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O,N,O′-tridentate ligands derived from carbohydrates in the V(IV)-promoted asymmetric oxidation of thioanisole

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Abstract

The simple synthesis of new O,N,O′-tridentate ligands derived from carbohydrates is illustrated. The ligands are obtained by condensing 2-amino-α-D-glucosides or 2-amino-α-D-alloside with several 3,5-disubstituted-2-hydroxybenzaldehydes. The efficiency of the imines in the V(IV)-promoted asymmetric oxidation of thioanisole has been examined and ee's up to 60% have been achieved.

Keywords: Sugars; Vanadium; Sulfide; Oxidation; Enantioselectivity; Catalysis

1. Introduction

The application of metal-promoted enantioselective catalysis in fine chemicals production is an increasing field of both academic and industrial activity [1]. Essential for this sector is the choice of the asymmetric coordination environment of the active centre, which must be accurately suited for achieving acceptable performances. Within this frame increasing attention is directed towards the use of carbohydrates as chiral auxiliaries, and their effective application in several reactions has been shown [2].

Recently, we have demonstrated [3] that a variety of nitrogen ligands can be straightforwardly prepared by suitable modification of common and inexpensive sugars such as D-glucose and D-mannose. In these cases, use of carbohydrates was also dictated by the assumption that the presence of more functionalisable hydroxyl groups allows the contemporaneous introduction of different type of functions, with tuneable polarity. These features are well-suited for developing catalysis in non-conventional conditions with reduced environmental impact [3a, 3c].

Within this field of activity, we have now addressed our attention towards tridentate O,N,O′-chelating ligands derived from sugars [4] of general formula **1** (Fig. 1). These molecules show a structural analogy with the imines developed a few years ago by Bolm [5] starting from chiral aminoalcohols (**2** in Fig. 1), which are effective in the asymmetric oxidation of sulfides to sulfoxides under convenient conditions [5]. On these grounds we have been prompted to prepare a family of ligands **1** for the asymmetric oxidation of thioanisole promoted by vanadium(IV), which to our knowledge represents the first application of carbohydrate-derived auxiliaries in this enantioselective transformation.

In this paper, we report the preparation of the new ligands along with the results regarding their catalytic activity.

2. Results and discussion

2.1. Synthesis and characterisation of the ligands

The O,N,O′-chelates are illustrated in Fig. 2. They are labelled with a number (**1**), followed by specification of the sugar (**G**, glucose; **A**, allose) and of the aryl ring (**a–f** according to Fig. 2). A prime indicates the presence of a benzylidene protector group at C4 and C6 in place of the here-preferred isopropylidene.

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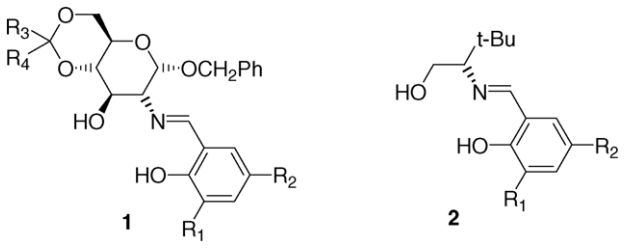


Fig. 1. General structure of ligands of types **1** and **2**.

With the only exception of **1A′b**, all the ligands were derived from glucose, since the equatorial–equatorial arrangement of the ligand positions at C2 and C3 has been found fruitful for the achievement of good performances in asymmetric catalysis [3]. As described below, also within this study this general observation has been confirmed.

The synthesis of the ligands requires a few simple steps (Scheme 1). Commercial *N*-acetyl-D-glucosamine (**3**) is protected in position C1, C4 and C6 through known procedures [6] (Scheme 1, paths i and ii). In the case of the glucose derivatives, the amido function of **4** is then easily hydrolysed (iii), and the resulting aminoderivative **5** is condensed with the appropriate benzaldehyde affording the goal ligands **1G** (iv). Alternatively, in the allose synthesis this step is anticipated by inversion of configuration at C3 (paths v and vi through **6** and **7**) with the achievement of the allosamine **8** [7] which is finally converted into **1A′b**.

