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Molybdenum(VI) *cis*-dioxo complexes bearing sugar derived chiral Schiff-base ligands: synthesis, characterization, and catalytic applications †

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Molybdenum(VI)–*cis*-dioxo complexes bearing sugar derived chiral Schiff-base ligands of general formula $MoO_2(L)(Solv)$ have been synthesized (with L = *N*-salicylidene-D-glucosamine; *N*-salicylidene-1,3,4,6-tetraacetyl-α-D-glucosamine; *N*-5-chlorosalicylaldehyde-1,3,4,6-tetraacetyl-α-D-glucosamine; *N*-salicylaldehyde-1,3,4,6-tetraacetyl-β-D-glucosamine; *N*-5-chlorosalicylaldehyde-1,3,4,6-tetraacetyl-β-D-glucosamine; *N*-salicylidene-4,6-*O*-ethylidene-β-D-glucopyranosylamine, and Solv = methanol or ethanol). Analytical data including IR, 1D- and 2D-NMR, MS and EA are in accord with their descriptions as monometallic compounds with one ligand L and a coordinated solvent molecule. One of the complexes and two of the chiral ligands have been examined by X-ray crystallography. In the case of the sugar –OH groups being protected as acetyl groups, one of them is selectively deacetylated and coordinates to the metal centre during the reaction process. Furthermore, an inversion takes place at the C1 carbon atom. This uncommon behaviour has been examined in some detail. The high catalytic activity of the title compounds for epoxidation is also described as well as the moderate enantiomeric induction of up to 30% ee for *cis*-β-methyl styrene.

Introduction

The recent years have seen an increasing interest in the synthesis of chiral oxometallate complexes and their use as catalysts for asymmetric olefin epoxidation.[1] The generally comparatively good catalytic activities of several molybdenum(VI)–oxo complexes in oxidation reactions make this type of complexes – in principle – promising candidates for asymmetric catalysis by using chiral ligands.[2] 2′-Pyridyl alcohols[3] and phosphino-alcohols[4] have been reported to induce epoxidation with 20-40% ee for functionalized olefins when coordinated to dioxo or peroxo molybdenum(VI) fragments. In this context, we and others have reported on the synthesis of a variety of *cis*-MoO_2^{2+} epoxidation catalysts bearing chiral ligands, such as bis-oxazoline,[5] *cis*-diol and *cis*-8-phenylthiomenthol.[6]

Carbohydrates are naturally occurring enantiomeric pure compounds ("chiral pool")[7] that might be of interest in metal-assisted or metal-catalyzed enantioselective synthesis. During the past decade, the nature of their interactions with metal ions has been delineated by the characterization of many complexes.[8] Furthermore, strategies for saccharide ligand modification have also been developed in order to make the isolation and characterization of the products more straightforward. In this respect, one of the most successful ligands are the Schiff-base analogues derived from the condensation of a saccharide containing a NH_2 group with a salicylaldehyde or one of its derivatives, in order to obtain a ligand prone to N,O coordination to the metal centre.[9,10]

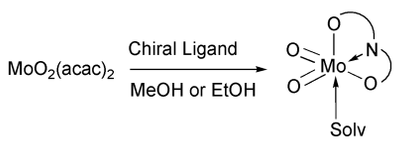
Still, catalytic applications of metal centres with sugar-derived ligands are quite rare. Among the few examples yet known are the hydroformylation of styrene with Rh(I)–diphosphine complexes,[11] catechol oxidation with Cu(II)–amino-carbohydrate β-ketoenaminic complexes,[12] hydrogenation with iridium–dithioether complexes[13] and allylic alkylation with palladium complexes.[14] However, despite some sugar derived ligands coordinated to *cis*-MoO_2^{2+} moieties have been reported recently,[9] the potential of this class of compounds as catalysts for olefin epoxidation, has not been, to the best of our knowledge, so far explored. In this work a study on the catalytic activity of molybdenum dioxo complexes bearing sugar containing Schiff-base ligands is presented and the first example of a molybdenum catalyzed deacetylation and an unusual ligand transformation during the coordination process with the molybdenum moiety is reported.

Results and discussion

Synthesis and spectroscopic examinations

The chiral Schiff-base ligands **1**–**6** (see Chart 1) were prepared by the condensation of salicylaldehyde and the corresponding D-glucose amines in water or methanol according to literature procedures.[15]

The corresponding Mo-complexes **7**–**10** of these ligands were synthesized by the reaction of $MoO_2(acac)_2$ and 1.1 equivalents of the corresponding chiral sugar ligands in methanol or ethanol, eqn. (1),



(1)

and could be isolated by precipitation on the addition of diethyl ether. All the new complexes are fairly air stable as solids, albeit decomposition occurs slowly in solution and the colour changes from yellow to green in the presence of moisture or moist air.

The infrared spectra of the product compounds **7**–**10** exhibit two strong $\nu_{Mo=O}$ bands in the region of *ca*. 920–940 and *ca*. 900–

† Electronic supplementary information (ESI) available: Analytical and spectroscopic data for ligand **1** and ORTEPS with selected bond lengths and angles for compounds **2** and **3**. See http://www.rsc.org/suppdata/dt/b3/b306039j/

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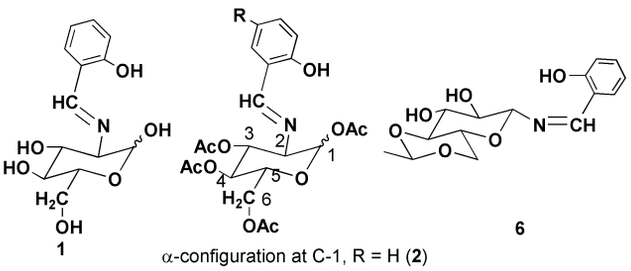


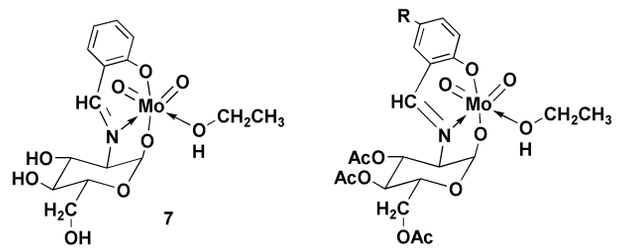
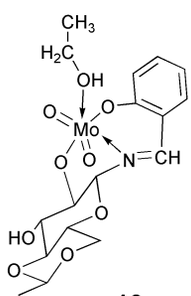


