

1,1'-Binaphthyl-2-methylpyridinium-Based Peroxophosphotungstate Salts: Synthesis, Characterization, and Their Use as Oxidation Catalysts

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A series of 1,1'-binaphthyl-2-methylammonium and pyridinium salts **6**, **7**, and **8** was synthesized through the coupling reaction of 2-(bromomethyl)-1,1'-binaphthalene (**5**) with the dendritic tetraallyl pyridinedicarbinol dendron **2** as well as triethylamine and 4-*tert*-butylpyridine. Tetraallyl pyridinedicarbinol dendron **2** was prepared by allylation of commercially available diethyl pyridine-3,5-dicarboxylate (**1**). The allylation of **2** with allyltrimethylsilane in the presence of boron trifluoride was unsuccessful, as tetraallyl pyridinedicarbinol trifluoroboron adduct **3** was obtained instead of expected hexaallylpyridine compound **4**. The catalytic hydrogenation of allyl groups of the ammonium salt of **2**, namely, tetraallyl 1,1'-binaphthyl-2-methylpyridinium salt **6**, successfully led to the corresponding tetra-*n*-propyl 1,1'-binaphthyl-2-methylpyridinium salt **9**. The reaction between salts **7**, **8**, and **9** and the heteropolyacid H₃PW₁₂O₄₀ in the presence of a large

excess of hydrogen peroxide afforded the corresponding 1,1'-binaphthyl-2-methylammonium-based polyoxometalate salts **10**, **11**, and **12**, which contain a catalytically active trianionic [H₃PW₁₂O₄₀]³⁻ in the core. These binaphthyl-POM salts are soluble in commonly used organic solvents, and their IR and ³¹P NMR spectroscopic and elemental analysis data indicate the presence of the POM unit in the frameworks. These POM hybrids are efficient, recoverable, and reusable catalysts in the oxidation of thioanisole, cyclooctene, and cyclohexanol, with H₂O₂ as the oxidant. A study of the countercation effects indicated that the reaction kinetics and the selectivity are sensitive to the structure of the cation. Two cycles of catalytic reactions were performed without a discernible loss in activity.

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Introduction

Dendritic catalysts have been developed during the last decade as a result of their potential applications in various areas.^[1] The use of these macromolecules in molecular catalysis, pioneered by van Leeuwen,^[2b,2d] is an emerging field of research. Their large size and molecular weight allow the easy recovery of the catalysts, an essential feature for reaction efficiency, resources economy, and environmental concern.^[2] In this context, a variety of dendritic compounds have been synthesized and used in different domains such as supramolecular chemistry,^[3] nanosciences,^[1c] drug delivery,^[4] and catalysis.^[2,5] Some relevant examples based on polyoxometalates (POMs) have been reported recently.^[6] POMs are effective catalysts in the oxidation of organic substrates such as alkenes, alcohols, and sulfides. POMs^[7] are a large class of inorganic compounds with interesting

properties that make them particularly attractive for applications in homogeneous catalysis, in biology, in magnetism, in optic, and in medicine.^[8] The properties of anionic POMs, in dendritic POM frameworks, such as their stability, solubility, catalytic efficiency, their recycling potential, and overall their catalytic efficiency, are closely related to the structure of the dendrimer. For instance, dendritic POM compounds in which the POM unit is encapsulated into the dendritic structures were found to be more stable than their homologues functionalized at the periphery with POM units.^[6b] In addition, the quest for new catalytic and highly enantioselective processes is one of the most intensively studied areas in chemical synthesis. Chiral ligands are crucial asymmetric inductors in active metal-organic catalysts.^[9] Therefore, the design of suitable innovative chiral ligands for a particular application remains a formidable challenge. In this context, we are interested in the synthesis of chiral dendritic polyoxometalate catalysts for asymmetric transformations. Binaphthylamino-containing ligands were chosen to introduce chirality into the dendritic structure. After the discovery of practical asymmetric catalysis by Knowles^[10] and Kagan,^[11] optically active binaphthyl-containing ligands of C₂ symmetry were confirmed to be of the highest interest for asymmetric catalysis.^[12] From the development of binap [2,2'-bis(diphenylphosphino)-1,1'-bi-

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naphthyl] chemistry by Noyori in 1980,^[13] binaphthyl, bi-phenyl, and other biaryl groups have been used as chiral sources to introduce many highly efficient asymmetric environments.^[14] A fine-tuning of the stereoelectronic properties of such ligands is easy to perform through the use of either substituted and/or partially hydrogenated aromatic units, resulting in spectacular variations in the efficiency and selectivity of the corresponding catalysts. In the case of dendrimers, the dihedral angles of the biaryl ligands have proven to exert a decisive influence on the reaction kinetics and/or enantioselectivity.^[15] It was found that the size of the dendritic wedges influenced the reactivity and/or the enantioselectivity of the catalytic species. Similar effects might be anticipated in the case of catalytic systems incorporating chiral dendritic POMs. Contrary to chiral dendritic binaphthylphosphane ligands that have been extensively used in asymmetric catalysis, binaphthylamino-containing ligands have been only scarcely reported.^[16] Thus, pursuing our investigation on the synthesis and catalytic applications of dendritic POM frameworks, we report the synthesis and characterization of dendritic and nondendritic 1,1'-binaphthyl-2-methylammonium-based peroxophosphotungstate $[\text{H}_3\text{PW}_{12}\text{O}_{40}]^{3-}$ salts^[6d–6h,17] in their racemic form. These organic–inorganic hybrids have shown to be efficient, recoverable, and reusable catalysts in the oxidation of thioanisole, cyclooctene, and cyclohexanol with hydrogen peroxide. We have investigated the synthesis of the racemic mixtures of dendritic POM hybrids with the intention to extend this synthetic route to enantiomerically pure dendritic 1,1'-binaphthyl-based POM frameworks.

