



Cite this: *Green Chem.*, 2021, **23**, 7361

Porous organic polymers as metal free heterogeneous organocatalysts

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Efficient catalysis is essential from a green chemistry perspective. Porous organic polymers (POPs) have recently emerged as highly effective materials for catalytic applications. POPs possess controllable compositions and functionalities, high surface areas and can be very stable. In this review we focus on the application of POPs as metal free heterogeneous organocatalysts, a booming field in green chemistry. Acid, base, combined acid–base and hydrogen bonding catalysis are addressed. In addition, chiral catalysis and CO₂ utilization with POPs are discussed. The aim is to provide a comprehensive overview of the field, exploring all different types of POPs as metal free catalysts. Special attention is given to the synthesis conditions to provide the reader with more insight into the construction of these types of materials.

Received 30th June 2021,
Accepted 9th September 2021

DOI: 10.1039/d1gc02319e

rsc.li/greenchem

1. Introduction

Modern life is impossible without catalysis, it is central to the products we use, the air we breathe, the food we eat... Catalysis stands at the core of the chemical industry and forms a central field of current science with enormous importance and challenges.¹ Due to the booming economy and the rising world

population, producing in the most environmentally friendly way possible is of critical importance and here catalysis plays a central role. The 9th principle of green chemistry highlights this: ‘Catalytic reagents, as selective as possible, are superior to stoichiometric reagents’.² Of the processes that take place in the chemical industry 85% are catalytic and in 80% of those processes heterogeneous catalysts are used.^{3,4}

The importance of catalysis doesn’t have to surprise. Without a catalyst driving the transformation many reactions either don’t work at all, or give mixtures of products. Selective catalysts on the other hand can reduce by-products, waste and lead to milder process conditions.⁵ For example, catalysts allow replacing stoichiometric oxidizing agents (e.g. PCC, K₂Cr₂O₇, KMnO₄...) with catalytic oxidations using O₂ or H₂O₂

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research is focussed on the application of porous organic polymers as heterogeneous (photo)catalysts.

Maarten Debruyne graduated in 2018 as a Bioengineer in Chemistry and Bioprocess technology at Ghent University. His research career started with his master thesis, during which he developed enzymatic glycosylations of β -lactams. Currently he is pursuing his PhD under the guidance of Professor Stevens at the SynBioC (Synthesis, Bioresources and Bioorganic Chemistry) research group (Ghent University), where his



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Veronique Van Speybroeck is full professor at Ghent University and head of the Center for Molecular modeling (<http://molmod.ugent.be>). She obtained her PhD in 2001 from Ghent University. She is recipient of two flagship grants from the European Research Council: a Starting and Consolidator grant. Her expertise lies in first principle kinetics and molecular dynamics simulations of complex chemical transformations in

or catalytic carbonylation utilizing CO instead of toxic and corrosive phosgene.^{6,7} Heterogeneous catalysts are generally preferred over homogeneous catalysts. These catalysts are recyclable, provide easier separation and work up of reaction mixtures, lower leaching of metals and they lend themselves exceptionally well to continuous production.^{5,8,9}

Porous materials are often used as heterogeneous catalysts due to their high internal surface where reactions can occur. These porous solids contain voids and thus the material will have an internal surface area and pores. IUPAC classifies the pores into three types: microporous ($d < 2$ nm), mesoporous ($2 \text{ nm} < d < 50$ nm) and macroporous ($d > 50$ nm).¹⁰ Many natural occurring porous materials exist: rocks, soils, zeolites, biological tissues (e.g. bones, wood), and many more have been made by man: bricks, textiles, sponges... Porosity is typically measured by argon or nitrogen physisorption and is characterized by a large (BET) surface area and pore volume.^{11,12}

Zeolites are microporous, aluminosilicate minerals with widespread applications as adsorbents and catalysts and serve as the workhorse heterogeneous catalysts in the chemical industry. They are naturally occurring, but are also produced industrially.¹³ However, many other porous materials can be utilized and are currently being developed for catalytic applications, for example, mesoporous silicas, polystyrene resins and metal organic frameworks (MOFs). The mesoporous silicas are normally alkaline sensitive and polystyrene resins often have low surface areas. MOFs are extended crystalline frameworks consisting of metal ions or clusters as the nodes, providing direction to the charged organic linkers.^{14–16} Examples of stable MOFs are known, however for widespread catalytic applications they are often still hampered by their generally low stability.¹⁷ Therefore, research into stable, light-

weight, highly porous and purely organic materials is gaining a lot of traction. This field of porous organic polymers (POPs) has exploded in the last years. POPs all share the following defining characteristics: high porosity, being composed of lightweight elements and strong covalent bonds holding their 2/3D structures together.¹⁸ In what follows, a short historical overview is given and a typical example of each class of POPs is shown (Scheme 1). POPs are classified depending on their degree of long range order (amorphous or crystalline) and the type of linkages used in their synthesis.

The oldest POPs are the hypercrosslinked polymers (HCPs). Crosslinked polystyrene networks were already reported in the 1930s.¹⁹ Development of a truly porous crosslinked polymer took place by Davankov *et al.* in the 1970s, by crosslinking linear polystyrene **1** with crosslinkers such as α,α' -dichloro-*p*-xylene **2** or chloromethyl methyl ether. The high level of crosslinks led to porous structures, with the rigid backbones preventing the structure from collapse and providing BET surface areas up to $1106 \text{ m}^2 \text{ g}^{-1}$.^{20,21} HCPs can also be formed by Friedel–Crafts type crosslinking of monomers, typically using Lewis acids such as FeCl_3 or AlCl_3 .²²

Polymers of intrinsic microporosity (PIMs), reported for the first time in 2004, are one-dimensional polymers containing twisted polymer backbones which result in inefficient packing and porosity. Unlike typical POPs, these polymers are able to dissolve in solvents, making them solution processable, a very attractive property.^{23,24}

Covalent organic frameworks (COFs), first reported in 2005 by Yaghi *et al.*, are crystalline extended 2D or 3D organic solids formed by reversible condensation reactions.²⁵ The first COF was formed by condensation of 1,4-phenylenediboronic acid **5** in sealed ampoules at 120 degrees for three days. In the years after the discovery of the first crystalline 2D (2005) and 3D



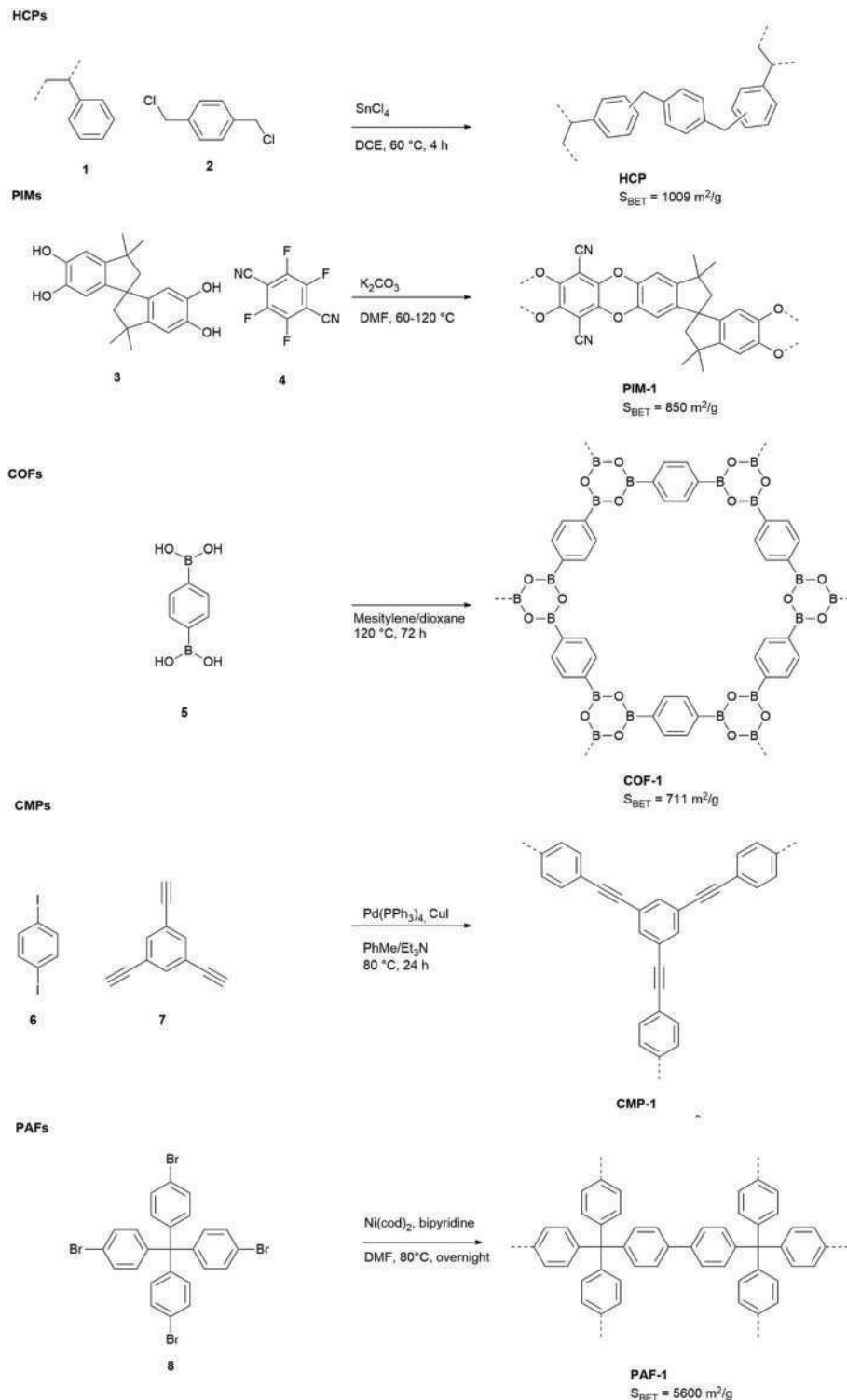
Pascal Van Der Voort

Pascal Van Der Voort is a full professor at Ghent University and the director of the Center for Ordered Materials, Organometallics and Catalysis (COMOC). His research focuses on the development of novel (hybrid) ordered porous materials, including PMOs, MOFs, COFs and CTFs. Application fields of these materials are heterogeneous catalysis, sorption, gas separation, luminescence, sensing, photocatalysis and electrocatalysis.



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Scheme 1 Examples of the different classes of POPs.^{20,23,25,30,32}

COFs (2007), research in this area has boomed. A lot of this effort has gone into identifying new suitable reactions for the synthesis of COFs. For every new reaction suitable conditions have to be developed, ensuring the formation of crystalline materials. The reactions need to be sufficiently reversible, so

that self-correction of defects is possible. One class of COFs are the covalent triazine frameworks (CTFs). These materials are typically formed by trimerization of aromatic nitriles in zinc chloride at elevated temperatures (400–500 °C) to ensure reversibility, however these harsh conditions lead to partial

carbonization and loss of crystallinity. CTFs are therefore typically amorphous with only some CTFs being crystalline.^{26–28}

Conjugated microporous polymers (CMPs) are porous polymers with fully conjugated skeletons, they can be viewed as amorphous analogues of COFs. These are typically synthesized *via* palladium catalyzed coupling reactions (Sonogashira–Hagihara, Suzuki–Miyaura, Heck) or nickel catalyzed Yamamoto couplings, but many more reaction types are known such as oxidative coupling, Schiff base formation, phenazine ring fusion, cyclotrimerization of alkynes or nitriles...^{18,29} A first example in 2007 consisted of the synthesis of **CMP-1**, formed by Sonogashira cross-coupling between 1,4-diiodobenzene **6** and 1,3,5-triethynylbenzene **7**.³⁰ Analogous to CMPs are porous aromatic frameworks (PAFs), which are formed using similar reactions. PAFs however do not possess extended π -conjugation because of the inclusion of tetrahedral, sp^3 hybridized tetraphenylmethane nodes.^{18,31} **PAF-1** was synthesized in 2009, by nickel(0)-catalyzed Yamamoto coupling of tetrakis(4-bromophenyl)methane **8** as the tetrahedral building block, leading to a porous material with extremely high surface areas ($5600\text{ m}^2\text{ g}^{-1}$).³² The silane, bismuth, tin and antimony analogues of PAFs are called element organic frameworks (EOFs).^{33,34}

POPs, together with the other porous materials, have widespread uses in adsorption, catalysis, separation, purification and energy storage or production.³⁵ Catalytically POPs can be useful as a support for metal complexes or nanoparticles,³⁶ but also as metal free catalysts. Due to their massive popularity many reviews concerning the use of POPs as catalysts have been published. However, these reviews either concern a single type of POP (*e.g.* COFs,^{37,38} CMPs...³⁹) or a single type of reaction (*e.g.* CO_2 conversion,^{40–42} chiral catalysis,⁴³ photocatalysis...^{44–48}) and more general reviews mainly discuss metal based catalysis.^{36,49–51} We therefore believe that there is room for a review offering an extensive overview on the complete field of POPs as metal free organocatalysts. POPs have been reported as metal free acid, base, hydrogen bonding and nucleophilic catalysts for a plethora of applications which we will discuss in this review. Catalytical applications where a metal is used in combination with an organocatalytical POP will also be reviewed. Next to this, special attention is given to chiral catalysis and CO_2 conversion. Lastly, we also take a critical look at the green character of these materials.

2. Acid catalysis

The catalysts now generally used for acid catalyzed reactions in industry are homogeneous, liquid acids (H_2SO_4 , HF, H_3PO_4 ...). Replacing these mineral liquid acids with porous acidic materials has many advantages, such as easy separation of the catalyst, recyclability, reduction of corrosion... all leading to greener chemical synthesis.^{52,53} Heterogeneous solid acids can be created by incorporating acidic groups in solid materials, either through direct synthesis or postfunctionalization. Many types of heterogeneous acids such as resins, zeolites and meso-

porous silicas (MCM-41,^{54,55} SBA-15⁵⁶) have been developed. In general, silicas possess a lower catalytic activity than concentrated sulfuric acid or zeolites due to the presence of hydrophilic silanol groups on the surface of these materials. In many acid catalyzed reactions (*e.g.* esterification) water is a byproduct and adsorption of this byproduct near the acidic catalytic centers will compete with the reagents (*e.g.* an alcohol) resulting in reduced catalytic activity.^{57,58} Zeolites generally possess pores that are quite small resulting in slow conversion of bulky substrates.⁵⁹ Sulfonated resins such as Amberlyst 15 can be effective acidic catalysts, but are challenged by their low surface areas and stabilities as the BET surface area of Amberlyst 15 amounts to only about $50\text{ m}^2\text{ g}^{-1}$.⁶⁰ Therefore, a lot of research has been performed to develop new, porous, fully organic acidic catalysts. This part will cover heterogeneous achiral acids, heterogeneous chiral phosphoric acids will be addressed in the part on chiral catalysts.

2.1 Sulfonic acids

In 2007, the Wu group introduced sulfonic acid moieties into purely organic mesoporous materials for the first time. To this end Fudan University (FDU)-type mesoporous polymers with cubic and hexagonal mesostructures **FDU-14** and **FDU-15** were prepared and sulfonated (Table 1, entry 1). FDU-type polymers are hydrothermally synthesized by a soft templating method where phenol **9** and formaldehyde **10** are polymerized around a templating agent, a triblock copolymer such as pluronic P123. The template is then removed, by thermal decomposition under vacuum at $350\text{ }^\circ\text{C}$, obtaining porous ($463\text{--}545\text{ m}^2\text{ g}^{-1}$) and well-ordered polymeric materials.⁶¹ Sulfonation was carried out by contacting the polymer powders with vapors from 50% oleum, as to not destroy the ordered structures by direct contact with the acid. Following this, the porosity was well retained ($447\text{--}539\text{ m}^2\text{ g}^{-1}$). The catalytic activity was evaluated for the liquid-phase Beckmann rearrangement of cyclohexanone oxime and the acetalization of hindered aldehydes. The sulfonated polymers performed much better than conventional acid resins (Dowex) or microporous zeolites (Beta, ZSM-5 or USY), especially when moving from benzaldehyde to the much more bulky 1-pyrenecarboxyaldehyde (Fig. 1). Microporous materials pose much more stringent size limitations, and thus for bulky substrates only the external surface and the area nearby the pore entrances are accessible. However FDU type polymers possess much larger pore dimensions ($>2\text{ nm}$), and therefore can accept bulkier substrates.⁵⁷

The first acid functionalized HCP was prepared by Xiao and coworkers in 2010 by sulfonation of superhydrophobic mesoporous polydivinylbenzenes (PDVB). These materials were prepared by hydrothermal polymerization of divinylbenzene (DVB) **11** in a sealed reaction medium at high temperatures and pressures (Table 1, entry 2). The solvent acts as a template and the polymer network is formed around it. Depending on the water/THF ratio different porosities were obtained. Functionalization by sulfonation was carried out by treatment with chlorosulfonic acid in dichloromethane or with sulfuric acid leading to **PDVB-*x*-SO₃H** possessing large surface areas

Table 1 POPs as acidic or hydrogen bonding catalysts

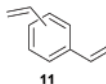
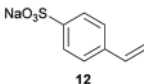
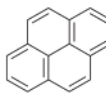
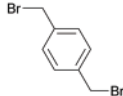
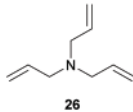
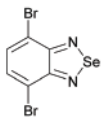
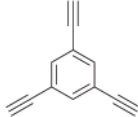
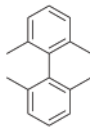
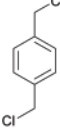
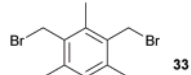
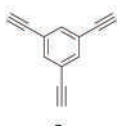
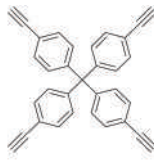
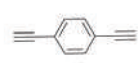
Entry: name	Monomers	Linkage	Conditions	Surface area (m ² g ⁻¹)	Ref.
1: FDU14-SO ₃ H, FDU15-SO ₃ H	  9 10	C-C	(1) 0.1 M NaOH, H ₂ O, 72 °C, 1.5 h	447–539	57
2: PDVB-x-SO ₃ H	 11	C-C	(2) Pluronic P123, H ₂ O, 72 °C, 120 h, then 80 °C, 48 h (3) 350 °C, 6 h (4) 50% SO ₃ /H ₂ SO ₄ vapors, 60 °C, 24 h (1) AIBN, THF/H ₂ O (x), r.t., 3 h, then 100 °C, 2 d	280–380	62
3: H-PDVB-x-SO ₃ H	  11 12	C-C	(2) ClSO ₃ H, CH ₂ Cl ₂ , 0 °C, 12 h (1) AIBN, THF/H ₂ O, r.t., 3 h then 100 °C, 24 h	143–535	63
4: SPPOP-1,2,3	  24 25	C-C	(2) 1 M H ₂ SO ₄ , r.t., 24 h (1) FeCl ₃ , DCE, 80 °C, 20 h	205–280	72
5: PDVTA-SO ₃ H	  26 11	C-C	(2) ClSO ₃ H, CH ₂ Cl ₂ , r.t., 48 h (1) AIBN, acetone, 120 °C, 24 h	406	73
6: COP-2	  26 7	C-C	(2) ClSO ₃ H, CH ₂ Cl ₂ , r.t., 4 h (1) Pd(PPh ₃) ₂ Cl ₂ , CuI Et ₃ N, 3 d	159	74
7: MeBP@H	  27 2	C-C	(2) ClSO ₃ H, CH ₂ Cl ₂ , 0 °C, 48 h (1) FeCl ₃ , DCE, 80 °C, 48 h	766	76
8: COP-A	  33 34	C-C	(2) ClSO ₃ H, CH ₂ Cl ₂ , 0 °C to r.t., 72 h (1) FDMA, FeCl ₃ , DCE, reflux, 20 h	1020	77
9: P(DEB), P(TEB), P(TEPM)	   7 42 41	C-C	(2) KMnO ₄ , NaOH, H ₂ O/EtOH, 30–32 h, 80 °C Rh(nbd)(acac), CH ₂ Cl ₂ , 70 °C, 72 h	711–1007	78

Table 1 (Contd.)

Entry: name	Monomers	Linkage	Conditions	Surface area (m ² g ⁻¹)	Ref.
10: mPMF		Amidine	Paraformaldehyde, DMSO, 120 °C, 1 h, then 170 °C, 72 h	930	100
11: M-POP		Amidine	MW, DMSO, 160 °C, 2 h	811	101
12: COF-SQ		Imine	6 M AcOH, mesitylene/dioxane (1/1) 120 °C, 3 d	1195	83
13: POP-TUs		Thio-urea	DMF, dioxane, EtOH or EtOH/dioxane, 60 °C, 3 d	23–49	84

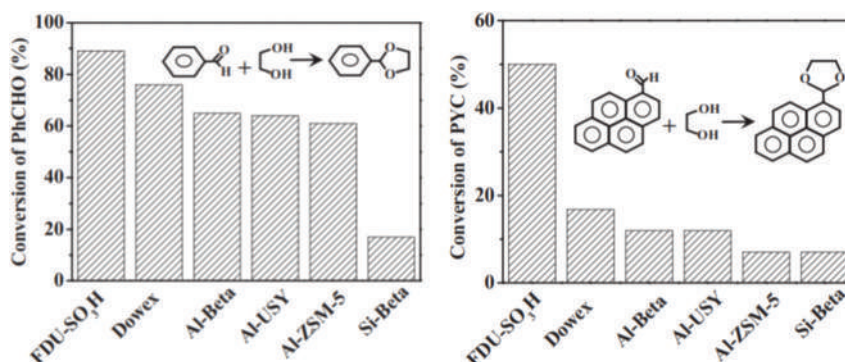


Fig. 1 FDU14-SO₃H is a more active catalyst than other acidic heterogeneous catalysts for acetalization reactions, especially for bulky substrates. Reproduced from ref. 57.

(280–380 m² g⁻¹), mesoporosity and a high density of sulfonic acid groups (3.9–4.1 mmol g⁻¹). The catalytic activity was evaluated by esterification of acetic, hexanoic and lauric acid with ethanol or cyclohexanol and by acylation of anisole with acetyl chloride. Higher activities than solid catalysts such as Amberlyst 15 or silicas (SBA-15-Pr-SO₃H, SBA-15-Ar-SO₃H) were obtained.⁶²

Liu *et al.* prepared HCPs by copolymerization of a sulfonated monomer, sodium *p*-styrene sulfonate **12**, with DVB **11** resulting in very hydrophobic acid catalysts **H-PDVB-*x*-SO₃H**'s where *x* is the molar ratio sulfonate to DVB ranging from 0.05 to 1.5 (Table 1, entry 3). Polymerization took place under solvothermal conditions and after ion-exchange by washing with sulfuric acid highly porous networks (143–535 m² g⁻¹) with abundant acidic sites (0.26–1.86 mol g⁻¹) were formed. The

hydrophobicity of the polymers was studied by measurement of the contact angle of a water droplet in contact with the material. This angle ranged from 118° to 148° pointing to the high hydrophobicity of **H-PDVB-*x*-SO₃H**'s. **PDVB-SO₃H** and Amberlyst 15 possess much lower contact angles of, respectively, 38° and 8°. These polymers are much more hydrophilic which correlates well with their higher acid loading of 4 and 4.7 mmol acid sites per g. The catalytic activity was evaluated for the esterification of acetic acid with cyclohexanol or 1-butanol, with conversion depending on the acid loading reaching, respectively, 55–78% and 70–90%. The acetalization of benzaldehyde with ethylene glycol could also be efficiently catalyzed, reaching 77–91% conversion. **H-PDVB-*x*-SO₃H**'s performed ~20–30% better than **PDVB-SO₃H** or Amberlyst 15 and comparable to sulfuric acid, the homogeneous analogue.

Importantly the most hydrophobic POP, **H-PDVB-0.05-SO₃H**, showed the highest turnover frequency (TOF). This proves that the isolation of water from the catalytic sites leads to a significant enhancing of the reaction rate.⁶³

The same group then used these superhydrophobic acid catalysts for hydroxymethylfurfural (HMF) **15** production by acid catalyzed dehydration of fructose **14**. Fructose, a simple carbohydrate that can be obtained from glucose **13** and thus also from cellulose, can in this way be transformed to a potential platform chemical. However this reaction typically is accompanied by yield reduction by hydration of HMF **15** to levulinic acid **16** and formic acid **17** (Scheme 2).^{64–66} Using a superhydrophobic **H-PDVB-0.05-SO₃H** based catalyst the hydration can be prevented by isolating the acidic sites from water. In this way high yields (>99%) with HMF as a sole product were reached. Using H₂SO₄ or Amberlyst 15, much lower yields of 54–62% and 46–66%, respectively, with formation of side products by hydration were observed. Furthermore, the authors developed a one-pot procedure directly converting glucose **13** *via* fructose **14** into HMF **15** by combining this acid catalyst with a hydrophilic solid base synthesized by copolymerization of divinylbenzene, 1-vinylimidazole, and *N,N*-methylenediacrylamide and this combined system could reach high yields of up to 95%.⁶⁷

Noncovalent interactions around catalytic centers have an enormous influence on the selectivity and activity of catalysts. In enzymes, multiple non-covalent substrate–catalyst interactions, individually weak but collectively strong, stabilize transition states.⁶⁸ Synthetically precise control over the environment of a catalytic site, particularly in heterogeneous catalysts, remains a big challenge. In this light, Sun *et al.* encapsulated a polymeric solvent analogue in a COF functionalized with acidic sites to modulate the reaction environment (Scheme 3). These authors synthesized intermediate COFs *via* a three component condensation reaction with 1,3,5-tris(4-aminophenyl)benzene **18**, 2,5-dihydroxyterephthalaldehyde **19** and 2,5-dimethoxyterephthalaldehyde **20**. The phenolic groups of these COFs were then functionalized by reaction with 1,2,2-trifluoro-2-hydroxy-1-trifluoromethylethane-sulfonic acid sultone **21**. Polyvinylpyrrolidone (PVP) could subsequently be encapsulated by *in situ* polymerization of 1-vinyl-2-pyrrolidone **22** in the presence of the COF. PVP **23** is a polymeric ana-

logue of *N*-methyl-pyrrolidinone (NMP), a high boiling and difficult to remove solvent known to suppress formation of side products in fructose dehydration to HMF.^{69,70} Using **PVP@[SO₃H]_{0.17}-COF** 100% conversion of fructose with 99% HMF yield was possible using THF as an easily removable solvent. This compared favorably to sulfonated resins such as Nafion™ NR50, Amberlyst 15 or homogeneous *p*-toluenesulfonic acid which only reached 9–29% fructose conversion and 5–21% HMF yield.⁷¹

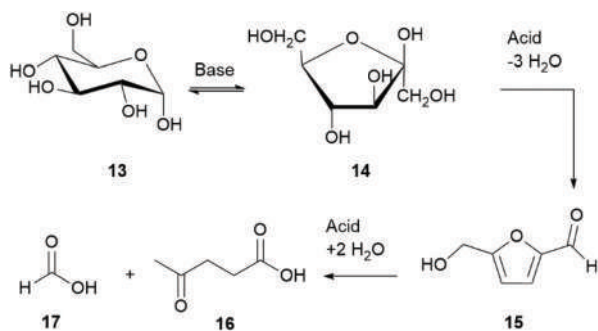
Staying in the field of the renewable resources, Kundu *et al.* synthesized pyrene-based pops **PPOP-1,2,3** through Friedel–Crafts alkylation between pyrene **24** and 1,4-bis-(bromomethyl)benzene **25** at different molar ratio's in the presence of FeCl₃ as a catalyst. These materials were functionalized with sulfonic acid groups (2.15–3.22 mmol g^{−1}) by treatment with chlorosulfonic acid (Table 1, entry 4). These sulfonated polymers **SPPOP-1,2,3** were efficient catalysts for the synthesis of biodiesels at room temperature *via* (trans)esterification.⁷² The same group prepared another sulfonated POP by postfunctionalization of **PDVTA-1**, a porous co-polymer prepared from divinylbenzene **11** and triallylamine **25** (Table 1, entry 5). Similar to the pyrene based materials these were highly active esterification catalysts for biodiesel production at room temperature.⁷³

Another sulfonated POP for biodiesel production was prepared by Maiti *et al.* by Sonogashira coupling of triethynylbenzene **7** with brominated benzoselenadiazole **26** leading to **COP-1**. This material was then sulfonated furnishing **COP-2** (Table 1, entry 6) and used as an effective catalyst for the transesterification of free fatty acids at room temperature with yields reaching up to 100%.⁷⁴

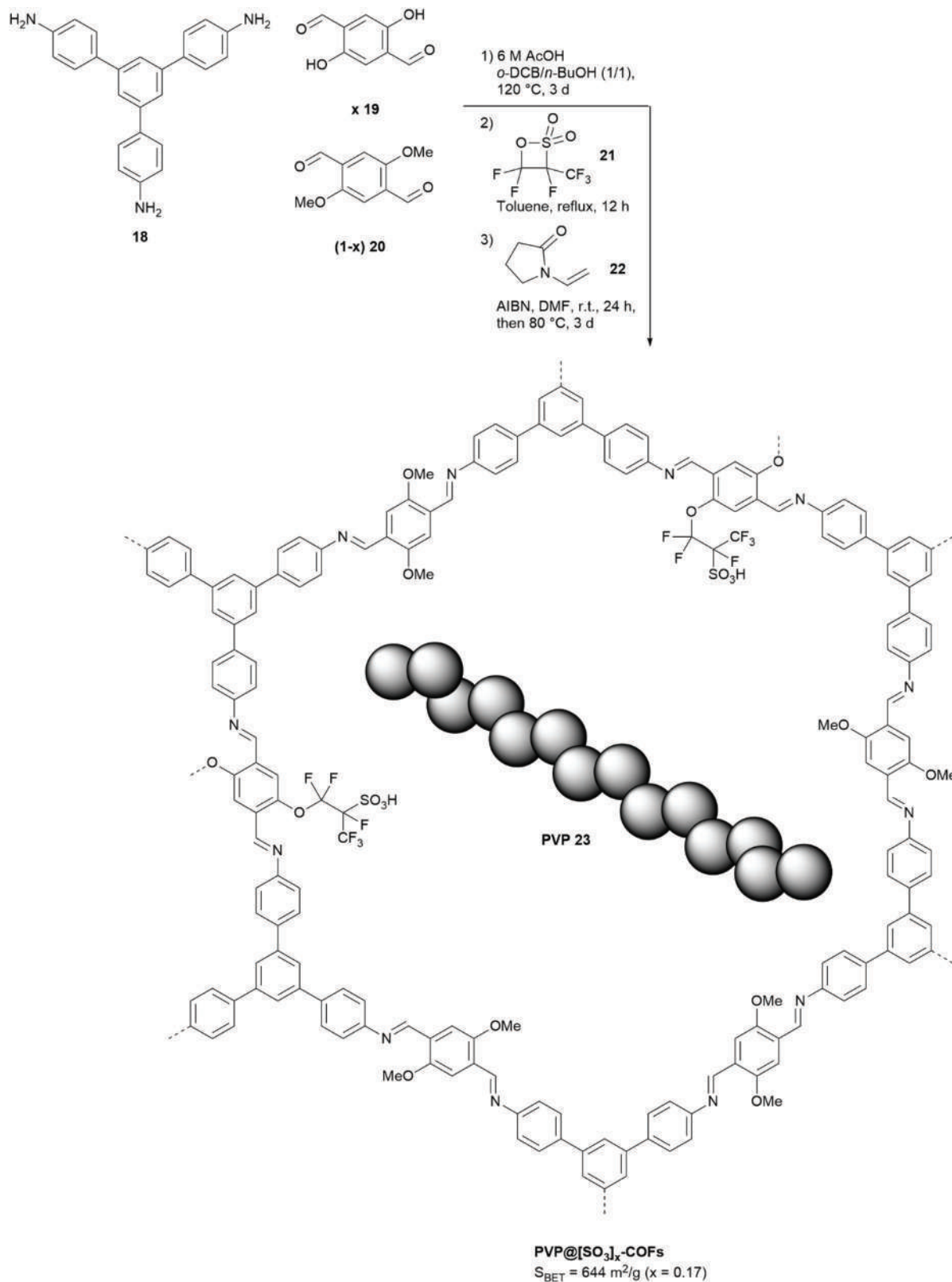
Yadav *et al.* prepared a sulfonated HCP **MeBP@H** through postmodification of a HCP consisting of tetramethylbiphenyl **27** crosslinked with 1,4-bis(chloromethyl)benzene **2** (Table 1, entry 7). **MeBP@H** was used as an acid catalyst for the synthesis of photochromic diphenylbenzo/naphthopyrans **30** from phenols or naphthol's **29** and propargyl alcohols **28** (Scheme 4).⁷⁵ A wide range of substrates could be prepared in generally very good yields (54–95%). Triazole synthesis by cycloaddition of sodium azide to β-nitrostyrenes **31** could also be efficiently catalyzed, with a wide range of substituted β-nitrostyrenes **31** showing good conversion (86–95%). The authors reported that **MeBP@H** could be recycled at least ten times with no loss of activity.⁷⁶

2.2 Carbon based acids

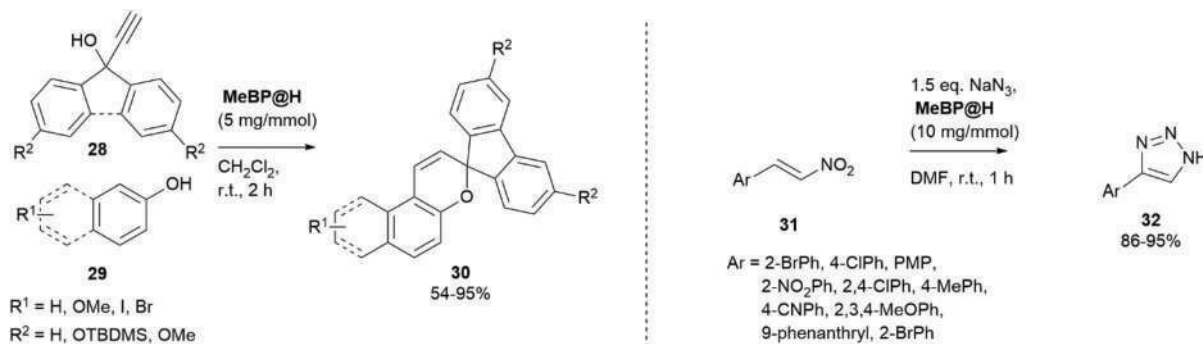
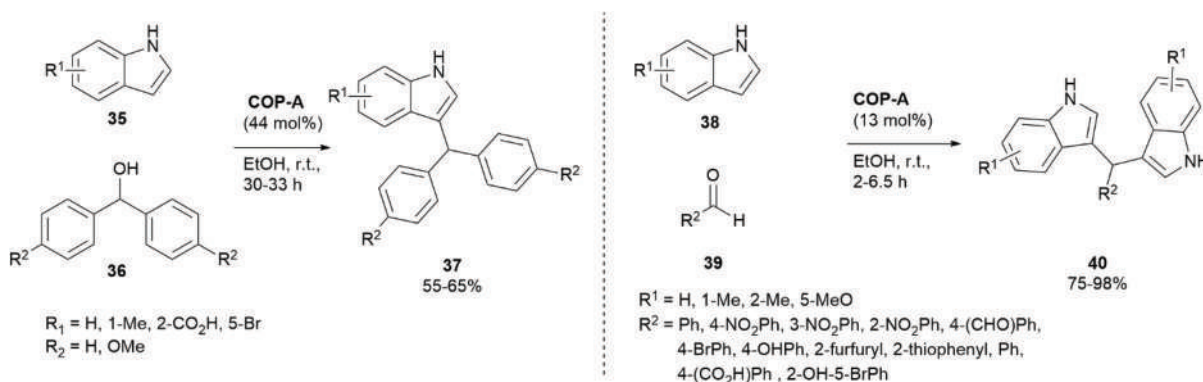
Weaker, carbon based acids can also be immobilized on porous polymers. In 2014, the Bhaumik group prepared POPs with free carboxylic acids by post-synthetic benzylic oxidation. A porous polymer was synthesized through Friedel–Crafts based FeCl₃ catalyzed crosslinking between 2,4,6-tris(bromomethyl)mesitylene **33** and 4,4'-bis(bromomethyl)-1,1'-biphenyl **34**. Treatment of this material with alkaline KMnO₄ oxidized the benzylic carbons furnishing **COP-A** with a high surface area of 1020 m² g^{−1} (Table 1, entry 8). **COP-A** possessed abundant acidic sites (4.4 mmol g^{−1}) and could be used as an effective heterogeneous catalyst for indole C3 functionalization



Scheme 2 HMF production by isomerization and dehydration of glucose.



Scheme 3 Synthesis and postfunctionalization of a COF for HMF production.⁷¹

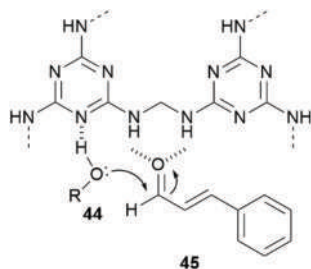
Scheme 4 Pyran and triazole synthesis catalyzed by MeBP@H.⁷⁶Scheme 5 Indole C3 functionalization with benzhydrols 37 or aldehydes 40 using COP-A as a catalyst.⁷⁷

using benzhydrols 36 or aldehydes 39 as electrophiles (Scheme 5). For benzhydrols high catalyst loadings (44 mol%) and rather long reaction times were used and only moderate yields (55–65%) were attained. The aromatic aldehydes gave better results reaching high yields with lower catalyst loading and reaction times for a wide range of aldehydes. COP-A could be recycled at least five times, however yield reduction and reduction of the surface area to 740 m² g^{−1} was observed.⁷⁷ Even weaker acidic groups, such as terminal ethynyl hydrogens, can serve as acid catalysts. Sekerová *et al.* prepared HCPs by rhodium catalyzed crosslinking of monomers with two, three or four terminal ethynyl groups: 1,4-diethynylbenzene (DEB) 41, 1,3,5-triethynylbenzene (TEB) 7, tetrakis(4-ethynylphenyl)methane (TEPM) 42 (Table 1, entry 9). The resulting polymers were highly porous (711–1007 m² g^{−1}) and possessed residual, unreacted acidic ethynyl groups (0.58–0.8 mmol g^{−1}). The acetalization of methanol with aldehydes gave moderate to high yields (50–98%) for the best performing network **P** (TEB). Ketones, however, reacted much more sluggishly (13–36%) and esterification of acetic, propionic and *cis*-hex-3-enoic acid gave only low yields (30–39%). The heterogeneous catalysts however were more active than their homogeneous counterpart phenylacetylene. The higher reactivity was explained by the increased acidity of the terminal hydrogen in the porous network due to the larger conjugated system formed by polymerization.⁷⁸

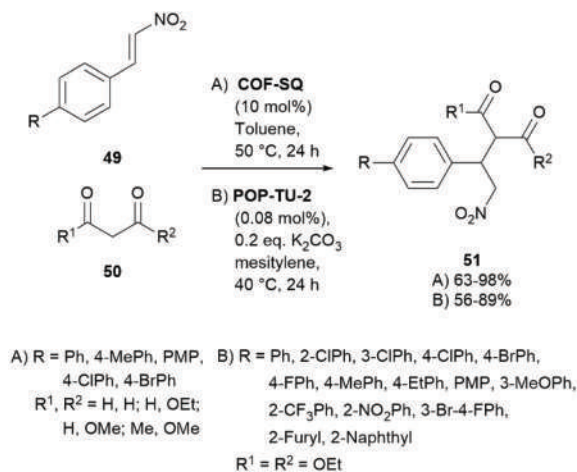
2.3 Hydrogen bond catalysis

Hydrogen bonding organocatalysis forms an attractive alternative to Lewis acids.⁷⁹ The difference between polymers that catalyze reactions *via* hydrogen bonds and polymers containing basic nitrogens is not always very pronounced. Hydrogen bond forming polymers that act as catalysts in typically acidic transformations (*e.g.* acetalization) or hydrogen bond catalyzed transformations (*e.g.* Michael addition) will be discussed here. N-Based polymers for other reactions will be discussed with the basic catalysts.

Zhang and coworkers prepared an aminated linked POP **mPMF** by polymerization of melamine 43 with formaldehyde 10 in DMSO (Table 1, entry 10). This material possessed high porosity and served as an efficient hydrogen-bonding catalyst for the chemoselective acetalization of aldehydes, converting aldehydes, but not the less reactive ketones or esters. The catalytic activity is explained by dual activation: hydrogen bonding of the melamine nitrogens activating the alcohol 44 and hydrogen bonding of the aminated moieties activating the aldehyde 45 (Scheme 6).⁸⁰ Analogously, **MPOP** was synthesized by condensation of melamine 43 with terephthalaldehyde 46 in DMSO under microwave irradiation (Table 1, entry 11). This material possessed a high surface area (811 m²/g) and was an effective catalyst for the acetalization of three different aldehydes with methanol or ethylene glycol in high yields (68–95%).⁸¹



Scheme 6 Catalytic activity of mPMF by alcohol and carbonyl activation.¹⁰⁰



Scheme 7 Michael addition catalyzed by COF-SQ or POP-TU-2.^{83,84}

The same POP has also been reported as a catalyst for the Knoevenagel condensation and styrene oxidation (*vide infra*).^{82,83}

Squaramide moieties can be excellent hydrogen bond catalysts, possessing hydrogen bond donating and accepting functionalities owing to their carbonyl and N–H groups. Self-aggregation can pose availability problems however, but can be solved conveniently by incorporating the catalytic moieties in heterogeneous frameworks, such as in MOFs constructed with squaramide based linkers.^{80–82} A squaramide decorated framework **COF-SQ** was synthesized by Li *et al.* through condensation of squaramide amine linker **47** and tritopic aldehyde **48** (Table 1, entry 12). This material was reported as a good catalyst for the Michael addition of dicarbonyl compounds **50** with nitrostyrenes **49** (Scheme 7A). A wide range of electrophiles and nucleophiles could be converted in high yields (63–98%). **COF-SQ** was stable, could be reused at least four times and showed much higher activity than the homogeneous monomer **47** and a model compound consisting of the monomer condensed with benzaldehyde.⁸³

Recently, Wu *et al.* synthesized novel POPs based on the condensation of amine **52** with isothiocyanate **53** (Table 1, entry 13). These materials **POP-TUs** possessed rather low porosities, which seems to be a general issue with urea or thiourea based POPs. This is postulated to be caused by hydrogen bonding interactions between reactant and solvent molecules during framework syn-

thesis. The formed thiourea networks were active catalysts in the Michael reaction of nitrostyrenes **49** with diethylmalonate **50** (Scheme 7B). A very wide range of substrates could be converted in high yields (56–89%) using low catalyst loadings.⁸⁴

2.4 Outlook on POPs as acid catalysts

To conclude, sulfonated POPs reach efficiencies comparable to or higher than sulfuric acid, the homogeneous analogue and typically higher than sulfonated resins such as Amberlyst-15. This resin is a commonly available solid acid for which many applications as a green catalyst have been described: etherification, olefin hydration, esterification...^{85–87} The higher efficiency of the POPs is caused by: their generally higher porosity, in some cases a more pronounced mesoporosity (*e.g.* the FDU type polymers) and in other cases the highly hydrophobic character of the used POPs.

A plethora of catalytic systems have already been described for the production of HMF, however, unless when using harsh conditions (such as heating at 160 °C under microwave irradiation) quite low yields are reached.^{88,89} A state of the art heterogeneous (metal free) catalyst would be an Amberlyst resin used in DMSO at 120 °C.^{89,90} The performance of the two catalytic systems described, which worked well at 100 °C in THF, giving no side reactions, can thus be considered as state of the art.

Catalytic biodiesel production has been extensively reviewed and typical catalysts are acids, bases or enzymes (lipases).^{91–93} Homogeneous cheap bases, such as KOH or NaOH, are preferred in industry. However, they pose environmental concerns and no regeneration of these catalysts is possible. Moreover, alkali catalysts, while more active than acidic catalysts^{92,93} are incompatible with the presence of water and free fatty acids (FFAs) due to saponification reducing the yield and quality of the resulting biodiesel.^{94,95} Acids, whilst less active than bases for this transformation tolerate FFAs because they also catalyze esterification, allowing the use of lower quality waste oil.⁹³ Generally, in literature very harsh conditions are reported for acceptable conversions under acidic catalysis. Sulphated metal oxides, metal oxide mixtures and supported heteropolyacids are reported, however, they suffer from high required temperatures, leaching or deactivation in the presence of water.⁹³ The organic solid acids consist mainly of resins such as Amberlyst-15 and these are less effective than the POPs we discussed, providing lower conversions or requiring higher temperatures.⁹⁶

The POPs discussed here as hydrogen bond catalysts, whilst interesting materials, are lagging behind the state of the art for homogeneous hydrogen bond mediated catalysis, which is definitely already in the catalysis of enantioselective transformations.

