http://dx.doi.org/10.5935/0103-5053.20140233

*J. Braz. Chem. Soc.*, Vol. 26, No. 1, 165-170, 2015.
Printed in Brazil - ©2015 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

# Stereoselective Addition of Diethylzinc to Aldehydes Using Chiral β-Hydroxy-2-oxazolines as Catalysts

*Francisco A. Marques,*,[a] Celso L. Wosch,[a] Gustavo Frensch,[a] Ricardo Labes,[a] Beatriz H. L. N. S. Maia,[a] Kahlil S. Salomé,[a] Andersson Barison[a] and Palimécio G. Guerrero Jr.[b]*

[a]*Departamento de Química, Universidade Federal do Paraná, P.O. Box 19081, 81531-990 Curitiba-PR, Brazil*

[b]*Departamento de Química e Biologia, Universidade Tecnológica Federal do Paraná, P.O. Box 81280-340 Curitiba-PR, Brazil*

β-Hidroxi-2-oxazolinas quirais foram sintetizadas e avaliadas como catalisadores na adição de dietilzinco a aldeídos. Todas as oxazolinas se mostraram eficientes na obtenção dos produtos de adição. Os melhores excessos enantioméricos (69 a 78%) foram obtidos quando se empregou a β-hidroxi oxazolina quiral derivada da (−)-mentona e do amino álcool 2-amino-2-metilpropan-1-ol.

Chiral β-hydroxy-2-oxazolines were synthesized and evaluated as catalysts for the addition of diethylzinc to aldehydes. All oxazolines proved effective in obtaining the addition products. The best enantiomeric excesses (69-78%) were obtained using the chiral β-hydroxy oxazoline derived from (−)-menthone and the amino alcohol 2-amino-2-methylpropan-1-ol.

**Keywords:** (−)-menthone, chiral β-hydroxy-2-oxazolines, catalysts, diethylzinc, aldehydes

## Introduction

The enantioselective addition of organometallic reagents to carbonyl compounds is one of the fundamental reactions to form a new carbon-carbon bond in asymmetric synthesis.[1] The asymmetric addition of organolithium and Grignard reagents to carbonyl substrates usually occurs with low stereoselectivity, due to their high reactivities.[2] On the other hand, the catalytic asymmetric addition of diorganozinc compounds to aldehydes is by far one of the most studied asymmetric transformations, and consists of a very useful method for the enantioselective preparation of secondary alcohols.[1,3-6] Chiral alcohols are widely found in nature and are also important building blocks in organic synthesis.[6]

Recently, the catalytic asymmetric addition of diethylzinc to aldehydes was applied to obtain optically active lactones,[7] cyclopropyl alcohols,[8] and also in the synthesis of the natural product (+)-(*R*)-gossonorol, which shows antifungal, anticancer and antioxidant activities.[9]

The chiral catalysts developed so far can induce good to excellent selectivities; they include primary amino alcohols,[10-17] diamines,[18,19] disulfonamides,[20,21] diols[22-24] and others.[25-36] The synthesis of these catalysts usually involves more than one step, so the development of new catalysts, readily available and versatile, remains an important challenge in this field.

Natural ketones such as camphor, fenchone and menthone have been widely used in the synthesis of chiral ligands employed in the asymmetric addition of organozinc reagents to carbonyl compounds, furnishing good to excellent results.[35,37-54] They represent an inexpensive and readily available source of chirality, which makes their use in the synthesis of the catalysts very advantageous.

Oxazolines have been extensively used in asymmetric catalysis, especially 2-oxazolines.[55-58] There are a few examples of oxazoline-based catalysts used in the addition of organozinc reagents to carbonyl compounds, most of them employing α-hydroxy-2-oxazolines.[28,59-62]

Herein we describe the synthesis of some β-hydroxy-2-oxazolines derived from (−)-menthone, and their application as chiral ligands in the enantioselective addition of diethylzinc to aldehydes.

## Results and Discussion

To obtain the oxazolines derived from 2-amino-2-methylpropan-1-ol we used the method proposed by

*e-mail: tic@ufpr.br

Meyers, in which a carboxylic acid, in this case acetic acid, is reacted with an amino alcohol under heating.[63] The 2-oxazoline derivatives from (+) or (–)-valinol were obtained by another method, also developed by Meyers, in which an amino alcohol reacts with an orthoester, in this case triethyl orthoacetate, under reflux.[64]

With the 2-oxazolines in hand, we performed the addition of their anions, generated by reaction with *n*-butyllithium,[65] to (–)-menthone, affording the chiral β-hydroxy-2-oxazolines outlined below (Figure 1).

