https://dx.doi.org/10.21577/0103-5053.20230047

J. Braz. Chem. Soc., Vol. 34, No. 9, 1353-1359, 2023

Article

New Catalysts Derived from Natural Products as Highly Stereoselective Chiral Inductors for Diethylzinc Addition to Aromatic Aldehydes

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Asymmetric addition of organozinc compounds to carbonyl groups is one of the most useful methods for the synthesis of alcohols with high enantioselectivity. There is a wide range of chiral catalysts, although their synthesis requires more than one step and not often readily available starting materials. In this work, chiral β-hydroxy oxazolines derived from (+)-camphor and (−)-fenchone were easily synthesized through a one-step method, with good yields. Both ligands were evaluated as catalysts for the stereoselective addition of diethylzinc to aromatic aldehydes. All ligands showed good catalytic activity, leading both to the preparation of the *R* enantiomer of chiral secondary alcohols. As ligand **2** provided slightly better enantioselectivities, it was used as chiral inductor for the addition of diethylzinc for a larger number of aldehydes, resulting in good to excellent yields (88-98%) and enantiomeric excess up to 96%.

Keywords: diethylzinc, (+)-camphor, (−)-fenchone, catalyst, oxazolines, chiral alcohol

Introduction

The enantioselective addition of organometallic reagents to carbonyl compounds is a powerful methodology to form a new carbon-carbon bond.[1,2] Generally, due to their higher reactivity, the asymmetric addition of organolithium and organomagnesium to aldehydes and ketones remains a challenge and few examples have been reported, including the use of very low temperatures and/or high amounts of chiral inductors.[3-5] On the other hand, the enantioselective addition of organozinc compounds to carbonyl group is one of the most useful methods for the asymmetric synthesis of secondary alcohols with high enatioselectivity.[2,3,6-11]

The synthesis of catalysts and their applications as chiral inductors in carbonyl organometallic addition have been studied in the last decades. In this way, there is a wide range of chiral catalysts, such as primary alcohols,[12-16] diamines,[17-20] disulfonamides,[21] diols,[22-26] oxazolines,[27-34] aminoalcohols,[35-40] and others.[41-56] However, the synthesis of those catalysts usually requires more than one step and not often readily available starting materials. So, the development of new catalysts, synthesized from easily available and inexpensive starting materials, through simple synthetic methods, remains an important challenge (Figure 1).

Natural chiral ketones, such as camphor, fenchone and menthone are inexpensive and have been applied in the synthesis of chiral inductors used in the asymmetric addition reactions of organozinc reagents to carbonyl compounds, furnishing good to excellent enantioselectivity.[50,57-63] Oxazolines have been extensively used in asymmetric

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Editor handled this article: Albertina Moglioni (Associate)

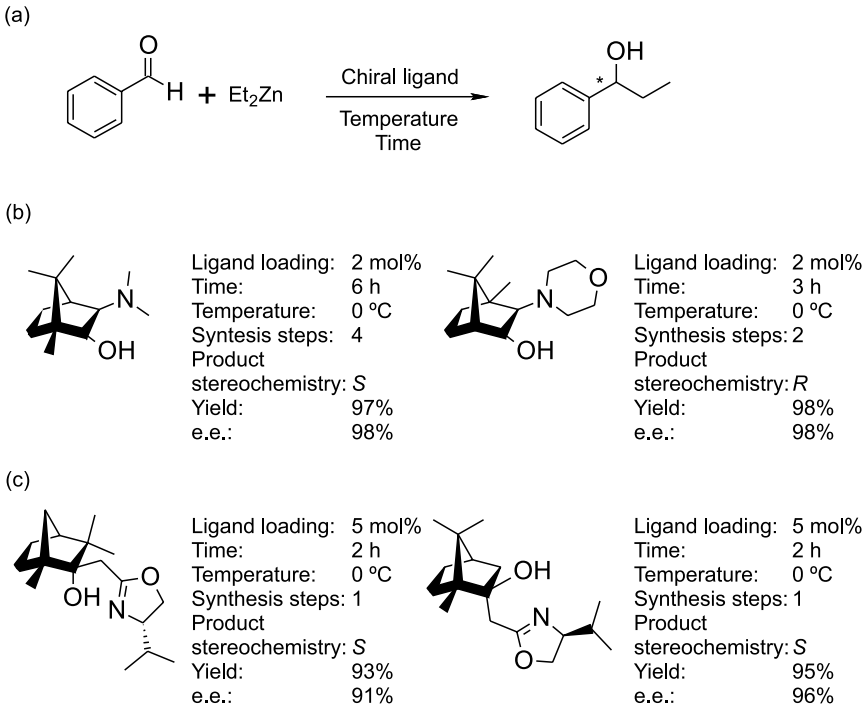


Figure 1. Known and new (+)-camphor and (−)-fenchone derived ligands for the addition of diethylzinc to aldehydes. (a) Stereoselective addition of Et_2Zn to benzaldehyde; (b) notable chiral ligands derived from (−)-camphor and (+)-fenchone; (c) this work: synthesis and evaluation of β-hydroxyoxazolines as ligands.

