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Synthesis of chiral bis(oxazolinyl)bipyridine ligands and related helical metal complexes

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Abstract—Enantiomerically pure tetradentate bis(oxazolinyl)bipyridine ligands **1** have been synthesized in high yields. X-Ray analysis showed that the copper(I) complexes of ligands **1** had a C_2-symmetric helical structure. Ruthenium complexes of ligands **1** prepared in situ were found to be efficient in the asymmetric cyclopropanation of styrene with ethyl diazoacetate.

1. Introduction

The design and synthesis of suitable chiral catalytic ligands is a key goal in the field of asymmetric catalysis and a number of very efficient chiral catalysts have been developed.[1] Among the tremendous number of reported ligands for chiral catalysis, those possessing central chirality, axial chirality and planar chirality occupy a predominant position.[2] Chiral helical ligands,[3] catalysts[4] and inducers[5] have recently been used in asymmetric catalysis, and some have provided encouraging enantioselectivities. Of these compounds, we are particularly interested in ligands which, upon coordination with metal ions, form chiral helical metal complexes for use as chiral catalysts in asymmetric catalysis. The well-designed examples of this type of ligand include binaphthol derivatives[3d] and bisamides.[4c] Herein we describe the synthesis of a new class of tetradentate chiral bipyridine ligands **1** and the related helical metal complexes **2**.

2. Results and discussion

The bis(oxazolinyl)bipyridine ligands **1** were synthesized in high yields from enantiomerically pure amino alcohols and the diethyl bipyridinedicarboxylate **4** which was prepared from the dibromobipyridine **3** as shown in Scheme 1. The reaction of 6,6-dibromo-2,2-bipyridine, prepared from the coupling of 2,6-dibromopyridine,[6] with the anion of ethyl isobutyrate gave diester **4** in 98% yield. Ester exchange of **4** with amino alcohols in xylene provided diamides **5** in 75–81% yield. Conversion of hydroxyl groups of **5** to chlorides **6** followed by treatment with NaOH in methanol produced the desired tetradentate ligands **1** in 62–76% overall yield from **5**.

To investigate the coordination behavior of tetradentate ligands **1** and the structures of their metal complexes, the copper(I) complexes **2** were synthesized. The bis(oxazolinyl)bipyridine ligands **1** were mixed with $Cu(CH_3CN)_4PF_6$ (1:1) in CH_2Cl_2 and stirred at room temperature for 2 h. After evaporation of solvent, the crude solid was recrystallized with anhydrous methanol to give a reddish-brown crystalline **2** (Scheme 2).

The single-crystal structure of complex **2a** was determined by X-ray analysis shown in Fig. 1.[7] Selected bond lengths and bond angles are listed in Table 1. As expected, the ligand **1a** assembled with Cu(I) through the coordination of four nitrogen atoms to form a helical complex **2a**. The complex in the crystal is C_2-symmetric and the configuration of helical ring is *P*, and the angles between the $Cu–N_{(oxazoline)}$ bond and the coordination plane (N1–Cu–N1A) are 36.3°. The dis-