Results and Discussion

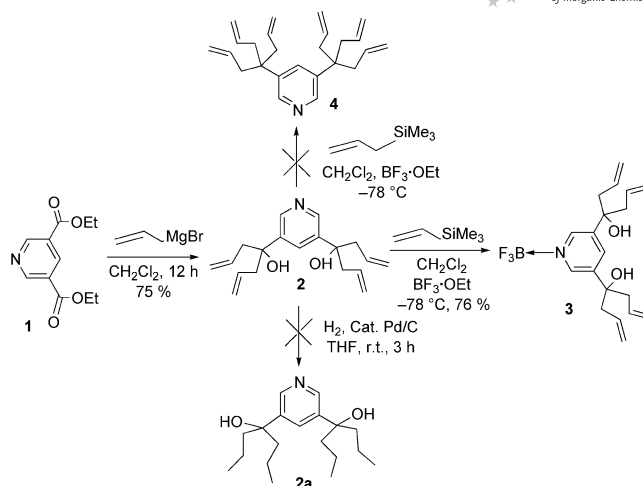
Synthesis and Spectroscopic Characterization of 1,1'-Binaphthyl-2-methylpyridinium and 1,1'-Binaphthyl-2-methyltriethylammonium Salts

The strategy used to prepare 1,1'-binaphthyl-2-methylpyridinium salts involved the coupling reaction of 2-(bromomethyl)-1,1'-binaphthalene (**5**)^[18] with designed dendritic pyridine compounds.

Synthesis of the Tetraallyl Pyridinedicarbinol Compound **2**

The synthesis of tetraallyl pyridine **2** was based on the allylation of commercially available diethyl pyridine-3,5-dicarboxylate (**1**) as summarized in Scheme 1. This strategy, recently reported by our group, enables a large-scale preparation of aryl polyallyl dendrons and dendrimers.^[19]

The reaction of **1** with allylmagnesium bromide led to tetraallyl pyridinedicarbinol compound **2** in 75% yield. The reaction of **2** with allyltrimethylsilane in the presence of $\text{Et}_2\text{O} \cdot \text{BF}_3$ led to tetraallyl dicarbinol boron adduct **3**. Expected hexaallylpyridine compound **4** was not obtained, even in the presence of a large excess of allyltrimethylsilane. The coordination of the pyridine moiety to the electron-withdrawing boron atom prevented the formation of the



Scheme 1. Syntheses of tetraallyl pyridinedicarbinol compounds **2** and **3**.

carbenium ion generated in the ionization process of the carbinol with boron trifluoride, thus avoiding the allylation reaction. Dendritic pyridine compound **2** and boron adduct **3** were characterized by standard NMR spectroscopic and mass spectrometric analysis. Whereas the aromatic region of **2** in its ^1H NMR spectrum exhibits two singlet at $\delta = 8.53$ (2H) and 7.74 ppm (1 H) assigned to the two different aromatic protons of the pyridine moieties, the spectrum of tetraallyl dicarbinol boron adduct **3** exhibits a broad doublet at $\delta = 8.77$ ppm and a singlet at $\delta = 8.30$ ppm assigned to the aromatic protons of the pyridine group. In addition, the ^1H NMR spectrum of boron adduct **3** shows a marked downfield shift of the two aromatic signals, probably due to the coordination of dendritic pyridine **2** (Lewis base) to boron trifluoride (Lewis acid). Further data in support of the formation of **3** were obtained by ^{11}B NMR (broad quadruplet at $\delta = 0.21$ ppm) and ^{19}F NMR (broad multiplet at -151.6 ppm) spectroscopy. Attempts to prepare *n*-propyl compound **2a** by catalytic hydrogenation of the allyl groups of **2** by using a Pd/C catalyst failed. Presumably, the pyridine moieties are potentially poisonous ligands for the Pd/C catalyst and possibly act as activity inhibitors. Thus, access to *n*-propyl pyridine derivatives was not possible under the reaction conditions. The mass spectrometric analysis of boron adduct **3** shows prominent peaks at $m/z = 300.18$ (calcd. 300.42) $[\text{M} - \text{BF}_3 + \text{H}]^+$ and 322.17 (calcd. 322.40) $[\text{M} - \text{BF}_3 + \text{Na}]^+$. For compound **2**, four prominent peaks were obtained in the mass spectrum at $m/z = 300.18$ (calcd. 300.42) $[\text{M} + \text{H}]^+$, 322.17 (calcd. 322.40) $[\text{M} + \text{Na}]^+$, 621.35 (calcd. 621.81) $[2\text{M} + \text{Na}]^+$, and 920.57 (calcd. 921.22) $[3\text{M} + \text{Na}]^+$. We assume these prominent peaks to be the mono(pyridine), bis(pyridine), and tris(pyridine) adducts of sodium. In contrast to **2**, the mass spectrum of tetraallylpyridine boron adduct **3** shows only an extra peak assigned to the bis(pyridine) adduct of sodium. In this case, the formation of the bis- and tris(pyridine) adducts of sodium in the mass spectrometer is probably avoided by the presence of the nitrogen–boron bond.

Synthesis of 1,1'-Binaphthyl-2-methylpyridinium and 1,1'-Binaphthyl-2-methyltriethylammonium Salts

