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Molybdenum(VI)-complexes with chiral *N*,*O*-ligands derived from carbohydrates: synthesis, structure and catalytic properties in asymmetric olefin epoxidation

Jörg Fridgen [a], Wolfgang A. Herrmann [a,*], Georg Eickerling [a,b], Ana M. Santos [a], Fritz E. Kühn [a,*]

[a] *Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching bei München, Germany*
[b] *Lehrstuhl für Chemische Physik und Materialwissenschaften, Institut für Physik der Universität Augsburg, Universitätsstrasse 1, 86135 Augsburg, Germany*

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Abstract

Novel chiral 2′-pyridinyl alcohols derived from isopropylidene-protected carbohydrates are reported. They show different characteristics at the hydroxy group, but are all suitable ligands for chiral molybdenum(VI) complexes of the type MoO_2L_2 (L = chiral 2′-pyridinyl alcoholate). $MoO_2(acac)_2$ served as starting material in the complex syntheses. The structure of one ligand and one dioxo complex were exemplary established by X-ray crystallography. For catalytic runs in the enantioselective epoxidation catalysis *trans*-methylstyrene was used as model substrate, *tert*-butylhydroperoxide and cumolhydroperoxide, resp., as the oxidant.

Keywords: Molybdenum; Carbohydrate; 2′-Pyridinyl alcohol; Enantioselective synthesis; Asymmetric catalysis; Epoxidation

1. Introduction

Molybdenum(VI) complexes have already been used successfully in enantioselective epoxidation using different types of chiral ligands, among them diisopropyltartrate, lactamides and several other chiral hydroxyacid amides [1].

Previous results of our research group had shown that molybdenum(VI) and tungsten(VI) complexes of the type MO_2L_2 (M = Mo, W; L = 2′-pyridinyl alcoholate) are useful catalysts for the epoxidation of unfunctionalised olefins using organic hydroperoxides as oxidants [2,3]. 2′-Pyridinyl alcoholates can easily be prepared by the reaction of 2-lithiopyridine with ketones and are strongly resistant to ligand degradation. We have also demonstrated the diastereoselective synthesis of chiral 2′-pyridinyl alcohols before [4]. Corresponding to the model of Felkin and Ahn, the nucleophilic attack of 2-lithiopyridine on carbonyl groups is always preferred from the sterically less hindered side [5] (Scheme 1). Using the monoterpenes (+)-camphor, (−)-camphor, (±)-fenchone, (−)-fenchone, and (−)-menthone we obtained enantiomerically pure 2′-pyridinyl alcoholates that could be applied as chiral *N*,*O*-Ligands in molybdenum(VI) and tungsten(VI) complexes. Especially, the molybdenum(VI) complexes exhibit good catalytic activity and substantial optical induction in the asymmetric epoxidation catalysis of *trans*-methylstyrene [4].

Carbohydrates represent a wide reservoir of easily accessible chiral compounds. Interactions between carbohydrates and metal ions have been studied since the

* Corresponding authors. Fax: +49-89-289-13473.
E-mail address: fritz.kuehn@ch.tum.de (W.A. Herrmann).

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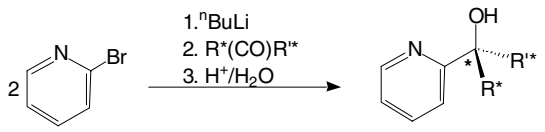


Scheme 1. Diastereoselective synthesis of chiral 2′-pyridinyl alcohols utilising the prochiral carbonyl function of (in the depicted particular case chiral) ketones.

early 19th century [6], but until about 20 years ago research was mainly focused on alkali and alkaline-earth metals [7]. Since then interactions of transition metals with carbohydrate derivatives in solution have largely been studied [8], but there are only few examples of transition metal compounds of that particular type that could be isolated and fully characterized [9]. In the last years Rao and co-workers [10] carried out detailed studies about the interactions between transition metals and carbohydrates and published several complexes both with simple carbohydrates and their derivatives. However, only very recently some X-ray crystal structures of such compounds could be obtained and reported [11].

We focused on carbohydrates as promising precursor compounds for the synthesis of chiral ligands similar to the ones we had obtained from monoterpenes because of their functional groups and well-defined stereochemistry.

2. Results and discussion

2.1. Synthesis of 2′-pyridinyl alcohols from carbohydrates

In order to get prochiral ketones for ligand synthesis, modifications of the carbohydrates are necessary. In fact, the resulting ligand must not contain functional groups that can easily be oxidized. This means that the hydroxy groups need to be protected. Furthermore, one single hydroxy group has to be oxidized to obtain a prochiral carbonyl group. Vicinal hydroxy groups can easily be protected as isopropylidene derivatives. Some of those protected carbohydrates are even commercially available. 1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (**1**), 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose (**2**) and 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose (**3**) were applied as starting compounds (Fig. 1). All three of them are hexoses with two furanoses and one pyranose. In compound **1** the nonprotected hydroxy group represents a secondary alcohol, in derivative **2** a semiacetal, and in complex **3** a primary alcohol.

The corresponding carbonyl derivatives were obtained by oxidation of the nonprotected hydroxy groups in compounds **1**–**3** (Scheme 2). The chromium trioxide–pyridin complex, which is formed in situ, is a