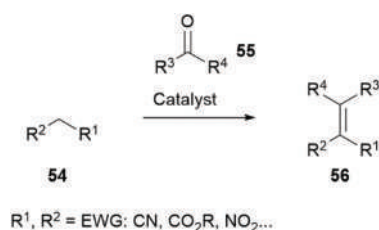
Regarding the synthesis of the polymers, in the case of the HCPs synthesized by radical crosslinking, **PDVB-x-SO₃H**, **H-PDVB-x-SO₃H**, **PDVTA-SO₃H** (Table 1, entries 2, 3 and 5), this was comparable to that of Amberlyst-15, *i.e.* crosslinking by co-polymerization with divinylbenzene followed by sulfonation. In the case of the amidine linked polymers **mPMF** and **M-POP** (Table 1, entries 10 and 11) no catalysts or dangerous solvents were needed, however, in many cases the synthesis is more problematic. The HCPs synthesized by Friedel–Crafts

crosslinking **SPPOP-1,2,3**, **MeBP@H** and **COP-A** (Table 1, entries 4, 7 and 8) typically use very large excesses of corrosive Lewis acids (FeCl_3 , AlCl_3) and toxic and carcinogenic DCE as a solvent. The CMPs **COP-2** and **P(DEB)**, **P(TEB)** and **P(TEPM)** (Table 1, entries 6 and 9) use precious metal based catalysts and non-recommended solvents (DCE, CH_2Cl_2 , Et_3N).⁹⁷ The ethynyl functionalized building blocks **7**, **41** and **42** also pose problems, being very expensive or even commercially unavailable. The COF **PVP@[SO₃H]_{0.17}-COF** (Scheme 3) while being very performant, has a problematic synthesis, which extends into COF synthesis in general. All three building blocks **18**, **19** and **20** are barely commercially available and require multiple step synthesis, using hazardous reagents. Triflic acid and hydrazine were used in the synthesis of the amine **18**. A blanc chloromethylation, known to produce highly carcinogenic bis (chloromethyl)ether as a side product⁹⁸ is one of the steps to synthesize the aldehydes **19** and **20**. Moreover, the polymerization itself is only reported (as is typical for COFs) on a small scale (0.5 mmol, ~200 mg), required heating at 120 °C for three days and three more postfunctionalization steps. **COF-SQ** (Table 1, entry 12) is similarly hampered by difficult to synthesize building blocks. Aldehyde **48** is typically produced by a very inefficient synthesis starting from 1,3,5-benzenetricarboxylic acid requiring esterification to the triester, reduction to the triol with hazardous LiAlH_4 and oxidation with carcinogenic hexavalent chromium based PCC.⁹⁹ The polymerization into the COF itself used non-recommended solvents, required heating at 120 °C for three days and at was again performed at a very small scale (0.15 mmol, ~50 mg).

3. Basic and nucleophilic catalysts

3.1 The Knoevenagel condensation

The condensation between a carbonyl group **55** and active methylene compounds **54**, or the Knoevenagel condensation, is a powerful and frequently used reaction for the formation of C=C bonds and is applied in industry (Scheme 8).^{102,103} Typically homogeneous catalysts^{104–107} are used, but many heterogeneous catalysts such as MOFs,^{108,109} PMOs,¹¹⁰ zeolites¹¹¹ and graphene-based materials^{112,113} have been developed. The Knoevenagel condensation serves as a reference reaction of sorts for heterogeneous basic catalysts. In general these materials contain high amounts of nitrogen and have high CO_2 absorption and selectivity.



Scheme 8 The Knoevenagel condensation.¹⁰³

In one of the earliest reports on porous polymers applied in the field of heterogeneous organocatalysis, Makowski *et al.* utilized a mesoporous polybenzimidazole network **mp-PDI** as a catalyst for the Knoevenagel condensation. **mp-PDI** was synthesized by LUDOX templated polybenzimidazole synthesis of monomers **57**, **58** and **59** (Table 2, entry 1).¹¹⁴ LUDOX HS-40 is a commercially available 40 wt% dispersion of silica nanoparticles, with a diameter of about 13 nm, which act as a hard template in the polymerization reaction. By heating of the monomer mixture up to 400 °C, complete ring closure could be achieved. The template was then removed by etching with ammonium hydrogen difluoride (NH_4HF_2), followed by washing with dilute sodium hydroxide to deprotonate the imidazolium moieties. High yields of up to 100% were reported for the reaction of ethyl cyanoacetate or malononitrile with a range of aldehydes at room temperature or at 100 °C.¹¹⁵

Liu *et al.* synthesized another porous polymer **JUC-Z12** by benzimidazole formation between tetra(4-formylphenyl) methane **61** and 3,3'-diaminobenzidine **60** (Table 2, entry 2). **JUC-Z12** possessed a large surface area of $750 \text{ m}^2 \text{ g}^{-1}$ and by virtue of its basic benzimidazole moieties could serve as an efficient catalyst for the Knoevenagel reaction.¹¹⁶

Another benzimidazole containing polymer was synthesized by Wang and coworkers through Sonogashira coupling of brominated benzimidazole **64** with tritopic building block **62** or tetratopic building block **63** furnishing **BPOP-1** and **BPOP-2** (Table 2, entry 3). The latter possessed good porosity ($668 \text{ m}^2 \text{ g}^{-1}$), however the former was non-porous for nitrogen. Both POPs were capable of CO_2 absorption with **BPOP-1** and **BPOP-2** absorbing, respectively, 50 mg g^{-1} and $103 \text{ mg g}^{-1} \text{ CO}_2$ (273 K, 1 bar). Predictably due to its higher porosity **BPOP-2** was able to catalyze the Knoevenagel condensation better.¹¹⁷

Dang *et al.* synthesized heptazine based polymer networks **Cy-pip** via coupling of cyameluric chloride **66** and piperazine **65** (Table 2, entry 4). Heptazines, with their large conjugated systems consisting of three condensed triazine rings have already found widespread application in heptazine based carbon nitrides. The resulting framework had a relatively low BET surface area of $116 \text{ m}^2 \text{ g}^{-1}$. The large nitrogen content furnished **Cy-pip** with a big CO_2 uptake capacity (103 mg g^{-1} , 1 bar, 273 K) and catalytic activity for the Knoevenagel reaction, converting a range of aldehydes in generally good yields (up to 97%).¹¹⁸

Carta *et al.* applied a polymerization reaction based on the formation of Tröger's base on triamino-triptycene monomers **67** (Scheme 9 and Table 2, entry 5). Tröger's base is a bridged bicyclic amine, formed by condensation of *p*-toluidine and formaldehyde dimethyl acetal (FDMA) **68**. The basicity of its nitrogen is enhanced due to the constraints in the rigid bicyclic system reducing the conjugation of the free nitrogen electrons into the aromatic rings.¹¹⁹ After polymerization of monomers **67** in trifluoroacetic acid, polymers **PIM-Tb-Trip1,2** with a high density of basic amine sites of up to 8.5 mmol g^{-1} and high surface areas of up to $1035 \text{ m}^2 \text{ g}^{-1}$, were obtained. Copolymerization with a flexible, bis-amine co-monomer **69** led to **PIM-Tb-Trip1**. The co-monomer allows formation of a more flexible network that is able to fill space more efficiently,

Table 2 POPs for the Knoevenagel condensation

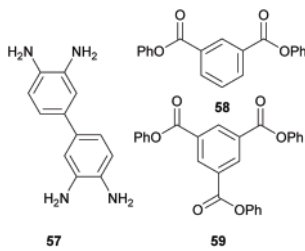
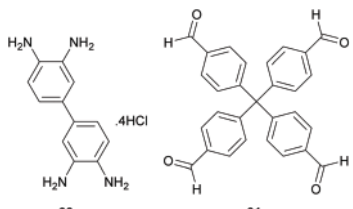
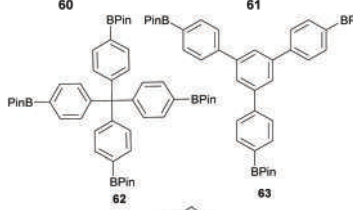
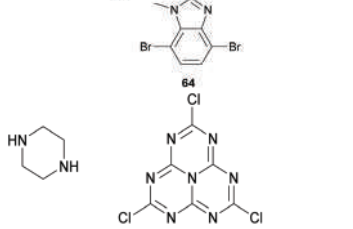
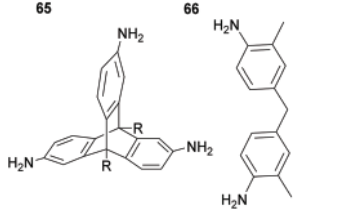
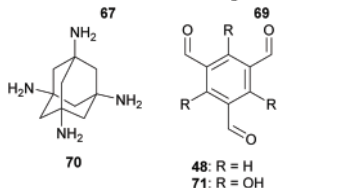
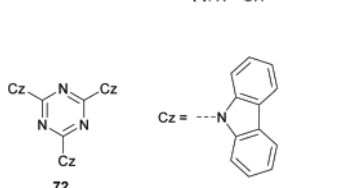
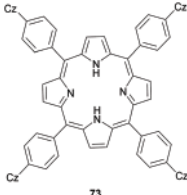
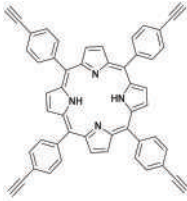
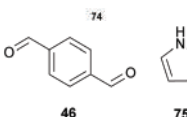
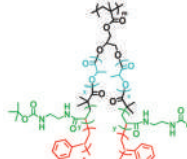
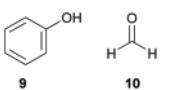
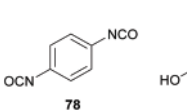
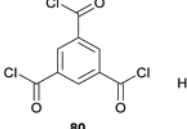
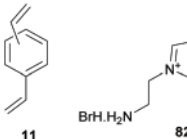
Entry: name	Monomers	Linkage	Conditions	Surface area (m ² g ⁻¹)	Ref.
1: Mp-PDI		Benzimidazole	(1) LUDOX-HS-40, 200 °C, 1.5 h then 400 °C, 0.5 h	180	114 and 115
2: JUC-Z12		Benzimidazole	(2) 4 M NH ₄ HF ₂ , r.t., 3 d (3) 0.1 M NaOH DMF, -40 °C to r.t., 130 °C, 3 d	750	116
3: BPOP-1/2		C-C	Pd(PPh ₃) ₄ , K ₂ CO ₃ , dioxane, 110 °C, 24 h	0–668	117
4: Cy-pip		N-C	DIPEA, THF, 0 °C, 4 h then r.t., 4 h then reflux, overnight	116	118
5: PIM-Tb-Trip1/2/3		N-C	FDMA, TFA, r.t., 24 h	1.5–1035	120
6: BF-COF-1/2		51: imine	3 M AcOH, mesitylene, 120 °C, 5 d	51 (BF-COF-1): 730	121
7: MFCMP-1		52: β-keto enamine C-C	FeCl ₃ , CHCl ₃ , reflux, 72 h	52 (BF-COF-2): 680 843	123

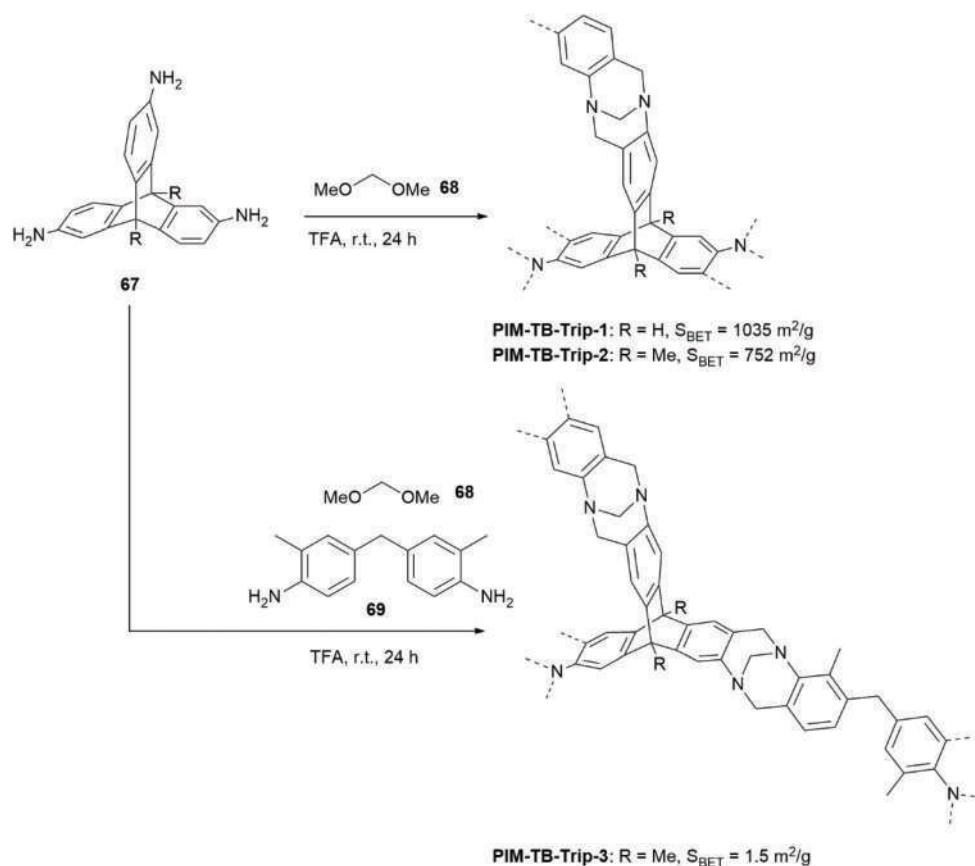
Table 2 (Contd.)

Entry: name	Monomers	Linkage	Conditions	Surface area (m ² g ⁻¹)	Ref.
8: HCP-TCPP		C-C	FDMA, TfOH, <i>o</i> -DCB, 100 °C, 12 h	1050	124
9: HPE-CMP		C-C	Pd(PPh ₃) ₂ Cl ₂ , CuI, THF/Et ₃ N, 80 °C, 72 h	662	125
10: Fe-PoP-1		Porphyrin	FeCl ₃ , AcOH, r.t., 3 h then 180 °C, 72 h	875	126 and 127
11: NH2-MONNs		C-C	(1) FDMA, FeCl ₃ , DCE, 80 °C, 14 h	936	129
12: Urea-MPs		N-C, C-C	(2) Aq. HCl, dioxane, 90 °C, 24 h, then NaOH/H ₂ O, MeOH, r.t., 12 h (1) NaOH, 70 °C, 2 h	258–403	130
13: MPU		Urethane	(2) F127, EtOH, 120 °C, 24 h (3) 350 °C, 4 h DMSO, 150 °C, 72 h	312	131
14: Am-POP		Amide	Et ₃ N, THF, 0 °C to r.t., 18 h	—	132
15: PAMBn (<i>n</i> = 82/11, 0.5–5)		C-C	(1) AIBN, EtOH/H ₂ O (3/1), 80 °C, 24 h (2) 1 M NaOH, H ₂ O, r.t., 72 h	123–429	134

and thus the resulting material possessed no surface area. All three materials were able to catalyze the Knoevenagel condensation. **PIM-Tb-Trip3** was as active as homogeneous Tröger's base, while for **PIM-Tb-Trip1,2** the turnover number and frequency (TON and TOF) indicate that the catalytic units embedded in the polymer are more than twice as active then when freely soluble as a homogeneous catalyst.¹²⁰

The first application of a 3D COF as a heterogeneous catalyst was reported by Fang *et al.* in 2014. These authors utilized adamantylamine based COFs as amine base catalysts for the

Knoevenagel condensation. Two 3D COFs were formed by condensation of tetrahedral alkyl amine 1,3,5,7-tetraaminoadamantane **70** with 1,3,5-triformylbenzene **48** or triformylphloroglucinol **71** (Table 2, entry 6). Due to the alkylamine building block being endowed with higher basicity than aromatic amines, the formed imines were more basic than in the typically fully aromatic imine linked COFs. **BF-COF-1** and **BF-COF-2** were active in the Knoevenagel condensation and importantly showed very high size selectivity. The reaction of benzaldehyde with malononitrile gave almost full conversion of 96% or 98% for **BF-COF-1**



Scheme 9 Synthesis of PIM-TB-Trip-1–3 by Tröger's base formation.¹²⁰

and **BF-COF-2**, respectively, however larger substrates such as 4-methylbenzaldehyde, 4-phenylbenzaldehyde, 4-(4-methylphenyl)benzaldehyde showed almost no conversion (2–4%). The product of the reaction with benzaldehyde has a size of $7.6 \times 10.4 \text{ \AA}^2$ and is small enough to fit inside the pores, which have a size of $7.8 \times 11.3 \text{ \AA}^2$ and $7.7 \times 10.5 \text{ \AA}^2$ for **BF-COF-1** and **BF-COF-2**, respectively. However for the larger substrates, the products no longer fit inside the pores, thus the reaction is only possible at the outer surface of the materials and therefore is much slower.¹²¹ The aminated linked POP formed by condensation of melamine **43** with terephthalaldehyde **46** in DMSO (Table 2, entry 11) could also efficiently catalyze the Knoevenagel condensation of aromatic aldehydes with ethyl cyanoacetate in a green solvent, water, at 120°C under microwave showing good conversions and selectivities of 44–99% and 65–99%, respectively, after only ten minutes of reaction.¹²²

Zhang *et al.* synthesized a carbazole based polymer **MFCMP-1** by oxidative polymerization of easily synthesized 2,4,6-tris-(carbazolo)-1,3,5-triazine **72** (Table 2, entry 7). The resulting highly porous ($843 \text{ m}^2 \text{ g}^{-1}$) material was multifunctional, showing high CO_2 absorption capacity of 16.2 wt% or 3.69 mmol g^{-1} (273 K, 1 bar) and great catalytic activity for a range of aldehydes in the Knoevenagel condensation. Next to this, it demonstrated selective fluorescence quenching in presence of nitroaromatic compounds, an useful luminescent property for the detection of explosive compounds.¹²³

A hypercrosslinked porous polyporphyrin was prepared by Feng *et al.* by crosslinking of tetracarbazole substituted porphyrin **73** with FDMA **68** (Table 2, entry 8). The resulting material **HCP-TCPP** possessed a high surface area of $1050 \text{ m}^2 \text{ g}^{-1}$ and was an effective catalyst for the Knoevenagel condensation between various aldehydes and malononitrile with yields ranging from 85 to 95%.¹²⁴ Liu *et al.* synthesized a metal free porphyrin linked polymer **HP_E-CMP** by alkyne–alkyne homocoupling of building block **74** furnishing a highly porous ($662 \text{ m}^2 \text{ g}^{-1}$) material with a high carbon dioxide uptake of 3.58 mmol g^{-1} (273 K, 1 bar) and good activity in the Knoevenagel reaction (Table 2, entry 9). The material could be recycled at least ten times and in a large scale experiment with one gram of benzaldehyde, only a milligram of catalyst resulted in a high yield of 92% after ten hours.¹²⁵ Another porphyrin POP **Fe-PoP-1** was synthesized by Bhaumik and coworkers through FeCl_3 catalyzed aromatic substitution of pyrrole **75** and terephthalaldehyde **46** (Table 2, entry 10).¹²⁶ It should be mentioned that this polymerization reaction resulted in very low yields (21–44%). Nevertheless, the resulting bifunctional material possessed basic sites able to catalyze Knoevenagel condensations of malononitrile with a range of aldehydes. Furthermore, the Fe^{III} sites were able to catalyze selective oxidation reactions of a wide range of alcohols to aldehydes or ketones using *tert*-butyl-hydroperoxide as oxidant.¹²⁷

Most existing POPs possess monomodal porosity. Constructing materials with well controlled hierarchical poro-

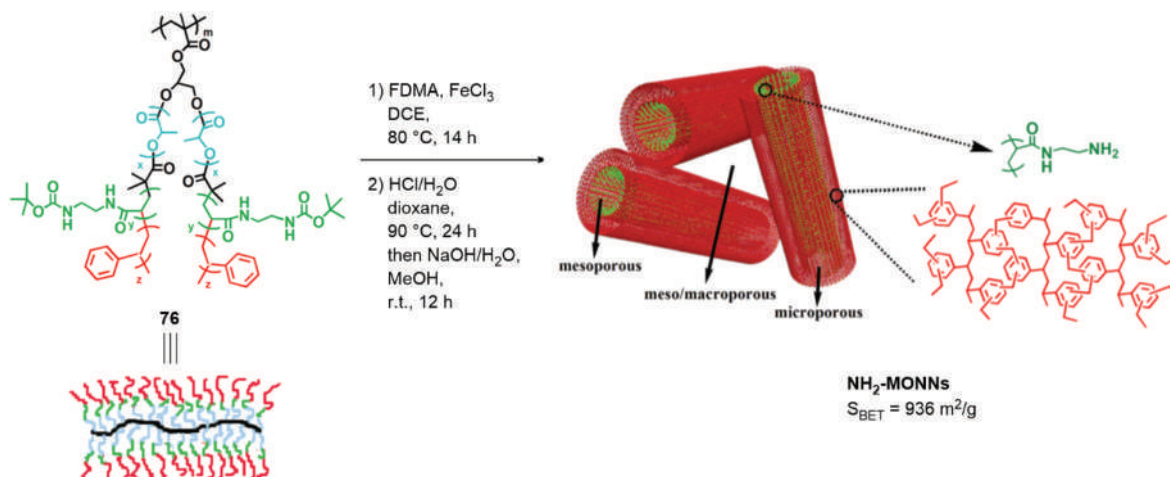
sity can lead to higher surface areas and better mass transfer. Ideally continuous macroporous channels are combined with micro- and mesopores. Zhang *et al.* developed a promising methodology to synthesize hierarchical porous materials by templating of core-shell bottlebrushes. Bottlebrush copolymers are highly branched macromolecules, possessing comb like architectures with steric repulsions of the side chains constraining the backbone of the polymer in an extended chain conformation.¹²⁸ Hypercrosslinking of the styrene shell of bottlebrush **76** followed by etching of the PLA core and Boc-deprotection led to formation of amino functionalized microporous organic nanotube networks **NH₂-MONNs** with a BET surface area of 936 m² g⁻¹ (Scheme 10 and Table 2, entry 11). This material could serve as a highly efficient catalyst in the Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate with conversion reaching 97% after only fifteen minutes. A nonporous polymer analogue and the homogeneous NH₂-bottlebrush reacted much slower with conversions reaching only 14% and 81%, respectively, after 45 minutes. The **NH₂-MONNs** could be recycled more than ten times with no significant decrease in catalytic activity and a range of aldehydes were reacted in high yields (85–99%). Moreover, **NH₂-MONNs** could also catalyze the Henry reaction between *p*-nitrobenzaldehyde and nitromethane in 99% yield after seventeen hours. Analogous polymers have also been used to perform one-pot deacetalization-Knoevenagel reactions (*vide infra*).¹²⁹

Similarly, Zhu *et al.* prepared urea functionalized mesoporous polymers **urea-MPs** through polymerization of phenol **9**, formaldehyde **10** and urea **77** around a block copolymer (F127), followed by calcination at 350 °C to remove the template. Depending on the urea content surface areas of 258 to 403 m² g⁻¹ were reached (Table 2, entry 12). **Urea-MPs** were good catalysts for the Knoevenagel condensation in water, reaching high yields (up to 94%) for both aryl aldehydes substituted with electron donating (*e.g.* methoxy) and electron withdrawing (*e.g.* nitro) substituents and different active

methylene compounds (1,3-diketone, β -keto-ester and 1,3-diester).¹³⁰ Dey *et al.* synthesized a microporous polyurethane **MPU** by reaction between di-isocyanate **78** and triol **79** in DMSO (Table 2, entry 13). Interestingly, as was the case with **BF-COF-1** and **BF-COF-2**, size selectivity was observed. **MPU** was able to catalyze the Knoevenagel condensation (95–99%) for a wide range of substituted benzaldehydes. However 9-anthracenecarboxaldehyde and biphenyl-4-carboxaldehyde did not react at all, suggesting that the reaction occurs in the pores of the materials.¹³¹

An amide linked polymer **Am-POP** was synthesized by reaction of *p*-phenylenediamine **81** with trimesoyl chloride **80** (Table 2, entry 14). **Am-POP** possessed no surface or uptake for N₂ or other gases such H₂ or Ar, however it did show CO₂ affinity (36 mg g⁻¹, 273 K, 1 bar). This was calculated to occur mainly through Lewis acid-base interaction of CO₂ with the amide oxygen, weak hydrogen bonding with the phenyl C-H and π - π stacking. Furthermore, **Am-POP** demonstrated good activity in the Knoevenagel reaction. This contrasts with its homogeneous analogue triphenylbenzamide, which showed no appreciable conversion.¹³²

Base functionalized ionic liquids are known alternatives for traditional bases.¹³³ Therefore, Wang *et al.* prepared basic mesoporous poly(ionic liquid)s **PAMBn** by radical copolymerization of 1-aminoethyl-3-vinylimidazolium bromide **82** with divinylbenzene **11** followed by ion exchange of the bromine with sodium hydroxide (Table 2, entry 15). The resulting materials possessed surface areas of 123 to 429 m² g⁻¹, depending on the ratio of imidazolium monomer to crosslinker. These polymers were good catalysts in the Knoevenagel and aldol condensations. A range of aldehydes were converted with ethyl cyanoacetate or malononitrile in short reaction times and good yields (93–99%). Very high TOFs of up to 572 h⁻¹ were reported, about five times more than the homogeneous monomer. The reaction is enhanced by the combination of nucleophilic (NH₂) and basic (OH⁻) moieties. Like the already discussed sulfonated HCPs these polymers are superhydropho-



Scheme 10 Synthesis of **NH₂-MONNs** by crosslinking, etching and deprotection of bottlebrush polymer **76**. Adapted from ref. 129.

bic. This property prevents poisoning by moisture if stored in air, and allows for the quick release of the formed water during the reaction. Moreover, the material was able to catalyze the aldol condensation between benzaldehyde and acetophenone, under solvent free conditions at 120 °C, furnishing 85% conversion to chalcone.¹³⁴

3.1.1 Outlook on POPs catalyzing the Knoevenagel reaction. Enormous amounts of (heterogeneous) catalysts have been reported to catalyze the Knoevenagel condensation: zeolites, MOFs, mesoporous silicas, metal oxides, carbon nitrides...^{135,136} However, homogeneous simple bases such as piperidine, β -alanine, pyridine or even NaOH are still used most often for this transformation. For example, β -alanine is used in the synthesis of atorvastatin (Lipitor), Pfizer's blockbuster, cholesterol lowering drug. Piperidine is applied in the synthesis of pioglitazone, an anti-diabetic medication.¹³⁷ NaOH is being used in the commercial production of lumefantrine, an antimalarial drug.¹³⁸ These homogeneous catalysts are commonly available, cheap and perform well, making it harder for more complex, heterogeneous catalysts to find widespread adaptation. The POPs described in this review generally showed very good activity. However, often there was no comparison being done with other catalysts and the results are also difficult to compare with each other with barely any (initial) TOFs or TONs being reported. Similarly as with many basic MOFs the reaction was frequently only performed as a proof of concept and not studied in detail.¹³⁵

Regarding the synthesis of the materials many of the same remarks as before can be made. In many cases very harsh conditions and hazardous reagents were being used. For example, the HCP **MFCMP-1** (Table 2, entry 7) required a very large excess (>15 equivalents) of hazardous FeCl₃, which is typical for HCPs produced by Friedel–Crafts crosslinking. The CMPs (Table 2, entries 3 and 9) required precious metal based couplings. Moreover, many difficult to access monomers were being used such as the borolated compounds **62** and **63**, amine **70**, aldehydes **48** and **71**, porphyrins **73** and **74** and bottlebrush copolymer **76**.

3.2 Transesterification

As stated before, a problem with base catalyzed transesterification of oils is the incompatibility of the basic catalysts with water and FFAs, common contaminants in waste oil.^{94,95} To obtain a water-tolerant basic catalyst Liu *et al.* prepared **PDVB-VI-*n*** by hydrothermal co-polymerization of divinylbenzene **11** and 1-vinylimidazole (vim) **83** in different molar ratios. These materials possessed high surface areas (513–680 m² g⁻¹) and very high contact angles (152 °C for **PDB-VI-0.5**) with a water droplet, indicating their superhydrophobicity. Transesterification of tripalmitin as well as virgin plant oil with methanol was efficiently carried out by the imidazole sites. Under very mild conditions, at 65 °C and atmospheric pressure, 97% yield after three hours was obtained for the transesterification of tripalmitin. Importantly, cheap vegetable oil, containing water and FFAs, could be used without

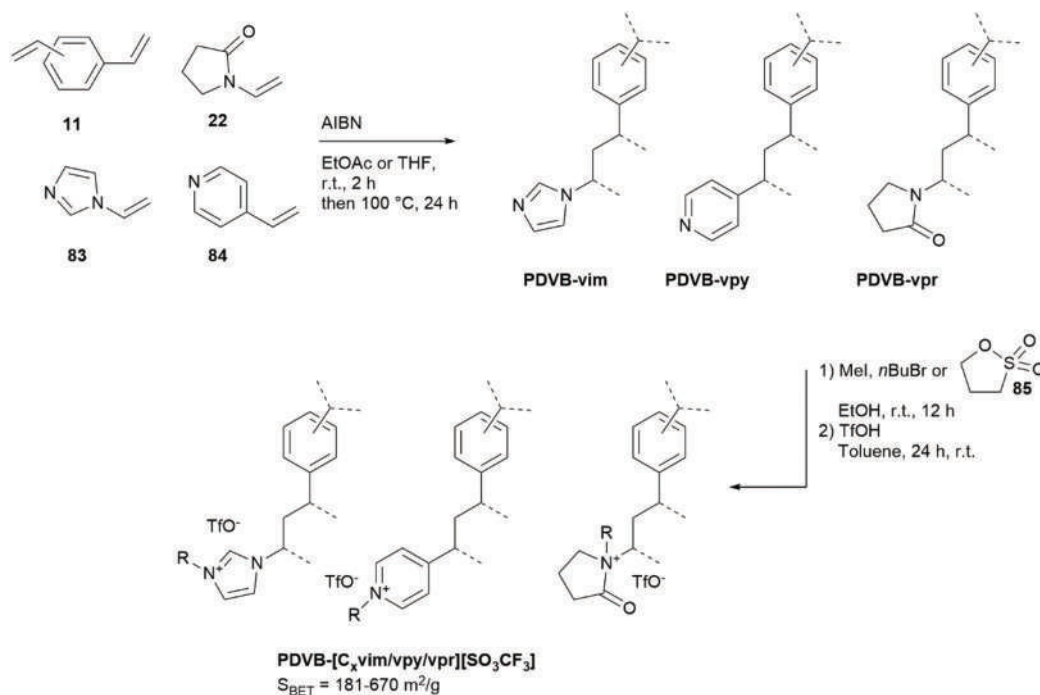
side reactions such as saponification or slower reaction speeds.¹³⁹

Analogously, the same authors prepared mesoporous polymers by hydrothermal polymerization of divinylbenzene **11** with 1-vinylimidazolate (vim) **83**, 4-vinylpyridine (vpy) **84** or 1-vinyl-2-pyrrolidone (vpr) **22**. These were further quaternized with methyl iodide, butyl bromide or 1,3-propanesultone **85** and anion exchanged furnishing ionic liquids immobilized on superhydrophobic polymers **PDVB-[C_xvim/vpy/vpr][SO₃CF₃]** (Scheme 11). Though not basic catalysts, they catalyze similar transformations and therefore are mentioned here. These materials were highly active catalysts, reaching up to 99.9% yield after sixteen hours for the transesterification of tripalmitin with methanol at 65 °C. The activity was even higher than the analogous homogeneous catalyst. In general, heterogeneous catalysts have a lower accessibility of the catalytic sites and thus often exhibit lower activities than their homogeneous counterparts. However, these polymers concentrate the reactants close to the catalytic sites and thus provide higher catalytic efficiencies. Furthermore these materials were also able to catalyze the Peckmann reaction between ethyl acetoacetate and resorcinol, the Kharasch addition between styrene and tetrachloromethane, the esterification of cyclohexanol with acetic acid and the hydration of propylene oxide.¹⁴⁰

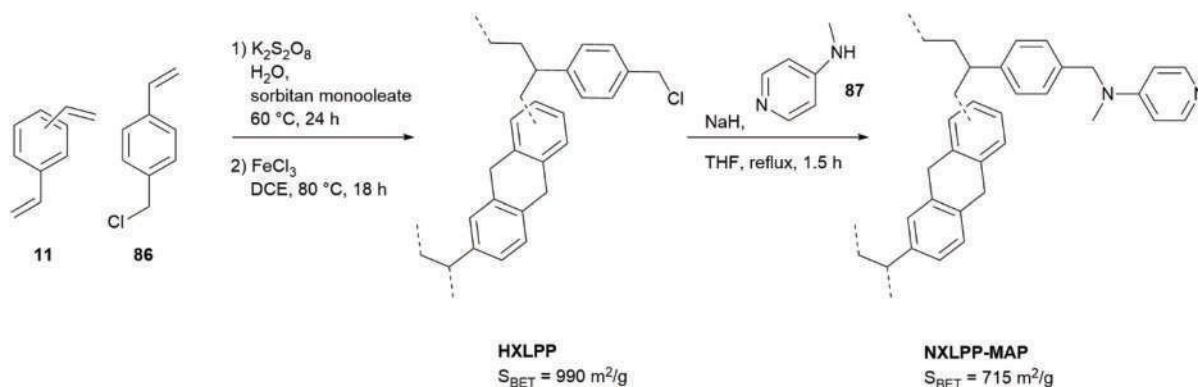
3.3 Reactions catalyzed by heterogeneous 4-dimethylaminopyridine

4-Dimethylaminopyridine (DMAP) is an important nucleophilic catalyst for a variety of reactions such as acylation, silylation, tritylation...¹⁴¹ A DMAP containing HCP was obtained by polymerization of divinylbenzene **11** with 4-(chloromethyl)styrene **86** by emulsion templating, followed by FeCl₃ catalyzed partial hypercrosslinking of the chloromethyl groups. This gave rise to a highly micro- and macroporous polymer **HXLPP**, with a BET area of 990 m² g⁻¹ and residual chloromethyl groups. These groups were then post-synthetically functionalized by nucleophilic substitution with 4-methylaminopyridine **87** (Scheme 12). The resulting polymer **NXLPP-MAP** was a highly active catalyst for the acylation of sterically hindered 1-methylcyclohexanol with acetic anhydride, reaching 100% conversion after three hours with a low catalyst loading of 1 mol%. This material clearly outperformed its nonporous analogues, unfortunately a comparison with homogeneous DMAP was not made.¹⁴²

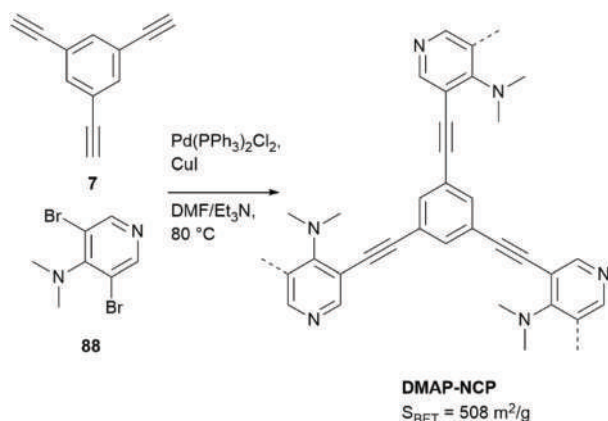
DMAP was also immobilized in CMPs by palladium catalyzed Sonogashira cross-coupling between 1,3,5-triethynylbenzene **7** and dibrominated DMAP **88**, thus incorporating a high loading of catalyst (2.02 mmol g⁻¹) into the porous framework **DMAP-NCP** (Scheme 13). The polymer showed good catalytic activity for the acylation of a wide range of alcohols obtaining high yields of 92 to 99% using 20 mol% loading and could be reused for at least fourteen times without loss of activity. Interestingly, the transformation could also be performed in continuous flow, with the catalyst staying fully active after more than 22 days of operation. **DMAP-NCP** was also a good



Scheme 11 Synthesis of ionic liquid functionalized HCPs by postsynthetic quaternization and ion exchange.¹⁴⁰



Scheme 12 DMAP immobilized by postsynthetic functionalization of a HCP.¹⁴²

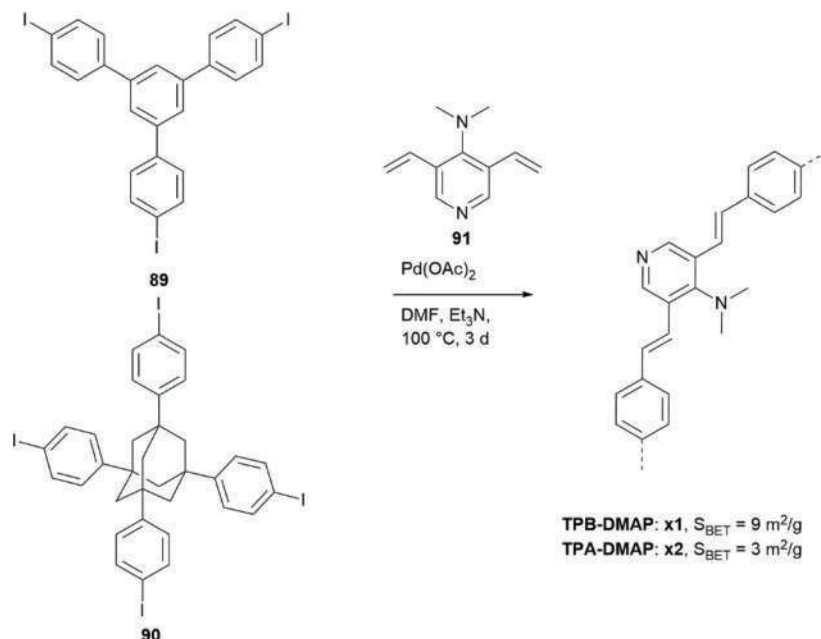


Scheme 13 Synthesis of a DMAP containing CMP by Sonogashira coupling.¹⁴³

catalyst for the silylation of alcohols and possessed a desirable selectivity for primary alcohols.¹⁴³

Lastly, Xu *et al.* synthesized polymers *via* Heck coupling between divinyl substituted DMAP **91** and 1,3,5-tris(4-iodophenyl)benzene **89** or 1,2,3,5-tetrakis(4-iodophenyl)adamantane **90** (Scheme 14). These networks possessed very low surface areas, however, they showed excellent catalytic activity for acylation reactions due to good solvent swelling properties.¹⁴⁴

Many non-porous polymers or resins containing immobilized DMAP have been reported in the literature. However, whilst these possess good recoverability and reusability, in general these exhibit lower activities than homogeneous DMAP.^{145–147} For example, D'Elia *et al.* resorted to immobilizing much more nucleophilic derivatives of DMAP on resins to obtain a heterogeneous catalyst with comparable activity to

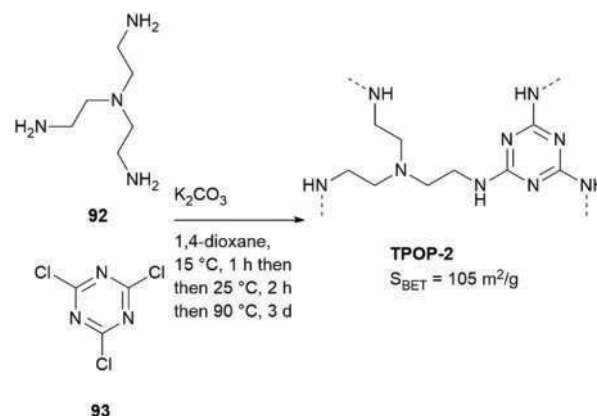


Scheme 14 Synthesis of DMAP containing polymers by Heck coupling.^{143,144}

homogeneous DMAP. This lowered activity is caused by changing of the catalytic micro environment and due to mass transfer limitations: the increased difficulty of the reactants to diffuse to the catalytic center.¹⁴⁷ Permanently porous materials, such as POPs, possess intrinsic porosity, making them less dependent on swelling properties in organic solvents and increasing mass transfer. They can thus be used in a variety of solvents without changing their mass transfer properties much.^{148,149} POPs, and especially COFs also can provide more precise control over the catalytic micro environment. Unfortunately, in the examples we discussed, no clear comparison to homogeneous DMAP was made. Furthermore, while the synthesis of **NXLPP-MAP** is comparable to that of DMAP containing polystyrene resins, the building blocks for **DMAP-NCP**, **TPB-DMAP** and **TPA-DMAP** are not commonly available. The structural building blocks **7**, **89** and **90** are available commercially, but are very expensive and the functional building blocks **88** and **91** require extra steps starting from DMAP, bromination to synthesize compound **88** and further Heck coupling to synthesize compound **91**.