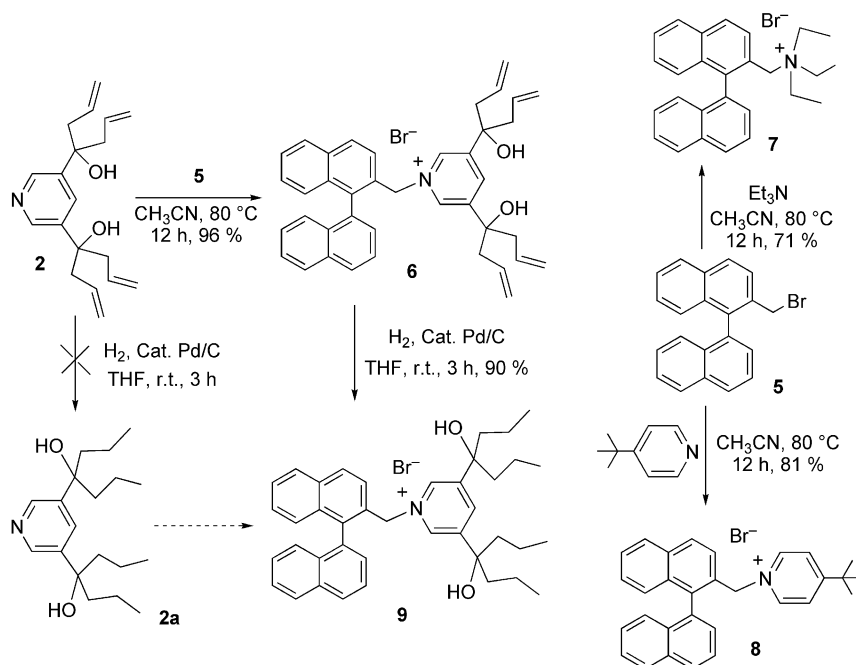
The 1,1'-binaphthyl-2-methylammonium salts were synthesized by using the strategy described in Scheme 2. The amino derivative (tetraallyl pyridinedicarbinol **2**, triethylamine, and *p*-*tert*-butylpyridine) was treated with 2-(bromomethyl)-1,1'-binaphthalene (**5**) and the corresponding 1,1'-binaphthylpyridinium compounds **6**, **7**, and **8** were obtained in 96, 71, and 81% yield, respectively. Triethylammonium salt **7** and *tert*-butylpyridinium salt **8** were synthesized to point out the effect of the dendritic cation on the anionic POM species in dendritic POM frameworks. The hydrogenation of **6** with the use of a Pd/C catalyst (10% Pd) gave the tetra-*n*-propyl 1,1'-binaphthyl-2-methylpyridinium salt **9** in 90% yield. Interestingly, whereas compound **2** was found to be inert towards hydrogen in the presence of the Pd/C catalyst, its ammonium derivative reacted with hydrogen under similar conditions to give **9**. Thus, the preparation of the ammonium salt is an essential step before the catalytic hydrogenation of alkenes groups, possibly because it avoids poisoning of the ligands by the Pd/C catalyst that could inhibit the hydrogenation reaction under these conditions (Scheme 2). Access to *n*-propyl-based pyridinium salts is essential, as they increase the solubility of POM frameworks in organic solvents, an important feature for their use in homogeneous catalysis. Characterization of all the compounds was carried out by using standard NMR spec-

troscopic techniques, as well as elemental analysis. The data are consistent with the structure proposed for these pyridinium salts.

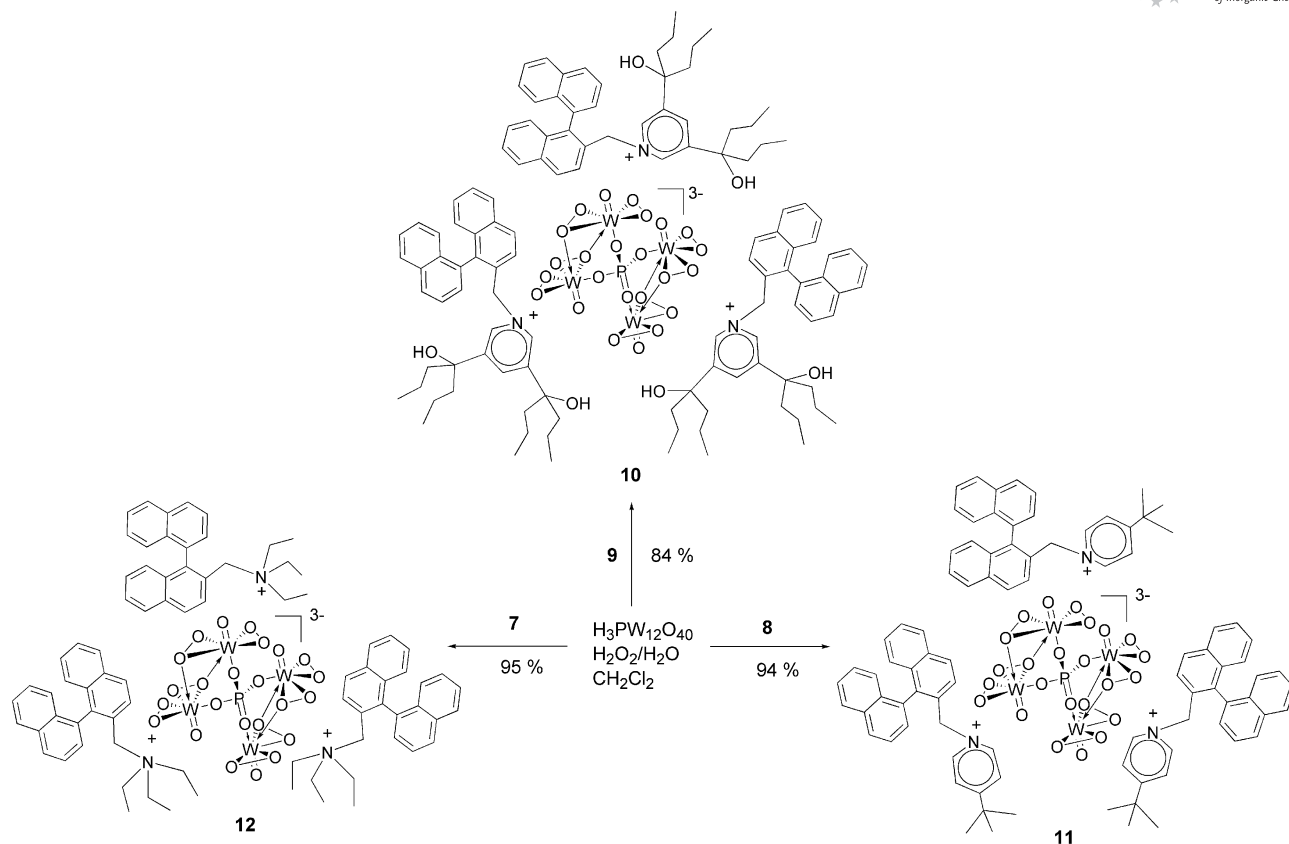
Synthesis and Characterization of 1,1'-Binaphthyl-2-methylpyridinium and 1,1'-Binaphthyl-2-methyltriethylammonium POM Salts

The 1,1'-binaphthyl-based POM-cored salts were synthesized according to the procedure involving peroxide-mediated decomposition of the heteropolyacid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in the presence of H_2O_2 to form the dinuclear peroxotungstate $[\text{WO}(\text{O}_2)_2(\text{H}_2\text{O})\text{O}]^{2-}$ and the trianionic peroxotungstate $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]^{3-}$. The latter reacts selectively with dendritic 1,1'-binaphthyl-2-methylpyridinium salt **9** as well as nondendritic pyridinium salt **8**, and triethylammonium salt **7** in a biphasic mixture of water and dichloromethane to give dendritic 1,1'-binaphthyl-2-methylpyridinium POM framework **10**, nondendritic *tert*-butylpyridinium POM salt **11**, and triethylammonium POM salt **12** containing the trianionic $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]^{3-}$ at the core (Scheme 3).

