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Optically Active Tripodal Dendritic Polyoxometalates: Synthesis, Characterization and Their Use in Asymmetric Sulfide Oxidation with Hydrogen Peroxide

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A series of structurally well-defined enantiopure tripodal allyl dendritic structures bearing three amine groups have been synthesized. The hydrogenation of the allyl groups in the presence of a Pd/C catalyst gave the corresponding enantiopure *n*-propyl counterparts. Treatment of these *n*-propyl amino dendrimers with heteropolyacid $H_3PW_{12}O_{40}$ and excess H_2O_2 gave the enantiopure *n*-propyl $\{PO_4[WO(O_2)_2]_4\}^{3-}$ salts. Characterization of these dendritic POM hybrids in solution by NMR spectroscopy, elemental analysis, UV/Vis spectrophotometry, circular dichroism (CD), vibrational circular dichroism (VCD) and fluorimetry indicates the presence of POM–ligand interactions and confirms their optical and chiroptical properties. The hybrid compounds selectively oxidized sulfides to the corresponding chiral sulfoxides with up to 13 % enantiomeric excess (*ee*), highlighting the transfer of chirality from the dendritic wedges to the inorganic cluster. The properties of the POM anion, especially its solubility and regio- and stereoselectivity, are sensitive to the structure of the cation. The catalyst was recovered by precipitation without any discernible loss in activity, selectivity or enantioselectivity over three catalytic cycles at –50 °C. Interestingly, a dendritic effect was noted in the enantioselectivity as the dendritic-POM hybrids are more selective than their non-dendritic counterparts. The *ee* resulting from chirality transfer to the anionic POM unit is comparable to that obtained in our previous work with monopodal dendritic polyoxometalates (14 %) despite the polyvalency of the highly charged tripodal ligand, which is rationalized by different spectroscopic methods.

Introduction

The quest for new catalytic and highly enantioselective processes[1] is currently one of the primary challenges in chemical synthesis. In this context, chiral polyoxometalates (POMs) have recently become a topic of interest due to their potential applications in medicine and stereoselective catalysis.[2] As a result, enantioselective organic transformations can also be investigated by using POM compounds. Among numerous applications of POMs,[3–7] catalysis is by far the most studied owing to the enormous versatility that POMs offer in the clean synthesis of fine chemicals, including their ability to catalyse environmentally friendly reactions. Many POMs are able to activate molecular oxygen or hydrogen peroxide as primary oxidants in reactions with water as the byproduct. In addition, many elements of the oxidant are incorporated into the final product (atom economy). On the other hand, for sustainable economic development, preventing waste, rather than treating it or cleaning it up, is the key requirement. Thus, one of the most imperative issues for chemists is the search for green chemical transformations. In particular, waste reduction is a key requirement in the development of new attractive industrial processes. In this context, a variety of metallodendritic compounds used as recoverable catalysts have been reported.[8–10] This area of research was pioneered in industry by van Leeuven in the early 1990s and in the academic world by the groups of Brunner, van Koten, Ford, and DuBois. However, in terms of green chemistry these systems have deficiencies on several accounts, especially the contamination of the reaction mixture by metal leaching, and hence the development of more environmentally friendly catalytic systems remains a major challenge for chemists. In this context, the combination of POMs with dendritic structures can result in catalysts with improved properties. The fixation of POM catalysts onto dendrimers is a very promising route that allows the coupling of molecular control, mechanistic knowledge and the catalytic efficiency of the POM unit with indispensable methods of recovery and recycling.[11] To date, numerous inorganic chiral POMs have been developed by two main synthetic approaches. The first involves the use of chiral species (organic moieties or metal complexes) as chirality transfer agents[12] whereas the second strategy is based upon spontaneous resolution upon

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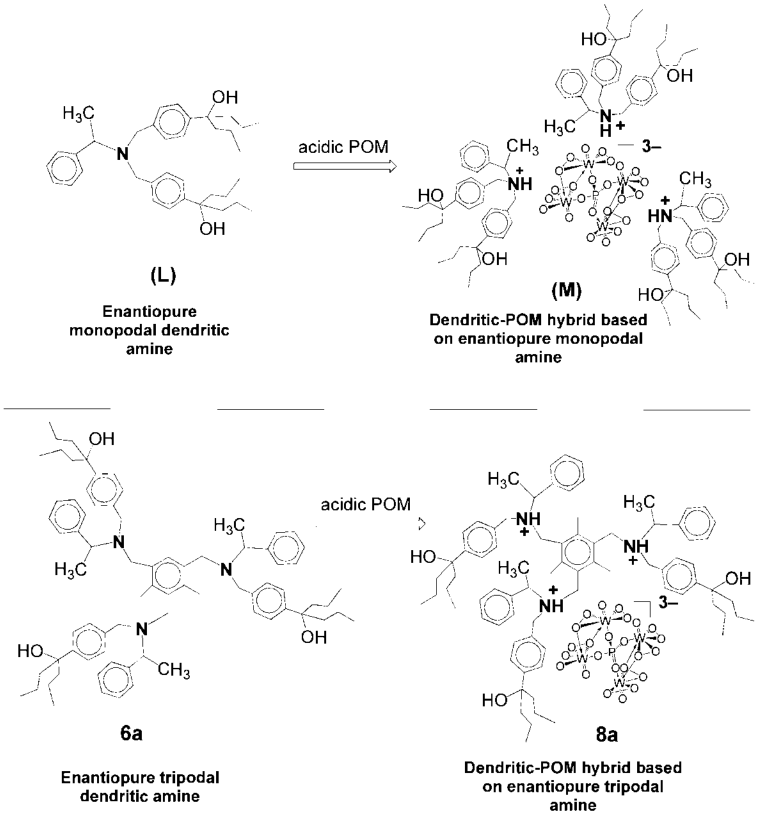
crystallization in the absence of any chiral auxiliary to yield conglomerates.[13] However, the resolution of the enantiomeric structure is frequently complicated by racemization such that only in a few cases has the spontaneous resolution of enantiopure conglomerates been successfully achieved. Recently, an elegant and promising approach to enantiopure POMs based on the kinetic resolution of α_1-substituted Dawson polyoxometalates by their chiral recognition by peptides was reported.[14] However, this approach could be restricted by the overall modest yield (20%) of the isolated enantiopure POM. Therefore an alternative strategy for the large-scale synthesis of enantiopure systems is the direct attachment of chiral organic structures onto the POM species. The optical and chiroptical properties of a few enantiopure POMs based on the electrostatic coupling of chiral cations to achiral anionic POM species have been described.[12] To the best of our knowledge, there is only one report describing the synthesis and characterization of enantiopure dendritic POM frameworks and their application in an enantioselective transformation. Indeed, in a preliminary communication, we reported the first example of enantiopure dendritic POM hybrids, prepared by the ionic coupling of enantiopure monopodal dendritic cations and the anionic POM, selectively oxidizing thioanisole to the corresponding chiral sulfoxide with up to 14% enantiomeric excess (*ee*).[15] This proof-of-principle catalytic experiment demonstrated and confirmed the transfer of chiroptical properties from the organic moieties to a catalytically active POM unit. Recently, Bonchio and co-workers published details of the preparation of non-dendritic optically active polyoxotungstophosphonates by covalent functionalization of a Keggin-type POM with a chiral organophosphonate. These compounds oxidized methyl *p*-tolyl sulfide to the corresponding chiral sulfoxide with up to 75% conversion and a maximum of 8% *ee*.[16] In addition, our preliminary results showed that the dendritic POM compound was more selective (14 vs. 4% *ee*) than the non-dendritic counterpart. Bonchio and co-workers also observed the dependence of the enantioselectivity of the reaction on the nature of the ligand. These promising results clearly indicate that the catalytic properties of the POM unit are dependent upon the nature of the organic cation. In this context, we need to understand the parameters that play a decisive role in achieving maximum activity and selectivity. Thus, an understanding of the relationship between the structure of the dendritic wedge, the structure of the POM cluster and the properties of the resulting dendritic POM hybrids will be of great interest as they will allow the development of enantiopure dendritic POM-based catalysts that are able to catalyse enantioselective transformations with excellent yields and enantiomeric excesses. Our first approach was to tune the structure of the chiral dendritic counter-cation. Thus, in our preliminary work we reported the synthesis and study of enantiopure dendritic POM hybrid catalysts, built by the electrostatic coupling of enantiopure monopodal dendritic cations with an achiral trianionic POM (Scheme 1, top). Now we compare the chiroptical and catalytic properties of this prototype family of hybrids with



Scheme 1. Dendritic POM hybrids **M** and **8a** based on monopodal dendritic amine **L** and tripodal dendritic amine **6a**, respectively.

those of a new series of enantiopure dendritic POMs built by assembling enantiopure tripodal dendritic amines and trianionic POM moieties (Scheme 1, bottom). In this way, the triply-charged anionic POM will be encapsulated by a single dendritic structure bearing three ammonium groups.

Herein we describe the synthesis and characterization of a novel series of chiral dendritic POM hybrids by assembling chiral tripodal dendritic amines and acidic POM moieties. Electronic absorption experiments as well as circular dichroism (CD), vibrational circular dichroism (VCD) and fluorimetry have been performed to obtain information on the interactions between the dendritic cation and the anionic POM in homogeneous solution. These compounds were used as recoverable catalysts in the oxidation of sulfides, which yielded sulfoxides with enantiomeric excess. The effects of the structural modifications induced by the dendritic wedge on the properties of the POM are emphasized.

