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Adamantyl-BINOL as platform for chiral porous polymer aromatic frameworks. Multiple applications as recyclable catalysts

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ABSTRACT

Herein, we report the synthesis of adamantyl-BINOL-based chiral porous aromatic polymers (Ad-BINOL-PAFs) for heterogeneous catalysis. Ad-BINOL-OH-PAF (365 $m^2 \cdot g^{-1}$ SA_{BET}) was built through the covalent bonds among of 4,4′-dibromo-O-ethyl-protected adamantyl-BINOL with 1,3,5-Triphenylbenzene-4′,4″,4‴-triboronic acid and in the presence of $[Ti(OiPr)_4]$ results an effective recyclable catalyst in the asymmetric addition of diethylzinc to aromatic aldehydes (ee up to 88%). The corresponding heterogenized phosphoric acid (Ad-BINOL-PO_2H-PAF) was applied as heterogeneous recyclable organocatalyst for the cascade condensation/amine addition of anthranilamide with aldehydes and transfer hydrogenation reactions obtaining high yields but low enantioselectivity. On the other hand, heterogeneous phosphoric acid (Ad-BINOLs-PO_2H-PAF) was also used as effective phosphate ligands for synthesis of rhodium(II) complexes which were effective catalysts in cyclopropanation of styrene affording chiral cyclopropanes in good yield and high diastereoselectivity (>99%) and moderate enantioselectivity (ee < 50%).

1. Introduction

Porous organic polymers as covalent organic frameworks (COFs) [1], hypercross-linked polymers (HCPs) [2,3], conjugated microporous polymers (CMPs) [4], and polymers of intrinsic microporosity (PIMs) [5], have been prepared from different building blocks and have been applied for gas storage [6,7], catalysis [8–12], sensors [13] and organic optoelectronics [14]. These materials usually present excellent porosity properties (large surface area and different networks) which allows them to accommodate different accessible catalytic centers and control their environment. Many polymers have been obtained by anchoring of a monomer to a polymer backbone [15,16]. The "bottom-up" approach is a more effective strategy to heterogenize molecular catalysts in comparison with the classical supported catalysts [17] and the resulting porous polymers catalysts possess the catalytic centers more accessible and homogeneously distributed [18]. There are different examples of porous organic polymers (POPs) with catalytic chiral sites, which act as heterogeneous catalysts combined with a metal [19–24], and some examples of metal-free catalytic systems as the Jogensen–Hayashi catalyst or BINOL-derived phosphoric acid introduced into nanoporous polymeric networks [25,26] or COFs [27,28].

Herein, we report the easy and fast "bottom-up" designed synthesis and characterization, of hindered BINOL-derivatives bearing bulky groups embedded into a porous Polymeric Aromatic Framework (PAF), and their application as catalysts for different reactions. The chiral BINOL moieties were incorporated into the network in three steps from the available reagents. The congested soluble and heterogenized Ad-BINOLs-OH exhibit high catalytic activity and enantioselectivity for the asymmetric addition reaction of Et_2Zn to benzaldehyde in combination with $Ti(OiPr)_4$; the BINOLs-PO_2H show high activity for several reactions but moderate chiral selectivity and the corresponding rhodium complexes show moderate activity and selectivity for cyclopropanation of styrene.

2. Results and discussion

2.1. Synthesis and characterization of porous aromatic frameworks incorporating Ad-BINOL platforms (Ad-BINOL-OH-PAF)

Enantiomeric pure BINOL (1,1′-binaphth-2,2′-diol) [29–34] and its derivatives are important auxiliaries and ligands for asymmetric

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reactions and have been applied in different model reactions [35–38]. BINOL skeleton was select as building block because it presents a structural rigidity which can contribute to the assembly of the rigid PAF networks, and has available the 4-positions on the naphthalene ring; these positions could be easily functionalized, by iodine or bromine, for further cross-coupling with boronic acids to build the chiral framework.

The synthesis of chiral polymer **Ad-BINOL-OH-PAF** and their soluble counterpart **Ad-BINOL-OH** (**D**) is outlined in Scheme 1. The precursor (**B**) was easily prepared at multigram scale from commercially available (*R*)-BINOL and 1-adamantanol and characterized by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry [39]. Robust BINOL-frameworks (BINOL-PAFs) were prepared via palladium-catalyzed Suzuki cross-coupling reaction between (*R*)-4,4′-dibromo-2,2′-diethoxy-6,6′-adamantyl (**B**) or chloro-1,1′-binaphthyl and the triboronic acid structural building block using $Pd(dppf)_2Cl_2$ as catalyst under microwave heating (Scheme 1). The resulting precipitate was filtered and washed several times with water and treated with aqueous KCN for total removing of palladium traces. The resulting precipitate was filtered and washed several times with water and treated with aqueous KCN for total removing of palladium traces. The ethoxy groups were deprotected by treatment with BBr_3 in CH_2Cl_2 affording Ad-BINOL-OH-PAF that contain chiral dihydroxy groups. The polymers were obtained as yellow powders insoluble in all the most common organic solvents in quantitative yields. Following a similar method, we prepared a soluble BINOL-OH, **D** (reference homogeneous catalyst) by a Suzuki coupling between **B** and the phenylboronic acid followed by deprotection of the ethyl derivative **C** as shown in Schemes 1 and S2. Details for characterization of soluble BINOL, D, can be found in supplementary information. Ad-BINOL-OH-PAF was characterized by ^{13}C NMR, infrared spectroscopy (FT-IR), nitrogen adsorption, etc. The IR spectra of Ad-BINOL-OH-PAF is consistent with the incorporation of both monomers into the framework and it can be observed a band at 3529 cm^{-1} corresponding to free O-H (Fig. S60). ^{13}C NMR spectrum shows signals at 150–110 ppm corresponding to the aromatic carbons and three signals from adamantyl aliphatic carbons at 45–25 ppm.