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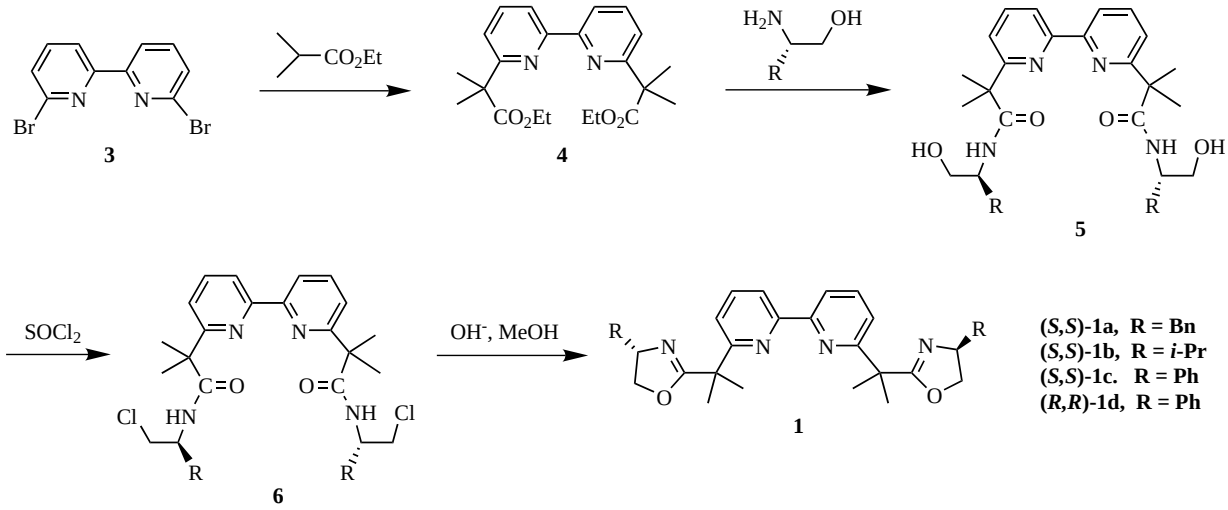
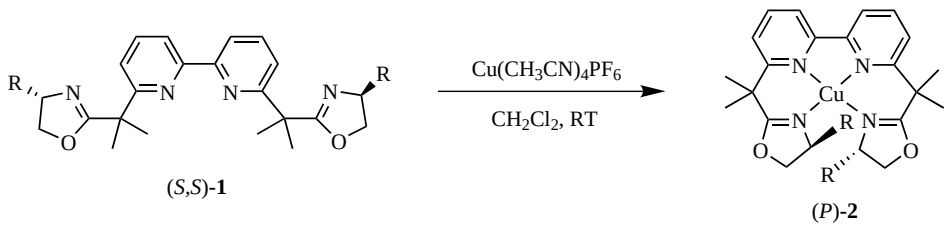


Scheme 1.



Scheme 2.

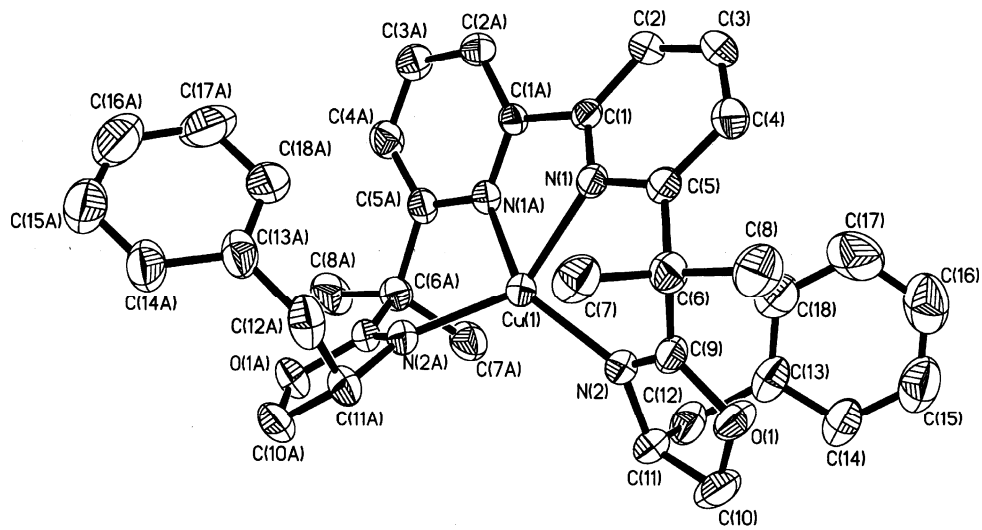


Figure 1. Crystal structure of complex **2a**.

tances between the copper atom and pyridine nitrogen are 2.096(3) Å which lie within the range reported in the copper(I) complexes of bipyridine.[8] While the lengths of Cu–$N_{(oxazoline)}$ bonds [1.988(3) Å] are slightly longer than those in the copper complexes of bisoxazoline.[4c,9]

Transition metal-catalyzed asymmetric cyclopropanation of olefins with diazo acetates is one of the most important methods for the construction of chiral cyclopropane structures in organic synthesis.[10] A few examples have demonstrated that the multinitrogen ligands induce good enantioselectivity in copper- or ruthenium-catalyzed cyclopropanation.[11] To investigate the efficiency of ligands **1** for enantiocontrol in the cyclopropanation reaction, the complexes **2** were first tested for catalytic ability in the asymmetric cyclopropanation of styrene with ethyl diazoacetate. No reaction was observed in refluxing $CHCl_3$; however, the ruthenium complexes, prepared in situ from [Ru(*p*-cymene)Cl_2]$_2$

