J. Braz. Chem. Soc., Vol. 26, No. 1, S1-S10, 2015.
Printed in Brazil - ©2015 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Supplementary Information

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

Experimental

General

All air and moisture-sensitive reactions were carried out under a 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 Aldrich in 1 mol L^{-1} and 1.6 mol L^{-1}, respectively. All other materials were obtained commercially with analytical purity.

Purification of reaction products was carried out by flash column chromatography manually using Merck 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 P-2000.

Nuclear magnetic resonance (NMR) spectra were obtained on a BRUKER AC 200 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 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 chromatograph Varian 3800 equipped with flame ionization detector, helium as the carrier gas and Chirasil-Dex CB-β-ciclodextrin (30 m × 0.25 mm × 0.25 μm) as stationary phase.

High-resolution mass spectra of compound **1** was obtained by a LTQ Orbitrap XL ETD (mass spectrometry facility RPT02H PDTIS/Carlos Chagas Institute - Fiocruz Parana), with an atmospheric pressure electronspray ionization source operating in positive mode (ESI +), the samples were diluted to concentrations of 3 mg L^{-1} an introduced into the system through a syringe infusion at 10 μL min^{-1}. The high-resolution mass spectra of compounds **2** and **3** were obtained by a microTOF Q II - ESI-TOF Mass Spectometer (Bruker Daltonics) in positive mode. The samples were introduced into the system through an infusion pump at 300 μL min^{-1} using methanol/water as solvent.

*e-mail: tic@ufpr.br

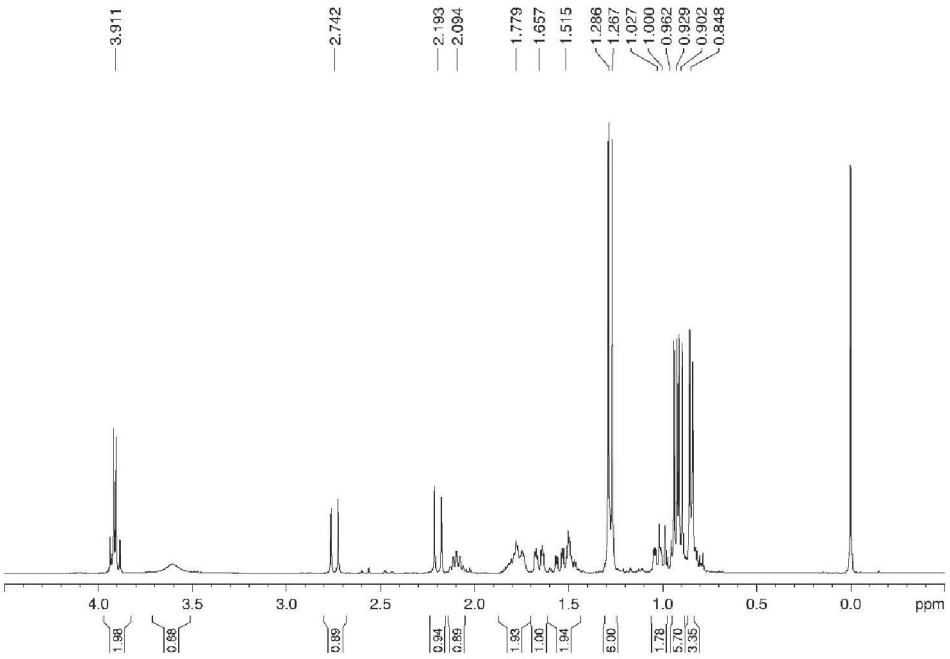

Figure S1. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of **1**.

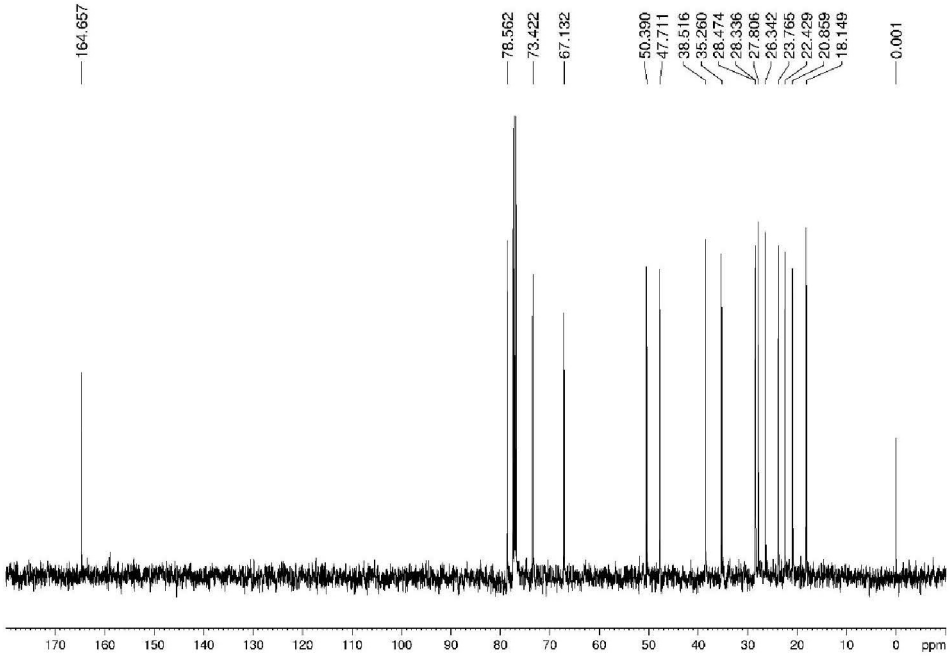

Figure S2. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of **1**.

