Pergamon

Tetrahedron: *Asymmetry* 12 (2001) 2467–2471

TETRAHEDRON: *ASYMMETRY*

Novel chiral diimines and diamines derived from sugars in copper-catalysed asymmetric cyclopropanation

Carmela Borriello, Maria Elena Cucciolito, Achille Panunzi and Francesco Ruffo*

Dipartimento di Chimica, Università di Napoli 'Federico II', Complesso Universitario di Monte S. Angelo, via Cintia, I-80126 Naples, Italy

Received 7 September 2001; accepted 8 October 2001

Abstract—New chiral diimino and diamino ligands derived from α-D-mannose and α-D-glucose are described. The ligands are obtained by introducing the appropriate nitrogen functions at C(2) and C(3) of the sugar rings. The ability of the new chelates to promote the asymmetric copper(I)-catalysed cyclopropanation of styrene has been investigated. The nature of both the sugars and the chelates is crucial in determining the enantioselectivity of the reaction.

1. Introduction

Homogenous catalysis by transition metals is an agile method for the formation of several organic functionalities. To date, the formation of C–C, C–H, C–N, C–S or C–O bonds can be accomplished with high enantioselectivity,[1] provided an appropriate choice of the active metal and of its chiral coordination environment is made. Within this field, great importance is currently attributed to nitrogen ligands,[2,3] which in several cases are even more effective than the classic phosphanes. Particularly, chelates of general type **1** and **2** (Fig. 1) derived from 1,2-cyclohexanediamine or 1,2-diphenylethanediamine are suitable ancilliary donors in very important processes such as olefins dihydroxylation,[4] cyclopropanation[5–7] and aziridination.[8]

Recently, we became interested in the synthesis of new chiral nitrogen chelates derived from carbohydrates.[9–11]

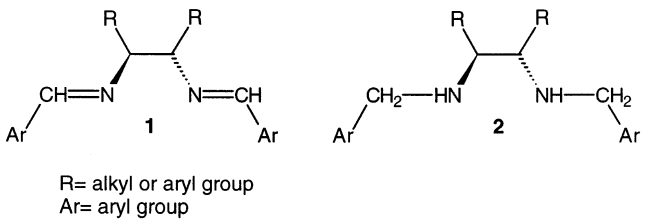


Figure 1. General formula for ligands of type **1** and **2**.

This choice was prompted by the assumption that sugars could be a very convenient source of chiral auxiliaries.

As part of this research and given the above considerations, we have devised a synthetic strategy[12] aimed to prepare new chiral diimines and diamines with a '1,2-cyclohexanediamine-like' skeleton derived from the inexpensive monoses, α-D-glucose and α-D-mannose. Herein, we describe these new compounds, which represent the first class of *N*,*N*-chelates with a chiral backbone generated form a sugar ring. As described in detail below, their use as ancilliary ligands in the cyclopropanation of styrene deserves interest, since the selectivity of the reaction depends on both the nature of the ligand (diimine or diamine) and the carbohydrate skeleton (α-D-mannose or α-D-glucose).

2. Results and discussion

2.1. Preparation and characterisation of the ligands

The new ligands of type **1** and **2** are shown in Fig. 2.

The Aryl substituents, namely phenyl (Ph), *o*-tolyl (Tol) and mesityl (Mes), were chosen with a view to varying the steric bulk of the ligands. In all cases, the relative configurations of the carbon atoms are suitable for chelating a metal centre with formation of a five-membered ring. More precisely, the glucose ligands have a *trans*-1,2-(*S*,*S*)-cyclohexanediamine like structure, while

* Corresponding author. Tel.: +39-081-674460; fax: +39-081-674090; e-mail: ruffo@unina.it