Table 1. Selected bond lengths (Å) and bond angles (°) in the complex **2a**

Bond lengths (Å)		Bond angles (°)	
Cu–N(1)	2.096(3)	N(1)–Cu–N(1A)	79.8(2)
Cu–N(2)	1.988(3)	N(1)–Cu–N(2)	88.3(1)
N(1)–C(1)	1.345(4)	N(2)–Cu–N(2A)	120.7(2)
N(1)–C(5)	1.353(4)	N(1A)–Cu–N(2A)	88.3(1)
N(2)–C(9)	1.273(5)	N(2)–Cu–N(1)–C(1)	136.12
N(2)–C(11)	1.490(5)	N(1A)–Cu–N(1)–C(1)	−7.57
C(1)–C(1A)	1.497(7)	N(2A)–Cu–N(1)–C(1)	−81.48

and the ligands **1** were found to be effective in this reaction. As an example, the cyclopropanation of styrene with ethyl diazoacetate catalyzed by the Ru complex of ligand **1a** (1 mol%) provided cyclopropanation products in 56% yield (*cis*/*trans* 34:66) with 24% e.e. for the *trans* isomer.

3. Conclusion

In summary, a series of new chiral tetradentate bis(oxazolinyl)bipyridine ligands **1** have been synthesized in high yields. These ligands, upon coordination with copper(I), formed C_2-symmetric helical complexes. The ligands **1** were proven to be efficient in the ruthenium-catalyzed asymmetric cyclopropanation of styrene. Although the enantioselectivity of the reaction was not high, it clearly shows the potential of these ligands and their helical complexes for enantiocontrol in asymmetric catalysis.

4. Experimental

4.1. General

THF and xylene were distilled from sodium–benzophenone, $CHCl_3$ and CH_2Cl_2 were distilled from CaH_2. All enantiomerically pure amino alcohols were prepared by reduction of the corresponding commercially available amino acids with $NaBH_4/H_2SO_4$ in THF.[12] 6,6′-Dibromo-2,2′-bipyridine was synthesized according to the literature method.[6] Melting points were measured with a Yanaco MP-500 apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AMX-300AC instrument using tetramethylsilane as an internal standard in deuterochloroform. IR spectra were obtained as KBr plates on a Shimadzu 435 spectrophotometer. Mass spectra were measured on a VG-7070E spectrometer using a solid probe at 70 eV. Elemental analyses were carried out on a Yanaco MT-3 analyzer. Optical rotations were measured on a Perkin–Elmer 241 rotation apparatus.

4.2. Synthesis of 6,6′-bis-(1-ethoxycarbonyl-1-methyl-ethyl)-[2,2′]bipyridinyl 4

A solution of *n*-BuLi/hexane (1.5 M, 16 mL, 24 mmol) was added dropwise into a solution of diisopropylamine (2.42 g, 24 mmol) in anhydrous THF (24 mL) at −10°C under nitrogen. The mixture was stirred at the same temperature for 30 min and then cooled to −78°C. Ethyl isobutyrate (2.78 g, 24 mmol) was added. At this temperature the mixture was allowed to stand for a further 45 min, and 6,6′-dibromo-2,2′-bipyridyl (3.14 g, 10 mmol) was added. Under the light of a 200 W tungsten lamp, the mixture was kept at −78°C for 10 min and then allowed to stir overnight at rt. The mixture was treated with saturated aqueous NH_4Cl solution, and extracted with diethyl ether. The organic layer was washed with saturated NaCl and dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with PE/EtOAc (10:1) to give **4** as a white solid (3.76 g, 98%). Mp 57–59°C. IR: 2983m, 1734vs, 1567s, 1436s, 1254s, 1148s, 1124m, 1022m, 808m, 760m. ^{1}H NMR: 8.33 (d, J=7.8 Hz, 2H), 7.75 (t, J=7.8 Hz, 2H), 7.28 (d, J=7.8 Hz, 2H), 4.16 (q, J=7.2 Hz, 4H), 1.66 (s, 12H), 1.88 (t, J=7.2 Hz, 6H). MS (m/z, %): 384 (45, M^+), 355 (14), 311 (68), 237 (100). Anal. calcd for $C_{22}H_{28}N_2O_4$: C, 68.75; H, 7.29; N, 7.29. Found: C, 68.71; H, 6.88; N, 7.51%.