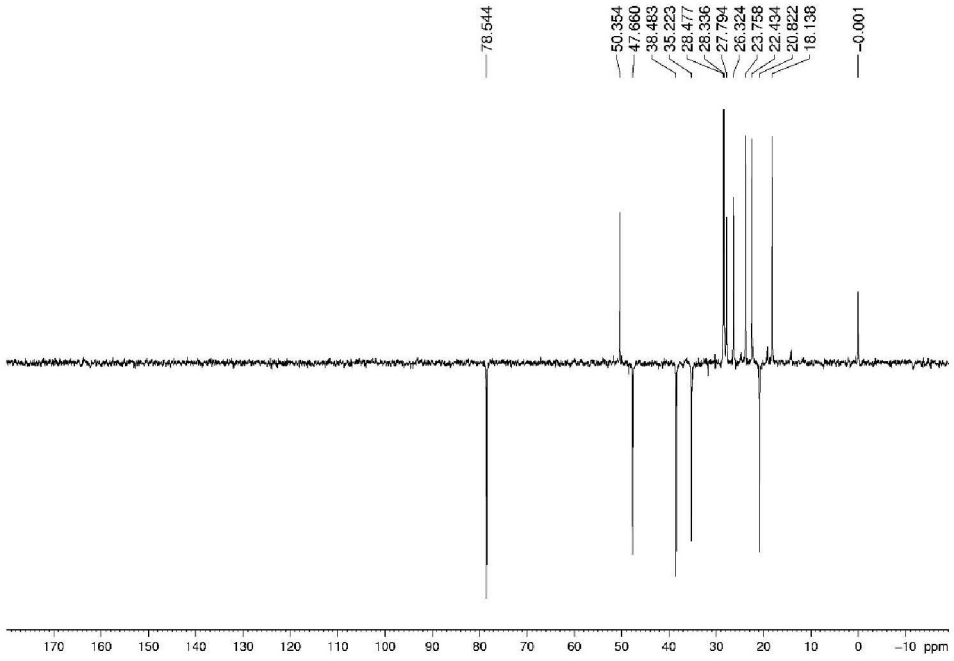

Figure S3. DEPT 135 NMR spectrum (50 MHz, $CDCl_3$) of **1**.

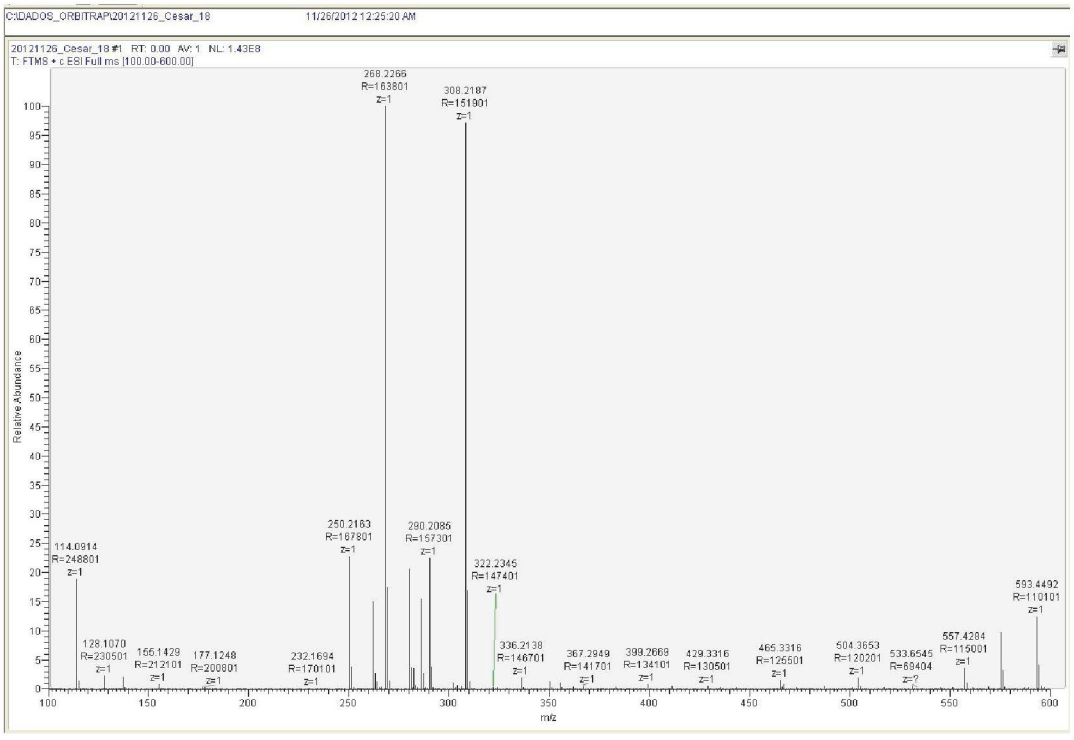

Figure S4. HRMS (ESI-TOF) *m/z* $[M + H]^+$ for $C_{16}H_{29}NO_2$ of **1**, calcd. 268.2271, observed 268.2266.