3.4 Multicomponent reactions

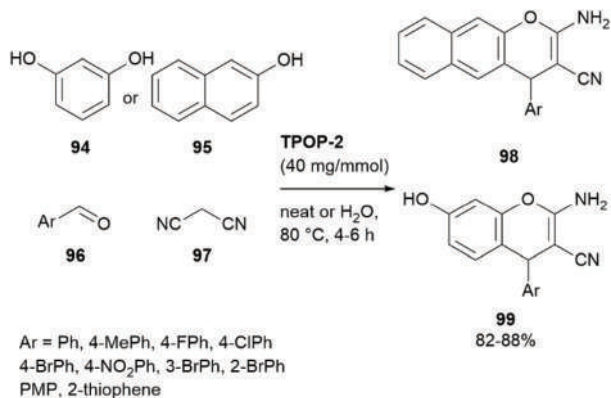
Multicomponent reactions (MCRs) are an exciting field in organic chemistry. In MCRs, simple reaction procedures allow the formation of many bonds and complex structures in one-pot. MCRs are powerful tools in drug development allowing rapid generation of libraries of compounds.^{150,151} In 2015, Bhaumik and coworkers developed a new triazine polymer **TPOP-2**, based on the condensation of tris (2-aminoethyl) amine **92** with cyanuric chloride **93** (Scheme 15). **TPOP-2** features a high density of amine and triazine nitrogens and a corresponding high surface basicity, allowing its use as a cata-



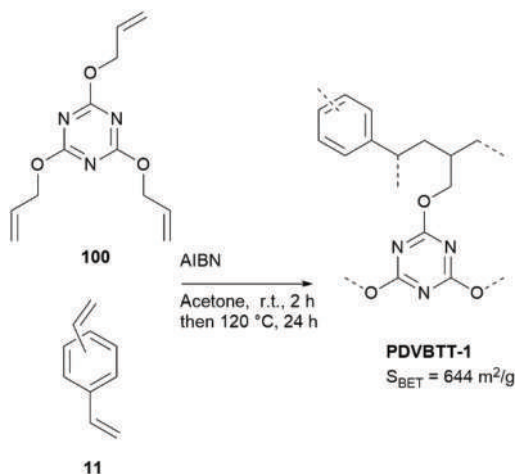
Scheme 15 Synthesis of **TPOP-2** by nucleophilic substitution of amine **92** with cyanuric chloride **93**.¹⁵³

lyst for the one-pot three component condensation reaction between aromatic aldehydes **96**, activated phenols (resorcinol **94** or 2-naphthol **95**) and malononitrile **97** leading to 2-aminochromenes **98–99** (Scheme 16). These compounds are typically prepared with homogeneous organic bases such as piperidine.¹⁵² **TPOP-2** proved to be a highly effective catalyst, obtaining high (82–88%) yields. With conventional basic catalysts, such as piperidine, pyridine, imidazole and tris(2-aminoethyl) amine, much lower yields of 35 to 46% were reported. A wide range of aromatic aldehydes with various electron withdrawing and donating groups were able to react and the catalyst could be recycled for at least five times without affecting the yield.¹⁵³

In 2016, the same group developed a porous organic polymer **PDVBTT-1** (poly-divinylbenzene-*co*-triallyloxytriazine)



Scheme 16 2-Amino-chromene synthesis catalyzed by TPOP-2.¹⁵³



Scheme 17 HCP synthesis by radical polymerization of DVB **11** with allyl substituted triazine **100**.¹⁵⁴

through radical co-polymerization of 2,4,6-triallyloxy-1,3,5-triazine **100** and divinylbenzene **11** (Scheme 17). The obtained surface areas were dependent on monomer ratios. Using only triazine **100**, the surface area obtained amounted to just 18 m² g⁻¹, whilst using four equivalents of DVB **11** a surface area of 644 m² g⁻¹ was reached. This catalyst was also active in forming 2-amino-chromenes **98–99** obtaining high yields (82–86%) for a range of aldehydes.¹⁵⁴ Interestingly, this same polymer has also been synthesized with surfactant P123 as a templating agent. In this way ordered 2D hexagonal mesopores along with micropores were obtained after template removal by refluxing in EtOH. This material possessed a higher surface area of 1016 m² g⁻¹ and was a good catalyst for the Knoevenagel condensation under microwave radiation.¹⁵⁵

In further research from the Bhaumik group, the synthesis of a porous base **TrzMOP** was reported by reaction between tetra-*tert*-butylamine **101** and 2,5-thiophenedicarboxaldehyde **103**, creating amination linkages (Scheme 18). This catalyst was used in another MCR, the polyhydroquinoline synthesis through

four component one-pot Hantzsch condensation. A series of aldehydes could be converted with good to excellent yields (72–98%), comparable to morpholine, a homogeneous counterpart (Scheme 19). The catalyst was highly reusable and after the 7th run only a minor yield loss of 3% was observed.¹⁵⁶ The same group prepared another amination linked material **TrzPyPOP** by condensation of tetraamine **101** and pyrene-1-carboxyaldehyde **102** (Scheme 18). This material was used in a three component Biginelli condensation furnishing a range of dihydropyrimidones **109** (Scheme 20).¹⁵⁷ Lastly, Zaharani *et al.* utilized mesoporous poly melamine formaldehyde **mPMF** (*vide supra*) as a catalyst for the mechanochemical synthesis of 2-amino-4*H*-benzo[*b*]pyrans **112** (Scheme 21). These authors reported the conversion of a wide range of substrates in good yields (62–92%).¹⁵⁸

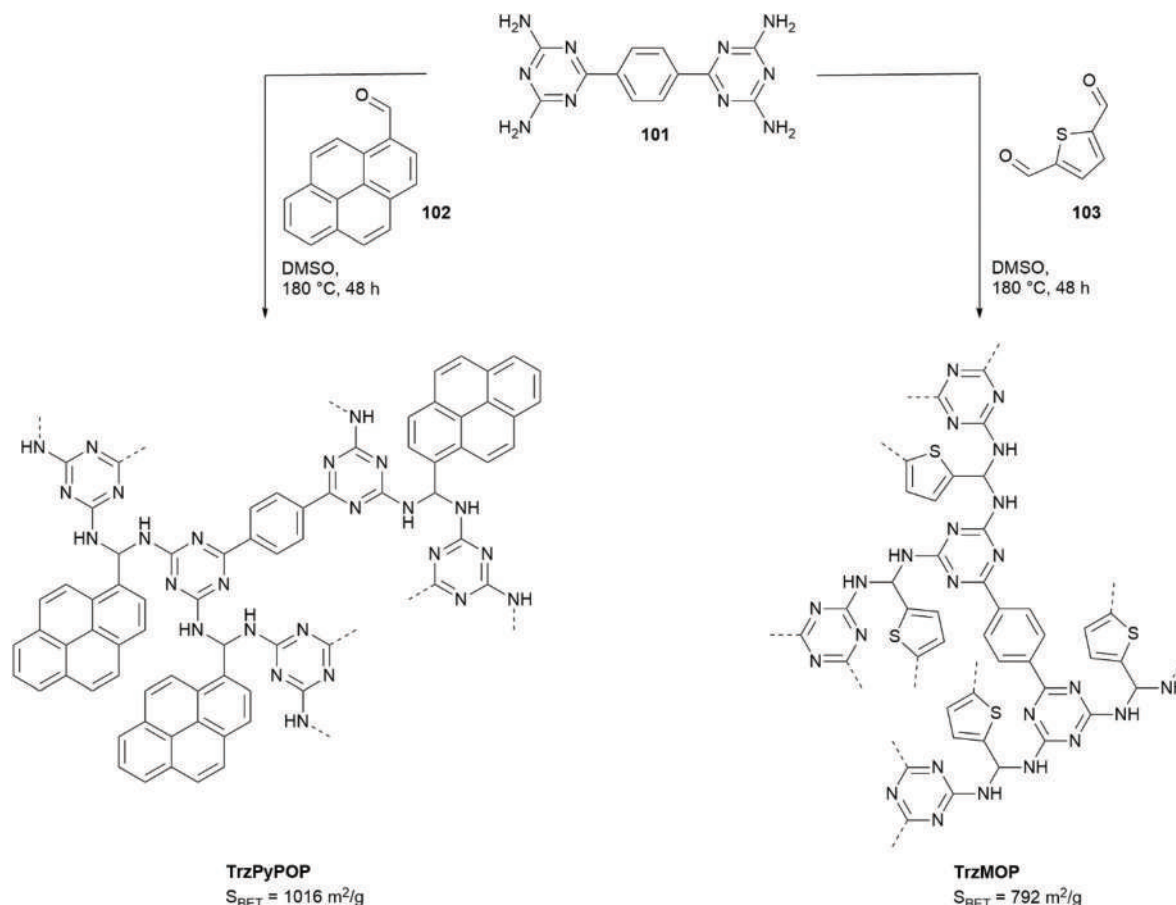
In general the polymers catalyzing these multi-component reactions possess interesting reactivities and work well. Regarding the TPOP-2 catalyzed synthesis of 2-amino-chromenes: typically homogeneous bases are used in literature.¹⁵⁹ However, some other (green) catalysts are also available such as expanded perlite, a cheap green heterogeneous catalyst, that doesn't require any chemical synthesis, but does require regeneration by calcination at 800 °C.¹⁶⁰

In the polyhydroquinoline synthesis through Hantzsch condensation **TrzMOP** performed comparable to a homogeneous base. Other (heterogeneous) catalysts have also been described for this transformation such as HClO₄-SiO₂, PW/SiO₂, barium nitrate, CeCl₃·7H₂O...¹⁶¹ Moreover, a very green protocol requiring only ammonium carbonate in water with mild heating to 55–60 °C has been reported, which of course makes a more difficult to synthesize heterogeneous catalyst less attractive.¹⁶² Similarly, for the three component Biginelli condensation several other (green) methodologies exist using many possible catalyst and solvent combinations, ionic liquids, microwave technology...^{163,164}

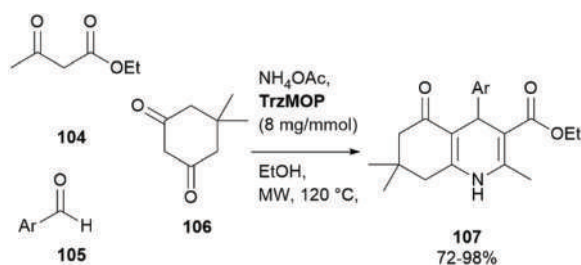
The described polymers were made using rather easily accessible reagents, especially for **PDVBTT1** and **TPOP-2** and under relatively mild conditions. In the case of the amidine linked polymers **TrzMOP** and **TrzPyPOP** no catalysts are needed to prepare them, only intense heating.

3.5 NHC catalysis

N-Heterocyclic carbenes (NHCs) are tunable and strong ligands for transition metal complexes, but can also be nucleophilic or basic organocatalysts by themselves.^{165–167} Rose *et al.* synthesized N-heterocyclic carbene containing element organic frameworks **EOF-15** and **EOF-16** by Suzuki coupling of a bifunctional imidazolium linker **113** with tetrafunctional boronic acids **114** and **115** (Scheme 22). The EOFs were used as nucleophilic catalysts in the conjugated umpolung of cinnamaldehyde **116** and coupling with trifluoroacetophenone **117** (Scheme 23). The heterogeneous catalytic NHC species was generated *in situ* by deprotonation of the imidazolium salt with diazabicycloundecene (DBU). Moderate (46–84%) yields were obtained, comparable or slightly lower than homogeneous counterparts (83–85%).¹⁶⁸

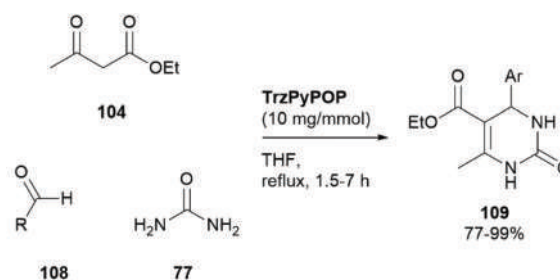


Scheme 18 Synthesis of TrzMOP and TrzPyPOP by aminal formation between amine **101** and aldehydes **102** and **103**.^{156,157}



Ar = Ph, 4-MePh, PMP, 3,4-MeOPh,
 3,4-OHPh, 4-CNPh, 3-NO₂Ph,
 4-NO₂Ph, 4-ClPh, 4-BrPh, thiophen-2-yl

Scheme 19 Polyhydroquinoline synthesis mediated by TrzMOP.¹⁵⁶



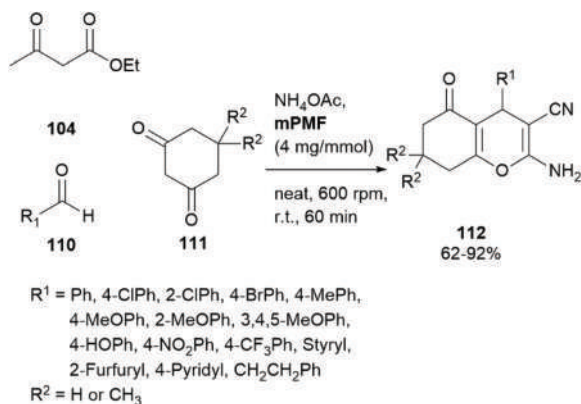
R = 4-MePh, 4-BrPh, 4-ClPh,
 4-NO₂Ph, 4-CNPh,
 2-furyl, pyren-1-yl

Scheme 20 Three component Biginelli condensation catalyzed by TrzPyPOP.¹⁵⁷

CTFs with embedded cationic imidazolium species have also been reported, yet these were always synthesized at the high (>400 °C) temperatures required for the ionothermal trimerization of nitriles utilized in typical CTF synthesis.¹⁶⁹⁻¹⁷²

However, Troschke *et al.* showed *via* thermogravimetric analysis of imidazolium precursors that substantial decomposition of these monomers already begins to occur at 300 °C, which raises doubts on the structural integrity of these CTFs.

Therefore, these authors devised a finely adjusted synthetic protocol utilizing long reaction times but relatively low temperatures to preserve the imidazolium functionality of building block **120** in the resulting **imid-CTF** (Scheme 24). This CTF was non-porous for nitrogen and thus is not permanently porous. However, a significant uptake of CO₂ was measured (2.05 mmol, 1 bar, 273 K). The authors performed vapor sorp-



Scheme 21 mPMF catalyzed synthesis of 2-amino-4H-benzo[b]pyrans **112**.¹⁵⁸

tion experiments to evaluate catalytic applications in the liquid phase. Significant swelling of the CTF and absorption of organic solvents such as EtOH or CH₃CN was found over the whole pressure range at 298 K. These very polar and small solvents were well absorbed, due to interaction of the nitrogen

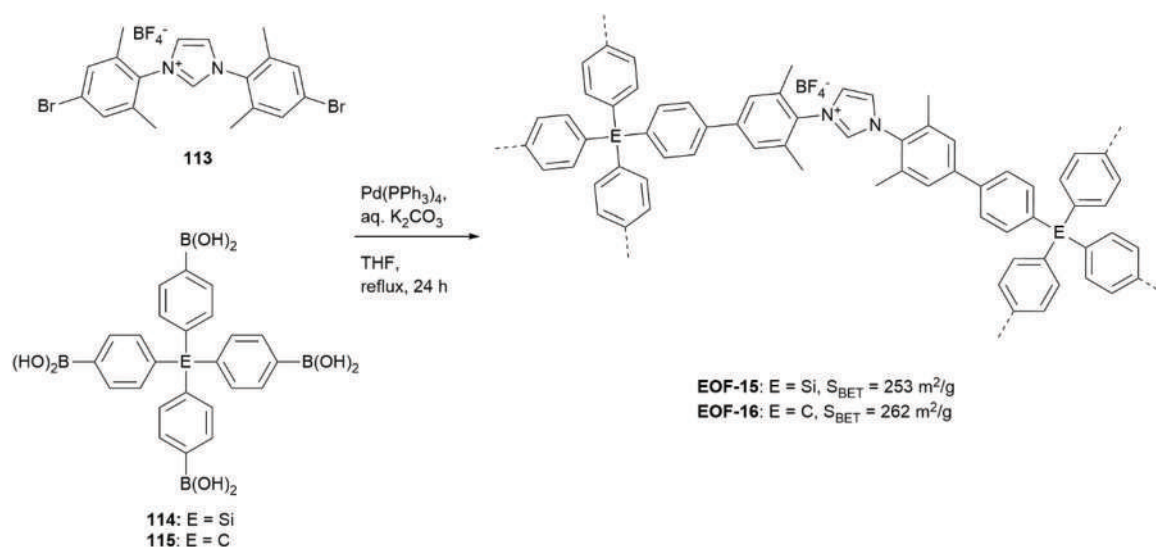
rich polymer with polar solvents, analogous to the quadrupole interactions of CO₂ with the framework. Apolar solvents, such as toluene, showed a negligible uptake. This was reflected in the catalytic activity for the umpolung reaction being solvent dependent, with the reaction working well in CH₃CN and EtOH, but *t*BuOH (too bulky) or apolar solvents resulting in very low yields. High yields (81%) were reached for the conjugated umpolung catalyzed by imid-CTF in CH₃CN (Scheme 23). However, when the CTF was fabricated at higher temperatures no significant product formation was observed. CTFs produced at slightly higher temperatures of 320 or 330 °C, respectively, already resulted in 8% or 1% yield only.¹⁷³

This refutes recent findings in literature^{169–172} proposing intact imidazolium moieties in CTFs produced at high temperatures.

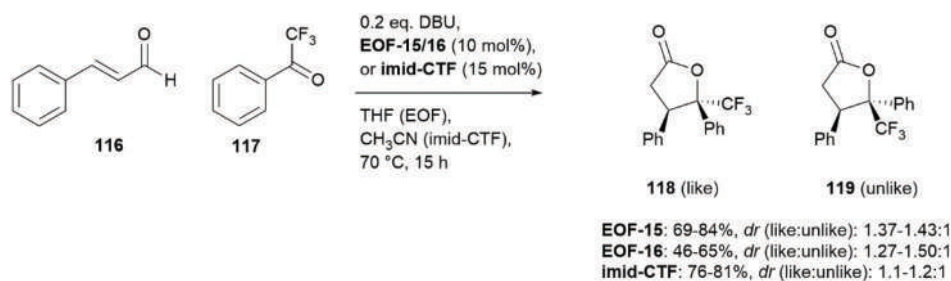
4 Cascade reactions

4.1 Simultaneous acid and base catalysis

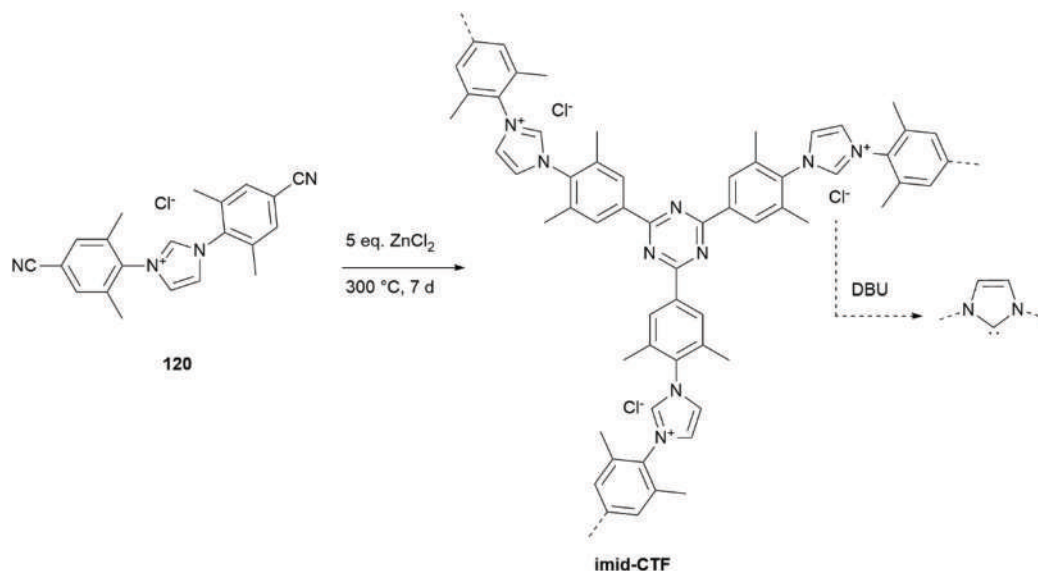
Cascade reactions, incorporating several reactions to give the final product in one operation, are a promising approach



Scheme 22 Synthesis of imidazolium containing EOFs by Suzuki coupling.¹⁶⁸



Scheme 23 Heterogeneous NHC catalyzed umpolung reaction.^{168,173}



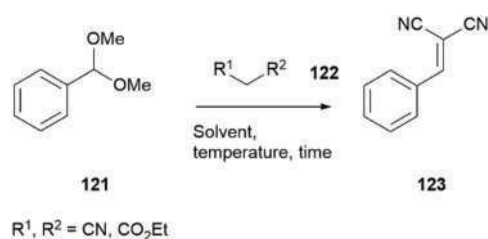
Scheme 24 Synthesis of imid-CTF by ionothermal polymerization at lower temperatures preserving the imidazolium structure.¹⁷³

towards more sustainable chemistry since they reduce both waste and time.¹⁷⁴ Generally, several active components (catalysts, acids, bases, ligands...) are involved in such a multistep process.¹⁷⁵ Integrating multiple catalytic sites into a single recyclable material is of course of huge interest.

Nature regularly employs multistep cascade reactions in enzymes. These often employ multiple acid–base sites in one

catalyst, for example, catalytic triads in serine proteases.¹⁷⁶ Simultaneous acid and base catalysis is impossible with homogeneous catalysts, as they will neutralize each other. Heterogeneous systems however can overcome this limitation. Quite some bifunctional acid–base POPs have been reported and often a one-pot deacetalization-Knoevenagel of dimethyl acetal protected benzaldehyde **121** is carried out as a reference reaction for these materials (Scheme 25 and Table 3).

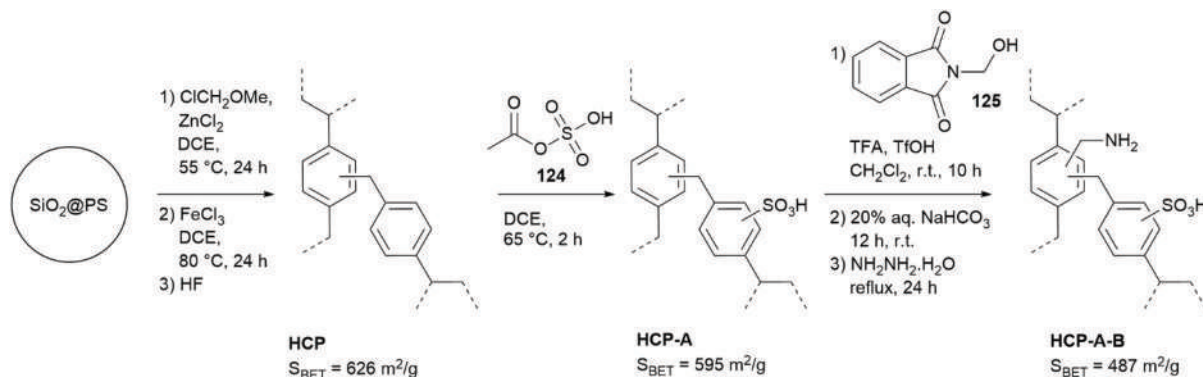
Jia *et al.* synthesized hypercrosslinked hollow spheres with acidic and basic sites **HCP-A-B** (Scheme 26). Firstly, a microporous hollow nanosphere **HCP** was synthesized using silica polystyrene composite particles, SiO₂@PS, as a precursor. The polystyrene was alkylated using methoxymethyl chloride, followed by hypercrosslinking of the chloromethyl moieties and etching of the silica template. Sulfonic acid groups were introduced in this **HCP** using acetyl sulfate **124**. Reaction with *N*-(hydroxymethyl)phthalimide **125** followed by deprotection with hydrazine led to the incorporation of amine functional-



Scheme 25 The one-pot deacetalization-Knoevenagel reaction.

Table 3 The one-pot deacetalization-Knoevenagel reaction

Entry	Conditions	Yield (%)	Ref.
1	2-(2-Bromophenyl)-1,3-dioxolane instead of 121 , HCP-A-B (133 mg mmol ⁻¹), H ₂ O, r.t., 8 h	95	177
2	1.2 eq. malononitrile, 250 mol% P(DVB-0.2-VBS) , 500 mol% P(DVB-0.2-VBA) , toluene, 80 °C, 30 min	99	178
3	1.2 eq. malononitrile, 10 mol% PPAF-SO₃H-NH₂ , toluene, water, 90 °C, 1 h	100	179
4	2 eq. malononitrile, PAF-1-NHCH₂CH₂NH₂-SO₃H (50 mg mmol ⁻¹), toluene, 90 °C, 3 h	99	180
5	1.2 eq. malononitrile, TxPPs-SO₃H-NH₂ (130 mg mmol ⁻¹), toluene, water, 90 °C, 1 h	75	181
6	1.1 eq. malononitrile, 2 mol% PP-x (8 mg mmol ⁻¹), toluene, water, 90 °C, 1 h	>95	182
7	4 eq. malononitrile, 10 mol% MONNs-SO₃H-NH₂ , toluene, 80 °C, 2 h	>99	187
8	4 eq. ethyl cyanoacetate, 10 mol% SO₃-MONNs and NH₂-MONNs , toluene, 80 °C, 2 h	>99	184
9	4 eq. ethyl cyanoacetate, 10 mol% NH₂-SO₃-H-ONTs , toluene, 80 °C, 2 h	>99	185
10	10 eq. ethyl cyanoacetate, acid base nanotubes (231 mg mmol ⁻¹), water, r.t., 24 h	100	186
11	1.1 eq. malononitrile, COF-OH (10 mg mmol ⁻¹), toluene/water (1.5/5), 80 °C, 85 min	96	188
12	1.1 eq. malononitrile, COF-OMe (10 mg mmol ⁻¹), toluene/water (1.5/5), 80 °C, 90 min	52	188
13	2-(2-Bromophenyl)-1,3-dioxolane instead of 121 , 1.2 eq. malononitrile, HCPs-SO₃H-50 (33 mg mmol ⁻¹) and HCPs-CH₂NH₂-50 (133 mg mmol ⁻¹), toluene, H ₂ O	96	183

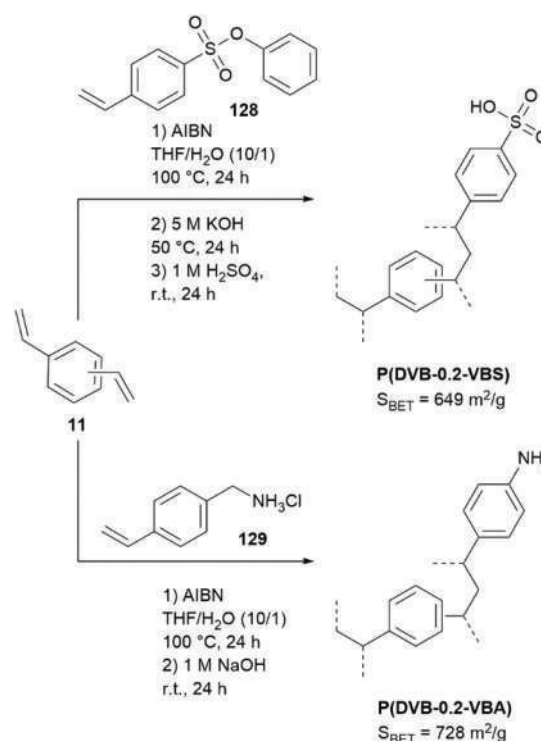


Scheme 26 Synthesis of hypercrosslinked nanospheres by crosslinking, etching, sulfonation and amination.¹⁷⁷

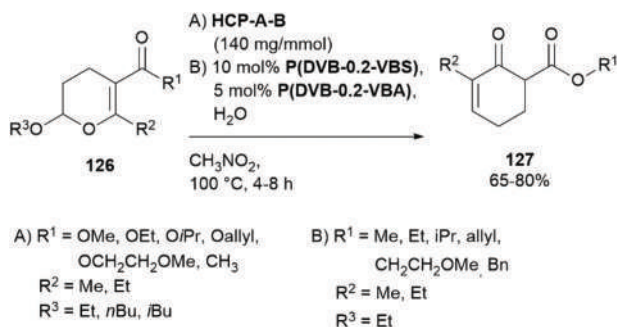
ities. **HCP-A-B** displayed high catalytic efficiency in both a deacetalization/Henry and a deacetalization/Knoevenagel reaction of 2-(2-bromophenyl)-1,3-dioxolane. The Knoevenagel reaction took place under very mild conditions, in water at room temperature (Table 3, entry 1). Moreover, these authors developed a new reaction, the synthesis of 2-cyclohexen-1-ones **127** from 2-alkoxy-3,4 dihydropyran derivatives **126** by a ring opening-aldol condensation-dehydration sequence (Scheme 27A).¹⁷⁷

Physical combinations of solid acids and bases can also be applied. Sun *et al.* synthesized amino or sulfonic acid functionalized POPs through radical polymerization of protected sulfonic acid functionalized building block **128** or amino containing compound **129** with divinylbenzene **11** (Scheme 28). The physical combination of these two materials was used as a simultaneous acid base catalyst for one-pot deacetalization-Henry condensation reactions with yields reaching up to 100%. These materials were also able to catalyze the deacetalization-Knoevenagel condensation (Table 3, entry 2) and transformation of 3,4-dihydropyran derivatives **126** to α -ester cyclohexenones **127** (Scheme 27B).¹⁷⁸

In 2013, Félix Sánchez *et al.* reported the functionalization of a spirobisfluorene PAF with both acidic and basic sites and its utilization as a catalyst. To this end 2,2',7,7'-tetraiodo/bromo-9,9'-spirobisfluorene **130-131** was polymerized with



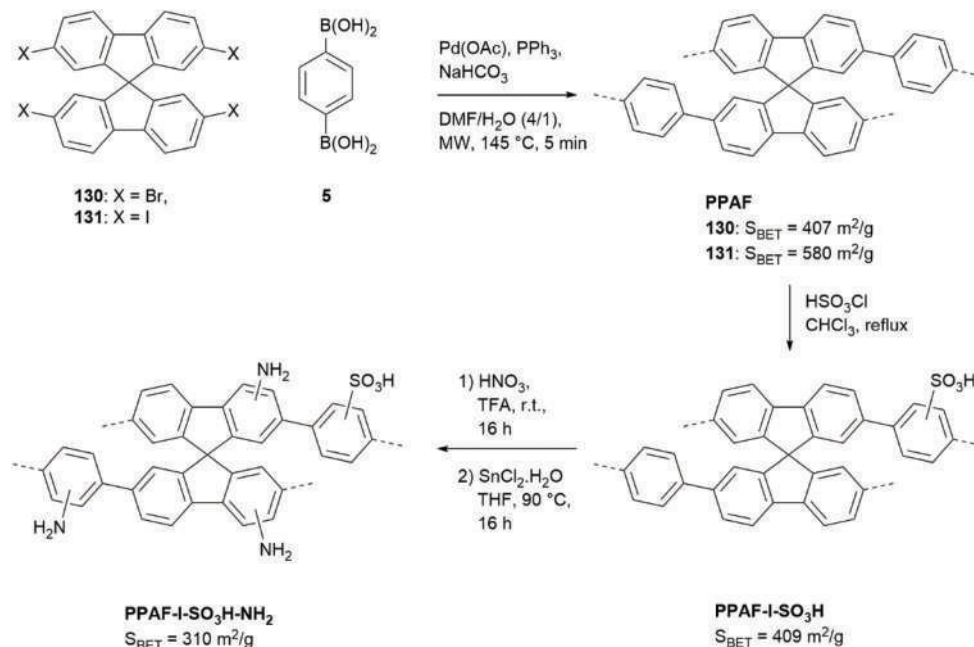
Scheme 28 Synthesis of amino or sulfonic acid functionalized HCPs.¹⁷⁸



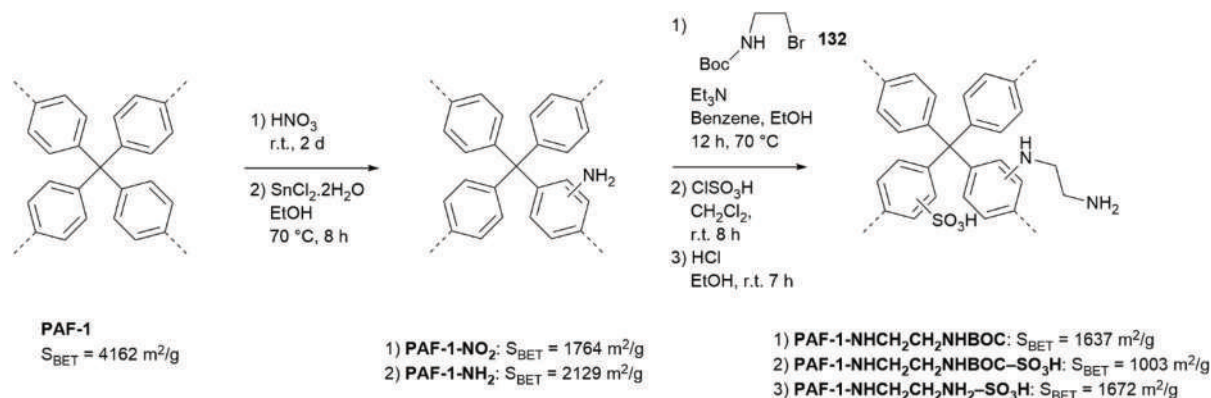
Scheme 27 Acid-base mediated rearrangement of 3,4-dihydropyrans **126** to α -ester cyclohexenones **127**.^{177,178}

benzene-1,4-diboronic acid **DBA** through a Suzuki coupling (Scheme 29). The more reactive iodo-substituted building block **131** resulted in slightly higher surface areas. Subsequent sulfonation, nitration and reduction of the nitro groups gave rise to **PPAF-SO₃-NH₂** with a BET surface area of $310 \text{ m}^2 \text{ g}^{-1}$. This acid and base functionalized porous catalyst was used in the one-pot deacetalization-Knoevenagel reaching 100% yield after one hour using 10 mol% catalyst (Table 3, entry 3).¹⁷⁹

Similarly Zhang *et al.* prepared another acid and base functionalized PAF starting from **PAF-1**. Firstly, an amine functionalized **PAF-1-NH₂** was synthesized by nitration and reduction. The amino groups of this material were then reacted with Boc protected compound **132**, followed by sulfonation and deprotection furnishing **PAF-1-NHCH₂CH₂NH₂-SO₃H**.



Scheme 29 Synthesis of bifunctional spirobisfluorene based POPs by Suzuki coupling and postfunctionalization by sulfonation, nitration and reduction.¹⁷⁹

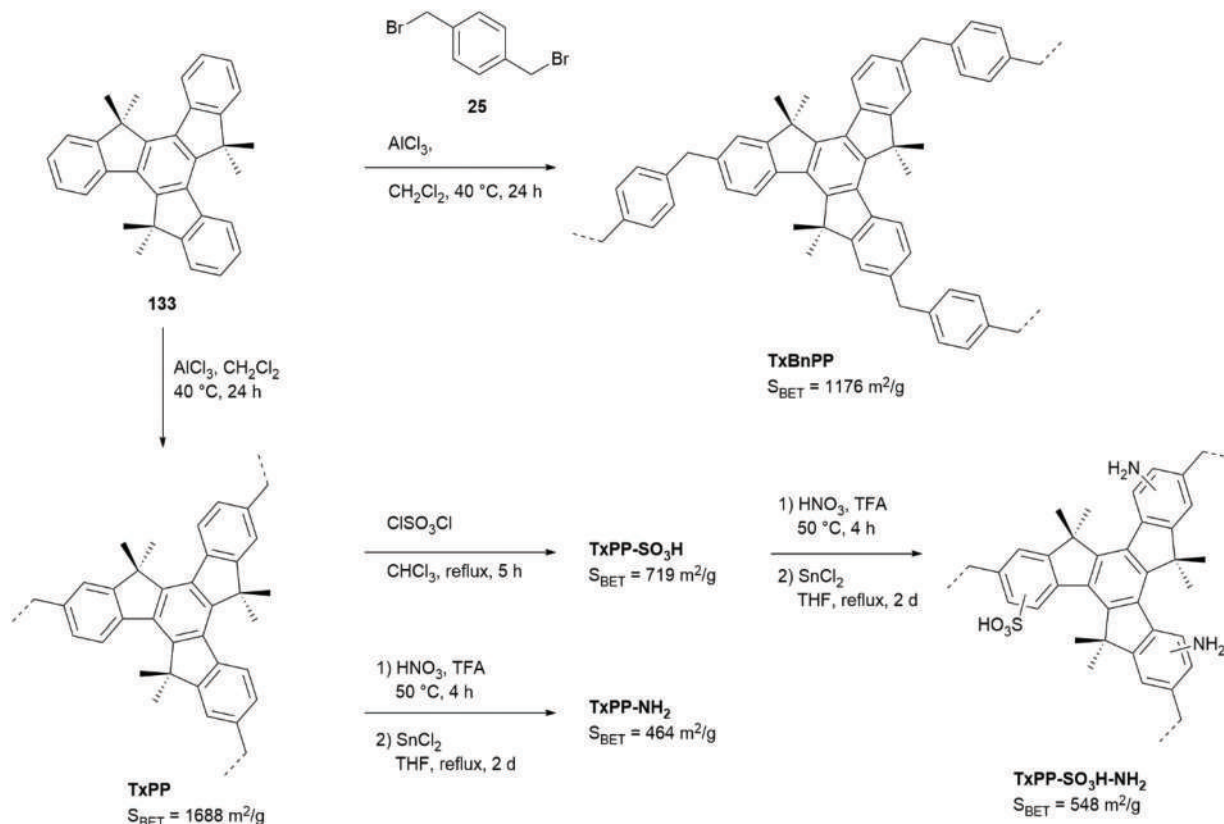


Scheme 30 Synthesis of amino and sulfonic acid functionalized PAFs by postfunctionalization.¹⁸⁰

(Scheme 30). The functionalized material still possessed a BET Surface area of $1672 \text{ m}^2 \text{ g}^{-1}$, which is higher than other bifunctional POPs. In deacetalization-Henry reactions up to 97% yield was reported, and for the deacetalization-Knoevenagel condensation a 99% yield was obtained (Table 3, entry 4).¹⁸⁰

Similarly, Guadalupe *et al.* prepared acid-base functionalized truxene based POPs *via* AlCl₃ catalyzed crosslinking followed by functionalization. As a crosslinker for the hexamethyltruxene monomer **133** the solvent dichloromethane, or an extra crosslinker 1,4-bis(bromomethyl)benzene **25** could be used, resulting in polymers **TxPP** and **TxBnPP** (Scheme 31). When more sterically hindered truxene monomers (*e.g.* hexabutyltruxene) were reacted, no polymeric materials were obtained, and starting material was recovered almost quanti-

tively. Truxene possesses intrinsic photoactivity, therefore **TxPP** itself could be used as a heterogeneous photocatalyst for the oxidative dimerization of benzylamine. High conversion (91%) was attained after 24 hours and the catalyst was recyclable up to five times with no loss of yield. Furthermore, **TxPP** was postfunctionalized with amines, sulfonic acids or both resulting in **TxPPs-SO₃H**, **TxPPs-NH₂** or **TxPPs-SO₃H-NH₂**, respectively. **TxPPs-SO₃H** was applied as a catalyst for esterification and transesterification reactions. A range of long chain fatty acids could be converted into their corresponding methyl esters in generally high to quantitative yields (91–99%) in methanol at room temperature in three hours. Ethyl cyanoacetate could be transesterified with methanol to its corresponding methyl ester in 88% yield under the same conditions.



Scheme 31 Synthesis and functionalization of truxene based POPs.¹⁸¹

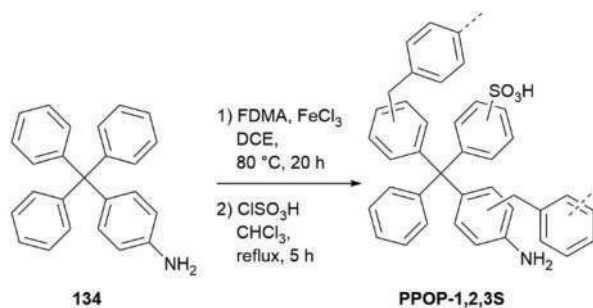
For the deacetalization-Knoevenagel reaction, after optimization of the ratio of acid and base catalysts, 75% yield could be reached after one hour (Table 3, entry 5). Interestingly, a physical mixture of acid and base functionalized catalysts performed better than the bifunctional catalyst.¹⁸¹

Bhaumik and coworkers polymerized 4-tritylaniline **134** under Lewis acidic conditions with dimethoxymethane obtaining porous polymers **PP-1,2,3** whose morphology depended on the amount of crosslinker used (Scheme 32). **PP1** was obtained as hollow tubes, whereas **PP-2** formed microflowers and **PP-3** formed larger interconnected hollow tubes. The authors proposed that the residual alkoxy groups from the crosslinker interacted with the amino groups and thus influenced the

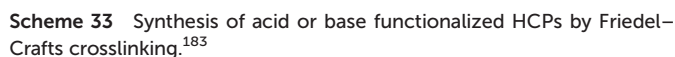
morphology, as these hollow structures are generally only formed when a template is used. **PP-1,2,3** were grafted with sulfonic acid groups forming **PP-1,2,3S** and used in the one-pot acetalization-Knoevenagel reaction giving high yield (>95%, Table 3, entry 6).¹⁸²

Wang *et al.* prepared acid or base functionalized microporous polymers **HCP-NH₂-x** and **HCP-SO₃-x** from simple pre-functionalized aromatic building blocks **136** or **137** and benzene **135** through FeCl₃ catalyzed crosslinking with dimethoxymethane (Scheme 33). As the amount of benzene decreases the surface areas decrease dramatically. These materials were able to catalyze one-pot deacetalization-Knoevenagel (Table 3, entry 13) and Henry reactions. Predictably, combining heterogeneous acid with homogeneous base or *vice versa* resulted in very low yields. This is caused by neutralization when one of the catalysts is in the homogeneous phase, resulting in cascade failure.¹⁸³

The Huang group, who prepared the amino functionalized microporous organic nanotube networks **NH₂-MONNs** (Scheme 10), used very similar materials as catalysts for the one-pot deacetalization-Knoevenagel reaction. Starting from bottlebrush polymer **138** (Fig. 2) containing phenoxy protected sulfonic acid or Boc protected amines **SO₃-MONNs** and **NH₂-MONNs** were synthesized by Friedel-Crafts hypercrosslinking followed by etching of the PLA core and deprotection. A physical mixture of those two catalysts was then successfully applied in de acetalization Knoevenagel reaction (Table 3, entry



Scheme 32 Preparation of sulfonic acid and amino functionalized HCPs by polymerization of 4-trityl aniline **134**.¹⁸²



In 2015, the Banerjee group synthesized a COF able to perform simultaneous acid and base catalysis due to the incorporation of acidic (catechol) and basic (porphyrin and imine) sites. Two highly crystalline and acid and base stable COFs **2,3-DhaTph** and **2,3-DmaTph** were synthesized by Schiff-base reaction between 2,3-dihydroxyterephthalaldehyde (2,3-Dha) **143** or 2,3-dimethoxyterephthalaldehyde (2,3-Dma) **144** and 5,10,15,20-tetrakis(4-aminophenyl)-21*H*-23*H*-porphine (Tph) **145** under solvothermal conditions (Scheme 36). The model reaction between benzaldehyde dimethyl acetal and malononitrile worked very well with the bifunctional COF **2,3-DhaTph** (Table 3, entry 11). **2,3-DmaTph** lacking the acidic functionalities showed much lower activity (Table 3, entry 12), proving the necessity of both functionalities. **2,3-DhaTph** could be recycled at least five times, however the yield dropped by 10–15%.¹⁸⁸

A bifunctional COF was synthesized by metalation of a β -ketoenamine linked **COF-TpPa-Py** with $\text{Pd}(\text{OAc})_2$ (Scheme 39). By virtue of the metal loading and the basic pyridine units this **COF-TpPa-Py** could oxidize a range of alcohols to their corresponding aldehydes which were then reacted with malononitrile in one-pot to form the Knoevenagel products in high yields (91–99%).¹⁹⁰

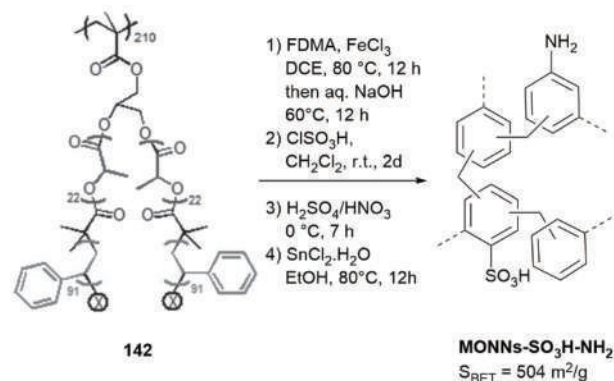
4.3 Outlook on POPs as bifunctional catalysts

The combination of a strong acid with a base is of course only possible in heterogeneous systems, where there is spatial separation of the catalytic sites. Similar materials to these POPs also exist based on silicas or PMOs^{191,192} and bifunctional MOFs^{193,194} containing both acidic and basic sites. These are used in analogous transformations with similar performances, however, POPs possess the advantages of being metal free and highly stable.

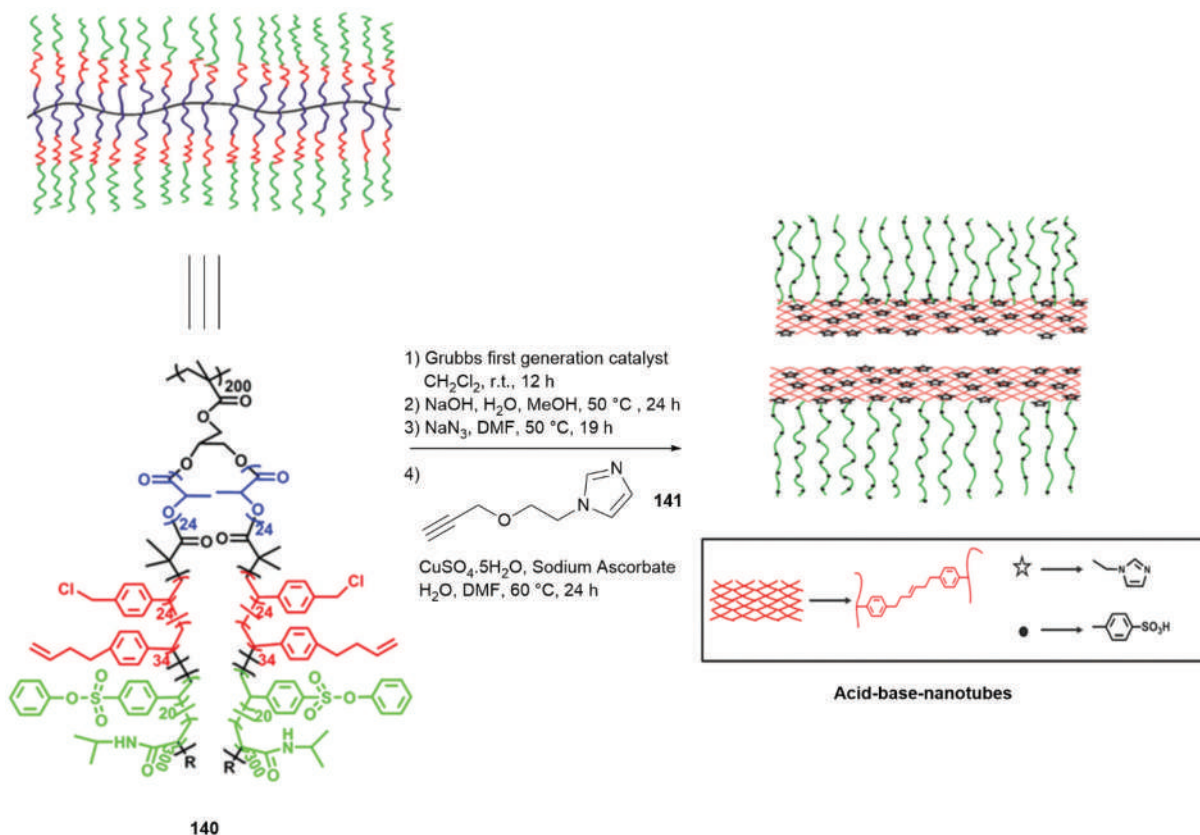
The synthesis of bi- or multifunctional POPs, combining different catalytic sites on a single material functioning in tandem, is still in its infancy. It can be considered an ideal avenue for further POP research, as it leverages many of the advantages of POPs such as good mass transfer, excellent stability and designability.

