SUPPORTING INFORMATION

The selective catalytic formation of β-boryl aldehydes through a base-free approach

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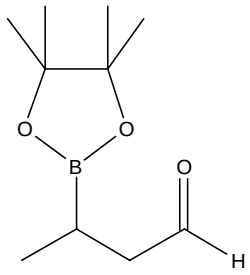
General. All reactions and manipulations were carried out under an atmosphere of dry nitrogen, and the necessary organic solvents were dried, distilled and degassed before use. Bis(pinacolato)diboron was used as purchased from Lancaster. The rest of reagents were purchased from SigmaAldrich. NMR spectra were recorded on Varian Gemini 300 and Varian Mercury 400. Chemical shifts were reported relative to tetramethylsilane for ^{1}H, 85% H_3PO_4 for ^{31}P and BF_3·ether for ^{11}B.

Typical catalytic β-boration of α,β-unsaturated aldehydes with base: Bis(pinacolato)diboron (1.1 eq.) was added to a solution of the catalyst (2 mol%) and base (3 mol%) in tetrahydrofurane (2 mL) under nitrogen. The solution was stirred for 5 minutes and the substrate (0.05 mmol) was then added with 2mL of MeOH. The mixture was stirred for 6 hours at room temperature. The products obtained were analyzed by ^{1}H NMR spectroscopy to determine the degree of conversion and the nature of the reaction products. Purification was carried out by silica gel chromatography (8:1=ether:ethyl acetate).

Typical catalytic β-boration of α,β-unsaturated aldehydes without base: Bis(pinacolato)diboron (1.1 eq.) was added to a solution of the catalyst IPrCuOR (OR= OMe, O^{t}Bu), (2 mol%) in tetrahydrofurane (2 mL) under nitrogen. The solution was stirred for 5 minutes and the substrate (0.05 mmol) was then added with 2mL of MeOH. The mixture was stirred for 1 hour at 90ºC. The products obtained were analyzed by ^{1}H NMR spectroscopy to determine the degree of conversion and

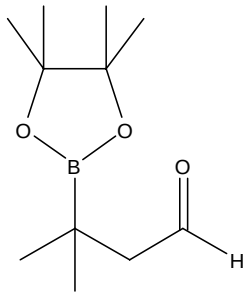
the nature of the reaction products. Purification was carried out by silica gel chromatography (8:1=ether:ethyl acetate).

Characterization of boryl products.



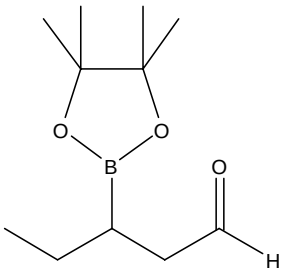
^{1}H NMR (300 MHz, $CDCl_3$) = δ 9.75 (s, 1H), 2.64-2.45 (m, 2H), 1.33 (m, 1H), 1.20 (s, 12H), 1.02 (d, *J* = 7.5 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) = δ 202.8, 83.3, 47.9, 25.2, 24.9, 14.4. ^{11}B NMR (96.27 MHz, $CDCl_3$) = δ 33.4

MS: M^+= 198; M^+-CH_3=183, M^+-CH_2CHO=155, M^+-CH_3-CH_2CHO= 140



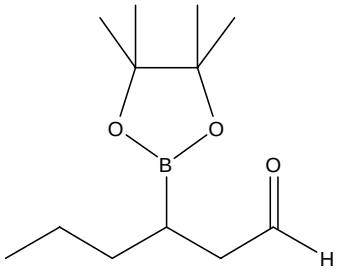
^{1}H NMR (300 MHz, $CDCl_3$) = δ 9.72 (s, 1H), 2.45 (s, 2H), 1.23 (s, 12H), 0.98 (s, 6H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) = δ 203.0, 83.5, 45.2, 29.9, 29.3, 28.6, 24.7. ^{11}B NMR (96.27 MHz, $CDCl_3$) = δ (96,27 MHz, $CDCl_3$)=34.1

