of Hf-PCN-222(Pd), also under solvothermal conditions.⁹⁴ However, the pre-metallation approach is only applicable when the metal (M) in the porphyrin does not interfere with the carboxylate functionalities of the linker, and when metal does not leach from the porphyrin to the MOF structure under synthetic conditions resulting in lower metal (M) incorporation. Preparing these PCN-222(M) MOFs requires complex and long procedures, involving preparation of the metallated porphyrin linkers prior to the MOF synthesis. Commonly, carboxylic group protection – deprotection steps to prevent metal (M)-carboxylate coordination (M = Fe and Mn), are needed. Therefore, we first focused on developing a method to prepare Hf-PCN-222(M), (M = Mn or Co). For that, we used a modified strategy for the preparation of the related Zr-PCN-222(M) MOFs (Fig. 2A).⁷⁶

First, the non-metallated Hf-PCN-222(H₂) was obtained using a microwave-assisted strategy. The Hf₆-oxo clusters were prepared by reacting commercially available bis(cyclopentadienyl)hafnium(IV) dichloride (HfCp₂Cl₂) with 2-fluorobenzoic acid (2-FBA), the modulator, for 5 min at 140 °C in DMF under microwave irradiation. This mixture was then treated with tetrakis(4-carboxyphenyl)porphyrin (H₂TCPP) and trifluoroacetic acid (TFA) for 3 h at 150 °C under microwave irradiation. An acidic treatment (2 M HCl at 100 °C, see the ESI† for a full optimization of this step) of as-synthesized Hf-PCN-222(H₂) is essential to remove the unreacted linkers trapped within the pores, as well as to remove 2-FBA modulators on Hf₆-oxo clus-

ters. The activated non-metallated Hf-PCN-222(H₂), obtained as bright purple crystals in 81% yield from H₂TCPP, has increased surface area compared to that of the as-synthesized MOF, and high crystallinity (Fig. S1†). The use of DMF to prepare PCN-222-MOFs is essential, and unsuccessful efforts to replace it by a greener alternative⁹⁵ have been reported.⁹⁶ Its role is to modulate the structure of the MOF, ensure mixture homogeneity and regular crystal growth, among others.⁹⁶ Replacement by DMSO resulted in a MOF structure with low crystallinity,⁹⁶ that influences the MOF catalytic and CO₂ capture capabilities. Although the DMF solvent could not be replaced during catalyst synthesis, the microwave method reported here requires reduced reaction time and lower amounts of DMF and of modulators than those reported for the preparation of Hf-PCN-222(M) structures (see ESI, Table S1†).

With the optimized preparation of Hf-PCN-222(H₂) in hand, we could implement a divergent metalation protocol, opening up the possibility of introducing many metals in a facile manner without the need to consider possible interferences or incompatibilities with the MOF structure. Thus, by reaction in aqueous solutions with either MnCl₂ or CoCl₂ under hydrothermal conditions, Hf-PCN-222(Mn) and Hf-PCN-222(Co) were obtained in 80% overall yield and >95% metalation efficiency in both instances (see ESI 2.3†).

The crystallinity and phase purity of activated Hf-PCN-222(H₂) was confirmed by powder X-ray diffraction (PXRD) analysis (Fig. 2B). Additionally, the diffraction patterns of Hf-PCN-222(Mn) and Hf-PCN-222(Co) closely matched with those of Hf-PCN-222(H₂) as well as with the simulated pattern, proving evidence of the preservation of the framework structure and crystallinity after the post-synthetic metalation. N₂

