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Enantioselective sulfoxidation catalyzed by polymer-supported chiral Schiff base–$VO(acac)_2$ complexes

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Abstract—The preparation of a series of polymer supported chiral Schiff bases derived from salicylic aldehydes and optically active amino alcohols is reported. These heterogeneous ligands have been complexed with $VO(acac)_2$ and employed to catalyze the enantioselective oxidation of sulfides to sulfoxides with hydrogen peroxide as an environmentally acceptable oxidant. The procedure affords the sulfoxides in good yield and selectivity and with ee values comparable to those obtained with the homogeneous counterparts. The catalyst can be used for at least four cycles without any significant decrease in both efficiency or enantioselectivity.

1. Introduction

Optically active sulfoxides are an important class of compounds useful as synthetic intermediates, chiral auxiliaries in asymmetric synthesis[1] as well as bioactive ingredients in the pharmaceutical industry.[2] The asymmetric oxidation of sulfides represents a convenient chemo and stereoselective route to optically active sulfoxides.

The reaction has been performed by using electrophilic oxidants because the initial oxidation of the highly nucleophilic sulfide to a sulfoxide is an easier process than the subsequent oxidation of the resulting much less nucleophilic sulfoxide to sulfone.[3]

In recent years the reaction has been carried out with a large number of homogeneous and heterogeneous catalysts with particular attention to the use of eco-compatible oxidants. Thus, the aerobic highly selective oxidation of sulfides to sulfoxides has been carried out in the presence of $Fe(NO_3)_3$–$FeBr_3$.[4]

Moreover, different solid catalysts were utilized to efficiently and selectively perform the reaction with hydrogen peroxide or its adduct with urea. Among them, which are worthy of note, are Ti-beta zeolite,[5] silica supported titanium/tartaric acid,[6] a composite metal oxide catalyst $LiNbMoO_6$[7] and tungstate-exchanged Mg–Al layered double hydroxide.[8] The photochemical oxidation has also been reported to occur with oxygen in the presence of a nafion membrane doped with a lead ruthenate pyrochlore catalyst[9] or a clay-bound methylene blue.[10]

Particular attention has been paid to the asymmetric sulfoxidation with some efficient procedures being reported.[11] Kagan, in continuation of his early studies, described the enantioselective oxidation of sulfides by cumyl hydroperoxide in the presence of $Ti(OPr^i)_4$/(*R*,*R*)-diethyltartrate with ee values up to 96%.[12] This methodology has been further developed by using hydroperoxyfurans and pyrans as oxygen donors.[13]

Much effort has also been directed towards the development of methods for the enantioselective synthesis of mono-oxides of cyclic dithioacetals, since these compounds serve as chiral masked acyl groups.[14]

Although different oxidants and metal catalysts have been described and continue to receive attention, current efforts are mainly devoted to the development of oxidation reactions using hydrogen peroxide, as this is an inexpensive, readily available, environmentally benign and atom efficient reagent. In this respect, the catalytic system of a vanadium/chiral Schiff base described by

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Bolm and Bienewald in 1995 is particularly attractive[15] and consequently it was further studied and applied to different substrates.[16]

Due to the great interest in the present topic, some groups faced the problem of performing the reaction in the presence of solid supported vanadium[17] and titanium[18] chiral Schiff base catalysts performing the oxidation of aryl alkyl sulfides in good yields and promising ee values. Therefore, it is desirable to develop further studies with the goal of making new solid catalysts and achieving information on their efficiency on the stereoselective sulfoxidation reaction.

In continuation of our involvement in this area,[19] we report herein the preparation of a small library of solid supported chiral salicylaldimines and its use in the vanadium-catalyzed enantioselective oxidation of sulfides to sulfoxides with hydrogen peroxide.

