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# Chiral dioxomolybdenum(VI) complexes for enantioselective alkene epoxidation

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Dedicated to Professor Dr Henri Brunner on the occasion of his 65th birthday

**Abstract**

Chiral dioxomolybdenum(VI) complexes of the type $MoO_2Cl_2(L^*)$ ($L^*$ = oxime), $MoO_2(THF)_2L^*$ ($L^*$ = *cis*-*p*-menthane-3,8-diol) and $MoO_2Cl(THF)L^*$ ($L^*$ = 8-phenylthioneomenthol and 8-phenylthioisoneomenthol) have been prepared in good yields by reacting $MoO_2Cl_2(THF)_2$ with the appropriate chiral organic bidentate O,O-, O,N- and O,S-ligands. The complexes were characterised by solution NMR ($^1H$, $^{13}C$, $^{95}Mo$) and IR spectroscopy as well as elementary analysis, and were evaluated as catalysts in solution for the asymmetric epoxidation of *cis*-β-methylstyrene by *tert*-butylhydroperoxide (TBHP). The *cis*-diol complex shows high catalytic activity and enantiomeric excesses of up to 25%. An attempt was made to immobilise the complex $MoO_2(THF)Cl[(-)$-8-phenylthioneomenthol] within the channels of MCM-41 mesoporous silica by using a tethering ligand [$L = NC(CH_2)_3Si(OEt)_3$]. The material was characterised by powder X-ray diffraction (XRD), IR spectroscopy and magic-angle-spinning (MAS) NMR ($^{13}C$, $^{29}Si$). Catalytic examinations demonstrated that it was active in the epoxidation of cyclooctene by TBHP. 

*Keywords:* Molybdenum complexes; Chiral ligands; Enantioselective epoxidations; Heterogeneous catalysis; Mesoporous materials; Supported catalysts

## 1. Introduction

The well recognized catalytic activity of the oxomolybdenum(VI) complexes in oxidation reactions and the recent increasing importance of enantioselective catalytic processes led to the search of oxomolybdenum catalysts able to perform enantioselective oxidation reactions [1]. Following the simplest approach to obtain enantioselective transformations at a metal center, chiral ligands like 2′-pyridyl alcohols [2,3] and phosphinoylalcohols [4] have been reported recently to induce enantioselective epoxidation of unfunctionalized olefins when coordinated to dioxo and peroxomolybdenum(VI) fragments. However, the reported enantiomeric excess (ee) values are modest (ca. 20–40%). In the context of olefin epoxidation, some of us recently reported the synthesis of a broad variety of *cis*-$MoO_2^{2+}$ epoxidation catalysts of the type $MoO_2X_2L_n$ (X = Cl, Br, $CH_3$) with mono- and bidentate nitrogen and oxygen ligands [5]. This work was subsequently extended to include chiral bis(oxazoline) and 2′-pyridyl alcohol ligands [6]. The resulting chiral dioxomolybdenum(VI) complexes exhibited good catalytic activity for the epoxidation of *trans*-β-methylstyrene with *t*-butylhydroperoxide (TBHP) with optical induction values in the range of those mentioned above. In these studies it

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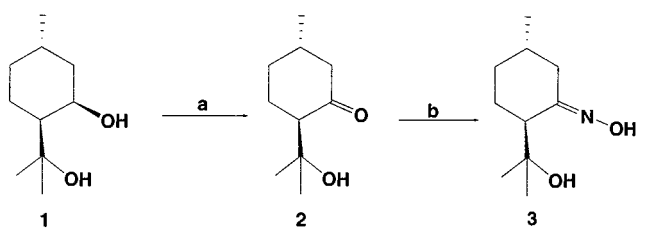
was observed that the catalytic activity strongly depends on the nature of the ligands X and L in the $MoO_2X_2L_n$ complexes. The higher electronegativity of X clearly accelerates the epoxidation reaction but the decisive effects of the ligands L are unclear either upon the activity or upon the enantioselectivity.

In this situation we decided to take a further step in the characterization of new $MoO_2X_2L_n$ catalysts bearing other simple chiral ligands of readily accessible preparation before attempting the upgrade of this system by means of the more recently elaborated concepts on the mechanism of chirality control in enantioselective synthesis [1b]. The nature of the best performing simple ligands in terms of activity and chiral properties will certainly be of use for the design of more efficient ligand sets.

Under this light we now wish to report on the exploration of the catalytic behaviour of a series of dioxomolybdenum(VI) complexes with chiral *cis*-diol and *cis*-8-phenylthiomenthol ligands derived from (*R*)-(+)-pulegone, and their corresponding oxime derivatives both in homogeneous and heterogeneous (supported) conditions with respect to olefin epoxidation. These ligands, e.g. oximes, thioethers, were chosen because they represent less studied types of ligands in this field of chemistry, are very easily accessible and have appropriate properties for the heterogenization in mesoporous supports. In fact, the relatively small size of these ligands allows their confinement in the large-pore molecular sieves, a process that may provide a route to effective asymmetric heterogeneous catalysts [7]. As an example, the tethering of chiral dioxomolybdenum(VI) complexes with bidentate *O,O*-ligands to the internal surface of a mesoporous USY-zeolite afforded a catalyst for the asymmetric epoxidation of allylic alcohols [8]. We recently described the heterogenisation of the dioxomolybdenum(VI) fragment $MoO_2X_2$ within ordered mesoporous MCM-41 silica by using a tethering ligand [$L = NC(CH_2)_2Si(OEt)_3$] [9]. We have applied the same methodology in the work reported here to try to immobilize a chiral dioxomolybdenum(VI) complex.




Scheme 1. (a) $CrO_3$/Py/$Ch_2Cl_2$/r.t./45 min. (b) $H_2NOH{\cdot}HCl$/DMAP/MeOH/r.t./24 h.

## 2. Results and discussion

### 2.1. Chiral ligand synthesis

The starting materials used for the synthesis of the chiral ligands were *cis*-*p*-menthane-3,8-diol (**1**) and (*R*)-(+)-pulegone (**4**), a commercially available natural product. Oxidation of **1** with $CrO_3$ in pyridine/dichloromethane gave the ketone derivative (+)-(2*R*,5*S*)-2-(1-hydroxy-1-methylethyl)-5-methylcyclohexanone (**2**) [10]. Treatment of **2** with hydroxylamine hydrochloride and 4-dimethylaminopyridine in methanol then gave the chiral oxime **3** (Scheme 1) [11].