catalysis, including some α-hydroxy-2-oxazolines[64-67] and β-hydroxy-2-oxazolines.[32]

The enantioselective catalytic addition of organozinc reagents to carbonyl groups has been used for the synthesis of optically active thiazolidines,[68] lactones,[13] cyclopropyl alcohols,[14,15,69,70] and natural products such as (+)-(*R*)-gossonorol, which shows antifungal, anticancer and antioxidant activities.[16]

Following our previous studies,[37,38] we envisioned that bulkier natural ketones like camphor and fenchone could enhance the steric induction when applied to the addition of organozinc compounds. Combining the aforementioned natural ketones with chiral oxazolines, which can be prepared from natural amino acids, provided access to two readily available chiral sources, that can be manipulated for the ligand design.

Herein we describe the synthesis of β-hydroxy-2-oxazolines, easily prepared from (−)-fenchone and (+)-camphor and their application as chiral inductors in the enantioselective addition of diethylzinc to aldehydes.

Experimental

General

All air- and moisture-sensitive reactions were carried out under dry argon atmosphere. Tetrahydrofuran (THF), hexane, toluene, and diethyl ether were dried by distillation from sodium using benzophenone as indicator. Diethylzinc and *n*-butyllithium solutions (in hexane) were purchased from Sigma-Aldrich (Saint Louis, USA) in 1 and 1.6 M, respectively. All other materials were commercially obtained with analytical purity.

Purification of reaction products was carried out manually by flash column chromatography using Merck (Darmstadt, Germany) 9385 Silica gel-Breckland 60 (0.040-0.063 mm). Analytical thin-layer chromatography was performed on silica gel 60 and GF (5-40 μm thickness) plates. Optical rotations were measured in a Jasco (Tokyo, Japan) P-2000 polarimeter.

The nuclear magnetic resonance (NMR) spectra were obtained on a Bruker (Billerica, USA) AC 200 spectrometer operating at 4.7 Tesla (200 MHz for ^1H) at 293 K, using $CDCl_3$ as solvent. The chemical shifts (δ) are given in ppm, related to tetramethylsilane (TMS) signal at 0.00 ppm as internal reference, and the coupling constants (*J*) are given in hertz (Hz).

Chiral gas chromatography (GC) analyses were performed in a Varian (Palo Alto, USA) 3800 chromatograph equipped with a flame ionization detector, helium as carrier gas, and Chirasil-Dex CB-β-cyclodextrin (30 m × 0.25 mm × 0.25 μm) as stationary phase. The carrier gas was helium, used at a constant pressure of 59 kPa and a constant flow of 1 mL min^{-1}. The injector temperature

was 280 °C, with the initial temperature set at 60 °C and a temperature ramp of 3 °C min^{-1} rising to a final temperature of 280 °C for 10 min.

High-resolution mass spectrometry (HRMS) data were obtained on a Waters (Mildford, USA) liquid chromatography time-of-flight (LC-TOF) mass spectrometer (LCT-XE Premier) with electrospray ionization (ESI) in the positive mode.

Synthesis of ligands

(1*S*,2*R*,4*S*)-2-(((*S*)-4-Isopropyl-4,5-dihydrooxazol-2-yl) methyl)-1,3,3-trimethylbicyclo[2,2,1]heptan-2-ol (**1**)