Chart 1

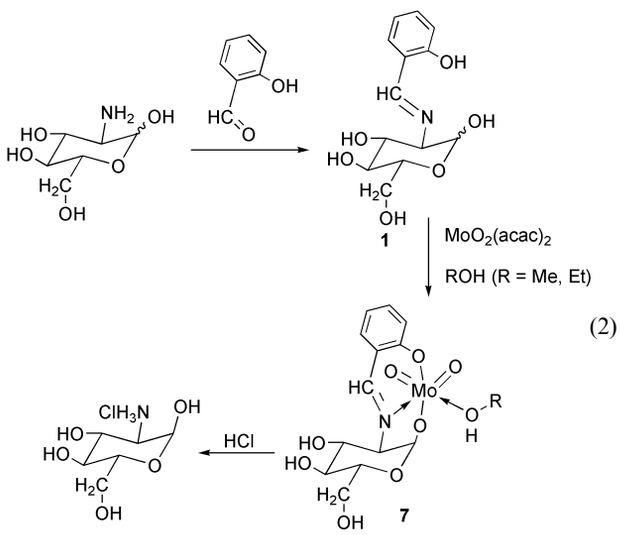


910 cm^{-1}, characteristic of the symmetric and asymmetric stretching vibrations of the *cis*-$[MoO_2]^{2+}$ fragments.[2,3,5,6] The most indicative newly appearing bonds are the ν(Mo–O) vibrations belonging to the molybdenum coordinated sugar-oxygen observed around 420 and 385 cm^{-1}, the ν(Mo–N) vibrations around 340 and 310 cm^{-1} and the ν(Mo–O) vibration coming from the molybdenum bound phenolic oxygen, observed at *ca*. 285 cm^{-1}.

Compounds **7**–**9** exhibit their ^{95}Mo NMR resonances shifted to higher field (−15 to −29 ppm) in comparison with the starting material $MoO_2(acac)_2$ (0 ppm). As expected, compound **7** with the ligand bearing free –OH groups exhibits the shift at highest field. These values can be compared with those reported in the literature for complexes bearing the *cis*-$[MoO_2]^{2+}$ moiety and two bidentate N–O ligands.[1b]

Spectroscopic and elemental analyses are consistent with monomeric complexes with a ligand:Mo ratio of 1 : 1. The mass spectra give no hint of the presence of dimeric species[16] or indicative fragments. For example, the molecular mass *m*/*z* = 409 and 536 was found in the mass spectra for the complexes **7** and **8**, respectively, and there are no other peaks in the higher mass region. When the synthesis reactions were performed using two equivalents of ligands, the same products were formed as observed with 1.1 equiv. ligand.

Interestingly, complex **7** is found to be a pure α-configurated compound according to the ^{1}H and ^{13}C NMR spectral study and could be obtained with yields of around 80% from ligand **1**. The ^{1}H NMR spectra of ligand **1**, however, shows two sets of signals, which represent α- and β-configuration with an integration area relationship of 1 : 2, while the $J_{1,2}$ coupling constants are 3.5 and 7.8 Hz for the *cis*-configuration of the α-sugar ring and the *trans*-configuration of the β-sugar ring, respectively.[17] After coordination, the ^{1}H NMR spectrum of complex **7** consists of only one set of peaks. The chemical shift of H1 changes to 5.58 ppm and the coupling constant $J_{1,2}$ is 3.04 Hz, indicating H1 and H2 to be in a *cis*-configuration. Furthermore, this demonstrates that the inversion of β-configuration into α-configuration occurs during the coordination of Mo, because the product yield is much higher than the content of α-configuration in the ligand precursor. To the best of our knowledge, such a phenomenon has not yet been reported in molybdenum coordination chemistry. The most possible structure of compound **7** with respect to the configuration of the coordinated tridentate ligand is shown below. Furthermore, the coordination of an ethanol molecule to the Mo centre is observed in the ^{1}H NMR and IR spectra and confirmed by elemental analysis. It can be concluded from the above described observations that the reaction outlined in eqn. (2)



(2)

could be even used as a possible method for the resolution of a diastereomeric sugar-derived Schiff base into an enantiomeric pure chiral one.

This interesting configuration transformation prompted us to a further examination of the interaction between the Molybdenum dioxo moiety and the protected sugar ligands **2** and **4**, which have differently configurated acetyl groups at their C1 positions. Again, inversion takes place when the β-configuration ligand is used, while the α-analogue remains in its original configuration, as can be seen by comparison of the coupling constants between H1 and H2 of the ligands **2** and **4** and the complex resulting from both reactions, **8**. The complex formed in both cases has an identical structure, since a deacetylation process occurs in both coordinations. The NMR spectra of complex **8** (obtained by different routes) demonstrate that in both cases one of the methyl groups and one of the carbonyl groups, which belong to the acetyl group, disappeared. By comparison of the ^{13}C NMR spectra of complex **8** with the ligands **2** and **4**, it is found that the chemical shift of the C1 in the ligand increases by about 8 ppm after the coordination to Mo, while the other ^{13}C-signals of the sugar ring remain almost unchanged. This observation indicates that the deacetylation reaction occurs solely at the C1 position during the coordination. Furthermore, pure complex **8** can be obtained when ligands **2** and **4** are mixed and used together. When a 1 : 1 mixture of the ligands **2** and **4** is reacted with $MoO_2(acac)$, only the C1-α-configurated ligand is consumed while the C1-β-configurated ligand remains in solution. Obviously the deacetylation/coordination reaction runs considerably faster than the inversion at C1 position. The same phenomenon can be also found in the case of ligands **3** and **5** to give the same

Table 1 Selected ^{1}H NMR chemical shifts (ppm) and coupling constants (Hz)

	1 (α-)	**1** (β-)	**7**	**2** (α-)	**4** (β-)	**8**	**3** (α-)	**5** (β-)	**9**
δ (H-1)	5.09	4.74	5.58	6.25	5.88	5.87	6.24	5.87	5.84
$J_{1,2}$	3.52	7.80	3.04	3.74	8.05	3.74	3.66	8.32	3.56
δ (CH=N)	8.32	8.31	8.54	8.37	8.30	8.37	8.30	8.24	8.27