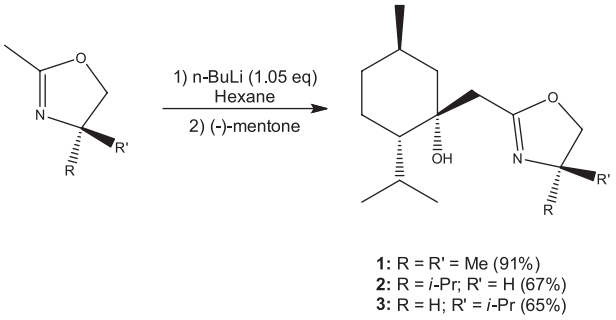



**Figure 1.** Preparation of the chiral β-hydroxy-2-oxazolines.

Ligand **1** was obtained as a mixture of diastereomers in a 75:25 ratio (Figure 2a), the same stereoselectivity observed in the synthesis of the other two ligands.

Using ligand **1** as a model, we determined the stereoselectivity of the major addition product obtained by nuclear Overhauser effect (NOE) experiment. The $CH_2$ (2.74 ppm) alpha to the hydroxyl group was strongly correlated with Ha and Hb (2.09 and 2.19 ppm), as shown in Figure 3. This confirmed that the oxazoline anion attacked the carbonyl moiety mainly via an equatorial approach, in accordance with previous reports.[38,44]

In order to evaluate the effect of the stereochemistry of the generated stereocenters of the new ligands on the stereoselective course of the addition of diethylzinc to aldehydes, the diastereomeric mixture was enriched in the

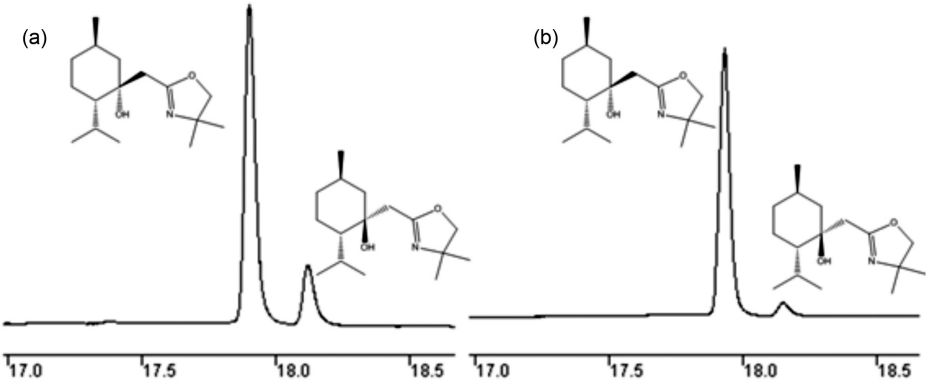



**Figure 2.** Chromatogram obtained with a fused silica column coated with Chirasil-Dex CB-β-cyclodextrin (30 m × 0.25 mm × 0.25 μm) showing the area of elution of ligand **1** in (a) 75:25 diastereomeric ratio and (b) after diastereomeric purification, at 95:5 diastereomeric ratio.

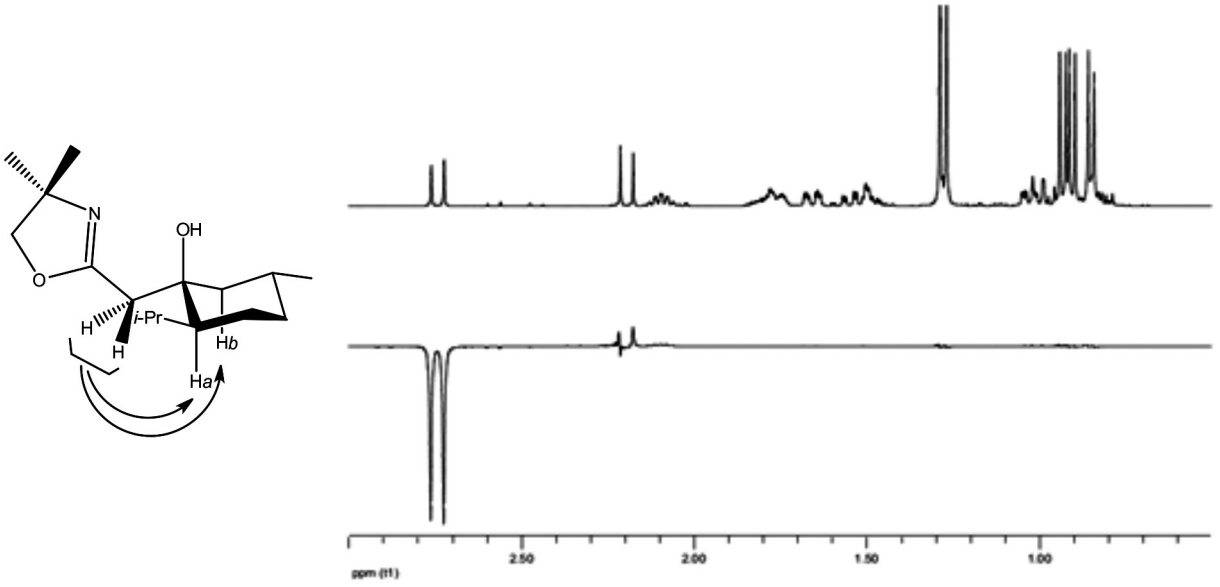
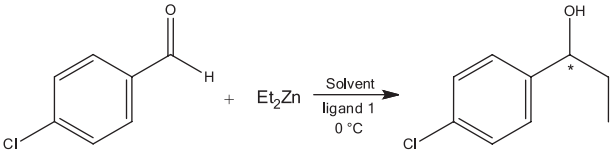