In a 25 mL round bottom flask equipped with a stir bar under argon atmosphere, anhydrous THF (4.0 mL) and (*S*)-(−)-2-methyl-4-isopropyloxazoline (0.254 g, 2.00 mmol) were added and the temperature reduced to −78 °C. After temperature stabilization, *n*-BuLi (2.10 mmol) in hexane was added at once. The reaction mixture was stirred for 15 min followed by addition, drop by drop, of a (−)-fenchone (0.308 g, 2.00 mmol) solution dissolved in anhydrous THF (4.0 mL). The mixture was stirred at −78 °C for 30 min and the cooling bath was removed. After reaching room temperature, the reactional mixture was washed with saturated $NaHCO_3$ aqueous solution (10 mL) and the aqueous layer was extracted with hexane/ethyl ether (1:1, 10 mL). The organic layers were combined, dried with anhydrous Na_2SO_4, filtrated, and evaporated. The crude product was purified by flash column chromatography using ethyl ether/ethyl acetate/hexane (0.25:0.25:9.5) to obtain the pure β-hydroxyoxazoline **1**. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.91 (d, *J* 6.8 Hz, 3H), 0.93 (d, *J* 5.6 Hz, 3H), 0.97 (m, 2H), 1.00 (s, 6H), 1.02 (d, *J* 5.6 Hz, 3H), 1.10 (dd, *J* 10.46 and 1.56 Hz, 1H), 1.52 (m, 5H), 2.16 (m, 1H), 2.40 (d, *J* 1.14 Hz, 2H), 3.86 (dd, *J* 8.75 and 7.61 Hz, 1H), 4.23 (dd, *J* 8.00 and 7.61 Hz, 1H), 5.70 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 17.80, 19.11, 19.55, 22.89, 25.44, 27.31, 29.45, 32.20, 33.27, 40.67, 44.22, 49.86, 52.07, 70.06, 72.53, 79.66, 168.05; GC-MS *m/z* (%), 154 (16.64), 127 (8.51), 109 (5.10), 95 (2.50), 81 (100), 69 (61.65), 56 (49.43), 41 (50.53); HRMS *m/z*, calcd. for $C_{17}H_{30}NO_2$ $[M + H]^+$: 280.2271, found: 280.2277; $[\alpha]_D^{25}$ −34.57 (*c* 1.20, CH_3Cl).

(1*S*,2*S*,4*R*)-2-(((*S*)-4-Isopropyl-4,5-dihydrooxazol-2-yl) methyl)-1,7,7-trimethylbicyclo[2,2,1]heptan-2-ol (**2**)

In a 25 mL round bottom flask equipped with a stir bar under argon atmosphere, anhydrous THF (4.0 mL) and (*S*)-(−)-2-methyl-4-isopropyloxazoline (0.254 g, 2.00 mmol) were added and the temperature reduced to −78 °C. After temperature stabilization, *n*-BuLi (2.10 mmol) in hexane was added at once. The reactional mixture was stirred for 15 min followed by addition, drop by drop, of a (+)-camphor (0.308 g, 2.00 mmol) solution dissolved in anhydrous THF (4.0 mL). The reaction mixture was kept under agitation at −78 ºC for 30 min and the cooling bath was removed. After reaching room temperature, the reactional mixture was washed with saturated $NaHCO_3$ aqueous solution (10 mL) and the aqueous layer was extracted with hexane/ethyl ether (1:1, 10 mL). The organic layers were combined, dried with anhydrous Na_2SO_4, filtrated, and evaporated. The crude product was purified with flash column chromatography using acetone/hexane (0.5:9.5), yielding 0.455 g (81%) of pure β-hydroxyoxazoline **2**. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (s, 6H), 0.89 (d, *J* 6.96 Hz, 3H), 0.97 (m, 1H), 0.98 (d, *J* 6.96 Hz, 3H), 1.15 (s, 3H), 1.40 (m, 3H), 1.70 (m, 4H), 2.11 (dt, *J* 13.2 and 3.7 Hz, 1H), 2.35 (d, *J* 15.6 Hz, 1H), 2.55 (d, *J* 15.6 Hz, 1H), 3.87 (m, 1H), 3.94 (dd, *J* 8.5 and 6.8 Hz, 1H), 4.24 (dd, *J* 8.5 and 6.8 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 10.71, 18.53, 19.01, 21.07, 21.54, 26.88, 30.51, 32.92, 36.59, 45.17, 46.93, 49.23, 52.19, 69.80, 72.09, 78.67, 166.62; GC-MS *m/z* (%), 169 (1.60), 127 (18.57), 108 (33.76), 95 (89.28), 84 (100), 81 (50.58), 70 (6.16), 69 (38.95), 56 (63.59), 55 (41.75), 43 (31.23), 41 (52.81); HRMS *m/z*, calcd. for $C_{17}H_{30}NO_2$ $[M + H]^+$: 280.2271, found: 280.2273; $[\alpha]_D^{25}$ −69.00 (*c* 2.50, CH_3Cl).

General procedure for addition of diethylzinc to aldehydes

A 10 mL reaction vial with a stir bar was loaded with β-hydroxyoxazoline (0.05 mmol), anhydrous hexane (1.0 mL), and diethylzinc solution in hexane (2.50 mL, 2.50 mmol) under argon atmosphere. The solution was stirred at 20 °C for 20 min. After that, the temperature was reduced to 0 °C and aldehyde (2.00 mmol) in anhydrous hexane (4.0 mL) was added to the vial. After 2 h, the temperature was raised to room temperature and an $NaHCO_3$ saturated aqueous solution (4.0 mL) was added to the vial. The layers were separated, and the aqueous layer was extracted with hexane/ethyl ether (1:1, 5.0 mL) three times. All organic layers were combined, dried with anhydrous Na_2SO_4, filtrated, and concentrated in a rotatory evaporator. The crude product was purified using flash column chromatography.