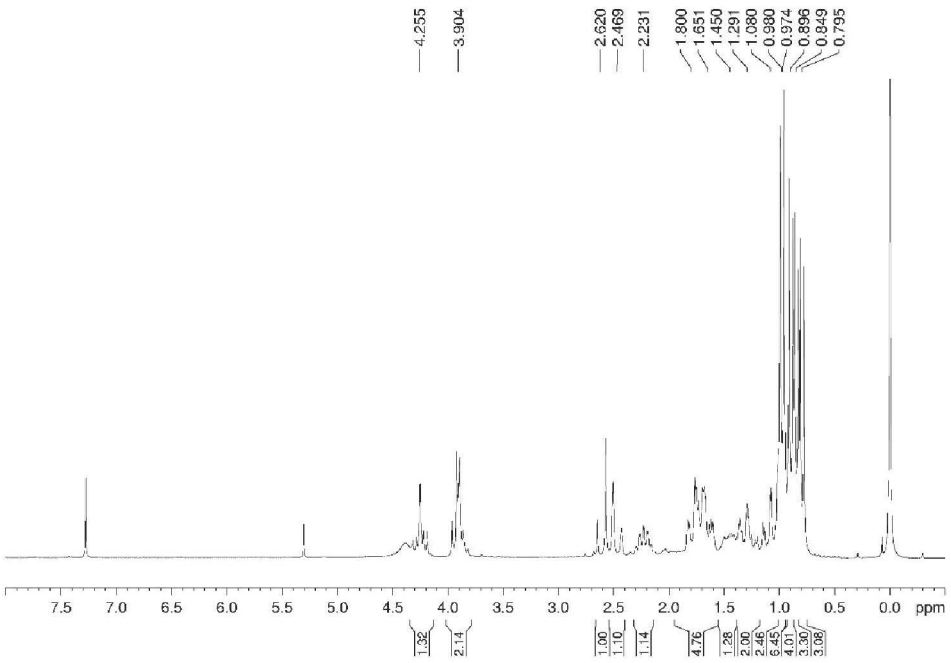

Figure S5. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of **2**.

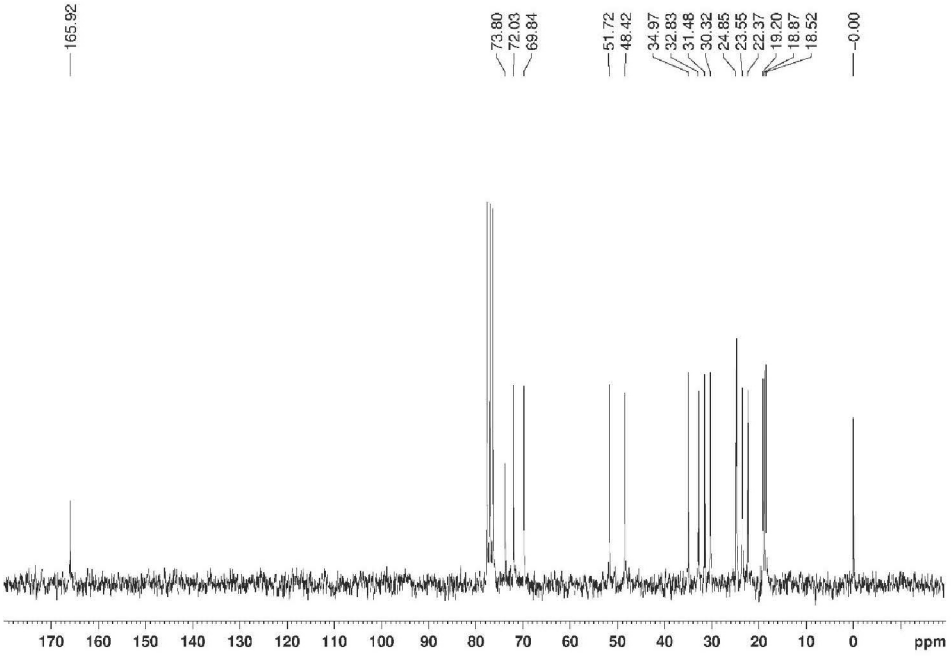

Figure S6. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of **2**.