In the dendritic series, we only considered the synthesis and investigation of the catalytic properties of *n*-propyl 1,1'-binaphthylpyridinium POM salt **10**, because of its high solubility in organic solvents, contrary to insoluble polyepoxy-POM hybrids usually obtained from polyallyl ammonium salts. All the POM compounds described herein were isolated from the CH_2Cl_2 layer and fully characterized by



Scheme 2. Syntheses of the tetraarmed 1,1'-binaphthyl-2-methylpyridiniumdicarbinol salts **6** and **9**.



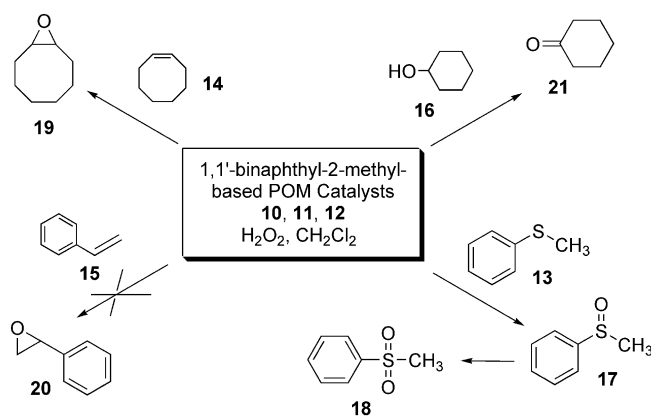
Scheme 3. Syntheses of 1,1'-binaphthyl-2-methylpyridinium POM salts **10** and **11** and 1,1'-binaphthyl-2-methyltriethylammonium POM salt **12**.

NMR spectroscopy, elemental analysis, and IR spectroscopy. The data obtained (see Experimental Section) are fully consistent with the proposed structures.

Oxidation of Sulfides, Alkenes, and Alcohols by Using 1,1'-Binaphthyl-Based POM Salts **10–12**

The performances of 1,1'-binaphthyl-based POM salts **10–12** were tested in the oxidation of thioanisole (**13**), cyclooctene (**14**), styrene (**15**), and cyclohexanol (**16**) (Scheme 4). The results reported in Tables 1 and 2 clearly show that compounds **10–12** oxidize **13** to corresponding sulfoxide **17** and sulfone **18**. The oxidation of **13** presumably gives, in a first step, sulfoxide **17**, which is in turn oxidized into sulfone **18** either through a POM-catalyzed process or directly by the action of hydrogen peroxide.

In order to optimize the selectivity of sulfoxide **17** formation, we carried out a series of experiments, which are summarized in Table 1. When **13** was treated with H_2O_2 at 30 °C without a catalyst, only 4% of sulfoxide was obtained after 5 d (Table 1, Entry 1). When the reaction was carried out in the presence of POM compound **12** and H_2O_2 (2.8 equiv.) it was completed within 1 h, with a selectivity of 31% for sulfoxide **17** and 69% for sulfone **18** (Table 1, Entry 2). By diminishing the oxidant/substrate ratio down to 1.1, we observed an increase in the selectivity of the sulfoxide (Table 1, Entries 3 and 4). The concentration of hy-



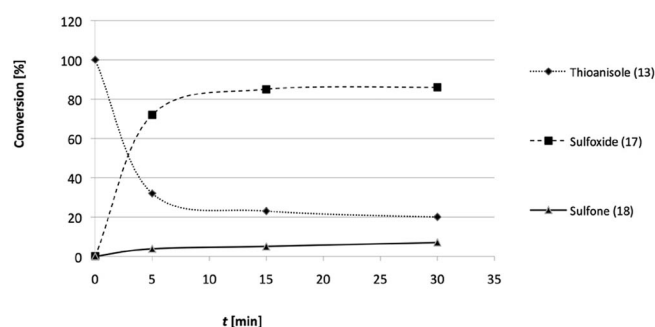
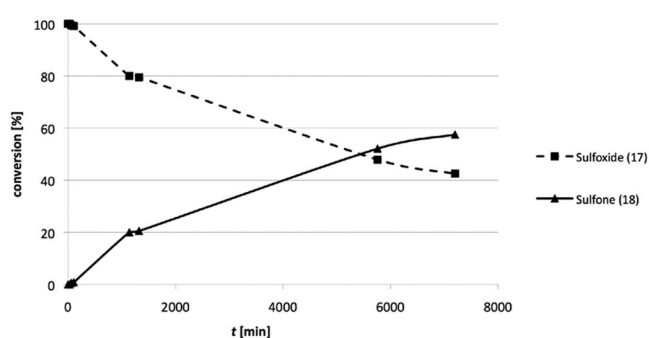
Scheme 4. Catalytic oxidation of thioanisole (**13**), cyclooctene (**14**), styrene (**15**) and cyclohexanol (**16**) with the use of 1,1'-binaphthyl-based POM salts **10–12**.

drogen peroxide had clearly a great effect on the kinetics and the selectivity of the reaction (Figure 1). For the oxidations mentioned so far, the POM was allowed to react with hydrogen peroxide for 30 min at room temperature before addition of the substrate. Following the evolution of the reaction mixture with time indicated that preactivation of POM catalyst **12** with H_2O_2 gave an active species. However, when the substrate was added immediately after hydrogen peroxide, an increase in the activity and selectivity was observed (Table 1, Entry 5).