Results and Discussion

Synthesis and Characterization of Enantiopure Dendritic POM Hybrids

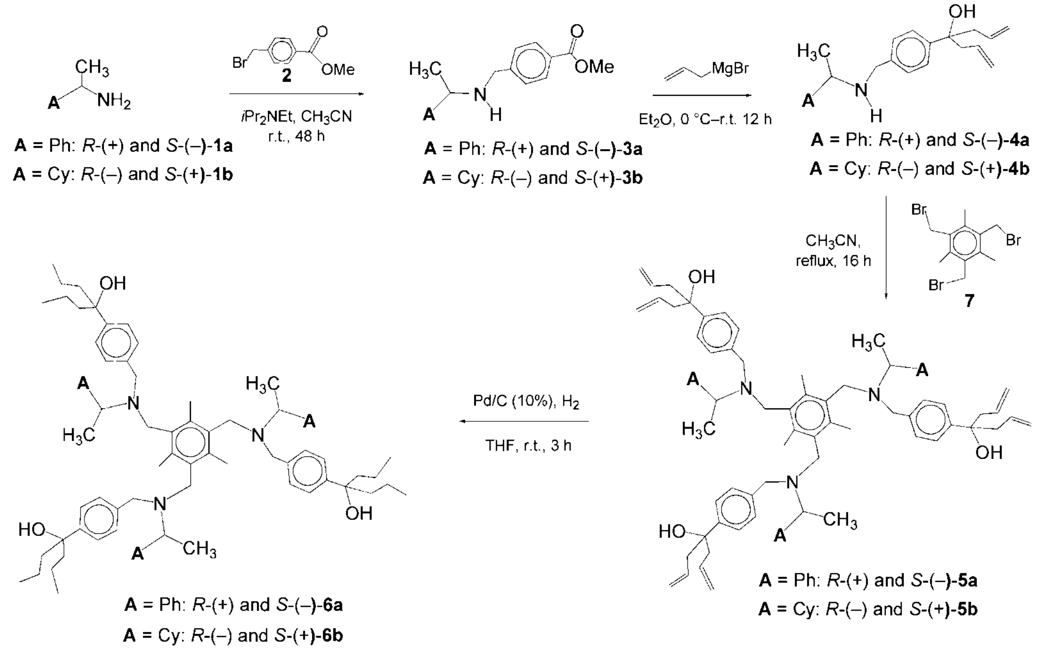
Enantiopure dendritic POM-based frameworks were constructed by ionic assembly of the trianionic $\{PO_4[WO(O_2)_2]_4\}^{3-}$ with enantiopure tripodal dendritic ammoniums obtained by functionalization of enantiopure commercially available 1-phenylethylamine (**1a**) and 1-cyclohexylethylamine (**1b**). To compare the work described in this manuscript and that reported in ref.[15], we focused on the Venturello species.

Synthesis of Enantiopure Tripodal Dendritic Amines 6a,b

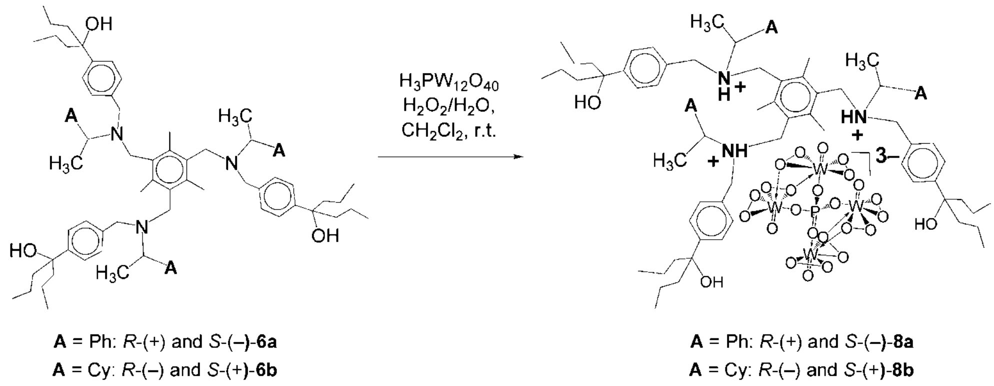
Enantiopure tripodal *n*-propyl dendritic amines (*R*)-(+)-**6a**, (*S*)-(–)-**6a** and (*R*)-(–)-**6b**, (*S*)-(+)-**6b** were obtained from methyl 4-(bromomethyl)benzoate (**2**) and enantiopure 1-phenylethylamine (**1a**) and 1-cyclohexylethylamine (**1b**; Scheme 2), respectively. The first step involved the reaction of 4-(bromomethyl)benzoate (**2**) with amines **1a** and **1b** (in excess), which selectively gave the amino benzoates (*R*)-(+)-**3a**, (*S*)-(–)-**3a** and (*R*)-(–)-**3b**, (*S*)-(+)-**3b**, respectively. These were allylated with allylmagnesium bromide to give the corresponding enantiomerically pure diallyl carbinols (*R*)-(+)-**4a**, (*S*)-(–)-**4a** and (*R*)-(–)-**4b**, (*S*)-(+)-**4b**. The hexaallyl triamino tricarbinol dendrimers (*R*)-(+)-**5a**, (*S*)-(–)-**5a** and (*R*)-(–)-**5b**, (*S*)-(+)-**5b** were then obtained in good yields by the coupling reaction of diallyl carbinols **4a** and **4b** with 2,4,6-tris(bromomethyl)mesitylene (**7**). The hydrogenation of hexaallyl **5a** and **5b** in the presence of Pd/C as catalyst gave the corresponding *n*-propyl compounds (*R*)-(+)-**6a**, (*S*)-(–)-**6a** and (*R*)-(–)-**6b**, (*S*)-(+)-**6b** in excellent yields. Spectroscopic studies and elemental analysis data are consistent with the proposed dendritic structures. Interestingly, the molecular peaks of amino dendrimers **6a** and **6b** were observed in their MALDI-TOF mass spectra at *m*/*z* = 1130.60 (calcd. 1130.69, $[M - 2H]^+$) and 1148.86 (calcd. 1148.83, $[M - 2H]^+$), respectively.

Synthesis of Enantiopure Dendritic POM Hybrids 8a,b

Enantiopure dendritic POM salts were prepared by a procedure involving the peroxide-mediated decomposition of $H_3PW_{12}O_{40}$.[11d,11f–11i,17] Following the procedure described in ref.[5], the hexa-*n*-propyl dendritic POM hybrids



Scheme 2. Synthesis of enantiopure tripodal dendritic amines **6a**,**b**.



Scheme 3. Synthesis of enantiopure tripodal dendritic POM hybrids **8a** and **8b**.

(*R*)-(+)-**8a**, (*S*)-(–)-**8a** and (*R*)-(–)-**8b**, (*S*)-(+)-**8b** were prepared from the tripodal dendritic amines **6a** and **6b** and the commercial heteropolyacid $H_3PW_{12}O_{40}$ in the presence of an excess of H_2O_2 in a biphasic mixture of water and dichloromethane (Scheme 3). The dendritic POM hybrids (*R*)-(+)-**8a**, (*S*)-(–)-**8a** and (*R*)-(–)-**8b**, (*S*)-(+)-**8b** were isolated as light-yellow solids in good yields. In contrast to the series of hybrids built with monopodal amines (Scheme 1, top) previously reported by our group, compounds **8a** and **8b** are insoluble in chloroform and slightly soluble in dichloromethane. Their solution investigations were performed either in acetone or in acetonitrile.

The ammonium chloride salts **6a**·3HCl (see the Supporting Information for detailed synthetic procedures and characterization) obtained from **6a** can also be used to prepare the dendritic POM salts **8a**. The NMR, IR and elemental analysis data reported for **8a**,**b** are in agreement with the structures proposed for these hybrids. The ^{31}P NMR spectra present only one signal for **8a** ([D$_6$]acetone, δ = 3.26 ppm) and **8b** ([D$_6$]acetone, δ = 3.32 ppm). In addition, the ^{1}H and ^{13}C NMR spectra confirm the presence of enantiopure cations around the POM species. Concerning the ^{183}W NMR measurements of these dendritic POM hybrids, we were unable to obtain spectra with a sufficiently high signal-to-noise ratio, probably because of the low receptivity of W in dilute systems. For certain POM systems we have observed ^{183}W NMR spectra, but this becomes increasingly difficult with dendritic POM frameworks even after accumulation for 1 week in 10 mm tubes. However, effort has been devoted to the characterization of these hybrids by ^{1}H and ^{13}C NMR and IR spectroscopy and especially elemental analysis. The structures and purity of these hybrids are supported by the analytical data presented in the Exptl. Sect.

The chiroptical properties of the enantiopure dendritic POM salts **8a** and **8b** were examined in solution by circular dichroism (CD) and polarimetry. The CD spectra of the enantiomers are mirror images of one another, as shown in Figure 1a for (*R*)-(–)-**8b** and (*S*)-(+)-**8b**, which confirms their enantiopurity. These spectra show strong and weak Cotton effects with maxima at 199, 224 and 302 nm. These can be compared with the CD spectra of the ammonium chloride counterparts (*R*)-(–)-**6b**·3HCl and (*S*)-(+)-**6b**·3HCl (Figure 1b), which exhibit strong and weak Cotton effects with maxima at 225 nm for (*R*)-(–)-**6b**·3HCl and (*S*)-(+)-**6b**·3HCl. These values are comparable to those obtained for the oxygen-to-tungsten charge-transfer bands of Keggin polyoxoanions[12k,18] as well as those obtained in our preliminary communication with the Venturello ion based hybrids prepared with monopodal dendritic amines.[15] To gain an insight into the interactions between the dendritic cation and the POM anion in solution, fluorescence and absorption experiments as well as electronic absorption and vibrational circular dichroism (VCD) spectroscopy of the enantiopure hybrids (*R*)-(+)-**8a** and (*S*)-(–)-**8a** were carried out.