2. Results and discussion

Bolm and Bienewald showed the apparent requirement for a hydroxy group and a *tert*-butyl group on the imine framework as well as a sterically demanding substituent, such as a *tert*-butyl group, at the C-6 of the aryl moiety.[15] For our purpose we needed a further OH group (at the C-4 position of the aromatic ring)[17] to be utilized in the supporting procedure. In agreement with previous studies from the literature, we decided to utilize hydroquinone derivatives as building blocks for the preparation of our chiral ligands.[20] Concerning the support, we decided to utilize organic polymers (i.e., polystyrene and polyesters) avoiding the use of silica since $VO(acac)_2$, the vanadium supplying compound, could react with the surface silanols and structural water[21] affording a nonchiral supported vanadium species.

In Scheme 1, the preparation of four polymer-supported ligands is depicted. First we prepared monomers **5**–**8** by applying synthetic methodologies reported in the literature with some adjustment. Compound **1**[20,22] was first converted into intermediates **2**–**4** in 45–94% yield by selective alkylation or acylation of the less hindered OH group with methacryloyl chloride, 4-iodomethylstyrene[23] and vinyl chloroformate, respectively, in the presence of pyridine or K_2CO_3. Salicylaldimines **5**–**8** were then prepared in 70–100% yield by simply mixing the selected aldehyde with (*S*)-*tert*-leucinol or (1*R*,2*R*)-2-amino-1-(4-nitrophenyl)-1,3-propanediol. All the thus obtained monomers were successively copolymerized affording rigid but porous copolymers useful as heterogeneous chiral ligands. In particular, compounds **5** and **8** were copolymerized with methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA) in toluene and in the presence of AIBN under a nitrogen atmosphere[24] giving the polymethacrylate-supported ligands **9** and **12**. Similarly compounds **6** and **7** were copolymerized with styrene and divinylbenzene (DVB) in toluene and in the presence of AIBN under a nitrogen atmosphere[25] affording polystyrene-supported ligands **10** and **11**. Vanadium complexes **9V**–**12V** were simply prepared by stirring the supported ligand (an amount corresponding to 0.150 mmol of imine) with $VO(acac)_2$ (0.100 mmol) in CH_2Cl_2 at room temperature for 4 h. During the reaction, the resins, originally yellow, turned to green. The supported vanadium catalysts were filtered, washed with CH_2Cl_2 several times and dried in vacuo for 2 h. The loading values of the imine ligand in polymers **9**–**12** and the vanadium in complexes **9V**–**12V** are reported in Table 1.