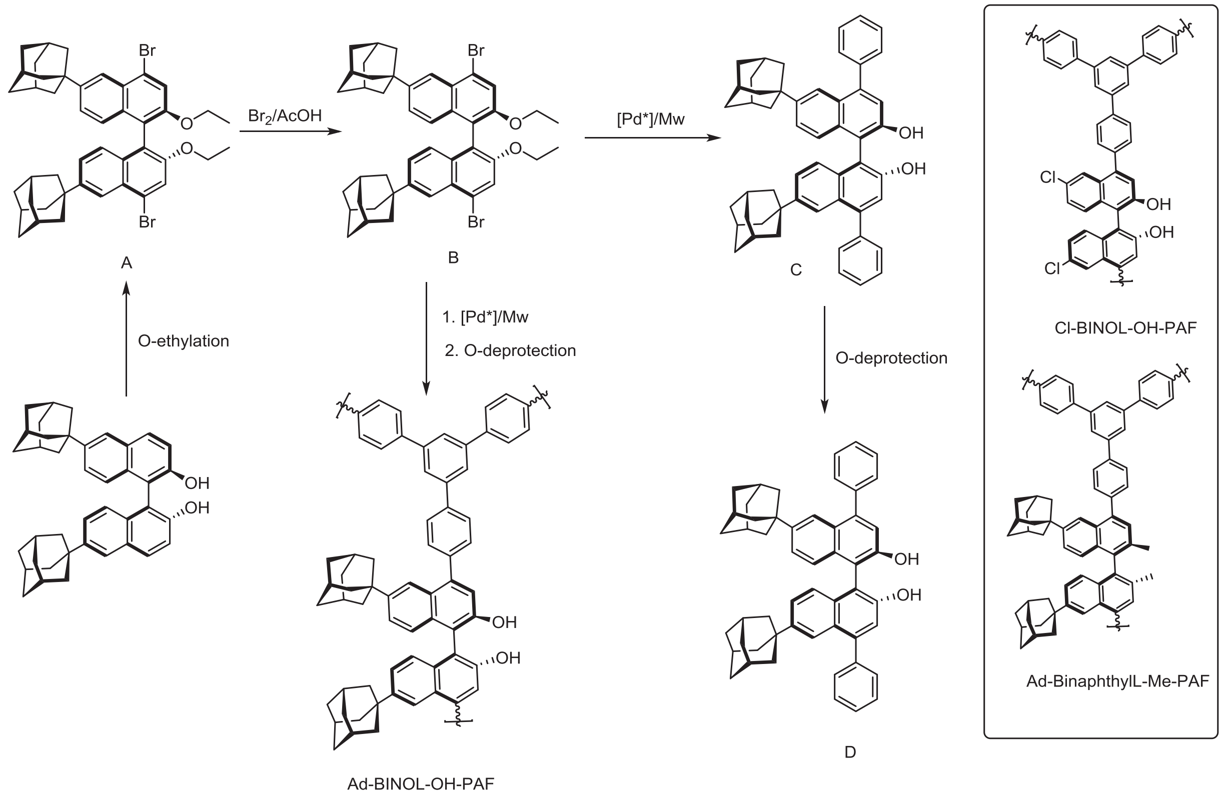
The porous properties measured by nitrogen adsorption/desorption isotherms at 77 k indicated that Ad-BINOL-OH-PAF is porous with Brunauer-Emmett-Teller (BET) surface areas of 365.5 $m^2 \cdot g^{-1}$ (Fig. 1, Table 1). To evaluate the effect of substituents on binaphthyl core on the porosity properties we prepared a 6,6′-Cl-substituted monomer and the corresponding polymer [40] which has a BET surface area of 405.7 $m^2 \cdot g^{-1}$ and other with methyl groups at 1,1′-position instead of OEt groups (**Ad-Binaphthyl-Me** in Scheme 1) with a BET of 196 $m^2 \cdot g^{-1}$ (Fig. 1). Pore size distributions are shown in Fig. S70.

2.2. Catalytic applications

2.2.1. Diethylzinc addition to benzaldehyde

Ad-BINOL-OH-PAF was used as heterogenized BINOL ligand for the formation of chiral catalysts by treating with excess $Ti(O^{i}Pr)_4$ (Scheme 2). Resulting Ti-catalyst was applied for the addition of diethylzinc to benzaldehyde and the results were compared with that obtained from the corresponding soluble **D-[Ti]**-catalyst (Table 2).

As shown in Table 2, when soluble D and heterogenized Ad-BINOLs were treated with $Ti(OiPr)_4$ are highly active catalytic system in the addition of diethylzinc to benzaldehyde to afford (R)-1-phenylpropan-1-ol. The reactions are quantitative conversions and selective for the secondary alcohol. The enantiomeric excess for the heterogenized catalyst was 88% similar to that obtained with the corresponding soluble D-[Ti]. Compared with other heterogenized systems, for example we found that Ad-BINOL-O[Ti]-PAF gives better enantiomeric excess than cross-linked polymers based on the 1,10-binaphthyl building



Scheme 1. Schematic preparation of embedded BINOL to porous aromatic framework.

