ELSEVIER

Journal of Molecular Catalysis A: Chemical 164 (2000) 173–179

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Chiral 8-substituted 2-(2-methoxyphenyl) and 2-(2-hydroxyphenyl)-5,6,7,8-tetrahydro-6,6-dimethyl-5,7-methanoquinolines as ligands for enantioselective catalysis: palladium catalyzed allylic substitution and addition of diethylzinc to benzaldehyde

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Received 10 April 2000; received in revised form 19 July 2000; accepted 19 July 2000

Abstract

Diastereomeric pure 8-substituted 2-(2-methoxyphenyl) and 2-(2-hydroxyphenyl)-5,6,7,8-tetrahydro-6,6-dimethyl-5,7-methanoquinolines were prepared and assessed in the enantioselective palladium catalyzed allylic substitution of 1,3-diphenyl-prop-2-enyl acetate with dimethyl malonate and addition of diethylzinc to benzaldehyde. Enantioselectivity up to 61% was obtained.

Keywords: Chiral tetrahydroquinolines; Palladium complex; Allylic substitution; Addition of diethylzinc; Enantioselectivity

1. Introduction

Though an increasing number of asymmetric reaction which employ electron tuning of the ligands as a control element to optimize a particular catalytic system are appearing in the literature [1,2], at present the major method to achieve this goal is the modulation of the steric requirements of the ligand so to provide optimum steric matching between the catalyst and the substrate(s) [3,4].

A very important class of chiral ligands for which steric factors have been well investigated is represented by the phosphinooxazolines **1** [5–7]. With this kind of ligands the steric control of a particular reaction (for instance palladium catalysed allylic substitutions) has been obtained both by a proper choice of the substituents bonded to the phosphorous atom and by modifying the oxazoline unit (for instance the examples **2**–**4** reported in Scheme 1) [8–12].

Continuing our interest in the synthesis and application of chiral pyridine derivatives as ligands for metal complexes in enantioselective catalysis [13–16], we have been attracted by the possibility to modify the structure of **1** by changing the oxazoline ring with a tetrahydroquinoline framework. This substitution brings to the new class of ligands **5** whose major feature, on the basis of a molecular modelling study of the related metal complexes (for instance a palladium(II) complex), is that the metal is wraped by the substituents bonded to the sterocentres of the tetrahydroquinoline framework on two sides (the upper and right parts in the more stable conformer). From

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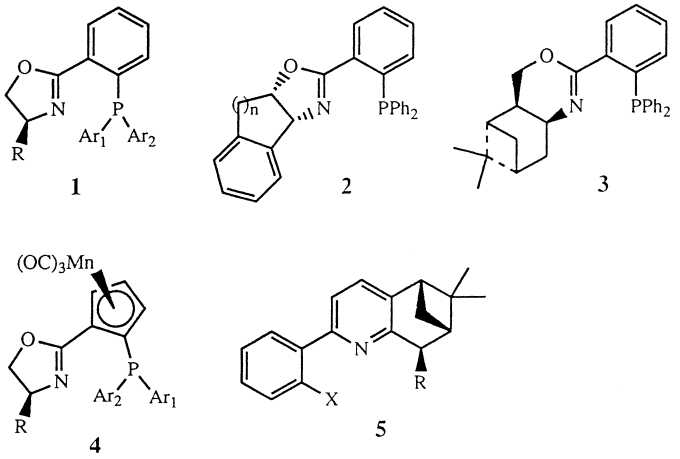
1381-1169/00/$ – see front matter
PII: S1381-1169(00)00373-3



Scheme 1. X = OR, SR, Par_2, etc.

our viewpoint, this characteristic would markedly effect the steric interactions between the ligand and the substrate, both coordinated to the metal, and so the stereoselectivity, which is expected to improve as the chirogenic element of the ligand gets closer to the metal centre.

In this paper, a part of a project for the synthesis of compounds of type 5, we report the synthesis of some diastereomeric pure 8-substituted 2-(2-methoxyphenyl) and 2-(2-hydroxyphenyl)-5,6,7,8-tetrahydro-6,6-dimethyl-5,7-methanoquinolines and the results obtained with these ligands in the enantioselective palladium catalysed allylic substitution of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate and in the addition of diethylzinc to benzaldehyde.