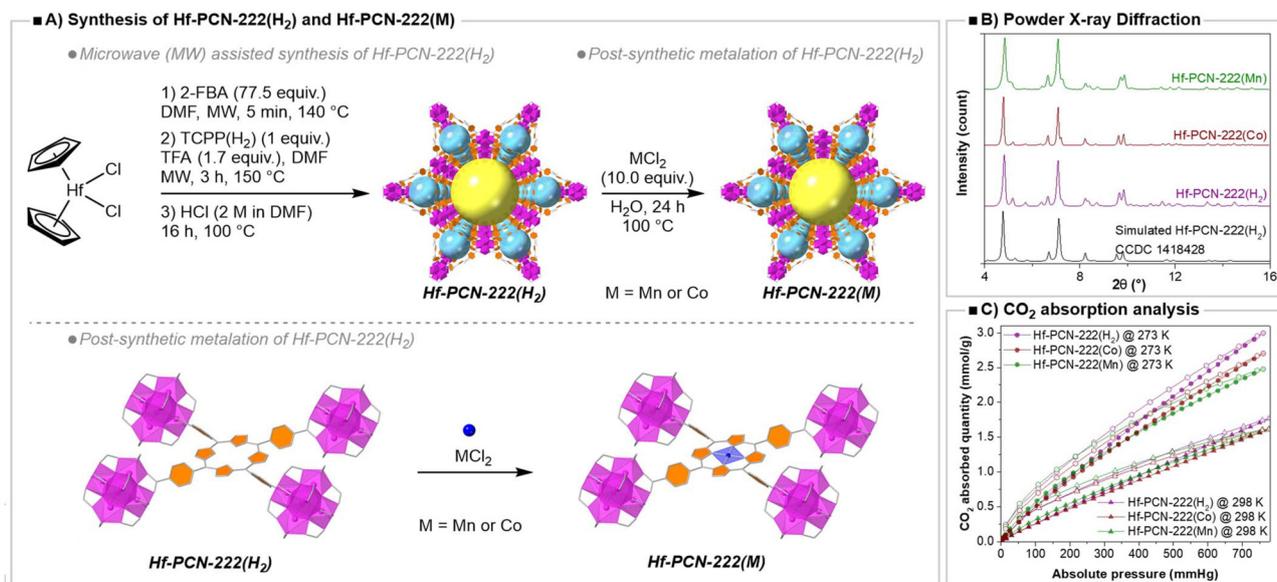


Fig. 2 Synthesis (A) and PXRD patterns (B) of Hf-PCN-222(H₂) and metalated Hf-PCN-222(M). (C) CO₂ adsorption – desorption isotherms of Hf-PCN-222(H₂) and metalated Hf-PCN-222(M).



gas adsorption–desorption analysis showed that metalated Hf-PCN-222(M) has only a slightly lower surface area compared to non-metalated Hf-PCN-222(H₂) (Fig. S4†), confirming that the porous structure of the MOFs is preserved.

Carbon dioxide adsorption isotherms of Hf-PCN-222(H₂), Hf-PCN-222(Mn) and Hf-PCN-222(Co) (Fig. 2C) showed excellent adsorption values: Hf-PCN-222(H₂) = 3.0 mmol g⁻¹ (273 K, 1 bar) and 1.8 mmol g⁻¹ (298 K, 1 bar); Hf-PCN-222(Mn) = 2.5 mmol g⁻¹ (273 K, 1 bar) and 1.6 mmol g⁻¹ (298 K, 1 bar); Hf-PCN-222(Co) = 2.7 mmol g⁻¹ (273 K, 1 bar) and 1.6 mmol g⁻¹ (298 K, 1 bar). The oxophilicity of Hf on the clusters^{97,98} and the confined structure of the MOF can be involved in the CO₂ adsorption *via* coordination, which may explain the good adsorption values observed. Additional information regarding the characterization of the synthesized materials is collected in the ESI,† including thermogravimetric analysis (Fig. S2†), scanning electron microscopy (Fig. S8†), elemental analysis (Table S3†), UV-Vis (Fig. S7†), and FT-IR spectroscopies (Fig. S6†).