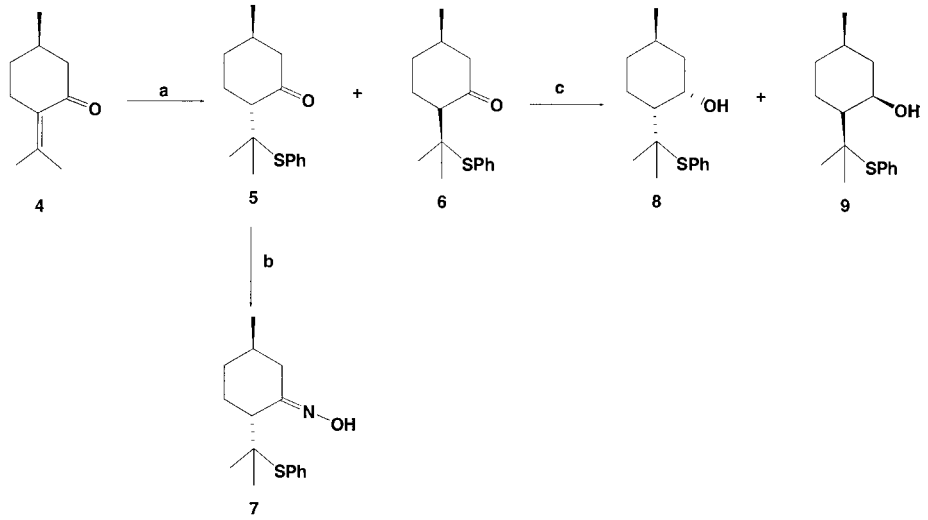
The 8-phenylthiomenthones **5** and **6** were obtained from **4** as a mixture of *cis* and *trans* isomers but otherwise highly pure as evidenced by spectral analysis (see experimental) (Scheme 2). Separation of the isomers was achieved by careful medium pressure chromatography on silica gel [12]. The chiral oxime **7** was prepared from **5** as described above for **3**. Following the method of Vollhardt [13a], reduction of **5** and **6** with L-Selectride gave the optically active 8-phenylthiomenthols **8** and **9** that were straightforwardly separated by chromatography on silica gel [13]. All the desired ligands were available in high optical purity and were fully characterised.

### 2.2. Synthesis of chiral dioxomolybdenum(VI) complexes

The complexes obtained by reacting the organic ligands **1**, **3** and **7**–**9**, with $MoO_2Cl_2(THF)_2$ in $CH_2Cl_2$ solvent, in a 1:1 molar ratio, are numbered **1a**, **3a** and **7a**–**9a**, respectively. They are formed in good yield after evaporation of the reaction mixture and washing with hexane. The complexes were characterized by elemental analysis and spectroscopic techniques.

Analysis of **1a** indicates the stoichiometry $MoO_2(THF)_2${(+)-*cis*-*p*-menthane-3,8-olato} implying that 2 equivalents of HCl were liberated during the reaction (Chart 1). With this stoichiometry the complex has a 6-coordinated environment with two THF ligands attached. The complex is very air sensitive decomposing within a few seconds when exposed to air. The IR indicates that this complex has a *cis*-$MoO_2$ stereochemistry. Since only one signal is observed in the $^{95}$Mo-NMR, either only one isomer is present or, most likely, the complex **1a** is fluxional or labile in solution. We did not pursue the definitive structural assigment further.

Treatment of one equivalent of the oxime ligands **3** and **7** with $MoO_2Cl_2(THF)_2$ gave the complexes of the type $MoO_2Cl_2L^*$ ($L^*$ = oxime ligand) in nearly quantitative yields (Chart 1). The product complexes **3a** and **7a** are soluble in dichloromethane and precipitated




Scheme 2. (a) HSPh/NaOH/Zn/CuBr/THF/Δ/8 h. (b) $H_2NOH{\cdot}HCl$/DMAP/MeOH/r.t./24 h. (c) (i) L-selectride/THF/0°C/4 h. (ii) $NaOH/H_2O_2$ (30%)

from the reaction mixture upon addition of ether. They are stable at room temperature and can be handled in air for brief periods of time (several minutes). The stoichiometry of **3a** and **7a** indicates that a simple adduct was formed and no HCl was liberated. Their IR spectra clearly show the presence of the OH groups but it is not easy to decide between a O/N and a O/O coordination. As depicted in Chart 1, we believe that the complexes have a O/N coordination based upon their higher stability, a more favorable chelating ring and the $^{95}$Mo data, discussed below.

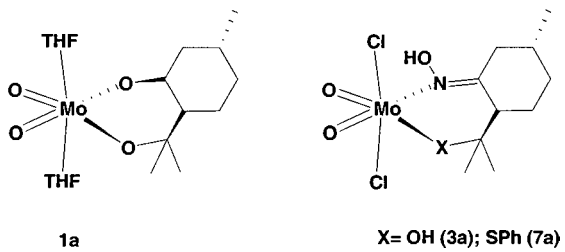
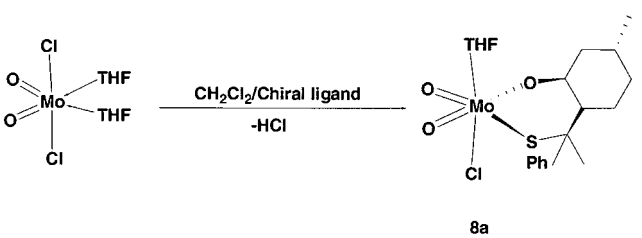



Chart 1.

The complexes of stoichiometry $MoO_2Cl(THF)L^*$ (**8a** and **9a**) were also prepared from $MoO_2Cl_2(THF)_2$ and the thioether-alcohol ligands (Scheme 3). Again, liberation of HCl took place and both complexes are air and moisture sensitive and can only be handled and stored under moisture-free inert gas atmosphere. Complex **9a** could be characterised in the solid state (analysis and IR) but a solution of the complex in deuterated solvent was too unstable and it was not possible to obtain consistent NMR data. These complexes (**8a** and **9a**) are more soluble in organic solvents compared to the oxime derivatives **3a** and **7a**, and do not precipitate from the reaction mixtures. They are soluble in diethyl ether and can only be purified by washing with hexane or pentane. These characteristics are similar to those reported by us for the corresponding chiral 2′-pyridyl alcoholate derivatives with the same general formula $MoO_2Cl(THF)L^*$ [6].

The complexes **1a**, **3a**, **6a**–**9a** display their symmetric and asymmetric IR Mo=O stretching vibrations in the expected range (916–962 $cm^{-1}$) [5,6,14]. The other bands in the IR spectra are assigned to the vibrational signals of the bound ligands. This shows that the thioether ligands were not oxidized by oxygen transfer from the Mo to the S atom. Besides, no colour change indicative of Mo(VI) reduction to Mo(IV) (or MoV) was observed. With this evidence in hand, the thioether ligands are considered to play their usual role as weak, labile ligands to the hard $Mo^{VI}O_2$ center.

The solubility of the dioxomolybdenum complexes enable good quality $^{95}$Mo-NMR spectra to be obtained, which displayed their signals in the region between 150 and 320 ppm (Table 1). The $^{95}$Mo-NMR signals of complexes **1a** and **8a**, with O,O- and O,S-ligands, respectively, appear at higher field [$\delta(^{95}Mo) = 183$ and 153 ppm] compared to complexes **3a** and **7a** with O,N-ligands [$\delta(^{95}Mo) = 241$ and 320 ppm]. These results are in agreement with data obtained for other $MoO_2Cl_2L_2$ complexes containing oxygen ligands L, e.g. $MoO_2Cl_2(CH_3COCHC(N(H)Me)CH_3)_2$




Scheme 3.