Results and Discussion

The β-hydroxy-2-oxazolines were easily obtained by the addition of 2-oxazoline anions to the respective ketones, as previously described.[32] The β-hydroxy-2-oxazoline **1** was obtained through an exo approach of the oxazoline anion

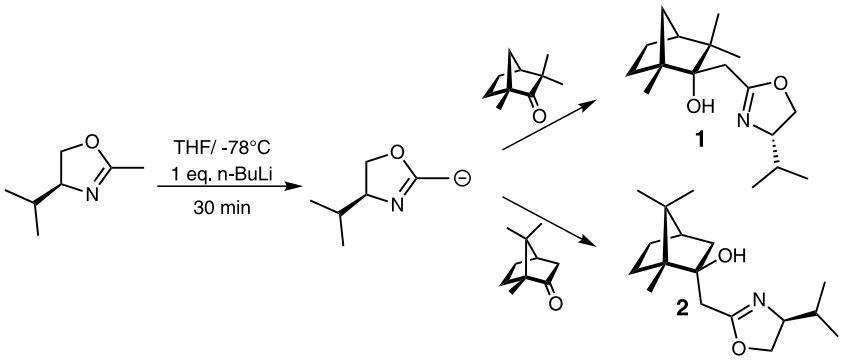


Figure 2. Synthesis of the β-hydroxy-2-oxazolines **1** and **2**.

to the carbonyl group of (–)-fenchone, as reported in the literature,[71,72] generating the endo-alcohol derivative with diastereomeric excess (d.e.) greater than 97%.

On the other hand, since (+)-camphor has a high steric hindrance caused by the methyl groups at the exo side of the bicyclic system, the addition of the oxazoline anion to the carbonyl group of (+)-camphor occurred via endo approximation (Figure 2) resulting in the exo-alcohol **2**, which was obtained with d.e. higher than 97%.

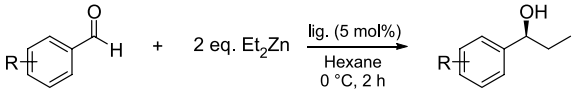
The stereochemistry and structure of both β-hydroxy-2-oxazolines **1** and **2** were determined using NMR analysis, such as coupling constants, heteronuclear single quantum coherence spectroscopy (HSQC), heteronuclear multiple bond correlation (HMBC) and nuclear Overhauser effect (NOE). For detailed information, see Supplementary Information (SI) section.

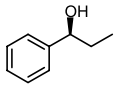
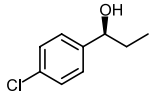
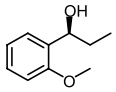
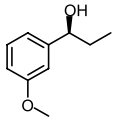
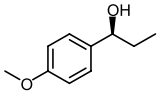
With the chiral inductors obtained, all stereoselective diethylzinc additions to aldehydes were carried out in hexane following reported procedures,[33,36] and the results are presented in Table 1.

As ligand **2** provided slightly better enantioselectivities in the previous study (up to 93%, e.e.), it was used as the chiral inductor for the addition of diethylzinc to some more aldehydes. The results are displayed in Table 2. Acceptable to good asymmetric inductions of 82-96% and good to excellent yields (88-98%) were reached.

The proposed mechanism for the addition of diethylzinc to aldehydes using the endo-β-hydroxy-2-oxazoline **2** as the chiral catalyst is shown in Figure 3. It is based on the generation of intermediate complexes, as previously described by several other research groups.[71-79] We believe that the mechanism consists of two steps. In the preceding step, diethylzinc reacts with the oxazoline **2** to generate the catalytically active species **3A** and **3B**, of which **3A** is energetically favored since it avoids steric repulsion of the ethyl zinc part with the isopropyl group of the oxazoline and the methyl group of camphor moiety, as it occurs in **3B**. Coordination of diethyl zinc and the aldehyde to **3A** leads to the favored transition state **4A**, which gives, in good agreement with the experimental results, highly enantioselectively the corresponding chiral alcohol with *S* configuration.