We first tested the newly prepared PCN-catalysts in the cycloaddition of CO₂. Reaction optimization was performed on styrene oxide (**2a**, Table 1), which was used as reagent and solvent simultaneously. We could observe that, when using Hf-PCN-222(Mn) (1 mol% based on porphyrin linker), tetrabutylammonium bromide (TBAB) (6 mol%), at 25 °C for 8 h (Fig. 3), 45% yield of styrene carbonate (**3a**) was obtained (Table 1, entry 1). Replacing Hf-PCN-222(Mn) by non-metalated Hf-PCN-222(H₂) or by the cobalt analogue Hf-PCN-222(Co) resulted in lower yields under otherwise identical conditions (Table 1, entries 2 and 3). Reaction with using Zr-PCN-222(Mn) analogue yielded only 17% of the desired COC (Table 1, entries 2 *vs.* 4). This behaviour can be attributed to the fact that Hf is more oxophilic than Zr.^{97,98} Indeed, negligible to no yields were observed in the absence of either MOF catalyst, TBAB co-catalyst, or CO₂ (Table 1, entries 5–7). Moreover, the

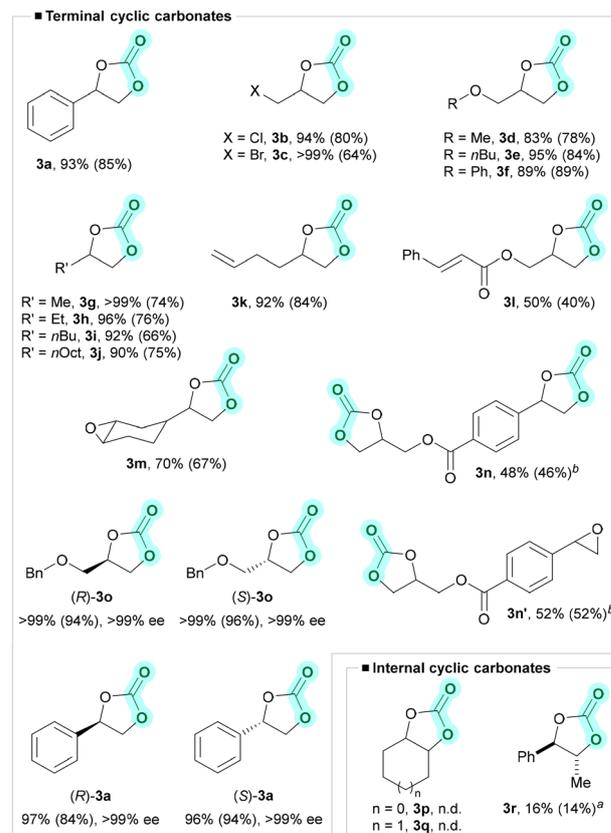


Fig. 3 Scope of CO₂ cycloaddition to epoxides **2**. Conditions: **2** (0.2 mmol), TBAB (6 mol%), Hf-PCN-222(Mn) (1 mol%), CO₂ (1 bar, balloon), neat, 25 °C, 24 h. ¹H NMR yields are reported. Isolated yields are in parentheses. ^aReaction carried out at 50 °C. ^bReaction carried out at 60 °C. **3n** and **3n'** were obtained from **2n** in the same reaction.

Table 1 Optimization of CO₂ cycloaddition to epoxides

| Entry | Deviations from standard conditions ^a | Yield 3a (%) |
|-------|---|---------------------|
| 1 | None | 45 |
| 2 | Hf-PCN-222(H ₂) instead of Hf-PCN-222(Mn) | 27 |
| 3 | Hf-PCN-222(Co) instead of Hf-PCN-222(Mn) | 29 |
| 4 | Zr-PCN-222(Mn) instead of Hf-PCN-222(Mn) | 17 |
| 5 | Absence of Hf-PCN-222(Mn) | 1 |
| 6 | Absence of TBAB | 6 |
| 7 | Absence of CO ₂ | n.d. |
| 8 | 24 h instead of 8 h | 93 |

^a Conditions: **2a** (0.2 mmol), Hf-PCN-222(Mn) (1 mol% based on porphyrin linker), TBAB (6 mol%), 25 °C, 8 h. ¹H NMR yields were obtained using 1,3,5-trimethoxybenzene as an internal standard.

yield could be increased to a remarkable 93% when the reaction time was prolonged from 8 to 24 h (Table 1, entry 8).