Even so, the synthesis of these bifunctional materials is plagued by long postmodification-sequences utilizing quite hazardous chemicals. For example, in the synthesis of **HCP-A-B** (Scheme 26) four separate postmodification steps are needed using hazardous chemicals such as TFA, TfOH, hydrazine... Moreover, the synthesis of the polymer itself requires highly dangerous MOMCl and HF. To produce acid-base functionalized materials by postfunctionalization generally three separate steps are needed: sulfonation, nitration and reduction,

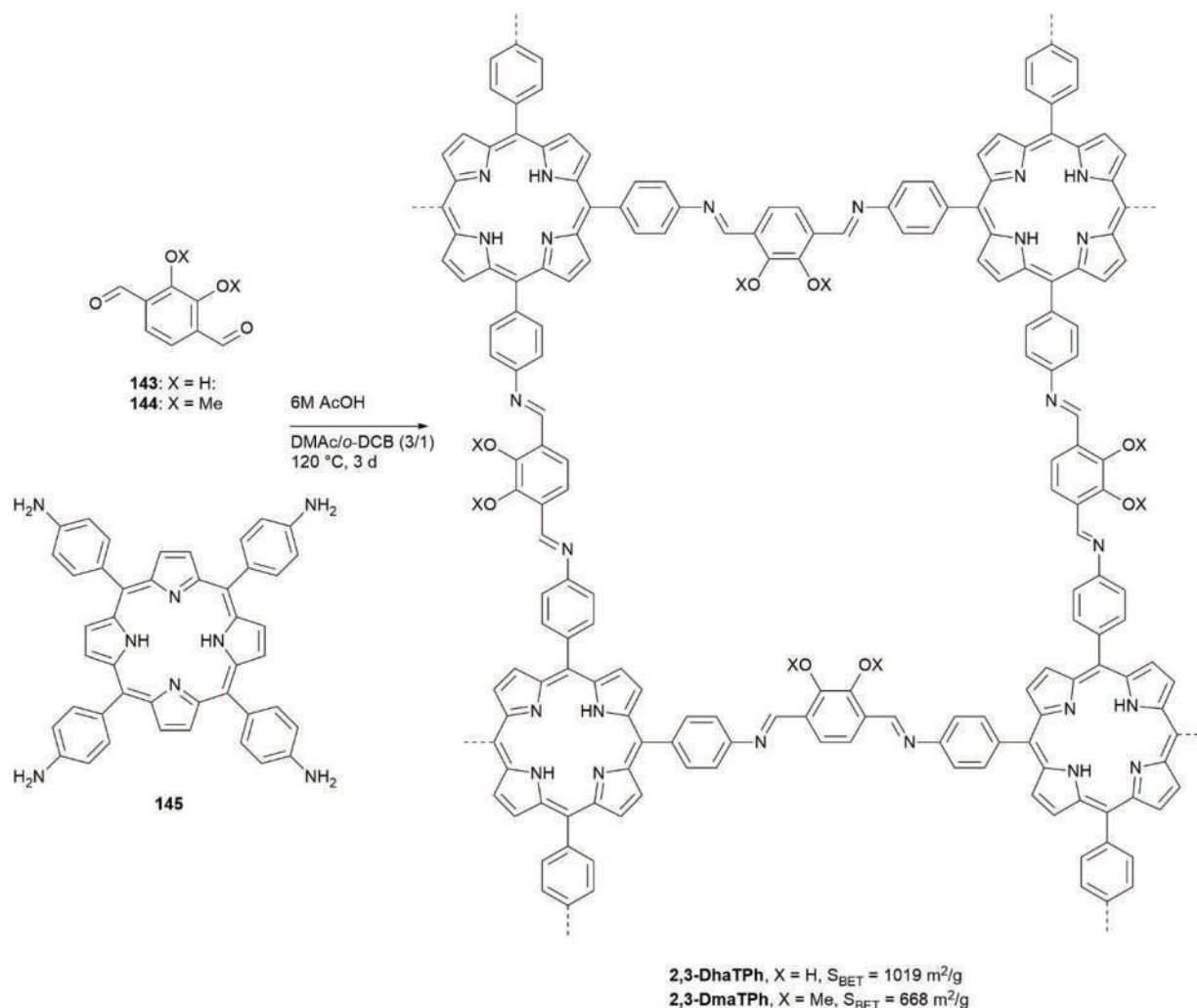
however, bottom up synthesis can alleviate this problem (Schemes 28, 33 and 36). Lastly, the nanotube networks (Fig. 2, Schemes 34 and 35) not only require complex postmodification but also a core removal step and a lengthy synthesis of the bottlebrush polymers themselves. For example, starting from poly (glycidyl methacrylate) six steps are needed to synthesize compound **140**.¹⁹⁵



Scheme 35 Synthesis of acid-base nanotubes by postfunctionalization.¹⁸⁷



Scheme 34 Synthesis of acid base nanotubes by double bond metathesis – sulfonic acid deprotection – nucleophilic substitution and click reaction.¹⁸⁶



Scheme 36 Synthesis of a bifunctional acid–base COF.¹⁸⁸

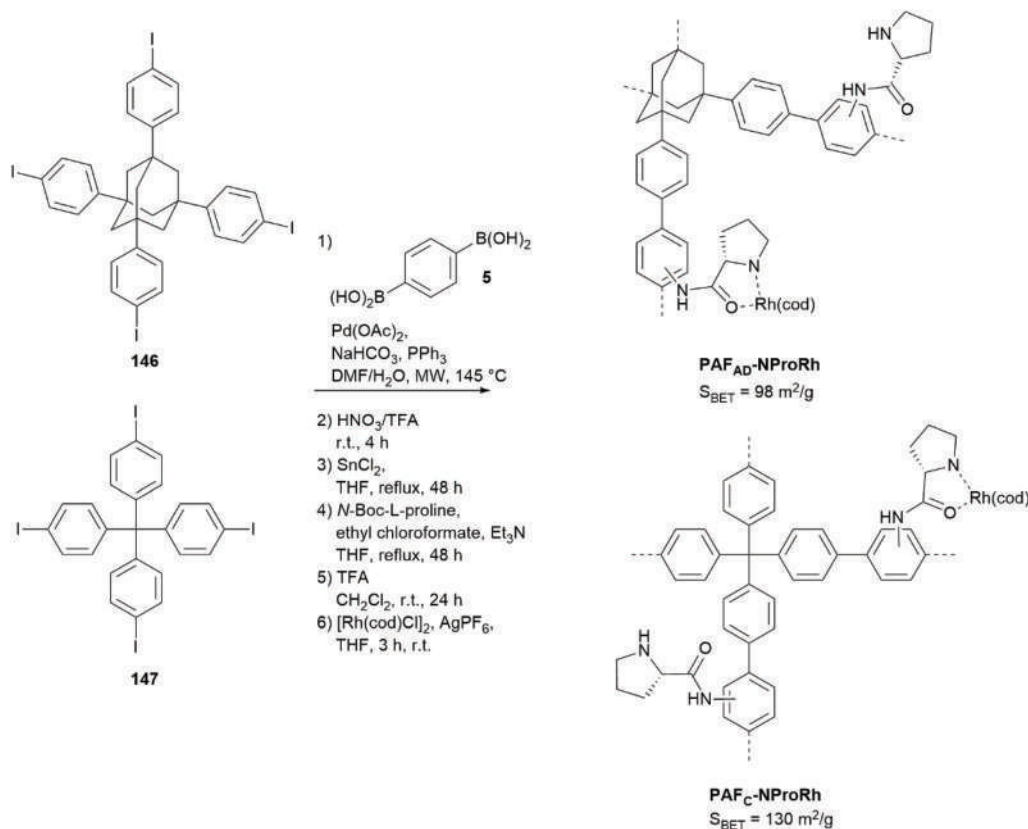
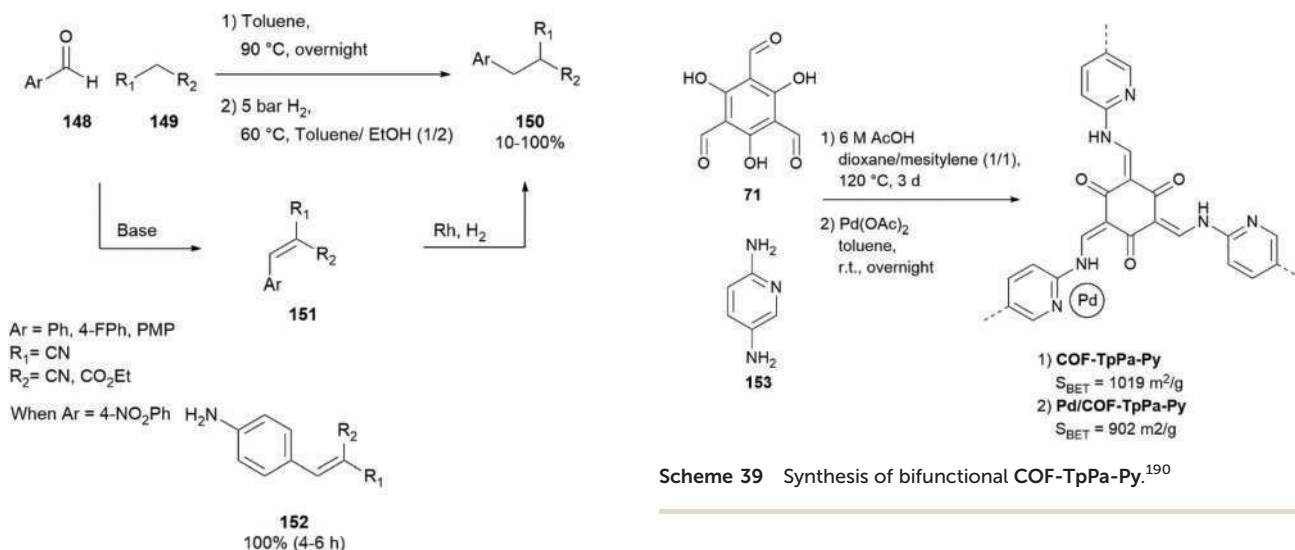
5 Chiral catalysts

For many applications in pharmaceuticals, agriculture and other chemical industries it is essential to obtain optically pure compounds.¹⁹⁶ Enantiomerically pure products are typically produced *via* multistep syntheses, on a relatively small scale (~1–10 000 ton per year for pharmaceuticals, 500–100 000 ton per year for agrochemicals) and typically in batch. These products have high purity requirements and high added values, thus tolerating higher process costs.¹⁴⁸

Asymmetric catalysis forms a convenient way to synthesize chiral molecules from achiral building blocks. This alleviates the need for costly resolution techniques or a chiral pool synthesis which can be long and convoluted. A good chiral catalyst should provide ee's in the range of 99% in the case of pharmaceuticals, if further enrichment is impossible. For agrochemicals lower ee's might be acceptable. TONs should range from 1000 to 50 000, depending on the scale and value of the products, but for a recyclable catalyst much lower limits are possible. The catalyst should of course be stable, both

mechanically and chemically (*i.e.* no leaching of the active component). Few homogeneous catalysts and ligands are commercially available in the needed, technical quantities and their synthesis is therefore often also a part of the process development. Heterogeneous catalysts are generally unavailable and their synthesis and characterization requires knowledge and machinery typically unavailable in a standard process lab, especially for newer types of catalysts.¹⁴⁸ However, heterogeneous catalysts can be a convenient alternative to expensive, not recyclable and difficult to synthesize homogeneous chiral catalysts and can even confer higher selectivity.⁸ The general advantages of a heterogeneous catalyst, such as easy work up and recycling of the catalyst, allows straightforward recovering and reuse of the chiral component, typically the most expensive part of the system.¹⁹⁷

Two main strategies exist for obtaining catalytic chiral POPs: postsynthetic modification or a bottom up approach. The first strategy entails the addition or immobilization of chiral catalytic moieties to the porous material, whereas in the second strategy the synthesis of the POPs starts from chiral

Scheme 37 Synthesis of bifunctional PAFs.¹⁸⁹Scheme 39 Synthesis of bifunctional COF-TpPa-Py.¹⁹⁰Scheme 38 One-pot Knoevenagel-reduction reaction catalyzed by rhodium and proline containing PAFs.¹⁸⁹

monomers, thus incorporating their chirality in the porous material and reducing the step count.

The postsynthetic modification or immobilization of homogeneous (chiral) catalysts on supports can be by covalent binding, adsorption, ion pair formation or entrapment.¹⁹⁸ The

examples of POPs in the literature thus far only used covalent binding.

As supports other than POPs linear, non-cross-linked polymers or dendrimers can be used. These require solvents that they are soluble in, but give catalysts with good mass transfer properties. Separation of the catalyst however requires precipitation or ultrafiltration and is therefore difficult or costly.¹⁹⁹ Swellable, slightly crosslinked polymers are easily separated, but these need to be used in solvents in which they swell

well.¹⁴⁸ The most widely used support of this type, and by far the most common support for immobilized chiral catalysts in general, are the Merrifield type resins (polystyrene and styrene/divinylbenzene copolymers).¹⁹⁷ These swellable polymers generally possess a lower activity compared to the non-supported homogeneous counterpart, as we have discussed earlier on the part on DMAP. This can, at least partially, be alleviated through the use of spacers.¹⁴⁶ Lastly, permanently porous materials (MOFs, metal oxides, POPs) barely swell and thus can be used regardless of solvent choice.¹⁴⁸

5.1 Heterogeneous chiral BINOL-derived phosphonic acids

Chiral 1,1'-bi-2-naphthol (BINOL) derived phosphonic acids are important homogeneous catalysts and form an active area of research.²⁰⁰ These chiral acids have been used as highly enantioselective catalysts in diverse reactions such as hydrogenations,²⁰¹ aza-Henry reactions,²⁰² Friedel-Crafts alkylations²⁰³... These BINOL-based catalysts however are expensive, suffer from tedious synthesis sequences and have a very high molecular weight. Heterogenizing these catalysts on porous supports could help alleviate these drawbacks.²⁰⁴ In 2010, Rueping *et al.* reported the first immobilized chiral Brønsted acids, by AIBN catalyzed radical crosslinking of catalysts **154**–**156** with styrene and divinylbenzene **11** resulting in

polymers **P154**–**156** (Fig. 3). The bulkier monomers **155** and **156** were synthesized to increase the enantioselectivity. The activity of the polymers was evaluated in the transfer hydrogenation of quinolines and benzoxazines. Yields and ee's of up to 96% were reported (Scheme 40 and Table 4, entry 1) and the catalysts did not lose enantioselectivity or activity upon reuse.²⁰⁵

In 2011, the group of Arne Thomas prepared a microporous polymer by oxidative FeCl₃ catalyzed polymerization of thiophene containing monomer **157** (Fig. 3). This polymerization increased the steric hindrance of the side groups and thus positively influenced the selectivity of the catalyst. Due to solubility reasons, the acid chloride was polymerized, which after aqueous wash of the polymer yielded the phosphoric acid containing polymer with a BET surface of 88 m² g⁻¹. These authors investigated the transfer hydrogenation of dihydro-2H-benzoxazine **161** (Scheme 40 and Table 4, entries 3 and 4). As predicted, the selectivity of the polymer **P157** (47%) was higher than that of the monomer **157** (34%), due to the crosslinking increasing the steric bulk close to the catalytic center. Interestingly, the enantioselectivity also was inverted. The reaction could be repeated three more times without loss in activity and with a slight increase in enantiomeric excess. This increase was hypothesized to be caused by the washing of

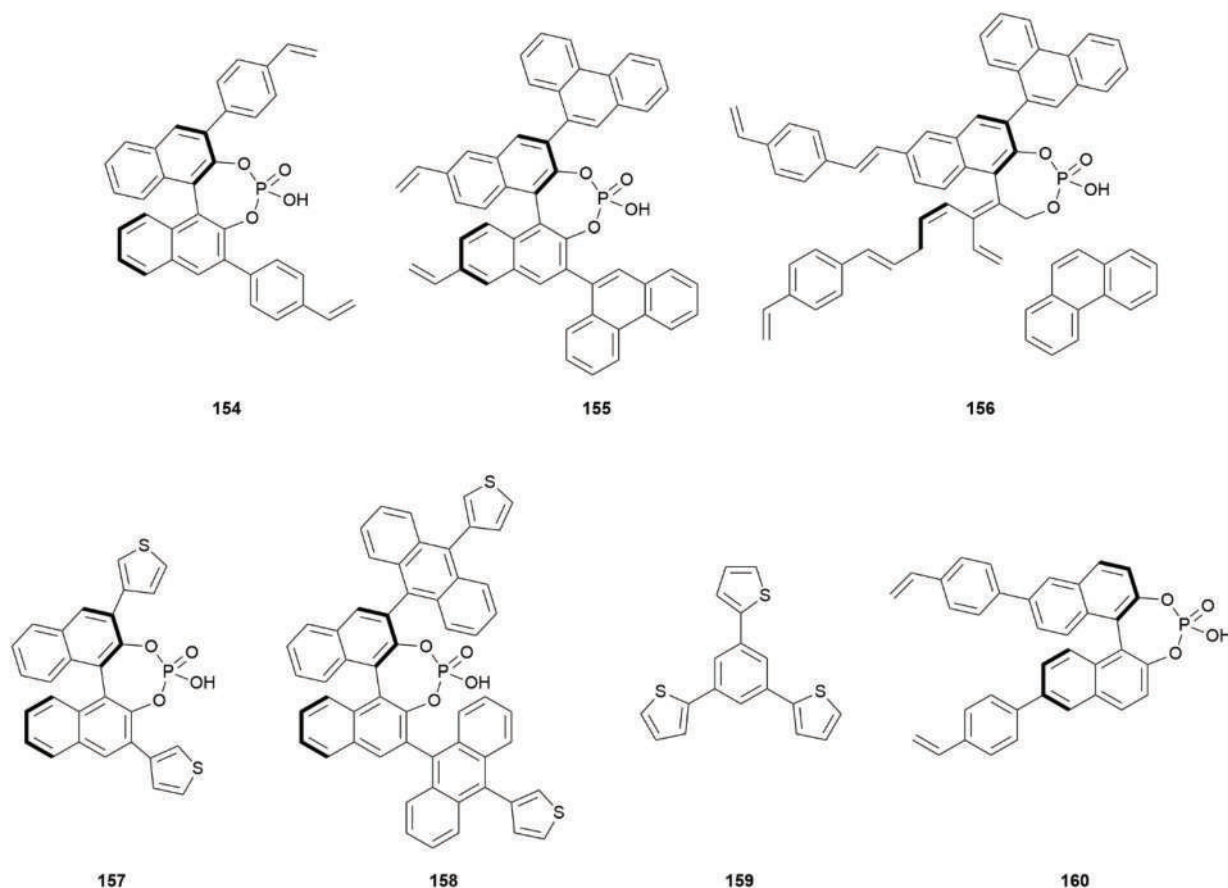
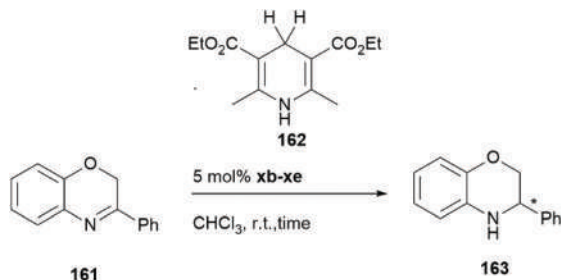


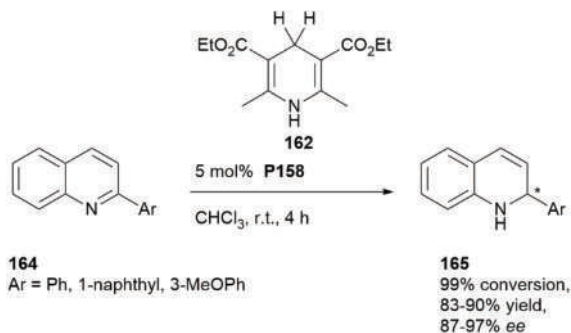
Fig. 3 Monomers used to synthesize heterogeneous chiral Brønsted acids.^{205–209}



Scheme 40 Catalytic asymmetric reduction of dihydro-2H-benzoxazine **161**.

Table 4 Catalytic asymmetric reduction of dihydro-2H-benzoxazine **161**

Entry	Catalyst, time	Yield (%)	ee (%)	Ref.
1	P155, 20 h	92	64	205
2	P156, 20 h	96	96	205
3	157, 24 h	99	34	206
4	P157, 24 h	99	47	206
5	158, 2 h	99	99	207
6	P158, 2 h	99	98	207



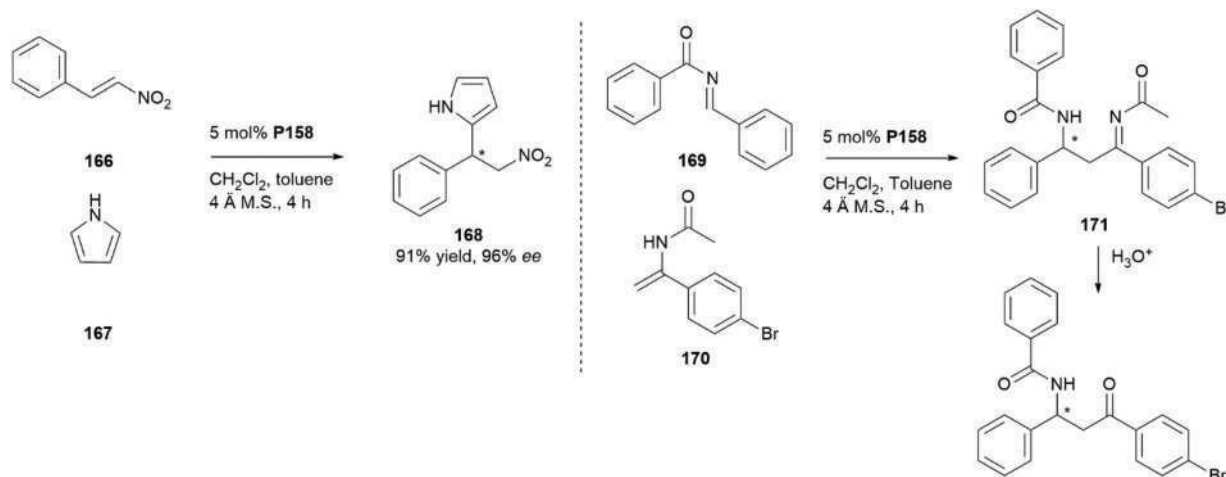
Scheme 41 Asymmetric reduction of 2-arylquinolines.²⁰⁷

residual acid from the pores which catalyzes the racemic background reaction.²⁰⁶

In further research, the same group extended the linker with a phenanthrene moiety, obtaining building block **158**, which after oxidative polymerization resulted in a porous polymer with a BET surface of $386 \text{ m}^2 \text{ g}^{-1}$. This polymer was highly active and selective, obtaining 99% yield and 98% ee for the benzoxazine reduction (Scheme 40 and Table 4, entry 6), comparable to the homogeneous version (Table 4, entry 5) and retains its full activity and enantioselectivity after ten runs. Furthermore, these authors studied the reduction of 2-arylquinolines **164**, for which also high conversions (99%) and ee's (87–97%) were reached (Scheme 41). The catalyst was also active in C–C bond formation by asymmetric Friedel–Crafts alkylation of pyrrole **167**, with nitrostyrene **166** and in an aza-ene reaction between substrates **169** and **170** (Scheme 42).²⁰⁷ The same group copolymerized building block **158** with 1,3,5-tris(2-thienyl)benzene **159** to obtain increased surface areas. For 1 : 1 and 1 : 5 ratios of **158** to **159** networks with surface areas of, respectively, 577 and $668 \text{ m}^2 \text{ g}^{-1}$ were reached. These increased surface areas translate into increased conversions compared to the polymer made from only monomer **158** for the reduction of 2-phenylquinoline.²⁰⁸ Lastly, Huangfu *et al.* synthesized a porous chiral binaphthyl phosphoric acid based material **PPO-BNPA** by polymerization of **160**. This material catalyzed the asymmetric reduction of phenyl methyl ketone with borane, with conversion reaching 99%, however only an ee of 70% was reported.²⁰⁹

5.2 Chiral amine organocatalysis

Asymmetric catalysis using chiral amines is a very useful way to generate chirality, and has gained tremendous attention since seminal works of List *et al.* and MacMillan *et al.* in 2000.^{210–212} However, applications on larger or industrial scales are limited by the amines low efficiency, the high catalyst loading of typically 10–30 mol% needed and the difficulty separating these high amounts of catalyst from the products.

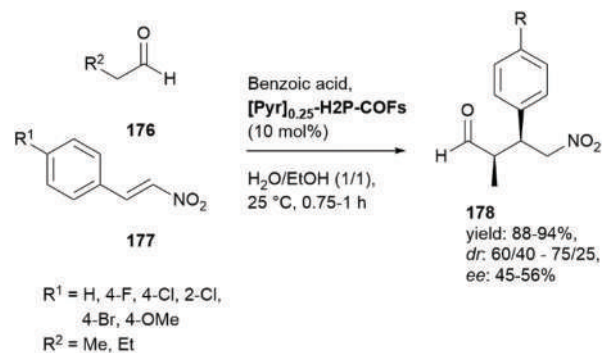


Scheme 42 Friedel–Crafts alkylation and aza-ene reaction catalyzed by P158.²⁰⁷

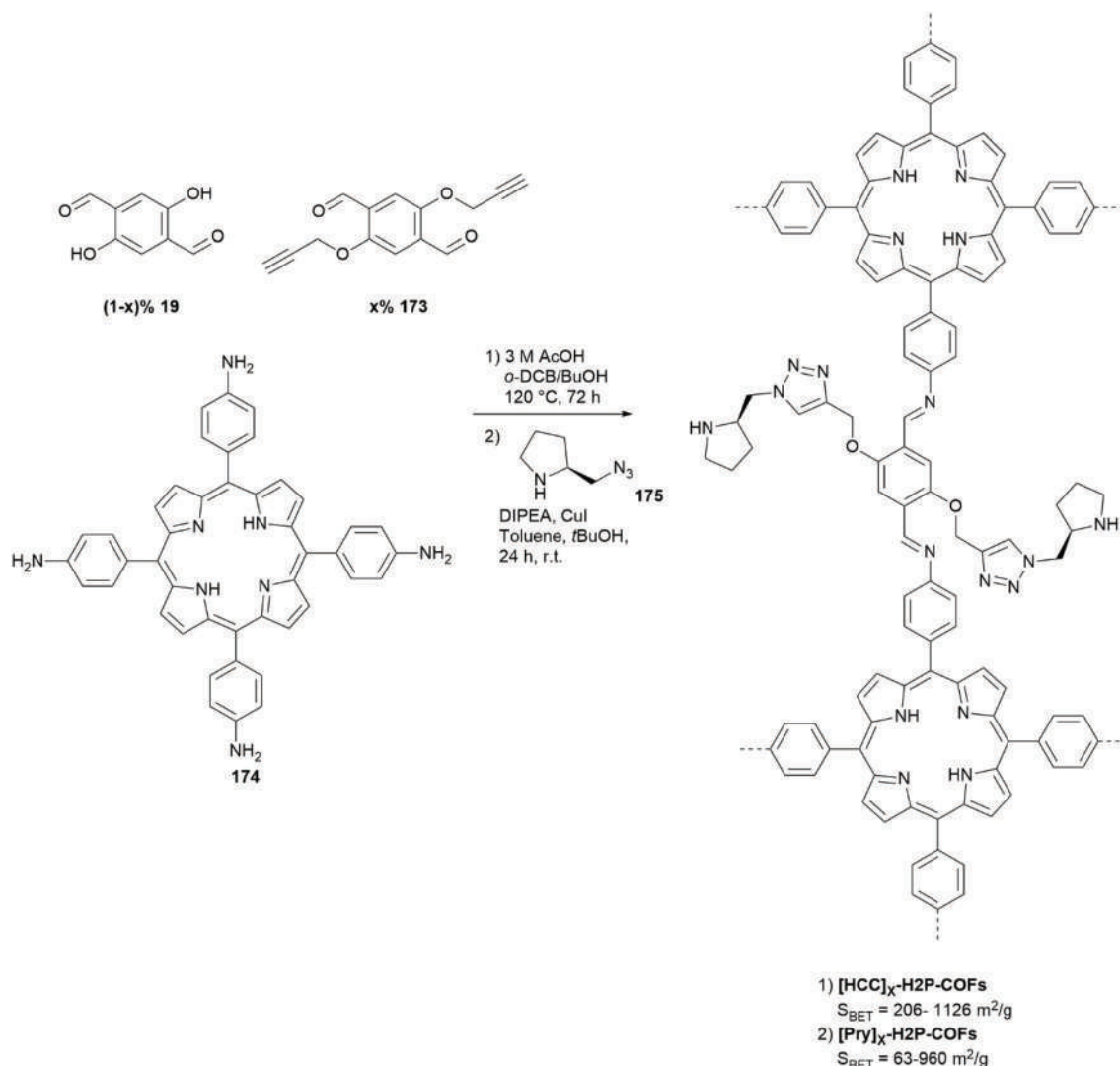
Therefore, the development of heterogeneous, recyclable chiral amine catalysts is a very hot topic.

5.2.1 Postsynthetic modification. Jiang *et al.* reported the first example of chiral organocatalytic COFs in 2013. These authors synthesized mesoporous imine linked porphyrin COFs [HC≡C]_x-H2P-COFs by condensation of 5,10,15,20-tetrakis(4'-tetraphenylamino) porphyrin (H2P) **174** with varying amounts of 2,5-dihydroxyterephthalaldehyde **19** and 2,5-bis(2-propynyloxy)terephthalaldehyde **173** (Scheme 43). A click reaction of chiral azide **175** with the ethynyl groups of the COF anchored the chiral catalytic moieties to the pore walls leading to [Pyr]_x-H2P-COFs. The disappearance of the typical alkyne vibration bands was observed in the infrared spectrum, proving that all the ethynyl groups had reacted. The COFs with increased ethynyl content led to a decreased crystallinity due to the larger number of amorphous units on the walls and a decreased surface area, which after click reaction declined further. [Pyr]_x-H2P-COFs were highly active catalysts for the

Michael addition reaction between nitrostyrenes **177** and propion- or butyraldehyde **176** with the least substituted COF, [Pyr]₂₅-H2P-COF, being the most active (Scheme 44). The orga-



Scheme 44 Asymmetric reaction between nitrostyrenes **177** and aldehydes **176**.²¹³



Scheme 43 Synthesis of chiral [Pyr]_x-H2P-COFs by click reaction with a chiral azide.²¹³

nocatalytic COF showed a much higher activity than a monomeric control. The authors hypothesize that the reagents, which are poorly soluble in the reaction mixture, accumulate on the walls of the COF, hereby increasing the activity. A variety of substrates were reacted and all reached full conversion in less than one hour with moderate ee's and dr's. The catalyst could be used at least four times, however the reaction time needed to be increased drastically. Upon the fourth time the required time had increased almost fivefold and the BET-area also showed a massive decrease with only $104 \text{ m}^2 \text{ g}^{-1}$ remaining. This could indicate that pore channels became blocked during the reaction. The authors also applied their catalyst in a continuous flow setup, and could maintain 100% conversion with 44% ee and 65/35 dr for more than two days.²¹³

In 2015, Jiang *et al.* reported the design of chiral COF based on analogous principles. Triphenylbenzene knots **179** were used with 2,5-dimethoxyterephthalaldehyde **20** and 2,5-bis(2-propynyloxy)terephthalaldehyde **173** linkers (Scheme 45). Interestingly, this resulted in extremely stable COFs originating from the methoxy substituted linkers. In imine COFs significant polarization of the C=N bond exists, due to the electronegativity difference between nitrogen and carbon. This polarization disrupts the interlayer force, responsible for keeping the structure together, and destabilizes the layered structures. The electron donating methoxy groups delocalize their oxygen lone pairs into the phenyl rings, hereby strengthening interlayer interactions, stabilizing the COF and aiding in crystallization.²¹⁴ The $[\text{HC}\equiv\text{C}]_x\text{-TPB-DMTB-COFs}$ were highly porous ($1297\text{--}1973 \text{ m}^2 \text{ g}^{-1}$) with large pore diameters and stable in boiling water, strong acid and base. After synthesis these materials were subjected to a click reaction with azide **180** furnishing $[(\text{S-Py})_x\text{-COFs}]$ without affecting the porosity much. The chiral COFs could act as catalysts for Michael additions of cyclohexanone **181** with nitrostyrenes **182** in water with high activity and selectivity (Scheme 46). The least substituted ($x = 0.17$) COF showed the highest activity, obtaining 100% conversion after six hours, performing better than the homogeneous control and was further used to transform a range of nitrostyrenes. When COFs with a higher loading of reactive sites were used, the reaction times needed were much longer. The high density of sites leads to overlap and reduces the accessibility of the active sites. Recycling was possible and selectivity was unchanged, however as in the previous example reaching full conversion required much longer reaction times.²¹⁵

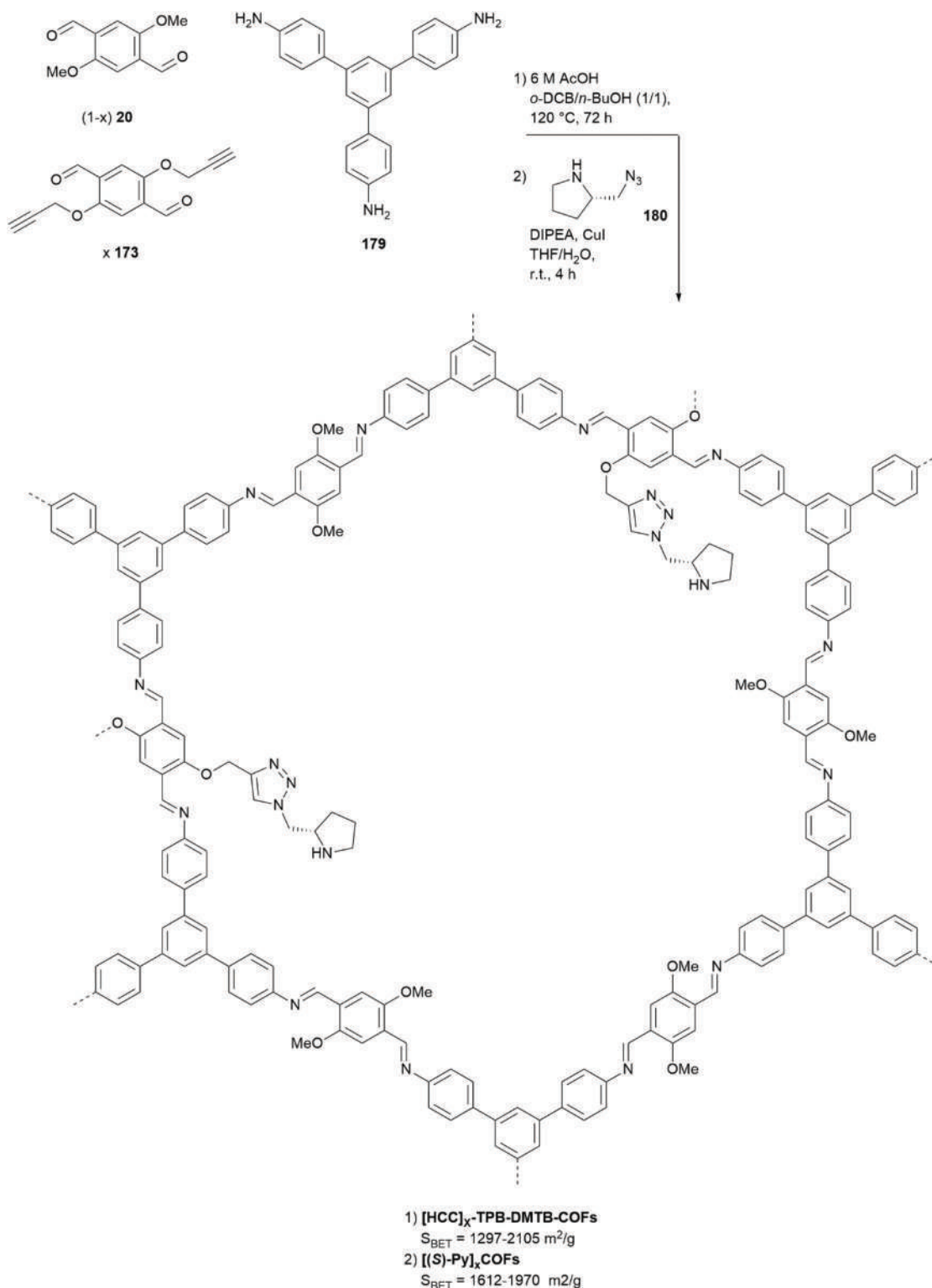
5.2.2 Bottom up approach. Building chiral polymers starting from chiral building blocks can have some advantages. The attachment of bulky amorphous groups onto the pore walls generally lowers the chemical stability, crystallinity and surface areas of the material. Starting from chiral building blocks also removes one extra step from the procedure, saving time, money and reducing possible complications. In 2016, Xu *et al.* constructed the first example of a chiral COF constructed by direct synthesis. Condensation followed by Boc-deprotection of chiral benzimidazolium monomer **184** with 1,3,5-triformylbenzene **48** or 2,4,6-triformylphloroglucinol **71**

led to highly crystalline imine linked **LZU-72** and β -ketoenamine linked **LZU-76**, with BET surface areas of respectively $1114 \text{ m}^2 \text{ g}^{-1}$ and $758 \text{ m}^2 \text{ g}^{-1}$ (Scheme 47). Due to its higher acid stability **LZU-76** was evaluated in the asymmetric aldol reaction of arylaldehydes **185** with acetone yielding β -hydroxyketones **186** in moderate to good yields and with high *e.r.* compared to an homogeneous catalyst analogue (Scheme 48). **LZU-76** could be recycled up to five times, however the yield dropped drastically.²¹⁶

The same group then developed a general strategy based on this benzimidazole scaffold to divergently synthesize a range of chiral COFs. Eight chiral aldehyde building blocks **188–195** were synthesized through nucleophilic substitution followed by Suzuki coupling of key building block **187**. From these monomers, different chiral COFs with identical framework structures were prepared through Schiff base condensation (Scheme 49). **MH-CCOF1-4** possess multiple hydrogen bonding sites, **TAH-CCOF1-2** possess both tertiary amine and hydrogen bonding sites. **SAH-CCOF-1-Boc** features secondary amine and hydrogen bonding sites and lastly **G-CCOF-1** has guanidine moieties. The authors studied the asymmetric amination reaction of ethyl 2-oxocyclopentane-1-carboxylate **196** with di-*tert*-butyl azodicarboxylate (DBAD) **197** to compare the performance of the different organocatalysts. **TAH-CCOF1** and **TAH-CCOF2** displayed the best activity, **TAH-CCOF2** was then used to convert a range of β -keto-esters in high yields and with high enantioselectivity of up to 98% and 91%, respectively (Scheme 50).²¹⁷

Zhang *et al.* reported the synthesis of another range of chiral COFs. Four L-proline and L-imidazoline based 1,3,5-tris(4-aminophenyl)benzene (TPB) **199** building blocks were condensed with DMTA **20**. Utilizing amine **TPB5**, no crystalline material could be obtained. The other, fully substituted COFs **DMTA-TPB1-4** were crystalline. However, after Boc and methyl ester deprotection only amorphous powders were formed. The high number of organocatalytic sites containing bulky groups probably interrupts the interlayer π - π interactions which stabilize the COFs. Especially after Boc-deprotection, the free amines can interact strongly with the methoxy and/or imine groups of the framework.²¹⁸ Co-synthesis with a substituent free building block **TPB-1** decreased the steric hindrance and weakened the interlayer repulsion, hereby increasing the crystallinity. When utilizing a 1/1 ratio of building blocks **TPB2-5** with **TPB1** highly crystalline COFs **DMTA-TPB1/2-5** were formed. Deprotection furnished crystalline **DMTA-TPB1/2'-5'** containing free amine and carboxylic acid groups (Scheme 51). The organocatalytic COFs were applied in asymmetric α -amino-oxylation, aldol and Diels-Alder reactions with good yields, selectivity and recyclability (Scheme 52). Amorphous analogous were much less active and needed extended reaction times, due to the non-uniform distribution and limited accessibility of catalytic moieties.²¹⁹

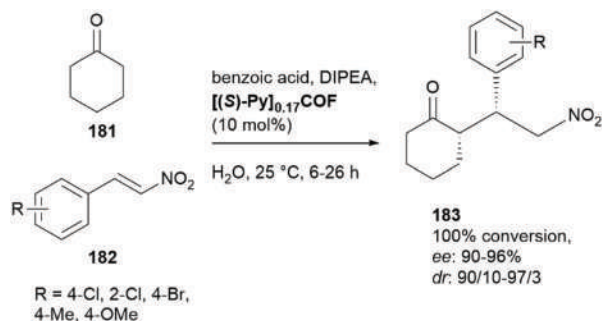
In 2019, Cui and coworkers reported the synthesis of two chiral COFs by condensation of chiral building blocks **210** and **211** containing 6,7-dihydro-5H-pyrrolo[1,2-*a*]imidazole or pyrrolidine moieties resulting in **TPB2-COF** and **Tfp2-COF**,



Scheme 45 Synthesis of chiral COFs by imine formation and click reaction.²¹⁵

respectively (Scheme 53). **TBP2-COF** was able to reach high conversions and good ee's, comparable to a homogeneous counterpart, in the Steglich rearrangement of oxazoles **212**, a rare way to generate quaternary stereocenters (Scheme 54).²²⁰

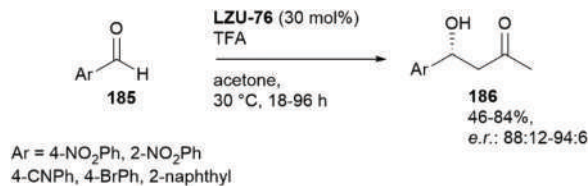
Tfp2-COF demonstrated good conversion and selectivity in the Michael reactions of nitrostyrenes **214** with cyclohexanone **181** (Scheme 54). Both COFs could be recycled at least five times and retained their porosity and crystallinity.²²¹



Scheme 46 Asymmetric Michael additions of cyclohexanone **181** with nitrostyrenes **182**.²¹⁵

Next to these aforementioned COFs many amorphous porous polymers with chiral moieties have been applied as catalysts. In 2012, Wang *et al.* reported a chiral POP containing diarylprolinol silyl ethers or Jørgensen–Hayashi catalysts.^{222,223,225} This porous polymer **JH-CPP** was synthesized by alkyne trimerization mediated by dicobalt octacarbonyl of a chiral functional building block **216** and structural building block (tetra(4-ethynylphenyl)methane **42** (Scheme 55). The catalytic activity was tested by an asymmetric Michael addition between nitrostyrenes **218** and aldehydes **217** (Scheme 56). High yields and good enantio- and diastereoselectivities were reported for a wide variety of substrates.