2. Results and discussion

2.1. Synthesis of the ligands

The key intermediate ligand **9** was readily accessible (82% yield) by reaction of (−)-pinocarvone **8**, obtained by oxidation [17] of (+)-α-pinene (90% ee), with 1-phenacylpyridinium iodide **7** which was in turn prepared by reaction of 2-methoxyacetophenone **6** with iodine in pyridine (Scheme 2).

Then, the red solution of lithiated **9**, obtained by treatment with lithium diisopropylamine (LDA) at −78°C for 1 h and then 1 h at 0°C, was quenched with the proper electrophile (*i*-PrI or *n*-BuBr or $PhCH_2Br$) to give the compounds **10a**–**c**. Finally, ligands **9** and **10a**–**c** were demethylated with pyridinium chloride at 200°C to afford the phenol derivatives **12** and **11a**–**c**, respectively.

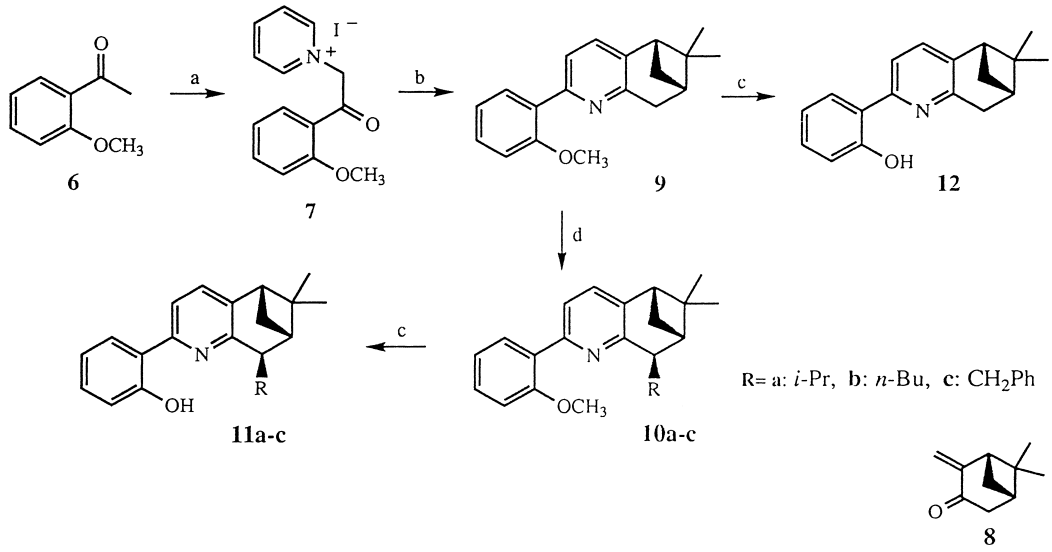
2.2. Palladium catalyzed allylic alkylation

In contrast to the great variety of P–P, P–N and N–N based ligands, with C_1 as well as C_2 symmetry, which have proven to induce impressive levels of enantioselectivity in the catalyzed asymmetric C–C bond forming reactions with allylic compounds [18–24], only a few examples of nitrogen–oxygen ligands have been reported so far [25,26].

Therefore, we decided to examine, in the enantioselective palladium catalysed allylic substitution of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate, these new pyridine–ethers which have two significantly different donor atoms.

Allylic substitutions were carried out employing $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ as procatalyst and a mixture of dimethyl malonate, N,O-bis(trimethylsilyl)acetamide (BSA) and potassium acetate in methylene chloride [27].

All assessed pyridine–ethers provided unreactive palladium catalysts at room temperature and thus no reaction product was detected after 12 days. In an attempt to increase the reaction rate a try was carried out



Scheme 2. (a) I_2, pyridine; (b) AcOH, $AcONH_4$, 120°C, 4 h; (c) pyridine hydrochloride, 200°C, 14 h; (d) LDA, THF, 1 h at −78°C; and 1 h at 0°C; then *i*-PrI or *n*-BuBr or $PhCH_2Br$, THF, −78°C, then slowly r.t.

at reflux temperature (40°C) using ligand **10b**. Under these conditions a complete conversion of the starting material was achieved after 6 days, but the reaction product was obtained in low yield and as a racemic mixture.