Table 2 Selected bond lengths (pm) and bond angles (°) for compound **8**

Mo–O2	194.38(13)	Mo–O10	195.38(14)
Mo–O11	169.21(15)	Mo–O12	171.26(13)
Mo–O13	234.76(15)	Mo–N	228.48(15)
N–C2	146.6(3)	N–C15	128.9(2)
C17–O10	134.4(2)	C1–O2	141.1(2)
O2–Mo–O10	150.33(6)	O2–Mo–O11	99.09(6)
O2–Mo–O12	97.95(6)	O2–Mo–O13	79.98(5)
O2–Mo–N	74.60(6)	O10–Mo–O11	97.16(7)
O10–Mo–O12	101.31(6)	O10–Mo–O13	79.98(6)
O10–Mo–N	80.12(6)	O11–Mo–O12	105.74(8)
O11–Mo–O13	170.65(7)	O11–Mo–N	92.28(7)
O12–Mo–O13	83.59(6)	O12–Mo–N	161.50(7)
O13–Mo–N	78.48(5)	Mo–O2–C1	118.51(12)
C2–N–C15	119.20(16)	C2–C1–O2	108.29(15)
C1–O1–C5	115.16(13)	C1–C2–C3	110.63(15)

α-configurated product **9**. Representative chemical shifts and coupling constants are listed in Table 1.

An ester-exchange reaction catalyzed by a molybdenum moiety has been mentioned in the literature only once.[18] For the deacetylation of this kind of ligand, Lewis acids such as $ZrCl_2$ and $SnCl_4$ have also been successfully used.[19,20] Furthermore, by using $Ba(OMe)_2$ as catalyst, a similar process denoted Zemplén deacetylation[21] occurs, accompanied by a similar inversion at the C1 position.[17] The reaction described here provides another method for a selective deacetylation at the C1 position.[22] When complex **8** was decomposed in acids such as hydrochloric acid, the resulting amine salt was shown to display α-configuration by ^{1}H NMR spectroscopy and chiral GC.

Another important observation is the partial replacement of the ligand when compound **8** is stirred for prolonged times (24 h) at 40 °C with an excess of ligand **3** or **5** under formation of complex **9**. A similar observation is made when stirring compound **10** with excess ligand **2**. The ease of the ligand exchange in solution may account at least in part for the quite low ee's obtained in the catalytic reactions (see below).

The crystal structures of complex 8 and the ligands 2 and 3

In order to confirm the structure of the complexes described above derived from spectroscopic results, the X-ray crystal structure of compound **8** was exemplary determined. Selected bond distances and bond angles are given in Table 2 and an ORTEP style presentation is shown in Fig. 1. The bond distances between the Mo core and the terminal oxygens are around 170 pm and the bond distances to the sugar derived Schiff-base ligand oxygens *ca*. 195 pm. The ethanol OH group oxygen–Mo bond is, as expected, significantly longer (234.76(15) pm). While the terminal Mo–O bonds can be regarded as double bonds, the Mo–O ligand bonds are single bonds. The ethanol molecule, however, is only acting as a neutral donor ligand, which should therefore be replaceable quite easily. This ease of replacement might be the reason for both the good catalytic activity (high initial TOF, see below) and the moisture sensitivity of the complexes, it might, however, also be one of the reasons leading to the relatively low ee's in chiral catalysis (see catalysis section below). The nitrogen donor atom is 228.48(15) pm away from the Mo core. While the terminal oxygens occupy a *cis*-position, the ligand oxygens are located in a *trans* position to each other with an O–Mo–O angle of *ca*. 150°. Together with the ligand nitrogen atom they coordinate the Mo centre in a distorted T-fashion. The nitrogen atom and the ethanol-oxygen atom are in *trans*-position to the terminal, double bonded oxygen atoms. The coordination around the metal is a highly distorted octahedron, as is typical for six-coordinate molybdenum(VI) complexes. Compound **10**, first synthesized by Rao and co-workers has also been crystallographically examined by Rao's group.[9] Despite the higher steric rigidity of its ligand, the overall structure as well as the observed bond distances and angles are very similar to that of compound **8**.

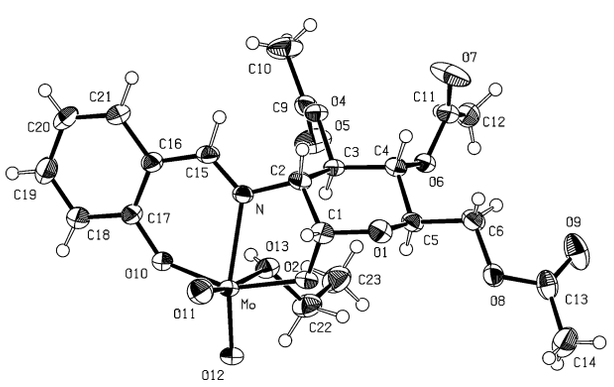


Fig. 1 ORTEP style drawing of the structure of compound **8**. The thermal ellipsoids are given at a 50% probability level.

For sake of completeness the structures of the sugar derived chiral Schiff-bases **2** and **3** have also been examined by X-ray crystallography (for details see ESI †). The bond angles and distances are only marginally influenced by the coordination to the Mo centre showing that the complex geometry is strongly influenced by the ligand geometry.

Complexes 7–10 in oxidation catalysis

The molybdenum–Schiff-base complexes **7**–**10** were examined as catalysts in the epoxidation of cyclooctene and both of *cis*- and *trans*-β-methylstyrene, with *tert*-butylhydroperoxide (TBHP) as the oxidant. Details about the conditions applied are given in the Experimental section. Blank runs were performed and, as expected, without catalyst, no significant epoxide formation was observed under the applied conditions.

In general, complexes **7**–**10** catalyzed the epoxidation of all three examined alkenes with good activity (TOFs up to 13000 h^{-1}) and complete stereo-retention, without significant by-product formation, the selectivity being close to 100%. In the case of epoxidation of cyclooctene, the yield reaches a value of 60–70% after 4 h, and after 22 h the reaction is completed in all cases (with the only exception of compound **7**), when the catalyst : substrate : oxidant ratio is 1 : 100 : 150. The activities obtained are similar to those reached by complexes of type $MoO_2X_2L_2$ (X = Cl, Br, L_2 = bidentate Lewis base ligand) which have been reported previously.[2d] Complexes **8** and **9** show the best catalytic activities with the highest TOFs of around 13000 h^{-1} with catalyst : substrate : oxidant ratios of 1 : 100000 : 150000. The substituent at the phenyl ring (H or Cl) seems to have little effect on the catalysis. The lowest activity is found for catalyst **7**: after 4 h only 20% yield could be obtained, while 70% was reached after 24 h, when the catalyst : substrate : oxidant ratio is 1 : 100 : 150. The main reason for this is probably the poor solubility of compound **7** in the oxidation solution. This explanation is supported by the observation that the general