All the imines are crystallised by adding hexane to the reaction mixture in toluene, and appear as yellow microcrystalline powders. They have been characterised through elemental analysis and NMR spectroscopy. Deuteriobenzene was used as solvent due to the general intolerance of the imino function towards acidic solvents such as chloroform. The coupling pattern typical of glucose and allose has been observed within the ring protons, and their correct attribution has been performed, when necessary, by using COSY spectra. As expected, the imino proton resonates between 8 and 9 ppm, while the corresponding carbon is found within 150–160 ppm in the ^{13}C NMR spectrum.

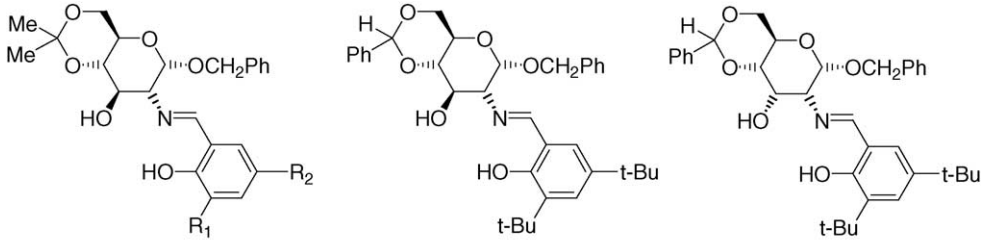
2.2. Oxidation reactions

Asymmetric oxidation of prochiral sulfides to sulfoxides is interesting because chiral sulfoxides [8] are biologically active and, due to the configurational stability, can also be used as chiral auxiliaries. Beside to enzymatic methods, metal-promoted asymmetric catalysis is a simple and convenient route for performing the oxidation of sulfides [8]. The advantages of this strategy comprise the possibility of tuning the properties of the metal catalyst, the oxidant and, in general, of the reaction conditions.

Though early studies refer to the use of chiral complexes of titanium and manganese as catalysts [9], other metal centres can be profitably used [5,10,11]. In particular, recent studies [5d, 11] have emphasised the remarkable skill of vanadium(IV) compounds containing chiral Schiff bases such as **2** in Fig. 1, and more sophisticated ligands with two or more independent chiral centers have been currently developed with even increasing effectiveness [12]. Experimental [13] and theoretical investigations [14] have also been addressed to the comprehension of the reaction mechanism, and the most important results within this sector have been reviewed [15].

Within this study, we have investigated the oxidation of thioanisole (SMePh) to methyl phenyl sulfoxide (MPSO). By-product of the reaction is methyl phenyl sulfone ($MPSO_2$), whose formation is due to further oxidation of the sulfoxide (Scheme 2). The convenient reaction conditions described by Bolm were employed, i.e. the reactions were performed in non-anhydrous dichloromethane by using hydrogen peroxide as oxidant. The enantiomeric excesses have been measured by ^{1}H NMR spectroscopy in deuteriochloroform in the presence of Eu(hfc)$_3$ by comparison with a sample of known chirality. In these conditions, the signals of all the aromatic protons do separate, and, in particular, the ortho protons are well resolved in the high frequency region and, hence, easy to be integrated. The results are summarised in Table 1.