Table 1
$^{95}$Mo-NMR data of the complexes ($CD_2Cl_2$, room temperature)

| Compound | $\delta(^{95}Mo)$ (ppm) | $\Delta\nu_{1/2}$ (Hz) |
|---|---|---|
| **1a** | 183 | 180 |
| **3a** | 241 | 210 |
| **7a** | 320 | 370 |
| **8a** | 153 | 102 |

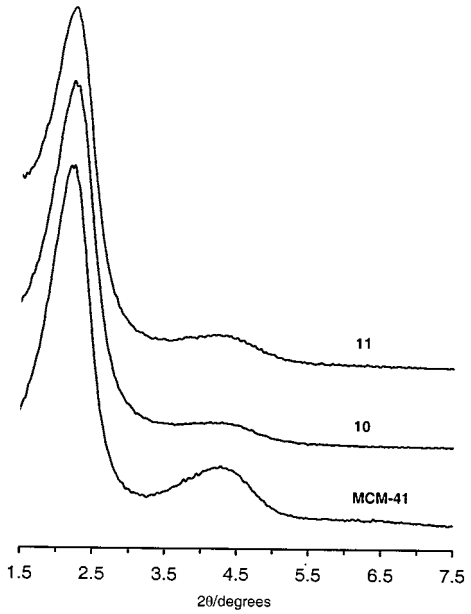
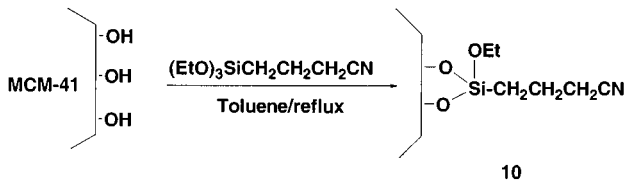



Fig. 1. Powder XRD patterns of calcined (pristine) MCM-41 and functionalised samples **10** and **11**.




Scheme 4.

[$\delta(^{95}Mo) = 160$ ppm] [5b] and also with data obtained for $MoO_2Cl_2L'_2$ complexes containing imine ligands L′ which give $\delta(^{95}Mo)$ signals in the region of 220 ppm [5b] and pyridine–alcoolate (py–O) derivatives of $MoO_2Cl$(py–O) which have these resonances at ca. 260 ppm [6].

### 2.3. Synthesis of derivatised mesoporous materials

Complex **8a** is labile. When prepared in dichloromethane or THF, the formulation $MoO_2Cl$(**THF**)L* (**8a**) is obtained but dissolution and recrystalisation from NCMe gave the NCMe adduct $MoO_2Cl$(**NCMe**)L* ($^1$H-NMR evidence). However, reaction of **8a** with pyridine in dichloromethane leads to decompostition to unidentified products with total displacement of the chiral ligand.

We recently showed that the dioxomolybdenum(VI) fragment $MoO_2X_2$ could be confined within the channels of the mesoporous silica MCM-41 by reaction of $MoO_2Cl_2(THF)_2$ with the nitrile-functionalised material MCM-41-Si(OEt)$_n$CH$_2$CH$_2$CN [9]. The nitrile groups replace coordinated THF molecules. Interest in the synthesis of asymmetric heterogeneous catalysts led us to examine whether this methodology could be used to immobilise the chiral complex **8a**.

MCM-41 was prepared as described in the literature using [($C_{14}H_{29}$)$NMe_3$]Br as the surfactant template. The powder XRD pattern of the calcined MCM-41 can be indexed on a hexagonal unit cell (using the strongest reflection, $d_{100}$, $a = 45.73$ Å). The pattern also displays a broad secondary feature at about 4.6° $2\theta$ where (110) and (200) reflections would be expected for a hexagonally ordered material such as MCM-41 (Fig. 1). The absence of resolved peaks indicates that any structural order of the material did not extend over a long range. A very similar result was obtained by Schmidt et al. for a purely siliceous MCM-41 prepared as in this work using the same surfactant [15].

The derivatised material MCM-41–Si(OEt)$_n$CH$_2$-CH$_2$CH$_2$CN (**10**) was prepared by diffusion of an excess of 4-(triethoxysilyl)butyronitrile in toluene, into calcined and dehydrated MCM-41 for 48 h (Scheme 4). The powder was washed repeatedly with dichloromethane to remove the unreacted nitrile and dried in vacuum at room temperature for several hours. Reaction of the nitrile-functionalised material **10** with the dioxomolybdenum complex **8a** in $CH_2Cl_2$ at room temperature gave a visibly air-sensitive pale blue powder (**11**) that contained 0.5 mass% Mo and 0.76% Cl. The powder XRD data for the functionalised materials **10** and **11** were consistent with retention of the hexagonal mesoporous structure throughout the grafting and tethering processes (Figure 1).

The $^{29}$Si-MAS and CP MAS-NMR spectra of MCM-41-Si(OEt)$_n$CH$_2$CH$_2$CH$_2$CN (**10**) displayed peaks between $\delta = -110$ and $-92$ assigned to $Q^n$ units of the silica framework [$Q^n = Si(OSi)_n(OH)_{4-n}$, $n = 2$–4] and additional peaks between $\delta = -62$ and $-54$ assigned to $T^m$ units of the grafted organosilica species [$T^m$ = R$Si(OSi)_m(OEt)_{3-m}$, $m = 1$–2] (Fig. 2). As expected, grafting of the triethoxysilyl ligand on the internal silica surface of MCM-41 resulted in a decrease in the relative intensity of the $Q^2/Q^3$ resonances and a concomitant increase in the intensity of the $Q^4$ resonance. This is consistent with the IR spectrum which showed characteristic absorption bands for the covalently-linked organic groups [$\nu$(N≡C) = 2257 cm$^{-1}$]. The $^{29}$Si-NMR spectra changed only slightly after material **10** was treated with complex **8a**. IR bands for the two *cis*-Mo=O stretching modes could not be seen clearly due to the small percentage of molybdenum in the material.

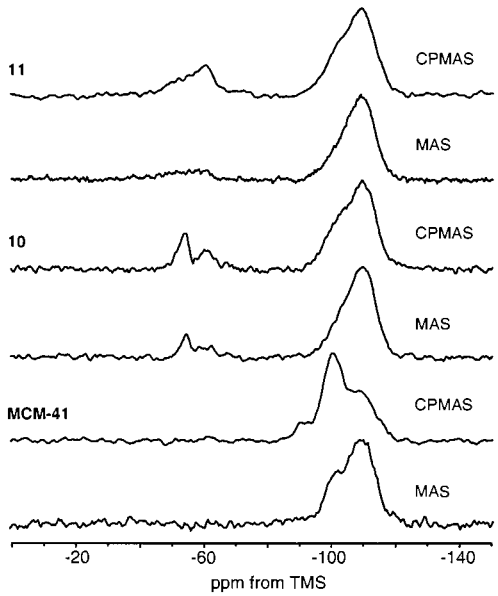



Fig. 2. $^{29}$Si-MAS and CP MAS-NMR spectra of calcined (pristine) MCM-41 and functionalised samples **10** and **11**.

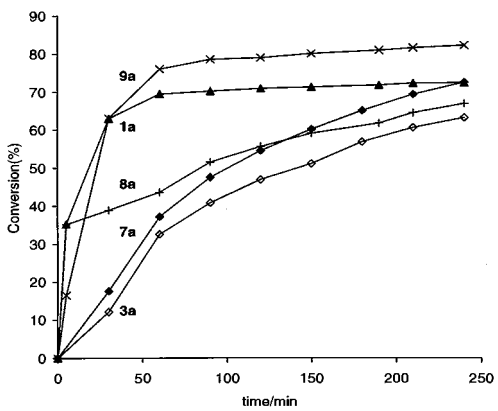



Fig. 3. Kinetic profile of epoxidation of *cis*-β-methylstyrene by TBHP at 55°C in the presence of the chiral *cis*-diol complex **1a** and oxime **3a**, *cis*-phenylthiomenthol complexes **8a** and **9a**, and oxime **7a**.