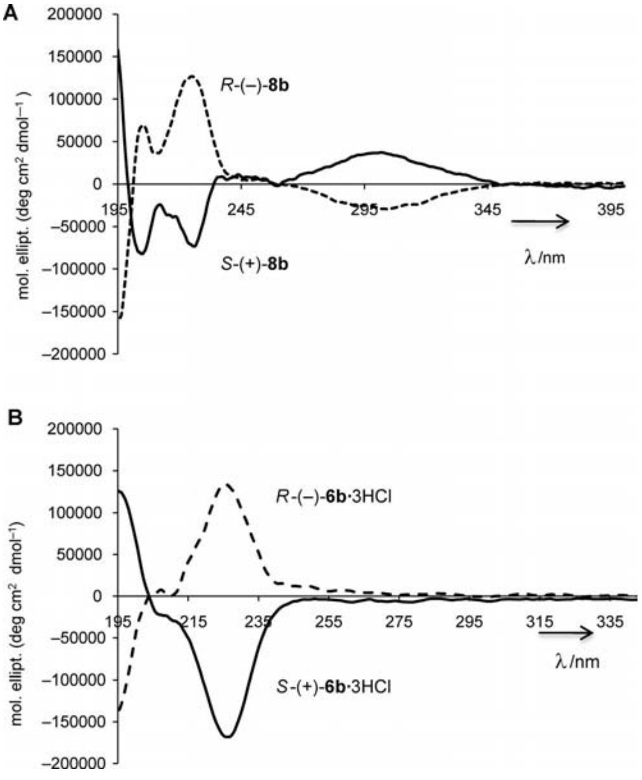


Figure 1. CD spectra in CH_3CN. **A**: enantiopure dendritic POMs (*R*)-(–)-**8b** and (*S*)-(+)-**8b** (c = 5.0×10^{-6} M); **B**: the precursor ammonium chloride salts (*R*)-(–)-**6b**·3HCl and (*S*)-(+)-**6b**·3HCl (c = 2.8×10^{-6} M).

Electronic Absorption and Emission Studies

The electronic absorption spectra of POM-Arquad and the tripodal ammonium salt **6a**·3HCl as well as the corresponding dendritic POM **8a** are shown in Figure 2. For the ligand salt **6a**·3HCl the intense high-energy band at 220 nm is ascribed to the peripheral aromatic groups whereas the band arising from the electronically isolated central aromatic lies at 260 nm. A significantly different absorption is observed for the dendritic POM **8a** compared with the parent POM (POM-Arquad) and tripodal ligand (in CH_2Cl_2 and CH_3CN). The absorption is not simply a summation of the absorption bands of the constituent POM and dendritic chromophores.

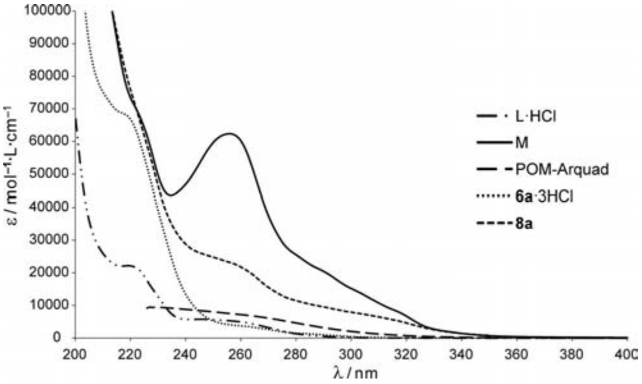


Figure 2. Electronic absorption spectra of POM-Arquad in CH_2Cl_2, the hydrochloride salts of the tripodal dendrimer (**6a**·3HCl) and monopodal ligand (**L**·HCl) as well as corresponding dendritic POMs **8a** and **M**, in CH_3CN ($c = 10^{-5}$ M).

The absorption spectrum of tripod–POM **8a** is altered upon dilution of an acetonitrile solution, especially below 10^{-4} M, notably in the region of the charge-transfer band, or on adding water, which indicates a decreased interaction/dissociation, consistent with the proposed interaction (Figure S37). The fluorescence emission and excitation spectra show that the structured POM-Arquad emission is slightly blueshifted when elaborated with dendritic wedges ($\Delta\omega \approx 1000\ \text{cm}^{-1}$) whereas the blue fluorescence of the ammonium ligand **6a**·3HCl ($\Phi_F = 0.004$, $\lambda_{max} = 303$ nm) appears partly quenched due to the close proximity of the POM in **8a**, although no sensitized emission arising from the POM part is detected (Figure S38).

All these results are consistent with a ground-state (and excited-state) complex comprising the anionic POM and at least one cationic dendritic wedge, necessitating a close interaction. The weaker charge-transfer interaction in the POM–tripod species may be due to differing charge densities within the dendron brick **6a**·3HCl compared with the monopodal ligand **L**·HCl. Indeed, protonation of the amino groups can have a dramatic effect on the neighbouring aromatics. The CH_2NMe_2 skeleton has a Hammett constant $\sigma_p = 0.01$ whereas on protonation the $CH_2N^+HMe_2$ group has a Hammett constant $\sigma_p = 0.43$ (for comparison, an aldehyde electroattractor has $\sigma_p = 0.42$).[19] In addition, the transmission of electric fields across a similarly short distance has previously been observed for an anthracene-containing species.[20] Thus, with three such electroattractors acting on the central cycle, significant perturbations may be anticipated on complex **8a**, provided this is the cycle that is interacting.[20c] This reduced charge-transfer interaction may be correlated with the catalytic behaviour (see below).

Vibrational Absorption and Circular Dichroism (VCD) Analyses

Vibrational absorption spectroscopy has been used to obtain information about the interaction between the dendritic structures and the POM unit. The infrared spectra of the ammonium chloride tripodal ligand **6a**·3HCl and the tripodal dendritic POM hybrid **8a** in CH_2Cl_2 solution are shown in Figure 3. Most of the bands of the POM complex are related to the corresponding tripodal ligand although broad bands from the POM unit are observed at around 1075 and 945 cm^{-1}. These spectral contributions are assigned to the stretching vibrations of the P–O and W=O bonds, respectively. This assignment was confirmed experimentally from the infrared spectrum of the non-dendritic

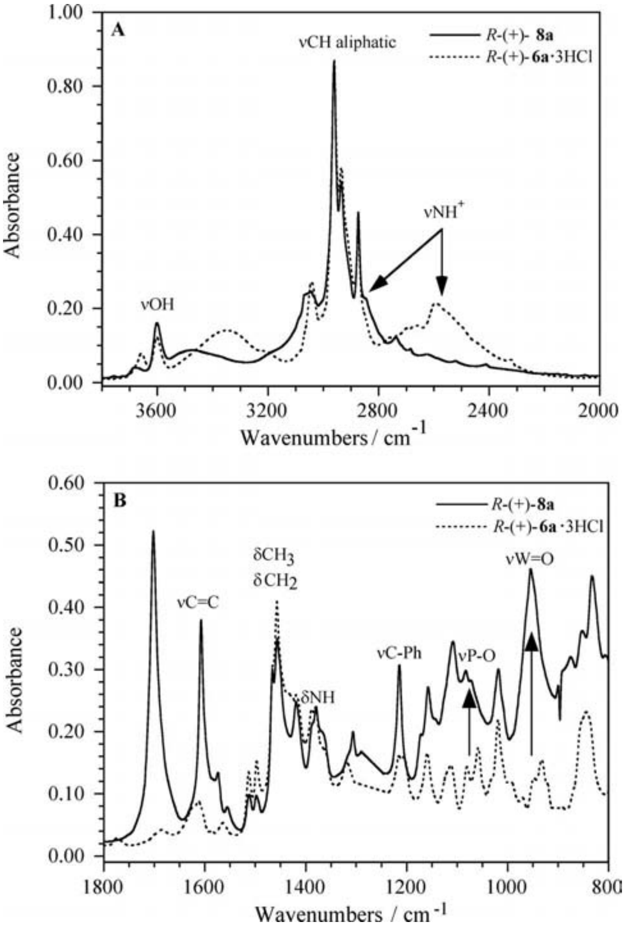


Figure 3. IR spectra. **A**: (*R*)-(+)-**6a**·3HCl and (*R*)-(+)-**8a** in the 3800–2000 cm^{-1} range; **B**: the 1800–800 cm^{-1} range under the following experimental conditions: co-addition of 50 scans, 4 cm^{-1} resolution, concentration 40 mM for (*R*)-(+)-**6a**·3HCl and (*R*)-(+)-**8a** in CH_2Cl_2 solution, path length 250 μm.

POM-Arquad compound (see Figure S39 in the Supporting Information) and by calculations using density functional theory (DFT) of the spectrum of the POM entity (see Figure S40 in the Supporting Information). The interaction between the tripodal ligand and the POM unit results in spectral modifications of several ligand bands.

Indeed, the broad band associated with the stretching vibration of the NH^+ group shifts from 2590 cm^{-1} for the ligand alone to 2900 cm^{-1} for the complex. A smaller interaction of the NH^+ group with the POM (with respect to the Cl^- anion for the ligand) explains this blueshift. A second important spectral modification upon complexation is the enhancement of the bands associated with the aromatic C=C stretching vibrations above 1500 cm^{-1} due to charge transfer between the POM entity and the aromatic rings.