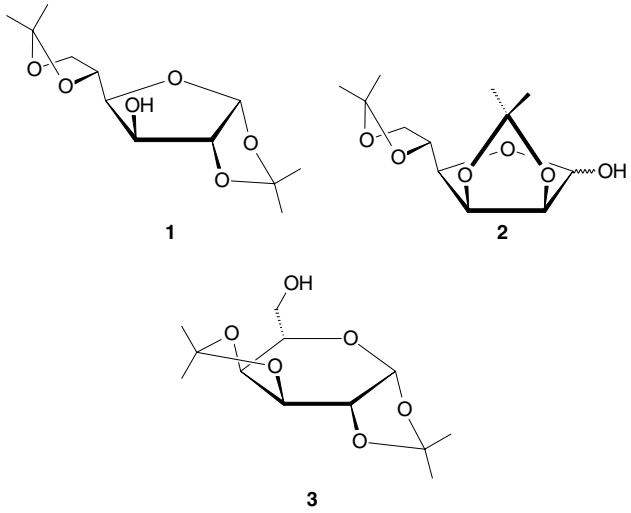


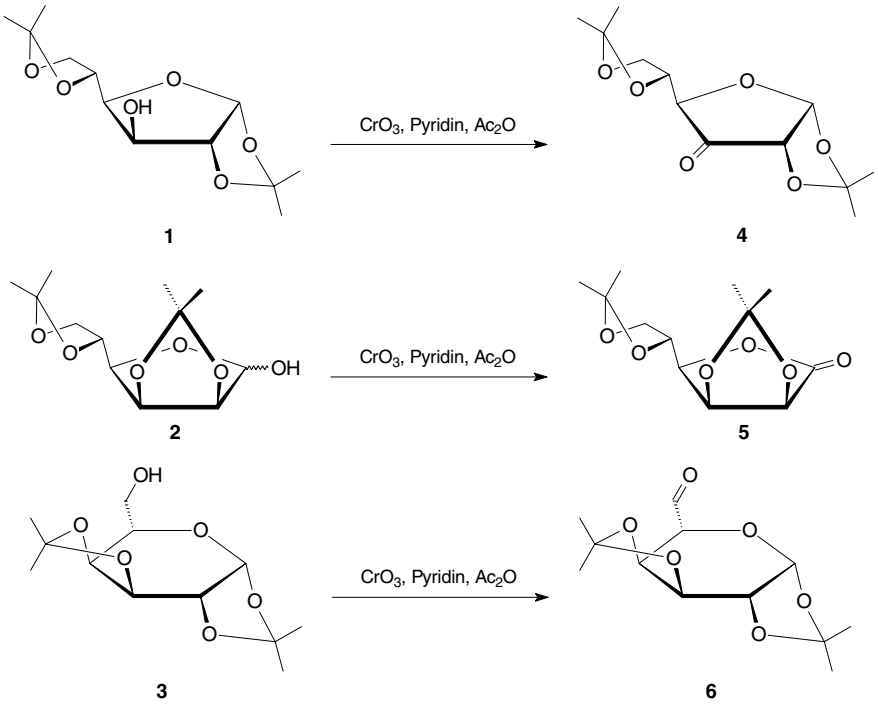
Fig. 1. Isopropylidene-protected carbohydrates as starting compounds.

well-established reagent for the oxidation of primary and secondary alcohols. Garegg and Samuelsson [12] applied it for the oxidation of partially isopropylidene-protected carbohydrates. The oxidation reactions were performed at room temperature with an excess of reagent. Compounds **1**–**3** were dissolved in dichloromethane and added dropwise. The oxidation products 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranos-3-ulose (**4**), 2,3:5,6-di-*O*-isopropylidene-D-manno-1,4-lactone (**5**) and 1,2:3,4-di-*O*-isopropyliden-D-galacto-6-aldehyde (**6**) could be isolated by a short column of silica gel. Yields between 46% and 70% were achieved.

The prochiral ketone **4** derived from β-D-glucofuranose seems comparable to the monoterpene ketones according to the nucleophilic attack of 2-lithiopyridine from the sterically less hindered side. The desired 2′-pyridinyl alcohol had already been isolated by Peterson and Mitchell [13]. In this case the comparatively rigid ring in position 1,2 is a more relevant obstacle than the free rotating ring in position 5,6 and therefore the nucleophile attacks on the *si*-side.

By reaction of compound **4** with 2-lithiopyridine (3*R*)-3-(2′-pyridinyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**7**, glupy) was obtained diasteriomerically pure in 35% yield (Fig. 2). The diastereomeric purity was proven by the detection of only one set of signals in the NMR-spectra. In the case of the lactone **5** derived from D-mannofuranose also cleavage of the intramolecular ester had to be taken into account, but the reaction of compound **5** with 2-lithiopyridine provides the desired 2′-pyridinyl alcohol (1*S*)-1-(2′-pyridinyl)-2,3:5,6-di-*O*-isopropylidene-D-mannofuranose (**8**, manpy) diastereomerically pure in 40% yield.

X-ray crystallography was used to determine the absolute configuration of **8** (Fig. 3). Surprisingly the



Scheme 2. Synthesis of prochiral carbonyl compounds.

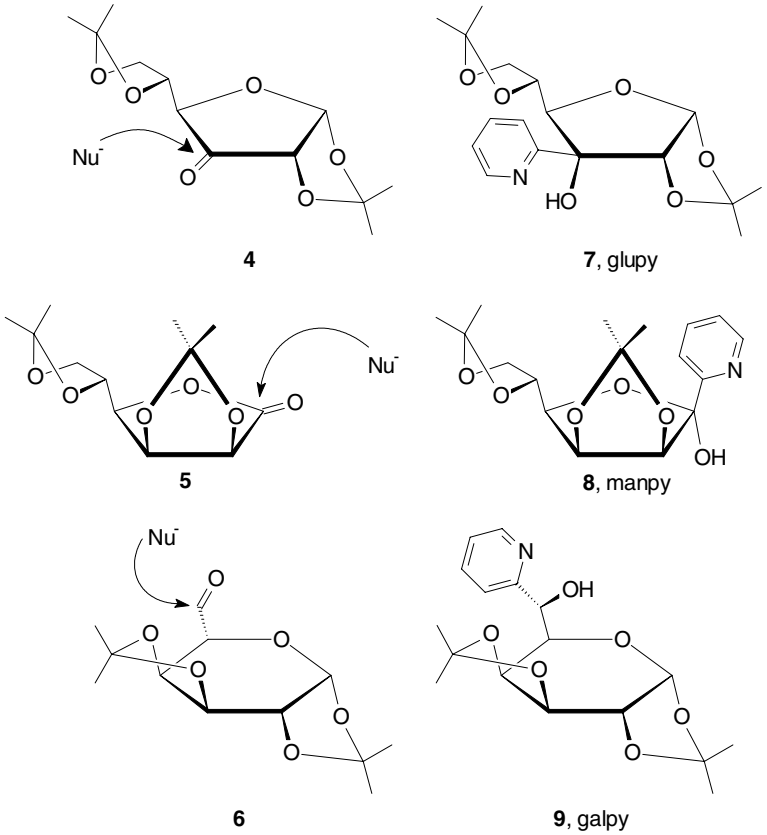


Fig. 2. Nucleophilic attack at prochiral carbonyl compounds to form chiral 2′-pyridinyl alcohols.

nucleophilic attack of 2-lithiopyridine on the carbonyl group is directed to the *si*-side, which looks sterically more hindered on the first glance. Obviously, the connection of the two hydroxy groups in 2,3-position and the intramolecular ester function are responsible for a special envelope configuration of the furanose ring that

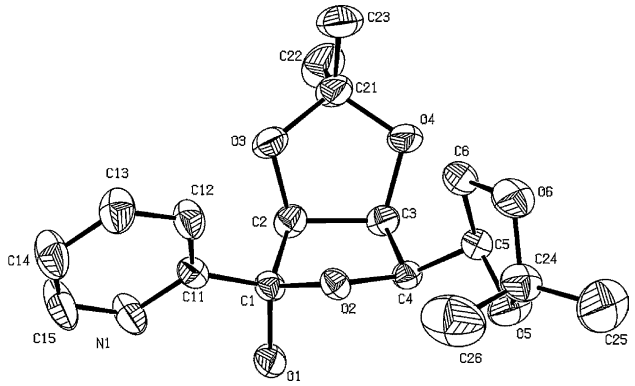


Fig. 3. ORTEP-representation of (1*S*)-1-(2′-pyridinyl)-2,3:5,6-di-*O*-isopropylidene-D-mannofuranose (**8**, manpy). Thermal ellipsoids represent 50% probability levels. Hydrogen atoms have been omitted for clarity.