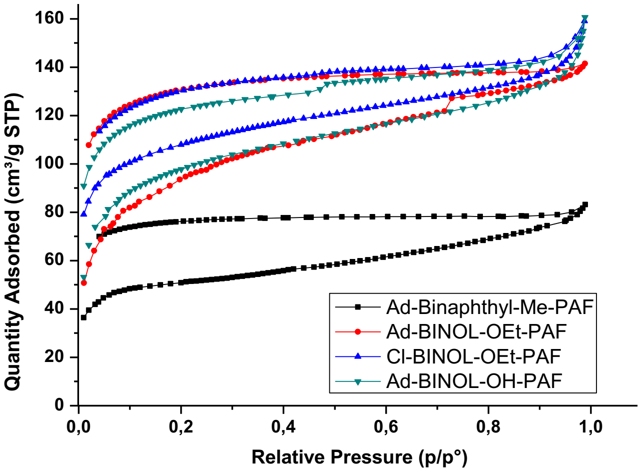


Fig. 1. Nitrogen adsorption isotherm of BINOLs-networks.

Table 1
Surface Areas and Pore Volumes of Ad-BINOL-PAFs.

Polymer	SA_{BET} $(m^2 \cdot g^{-1})$[a]	Pore volume $(cm^3 \cdot g^{-1})$[b]	Pore size (nm)
Ad-BINOL-OEt-PAF	337	0.219	2.60
Ad-BINOL-OH-PAF	365	0.248	2.96
Cl-BINOL-OEt-PAF	406	0.246	2.43
Ad-Binaphthyl-Me-PAF	196	0.128	2.62

[a] Calculated from the nitrogen adsorption isotherm.
[b] At P/P_0: 0.99.

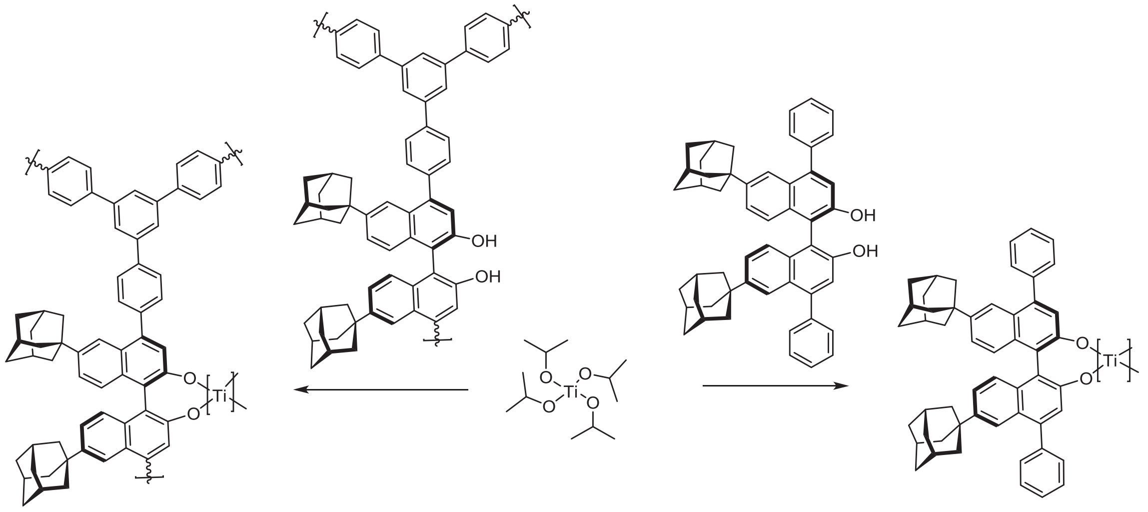
blocks prepared via the trimerization reaction of terminal alkyne groups for Lin et al. (entry 5) [21]. A BINOL supported on Zr-phosphonate gives only 59% ee (Table 2, entry 6) [41] and a (*R*, *R*)-tetraaryl-1,3-dioxolane-4,5-dimethanol (TADDOL)-based chiral porous polymer gives similar ee (91%) although the reaction in this case is done at −30 °C and 48 h reaction time (entry 7) [19]. Another example was reported when (R)-BINOL was incorporated in the mesoporous framework of organosilicas (PMOs) and after coordinating to $Ti(OiPr)_4$, catalyze the asymmetric addition of diethylzinc to benzaldehyde with high yields (99%) and moderate enantioselectivity (39.8%) (entry 8) [42]. However, when a 3-aryl H8-BINOL was grafted on the surface of silica gel and the resulting supported ligand was used in the alkylation of *p*-chlorobenzaldehyde in the presence of Ti(OiPr)4 affords the corresponding alcohol in high enantioselectivities and yields [43]. A pillar[5]arene-based-TADDOL was also applied for the addition reaction of $ZnEt_2$ to benzaldehyde at −30 °C affording the (S)-1-phenylpropan-1-ol in 88% yield and 94% ee after 48 h (entry 9) [44]. A Cu-MOF with a chiral tetracarboxylate ligand derived from 1,1′-bi-2-naphthol (CMOF) gives moderate selectivity towards the alcohol (68%) and 82% ee after reacting overnight (entry 10) [45]. As can be concluded, Ad-BINOL-O[Ti]-PAF results an effective and selective heterogeneous catalyst for the alkylation of benzaldehyde at room temperature and 3 h reaction time.

Concerning the mechanism of asymmetric ethylation of aldehydes catalyzed by a chiral ligand/$Ti(OiPr)_4$ system, it appears that the active species consists of a bimetallic titanium complex with a titanium coordinated to the BINOLate ligand and the other with an alkyl group ($[BINOLate)Ti(aldehyde)(O\text{-}i\text{-}Pr)_2]\text{-}[Ti(O\text{-}i\text{-}Pr)_3Et]$ [46,47].