**Figure 3.** Determination of the stereochemistry of the major diastereomer of ligand **1** by NOE.

major diastereomer by column chromatography, reaching a 95:5 diastereomeric ratio (Figure 2b). The addition of diethylzinc to *p*-chlorobenzaldehyde was performed with both diastereomeric mixtures in the same conditions (entry 1a, using the 75:25 and entry 1b, using the 95:5 diastereomeric ratio, Table 1). The results showed that the products were obtained with the same enantiomeric excess. This is probably a consequence of a non-linear effect between the diastereomeric ratio of the chiral ligand and the enantioselectivity obtained in the addition process catalyzed by the ligand, as has been described elsewhere.[66-69]

Ligand **1**, in a 75:25 diastereomeric ratio, was chosen in order to evaluate the influence of the solvent, temperature and amount of the catalyst in the stereoselective addition of diethylzinc to aromatic aldehydes, using *p*-chlorobenzaldehyde as a model (Table 1).

**Table 1.** Screening of the conditions to perform the addition of diethylzinc to *p*-chlorobenzaldehyde using **1** as catalyst




| entry | Solvent | Amount of **1** / % | time / h | Yield / %[a] | e.e. / %[b] |
|---|---|---|---|---|---|
| 1a | hexane | 5 | 2 | 93 | 69 (*R*)[c] |
| 1b[d] | hexane | 5 | 2 | 93 | 69 (*R*) |
| 2 | hexane:toluene (1:1) | 5 | 2 | 85 | 66 (*R*) |
| 3 | hexane:diethyl ether (1:1) | 5 | 2 | 80 | 68 (*R*) |
| 4 | hexane | 8 | 2 | 93 | 69 (*R*) |
| 5 | hexane | 2 | 2 | 85 | 69 (*R*) |
| 6 | hexane | 5 | 4 | 93 | 69 (*R*) |
| 7 | hexane | 5 | 6 | 93 | 69 (*R*) |
| 8 | hexane | 5 | 8 | 93 | 69 (*R*) |

[a]Yield of isolated product; [b]determined by chiral GC (column: β-cyclodextrin-CB); [c]absolute configuration determined by comparison of the optical rotation with published data;[70] [d]ligand used in a 95:5 diastereomeric mixture.

After the reaction conditions were optimized, all β-hydroxy-2-oxazolines prepared were tested, without diastereomeric purification, as chiral ligands to perform the stereoselective addition of diethylzinc to *p*-chlorobenzaldehyde (Table 2).

Interestingly, the ligand with the fewest stereogenic centers showed the best result. We assumed that the stereogenic center present in the oxazoline portion could improve the stereoselectivity, if acting in synergism with the steric hindrance provided by the menthane portion; however, both ligands **2** and **3** led to lower stereoselectivities.

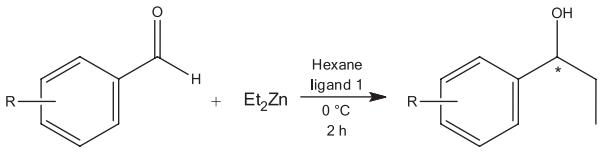
**Table 2.** Addition of diethylzinc to *p*-chlorobenzaldehyde using chiral β-hydroxy-2-oxazolines as catalysts[a]

| entry | Ligand | Yield / %[b] | e.e. / %[c] |
|---|---|---|---|
| 1 | 1 | 93 | 69 (*R*)[d] |
| 2 | 2 | 67 | 50 (*R*) |
| 3 | 3 | 62 | 25 (*R*) |

[a]The reaction was carried out using hexane as solvent, 5% molar ratio of ligand, 0 °C, for 2 h; [b]yield of isolated product; [c]determined by chiral GC (column: CB-cyclodextrin-β); [d]absolute configuration determined by comparison of the optical rotation with published data.[70]

Since ligand **1** showed the best results, it was used in the addition to other aromatic aldehydes (Table 3).