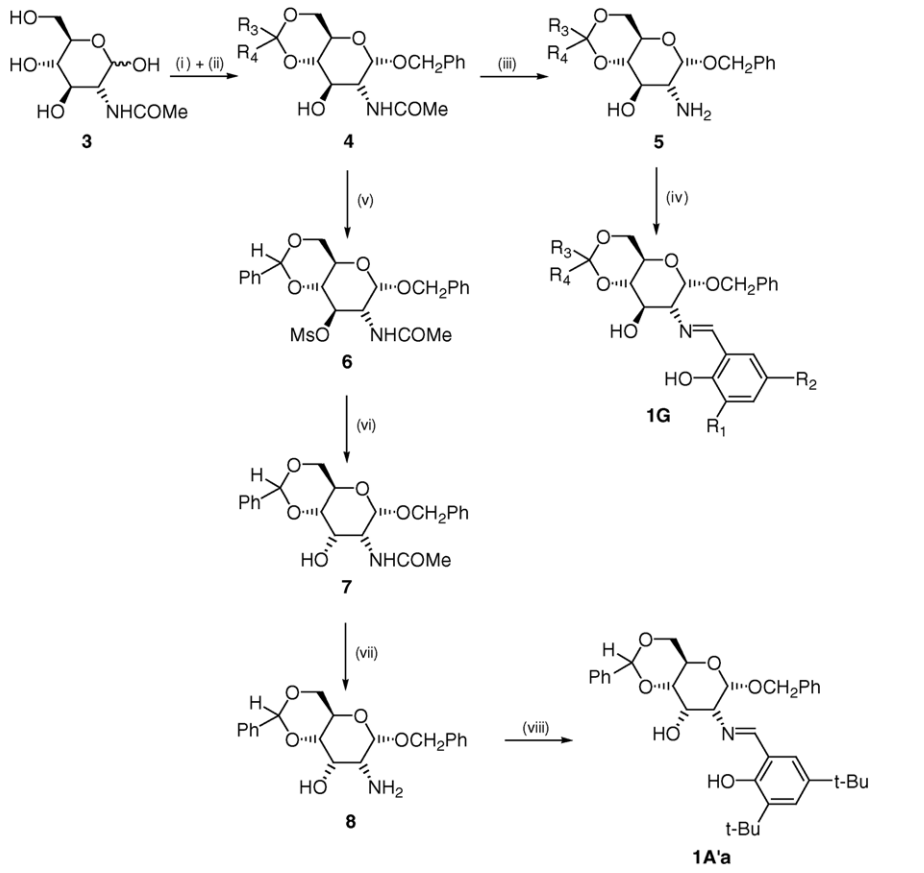
All the reactions were fast and completed within one hour. In most cases, conversion was superior to 80% after 15 min. Although a rationale of the electronic and steric effects on the



1Ga ($R_1 = R_2 = H$)
1Gb ($R_1 = R_2 =$ t-Bu)
1Gc ($R_1 = H; R_2 =$ t-Bu)
1Gd ($R_1 =$ t-Bu; $R_2 = H$)
1Ge ($R_1 =$ t-Bu ; $R_2 = NO_2$)
1Gf ($R_1 = R_2 = I$)

1G'b **1A'b**

Fig. 2. Labelling of ligands of type **1**.



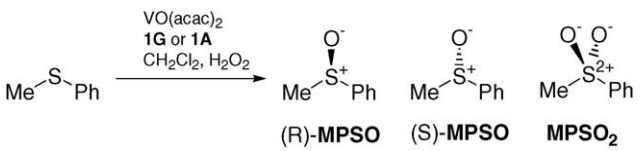
(i) $PhCH_2OH$, H^+; (ii) R_3= R_4= Me: $Me_2C(OMe)_2$; R_3= H, R_4= Ph: PhCHO; (iii) KOH;
(iv) $3R_1,5R_2$-2-hydroxybenzaldehyde; (v) MsCl; (vi) NaOAc; (vii) KOH; (viii) 3,5-di-t-Bu-2-hydroxybenzaldehyde

Scheme 1. The synthesis of ligands of type **1**.

reaction fate is not easily traceable, some general comments can be drawn as follows.

Taking as reference **1Ga**, where the aryl ring has no substituents, the enantioselectivity of the reaction is improved by adding two *t*-butyls in positions 3′ (R_1) and 5′ (R_2) (**1Gb**). In fact, the ee of the product goes from 42% to 60%. This value coincides with that obtained by using the analogous Bolm's ligand of type **2**. Furthermore, **1Gb** does also provide the highest selectivity in terms of ratio of sulfoxide/sulfone (97/3).

The beneficial effect of two substituents in 3′ and 5′ is not observed if they are both iodines (**1Gf**) or when one *t*-butyl is replaced by a NO_2 group (**1Ge**). Similarly, the presence of only one *t*-butyl, either in 3′ (**1Gd**) or in 5′ (**1Gc**), lowers the ee.



