



Porous aromatic frameworks containing binaphthyl-dihydroazepine units (cBAPAFs) as catalytic supports for asymmetric reactions

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ABSTRACT

We present the successful synthesis of a series of chiral polymeric aromatic frameworks containing novel enantiopure atropisomeric 1,1'-binaphthyl-dihydroazepine-based compounds as structural building units named cBAPAFs. Three porous materials with amino, pyridinic and amino-alcohol functionalities were successfully obtained from dibrominated monomers by Suzuki-Miyaura couplings. New porous materials present surface areas up to 619 m² g⁻¹ determined by Brunauer-Emmett-Teller (BET), and high thermal stability. The use of nitrogen-based structural units provides useful functional groups to allow a robust binding site for metal complexes. Thus, after post-synthetic metalation with Cu(OAc)₂, these materials have been applied as efficient heterogenized catalysts for the nitroaldol (Henry) reaction and a multicomponent reaction, affording chiral products with comparable enantioselectivity to that of the homogeneous system. The materials were also tested as organocatalysts for the asymmetric addition of diethylzinc to benzaldehyde and the reaction between nitro-styrene and nitroethane. These cBAPAFs could be recycled for the asymmetric nitroaldol reaction for at least 5 cycles without a significant loss in its catalytic efficiency.

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1. Introduction

Asymmetric catalysis is of essential significance because of the important demand for compounds with high optical purity. Over the last years, numerous efficient homogeneous chiral catalysts have been obtained [1]. The immobilization of these homogeneous chiral catalysts in a solid matrix (inorganic or polymers) gives rise to heterogenized systems that combine the characteristics of homogeneous and heterogeneous catalysts [2–5].

In the recent decade, different porous materials (porous organic frameworks, POPs, covalent organic frameworks, COFs or metal organic frameworks, MOFs) with high porosity have been developed and used in fields, such as, gas adsorption and storage, separation, drug delivery, sensing, and catalysis [6–8]. The heterogenization of soluble chiral catalysts on these materials has become very interesting and the last advances in this field have been reported for different authors [9–17]. POPs are formed by stable covalent bonds and in particular when formed by only aromatic rings linked by single carbon-carbon bond are named porous

aromatic frameworks (PAFs) and have been applied in different fields [18,19]. It was also found that these materials are good organic matrices to support organo and organometallic catalysts [20,21].

Dibenz[c,e]azepine derivatives have attracted the attention of synthetic and pharmaceutical chemists researches because of its possible application in medicine [22]. Chiral C2-3,5-dihydro-4H-dinaphth-[2,1-c:1'2'-e]azepines are interesting 1,1'-binaphthyl derivatives which up to date has only received limited attention in contrast to other binaphthyl compounds such as phosphoric acids [23,24], phosphoramidites [25], phosphites [26] or even 1,1'-binaphthol (binol) [27] etc. Dihydro-azepines have been employed as precursors of chiral ammonium phase-transfer catalysts, widely reported by Maruoka's group [28–31]. However, its use as organocatalyst [32,33] is scarce because of the relatively low basicity of this chiral secondary amine. Therefore its application as chiral organocatalyst requires some structural modifications to enhance its basicity. The azepine unit can be functionalized with different groups that make attractive mono and bidentate ligands, useful in asymmetric catalysis. These groups include phosphine [34], amine [35], pyridine [36] or alcohol [37] units among others etc. The idea of introducing a second coordinat-

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ing group anchored through the nitrogen of the dihydroazepine is to enable a further chelate effect. Aminopyridine and aminoalcohol derivatives have proven to be interesting active homogeneous catalysts for the nitroaldol (Henry) reaction and diethylzinc addition to aldehydes [38].

Our research interests involve the development of chiral polymeric materials to be used as catalysts [20]. To the best of our knowledge, the heterogenization of the homogeneous dihydroazepine-based catalysts have not been reported yet, and only the Maruoka phase-transfer catalyst has been copolymerized and employed as a solid catalyst in the enantioselective α -alkylation reaction with high enantiodiscrimination [39,40]. Herein, we design and prepared a novel family of binaphthyl-based chiral porous polymers, **cBAPAFs**, incorporating azepine moieties in the framework by a Suzuki-Miyaura cross-coupling between two building blocks, dibromotetrahydroazepine derivatives and 1,3,5-tris[(4-phenylboronic acid)]benzene. The resulting materials have been applied as catalysts in different reactions as the nitroaldol (Henry) reaction, the multicomponent A3 coupling (aldehyde-amine-nitromethane), diethylzinc addition to benzaldehyde and the nitro-Michael reaction between nitro-styrene and nitroethane, comparing both homogeneous and heterogeneous catalytic systems.

2. Experimental

2.1. Synthesis of the chiral azepine building blocks.

The synthesis and characterization of chiral-binaphthyl-dihydroazepine building blocks employed in this work (**3-NH**, **3-NPy** and **3-NOH**) are described in the [Supporting Information](#).