Table 2
Results of catalytic epoxidation of *cis*-β-methylstyrene by TBHP at 55°C in the presence of the chiral *cis*-diol complex **1a** and oxime **3a**, *cis*-phenylthiomenthol complexes **8a** and **9a**, and oxime **7a** [a]

| Compound | TOF [b]/mol ($mol_{cat}^{-1}$ $min^{-1}$) | Conversion [c] (%) | ee (%) |
|---|---|---|---|
| **1a** | 7.05 | 72 | 23.8 (*R*,*R*) |
| **3a** | 0.52 | 63 | 1.3 (*R*,*R*) |
| **7a** | 0.59 | 72 | 1.5 (*R*,*R*) |
| **8a** | 7.00 | 67 | 2.2 (*R*,*R*) |
| **9a** | 3.30 | 82 | – |

[a] See text and Section 3 for reaction details.
[b] Initial turnover frequency, calculated after 5 min reacting.
[c] Conversion and ee calculated after 4 h reacting.

The $^{13}$C CP MAS-NMR spectrum of MCM-41-Si(OEt)$_n$CH$_2$CH$_2$CH$_2$CN (**10**) exhibited one faint peak at $\delta = 118.3$ attributed to N*C*R, two peaks at $\delta = 58.3$ and 19.1 attributed to the ethoxide group, and two well-defined peaks at $\delta = 16.6$ and 10.5 attributed to NC–*C*H$_2$– and –*C*H$_2$–*C*H$_2$–Si respectively. The $^{13}$C CP MAS-NMR spectrum of material MCM-41-Si(OEt)$_n$(CH$_2$)$_3$CN/**8a** (**11**) was similar except that the peaks corresponding to the ethoxide group were relatively less intense compared to the peaks corresponding to the NC–(CH$_2$)$_3$–Si fragment. Also, the resonance at $\delta = 119.4$ attributed to N≡*C* was shifted downfield slightly compared to **10** as a result of coordination to the $MoO_2Cl$ fragment. The spectrum did not display any additional resonances that could be assigned to the chiral ligand, suggesting that the latter was lost during the reaction of **8a** with **10**.

### 2.4. Dioxomolybdenum(VI) complexes in epoxidation catalysis

The design of new metal catalysts for highly enantioselective epoxidation of unfunctionalised olefins is still an area of active research despite the success of Mn–salen and metalloporphyrin complexes [1]. Some effort has focussed on the isolation of highly reactive and chiral oxometal complexes. It is hoped that examination of their reactivities towards asymmetric alkene epoxidations will partly provide a clue to the factors affecting enantioselectivity [16]. A chiral dioxoruthenium(VI) porphyrin complex was recently shown to catalyse enantioselective aerobic oxidation of *cis*-β-methylstyrene with 70% ee [16c]. In the field of molybdenum(VI) chemistry, enantiomeric excesses of up to 53% are known with functionalised olefins as substrate, e.g. allylic alcohols [17], whereas for unfunctionalised olefins enantioselective epoxidation is much more difficult. For example, reaction of squalene with TBHP in the presence of 1 mol% of $MoO_2(acac)_2$/diisopropyl tartrate gives 2,3-oxidosqualene in only 14% ee [18]. More recent studies report ee's of up to 25% for the oxidation of *trans*-β-methylstyrene by TBHP in the presence of chiral dioxomolybdenum(VI) pyridyl alcoholate complexes [2,6].

Complexes **1a**, **3a** and **7a**–**9a** were evaluated as catalysts for the asymmetric epoxidation of *cis*-β-methylstyrene using *tert*-butylhydroperoxide as oxidant and toluene as solvent at 55°C. The ratio substrate:oxidant:catalyst used was 100:200:1. Catalytic runs are shown in Fig. 3 and results are summarized in Table 2. For the five complexes studied, the reactions proceeded with high retention of configuration and high selectivity to the epoxide but only the *cis*-diolato complex **1a** produces significant optical induction. The (1*R*,2*R*)-*cis*-β-methylstyrene oxide was formed in 20–24% ee from the initial stages of the reaction to the end (24 h). After a quick increase in the yield within the first

hour the reaction velocity slowed down and conversion reached 86% after 24 h. The complexes **7a**–**9a**, containing one alcoholate and one phenylthio ligand did not give rise to significant enantiomeric excesses in the epoxidation of *cis*-β-methylstyrene. However, complex **9a** proved to be the more active catalyst in this series. After 30 minutes the conversion was similar to that obtained with complex **1a** but it didn't slow down so rapidly, proceeding to complete conversion of the substrate within 24 h with 100% selectivity to the epoxide. Quite interestingly, complex **8a** with another enantiomeric form of the same ligand exhibited a slightly different kinetic profile in which, after a very rapid increase in yield in the first 5 min, product formation increased slowly but steadily from 40% after 30 min to 90% after 24 h reaction. These results deserve some comment in the context of exploring new ligands for the catalytic epoxidation with $MoO_2X_2L_2$ systems. In fact, at first sight sulfur ligands do not seem to be appropriate for this kind of oxidative chemistry since the S atom will quite likely be oxidized to a sulfoxide or a sulphone. In the present study we did not try to establish these facts but the results obtained with **9a** clearly show that the sulphur containing ligand **9** provides one of the most active, selective and chemically resistant catalyst of all the $MoO_2X_2L_2$ systems that we studied so far [5]. Unfortunately, it wasn't possible to ascertain the degree of lability of the thioether ligand in **9a**. However, it is quite likely that the dissociation of the SPh group under catalytic conditions leads to the formation of a S(O)Ph ligand which can bind the Mo(VI) center by its O atom in the same fashion as DMSO or DMF [22] or phosphine oxides [4] coordinate such centers to produce catalytic oxygen transfer systems. One can thus speculate that the expected lability of the sulphoxide ligand and its chemical resistance to oxidation may provide an explanation for the higher activity and chemical stability of this system since the Mo centre becomes easily accessible to reactants (by S(O)Ph dissociation) and readily protected (by ready association of the pendant S(O)Ph group.

In contrast, the reaction in the presence of the oxime derivatives **3a** and **7a** was sluggish and conversion of the substrate only reached ca. 30% after about 1 h. Nevertheless, the reaction proceeded smoothly and the product yield increased to 90% after 24 h. Both profiles are essentially parallel showing that the presence of an oxidizable sulfur in the thioether ligand is not important for the rate of the reaction. Instead, the presence of the N bound oxime ligand clearly slows down the reactivity of these complexes compared to the alcoholates. In any case, the optical induction of all the thioether and oxime containing complexes is very low.

The latter observation together with the fact that **9a** does not produce any optical induction seems to reinforce our belief that enantioselectivity in this systems requires the chiral ligand to remain chelated the $Mo^{VI}O_2$ center. Opening of the chelating ring will contribute to a faster reaction but to a loss of enantioselectivity. Such opening may be accelerated by the accumulation of excess *t*-BuOH in the reaction mixture as by product of the oxidation. A lowering of the enanstioselectivity along increasing conversion was described by Haider in the epoxidation of *cis*-β-methylstyrene catalysed by a chiral 2′-pyridine alcoholate derived from fenchone, $MoO_2(fenpy)_2$ [1c]. The loss of selectivity along the reaction evolution was attributed to opening of the chelation by protonation of the Mo–O bond of one fenpy ligand. A similar behaviour can be expected to take place in a diolate complex like **1a**.