Table 1. Catalytic oxidation of thioanisole (**13**) by using H₂O₂.^[a]

Entry	Catalyst	H ₂ O ₂ (equiv./substrate)	Time ^[c]	Conversion ^[d] [%]	Yield of 17 ^[d] [%]	Yield of 18 ^[d] [%]	50 % conversion [min]
1	—	1	5 d	4	4	—	—
2	12 ^[b]	2.8	60 min	100	31	69	—
3	12 ^[b]	2.4	60 min	100	56	44	5
4	12 ^[b]	1.1	210 min	99	82	17	7.5
5	12	1.1	30 min	80	75	5	3
6	11	2.8	35 min	80	42	38	4
7	11	1.1	75 min	98	90	8	9
8	10	2.8	65 min	100	53	47	13
9	10	1.1	75 min	96	92	4	13

[a] Catalytic conditions: in CH₂Cl₂ at 30 °C under vigorous stirring, reactants were added as follows: catalyst (0.4 mol-%), H₂O₂ (35% in H₂O), CH₂Cl₂, and substrate (1 mmol). [b] The catalysts were activated through reaction with H₂O₂ over 30 min at room temperature before addition of the substrate. [c] Nonoptimized reaction times. [d] Determined by GC analysis with an Alltech EC5 capillary column.

Figure 1. Kinetics of thioanisole (**13**) oxidation with 1,1'-biphenyl-2-methyltriethylammonium POM salts **12**.Figure 2. Kinetics of the oxidation of sulfoxide **17** into sulfone **18** with H₂O₂ without any POM salt.

This result indicates that the preactivation of the catalyst was not necessary, as half conversion of thioanisole was reached within 3 min without activation of the catalyst (Table 1, Entries 4 and 5).

To evaluate the ability of hydrogen peroxide to oxidize sulfoxide into sulfone without any assistance of the POM catalyst, we investigated the oxidation of sulfoxide **17** into sulfone **18** with H₂O₂ at 30 °C (Figure 2).^[20]

The reaction was found to be extremely slow, with only 0.8% (GC yield) of sulfone obtained after 90 min. This rate increased with barely a 20% conversion of sulfoxide **17** into sulfone **18** within 33 h, supporting the fact that there is no significant contribution of an uncatalyzed process to this over oxidation. Thus, when adapting the amount of oxidant to that of the substrate, the selectivity of sulfoxide **17** can be quite high (Table 1, Entries 7 and 9).

Table 2. Catalytic oxidation of cyclooctene (**14**), styrene (**15**), and cyclohexanol (**16**) using H₂O₂.^[a]

Entry	Catalyst	Substrate	Time	Conversion ^[c] [%]	Product, yield [%]	50 % conversion [h]
1	—	14	3 d	4	19 , 100	—
2	12 ^[b]	14	48 h	100	19 , 100	5
3	11 ^[b]	14	72 h	100	19 , 100	13
4	11	14	49 h	83	19 , 100	13
5	10 ^[b]	14	24 h	100	19 , 100	11.5
6	10	14	49 h	60	19 , 100	—
7	12	15	8 d	—	20 , 0	—
8	11	15	8 d	—	20 , 0	—
9	10	15	8 d	—	20 , 0	—
10	11	16	3 d	69	21 , 100	9.5
11	10	16	3 d	55	21 , 100	48

[a] All catalytic reactions were performed in CH₂Cl₂ at 30 °C under vigorous stirring. The reactants were added as follows: catalyst (0.4 mol-%), H₂O₂ (35% in H₂O, 3.2 equiv./substrate), CH₂Cl₂, and then the substrate (1 mmol). [b] The catalysts were activated through reaction with H₂O₂ over 30 min at room temperature before addition of the substrate. [c] Determined by GC with an Alltech EC5 capillary column.

Dendritic 1,1'-binaphthyl-2-methylpyridinium POM **10** and nondendritic *tert*-butylpyridinium POM salt **11** also oxidized thioanisole into sulfoxide with good selectivities (90 to 92%; Table 1, Entries 7 and 9). In comparison to nondendritic POM catalysts **11** and **12**, the highest selectivity of sulfoxide **17** (92%; Table 1, Entry 9) was obtained with dendritic compound **10**. Interestingly, a discernible negative dendritic effect was observed on the reaction kinetics, as 13 min were needed to convert 50% of the substrate with dendritic catalyst **10** (Table 1, Entry 9), whereas half conversion of sulfide **13** was reached after 9 min in the case of **11** (Table 1, Entry 7). This negative effect is probably caused by the increased bulk around the catalytic center. Two cycles of catalytic reactions were performed with the use of **13** and dendritic catalyst **10**, without a discernible loss in activity or selectivity.

We also performed the oxidation of cyclooctene (**14**), styrene (**15**), and cyclohexanol (**16**) with POM salts **10–12** with the use of H₂O₂ as oxidant (Scheme 4). The experimental results summarized in Table 2 clearly showed the efficiency of all the binaphthyl-POM salts in the oxidation of cyclooctene (**14**) into corresponding epoxide **19** (Table 2, Entries 2–6). Styrene (**15**) was not oxidized into epoxystyrene (**20**) with this series of catalysts (Table 2, Entries 7–9), whereas cyclohexanol (**16**) led to corresponding ketone **21** with 55 to 69% conversion after 3 d with POM salts **11** and **10**. In comparison to our initial experiments investigating the properties of POM-cored dendrimers, especially their solubility and catalytic efficiency,^[6g–6h] the results described here with a new series of POM compounds confirm that the microenvironment of the POM unit has a great effect on its properties.