0957-4166/01/$ - see front matter
PII: S0957-4166(01)00438-4

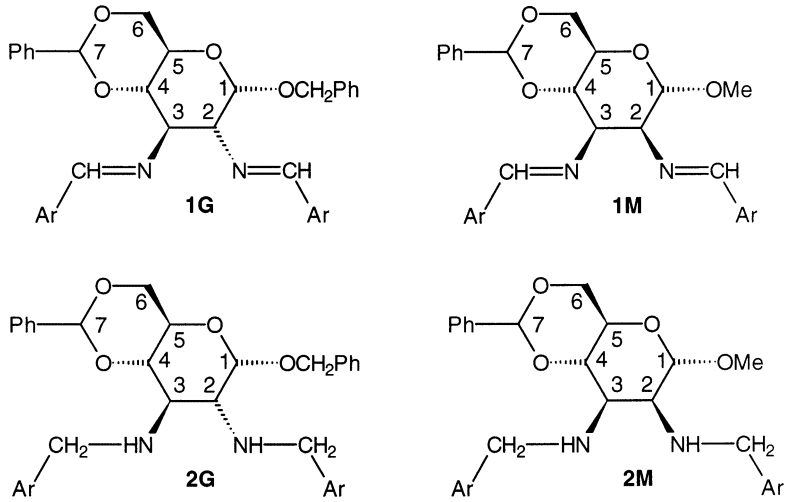


Figure 2. Ligands of type **1** and **2** derived from sugars. The ligands are indicated by a number (**1**, diimine or **2**, diamine), followed by a capital letter (**G**, α-D-glucose or **M**, α-D-mannose) and by specification of the Ar substituents.

the mannose species can be viewed as the corresponding *cis* derivatives.[13]

Our synthetic strategy involved initial protection of the ring positions C(1), C(4) and C(6) and successive insertion of the nitrogen atoms in positions C(2) and C(3). Thus, suitable precursors were found to be the corresponding diamino sugars **3**, readily available through a series of simple reactions by starting from inexpensive commercial sources.[14,15] Condensation of the amino functions with the appropriate aldehyde ArCHO afforded the corresponding type **1** diimines (Scheme 1, path i).

White crystalline compounds were obtained by simply grinding the crude reaction products in methanol. These ligands are very soluble in halogenated and aromatic solvents, while they are insoluble in alcohols and paraffins. They are stable under anhydrous conditions, and NMR spectra could be recorded in dry deuteriobenzene. Otherwise, hydrolysis of the imino bonds rapidly takes place in the presence of traces of water.

Ligands of the type **1** could be hydrogenated to the diamines **2** by reaction with excess sodium borohydride in a toluene/methanol mixture (Scheme 1, path ii). The products were isolated in good yield as white solids after an easy work-up of the reaction mixture. They display solubility properties similar to those of the parent diimines, and obviously do not degrade on exposure to moisture.

The characterisation of the products was carried out through NMR spectroscopy and elemental analyses. Due to crowding of the corresponding spectral region, the accurate attribution of the ring protons was accomplished by using 2-D NMR techniques. The main spectral features are as follows:

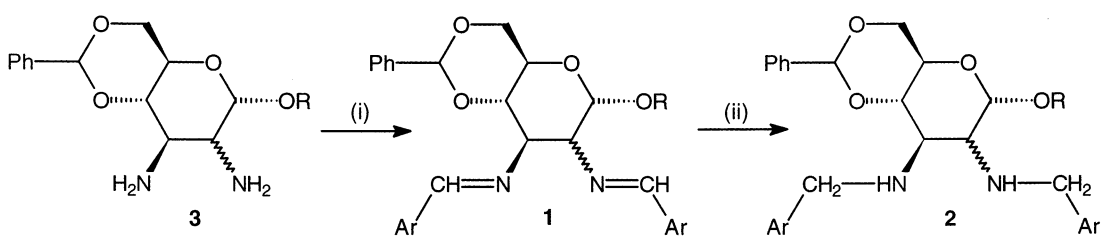
(i) the identity of the sugars was retained throughout the preparation. This was deduced by the presence of proton spectral patterns typical of *manno*- and *gluco*-configurations, respectively;

(ii) spectra of type **1** compounds display low field signals diagnostic of the CH(imino) nuclei;

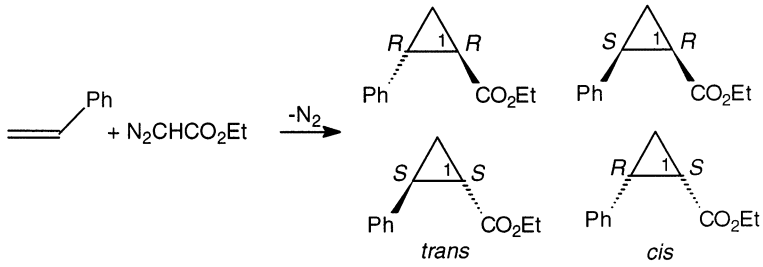
(iii) the aforementioned signals are not present in the spectra of the corresponding diamines, while signals accounting for the N-CH_2 moieties appear in the appropriate regions.