Vibrational circular dichroism (VCD) is a well-established method for obtaining information about the chirality of a sample and in particular for determining the absolute configuration and solution conformation of chiral molecules.[21] Compared with electronic circular dichroism (ECD) spectra, VCD spectra are more detailed because of the many bands contained in the mid-IR region. The VCD spectra of (*R*)-(+)-**8a** in CH_2Cl_2 solution is shown in Figure 4. The most important contributions to the VCD spectrum of the tripodal dendritic POM hybrid come from vibrational modes related to the ligand. In particular, the VCD bands at 1467 and 1454 cm^{-1} are associated with the CH_3 and CH_2 bending vibrations of the propyl groups. Likewise, the VCD band located at 1204 cm^{-1} is assigned to the chiral C–Ph stretching vibrations.

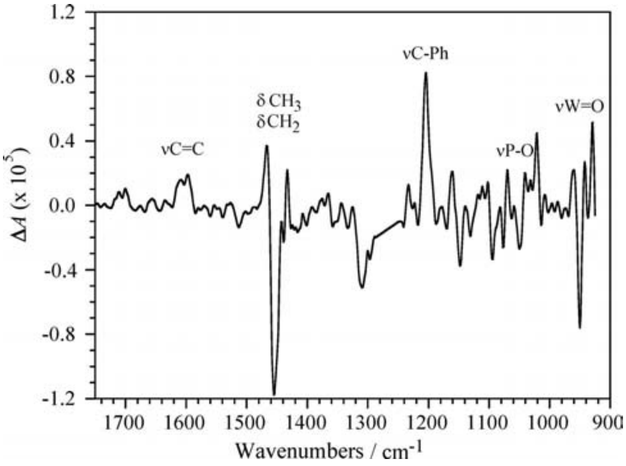


Figure 4. VCD spectrum of (*R*)-(+)-**8a** in CH_2Cl_2 solution.

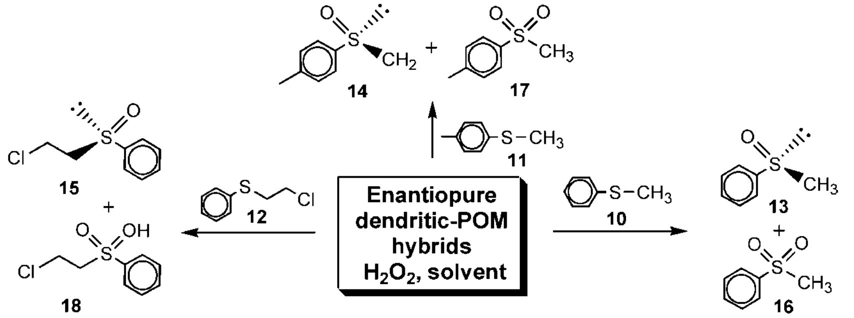
The investigation of chirality transfer from the ligand to the POM unit is not straightforward. Indeed, induced chirality on achiral molecules gives rise to very low VCD signals and is generally associated with a modified vibrational circular dichroism of the chiral inducer. This behaviour has been observed previously for the enantiopure monopodal dendritic POM hybrid.[15] Thus, a VCD band associated with the P–O bonds has been observed at around 1050 cm^{-1} with a very low intensity (similar to the noise of the VCD spectrum). Unfortunately, no additional information in the W=O spectral region (960–920 cm^{-1}) has been obtained due to solvent ($CDCl_3$) interference. To confirm the chirality transfer from the ligand to the POM cluster, we recorded the VCD spectrum of the enantiopure tripodal dendritic POM hybrid in CH_2Cl_2 solution, which allows spectral information up to 900 cm^{-1} to be acquired. A negative VCD band is observed at around 1050 cm^{-1} arising from the P–O bonds whereas a positive–negative–positive pattern is detected in the 960–920 cm^{-1} spectral range for the W=O bonds. The intensities of these latter bands are significantly greater than those observed for the P–O bonds, which indicates that the W=O mode seems to be a good probe for following the chirality transfer from the ligand to the POM cluster.

The POM molecule would thus display structural chirality in a chiral environment, which may be anticipated to be the origin of the *ee* in the sulfide oxidation. This structural chirality has been clearly evidenced by this VCD study. Moreover, DFT calculations of the optimized geometry of the chiral dendritic POM complex show this tendency of the POM unit to adopt a chiral structure. Indeed, significant VCD intensities have been calculated for the stretching vibrations of P–O and W=O bonds (see Figure S41 in the Supporting Information).

Catalytic Oxidation of Sulfides Using Enantiopure Tripodal Dendritic POM Hybrids 8a and 8b

To evaluate the catalytic efficiency of enantiopure dendritic POM hybrids **8a** and **8b** and demonstrate the chiroptical properties of the POM unit in an asymmetric reaction, we oxidized methyl phenyl sulfide (**10**), methyl *p*-tolyl sulfide (**11**) and 2-chloroethyl phenyl sulfide (**12**) with H_2O_2 (35%) in a biphasic mixture of water and organic solvents. Table 1 reports the results obtained with dendritic POM catalysts **8a**, **8b** and the non-dendritic counterpart **9** in terms of conversion, product selectivity (sulfoxide vs. sulfone) and enantiomeric excess (*ee*). The synthesis and characterization of the non-dendritic hybrid **9** have been reported in our previous work.[15] The reactions were performed in a mixture of water and $CDCl_3/CH_3CN$ (19:1, v/v) at 35, 0 and –50 °C. As shown in Table 1, the oxidation of methyl phenyl sulfide (**10**), methyl *p*-tolyl sulfide (**11**) and 2-chloroethyl phenyl sulfide (**12**) selectively gave the corresponding methyl phenyl sulfoxide (**13**), methyl *p*-tolyl sulfoxide (**14**) and 2-chloroethyl phenyl sulfoxide (**15**), together with a small amount of sulfones **16**, **17** and **18**, respectively. In all cases, the selectivity to sulfoxide and the enantiomeric excess increased with decreasing reaction temperature with yields ranging from 19 to 100% and the *ee* values ranging from 1 to 13% after 5 to 360 min depending on the nature of the substrate and the reaction temperature. The reaction efficiency, selectivity and enantioselectivity were dependent upon the nature of the substrate and the reaction temperature. A comparison between substrates **10**, **11** and **12** shows that methyl *p*-tolyl sulfide (**11**) substituted with an electron-donating group (CH_3) accelerated the oxidation reaction

Table 1. Oxidation of representative sulfides catalysed by tripodal dendritic enantiopure POM salts **8a**,**b** and the non-dendritic **9** using H_2O_2.[a]



Entry	Substrate	Catalyst	T [°C]	t [min][b]	Conversion [%][c]	Products (yield, %)		*ee* [%][d]
1	**10**	**8a**	35	5	100	**13** (36)	**16** (64)	2
2			0	30	100	(91)	(9)	11
3			–50	180	100	(81)	(19)	13
4		**8b**	35	5	100	(0)	(100)	–
5			–50	30	100	(81)	(19)	9
6		**9**	35	8	100	(68)	(28)	4
7			–50	30	100	(72)	(32)	4
8	**11**	**8a**	35	5	100	**14** (48)	**17** (52)	1
9			0	5	100	(66)	(34)	7
10			–50	5	100	(77)	(23)	9
11		**8b**	–50	120	72	(68)	(4)	3
12	**12**	**8a**	35	5	100	**15** (39)	**18** (61)	1
13			0	120	100	(70)	(30)	3
14			–50	360	19	(19)	(0)	4
15		**8b**	–50	360	70	(63)	(7)	2

[a] Reaction conditions: catalyst (0.4 mol-%), substrate (250 equiv.), 35% H_2O_2 (800 equiv.), solvent [1 mL, mixture of $CHCl_3/CH_3CN$ (19:1, v/v)]. [b] The reactions were monitored by ^1H NMR spectroscopy. [c] The conversions were determined from the relative intensities of the ^1H NMR signals of the substrate and the product. [d] The enantiomeric excesses were determined by chiral HPLC using a Chiralcel ASH column, UV detection (254 nm), eluting with hexane/2-propanol (1:1) at a flow rate of 0.5 mL min^{-1}.[22]

relative to methyl phenyl sulfide (**10**) and 2-chloroethyl phenyl sulfide (**12**; Table 1, entries 3, 10 and 14). The oxidation of methyl phenyl sulfide (**10**) with the phenylethylamine-based hexa-*n*-propyl dendritic POM hybrids **8a** was more enantioselective than the oxidation of **11** and **12** at –50 °C (13 vs. 9 and 4%, entries 3, 10 and 14). The high selectivity to sulfoxide implies that sulfide oxidation proceeds significantly faster than the corresponding sulfoxide oxidation under these reaction conditions. For example, in contrast to **10** and **11**, the oxidation of **12** led to a significant amount of sulfone (byproduct). This indicates that the mechanism operating in the system is electrophilic oxygen transfer as **11** is a more nucleophilic substrate than **10** and **12**. Overall, with all the catalysts tested, the catalytic experiments performed at 35 °C were extremely fast (100% conversion with reaction times between 5 and 8 min) in contrast to the reaction performed at –50 °C. However, the selectivity to sulfoxide and the enantioselectivity were lower under these conditions (Table 1). It is interesting to note that all the oxidation reactions performed did not proceed in the absence of the POM catalyst when carried out under similar conditions. The phenylethyl-based POM hybrid **8a** was more enantioselective than its cyclohexylethyl counterpart **8b** (Table 1, entries 3, 5, 10, 11, 14 and 15). Interestingly, as shown in Table 1, the enantioselectivity is dependent upon the nature of the organic cation. A slight dendritic effect was also observed in the *ee* as the dendritic POMs **8a** and **8b** are more enantioselective than their non-dendritic compounds **9** under similar conditions (13 and 9% vs. 4% *ee*; entries 3, 5 and 7). Studies on the amount of catalyst used in the oxidation of methyl phenyl sulfide (**10**) with POM hybrids **8a** showed that increasing the catalyst concentration increases the oxidation kinetics without significantly affecting the *ee* (see Figure S42 in the Supporting Information). As a result, the best reaction conditions found up to now to achieve a high yield of chiral sulfoxide product with a maximum *ee* are 0.4 mol-% of catalyst **8a**, a ratio of 1:3.2 substrate/hydrogen peroxide and 1 mL of $CHCl_3/CH_3CN$ (19:1, v/v) at –50 °C.