Table 3 Epoxidation of *cis*- and *trans*-β-methylstyrene catalyzed by molybdenum–sugar complexes[a]

		cis-β-Methylstyrene		*trans*-β-Methylstyrene	
Catalyst	Temp./°C	ee (%)	Yield (%)	ee (%)	Yield (%)
7	0	0	15	0	6
	55	0	72	0	11
8	0	17	29	5	38
	55	5	94	2	72
9	0	22	31	3	46
10	0	23	35	10	17
	0[b]	30	52	12	25
	55	4	96	3	70

[a] The reactions were carried out by using a catalyst : substrate : oxidant ratio of 1 : 100 : 200 unless specified otherwise, the reaction time was 22 h and toluene was the solvent. Lower temperature (−23 °C) has also been applied in this reaction, but the low reactivity precludes the attempts for the improvement of enantioselectivity. [b] Using a 5 mol% amount of catalyst.

catalyst activity remains fairly unchanged for a much longer time than in the case of the other catalysts described in this work. When the soluble part of the catalyst decomposes, other catalyst molecules are dissolved and maintain the overall catalyst activity for some more time.

For the epoxidation of *cis*- and *trans*-β-methylstyrene, as expected, the general observation is that the catalytic activity as well as the asymmetric induction for the *cis* substrates is much better than that for the *trans* analogues. The effects of temperature, solvent and the amount of catalyst used have also been studied, and indicate that low temperature is beneficial for the ee obtained in this reaction. Within experimental error the results are the same in both CH_2Cl_2 and toluene as solvent. Higher amounts of catalyst also improve both ee and yield values. Accordingly, the highest observed ee of *ca.* 30% could be obtained with compound **10** as catalyst at 0 °C (Table 3). The low-temperature effect is probably due to a slower ligand exchange rate (see also above). Another reason for the relatively low ee's might be the ease of the exchange of the alcohol ligand by TBHP. The steric situation at the Mo centre is not crowded after the loss of the alcohol ligand and the chiral centers of the ligand may be too far away from the oxygen transfer site to have a strong influence. Enantiomeric excesses found in the literature for compounds of the type $MoO_2L^*_2$ (L* = chiral 2′-pyridinyl alcoholate are up to 25% for unfunctionalised olefins, higher ee's (up to 53%) being reported only for functionalized olefins such as allylic alcohols.[3a]

Summary

Complexes of the type $MoO_2(L)(Solv)$ (with L = tridentate, sugar derived chiral Schiff base, Solv = alcohol) are easily prepared by the reaction of the ligands L with $MoO_2(acac)_2$ in alcohols. Depending on the position of the potential coordination sites of the ligand L, the reactions lead to selective inversion at the C1 atom of the sugar ligand in order to reach the optimal coordination geometry. When esterification is used to protect the –OH groups of the sugar ligand, Lewis-acid catalyzed deacetylation takes place to allow a tridentate coordination of the ligand. The coordination of two bidentate ligands is not observed, even if the ligand size would allow it, as in the case of the non-protected ligand **1**. It can be assumed that during the epoxidation catalysis, where the examined complexes can be used as catalysts, the weakly coordinating alcohol ligand is replaced by TBHP. The TOF at the beginning of the reaction is very high in the case of cyclooctene as the substrate. During the course of the reaction, however, the velocity slows down considerably since an increasing amount of *tert*-butyl alcohol molecules is competing for the same coordination sites as the TBHP molecules. Furthermore, a significant portion of the tiny amounts of catalyst, used to reach the high TOFs, falls victim to decomposition due to traces of water in the catalytic system. The catalytic epoxidation reaction is much slower with styrene as the substrate, but in case of *cis*-β-methylstyrene moderate enantiomeric excesses of up to 30% can be reached. The moderate enantiomeric excess may be – at least in part – due to an ongoing ligand exchange in solution, which can be slowed down at lower temperatures.

Experimental

The preparations and manipulations were carried out under an oxygen- and water-free argon atmosphere using standard Schlenk techniques. Solvents and substrates were dried by standard procedures, distilled, and kept under argon over molecular sieves. Elemental analyses were performed in the Mikroanalytisches Labor of the TU München in Garching (M. Barth). ^{1}H, ^{13}C, ^{1}H–^{1}H COSY and ^{95}Mo NMR (0.5 M solution of Na_2MoO_4 was used as reference) spectra were obtained with a Bruker Avance DPX-400 spectrometer. IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer using KBr pellets as IR matrix. Far-IR measurements were performed in a Bio-Rad FTS 525 system as Nujol mulls or polyethylene pellets using a 6 μm Mylar beam splitter. Mass spectra were carried out in a Finnigan MAT 311 A and a MAT 90 spectrometers.

The parent sugar, acetyl protected glucosamine derivatives, 1,3,4,6-tetraacetyl-α-D-glucosamine[23] and 1,3,4,6-tetraacetyl-β-D-glucosamine[24] were prepared as described previously. The sugar salicylaldimines **1**–**5** were all prepared analogous to the method of Irvine and Earl[15] by mixing vigorously the amino sugar and salicylaldehyde together in water, or in a methanol–water mixture, with one equivalent of sodium bicarbonate added. The analytical and spectroscopic data of the already known compound **1** is given in the ESI.† Compounds **6** and **10** can be obtained by a previously reported method.[9] The chemical shift of the protons of the sugar ring are partially assigned here according to ^{1}H NMR and ^{1}H–^{1}H COSY.

N-Salicylidene-1,3,4,6-tetraacetyl-α-D-glucosamine (2)

Yield 84%. Anal. Calc. for $C_{21}H_{25}NO_{10}$ (451.43): C 55.87; H 5.58; N 3.10. Found: C 55.35; H 5.54; N 3.05%. IR (KBr/Nujol, ν/cm^{-1}): 1751vs (acetyl), 1629vs (C=N), 1458m, 1368s, 1226vs, 1123m, 1037vs, 760m; ^{1}H NMR ($CDCl_3$, δ (ppm)) 12.39 (1H, s, OH), 8.37 (1H, s, CH=N), 7.35–6.86 (4H, m, Ar-H), 6.25 (1H, d, $J_{1,2}$ 3.74 Hz, sugar H-1), 5.60 (1H, t, sugar H-3), 5.17 (1H, t, sugar H-4), 4.37–4.33 (1H, q, sugar H-6), 4.24–4.213 (1H, q, sugar H-6′), 4.208–4.08 (1H, m, sugar H-5), 3.71–3.68 (1H, q, sugar H-2), 2.21 (3H, s, acetyl-1), 2.09 (3H, s, acetyl-3), 2,04 (3H, s, acetyl-4), 1.91 (3H, s, acetyl-6); ^{13}C NMR ($CDCl_3$, δ (ppm)) 170.58, 169.73, 169.70 and 168.94 (four C=O of acetyl), 168.89 (C=N), 161.05, 133.45, 131.92, 118.91, 118.11 and 117.30 (six carbons of aryl), 91.12 (sugar C-1), 71.00 (sugar C-5), 70.01 (sugar C-3), 69.46 (sugar C-4), 67.88 (sugar C-6), 61.66 (sugar C-2), 20.74, 20.67, 20.60 and 20.51 (four acetyl CH_3)