**Table 3.** Addition of diethylzinc to benzaldehydes using ligand **1** as catalyst




| entry | R | Yield / %[a] | e.e. / %[b] |
|---|---|---|---|
| 1 | H | 94 | 71 (*R*)[c] |
| 2 | *o*-$CH_3O$ | 90 | 69 (*R*)[c] |
| 3 | *m*-$CH_3O$ | 92 | 78 (*R*)[c] |
| 4 | *p*-$CH_3O$ | 93 | 71 (*R*)[c] |
| 5 | *p*-Cl | 93 | 69 (*R*)[c] |

[a]Yield of isolated product; [b]determined by chiral GC (column: CB-cyclodextrin-β); [c]absolute configuration determined by comparison of the optical rotation with published data.[70]

The best enantiomeric excess (e.e.) (78%) was achieved using 3-methoxybenzaldehyde. This result is probably related to the lower steric hindrance caused by the methoxy group when located at the 3-position, compared to the starting material with the methoxy group at the 2-position.

The e.e. achieved employing the other aldehydes were compared to those obtained using benzaldehyde.

This is the first report dealing with the use of chiral β-hydroxy-2-oxazolines as catalysts in the addition of diethylzinc to aldehydes; in the literature there are a few reports of the use of chiral α-hydroxy-2-oxazolines as catalysts in this reaction.[28,59-62] Although some e.e. obtained when using α-hydroxy-2-oxazolines are better than those reported herein, β-hydroxy-2-oxazolines are much easier to prepare, using less-expensive, commercially available materials. The results obtained in this study are being used by our group in order to synthesize other chiral β-hydroxy-2-oxazolines, aiming to improve the stereoselectivity of this process.

## Conclusions

We describe herein the synthesis of new chiral β-hydroxy-2-oxazolines, and their application in the asymmetric addition of diethylzinc to aromatic aldehydes. The best ligand **1**, which was readily synthesized from inexpensive and commercially available materials, showed good catalytic activity (up to 93% yield and 78% e.e.). Other chiral β-hydroxy-2-oxazolines are being synthesized in our laboratory, aiming at applications beyond the organozinc additions to aldehydes, such as in the asymmetric addition of alkynes to carbonyl compounds,[71] and in the asymmetric addition of boronic acids to carbonyl compounds.[72]

## Experimental

### Oxazolines

All three oxazolines (2,4,4-trimethyl-2-oxazoline and (*S*) and (*R*)-4-isopropyl-2-methyl-2-oxazoline) were synthesized, and afforded spectral data according with the literature.[63,64]

### General procedure for the preparation of β-hydroxy-2-oxazolines **1-3**

In a 25 mL flask equipped with magnetic stirring, a solution of *n*-butyllithium (1.31 mL, 2.1 mmol) in hexane was added at −78 °C to a solution of the corresponding 2-oxazoline (2 mmol) in tetrahydrofuran (THF) (4 mL). The reaction mixture was stirred for 30 min and then a solution of menthone (308 mg, 2 mmol) in THF (4 mL) was added dropwise. After the addition, the cooling bath was removed and the mixture was stirred for 2 h at 25 °C. The reaction mixture was quenched with aqueous saturated $NH_4Cl$ solution (10 mL), and extracted with diethyl ether (3 × 30 mL). The combined organic layer was dried over anhydrous $Na_2SO_4$. After filtration and evaporation of the solvent under reduced pressure, the crude product was purified by flash chromatography using a mixture of hexane/ethyl acetate (9:0.5) as eluent to give the corresponding chiral β-hydroxy-2-oxazolines.

(1*R*,2*S*,5*R*)-1-((4,4-dimethyl-4,5-dihydrooxazol-2-yl) methyl)-2-isopropyl-5-methylcyclohexanol (**1**): Yield 91% (486 mg); $[\alpha]_D^{25}$ –34.97 (c 1.25, $CHCl_3$, 90% e.e.); IR (KBr) ν/cm$^{-1}$ 3046, 2957, 1742, 1653, 1558, 1457, 1406, 1242, 1191, 982; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 0.85 (d, 3H, *J* 6.5 Hz, $CH_3$), 0.90 (d, 3H, *J* 6.9 Hz, $CH_3$), 0.93 (d, 3H, *J* 6.8 Hz $CH_3$), 0.96 (m, 1H, CH), 1.00 (dd, 1H, *J* 13.4 Hz, 1.1, CH), 1.02 (ddd, 1H, *J* 12.1 Hz, 3.9, 1.8, CH), 1.27 (s, 3H, $CH_3$), 1.29 (s, 3H, $CH_3$), 1.52 (m, 2H, $CH_2$), 1.66 (ddd, 1H, *J* 13.4 Hz, 3.3, 2.5, $CH_2$), 1.77 (m, 1H, $CH_2$), 1.79 (m, 1H, $CH_2$), 2.09 (qqd, 1H, *J* 6.9 Hz, 6.8, 1.4, CH), 2.19 (d, 1H, *J* 14.9 Hz, $CH_2$), 2.74 (d, 1H, *J* 14.9 Hz, $CH_2$), 3.89 (d, 1H, *J* 8.1 Hz, $CH_2$), 3.93 (d, 1H, *J* 8.1 Hz, $CH_2$); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 18.2, 20.9, 22.4, 23.8, 26.3, 27.8, 28.3, 28.5, 35.3, 38.5, 47.7, 50.4, 67.1, 73.4, 78.6, 164.7; HRMS (ESI-TOF) *m/z*, calcd. for $C_{16}H_{29}NO_2$ $[M + H]^+$: 268.2271, found 268.2266.