2.2. Styrene cyclopropanation

Olefin cyclopropanation is a very useful reaction for the preparation of building blocks for the synthesis of natural products (Scheme 2).



Scheme 1. (i) +2ArCHO, $-2H_2O$, PhMe, 333 K, 1 h; (ii) +10$NaBH_4$, PhMe/MeOH, 298 K, 24 h.



Scheme 2.

The best results in terms of both yields and selectivity have been achieved by using copper(I) as the metal catalyst and chiral nitrogen chelates as ligands.[2] Recent reviews[2,3] underline that several *N*,*N*-ligands have been designed aiming to optimise the performance of the catalytic cycle. Besides the oxazoline systems developed by Evans[16] and Pfaltz,[17] significant results were achieved using chiral diimines and diamines of type **1** and **2** (Fig. 1) derived from 1,2-cyclohexanediamine[5,8] or 1,2-diphenylethanediamine.[6,7]

The availability of the closely related ligands derived from sugars (Fig. 2) prompted us to test them in the cyclopropanation of styrene. Ethyl diazoacetate was used as the carbene generator (Scheme 2), and the results are summarised in Table 1.

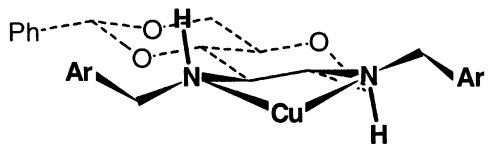
Table 1. Copper-catalysed cyclopropanation using ligands of type **1** and **2**

Entry	Ligand	Isolated yield (*trans*/*cis*)	E.e$_{trans}$[a]	E.e$_{cis}$[a]
1	**1G-Ph**	80% (65/35)	29 (*R*)	25 (*R*)
2	**1G-Mes**	85% (7/3)	20 (*R*)	19 (*R*)
3	**1M-Mes**	85% (6:4)	10 (*S*)	11 (*S*)
4	**2G-Ph**	75% (65/35)	36 (*S*)	40 (*S*)
5	**2G-Mes**	90% (72/28)	55 (*S*)	36 (*S*)
6	**2G-Tol**	85% (7/3)	18 (*S*)	7(*S*)
7	**2M-Ph**	80% (6/4)	0	0
8	**2M-Mes**	85% (11/9)	0	0

[a] Configuration at C(1) of the major enantiomer in parenthesis.

In all cases the reactions afforded good to high yields of the corresponding cyclopropane as a *trans*/*cis* mixture. Non-racemic products were observed in all the experiments performed with ligands based on glucose (entries 1, 2, and 4–6). On the other hand, chelates derived from mannose (entries 3, 7, and 8) were found to be less effective as a non-racemic product was observed in only one case (entry 3).

The results obtained with diamines (type **2**) are in line with the mechanism proposed for cyclopropanation.[17] Actually, substantial enantioselectivity is expected only if the *N*,*N*-ligand is able to create a chiral pocket with C_2 symmetry in the coordination environment of the metal ion. When appropriately viewed perpendicularly to the C(2)–C(3) axis, diamines based on glucose do display local C_2 symmetry since the nitrogen functions lie in equatorial positions. In other words, they resemble 1,2-(*S*,*S*)-diaminocyclohexane derivatives.[13] According to previous results,[18] this symmetry should be retained upon coordination to the copper ion, as the nitrogen atoms are expected to adopt the same relative configuration giving rise to a *transoid* geometry of the segments C(2)–C(3)–NH–CH_2Ar and C(3)–C(2)–NH–CH_2Ar (Fig. 3).