4.3. Synthesis of 5

4.3.1. General procedure. Anhydrous xylene (24 mL), amino alcohol (12 mmol), **4** (4 mmol) and NaCN (39 mg, 10 mol%) were added in sequence into a Schlenk flask equipped with a N_2 inlet. The mixture was heated under gentle reflux for 7 days. After cooling to rt, the mixture was diluted with $CHCl_3$, washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4, and filtered through a short silica gel column to give **5**. The crude products were pure enough for direct use in the next step.

4.3.2. 6,6′-Bis-{1-[*N*-((1*S*)-2-hydroxy-1-benzyl-ethyl)]-carbamoyl-1-methyl-ethyl}-[2,2′]bipyridinyl 5a. 78% yield. ^{1}H NMR: 8.14 (d, J=7.8 Hz, 2H), 7.84 (t, J=7.8 Hz, 4H), 7.46 (d, J=7.8 Hz, 2H), 7.05–7.15 (m, 10H), 4.03–4.10 (m, 2H), 3.47–3.53 (m, 4H), 2.73–2.77 (m, 2H), 1.67 (s, 12H).

4.3.3. 6,6′-Bis-{1-[*N*-((1*S*)-2-hydroxy-1-isopropyl-ethyl)]-carbamoyl-1-methyl-ethyl}-[2,2′]bipyridinyl 5b. 75% yield. ^{1}H NMR: 8.31 (d, J=7.8 Hz, 2H), 7.86 (t, J=7.8 Hz, 2H), 7.49 (d, J=7.8 Hz, 2H), 6.94 (d, 6.9 Hz, 2H), 3.48–3.66 (m, 6H), 1.70–1.79 (m, 14H), 0.82 (d, J=6.9 Hz, 6H), 0.74 (d, J=6.6 Hz, 6H).

4.3.4. 6,6′-Bis-{1-[*N*-((1*S*)-2-hydroxy-1-phenyl-ethyl)]-carbamoyl-1-methyl-ethyl}-[2,2′]bipyridinyl 5c. 81% yield. ^{1}H NMR: 8.15 (d, J=7.8 Hz, 2H), 7.71–7.74 (m, 4H), 7.36 (d, J=7.8 Hz, 2H), 7.09–7.26 (m, 10H), 4.94–4.98 (m, 2H), 3.68–3.74 (m, 4H), 1.77 (d, J=6.6 Hz, 12H).

4.3.5. 6,6′-Bis-{1-[*N*-((1*R*)-2-hydroxy-1-phenyl-ethyl)-carbamoyl]-1-methyl-ethyl}-[2,2′]bipyridinyl 5d. 79% yield. ^{1}H NMR: 8.15 (d, J=7.8 Hz, 2H), 7.68–7.76 (m, 4H), 7.46 (d, J=7.8 Hz, 2H), 7.08–7.20 (m, 10H), 4.93–4.98 (m, 2H), 3.70–3.72 (m, 4H), 1.76 (d, J=6.6 Hz, 12H).

4.4. General procedure for synthesis of ligands 6

To a solution of **5** (3 mmol) in $CHCl_3$ (15 mL) was added a solution of $SOCl_2$ (60 mmol) in $CHCl_3$ (15 mL) at −5°C over 0.5 h, and the mixture was allowed to stir overnight at rt. Then water (20 mL) was added slowly, the organic phase was separated, and the aqueous phase was extracted with chloroform. The combined organic phase was washed with aqueous $NaHCO_3$ and saturated NaCl solution, and dried over anhydrous Na_2SO_4. The organic phase was filtered through a short silica gel column and concentrated under reduced pressure to give **6**. The crude material was used directly to the next step.

4.4.1. 6,6′-Bis-{1-[*N*-((1*S*)-2-chloro-1-benzyl-ethyl)carbamoyl]-1-methyl-ethyl}-[2,2′]bipyridinyl 6a. 90% yield. ^{1}H NMR: 8.28 (d, J=7.8 Hz, 2H), 7.81 (t, J=7.8 Hz, 4H), 7.6 (d, J=7.38 Hz, 2H), 7.04–7.24 (m, 10H), 4.36–4.44 (m, 2H), 3.34–3.58 (m, 4H), 2.75–2.79 (m, 2H), 1.69 (d, J=9.0 Hz, 12H).