N-5-Chlorosalicylaldehyde-1,3,4,6-tetraacetyl-α-D-glucosamine (3)

Yield 78%. Anal. Calc. for $C_{21}H_{24}ClNO_{10}$ (485.86): C 51.91; H 4.98; N 2.88. Found: C 51.68; H 4.92; N 2.73%. IR (KBr/Nujol, ν/cm^{-1}): 1752vs, 1740vs (acetyl), 1636vs (C=N), 1576m, 1376s, 1222vs, 1139m, 1028s, 822m; ^{1}H NMR ($CDCl_3$, δ (ppm)) 12.37 (1H, s, OH), 8.30 (1H, s, CH=N), 7.29–6.85 (3H, m, Ar-H), 6.24 (1H, d, $J_{1,2}$ 3.66 Hz, sugar H-1), 5.58 (1H, t, sugar H-3), 5.16 (1H, t, sugar H-4), 4.37–4.31 (1H, q, sugar H-6), 4.24–4.17 (1H, q, sugar H-6′), 4.11–4.10 (1H, m, sugar H-5), 3.72–3.67 (1H, q, sugar H-2), 2.19 (3H, s, acetyl-1), 2.08 (3H, s, acetyl-4), 2.03

(3H, s, acetyl-3), 1.91 (3H, s, acetyl-6); ^{13}C NMR ($CDCl_3$, δ (ppm)) 170.55, 169.68, 169.65 and 168.86 (four carbonyl groups), 167.70 (C=N), 159.67, 133.32, 130.89, 123.58, 118.99, 118.82 (six carbons of aryl), 91.00 (sugar C-1), 70.91 (sugar C-5), 70.08 (sugar C-3), 69.47 (sugar C-4), 67.81 (sugar C-6), 61.63 (sugar C-2), 20.73, 20.68, 20.59 and 20.53 (four CH_3 of acetyl); m/z = 486.4 (M + 1).

N-Salicylaldehyde-1,3,4,6-tetraacetyl-β-D-glucosamine (4)

Yield 82%. Anal. Calc. for $C_{21}H_{25}NO_{10}$ (451.43): C 55.87; H 5.58; N 3.10. Found: C 55.55; H 5.52; N 3.07%. IR (KBr/Nujol, ν/cm^{-1}): 1746vs (acetyl), 1631vs (C=N), 1580m, 1370s, 1279s, 1215vs, 1155m, 1089s, 1065s, 1035vs, 760s; ^{1}H NMR ($CDCl_3$, δ (ppm)) 11.97 (1H, s, OH), 8.30 (1H, s, CH=N), 7.32–6.83 (4H, m, Ar-H), 5.88 (1H, d, $J_{1,2}$ 8.05 Hz, sugar H-1), 5.42 (1H, t, sugar H-3), 5.10 (1H, t, sugar H-4), 4.35–4.31 (1H, q, sugar H-6), 4.11–4.07 (1H, q, sugar H-6′), 3.96–3.93 (1H, m, sugar H-5), 3.47–3.41 (1H, q, sugar H-2), 2.04 (3H, s, acetyl-1), 1.99 (6H, s, acetyl-3,4), 1.87 (3H, s, acetyl-6); ^{13}C NMR ($CDCl_3$, δ (ppm)) 170.45, 169.67, 169.34 and 168.93 (four C=O of acetyl), 168.43 (C=N), 160.80, 133.31, 131.86, 118.84, 118.00, 117.26 (six carbons of aryl), 92.55 (sugar C-1), 72.95 (sugar C-5), 72.74 (sugar C-3), 71.66 (sugar C-4), 67.69 (sugar C-6), 61.54 (sugar C-2), 20.60, 20.59, 20.50 and 20.33 (four CH_3 of acetyl)

N-5-Chlorosalicylaldehyde-1,3,4,6-tetraacetyl-β-D-glucosamine (5)

Yield 78%. Anal. Calc. for $C_{21}H_{24}ClNO_{10}$ (485.86): C 51.91; H 4.98; N 2.88. Found: C 51.36; H 5.09; N 2.80%. IR (KBr/Nujol, ν/cm^{-1}): 1751vs (acetyl), 1636vs (C=N), 1576 m, 1466s, 1374s, 1265s, 1222vs, 1083s, 1040s, 978m, 756m; ^{1}H NMR ($CDCl_3$, δ (ppm)) 11.92 (1H, s, OH), 8.24 (1H, s, CH=N), 7.28–6.88 (3H, m, Ar-H), 5.87 (1H, d, $J_{1,2}$ 8.32 Hz, sugar H-1), 5.43 (1H, t, sugar H-3), 5.13 (1H, t, sugar H-4), 4.37–4.33 (1H, q, sugar H-6), 4.13–4.09 (1H, q, sugar H-6′), 3.97–3.93 (1H, m, sugar H-5), 3.50–3.45 (1H, q, sugar H-2), 2.07 (3H, s, acetyl-1), 2.03 (3H, s, acetyl-4), 2.02 (3H, s, acetyl-3), 1.91 (3H, s, acetyl-6); ^{13}C NMR ($CDCl_3$, δ (ppm)) 170.53, 169.72, 169.43 and 168.48 (four C=O of acetyl), 167.82 (C=N), 159.42, 133.24, 130.92, 123.58, 119.01, 118.75 (six carbons of aryl), 92.48 (sugar C-1), 72.90 (sugar C-5), 72.88 (sugar C-3), 71.80 (sugar C-4), 67.64 (sugar C-6), 61.56 (sugar C-2), 20.68, 20.67, 20.57 and 20.42 (four CH_3 of acetyl)

MoO_2(*N*-salicylidene-D-glucosamine) (7)