Conclusions

Dendritic and nondendritic 1,1'-binaphthyl-2-methylpyridinium- and 1,1'-binaphthyl-2-methyltriethylammonium-based POM salts were prepared in their racemic form and used in the oxidation of thioanisole, cyclooctene, and cyclohexanol with hydrogen peroxide. The corresponding sulfoxide, epoxide, and ketone, respectively, were obtained with good to excellent conversion and selectivity. Among these POM catalysts, it was observed that the reaction kinetics and the selectivity were sensitive to the structure of the cation. Despite the racemic form of these POM hybrids, we have set up an efficient protocol to recoverable 1,1'-binaphthyl-2-methyl-based polyoxometalate frameworks and showed their efficiency in the oxidation of a variety of substrates such as sulfides, alkenes, and alcohols. We believe that this synthetic procedure represents a promising approach to enantiopure dendritic 1,1'-binaphthyl-2-methyl-based POM salts that should be used as recoverable and highly enantioselective catalysts in oxidation reactions.^[21] Further work in this area 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 an argon atmosphere immediately prior to use. Acetonitrile (CH₃CN) was stirred under an argon atmosphere overnight over phosphorus pentoxide, distilled from sodium carbonate, and stored under an argon atmosphere. Methylene chloride (CH₂Cl₂) was distilled from calcium hydride just before use. All other chemicals were used as received. The ¹H, ¹³C, ³¹P, ¹¹B, and ¹⁹F NMR spectra were recorded at 25 °C with a Bruker AC, 400 FT spectrometer (¹H 250.13, ¹³C 62.91 MHz), 250 FT spectrometer (¹H 250.13, ¹³C 62.91 MHz), or a Bruker AC 200 FT spectrometer (¹H 200.16, ¹³C 50.33, ³¹P 81.02 MHz) at the CESAMO (Bordeaux, France). All chemical shifts are referenced to Me₄Si (TMS). Mass spectra were performed by the CESAMO with a QStar Elite mass spectrometer (Applied Biosystems). The instrument is 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 Vernaion CNRS center. The infrared spectra were recorded in KBr pellets with an FTIR Paragon 1000 Perkin-Elmer spectrometer, unless otherwise indicated. Organic oxidation products were identified by correlation to authentic samples. The synthesis and characterization of 2-(bromomethyl)-1,1'-binaphthalene (**5**) were performed according to a literature procedure.^[18]

Tetraallyl Pyridinedicarbinol 2: In a Schlenk tube, a solution of diethyl pyridine-3,5-dicarboxylate (**1**) (3.53 g, 15.84 mmol) in CH₂Cl₂ (10 mL) was added to a Schlenk tube containing allylmagnesium bromide (1 M in diethyl ether, 79.2 mL, 79.2 mmol) at 0 °C. After 12 h stirring at room temperature, a solution of NH₄Cl (6 M, 30 mL) was added to the reaction mixture. The product was extracted with CH₂Cl₂ (3 × 30 mL), and the organic phase was dried with sodium sulfate. The solvent was removed under vacuum, and the product was purified by column chromatography on silica gel (petroleum ether/diethyl ether, 1:1) to afford **2** as an orange oil. Yield: 3.6 g (75%). ¹H NMR (250.13 MHz, CDCl₃): δ = 8.53 (s, 2 H, *o*-H pyridine), 7.74 (s, 1 H, *p*-H pyridine), 5.55 (m, 4 H, CH allyl), 5.08 (m, 8 H, CH₂ allyl), 2.65 (m, 8 H, CH₂ allyl) ppm. ¹³C NMR (62.91 MHz, CDCl₃): δ = 145.3 (CH, pyridine), 140.6 (C_q, pyridine), 132.7 (CH=CH₂), 131.3 (C, pyridine), 119.7 (CH=CH₂), 74.2 (C-OH), 46.7 (CH₂) ppm. MS (ESI): *m/z* = 300.18 [M]⁺, 322.17 [M + Na]⁺, 621.35 [2M + Na]⁺, 920.57 [3M + Na]⁺. C₁₉H₂₅NO₂ (299.41): calcd. C 76.22, H 8.42; found C 76.01, H 8.58.

Pyridinedicarbinol Boron Adduct 3: In a Schlenk tube, allyltrimethylsilane (3.81 g, 33.40 mmol, 5.3 mL) was dissolved in anhydrous CH₂Cl₂ (8 mL), and the solution was cooled to -78 °C. Then, a solution of BF₃ (1 M in Et₂O, 33.40 mmol, 33.40 mL) was added to the reaction mixture. Then, a solution of **2** (1 g, 3.34 mmol) in CH₂Cl₂ (8 mL), also cooled to -78 °C, was added to the reaction mixture. After 12 h stirring, the solution was evaporated under vacuum and Et₂O (10 mL) was added. The product was extracted with CH₂Cl₂ (3 × 20 mL) and dried with sodium sulfate. The solvent was removed under vacuum, and the product was purified by column chromatography on silica gel (petroleum ether/diethyl ether, 9:1) to give an orange oil. Yield: 878 mg (71%). ¹H NMR (250.13 MHz, CDCl₃): δ = 8.77 (br. d, ³J_{H,B} = 1.5 Hz, 2 H, *o*-H pyridine), 8.30 (s, 1 H, *p*-H pyridine), 5.64 (m, 6 H, CH=CH₂), 5.11 (m, 12 H, CH=CH₂), 2.65 (m, 12 H, CH₂) ppm. ¹³C NMR (62.91 MHz, CDCl₃): δ = 146.5 (CH, pyridine), 141.6 (C_q, pyridine), 138.2 (CH, pyridine), 131.5 (CH=CH₂), 121.7 (CH=CH₂), 74.8 (C-OH), 46.4 (CH₂) ppm. ¹¹B NMR (128.38 MHz, CDCl₃): δ = 0.21 (br. q, BF₃) ppm. ¹⁹F NMR (376.46 MHz, CDCl₃): δ = -151.6 (br. m, BF₃)

ppm. MS (ESI): m/z = 300.18 $[M + H - BF_3]^+$, 322.17 $[M + Na - BF_3]^+$. $C_{19}H_{25}BF_3NO_2$ (367.21): calcd. C 62.15, H 6.86; found C 62.20, H 6.89.