Table 1
Selected bond lengths (pm) and bond angles (°) of manpy (**8**)

Bond length (pm)		Angle (°)	
O1–C1	140.2(2)	O1–C1–C11	111.96(13)
C1–C11	150.8(2)	O1–C1–O2	108.90(13)
N1–C11	132.5(2)	O1–C1–C2	107.46(14)
C1–C2	153.2(3)	O2–C1–C2	104.04(13)
C1–O2	141.2(2)	N1–C11–C1	115.34(15)
O2–C4	144.2(2)	C1–O2–C4	106.38(12)
C2–C3	153.4(3)	C1–C2–C3	103.80(13)
		O4–C3–C4	111.24(14)

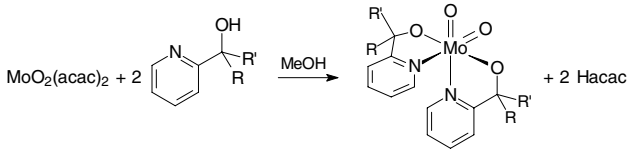
allows a nucleophilic attack only from the *exo*-side. In **8** the angle at the chiral carbon C1 between the hydroxy group and the pyridine ring is 112° compared to about 107° in ligands derived from monoterpenes [4] (see Table 1).

The bond distances between C1 and both hydroxy group and pyridine ring are only slightly shorter than in those ligands [4]. Therefore, sterically there is no significant difference between the lactone **8** and the known chiral 2′-pyridinyl alcohol ligands.

The third prochiral carbonyl compound **6** derived from D-galactopyranose represents an aldehyde and contrary to the former cases here a secondary alcohol is formed. The carbonyl function can easily rotate, and it can be considered that during the attack of the lithiumpyridine (approaching from outside the pyranose ring) it faces away from the substituents in 3,4-position. The chiral 2′-pyridinyl alcohol (6*S*)-6-(2′-pyridinyl)-1,2:3,4-di-*O*-isopropylidene-D-galactopyranose (**9**, galpy) was isolated diastereomerically pure in 40% yield.

2.2. Synthesis of the dioxomolybdenum(VI)-complexes

Several synthetic routes to dioxomolybdenum(VI) 2′-pyridinyl alcoholate complexes from metal precursors



Scheme 3. Synthesis of dioxomolybdenum(VI) complexes.

bearing a *cis*-dioxo metal fragment have been developed [2,4]. In this work, $MoO_2(acac)_2$ was chosen as the precursor compound to be put to reaction with the chiral ligands **7**–**9**, since previous results [1,3] showed that the acetylacetonato ligands can very easily be replaced by 2′-pyridinyl alcoholates (Scheme 3).

The resulting complexes exhibit a *cis*-dioxo metal unit with the pyridine nitrogen donor atoms placed *trans* to the oxo ligands and the alcoholate ligands placed *trans* to each other. According to these structure principles the complexes are chiral with Δ- and Λ-isomers being possible (Fig. 4) [4,14]. When chiral ligands are applied Δ- and Λ-isomers are diastereomers and can be distinguished in the NMR-spectra.

$MoO_2(acac)_2$ reacts with two equivalents of 2′-pyridinyl alcohol in dry methanol to form the pyridinyl alcoholate complexes **10**–**12** of analytical purity in high yields (Fig. 5). In the case of $MoO_2(glupy)_2$ two sets of signals are detected, showing that a mixture of Δ- and Λ-isomers (**10a** and **10b**) is formed.

Ligand **8** is a cyclic semiacetal and differs from the ligands we had applied until now. For $MoO_2(manpy)_2$ (**11**) we found only one set of signals in the NMR-spectra, so only one isomer was formed. The structure of **11** was established by X-ray crystallography, representing to the best of our knowledge only the third example of a crystal structure of a dioxomolybdenum complex with a *N*,*O*-ligand derived from a carbohydrate, and the first example in which two bidentate sugar derived ligands are coordinated to a MoO_2 moiety (Fig. 6 and Table 2) [11]. The metal centre obtains Λ-configuration. Also for the third complex, $MoO_2(galpy)_2$ (**12**), only one set of signals is detected in the NMR-spectra.

2.3. Catalytic results

We examined the complexes **10**–**12** for their catalytic activity in the asymmetric epoxidation of unfunctionalized *trans*-olefins. This class of substrates is particularly

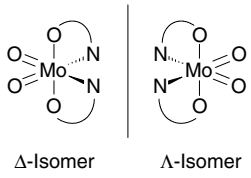


Fig. 4. Δ- and Λ-isomers.

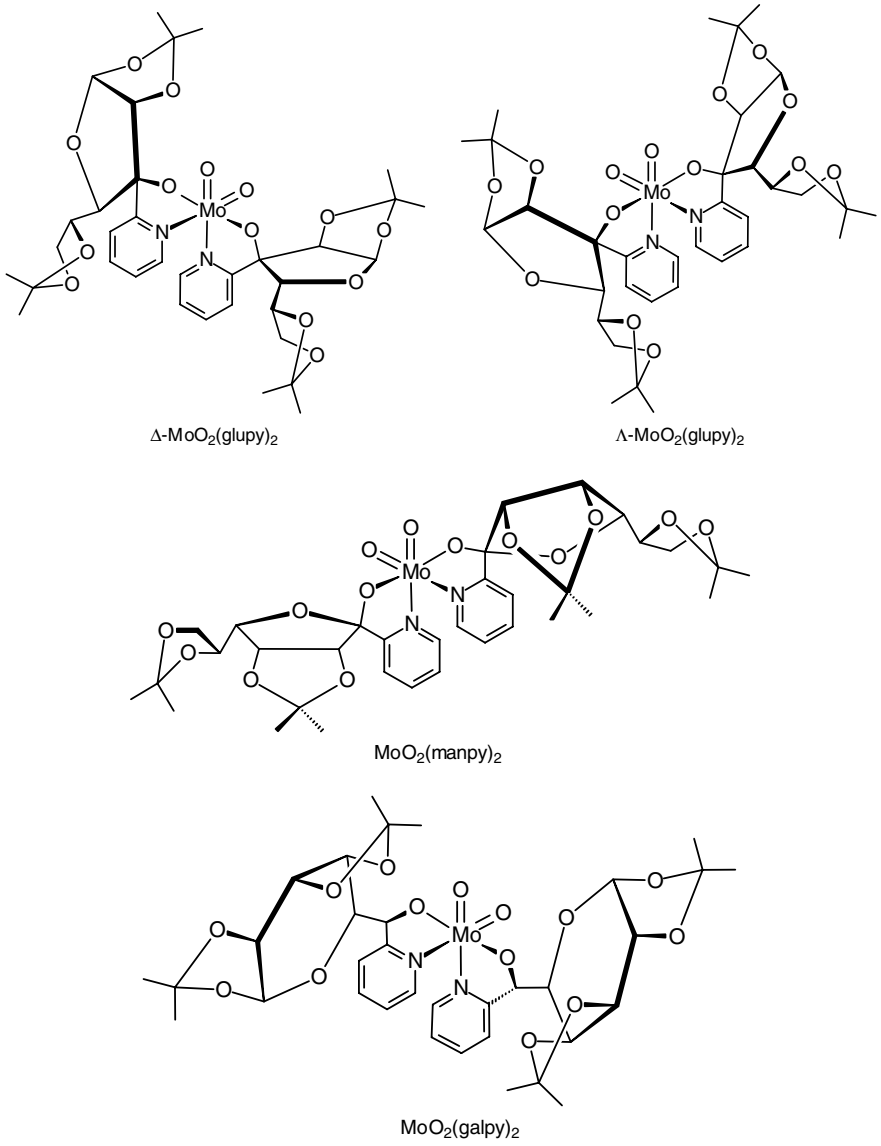


Fig. 5. Dioxomolybdenum(VI) complexes with chiral 2′-pyridinyl alcohol ligands derived from carbohydrates.