N-Salicylaldehyde-D-glucosamine **1** (0.300 g, 1.06 mmol) was dissolved in *ca*. 15 mL of dried methanol. After complete dissolution, $MoO_2(acac)_2$ (0.313 g, 0.954 mmol) was added to the yellow solution. The mixture was allowed to react for 4 h, then the volume was then reduced to *ca*. 5 mL and 20 mL of diethyl ether were added to precipitate the compound as a yellow solid. This solid was washed twice with diethyl ether and dried under vacuum. Yield 78%. Anal. Calc. for $C_{13}H_{15}NO_8Mo{\cdot}CH_3OH$ (441.25): C 38.11; H 4.34; N 3.17. Found: C 38.49; H 4.76; N 3.30%. IR (KBr/Nujol, ν/cm^{-1}): 3376 br (O–H), 1636vs (N=C), 1601s, 1558s, 1475s, 1448s, 1280vs, 1091vs, 1018vs, 919vs, sh (ν_{sym}(Mo=O)), 905vs (ν_{asym}(Mo=O)), 821m, 763m, 420m, 391w, 341m, 312w, 286w. ^{1}H NMR (CD_3OD, δ ppm) 8.54 (1H, s, CH=N), 7.47–6.84 (4H, m, Ar-H), 5.58 (1H, d, $J_{1,2}$ 3.04 Hz, sugar-H-1), 3.76–1.05 (9H, m, CH_3 of methanol and other sugar ring H);). ^{95}Mo NMR (CD_3OD, δ (ppm)) −29; m/z = 409 (M^+ − MeOH).

MoO_2(*N*-salicylidene-1,3,4,6-tetraacetyl-α-D-glucosamine) (8)

N-Salicylaldehyde-1,3,4,6-tetraacetyl-α-(or β-)D-glucosamine **2** (or **4**) (0.4736 g, 1.05 mmol) was dissolved in *ca*. 20 mL of dried methanol or ethanol. After complete dissolution, $MoO_2(acac)_2$ (0.3279 g, 1 mmol) was added to the yellow solution. The mixture was allowed to react for 12 h and then the solvent was partially evaporated. During this procedure a small amount of yellow precipitate formed. After the addition of 15 mL of diethyl ether, more compound precipitated as a yellow solid, which was washed with diethyl ether twice and dried under vacuum. Yield 62% for **8** and 70% for **10**. Anal. Calc. for $C_{19}H_{21}NO_{11}Mo{\cdot}CH_3OH$ (567.36): C 42.34; H 4.44; N 2.47. Found: C 42.40, H 4.33, N 2.55 or for $C_{19}H_{21}NO_{11}Mo{\cdot}CH_3$-$CH_2OH$. (581.38): C 43.38; H 4.68; N 2.41. Found: C 43.13, H 4.66, N 2.37%. IR (KBr/Nujol, ν/cm^{-1}): 3383s (ν(OH)), 1757vs, 1742vs (acetyl), 1630vs (C=N), 1600s, 1552s, 1367s, 1291vs, 1229vs, 1150s, 1131s, 1036vs, 931vs (ν_{sym}(Mo=O)), 902vs (ν_{asym}(Mo=O)) 419m, 382w, 343m, 311w, 282w. ^{1}H NMR ($CDCl_3$, δ (ppm)) 8.36 (1H, s, CH=N), 7.49–6.87 (4H, m, aryl H), 5.84 (1H, d, $J_{1,2}$ 3.75 Hz, sugar H-1), 5.43 (1H, t, sugar H-3), 5.10 (1H, t, sugar H-4), 4.41–4.35 (2H, m, sugar H-6, H-5), 4.12–4.07 (2H, m, sugar H-6′, H-2), 3.83 (2H, q, ethanol CH_2), 2.12 (3H, s, acetyl-3), 2,11 (3H, s, acetyl-4), 2.08 (3H, s, acetyl-6), 1.24 (3H, t, ethanol CH_3). ^{13}C NMR ($CDCl_3$, δ (ppm)) 170.67, 170.27, 166.68 (three C=O of acetyl groups), 166.71 (C=N), 162.06, 136.81, 134.15, 121.02, 120.37, 119.97 (six carbons of aryl), 99.65 (sugar C-1), 73.66 (sugar C-5), 70.75 (sugar C-3), 69.02 (sugar C-4), 67.66 (sugar C-6), 61.91 (sugar C-2), 59.36 (CH_2, ethanol), 20.70, 20.66, 20.23 (acetyl, CH_3), 17.98 (CH_3, ethanol). ^{95}Mo NMR (CD_3OD, δ (ppm)) −15; m/z = 536 (M^+ − EtOH + 1).

MoO_2(*N*-5-chlorosalicylidene-1,3,4,6-tetraacetyl-α-D-glucosamine) (9)

N-5-Chlorosalicylaldehyde-1,3,4,6-tetraacetyl-α-(or β-)-D-glucosamine **3** (or **5**) (0.5098 g, 1.05 mmol) was dissolved in *ca*. 30 mL of dried ethanol. After complete dissolution by heating to 40–50 °C, $MoO_2(acac)_2$ (0.3279 g, 1 mmol) was added to the yellow solution. The mixture was allowed to react for 12 h at 40–50 °C and then solvent was partially evaporated. During this time a small amount of yellow precipitate formed. After the addition of 15 mL of diethyl ether, the compound precipitated as a yellow solid, and was washed with diethyl ether twice and dried under vacuum. Yield 70%. Anal. Calc. for $C_{19}H_{20}NO_{11}ClMo{\cdot}CH_3CH_2OH$ (615.83): C 40.96; H 4.26; N 2.27. Found: C 41.13, H 4.66, N 2.37%. IR (KBr/Nujol, ν/cm^{-1}): 3378 br (ν(OH)), 1758vs, 1738vs (acetyl), 1637vs (C=N), 1544s, 1371s, 1283vs, 1230vs, 1213vs, 1139s, 1122s, 1033vs, 935vs (ν_{sym}(Mo=O)), 903vs (ν_{asym}(Mo=O)) 415w, 379m, 350m, 310w, 289w; ^{1}H NMR ($CDCl_3$, δ (ppm)) 8.27 (1H, s, CH=N), 7.43–6.84 (3H, m, aryl H), 5.84 (1H, d, $J_{1,2}$ 3.56 Hz, sugar H-1), 5.38 (1H, t, sugar H-3), 5.12 (1H, t, sugar H-4), 4.375 (2H, d, sugar H-6, H-5), 4.13–4.08 (2H, m, sugar H-6′, H-2), 3.82 (2H, q, methanol CH_2), 2.14 (1H, s, acetyl-3), 2.08 (6H, s, acetyl-4,6), 1.25 (3H, t, methanol CH_3). ^{13}C NMR ($CDCl_3$, δ (ppm)) 170.67, 170.00, 165.44 (three C=O of acetyl groups), 165.42 (C=N), 160.61, 136.51, 132.61, 125.48, 121.69, 120.92 (six carbons of aryl), 99.71 (sugar C-1), 73.53 (sugar C-5), 70.84 (sugar C-3), 69.04 (sugar C-4), 67.35 (sugar C-6), 61.81 (sugar C-2), 59.38 (CH_2, ethanol), 20.72, 20.69, 20.32 (three CH_3 of acetyl groups), 17.99 (CH_3, ethanol); ^{95}Mo NMR (CD_3OD, δ (ppm)) −22; m/z = 570 (M^+ − EtOH).