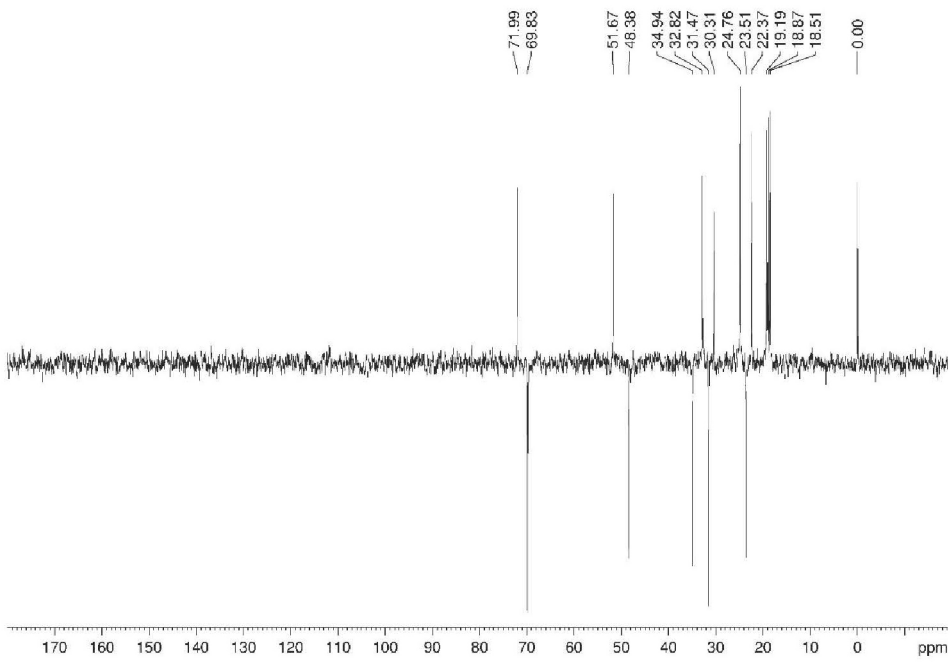

Figure S7. DEPT 135 NMR spectrum (50 MHz, $CDCl_3$) of **2**.

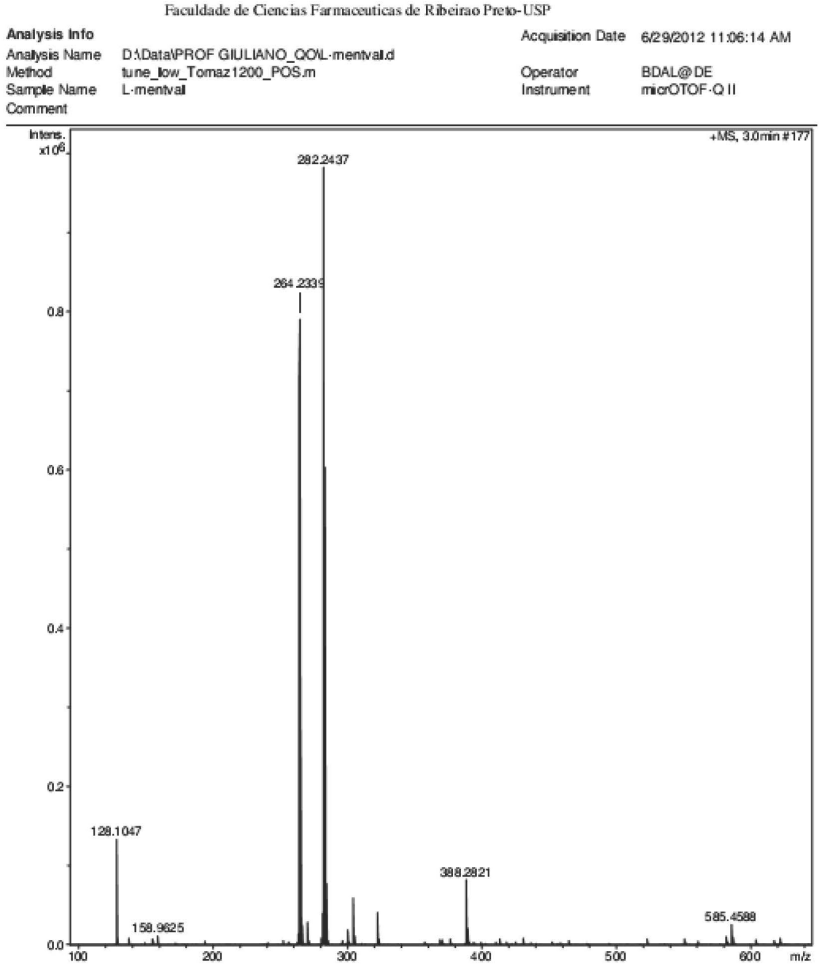

Figure S8. HRMS (ESI-TOF) *m/z* $[M + H]^+$ for $C_{17}H_{32}NO_2$ of **2**, calcd. 282.2428, observed 282.2437.

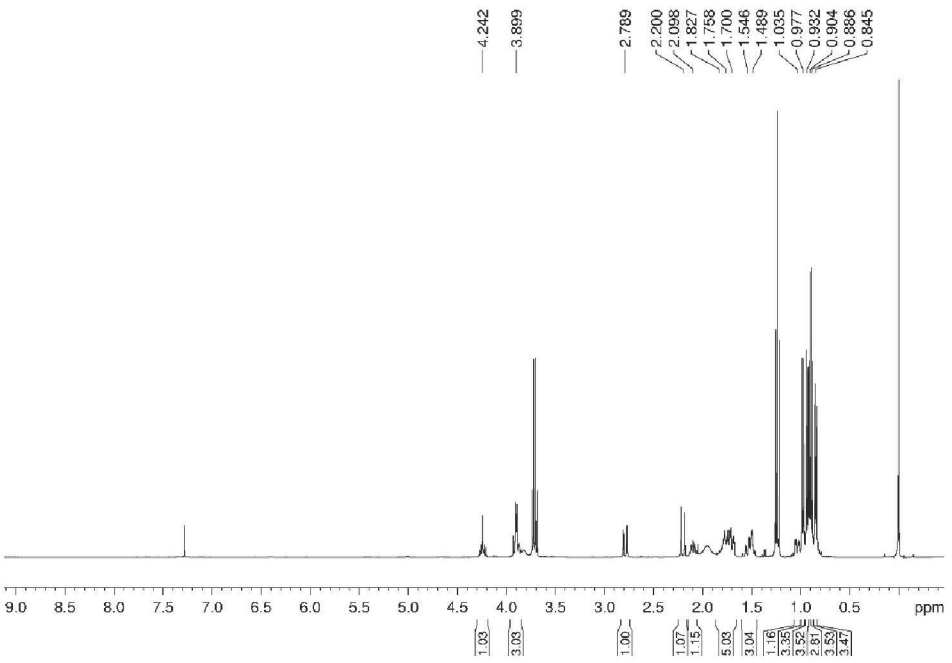

Figure S9. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of **3**.