The dioxomolybdenum-functionalised MCM (**11**) was tested as a catalyst for the epoxidation of cyclooctene with TBHP as oxygen source at 55°C (see Section 3 for more details). After a very quick increase in the yield within the first 5 min the reaction velocity slowed down. Similar results were obtained with MCM-41-grafted $MoO_2Cl_2NCCH_2CH_2Si(OEt)_3$ [9]. The yield of cyclooctene oxide formed was 31% after 15 min, increasing to 41% after 4 h (65–70% selectivity to the epoxide). An initial turnover frequency of 0.86 mmol cyclooctene oxide per g of catalyst per min was achieved, or 1.7 mol cyclooctene oxide per mol molybdenum atoms per min. A possible explanation for the sudden decrease in activity is the reaction of the tethered dioxomolybdenum complex with *tert*-butanol. It has previously been reported that the epoxidation of 1-octene by a $TiO_2$-on-$SiO_2$ catalyst and TBHP in benzene at 80 °C exhibits marked autoretardation, attributed to the formation of *tert*-butanol during the epoxidation process [17]. Reactions were also performed with parent calcined MCM-41 and the ligand-grafted material MCM-41-$Si(OEt)_n(CH_2)_3CN$ (**10**) and, as expected, neither material showed significant activity in the epoxidation of cyclooctene. After 4 h reacting, conversions were 5% for MCM-41 and 10% for **10**. MCM-41 was found previously to be inactive in cyclohexene epoxidation with TBHP [18].

In conclusion we note that the most active catalysts or catalyst precursors studied in this work, **1a** and **9a**, were very moisture sensitive alcoholates. Their overall activity in olefin epoxidation is among the best of all $MoO_2X_2L_2$ and $MoO_2(py–O)_2$ complexes studied so far. This excellence also complies for the enantioselectivity of **1a** (but not **9a)** which also ranks very high among all previous results with the above mentioned $MoO_2$ derived complexes. The difference in activity between **8a** and **9a** is most remarkable since the only noticeable difference between both complexes is the chirality of the ligand. Definitive benchmark tests as well as tests with other diols are presently under way in our laboratories. In particular, BINOL and other biaryl

alcohols are under careful observation because they can open an entry to more advanced configuration control as discussed by Bolm in his recent critical review [1b].

Theoretical and experimental studies are also being carried out in order to clarify the mechanism of oxidation with the $MoO_2X_2L^*$/TBHP system. NMR results ($^{17}O$, $^{1}H$, $^{95}Mo$) have shown that TBHP interacts with $MoO_2Cl_2L$ (L = 2′-pyridyl alcoholate) complexes to produce slightly displaced resonances which are reproducible experimentally [6]. A peroxometal reaction pathway is therefore assumed whereby the electron deficient $d^0$ metal center acts as a Lewis acid activating the hydroperoxide.

Due to the lability of the chiral ligands these complexes are not appropriate to prepare eneantioselective catalysts by support on mesoporous MCM-41 materials.

## 3. Experimental

### 3.1. Materials and methods

All preparations and manipulations were carried out using standard Schlenk techniques under an atmosphere of nitrogen. Solvents were dried by standard procedures (THF, *n*-hexane and $Et_2O$ over Na/benzophenone ketyl; $CH_2Cl_2$ and NCMe over $CaH_2$), distilled under argon and kept over 4Å molecular sieves (3Å for NCMe).

Microanalyses were performed at the ITQB and the Mikroanalytische Labor of the Technical University of Munich (M. Barth). IR spectra were measured on a Unican Mattson Mod 7000 FTIR spectrometer and a Perkin–Elmer FT-IR spectrometer using KBr pellets. Powder XRD data were collected on a Phillips X'pert diffractometer using Cu–$K_\alpha$ radiation filtered by Ni. $^{1}H$-NMR solution spectra were recorded at 300 MHz and 400 MHz on Bruker CXP 300 and Bruker Avance DPX-400 spectrometers respectively. $^{13}C$-NMR solution spectra were measured at 100.28 MHz on a JEOL JNM GX-400 and a Bruker Avance DPX-400. $^{95}Mo$-NMR solution spectra were measured at 26.07 MHz on a Bruker Avance DPX-400. $^{29}Si$- and $^{13}C$- solid-state NMR spectra were recorded at 79.49 and 100.62 MHz respectively, on a (9.4 T) Bruker MSL 400P spectrometer. $^{29}Si$ MAS-NMR spectra were recorded with 40° pulses, spinning rates 5.0–5.5 kHz and 60 s recycle delays. $^{29}Si$ CP MAS-NMR spectra were recorded with 5.5 ms $^{1}H$ 90° pulses, 8ms contact time, a spinning rate of 4.5 kHz and 4 s recycle delays. Chemical shifts are quoted in parts per million from TMS. $^{13}C$ CP MAS-NMR spectra were recorded with a 4.5 μs $^{1}H$ 90° pulse, 2 ms contact time, a spinning rate of 8 kHz and 4 s recycle delays. Chemical shifts are quoted in parts per million from TMS.

The hexagonal channel host MCM-41 was synthesised using $[(C_{14}H_{29})NMe_3]Br$ according to published procedures [19]. After calcination (540°C/6 h), the material was characterised by powder XRD and FTIR spectroscopy. The precursor materials $MoO_2Cl_2$ [20] and $MoO_2Cl_2(THF)_2$ [21] were prepared as described previously. (+)-*cis*-*p*-menthane-3,8-diol (**1**) and (*R*)-(+)-pulegone (**4**) were purchased from Aldrich and used as received.

### 3.2. Chiral ligand synthesis

#### 3.2.1. (+)-(2R,5S)-2-(1-Hydroxy-1-methylethyl)-5-methylcyclohexanone (**2**)

To a solution of pyridine (22.4 g, 278 mmol) in dichloromethane (230 ml) at 0°C was added $CrO_3$ (13.92 g, 139.20 mmol). The solution was stirred for 15 min at room temperature and then treated with a solution of (+)-*cis*-*p*-menthane-3,8-diol (4.0 g, 23.2 mmol) in dichloromethane (40 ml). After stirring for 45 min, the mixture was filtered through Celite and the residue washed several times with diethyl ether (150 ml). The combined filtrate and washings were concentrated and washed with 10% NaOH (2 × 60 ml) and brine (100 ml). The combined organic layers were dried over $Na_2SO_4$ and the solvent removed to give an oil (4.1 g) purified by flash chromatography (hexane:EtOAc; 3:7). Yield: 3.52 g (89%). Anal. Calc. for $C_{10}H_{18}O_2$ (170.25): C, 70.55; H, 10.66. Found: C, 70.23; H, 10.46%. $[\alpha]_D^{20}$ + 3.7 (*c* 1, $CDCl_3$). IR (neat, *v* $cm^{-1}$): 3479 vs, 2957 vs, 2930 vs, 2874 s, 1699 vs, 1458 s, 1377 s, 1362 s, 1160 s, 943 s, 804 m, 619 m, 548 m. $^{1}H$-NMR ($CDCl_3$, 300 MHz, r.t., $\delta$ ppm): 3.95 (s, 1H, OH); 2.40–2.32 (m, 2H); 2.22–1.89 (m, 4H); 1.57–1.40 (m, 2H); 1.23 (d, 6H, $CH_3$); 1.02 (d, 3H, $CH_3$). $^{13}C$-NMR ($CDCl_3$, 300 MHz, r.t., $\delta$ ppm): 216.44; 72.44; 60.17; 52.85; 36.92; 35.30; 30.09; 26.90; 23.37.