2.2.1.1. Recycling. We have examined recyclability and reusability of the Ad-BINOL-OH/Ti catalyst system. The solid was readily recovered from the reaction mixture via centrifugation, followed by repeated washing with HCl (1N), H_2O, MeOH, THF and acetone. The recovered catalyst was able to perform diethylzinc addition to benzaldehyde for seven cycles without loss of conversion. During the washing and recycling processes, residues of zinc and/or titanium oxides could have been immobilized inside the material, this would lead to a decrease in the enantioselectivity but not in the conversion (Table 2, entries 3 and 4). Similar results were reported previously a TADDOL-CPP catalyst [19] or a Cu-MOF [45].

2.3. Ad-BINOL-PO_2H: Synthesis and characterization of porous aromatic frameworks (Ad-BINOL-PO_2H-PAF) and their corresponding soluble phosphoric acids

With the Ad-BINOLs-OH in the hand, we have gone a step further and prepared a series of phosphoric acids to be used as organocatalysts and as ligands for rhodium(II) complexes. Brønsted-acid catalysts are important organocatalysts for a great number of carbon–carbon bond-forming reactions. Brønsted acids are classified as neutral (thiourea and TADDOL) and stronger

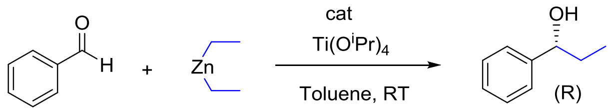


Ad-BINOL-O[Ti]-PAF

D-[Ti]

Scheme 2. Formation of chiral-[Ti]-catalyst.

Table 2
Asymmetric ethylation of benzaldehyde catalyzed by Ad-BINOL-[Ti].



Entry	Catalyst	Conv. (%)[c] (h)	ee (%)[d]
1	D-[Ti][a]	91 (1)	87.0
2	Ad-BINOL-O[Ti]-PAF[b]	100 (3)	88.0
3	2run (without regeneration)	50 (3)	35.4
4	7run (after regeneration)	90 (3)	65
5	CCP-2 [21]	94 (16)	68
6	ZrL_3 [41]	95 (16)	59
7	TADDOL-CPP [19]	86 (48)	91
8	MMB40-OTi [42]	99 (2)	39.8
9	TADP5 [44]	88 (48)	94
10	CMOF-3b [45]	99 (overnight)	82

[a] D/[Ti]/Aldehyde/[Zn] (0.1/1.0/1.0/3.0), 1 h.
[b] Ad-BINOL-O[Ti]/Aldehyde/[Zn] (20 mg/10/7.0/20), 3 h.
[c] Determined by GC (dodecane as internal reference).
[d] GC using a CP-Chirasil-Dex chiral column (100 °C 5 min; 2 °C/min to 130 °C); t_1 (R) = 21.3 min; t_2 (S) = 21.9 min [48].

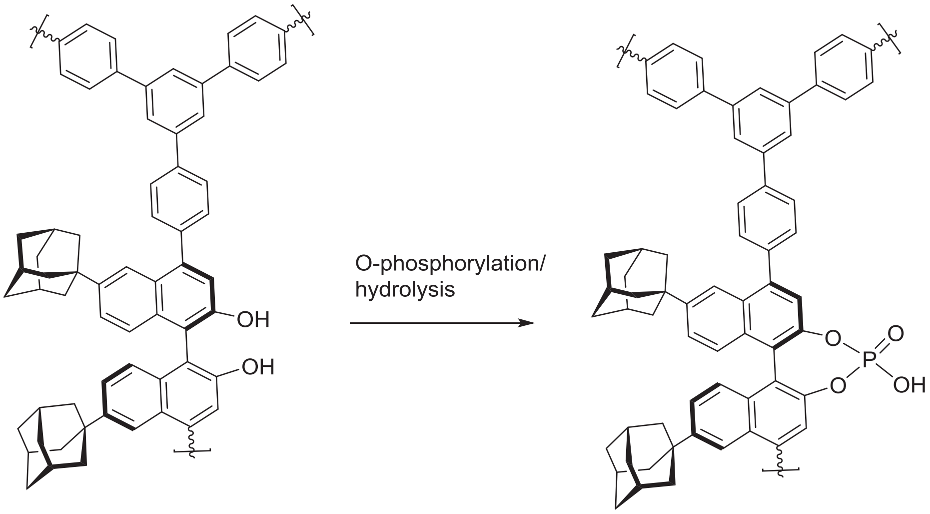
Brønsted acids, such as phosphoric acids [49]. Chiral phosphoric acids have attracted considerable attention in the preparation of efficient chiral environments in organocatalysis and in transition metal catalysis due to their Brønsted acid-base behavior, hydrogen bonding, counter-anions and ligands toward metals [33,50–54]. BINOL-phosphoric acids are among the most important catalysts being used for heterogeneous organocatalysis.

The heterogeneous and recyclable Ad-BINOL-phosphoric acid (Ad-BINOL-PO_2H-PAF) was prepared from the OH-material by reaction with $POCl_3$ followed by hydrolysis with aqueous H_2SO_4 (Scheme 3). The solid was thoroughly washed ($HCl_{aq.}$, ethanol, THF) to afford the acid polymer as an insoluble yellow powder. Thermogravimetric analysis (Fig. S65) reveals its high thermal stability with decomposition temperature at 475 °C under a nitrogen atmosphere. Solid-state CP/MAS ^{13}C NMR spectroscopy shows broad resonances peaks between 150 and 110 ppm, a peak at 146 ppm corresponds to the aryl carbons next to the oxygen atoms. The peak centered at 127 ppm can be attributed to substituted aryl carbons, and the aliphatic adamantyl groups appears at 43, 27 and 19 ppm (Fig. S62). The ^{31}P NMR shows a signal centered at 3.83 ppm, at similar position that soluble phosphoric acid **5** (Fig. S63). The FT-IR spectra also indicate successful functionalization (Fig. S64).