Table 1. Yield and products in the addition reaction of diethylzinc to aldehydes



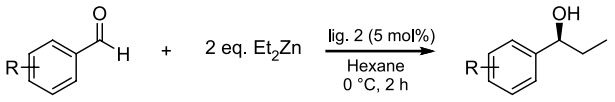
entry	Product	Ligand **1** yield / %	Ligand **1** e.e. / %	Ligand **2** yield / %	Ligand **2** e.e. / %
1		93	88 (*S*)	95	91 (*S*)
2		89	84 (*S*)	93	90 (*S*)
3		88	85 (*S*)	90	85 (*S*)
4		91	91 (*S*)	92	93 (*S*)
5		89	90 (*S*)	93	92 (*S*)

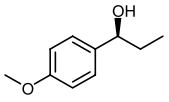
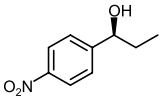
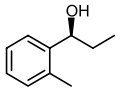
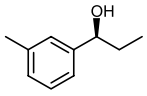
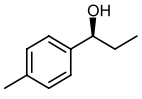
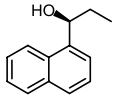
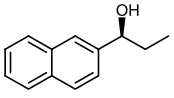
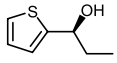
e.e.: enantiomeric excess.

Conclusions

In summary, we report the easy synthesis of new chiral inductors **1** and **2**, prepared from natural ketones through a one-step method, and their application as a catalyst in stereoselective addition of diethylzinc to aldehydes, which allowed the preparation of chiral secondary alcohols in good to excellent yields and enantiomeric excess up to 96%. We envisioned that this approach will enable further ligand

Table 2. Yield and products in the addition reaction of diethylzinc to aldehydes using ligand **2**



	Product	Yield / %	e.e. / %
1		93	92
2		91	82
3		88	88
4		95	95
5		90	89
6		93	93
7		95	96
8		98	90

e.e.: enantiomeric excess.

designs, that shall pave the way to new easily accessible chiral pre-catalysts.

Supplementary Information

Supplementary information (spectra and detailed mechanisms) is available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

The authors thank the National Council for Scientific and Technological Development-CNPq/INCT process 465357/2014-8, CAPES and the Paraná Research Foundation-Fundação Araucária for financial support.

Author Contributions

Celso L. Wosch, Palimecio G. Guerrero Jr., Gustavo Frensch, Beatriz H. L. N. S. Maia and Francisco A. Marques contributed to the study conception and design. Funding acquisition and project administration were performed by Francisco A. Marques, Beatriz H. L. N. S. Maia and Palimecio G. Guerrero Jr. Material preparation, investigation, data collection and analysis were performed by Celso L. Wosch, Ricardo Labes, Kahlil S. Salome, Vitor S. Melo, Renan R. Schorr and Nathalya K. Lima. The first draft of the manuscript was written by Celso L. Wosch and Gustavo Frensch and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

References

1. Wang, H.; Dai, X.-J.; Li, C.-J.; *Nat. Chem.* **2017**, *9*, 374. [Crossref]

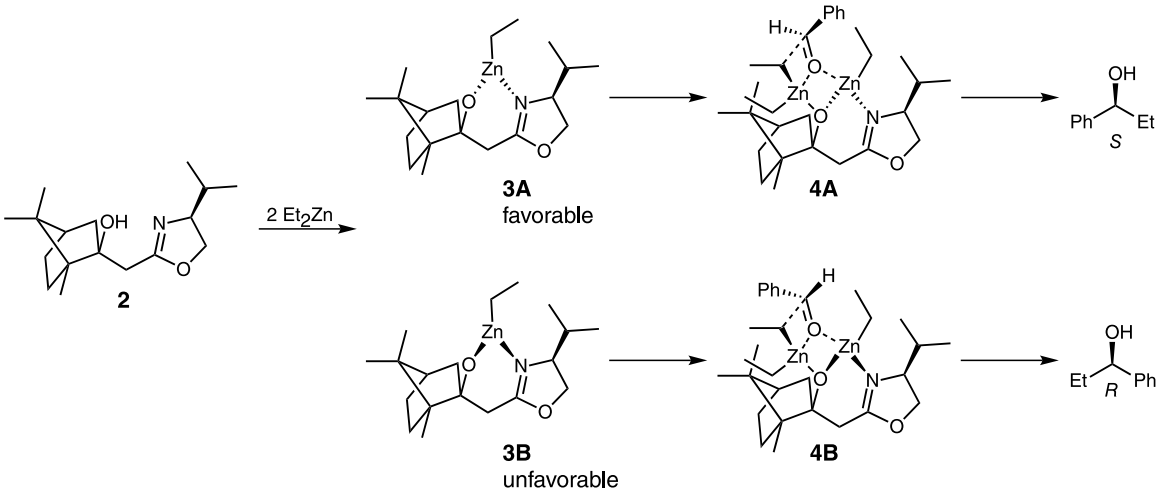


Figure 3. Proposed mechanism for the stereoselective addition of diethylzinc to aldehydes in the presence of the chiral inductor **2**.