#### 3.2.2. (+)-(2S,5S)-2-(1-Hydroxy-1-methylethyl)-5-methylcyclohexanone oxime (**3**)

Into a 100 ml round-bottomed flask containing an efficient stirring bar was added a solution of **2** (3.0 g, 17.62 mmol), hydroxylamine hydrochloride (6.18 g, 88.0 mmol), 4-dimethylaminopyridine (DAMP) (2.37 g, 19.4 mmol) and MeOH (58 ml). The reaction mixture was stirred for 24 h at room temperature (r.t.). The mixture was diluted with water (200 ml) and extracted with ether (4 × 80 ml). The combined organic layers were washed with 1.0 M HCl (2 × 60 ml) and brine (100 ml). The organic solution was dried over $Na_2SO_4$ and the solvent removed to give a yellow solid (3.2 g) purified by recrystallization from cyclohexane to yield a white solid (3.13 g, 96%). Anal. Calc. for $C_{10}H_{19}NO_2$ (185.27): C, 64.83; H, 10.34; N, 7.56. Found: C, 64.68; H, 10.22; N, 7.66%. M.p. 115–117°C. $[\alpha]_D^{20}$ + 34.5 (*c* 1, $CHCl_3$). IR (KBr, *v* $cm^{-1}$): 3416 vs (OH), 3234 vs, 3103

vs, 2971 vs, 2921 s, 2868 s, 1668 vs, 1467 s, 1402 s, 1381 s, 1251 s, 1170 s, 964 s, 941 s, 891 m, 768 m, 673 s, 642 s, 545 m. $^1$H-NMR ($CDCl_3$, 300 MHz, r.t., $\delta$ ppm): 8.43 (s, 1H, OH); 5.24 (s, 1H, OH); 3.45–3.39 (m, 2H); 2.20–2.15 (m, 2H); 2.01–1.95 (m, 2H); 1.81 (m, 2H); 1.19 (d, 6H, $CH_3$); 1.00 (d, 3H, $CH_3$).

### 3.2.3. (−)-(2R,5R)-2-[1-Methyl-1-(phenylthio)ethyl]-5-methylcyclohexanone (**5**)

A suspension of thiofenol (14.4 g, 130.7 mmol), zinc (1.0 g, 15.3 mmol), copper (I) bromide (1.8 g, 12.5 mmol), (*R*)-(+)-pulegone (18.1 g, 118.9 mmol), 10% NaOH (1 ml) and THF (60 ml) was stirred and refluxed for 8 h under a nitrogen atmosphere. The reaction was allowed to cool to ambient temperature, followed by the addition of 1.0 M HCl (200 ml) and diethyl ether (100 ml). The mixture was filtered through Celite and the residue washed several times with diethyl ether (100 ml). The combined organic layers were washed with 1.0 M HCl (2 × 100 ml), brine (200 ml), dried over $Na_2SO_4$, and the solvent removed to give a mixture of **5** and **6** (33.7 g) as indicated by NMR (**5**:**6** = 86:14). The mixture was purified by flash chromatography (hexane:ether; 9:1) to afford the pure phenylthioketone **5** (9.2 g, 29%) and a mixture of **5** + **6** (18.1 g, 58%) with a diastereomeric relation 79:21 as indicated by $^1$H-NMR. Anal. Calc. for $C_{16}H_{22}OS$ (262.41) **5**: C, 73.24; H, 8.45. Found: C, 73.03; H, 8.41%. M.p. 30–32 °C. $[\alpha]_D^{20}$ −38.2 (*c* 1, $CHCl_3$). IR (KBr, $\nu$ cm$^{-1}$): 3088 m, 3059 m, 3022 m, 2955 vs, 2926 vs, 2872 vs, 1710 vs, 1496 s, 1364 s, 1205 s, 1122 s, 1091 s, 771 s, 700 vs, 565 s. $^1$H-NMR ($CDCl_3$, 300 MHz, r.t., $\delta$ ppm): 7.51–7.31 (m, 5H, Ph); 2.83–2.77 (m, 2H); 2.36–2.25 (m, 2H); 1.96–1.94 (m, 2H); 1.63–1.57 (m, 2H); 1.39 (d, 6H, $CH_3$); 1.01 (d, 3H, $CH_3$). $^{13}$C-NMR ($CD_2Cl_2$, 300 MHz, r.t., $\delta$ ppm): 212.18; 151.63; 129.24; 127.28; 126.69; 60.63; 53.65; 40.26; 37.67; 36.06; 31.09; 27.07; 25.94; 23.44.

### 3.2.4. (+)-(2R, 5R)-2-[1-Methyl-1-(phenylthio)ethyl]-5-methyl cyclohexanone oxime (**7**)

Into a 50 ml round-bottomed flask containing an efficient stirring bar was added a solution of **5** (1.0 g, 3.81 mmol), hydroxylamine hydrochloride (1.34 g, 19.1 mmol), 4-dimethylaminopyridine (0.51 g, 4.19 mmol) and MeOH (13 ml). The reaction mixture was stirred for 24 h at r.t.. The mixture was diluted with water (70 ml) and extracted with diethyl ether (4 × 40 ml). The combined organic layers were washed with 1.0 M HCl (2 × 30 ml) and brine (50 ml). The organic solution was dried over $Na_2SO_4$ and the solvent removed to give a yellow solid (1.07 g) purified by recrystallization from cyclohexane to yield a white solid (1.03 g, 97%). Anal. Calc. for $C_{16}H_{23}NOS$ (277.43): C, 69.27; H, 8.36; N, 5.05. Found: C, 69.43; H, 8.45; N, 4.99%. M.p. 85–86°C. $[\alpha]_D^{20}$ + 35.5 (*c* 1, $CHCl_3$). IR (KBr, $\nu$ cm$^{-1}$): 3393 vs (OH), 3055 m, 2951 vs, 2924 vs, 2866 s, 1651 vs, 1445 s, 1381 s, 1229 s, 1134 s, 939 s, 899 m, 754 m, 695 s, 665 s, 594 m. $^1$H-NMR ($CDCl_3$, 300 MHz, r.t., $\delta$ ppm): 7.52 (s, 1H, OH); 7.51–7.26 (m, 5H, Ph), 3.31–3.26 (m, 1H); 2.57–2.52 (m, 1H); 2.17–2.12 (m, 1H); 1.92–1.87 (m, 1H); 1.61–1.57 (m 2H); 1.41 (d, 6H, $CH_3$); 1.35–1.31 (m, 1H); 1.27–1.15 (m, 1H); 0.98 (d, 3H, $CH_3$). $^{13}$C-NMR ($CDCl_3$, 300 MHz, r.t., $\delta$ ppm): 161.19; 138.06; 132.80; 128.83; 125.11; 52.63; 52.01; 34.94; 34.00; 30.07; 28.41; 25.47; 22.19.