2G

Figure 3. The chiral pocket possibly generated by ligands of type **2G** upon coordination to the copper ion. The -OCH_2Ph group in position 1 has been omitted for sake of clarity.

A chiral pocket with C_2 symmetry would be thus created, which, in this particular case, is apt to favour formation of the (*S*)-enantiomer.[18]

On the other hand, in mannose the configuration at C(2) is inverted and the sugar assumes a local *meso* configuration, which is not suited for promoting asymmetry in the reaction.

In all cases, the glucodiamines **2G** favoured the (*S*)-configuration at position 1 of the cyclopropane ring (Scheme 2), and the e.e. was greater in the case of the *trans* product. Both findings are in keeping with those found in cyclopropanation reactions catalysed by Cu(I)/(*S*,*S*)-1,2-diphenylethanediamine systems.[6]

Diamines **2G-Ph** and **2G-Mes** performed significantly better than the less symmetrical *o*-tolyl substituted **2G-Tol**. The first two chelates displayed also a different selectivity, as **2G-Mes** afforded the *trans* product with higher e.e. than **2G-Ph**, while the result was reversed for the *cis* isomer.

Quite surprisingly, diimines of the type **1G** were found to favour the formation of the opposite enantiomers. Although lower e.e.s were observed, both *cis* and *trans* products were preferentially obtained with (*R*)-configuration at position 1. Furthermore, the less hindered **1G-Ph** induced higher enantioselectivity than the bulky **1G-Mes**. These results are better than those obtained in an experiment performed under the same conditions by using the closely related 1,2-diphenylethanediimine

derivative (1*S*,2*S*)-Mes-CH=N-CH(Ph)-CH(Ph)-N=CH-Mes, which did not induce significant enantioselectivity.

Furthermore, the reverse influence from the bulk of the Ar groups was also found when (*S*,*S*)-1,2-cyclohexanediimines were used,[8] the phenyl derivative yielding a significantly lower e.e. than the corresponding mesityl analogue.

Within diimine ligands, the important role played by the nature of the sugar was also identified. Actually, diimine **1M-Mes**, which was the sole mannose derivative to afford a non-racemic product, induced opposite selectivity with respect to the corresponding glucose ligands.

3. Conclusion

We have reported the synthesis of new chiral diimino and diamino ligands derived from the most common carbohydrates. As far as we know, they form the first class of *N*,*N*-chelates with a chiral backbone generated from a sugar ring, although several related *P*,*P*- or mixed *P*,*N*-ligand systems have been reported.[19] The ability of the new chelates to promote the asymmetric copper(I)-catalysed cyclopropanation of styrene has been assessed, and e.e.s of up to 55% were obtained. Notably, diimines derived from α-D-glucose were found to favour the opposite enantiomers with respect to diamines derived from the same sugar. An analogous reverse effect was demonstrated by comparing the activity of diimines derived from different sugars. Further studies on modified type **1** and **2** ligands are in progress.

4. Experimental

4.1. General methods

NMR spectra were recorded in C_6D_6 or $CDCl_3$ with a 200 or a 300 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. Benzyl-4,6-*O*-2,3-diamino-2,3-dideoxy-α-D-glucoside[14] and methyl-4,6-*O*-benzylidene-2,3-diamino-2,3-dideoxy-α-D-mannoside[15] were prepared according to literature methods. Toluene was distilled from sodium, methanol from magnesium immediately before use.

4.2. Synthesis of type 1 ligands

The appropriate aldehyde (2 mmol) was added to a stirred solution of the 2,3-hexapyranosediamine **3** (1 mmol) in 4 ml of dry toluene under nitrogen. After stirring for 1 h at 333 K, the solvent was removed under vacuum. The addition of methanol to the crude reaction yielded a white microcrystalline solid which was separated, washed with methanol, petroleum ether, and dried under vacuum (yield >75%).