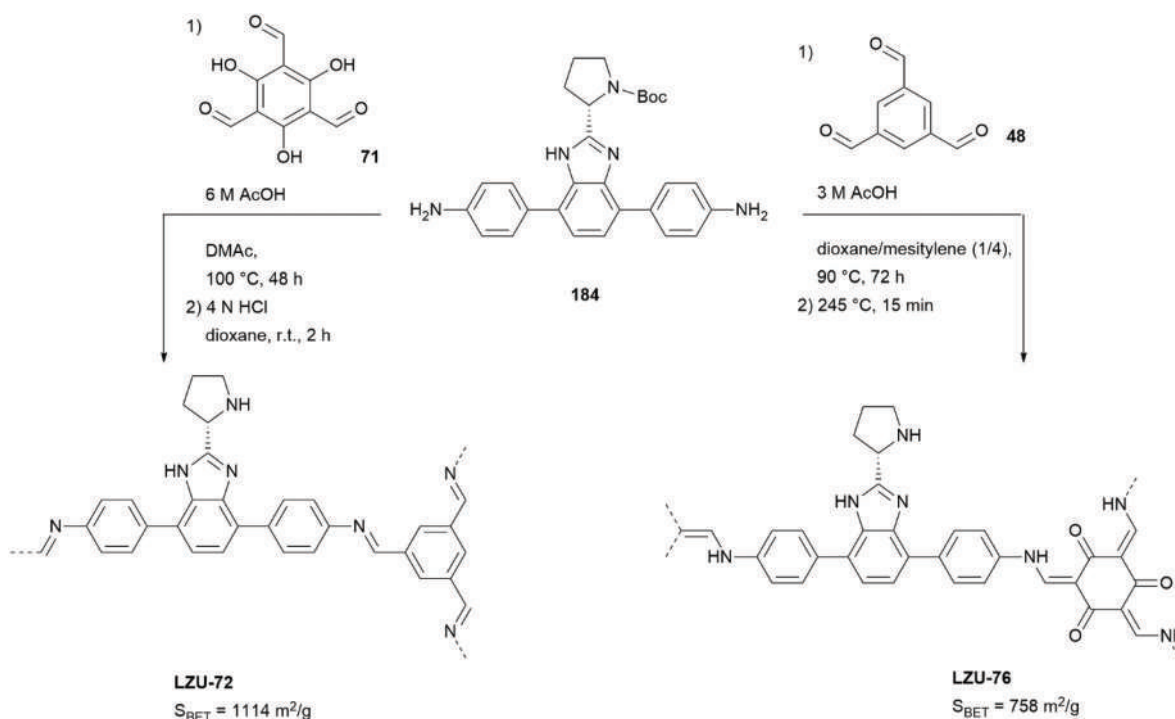
In recycling experiments the authors observed a lowering of the yield to 51% in the third run and a lowered surface area of 578 m² g⁻¹ after the fourth run. Structural analysis



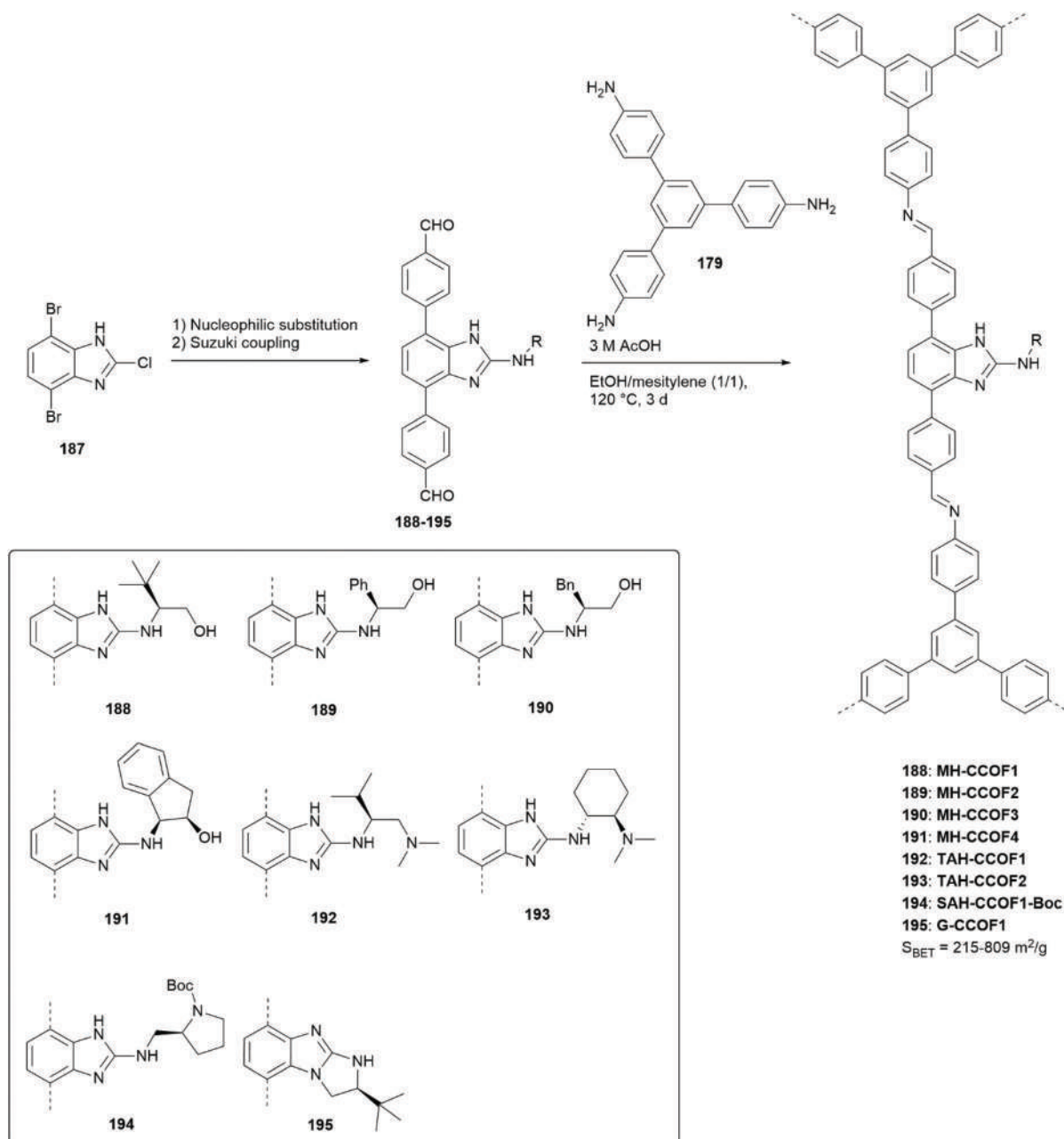
Scheme 48 LZU-76 catalyzed asymmetric aldol reaction of arylaldehydes **185** with acetone.²¹⁶

via solid state ¹³C-NMR showed that the structure of the material was retained, however new signals appeared. The authors state that a part of the substrates stays bound to **JH-CPP** in the form of the catalyst resting state **220**, the bulky cyclobutane intermediate.²²⁴ The inclusion of these bulky intermediates in the small pores slows down the reaction. This lowering of activity was also observed in similar proline containing polymers.²²⁵

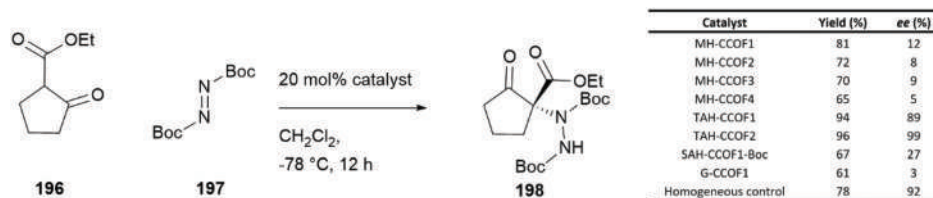
In 2017, the same group reported new chiral POPs based on a MacMillan catalyst containing building block. **Mac-CPOP-1** and **Mac-CPOP-2** were obtained by palladium catalyzed Sonogashira coupling of chiral building block **222** with tritopic linkers **7** or **221** (Scheme 57). **Mac-CPOP-2** possessed a surface area of 468 m² g⁻¹. However, **Mac-CPOP-1** showed no permanent porosity due to congestion of the imidazolidinone moieties inside the free volumes. These POPs showed good activity (64–95%) as enantioselective Diels–Alder catalysts for a wide range of β -unsaturated aldehydes **223** with cyclopentadiene **206** (Scheme 58).²²⁶



Scheme 47 Synthesis of chiral imine or β -ketoenamine linked COFs LZU-72 and LZU-76 starting from chiral amine **184**.²¹⁶



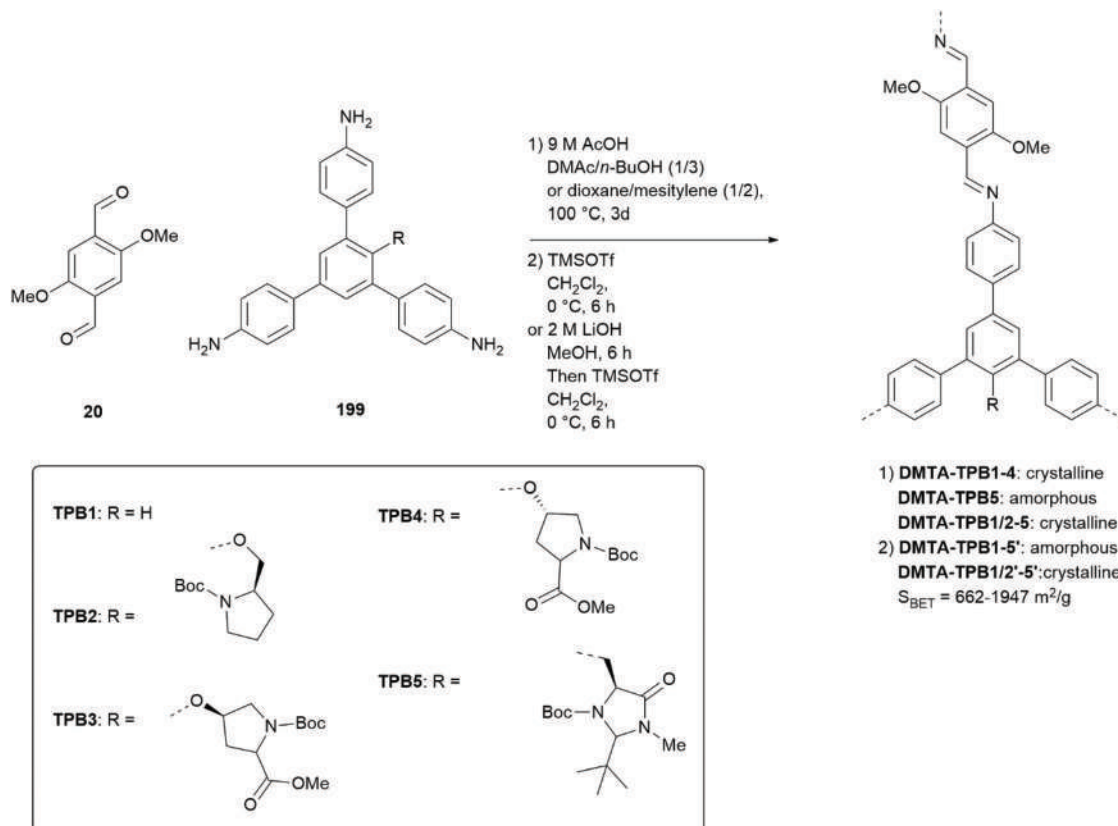
Scheme 49 Synthesis of a family of chiral COFs containing different types of organocatalytic moieties.²¹⁷



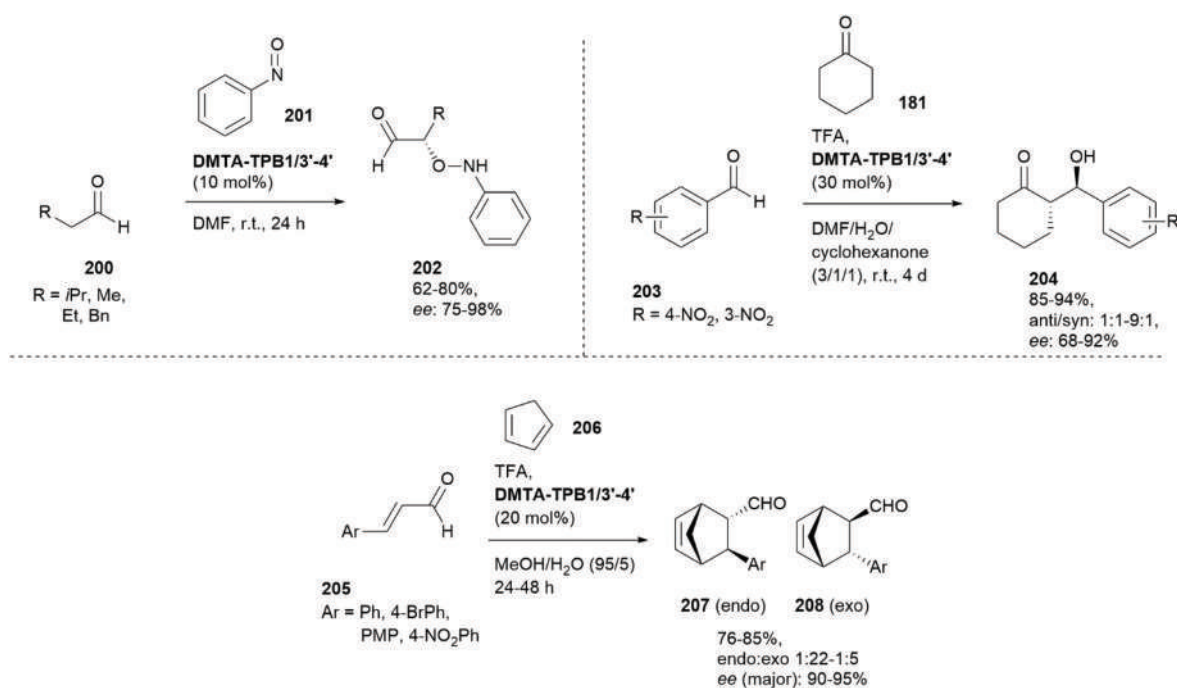
Scheme 50 Asymmetric amination reaction of ethyl 2-oxocyclopentane-1-carboxylate **196** with DBAD **197**.²¹⁷

In 2019, Lan *et al.* reported another direct synthesis of a chiral pyrrolidine based POP *via* a bottom up strategy to perform Michael additions in water. From a green chemistry

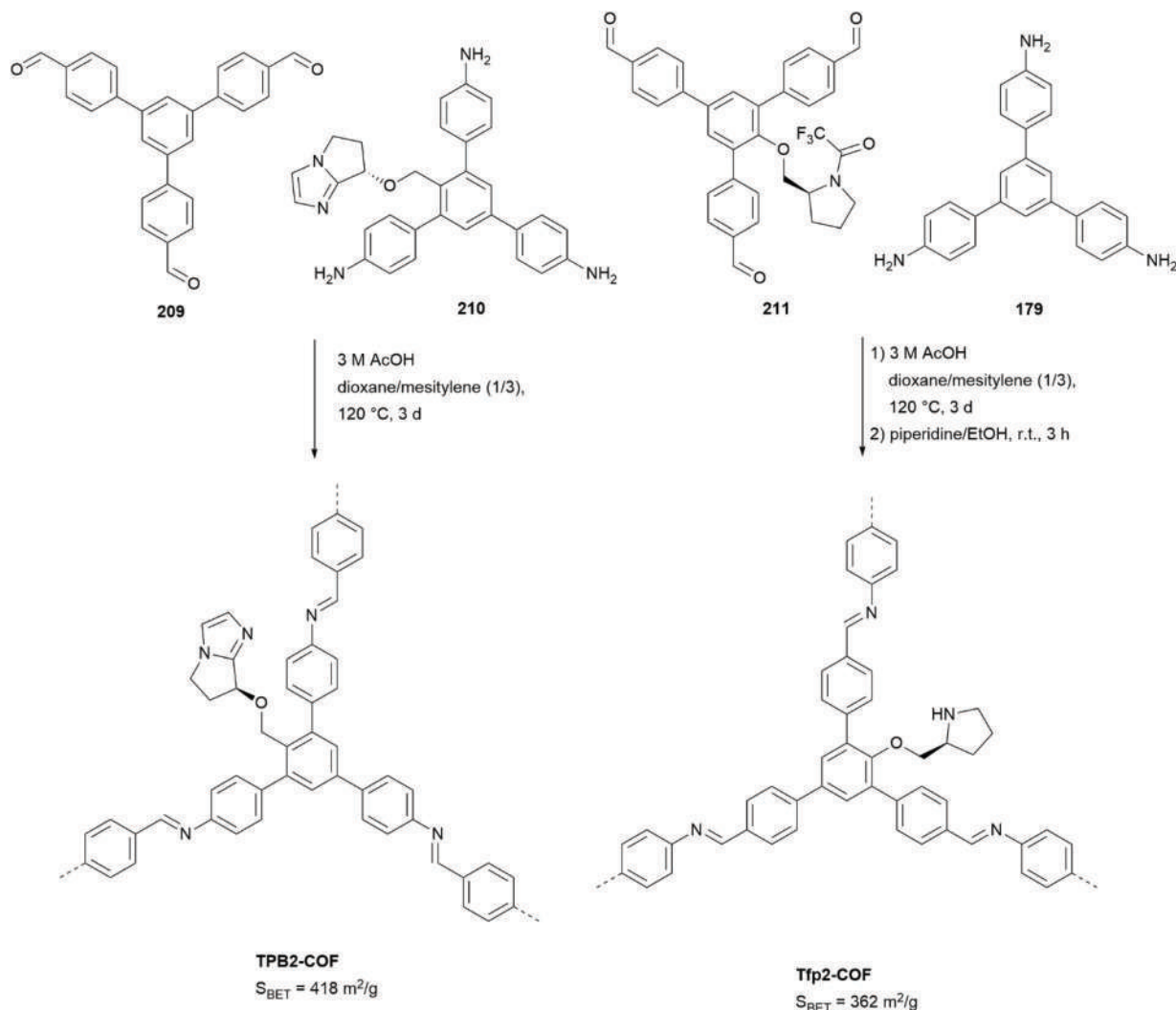
perspective, water is an extremely attractive solvent and therefore the development of effective organocatalytic Michael additions in water has attracted great interest. The followed



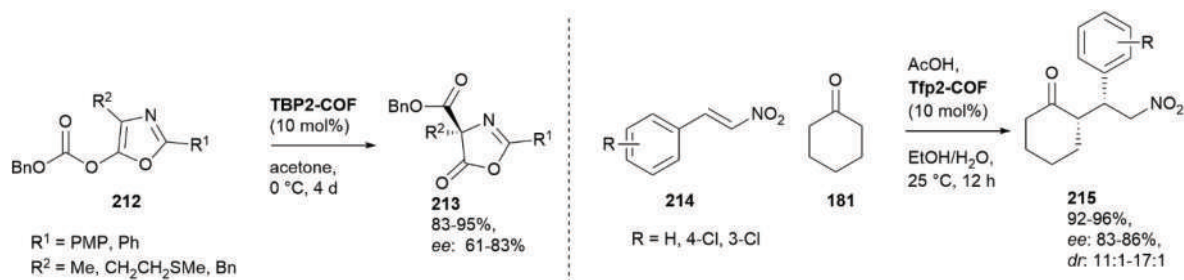
Scheme 51 Synthesis and deprotection of a range of chiral COFs based on 1,3,5-tris(4-aminophenyl)benzene **199**.²¹⁹



Scheme 52 Asymmetric α -amino-oxylation, aldol and Diels–Alder reactions catalyzed by DMTA-TPB1/3'-4'.²¹⁹



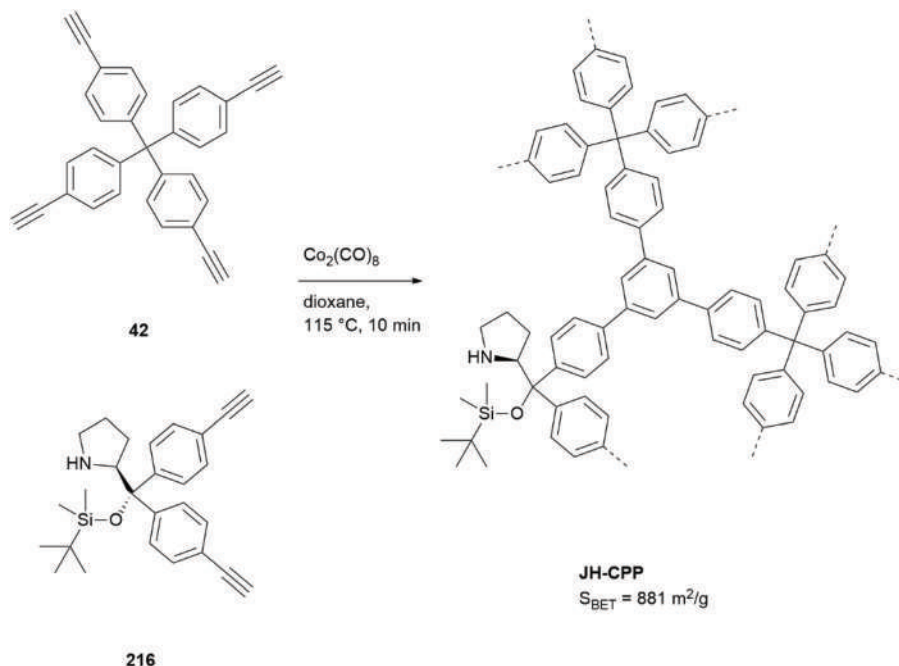
Scheme 53 Bottom up synthesis of chiral COFs with pyrrolidine and 6,7-dihydro-5H-pyrrolo[1,2-a]imidazole moieties.²²¹



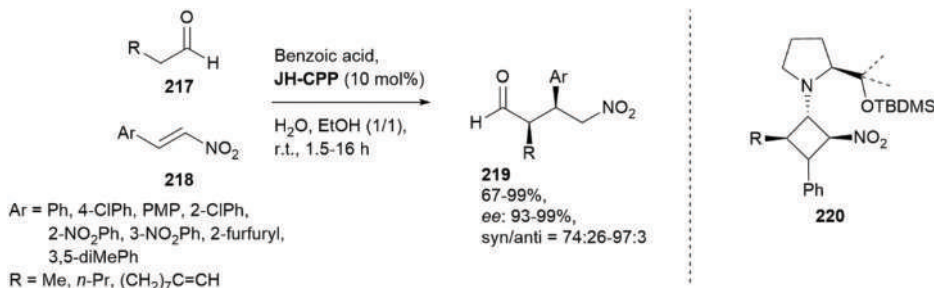
Scheme 54 Asymmetric Steglich rearrangement and Michael addition.²²¹

strategy typically entails linking the polar organocatalytic moiety with large hydrophobic groups. These groups are capable of aggregating the hydrophobic reactants and intermediates in water and hereby increase the reaction rate. *Via* Sonogashira coupling of tetratopic building block 42 with functional building block 226 a chiral CMP **Py-CPP** with a modest surface area of $228 \text{ m}^2 \text{ g}^{-1}$ was obtained

(Scheme 59). A wide range of Michael products could be formed with high yield and selectivity at room temperature in water (Scheme 60). The authors state that the incorporation of the triazole moiety led to high stereoselectivities due to it shielding the *si* face of the enamine double bond.²²⁷ This material also possessed size selectivity: a naphthyl substituted nitroolefin already showed a greatly decreased yield,



Scheme 55 Synthesis of JH-CPP by cobalt catalyzed alkyne trimerization.²²⁵



Scheme 56 Michael addition catalyzed by JH-CPP and proposed catalytic resting state intermediate **220**.²²⁵

and with a pyrene substituted substrate only trace amounts of product were observed.²²⁸

Cao *et al.* prepared chiral PAFs by Yamamoto cross-coupling between brominated tetraphenylmethane compound **229** and mono or ditopic functional building blocks **230** and **231** furnishing **dPOFs1-4** (Scheme 61). **dPOF4** formed from the low-connected, monotopic functional monomer **231**. Low connected building blocks are much more readily available or prepared. This greatly extends the type of POPs that can be easily prepared. These dPOFs catalyzed the aldol condensation between carbonyl compounds **233** and 2-, 3- or 4-nitrobenzaldehyde **232** with moderate yields and ee's (Scheme 62).²²⁹

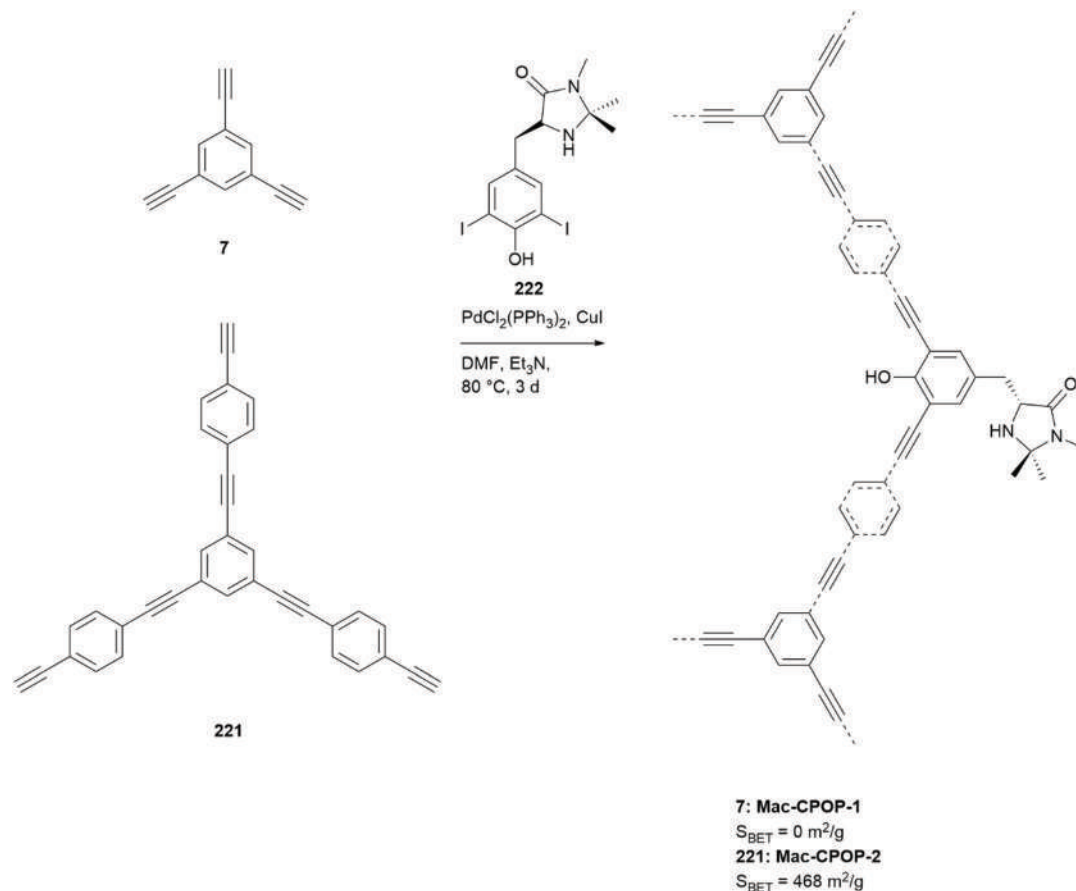
5.2.3 Asymmetric synthesis. Next to their direct synthesis and postsynthetic modification, chiral COFs can be synthesized by chiral induction or asymmetric catalysis.^{230,231} Recently, Wang *et al.* synthesized chiral COFs, (*R*)- or (*S*)-**DTP-COF** via a multicomponent one-pot polymerization of dialdehyde **20**, amine **18** and phenylacetylene **235**

catalyzed by chiral pyridine-2,6-bis(oxazolines)-Cu(I) complexes (Scheme 63). Circular dichroism spectra were taken to prove the chiral nature of these COFs. (*S*)-**DTP-COF** catalyzed the Michael addition between cyclohexanone and a wide range of nitrostyrenes with high yields (83–97%) and good selectivity (ee: 90–99% and dr: 68 : 32–88 : 12).²³¹

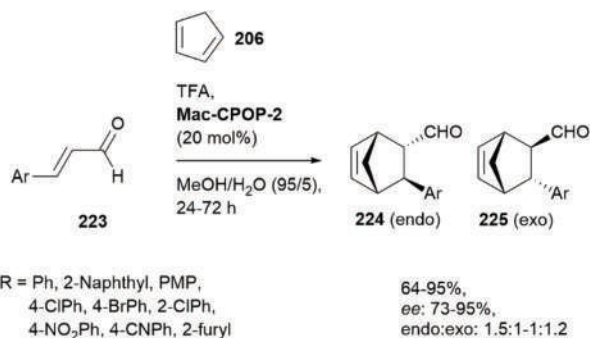
5.3 Other chiral catalysts

In a very early report in 2009 by Du *et al.* on metal free POP catalysts, diiodo functionalized Tröger's base **236** was polymerized through Sonogashira coupling with triethynylbenzene **7** (Scheme 64). The resulting POP had a relatively high surface area ($750 \text{ m}^2 \text{ g}^{-1}$) and showed reasonable activity (74% yield) for the addition of diethylzinc to 4-chlorobenzaldehyde. However, the polymer itself was not chiral and thus the reaction was not enantioselective.²³²

The same reaction has been asymmetrically catalyzed by porous polymers synthesized by trimerization of alkyne groups



Scheme 57 Synthesis of Macmillan catalyst containing chiral POPs Mac-CPOP-1 and Mac-CPOP-2.²²⁶

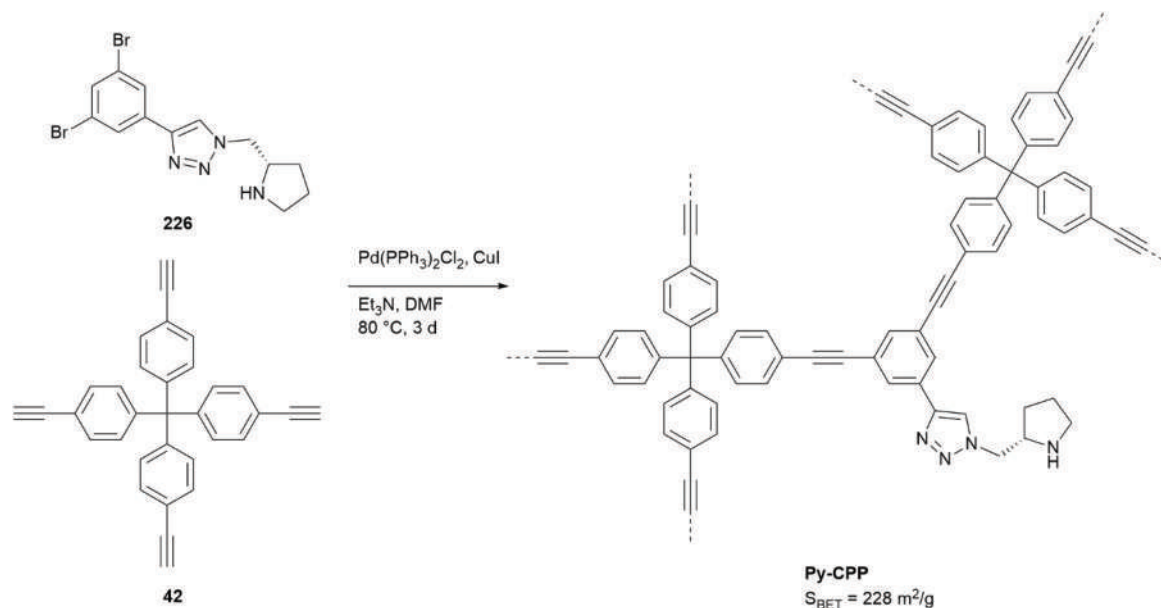


Scheme 58 Asymmetric Diels Alder reaction catalyzed by Mac-CPOP-2.²²⁶

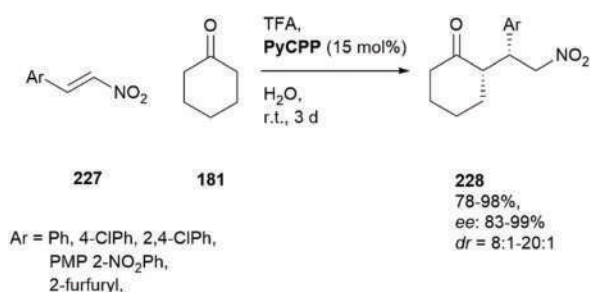
of BINOL derived building blocks. After treatment with titanium isopropoxide ($\text{Ti}(\text{OiPr})_4$), these polymers were converted into chiral heterogeneous Lewis acid catalysts, however only moderate ee's (up to 81%) were reached in the addition reaction.²³³ Analogously, $\alpha,\alpha,\alpha',\alpha'$ -tetraaryl-2,2-disubstituted 1,3-dioxolane-4,5-dimethanol (TADDOL) building blocks functionalized with alkynes were coupled *via* Sonogashira coupling with tetrakis(4-bromophenyl)methane. These materials were

treated with $\text{Ti}(\text{OiPr})_4$ or reacted in the presence of $\text{Ti}(\text{OiPr})_4$ which gave higher ee's (up to 91%).²³⁴ Two-dimensional COFs with embedded chiral functionalities were synthesized by imine condensations of TADDOL-derived tetra-aldehydes with 4,4'-diaminodiphenylmethane. After postsynthetic modification of the chiral dihydroxy groups with $\text{Ti}(\text{OiPr})_4$ these COFs were efficient and recyclable heterogeneous catalysts for asymmetric addition of diethylzinc to aldehydes with high enantioselectivity (up to 94%).²³⁵

Recently, Ma *et al.* developed a chiral COF (**R**)-CuTAPBN-COF for the catalytic asymmetric synthesis of a key intermediate, (*S*)-CIK **242**, in the synthesis of (*S*)-clopidogrel **243**, an antiplatelet medication used as a heart disease and stroke risk reducer. The chiral COF was synthesized by imine formation between chiral BINOL derived dialdehyde **239** and copper containing porphyrin based amine **238** (Scheme 65). (*S*)-CIK was obtained *via* an asymmetric (**R**)-CuTAPBN-COF catalyzed Strecker reaction between aldehyde **241** and amine **240** in 98% yield with 94% ee (Scheme 66). The BINOL derived moieties acted as chiral Lewis acids, whereas the porphyrin units acted as photothermal conversion units, converting light into heat, increasing the temperature in the reaction vessel from room temperature to 50 °C. In the dark, at this temperature, a similar high yield was obtained. However, in the dark,



Scheme 59 POP containing chiral pyrrolidine moieties synthesized by Sonogashira coupling.²²⁸

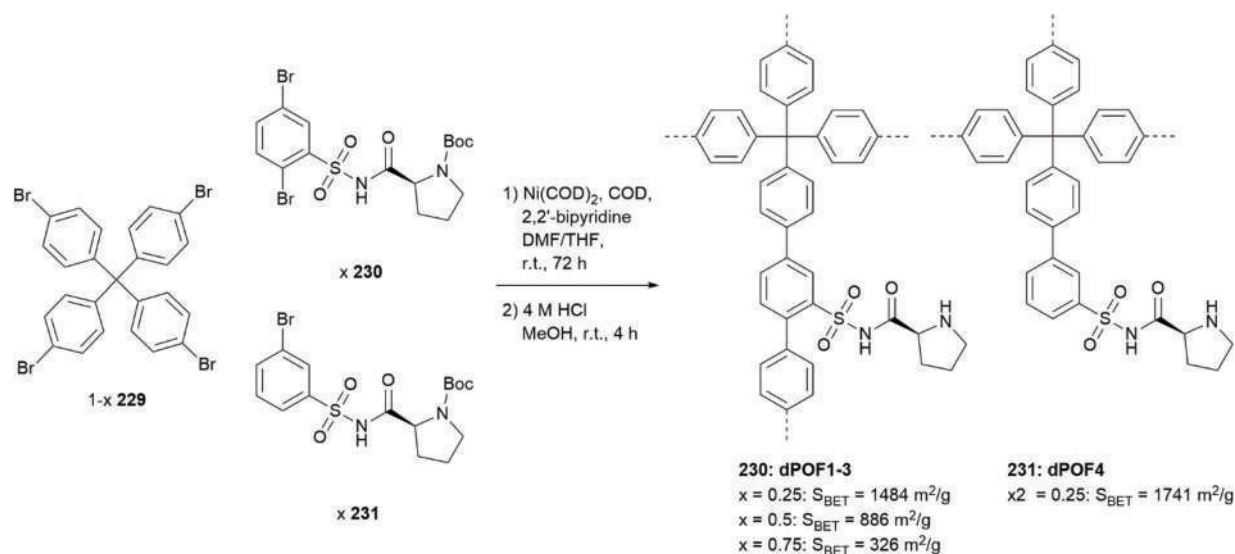


Scheme 60 Asymmetric Michael addition catalyzed by PyCPP.²²⁸

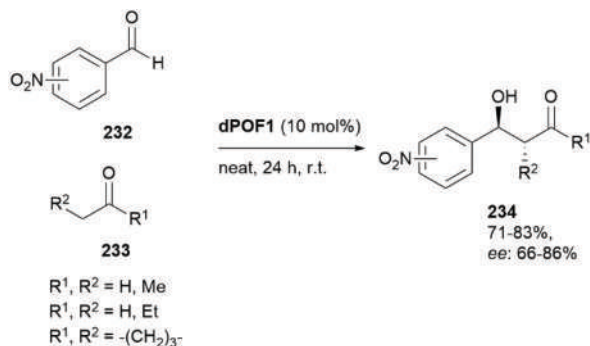
at room temperature no product could be detected. Moreover, these authors designed a model continuous flow-through setup for the gram scale preparation of (*S*)-CIK which proceeded smoothly, producing 1.29 grams in eight hours with a yield of 90% and 93% ee. Furthermore, a range of different aldehydes and secondary amines could be converted with excellent yield and ee's, except for larger substrates such as fluorene-2-carboxaldehyde or 9-anthracenecarboxaldehyde.²³⁶

5.4 Outlook on POPs as chiral catalysts

The aforementioned examples prove that POPs show great promise as chiral catalysts, with activities and selectivities



Scheme 61 Synthesis of chiral POPs by reactions with low connected building blocks.²²⁹

Scheme 62 dPOF1 catalyzed aldol condensation.²²⁹

often equal or greater than the homogeneous analogues. By varying the connectivity, size and geometry of the POP building blocks, theoretically, the catalytic environment can be very precisely controlled.¹⁹⁷ However, the full potential of these materials is yet to be realized. In most cases the POPs are used as a type of inert carrier material. Especially for COFs, the molecular structure is so well defined and allows precise manipulation that much more intricate and advanced designs should be possible. In enzymes multiple secondary interactions are responsible for stabilizing transition states and helping with substrate binding and such a tailored design of the catalytic sites would also be possible with COFs.⁴³ Moreover, the scope of the reactions covered still mainly focusses on enamine/iminium organocatalysis with other modes being underdeveloped.

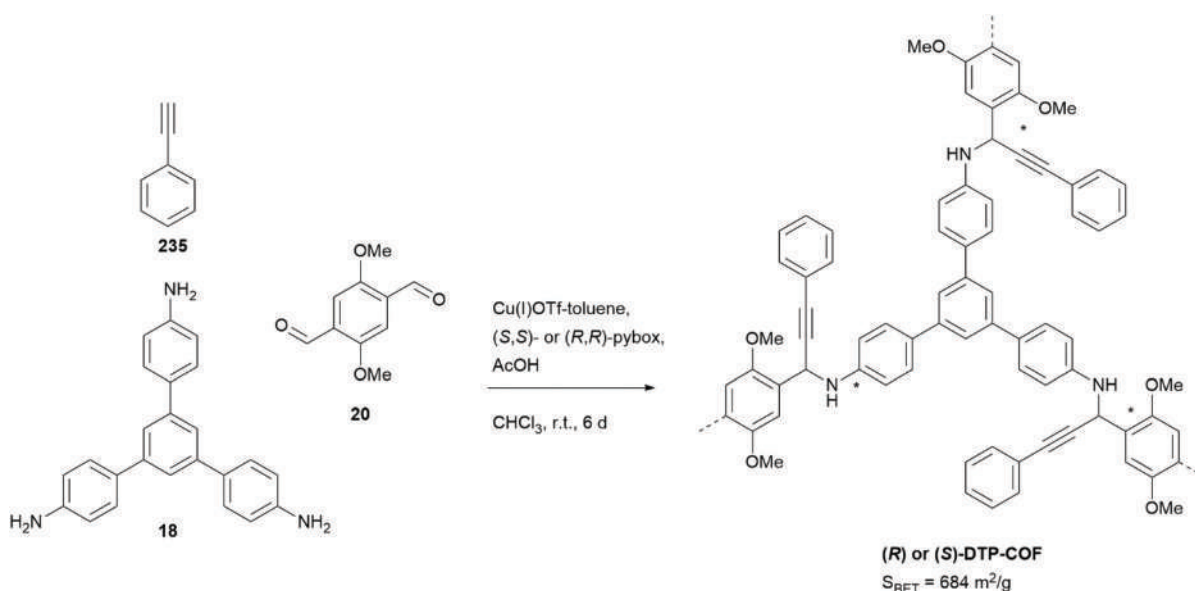
The synthesis of the materials also deserves comment. In the case of the chiral phosphoric acids the used building blocks require very long and hazardous synthesis sequences. Compounds 155 and 156 require a ten step complex synthesis

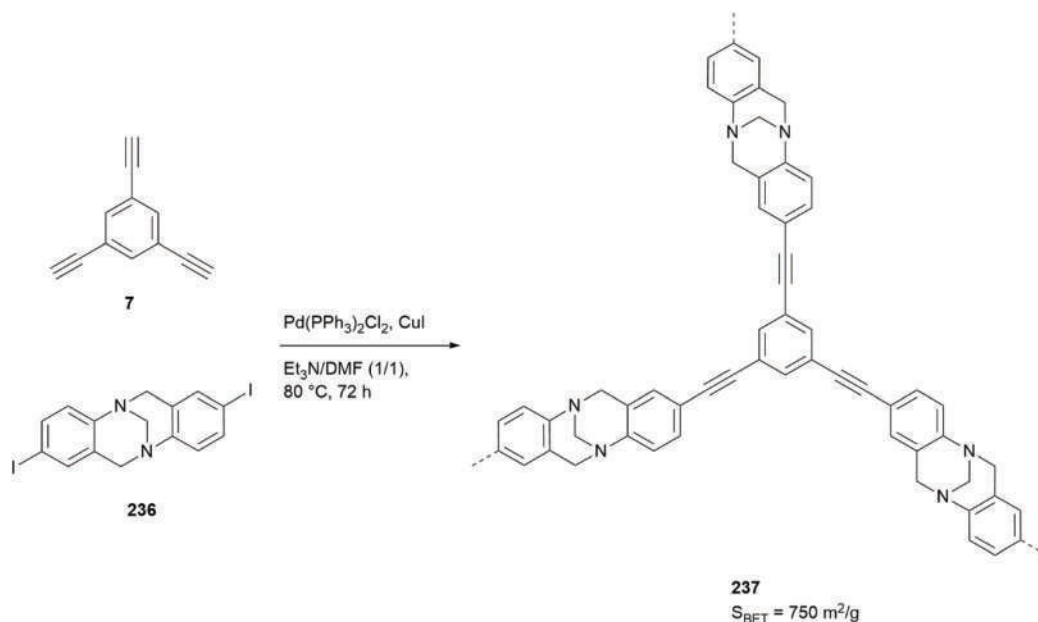
starting from BINOL, including hazardous chemicals such as MOMCl, BuLi, DIBAL, POCl₃, Br₂... Similarly, compounds 157 and 158 required a five step synthesis from BINOL. The other synthesized chiral COFs have the typical synthetic shortcomings of COFs. Namely, difficult to access monomers and synthesis in unattractive conditions on small scales. The other, amorphous chiral POPs can typically be produced on bigger scales, however their synthesis conditions are still rather unattractive: precious metal based cross-couplings at high temperatures for long times and the monomers can be rather exotic as well.

6 POPs as catalysts for CO₂ fixation

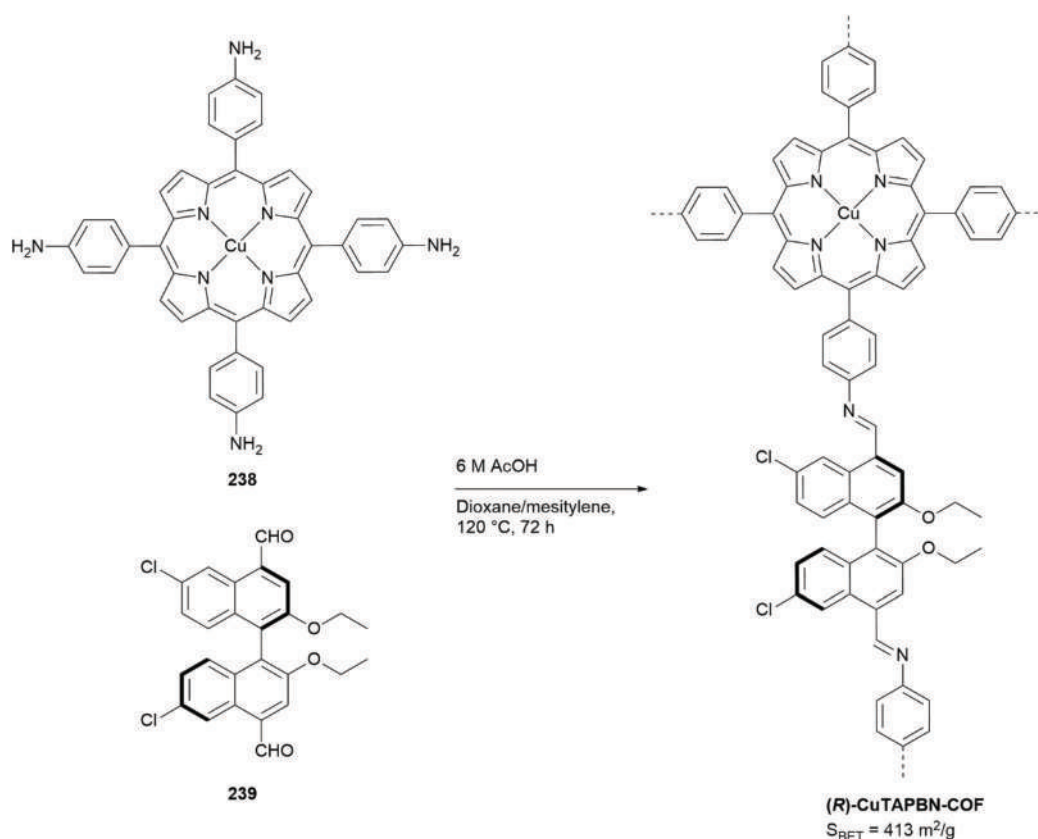
The accumulation of CO₂ in the atmosphere is the main cause of global warming. The reduction of CO₂ emissions is therefore a big challenge with many facets and possible solutions. Carbon capture and sequestration (CCS) forms one possible part of a solution, capturing and storing CO₂ as waste, or even better: turning this waste into high value chemicals.²³⁷ One promising strategy is the cycloaddition of CO₂ with an epoxide forming cyclic carbonates, a very atom efficient transformation (Scheme 67). The carbonate products have applications as degreasers, monomers, green aprotic solvents, electrolytes in lithium ion batteries...^{238–242}

The cycloaddition reaction is generally catalyzed by nucleophilic catalysts, to open the epoxide ring, and/or (Lewis) acid catalysts, to activate the epoxide towards nucleophilic attack. Industrially sodium iodide or tetra-*n*-butylammonium bromide (TBAB) are used as catalysts, but new, greener catalysts are being developed. Homogeneously, efforts have been focused on ionic liquids,²⁴³ transition-metal complexes²⁴⁴ and organocatalysts.²⁴⁵ Heterogeneously, the main challenge con-

Scheme 63 A chiral COF synthesized by asymmetric synthesis.²³¹



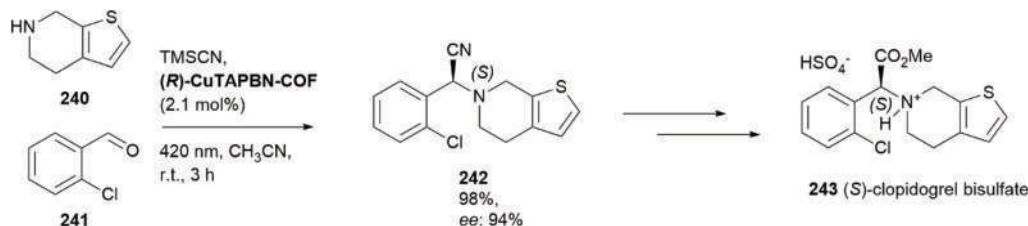
Scheme 64 Synthesis of a Tröger's base containing POP by Sonogashira coupling.²³²



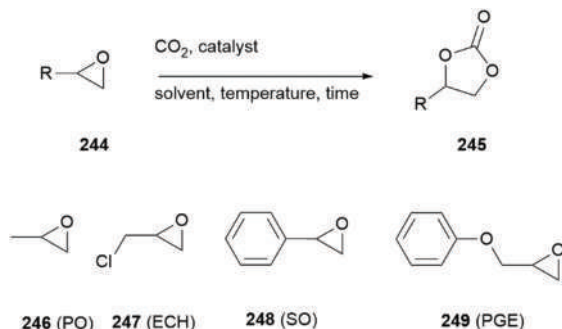
Scheme 65 Synthesis of a chiral COF by condensation between porphyrin 237 and BINOL based aldehyde 238.²³⁶

sists in constructing a (metal free) recyclable catalyst capable of performing under ambient conditions. This implies a good CO_2 enrichment capability, for which ionic sites providing

strong interactions, and micropores providing large surface areas are important. Most of the POPs used thus far have charged moieties. These ionic polymers possess intrinsic



Scheme 66 COF mediated asymmetric Strecker reaction towards (S)-clopidogrel bisulfate **242**.²³⁶

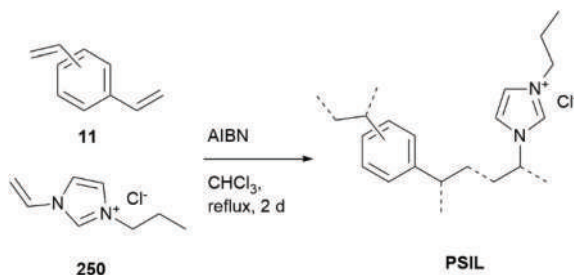


Scheme 67 The cycloaddition of CO₂ with epoxides and the most common substrates: propylene oxide (PO) **246**, epichlorohydrin (ECH) **247**, styrene oxide (SO) **248** and phenyl glycidyl ether (PGE) **249**.

affinity for CO₂ by virtue of the strong dipole-quadrupole interactions between their ionic moieties and CO₂. First, imidazolium containing POPs and the related carbenes will be discussed, then phosphonium based POPs followed by COFs, CTFs and other polymers are reviewed.