2.2. Preparation of polymeric aromatic frameworks (cBAPAFs).

Method A: In an Ace pressure tube (Merck), the binaphthyl-dihydroazepine monomer **3-NH** or **3-NPy** (0.40 eq.) and 1,3,5-triphenylbenzene-4',4'',4'''-triboronic acid (1.0 eq.) were added to a dimethylformamide (DMF) (4 mL)/tetrahydrofuran (THF) (2 mL) mixture and degassed with nitrogen for 20 min, then Pd(dppf)Cl₂ (0.02 eq.) and aqueous saturated solution of K₂CO₃ were added. The reaction mixture was stirred and heated at 120 °C for 24 h, filtered washed with DMF, water and H₂O/acetone in presence of KCN to remove the residual palladium. The solid was then washed with acetone dichloromethane (DCM) and THF and dried under reduced pressure at 100 °C.

Method B: For the case of cBAPAF-NOH, **3-NOH** (0.8 eq.), 1.10 eq. of co-linker 4,4'-diiodo-1,1'-biphenyl and 1,3,5-triphenylbenzene-4',4'',4'''-triboronic acid (1.10 eq.) were reacted and treated under the same conditions used in method A. Experimental details can be found in the [supplementary material](#).

2.3. Catalytic evaluation

Copper-catalyzed reactions: In general, ligand-copper catalysts were prepared in situ reacting the corresponding ligand (0.02 mmol) and Cu(OAc)₂ (0.02 mmol), the mixture was stirred in EtOH (1 mL) at room temperature overnight, then the resulting solid was filtered and washed with ethanol to eliminate unreacted copper salt and used for the chosen reaction. Experimental details and characterization data can be found in the [supplementary material](#).

3. Results and discussion

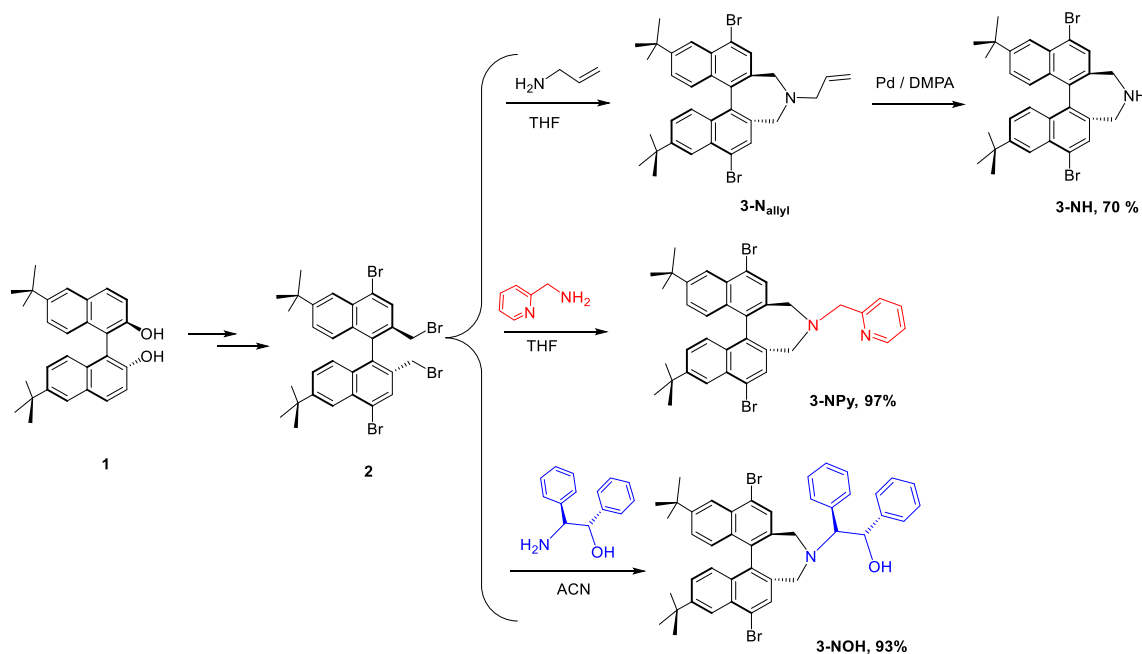
3.1. Synthesis of the chiral azepine building blocks.

1,1'-Binaphthyl based materials are typically grown in the 3,3'-positions of binaphthyl unit. This geometry affords more constraints around the chiral pocket and in some cases the enantioselectivities are increased [41,42]. We have prepared materials by growth from an axial position, and therefore it is necessary to synthesize the intermediate **2**, shown in [Scheme 1](#). The regioselectivity of the aromatic bromination is exclusively to the 4,4' positions due to the previous introduction of the *tert*-butyl groups in the 6,6' positions, this substitution was previously reported by our group for the case of binol as structural unit [43]. Details for the synthesis of precursor **2** are given in the [supplementary information](#). The dihydro-azepine monomer is formed by a nucleophilic substitution of the tetra-bromide compound **2** with the primary amine of choice. This route is similar to that previously reported [44].