Tetraallyl 1,1'-Binaphthyl-2-methylpyridiniumdicarbinol Salt 6: In a Schlenk tube, a mixture of **5** (0.290 g, 0.84 mmol) and the corresponding amine in acetonitrile (5 mL, 0.500 g, 1.67 mmol) was stirred for 12 h at 80 °C. After removal of the solvent under vacuum, the residue was washed with diethyl ether and dried under vacuum to afford the ammonium salt as a brown light solid. Yield: 515 mg (96%). 1H NMR (250.13 MHz, $CDCl_3$): δ = 8.70 (s, 1 H, *p*-H pyridine), 8.62 (s, 2 H, *o*-H pyridine), 8.20–7.02 (m, binaphthyl), 5.78 (dd, 2 H, CH_2 -N), 5.61 (m, 4 H, $CH=CH_2$), 4.96 (m, 8 H, $CH=CH_2$), 2.56 (br. m, 8 H, CH_2) ppm. ^{13}C NMR (62.91 MHz, $CDCl_3$): δ = 147.05 (C_q , pyridine), 140.81 (C_q , binaphthyl), 140.37 (CH, pyridine), 138.74 (CH, pyridine), 134.14 (C_q , binaphthyl), 133.72 (C_q , binaphthyl), 133.62 (C_q , binaphthyl), 133.01 (C_q , binaphthyl), 132.99 (C_q , binaphthyl), 132.30 ($CH=CH_2$), 132.29 (C_q , binaphthyl), 129.84 (CH, binaphthyl), 129.27 (CH, binaphthyl), 128.86 (CH, binaphthyl), 128.55 (CH, binaphthyl), 128.19 (CH, binaphthyl), 127.43 (CH, binaphthyl), 127.22 (CH, binaphthyl), 127.12 (CH, binaphthyl), 126.70 (CH, binaphthyl), 127.32 (CH, binaphthyl), 125.88 (CH, binaphthyl), 125.40 (CH, binaphthyl), 125.07 (CH, binaphthyl), 119.91 ($CH=CH_2$), 75.14 (C_q -OH), 63.00 (CH_2 -N), 45.84 (CH_2) ppm. MS (ESI): m/z = 566.30 $[M - Br]^+$, 567.31 $[M + H - Br]^+$. $C_{40}H_{40}BrN$ (646.66): calcd. C 74.29, H 6.13, N 2.17; found C 74.13, H 6.05, N 2.03.

1,1'-Binaphthyl 2-Methyltriethylammonium Salt 7: In a Schlenk tube, **5** (0.717 g, 2.06 mmol) was dissolved in triethylamine (4 mL) and stirred for 12 h at 80 °C. After removal of the solvent under vacuum, the residue was washed with diethyl ether and dried under vacuum to afford the corresponding ammonium salt as a brown light solid. Yield: 659 mg (71%). 1H NMR (250.13 MHz, $CDCl_3$): δ = 7.97–7.09 (m, binaphthyl), 4.62, (d, 2 H, CH_2 -N), 3.24 (m, 6 H, CH_2), 0.91 (t, 9 H, CH_3) ppm. ^{13}C NMR (62.91 MHz, $CDCl_3$): δ = 141.8–123.9 (binaphthyl), 59.1 (CH_2 -N), 53.7 (CH_2 -N), 46.25 (CH_2), 10.2 (CH_3) ppm. MS (ESI): m/z = 368.22 $[M - Br]^+$, 369.24 $[M + H - Br]^+$. $C_{27}H_{30}BrN$ (448.44): calcd. C 72.32, H 6.74, N 3.12; found C 71.98, H 6.56, N 3.01.

1,1'-Binaphthyl 2-Methylpyridinium Salt 8: In a Schlenk tube, **5** (0.524 g, 1.51 mmol) was dissolved in acetonitrile (2 mL) with 4-*tert*-butylpyridine (0.45 mL, 0.408 g, 3.02 mmol) and stirred for 12 h at 80 °C. After removal of the solvent under vacuum, the residue was washed with petroleum ether and dried under vacuum to afford ammonium salt **8** as a brown light solid. Yield: 580 mg (81%). 1H NMR (250.13 MHz, $CDCl_3$): δ = 8.41 (d, CH_{pyr}), 8.18 (d, CH_{pyr}), 8.00–6.962 (m, binaphthyl), 6.10 (dd, CH_2 -N), 1.316 (s, 9 H, CH_3) ppm. ^{13}C NMR (62.91 MHz, $CDCl_3$): δ = 170.0 (C_{pyr}), 143.7 (CH_{pyr}), 138.98 (CH_{pyr}), 134.4–123.8 (binaphthyl), 62.76 (CH_2 -N), 36.2 (C_q , *t*Bu), 29.89 (CH_3) ppm. MS (ESI): m/z = 402.20 $[M - Br]^+$, 403.22 $[M + H - Br]^+$. $C_{30}H_{28}BrN$ (482.46): calcd. C 74.69, H 5.85, N 2.90; found C 74.60, H 5.74, N 2.81.

Tetra-*n*-propyl 1,1'-Binaphthyl-2-methylpyridiniumdicarbinol Salt 9: 10% Pd/C catalyst (35 mg, 0.324 mmol) was added to a THF solution (5 mL) of ammonium compound **6** (0.350 g, 0.504 mmol) in a thick-walled tube capped with a Young's stopcock. The tube was flushed, pressurized with hydrogen, and sealed, and the mixture was 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 dichloromethane, **9** was obtained as a brown light solid. Yield: 315 mg (90%). 1H NMR (250.13 MHz, $CDCl_3$): δ = 8.95 (s, 1 H, CH_{pyr}), 8.63 (s, 2

H, CH_{pyr}), 8.95–6.95 (m, binaphthyl), 5.74 (br. m, CH_2 -N), 1.72 (br., CH and CH_2), 1.21 (br., CH_2), 0.76 (br., CH_3) ppm. ^{13}C NMR (62.91 MHz, $CDCl_3$): δ = 150.4–125.0 (C_{pyr} and $C_{binaphthyl}$), 75.8 (C -OH), 63.2 (CH_2 -N), 43.9 (CH_2), 16.8 (CH_2), 14.3 (CH_3) ppm. MS (ESI): m/z = 574.20 $[M - Br]^+$. $C_{40}H_{48}BrNO_2$ (654.73): calcd. C 73.38, H 7.39, N 2.14; found C 73.46, H 7.18, N 2.06.