Recovery and Reutilization of Enantiopure Dendritic POM Hybrid 8a and the Non-Dendritic POM 9

Three catalytic cycles were performed at –50 °C to test the stability of the dendritic POM hybrid **8a** in comparison with the non-dendritic counterpart **9**. Methyl phenyl sulfide (**10**) was used as a model substrate for the catalyst recycling experiments. The catalyst was recovered by precipitation after each catalytic cycle and checked by ^1H and ^{31}P NMR before a new catalytic experiment was performed. The enantiopure dendritic POM hybrid **8a** selectively oxidized

Table 2. Recovery and reuse of enantiopure dendritic POM catalyst **8a** and the non-dendritic POM **9** in the oxidation of methyl phenyl sulfide (**10**) with H_2O_2 in three catalytic cycles.[a]

Entry	Catalyst	Solvent	Cycles	T [°C]	t [min][b]	Conversion [%][c]	Products [%] **13**	**16**	ee [%][d]	Cat. yield [%][e]
1	**8a**	$CDCl_3/CH_3CN$[f]	1	–50	120	94	85	9	13	85
2			2	–50	120	93	86	7	13	83
3			3	–50	120	93	86	7	13	80
4	**9**	$CDCl_3/CH_3CN$[f]	1	–50	30	100	70	30	4	82
5			2	–50	30	100	70	30	4	84
6			3	–50	30	100	71	29	4	84

[a] Reaction conditions: catalyst (0.4 mol-%), substrate (250 equiv.), 35% H_2O_2 (800 equiv.), solvent (1 mL). [b] The reactions were monitored by ^{1}H NMR spectroscopy. [c] The conversions were determined from the relative intensities of the ^{1}H NMR signals of the substrate and the product. [d] The enantiomeric excesses were determined by chiral HPLC using a Chiralcel ASH column, UV detection (254 nm), eluting with hexane/2-propanol (1:1) at a flow rate of 0.5 mL min^{-1}.[22] [e] The isolated yields of POM hybrids **8a** and **9**. [f] Mixture of $CHCl_3/CH_3CN$ (9:1, v/v).

the methyl phenyl sulfide (**10**) to the corresponding sulfoxide **13** with 93–94% conversion after 120 min and with 13% *ee* for each of the three catalytic cycles, as shown in Table 2. The isolated yields of the recovered catalyst were in the range of 80 to 85% (Table 2, entries 1–3). The reaction kinetics revealed no discernible loss of activity, selectivity or enantioselectivity over the three catalytic cycles. As shown in Table 2 (entries 4–6), the recyclability of the non-dendritic POM hybrid **9** was also investigated. Equally, no discernible loss of activity, selectivity or enantioselectivity was observed in the oxidation of sulfide **10** at –50 °C. However, a positive dendritic effect was noted in the selectivity to the sulfoxide and the enantioselectivity (Table 2, entries 1–3 vs. 4–6) as the dendritic POM hybrid **8a** was more selective and more stereoselective than its non-dendritic counterpart **9**. This can be explained by the fact that in contrast to the non-dendritic cation, the dendritic wedges around the active POM unit lower the reaction kinetics and probably keep the chiral structure close to the achiral POM.

Conclusions

We have assembled enantiopure dendritic polyoxometalate frameworks derived from phenyl- and cyclohexyl-based chiral tripodal amino dendrimers and acidic POM moieties. The solution CD, UV/Vis and VCD data of the phenyl-based dendritic POM hybrid **8a** indicate an induction of optical activity in the POM cluster. Interestingly, these compounds selectively oxidize sulfides to the corresponding chiral sulfoxides with up to 13% *ee*. These results are comparable to those reported in our preliminary communication in which a series of dendritic POM hybrids bearing monopodal dendritic amino cations oxidized sulfides with up to 14% *ee*.[15] The properties of the POM unit, especially their selectivity in the oxidation of sulfides to sulfoxides and their enantioselectivity, are sensitive to the structure of the dendritic cation as well as the reaction temperature. Despite the increased potential for electrostatic interactions with the triply charged tripods compared with the monocationic monopodal species, a lower charge-transfer interaction is evidenced. We believe that the *ee* values can be increased by elaboration of dendritic structures from enantiopure amines such as amino acids or binaphthyl-based amines with greater potential for chiral induction along with optimized concomitant electrostatic and charge-transfer interactions. The development of catalytic systems for this purpose is in progress.

Experimental Section

General Remarks: Reagent-grade tetrahydrofuran (THF) and diethyl ether were predried with Na foil and distilled from sodium–benzophenone under argon immediately before use. Acetonitrile (CH_3CN) was stirred under argon overnight over phosphorus pentoxide, distilled from sodium carbonate and stored under argon. Methylene chloride (CH_2Cl_2) was distilled from calcium hydride just before use. All other chemicals were used as received. The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at 25 °C with Bruker AC 250 FT (^{1}H: 250.13; ^{13}C: 62.91 MHz) and AC 200 FT spectrometers (^{1}H: 200.16; ^{13}C: 50.33; ^{31}P: 81.02 MHz) at CESAMO (Bordeaux, France). All chemical shifts are referenced to Me_4Si (TMS). Mass spectra were performed at the CESAMO with a QStar Elite mass spectrometer (Applied Biosystems). The instrument was equipped with an ESI source and spectra were recorded in the positive mode. The electrospray needle was maintained at 4500 V and operated at room temperature. Samples were introduced by injection through a 10 µL sample loop into a 200 µL min^{-1} flow of methanol from the LC pump. Elemental analyses were carried out at the Vernaison CNRS centre. The infrared spectra were recorded in KBr pellets with a FT-IR Paragon 1000 Perkin–Elmer spectrometer unless otherwise indicated. Organic oxidation products were identified by correlation with authentic samples. CD analyses were performed with a Jasco J-715 instrument using CH_3CN solutions in 1 cm quartz cells with a resolution of 2 nm, a step size of 0.2 nm, a response time of 2 s and scan speed of 20–50 nm min^{-1}, collecting 6–16 acquisitions. Electronic absorption spectra were recorded with a Varian Cary 5000 spectrometer. Steady-state emission spectra were recorded with a Fluorolog 212 (SPEX) or Fluorolog-3 fluorimeter and were corrected for instrumental function. The quantum yield Φ of a dendron was calculated by using the equation $\Phi = \Phi_r(I/I_r)(A_r/A)(\eta^2/\eta_r^2)$ in which r refers to the reference, I is the integrated emission intensity, A is the absorbance at the excitation wavelength and η is the refractive index of the solvent. An optically dilute solution of naphthalene in degassed ethanol ($\Phi_r = 0.21$)[23] was used as the reference.

IR and VCD spectra were recorded with a ThermoNicolet Nexus 670 FTIR spectrometer equipped with a VCD optical bench.[24] In this optical bench the light beam was focused by a BaF_2 lens (191 mm focal length) onto the sample through an optical filter (depending upon the studied spectral range) and was equipped with a BaF_2 wire grid polarizer (Specac) and a ZnSe photoelastic modulator (Hinds Instruments, Type II/ZS50). The light was then focused by a ZnSe lens (38.1 mm focal length) onto a 1×1 mm^2 Hg CdTe (ThermoNicolet, MCTA* E6032) detector. IR and VCD spectra were recorded at a resolution of 4 cm^{-1} by co-adding 50 and 72000 scans (24 h acquisition time), respectively. The sample was held in a fixed pathlength cell (200 μm) with KBr windows. IR and VCD spectra of the two opposite enantiomers of ligands **6a**·3HCl and tripodal dendritic POM hybrid **8a** were measured in CH_2Cl_2 at a concentration of 40 mM. Baseline corrections of the VCD spectra were performed by subtracting the two opposite enantiomer VCD spectra (recorded under the same experimental concentration) and dividing by two. In all experiments, the photoelastic modulator was adjusted for a maximum efficiency at 1400 cm^{-1}. Calculations were performed with the standard ThermoNicolet software using Happ and Genzel apodization, de-Haseth phase correction and a zero-filling factor of one. Calibration spectra were recorded using a birefringent plate (CdSe) and a second BaF_2 wire grid polarizer following the experimental procedure previously published.[25] Finally, the solvent absorption has been subtracted from the IR spectra presented. The geometry optimizations, vibrational frequencies, absorption and VCD intensities were calculated by using the Gaussian 03 program[26] on the SGI Altix XE 1300 computer of the Pôle Modélisation of the Institut des Sciences Moléculaires (University Bordeaux I). Calculations of the optimized geometry of the POM unit and of the (*R*)-(+) monopodal dendritic POM hybrid were performed by using density functional theory using the B_3PW_{91} functional and 6-31G* basis set, except on the tungsten atom for which the SDD basis set was used. Vibrational frequencies, IR and VCD intensities were calculated at the same level of theory utilizing the magnetic field perturbation method with gauge-invariant atomic orbitals.[27] For comparison with experiment, the calculated frequencies were scaled by 0.968 and the calculated intensities were converted into Lorentzian bands with half-widths of 7 cm^{-1}.