4.4.2. 6,6′-Bis-{1-[*N*-((1*S*)-2-chloro-1-isopropyl-ethyl)-carbamoyl]-1-methyl-ethyl}-[2,2′]bipyridinyl 6b. 86% yield. ^{1}H NMR: 8.39 (dd, J=7.8 Hz and 0.9 Hz, 2H), 7.84 (t, J=7.8 Hz, 2H), 7.46 (dd, J=7.8 Hz and 0.9 Hz, 2H), 7.06 (d, 9.0 Hz, 2H), 3.85–3.91 (m, 2H), 3.53–3.64 (m, 4H), 1.73–1.80 (m, 12H), 0.85 (d, J=6.6 Hz, 6H), 0.69 (d, J=6.9 Hz, 6H).

4.4.3. 6,6′-Bis-{1-[*N*-((1*S*)-2-chloro-1-phenyl-ethyl)carbamoyl]-1-methyl-ethyl}-[2,2′]bipyridinyl 6c. 82% yield. ^{1}H NMR: 8.44 (d, J=7.8 Hz, 2H), 7.91–7.96 (m, 4H), 7.62 (d, J=7.8 Hz, 2H), 7.24–7.33 (m, 10H), 5.38–5.46 (m, 2H), 3.87–3.90 (m, 4H), 1.91 (d, J=8.7 Hz, 12H).

4.4.4. 6,6′-Bis-{1-[*N*-((1*R*)-2-chloro-1-phenyl-ethyl)carbamoyl]-1-methyl-ethyl}-[2,2′]bipyridinyl 6d. 83% yield. ^{1}H NMR: 8.29 (d, J=7.8 Hz, 2H), 7.76–7.83 (m, 4H), 7.49 (d, J=7.8 Hz, 2H), 7.14–7.19 (m, 10H), 5.23–5.31 (m, 2H), 3.74–3.76 (m, 4H), 1.78 (d, J=8.4 Hz, 12H).

4.5. Synthesis of ligands 1

4.5.1. General procedure. A mixture of **6** (2.7 mmol) and NaOH (0.32 g, 8 mmol) in methanol (27 mL) was heated under reflux for 6 h. After removal of methanol, chloroform (60 mL) and water (15 mL) were added to the residue, the organic phase was separated, and the aqueous phase was extracted with chloroform. The combined organic phase was washed with saturated NaCl solution, dried over anhydrous K_2CO_3 and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel with PE/EtOAc (4:1) to provide ligands **1**.

4.5.2. 6,6′-Bis-{1-[(4*S*,4′*S*)-4-benzyl-4,5-dihydro-oxazol-2-yl]-1-methyl-ethyl}-[2,2′]bipyridinyl 1a. White solid, 84% yield, mp 110–112°C. $[\alpha]_D^{20}$ −13 (c 1.0, $CHCl_3$). IR: 2974m, 1664vs, 1649s, 1575s, 1435s, 1382m, 1138m, 1109s, 1083s, 976s, 810s. ^{1}H NMR: 8.36 (d, J=8.0 Hz, 2H), 7.70 (t, J=8.0 Hz, 2H), 7.22–7.33 (m, 10H), 7.17 (d, J=8.0 Hz, 2H), 4.44–4.49 (m, 2H), 4.12–4.17 (m, 2H), 3.98–4.01 (m, 2H), 3.19 (dd, J=13.6 Hz and 4.0 Hz, 2H), 2.73 (dd, J=13.6 Hz and 8.8 Hz, 2H), 1.69 (d, J=18.0 Hz, 12H). MS (m/z, %): 558 (4, M^+), 467 (100), 399 (22), 333 (20), 306 (12), 264 (10), 237 (26), 91 (54). Anal. calcd for $C_{36}H_{38}N_4O_2$: C, 77.42; H, 6.81; N, 10.04. Found: C, 77.34; H, 6.84; N, 9.85%.

4.5.3. 6,6′-Bis-{1-[(4*S*,4′*S*)-4-isopropyl-4,5-dihydro-oxazol-2-yl]-1-methyl-ethyl}-[2,2′]bipyridinyl 1b. White solid, 79% yield, mp 47–49°C. $[\alpha]_D^{20}$ −62 (c 1.0, $CHCl_3$). IR: 2958s, 1655s, 1572s, 1432s, 1382m, 1366w, 1138m, 1113s, 977s, 809s, 757m. ^{1}H NMR: 8.35 (d, J=7.8 Hz, 2H), 7.72 (t, J=7.8 Hz, 2H), 7.29 (d, J=7.8 Hz, 2H), 4.14–4.19 (m, 2H), 3.93–4.04 (m, 4H), 1.83–1.95 (m, 2H), 1.70 (s, 12H), 0.97 (d, J=6.6 Hz, 6H), 0.89 (d, J=6.6 Hz, 6H). MS (m/z, %): 462 (8, M^+), 419 (100), 351 (68), 334 (25), 264 (19), 237 (31). Anal. calcd for $C_{28}H_{38}N_4O_2$: C, 72.73; H, 8.22; N, 12.12. Found: C, 72.72; H, 8.20; N, 11.96%.