2. Pu, L.; Yu, H.-B.; *Chem. Rev.* **2001**, *101*, 757. [Crossref]
3. Collados, J. F.; Solà, R.; Harutyunyan, S. R.; Maciá, B.; *ACS Catal.* **2016**, *6*, 1952. [Crossref]
4. Luderer, M. R.; Bailey, W. F.; Luderer, M. R.; Fair, J. D.; Dancer, R. J.; Sommer, M. B.; *Tetrahedron: Asymmetry* **2009**, *20*, 981. [Crossref]
5. Hatano, M.; Miyamoto, T.; Ishihara, K.; *Curr. Org. Chem.* **2007**, *11*, 127. [Crossref]
6. Wang, P.; Ma, G.-R.; Yu, S.-L.; Da, C.-S.; *Chirality* **2019**, *31*, 79. [Crossref]
7. Osakama, K.; Nakajima, M.; *Org. Lett.* **2016**, *18*, 236. [Crossref]
8. Bieszczad, B.; Gilheany, D. G.; *Angew. Chem., Int. Ed.* **2017**, *56*, 4272. [Crossref]
9. Buchcic-Szychowska, A.; Adamczyk, J.; Marciniak, L.; Pieczonka, A. M.; Zawisza, A.; Leśniak, S.; Rachwalski, M.; *Catalysts* **2021**, *11*, 968. [Crossref]
10. Geiger, Y.; Achard, T.; Maisse-François, A.; Bellemin-Laponnaz, S.; *Chirality* **2020**, *32*, 1250. [Crossref]
11. Raji, M.; Le, T. M.; Fülöp, F.; Szakonyi, Z.; *Catalysts* **2020**, *10*, 474. [Crossref]
12. Noyori, R.; *Asymmetric Catalysis in Organic Synthesis*, 1st ed.; John Wiley & Sons: New York, 1994.
13. Pisani, L.; Superchi, S.; D'Elia, A.; Scafato, P.; Rosini, C.; *Tetrahedron* **2012**, *68*, 5779. [Crossref]
14. Soai, K.; Niwa, S.; *Chem. Rev.* **1992**, *92*, 833. [Crossref]
15. Kim, H. Y.; Walsh, P. J.; *J. Phys. Org. Chem.* **2012**, *25*, 933. [Crossref]
16. González-López, S.; Yus, M.; Ramón, D. J.; *Tetrahedron: Asymmetry* **2012**, *23*, 611. [Crossref]
17. Liu, C.-L.; Wei, C.-Y.; Wang, S.-W.; Peng, Y.; *Chirality* **2011**, *23*, 921. [Crossref]
18. Bian, G.; Huang, H.; Zong, H.; Song, L.; *Chirality* **2012**, *24*, 825. [Crossref]
19. Cicchi, S.; Crea, S.; Goti, A.; Brandi, A.; *Tetrahedron: Asymmetry* **1997**, *8*, 293. [Crossref]
20. Szakonyi, Z.; Balázs, Á.; Martinek, T. a.; Fülöp, F.; *Tetrahedron: Asymmetry* **2006**, *17*, 199. [Crossref]
21. Conti, S.; Falorni, M.; Giacomelli, G.; Soccolini, F.; *Tetrahedron* **1992**, *48*, 8993. [Crossref]
22. Pini, D.; Mastantuono, A.; Uccello-Barretta, G.; Iuliano, A.; Salvadori, P.; *Tetrahedron* **1993**, *49*, 9613. [Crossref]
23. Yi-Shan, S.; Boobalan, R.; Chen, C.; Lee, G.-H.; *Tetrahedron: Asymmetry* **2014**, *25*, 327. [Crossref]
24. Serra, M. E. S.; Murtinho, D.; Paz, V.; *Tetrahedron: Asymmetry* **2017**, *28*, 381. [Crossref]
25. Paquette, L. A.; Zhou, R.; *J. Org. Chem.* **1999**, *64*, 7929. [Crossref]
26. Gonda, T.; Bérdi, P.; Zupkó, I.; Fülöp, F.; Szakonyi, Z.; *Int. J. Mol. Sci.* **2017**, *19*, 81. [Crossref]
27. Olsson, C.; Friberg, A.; Frejd, T.; *Tetrahedron: Asymmetry* **2008**, *19*, 1476. [Crossref]