X-Ray crystallography

Preliminary examination and data collection were carried out on a KappaCCD device (NONIUS MACH3) with an Oxford Cryosystems cooling device at the window of a rotating anode (NONIUS FR591) with graphite-monochromated Mo-Kα radiation (λ = 71.073 pm). Data collection was performed using the Collect Software.[25] The detector to crystal distance was 40 mm. A correction for absorption effects and/or decay was applied during the scaling procedure.[26] The structures were solved by a combination of direct methods[27] and difference-

Table 4 Crystal data and summary of intensity data collection and structure refinement of *N*-salicylidene-1,3,4,6-tetraacetyl-D-glucosamine [4(**2**)·H_2O], *N*-5-chlorosalicylaldehyde-1,3,4,6-tetraacetyl-D-glucosamine (**3**) and MoO_2(*N*-salicylidene-1,3,4,6-tetraacetyl-D-glucosamine) (**8**)

	4(**2**)·H_2O	**3**	**8**
Empirical formula	$C_{84}H_{102}N_4O_{41}$	$C_{21}H_{24}ClNO_{10}$	$C_{21}H_{27}MoNO_{12}$
Formula weight	1823.70	485.86	581.38
Color/shape	Colorless/fragment	Colorless/fragment	Yellow/fragment
Crystal size/mm	0.13 × 0.20 × 0.25	0.66 × 0.89 × 0.89	0.13 × 0.18 × 0.61
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$ (no. 19)	$P2_1$ (no. 4)	$P2_12_12_1$ (no. 19)
a/pm	788.53(1)	1225.73(1)	1605.32(1)
b/pm	1583.27(1)	714.73(1)	802.34(1)
c/pm	1871.71(2)	1449.14(2)	1888.65(1)
β/°	90	113.2552(4)	90
V/10^6 pm^3	2336.75(4)	1166.40(3)	2432.60(4)
Z	1	2	4
D_c/g cm^{-3}	1.296	1.383	1.587
F(000)	962	508	1192
μ/mm^{-1}	0.104	0.219	0.603
λ(Mo-Kα)/pm	71.073	71.073	71.073
T/K	173	173	173
Index ranges	*h*: ±9; *k*: ±19; *l*: ±22	*h*: ±14; *k*: ±8; *l*: ±17	*h*: ±19; *k*: ±9; *l*: ±22
Reflections collected	56775	25017	54662
Independent reflections (R_{int})	4268 (0.028)	4229 (0.040)	4450 (0.035)
Completeness (%)	99.8 (to Θ = 25.33°)	99.6 (to Θ = 25.28°)	100.0 (to Θ = 25.34°)
Observed reflections ($I > 2\sigma(I)$)	4058	4183	4386
Data/restraints/parameters	4268/0/398	4229/1/394	4450/0/424
*R*1 (observed/all data)	0.0267/0.0291	0.0267/0.0269	0.0179/0.0183
*wR*2 (observed/all data)	0.0647/0.0665	0.0712/0.0714	0.0455/0.0457
GOF (observed/all data)	1.063/1.063	1.055/1.055	1.081/1.081
Largest diff. peak and hole /e Å^{-3}	0.11 and −0.13	0.21 and −0.23	0.39 and −0.28
Flack parameter	−0.3(6)	0.03(5)	−0.02(2)

Fourier syntheses.[28] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found and refined with individual isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ and converged with a maximum shift/error < 0.001. The final difference-Fourier maps show no striking features. The absolute configuration was established by synthesis. Pertinent crystal data are given in Table 4.

CCDC reference numbers 211645–211647.

See http://www.rsc.org/suppdata/dt/b3/b306039j/ for crystallographic data in CIF or other electronic format.

Catalysis reactions with compounds 7–10 as catalysts

The catalytic reactions were performed under an air atmosphere, in a reaction vessel equipped with a magnetic stirrer, immersed into a thermostated bath.

Achiral catalytic epoxidation: *cis*-cyclooctene (800 mg, 7.2 mmol), mesitylene (1 g, internal standard), 1 mol% (72 μmol) of compounds **7**–**10** as catalyst were added to the reaction vessel. With the addition of TBHP (2 mL, 5.5–6.0 M in *n*-decane) the reaction was started. The course of the reactions was monitored by quantitative GC analysis. Samples were taken and diluted with CH_2Cl_2, and treated with a catalytic amount of $MgSO_4$ and MnO_2 to remove water and destroy the peroxide, respectively. The resulting slurry was filtered and the filtrate injected into a chiral GC column. The conversion of cyclooctene, and the formation of cyclooctene oxide were calculated from calibration curves (r^2 = 0.999) recorded prior to the reaction course.

Chiral catalytic epoxidation: *cis*-, or *trans*-β-methylstyrene (200 mg, 1.7 mmol), mesitylene (100 mg, 0.83 mmol, internal standard), and 1 mol% (17 μmol), 5 mol% and 10 mol% of the compounds **7**–**10** as catalysts and 2 mL toluene as solvent were added to the reaction vessel. With the addition of TBHP (450 μl, 7.5 M in toluene) the reaction started. The course of the reactions was monitored by quantitative GC analysis. The samples were processed as described above. The enantiomeric excess was calculated from the ratio of the peaks corresponding to both epoxides formed.

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References

1 (*a*) *Catalytic Asymmetric Syntheses*, ed. I. Ojima, VCH, Weinheim, 1993; (*b*) J. J. Haider, PhD Thesis, Technische Universität München, 1999; (*c*) A. K. Duhme-Klair, G. Vollmer, C. Mars and R. Fröhlich, *Angew. Chem., Int. Ed.*, 2000, **39**, 1626.