With the optimal conditions in hand, we proceeded to study the scope and limitations of the CO₂ cycloaddition to epoxides (Fig. 3). Styrene oxide (**2a**), epichlorohydrin (**2b**), and epibromohydrin (**2c**) yielded the corresponding cyclic carbonates in near quantitative yields. Furthermore, glycerol carbonate derivatives were obtained in 83% (MeO-, **3d**), 95% (nBuO-, **3e**), 89% (PhO-, **3f**) under identical conditions. Notably, alkyl-epoxides **2g–2j** underwent CO₂ cycloaddition to give cyclic carbonates **3g–3j** in excellent yield up to >99%. Unsaturated epoxides **2k** and **2l** yielded **3k** and **3l** in 92% and 50% yield, respectively, without interference of the double bond moiety present in their structure. Interestingly, when bis-epoxide **2m** bearing terminal and internal epoxide moieties was used, only the terminal epoxide underwent the cycloaddition reaction with CO₂, giving **3m** in 70% yield. Terminal bis-epoxide **2n** formed the bis(cyclic carbonate) **3n** in 48% yield, together with 52% yield of the mono carbonate by-product **3n'**. Formation of **3n'** indicates that the cycloaddition rate of alkyl epoxides is higher than that of aryl epoxides.



Obtaining chiral styrene carbonate **3a** in high enantiomeric purity from easily accessible chiral (*R/S*)-styrene oxide **2a** is challenging. That is due to the fact that the carbocation formed under Lewis acid conditions accounts for the racemization of chiral styrene oxide derivatives.⁹⁹ The reported procedures for the synthesis of chiral styrene carbonate (63% to 99% ee) usually require high temperature (100 to 150 °C) and/or high CO₂ pressure (10 to 80 bar).^{100–108} Despite that, we obtained (*R*)-**3a** and (*S*)-**3a** in quantitative yields and >99% ee at room temperature under atmospheric pressure of CO₂. Likewise, (*R*)-**3o** and (*S*)-**3o** with >99% ee were synthesized in quantitative yield under identical conditions.

Unfortunately, internal epoxides **2p** and **2q** did not yield the desired products. Low yield (16%) of internal carbonate **3r** was obtained when the CO₂ cycloaddition reaction was carried out at a higher temperature of 50 °C.

Catalyst recyclability experiments were conducted. We were happy to see that Hf-PCN-222(Mn) can be reused for 10 consecutive runs without significant loss in reactivity and at a comparable rate (see ESI, Fig. S17†).

Encouraged by the results in the cycloaddition of CO₂ into epoxides, we then turned into developing an efficient auto-relay catalytic oxidative carboxylation of alkenes. We started evaluating 4-chlorostyrene (**1a**) as model substrate to form COC **3s**, by performing the epoxidation and the cycloaddition catalytic reactions using Hf-PCN-222(Mn) as a sole catalyst and with all the reagents in one-pot fashion (Table 2). We were pleased to observe that 2 mol% of Hf-PCN-222(Mn) efficiently catalyzed the oxidation when using 1.5 equiv. of iodosobenzene (PhIO) as the oxidant. The reaction runs in neat conditions without the use of organic solvent using 1.5 equiv. of PhIO. Furthermore, COC **3s** was isolated in 75% at 40 °C,

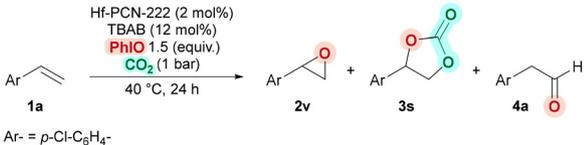
using a CO₂ atmosphere (1 bar) and in the presence of TBAB (12 mol%) (for full optimization, see the ESI, Table S6†). Notably, the reaction outcome was also highly selective, providing COC **3s** in 75% yield, with only traces of the corresponding epoxide intermediate **2v** (Table 2, entry 1). No other by-products were detected after 24 h of reaction time. This is quite remarkable, as side reactions, forming styrene diol, phenylacetaldehyde, benzaldehyde and polystyrene, during styrene epoxidation often limits high yield and selectivity of epoxidation reactions.^{88–91,109–112}