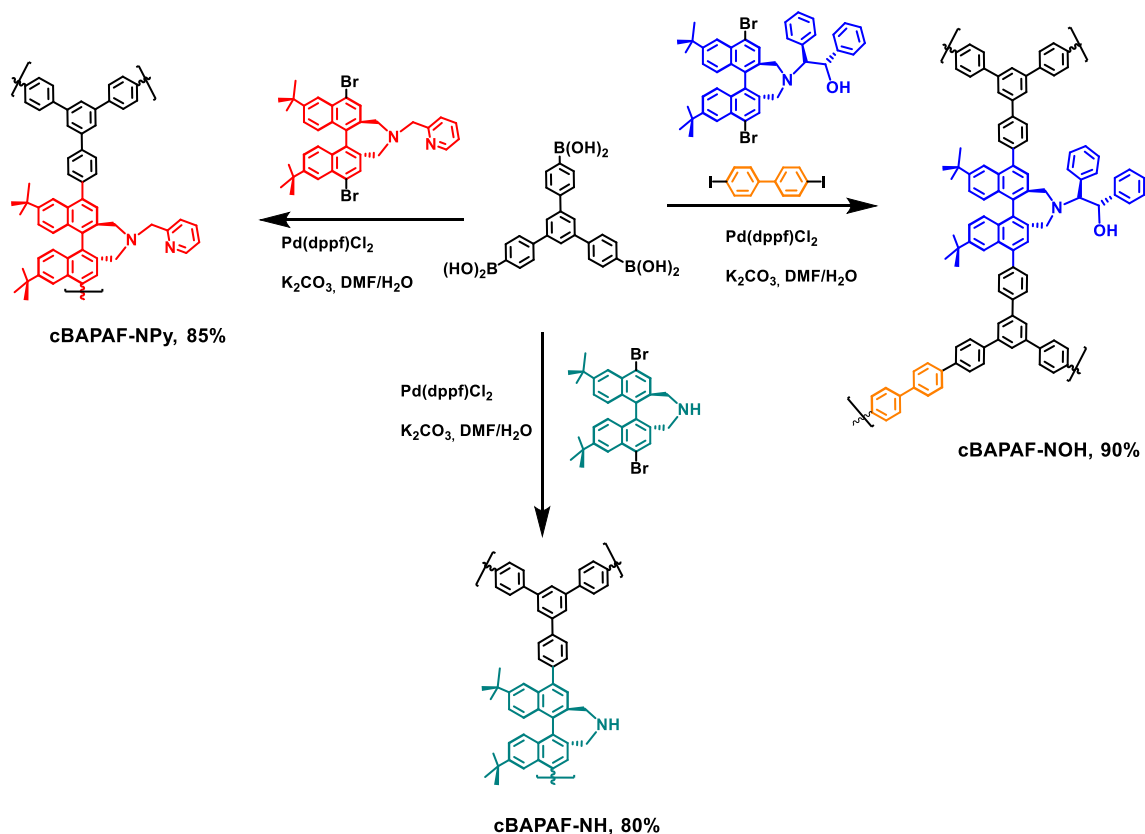
3.2. Synthesis of the binaphthyl-dihydro-azepine-based chiral porous aromatic frameworks (cBAPAFs)

Once 4,4'-bromide-dihydroazepine compounds, **3-NH**, **3-NPy** and **3-NOH**, were obtained, the corresponding polymers were prepared through a Suzuki-Miyaura coupling with 1,3,5-tris[(4-phenylboronic acid)]benzene under conventional heating at 120 °C in a mixture of THF/DMF as solvent and Pd(dppf)₂Cl₂ as catalyst ([Scheme 2](#)). The resulting solids were washed with DMF, water, acetone, DCM and THF and characterized by the common solid-state techniques. In the case of the bulkier precursor **3-NOH**, the synthesis was performed by copolymerization of boronic acid, **3-NOH** and 4,4'-diiodobiphenyl as co-linker, in order to avoid steric saturation of the polymer and the formation of bottlenecks which might causes the encapsulation of reactants during the polymerization process. Two materials were obtained depending on the amount of **3-NOH** (0.4 eq. or 0.8 eq.). The resulting cBAPAF-NOH obtained from 0.4 eq. of aminoalcohol gives a very low nitrogen value in its elemental analysis (0.5%). Furthermore, its solid ¹³C NMR spectrum shows only weak signals from the functional group and it is ruled out for use as a ligand (see [SI](#)). All final polymers were treated with KCN in acetone/water to eliminate the residual Pd(0) from the catalyst. Elemental analysis of the synthesized polymers shows that the binaphthyl units are successfully incorporated into the polymer (Table S1). As it is typically observed for this type of polymers carbon loading is lower than expected but the nitrogen loading is in agreement with the theoretical value expected. **cBAPAFs-NPy** shows a lower C/N ratio than expected probably due to the partial coordination of monomer to the Pd. ICP and EDX analysis shows that there is no palladium in **cBAPAF-NH** and **cBAPAF-NOH** however in the case of **CBPP-NPy** a 1.3% of Pd is obtained confirmed by the residue from the TGA analysis.