Scheme 2. Asymmetric oxidation of thioanisole.

This behaviour only partially matches that described for ligands of type **2** [5d, 11], which conversely significantly improve the catalyst activity upon introduction of halogens or electron-withdrawing groups in their aryl ring. The difference is particularly evident when the performances of **1Ge** (ee = 20%) and **1Gf** (ee = 18%) are compared to those of the corresponding Bolm's ligand **2** (R_1 = *t*-Bu, R_2 = NO_2: ee = 70%; R_1 = R_2 = I: ee = 90%) [11]. A simple explanation of these findings does not seem immediately accessible.

Although apparently remote from the metal centre, also the protecting groups in position C4 and C6 of the sugar ring appreciably influence the enantioselectivity. Thus, the presence of a benzylidene moiety reduces the ee with respect to the isopropylidene fragment (cf. **1Gb** versus **1G′b**).

Finally, changing the relative orientation of the coordinating positions, i.e. changing the sugar nature, has a remarkable effect on the enantioselectivity of the reaction. In fact, the use of D-allose as building block (**1A′b**) affords the sulfoxide as a racemic mixture. In this case, it is evident (Fig. 3a) that the C2 (equatorial)–C3 (axial) arrangement places the chair of the sugar nearly orthogonal to the plane containing the coordinating atoms O, N and O′. The geometry is completely different

Table 1
Results of the vanadium-catalysed oxidation of thioanisole

Entry	Ligand	Time (min)	Conversion (%)[a]	Selectivity[b] (MPSO/$MPSO_2$)	ee (%)[c]
1	**1Ga**	60	99	95/5	42(S)
2	**1Gb**	60	99	97/3	60(S)
3	**1Gc**	60	99	90/10	26(S)
4	**1Gd**	60	99	80/20	26(S)
5	**1Ge**	60	99	90/10	20(S)
6	**1Gf**	60	99	90/10	18(S)
7	**1G′b**	60	99	85/15	45(S)
8	**1A′b**	60	99	85/15	0

[a] The conversion has been calculated by integration of suitable peaks in the NMR spectrum of the crude product.
[b] MPSO: methyl phenyl sulfoxide; $MPSO_2$: methyl phenyl sulfone.
[c] The determination of the ee's was carried out by ^1H NMR analysis in $CDCl_3$ in the presence of $Eu(hfc)_3$ as shift reagent.

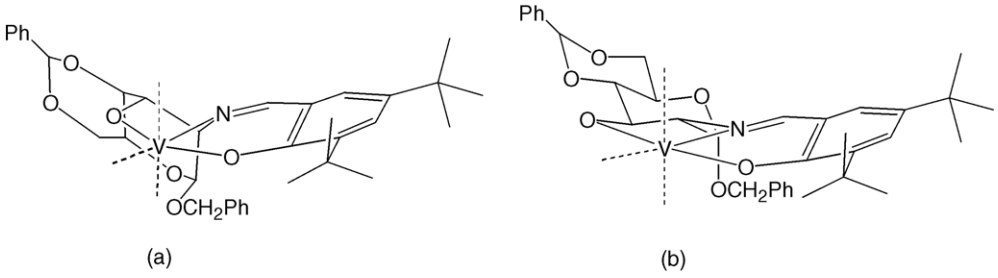


Fig. 3. The coordinating features of **1A′b** (a) and **1G′b** (b).

for **1G′b** (Fig. 3b) that approximately leaves the sugar chair in that plane. Though the origin of the enantioselectivity is complicated [14], these different geometric features do surely play a prominent role in determining the dramatic change of enantioselectivity, in keeping with the general observation [3] that a *cis* di-equatorial arrangement of the sugar coordinating functions (i.e. as in glucose) is propitious for stereoselectivity.

3. Conclusion

This paper validates the assumption that ligands for asymmetric catalysis can be obtained by simple functionalisation of common carbohydrates. Condensation of 2-amino-pyranoses with several 3,5-disubstituted-2-hydroxybenzaldehydes affords O,N,O′-tridentate ligands, whose activity in the V(IV)-catalysed oxidation of thioanisole is in some cases comparable to that of structurally related ligands, e.g. **2** [5,11].