interesting because the Jacobsen method [15] works highly efficient mainly for *cis*-olefins. For our catalytic experiments, we chose *trans*-methylstyrene as model substrate and *tert*-butylhydroperoxide or cumolhydroperoxide as oxidant (Scheme 4). Using dioxomolybdenum(VI) complexes and 2′-pyridinyl ligands derived from monoterpenes up to 26% e.e. had been achieved with *tert*-butylhydroperoxide [4]. The use of tridentate, sugar derived chiral Schiff-base ligands, led to e.e.'s up to 30% [11b]. Enantiomeric excesses in a similar order of magnitude have been reached with variety of *cis*-MoO_2^{2+} epoxidation catalysts bearing chiral ligands, such as bis-oxazoline, *cis*-diol, *cis*-8-phenylthiomenthol, etc. [16].

In a typical catalytic run one equivalent of substrate was mixed with 1 mol% catalyst and two equivalents of oxidant (substrate:catalyst ratio 100:1). The reaction was performed over 6 h at 50 and 70 °C. Aliquots were taken every 30 min and were quenched by addition of manganese dioxide, filtered and analyzed by chiral gas chromatography. The results are depicted in Table 3. A comparison of the catalytic activities reveals good conversions only at 70 °C. Enantiomeric excesses up to 23% were achieved, but both catalytic activities and enantiomeric excesses were somewhat lower than for complexes with ligands derived from terpenes [4].

The mixture of Δ- and Λ-isomers in **10** does not give any optical induction, as expected. When the catalysts **11** and **12** were employed, always the same epoxidation products (*R*,*R* or *S*,*S*) were preferred, no matter which oxidant was used. It should also be noticed that no indication of epimerization under catalytic conditions for compounds **11** and **12** was found. The influence of the oxidant can be seen at the enantiomeric excesses. With

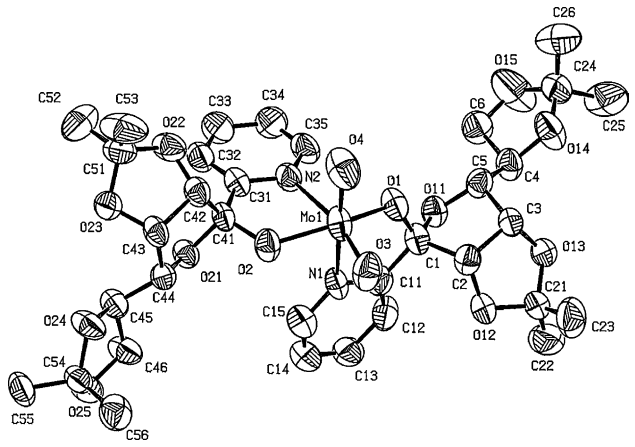
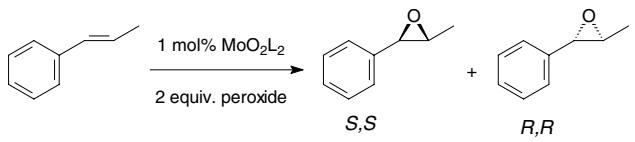


Fig. 6. ORTEP-representation of $MoO_2(manpy)_2$ (**11**). Thermal ellipsoids represent 50% probability levels. Hydrogen atoms were omitted for clarity.

Table 2
Selected bond lengths (pm) and bond angles (°) of $MoO_2(manpy)_2$ (**11**)

Bond length (pm)		Bond angle (°)	
Mo–O1	195.5(3)	O3–Mo–O4	105.9(3)
Mo–O2	193.5(3)	O1–Mo–O3	103.10(17)
Mo–O3	171.7(4)	O1–Mo–O2	147.62(18)
Mo–O4	171.4(4)	O1–Mo–N1	72.22(18)
Mo–N1	234.7(5)	O3–Mo–N1	86.9(2)
Mo–N2	235.1(4)	N1–Mo–N2	79.11(18)
O1–C1	139.5(7)	O1–C1–C11	110.0(4)
O11–C1	141.6(7)	N1–C11–C1	112.7(5)
N1–C11	133.9(8)		
C1–C11	153.4(8)		



Scheme 4. Epoxidation of *trans*-methylstyrene.

cumolhydroperoxide higher product selectivities were obtained, which might be a consequence of π-interactions between substrate and oxidant. This type of interactions has also been taken into account for the Jacobsen system [17].

3. Conclusion

Carbohydrates are promising precursor compounds for the synthesis of chiral ligands because of their functional groups and well-defined stereochemistry. Three isopropylidene-protected carbohydrates were transferred into prochiral ketones through oxidation of one hydroxy group. The corresponding carbonyl compounds are suitable precursor molecules for chiral 2′-pyridinyl alcohols, which can be employed as ligands in dioxomolybdenum(VI) complexes. In this type of complexes two configurations are possible. Using one of the three new ligands a mixture of Δ- and Λ-isomers was obtained. When the other ligands were employed, only one isomer was formed. In these cases the catalytic results show the suitability of dioxomolybdenum(VI) complexes with 2′-pyridinyl alcohol ligands derived from carbohydrates for asymmetric epoxidation. Further research to identify more effective catalysts within the group of carbohydrates is required and is currently under way in our laboratories.

4. Experimental

4.1. General remarks

Only freshly distilled, dry and oxygen-free solvents were used. The ^1H- and ^{13}C NMR spectra were recorded at 399.78 and 100.61 MHz on a Jeol JNM-GX-400 instrument. IR spectra were recorded on a Perkin–Elmer 1650 spectrometer (KBr). Elemental analyses were performed in the Mikroanalytische Labor of the Technical University Munich (M. Barth). Mass spectra were recorded on a Finnigan MAT 90-spectrometer by R. Dumitrescu. Catalytic runs were monitored by chiral GC methods on a Hewlett–Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphadex 120 and a Hewlett–Packard integration unit HP 3396 Series II by S. Mühl.

$MoO_2(acac)_2$, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose, 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose, 2-bromopyridine, *tert*-butylhydroperoxide, cumolhydroperoxide and *trans*-methylstyrene were purchased from Aldrich and used without further purification.

4.2. X-ray crystallography

Suitable single crystals for the X-ray diffraction studies were grown by standard techniques from saturated solutions in dichloromethane/methanol (**8**) or methanol (**11**) at room temperature.