[Fig. 1a](#), [1b](#) & [1c](#) show the solid state ¹³C NMR spectra of all polymers. The signals corresponding to the aromatic carbons can be observed at 120–150 ppm, the resonance due to the aliphatic *t*-butyl groups appears at ~34 (C) and ~30 (CH₃) ppm and weak signals in the range of 50–60 ppm are assigned to the azepine unit. The spectrum of **cBAPAF-NPy** shows a signal at 158.0 ppm corresponding to the pyridine ring and **cBAPAF-NOH** shows weak signals due to the amino alcohol group. The cBA-polymers were also characterized by FTIR-ATR (Fourier transformed IR from attenuated total reflectance) spectroscopy ([Fig. 1d](#)). The spectra show the characteristic signals of the monomers and functional groups at 650–850 cm⁻¹ (aromatic ring, the out-of-plane bending modes of the C-H bond), 1400–1650 cm⁻¹ (C=C), 3050 cm⁻¹ (C-H aromatic) and 2850–2950 cm⁻¹ (C-H aliphatic). The spectrum of



Scheme 1. Synthetic route to obtain 1,1'-Binaphthyl-dihydro-azepine-monomers.



Scheme 2. Synthesis of binaphthyl-azepine-based-PAFs.

NOH-polymers also shows a signal at 3680 cm^{-1} due to OH group from the amino alcohol.

The thermal stability of the materials was studied by thermogravimetric analysis (TGA). All showed good thermal stability being higher for NH- and NOH-derivatives which present a fast weight loss after $475\text{ }^{\circ}\text{C}$ and $453\text{ }^{\circ}\text{C}$ respectively (Fig. 1e). In the

case of **cBAPAF-NPy** it is observed two main steps at $320\text{ }^{\circ}\text{C}$ and $380\text{ }^{\circ}\text{C}$ and an inorganic residue, which is due to the remaining palladium coordinated at the pyridine chelate despite the exhaustive washing to which the material is subjected after synthesis. We have verified that this remaining palladium do not alter the catalytic activity, as it is commented *vide infra*.