The porous properties were analyzed by nitrogen adsorption/desorption isotherms at 77 k showing an isotherm characteristic of microporous materials (Fig. 2, Table 3). The final phosphoric acid derivative has a BET surface area of 248.0 $m^2 \cdot g^{-1}$; this fact indicates that phosphorylation does not alter too much the porosity properties of the material. Total pore volume result of 0.18 $cm^3 g^{-1}$ at $P/P_0 = 0.99$.

The morphology and texture was also studied by field-emission scanning electron microscopy (SEM) showing the typical aggregates of spherical structures described for this type of porous polymers (Fig. 3).

We also have prepared a series of soluble bulky alkyl substituted R-BINOL-phosphoric acids (R-BINOLs-PO_2H) (**1**–**5** in Scheme 4) from R-BINOLs-OH [39] by reaction with $POCl_3$ followed by hydrolysis to yield the corresponding enantiopure solid white crystalline phosphoric acids in high yield (details in supporting information).



Ad-BINOL-OH-PAF

Ad-BINOL-PO_2H-PAF

Scheme 3. Schematic preparation of Ad-BINOL-PO_2H-PAF.

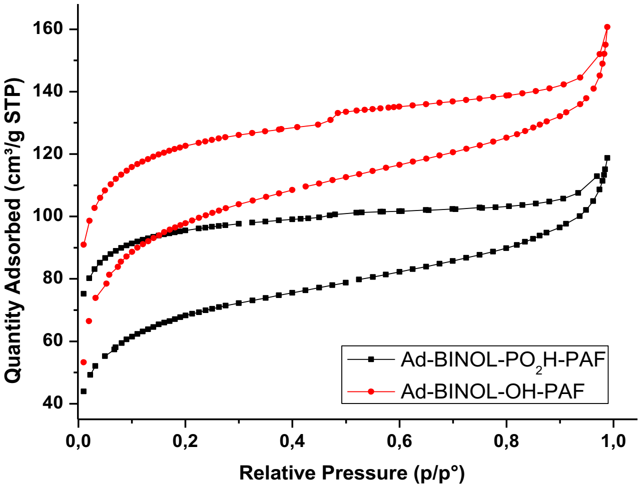


Fig. 2. Nitrogen adsorption isotherm of Ad-BINOLs network.

Table 3
Porous properties.

Polymer	SA_{BET} ($m^2 \cdot g^{-1}$)[a]	Pore volume ($cm^3 \cdot g^{-1}$)[b]	Pore size (nm)
Ad-BINOL-OH-PAF	365	0.25	2.72
Ad-BINOL-PO_2H-PAF	248	0.18	2.96

[a] BET surface area calculated from the nitrogen adsorption isotherm.
[b] At P/P_0: 0.99.

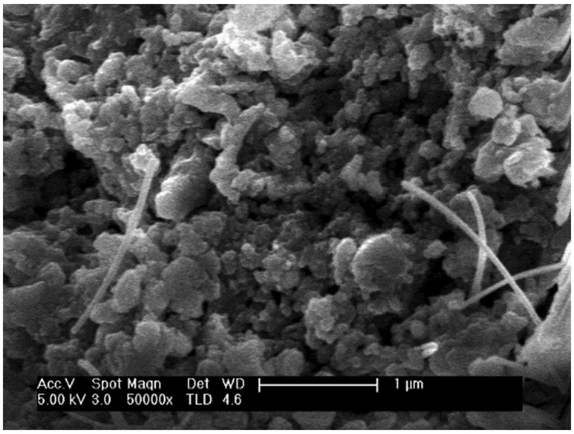
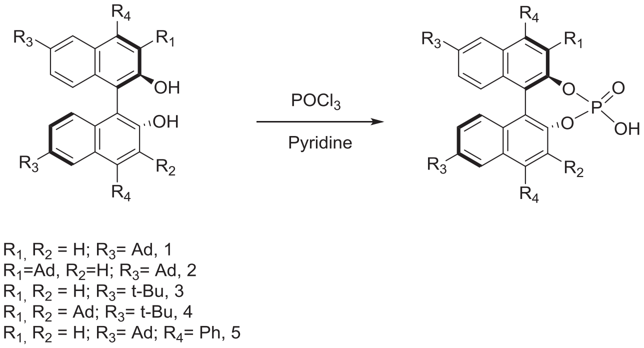


Fig. 3. SEM image of Ad-BINOL-PO_2H-PAF.



Scheme 4. Synthesis of soluble R-BINOLs-PO_2H.

2.3.1. Catalytic application of soluble and heterogenized BINOL-phosphoric acids

We have tested soluble (R-BINOL-PO_2H) and heterogenized Ad-BINOL-PO_2H-PAF in a series of model organocatalyzed reactions.

2.3.1.1. Cyclization of anthranilamide with aldehydes. 2,3-Dihydroquinazolinones are the family of compounds in which different substitutions displays important pharmacological, biological and medicinal activity [55–59]. In addition, it has been reported that their enantiomers have different bioactivities [60]. The 2,3-disubstituted quinazolinones have been expected to have antiviral and antihypertensive activities [56,61].