6.1 Imidazolium based POPs

In 2007, Xie *et al.* immobilized ionic liquids through radical copolymerization of 3-butyl-1-vinylimidazolium chloride **250** with cross linker divinylbenzene **11**. Hereby highly cross-linked polymer supported ionic liquids **PSIL** with an ionic site loading of about 1 mmol g⁻¹ were prepared, a surface area was not reported (Scheme 68). **PSIL** was able to promote the cycloaddition of CO₂ with PO, reaching 97% yield after seven hours under high (6 MPa) CO₂ pressure (Table 5, entry 1), and could be recycled five times with no considerable reduction in yield. Furthermore, a wide range of epoxides could be converted



Scheme 68 Synthesis of **PSIL** by radical copolymerization.²⁴⁶

with good yields (79–96%). **PSIL** performed better than homogeneous counterparts, which formed a separate phase in the reaction medium. The heterogeneous catalyst formed a dispersion leading to much better mass transfer and thus higher yields.²⁴⁶

Polymerization of *e.g.* divinylimidazolium or similar building blocks without external crosslinkers, such as divinylbenzene, doesn't generate sufficient porosity. However, some methods exist to increase the surface area. Hard templating consists of the polymerization around additive inorganic components (generally silica), which are then etched away with acid or base.^{247–249} Soft templating involves polymerization around an organic tri-block polymer template, which is afterwards removed *via* extraction.²⁵⁰ Another option is electrostatic, template free crosslinking by complexation between polymerized (linear) ionic liquids with polyanions, thus forming a three dimensional net by polyelectrolyte complexation.^{251–254}

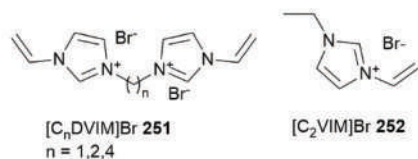
In 2015, Wang *et al.* prepared ionic POPs by free radical polymerization of bis-vinyl imidazolium salts ([C_nDVIM]Br) **251** without adding external templates or crosslinkers by means of ionothermal polymerization in a mixture of ionic liquid **253** with water (Fig. 4). The spacer length *n* between the imidazolium moieties was critical in achieving porous structures. For *n* = 1 a porous polymer **PDMBr** was obtained with a surface area of 205 m² g⁻¹. With more flexible monomers (*n* = 2 or 4) low porosities were obtained. The influence of the alkyl length of the polymerization solvent **253** was also pronounced, with porosity increasing as alkyl length went up. But when *n* = 8 no porosity was obtained, pointing to pore collapse. Other ionic solvents such as [C₄Py]Br **254** and [P₄₄₄₄]Br **255** produced nonporous polymers. However, tetrabutyl/propyl ammonium bromide (TBAB or TPAB) were successful in generating porous structures, for TPAB an even higher porosity of 260 m² g⁻¹ was reported. The used co-solvent was also essential, when water was replaced with other solvents (EtOH, AcOH, DMF, DMSO) poor porosities were obtained. The water containing IL contains both polar (imidazolium) and apolar (alkyl) moieties. The polar domain is where polymerization takes place and the apolar domains act as a template for pore formation. Larger alkyl chains thus lead to an expansion of the pore volumes due to the polymer being formed around a larger template. For **PDMBr** a high CO₂ absorption of 1.02 mmol g⁻¹ (25 °C, 1 atm) was measured and it proved to be highly active at catalyzing the cycloaddition reaction. The conversion of allyl glycidyl

Table 5 Cycloaddition of CO₂ with epoxides

Entry: name	Active site	Substrate	Reaction conditions	Yield (%)	Ref.
<i>Imidazolium</i>					
1: PSIL	Cl [−]	PO	0.68 mol% PSIL , 6 MPa CO ₂ , 110 °C, 7 h	97	246
2: PDMBr	Br [−]	Allyl glycidyl ether	1.3 mol% PDMBr , 1 MPa CO ₂ , 110 °C, 3 h	99	255
			2.6 mol% PDMBr , 0.1 MPa, 120 °C, 12 h	99	
			2.6 mol% PDMBr , 0.1 MPa, 70 °C, 48 h,	95	
3: AE-PIL-Cl	Cl [−]	PO	1 mol% AE-PIL-Cl , 1 MPa CO ₂ , 140 °C, 6 h	100	256
		ECH		93	
4: HIP-Br-2 , GHIP-Br	Br [−]	SO	0.2 mol% HCP-Br-2/GHIP-Br , 10 bar CO ₂ , 120 °C, 6 h	99	257
				86	
5: HIP-Br-2/ZnBr₂	Br [−] , Zn ²⁺	SO	4 mol% HIP-Br-2 , 4 mol% ZnBr ₂ , 1 bar CO ₂ , DMF, 25 °C, 120 h	93	257
6: I_{C2}HCP-5b	Br [−]	ECH	0.05 mol% I_{C2}HCP-5b , 3 MPa (15% CO ₂), 120 °C, 4 h	81	258
7: POM3IM	Cl [−]	PO	0.005 mol% POM3IM , 1 MPa CO ₂ , EtOH, 120 °C, 8 h	92	259
		ECH		90	
8: T-Im	I [−]	ECH	0.065 mol% T-Im , 1 MPa CO ₂ , 150 °C	85	260
9: IT-POP-1	Cl [−]	PO	0.1 mol% IT-POP-1 , 1 MPa CO ₂ , 130 °C, 10 h	96	261
11: PImCl	Cl [−]	ECH	5.6 mg PImCl or PNHC per mmol, 6.9 bar CO ₂ , 130 °C, 4 h	86	262
12: PNHC	Carbene	ECH		94	
13: NP-NHC	Carbene	ECH	5 w/w% NP-NHC , 1 bar CO ₂ , 120 °C, 24 h	98	263
14: PEAMC1	Carbene	ECH	10 mg PEAMC1 per mmol, 10 bar CO ₂ , 120 °C, 2 h	99	264
		ECH	10 mg PEAMC1 per mmol, 1 bar CO ₂ , 120 °C, 8 h	93	
15: PPh₃-ILBr-ZnBr₂@POPs	Br [−] , Zn ²⁺	PO	0.0125 mol% PPh₃-ILBr-ZnBr₂@POPs , 3 MPa CO ₂ , 120 °C, 1 h	44	265
<i>Phosphonium</i>					
16: PP-Br	Br [−]	PGE	1 mol% PP-Br , 1 atm CO ₂ , DMF, 140 °C, 20 h	99	267
17: 2	Br [−]	PO	0.0005 mol% 2 , 1 MPa CO ₂ , DMF, 100 °C, 9 h	94	268
18: 2 + 6	Br [−] + ZnBr ₂	PO	0.0005 mol% 2 + 6 , 1 MPa CO ₂ , DMF, 100 °C, 4 h	90	268
19: PIP-Bn-Cl	Cl [−]	ECH	0.46 mol% PIP-Bn-Cl , 0.1 MPa CO ₂ , 25 °C, 80 h	95	269
			0.46 mol% PIP-Bn-Cl , 0.1 MPa CO ₂ , 100 °C, 3 h	>99	
<i>COFs</i>					
20: 2,3-DhaTph COF	Catechol	SO	0.2 mol% 2,3-DhaTph COF , 0.5 mol% TBAL, 1 atm CO ₂ , 110 °C, 12 h	94	270
		PO		78	
		ECH		88	
21: PPSCCOF-TpBpy-Cu	Cu ²⁺ , Br [−]	ECH	0.17 ^a /0.14 ^b mol % PPSCCOF-TpBpy-Cu , 1 atm CO ₂ , 40 °C, 24 h	95	271
22: ImIP@TT-COF	N-H, Br [−]	ECH	3 mg ImIP@TT-COF per mmol, 0.15 atm CO ₂ , 24 h, 120 °C	99	272
23: COF-JLU6 , COF-JLU7	OH, Br [−]	ECH	0.5 mol% COF-JLU6/7 , 0.5 mol% TBAB, 0.1 MPa CO ₂ , 40 °C, 48 h	86	273
				92	
24: OMe-OH-TPBP-COF , OH-TPBP-COF , OMe-TPBP-CF	OH, Br [−]	ECH	1 mol% OMe/OH-TPBP-COF , 5 mol% TBAB, 0.1 MPa CO ₂ , 40 °C, 24 h	91	274
				89	
				41	
<i>CTFs</i>					
25: CTF1 , CTF1-HAS , CTFP-HAS	Basic N	ECH	5.6 mg CTF per mmol, 6.9 bar CO ₂ , 130 °C, 4 h	76	281
				96	
				95	
26: CTF0-400/600-20/20-5	Basic N	ECH	5.6 mg CTF0-400/600-20/20-5 per mmol, 6.9 bar CO ₂ , 130 °C, 4 h	93	27
27: 2,5-DCP-CTF-0	Basic N	ECH	5.6 mg 2,5-DCP-CTF-0 per mmol, 6.9 bar CO ₂ , 130 °C, 4 h	95	282
28: cCTF-500	Basic N, Cl [−]	PO	4 wt% cCTF-500 , 1 MPa CO ₂ , 90 °C, 12 h	99	283
		ECH		95	
		SO		36	
29: IPF-CSU-1	Cl [−] , Br [−]	PO	1 mol% IPF-CSU-1 , 11.5 mol% TBAB, 0.1 MPa CO ₂ , 25 °C, 48 h	99	284
30: HB-CTP	Basic N, Br [−]	PO	5 mg HB-CTP per mmol, 5 mol% TBAB, 2 MPa CO ₂ , 80 °C, 12 h	97	285
		ECH		99	
		SO		88	
		PGE		91	
31: CYA-ANIS	Basic N, I [−]	ECH	6.7 mg CYA-ANIS per mmol, 1.67 mol% TBAL, 1.02 atm CO ₂ , 105 °C, 20 h	100	286
		SO		100	
		PGE		100	
<i>Other</i>					
32: POF-PNA-Br[−]	Br [−] , COOH	PO	1.7 mg POF-PNA-Br[−] per mmol, 0.1 MPa CO ₂ , 40 °C, 48 h	92	287
33: PCP-Cl	Cl [−]	PO	5 wt% PCP-Cl , 3 MPa CO ₂ , 100 °C, 12 h	99	288
		SO		16	
34: COP-(114-CH₂NMe₃⁺)Cl[−]	Cl [−]	ECH	4 mg COP-(114-CH₂NMe₃⁺)Cl[−] per mmol, 1 bar CO ₂ , 100 °C, 24 h	>99	289
		SO		90	
35: PhCH₂TMG	Basic N	SO	0.1 mol% PhCH₂TMG , 7 bar CO ₂ , 100 °C, 4–20 h	90	290
				100	
36: CBAP-1(EDA)	Basic N	ECH	2 mg CBAP-1(EDA) per mmol (2 mol%), 1 MPa CO ₂ , 130 °C, 4 h	98	291
37: MOP-0	Basic N	ECH	5 mg MOP-0 per mmol, 1 MPa CO ₂ , 100 °C, 24 h	89	292

^a mmol of Cu²⁺. ^b mmol of Br[−].

Monomers



Solvents

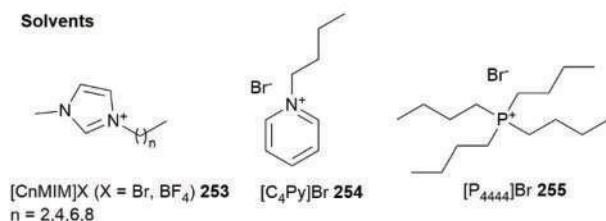
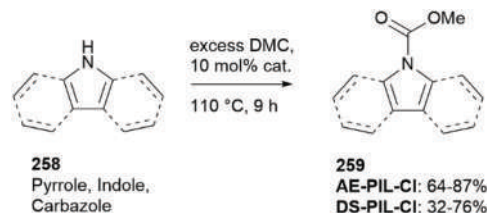


Fig. 4 Monomers and solvents used in the synthesis of porous ionic liquids.²⁵⁵

ether, for example, reached 99% after three hours under 1 MPa CO₂ pressure. Interestingly **PDMBR** was also active under lower pressures and temperatures only requiring extended reaction times and catalyst loading (Table 5, entry 2).²⁵⁵

In 2017, Qin *et al.* developed a novel strategy to increase the surface area of ionic polymers prepared through radical cross-linking, by utilizing monomers with bulky salicylate counterions followed by ion exchange with smaller ions (Scheme 69). Polymers prepared through direct synthesis with bromine/chlorine/acetate counterions had much lower surface areas (18–26 m² g⁻¹) than the ones prepared through anion exchange **AE-PIL-X** (129–228 m² g⁻¹). These higher surface area materials were more active in the cycloaddition reaction and **AE-PIL-Cl** was the most active (Table 5, entry 3). A range of substrates with increasing chain length were tested and activity generally decreased, but the decline was more pronounced for less porous polymers. Furthermore, these POPs catalyzed N-heterocyclic carbomethoxylation reactions of heterocycles **258** with dimethyl carbonate (Scheme 70).²⁵⁶

The Wang group reported ionic HCPs **HIP-Cl/Br-1/2** by one-pot quaternization-Friedel-Crafts-alkylation reactions between 2-phenylimidazole **260** and crosslinkers dichloro/bromoxyl-

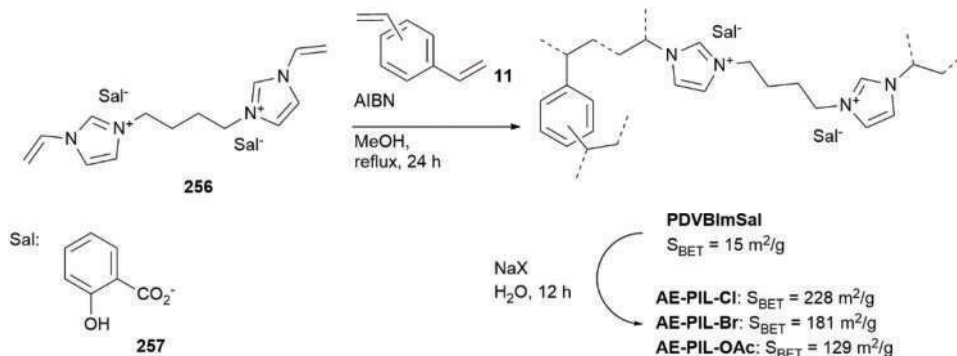


Scheme 70 Carbomethoxylation of N containing heterocycles.²⁵⁶

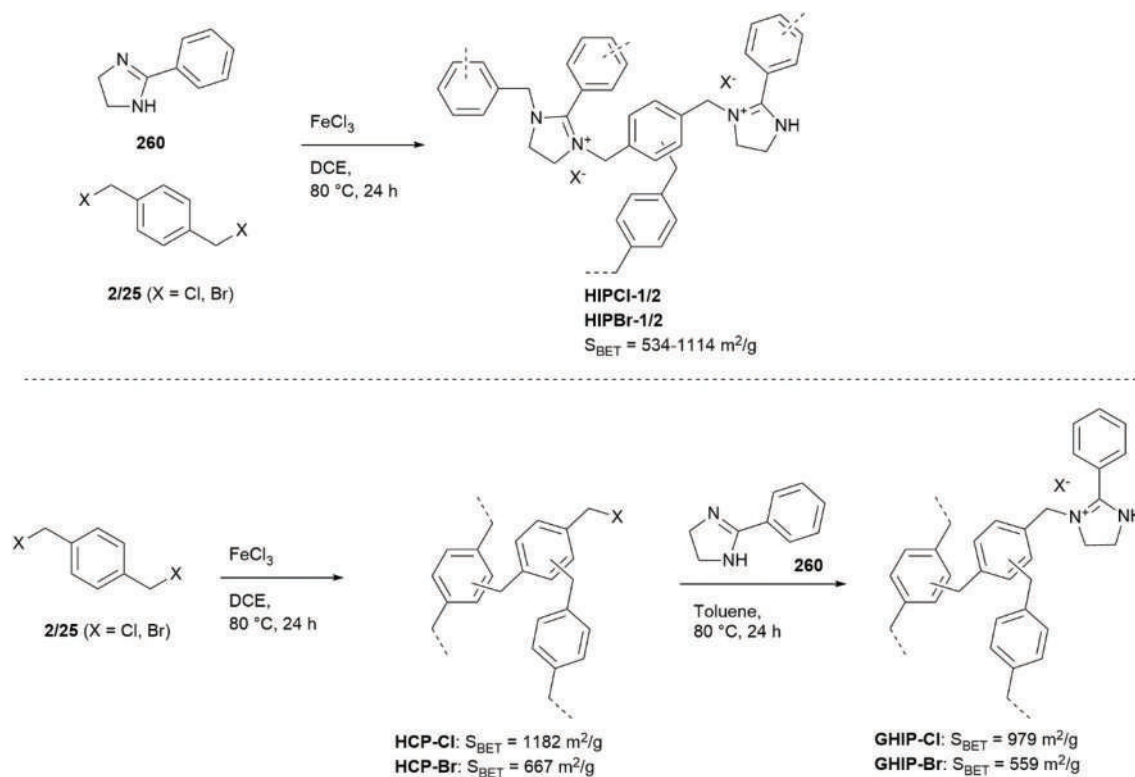
lene (DCX,DBX) **2/25**. Nonionic HCPs **HCP-Cl/Br** were synthesized using only the crosslinker and the residual chloro- or bromomethyl groups were then reacted with 2-phenylimidazole **260** forming ionic liquid grafted polymers **GHIP-Cl/Br** (Scheme 71). Of these catalysts **HIP-Br-2** was the most active (99%, Table 5, entry 4) for the conversion of styrene oxide, more active than the grafted polymers **GHIP-Cl** or **GHIP-Br** (75–86%), a polystyrene resin supported imidazolium salt (59%) or a homogeneous analogue (69%). Utilizing ZnBr₂ as Lewis acid co-catalyst (Table 5, entry 5) high yields could be obtained at room temperature using a flue gas analogue consisting of 15% CO₂ and 85% N₂. Direct capture of CO₂ from flue gas is highly advantageous due to the avoidance of energy intensive gas separation.²⁵⁷

The same group prepared a range of analogous imidazolium-functionalized ionic HCPs with diverse substituents by hypercrosslinking of substituted imidazolium salts **261** with crosslinker **2** (Scheme 72). Surface areas of 360–722 m² g⁻¹ were reported and the ethyl substituted polymer, **I_{C2}HCP**, was further optimized. By varying the monomer composition and FeCl₃ amounts surface areas of up to 1017 m² g⁻¹ were reached. This optimized **I_{C2}HCP-5b** also possessed the highest CO₂ uptake of 3.05 mmol g⁻¹ (1 bar, 0 °C) and was also the highest performing catalyst. Using 3 MPa pressure of simulated flue gas 81% yield was reached using low catalyst loadings (Table 5, entry 6).²⁵⁸

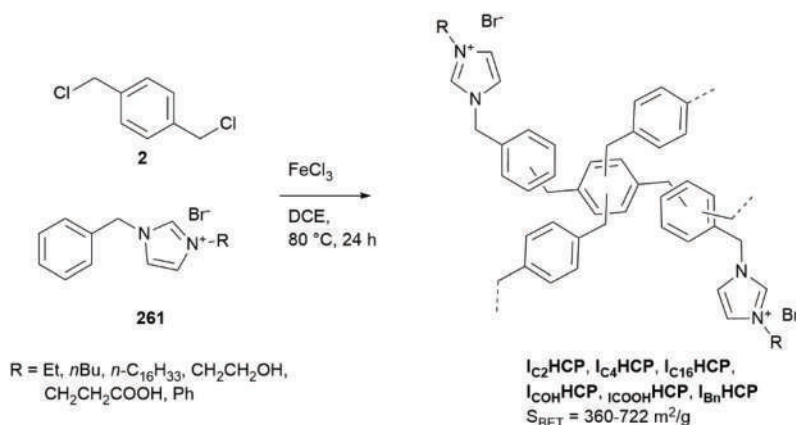
Imidazolium grafted HCPs were reported by crosslinking of benzylhalides **2,25,262–265** and subsequent reaction of N-methylimidazole **266** with the residual bromo- or chloromethyl groups, leading to **POM1-6-Im** (Scheme 73). Of these catalysts **POM3IM** was the most effective in the conversion of a



Scheme 69 Synthesis of porous ionic liquids by postsynthetic exchange of bulky anions.²⁵⁶



Scheme 71 Synthesis of porous ionic liquids by one quaternization-Friedel-Crafts crosslinking (above) or grafting (below).²⁵⁷



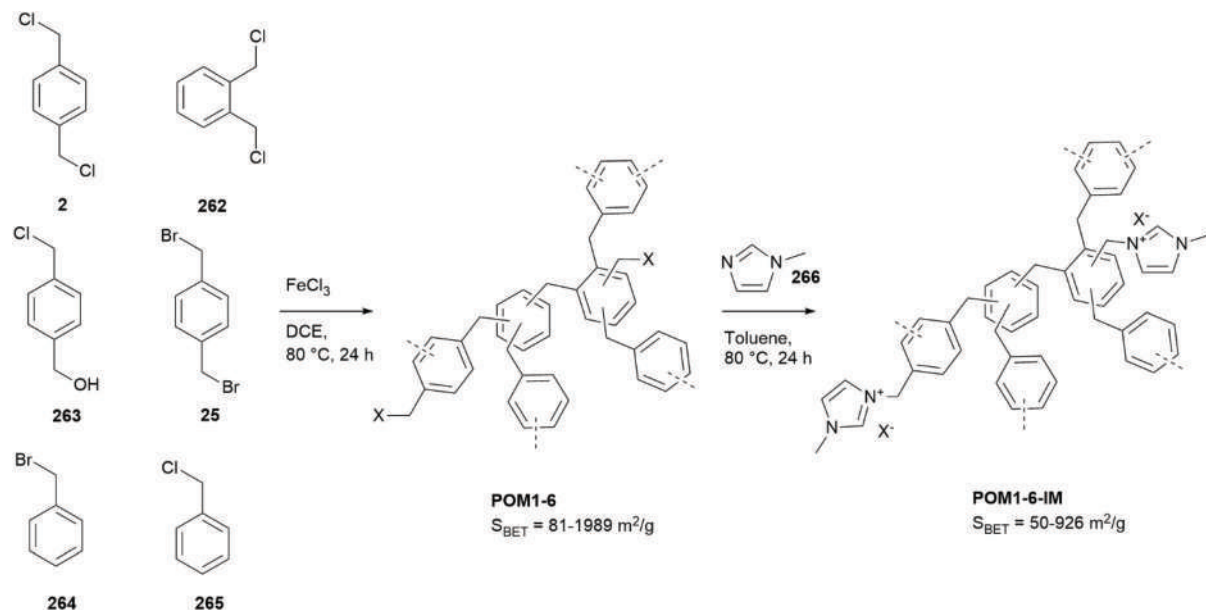
Scheme 72 Synthesis of a range of imidazolium HCPs by Friedel-Crafts crosslinking.²⁵⁸

range of epoxides, reaching 92% conversion of PO (Table 5, entry 7).²⁵⁹

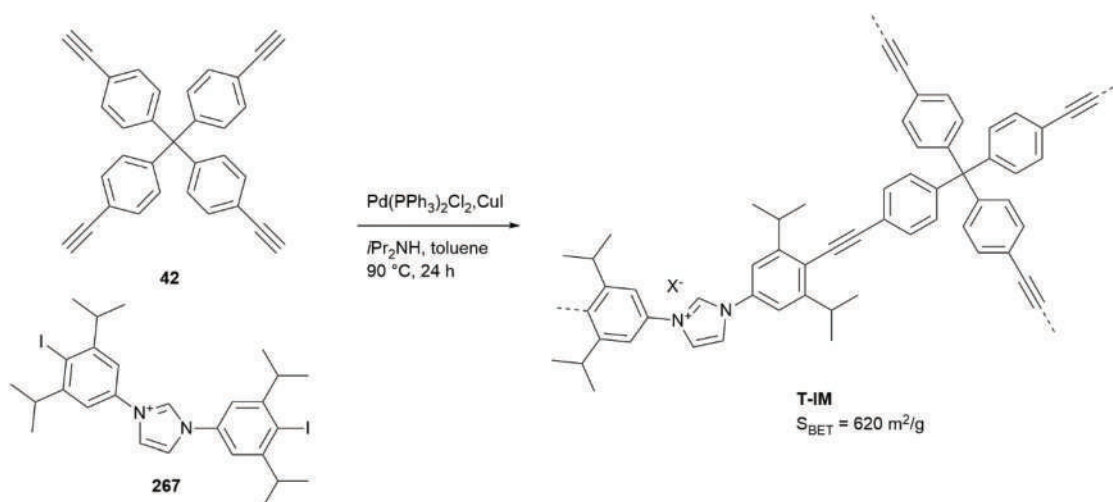
In 2010, Cho *et al.* prepared tubular, ionic CMPs through Sonogashira coupling of tetrakis(4-ethynylphenyl)methane **42** and functional imidazolium building block **267** (Scheme 74). The morphology and growth process of the obtained material, **T-Im**, was studied through transmission and scanning electron microscopy (TEM and SEM). All materials had a hollow inner space and formed tubes. The formation of hollow spheres happened through Oswald ripening. In the beginning of the reaction rods with a thin average diameter and a dense inner struc-

ture were observed and the diameter gradually increased as a hollow inner sphere was formed. **T-Im** was an active catalyst for a range of epoxides, for example, ECH could be converted in 85% yield utilizing 1 MPa CO₂ at 150 °C (Table 5, entry 8).²⁶⁰

Other ionic CMPs were reported by Sonogashira coupling of triazine based building block **268** with tetratopic **42**, thus incorporating two functionalities, triazines and imidazoliums, with high affinity for CO₂ in the resulting material (Scheme 75). This **IT-POP-1** was ion exchanged, replacing the small chlorine anions with larger iodine or hexafluoro-



Scheme 73 Synthesis of ionic HCPs by postsynthetic functionalization of residual chloro/bromomethyl groups.²⁵⁹



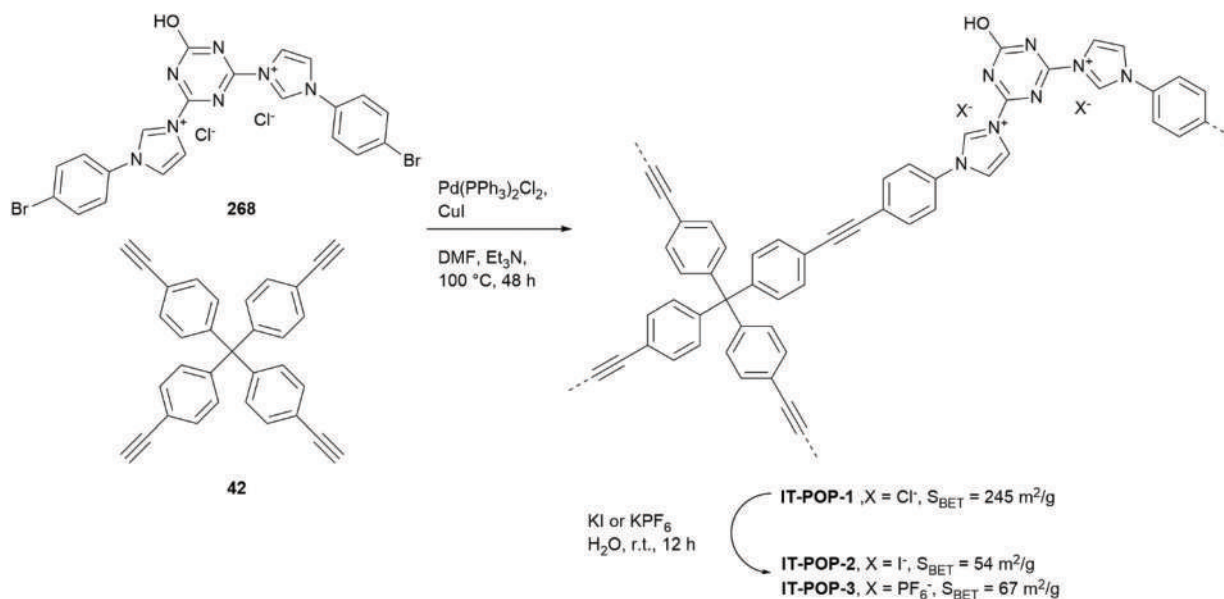
Scheme 74 Synthesis of an imidazolium containing CMP T-IM via Sonogashira coupling.²⁶⁰

phosphate anions forming **IT-POP-2/3**. The surface areas are hereby drastically lowered and pore size distribution analysis showed that the micropores are blocked. **IT-POP-1** was the most active catalyst by far, reaching 99% yield at 120 °C and 1 MPa CO₂ for the conversion of ECH (Table 5, entry 9). Due to their lower surface area **IT-POP-2** (89%) and **IT-POP-3** (33%) were much less active. For **IT-POP-3** the much lower nucleophilicity of the hexafluorophosphate anion lowered the activity drastically.²⁶¹

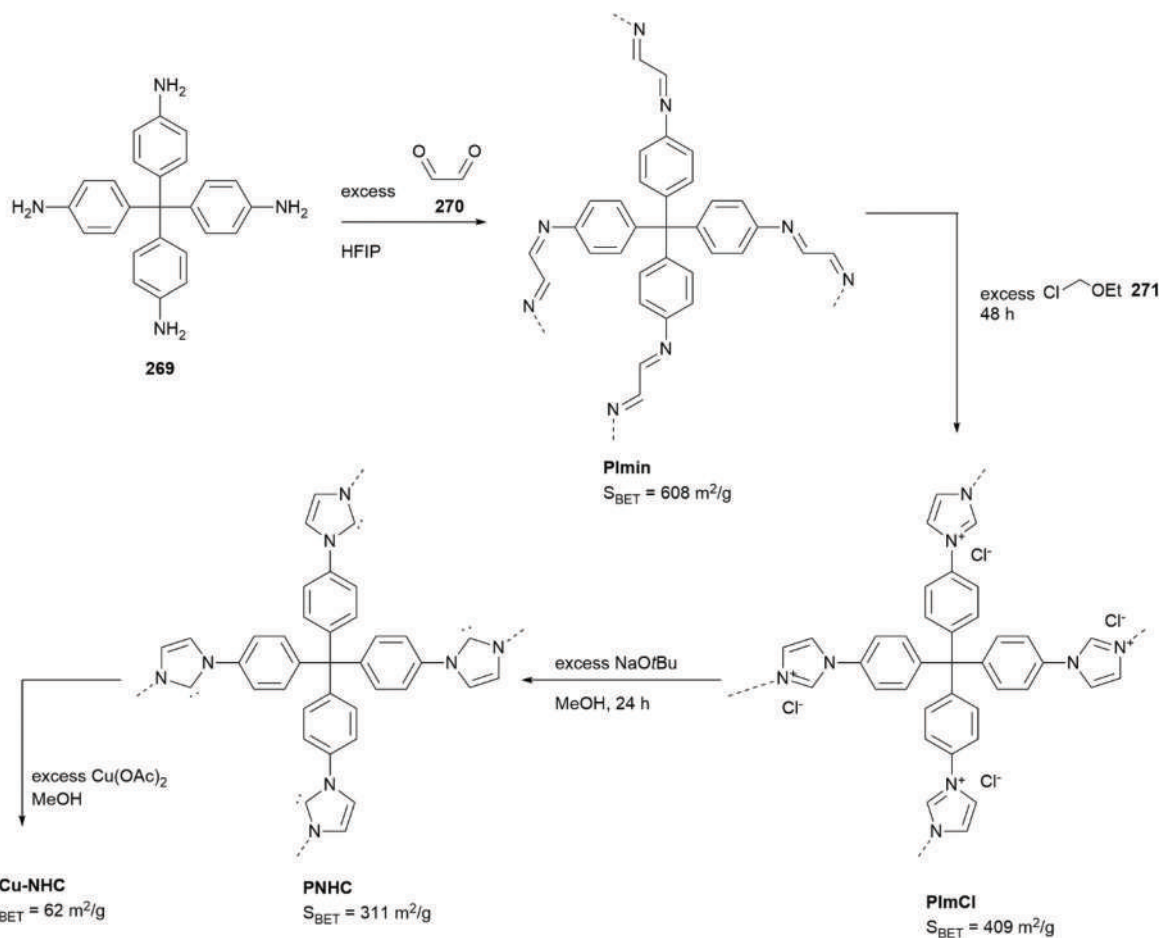
Imidazolium moieties can also be generated post synthetically. In 2012 the Thomas group generated a POP with N-heterocyclic carbenes (NHCs) in the backbone using a step-wise approach (Scheme 76). Polymerization of tetrakis(4-aminophenyl)methane **269** with glyoxal **270** generated an imine

network **Pimin**, which was converted with chloromethyl ethyl ether **271** to the imidazolium polymer **PimCl**, which after deprotonation generated **PNHC**. Furthermore, copper could be immobilized and this polymer **PCuNHC** could serve as a catalyst for the deoxygenation of organic sulfoxides. Both **PNHC** and **PimCl** showed activity for the cycloaddition reaction with **PNHC** giving slightly higher yield (Table 5, entries 11 and 12).²⁶²

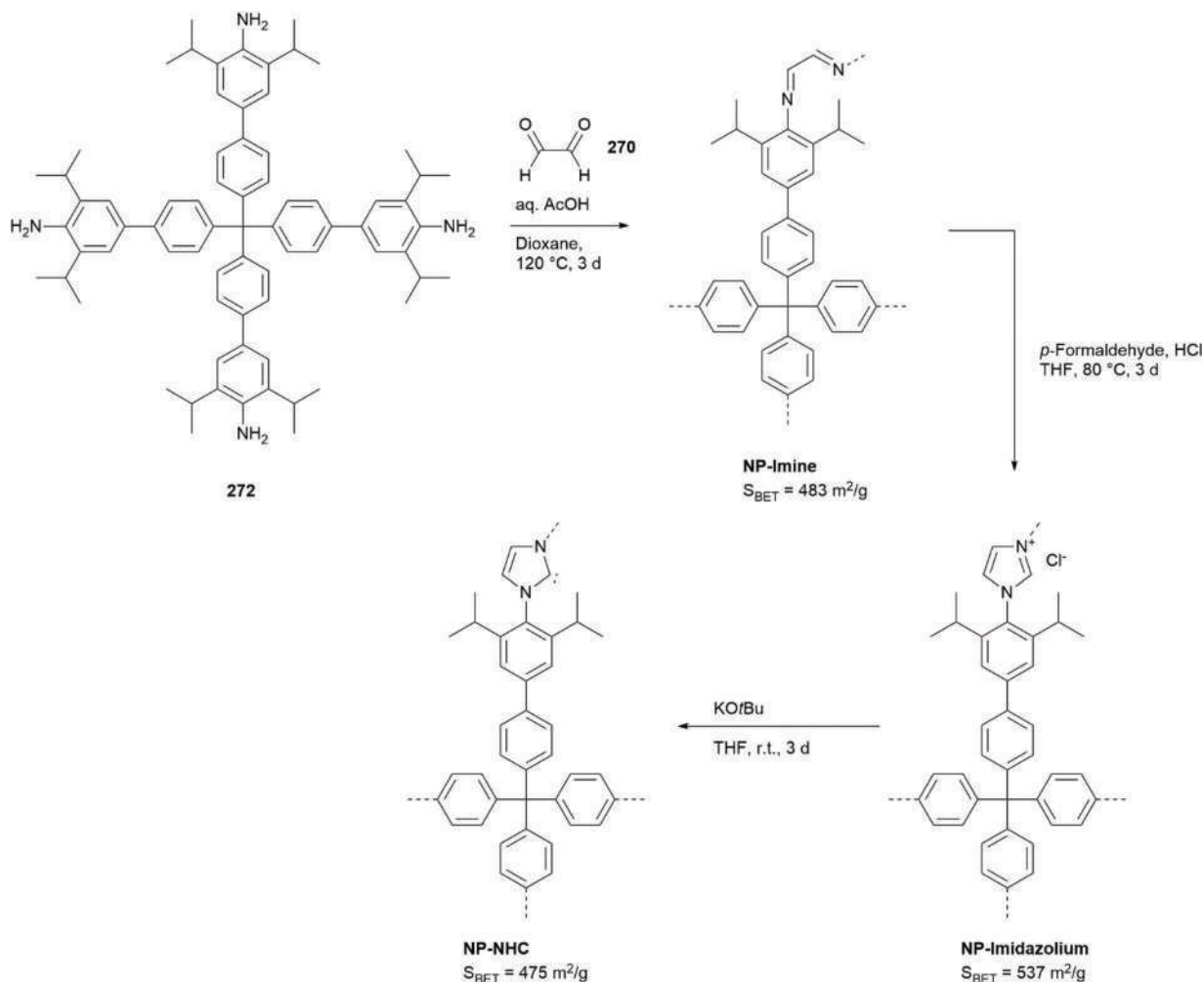
Similarly, Talapaneni *et al.* generated imidazolium and NHC moieties post synthetically in a three step approach using a much more sterically hindered building block **272** (Scheme 77). In this way the NHC moieties were stabilized by sterical confinement, inhibiting dimerization and other side reactions. The authors proved the existence of the free car-



Scheme 75 Synthesis of an imidazolium and triazine containing CMP through Sonogashira coupling.²⁶¹



Scheme 76 Synthesis of NHC containing POPs by Schiff base reaction, ring closure and deprotonation.²⁶²



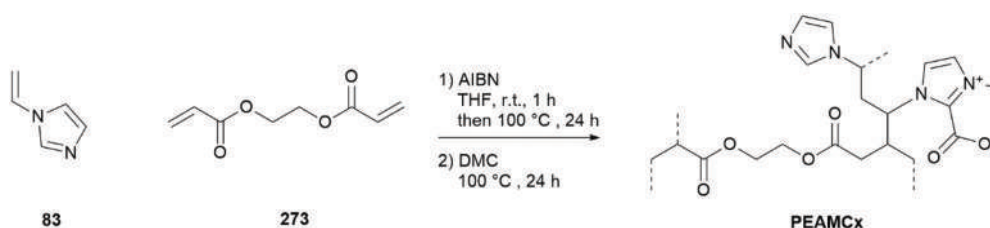
Scheme 77 Generation of a polymer network containing sterically confined NHCs.²⁶³

benes by observing the formation of imidazolium carboxylates in solid state ^{13}C -NMR. Unlike in most postmodification sequences, here the surface areas increased due to the steric size of the imidazolium rings and the increasing rigidity of the framework. **NP-NHC** could catalyze the conversion of PO at atmospheric pressures of CO_2 in high yield (98%, Table 5, entry 13).²⁶³

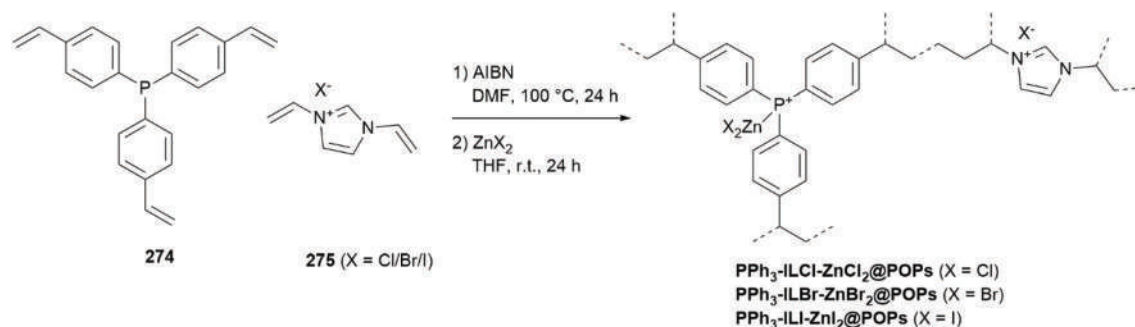
Wang *et al.* synthesized a series of POPs incorporating NHC- CO_2 adducts *via* copolymerization of *N*-vinylimidazolate 83 with ethyleneglycol dimethacrylate 273, followed by post-

synthetic modification with dimethyl carbonate (Scheme 78). Under high pressure and temperature a good conversion of ECH was reached after only two hours, under ambient pressure longer reaction times were needed (Table 5, entry 14).²⁶⁴

Lastly, in 2016 Wang *et al.* prepared a series of imidazolium, zinc halide and triphenylphosphine integrated POPs through radical polymerization of vinyl functionalized triphenylphosphine 274 and divinylimidazolium 275, followed by zinc halide immobilization (Scheme 79). These materials were effective cooperative catalysts, with $\text{PPh}_3\text{-ILBr-ZnBr}_2$ being



Scheme 78 Synthesis of polymers containing NHC- CO_2 adducts.²⁶⁴



Scheme 79 Synthesis of imidazolium-triphenylphosphine polymers by radical copolymerization.²⁶⁵

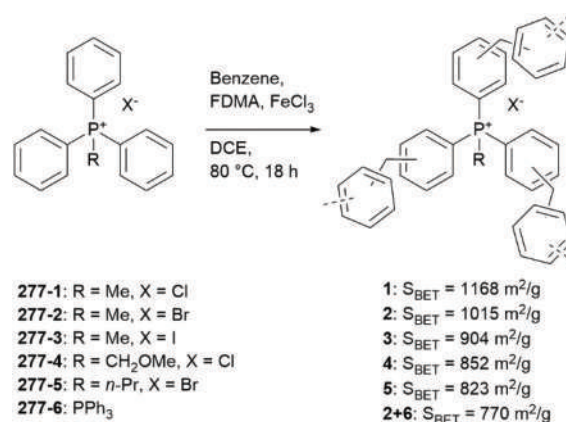
the most effective, reaching a very high TON of 2120 h⁻¹ at 40 °C and an extremely high initial TOF of 5200 h⁻¹ at 120 °C (Table 5, entry 15) which were at that time the highest reported for a heterogeneous catalyst.²⁶⁵

6.2 Phosphonium based POPs

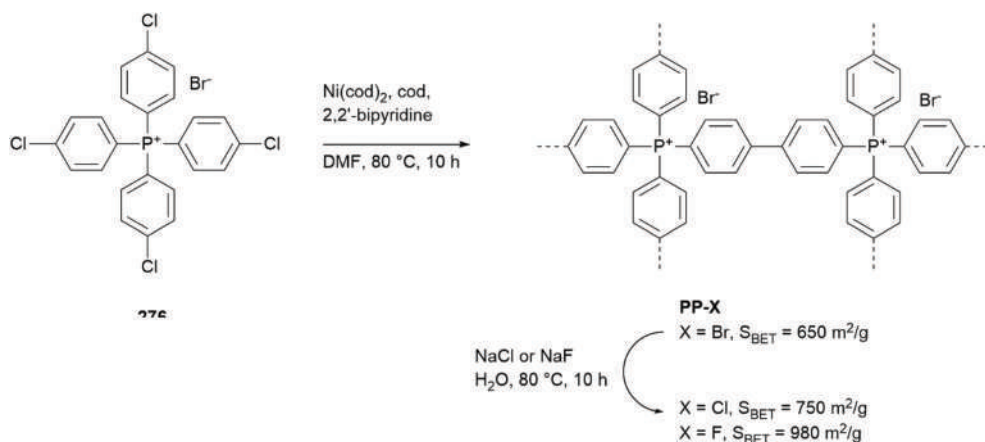
Phosphonium salt based CO₂ conversions are already applied in the OMEGA process by Shell and Mitsubishi chemicals where ethylene glycol is produced from ethylene oxide by reaction with CO₂ followed by hydrolysis of ethylene carbonate.²⁶⁶ In 2012, Zhang *et al.* prepared the first phosphonium containing POP, by nickel catalyzed Yamamoto coupling of monomer 276. The resulting porous polymer, **PP-Br**, had a surface area of 650 m² g⁻¹ that could be tuned further *via* anion exchange (Scheme 80). This material was an effective catalyst for the cycloaddition reaction under atmospheric pressure with a reported yield of 98% for phenyl glycidyl ether (Table 5, entry 16).²⁶⁷