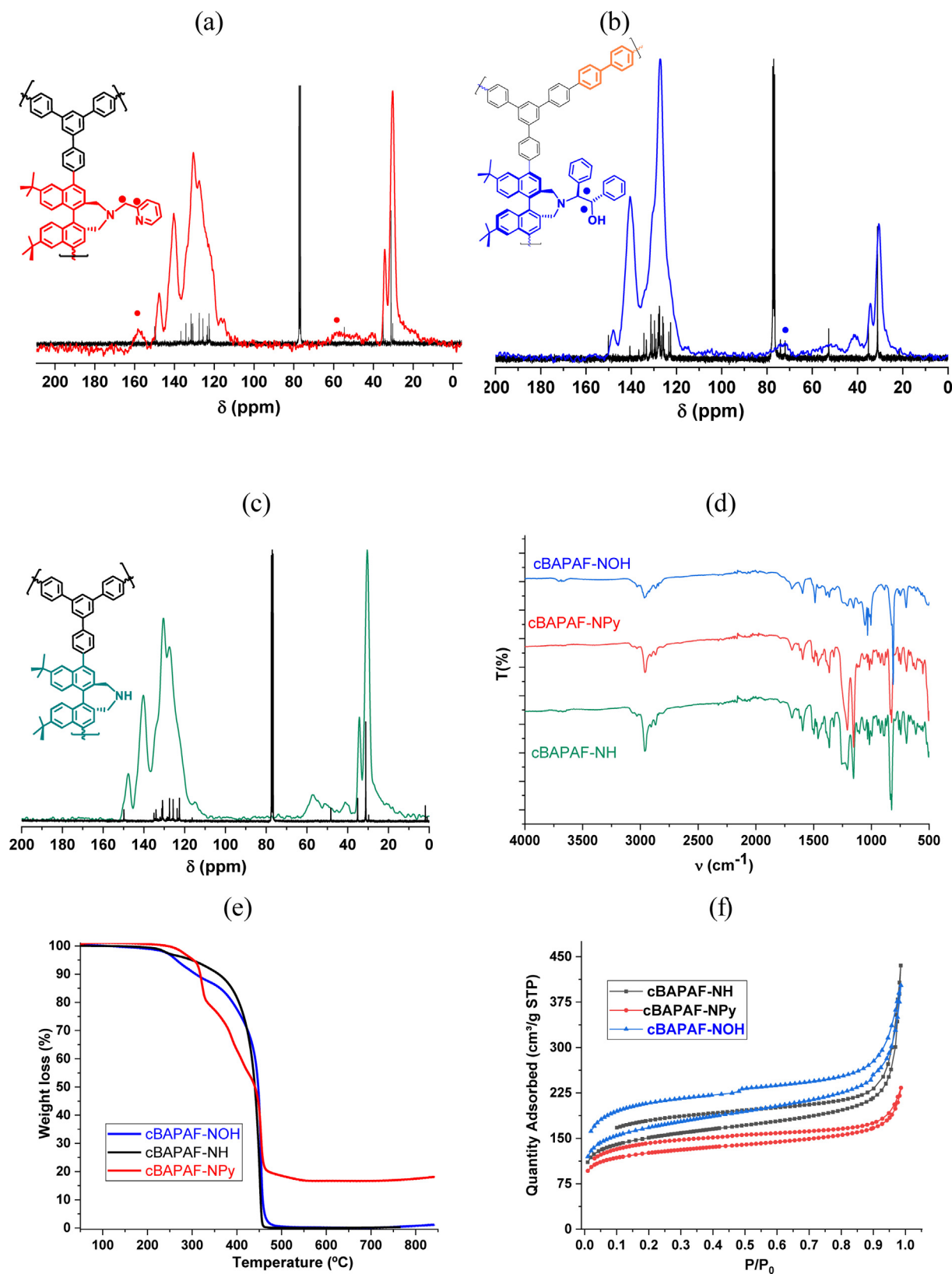


Fig. 1. Characterization data of cBAPAFs: a), b), c) ^{13}C NMR spectra of material and ligands; d) FT-IR, e) TGA of materials. f) N_2 adsorption measurements.

Porosity has been studied by isothermal nitrogen sorption measurements at 77 K, showing the adsorption-desorption isotherms the typical IV aspect that implies the existence of mesopores and

micropores (Fig. 1f). The specific surface areas have been obtained by Brunauer-Emmett-Teller (BET) methods and the calculated surface area of the **cBAPAF-NPy** and **cBAPAF-NOH** reached 472 m^2

g^{-1} and $619 \text{ m}^2 \text{ g}^{-1}$ respectively ($560 \text{ m}^2 \text{ g}^{-1}$ for **cBAPAF-NH**), all materials have porous structures with average pore sizes of 2.75, 3.50 and 3.90 nm, respectively (Table 1).

Finally, the morphology of the polymers was observed by field-emission scanning electron microscopy (FE-SEM; Fig. 2) and it showed the spherical aggregates characteristic for these porous materials.

3.3. Evaluation of cBAPAFs catalysts in asymmetric catalysis

cBAPAF-NH, **cBAPAF-NPy** and **cBAPAF-NOH** have been applied as ligands to obtain the corresponding heterogenized ligand/[Cu]-catalysts which have been evaluated for the nitroaldol(Henry) and a multicomponent A^3 coupling (aldehyde-amine-nitromethane) reactions. They have also been applied as organocatalysts for the asymmetric addition of diethylzinc to benzaldehyde and the reaction between nitro-styrene and nitroethane. Experimental details can be found in the [supplementary material](#). We have compared the catalytic behavior of the corresponding soluble catalysts (**3-NH**, **3-NPy** and **3-NOH**) with that of the corresponding heterogenized cBAPAFs.

3.3.1. Copper-catalyzed-reactions

The nitroaldol (Henry) reaction is a classical reaction to obtain β -nitroalcohol products by a reaction between an alkyl nitro compound and a carbonyl function [45]. The asymmetric version has been extensively studied and generally implies copper precursors [46–49]. Heterogenization and recyclability of soluble catalysts have been also performed for this reaction [50,51]. We decided to apply the azepine-based polymers as ligands for the Cu-catalyzed Henry reaction. The ligand/[Cu] catalysts were prepared in situ by reaction of the soluble or heterogenized ligand with copper acetate in ethanol, being used directly in the corresponding reaction.

To confirm that the catalyst has been effectively obtained, we have isolated and characterized the cBAPAF-NOH-[Cu] catalyst (Figure S1). cBAPAF-NOH-[Cu] has similar bands to that of the free ligand in the ATR spectrum and has similar thermal stability with a fast weight loss after 450°C giving an inorganic residue corresponding to copper oxide. XPS analysis was also performed (Figure S1d). Main peaks of Cu 2p_{3/2} at 935.0 eV and Cu 2p_{1/2} at 955.0 eV and the corresponding satellites lines are typical for Cu

(II) compounds [52] and confirmed the successful incorporation of copper into the PAF. EPR spectrum was also obtained showing the typical X-band for copper with a $g = 2.15$ (Figure S1c). Elemental analysis of nitrogen and copper (determined by ICP-OES and TGA) indicates that copper complex is effectively obtained.