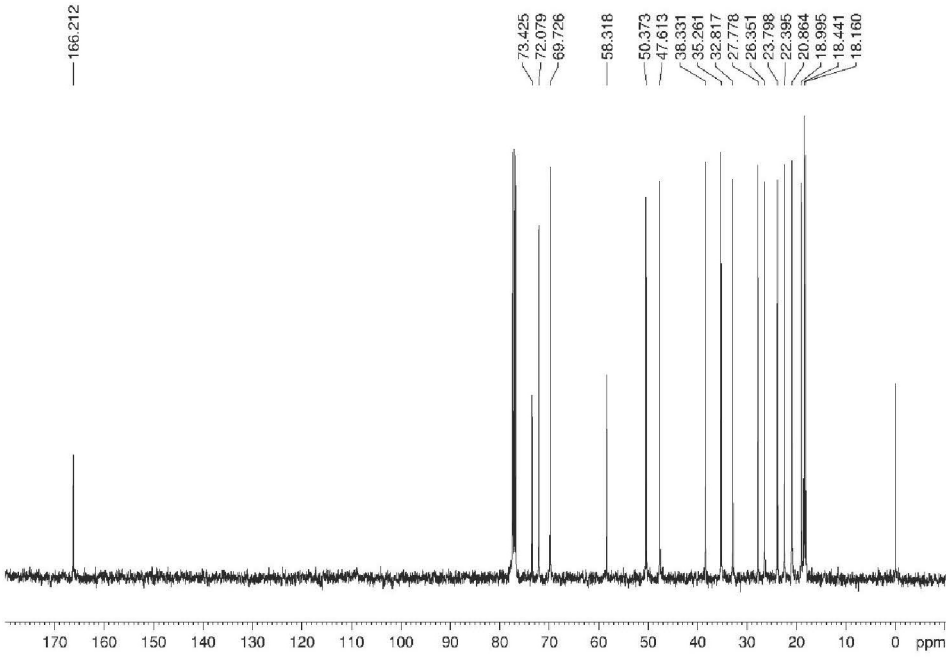

Figure S10. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of **3**.

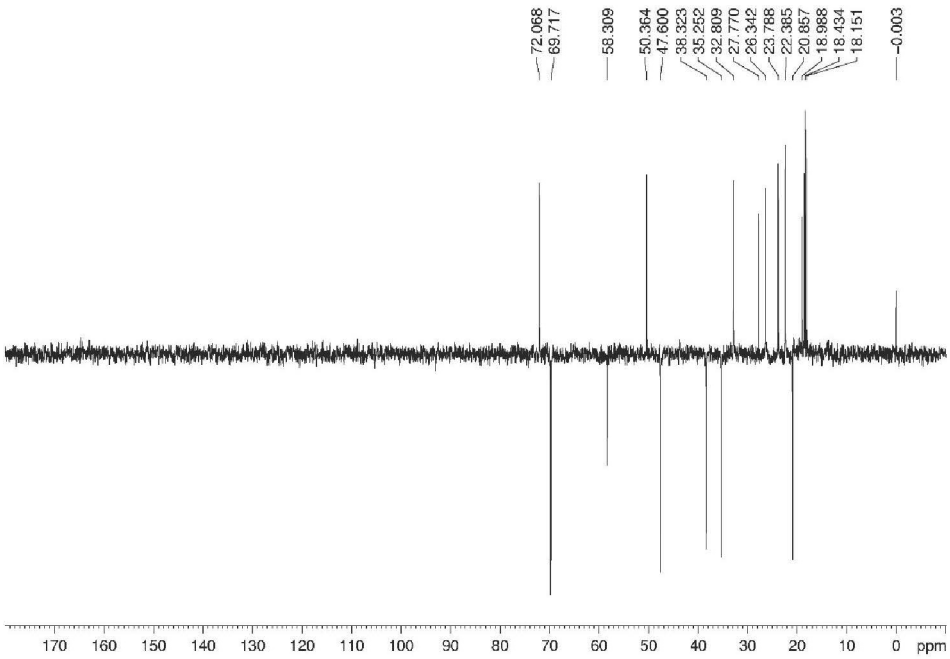

Figure S11. DEPT 135 NMR spectrum (50 MHz, $CDCl_3$) of **3**.