Synthesis of Enantiopure Tripodal Dendritic Amines 6a and 6b

General Procedure for the Synthesis of the Amino Benzoates 3a and 3b: A mixture of 1 equiv. of the corresponding enantiopure amine **1** (3 equiv.), methyl 4-(bromomethyl)benzoate (**2**; 1 equiv.) and *N*,*N*-diisopropyl(ethyl)amine (3 equiv.) in CH_3CN (15 mL) was stirred for 48 h at room temperature. After removal of the solvent under vacuum, the residue was extracted with diethyl ether, washed with water and dried with sodium sulfate. The solvent was removed under vacuum and the product was purified by silica gel column chromatography, eluting with petroleum ether/diethyl ether (9:1, v/v).

Phenylethylamino Benzoates (*R*)-(+)-3a and (*S*)-(–)-3a: Colourless oil; yield 3.51 g, 95%. ^{1}H NMR (250.13 MHz, $CDCl_3$, TMS): δ = 8.00 (d, 2 H, Ar), 7.32 (m, 7 H, Ar), 3.91 (s, 3 H, O-CH_3), 3.80 (q, 1 H, CH), 3.68 (dd, 2 H, CH_2-N), 1.39 (d, 3 H, CH_3) ppm. ^{13}C NMR (62.91 MHz, $CDCl_3$, TMS): δ = 167.1 (C=O), 146.2 (C_q, Ar), 145.4 (C_q, Ar), 129.7 (CH, Ar), 128.6 (CH, Ar), 128.0 (CH, Ar), 127.1 (CH, Ar), 126.7 (CH, Ar), 57.7 (CH), 52.1 (CH_2-N), 51.3 (O-CH_3), 24.6 (CH_3) ppm. MS (ESI): calcd. for $[M + H]^+$ 270.35; found 270.16. $C_{17}H_{19}NO_2$ (269.34): calcd. C 75.81, H 7.11, N 5.20; found C 76.46, H 7.23, N 5.43. (*R*)-(+)-**3a**: $[\alpha]_D^{20}$ = 30.0 (*c* = 10^{-2} g mL^{-1}, $CHCl_3$). CD (*c* = 3.8×10^{-5} M, CH_3CN): λ ($\Delta\varepsilon$) = 207 (–8.0), 218 (–2.3), 235 (3.3 M^{-1} cm^{-1}) nm. (*S*)-(–)-**3a**: $[\alpha]_D^{20}$ = –30.0 (*c* = 10^{-2} g mL^{-1}, $CHCl_3$). CD (*c* = 3.8×10^{-5} M, CH_3CN): λ ($\Delta\varepsilon$) = 207 (5.6), 218 (1.9), 235 (–3.6 M^{-1} cm^{-1}) nm.

Cyclohexylethylamino Benzoates (*R*)-(–)-3b and (*S*)-(+)-3b: White solid; yield 1.35 g, 98%. ^{1}H NMR (250.13 MHz, $CDCl_3$, TMS): δ = 7.97 (d, 2 H, Ar), 7.39 (d, 2 H, Ar), 3.89 (s, 3 H, O-CH_3), 3.81 (dd, 2 H, CH_2-N), 2.46 (q, 1 H, CH), 1.71 (m, 5 H, CH_2 and CH), 1.26 (m, 6 H, CH_2), 0.98 (d, 3 H, CH_3) ppm. ^{13}C NMR (62.91 MHz, $CDCl_3$, TMS): δ = 166.9 (C=O), 146.7 (C_q, Ar), 129.6 (CH, Ar), 128.5 (C_q, Ar), 127.9 (CH, Ar), 57.1 (CH), 52.1 (CH_2-N), 51.1 (O-CH_3), 42.9 (CH), 29.8, 28.0, 26.8, 26.6, 26.5 (CH_2), 16.7 (CH_3) ppm. MS (ESI): calcd. for $[M + H]^+$ 276.34; found 276.20. $C_{17}H_{25}NO_2$ (275.39): calcd. C 74.14, H 9.15, N 5.09; found C 73.78, H 9.08, N 4.89. (*R*)-(–)-**3b**: $[\alpha]_D^{20}$ = –18.7 (*c* = 10^{-2} g mL^{-1}, $CHCl_3$). CD (*c* = 1.7×10^{-5} M, CH_3CN): λ ($\Delta\varepsilon$) = 200 (5.1), 208 (–0.7), 227 (–2.9), 245 (4.7 M^{-1} cm^{-1}) nm. (*S*)-(+)-**3b**: $[\alpha]_D^{20}$ = 18.2 (*c* = 10^{-2} g mL^{-1}, $CHCl_3$). CD (*c* = 1.7×10^{-5} M, CH_3CN): λ ($\Delta\varepsilon$) = 200 (–5.1), 208 (+0.7), 227 (+2.9), 245 (–4.7 M^{-1} cm^{-1}) nm.

General Procedure for the Synthesis of the Amino Diallyl Carbinols 4a and 4b: In a Schlenk tube, allyl bromide (2.5 equiv.) was slowly added to a mixture of magnesium (3 equiv.) in anhydrous diethyl ether (25 mL) cooled to 0 °C. Then a solution of amino benzoate **3** (1 equiv.) in anhydrous diethyl ether (20 mL) was added to the reaction mixture at 0 °C. The mixture was stirred for 12 h at room temperature. Then a solution of 6 M NH_4Cl (10 equiv.) was added to the reaction mixture and the product was extracted with diethyl ether and dried with sodium sulfate. The solvent was removed under vacuum and the product purified by silica gel column chromatography, eluting with a petroleum ether/diethyl ether (7:3, v/v) to give the corresponding amino diallyl dicarbinol.

Phenylethylamino Diallyl Carbinols (*R*)-(+)-4a and (*S*)-(–)-4a: Colourless oil; yield 4.78 g, 96%. ^{1}H NMR (250.13 MHz, $CDCl_3$, TMS): δ = 7.34 (m, 9 H, Ar), 5.63 (m, 2 H, CH=CH_2), 5.12 (m, 4 H, CH=CH_2), 3.85 (q, 1 H, CH), 3.63 (dd, 2 H, CH_2-N), 2.61 (dd, 4 H, CH_2-CH=CH_2), 1.40 (d, 3 H, CH_3) ppm. ^{13}C NMR (62.91 MHz, $CDCl_3$, TMS): δ = 145.4 (C_q, Ar), 144.4 (C_q, Ar), 138.8 (C_q, Ar), 133.5 (CH=CH_2), 128.5 (CH, Ar), 128.1 (CH, Ar), 127.9 (CH, Ar), 126.9 (CH, Ar), 126.7 (CH, Ar), 125.4 (CH, Ar), 119.1 (CH=CH_2), 75.0 (C_q, C-OH), 57.8 (CH), 51.3 (CH_2-N), 46.8 (CH_2-CH=CH_2), 24.5 (CH_3) ppm. MS (ESI): calcd. for $[M + H]^+$ 322.47; found 322.22. $C_{22}H_{27}NO$ (321.46): calcd. C 82.20, H 8.47, N 4.36; found C 81.88, H 8.39, N 4.55. (*R*)-(+)-**4a**: $[\alpha]_D^{20}$ = 28.0 (*c* = 10^{-2} g mL^{-1}, $CHCl_3$). CD (*c* = 2.5×10^{-5} M, CH_3CN): λ ($\Delta\varepsilon$) = 216 (–0.6), 235 (+0.8 M^{-1} cm^{-1}) nm. (*S*)-(–)-**4a**: $[\alpha]_D^{20}$ = –28.0 (*c* = 10^{-2} g mL^{-1}, $CHCl_3$). CD (*c* = 2.5×10^{-5} M, CH_3CN): λ ($\Delta\varepsilon$) = 216 (0.7), 235 (–0.5 M^{-1} cm^{-1}) nm.

Cyclohexylethylamino Diallyl Carbinols (*R*)-(–)-4b and (*S*)-(+)-4b: Colourless oil; yield 2.29 g, 95%. ^{1}H NMR (250.13 MHz, $CDCl_3$, TMS): δ = 7.30 (m, 4 H, Ar), 5.59 (m, 2 H, CH=CH_2), 5.07 (m, 4 H, CH=CH_2), 3.73 (dd, 2 H, CH_2-N), 2.62 (dd, 4 H, CH_2-CH=CH_2), 2.43 (q, 1 H, CH), 1.68 (m, 5 H, CH_2 and CH), 1.23 (m, 6 H, CH_2), 0.96 (d, 3 H, CH_3) ppm. ^{13}C NMR (62.91 MHz, $CDCl_3$, TMS): δ = 144.3 (C_q, Ar), 139.3 (C_q, Ar), 133.6 (CH=CH_2), 127.9 (CH, Ar), 125.4 (CH, Ar), 119.1 (CH=CH_2), 75.0 (C_q-OH), 57.3 (CH), 51.2 (CH_2-N), 46.9 (CH_2-CH=CH_2), 42.9 (CH), 29.9, 28.0, 26.8, 26.7, 26.5 (CH_2), 16.8 (CH_3) ppm. MS (ESI): calcd. for $[M + H]^+$ 328.18; found 328.27. $C_{22}H_{33}NO$ (327.51): calcd. C 80.68, H 10.16, N 4.89; found C 79.24, H 9.87, N 4.28. (*R*)-(–)-**4b**: $[\alpha]_D^{20}$ = –20.2 (*c* = 10^{-2} g mL^{-1}, $CHCl_3$). (*S*)-(+)-**4b**: $[\alpha]_D^{20}$ = 20.7 (*c* = 10^{-2} g mL^{-1}, $CHCl_3$).