Dendritic *n*-Propyl 1,1'-Binaphthyl-2-methylpyridinium POM 10: H_2O_2 (35% in water, 14 mL) was added to a solution of commercial heteropolyacid $H_3PW_{12}O_{40}$ (804 mg, 0.280 mmol) in water (0.500 mL). The mixture was stirred at room temperature for 30 min. A solution of ammonium bromide salt **9** (450 mg, 0.730 mmol) in CH_2Cl_2 (3 mL) was added, and the mixture was stirred for 40 min. The CH_2Cl_2 layer was washed with water and dried with sodium sulfate. The product was obtained by removing the solvent under vacuum to give a yellow solid. Yield: 652 mg (84%). 1H NMR (300 MHz, $CDCl_3$, broad signal): δ = 9.00 (br., CH_{pyr}), 8.44 (br., CH_{pyr}), 8.13–6.96 (br. m, binaphthyl), 5.83 (br., CH_2 -N), 1.67 (br., CH and CH_2), 1.25 (br., CH_2), 0.79 (br., CH_3) ppm. ^{13}C NMR (62.91 MHz, $CDCl_3$): δ = 148.2 (C_{pyr}), 139.96 (C_{pyr}), 139.06 (C_{pyr}), 134.5–125.0 (binaphthyl), 75.05 (C -OH), 63.74 (CH_2 -N), 42.94 (CH_2), 16.7 (CH_2), 14.4 (CH_3) ppm. ^{31}P NMR (81.02 MHz, $CDCl_3$): δ = 2.97 (br., PO_4) ppm. MS (MALDI-TOF): m/z = 2868.31 $[M]^+$. FTIR (KBr): $\tilde{\nu}$ = 1094.72 (P–O), 944.42 (W=O), 864.05 (O–O), 605.32 and 525.46 $\{[W(O)_2]_{s,as}\}$ cm^{-1} . $C_{120}H_{144}N_3O_{30}PW_4$ (2874.83): calcd. C 50.14, H 5.05, P 1.08, W 25.58; found C 50.02, H 4.85, P 1.1, W 25.82.

1,1'-Binaphthyl-2-methylpyridinium POM 11: H_2O_2 (35% in water, 8.0 mL) was added to a solution of commercial heteropolyacid $H_3PW_{12}O_{40}$ (465 mg, 0.161 mmol) in water (0.300 mL). The mixture was stirred at room temperature for 30 min. A solution of ammonium bromide salt **8** (200 mg, 0.420 mmol) in CH_2Cl_2 (3 mL) was added, and the mixture was stirred for 40 min. The CH_2Cl_2 layer was washed with water and dried with sodium sulfate. The product was obtained by removing the solvent under vacuum to give a yellow solid. Yield: 356 mg (94%). 1H NMR (200 MHz, $CDCl_3$, broad signal): δ = 9.15 (br., CH_{pyr}), 8.70 (br., CH_{pyr}), 8.22–7.07 (binaphthyl), 5.95 (br. m, CH_2 -N), 0.99 (s, CH_3) ppm. ^{13}C NMR (62.91 MHz, $CDCl_3$): δ = 143.6 (C_{pyr}), 138.83 (C_{pyr}), 134.4–123.9 (binaphthyl), 63.10 (CH_2 -N), 36.0 (C_q , *t*Bu), 29.8 (CH_3) ppm. ^{31}P NMR (81.02 MHz, $CDCl_3$, broad signal): δ = 3.06 (br., PO_4) ppm. FTIR (KBr): $\tilde{\nu}$ = 1111.96 and 1053.06 (P–O), 954.33 (W=O), 830.66 (O–O), 590.95 and 508.25 $\{[W(O)_2]_{s,as}\}$ cm^{-1} . $C_{90}H_{84}N_3O_{24}PW_4$ (2357.99): calcd. C 45.84, H 3.59, P 1.31, W 31.19; found C 45.66, H 3.48, P 1.1, W 31.40.

1,1'-Binaphthyl-2-methyltriethylammonium POM 12: H_2O_2 (35% in water, 8.0 mL) was added to a solution of commercial heteropolyacid $H_3PW_{12}O_{40}$ (498 mg, 0.173 mmol) in water (0.300). The mixture was stirred at room temperature for 30 min. A solution of ammonium bromide salt **7** (200 mg, 0.450 mmol) in CH_2Cl_2 (3 mL) was added, and the mixture was stirred for 40 min. The CH_2Cl_2 layer was washed with water and dried with sodium sulfate. The product was obtained by removing the solvent under vacuum to give a yellow solid. Yield: 370 mg (95%). 1H NMR (200 MHz, $CDCl_3$): δ = 7.92–7.04 (binaphthyl), 4.51 (br. m, CH_2 -N), 3.12 (br., CH_2 -N), 0.86 (br., 9 H, CH_3) ppm. ^{13}C NMR (62.91 MHz, $CDCl_3$): δ = 141.5–124.7 (binaphthyl), 58.9 (CH_2 -N), 53.89 (CH_2 -N), 8.21 (CH_3) ppm. ^{31}P NMR (81.02 MHz, $CDCl_3$): δ = 2.77 (PO_4) ppm. FTIR (KBr): $\tilde{\nu}$ = 1117.28 and 1048.59 (P–O), 956.44 (W=O), 828.02 (O–O), 603.26 and 523.04 $\{[W(O)_2]_{s,as}\}$ cm^{-1} . $C_{81}H_{90}N_3O_{24}PW_4$ (2255.94): calcd. C 43.12, H 4.02, P 1.37, W 32.60; found C 42.87, H 3.97, P 2.03, W 32.11.

General Procedure for the Catalytic Oxidation Reactions with the Use of Ammonium POM Salts 10–12 and Catalyst Recovery Experiments: To a CH_2Cl_2 solution of the catalyst (0.4 mol-%) was added the substrate (1 mmol) and the corresponding equivalents of 35% H_2O_2 . The reaction mixture was stirred at 30 °C and monitored by GC with an Alltech EC5 capillary column. Upon completion, the CH_2Cl_2 layer was separated and concentrated under vacuum. The catalyst was precipitated by addition of Et_2O . The solid was filtered and washed with Et_2O , giving quantitatively the POM catalyst. The catalyst recycling was carried out following the typical procedure and conditions described above for the first cycle, CH_2Cl_2 and reactants being adjusted to the amount of catalyst used. The reaction was performed with thioanisole (**13**) by using dried recovered dendritic compound **10**. The catalyst was completely dissolved in CH_2Cl_2 , and the reactants were added to the solution. After completion, the kinetics remained unchanged, as the data collected were comparable to that summarized in Table 1 for the first cycle. The catalyst was recovered and checked by ^1H and ^{31}P NMR spectroscopy.

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