2.3. Asymmetric addition of diethylzinc to benzaldehyde

The enantioselective formation of carbon–carbon bonds through the asymmetric addition of dialkylzinc to aldehydes continue to be a very important area in current enantioselective methodology development [28,29]. Since a number of pyridine–carbinol derivatives have proved to be effective chiral catalysts [30–32], following our research in this field [33–36], we have been evaluating the potential utility of new ligands **12** and **11a**–**c** in this catalytic process. The reactions were carried out in hexane–toluene solution in the presence of 5 mol% of ligands at room temperature. All catalysts gave (*S*)-l-phenyl-1-propanol in good yield and in moderate enantioselectivities (Table 1). The stereochemical outcome mainly depends on the stereogenic centres in the 5,7-position of the tetrahydroquinoline ring (ligand **12**). In fact, with the ligands bearing a further substituent on the eighth position only a moderate increasing of the stereoselectivity is obtained. The best enantioselectivity is achieved with the 8-*n*-butyl substituted ligand **11b** (61% ee).

Table 1
Enantioselective addition of diethylzinc to benzaldehyde[a]

C_6H_5-CHO $\xrightarrow{Zn(C_2H_5)_2 / L^*}$ C_6H_5-C*H(OH)-C_2H_5

Ligand	Time (h)	Yield (%)[b]	Ee (%)[c]	Configuration[d]
12	7	95	44	*S*
11a	14	98	49	*S*
11b	19	94	61	*S*
11c	14	95	52	*S*

[a] Reaction carried out at r.t. in hexane/toluene with a molar ratio Et_2Zn/aldehyde/ligand = 2/1/0.05.
[b] Isolated yield.
[c] Determined by chiral GC (30 m Beta Dex-120 column, Supelco).
[d] Determined from the specific rotation of (*S*)-1-phenylpropanol: $[\alpha]_D^{25}$ − 47.6 ($CHCl_3$): [38].

In summary, we have prepared the oxygen derivatives of a new class of chelating ligands of the type **5** and demonstrated their catalytic activity in enantioselective palladium catalysed allylic substitutions and asymmetric addition of diethylzinc to benzalde-

hyde. Further efforts aimed at the preparation and application to catalytic asymmetric reactions of sulphur and phosphorous derivative ligands of type **5** are in progress.

3. Experimental

3.1. General methods

Melting points were determined on a Büchi 510 capillary apparatus and are uncorrected. The ^{1}H NMR (300 MHz) spectra were obtained with a Varian VXR-300 spectrometer. Optical rotations were measured with a Perkin-Elmer 241 polarimeter in a 1 dm tube. Elemental analyses were performed on a Perkin-Elmer 240 B analyser. Gas chromatographic analyses were performed by a Perkin-Elmer 8600 chromatograph using He_2 as a carrier gas. A 30 m Beta Dex-120 column (Supelco) was employed.

(−)-Pinocarvone **8** was obtained by oxydation of (1R)-(+)-α-pinene (90% ee by GLC, Aldrich) [17]. 1-[2-(2-Methoxyphenyl)-2-oxoethyl] pyridinium iodide **7** was prepared according to a reported procedure [37].

3.2. (5S,7S)-(+)-5,6,7,8-T etrahydro-6,6-dimethyl-2-(2-methoxyphenyl)-5,7-methanoquinoline ***9***

A mixture of 1-[2-(2-methoxyphenyl)-2-oxoethyl] pyridinium iodide **7** (12 g, 33.8 mmol), ammonium acetate (20 g) and glacial acetic acid (46 ml) was heated at 100°C for 10 min. Then a solution of (−)-pinocarvone 8 (5.1 g, 33.8 mmol) in glacial acetic acid (5 ml) was added dropwise and the resulting solution was heated at 120°C for 4 h. After cooling the mixture was taken up in H_2O (1 l) and extracted with ethyl ether (3 ml × 200 ml). The combined organic phases were dried over anhydrous Na_2SO_4, the solvent was evaporated and the residue was purified by flash chromatography (petroleum ether:ethyl acetate = 7:3) to give: 4.15 g (44%); mp 103–4°C; $[\alpha]_D^{25}$ + 63.7 (*c* 1.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.77 (dd, ^{1}H, J = 7.8, 1.8 Hz), 7.50 (d, 1H, J = 7.8 Hz), 7.33 (dt, 1H, J = 8.1, 1.8 Hz), 7.22 (d, 1H, J = 8.1 Hz), 7.06 (dt, 1H, J = 7.5, 0.9 Hz), 6.98 (d, 1H, J = 8.1 Hz), 3.85 (s, 3H), 3.18 (d, 2H, J = 3.0 Hz), 2.78 (t, 1H, J = 5.7 Hz), 2.69 (m, 1H), 2.38 (m, 1H), 1.42 (s, 3H), 1.33 (d, 1H, J = 9.6 Hz), 0.7 (s, 3H). Anal. calcd for $C_{19}H_{21}NO$: C, 81.67; H, 7.58; N, 5.02. Found C, 81.76; H, 7.81; N, 5.11.