The structure solution of **8** was carried out at the window of a rotating anode X-ray generator (Nonius FR591) using graphite monochromated Mo Kα radiation on an Enraf-Nonius KappaCCD diffractometer. A suitable crystal was selected in a perfluorinated polyether and transferred into a glass capillary, which was mounted in a N_2 cooling stream. The data was corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods using the program SIR-92 and refined by full-matrix

Table 3
Conversions, enantiomeric excesses (e.e.) and main products in the asymmetric epoxidation of *trans* methylstyrene with TBHP or cumolhydroperoxide and 1.0 mol% of compounds **10**–**12** after 6 h at 50 or 70 °C in %

	TBHP, 50 °C		TBHP, 70 °C		CHP, 50 °C		CHP, 70 °C	
	Conversion	e.e.	Conversion	e.e.	Conversion	e.e.	Conversion	e.e.
10	38	0	65	0	29	0	58	0
11	29	8 *R*,*R*	52	7 *R*,*R*	20	17 *R*,*R*	47	23 *R*,*R*
12	32	7 *S*,*S*	56	5 *S*,*S*	23	8 *S*,*S*	52	6 *S*,*S*

least-square techniques against F^2 using the program SHELXL-97 [18,19]. The absolute structure was determined using the Flack parameter and by refinement of an assumed racemic twin. The Flack parameter of −0.1(9) (1.1(9) for the inverted structure) is not a satisfactory criterion in this case because of its high standard deviation. An additional twin refinement of both enantiomers was carried out and a value of 0.00001 is obtained for the fractional contribution of the two components, showing that the correct absolute structure was assumed.

The structure solution of **11** was carried out on an IPDS diffractometer (STOE) using graphite monochromated Mo Kα radiation of a rotating anode X-ray generator (Nonius FR591). The crystal was selected in a perfluorinated polyether and transferred into a glass capillary. During cell determination two twin domains have been found and integrated separately. The two datasets were then merged together. The structure was solved by direct methods using the program SIR-92 and refined by full-matrix least-square techniques against F^2 using the program SHELXL-97 [18,19]. The Flack parameter of −0.03(5) shows, that the correct absolute structure was assumed.

The molecular illustrations were drawn using PLATON [20]. The crystallographic details are given in [21,22].

4.3. General procedure for the synthesis of the prochiral carbonyl compounds *4*–*6*

15.35 g (153 mmol) CrO_3 was added carefully to a stirred solution of 25.50 (307 mmol) pyridine in 350 ml dichloromethane in a 1000 ml flask equipped with a reflux condenser. The mixture was stirred for 20 min to produce a deep-red solution. 10 g (28.4 mmol) of the appropriate isopropylidene-protected carbohydrate (**1**–**3**) was dissolved in 50 ml dichloromethane and added dropwise with stirring at room temperature. The color of the mixture changed to dark-brown. 14.5 ml (153 mmol) acetic anhydride was added at once. The formation of the product was monitored by TLC using ethyl acetate as solvent and 2,4-dinitrophenylhydrazine to mark the product. After 30 min, the volume was reduced to 100 ml and the dark-brown tarry mixture was transferred to the top of a short column of silica gel in ethyl acetate, with a layer of ethyl acetate above the gel in which chromium compounds were precipitated before elution. The eluate was concentrated to produce colourless oils (**4**, **6**) or a colourless solid (**5**).

4.4. 1,2:5,6-Di-O-isopropylidene-α-D-glucofuranos-3-ulose (*4*)

Yield: 4.61 g, 46%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): $\delta = 6.33$ (H^1, d, $^3J(H^1, H^2) = 4$ Hz, 1H), 4.82 (H^2, d, $^3J(H^2, H^1) = 4$ Hz, 1H), 4.27 (H^4, d, $^3J(H^4, H^5) = 7$ Hz, 1H), 3.81 (H^5, m, $^3J(H^5, H^4) = 7$ Hz, $^3J(H^5, H^{6ax}) = 8$ Hz, $^3J(H^5, H^{6eq}) = 6$ Hz, 1H), 3.61 (H^{6ax}, dd, $^2J(H^{6ax}, H^{6eq}) = 13$ Hz, $^3J(H^{6ax}, H^5) = 8$ Hz, 1H), 3.51 (H^{6eq}, dd, $^2J(H^{6eq}, H^{6ax}) = 13$ Hz, $^3J(H^{6eq}, H^5) = 6$ Hz, 1H), 1.68 ($H^{8/9}$, s, 3H), 1.42 ($H^{8/9}$, s, 3H), 1.37 ($H^{11/12}$, s, 3H), 1.16 ($H^{11/12}$, s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, ppm): $\delta = 208.74$ (C^3), 114.09 (C^7), 110.18 (C^{10}), 102.97 (C^1), 78.81 (C^2), 77.11 (C^4), 76.24 (C^5), 66.13 (C^6), 27.41 ($C^{8/9}$), 27.01 ($C^{8/9}$), 25.82 ($C^{11/12}$), 25.14 ($C^{11/12}$).

4.5. 2,3:5,6-di-O-isopropylidene-D-manno-1,4-lactone (*5*)

Yield: 6.42 g, 64%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): $\delta = 4.85$ (H^3, dd, $^3J(H^3, H^2) = 5$ Hz, $^3J(H^3, H^4) = 3$ Hz, 1H), 4.81 (H^2, d, $^3J(H^2, H^3) = 5$ Hz, 1H), 4.41 (H^5, m, $^3J(H^5, H^4) = 8$ Hz, $^3J(H^5, H^{6ax}) = 6$ Hz, $^3J(H^5, H^{6eq}) = 4$ Hz, 1H), 4.35 (H^4, dd, $^3J(H^4, H^3) = 3$ Hz, $^3J(H^4, H^5) = 8$ Hz, 1H), 4.13 (H^{6ax}, dd, $^2J(H^{6ax}, H^{6eq}) = 10$ Hz, $^3J(H^{6ax}, H^5) = 6$ Hz, 1H), 4.06 (H^{6eq}, dd, $^2J(H^{6eq}, H^{6ax}) = 10$ Hz, $^3J(H^{6eq}, H^5) = 4$ Hz, 1H), 1.46 ($H^{8/9}$, s, 3H), 1.45 ($H^{8/9}$, s, 3H), 1.41 ($H^{11/12}$, s, 3H), 1.37 ($H^{11/12}$, s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, ppm): $\delta = 173.41$ (C^1), 114.50 (C^7), 109.92 (C^{10}), 78.14 (C^2), 76.06 (C^3), 75.81 (C^4), 72.57 (C^5), 66.45 (C^6), 26.97 ($C^{8/9}$), 26.77 ($C^{8/9}$), 25.91 ($C^{11/12}$), 25.07 ($C^{11/12}$).

4.6. 1,2:3,4-di-O-isopropylidene-D-galacto-6-aldehyde (*6*)

Yield: 7.04 g, 70%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): $\delta = 5.63$ (H^1, d, $^3J(H^1, H^2) = 4$ Hz, 1H), 4.60

(H^5, d, $^3J(H^5, H^4)=3$ Hz, 1H), 4.56 (H^4, dd, $^3J(H^4, H^3)=5$ Hz, $^3J(H^4, H^5)=3$ Hz, 1H), 4.34 (H^2, dd, $^3J(H^2, H^1)=4$ Hz, $^3J(H^2, H^3)=2$ Hz, 1H), 4.28 (H^3, dd, $^3J(H^3, H^2)=2$ Hz, $^3J(H^3, H^4)=5$ Hz, 1H), 1.48 ($H^{8/9}$, s, 3H), 1.40 ($H^{8/9}$, s, 3H), 1.31 ($H^{11/12}$, s, 3H), 1.28 ($H^{11/12}$, s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, ppm): $\delta=200.19$ (C^6), 110.03 (C^7), 109.01 (C^{10}), 96.19 (C^1), 73.17 (C^5), 71.67 (C^2), 70.67 (C^4), 70.34 (C^3), 25.94 ($C^{8/9}$), 25.74 ($C^{8/9}$), 24.74 ($C^{11/12}$), 24.18 ($C^{11/12}$).