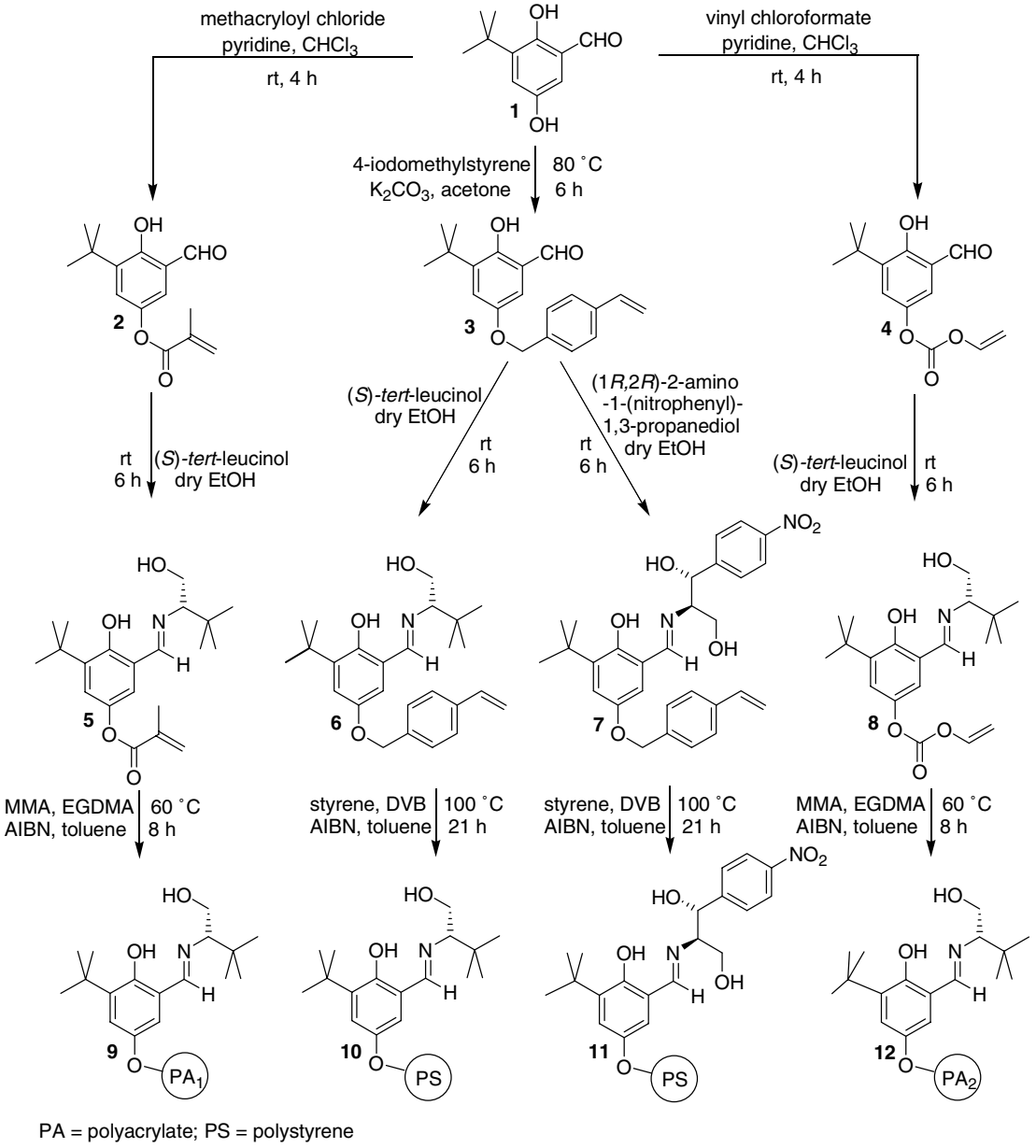
In all materials, the vanadium content was considerably lower than that of the Schiff base. This is probably due to the fact that, during the polymerization process, variable amounts of the ligand molecules are incorporated within the framework of the material in hard to reach regions, despite the use of toluene as porogen molecule.

Initially we investigated the performances of catalysts **9V**–**12V** in comparison with those of the homogeneous monomers **5V**–**8V** in situ prepared by adding $VO(acac)_2$ (0.010 mmol) to the ligand (0.015 mmol) in CH_2Cl_2 as previously reported[15] in the model oxidation of thioanisole (1.0 mmol) with H_2O_2 (1.1 mmol) in the presence of the catalyst (1 mol% with respect to the thioether) in CH_2Cl_2 (6 mL) at 25 °C for 16 h (see Table 2). In all cases, product (***S***)-**14a** was detected as the major isomer.

As previously observed in the liquid phase,[15] the reaction with supported catalysts shows some ligand acceleration[26] and similarly the polymeric support (i.e., PS) plays an activating effect [compare entries 1 and 2 of Table 2 showing the activity of $VO(acac)_2$ alone and in the presence of a 50 mg of copolymer styrene/DVB per millimole of sulfide]. Moreover sulfoxide **14a** was produced in quite similar yields by using the homogeneous catalyst and the heterogeneous counterpart. Interestingly, satisfactory and similar ee values were observed when the ligand was supported on a polystyrene matrix (compare entries 5 and 6 or 7 and 8 of Table 2), whereas the use of polyester supports resulted in a considerable lowering in yield and ee values (compare entries 3 and 4 or 9 and 10 of Table 2). This negative effect could be the consequence of the fact that some $VO(acac)_2$ is held by the polar ester functional groups on the matrix affording the racemic sulfoxide **14a**. Moreover the polystyrene utilized, containing 17% DVB, undergoes a good level of swelling in CH_2Cl_2 and consequently, space is available within the resin, allowing easy access of reactants to the surface active sites, whereas a lower swelling factor is expected for polyesters in the same solvent.[24]