Control experiments conducted without PhIO, TBAB, or Hf-PCN-222(Mn) confirmed that each component is essential to achieve the auto-relay oxidative carboxylation (Table 2, entries 2–6). In these instances, although high conversions were obtained, unidentified by-products (likely polymers) are produced, along with small amounts (<15%) of epoxide **2v**, carbonate **3s**, or aldehyde **4a**. Additionally, these experiments proved that Hf-PCN-222(Mn) was involved not only in the cycloaddition step, but also in the epoxidation⁹² as only traces of COC **3s** and epoxide **2v** were detected without this catalyst (Table 2, entry 5). The use of the analogous cobalt catalyst, Hf-PCN-222(Co), resulted in negligible amount of product **3s** (Table 2, entry 6). Further, since Hf-PCN-222(Co) is active in the cycloaddition reaction (Table 1, entry 3) we attributed this lack of activity to the so-called “oxo-wall effect”, which prevented the formation of the epoxide intermediate.¹¹³

Then, the scope and limitations of the tandem oxidative carboxylation of a range of alkenes was explored (Fig. 4). Halide handles are important functional groups as they enable further diversification *via* well-known procedures.^{114,115} Thus, *para*-Cl, -Br and -F-substituted styrene derivatives were tested, affording COCs **3s–3u** in good, isolated yields. Electron-poor (R = CF₃, CN, NO₂) and electron-rich (R = Me, *t*Bu, OMe) *para*-substituted styrenes gave COCs **3a**, **3v–3aa** in moderate to good yields. *meta*-Me **3ab** and *ortho*-Me **3ac** COCs were synthesized in 47% and 54% yield, respectively. *meta*-OMe styrene carbonate **3ac** was formed in 39%. Likewise, *meta*-NO₂ **3ad** and *ortho*-NO₂ **3af** COCs were obtained in 51% and 38% yield, respectively. Pentafluorobenzene COC **3ag** was obtained in 40% yield under the optimized conditions. Heterocycles such as pyridine (**3ah**) and benzofuran (**3ai**) were obtained moderate to low yields. Interestingly, (*E*)-1,3-Butadien-1-ylbenzene underwent oxidative carboxylation yielding unsaturated cyclic carbonate **3aj** in 42% yield. Although the yields range from moderate to good, with most being moderate, it is important to highlight that we could achieve synthetically useful yields for a wide scope of olefins in a two-steps one-pot process. This kind of methodology eliminates the need for isolation, purification, and handling of epoxides which is a significant advantage from an atom-economy perspective.

Several attempts were made to convert non-conjugated alkenes to the corresponding COCs (**3ak–3ap**); however, they were unproductive. The exception was pentafluorobenzyl-substituted ethylene carbonate **3ak**, obtained in 26% yield. In any case, we decided to take advantage of this apparent limitation

Table 2 Optimization of oxidative carboxylation of alkenes



| Entry | Deviations from standard conditions ^a | Conv. (%) | Yield (%) | | |
|----------------|--|-----------|-----------|-----------|-----------|
| | | | 2v | 3s | 4a |
| 1 | None | 96 | 2 | 75 | n.d. |
| 2 | No TBAB | 90 | 3 | n.d. | 15 |
| 3 | No PhIO | 91 | n.d. | n.d. | n.d. |
| 4 ^b | PhI(OAc) ₂ + H ₂ O instead of PhIO | 92 | n.d. | n.d. | n.d. |
| 5 | No Hf-PCN-222(Mn) | 97 | 7 | 2 | 4 |
| 6 ^c | Hf-PCN-222(Co) instead of Hf-PCN-222(Mn) | 67 | n.d. | 8 | 1 |