There are different synthetic methods to prepare these compounds using catalysts as ionic liquids [62], [bmim]HSO_4 [63], some Brønsted acids [64], phosphoric acid [65,66], etc. These procedures present disadvantages such as harsh reaction conditions, long reaction times, and poor yields beside the use of non-recyclable and toxic catalysts associated with demands of development of greener process involving easily available, easy to handle and efficient catalysts. In this context, we reported the catalytic performance of BINOL-phosphoric acids for the formation of dihydroquinazolinones by reaction of anthranilamide and benzaldehydes (Table 4). Soluble and heterogenized catalysts result effective catalysts, we found excellent activity with quantitative yields; however, only marginal ee's were obtained. When precursor BINOL-OH was the catalysts, we obtain selectively the imine (entry 9). The possible transition state for the cyclization reaction may be as proposed for a SPINOL-phosphoric acid by Lin et al. [67].

2.3.1.1.1. Recycling of solid catalyst Ad-BINOL-PO_2H-PAF. The heterogeneous Ad-BINOL-PO_2H-PAF can be easily separated by centrifugation and reused for further repeating runs. For each run, >99% conversion was observed (see Table 5). The selectivity decreases after five cycles yielding the imine. After a regeneration process with $HClO_4$ the selectivity to cyclic product was recovered. Furthermore, we performed hot extraction experiments to check the heterogeneity of catalyst. After 20% conversion of substrate, we separated the catalyst, and even after 24 h no further conversion was observed, which demonstrates that the catalyst is mainly heterogeneous.

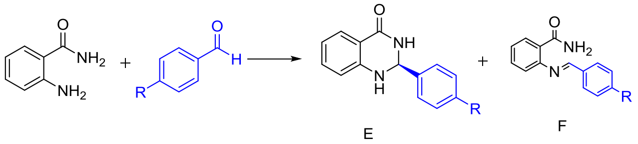
2.3.1.2. Transfer hydrogenation. To establish the versatility of these easy available adamantyl-BINOL-PO_2H catalysts, they were also applied in a reaction type catalyzed by Brønsted acids: the transfer hydrogenation [68] (Table 6). The substrates of choice are *N*-Heterocycles [69] (2-phenylquinoline, 2-phenylbenzoxazine and 2-phenylbenzothiazine) and as hydrogen source we use the Hantzsch ester (diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate). As can be observed, high yields were obtained in short reaction times with low enantiomeric excess. Lower temperatures did not affect the selectivity but did decrease the product yield. It can be observed that 2-phenylbenzothiazine is easily reduced without poisoning of the catalyst.

A possible mechanism will be similar to that described previously for transfer hydrogenation of benzoxazines and quinolones [70,71]. First, the protonation of the cyclic imine by phosphoric acid takes place giving a iminium-phosphate ion pair. Second, hydride transfer from Hantzsch ester give the product and pyridinium salt and finally a proton transfer close the cycle yielding the Hantzsch pyridine.

2.4. Synthesis and characterization of tetrakis(binaphthyl-phosphate) dirhodium(II,II) complexes

Chiral dirhodium complexes are effective catalysts for decomposition of diazo compounds. Those complexes are generally obtained

Table 4
Cyclization of anthranilamide with benzaldehydes.[a]



Entry	Catalyst	R	Conv. (%)[b]	Product	ee (%)[b]
1	1	H	>99	E	1.3
2	2	H	>99	E	8.3
3	3	H	>99	E	0.6
4	4	H	>99	E	4.2
5	5	H	>99	E	2.3
6	Ad-BINOL-PO_2H-PAF	H	>99	E	10.1
7		OMe	>99	E	12.0
8		Br	>99	E	13.0
9	Ad-BINOL-OH-PAF	H	>99	F	–
10	CF_3COOH	H	99	E	–
11	4d in [66]	H	67		26
12	4a-4g in [64]	H	90		6–93

[c] Determined by HPLC using a Chiralcel-OD column.

[a] BINOL-PO_2H/Substrate (1:100), in $CHCl_3$ at −20 °C, 24 h.

[b] Determined by ^1H NMR.

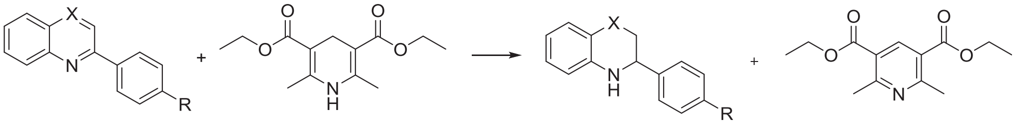
Table 5
Recycling of Ad-BINOL-PO_2H-PAF.[a]

Run	Conversion (%)	Product
1	>99	E
2	>99	E
3	>99	E
4	>99	E
5	>99	F
6	>99	F

[a] Binol-PO_2H/Substrate (1:100), in $CHCl_3$ at −20 °C, 24 h.

with four chiral ligands as carboxylates, imidates or biaryl phosphates. The Rh_2(biarylphosphate)$_4$ complexes are prepared by reaction of $Rh_2(OAc)_4$ with the corresponding hydrogen phosphate and used as chiral catalysts for different reactions [73–79]. Dirhodium complexes with substituents at the 3,3′-positions of the BINOL moiety are scarce [77] and it has been demonstrated the importance of such substitution in chiral phosphoric acid catalysis [80]. Herein we described the synthesis of a series of dirhodium complexes with different substituents at 3,3′- and 6,6′-positions of the BINOL to evaluate the effect of such groups on the reactivity

Table 6
Transfer hydrogenation reactions catalyzed by Adamantyl-BINOLs-PO_2H.[a]