4.7. General procedure for the synthesis of the 2′-pyridinyl alcohols 7–9

To 40 ml dry THF was added 7.5 ml (12 mmol) 1.6 M *n*-buthyllithium/hexane under nitrogen. The mixture was cooled to −40 °C (dry ice/isopropanol). A solution of 0.95 ml (10 mmol) 2-bromopyridine in 10 ml dry diethylether was added dropwise under vigorous stirring and the clear solution turned dark-red. After stirring for additional 30 min at −40 °C, a solution of the oxidized carbohydrate compound (**4**–**6**) (2.3 g, 9 mmol) in 10 ml THF was added dropwise. The mixture turned brown and was stirred for 2 h at −40 °C. Then it was allowed to warm up to 0 °C within 1 h and carefully hydrolyzed by addition of 5 ml of saturated aqueous ammonium chloride solution. For the isolation of the reaction product the volume was reduced to 15 ml and the yellow suspension was transferred to the top of a column of silica gel in hexane/ethyl acetate (7:3). The eluate was concentrated to produce a yellow solid. Recrystallisation from dichloromethane/methanol (3:1) gives colourless crystals of analytical purity.

4.8. (3R)-3-(2′-pyridinyl)-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (7)

Yield: 1.06 g, 35%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): $\delta=8.68$ ($H^{6'}$, d, $^3J(H^{6'}, H^{5'})=5$ Hz, 1H), 7.89 ($H^{4'}$, dd, $^3J(H^{4'}, H^{5'})=8$ Hz, $^3J(H^{4'}, H^{3'})=8$ Hz, 1H), 7.75 ($H^{3'}$, d, $^3J(H^{3'}, H^{4'})=8$ Hz, 1H), 7.40 ($H^{5'}$, dd, $^3J(H^{5'}, H^{4'})=8$ Hz, $^3J(H^{5'}, H^{6'})=5$ Hz, 1H), 6.26 (H^1, d, $^3J(H^1, H^2)=4$ Hz, 1H), 4.74 (H^2, d, $^3J(H^2, H^1)=4$ Hz, 1H), 4.18 (H^4, d, $^3J(H^4, H^5)=7$ Hz, 1H), 3.95 (OH, s, 1H), 3.67 (H^5, m, $^3J(H^5, H^4)=7$ Hz, $^3J(H^5, H^{6ax})=8$ Hz, $^3J(H^5, H^{6eq})=6$ Hz, 1H), 3.55 (H^{6ax}, dd, $^2J(H^{6ax}, H^{6eq})=13$ Hz, $^3J(H^{6ax}, H^5)=8$ Hz, 1H), 3.45 (H^{6eq}, dd, $^2J(H^{6eq}, H^{6ax})=13$ Hz, $^3J(H^{6eq}, H^5)=6$ Hz, 1H), 1.65 ($H^{8/9}$, s, 3H), 1.41 ($H^{8/9}$, s, 3H), 1.35 ($H^{11/12}$, s, 3H), 1.14 ($H^{11/12}$, s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, ppm): $\delta=157.74$ ($C^{2'}$), 146.62 ($C^{6'}$), 138.91 ($C^{4'}$), 123.59 ($C^{3'}$), 122.58 ($C^{5'}$), 113.14 (C^7), 109.25 (C^{10}), 105.72 (C^1), 83.90 (C^3), 83.82 (C^2), 81.37 (C^4), 73.64 (C^5), 66.44 (C^6), 26.78 ($C^{8/9/11/12}$), 26.72 ($C^{8/9/11/12}$), 26.61 ($C^{8/9/11/12}$), 25.25 ($C^{8/9/11/12}$).

4.9. (1S)-1-(2′-Pyridinyl)-2,3:5,6-di-O-isopropylidene-D-mannofuranose (8)

Yield: 1.21 g, 40%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): $\delta=8.52$ ($H^{6'}$, d, $^3J(H^{6'}, H^{5'})=4$ Hz, 1H), 7.73 ($H^{4'}$, dd, $^3J(H^{4'}, H^{5'})=8$ Hz, $^3J(H^{4'}, H^{3'})=8$ Hz, 1H), 7.61 ($H^{3'}$, d, $^3J(H^{3'}, H^{4'})=8$ Hz, 1H), 7.30 ($H^{5'}$, dd, $^3J(H^{5'}, H^{4'})=8$ Hz, $^3J(H^{5'}, H^{6'})=4$ Hz, 1H), 5.21 (H^3, dd, $^3J(H^3, H^2)=5$ Hz, $^3J(H^3, H^4)=3$ Hz, 1H), 4.66 (H^2, d, $^3J(H^2, H^3)=5$ Hz, 1H), 4.40 (H^5, m, $^3J(H^5, H^4)=8$ Hz, $^3J(H^5, H^{6ax})=6$ Hz, $^3J(H^5, H^{6eq})=4$ Hz, 1H), 4.31 (H^4, dd, $^3J(H^4, H^3)=3$ Hz, $^3J(H^4, H^5)=8$ Hz, 1H), 4.12 (H^{6ax}, dd, $^2J(H^{6ax}, H^{6eq})=10$ Hz, $^3J(H^{6ax}, H^5)=6$ Hz, 1H), 4.08 (H^{6eq}, dd, $^2J(H^{6eq}, H^{6ax})=10$ Hz, $^3J(H^{6eq}, H^5)=4$ Hz, 1H), 4.04 (OH, s, 1H), 1.48 ($H^{8/9}$, s, 3H), 1.42 ($H^{8/9}$, s, 3H), 1.34 ($H^{11/12}$, s, 3H), 1.27 ($H^{11/12}$, s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, ppm): $\delta=155.10$ ($C^{2'}$), 147.12 ($C^{6'}$), 136.48 ($C^{4'}$), 123.97 ($C^{3'}$), 123.85 ($C^{5'}$), 112.88 (C^7), 109.25 (C^{10}), 103.36 (C^1), 87.11 (C^2), 80.25 (C^3), 79.97 (C^4), 73.32 (C^5), 67.06 (C^6), 26.90 ($C^{8/9/11/12}$), 25.67 ($C^{8/9/11/12}$), 25.37 ($C^{8/9/11/12}$), 23.98 ($C^{8/9/11/12}$).