n.d. = not detected. ^a Conditions: **1a** (0.2 mmol), Hf-PCN-222(Mn) (2 mol% based on porphyrin linker), TBAB (12 mol%), 40 °C, 24 h. ¹H NMR yields and conversions were obtained using 1,3,5-trimethoxybenzene as an internal standard. ^b PhI(OAc)₂ (1.5 equiv.) and H₂O (1.5 equiv.) was used instead of PhIO (1.5 equiv.). ^c Hf-PCN-222(Co) (2 mol%) was used instead of Hf-PCN-222(Mn) (2 mol%).



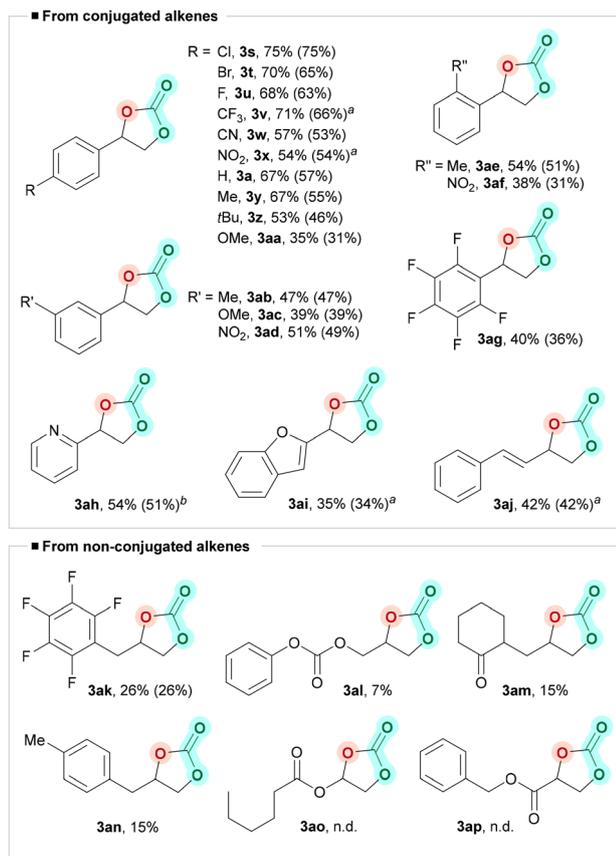


Fig. 4 Scope of oxidative carboxylation of alkenes **1**. Conditions: **1** (0.2 mmol), TBAB (12 mol%), Hf-PCN-222(Mn) (2 mol%), CO₂ (1 bar, balloon), neat, 40 °C, 24 h. ¹H NMR yields are reported. Isolated yields are in parentheses. ^aReaction carried out for 48 h. ^bReaction carried out for 72 h.

Table 3 Optimization of chemoselective oxidative carboxylation of dienes

| Entry | Time ^a (h) | Conv. (%) | Yield 2w (%) | Yield 3aq (%) |
|-------|-----------------------|-----------|---------------------|----------------------|
| 1 | 24 | 83 | 41 | 26 |
| 2 | 48 | 83 | 21 | 46 |
| 3 | 72 | 83 | 4 | 68 |

^a Conditions: **1aj** (0.2 mmol), Hf-PCN-222(Mn) (2 mol% based on porphyrin linker), TBAB (12 mol%), 40 °C, 24–72 h. ¹H NMR yields and conversions were obtained using 1,3,5-trimethoxybenzene as an internal standard.