(1*R*,2*S*,5*R*)-2-isopropyl-1-(((S)-4-isopropyl-4,5-dihydrooxazol-2-yl)methyl)-5-methylcyclohexanol (**2**): Yield 67% (342 mg); $[\alpha]_D^{25}$ –34.34 (c 1.15, $CHCl_3$, 98% e.e.); IR (KBr) ν/cm$^{-1}$ 3413, 2957, 2925, 1742, 1660, 1603, 1451, 1362, 1261, 1160, 1046, 982, 881, 780, 698; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 0.80 (d, 3H, *J* 6.9 Hz, $CH_3$), 0.85 (d, 3H, *J* 6.4 Hz, $CH_3$), 0.90 (d, 3H, *J* 6.8 Hz, $CH_3$), 0.97 (d, 3H, *J* 6.7 Hz, $CH_3$), 0.98 (d, 3H, *J* 7.0 Hz, $CH_3$), 1.08 (m, 2H, $CH_2$), 1.29 (m, 2H, $CH_2$), 1.45 (m, 1H, $CH_2$), 1.65 (m, 1H, $CH_2$), 1,78 (m, 1H, CH), 1.80 (m, 1H, CH), 1,82 (m,1H, CH), 2.23 (qqd, 1H, *J* 6.9 Hz, 6.8, 1.9, CH), 2.47 (dt, 1H, *J* 15.3 Hz, 1.6, $CH_2$), 2.62 (d, 1H, *J* 15.3 Hz, $CH_2$), 3.90 (m, 2H, $CH_2$), 4.26 (m, 1H, CH); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 18.5, 18.9, 19.2, 22.4, 23.5, 24.8, 24.9, 30.3, 31.5, 32.8, 35.0, 48.4, 51.7, 69.8, 72.0, 73.8, 166.2; HRMS (ESI-TOF) *m/z*, calcd. for $C_{17}H_{32}NO_2$ $[M + H]^+$ 282.2428, found 282.2437.

(1*R*,2*S*,5*R*)-2-isopropyl-1-(((R)-4-isopropyl-4,5-dihydrooxazol-2-yl)methyl)-5-methylcyclohexanol (**3**): Yield 65% (365 mg); $[\alpha]_D^{25}$ 6.73 (c 1.22, $CHCl_3$, 97% e.e.); IR (KBr) ν/cm$^{-1}$ 3447, 2935, 2901, 1842, 1650, 1633, 1479, 1352, 1252, 1147, 1081, 978, 869, 802, 678; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.84 (d, 3H, *J* 6.5 Hz, $CH_3$), 0.89 (d, 3H, *J* 7.1 Hz, $CH_3$), 0.90 (d, 3H, *J* 7.2 Hz, $CH_3$), 0.93 (d, 3H, *J* 6.9 Hz, $CH_3$), 0.98 (d, 3H, *J* 6.7 Hz, $CH_3$), 1.03 (ddd, 1H, *J* 12.1 Hz, 4.2, 1.9, CH), 1.48 (m, 1H, $CH_2$), 1.55 (m, 2H, $CH_2$), 1.70 (m, 2H, $CH_2$), 1.75 (m, 1H, CH), 1,77 (m, 1H, CH) 1.83 (m, 1H, CH), 2.10 (qqd, 1H, *J* 7.2 Hz, 6.9, 1.9, CH), 2.20 (d, 1H, *J* 15.1 Hz, $CH_2$), 2.79 (dd, 1H, *J* 15.1 Hz, 1.2, $CH_2$), 3.90 (m, 2H, $CH_2$), 4.24 (m, 1H, CH); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 18.41, 18.44, 19.0, 20.9, 22.4, 23.8, 26.4, 27.8, 32.8, 35.3, 38.3, 47.6, 50.4, 69.7, 72.1, 166.2; HRMS (ESI-TOF) *m/z*, calcd. for $C_{17}H_{32}NO$ $[M + H]^+$ 282.2428, found 282.2437.