MS: M^+=212; M^+-CH_3=197; M^+-CH_2CHO=169; M^+-CH_3CH_2CHO=154



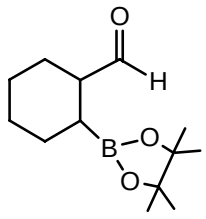
^{1}H NMR (300 MHz, $CDCl_3$) = δ 9.76 (s, 1H), 2.63-2.48 (m, 2H), 1.53-1.20 (m, 3H), 1.23 (s, 6H), 1.22 (s, 6H), 0.92 (t, *J*=7.6, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) = δ 203.2, 83.4, 45.8, 24.9, 24.8, 23.6, 13.3. ^{11}B NMR (96.27 MHz, $CDCl_3$) = δ 33.2

MS: M^+=212; M^+-CH_3=197; M^+-CH_2CH_3=183; M^+-CH_2CHO=169; M^+-CH_3CH_2CHO=154



^{1}H NMR (300 MHz, $CDCl_3$) = δ 9.75 (s, 1H), 2.61-2.40 (m, 2H), 1.46-1.25 (m, 5H), 1.25 (s, 6H), 1.24 (s, 6H), 0.88 (t, *J*=7.6, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) = δ 203.1, 83.4, 46.0, 32.9, 24.9, 24.8, 22.1, 11.4. ^{11}B NMR (96.27 MHz, $CDCl_3$) = δ 33.6

MS: M^+=226; M^+-CH_3=211; M^+-CH_2CH_3=197; M^+-CH_2CHO=183; M^+-CH_3CH_2CHO=168



^{1}H NMR (300 MHz, $CDCl_3$) = δ 9.65 (s, 1H), 2.84 (dt, 1H, C*H*-CHO), 1.65-1.25 (m, 9H), 1.15 (s, 6H), 1.14 (s, 6H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) = δ 201.1, 86.4, 43.0, 32.6, 31.8, 24.9, 24.8, 22.1, 21.4. ^{11}B NMR (96.27 MHz, $CDCl_3$) = δ 33.5

Synthesis of IPrCuOMe: In a glove box a 100 mL Schenk flask was charged with 488.5 mg (1 mmol) of IPrCuCl and 15 mL MeOH anhydrus and then 1.25 equvi of NaOMe was added. The resulting mixture was stirred at room temperature for 45 min. The solvent was reduced to dryness under vacuum and 20 ml of benzene was added to extract the compound. The colorless solution was filtered and the solvent was removed under vacuum to give an off-white solid. The complex was washed with hexane and dried under vacuum. Yield: 378 mg (78 %).

Spectroscopic data for the copper complex IPrCu-OMe:

^{1}H NMR (400 MHz, C_6D_6) = δ 1.10 (d, *J*= 6.9 Hz, 12H, -CH(C*H*$_3$)$_2$), 1.38 (d, *J*= 6.9 Hz, 12H, -CH(C*H*$_3$)$_2$), 2.58 (sep, 4H, *J*= 6.9 Hz, -C*H*(CH$_3$)$_2$), 3.79 (bs, 3H, -OC*H*$_3$), 6.21 (bs, 2H, NC*H*), 7.05 (d, *J*= 7.7 Hz, 4H, *meta*-C*H*), 7.18 (t, 2H, *J*= 7.7 Hz, *para*-C*H*). $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6) = δ 24.1 (4C, -CH(*C*H$_3$)$_2$), 25.2 (4C, -CH(*C*H$_3$)$_2$), 29.3 (2C, -*C*H(CH$_3$)$_2$), 51.3 (-O*C*H$_3$), 113.0 (2C, N*C*H), 123.1, 130.9, 134.1, 146.1 (*C* arom.), 199.7 (C, N*C*N).

Note: The copper complex is highly sensitive to water and we have been unable to obtain satisfactory elemental for the complex