General Procedure for the Synthesis of the Hexaallyl Triamino Tricarbinols 5a and 5b: 2,4,6-Tris(bromomethyl)mesitylene (**7**; 1 equiv.) and K_2CO_3 (4 equiv.) were added to a solution of the corresponding enantiopure amino diallyl carbinol (3.6 equiv.) in CH_3CN (10 mL). The mixture was stirred for 16 h at reflux. After removal of the solvent under vacuum, the product was extracted with dichloromethane, washed with water and dried with sodium sulfate. The solvent was removed under vacuum and the product was purified by silica gel column chromatography, eluting with petroleum ether/diethyl ether (7:3, v/v).

Phenylethyl Hexaallyl Triamino Tricarbinols (*R*)-(+)-5a and (*S*)-(–)-5a: White solid; yield 1.0 g, 91%. ^{1}H NMR (250.13 MHz, $CDCl_3$, TMS): δ = 7.18 (m, 27 H, Ar), 5.55 (m, 6 H, $CH=CH_2$), 5.07 (m, 12 H, $CH=CH_2$), 3.86 (q, 3 H, CH), 3.58 (m, 6 H, CH_2-N), 3.46 (m, 6 H, CH_2-N), 2.55 (dd, 12 H, CH_2-$CH=CH_2$), 2.16 (s, 3 H, OH), 2.12 (s, 9 H, CH_3 Ar), 1.49 (d, 9 H, CH_3) ppm. ^{13}C NMR (62.91 MHz, $CDCl_3$, TMS): δ = 144.0 (C_q, Ar), 142.6 (C_q, Ar), 139.1 (C_q, Ar), 138.1 (C_q, Ar), 133.7 ($CH=CH_2$), 133.3 (C_q, Ar), 129.0 (CH, Ar), 128.5 (CH, Ar), 127.7 (CH, Ar), 126.6 (CH, Ar), 124.9 (CH, Ar), 119.0 ($CH=CH_2$), 75.1 (C_q, C-OH), 56.5 (CH), 52.6 (CH_2-N), 47.4 (CH_2-N), 46.8 (CH_2-$CH=CH_2$), 16.5 (CH_3), 12.6 (CH_3, Ar) ppm. MS (MALDI-TOF): calcd. for $[M - 2H]^+$ 1118.60; found 1118.75. $C_{78}H_{93}N_3O_3$ (1120.61): calcd. C 83.60, H 8.36; found C 83.46, H 8.38. (*R*)-(+)-**5a**: $[\alpha]_D^{20}$ = 60.0 (c = 10^{-2} g mL^{-1}, $CHCl_3$). CD (c = 3.5×10^{-6} M, CH_3CN): λ ($\Delta\varepsilon$) = 195 (3), 206 (–0.2), 223 (+1.7 M^{-1} cm^{-1}) nm. (*S*)-(–)-**5a**: $[\alpha]_D^{20}$ = –60.0 (c = 10^{-2} g mL^{-1}, $CHCl_3$). CD (c = 3.5×10^{-6} M, CH_3CN): λ ($\Delta\varepsilon$) = 195 (–2.4), 206 (0.6), 223 (–1.9 M^{-1} cm^{-1}) nm.

Cyclohexylethyl Hexaallyl Triamino Tricarbinols (*R*)-(–)-5b and (*S*)-(+)-5b: White solid; yield 1.04 g, 92%. ^{1}H NMR (250.13 MHz, $CDCl_3$, TMS): δ = 7.03 (m, 12 H, Ar), 5.36 (m, 6 H, $CH=CH_2$), 4.86 (m, 12 H, $CH=CH_2$), 3.41 (dd, 6 H, CH_2-N), 3.00 (dd, 6 H, CH_2-N), 2.46 (q, 3 H, CH), 2.38 (dd, 12 H, CH_2-$CH=CH_2$), 1.98 (s, 9 H, CH_3, Ar), 1.34 (m, 15 H, CH_2 and CH), 1.10 (m, 12 H, CH_2), 0.82 (d, 9 H, CH_3), 0.64 (m, 6 H, CH_2) ppm. ^{13}C NMR (62.91 MHz, $CDCl_3$, TMS): δ = 143.9 (C_q, Ar), 138.8 (C_q, Ar), 138.1 (C_q, Ar), 138.1 (C_q, Ar), 133.5 ($CH=CH_2$), 133.1 (C_q, Ar), 129.9 (CH, Ar), 124.7 (CH, Ar), 119.0 ($CH=CH_2$), 75.2 (C_q, C-OH), 57.1 (CH), 53.1 (CH_2-N), 48.4 (CH_2-N), 46.9 (CH_2-$CH=CH_2$), 41.4 (CH), 31.2 (CH_2), 30.6 (CH_2), 26.6 (CH_2), 26.5 (CH_2), 26.4 (CH_2), 16.0 (CH_3), 11.0 (CH_3, Ar) ppm. MS (MALDI-TOF): calcd. for $[M - 2H]^+$ 1136.74; found 1136.93. $C_{78}H_{111}N_3O_3$ (1138.76): calcd. C 82.27, H 9.82; found C 83.02, H 9.56. (*R*)-(–)-**5b**: $[\alpha]_D^{20}$ = –58.0 (c = 10^{-2} g mL^{-1}, $CHCl_3$). CD (c = 3.5×10^{-6} M, CH_3CN): λ ($\Delta\varepsilon$) = 197 (–9.3), 208 (–2.0), 225 (+3.3 M^{-1} cm^{-1}) nm. (*S*)-(+)-**5b**: $[\alpha]_D^{20}$ = 58.0 (c = 10^{-2} g mL^{-1}, $CHCl_3$). CD (c = 3.5×10^{-6} M, CH_3CN): λ ($\Delta\varepsilon$) = 197 (11.3), 208 (0.7), 225 (–3.8 M^{-1} cm^{-1}) nm.

General Procedure for the Synthesis of Hexa-*n*-propyl Triamino Tricarbinols 6a and 6b: Pd/C catalyst (10%) was added to a THF solution (20 mL) of the corresponding triamine hexaallyl tricarbinol **5** in a thick-walled tube capped with a Young's stopcock. The tube was flushed, pressurized with hydrogen, sealed and stirred at room temperature for 3 h. The solvent was removed under vacuum and the residue was extracted with dichloromethane and filtered through Celite. After evaporation of the solvent, the hexa-*n*-propyl triamino tricarbinol compound was purified by silica gel column chromatography with petroleum ether/diethyl ether (6:4, v/v) as eluent.

Phenylethyl Hexa-*n*-propyl Triamino Tricarbinols (*R*)-(+)-6a and (*S*)-(–)-6a: White solid; yield 2.6 g, 93%. ^{1}H NMR (250.13 MHz, $CDCl_3$, TMS): δ = 7.21 (m, 27 H, Ar), 3.85 (q, 3 H, CH), 3.62 (dd, 6 H, CH_2-N), 3.40 (m, 6 H, CH_2-N), 2.12 (s, 9 H, CH_3, Ar), 1.75 (m, 12 H, CH_2), 1.48 (m, 9 H, CH_3), 1.26 (m, 6 H, CH_2), 1.04 (m, 6 H, CH_2), 0.84 (t, 18 H, CH_3) ppm. ^{13}C NMR (62.91 MHz, $CDCl_3$, TMS): δ = 144.8 (C_q, Ar), 142.6 (C_q, Ar), 138.7 (C_q, Ar), 138.1 (C_q, Ar), 133.3 (C_q, Ar), 128.9 (CH, Ar), 128.5 (CH, Ar), 127.7 (CH, Ar), 126.6 (CH, Ar), 124.9 (CH, Ar), 77.1 (C_q, C-OH), 56.4 (CH), 52.6 (CH_2-N), 47.4 (CH_2-N), 45.3 (CH_2), 16.9 (CH_2), 16.5 (CH_3), 14.7 (CH_3), 12.6 (CH_3, Ar) ppm. MS (MALDI-TOF): calcd. for $[M - 2H]^+$ 1130.69; found 1130.60. $C_{78}H_{105}N_3O_3$ (1132.71): calcd. C 82.71, H 9.34; found C 81.64, H 9.34. (*R*)-(+)-**6a**: $[\alpha]_D^{20}$ = 60.0 (c = 10^{-2} g mL^{-1}, $CHCl_3$). CD (c = 3.6×10^{-6} M, CH_3CN): λ ($\Delta\varepsilon$) = 194 (34.5), 205 (–8.0), 222 (+18.0 M^{-1} cm^{-1}) nm. (*S*)-(–)-**6a**: $[\alpha]_D^{20}$ = –60.0 (c = 10^{-2} g mL^{-1}, $CHCl_3$). CD (c = 3.6×10^{-6} M, CH_3CN): λ ($\Delta\varepsilon$) = 194 (–36.0), 205 (6.0), 222 (–17.0 M^{-1} cm^{-1}) nm.