Among the heterogeneous catalysts, **10V** showed the best stereocontrol in the model reaction (50% ee); this value could be progressively improved by carrying out the reaction in the presence of traces of methanol (Table 2, entry 11: 53% ee) at 0 °C (Table 2, entry 12: 56% ee).[17] The lower ee values observed with catalysts **7V** and **11V** could be attributed to a competitive process caused by different complexes involving the additional OH group.

The efficiency of the catalyst **10V** in the present reaction was shown by the possibility of recycling it for almost



Scheme 1. Preparation of four polymer-supported ligands.

Table 1. Loading values of imine and vanadium complexes

Entry	Ligand	Imine loading (mmol/g)	Complex	Vanadium loading (mmol/g)
1	**9**	0.220	**9V**	0.032
2	**10**	0.328	**10V**	0.175
3	**11**	0.587	**11V**	0.115
4	**12**	0.093	**12V**	0.023

three further cycles after filtration, washing with CH_2Cl_2 and immediately reusing (first cycle: 75% yield, 56% ee; second cycle: 76% yield, 57% ee; third cycle: 72% yield, 55% ee; fourth cycle: 70% yield, 51% ee).

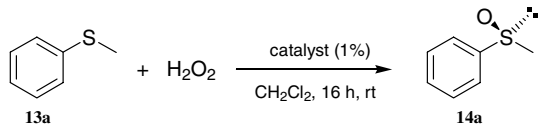
The above reported results show that (i) the Schiff base ligands utilized are stable enough to be polymerized under radical polymerization reactions and (ii) the supported catalysts can be reused several times without lowering their efficiency.

The solid catalyst was then applied to the oxidation of some other methyl aryl sulfides with good yields and satisfactory ee values (see Table 3).

3. Conclusion

In conclusion, we have shown a simple method for the preparation of vanadium-Schiff base chiral complexes supported on polymeric materials. These heterogeneous and reusable catalysts promoted the oxidation of some thioanisoles to the corresponding sulfoxides in good yields and satisfactory ee values. Even if in the literature

Table 2. Efficiency of vanadium-based catalysts in the enantioselective oxidation of thioanisole

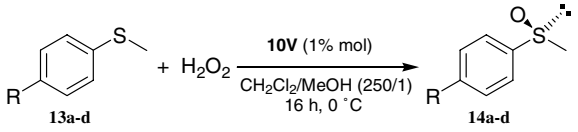


13a 14a

Entry	Catalyst	Yield (%)	Ee[a] (%)
1	$VO(acac)_2$	21	—
2	$VO(acac)_2$/PS[b]	53	—
3	**5V**	79	61
4	**9V**	61	39
5	**6V**	73	60
6	**10V**	72	50
7	**7V**	66	18
8	**11V**	64	12
9	**8V**	70	56
10	**12V**	51	35
11	**10V**[c]	78	53
12	**10V**[d]	75	56

[a] Determined by polarimeter.
[b] The amount of PS was 50 mg/mmol of **13a**.
[c] Reaction in CH_2Cl_2/MeOH (250/1).
[d] Reaction in CH_2Cl_2/MeOH (250/1) at 0 °C.

Table 3. Synthesis of chiral sulfoxides



13a-d 14a-d

Entry	R	Yield (%)	Ee[a] (%)
1	H	75	56 (*S*)
2	Me	70	52 (*S*)
3	Br	80	45 (*S*)
4	Cl	79	51 (*S*)
5	OMe	76	52 (*S*)
6	NO_2	54	57 (*S*)

[a] Determined by polarimeter.

more stereoselective homogeneous catalysts are described to promote the reaction, this note represents the first step towards a safe and economical route for performing the enantioselective sulfoxidation reaction.