4.10. (6S)-6-(2′-Pyridinyl)-1,2:3,4-di-O-isopropylidene-D-galactopyranose (9)

Yield: 1.22 g, 40%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): $\delta=8.38$ ($H^{6'}$, d, $^3J(H^{6'}, H^{5'})=4$ Hz, 1H), 7.75 ($H^{4'}$, dd, $^3J(H^{4'}, H^{5'})=8$ Hz, $^3J(H^{4'}, H^{3'})=8$ Hz, 1H), 7.62 ($H^{3'}$, d, $^3J(H^{3'}, H^{4'})=8$ Hz, 1H), 7.31 ($H^{5'}$, dd, $^3J(H^{5'}, H^{4'})=8$ Hz, $^3J(H^{5'}, H^{6'})=4$ Hz, 1H), 5.41 (H^1, d, $^3J(H^1, H^2)=4$ Hz, 1H), 4.51 (H^5, d, $^3J(H^5, H^4)=3$ Hz, 1H), 4.45 (OH, s, 1H), 4.44 (H^4, dd, $^3J(H^4, H^3)=5$ Hz, $^3J(H^4, H^5)=3$ Hz, 1H), 4.18 (H^2, dd, $^3J(H^2, H^1)=4$ Hz, $^3J(H^2, H^3)=2$ Hz, 1H), 4.04 (H^3, dd, $^3J(H^3, H^2)=2$ Hz, $^3J(H^3, H^4)=5$ Hz, 1H), 1.31 ($H^{8/9}$, s, 3H), 1.23 ($H^{8/9}$, s, 3H), 1.15 ($H^{11/12}$, s, 3H), 1.13 ($H^{11/12}$, s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, ppm): $\delta=155.92$ ($C^{2'}$), 144.96 ($C^{6'}$), 139.02 ($C^{4'}$), 126.76 ($C^{3'}$), 122.61 ($C^{5'}$), 110.17 (C^7), 109.79 (C^{10}), 97.92 (C^1), 79.98 (C^6), 73.84 (C^5), 72.16 (C^2), 71.99 (C^4), 70.39 (C^3), 26.26 ($C^{8/9/11/12}$), 25.10 ($C^{8/9/11/12}$), 24.53 ($C^{8/9/11/12}$), 24.24 ($C^{8/9/11/12}$).

4.11. General procedure for the synthesis of the dioxomolybdenum(VI) complexes 10–12

1 g (3 mmol) 2′-pyridinyl alcohol (**7**–**9**) was added to a suspension of 0.49 g (1.5 mmol) $MoO_2(acac)_2$ in 20 ml dry methanol. After stirring for 30 min at 30 °C the volume of the solution was reduced to 5 ml and the reaction products precipitated as white solids. The supernatant was filtered off with a Whatman filter-wrapped cannula and the obtained solid was washed with few cold methanol. Finally, the product was dried under high vacuum to give a white powder of analytical purity. For X-ray

diffraction studies compound **11** was recrystallized from methanol to give colourless crystals.

4.12. Dioxomolybdenum(VI)-bis[(3R)-3-(2′-pyridinyl)-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose] (mixture of Δ- and Λ-isomer) (10)

Yield: 1.07 g, 89%. Anal. Calc. for $C_{34}H_{44}N_2O_{14}Mo$: C, 51.00; H, 5.54; N, 3.50. Found: C, 51.70; H, 5.83; N, 3.46%. FAB-MS (*m*/*z*): 802.4 ($[M]^+$), 744.5. IR (KBr, cm^{-1}): *v*(Mo=O) = 925, 906. ^1H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 9.25/9.16 ($H^{6'}$, d, $^3J(H^{6'}, H^{5'})$ = 5 Hz, 2H), 7.82/78 ($H^{4'}$, dd, $^3J(H^{4'}, H^{5'})$ = 8 Hz, $^3J(H^{4'}, H^{3'})$ = 8 Hz, 2H), 7.67/7,58 ($H^{3'}$, d, $^3J(H^{3'}, H^{4'})$ = 8 Hz, 2H), 7.36/7.27 ($H^{5'}$, dd, $^3J(H^{5'}, H^{4'})$ = 8 Hz, $^3J(H^{5'}, H^{6'})$ = 5 Hz, 2H), 6.16/6.06 (H^1, d, $^3J(H^1, H^2)$ = 4 Hz, 2H), 4.80/4.73 (H^2, d, $^3J(H^2, H^1)$ = 4 Hz, 2H), 4.67/4.63 (H^4, d, $^3J(H^4, H^5)$ = 7 Hz, 2H), 4.17/4.08 (H^5, m, $^3J(H^5, H^4)$ = 7 Hz, $^3J(H^5, H^{6ax})$ = 8 Hz, $^3J(H^5, H^{6eq})$ = 6 Hz, 2H), 3.62/3.55 (H^{6ax}, dd, $^2J(H^{6ax}, H^{6eq})$ = 13 Hz, $^3J(H^{6ax}, H^5)$ = 8 Hz, 2H), 3.33/2.87 (H^{6eq}, dd, $^2J(H^{6eq}, H^{6ax})$ = 13 Hz, $^3J(H^{6eq}, H^5)$ = 6 Hz, 2H), 1.74/1.68 ($H^{8/9}$, s, 6H), 1.42/1.40 ($H^{8/9}$, s, 3H), 1.32/1.29 ($H^{11/12}$, s, 6H), 1.23/1.16 ($H^{11/12}$, s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, ppm): δ = 161.56/160.40 ($C^{2'}$), 150.02/148.78 ($C^{6'}$), 139.25/139.19 ($C^{4'}$), 124.49/123.87 ($C^{3'}$), 121.14/120.71 ($C^{5'}$), 113.97/113.70 (C^7), 110.06/108.29 (C^{10}), 104.53/102.78 (C^1), 94.36/93.34 (C^3), 84.71/82.41 (C^2), 81.79/81.62 (C^4), 73.89/72.47 (C^5), 68.71/63.84 (C^6), 27.05/26.92/26.85/26.78/26.56/26.33/26.27/25.30 ($C^{8/9/11/12}$).