Cyclohexylethyl Hexa-*n*-propyl Triamino Tricarbinols (*R*)-(–)-6b and (*S*)-(+)-6b: White solid; yield 3.2 g, 92%. ^{1}H NMR (250.13 MHz, $CDCl_3$, TMS): δ = 7.04 (m, 12 H, Ar), 3.42 (dd, 6 H, CH_2-N), 3.01 (dd, 6 H, CH_2-N), 1.97 (m, 6 H, CH and OH), 1.79 (s, 9 H, CH_3, Ar), 1.56 (m, 15 H, CH_2 and CH), 1.34 (m, 12 H, CH_2), 1.12 (m, 12 H, CH_2), 0.86 (m, 6 H, CH_2), 0.72 (m, 6 H, CH_2), 0.64 (t, 18 H, CH_3) ppm. ^{13}C NMR (62.91 MHz, $CDCl_3$, TMS): δ = 144.5 (C_q, Ar), 138.3 (C_q, Ar), 138.0 (C_q, Ar), 133.1 (C_q, Ar), 129.7 (CH, Ar), 124.5 (CH, Ar), 77.1 (C_q, C-OH), 57.0 (CH), 53.1 (CH_2-N), 48.4 (CH_2-N), 45.4 (CH_2), 41.3 (CH), 31.2 (CH_2), 30.5 (CH_2), 26.6 (CH_2), 26.4 (CH_2), 16.7 (CH_2), 15.9 (CH_3), 14.4 (CH_3), 10.9 (CH_3, Ar) ppm. MS (MALDI-TOF): calcd. for $[M - 2H]^+$ 1148.83; found 1148.86. $C_{78}H_{123}N_3O_3$ (1150.85): calcd. C 81.41, H 10.77; found C 80.52, H 10.80. (*R*)-(–)-**6b**: $[\alpha]_D^{20}$ = –54.0 (c = 10^{-2} g mL^{-1}, $CHCl_3$). CD (c = 2.8×10^{-6} M, CH_3CN): λ ($\Delta\varepsilon$) = 197 (–16.0), 209 (–4.0), 224 (7.5 M^{-1} cm^{-1}) nm. (*S*)-(+)-**6b**: $[\alpha]_D^{20}$ = 54.0 (c = 10^{-2} g mL^{-1}, $CHCl_3$). CD (c = 2.8×10^{-6} M, CH_3CN): λ ($\Delta\varepsilon$) = 197 (19.0), 209 (4.0), 224 (–9.0 M^{-1} cm^{-1}) nm.

General Procedure for the Synthesis of the Enantiopure Dendritic POM Salts 8a and 8b: H_2O_2 (35% in water) was added to an aqueous solution of commercial heteropolyacid $H_3PW_{12}O_{40}$. The mixture was stirred at room temperature for 30 min and then a CH_2Cl_2 solution of the corresponding amino tricarbinol compound was added and the mixture was stirred for an additional hour. The organic layer was dried with Na_2SO_4 and the solvents evaporated under vacuum to provide the desired dendritic POM material as a light-yellow solid.

Tris(phenylethyl) Hexa-*n*-propyl Tricarbinol Dendritic POM Salts (*R*)-(+)-8a and (*S*)-(–)-8a: Yield 1.9 g, 86%. ^{1}H NMR (250.13 MHz, [D$_6$]acetone, TMS): δ = 7.56 (br., 27 H, Ar), 4.56 (br., 12 H, CH_2-N), 3.70 (br., 3 H, CH), 2.93 (br., 9 H, CH_3, Ar), 1.75 (br., 12 H, CH_2), 1.41 (br., 9 H, CH_3), 1.29 (br., 12 H, CH_2), 0.79 (br., 18 H, CH_3) ppm. ^{13}C NMR (62.91 MHz, CD_3CN, TMS): δ = 145.1 (C_q, Ar), 142.7 (C_q, Ar), 137.7 (C_q, Ar), 137.6 (C_q, Ar), 133.0 (C_q, Ar), 128.2 (CH, Ar), 127.9 (CH, Ar), 127.3 (CH, Ar), 126.1 (CH, Ar), 124.6 (CH, Ar), 75.8 (C_q, C-OH), 66.0 (CH), 51.8 (CH_2-N), 46.8 (CH_2-N), 45.0 (CH_2), 16.2 (CH_2), 15.6 (CH_3), 14.3 (CH_3), 13.6 (CH_3, Ar) ppm. ^{31}P NMR (81.02 MHz, [D$_6$]acetone, 85% H_3PO_4): δ = 3.26 (PO_4) ppm. IR (KBr): $\tilde{\nu}$ = 3489 (br, s), 2957 (s), 2928 (s), 2871 (s), 1701 (m), 1604 (m), 1455 (m), 1108 (m), 1081 (m, P–O), 1062 (m, P–O), 951 (m, W=O), 834 (m, O–O) cm^{-1}. $C_{78}H_{108}N_3O_{27}PW_4$ (2286.05): calcd. C 40.98, H 4.76, W 32.17; found C 41.85, H 4.80, W 34.70. (*R*)-(+)-**8a**: $[\alpha]_D^{20}$ = 9.0 (c = 10^{-2} g mL^{-1}, $CHCl_3$). CD (c = 5.0×10^{-6} M, CH_3CN): λ ($\Delta\varepsilon$) = 196 (10.0) 220 (6.0 M^{-1} cm^{-1}) nm. (*S*)-(–)-**8a**: $[\alpha]_D^{20}$ = –9.0 (c = 10^{-2} g mL^{-1}, $CHCl_3$). CD (c = 5.0×10^{-6} M, CH_3CN): λ ($\Delta\varepsilon$) = 196 (–12.9), 220 (–9.6 M^{-1} cm^{-1}) nm.

Tris(cyclohexylethyl) Hexa-*n*-propyl Tricarbinol Dendritic POM Salts (*R*)-(–)-8b and (*S*)-(+)-8b: Yield 2.3 g, 86%. ^{1}H NMR (250.13 MHz, $CDCl_3$, TMS): δ = 7.73 (br., 18 H, Ar), 7.31 (br., 18 H, Ar), 4.41 (br., 12 H, CH_2-N), 3.00 (br., 3 H, CH), 2.17 (br., 9 H, CH_3, Ar), 1.67 (br., 36 H, CH_3, Ar and CH_2), 1.13 (br., 27 H,

CH_3), 0.89 (br., 18 H, CH_2), 0.81 (br., 54 H, CH_3) ppm. ^{13}C NMR (62.91 MHz, $CDCl_3$, TMS): δ = 147.4 (C_q, Ar), 139.6 (C_q, Ar), 139.4 (C_q, Ar), 134.8 (C_q, Ar), 131.3 (CH, Ar), 126.8 (CH, Ar), 77.7 (C_q, C-OH), 58.6 (CH), 54.8 (CH_2-N), 50.1 (CH_2-N), 47.8 (CH_2), 47.4 (CH_2), 43.1 (CH), 33.0 (CH_2), 32.3 (CH_2), 28.2 (CH_2), 28.0 (CH_2), 18.4 (CH_2), 17.5 (CH_3), 15.9 (CH_3), 12.2 (CH_3, Ar) ppm. ^{31}P NMR (81.02 MHz, [D$_6$]acetone, 85% H_3PO_4): δ = 3.32 (PO_4) ppm. IR (KBr): $\tilde{\nu}$ = 3458 (br, s), 2965 (s), 2876 (s), 1701 (m), 1609 (m), 1465 (m), 1089 (m, P–O), 1058 (m, P–O), 964 (m, W=O), 843 (m, O–O) cm^{-1}. $C_{78}H_{126}N_3O_{27}PW_4$ (2304.20): calcd. C 40.66, H 5.51, W 31.92; found C 41.57, H 5.39, W 30.90. (*R*)-(–)-**8b**: $[\alpha]_{\mathrm{D}}^{20}$ = –12.0 (c = 10^{-2} gmL^{-1}, $CHCl_3$). CD (c = 5.0×10^{-6} M, CH_3CN): λ ($\Delta\varepsilon$) = 199 (7.0), 224 (12.9), 302 (–2.7 M^{-1} cm^{-1}) nm. (*S*)-(+)-**8b**: $[\alpha]_{\mathrm{D}}^{20}$ = +12.0 (c = 10^{-2} gmL^{-1}, $CHCl_3$). CD (c = 5.0×10^{-6} M, CH_3CN): λ ($\Delta\varepsilon$) = 199 (–8.4), 224 (–7.7), 302 (3.6 M^{-1} cm^{-1}) nm.

General Procedure for the Catalytic Oxidation Reactions with Enantiopure Dendritic POM Hybrids and for the Catalyst Recovery Experiments: The POM catalyst and the substrate (250 equiv.) were dissolved in solvent (1 mL). An aqueous solution of H_2O_2 (35% in water) was added to the reaction mixture at the appropriate temperature. The latter was stirred and monitored by ^{1}H NMR spectroscopy. Upon completion of the reaction, the organic layer was separated and concentrated under vacuum to about 1 mL. The catalyst was precipitated by addition of Et_2O (5 mL). The solid was filtered, washed with diethyl ether (3 × 2 mL) and dried under vacuum to yield the POM catalyst as a white solid (see Table 2), which was analysed by ^{1}H and ^{31}P NMR spectroscopy before its use in a new catalytic experiment. The diethyl ether solution was evaporated under vacuum and the oxidized product was purified by silica gel column chromatography (petroleum ether/diethyl ether, 1:9, v/v). The enantiomeric excesses were determined by chiral HPLC using a Chiralcel ASH column and UV detector (254 nm), eluting with hexane/2-propanol (1:1) at a flow rate of 0.5 mL min^{-1}. Retention times [min]: (*R*)-**13**: 22.5; (*S*)-**13**: 30.9; (*R*)-**14**: 21.4; (*S*)-**14**: 31.2; (*R*)-**15**: 28.5; (*S*)-**15**: 39.1.[21] The catalyst was recovered following the typical procedure and conditions described above for the first cycle, the organic solvent and the reactants being adjusted to the amount of catalyst used.

Supporting Information (see footnote on the first page of this article): NMR, IR, CD, fluorescence, and absorption spectra of amines and dendritic-POM compounds are given. Theoretical VCD spectra of the Venturello species $[PW_4O_{24}]^{3-}$ and detailed catalytic experiments data are also presented.

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