Further investigations are currently underway to rationalize the role of the heterogeneous support and to improve the stereochemical control of the process.

4. Experimental section

4.1. General

Elemental analyses were performed by a Carlo Erba CHNS-0 EA 1108 Elemental Analyzer. Optical Rotatory Power (ORP) determination was obtained by using a Perkin Elmer 341 polarimeter. Analytical measures on vanadium content were obtained by using an Ultima 2 Jobin Yvon Horiba instrument (ICP–AES). Silica gel chromatography was performed with Merck silica gel 60 PF_{254}. All chemicals and solvents were purchased from commercial sources and used without further purification.

All ^1H NMR spectra were recorded on a Bruker AC-300 instrument in $CDCl_3$ with tetramethylsilane as the internal standard. Data are reported as follows: chemical shift in parts per million (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz) and integration. Infrared spectra (IR) were obtained on a Nicolet PC 5 spectrophotometer and absorptions are reported in reciprocal centimetres. Mass spectra were obtained on an HP 5971 A spectrometer (CI).

4.2. Preparation of aldehydes 2–4

4.2.1. 3-*tert*-Butyl-4-hydroxy-5-oxomethylphenyl methacrylate 2. Toz a stirred solution of 3-*tert*-butyl-2,5-dihydroxybenzaldehyde (5 mmol, 970 mg) in dry chloroform (4 mL), pyridine (6 mmol, 484 mg, 0.48 mL) and methacryloyl chloride (10 mmol, 1045 mg, 0.97 mL) were successively added. After the mixture was stirred for 4 h at room temperature, the solvent was removed under reduced pressure and the crude residue chromatographed on a silica gel column using hexane/ethyl acetate 96/4 as eluant to afford product **2** (590 mg, 45%) as a white solid; mp 53–54 °C; IR (KBr) 2953, 1727 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.42 (s, 9H), 2.07 (d, J = 1.4 Hz, 3H), 5.77 (q, J = 1.4 Hz, 1H), 6.35 (s, 1H), 7.21 (d, J = 2.8 Hz, 1H), 7.25 (d, J = 2.8 Hz, 1H), 9.82 (s, 1H), 11.71 (s, 1H); MS (CI, *m*/*z*) 263 ($M^+ + 1$), 262 (M^+), 89, 61; Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.69; H, 6.92. Found: C, 68.75; H, 6.87.

4.2.2. 3-*tert*-Butyl-2-hydroxy-5-(*p*-vinylbenzyloxy)benzaldehyde 3. To a stirred solution of 3-*tert*-butyl-2,5-dihydroxybenzaldehyde (5 mmol, 970 mg) in dry acetone (30 mL), potassium carbonate (5 mmol, 691 mg) and 4-iodomethylstyrene (6.5 mmol, 1590 mg) were successively added. The mixture was stirred for 6 h at 80 °C and after cooling to room temperature, the inorganic salts were filtered off, the solvent removed under reduced pressure and the crude residue chromatographed on a silica gel column using hexane as eluant to afford product **3** (1133 mg, 73%) as a pale red solid; mp 30–33 °C; IR (KBr) 2957, 1727 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.42 (s, 9H), 5.03 (s, 2H), 5.28 (dd, J = 10.9 and 0.6 Hz, 1H), 5.78 (dd, J = 17.6 and 0.6 Hz, 1H), 6.74 (dd, J = 17.6 and 10.9 Hz, 1H), 6.87 (d, J = 3.0 Hz, 1H), 7.26 (d, J = 3.0 Hz, 1H), 7.40 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.2 Hz, 2H), 9.80 (s, 1H), 11.54 (s, 1H); MS (CI, *m*/*z*) 310 (M^+), 117, 91; Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.46; H, 7.08.