28. Kostova, K.; Genov, M.; Philipova, I.; Dimitrov, V.; *Tetrahedron: Asymmetry* **2000**, *11*, 3253. [Crossref]
29. Gök, Y.; Kekeç, L.; *Tetrahedron Lett.* **2014**, *55*, 2727. [Crossref]
30. Gök, Y.; Küloğlu, S.; Gök, H. Z.; Kekeç, L.; *Appl. Organomet. Chem.* **2014**, *28*, 835. [Crossref]
31. Mohebbi, M.; Salehi, P.; Bararjanian, M.; Ebrahimi, S. N.; *J. Iran. Chem. Soc.* **2018**, *15*, 47. [Crossref]
32. Gant, T. G.; Meyers, A. I.; *Tetrahedron* **1994**, *50*, 2297. [Crossref]
33. Ranu, B. C.; Ghosh, S.; Das, A.; *Mendeleev Commun.* **2006**, *16*, 220. [Crossref]
34. Johnson, J. S.; Evans, D. A.; *Acc. Chem. Res.* **2000**, *33*, 325. [Crossref]
35. Werner, H.; Vicha, R.; Gissibl, A.; Reiser, O.; *J. Org. Chem.* **2003**, *68*, 10166. [Crossref]
36. Nottingham, C.; Benson, R.; Müller-Bunz, H.; Guiry, P. J.; *J. Org. Chem.* **2015**, *80*, 10163. [Crossref]
37. Marques, F. A.; Wosch, C. L.; Frensch, G.; Labes, R.; Maia, B. H. L. N. S.; Salomé, K. S.; Barison, A.; Guerrero Jr., P. G.; *J. Braz. Chem. Soc.* **2015**, *26*, 165. [Crossref]
38. Frensch, G.; Labes, R.; Wosch, C. L.; Munaretto, L. S.; Salomé, K. S.; Guerrero Jr., P. G.; Marques, F. A.; *Tetrahedron Lett.* **2016**, *57*, 420. [Crossref]
39. Sasaki, S.; Yamauchi, T.; Kanai, M.; Ishii, A.; Higashiyama, K.; *Bull. Chem. Soc. Jpn.* **2015**, *88*, 200. [Crossref]
40. Szakonyi, Z.; Csőr, Á.; Csámpai, A.; Fülöp, F.; *Chem. - Eur. J.* **2016**, *22*, 7163. [Crossref]
41. Asami, M.; Miyairi, N.; Sasahara, Y.; Ichikawa, K.; Hosoda, N.; Ito, S.; *Tetrahedron* **2015**, *71*, 6796. [Crossref]
42. Asami, M.; Hasome, A.; Yachi, N.; Hosoda, N.; Yamaguchi, Y.; Ito, S.; *Tetrahedron: Asymmetry* **2016**, *27*, 322. [Crossref]
43. Huang, W.-M.; Uang, B.-J.; *Chem.-Asian J.* **2015**, *10*, 998. [Crossref]
44. Zhang, W.; Tang, R.; Yu, H.; Gao, S.; *Appl. Organomet. Chem.* **2014**, *28*, 545. [Crossref]
45. Faigl, F.; Deák, S. Z.; Erdélyi, Z. S.; Holczbauer, T.; Czugler, M.; Nyerges, M.; Mátravölgyi, B.; *Chirality* **2015**, *27*, 216. [Crossref]
46. Olubanwo, O. B.; Golen, J. A.; Rheingold, A. L.; Nevalainen, V.; Olubanwo, O. B.; Golen, J. A.; Rheingold, A. L.; Nevalainen, V.; *Int. J. Org. Chem.* **2018**, *8*, 240. [Crossref]
47. Burguete, M. I.; Collado, M.; Escorihuela, J.; Luis, S. V.; *Angew. Chem., Int. Ed.* **2007**, *46*, 9002. [Crossref]
48. Leśniak, S.; Rachwalski, M.; Sznajder, E.; Kiełbasiński, P.; *Tetrahedron: Asymmetry* **2009**, *20*, 2311. [Crossref]
49. Murtinho, D.; Ogihara, C. H.; Serra, M. E. S.; *Tetrahedron: Asymmetry* **2015**, *26*, 1256. [Crossref]
50. Yang, X.; Shen, J.; Da, C.; Wang, R.; Choi, M. C. K.; Yang, L.; Wong, K.; *Tetrahedron: Asymmetry* **1999**, *10*, 133. [Crossref]