4.13. Dioxomolybdenum(VI)-bis[(1S)-1-(2′-pyridinyl)-2,3:5,6-di-O-isopropylidene-D-mannofuranose] (11)

Yield: 1.09 g, 91%. Anal. Calc. for $C_{34}H_{44}N_2O_{14}Mo$: C, 51.00; H, 5.54; N, 3.50. Found: C, 50.64; H, 5.70; N, 3.39%. EI-MS (*m*/*z*): 803.4 ($[M]^+$), 585.0. IR (KBr, cm^{-1}): *v*(Mo=O) = 922, 899. ^1H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 8.56 ($H^{6'}$, d, $^3J(H^{6'}, H^{5'})$ = 4 Hz, 2H), 7.74 ($H^{4'}$, dd, $^3J(H^{4'}, H^{5'})$ = 8 Hz, $^3J(H^{4'}, H^{3'})$ = 8 Hz, 2H), 7.47 ($H^{3'}$, d, $^3J(H^{3'}, H^{4'})$ = 8 Hz, 2H), 7.21 ($H^{5'}$, dd, $^3J(H^{5'}, H^{4'})$ = 8 Hz, $^3J(H^{5'}, H^{6'})$ = 4 Hz, 2H), 5.05 (H^3, dd, $^3J(H^3, H^2)$ = 5 Hz, $^3J(H^3, H^4)$ = 3 Hz, 2H), 4.93 (H^2, d, $^3J(H^2, H^3)$ = 5 Hz, 2H), 4.57 (H^5, m, $^3J(H^5, H^4)$ = 8 Hz, $^3J(H^5, H^{6ax})$ = 6 Hz, $^3J(H^5, H^{6eq})$ = 4 Hz, 2H), 4.54 (H^4, dd, $^3J(H^4, H^3)$ = 3 Hz, $^3J(H^4, H^5)$ = 8 Hz, 2H), 4.18 (H^{6ax}, dd, $^2J(H^{6ax}, H^{6eq})$ = 10 Hz, $^3J(H^{6ax}, H^5)$ = 6 Hz, 2H), 4.13 (H^{6eq}, dd, $^2J(H^{6eq}, H^{6ax})$ = 10 Hz, $^3J(H^{6eq}, H^5)$ = 4 Hz, 2H), 1.52 ($H^{8/9}$, s, 6H), 1.49 ($H^{8/9}$, s, 6H), 1.42 ($H^{11/12}$, s, 6H), 1.29 ($H^{11/12}$, s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, ppm): δ = 157.04 ($C^{2'}$), 146.50 ($C^{6'}$), 138.43 ($C^{4'}$), 125.33 ($C^{3'}$), 125.14 ($C^{5'}$), 113.41 (C^7), 112.96 (C^{10}), 109.40 (C^1), 83.79 (C^2), 80.45 (C^3), 80.20 (C^4), 73.42 (C^5), 66.99 (C^6), 26.87 ($C^{8/9/11/12}$), 25.69 ($C^{8/9/11/12}$), 25.39 ($C^{8/9/11/12}$), 24.01 ($C^{8/9/11/12}$).

4.14. Dioxomolybdenum(VI)-bis[(6S)-6-(2′-pyridinyl)-1,2:3,4-di-O-isopropylidene-D-galactopyranose] (12)

Yield: 0.77 g, 64%. Anal. Calc. for $C_{34}H_{44}N_2O_{14}Mo$: C, 51.00; H, 5.54; N, 3.50. Found: C, 50.78; H, 5.61; N, 3.44%. FAB-MS (*m*/*z*): 802.4 ($[M]^+$), 785.4. IR (KBr, cm^{-1}): *v*(Mo=O)=925, 897. ^1H NMR (400 MHz, D_4-MeOH, 298 K, ppm): δ = 8.39 ($H^{6'}$, d, $^3J(H^{6'}, H^{5'})$ = 4 Hz, 2H), 7.75 ($H^{4'}$, dd, $^3J(H^{4'}, H^{5'})$ = 8 Hz, $^3J(H^{4'}, H^{3'})$ = 8 Hz, 2H), 7.46 ($H^{3'}$, d, $^3J(H^{3'}, H^{4'})$ = 8 Hz, 2H), 7.24 ($H^{5'}$, dd, $^3J(H^{5'}, H^{4'})$ = 8 Hz, $^3J(H^{5'}, H^{6'})$ = 4 Hz, 2H), 5.71 (H^1, d, $^3J(H^1, H^2)$ = 4 Hz, 2H), 5.42 (H^5, d, $^3J(H^5, H^4)$ = 3 Hz, 2H), 4.63 (H^4, dd, $^3J(H^4, H^3)$ = 5 Hz, $^3J(H^4, H^5)$ = 3 Hz, 2H), 4.28 (H^2, dd, $^3J(H^2, H^1)$ = 4 Hz, $^3J(H^2, H^3)$ = 2 Hz, 2H), 4.10 (H^3, dd, $^3J(H^3, H^2)$ = 2 Hz, $^3J(H^3, H^4)$ = 5 Hz, 2H), 1.50 ($H^{8/9}$, s, 6H), 1.40 ($H^{8/9}$, s, 6H), 1.14 ($H^{11/12}$, s, 6H), 1.05 ($H^{11/12}$, s, 6H). ^{13}C NMR (100 MHz, D_4-MeOH, 298 K, ppm): δ = 163.52 ($C^{2'}$), 148.52 ($C^{6'}$), 139.72 ($C^{4'}$), 125.12 ($C^{3'}$), 124.59 ($C^{5'}$), 110.50 (C^7), 110.14 (C^{10}), 97.89 (C^1), 83.06 (C^6), 72.16 ($C^{2/4/5}$), 72.13 ($C^{2/4/5}$), 72.10 ($C^{2/4/5}$), 68.03 (C^3), 26.39 ($C^{8/9/11/12}$), 25.80 ($C^{8/9/11/12}$), 25.20 ($C^{8/9/11/12}$), 24.53 ($C^{8/9/11/12}$).

4.15. General procedure for the epoxidation of trans-methylstyrene with the dioxomolybdenum(VI) complexes 10–12

A total of 200 mg (1.7 mmol) of *trans*-methylstyrene, 14 mg (1.0 mol%) catalyst and 100 mg mesitylene as internal standard was dissolved in 2 ml toluene. After the addition of 0.615 μl (3.4 mmol) of a 5.5 M *tert*-butylhydroperoxide solution in decane (0.628 μl of cumolhydroperoxide, respectively) the reaction mixture was stirred for 6 h at 50 °C (70 °C, respectively). For GC-analysis aliquots of 10 μl were taken every 30 min, quenched with manganese dioxide, diluted with 0.5 ml dichloromethane and dried over magnesium sulfate. The enantiomeric excess and conversion was determined on a chiral GC column. The products were identified by co-injection of reference substances.

5. Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC-221597 (**8**) and CCDC-221598 (**11**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

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[21] Crystallographic details for **8**: 183 K, crystal color: brown, crystal size: 0.4×0.3×0.2 mm, orthorhombic, $a=8.3536(1)$ Å, $b=19.4311(2)$ Å, $c=21.0334(2)$ Å, $V=3414.3(6)$ Å^3, $Z=8$, $F(000)=1440$, $\rho_{calc}=1.314$ g cm^{-3}, space group $C222_1$, absorption coefficient 0.100 mm^{-1}, Θ limit 2.10–25.02°, γ- and ω-scan, 67325 reflections measured, 3008 independent reflections, 2836 reflections $F_o^2 > 2\sigma(F_o^2)$, 265 parameters, GOOF = 1.061, $R_1=0.0374$, $wR_2=0.0864$, final difference map residual electron density (e Å^{-3}) 0.26/−0.19.

[22] Crystallographic details for **11**: 293 K, crystal color: colorless, crystal size: 0.5×0.1×0.1 mm, orthorhombic, $a=10.2845(5)$ Å, $b=17.6287(13)$ Å, $c=20.3331(13)$ Å, $V=3686.4(7)$ Å^3, $Z=4$, $F(000)=1664$, $\rho_{calc}=1.443$ g cm^{-3}, space group $P2_12_12_1$, absorption coefficient 0.425 mm^{-1}, Θ limit 2.22–23.25°, γ-scan, 17388 reflections measured, 5022 independent reflections, 3787 reflections $F_o^2 > 2\sigma(F_o^2)$, 468 parameters, GOOF = 0.898, $R_1=0.0617$, $wR_2=0.0890$, final difference map residual electron density (e Å^{-3}) 0.35/−0.44.