In 2015, Wang *et al.* prepared HCPs with phosphonium moieties through Friedel-Crafts polymerization of phosphonium salt monomers 277 with benzene and FDMA as a crosslinker. The co-monomer benzene is necessary due to the limited reactivity of the phosphonium benzene rings. Highly porous HCPs (770–1168 m² g⁻¹) were reported and surface

areas decreased as the counterions and substituents got bigger (Scheme 81). Polymers with bromine as the anion and a small methyl substituents gave the best results, reaching 94% conversion of PO after nine hours (Table 5, entry 17). Co-polymerization of triphenylphosphine 277-6 with phosphonium salt 277-2 resulted in triphenylphosphine containing polymer 2 + 6, onto which Lewis acid ZnBr₂ was immobilized and this



Scheme 81 Synthesis of phosphonium HCPs by Friedel-Crafts crosslinking.²⁶⁸



Scheme 80 Synthesis of phosphonium salt containing polymers by Yamamoto coupling.²⁶⁷

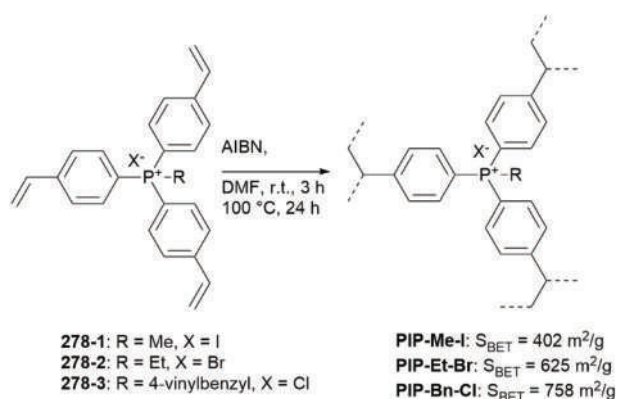
proved to be a very effective combination, reaching 90% yield after only four hours (Table 5, entry 18).²⁶⁸

Sun *et al.* prepared ionic polymers by radical polymerization of vinyl functionalized quaternary phosphonium salt monomers **278**, leading to POPs with high surface areas (402–758 m² g^{−1}) (Scheme 82). Polymers with different substituents and counterions were tested, and of these the highest catalytic activity was found for **PIP-Bn-Cl** containing the more hindered benzyl substituent and chloride anion. A more sterically hindered substituent can lead to looser ion binding and thus higher catalytic activity. This material could catalyze the cycloaddition of CO₂ with ECH in high yield (95%) under extremely mild conditions at room temperature under atmospheric CO₂ pressure and very low catalyst loadings, however requiring long reaction times. Heating at 100 °C shortened the reaction time to only three hours with >99% yield (Table 5, entry 19). Furthermore, the catalyst could be recycled at least ten times without any noticeable reduction of yield.²⁶⁹

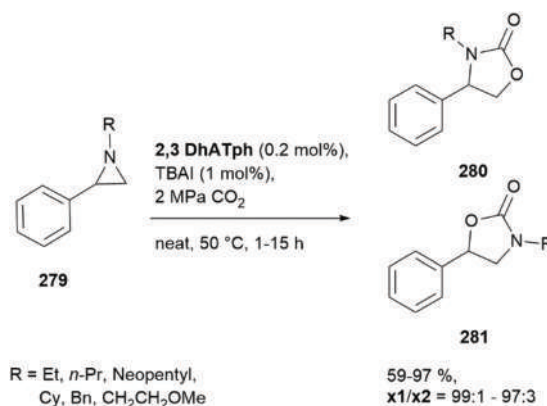
6.3 COFs

The **2,3-DhaTph** and **2,3-DmaTph** COFs (Scheme 36) reported by the Banjeree group were not only simultaneous acid base catalysts for the deacetalization-Knoevenagel reaction but also for CO₂ conversion. **2,3-DhaTph** is a stable, highly porous COF and possesses both acidic (catechol) and basic (porphyrin) active sites. The catechol moieties activate the epoxide through hydrogen bonding and stabilize the oxyanion. Furthermore, the porphyrins have good affinity for CO₂. **2,3-DhaTph** performed well in the cycloaddition of epoxides at atmospheric CO₂ pressure when TBAI was used as a co-catalyst and as expected **DmaTph** was less effective (Table 5, entry 20). **2,3-DhaTph** also catalyzed the conversion of a wide range of substituted aziridines **279** to oxazolidinones **280** and **281** in high yield and with good regioselectivity (Scheme 83).²⁷⁰

Two or more catalytic centers working together to perform a single transformation can be considered state of the art in modern catalysis. However, for heterogeneous catalysts such as POPs the spatial separation in rigid frameworks makes this



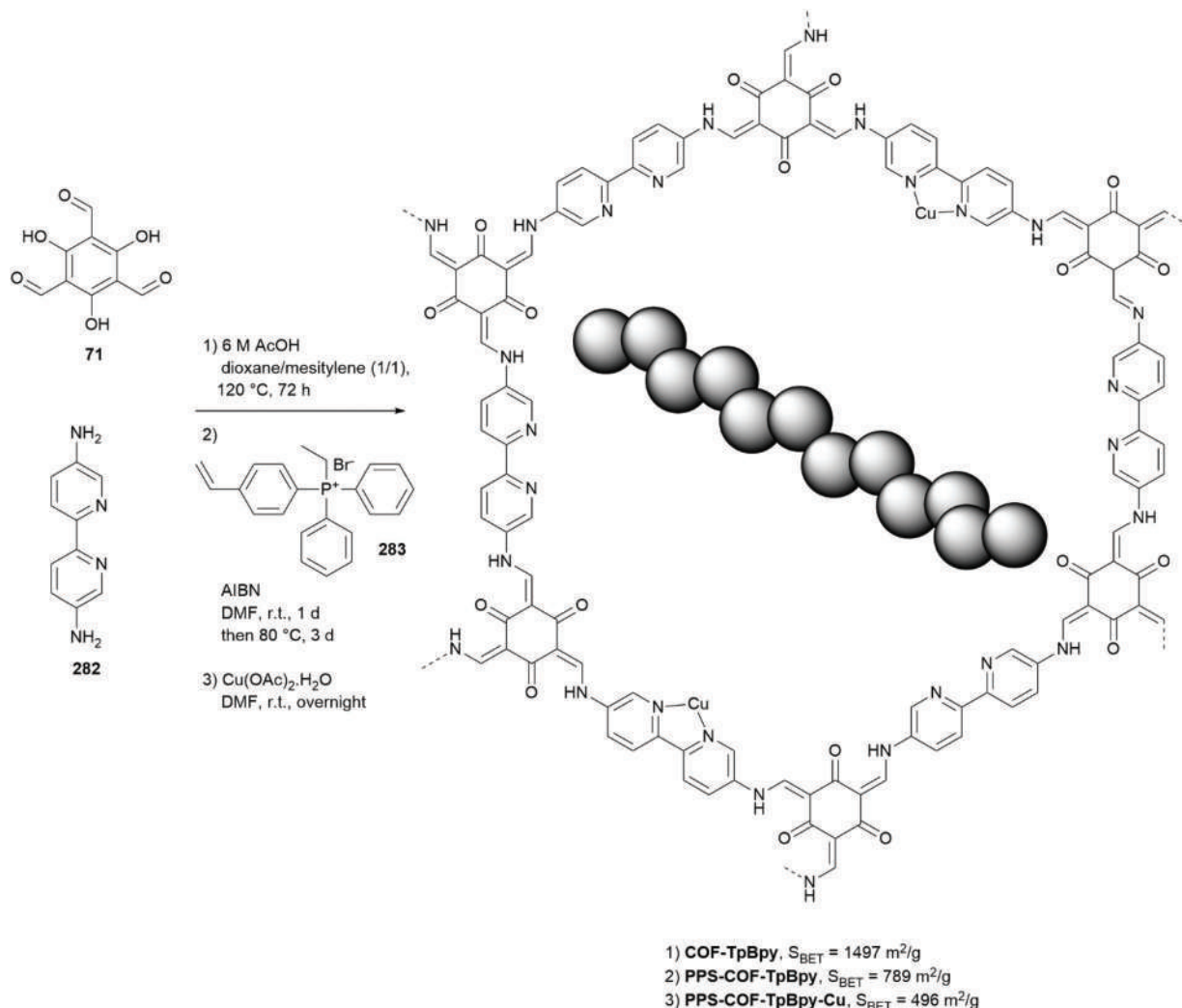
Scheme 82 Synthesis of phosphonium containing HCPs by radical polymerization.²⁶⁹



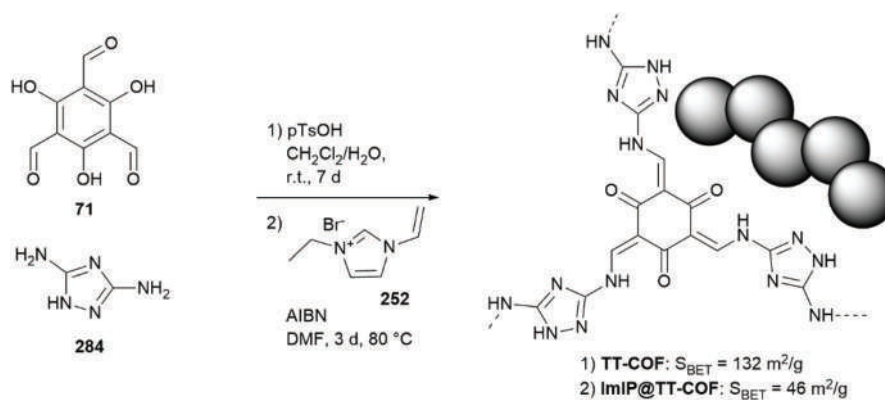
Scheme 83 COF mediated synthesis of oxazolidinones **280** and **281** by CO₂ cycloaddition to aziridines **279**.²⁷⁰

cooperation difficult. Sun *et al.* devised an elegant solution to this problem by encapsulating flexible ionic polymers with halide catalytic sites in a Lewis acid functionalized COF. These authors synthesized **COF-TpBpy** by Schiff base condensation between 5,5'-diamino-2,2'-bipyridine (Bpy) **282** and 1,3,5-triformylphloroglucinol (Tp) **71**. Following this, *in situ* radical polymerization of phosphonium salt **283** encapsulated linear PS chains in the COF channels. Copper was then immobilized on the bipyridines sites forming **PPSCOF-TpBpy-Cu** (Scheme 84). The ionic polystyrene chains retained their flexibility, as signified by their sharp ³¹P-NMR signals when contacted with solvent, and could be viewed as quasi homogeneous catalysts. The catalytic activity was tested for the conversion of ECH under atmospheric CO₂ pressure which reached a high yield (95%, Table 5, entry 21). Isolating the Br[−] and Cu²⁺ active species, by using a physical mixture of **COF-TpBpy-Cu** and the phosphonium polymer, was much less effective (16%). A soluble ionic co-catalyst (PPh₃EtBr) only reached 73% conversion of ECH. A molecular catalyst is homogeneously distributed in solution, whereas the ionic catalytic component of the polystyrene chains are only present in the COF channels, increasing the chance of concerted catalysis. When divinylbenzene was copolymerized with the phosphonium salt **283** much more rigid chains were obtained, drastically lowering the yield (49%). The catalyst could be recycled at least ten times with negligible loss of activity. In a large scale experiment extremely high TONs (>28 000) were obtained indicating possible practical applications.²⁷¹

Recently, a fully metal free variant of this concept was reported by Zhong *et al.* who synthesized a nitrogen rich COF integrated with an imidazolium-based ionic polymer **ImIP@TT-COF**. The COF was produced by layering of an aqueous solution of 1*H*-1,2,4-triazole-3,5-diamine (TDA) **284** and *p*-toluenesulfonic acid on top of a dichloromethane solution of the aldehyde **71**. Free-radical polymerization of imidazolium **252** in presence of the COF gave rise to **ImIP@TT-COF** (Scheme 85). The COF served as a catalyst by virtue of its hydrogen bonding donor capabilities and CO₂ concentrating



Scheme 84 Synthesis of a functionalized COF for CO₂ conversion by postfunctionalization with an ionic polymer and metalation with copper.²⁷¹



Scheme 85 Synthesis of a COF with integrated imidazolium polymers for CO₂ conversion.²⁷²

properties. The anions of the imidazolium polymers served as nucleophilic catalysts. Quantitative conversion of ECH was reported under atmospheric or even lower CO₂ pressures

(Table 5, entry 22) with negligible loss of activity after six runs. Just as reported in similar examples the activity of this system is superior to the sum of its parts.²⁷²

Zhi *et al.* reported two triazine based covalent organic frameworks (COF-JLU6 and COF-JLU7) that were synthesized by Schiff base condensation between aldehyde **19** and tritopic amines **285** and **286** (Scheme 86). The high nitrogen content of the pore walls increased the affinity for CO₂ and a high density of hydroxyl groups as Brønsted acids served to activate epoxides. Therefore both COFs were effective at mild conditions (Table 5, entry 23) in the presence of co-catalyst TBAB.²⁷³

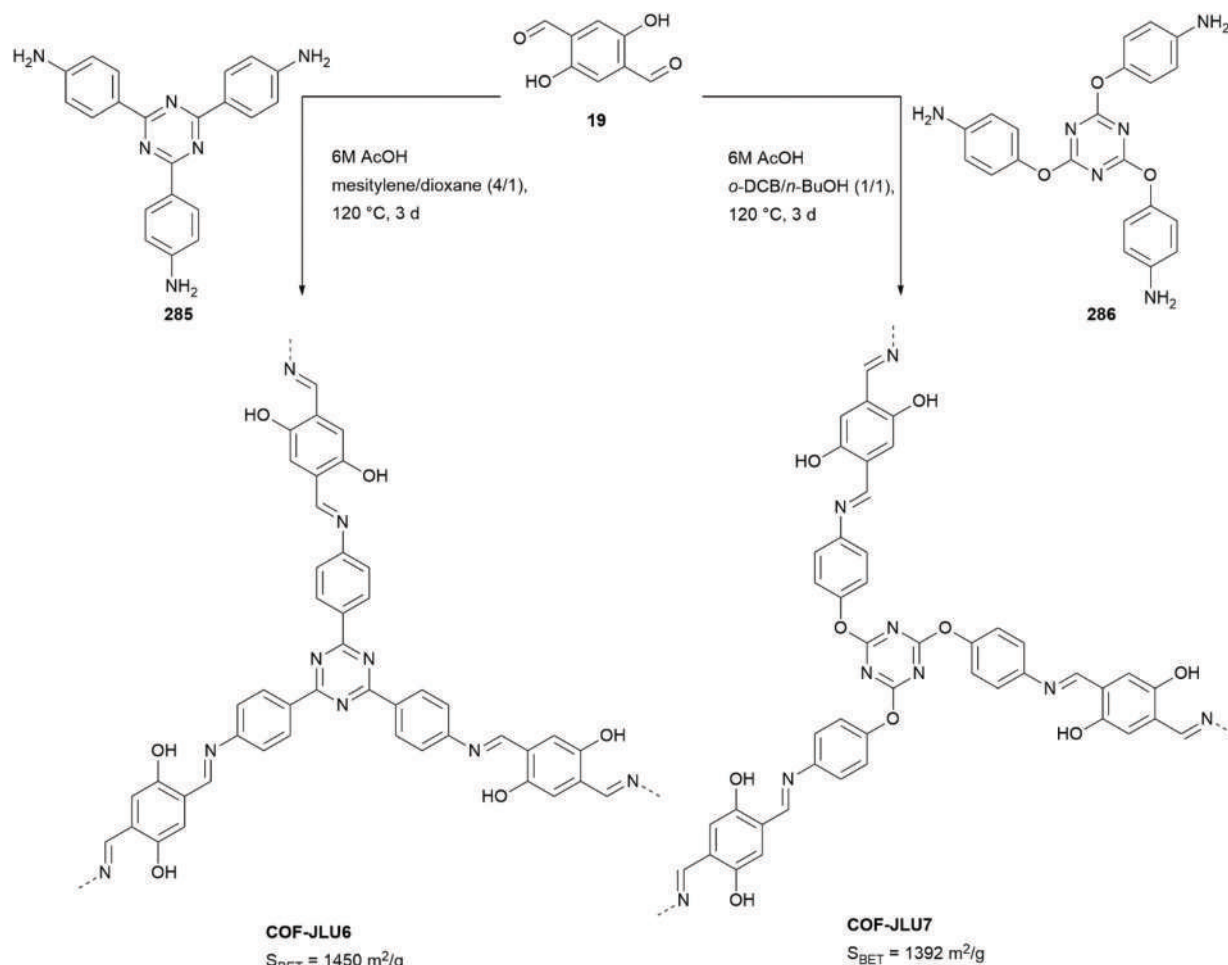
Yang *et al.* prepared three isostructural COFs based on the rigid 3,3',5,5'-tetrakisphenylbiphenyl (TPBP) aromatic core with either hydroxyl (OH-TFBP-COF), methoxy (OMe-TFBP-COF) or both (OMe-OH-TFBP-COF) groups (Scheme 87). OMe-OH-TFBP-COF performed best in the cycloaddition of ECH with CO₂ under very mild conditions, with TBAB as co-catalyst reaching 91% yield (Table 5, entry 24), slightly higher than OH-TPBP-COF (89%) and much higher than OMe-TFBP-COF which showed negligible activity.²⁷⁴

Recently the zwitterion glycine betaine proved to be an efficient organocatalyst for the reduction of CO₂.²⁷⁵ Mu *et al.* synthesized zwitterionic COFs as catalysts for the controllable reduction of CO₂ with hydrosilane, selectively forming

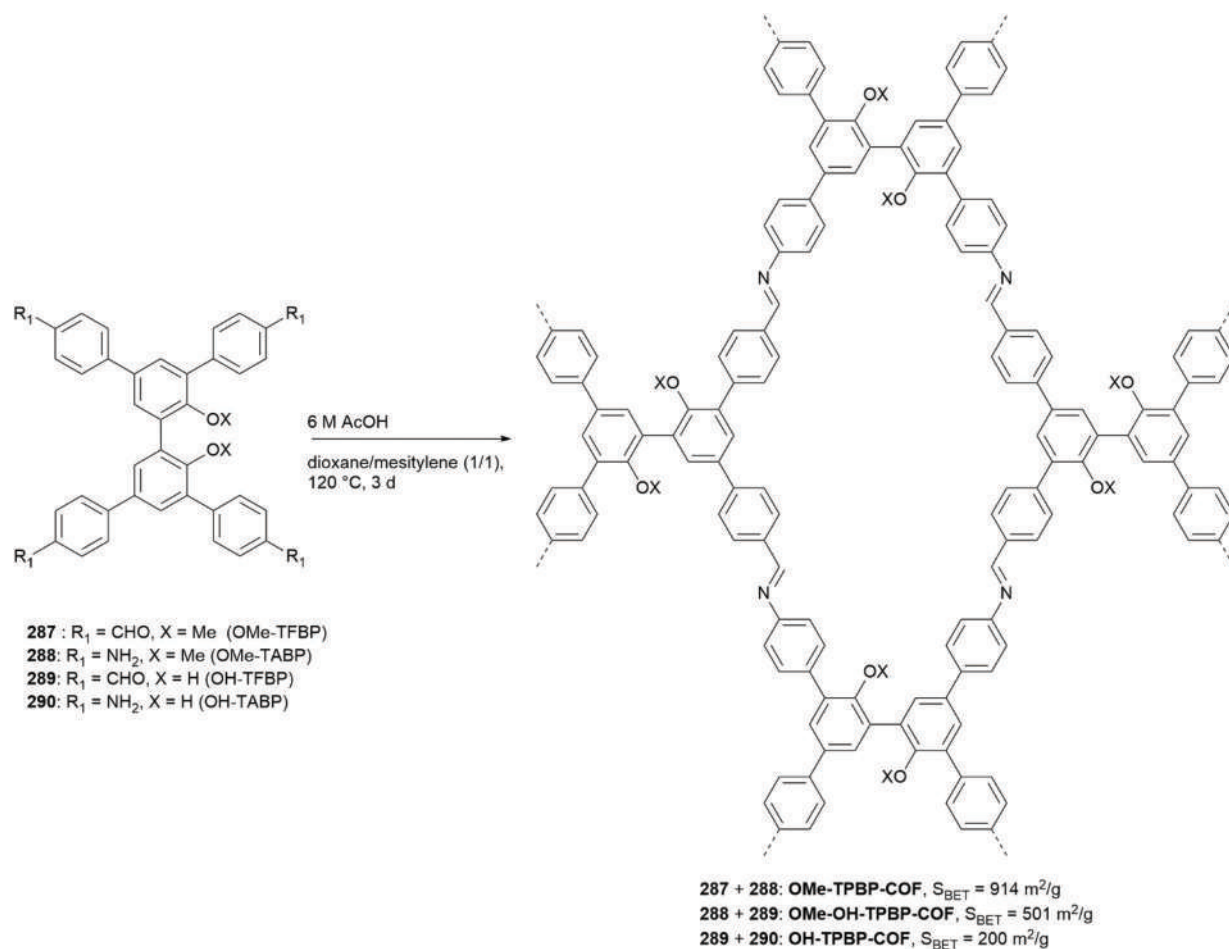
different products depending on the reaction conditions. Through Schiff base condensation of tritopic amine with aldehydes **19** and **20** [OH]_x-TD-COFs with variable amounts of hydroxyl groups were synthesized. These were then postfunctionalized through Williamson ether synthesis with brominated compound **291** forming [BE]_x-TD-COFs with good preservation of crystallinity and porosity (Scheme 88). Using these COFs, with hydrosilane as reducing agent and CO₂ as carbon donor, amines **292** could be selectively transformed into formamides **293**, methylamines **294** or amins **295** (Scheme 89). The carboxylate group of betaine activates CO₂ and enhances the reducing power of hydrosilane by forming hypervalent silicon species.²⁷⁵ [BE]_{50%}-TD-COF possessed the highest activity, probably it has the ideal balance of sufficient functionalization without hindering mass transport by blocking of the pores.²⁷⁶

6.4 CTFs

The unique properties of CTFs for CO₂ conversion were recognized in 2012 by the Thomas group. CTFs are typically synthesized through reversible ionothermal trimerization of aromatic polynitriles. These materials possess several interesting charac-



Scheme 86 Synthesis of triazine based COFs for CO₂ conversion.²⁷³

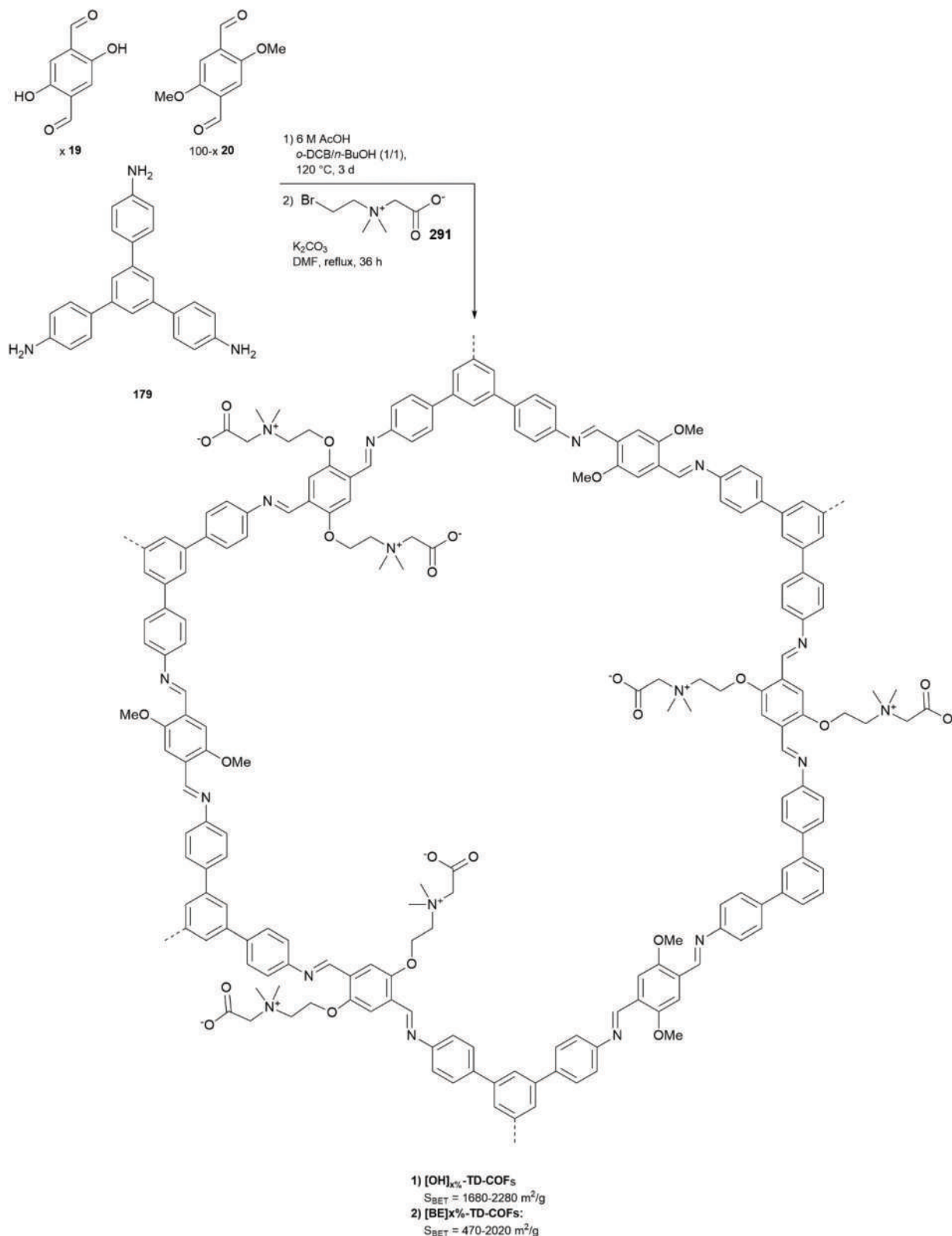


Scheme 87 Synthesis of three isostructural COFs for CO_2 conversion.²⁷⁴

teristics for catalytic applications, such as high thermal and chemical stability and tunable properties by the choice of the monomer and the synthetic procedure. These polymers can be used as support for catalytically active metal complexes or nanoparticles, however the materials themselves are also efficient basic catalysts by virtue of their basic nitrogen sites. Ionothermal synthesis typically takes place in a molten salt, ZnCl_2 , at high temperatures ($\geq 400^\circ\text{C}$), with the salt acting as a solvent, catalyst and template. The products are typically amorphous, especially at higher temperatures ($>400^\circ\text{C}$) and when utilizing more equivalents of ZnCl_2 . Heating at higher temperatures, *e.g.* 600°C , leads to higher surface areas and mesoporosity, however increased carbonization also takes place, hereby lowering the nitrogen content of the material.²⁷⁷ It is worth nothing that CTFs can also be synthesized by solvothermal reaction between amidines and aldehydes,²⁷⁸ Friedel-Crafts reactions of aromatics with cyanuric chloride²⁷⁹ and nucleophilic substitutions of amines or alcohols with cyanuric chloride.²⁸⁰

Thomas and co-workers synthesized three CTFs to compare the influence of porosity and chemical composition on the CO_2 cycloaddition. CTF-1 and CTF-1-HAS were prepared by trimerization of 1,4-dicyanobenzene **296** at 400°C or 600°C and

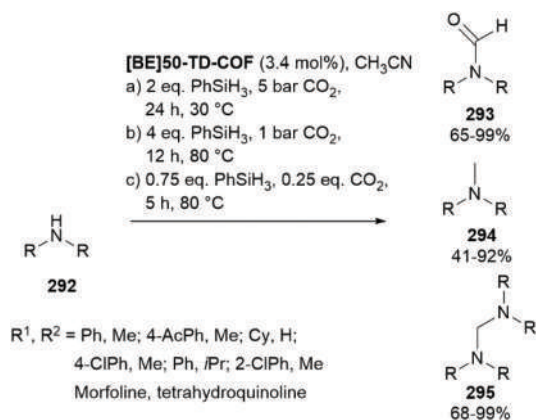
CTF-P-HAS by trimerization of 2,6-dicyanopyridine **297** at 600°C (Scheme 90). The higher synthesis temperature of CTF-1-HAS compared with CTF-1 led to a higher surface area but much lower nitrogen content due to carbonization. CTF-P-HSA possessed both a high surface area and nitrogen content, due to the nitrogen containing pyridinic monomer. The differences in structure can be attributed to incomplete condensation at lower temperatures and partial carbonization and removal of triazine at higher temperatures. The complete removal of potentially catalytically active ZnCl_2 was achieved by washing under concentrated acidic conditions. The structural differences had a major influence on the catalytic efficiency for the conversion of CO_2 to cyclic carbonates. Both high nitrogen amounts and high porosity are desired to obtain a high density of catalytic sites and good mass transfer. For the reaction of epichlorohydrin with CO_2 both CTF-1-HAS and CTF-P-HAS reached 100% conversion, whereas CTF-1 could only manage 81% (Table 5, entry 25). However, for styrene carbonate and cyclohexene carbonate a very low selectivity was reported of only 14% and 48% respectively, with both epoxide hydrolysis and carbonate dimerization as side reactions. A two-step conversion of epoxides into cyclic carbonates, followed by transesterification with methanol furnishing dimethyl carbon-



Scheme 88 Synthesis of betaine containing COFs for amine functionalization through CO_2 reduction.²⁷⁶

ate and vicinal diols, was also reported. The CTFs could reach high conversions, however with low selectivities (2–18%) for dimethylcarbonate.²⁸¹

The Thomas group also prepared CTFs through trimerization of 1,3,5-tricyanobenzene **298** leading to **CTF-0** (Scheme 91). Crystalline frameworks with surface areas of



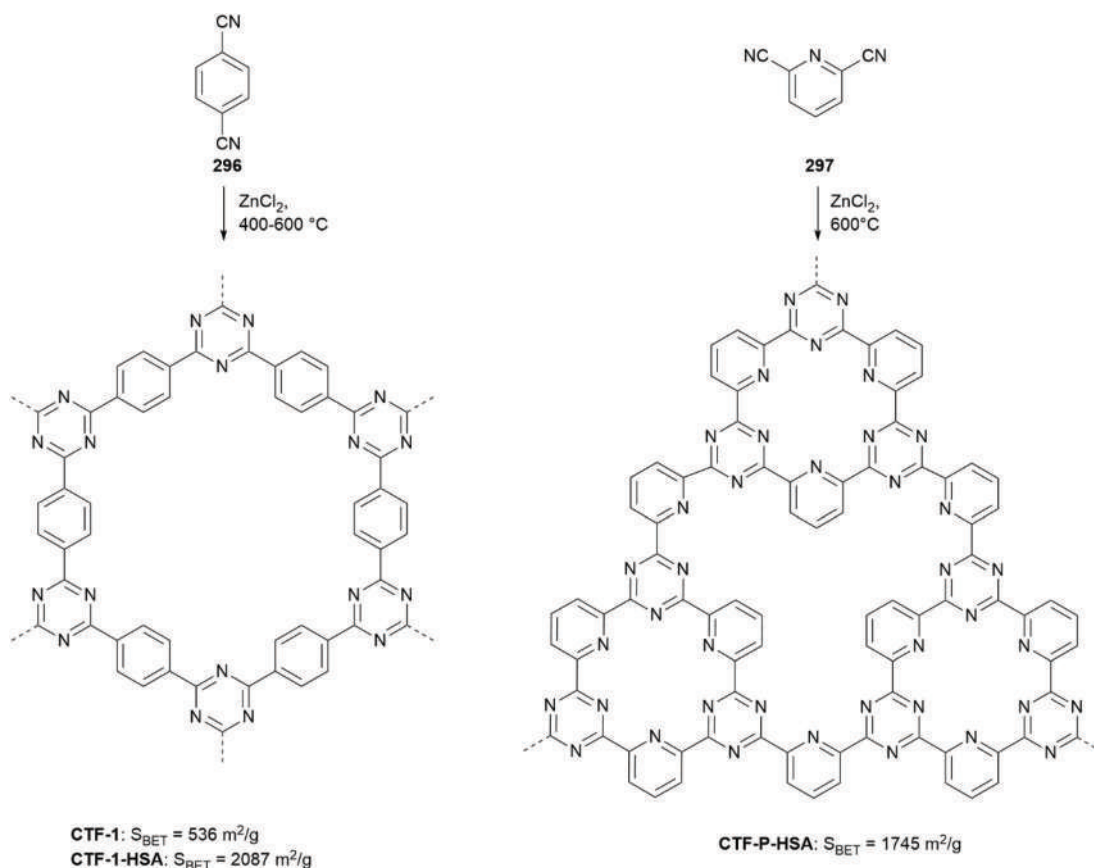
Scheme 89 Betaine containing COFs catalyze the functionalization of amines **292** with CO_2 , selectively synthesizing formamides **293**, methylamines **294** or amins **295**.²⁷⁶

around $500 \text{ m}^2 \text{ g}^{-1}$ could be formed after careful optimization of the monomer/ ZnCl_2 ratio, the reaction time and temperature. Increasing the reaction temperature to 600 °C furnished materials with a higher surface area ($>500 \text{ m}^2 \text{ g}^{-1}$). Interestingly, the ideal structure was simulated to possess pores so small that they are inaccessible to N_2 and should

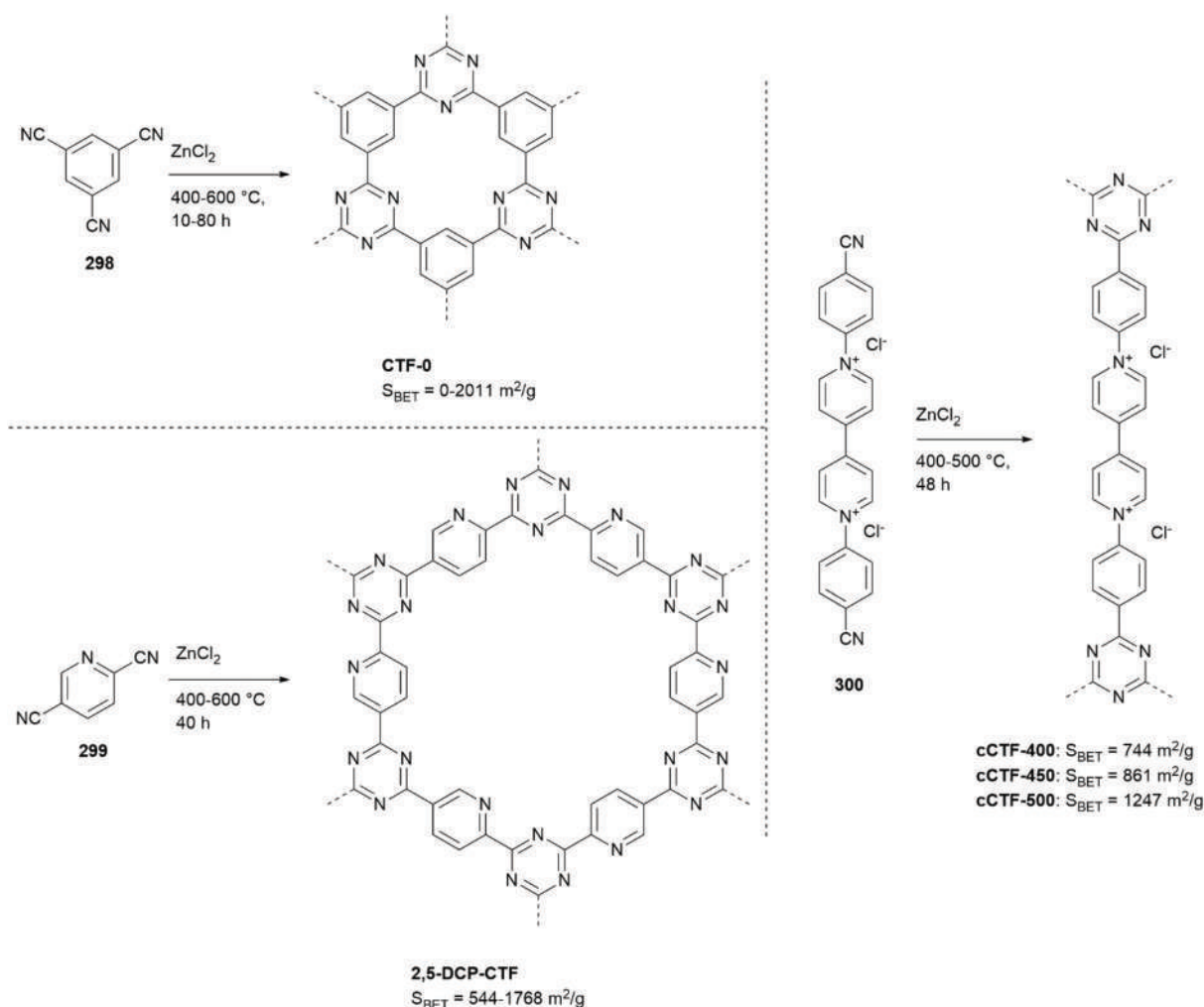
therefore have zero surface area for nitrogen. This 'ideal' material could be synthesized by extending the reaction time to 80 hours after which a crystalline material with no porosity for N_2 was formed, however this material could still absorb CO_2 . **CTF-0** possessed an exceptionally high thermal stability, up to 600 °C in air. The high surface area variant of **CTF-0** showed good activity for CO_2 cycloaddition of ECH reaching 100% conversion with 93% selectivity (Table 5, entry 26).²⁷

Another CTF was synthesized from 2,5-dicyanopyridine **299** at 400–600 °C with 10–12 equivalents of ZnCl_2 (Scheme 91). The **2,5-DCP-CTF** with the lowest porosity but highest nitrogen content was the most active and reached 95% yield for ECH (Table 5, entry 27), contrasting with other CTFs were in general the ones with the highest surface area were the most active.²⁸²

A charged, ionic CTF was synthesized by trimerization of dicationic viologen derivative **300** (Scheme 91). The surface areas and pore volumes were controlled by varying the temperature and ZnCl_2 content. The resulting CTF **cCTF-400/450/500** had high surface areas, up to $1247 \text{ m}^2 \text{ g}^{-1}$, and high stability, whilst the incorporation of the ionic moieties furnished a good CO_2 uptake (133 mg g^{-1} , 1 bar, 0 °C) and catalytic activity. Higher yields in the cycloaddition reaction than previously reported CTFs could be obtained, for example, for PO 99% yield was obtained (Table 5, entry 28).²⁸³



Scheme 90 CTF synthesis by ionothermal trimerization.²⁸¹



Scheme 91 Synthesis of CTF-0, cCTFs and 2,5-DCP-CTF by ionothermal trimerization.^{27,282,283}

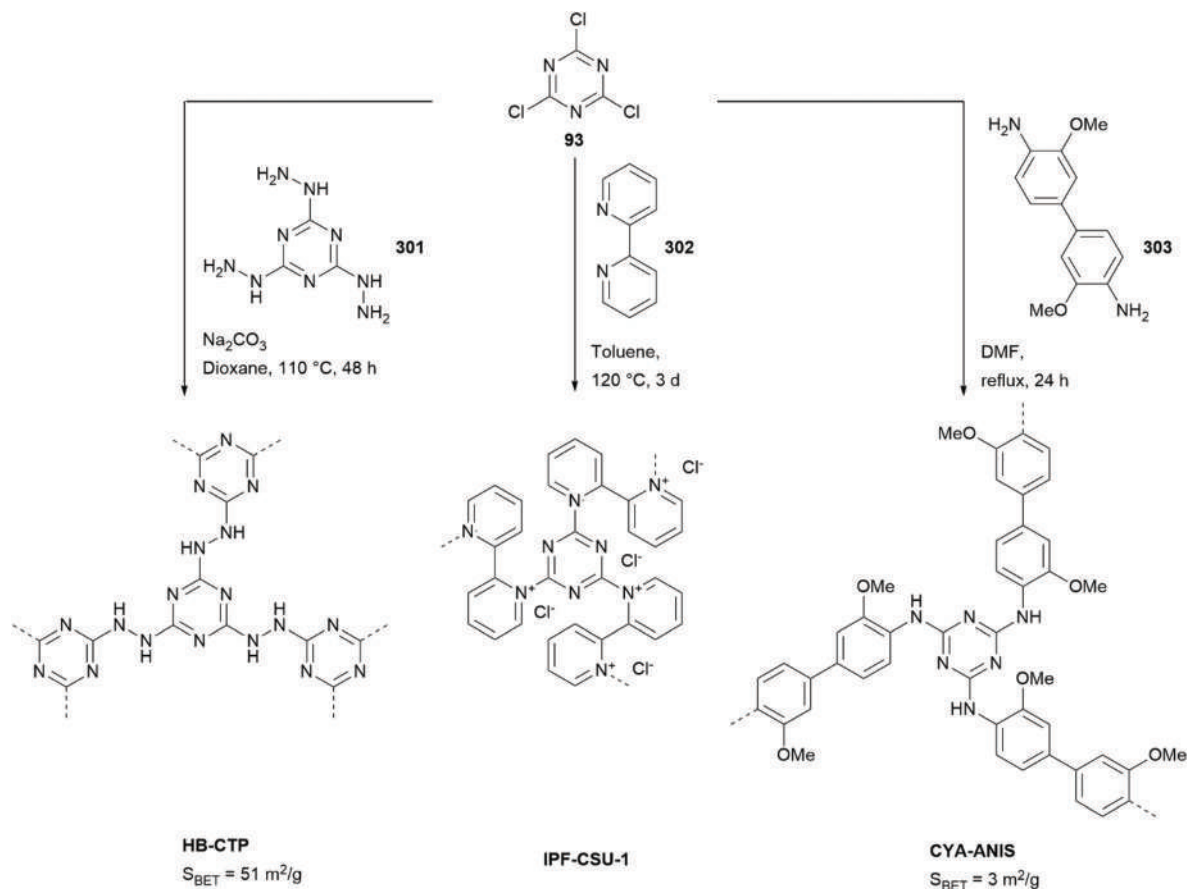
Yu *et al.* synthesized porous ionic CTFs **IPF-CSU-1** by condensation of 2,2'-bipyridine **302** with cyanuric chloride **93**, without using any templates, metals, acids or bases (Scheme 92). The resulting polymer possessed an abundance of ionic sites and a high nitrogen content of 20.3 wt%. This polymer was an active catalyst at atmospheric pressure and ambient temperature, however a very large amount of TBAB as a co-catalyst was used to reach high conversions (99%, Table 5, entry 29).²⁸⁴ Liu *et al.* prepared a hydrazine bridged CTF by reaction of cyanuric chloride **93** with 2,4,6-trihydrazinyl-1,3,5-triazine **301** resulting in **HB-CTP** (Scheme 92). This CTF possessed a rather low surface area ($51 \text{ m}^2 \text{ g}^{-1}$) postulated to be caused by interlayer hydrogen bonding. However, this CTF exhibited good CO_2 capture capacity ($8.2 \text{ wt\%}$, 0°C , 0.1 MPa) and catalytic activity for the cyclo-addition of CO_2 with various epoxides in good to excellent yields (67%–99%), although high temperatures, CO_2 pressures and a TBAB as co-catalyst were used (Table 5, entry 30).²⁸⁵ Similarly Biswas *et al.* prepared a CTF, **CYA-ANIS**, from cyanuric chloride **93** and *o*-dianisidine **303** (Scheme 92). This material possessed a very low surface

area of only $3 \text{ m}^2 \text{ g}^{-1}$. However, it catalyzed the cycloaddition well, reaching full conversions with co-catalyst TBAB under atmospheric pressures (Table 5, entry 31).²⁸⁶

While the building blocks of CTFs, typically aromatic polynitriles, are often quite accessible, the synthesis conditions themselves are harsh and not suited to larger scales. The typical ionothermal synthesis requires very high temperatures, large amounts of zinc chloride and takes place in vacuum sealed glass ampoules. The CTFs synthesized through nucleophilic addition of cyanuric chloride (Scheme 92) can be synthesized under milder conditions, but possess much lower surface areas and use a TBAX co-catalyst for the CO_2 cycloaddition.

6.5 Other POPs

Ma *et al.* prepared a bifunctional polymer **POF-PNA-Br⁻** by Sonogashira coupling between monomers **42** and **304** followed by quaternization with bromoacetic acid **305** (Scheme 93). This led to a highly effective catalyst due to the synergy of the Brønsted acidic site of the carboxylic acid and the Br^- anion of the ionic moiety as a nucleophilic site. **POF-PNA-Br⁻** was able



Scheme 92 Synthesis of CTFs by nucleophilic substitutions with cyanuric chloride **93**.^{284,285,286}

to effectively catalyze the conversion of epoxides at atmospheric CO_2 pressure and 40°C with yields up to 94% (Table 5, entry 32). Both Cl^- and I^- containing **POF-PNA-Cl** and **POF-PNA-I** were less effective. The chlorine anion possesses a much lower nucleophilicity, whilst the iodine has a very large radius, blocking pores and reducing mass transfer.²⁸⁷

Buyukcakil *et al.* prepared **PCP-Cl/BF₄/PF₆** with a viologen backbone through Sonogashira coupling between tetratopic building block **42** and the dichloride (Cl^-), ditetrafluoroborate (BF_4^-) and dihexafluorophosphate (PF_6^-) viologen salts **306** (Scheme 93). The surface area decreased as the radius of the anions increased. **PCP-Cl** possessed both the highest surface area, CO_2 absorption capacity and catalytic activity.