3.3. General procedure for the preparation of **10*a*–*c***

A solution of the pyridine **9** (2 mmol) in anhydrous THF (2 ml) was added at −78°C to a solution of lithium diisopropylamine (2 mmol) in anhydrous THF (10 ml). The resulting solution was stirred at −78°C for 1 and 3 h at 0°C. Then a solution of the proper electrophile (*i*-PrI or *n*-BuBr or $PhCH_2Br$) (2 mmol) in THF (2 ml) was added dropwise at −78°C. After 0.5 h at −78°C, the solution was allowed to reach slowly room temperature and then treated with H_2O. The organic phase was separated and the aqueous phase extracted twice with CH_2Cl_2. The combined organic phases were dried over anhydrous Na_2SO_4, the solvent was evaporated and the residue was purified by flash chromatography.

3.4. (5S,7S,8R)-(+)-5,6,7,8-Tetrahydro-6,6-dimethyl-8-(1-methylethyl)-2-(2-methoxyphenyl)-5,7-methanoquinoline ***10a***

Chromatografic eleuent: petroleum ether:ethyl acetate = 95:5; 0.290 g (45%); mp 75–6°C; $[\alpha]_D^{25}$ +15.2 (*c* 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.90 (dd, 1H, J = 7.5, 1.5 Hz), 7.59 (d, 1H, J = 7.8), 7.30 (dt, 1H, J = 7.5, 1.2 Hz), 7.19 (d, 1H, J = 7.5 Hz), 7.06 (t, 1H, J = 7.5 Hz), 6.97 (d, 1H, J = 8.1), 3.80 (s, 3H), 2.90 (m, 2H), 2.70 (t, 1H, J = 5.3 Hz), 2.60 (m, 1H), 2.52 (dt, 1H, J = 6.0, 1.8 Hz), 1.42 (s, 3H), 1.41 (d, 1H, J = 9.6 Hz), 1.2 (d, 3H, J = 6.6 Hz), 0.86 (d, 3H, J = 6.6 Hz), 0.65 (s, 3H). Anal. calcd for $C_{22}H_{27}NO$: C, 82.20; H, 8.47; N, 4.36. Found C, 82.15; H, 7.59; N, 4.21.

3.5. (5S,7S,8R)-(+)-5,6,7,8-Tetrahydro-6,6-dimethyl-8-butyl-2-(2-methoxy phenyl)-5,7-methanoquinoline ***10b***

Chromatografic eleuent: petroleum ether:ethyl acetate = 95:5; 0.396 g (59%); oil; $[\alpha]_D^{25}$ + 15.7 (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.89 (dd, 1H, J = 7.8, 2.1 Hz), 7.55 (d, 1H, J = 7.8 Hz), 7.32 (dt, 1H, J =

8.4, 1.8 Hz), 7.18 (d, 1H, $J = 7.8$ Hz), 7.08 (t, 1H, $J = 7.5$, 0.9 Hz), 6.98 (d, 1H, $J = 8.1$ Hz), 3.85 (s, 3H), 3.04 (m, 1H), 2.76 (t, 1H, $J = 5.7$ Hz), 2.53 (m, 1H), 2.34 (m, 2H), 1.60–1.24 (m, 5H), 1.42 (s, 3H), 1.34 (d, 1H, $J = 9.9$ Hz), 0.94 (t, 3H, $J = 7.2$ Hz), 0.70 (s, 3H). Anal. calcd for $C_{23}H_{29}NO$: C, 82.34; H, 8.71; N, 4.17. Found C, 82.55; H, 7.89, N, 4.11.