### General procedure for the addition of diethylzinc to aldehydes

The chiral β-hydroxy-2-oxazoline (0.05 mmol) was dissolved in the desired solvent (1 mL) then a solution of diethylzinc was added (2.5 mL, 2.5 mmol, 1 mol L$^{-1}$ in hexane) at 25 °C. The mixture was stirred for 20 min and then cooled to 0 °C. A solution of the aldehyde (2 mmol

in 3 mL of solvent) was added dropwise. After 2 h, the cooling bath was removed and the reaction was quenched with an aqueous saturated solution of $NH_4Cl$ (5 mL), extracted with a mixture of hexane (2 mL) and diethyl ether (2 mL).The organic layer was dried over anhydrous $Na_2SO_4$, and after filtration, the solvent was eliminated under reduced pressure. The product was purified by flash chromatography using hexane/ethyl acetate 9:1 as eluent leading to the corresponding secondary alcohol. The enantiomeric excess was determined by chiral gas chromatography.

1-phenylpropan-1-ol: The reaction was performed as described above to give the product as a colorless oil (255 mg, 94% yield); $[\alpha]_D^{25}$ +32.6 (c 1.00, $CHCl_3$). The NMR data match those previously reported.[73]

1-(2-methoxyphenyl)propan-1-ol: The reaction was performed as described above to give the product as a colorless oil (298 mg, 90% yield); $[\alpha]_D^{25}$ +21.2 (c 1.00, $CHCl_3$). The NMR data match those previously reported.[73]

1-(3-methoxyphenyl)propan-1-ol: The reaction was performed as described above to give the product as a colorless oil (305 mg, 92% yield); $[\alpha]_D^{25}$ +39.1 (c 1.00, toluene). The NMR data match those previously reported.[74]

1-(4-methoxyphenyl)propan-1-ol: The reaction was performed as described above to give the product as a colorless oil (309 mg, 93% yield); $[\alpha]_D^{25}$ +21.9 (c 1.00, toluene). The NMR data match those previously reported.[73]

1-(4-chlorophenyl)propan-1-ol: The reaction was performed as described above to give the product as a colorless oil (316 mg, 93% yield); $[\alpha]_D^{25}$ +27.0 (c 1.00, toluene). The NMR data match those previously reported.[73]

## Supplementary Information

Experimental detail and supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

## Acknowledgments

The authors thank CNPq-INCT "Controle Biorracional de Insetos Pragas", CAPES and Fundação Araucária for financial support.