As far as we know, this is the first example in which carbohydrates are used as ancillary ligands for asymmetric oxidation of sulfides. Further development of the work will involve the functionalisation of the sugar functions not involved in coordination for (i) anchoring the ligands to a solid matrix or (ii) tuning the polarity of the chelates for the extension of catalysis to non-conventional solvents.

4. Experimental

4.1. General methods

NMR spectra were recorded in C_6D_6 (C_6D_5H, δ 7.15, and $^{13}C_6D_6$, δ 128, as internal standards) with a 200 MHz spectrometer (Varian Model Gemini). The following abbreviations were used for describing NMR multiplicities: s, singlet; d, doublet; t, triplet; dd, double doublet; dt, double triplet; m, multiplet; app, apparent. Specific optical rotatory powers [α] were measured with a Perkin-Elmer Polarimeter (model 141) at 298 K and 589 nm in toluene (c = 1.0 g per 100 mL). Benzyl-4,6-*O*-benzylidene-2-amino-2-deoxy-α-D-glucoside [16], benzyl-4,6-*O*-isopropylidene-2-amino-2-deoxy-α-D-glucoside [17] and methyl-4,6-*O*-benzylidene-2-amino-2-deoxy-α-D-alloside [7] are described in literature.

4.2. Synthesis of ligands of type *1*

A solution of the appropriate 2-hydroxybenzaldehyde (0.25 mmol) in toluene (2 mL) is added to a solution of the amino sugar derivative **5** or **8** (0.25 mmol) in the same solvent (2 mL). The resulting mixture is stirred for 2 h at 80 °C affording a yellow solution. The volume of the solvent is reduced under vacuum at ca. 1 mL and hexane (5–6 mL) is slowly added to afford the product as a yellow microcrystalline powder, which is washed with hexane and dried under vacuum (yield: 80–90%).

1Ga: Selected ^{1}H NMR data: δ 7.94 (s, 1 H, N=CH), 4.60 (d, 1H, H1, $^3J_{H1–H2}$ = 3.8 Hz), 4.51 (d, 1H, C*H*HPh, $^2J_{gem}$ = 12.2 Hz), 4.27 (d, 1H, CH*H*Ph), 4.04–3.82 (m, 3H, H3, H5 and H6eq), 3.69 (t, 1 H, H6ax, $^3J_{H6ax–H5}$ = 10.0 Hz), 3.52 (t, 1H, H4, $^3J_{H5–H4}$ = 9.2 Hz), 3.07 (dd, 1 H, H2). Selected ^{13}C NMR data: δ 167.7, 98.4, 97.7, 75.3, 72.9, 69.4(2C), 64.3, 62.7. Anal. calcd. for $C_{27}H_{34}N_2O_8$ C, 66.81; H, 6.58; N, 3.39; found: C, 67.00; H, 6.36; N, 3.24. $[\alpha]$ = +93° mL g^{-1} dm^{-1}.

1Gb: Selected ^{1}H NMR data: δ 8.05 (s, 1H, N=CH), 4.67 (d, 1H, H1, $^3J_{H1–H2}$ = 3.6 Hz), 4.54 (d, 1 H, C*H*HPh, $^2J_{gem}$ = 12.4 Hz), 4.29 (d, 1 H, CH*H*Ph), 4.03 (t, 1H, H3, $^3J_{H3–H2}$ = $^3J_{H3–H4}$ = 9.4 Hz), 3.98–3.82 (m, 2 H, H5 and H6eq), 3.70 (t, 1 H, H6ax, $^3J_{H6ax–H5}$ = 9.4 Hz), 3.14 (dd, 1 H, H2). Selected ^{13}C NMR data: δ 168.7, 100.0, 98.7, 75.3, 72.3, 72.9, 69.6, 69.4, 64.3, 62.7. Anal. calcd. for $C_{31}H_{43}NO_6$C, 70.83; H, 8.24; N, 2.66; found: C, 70.65; H, 8.49; N, 2.33. $[\alpha]$ = +55° mL g^{-1} dm^{-1}.