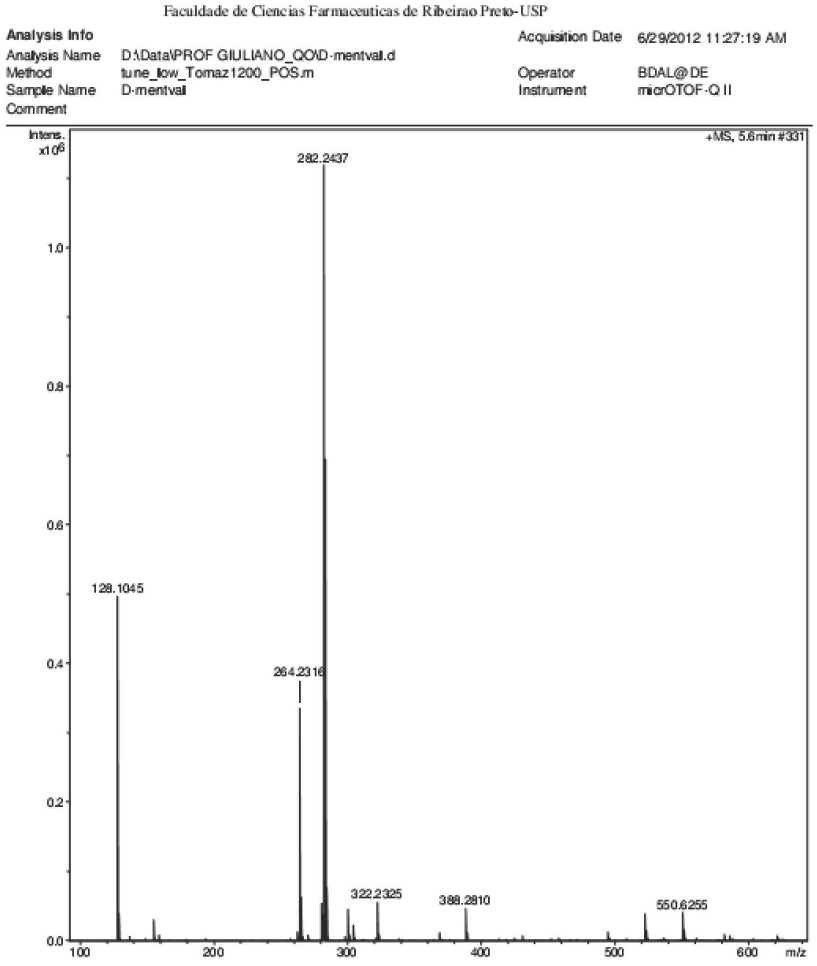

Figure S12. HRMS (ESI-TOF) *m/z* $[M + H]^+$ for $C_{17}H_{32}NO_2$ of **3**, calcd. 282.2428, observed 282.2437.

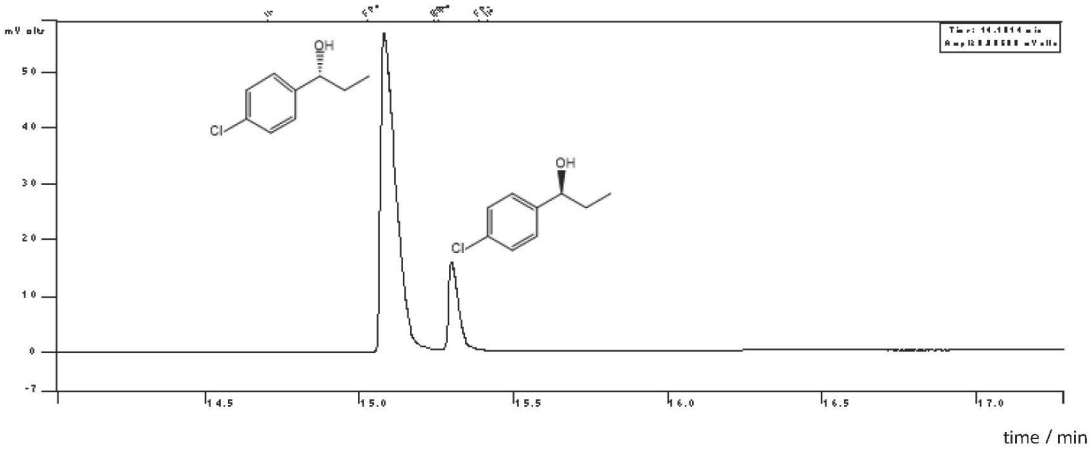

Figure S13. Chromatogram obtained with a fused silica column coated with Chirasil-Dex CB-β-cyclodextrin (30 m × 0.25 mm × 0.25 μm) showing the area of elution of 1-(4-chlorophenyl)propan-1-ol using ligand 1 as catalyst in the diethylzinc addition.