### 3.2.5. (−)-(1S,2R,5R)-2-[1-Methyl-1-(phenylthio)ethyl]-5-methylcyclohexanol (**8**) and (−)-(1R,2S,5R)-2-[1-methyl-1-(phenylthio)ethyl]-5-methylcyclohexanol (**9**)

Method (a): to an L-Selectride solution (2.86 ml 1.0 M in THF, 2.86 mmol) at 0°C was added dropwise via syringe a solution of **5** (0.5 g, 1.9 mmol) in THF (4 ml). The reaction mixture was stirred for 4 h at 0°C after which aqueous 3 M NaOH (1 ml) was added dropwise followed by slow addition of 30% $H_2O_2$ (1 ml), resulting in an exothermic reaction. The solution was allowed to warm to ambient temperature, stirred for 30 min, and extracted with diethyl ether (4 × 40 ml). The combined organic portions were washed with water (50 ml), brine (60 ml) and dried over $Na_2SO_4$. The solvent was removed to give an oil (0.51 g) purified by flash chromatography (hexane:ether; 9:1) to afford the pure phenylthioalcohol **8** (0.49g, 99%).

Method (b): to an L-Selectride solution (97.0 ml 1.0 M in THF, 97.1 mmol) at 0°C was added dropwise via syringe a solution of the diastereomeric mixture (**5**:**6** = 79:21) (16.98 g, 64.75 mmol) in THF (75 ml). Using the treatment from method (a) we isolated a mixture of diastereomers of the two alcohols (**8**:**9** = 78:22 by NMR) which were purified by flash chromatography (hexane:ether; 19:1). The first fraction was identified as **9** (3.55 g, 20.7%). Anal. Calc. for $C_{16}H_{24}OS$ (264.43): C, 72.68; H, 9.15. Found: C, 72.47; H, 9.02%. M.p. 60–61°C. $[\alpha]_D^{20}$ −1.2 (*c* 1, $CHCl_3$). IR (KBr, $\nu$ cm$^{-1}$): 3545 vs, 3065 m, 2943 vs, 2912 vs, 2872 s, 2852 m, 1651 vs, 1456 s, 1437 s, 1359 s, 1257 m, 1203 s, 1130 s, 1069 m, 958 s, 833 m, 750 s, 705 s, 692 s, 536 m. $^1$H-NMR ($CDCl_3$, 300 MHz, r.t., $\delta$ ppm): $^1$H-NMR ($CDCl_3$, 300 MHz, r.t., $\delta$ ppm): 7.52–7.29 (m, 5H, Ph); 4.36 (s, 1H, OH); 2.27–2.25 (m, 1H); 1.95–1.55 (m, 8H); 1.57 (s, 3H, $CH_3$); 1.27 (s, 3H, $CH_3$); 1.20 (d, 3H, $CH_3$). $^{13}$C-NMR ($CDCl_3$, 300 MHz, r.t., $\delta$ ppm): 137.08; 131.34; 127.84; 127.76; 124.06; 68.33; 50.01; 39.06; 31.89; 27.63; 26.63; 25.94; 20.31; 17.95.

A second fraction was identified as pure **8** (11.1 g, 64.9%). Anal. Calc. for $C_{16}H_{24}OS$ (264.43): C, 72.68; H, 9.15. Found: C, 72.47; H, 9.02%. $[\alpha]_D^{20}$ −5.0 (*c* 1, $CHCl_3$). IR (KBr, $\nu$ cm$^{-1}$): 3448 vs, 3059 m, 2947 vs, 2922 vs, 2868 s, 2845 m, 1651 vs, 1456 s, 1363 s, 1253 s, 1190 m, 1126 s, 1026 s, 950 s, 841 m, 750 s, 694 s.

$^1$H-NMR ($CDCl_3$, 300 MHz, r.t., $\delta$ ppm): 7.52–7.32 (m, 5H, Ph); 4.37 (s, 1H, OH); 2.38–2.37 (m, 1H); 1.90–1.69 (m, 6H); 1.43 (s, 3H, $CH_3$); 1.26 (s, 3H, $CH_3$); 1.09–0.89 (m, 2H); 0.88 (d, 3H, $CH_3$). $^{13}$C-NMR ($CD_2Cl_2$, 300 MHz, r.t., $\delta$ ppm): 137.86; 132.08; 128.94; 128.64; 124.06; 68.18; 50.39; 43.43; 35.57; 28.65; 27.36; 26.19; 22.11; 21.08.

### 3.3. Synthesis of chiral dioxomolybdenum(VI) complexes

#### 3.3.1. General procedure

A solution of $MoO_2Cl_2(THF)_2$ (1.36 g, 4.00 mmol) in $CH_2Cl_2$ (15 ml) was treated with one equivalent of ligand. The resulting turbid solution was stirred for a further 2 h. The solvent was evaporated, and the product washed with hexane and dried under vacuum.

#### 3.3.2. $MoO_2(THF)_2$\{(+)-cis-p-menthane-3,8-olato\} (**1a**)

Yield, 82%. Anal. Calc. for $C_{18}H_{32}MoO_6$ (440.39): C, 49.09; H, 7.32. Found: C, 48.78; H, 6.80%. IR (Nujol, $\nu$ cm$^{-1}$): 1653 s, 1540 m, 1456 s, 1376 m, 1310 m, 1256, 1217 m, 1152 s, 1024 m, 997 m, 957 vs $\nu$(Mo=O), 920 vs $\nu$(Mo=O), 891 m, 866 m, 721 s, 580 m. $^1$H-NMR ($CD_2Cl_2$, 300 MHz, r.t., $\delta$ ppm): 3.90 (THF); 1.96 (THF); 1.96–1.69 (m, 6H); 1.36 (s, 3H); 1.29 (d, 3H, $CH_3$); 1.00–0.96 (m, 1H); 0.92 (d, 3H, $CH_3$).

#### 3.3.3. $MoO_2Cl_2$\{(+)-(2S,5S)-2-(1-olato-1-methylethyl)-5-methylcyclohexanone oxime\} (**3a**)

Yield, 92%. Anal. Calc. for $C_{10}H_{19}MoCl_2O_4N$ (384.11): C, 31.27; H, 4.99; N, 3.65. Found: C, 31.70; H, 5.02; N, 3.34%. IR (KBr, $\nu$ cm$^{-1}$): 3421 vs (OH), 3151 m, 3103 m, 2964 s, 2870 m, 1651 s, 1475 s, 1394 m, 1334 m, 1168 s, 1143 s, 1124 s, 1091 s, 1052 m, 943 vs (Mo=O), 918 vs (Mo=O), 833 s, 802 m, 763 m, 663 s, 553 s. $^1$H-NMR ($CD_2Cl_2$, 300 MHz, r.t., $\delta$ ppm): 4.05 (br, 1H); 3.61 (br, 1H); 3.29–3.22 (m, 2H); 3.09–3.05 (br, 2H); 2.89–2.87 (m, 1H); 2.77–2.62 (m, 2H); 1.95–1.89 (m, 1H); 1.45 (s, 3H, $CH_3$); 1.37 (s, 3H, $CH_3$); 1.06 (s, 3H, $CH_3$).