1Gc: Selected ^{1}H NMR data: δ 8.02 (s, 1 H, N=CH), 4.68 (d, 1 H, H1, $^3J_{H1–H2}$ = 4.0 Hz), 4.55 (d, 1 H, C*H*HPh, $^2J_{gem}$ = 12.0 Hz), 4.30 (d, 1 H, CH*H*Ph), 4.10 (t, 1H, H3, $^3J_{H3–H2}$ = $^3J_{H3–H4}$ = 9.2 Hz), 3.98–3.82 (m, 2 H, H5 and H6eq), 3.69 (t, 1H, H6ax, $^3J_{H6ax–H5}$ = 10.0 Hz), 3.58 (t, 1 H, H4, $^3J_{H5–H4}$ = 9.2 Hz), 3.16 (dd, 1 H, H2). Selected ^{13}C NMR data: δ 168.1, 100.0, 98.5, 75.3, 73.1, 69.6, 69.5, 64.3, 62.7. Anal. calcd. for $C_{27}H_{35}NO_6$ C, 69.06; H, 7.51; N, 2.98; found: C, 68.78; H, 7.63; N, 3.03. $[\alpha]$ = +93° mL g^{-1} dm^{-1}.

1Gd: Selected ^{1}H NMR data: δ 8.05 (s, 1 H, N=CH), 4.58 (d, 1 H, H1, $^3J_{H1–H2}$ = 3.8 Hz), 4.50 (d, 1 H, C*H*HPh, $^2J_{gem}$ = 12.4 Hz), 4.25 (d, 1 H, CH*H*Ph), 4.05 (t, 1 H, H3, $^3J_{H3–H2}$ = $^3J_{H3–H4}$ = 9.4 Hz), 3.98–3.79 (m, 2 H, H5 and H6eq), 3.65 (t, 1 H, H6ax, $^3J_{H6ax–H5}$ = 10.2 Hz), 3.52 (t, 1 H, H4, $^3J_{H5–H4}$ = 10.2 Hz), 3.03 (dd, 1 H, H2). Selected ^{13}C NMR data: δ 168.4, 100.1, 98.7, 75.3, 72.3, 69.5, 64.3, 64.7. Anal. calcd. for $C_{27}H_{35}NO_6$ C, 69.06; H, 7.51; N, 2.98; found: C, 69.41; H, 7.29; N, 3.15. $[\alpha]$ = +108° mL g^{-1} dm^{-1}.

1Ge: Selected ^{1}H NMR data: δ 8.31 (s, 1 H, N=CH), 4.61 (d, 1 H, H1, $^3J_{H1–H2}$ = 4.2 Hz), 4.52 (d, 1 H, C*H*HPh, $^2J_{gem}$ = 11.8 Hz), 4.25 (d, 1H, CH*H*Ph), 3.93–3.64 (m, 4 H, H3, H5, H6ax and H6eq), 3.51 (t, 1 H, H4, $^3J_{H4–H3}$ = $^3J_{H4–H5}$ = 9.2 Hz), 3.04 (dd, 1 H, H2, $^3J_{H2–H3}$ = 9.2 Hz). Selected ^{13}C NMR data: δ 170.0, 100.0, 97.4, 75.0, 70.2, 69.4(2C), 64.2, 62.5. Anal. calcd. for $C_{27}H_{34}N_2O_8$ C, 63.02; H, 6.66; N, 5.44; found: C, 63.20; H, 6.87; N, 5.34. $[\alpha]$ = +44° mL g^{-1} dm^{-1}.