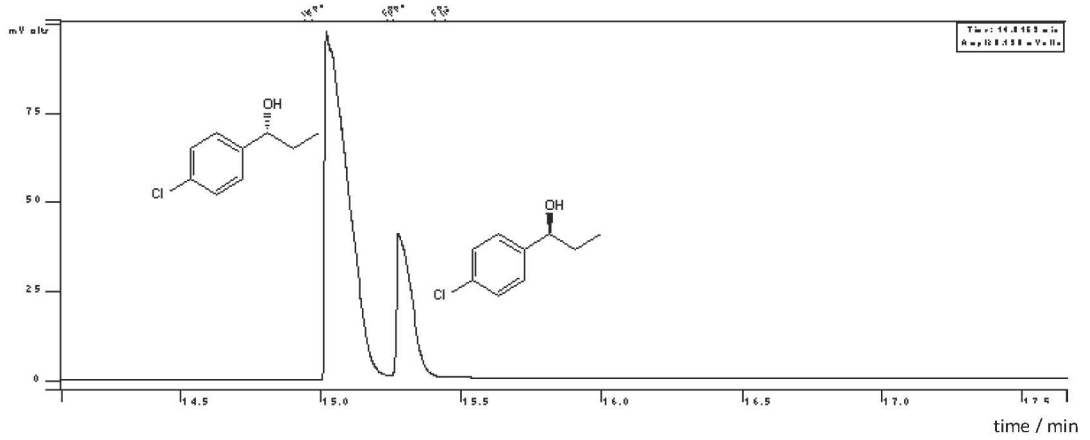

Figure S14. Chromatogram obtained with a fused silica column coated with Chirasil-Dex CB-β-cyclodextrin (30 m × 0.25 mm × 0.25 μm) showing the area of elution of 1-(4-chlorophenyl)propan-1-ol using ligand **2** as catalyst in the diethylzinc addition.

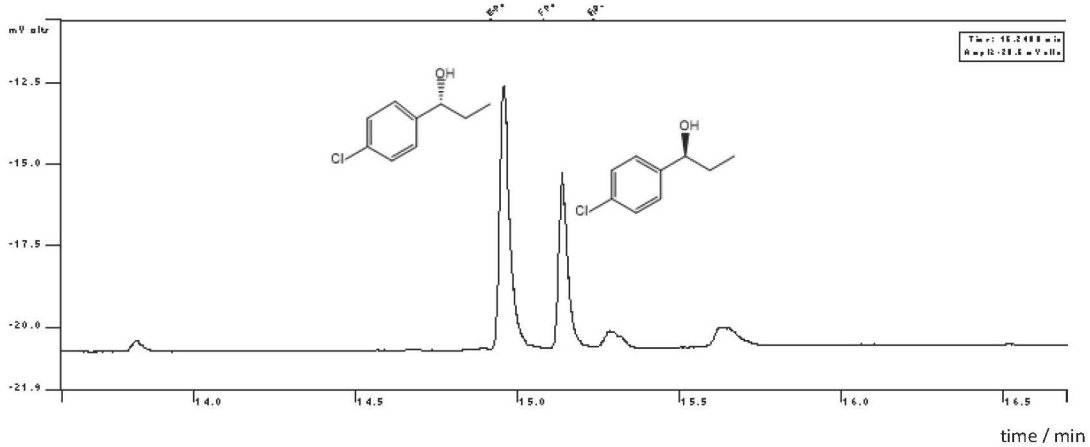

Figure S15. Chromatogram obtained with a fused silica column coated with Chirasil-Dex CB-β-cyclodextrin (30 m × 0.25 mm × 0.25 μm) showing the area of elution of 1-(4-chlorophenyl)propan-1-ol using ligand **3** as catalyst in the diethylzinc addition.

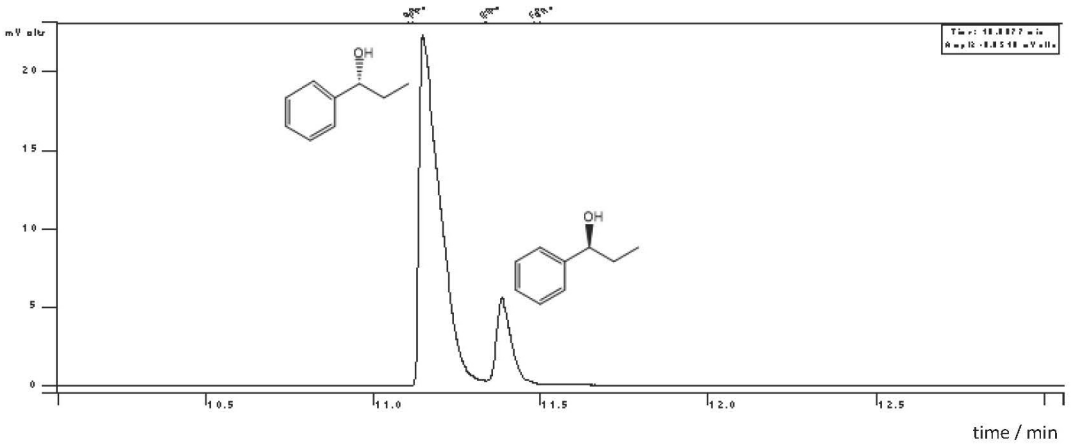

Figure S16. Chromatogram obtained with a fused silica column coated with Chirasil-Dex CB-β-cyclodextrin (30 m × 0.25 mm × 0.25 μm) showing the area of elution of 1-phenylpropan-1-ol using ligand **1** as catalyst in the diethylzinc addition.