3.6. (5S,7S,8R)-(+)-5,6,7,8-Tetrahydro-6,6-dimethyl-8-phenylmethyl-2-(2-methoxyphenyl)-5,7-methanoquinoline ***10c***

Chromatografic eleuent: petroleum ether:ethyl acetate = 95:5; 0.340 g (46%); oil; $[\alpha]_D^{25} + 73.8$ (*c* 2.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.98 (dd, 1H, $J = 7.5$, 1.5 Hz), 7.63 (d, 1H, $J = 7.8$ Hz), 7.33–7.22 (M, 6H), 7.18 (d, 1H, $J = 7.8$ Hz), 7.07 (t, 1H, $J = 7.35$ Hz), 6.95 (d, 1H, $J = 8.1$ Hz), 3.88 (dd, 1H, $J = 13.5$, 3.6 Hz), 3.8 (s, 3H), 3.4 (d, 1H, $J = 11.1$ Hz), 2.73 (m, 2H), 2.52 (m, 1H), 2.09 (m, 1H), 1.44 (d, 1H, $J = 9.6$ Hz), 1.33 (s, 3H), 0.62 (s, 3H). Anal. calcd for $C_{26}H_{27}NO$: C, 84.51; H, 7.37; N, 3.79. Found C, 84.55; H, 7.49; N, 3.65.

3.7. General procedure for the demethylalation of **9***and* ***10a–c***

A mixture of the methoxy derivatives **9** or **10a–c** (0.85 mmol) and pyridine hydrochloride (0.13 g, 1.1 mmol) was heated at 200°C for 14 h under a nitrogen atmosphere. After cooling the mixture was treated with 5% sodium hydroxyde and then neutralized with glacial acetic acid and finally extracted with chloroform. The organic phase was dried on anhydrous Na_2SO_4, the solvent was evaporated and the residue was purified by flash chromatography to give pure phenol derivatives.

3.8. (5S,7S)-(+)-5,6,7,8-Tetrahydro-6,6-dimethyl-2-(2-hydroxyphenyl)-5,7-methanoquinoline ***12***

Chromatografic eleuent: petroleum ether:ethyl acetate = 40:1; 1.62 g (72%); mp 122–4°C; $[\alpha]_D^{25} + 98.5$ (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.77 (d, 1H, $J = 6.9$ Hz), 7.62 (d, 1H, $J = 8.1$ Hz), 7.37 (d, 1H, $J = 8.1$ Hz), 7.26 (m, 1H), 7.00 (d, 1H, $J = 7.8$ Hz), 6.89 (t, 1H, $J = 7.8$ Hz), 3.14 (d, 2H, $J = 2.7$ Hz), 2.84–2.68 (m, 2H), 2.40 (m, 1H), 1.43 (s, 3H), 1.31 (d, 1H, $J = 9.6$ Hz), 0.68 (s, 3H). Anal. calcd for $C_{18}H_{19}NO$: C, 81.48; H, 7.22; N, 5.28. Found C, 81.65; H, 7.39; N, 5.15.

3.9. (5S,7S,8R)-(−)-5,6,7,8-Tetrahydro-6,6-dimethyl-8-(1-methylethyl)-2-(2-hydroxyphenyl)-5,7-methanoquinoline ***11a***

Chromatografic eleuent: petroleum ether:ethyl acetate = 20:1; 1.96 g (75%); oil; $[\alpha]_D^{25} - 9.7$ (*c* 0.4, $CHCl_3$); ^{1}H NMR (CDCl3) δ: 7.76 (dd, 1H, $J = 8.1$, 1.5 Hz), 7.60 (d, 1H, $J = 8.1$ Hz), 7.34 (d, 1H, $J = 8.1$ Hz), 7.26 (m, 1H), 7.01 (dd, 1H, $J = 6.9$, 1.2 Hz), 6.88 (dt, 1H, $J = 7.8$, 1.2 Hz), 2.98 (m, 1H), 2.84–2.70 (m, 2H), 2.60 (m, 1H), 2.37 (dt, 1H, $J = 5.7$, 1.8 Hz), 1.42 (s, 3H), 1.40 (d, 1H, overlapping), 1.14 (d, 3H, $J = 7.2$ Hz), 0.82 (d, 3H, $J = 7.2$ Hz), 0.62 (s, 3H). Anal. calcd for $C_{21}H_{25}NO$: C, 82.04; H, 8.20; N, 4.56. Found C, 82.15; H, 8.39; N, 4.45.