4.2.3. 3-*tert*-Butyl-4-hydroxy-5-oxomethylphenyl vinylcarbonate 4. To a stirred solution of 3-*tert*-butyl-2,5-dihydroxybenzaldehyde (5 mmol, 970 mg) in dry chloroform (4 mL), pyridine (6 mmol, 484 mg, 0.48 mL) and vinyl chloroformate (10 mmol, 1065 mg, 0.91 mL) were

successively added. After the mixture was stirred for 4 h at room temperature, the solvent was removed under reduced pressure and the crude residue chromatographed on a silica gel column using hexane/ethyl acetate 96/4 as eluant to afford product **4** (1242 mg, 94%) as a pale yellow solid; mp 59–60 °C; IR (KBr) 2958, 1780, 1761 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.41 (s, 9H), 4.71 (dd, $J = 6.9$ and 2.3 Hz, 1H), 5.06 (dd, $J = 13.7$ and 2.3 Hz, 1H), 7.14 (dd, $J = 13.7$ and 6.9 Hz, 1H), 7.30 (d, $J = 2.9$ Hz, 1H), 7.33 (d, $J = 2.9$ Hz, 1H), 9.84 (s, 1H), 11.76 (s, 1H); MS (CI, *m/z*) 265 ($M^+ + 1$), 264 (M^+), 249, 61; Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10. Found: C, 63.72; H, 6.07.

4.3. General procedure for the preparation of ligands 5–8

To a stirred solution of the selected benzaldehyde **2**–**4** (2 mmol) in dry ethanol (20 mL), the selected amino alcohol (2 mmol) was added. The stirring was continued for 6 h at room temperature, the solvent removed under reduced pressure and the crude residue chromatographed on a silica gel column using hexane/ethyl acetate mixtures to afford the products **5**–**8**.

4.3.1. (*S*)-3-*tert*-Butyl-4-hydroxy-5-[(1-*tert*-butyl-2-hydroxy-ethylimino)-methyl]-phenyl methacrylate 5. (723 mg, 100%). Pale yellow foam; mp 52–52.5 °C; $[\alpha]_D^{20} = 4.1$ (*c* 1, EtOH); IR (KBr) 3425, 1735 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.98 (s, 9H), 1.43 (s, 9H), 2.06 (s, 3H), 2.93 (dd, $J = 9.4$ and 2.8 Hz, 1H), 3.74 (dd, $J = 11.1$ and 9.4 Hz, 1H), 3.94 (dd, $J = 11.1$ and 2.8 Hz, 1H), 5.74 (m, 1H), 6.33 (s, 1H), 6.95 (d, $J = 2.9$ Hz, 1H), 7.05 (d, $J = 2.9$ Hz, 1H), 8.29 (s, 1H), 11.4 (br s, 1H); MS (CI, *m/z*) 362 ($M^+ + 1$), 361 (M^+), 292; Anal. Calcd for $C_{21}H_{31}NO_4$: C, 69.78; H, 8.64; N, 3.87. Found: C, 69.72; H, 8.57; N, 3.93.

4.3.2. (*S*)-2-[*N*-3-*tert*-Butyl-5-(*p*-vinylbenzyloxy)salicyden]amino-3,3-dimethyl-1-butanol 6. (573 mg, 70%). Pale yellow foam; mp 129–130 °C; $[\alpha]_D^{20} = -6.5$ (*c* 1, EtOH); IR (KBr) 3440 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.98 (s, 9H), 1.43 (s, 9H), 2.92 (dd, $J = 10.9$ and 2.9 Hz, 1H), 3.76 (t, $J = 10.9$ Hz, 1H), 3.94 (br d, $J = 10.9$ Hz, 1H), 5.00 (s, 2H), 5.25 (d, $J = 10.9$ Hz, 1H), 5.76 (d, $J = 17.6$ Hz, 1H), 6.70 (d, $J = 3.0$ Hz, 1H), 6.73 (dd, $J = 17.6$ and 10.9 Hz, 1H), 7.06 (d, $J = 3.0$ Hz, 1H), 7.39 (d, $J = 8.4$ Hz, 2H), 7.43 (d, $J = 8.4$ Hz, 2H), 8.29 (s, 1H); MS (CI, *m/z*) 410 ($M^+ + 1$), 409 (M^+), 292; Anal. Calcd for $C_{26}H_{35}NO_3$: C, 76.25; H, 8.61; N, 3.42. Found: C, 76.29; H, 8.56; N, 3.49.