Selected data for **1G-Ph**: ^{1}H NMR (200 MHz, C_6D_6): δ 8.15 (s, 1H, N=CH), 8.00 (s, 1H, N=CH), 5.42 (s, 1H, H7), 4.86 (d, 1H, H1), 4.75 (d, 1H, C*H*HPh), 4.50 (m, 3H, H3, H5 and CH*H*Ph), 4.32 (dd, 1H, $H6_{eq}$), 4.11 (t, 1H, H4), 3.94 (dd, 1H, H2), 3.72 (t, 1H, $H6_{ax}$); ^{13}C NMR (75.5 MHz, C_6D_6): δ 164.7, 164.1, 138–127 (16 C, aromatics), 102.1, 99.5, 80.9, 73.9, 70.0, 69.7, 69.6, 63.9. Anal. calcd for $C_{34}H_{32}N_2O_4$: C, 76.67; H, 6.06; N, 5.26. Found: C, 76.89; H, 6.10; N, 5.15%.

Selected data for **1G-Mes**: ^{1}H NMR (300 MHz, C_6D_6): δ 8.60 (s, 1H, N=CH), 8.50 (s, 1H, N=CH), 5.51 (s, 1H, H7), 5.00 (d, 1H, H1), 4.81 (d, 1H, C*H*HPh), 4.5 (m, 4H, H3, H5, $H6_{eq}$ and CH*H*Ph), 4.08 (t, 1H, H4), 3.99 (dd, 1H, H2), 3.84 (t, 1H, $H6_{ax}$); ^{13}C NMR (50.3 MHz, C_6D_6): δ 164.5, 163.6, 139–127 (16 C, aromatics), 102.2, 99.9, 80.8, 75.8, 71.7, 69.9, 69.7, 63.9, 21.2, 21.0, 20.7. Anal. calcd for $C_{40}H_{44}N_2O_4$: C, 77.89; H, 7.19; N, 4.54. Found: C, 78.01; H, 7.20; N, 4.48%.

Selected data for **1G-Tol**: ^{1}H NMR (200 MHz, C_6D_6): δ 8.50 (s, 1H, N=CH), 8.46 (s, 1H, N=CH), 5.53 (s, 1H, H7), 4.96 (d, 1H, H1), 4.78 (d, 1H, C*H*HPh), 4.55 (m, 2H, H3 and H5), 4.48 (d, 1H, CH*H*Ph), 4.36 (dd, 1H, $H6_{eq}$), 4.14 (t, 1H, H4), 3.96 (dd, 1H, H2), 3.76 (t, 1H, $H6_{ax}$); ^{13}C NMR (75.5 MHz, C_6D_6): δ 163.5, 163.0, 139–126 (16 C, aromatics), 102.0, 99.4, 81.0, 74.3, 70.2, 69.7, 63.9, 19.3, 19.0. Anal. calcd for $C_{36}H_{36}N_2O_4$: C, 77.12; H, 6.47; N, 5.00. Found: C, 77.20; H, 6.42; N, 5.04%.

Selected data for **1M-Mes**: ^{1}H NMR (200 MHz, C_6D_6): δ 8.62 (s, 1H, N=CH), 8.56 (s, 1H, N=CH), 5.46 (s, 1H, H7), 4.71 (t, 1H, H4), 4.66 (d, 1H, H1), 4.25 (m, 3H, H3, H5 and $H6_{eq}$), 3.86 (t, 1H, $H6_{ax}$), 3.77 (dd, 1H, H2), 3.18 (s, 3H, OMe); ^{13}C NMR (75.5 MHz, C_6D_6): δ 161.7, 160.9, 137–125 (12 C, aromatics), 101.1, 100.2, 76.0, 74.9, 69.1, 67.7, 63.8, 52.7, 19.4, 19.2, 19.0, 18.4. Anal. calcd for $C_{34}H_{40}N_2O_4$: C, 75.53; H, 7.46; N, 5.18. Found: C, 75.44; H, 7.43; N, 5.12%.

4.3. Synthesis of type 2 ligands

To a solution of the appropriate diimine of type **1** (1 mmol) in a 1:1 mixture of dry toluene and dry methanol (20 mL) was added excess sodium borohydride (0.55 g, 14 mmol) at 273 K under a nitrogen atmosphere. After stirring for 24 h at 298 K, saturated aqueous ammonium chloride (10 mL) was added to the mixture. The organic phase was extracted with dichloromethane (2×10 mL) and dried over sodium sulphate. The solvent was removed under vacuum leaving the product as a white solid (yield >70%).