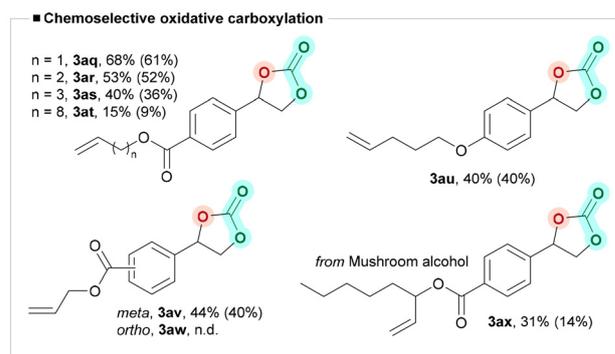


Fig. 5 Scope of chemoselective oxidative carboxylation of dienes.

and develop a chemoselective carboxylation of dienes with both conjugated and non-conjugated alkenes present in the same molecule.

Therefore, diene **1aj**, was used as the model substrate (Table 3). First catalytic tests showed that, the en-cyclic carbonate **3aq** was formed in 26% yield, together with 41% yield of monoepoxide **2w** after 24 h at 40 °C (Table 3, entry 1). No oxidized products related to the non-conjugated alkene moiety of **1aj** were observed. Hence, to get a higher yield of **3aq**, the reaction time was extended. We were pleased to see, **3aq** was formed in 46% and 68% yields after 48 h and 72 h, respectively (Table 3, entries 2 and 3). Then, with optimized reaction conditions, several dienes with different length of the unsaturated alkyl chain were tested (Fig. 5). In all cases, only the conjugated alkene underwent oxidative carboxylation. Notably, as the size of the diene substrates increased, a steady decrease in yield was observed, likely due to the confined space effects within the MOF's channels (see the ESI, Table S8 and Fig. S22, S23[†]); en-cyclic carbonates **3aq–3at** were formed in 68%, 53%, 40%, and 15% yield for *n* = 1, 2, 3,

and 8, respectively. Ether **3aw** was obtained in 40% yield under identical conditions. The reaction showed high sensitivity to steric effects in the aryl ring, as no yield was obtained for *ortho*-**3aw**, in comparison to 44% yield for *meta*-**3av** and 68% yield for *para*-**3aq**. Unsaturated mono-cyclic carbonate derived from mushroom alcohol **3ax** was also obtained in full selectivity, albeit in low yields likely due to their large size.

Finally, the recyclability of the catalyst Hf-PCN-222(Mn) used for the oxidative carboxylation of 4-chlorostyrene (**1a**) was investigated (Fig. 6). After 5 consecutive runs, Hf-PCN-22(Mn) keeps a stable activity, affording **3s** in a remarkable 61% yield and epoxide **2v** in 8% yield after the fifth run. This is comparable to the results after the first run, namely 68% of **3s** and 1% yield of **2v**. PXRD pattern and SEM analysis showed that the recycled Hf-PCN-222(Mn) samples after 1 run and 5 runs have similar crystallinity and morphology compared to the pristine MOF. SEM-EDS showed that the leaching of Mn from the MOF structure is negligible (see ESI, Table S9[†]).