Entry	Catalyst	X	Solvent	T (°C)	Conv (%)[b]	ee (%)[c]
1	5	CH	THF	35	77.2	19.5
2		CH	THF	RT	64.8	19.8
3	2	CH	THF	35	20.0	41.9
4		CH	THF	−15	3.7	36.0
5		CH	Toluene	35	94.1	15.0
6		CH	Toluene	10	96.7	22.0
1	2	O	$CHCl_3$	RT	99 (80)[d]	31.4
2		O	CH_2Cl_2	RT	99	34.5
3		O	Toluene	RT	99	24.4
4		O	THF	RT	99	23.0
5		O	$CHCl_3$	0	99	34.6
6		O	$CHCl_3$	−78	99	35.6
7	1	O	$CHCl_3$	RT	99	12.7
8	5	O	$CHCl_3$	RT	99	15.1
9	PO_2H-PAF	O	$CHCl_3$	RT	99	2.5
10	2	S	$CHCl_3$	RT	99[d]	9.9
11[e]	2	O	$CHCl_3$	RT	73[d]	12.6

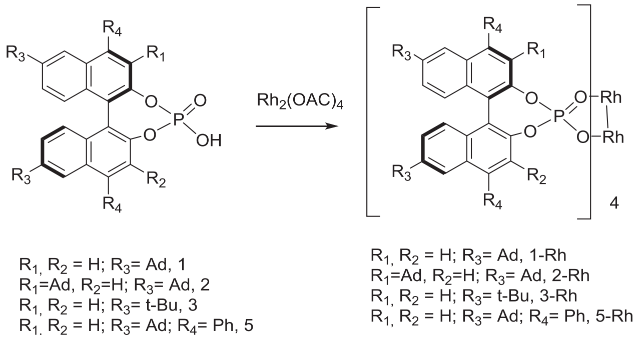
[a] Reaction conditions: substrate [72] (1.0 eq.), Hantzsch ester (1.25 eq.) catalyst (5%) in chloroform (2 mL).

[b] Determined by GC and ^1H NMR.

[c] Determined by HPLC using a Chiralcel-OD column.

[d] Isolated yield.

[e] R = CN.



Scheme 5. Synthesis of soluble phosphate-dirhodium complexes.

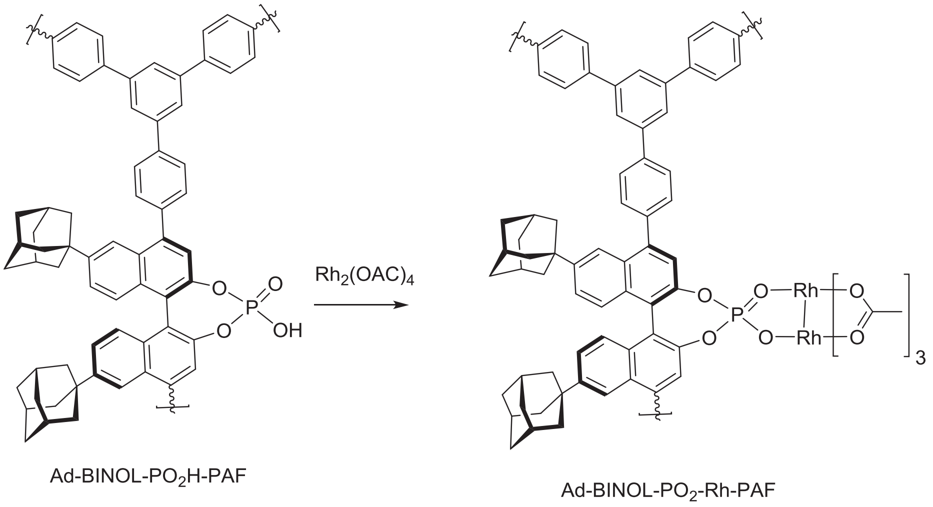
and enantioselectivity for the enantioselective cyclopropanation of styrene.

Dirhodium(II) complexes were prepared according to the reported procedures by refluxing eight equivalents of corresponding enantiopure (*R*)-binaphthyl phosphate with $Rh_2(OAc)_4$ in chlorobenzene (Scheme 5) [73–79]. This method is an efficient method for the introduction of bulky ligands because using a system Soxhlet with sand and Na_2CO_3, the acetic acid is removed. The desired complex was isolated in 50% yield. The effect of substitution at the 3-position was examined using tri-adamantylbinaphthol (2) as ligand, the corresponding 2-Rh-complex was prepared with 45% yield. Details of characterization data and NMR, FTIR and MS spectra can be found in supplementary.

PAF-BINOL-PO_2-dirhodium(II) complex was prepared as described for soluble **PO_2-Rh** complexes by refluxing the corresponding PAF-binaphthyl phosphate with $Rh_2(OAc)_4$ in chlorobenzene (see Scheme 6). The desired complex was isolated as a greenish solid with an Rh loading of 1.5% (determined by ICP analysis). The molecular structure corresponds to a phosphate ligand and the acetate ligands remains coordinated to rhodium as can be observed in the ^{13}C NMR spectrum (Fig. S66) with signals corresponding to the aromatic carbons (between 151 and 115 ppm), adamantyl groups (43.27, 36.69 and 29.33 ppm) and CH_3 from acetate at 23.65 ppm. ^{31}P NMR shows a signal at 6.52 ppm (Fig. S67). TGA (Fig. S69) shows the high thermal stability of this complex (500 °C). Nitrogen adsorption/desorption isotherms at 77 k shows a decrease of surface area to 54 m^2/g.

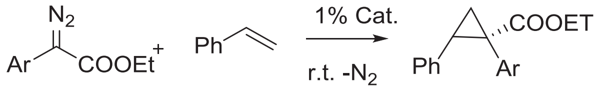
2.4.1. Cyclopropanation of styrene

Preparation of cyclopropanes by catalytic enantioselective methods have been of important pharmaceutical interest. With Rh-complexes in hand, we evaluated their catalytic efficiency for



Scheme 6. Synthesis of dirhodium-polymer.

