SUPPORTING INFORMATION

Ni and Pd mediate asymmetric organoboron synthesis with ester functionality at the β position

Vanesa Lillo, ‡ Michael J. Geier, † Stephen A. Westcott, † Elena Fernandez * ‡

Universitat Rovira i Virgili, C/Marcel.lí Domingo s/n. 43005 Tarragona, Spain. Mount Allison University, 63C York Street, Sackville, New Brunswick, E4L 1G8, Canada

mariaelena.fernandez@urv.cat

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All reactions and manipulations were carried out under a nitrogen atmosphere by using Schlenk-type techniques. The solvents were distilled over dehydrating reagents (toluene was distilled over Na using benzophenone as dryness indicator), and were deoxygenated before use. Toluene was stored over slices of sodium. Bis(pinacolato)diboron was used as purchased from Lancaster. (S)-QUINAP was provided by Across. (R)-(S)-Mandyphos, (R)-(S)-Josiphos, (R)-Ph-MeOBiphep, (R)-(R)-Walphos and (R)-(S)-
Taniaphos were supplied by Solvias. The α,β-unsaturated esters and the Ni(cod)$_2$, NiCl$_2$, Pd$_2$(dba)$_3$, and Pd(OAc)$_2$ complexes were used as purchased by Sigma-Aldrich.

NMR spectra were obtained on either a Varian Gemini 300 or a Varian Mercury 400 spectrometer. $^1$H NMR and $^{13}$C NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane, references to the chemical shift of residual solvents resonances. $^{31}$P NMR chemical shifts are reported in ppm (δ) relative to H$_3$PO$_4$. $^{11}$B NMR chemical shifts are reported in ppm (δ) relative to BF$_3$(CH$_3$)$_2$O. HPLC-MS equipped with chiral column Chiracel OD-H.

**Experimental procedure for the metal-catalyzed asymmetric β-boration of α,β-unsaturated esters with bis(pinacolato)diboron**

Ni(cod)$_2$ or NiCl$_2$ or Pd$_2$(dba)$_3$ or Pd(OAc)$_2$ complexes (0.025 mmol of metal) and diphosphine (0.025 mmol) were placed in a schlenck and dissolved with toluene (3 mL) under nitrogen. The suspension was stirred for 10 minutes and Cs$_2$CO$_3$ (244 mg, 0.75 mmol) was added. Afterwards, a solution of alkyl (E)-crotonate, (0.5 mmol of methyl (E)-crotonate, or ethyl (E) crotonate or i-butyl (E)-crotonate) and bis(pinacolato)diboron (191 mg, 0.75 mmol) in toluene (2 mL) was then added. Finally MeOH (0.25 mL) and water (14 mL, 0.75 mmol) were added, and the mixture was allowed to stir at room temperature for 4h. The resulting mixture was poured into water (10 mL) and the product was extracted with hexane/ethyl acetate (20:1). The combined organic layer was dried over sodium sulphate, and concentrated in vacuo. Silica gel column purification (hexane: ethyl acetate = 40:1) have the alkyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate in 80% for methyl derivative, 75% for ethyl derivative and 77% for i-butyl derivative.

**The oxidation protocol.** A solution of sodium perborate (2.5 mmol) in THF/water (1/1, 4 mL), was added to the reaction mixture of the β-boration before product purification. The mixture was stirred vigorously during 4h. After this time, it was quenched with a saturate solution of NaCl and then...
extracted into AcOEt (3 x 20ml). The organic phase was dried over MgSO₄, followed by evaporation under reduced pressure to remove the solvent. The methyl 3-hydroxybutanoate was purified with hexane/ethyl acetate (5:1) as an eluent in 57% yield. To determine the e.e. values of the β-alcohol it was analyzed in HPLC-MS equipped with chiral column Chiracel OD-H.

**The acylation protocol.** A solution of 3mL of acetic anhydride and 5 mL of acetic acid in 25 mL of CHCl₃, were added to ethyl 3-hydroxybutanoate and ethyl 3-hydroxybutanoate products. The reaction was stirring overnight at 50ºC. The next day the mixture was extracted with AcOEt (3 x 20ml). The organic phase was dried over MgSO₄, followed by evaporation under reduced pressure to remove the solvent. The solution was analyzed in the G.C.-MS equipped with chiral column β-cyclodex to determine the e.e. values.

**Characterization data for products:** Boronates, alcohols and acetylated products are known products,¹⁻⁵ but related data are included in this section.

![Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate](image.png)

**Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate:** NMR ¹H (400 MHz, CDCl₃) = δ 3.8 (s, 3H), 2.4 (dd, J=16.4 Hz, J=7.6 Hz, 1H), 2.3 (dd, J=16.3, 8.7, 1H), 1.4 (q, J=7.2 Hz, 1H), 1.2 (m, 12H), 1.0 (d, J=7.2 Hz, 3H). ¹³C NMR (100,62 MHz, CDCl₃) = 173.6, 82.4, 61.4, 39.5, 25.1, 25.0, 15.8, 13.8(C-B).
**Ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate:** $^1$H NMR (300 MHz, CDCl$_3$) = $\delta$ 4.12 (q, $J = 7.2$ Hz, 2H), 2.43 (dd, $J = 16.3$, 7.6 Hz, 1H), 2.36 (dd, $J = 16.3$, 6.6 Hz, 1H), 1.41–1.34 (m, 1H), 1.27–1.22 (m, 15H), 1.00 (d, $J = 7.5$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) = 173.9, 83.4, 60.4, 38.0, 25.1, 25.0, 15.5, 14.7, 13.8(C-B).

**Isobutyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate:** NMR $^1$H (400 MHz, CDCl$_3$) = $\delta$ 3.8 (dd, $J = 6.5$, 3.6 Hz, 2H), 2.4 (dd, $J = 16.8$ Hz, $J = 7.6$ Hz, 1H), 2.3(dd, $J = 16.3$, 6.9Hz, 1H), 1.8 (m, 1H), 1.4 (q, $J = 7.2$ Hz, 1H), 1.2 (m, 12H), 1.0 (d, $J = 7.2$ Hz, 3H), 0.9 (d, $J = 6.8$, 6H).

**Methyl 3-hydroxybutanoate:** $^1$H NMR (CDCl$_3$): 4.21 (m, 1H), 3.72 (s, 3H), 2.8 (br, 1H), 2.51 (dd, $J = 3.8$Hz, 16.5Hz, 1H), 2.43 (dd, $J = 7.4$Hz, 16.5Hz, 1H), 1.24 (d, $J = 6.3$Hz, 3H). Enantiomeric excess were determinated by HPLC-TOF/MS; Chiralcel OD-H, $R_T = 15.6$min ($R$), 11.9 ($S$)

**Ethyl 3-hydroxybutanoate:** $^1$H NMR (400 MHz, CDCl$_3$) = $\delta$ 4.06-4.22 (m, 3H), 3.22 (bs, 1H), 2.22-2.48 (m,2H), 1.23 (d, $J = 6.2$ Hz, 3H), 1.17 (d, $J = 7$ Hz, 3H). $^{13}$C NMR (100,62 MHz, CDCl$_3$) = 172.9, 64.2, 60.6, 42.7, 22.3, 14.0

**Isobutyl 3-hydroxybutanoate:** $^1$H NMR (400 MHz, CDCl$_3$) = $\delta$ 4.06-4.19 (m, 1H), 3.84 (d, $J = 6.7$ Hz, 2H), 3.22 (bs, 1H), 2.31-2.52 (m, 2H) 1.82-1.98 (m, 1H), 1.18 (d, $J = 6.3$ Hz, 3H), 0.88 (d, $J = 6.7$ Hz, 6H)
Ethyl 3-acetoxybutanoate $^1$H NMR (CDCl$_3$): 5.30-5.20 (m, 1H), 3.60 (q, J = 7.28Hz, 2H), 2.57 (dd, J = 7.4Hz, 15.4 Hz, 1H), 2.54 (dd, J = 8.0Hz, 15.4Hz, 1H), 2.01 (s, 3H), 1.29 (t, J = 7.2Hz, 3H), 1.22 (d, J = 7.4Hz, 3H). Enantiomeric excess were determinated by GC; β-DEX 120, R$_t$= 16.1min (S), 15.2min (R)

Isobutyl 3-acetoxybutanoate $^1$H NMR (CDCl$_3$): 5.31-5.19 (m,1H), 3.85 (d, J = 6.6Hz, 2H), 2.56 (dd, J = 7.5Hz, 15.5 Hz, 1H), 2.54 (dd, J = 5.6Hz, 15.5Hz, 1H), 1.99 (s, 3 H), 1.95-1.82 (m, 1H), 1.28 (d, J = 6.3Hz, 3H), 0.90 (d, J = 6.7Hz, 6H). Enantiomeric excess were determinated by GC; β-DEX 120, R$_t$= 47.3min (S), 43.6min (R).

References
Qualitative Analysis Report

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