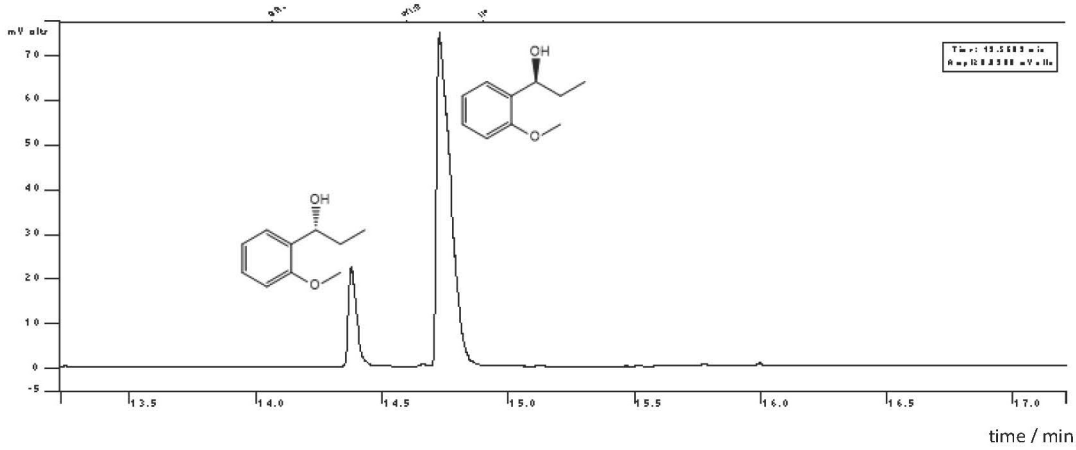

Figure S17. Chromatogram obtained with a fused silica column coated with Chirasil-Dex CB-β-cyclodextrin (30 m × 0.25 mm × 0.25 μm) showing the area of elution 1-(2-methoxyphenyl)propan-1-ol using ligand **1** as catalyst in the diethylzinc addition.

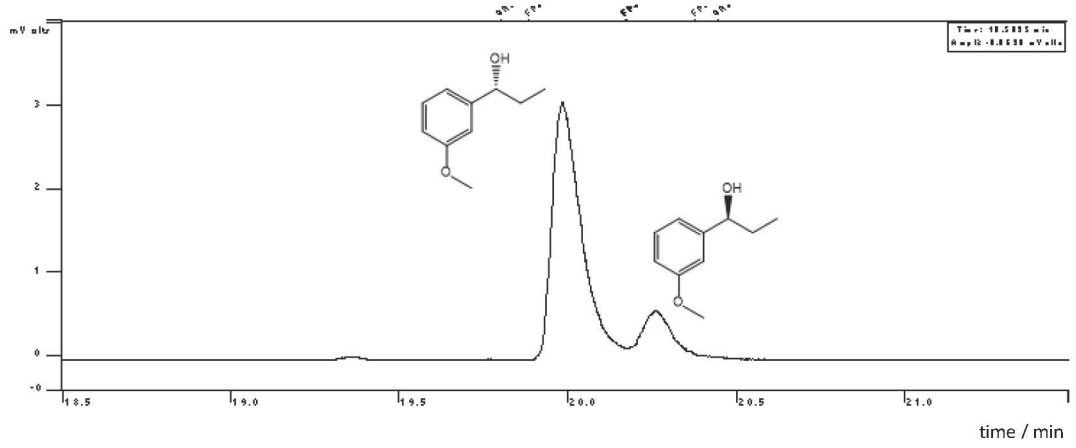

Figure S18. Chromatogram obtained with a fused silica column coated with Chirasil-Dex CB-β-cyclodextrin (30 m × 0.25 mm × 0.25 μm) showing the area of elution of 1-(3-methoxyphenyl)propan-1-ol using ligand **1** as catalyst in the diethylzinc addition.

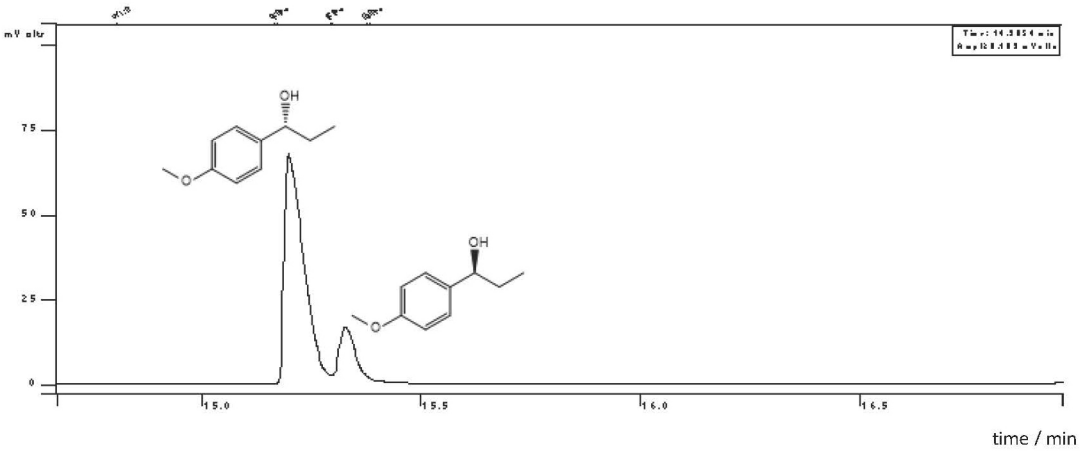

Figure S19. Chromatogram obtained with a fused silica column coated with Chirasil-Dex CB-β-cyclodextrin (30 m × 0.25 mm × 0.25 μm) showing the area of elution of 1-(4-methoxyphenyl)propan-1-ol using ligand **1** as catalyst in the diethylzinc addition.