51. Ueda, Y.; Yagishita, F.; Ishikawa, H.; Kaji, Y.; Baba, N.; Kasashima, Y.; Mino, T.; Sakamoto, M.; *Tetrahedron* **2015**, *71*, 6254. [Crossref]
52. Liu, L.; Long, Q.; Aoki, T.; Zhang, G.; Kaneko, T.; Teraguchi, M.; Zhang, C.; Wang, Y.; *Chirality* **2015**, *27*, 454. [Crossref]
53. Bouhachicha, M.; Ngo Ndimba, A.; Roisnel, T.; Lalli, C.; Argouarch, G.; *New J. Chem.* **2017**, *41*, 4767. [Crossref]
54. Li, J.; Zhou, B.; Jiang, Y.; Liu, X.; *Catalysts* **2018**, *8*, 46. [Crossref]
55. Sweetman, B. A.; Guiry, P. J.; *Tetrahedron* **2018**, *74*, 5567. [Crossref]
56. Lombardo, M.; Chiarucci, M.; Trombini, C.; *Chem.-Eur. J.* **2008**, *14*, 11288. [Crossref]
57. Pastor, I. M.; Adolfsson, H.; *Tetrahedron Lett.* **2002**, *43*, 1743. [Crossref]
58. Pathak, K.; Bhatt, A. P.; Abdi, S. H. R. R.; Kureshy, R. I.; Khan, N. H.; Ahmad, I.; Jasra, R. v.; Kahn, N. H.; Ahmad, I.; Jasra, R. V.; *Tetrahedron: Asymmetry* **2006**, *17*, 1506. [Crossref]
59. Pisani, L.; Superchi, S.; *Tetrahedron: Asymmetry* **2008**, *19*, 1784. [Crossref]
60. Roudeau, R.; Gomez Pardo, D.; Cossy, J.; *Tetrahedron* **2006**, *62*, 2388. [Crossref]
61. Wang, M.-C.; Liu, L.-T.; Zhang, J.-S.; Shi, Y.-Y.; Wang, D.-K.; *Tetrahedron: Asymmetry* **2004**, *15*, 3853. [Crossref]
62. Wang, M.-C.; Zhang, Q.-J.; Li, G.-W.; Liu, Z.-K.; *Tetrahedron: Asymmetry* **2009**, *20*, 288. [Crossref]
63. Wu, Z.-L.; Wu, H.-L.; Wu, P.-Y.; Uang, B.-J.; *Tetrahedron: Asymmetry* **2009**, *20*, 1556. [Crossref]
64. Chelucci, G.; *Chem. Soc. Rev.* **2006**, *35*, 1230. [Crossref]
65. Cheng, G.; Shei, C.; Sung, K.; *Chirality* **2007**, *19*, 235. [Crossref]
66. 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. [Crossref]
67. Kozakiewicz, A.; Ullrich, M.; Wełniak, M.; Wojtczak, A.; *J. Mol. Catal. A: Chem.* **2010**, *326*, 128. [Crossref]
68. Tavares, N. C. T.; Neves, C. T.; Milne, B. F.; Murtinho, D.; Pais, A. A. C. C.; Serra, M. E. S.; *J. Organomet. Chem.* **2018**, *878*, 1. [Crossref]
69. Kim, H. Y.; Walsh, P. J.; *Acc. Chem. Res.* **2012**, *45*, 1533. [Crossref]
70. Laroche, M.-F.; Belotti, D.; Cossy, J.; *Org. Lett.* **2005**, *7*, 171. [Crossref]
71. Leven, M.; Schlörer, N. E.; Neudörfl, J. M.; Goldfuss, B.; *Chem. - Eur. J.* **2010**, *16*, 13443. [Crossref]
72. Dobrikov, G. M.; Philipova, I.; Nikolova, R.; Shivachev, B.; Chimov, A.; Dimitrov, V.; *Polyhedron* **2012**, *45*, 126. [Crossref]
73. de Las Casas Engel, T.; Sánchez-carnerero, E. M.; Sokolovskaya, E.; Gallardo-araya, C. M.; JimÉnez, F. M.; Maroto, B. L.; de la Moya Cerero, S.; *Chirality* **2012**, *24*, 771. [Crossref]
74. Bauer, M.; Kazmaier, U.; *J. Organomet. Chem.* **2006**, *691*, 2155. [Crossref]
75. Bolm, C.; Zani, L.; Rudolph, J.; Schiffers, I.; *Synthesis* **2004**, *2004*, 2173. [Crossref]
76. Schinnerl, M.; Seitz, M.; Kaiser, A.; Reiser, O.; *Org. Lett.* **2001**, *3*, 4259. [Crossref]
77. 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. [Crossref]
78. Goldfuss, B.; Steigelmann, M.; Rominger, F.; *Eur. J. Org. Chem.* **2000**, *2000*, 1785. [Crossref]
79. Goldfuss, B.; Steigelmann, M.; Khan, S. I.; Houk, K. N.; *J. Org. Chem.* **2000**, *65*, 77. [Crossref]

Submitted: October 28, 2022
Published online: April 4, 2023