Selected data for **2G-Ph**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.70 (s, 1H, H7), 5.05 (d, 1H, H1), 4.84 (d, 1H, C*H*HPh), 4.60 (d, 1H, CH*H*Ph), 4.35 (dd, 1H, $H6_{eq}$), 4.26 (d, 1H, NC*H*H), 3.99 (d, 1H, NCH*H*), 3.98 (m, 1H, H5), 3.86 (d, 1H, NC*H*H), 3.75 (m, 2H, H4 and $H6_{ax}$), 3.67 (d, 1H, NCH*H*), 3.12 (t, 1H, H3), 2.78 (dd, 1H, H2); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 149–126 (16 C, aromatics), 101.1, 95.3, 84.3, 69.2, 69.1, 62.9, 60.0, 57.4, 53.9, 51.3. Anal. calcd for $C_{34}H_{36}N_2O_4$: C, 76.09; H, 6.76; N, 5.22. Found: C, 76.11; H, 6.85; N, 5.30%.

Selected data for **2G-Mes**: ^{1}H NMR (300 MHz, C_6D_6): δ 5.60 (s, 1H, H7), 5.08 (d, 1H, H1), 4.67 (d, 1H, C*H*HPh), 4.48 (d, 1H, NC*H*H), 4.30 (dd, 1H, $H6_{eq}$), 4.26 (d, 1H, CH*H*Ph), 4.16 (dt, 1H, H5), 3.80 (d, 1H, NCH*H*), 3.76 (2 t, 2H, H4 and $H6_{ax}$), 3.67 (d, 1H, NC*H*H), 3.33 (d, 1H, NCH*H*), 3.12 (t, 1H, H3), 2.77 (dd, 1H, H2); ^{13}C NMR (75.5 MHz, C_6D_6): δ 137–127 (16 C, aromatics), 101.9, 96.2, 85.9, 69.8, 69.5, 63.4, 61.6, 59.6, 49.2, 45.6, 20.9, 19.8, 19.5. Anal. calcd for $C_{40}H_{48}N_2O_4$: C, 77.39; H, 7.79; N, 4.51. Found: C, 77.47; H, 7.78; N, 4.45%.

Selected data for **2G-Tol**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.60 (s, 1H, H7), 5.09 (d, 1H, H1), 4.72 (d, 1H, C*H*HPh), 4.48 (d, 1H, CH*H*Ph), 4.23 (dd, 1H, $H6_{eq}$), 4.16 (d, 1H, NC*H*H), 3.95 (dt, 1H, H5), 3.82 (d, 1H, NCH*H*), 3.78 (t, 1H, $H6_{ax}$), 3.68 (d, 1H, NCH*H*), 3.64 (t, 1H, H4), 3.57 (d, 1H, NCH*H*), 3.02 (t, 1H, H3), 2.75 (dd, 1H, H2); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 138–126 (18 C, aromatics), 101.2, 95.4, 84.7, 69.4, 69.2, 62.9, 60.5, 57.8, 51.7, 49.4, 18.9, 18.8. Anal. calcd for $C_{36}H_{40}N_2O_4$: C, 76.57; H, 7.14; N, 4.96. Found: C, 76.70; H, 7.18; N, 4.91%.

Selected data for **2M-Mes**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.46 (s, 1H, H7), 4.89 (d, 1H, H1), 4.22 (m, 1H, $H6_{eq}$), 3.80 (m, 5H, H4, H5, $H6_{ax}$, NCH_2), 3.72 (d, 1H, NC*H*H), 3.53 (d, 1H, NCH*H*), 3.46 (s, 3H, OMe), 3.31 (dd, 1H, H3), 3.15 (dd, 1H, H2); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 138–125 (12 C, aromatics), 101.7, 99.3, 69.2, 64.0, 58.6, 57.9, 55.1, 45.9, 20.8, 19.7, 19.4. Anal. calcd for $C_{34}H_{44}N_2O_4$: C, 74.97; H, 8.14; N, 5.14. Found: C, 75.06; H, 8.19; N, 5.07%.