To evaluate the catalytic performance of cBAPAFs as ligands, first, we have tested the corresponding soluble catalytic system ligand/[Cu]. The catalytic activity of the soluble binaphthyl azepines was firstly tested in the reaction between different aldehydes and nitromethane. To optimize the reaction conditions, we chose ligand **3NPy** and we examine temperature reaction and solvent. Table S2 shows that the reaction temperature does not affect significantly the enantioselectivity obtained for this reaction, only less conversion is achieved at lower temperatures. However, the solvent does and it was found that non-protic solvents such as DCM or dichloroethane did not enable enantioselectivity being ethanol the most effective. Lastly, different copper salts were proved and oxidation state of the copper salt seems also key to affords high conversion being $\text{Cu}(\text{OAc})_2$ the salt of choice to perform the Henry reaction (Table S2). In all experiments we have used a ratio of reagents of aldehyde/nitromethane/[metal salt]: 0.2/0.2/0.02. We have also evaluated the influence of the amount of catalyst in the reaction and when 0.01 mmol of copper salt was used, the yield decreases to 50%.

Once the standard conditions have been chosen (solvent: EtOH, temperature: r.t., copper salt: $\text{Cu}(\text{OAc})_2$), we studied the behavior of the different soluble catalytic systems in the reaction between different aldehydes and nitromethane or nitroethane (Table 2). Bare binaphthyl-dihydroazepine-[Cu] (**3-NH**-[Cu]) results inactive for the reaction between benzaldehyde and nitromethane due to the absence of chelating effect. However, when picoline derivative was used as ligand (**3-NPy**-[Cu]) a quantitative yield was obtained with 60% ee, this is due to the more favorable copper(II) complex formed. This catalytic system also results effective for other aldehydes with excellent yields and moderate enantioselectivity. After these results, we opted to prepare and apply as ligand the *N*-substituted binaphthyl-dihydroazepine incorporating (1*S*,2*R*)-2-amino-1,2-diphenylethanol as a second chiral moiety. In this case high enantioselectivities were achieved with values up to 97%.

With these results in hand, the heterogenized cPAFs-ligands were reacted with $\text{Cu}(\text{OAc})_2$ for 3 h and thoroughly washed to remove the uncoordinated copper species and the corresponding **cBAPAF**-[Cu] catalytic systems were studied for the same model reaction (Table 2). As can be observed the catalysts show a good activity and the highest enantioselectivities were also obtained with **cBAPAF-NOH**-[Cu] catalyst, although the e.e. values were slightly lower than that obtained with its homogeneous counterpart. **cBAPAF-NPy**-[Cu] gives the same e.e. than its homogeneous analogous. As it was commented above, the fact that cBAPAF-NPy is purely made with 3-NPy monomer, which is such a bulky mono-

Table 1

BET surface area and total pore volume.

Material	$\text{SA}_{\text{BET}}(\text{m}^2 \cdot \text{g}^{-1})^a$	$\text{V}_{\text{pore}}(\text{cm}^3 \cdot \text{g}^{-1})^b$	Pore size (nm) ^c
cBAPAF-NOH	619	0.542	3.50
cBAPAF-NH	560	0.545	3.90
cBAPAF-NPy	472	0.320	2.75

^aCalculated from BET methods. ^b At P/P_0 0.98. ^c From DFT.

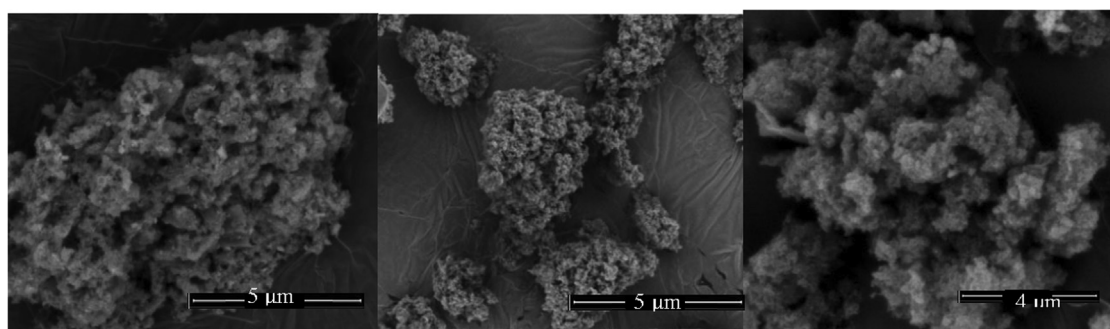


Fig. 2. SEM images of, from left to right: cBAPAF-NPy, cBAPAF-NOH and cBAPAF-NH.