4.3.3. (1′*R*,2′*R*)-2-[*N*-3-*tert*-Butyl-5-(*p*-vinylbenzyloxy)-salicyden]amino-1′-(*p*-nitrophenyl)-1′,3′-propandiol 7. (908 mg, 90%). Pale yellow foam; mp 117–118 °C; $[\alpha]_D^{20} = -107.5$ (*c* 1, EtOH); IR (KBr) 3439 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.43 (s, 9H), 2.7–2.8 (m, 1H), 3.49 (q, $J = 5.5$ Hz, 1H), 3.78 (d, $J = 5.4$ Hz, 2H), 4.98 (s, 2H), 5.1–5.2 (m, 1H), 5.26 (d, $J = 10.9$ Hz, 1H), 5.76 (d, $J = 17.6$ Hz, 1H), 6.63 (d, $J = 3.0$ Hz, 1H), 6.73, (dd, $J = 17.6$ and 10.9 Hz, 1H), 7.09 (d, $J = 3.0$ Hz, 1H), 7.37 (d, $J = 8.3$ Hz, 2H), 7.42 (d, $J = 8.3$ Hz, 2H), 7.58 (d, $J = 8.7$ Hz, 2H), 8.22 (d, $J = 8.7$ Hz, 2H), 8.27 (s, 1H); MS (CI, *m/z*) 506 ($M^+ + 1$), 505 (M^+), 449, 387, 152; Anal. Calcd for $C_{29}H_{32}N_2O_6$: C, 69.03; H, 6.39; N, 5.55. Found: C, C, 69.12; H, 6.45; N, 5.47.

4.3.4. (*S*)-3-*tert*-Butyl-4-hydroxy-5-[(1-*tert*-butyl-2-hydroxy-ethylimino)-methyl]-phenyl vinyl carbonate 8. (727 mg, 100%). Pale yellow foam; mp 51–52 °C; $[\alpha]_D^{20} = -4.0$ (*c* 1, EtOH); IR (KBr) 3415, 1775 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.99 (s, 9H), 1.43 (s, 9H), 2.92 (dd, $J = 9.4$ and 2.9 Hz, 1H), 3.75 (dd, $J = 11.0$ and 9.4 Hz, 1H), 3.95 (br d, $J = 11.0$ and 2.9 Hz, 1H), 4.68 (dd, $J = 6.2$ and 1.9 Hz, 1H), 5.04 (dd, $J = 13.8$ and 1.9 Hz, 1H), 7.02 (d, $J = 3.0$ Hz, 1H), 7.14 (dd, $J = 13.8$ and 6.2 Hz, 1H), 7.14 (d, $J = 3.0$ Hz, 1H), 8.30 (s, 1H); MS (CI, *m/z*) 364 ($M^+ + 1$), 363 (M^+), 276; Anal. Calcd for $C_{20}H_{29}NO_5$: C, 66.09; H, 8.04; N, 3.85. Found: C, 66.17; H, 8.13; N, 3.80.

4.4. General procedure for the preparation of polymers 9 and 12

To a stirred solution of the selected ligand **5** or **8** (1 mmol) in dry toluene (15 mL), MMA (2.33 mmol, 233 mg, 0.25 mL), EGDMA (13.80 mmol, 2735 mg, 2.60 mL) and AIBN (0.19 mmol, 31 mg) were successively added at room temperature under nitrogen. The mixture was heated at 60 °C for 8 h, the resulting solid crushed in a mortar and the powder washed with dichloromethane (100 mL) and dried under vacuo for 6 h.