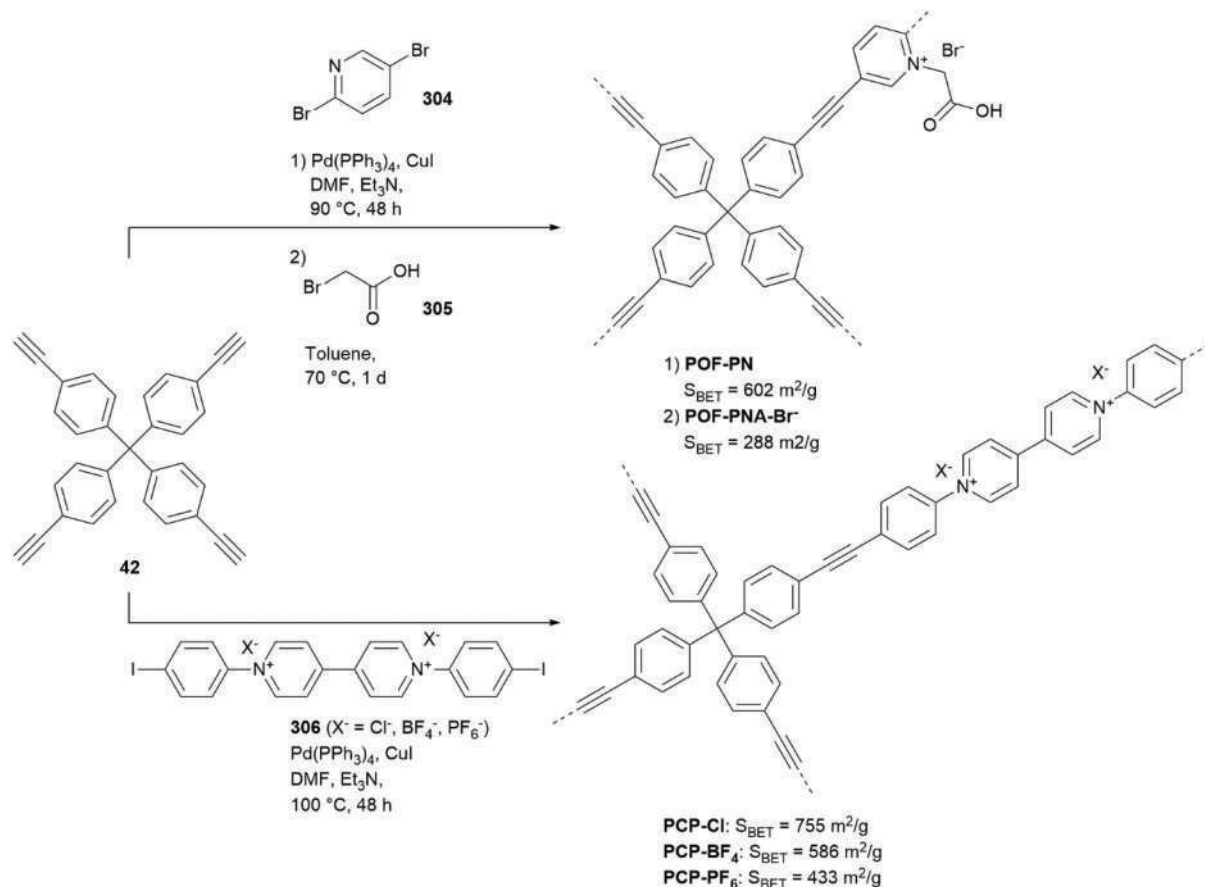
Good yields were obtained for the cycloaddition reaction when using high temperatures and CO_2 pressures (Table 5, entry 33). Moreover, due to the pronounced microporosity of the material bigger substrates such as styrene oxide (SO) could not react efficiently.²⁸⁸

Kim *et al.* prepared quaternary ammonium salt grafted HCPs *via* a two-step postfunctionalization sequence. The starting polymer, **COP-114** was prepared *via* a Friedel–Crafts reaction. Chloromethyl groups were then introduced by reaction with chloromethyl methyl ether (MOMCl) and these were further functionalized by reaction with tertiary amines (Scheme 94). The material with the least sterically hindered tri-

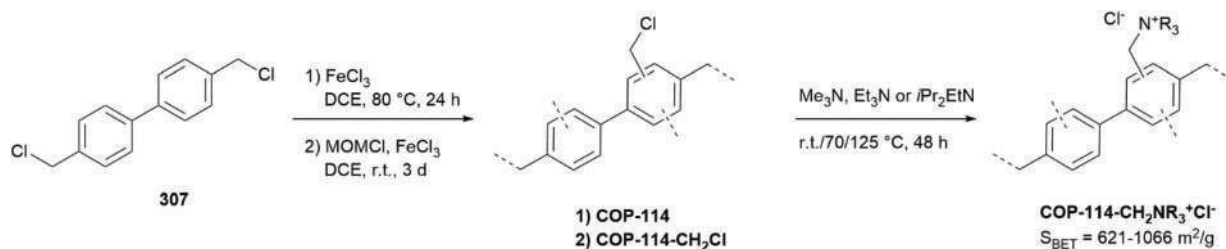
methylammonium groups **COP-(114-CH₂NMe₃⁺)Cl[−]** was tested for the cycloaddition of CO_2 to epoxides. High conversion and yield were reported under atmospheric pressure, but a high temperature of 100°C was required (Table 5, entry 34).²⁸⁹

Recently, Maya *et al.* prepared tetramethylguanidine functionalized polyphenylene POPs (Scheme 95). Amino groups were either directly incorporated in the monomers or introduced by postfunctionalization. These amine groups were then reacted with tetramethylurea in the presence of oxalyl chloride furnishing tetramethylguanidine substituted polymers: **5PhTMG**, **2PhTMG** and **2PhCH₂TMG**. Only the polymer with the methylene spacer, **PhCH₂TMG**, possessed sufficient activity in the cycloaddition reaction. For SO 90% conversion was reported, however quite harsh conditions were applied (Table 5, entry 35).²⁹⁰

A carbonyl containing aromatic polymer **CBAP-1** was synthesized by Ravi *et al.* *via* a Friedel–Crafts acylation reaction (Scheme 96). Post synthetically functionalization by reductive amination led to **CBAP-1(EDA)**. Zn^{2+} and Co_2^{+} were also immobilized to enhance the catalytic activity by introduction of Lewis acidic sites. **CBAP-1(EDA)** reached high conversions for ECH (99%), however it required harsh conditions (Table 5, entry 36). Using TBAB as a co-catalyst, together with the Lewis acid functionalized polymers, reduced temperatures were possible.²⁹¹



Scheme 93 Synthesis of ionic CMPs by Sonogashira coupling.^{287,288}



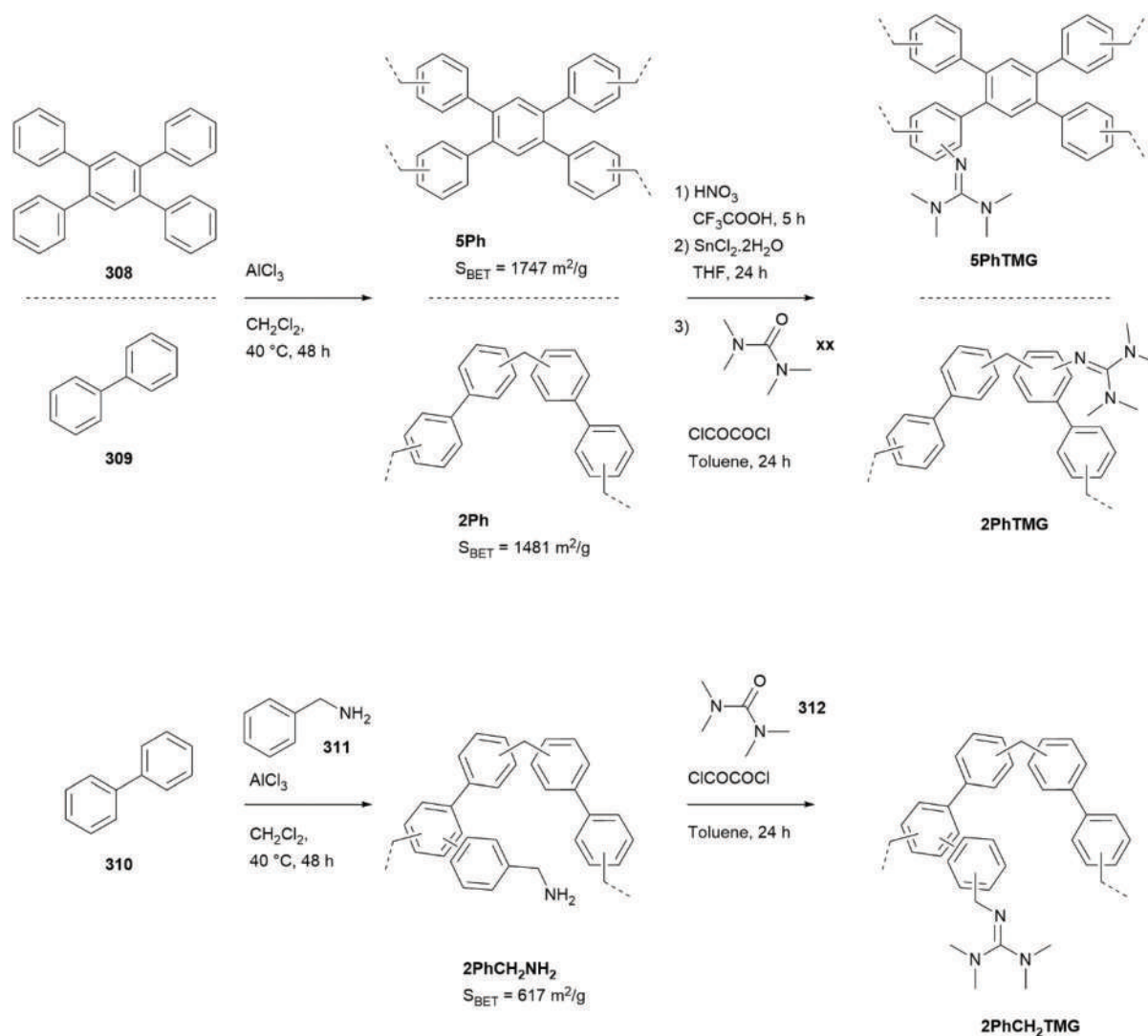
Scheme 94 Synthesis of ammonium grafted HCPs by polymerization, chloromethylation and substitution with amines.²⁸⁹

Zhang *et al.* synthesized a series of mesoporous POPs, **MOP-0-4**, by polycondensation of melamine **43** and aryl aldehydes **316**, forming amidine linkages (Scheme 97). By increasing the hydroxyl substitution of the aldehyde the CO₂ absorption capacity increased, but the surface areas and catalytic activity decreased. **MOP-0** was the most active and reached 89% ECH conversion under high temperature and pressure (Table 5, entry 37).²⁹²

6.6 Outlook on POPs catalyzing CO₂ fixation

As stated in the introduction to this part, homogeneous catalysts used for the cycloaddition of CO₂ to epoxides are typically

organic halides such as quaternary ammonium, phosphonium and imidazolium salts (ionic liquids). Next to these, strong organic bases are used. These catalysts generally need high temperatures (>80 °C) to achieve good yields, which next to being energy intensive can also lead to de-quaternization, sometimes thwarting their reuse.^{293–295} To enable more effective catalysts the nucleophilic Lewis bases can be combined with Lewis acids, typically metal cations with ligands. Some of the most well studied examples of this class consist of the metal-porphyrins, zinc β -diiminates and salen/salphen based complexes and the best of this class work well at mild conditions (≤ 60 °C, ≤ 10 bar).^{296,297} However, such metal com-



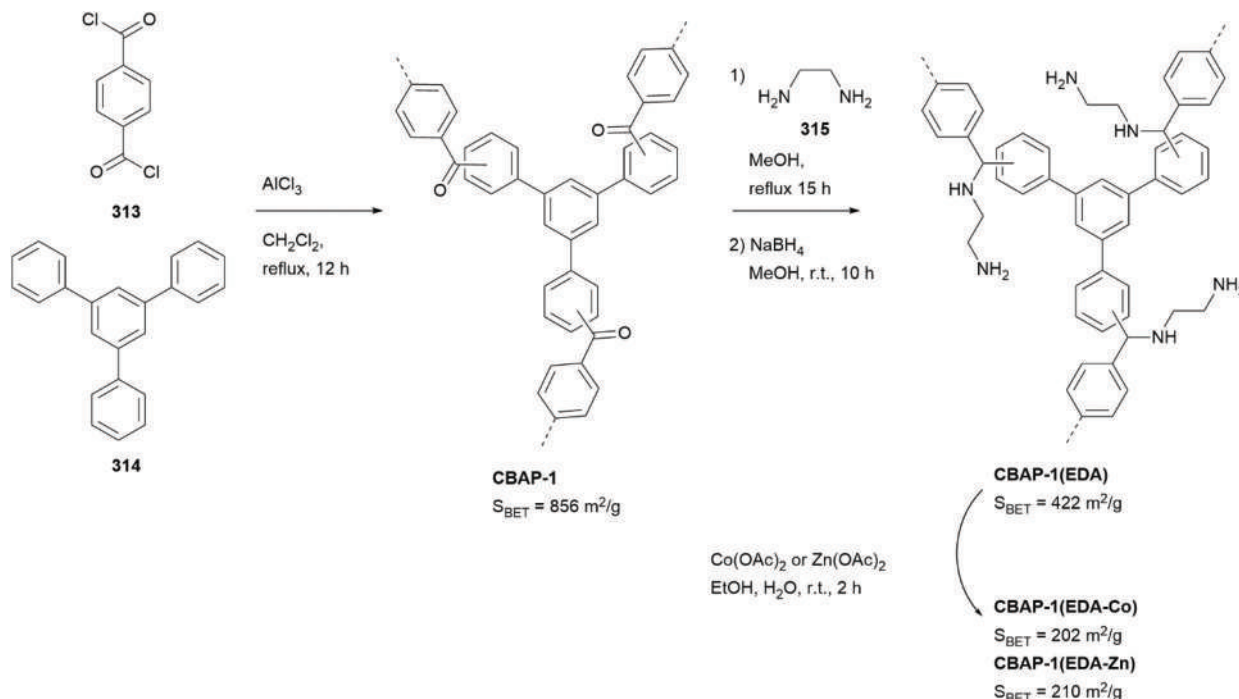
Scheme 95 Synthesis of tetramethyl urea functionalized HCPs by Friedel–Crafts polymerization of polyphenyl building blocks and reaction with tetramethylurea.²⁹⁰

plexes are hampered by instability and long and costly synthesis routes.²⁹⁸ Organocatalysts can be more economical, generally less toxic and minimize metal residues in products.²⁴⁵ Therefore, homogeneous organocatalysts combining Lewis acids with Lewis bases are being developed, for example, ionic liquids with hydroxyl, carboxyl acid or amino groups that act as Lewis acids.^{298,299}

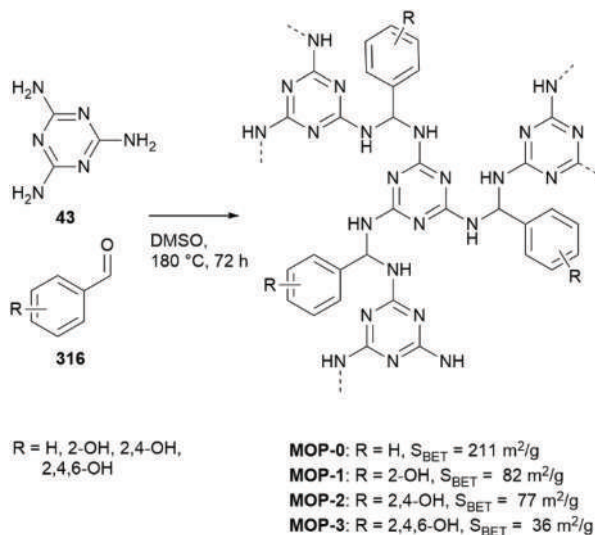
Lewis basic heterogeneous catalysts for this transformation mainly consist of immobilized ionic liquids, onium salts and organic bases on polymers and silica based materials,^{300–304} including ordered mesoporous silicas such as MCM-41³⁰⁵ and SBA-15³⁰¹ as the carrier material.²⁹⁸ Polystyrene resins have been used to immobilize 3,4-diaminopyridine analogues.³⁰⁶ These purely Lewis basic heterogeneous catalysts also typically require high temperatures and pressures. Combinations of these types of catalysts with extra Lewis acidic metals exist, such as Zn/SBA-15 supported

ammonium salt³⁰⁷ or bifunctional ammonium–aluminum salen complexes supported on polystyrene or silica. These can work at milder conditions, up to ambient pressure and room temperature, however, in some cases lowered activity upon recycling was detected.^{308,309}

Another class of materials that has been studied intensely for this transformation are the MOFs. Their metal nodes, when coordinatively unsaturated, can act as Lewis acidic sites or their organic linkers can coordinate Lewis acidic metals.³¹⁰ Harsh conditions and large amounts of an organic halide (TBAX) co-catalyst are often needed and the frameworks can be unstable under the required temperature or pressure.^{311–315} A state of the art MOF, such as MIL-101-IP consisting of a chromium terephthalate MOF with an incorporated ionic polymer, was able to catalyze this transformation under atmospheric CO_2 pressure at room temperature, but still required a long time (48 h) to achieve full conversion.³¹⁶



Scheme 96 Synthesis of a carbonyl containing polymer **CBAP-1** by Friedel–Crafts acylation, followed by reductive amination and metalation.^{291,345}



Scheme 97 Synthesis of a series of POPs by amidine formation.²⁹²

Next to this, and most importantly in the context of this review are the heterogeneous, fully metal free organocatalysts that combine Lewis acidic and basic modes of activation. An early example of this were the silica supported phosphonium salts whose free silanol groups can act as Lewis acids, however, these catalysts required harsh conditions (100°C , 10 MPa).³¹⁷ Ionic liquids containing hydroxyl or carboxylic acid moieties have also been immobilized on silica. For example, hydroxy containing triazolium compounds on SBA-15³¹⁸ or carboxyl-

functionalized imidazolium-based ionic liquids grafted on silica,³¹⁹ but both still required high pressures and temperatures (110°C , $>1.6 \text{ MPa}$). A similar catalyst has been reported in flow, using supercritical CO_2 at high temperatures and this material was unstable in the presence of even traces of water due to hydrolysis.³²⁰ Polystyrene supported imidazolium based ionic liquids with incorporated hydroxy or vicinal diol groups have also been reported, but also required harsh conditions ($\geq 120^\circ\text{C}$, $\geq 2 \text{ MPa}$).^{321,322} Resorcinarene containing quaternary ammonium groups with halide counterions have been immobilized on polystyrene resins and likewise required quite harsh conditions (80°C , 0.5 MPa).³⁰⁶ A triazolium ionic liquid combined with Lewis acidic pyrogallol moieties has been immobilized on a polystyrene resin and, interestingly, achieved full conversion at low temperature but high pressure (45°C , 1 MPa).³²³

Lastly, cellulose and chitosan have been used as green materials to immobilize ionic moieties for this transformation. These catalysts again required high temperatures and pressures ($\geq 120^\circ\text{C}$, $\geq 1.2 \text{ MPa}$).^{324–326}

To conclude, while this transformation has received widespread attention, not only in the POP field but in many other fields, the ‘holy grail’ of metal free, efficient cycloaddition of CO_2 to epoxides at ambient temperature and pressure is still not achieved. The best in class fully metal free POPs could achieve good conversion at atmospheric pressures and temperatures as low as 25°C , but then required long reaction times (Table 5, entries 2, 19 and 32). This does compare favorably to other materials such as polystyrene resins and silicas where typically higher temperatures and pressures were used. Another

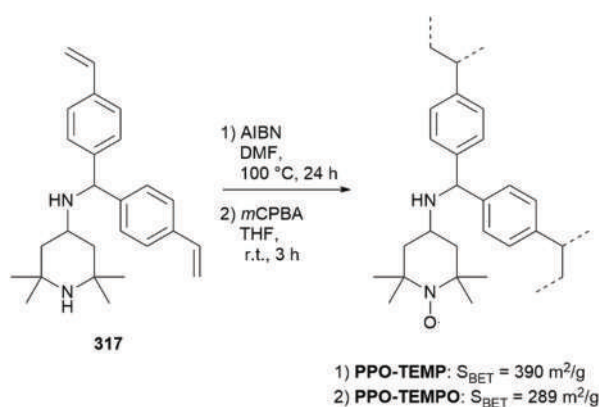
fully metal free catalytic system that worked at low pressure and temperature (Table 5, entry 29) required a very high amount of organic halide, diminishing its green potential.

It does seem that organocatalysis, in this case, is (still) not able to achieve the epoxide activating power of Lewis acidic metals. When combined with metals such as in **PPSCOF-TpBpy-Cu** (Table 5, entry 21) POPs can achieve extremely promising results, similar to or better than other state of the art catalysts such as MOFs.

7 Other reactions

7.1 Oxidation reactions

The reports on POPs as catalysts for oxidation reactions are rather limited. Huangfu *et al.* reported the synthesis of a (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) containing porous organocatalyst **PPO-TEMPO**. This material was synthesized by polymerization and oxidation of vinyl functionalized monomer **317** (Scheme 98) and catalyzed the oxidation of alcohols to aldehydes or ketones. A range of alcohols, both



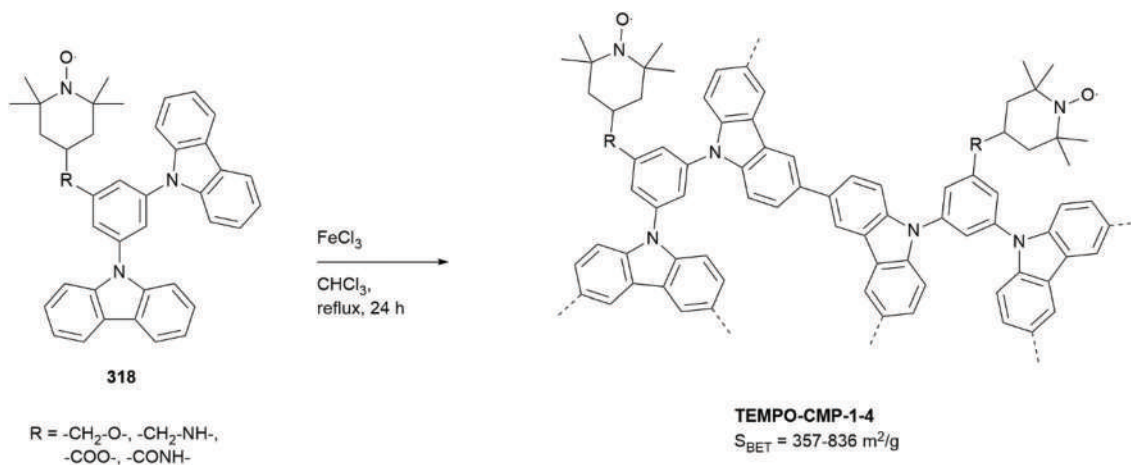
Scheme 98 Synthesis of a TEMPO based heterogeneous catalyst by crosslinking and postsynthetic oxidation.²⁰⁹

benzylic and aliphatic, could be reacted with conversions and selectivities up to 99%, using hypochlorite as an oxidant in dichloromethane. Due to enrichment of reagents in the pores of the material its activity was much higher than the homogeneous equivalent.²⁰⁹

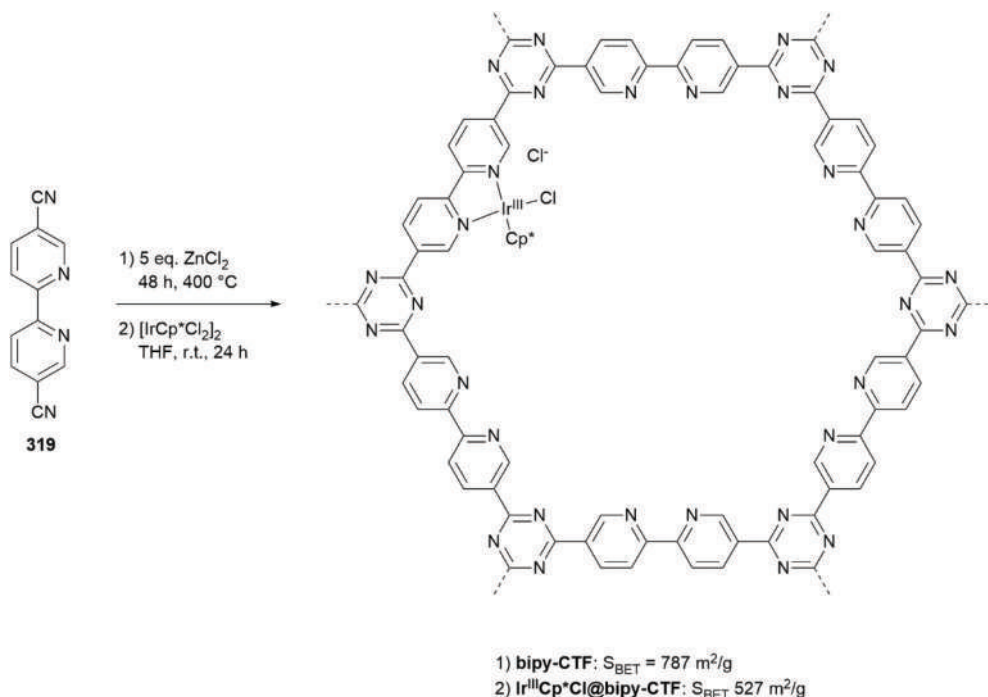
Another TEMPO containing polymer was synthesized by FeCl_3 catalyzed oxidative polymerization of carbazolic building blocks **318**, with different linkages between the structural and functional (TEMPO) component (Scheme 99). Allylic, benzylic and aliphatic primary alcohols were able to react in acetic acid at room temperature under oxygen or air. NaNO_2 and 1,3-dibromo-5,5-dimethylhydantoin were used as a co-catalyst and auxiliary, respectively. The most active polymer, **TEMPO-CMP-4**, with the amide linker possessed a higher activity than the homogeneous monomer and could be recycled at least twenty times with retention of the activity.³²⁷

Abednatanzi *et al.* synthesized a bipyridine CTF **bipy-CTF** as a support for an Ir^{III} complex for the aerobic oxidation of alcohols (Scheme 100). Interestingly the activity of the metal catalyst was hugely increased by the solid CTF support, by virtue of its nitrogen rich sites activating oxygen and the alcohol substrates. A wide range of benzylic alcohols could be converted into the corresponding aldehydes in generally high yields, using only the catalyst and the most environmentally friendly oxidant: molecular oxygen, aliphatic alcohols however gave much lower conversions.³²⁸

In further research by the same group metal free CTFs were used for the oxidation of benzylic alcohols and amines. Using easily prepared **CTF-1** (Scheme 90) and under similar conditions as the aforementioned iridium catalyzed reactions, a wide range of alcohols were converted in generally good yields. Furthermore, this material catalyzed the oxidative coupling of amines to imines for a wide range of substrates with high conversion (99%) and selectivity (>85%). The nitrogen composition of a range of CTFs was determined by XPS analysis and the conversion corresponded with the amount of quaternary nitrogens in the materials.³²⁹ The mechanism of the oxygen



Scheme 99 Synthesis of TEMPO containing polymers by oxidative polymerization of carbazoles.³²⁷

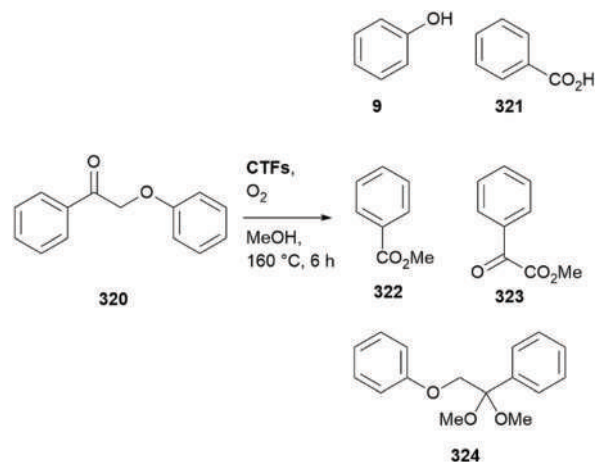


Scheme 100 Synthesis and postsynthetic metalation of a bipyridine based CTF.³²⁸

activation is proposed to go by adsorption of oxygen on a carbon atom neighboring the quaternary N, resulting in formation of oxygen radicals as hypothesized by Arai and co-workers who studied a similar reaction using nitrogen doped carbon as a catalyst.³³⁰ It is worth noting that these oxidation reactions have also been reported photocatalytically by CTFs synthesized from thiophene containing building blocks.³³¹

CTFs have also been applied for the oxidative depolymerization of lignin, a main constituent of biomass. Lignin is made up of methoxylated phenylpropane monomers and is a potential renewable source of aromatic building blocks for the chemical industry. However, its depolymerization is not a trivial process. To study the oxidative cleavage of a lignin model compound **320** several CTFs based on 1,4-dicyanobenzene, 1,3-dicyanobenzene and 4,4'-dicyanobiphenyl were synthesized. Phenoxyacetophenone **320** was converted into the cleavage products: phenol **9**, benzoic acid **321**, methyl benzoate **322**, methyl benzoylformate **323** and the ketal **324** (Scheme 101). The conversion stayed under 20% when no catalyst was used, applying CTFs the conversion could reach up to 99%. Furthermore, a range of different β -O-4 ketone compounds could be converted by the CTFs. The mechanism is proposed to go through generation of a peroxide from the β -H, followed by decomposition with C–C or C–O bond cleavage and further reaction to the products.³³²

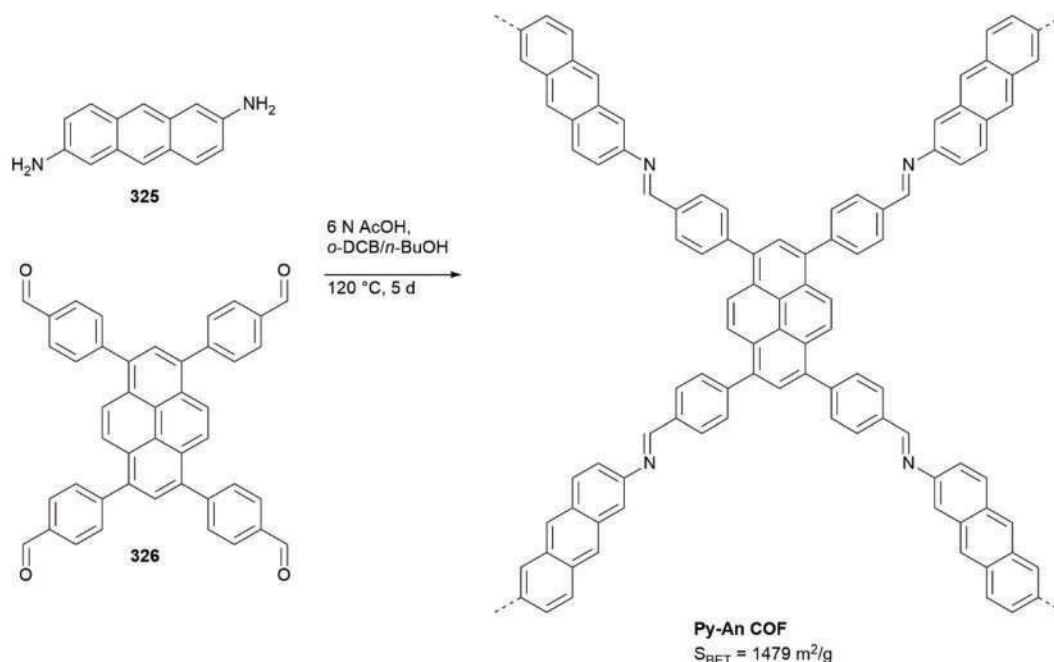
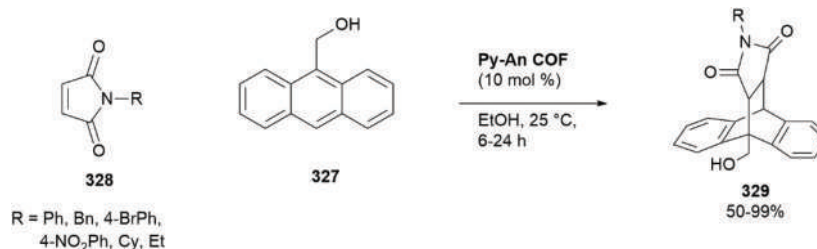
Lastly, Ansari *et al.* used the earlier mentioned polymer formed by condensation of formaldehyde with melamine (Table 1, entry 10) as a catalyst for the epoxidation of styrene to styrene oxide. Using hydrogen peroxide in presence of NaHCO_3 90% conversion and 98% selectivity was obtained.³³³



Scheme 101 CTF catalyzed decomposition of lignin model compound **320**.³³²

7.2 Miscellaneous

Wu *et al.* synthesized **Py-An** COF by solvothermal condensation of 1,3,6,8-tetrakis(*p*-formylphenyl)pyrene **326** with 2,6-diaminoanthracene **325** (Scheme 102). This COF with open one-dimensional channels and columnar π -walls promoted Diels Alder reactions of 9-hydroxymethylantracene **327** and *N*-substituted maleimide derivatives **328** under ambient conditions (Scheme 103). The authors suggest the COF increases both the effective concentration of the reactants within their pores and activates the substrates through C–H π -interactions, reducing the entropy loss and activation energy of the reaction.³³⁴

Scheme 102 Synthesis of Py-An COF.³³⁴Scheme 103 Diels Alder reactions catalyzed by Py-An COF.³³⁴

8 Summary and perspectives

This review summarized the literature concerning metal free porous organic polymers (POPs) as heterogeneous catalysts, to help serve as a guide in this new and exciting field. POPs are a class of polymers that have attracted tremendous interest these past few years. POPs are being researched for many different applications: organic semiconductors, sensors, energy storage, proton conduction, gas adsorption and separation... and of course heterogeneous catalysis.

Their attractive properties such as good stability, high surface areas and accompanying good mass transfer make them especially interesting for catalysis and gas sorption applications. The tailorable design and functionality by the large choice of building blocks and linkages available, allows for an unprecedented control of the structure and function of these materials. A lot of research thus far has been focused on using POPs as a support for metal complexes or nanoparticles. However, when suitable building blocks or postsynthetic

functionalization strategies are used, metal free POPs can be highly effective heterogeneous organocatalysts. This review offered an in depth overview on the literature concerning POPs, including CTFs and COFs, as metal free catalysts. The main topics covered concerned acid and base catalysis, chiral catalysis and the cycloaddition of CO₂ with epoxides.

We have seen that metal free POPs can be effective catalysts for a wide variety of transformations, forming an alternative for homogeneous catalysts and other types of heterogeneous materials. Often when immobilizing catalysts on carrier materials, such as polystyrene resins, the activity is lowered considerably, through mass transfer limitations and changes in the chemical environment. However, POPs generally possess good mass transfer and do not require specific solvents to swell because of their permanent porosity. They also possess much finer control over the chemical environment than other carrier materials, allowing activities that are similar and even in some cases higher than the corresponding homogeneous catalysts. Moreover, this fine control allows very advanced

types of materials, combining catalytic units (e.g. Scheme 37) and providing an ideal chemical space for certain transformations (e.g. Schemes 3, 84 and 85).

Next to these advantages, many challenges remain on the way to more widespread (industrial) application and to be able to speak of truly green or sustainable materials (Fig. 5). In general, large scale synthesis of the more complex materials is a big problem, especially for COFs. Expensive or commercially unavailable monomers, toxic or expensive catalysts and the harsh conditions that are often used still form major hurdles towards large scale applications.

Many POPs require very specific, highly functionalized, expensive or synthetically challenging building blocks. As mentioned several times in this review many of the monomers are not commonly available and require multiple, often inefficient synthesis steps utilizing toxic and hazardous reagents, challenging the green potential of the materials themselves. For example, in the case of some of the discussed chiral phosphoric acid containing polymers up to ten steps were required to synthesize some monomers (155 and 156). But even more commonly used building blocks such as 5,5'-diamino-2,2'-bipyridine **282**, 2,4,6-triformylphloroglucinol **71**, 1,3,5-triformylbenzene **48** and many more require inefficient chemical synthesis using hazardous reagents. Moreover, not much effort has been made to incorporate building blocks based on renewable resources into these materials, for example, 2,5-furandicarboxaldehyde could be used to synthesize imine COFs, a further avenue for enhancing the sustainability of these materials.

The actual polymerization of the monomers into POPs is also, in many cases, not (yet) scalable or green. The synthesis of HCPs prepared through radical crosslinking is comparable

to that of polystyrene resins and can be performed on larger scales, under relatively mild conditions. However, HCPs based on Friedel–Crafts crosslinking typically use DCE, a non-recommended solvent, and large excesses (up to more than ten equivalents) of corrosive Lewis acids such as AlCl_3 or FeCl_3 . CMPs and PAFs are typically prepared by precious-metal based crosslinking in non-recommended solvents such as toluene, THF, DMF, Et_3N or DIPEA... for several days at high temperatures.

COFs and CTFs in particular are in this case the biggest offenders, these are still mainly made in vacuum sealed glass ampoules placed in ovens at high temperatures (typically 120 °C for COFs) at very small scales (<100 mg). In the case of the CTFs extremely high temperatures (≥ 400 °C) are applied, which forms a safety hazard due to the possibility of the ampoules exploding. Moreover, these extremely high temperatures lead to carbonization of parts of the material making characterization difficult and obscuring their structure. To help solve these problems a lot of research has been done to improve the synthesis. For CTFs an alternative to the high temperature ionothermal reaction consists of superacid catalyzed trimerization at room temperature³³⁵ or the condensation of alcohols or aldehydes with amidines in DMSO at 120 °C, with the latter method even capable of producing crystalline materials.^{278,336}

Obtaining truly crystalline COFs still forms a tremendous challenge. Every new COF requires a large amount of trial and error based optimization of the reaction conditions to obtain a crystalline material, and even then the synthesis typically only works on a small scale.^{37,337,338} Furthermore, many of the common solvents to synthesize COFs are non-recommended,⁹⁷ e.g. DMAc, DMF, mesitylene, 1,4-dioxane, 1,2-DCB... Progress

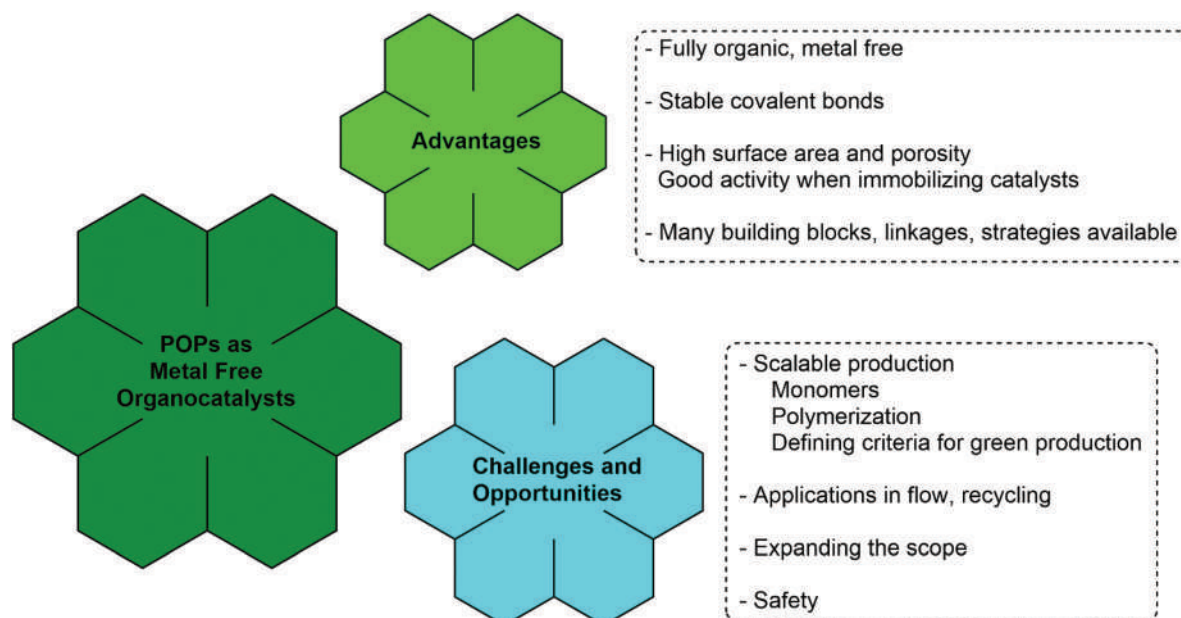


Fig. 5 Advantages and future challenges applying POPs as metal free organocatalysts.

is being made to develop new synthetic strategies to help overcome these challenges, such as microwave or mechanochemical synthesis, linker exchange, multicomponent reaction and multistep synthesis.³³⁸ However, a truly large scale, green synthesis method for COFs (and most POPs in general) has not been found yet.

Similarly as with MOFs, POPs are touted as 'green materials' enabling sustainable technologies. For this to happen however the availability of clean and sustainable synthesis methodologies that work on larger scales is of paramount importance. While criteria for green, sustainable and industrially-acceptable MOF synthesis have been developed,^{339–341} for POPs this has not yet been done. These criteria include the costs and availability of raw materials, the space time yield (STY), reaction and work up (filtration–washing–drying) conditions, total cost and the safety or environmental concerns for all steps of the production process. For MOFs examples already exist of ton-scale production in a green way, for example, Basolite A520.^{340,342} For its production, DMF, the classical solvent for MOF synthesis, was replaced by water. The STY was increased by more than 500-fold, to more than 3600 kg per m³ per day and the synthesis was so easy and safe that it could be performed in a high school laboratory.³⁴⁰ This does raise the hope that similar enhancements for POP synthesis could be possible to enable the transition from the small, academic scale to the larger industrial scale.

Next to the synthesis of the POPs another important aspect is their toxicity when handled or disposed. There is a lack of studies addressing these points. It is of course not unthinkable that porous (crystalline) powders such as POPs would form breathing hazards. The degradation of POPs in the environment is also uncharted terrain. While some, more unstable materials such as certain imine COFs, could degrade quite quickly, others such as CTFs could prove to be quite persistent.

Another important aspect is the exploration of the catalytic applications of POPs in flow chemistry. Almost all applications were reported in batch, whilst due to the insolubility of POPs they are perfectly suited for applications in flow. Continuous flow chemistry has several advantages over batch. The efficient mass and heat transfer allows a very precise temperature control over the reactor and thus avoids uncontrolled exotherms and ensures process safety. The quality of the end product is very consistent and continuous production can lead to long term economic savings.^{343,344} For this application the stability, recyclability or possibility of regeneration of the heterogeneous catalyst is extremely important. While for many of the discussed catalysts the activity was constant, even after many runs, this is not always the case. Especially in the case of the chiral POPs yields sometimes dropped dramatically. The production of these difficult to make heterogeneous catalysts is of course only justified if they can be recycled many times.

Furthermore, the reaction scope is still quite limited. In many papers the catalytic applications are only reported as an afterthought to probe, for example, the basicity of the material.

For some transformations that are already well established with POPs, for example, Knoevenagel type reactions, CO₂ cycloadditions to epoxides, chiral amine organocatalysis... it is time to move beyond these proof of concept studies into larger, scale up studies, to truly establish these materials as an important class of catalysts for practical applications. Moreover, it is challenging to compare catalyst performance due to uninformed reporting. The kinetics of the reactions should be studied and reported better: (initial) turnover frequencies and numbers should be determined under as uniform conditions as possible to enable clear comparisons between catalysts.

Next to this, more truly novel types of reactions should be performed with POPs. It may be time to move away from simply heterogenizing homogenous catalysts on POPs for the increased stability and recyclability as a primary reason to investigate these catalysts. POPs can provide control of the shape and chemical environment of the pores and thus the catalytic moieties, enabling mechanisms and reactivities not possible with homogeneous catalysts and this should be researched and developed further.⁴⁹ COFs especially enable truly unprecedented control of the microenvironment of fully organic extended materials. This allows for the construction of catalysts utilizing multiple substrate binding and transition state stabilizing interactions, enabling extremely efficient catalysis of new transformations.

As stated in the beginning of this review, efficient catalysis is essential to perform green chemistry and for the modern world in general. We have seen throughout this review that as a class of materials metal free POPs can have tremendous potential as heterogeneous catalysts. However, as we discussed, many challenges remain on the way to widespread adaptation. In the coming years this field will develop further and many more exciting applications will be reported, to help pave the way to a more sustainable chemical industry.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors acknowledge the Research Board of Ghent University (BOF GOA20177000303) for funding.

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