#### 3.3.4 $MoO_2Cl_2$\{(+)-(2R,5R)-2-[1-methyl-1-(phenylthio)ethyl]-5-methylcyclohexanone oxime\} (**7a**)

Yield, 96%. Anal. Calc. for $C_{16}H_{23}MoCl_2O_3NS$ (476.27): C, 40.35; H, 4.87; N, 2.94. Found: C, 40.63; H, 4.75; N, 3.06%. IR (KBr, $\nu$ cm$^{-1}$): 3395 vs (OH), 3140 m, 3087 m, 2959 s, 2928 s, 2870 m, 1587 s, 1447 vs, 1395 m, 1375 m, 1138 s, 1084 s, 949 vs (Mo=O), 916 vs (Mo=O), 752 s, 691 s, 559 m. $^1$H-NMR ($CD_2Cl_2$, 300 MHz, r.t., $\delta$ ppm): 7.81–7.35 (m, 5H, Ph); 3.94 (br, 1H); 3.49 (d, 1H); 3.32 (d, 1H); 2.74–2.47 (m, 2H); 2.17–2.12 (m, 1H); 2.06–1.51 (m, 2H); 1.38 (s, 3H, $CH_3$); 1.35–1.31 (m, 1H); 1.25 (s, 3H, $CH_3$); 1.17 (d, 3H, $CH_3$).

#### 3.3.5. $MoO_2(THF)Cl$\{(−)-(1S,2R,5R)-2-[1-methyl-1-(phenylthio)ethyl]-5-methylcyclohexanolato\} (**8a**)

Yield, 88%. Anal. Calc. for $C_{20}H_{31}MoClO_3S$ (498.92): C, 48.15; H, 6.26. Found: C, 47.88; H, 5.98%. IR (Nujol, $\nu$ cm$^{-1}$): 962 vs (Mo=O), 922 vs (Mo=O). $^1$H-NMR ($CD_2Cl_2$, 300 MHz, r.t., $\delta$ ppm): 7.51–7.31 (m, 5H, Ph); 4.14 (THF); 2.07 (THF); 2.07–1.71 (m, 6H); 1.34 (s, 3H, $CH_3$); 1.25 (s, 3H, $CH_3$); 1.04–0.93 (m, 2H); 0.86 (d, 3H, $CH_3$).

#### 3.3.6. $MoO_2(THF)Cl$\{(−)-(1R,2S,5R)-2-[1-methyl-1-(phenylthio)ethyl]-5-methylcyclohexanolato\} (**9a**)

Yield, 74%. Anal. Calc. for $C_{20}H_{31}MoClO_3S$ (498.92): C, 48.15; H, 6.26. Found: C, 47.88; H, 5.98%. IR (Nujol, $\nu$ cm$^{-1}$): 960 vs (Mo=O), 920 vs (Mo=O).

### 3.4. Synthesis of derivatised mesoporous materials

#### 3.4.1. Preparation of MCM-41-$Si(OEt)_nCH_2CH_2CH_2CN$ (**10**)

Calcined MCM-41 (1.0 g) was activated at 180°C under vacuum ($10^{-2}$ mbar) for 2 h and treated with excess of a solution of $NCCH_2CH_2CH_2Si(OEt)_3$ in toluene (30 ml). The mixture was stirred under reflux for 48 h. The solution was filtered off and the white solid washed four times with 20 ml portions of diethyl ether, before drying under vacuum at 100°C for several hours. Anal. Found: C, 12.46; H, 2.37; N, 2.11%. IR (KBr, $\nu$ cm$^{-1}$): 2980 m, 2940 m, 2898 m, 2257 m $\nu$(C≡N). $^{29}$Si MAS-NMR spectrum exhibited broad resonances at $\delta = -109.6$, $-61.9$ and $-54.3$. $^{29}$Si CP MAS-NMR spectrum exhibited two broad resonances at $\delta = -109.5$ ($Q^4$) and $\delta = -100.8$ ($Q^3$), a faint peak at $\delta = -91.9$ ($Q^2$), and two broad overlapping signals at $\delta = -59.9$ and $-53.6$. $^{13}$C CP MAS-NMR (r.t., $\delta$ ppm): 118.3 (*C*≡N); 58.3 (O–*C*H$_2$–); 19.1 (–*C*H$_3$); 16.6 (NC–*C*H$_2$–); 10.5 (broad signal).

#### 3.4.2. Reaction of MCM-41-$Si(OEt)_nCH_2CH_2CH_2$-CN with $MoO_2(THF)Cl$\{(−)-(1R,2S,5R)-2-[1-methyl-1-(phenylthio)ethyl]-5-methylcyclohexanolato\} (**11**)

A suspension of MCM-41-$Si(OEt)_nCH_2CH_2CH_2CN$ (0.8 g) was treated with excess of a solution of $MoO_2(THF)Cl$\{(−)-(1*S*,2*R*,5*R*)-2-[1-methyl-1-(phenylthio)ethyl]-5-methylcyclohexanol\} (**8a**) (0.4 g) in $CH_2Cl_2$ (30 ml). The mixture was stirred at r.t. for 24 h. The solution was filtered off and the pale blue solid washed four times with 30 ml portions of $CH_2Cl_2$ (20 ml), before drying under vacuum at r.t. for several hours. Anal. Found: C, 10.49; H, 3.09; Cl, 0.76; Mo, 0.5; N, 1.92%. IR (KBr, $\nu$ cm$^{-1}$): 2982 m, 2937 m, 2896 m, 2254 m $\nu$(C≡N). $^{29}$Si MAS-NMR spectrum exhibited broad resonances at $\delta = -108.9$, $-60.8$ and $-51.4$. $^{29}$Si CP MAS-NMR spectrum exhibited two broad resonances at $\delta = -109.3$ ($Q^4$) and $\delta = -101.5$ ($Q^3$), a faint peak at $\delta = -91.9$ ($Q^2$), and two broad over-

lapping signals at $\delta = -60.3$ and $-51.4$. $^{13}C$ CP MAS-NMR (r.t., $\delta$ ppm): 119.4 (C≡N); 58.6 (O–$CH_2$–); 19.0 (–$CH_3$); 16.2 (NC–$CH_2$–); 10.8 (broad signal).

### 3.5. Dioxomolybdenum(VI) complexes in epoxidation catalysis

#### 3.5.1. Chiral dioxomolybdenum(VI) complexes in solution

A total of 200 mg *cis*-$\beta$-methylstyrene (1.7 mmol), 100 mg mesitylene (internal standard) and 1.0 mol% **1a**, **3a**, **7a**–**9a** as catalyst (17 μmol) were dissolved in 2 ml of dry toluene. After addition of 615 μl *tert*-butylhydroperoxide solution (5.5 M in decane) the reaction mixture was stirred for up to 24 h at 55°C.

#### 3.5.2. MCM-41-supported dioxomolybdenum(VI) catalyst

A total of 800 mg (7.3 mmol) *cis*-cyclooctene, 800 mg *n*-dibutylether (internal standard), 175 mg **11** as catalyst and 2 ml 5.5 M TBHP were added to a thermostated reaction vessel and stirred for 24 h at 50°C.

The course of the reactions were monitored by quantitative GC-analysis. Samples were taken every thirty minutes, diluted with chloroform, and chilled in an icebath. For the destruction of hydroperoxide and removal of water a catalytic amount of manganese dioxide and manganese sulfate was added. After the gas evolution ceased the resulting slurry was filtered over a filter equipped Pasteur pipette and the filtrate injected into the GC column. The enantiomeric excesses and conversions were determined by chiral GC methods on a Hewlett–Packard (HP5970 B) instrument equipped with a Chiraldex $\gamma$-TA column (Alltech), a mass-selective detecter (HP5970 B) and integration unit (HP 3394).

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