## References

1. Pu, L.; Yu, H. B.; *Chem. Rev.* **2001**, *101*, 757.
2. Luderer, M. R.; Bailey, W. F.; Luderer, M. R.; Fair, J. D.; Dancer, R. J.; Sommer, M. B.; *Tetrahedron: Asymmetry* **2009**, *20*, 981.
3. Hatano, M.; Miyamoto, T.; Ishihara, K.; *Curr. Org. Chem.* **2007**, *11*, 127.
4. Knochel, P.; Singer, R. D.; *Chem. Rev.* **1993**, *93*, 2117.
5. Noyori, R.; *Asymmetric Catalysis in Organic Synthesis*, 1st ed.; John Wiley & Sons: New York, 1994.
6. Soai, K.; Niwa, S.; *Chem. Rev.* **1992**, *92*, 833.
7. Pisani, L.; Superchi, S.; D'Elia, A.; Scafato, P.; Rosini, C.; *Tetrahedron* **2012**, *68*, 5779.
8. Kim, H. Y.; Walsh, P. J.; *J. Phys. Org. Chem.* **2012**, *25*, 933.
9. González-López, S.; Yus, M.; Ramón, D. J.; *Tetrahedron: Asymmetry* **2012**, *23*, 611.
10. Liu, C. L.; Wei, C. Y.; Wang, S. W.; Peng, Y. G.; *Chirality* **2011**, *23*, 921.
11. Bian, G.; Huang, H.; Zong, H.; Song, L.; *Chirality* **2012**, *24*, 825.
12. Cicchi, S.; Crea, S.; Goti, A.; Brandi, A.; *Tetrahedron: Asymmetry* **1997**, *8*, 293.
13. Martinez, A. G.; Vilar, E. T.; Fraile, A. G.; Cerero, S. D.; Maroto, B. L.; *Tetrahedron* **2005**, *61*, 3055.
14. Olsson, C.; Helgesson, S.; Frejd, T.; *Tetrahedron: Asymmetry* **2008**, *19*, 1484.
15. Panda, M.; Phuan, P. W.; Kozlowski, M. C.; *J. Org. Chem.* **2003**, *68*, 564.
16. Szakonyi, Z.; Balazs, A.; Martinek, T. A.; Fulop, F.; *Tetrahedron: Asymmetry* **2006**, *17*, 199.
17. You, J. S.; Shao, M. Y.; Gau, H. M.; *Tetrahedron: Asymmetry* **2001**, *12*, 2971.
18. Conti, S.; Falorni, M.; Giacomelli, G.; Soccolini, F.; *Tetrahedron* **1992**, *48*, 8993.
19. Pini, D.; Mastantuono, A.; Uccello-Barretta, G.; Iuliano, A.; Salvadori, P.; *Tetrahedron* **1993**, *49*, 9613.
20. Cernerud, M.; Skrinning, A.; Bérgère, I.; Moberg, C.; *Tetrahedron: Asymmetry* **1997**, *8*, 3437.
21. Paquette, L. A.; Zhou, R.; *J. Org. Chem.* **1999**, *64*, 7929.
22. Kostova, K.; Genov, M.; Philipova, I.; Dimitrov, V.; *Tetrahedron: Asymmetry* **2000**, *11*, 3253.
23. Nakamura, Y.; Takeuchi, S.; Ohgo, Y.; Curran, D. P.; *Tetrahedron Lett.* **2000**, *41*, 57.
24. Omote, M.; Kominato, A.; Sugawara, M.; Sato, K.; Ando, A.; Kumadaki, I.; *Tetrahedron Lett.* **1999**, *40*, 5583.
25. Burguete, M. I.; Collado, M.; Escorihuela, J.; Luis, S. V.; *Angew. Chem., Int. Ed.* **2007**, *46*, 9002.
26. Lesniak, S.; Rachwalski, M.; Sznajder, E.; Kielbasinski, P.; *Tetrahedron: Asymmetry* **2009**, *20*, 2311.
27. Lombardo, M.; Chiarucci, M.; Trombini, C.; *Chem. Eur. J.* **2008**, *14*, 11288.
28. Pastor, I. M.; Adolfsson, H.; *Tetrahedron Lett.* **2002**, *43*, 1743.
29. Pathak, K.; Bhatt, A. P.; Abdi, S. H. R.; Kureshy, R. I.; Khan, N. H.; Ahmad, I.; Jasra, R. V.; *Tetrahedron: Asymmetry* **2006**, *17*, 1506.
30. Pisani, L.; Superchi, S.; *Tetrahedron: Asymmetry* **2008**, *19*, 1784.
31. Pu, L.; *Tetrahedron* **2003**, *59*, 9873.