4.5.4. 6,6′-Bis-{1-[(4*S*,4′*S*)-4-phenyl-4,5-dihydro-oxazol-2-yl]-1-methyl-ethyl}-[2,2′]bipyridinyl 1c. White solid, 75% yield, mp 150–152°C. $[\alpha]_D^{20}$ −151 (c 1.0, $CHCl_3$). IR: 2972m, 1662vs, 1563m, 1431s, 1136s, 1121s, 979m, 810m, 759s, 702s. ^{1}H NMR: 8.42 (d, J=7.8 Hz, 2H), 7.77 (t, J=7.8 Hz, 2H), 7.40 (d, J=7.8 Hz, 2H), 7.26–7.30 (m, 10H), 5.23–5.32 (m, 2H), 4.56–4.63 (m, 2H), 4.04–4.11 (m, 2H), 1.80 (d, J=4.8 Hz, 12H). MS (m/z, %): 530 (12, M^+), 385 (100), 264 (34), 237 (38), 103 (28), 91 (25). Anal. calcd for $C_{34}H_{34}N_4O_2$: C, 76.98; H, 6.42; N, 10.57. Found: C, 76.81; H, 6.36; N, 10.34%.

4.5.5. 6,6′-Bis-{1-[(4*R*,4′*R*)-4-phenyl-4,5-dihydro-oxazol-2-yl]-1-methyl-ethyl}-[2,2′]bipyridinyl 1d. White solid, 75% yield, mp 150–152°C. $[\alpha]_D^{20}$ +149 (c 1.0, $CHCl_3$). IR: 2972m, 1662vs, 1563m, 1455m, 1431m, 1383w, 1136s, 1121s, 979m, 810m, 759s, 702s. ^{1}H NMR: 8.38 (d, J=7.8 Hz, 2H), 7.74 (t, J=7.8 Hz, 2H), 7.35 (d, J=7.8 Hz, 2H), 7.23–7.29 (m, 10H), 5.20–5.28 (m, 2H), 4.50–4.60 (m, 2H), 3.98–4.07 (m, 2H), 1.78 (d, J=4.8 Hz, 12H). MS (m/z, %): 530 (12, M^+), 385 (100), 264 (32), 237 (37), 103 (26), 91 (24). Anal. calcd for $C_{34}H_{34}N_4O_2$: C, 76.98; H, 6.42; N, 10.57. Found: C, 76.86; H, 6.38; N, 10.49%.

4.6. Enantioselective cyclopropanation catalyzed by Ru complex of ligand 1a

To a Schlenk flask were added $[Ru(p\text{-cymene})Cl_2]_2$ (3.1 mg, 0.005 mmol), ligand **1a** (5.6 mg, 0.01 mmol) and $CHCl_3$ (2 mL) under nitrogen. The mixture was stirred for 3 h at rt, then filtered to a three-neck flask equipped with a dropping funnel. To the filtrate $AgBF_4$ (8.0 mg, 0.02 mmol) was added, the mixture was stirred for 20 h at rt, then filtered to a three-neck flask equipped with a dropping funnel. After addition of styrene, ethyl diazoacetate (114 mg, 1 mmol) in $CHCl_3$ (10 mL) was added over 3 h. The resulting mixture was stirred for 24 h at rt, and the solvent was evaporated under reduced pressure. The residue was purified by a column chromatography on silica gel to give cyclopropanation products. Diastereoselectivities (*cis*:*trans* ratio) of products were analyzed by GC using a capillary column

(HP-1, 30 m, 0.32 mm ID). The enantiomeric excesses were measured by GC after re-esterification with (−)-menthol.[13]

Acknowledgements

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7. *Crystal data*: Tetragonal, space group $P4(1)2(1)2$; $a=13.053(2)$, $b=13.053(2)$, $c=21.702(5)$ Å; $V=3697.4(13)$ Å^3, $Z=4$, crystal dimensions $=0.30\times0.28\times0.25$ mm, $T=293(2)$ K, radiation $=$ MoKα, $\lambda=0.71073$ Å, unique data $=3272$, $R=0.0535$.
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