4.4. Cyclopropanation reactions

All reactions were performed at 298 K. To a stirred solution of the *N*,*N*-chelate (0.20 mmol) and $[Cu(MeCN)_4]BF_4$ (0.10 mmol) in dry dichloromethane (10 mL) was added styrene (30.0 mmol). A solution of ethyl diazoacetate (10.0 mmol) in dry dichloromethane (20 mL) was added via syringe pump to the amine/tetrafluoroborate/styrene solution. The addition was completed in 16 h. The solvent was removed under vacuum and the residue chromatographed on aluminium oxide, ethyl acetate: hexane 1:5 as eluent. E.e.s were evaluated by NMR spectroscopy by using the shift reagent $Eu(hfc)_3$, and by comparing the spectra with those obtained with original samples of known configuration. The results were confirmed by measurements of the optical rotation of the products.[20]

Acknowledgements

The authors thank the Consiglio Nazionale delle Ricerche, the MURST (Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale, Cofinanziamento 2000–2001) for financial support, and the Centro Interdipartimentale di Metodologie Chimico-Fisiche, Università di Napoli 'Federico II' for the NMR facilities.

References

1. Trost, B. M.; Lee, C. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 2000.
2. Fache, F.; Schulz, E.; Tommasino, M. L.; Lemaire, M. *Chem. Rev.* **2000**, *100*, 2159–2231.
3. Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 497–526.
4. Corey, E. J.; Jardine, P. D.; Virgil, S.; Yuen, P. W.; Connell, R. D. *J. Am. Chem. Soc.* **1989**, *111*, 9243–9244.
5. Denmark, S. E.; Christenson, B. L.; Coe, D. M.; O'Connor, S. P. *Tetrahedron Lett.* **1995**, *36*, 2215–2218.
6. Kanemasa, S.; Hamura, S.; Harada, E.; Yamamoto, H. *Tetrahedron Lett.* **1994**, *35*, 7985–7988.
7. Kanemasa, S. *Jpn. Kokai Tokkyo Koho* **1994**, CAN 121:255288.
8. Li, Z.; Quan, R. W.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5889–5890.
9. Borriello, C.; Ferrara, M. L.; Orabona, I.; Panunzi, A.; Ruffo, F. *J. Chem. Soc., Dalton Trans.* **2000**, 2545–2550.
10. Ferrara, M. L.; Giordano, F.; Orabona, I.; Panunzi, A.; Ruffo, F. *Eur. J. Inorg. Chem.* **1999**, 1939–1947.
11. Ferrara, M. L.; Funicello, M.; Orabona, I.; Panunzi, A.; Ruffo, F. *Organometallics* **1998**, *17*, 3832–3834.
12. The synthesis of one ligand based on mannose has been previously given. See: Borriello, C.; De Renzi, A.; Fusto, M.; Molinaro, A.; Ruffo, F. *Carbohydr. Res.* **2001**, *331*, 209–212.
13. Actually, it should be noted that according to the stereochemical rules the configurations at C(2) and C(3) are (*R*,*R*) and (*S*,*R*) for 2,3-D-glucodiamines and 2,3-D-mannodiamines, respectively.
14. Meyer zu Reckendorf, W.; Weber, R.; Hehenberger, H. *Chem. Ber.* **1981**, *14*, 1306–1317.
15. Guthrie, R. D.; Murphy, D. *J. Chem. Soc.* **1965**, 6956–6960.
16. Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726–728.
17. Pfaltz, A. In *Advances in Catalytic Processes*; Doyle, M. P., Ed.; JAI Press: London, 1993; Vol. 1, pp. 61–94.
18. Cavallo, L.; Cucciolito, M. E.; De Martino, A.; Giordano, F.; Orabona, I.; Vitagliano, A. *Chem. Eur. J.* **2000**, *6*, 1127–1139.
19. Steinborn, D.; Junicke, H. *Chem. Rev.* **2000**, *100*, 4283–4317.
20. Evans, D. A.; Woerpel, K. A.; Scott, M. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 430–432.