32. Roudeau, R.; Pardo, D. G.; Cossy, J.; *Tetrahedron* **2006**, *62*, 2388.
33. Wang, M. C.; Liu, L. T.; Zhang, J. S.; Shi, Y. Y.; Wang, D. K.; *Tetrahedron: Asymmetry* **2004**, *15*, 3853.
34. Wang, M. C.; Zhang, Q. J.; Li, G. W.; Liu, Z. K.; *Tetrahedron: Asymmetry* **2009**, *20*, 288.
35. Wu, Z. L.; Wu, H. L.; Wu, P. Y.; Uang, B. J.; *Tetrahedron: Asymmetry* **2009**, *20*, 1556.
36. Yang, X. W.; Shen, J. H.; Da, C. S.; Wang, R.; Choi, M. C. K.; Yang, L. W.; Wong, K. Y.; *Tetrahedron: Asymmetry* **1999**, *10*, 133.
37. Genov, M.; Dimitrov, V.; Ivanova, V.; *Tetrahedron: Asymmetry* **1997**, *8*, 3703.
38. Kwong, H. L.; Lee, W. S.; *Tetrahedron: Asymmetry* **1999**, *10*, 3791.
39. Goldfuss, B.; Steigelmann, M.; Khan, S. I.; Houk, K. N.; *J. Org. Chem.* **2000**, *65*, 77.
40. Goldfuss, B.; Steigelmann, M.; Rominger, F.; *Eur. J. Org. Chem.* **2000**, 1785.
41. Hanyu, N.; Aoki, T.; Mino, T.; Sakamoto, M.; Fujita, T.; *Tetrahedron: Asymmetry* **2000**, *11*, 4127.
42. Dimitrov, V.; Dobrikov, G.; Genov, M.; *Tetrahedron: Asymmetry* **2001**, *12*, 1323.
43. Panev, S.; Linden, A.; Dimitrov, V.; *Tetrahedron: Asymmetry* **2001**, *12*, 1313.
44. Xu, Q.; Wang, G.; Pan, X.; Chan, A. S. C.; *Tetrahedron: Asymmetry* **2001**, *12*, 381.
45. Xu, Q. Y.; Wu, X. M.; Pan, X. F.; Chan, A. S. C.; Yang, T. K.; *Chirality* **2002**, *14*, 28.
46. Chelucci, G.; *Chem. Soc. Rev.* **2006**, *35*, 1230.
47. Cheng, G. I.; Shei, C. T.; Sung, K. S.; *Chirality* **2007**, *19*, 235.
48. Martinez, A. G.; Vilar, E. T.; Fraile, A. G.; Cerero, S. D.; Ruiz, P. M.; Morillo, C. D.; *Tetrahedron: Asymmetry* **2007**, *18*, 742.
49. Martínez, A. G.; Vilar, E. T.; Fraile, A. G.; de la Moya Cerero, S.; Martínez Ruiz, P.; Díaz Morillo, C.; *Tetrahedron: Asymmetry* **2007**, *18*, 742.
50. Kamenova-Nacheva, M.; Dobrikov, G.; Dimitrov, V.; *Arkivoc* **2009**, 141.
51. Kozakiewicz, A.; Ullrich, M.; Welniak, M.; Wojtczak, A.; *J. Mol. Catal. A: Chem.* **2010**, *326*, 128.
52. Leven, M.; Schlorer, N. E.; Neudorfl, J. M.; Goldfuss, B.; *Chem. Eur. J.* **2010**, *16*, 13443.
53. Dobrikov, G. M.; Philipova, I.; Nikolova, R.; Shivachev, B.; Chimov, A.; Dimitrov, V.; *Polyhedron* **2012**, *45*, 126.
54. Engel, T. D.; Sanchez-Carnerero, E. M.; Sokolovskaya, E.; Gallardo-Araya, C. M.; Jimenez, F. M.; Maroto, B. L.; Cerero, S. D.; *Chirality* **2012**, *24*, 771.
55. Gant, T. G.; Meyers, A. I.; *Tetrahedron* **1994**, *50*, 2297.
56. Ghosh, A. K.; Mathivanan, P.; Cappiello, J.; *Tetrahedron: Asymmetry* **1998**, *9*, 1.
57. Johnson, J. S.; Evans, D. A.; *Acc. Chem. Res.* **2000**, *33*, 325.
58. Werner, H.; Vicha, R.; Gissibl, A.; Reiser, O.; *J. Org. Chem.* **2003**, *68*, 10166.
59. Bauer, M.; Kazmaier, U.; *J. Organomet. Chem.* **2006**, *691*, 2155.
60. Bolm, C.; Zani, L.; Rudolph, J.; Schiffers, I.; *Synthesis* **2004**, 2173.
61. Schinnerl, M.; Seitz, M.; Kaiser, A.; Reiser, O.; *Org. Lett.* **2001**, *3*, 4259.
62. Zhang, X. M.; Zhang, H. L.; Lin, W. Q.; Gong, L. Z.; Mi, A. Q.; Cui, X.; Jiang, Y. Z.; Yu, K. B.; *J. Org. Chem.* **2003**, *68*, 4322.
63. Meyers, A. I.; *J. Org. Chem.* **2005**, *70*, 6137.
64. Kamata, K.; Agata, I.; Meyers, A. I.; *J. Org. Chem.* **1998**, *63*, 3113.
65. Meyers, A. I.; Knaus, G.; *Tetrahedron Lett.* **1974**, *15*, 1333.
66. Page, P. C. B.; Allin, S. M.; Maddocks, S. J.; Elsegood, M. R. J.; *J. Chem. Soc., Perkin Trans. 1* **2002**, 2827.
67. Kitamura, M.; Okada, S.; Suga, S.; Noyori, R.; *J. Am. Chem. Soc.* **1989**, *111*, 4028.
68. Long, J.; Ding, K.; *Angew. Chem., Int. Ed.* **2001**, *40*, 544.
69. Girard, C.; Kagan, H. B.; *Angew. Chem., Int. Ed.* **1998**, *37*, 2922.
70. Kang, J.; Lee, J. W.; Kim, J. I.; *J. Chem. Soc., Chem. Commun.* **1994**, 2009.
71. Trost, B. M.; Weiss, A. H.; *Adv. Synth. Catal.* **2009**, *351*, 963.
72. Braga, A. L.; Paixao, M. W.; Westermann, B.; Schneider, P. H.; Wessjohann, L. A.; *J. Org. Chem.* **2008**, *73*, 2879.
73. Yue, H.; Huang, H.; Bian, G.; Zong, H.; Li, F.; Song, L.; *Tetrahedron: Asymmetry* **2014**, *25*, 170.
74. Zhang, A.; Yang, N.; Yang, L.; Peng, D.; *Chem. Lett.* **2014**, *43*, 462.

*Submitted: July 24, 2014*
*Published online: October 3, 2014*