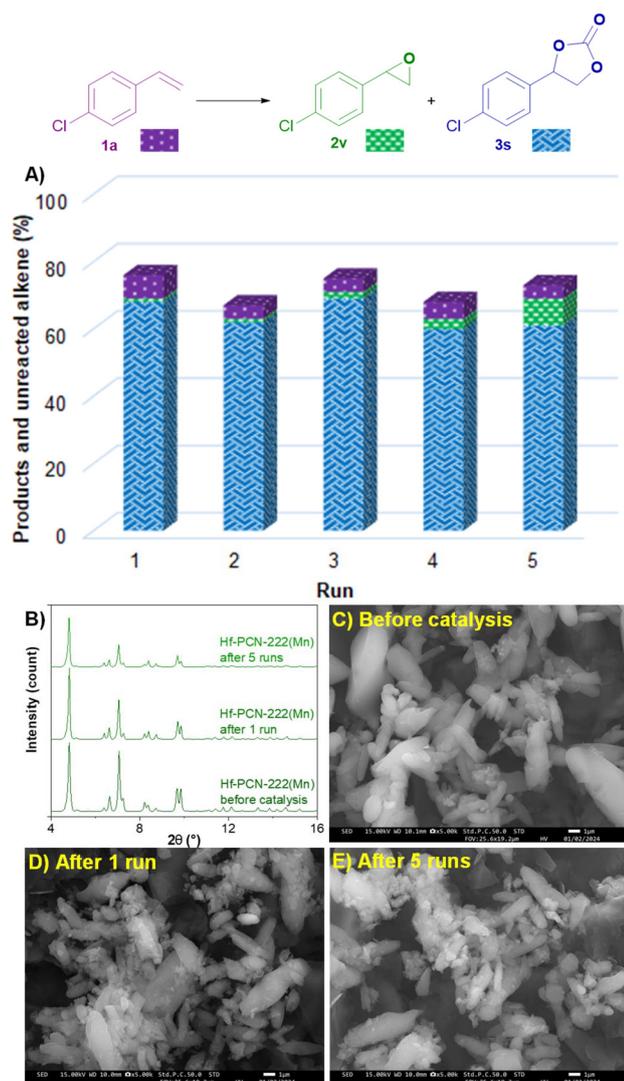


Fig. 6 Recyclability experiment. (A) Reaction outcome. (B) PXRD patterns of Hf-PCN-222(Mn) before and after catalyst. SEM images of Hf-PCN-222(Mn) before catalysis (C), after 1 run (D), and after 5 runs (E).

Conclusions

The porous Hf-based MOF with manganoporphyrin carboxylate linkers, namely Hf-PCN-222(Mn), has been prepared for the first time using a post-metalation synthetic approach, enabled by microwave radiation. This methodology reduces the synthesis time and overall quantity of reagents used. Furthermore, the development of a post-metalation approach of the Hf-PCN-222(H₂) makes possible the introduction of a wide metal diversity avoiding interferences between the MOF structure and the metal of choice. Through this method, elusive porphyrin-MOFs metallated with Mn can be prepared with high metalation yield.

Hf-PCN-222(Mn) proved to be active in the cycloaddition of CO₂ to over 20 epoxides, achieving excellent yields (up to >99% yield) using mild pressure and temperature conditions.

Furthermore, when applied to the tandem oxidative carboxylation of alkenes with CO₂, Hf-PCN-222(Mn) provided organic cyclic carbonates from 23 alkenes, as well as the chemo-selective and size-selective carboxylation of 7 dienes using the same mild conditions.

Furthermore, a comparison of the reaction conditions, catalytic activity and scope with other relevant MOF-based systems reveals that our system is able to perform the oxidative carboxylation of alkenes under mild temperatures and at ambient pressure without sacrificing efficiency. Thus, enabling the exploration of a broader scope for the one-step synthesis of cyclic carbonates from different readily accessible olefins with a variety of functional groups. We also eliminated completely the use of solvent in the catalysis, contributing in the overall sustainability of the process.

Furthermore, Hf-PCN-222(Mn) could be reused 5 times without loss of activity in the tandem oxidative carboxylation of alkenes with CO₂. This is quite remarkable, as the MOF is not degraded by the oxidative reaction conditions, and keeps its catalytic activity for several runs, increasing the sustainability of the process.

Author contributions

All authors have given approval to the final version of the manuscript.

Data availability

The data supporting the submitted work can be found in the ESI† of the article.

The ESI† also contains further details regarding safety, as well as characterization information of the prepared compounds (¹H NMR, ¹³C NMR, ¹⁹F NMR, and HRMS).

The raw NMR data files for all compounds reported in the article are deposited at Zenodo and will be made publicly available after acceptance (DOI: [10.5281/zenodo.13365877](https://doi.org/10.5281/zenodo.13365877)). The numbering of the files will then be matched to those in the article.

Each parent folder in Zenodo will contain subfolders with different files. In order to process the data, the full parent folder must be dragged into either Mestrenova or Topspin and then the data is automatically processed. If the name of the raw data files are renamed, the software (Mestrenova or Topspin) will not be able to process the files.

Conflicts of interest

There are no conflicts to declare.

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