3.10. (5S,7S,8R)-(−)-5,6,7,8-Tetrahydro-6,6-dimethyl-8-butyl-2-(2-hydroxy phenyl)-5,7-methanoquinoline ***11b***

Chromatografic eleuent: petroleum ether:ethyl acetate = 7:3; 1.67 g (61%); oil; $[\alpha]_D^{25} - 9.6$ (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.76 (dd, 1H, $J = 8.1$, 1.5 Hz), 7.60 (d, 1H, $J = 8.1$ Hz), 7.34 (d, 1H, $J = 7.8$ Hz), 7.30 (dt, 1H, $J = 6.6$, 1.5 Hz), 7.00 (d, 1H, $J = 8.1$ Hz), 6.88 (dt, 1H, $J = 8.1$, 1.2 Hz), 3.03 (m, 1H), 2.79 (m, 1H), 2.57 (m, 1H), 2.34 (m, 1H), 1.60–1.20 (m, 6H), 1.44 (s, 3H), 1.33 (d, 1H, $J = 9.9$ Hz), 0.95 (t, 3H, $J = 7.3$ Hz), 0.64 (s, 3H). Anal. calcd for $C_{22}H_{27}NO$: C, 82.20; H, 8.47; N, 4.36. Found C, 82.35; H, 8.39; N, 4.47.

3.11. (5S,7S,8R)-(+)-5,6,7,8-Tetrahydro-6,6-dimethyl-8-(1-methylphenyl)-2-(2-hydroxyphenyl)-5,7-methanoquinoline ***11c***

Chromatografic eleuent: petroleum ether:ethyl acetate = 20:1; 1.60 g (53%); oil; $[\alpha]_D^{25} + 82.1$ (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.76 (dd, 1H, $J = 8.1$, 1.5 Hz), 7.60 (d, 1H, $J = 8.1$ Hz), 7.36–7.16 (m, 7H); 7.04 (d, 1H, $J = 8.1$ Hz), 6.88 (t, 1H, $J = 7.2$ Hz), 3.62 (dd, 1H, $J = 13.2$, 2.7 Hz), 3.30 (d, 1H, $J =$

11.1 Hz), 2.80–2.62 (m, 2H), 2.56 (m, 1H), 2.10 (dt, 1H, $J = 6.0, 2.1$ Hz), 1.40 (d, 2H, $J = 10.8$ Hz), 1.31 (s, 1H), 0.56 (s, 3H). Anal. calcd for $C_{25}H_{25}NO$: C, 84.47; H, 7.09; N, 3.94. Found C, 84.35; H, 7.29; N, 3.78.

3.12. Allylic alkylation of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate: general procedure

A solution of ligand (0.04 mmol, 10 mol%) and $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ (4 mg, 2.5 mol%) in dry CH_2Cl_2 (2 ml) was stirred at room temperature for 1 h. This solution was treated successively with a solution of *rac*-(E)-1,3-diphenyl-2-propenyl acetate (0.4 mmol) in CH_2Cl_2 (1 ml), dimethyl malonate (1.2 mmol), N,O-bis(trimethylsilyl)acetamide (1.2 mmol) and anhydrous potassium acetate (3.5 mol%). The reaction mixture was stirred until conversion was complete as shown by TLC analysis (light petroleum:ether = 3:1). The reaction mixture was diluted with ether (25 ml) and washed with ice-cold saturated aqueous ammonium chloride. The organic phase was dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash chromatography (light petroleum:ether/3:1) to afford dimethyl 1,3-diphenylprop-2-enylmalonate. The enantiomeric excess was determined from the ^{1}H-NMR spectrum in the presence of enantiomerically pure shift reagent Eu(hfc)$_3$; splitting of the signals for one of the two methoxy groups was observed.

3.13. Addition of diethylzinc to benzaldehyde: typical procedure

A solution of ligand (0.15 mmol) in toluene (3 ml) was cooled at 0°C. A 1M solution of diethylzinc in hexane (6 ml, 6 mmol) was added over a period of 5 min. The mixture was stirred at room temperature for 20 min, cooled at 0°C, added with benzaldehyde (0.3 ml, 0.323 g, 3 mmol) and then stirred at room temperature for the appropriate time. The reaction mixture was quenched with 5% H_2SO_4 (5 ml) and extracted with ether. The organic layer was washed with 5% H_2SO_4, saturated $NaHCO_3$, and dried over Na_2SO_4. The solvent was evaporated and the residue purified by flash chromatography (petroleum ether:ethyl acetate = 4:1) to afford pure 1-phenylpropanol. The enantiomeric excess was determined by chiral GC.

Acknowledgements

Financial support by M.U.R.S.T. and by Regione Autonoma Sardegna is gratefully acknowledged.

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