Table 7
Ad-BINOL-[Rh]-catalyzed-cyclopropanation of styrene.[a]



Entry	Catalyst	Ar	Conv. (%)[b] (h)	d.r.(%)[b]	ee (%)[c]
1	1-Rh	ClPh	100	97.8	48.9
2	2-Rh		97	97.7	37.2
3	3-Rh		96	98.0	49.9
4	5-Rh		91	98.0	17.9
5	Ad-BINOL-PO_2-[Rh]-PAF		90	99.0	12.0
6	Rh_2(R-BNP)$_4$ [84]	Ph	85	–	40.0
7	1a, 2a, 2b [77]	Ph	74–82	–	23–43
8	Rh_2(R-BNP)$_4$ [81]	ClPh	89		57

[a] Reaction conditions: styrene (1 eq.), 2-(4-chlorophenyl)-2-diazoacetate (1.5 eq.), toluene (1 mL), catalyst (1 mol% based on Rh).

[b] Determined by GC (hexadecane as internal reference).

[c] HPLC using a Chiralcel (OD) chiral column.

the cyclopropanation of styrene with Cl-phenyldiazoacetate (Table 7). Soluble catalysts have excellent reactivity (conversion 100% and 96%) and the cyclopropane was obtained as a single diastereomer (>98:2 dr), these data are comparable to that described previously for dibromobinaphtholphosphate-Rh-catalysts [76,77].

1, **3** and **5-Rh**-catalysts afforded the cyclopropane in the same predominant enantiomeric form (1*S*, 2*R*) [81,82]; however it is important to note that **2-Rh** (with an adamantyl group at 3-position) gives the contrary enantiomer.

Heterogeneous Ad-BINOL-PO_2-[Rh]-PAF shows excellent reactivity (conversion > 90%) and the cyclopropane was obtained as a single diastereomer (99: 1 dr) with 13.7%.

The mechanism of PO_2-Rh(II)-catalysed cyclopropanation should be similar to that investigated computationally using $Rh_2(formate)_4$ as a model [83].

3. Experimental section

3.1. Synthesis of soluble BINOLs phosphoric acids (1–5)

The corresponding (*R*)-adamantyl-BINOL (1.0 eq.) [39] was dissolved in dry pyridine (2 mL) and then $POCl_3$ (2.0 eq.) was added at room temperature. The reaction mixture was stirred overnight; then, water was added and the mixture stirred for 6 h and extracted with dicloromethane and HCl (2 M) several times. The organic layer was dried over Na_2SO_4 and the solvent eliminated under vacuum to yield a solid (Yield 90%).

3.2. Adamantyl–BINOL-polymers (Ad-BINOL-PO_2H-PAF)

The adamantly polymer was prepared following a similar procedure to that used to obtain the soluble reference ((*R*)-6,6′-di(1-adamantyl)-2,2′-diethoxy-4,4′-diphenyl-1,1′-binaphthyl (**C**) in Scheme 1) [39]. Thus, (*R*)-6,6′-di(1-adamantyl)-2,2′-diethoxy-4,4′-dibromo-1,1′-binaphthyl (**B**) (40 mg, 0.052 mmol), 1,3,5-triphenylbenzene-4′,4″,4‴-triboronic acid (22.7 mg, 0.078 mmol), K_2CO_3 (0.4 mL, 2 M, 4.20 eq.) and dry THF (1.6 mL) were introduced in a microwaves tube and deaerated with argon for 15 min. After that catalyst $Pd(dppf)_2Cl_2$ (1.1 mg, 2.5 μmol, 3%) was added. The reaction was performed in two steps: (1) 12 bar, 75 W; (2) 145 °C, 15 min, 75 W. The process was repeated at least ten times. The resulting solid was filtered and thoroughly washed with H_2O. The solid was stirred with H_2O and KCN overnight to remove the Pd (0) residues. Then, it was filtered under vacuum and dried to yield the final solid product. Deprotection was performed with BBr_3 in CH_2Cl_2 at −78 °C and subsequent phosphorylation under similar conditions to those used for soluble Ad-PO_2H-compounds. Yield (60%).

3.3. Synthesis of tetrakis[BINOLs-phosphate] dirhodium complexes [76,77]

General method: $Rh_2(OAc)_4$ (1.0 eq.) and the corresponding binol phosphoric acid ligand (8.0 eq.) were dissolved in clorobenzene (70 mL). A system Soxhlet with sand and Na_2CO_3 was adapted to the reaction flask. The reaction mixture was heated under reflux during 48 h. After that, the solvent was removed under reduced pressure and the compound crystallized by co-precipitation with 1,4-dioxane and methanol to give a black solid. Ad-BINOL-PO_2[Rh]-PAF was synthetized following the general method described for soluble Rh-phosphate-complexes.

3.4. Catalytic activity

Details for catalytic experiments are found in supplementary information.

4. Conclusions

We have successfully prepared a new embedded chiral adamantyl-BINOL-polymer (365 m^2/g SA_{BET}) which results highly active and selective for the asymmetric addition of Et_2Zn to benzaldehyde (88% *ee*); these homochiral **Ad-BINOL-PAFs** materials are stable, easily separable, and can be reused several times. The Ad-BINOLs were easily converted into BINOL-phosphoric acids which are effective Brønsted acid organocatalysts (soluble and heterogeneous) and phosphate ligands to prepare rhodium(II) complexes. The corresponding phosphate dirhodium complexes were also applied as effective catalysts for cyclopropanation of styrene affording chiral cyclopropanes in good yields with high diastereoselectivity (>99%) and moderate enantioselectivity (ee < 50%).

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.07.059.

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