Table 2
Ligand/[Cu]-catalyzed Henry reaction.^a

3NPy[Cu]:	60%	ee,	100% conv.
cBAPAF-NPy[Cu]:	60%	ee,	100% conv.
3NOH[Cu]:	97%	ee,	95% conv.
cBAPAF-NOH[Cu]:	90%	ee,	85% conv.
3NH[Cu]:	0%	ee,	10% conv.
3NPy[Cu]:	40%	ee,	99% conv.
cBAPAF-NPy[Cu]:	30%	ee,	95% conv.
3NOH[Cu]:	94%	ee,	100% conv.
cBAPAF-NOH[Cu]:	10%	ee,	98% conv.
3NPy[Cu]:	60%	ee,	99% conv.
cBAPAF-NPy[Cu]:	60%	ee,	100% conv.
3NOH[Cu]:	95%	ee,	99% conv.
cBAPAF-NOH[Cu]:	<10%	ee,	100% conv.
3NPy[Cu]:	<10%	ee,	99% conv.
cBAPAF-NPy[Cu]:	<10%	ee,	100% conv.
3NOH[Cu]:	81/60%	ee,	90% dr, 70% conv.
cBAPAF-NOH[Cu]:	80/60%	ee,	70% dr, 50% conv.

^a Reaction conditions: aldehyde (0.2 mmol), nitromethane (0.2 mmol), EtOH (1 mL), catalyst (Cu(OAc)₂ (0.02 mmol), ligand (0.02 mmol based on nitrogen found); ee determined by HPLC: a CHIRACEL OD-H column, eluent: 90:10 hexane/2-propanol, flow rate of 1 mL/min.

mer, favored the creation of bottlenecks that seem to have encapsulated traces of palladium (required during Suzuki-mediated polymerization). Thus, so as to conclude the inert nature of this palladium residue, it was tested the Henry reaction with cBAPAF-NPy as catalyst, but in absence of copper, and the reaction do not take place.

Moreover, the recyclability of the heterogenized cPAF-[Cu] catalysts was studied for the reaction between benzaldehyde and nitromethane (Fig. 3, table S3). Whereas **cBAPAF-NPy[Cu]** remains stable for 5 cycles, with a little decrease of enantioselectivity in the last one. **cBAPAF-NOH-[Cu]** required to get activated after the 4th cycle by heating at 145 °C and refluxing again with Cu(OAc)₂. A hot filtration test was carried out to examine the heterogeneity of the catalyst and no further reaction occurred upon removal of the catalyst, which demonstrate the heterogeneous nature of our catalyst. IR spectrum and SEM images show that the recovered Cu-catalyst has not changed significantly (Figure S2). The XPS displays the expected signals, which further confirm the stability of the copper complex.

The applicability of the **cBAPAFs-[Cu]** to other reactions was also studied, we considered, as a proof of concept and as one step forward of the Henry reaction, the multicomponent reaction (A³ coupling) between *para*-nitro-benzaldehyde, *para*-methoxyaniline and nitromethane [53] and the results are shown in Table 3. The homogeneous catalytic systems result very effective in enantioselectively afford the 4-methoxy-*N*-(2-nitro-1-(4-nitrophenyl)-1-ethyl)aniline with 3NOH-[Cu], with 96% e.e. Although full conversion was observed, the selectivity towards the A3 product was

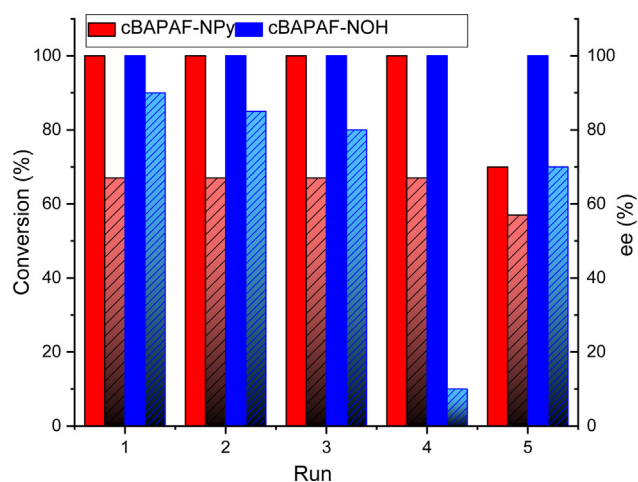
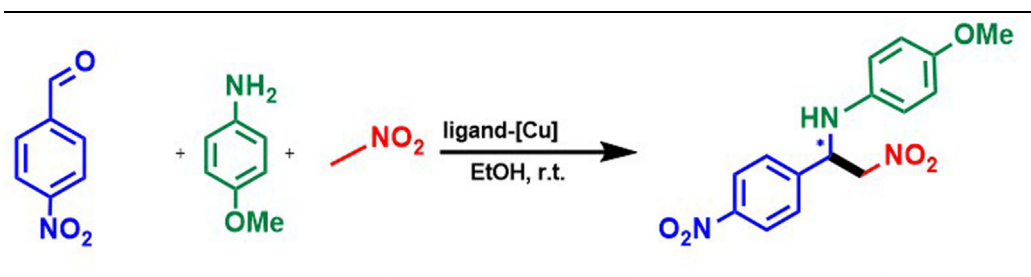
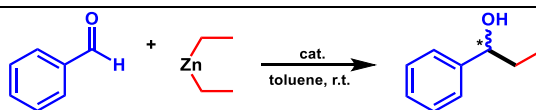
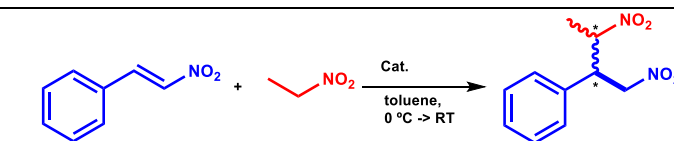


Fig. 3. Catalytic activity of NPy- and NOH-cBAPAFs in the reaction between benzaldehyde and nitromethane over 5 runs.

moderate, observing also the imine precursor. The others systems afforded the desired product with very low yield and enantioselectivity.