2 (*a*) R. A. Sheldon, *J. Mol. Catal.*, 1980, **7**, 107; (*b*) W. R. Thiel and T. Priermeier, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1737; (*c*) W. R. Thiel, *J. Mol. Catal.*, 1997, **117**, 449; (*d*) F. E. Kühn, A. D. Lopes, A. M. Santos, E. Herdtweck, J. J. Haider, C. C. Romão and A. G. Santos, *J. Mol. Catal. A: Chem.*, 2000, **151**, 147; (*e*) M. Abrantes, A. A. Valente, M. Pillinger, I. S. Gonçalves, J. Rocha and C. C. Romão, *Inorg. Chem. Commun.*, 2002, **5**, 1069; (*f*) M. Abrantes, A. A. Valente, M. Pillinger, I. S. Gonçalves, J. Rocha and C. C. Romão, *J. Catal.*, 2002, **209**, 237; (*g*) C. D. Nunes, A. A. Valente, M. Pillinger, A. C. Fernandes, C. C. Romão, J. Rocha and I. S. Gonçalves, *J. Mater. Chem.*, 2002, **12**, 1735; (*h*) M. J. Jia and W. R. Thiel, *Chem. Commun.*, 2002, 2392.

3 (*a*) W. A. Herrmann, J. J. Haider, J. Fridgen, G. M. Lobmaier and M. Spiegler, *J. Organomet. Chem.*, 2000, **603**, 69; (*b*) S. Bellemin-Caponnaz, K. S. Coleman and J. A. Osborn, *Polyhedron*, 1999, **18**, 273.

4 R. J. Cross, P. D. Newman, R. D. Peacock and D. Stirling, *J. Mol. Catal. A: Chem.*, 1999, **144**, 273.

5 (*a*) F. E. Kühn, A. M. Santos, A. D. Lopes, I. S. Gonçalves, J. E. Rodriguez-Borges, M. Pillinger and C. C. Romão, *J. Organomet. Chem.*, 2001, **621**, 207; (*b*) A. A. Valente, I. S. Gonçalves, A. D. Lopes, J. E. Rodriguez-Borges, M. Pillinger, C. C. Romão, J. Rocha and X. García-Mera, *New. J. Chem.*, 2001, **25**, 959.

6 I. S. Gonçalves, A. M. Santos, C. C. Romão, A. D. Lopes, J. E. Rodriguez-Borges, M. Pillinger, P. Ferreira, J. Rocha and F. E. Kühn, *J. Organomet. Chem.*, 2001, **626**, 1.

7 D. Steinborn and H. Junicke, *Chem. Rev.*, 2000, **100**, 4283.

8 (*a*) S. Yano and K. Ohtsuka, *Metal Ions in Biological Systems*, ed. H. Sigel and A. Sigel, Marcel Dekker, New York, 1996, vol. 32, p. 113; (*b*) D. M. Whitfield, S. Stojkovsky and B. Sarkar, *Coord. Chem. Rev.*, 1993, **122**, 171.
9 A. K. Sah, C. P. Rao, P. K. Saarenketo, E. K. Wegelius, E. Kohlemainen and K. Rissanen, *Eur. J. Inorg. Chem.*, 2001, 2773.
10 (*a*) J. Kuduk-Jaworska and B. Jezowska-Trzebiatowska, *Inorg. Chim. Acta*, 1986, **123**, 209; (*b*) M. J. Adam and L. D. Hall, *Can. J. Chem.*, 1982, **60**, 2229; (*c*) J. Kuduk-Jaworska, *Transition Met. Chem.*, 1994, **19**, 296.
11 (*a*) M. Diegnez, O. Pamies, A. Ruiz and C. Claver, *New J. Chem.*, 2002, **26**, 827; (*b*) M. Diegnez, O. Pamies, A. Ruiz and C. Claver, *J. Organomet. Chem.*, 2001, **629**, 77.
12 R. Wegner, M. Gottschaldt, H. Gorls, E. G. Jager and D. Klemm, *Chem. Eur. J.*, 2001, **7**, 2143.
13 O. Pamies, M. Diegnez, G. Net, A. Ruiz and C. Claver, *J. Chem. Soc., Dalton Trans.*, 1999, **19**, 3439.
14 K. Boog-Wick, P. S. Pregosin and G. Trabesinger, *Magn. Reson. Chem.*, 1998, **36**, 189.
15 J. C. Irvine and J. C. Earl, *J. Chem. Soc.*, 1922, **121**, 2376.
16 M. J. Adam and L. P. Hall, *Can. J. Chem.*, 1982, **60**, 2229.
17 A. G. Sánchez, A. C. Ventulá and U. Scheidegger, *Carbohydr. Res.*, 1971, **18**, 173.
18 M. Fumiki, T. Soichi and Y. Toshihiko, *Jpn. Kokai Tokkyo Koho*, 1977, JP 2111512.
19 M. O. Contour, J. Defaye, M. Little and E. Wong, *Carbohydr. Res.*, 1989, **193**, 283.
20 (*a*) J. Banoub and D. R. Bundle, *Can. J. Chem.*, 1979, **57**, 2085; (*b*) S. Hanessian and J. Banoub, *Carbohydr. Res.*, 1977, **59**, 261.
21 G. Zemplén and E. Pacsu, *Chem. Ber.*, 1929, **62**, 1613.
22 (*a*) E. Petráková and C. P. J. Glaudemans, *Carbohydr. Res.*, 1995, **268**, 135; (*b*) A. Nudelman, J. Herzig, H. E. Gottlieb, E. Keinan and J. Sterling, *Carbohydr. Res.*, 1987, **162**, 145; (*c*) J. Herzig and A. Nudelman, *Carbohydr. Res.*, 1986, **153**, 162.
23 F. Micheel and W. Lengsfeld, *Chem. Ber.*, 1956, **89**, 1246.
24 M. Bergmann and L. Zervas, *Chem. Ber.*, 1931, **64**, 975.
25 Data Collection Software for NONIUS KappaCCD devices, Delft, The Netherlands, 2001.
26 Z. Otwinowski and W. Minor, in *Methods in Enzymology* : *Macromolecular Crystallography, Part A*, ed., C. W. Carter, Jr. and R. M. Sweet, Academic Press, San Diego, CA, 1997, vol. 276, pp. 307—326.
27 SIR92: A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Crystallogr.*, 1994, **27**, 435.
28 G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.