1Gf: Selected ^{1}H NMR data: δ 7.92 (s, 1 H, N=CH), 5.49 (d, 1H, C*H*HPh, $^2J_{gem}$ = 12.2 Hz), 4.71 (d, 1 H, H1, $^3J_{H1–H2}$ = 3.4 Hz), 4.65 (d, 1 H, CH*H*Ph), 4.55 (t, 1 H, H3, $^3J_{H3–H4}$ = $^3J_{H3–H2}$ = 9.2 Hz), 4.15 (dt, 1 H, H5, $^3J_{H5–H4}$ = $^3J_{H5–H6ax}$ = 10.4 Hz, $^3J_{H5–H6eq}$ = 5.0 Hz), 3.92 (dd, 1H, H6eq, $^3J_{H6eq–H6ax}$ = 10.8 Hz), 3.75 (app t, 2 H, H4 and H6ax), 2.87 (dd, 1 H, H2). Selected ^{13}C NMR data: δ 169.4, 100.2, 94.5, 74.6, 69.5, 69.2, 68.5, 65.0, 62.7. Anal. calcd. for $C_{23}H_{25}I_2NO_6$ C, 41.53; H, 3.79; N, 2.11; found: C, 41.42; H, 3.91; N, 2.19. $[\alpha]$ = −173° mL g^{-1} dm^{-1}.

1G′b: Selected ^{1}H NMR data: δ 8.02 (s, 1H, N=CH), 5.30 (s, 1 H, PhC*H*), 4.61 (d, 1 H, H1, $^3J_{H1–H2}$ = 4.0 Hz), 4.53 (d, 1 H, C*H*HPh, $^2J_{gem}$ = 11.6 Hz), 4.28 (d, 1 H, CH*H*Ph), 4.20–4.0 (m, 3 H, H3, H5 and H6eq), 3.53 (t, 1 H, H4, $^3J_{H4–H5}$ = $^3J_{H4–H3}$ = 8.6 Hz), 3.39 (t, 1 H, H6ax, $^3J_{H6–H5}$ = 9.6 Hz), 3.10 (dd, 1H, H2, $^3J_{H2–H3}$ = 8.6 Hz). Selected ^{13}C NMR data: δ 168.9, 98.7, 97.0, 82.4, 72.8, 69.7, 69.5, 69.4, 63.3. Anal. calcd. for $C_{35}H_{43}NO_6$ C, 73.27; H, 7.55; N, 2.44; found: C, 73.06; H, 7.39; N, 2.60. $[\alpha]$ = +72° mL g^{-1} dm^{-1}.

1A′b: Selected ^{1}H-NMR data: δ 7.92 (s, 1 H, N=CH), 5.45 (s, 1 H, PhC*H*) 4.61 (d, 1H, H1, $^3J_{H1–H2}$ = 3.4 Hz), 4.40–4.10 (m, 5 H, H3, H5, H6eq and C*H*HPh), 3.58 (t, 1 H, H6ax, $^3J_{H6ax–H5}$ = 10.0 Hz), 3.16 (dd, 1H, H4, $^3J_{H4–H5}$ = 9.2, $^3J_{H4–H3}$ = 2.4 Hz), 3.0 (t, 1 H, H2). Selected ^{13}C NMR data: δ 167.8, 102.3, 98.8, 80.0, 69.4, 67.0, 58.7. Anal. calcd. for $C_{35}H_{43}NO_6$ C, 73.27; H, 7.55; N, 2.44; found: C, 73.02; H, 7.71; N, 2.47. $[\alpha]$ = −2° mL g^{-1} dm^{-1}.

4.3. Oxidation reactions

To a solution of [VO(acac)$_2$] (5.3 mg, 0.02 mmol) in dichloromethane (1.5 mL) is added a solution of the appropriate ligand of type **1** (0.03 mmol) in the same solvent (1.5 mL). After 10 min of stirring, thioanisole (118 μL, 1 mmol) is added followed by hydrogen peroxide (100 μL, 35%, w/w, 1.1 mmol). After the desired reaction time, the addition of a saturated solution of sodium sulphite quenches the reaction. The organic phase is dried over sodium sulphate and the solvent evaporated under vacuum. The crude reaction product is analysed by NMR spectroscopy in $CDCl_3$ as solvent. The enantiomeric excesses have been determined by using the shift reagent Eu(hfc)$_3$. The absolute configuration has been obtained by comparison with a sample of known chirality.

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