3.3.2. cBAPAFs as organocatalysts

Diethylzinc addition to aldehydes is one of the typical proof of concept reaction to explore the enantioselectivity of chiral

Table 3
Multicomponent A³ coupling.^a**3NPy-[Cu]:** <10% ee, <10% select.**cBAPAF-NPy-[Cu]:** <10% ee, <10% select.**3NOH-[Cu]:** 96% ee, 35% select.**cBAPAF-NOH-[Cu]:** <10% ee, 30% select.^a Reaction conditions: aldehyde (0.2 mmol), amine (0.21 mmol), nitromethane (0.22 mmol), EtOH (1 mL), catalyst (Cu(OAc)₂ (0.02 mmol)/ligand (0.02 mmol); ee determined by HPLC: CHIRACEL OD-H column, 90:10 hexane/2-propanol, 1 mL/min.**Table 4**
Diethylzinc addition to benzaldehyde.^a**3NOH:** 80% ee, 70% conv.**cBAPAF-NOH:** 70% ee, 99% conv.**3NPy:** 0% ee, 95% conv.**cBAPAF-NPy:** 0% ee, 90% conv.^a Reaction conditions: aldehyde (0.07 mmol), Et₂Zn (0.140 mmol), cat. (0.007 mmol, based on functional group), toluene (1 mL), r.t.; ee determined by HPLC: CHIRACEL OD-H column, a mobile phase composition of 90:10 hexane/2-propanol and a flow rate of 0.5 mL/min.**Table 5**
Michael reaction.^a**3NOH:** 50% ee, 86 % dr, 75% conv.**cBAPAF-NOH:** 10% ee, 100% dr, 40% conv.^a Reaction conditions: β-nitro-styrene (0.03 mmol), nitroethane (0.38 mmol) and catalyst (0.003 mmol, based on functional group), toluene (1 mL) at r.t. ee determined by HPLC: CHIRALPAK IB column, a mobile phase composition of 95:5 hexane/2-propanol and a flow rate of 1 mL/min.

organocatalysts [54,55]. Under conventional conditions, all catalysts were evaluated using toluene as solvent and room temperature, all of them afforded the corresponding products in high yields (70–100%) (Table 4). The enantioselectivity was good obtaining 80% e.e. when cBAPAF-NOH was the catalyst. The aminopyridine-based catalyst did not afford any enantioselectivity, and we consider that the fact that the ligand cannot neutralize the Zn(II) charge, makes the corresponding coordination complex not enough stable. The recyclability of cBAPAF-NOH as organocatalyst was also studied. In this case, it is also necessary the reactivation of the catalyst to eliminate the inorganic residues being effective only for three runs (Figure S3).

The organocatalytic efficiency of these chiral cBAPAFs was finally evaluated in another standard process as a Michael reaction [56]. As substrates we have chosen nitro-styrene and nitroethane and the reaction was done in toluene at 0 °C temperature (Table 5). Soluble 3-NOH catalyst results more effective (75% conv., 50% ee) than the corresponding heterogenized cBAPAF-NOH (40% conv, 10% ee); however, higher diastereoselectivities were obtained with cBAPAF compared to homogeneous counterpart (100% for CBPP-NOH versus 86% for 3-NOH).

4. Conclusions

We have obtained three robust chiral 1,1'-binaphthyl-dihydroazepine-based porous polymeric aromatic frameworks (cBAPAFs) via a palladium catalyzed Suzuki-Miyaura coupling. These materials are found to have high stability, specific surface areas up to 619 m²·g⁻¹ and show great potential for applications in heterogeneous asymmetric catalysis. The functionalized cBAPAFs-[Cu] exhibit an excellent catalytic performance in the Henry reaction with a high stability and could be reused at least five times. The results demonstrate the potential of cBAPAFs as organocatalysts and/or as catalyst supports providing a high loading of accessible active sites. The results presented highlights the huge opportunities that these polymers offer in the development on new heterogeneous catalysts by benefiting not only intrinsic chirality of binaphthylazepine but also that of post-synthetically incorporated of functional groups and opens the possibility to explore new catalytic applications by combining the intrinsic properties of the azepine unit with those of integrated functionalities.

Declaration of Competing Interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcat.2022.06.034>.

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