4.5. General procedure for the preparation of polymers 10 and 11

To a stirred solution of the selected ligand **6** or **7** (1 mmol) in dry toluene (15 mL), styrene (6.97 mmol, 726 mg, 0.80 mL), DVB 80% (1.50 mmol, 196 mg, 0.21 mL) and AIBN (0.19 mmol, 31 mg) were successively added at room temperature under nitrogen. The mixture was heated at 100 °C for 21 h, the resulting solid crushed in a mortar and the powder washed with dichloromethane (100 mL) and dried under vacuo for 6 h.

4.6. General procedure for the preparation of complexes 5V–8V

To a stirred solution of the selected ligand **5**–**8** (0.015 mmol) in dry dichloromethane (6 mL), $VO(acac)_2$ (0.010 mmol, 2.65 mg) was added at room temperature. The mixture was stirred at room temperature for 4 h and the resulting complex in solution employed for the reaction.

4.7. General procedure for the preparation of complexes 9V–12V

To a stirred mixture of the selected polymer **9**–**12** (0.015 mmol of supported ligand) in dry dichloromethane (6 mL), $VO(acac)_2$ (0.010 mmol, 2.65 mg) was added at room temperature. The mixture was stirred at room temperature for 4 h and then the resulting complex filtered, washed with dichloromethane (2×10 mL) and dried under vacuo.

4.8. General procedure for the preparation of chiral sulfoxides 14

To a mixture of the supported catalyst **10V** (46 mg) in dichloromethane/methanol 250/1 (6 mL) at 0 °C in a Schlenk tube equipped with a magnetic stirrer, the selected sulfide (1.0 mmol) and H_2O_2 30% (1.1 mmol, 0.11 mL) were successively added. The mixture was stirred at 0 °C for 16 h and then the catalyst removed by filtration on a Büchner funnel and washed with dichloromethane (3 × 5 mL). The organic phase was washed with distilled water (20 mL), dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure. The crude residue was chromatographed on silica gel plates (25 × 25 cm) using hexane/ethyl acetate 20/80 to afford the products.

4.8.1. (*S*)-Methyl phenyl sulfoxide 14a.[27] Colourless oil, yield: 75%, ee 56%, $[\alpha]_D = -80.1$ (*c* 0.69, abs EtOH) {Lit. $[\alpha]_D = 143$ (*c* 0.69, abs EtOH)}.

4.8.2. (*S*)-Methyl *p*-methylphenyl sulfoxide 14b.[28] White solid, yield: 70%, ee 52%, $[\alpha]_D = -77.8$ (*c* 2.00, acetone) {Lit. $[\alpha]_D = +145$, ee 99.5% (*c* 2, acetone)}.

4.8.3. (*S*)-Methyl *p*-bromophenyl sulfoxide 14c.[29] White solid, yield: 80%, ee 45%, $[\alpha]_D = -58.7$ (*c* 1.50, $CHCl_3$) {Lit. $[\alpha]_D = -75.7$, ee 58% (*c* 1.50, $CHCl_3$)}.

4.8.4. (*S*)-Methyl *p*-chlorophenyl sulfoxide 14d.[30] White solid, yield: 79%, ee 51%, $[\alpha]_D = -80.6$ (*c* 0.95, $CHCl_3$) {Lit. $[\alpha]_D$:−158 (*c* 0.95, $CHCl_3$)}.

4.8.5. (*S*)-Methyl *p*-methoxyphenyl sulfoxide 14e.[31] White solid, yield: 76%, ee 52%, $[\alpha]_D = -88.0$ (*c* 1.20, $CHCl_3$) {Lit. $[\alpha]_D = -162.4$, ee 96% (*c* 1.2, $CHCl_3$)}.

4.8.6. (*S*)-Methyl *p*-nitrophenyl sulfoxide 14f.[28] White solid, yield: 54%, ee 57%, $[\alpha]_D = -90.1$ (*c* 0.75, $CHCl_3$) {Lit. $[\alpha]_D = +156.9$, ee 99.3% (*c* 0.75, $CHCl_3$)}.

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