Supporting Information

Nickel-catalyzed Alkylation of Aldehydes with Trialkylboranes

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Instrumentation and Materials

^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on Varian UNITY INOVA 500 and Mercury 300 spectrometers. ^1H NMR and ^{13}C NMR spectra were obtained in CDCl_3 with tetramethylsilane as an internal standard. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel (Wakogel 200 mesh) was used for column chromatography. The analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene was dried over slices of sodium and degassed before use. Et_3B and $n\text{-Bu}_3\text{B}$ were purchased from Aldrich. 9-Borabicyclo[3.3.1]nonane (9-BBN) and $t\text{-Bu}_3\text{P}$ were obtained from Wako. Et_3B and $t\text{-Bu}_3\text{P}$ were diluted to prepare 1.0 M hexane solutions, which were stored strictly under argon. Bis(1,5-cyclooctadiene)nickel was available from Strem.

Experimental Section

General Procedure for Ethylation of Benzaldehyde (**1a**)

With a glovebox, Ni(cod)₂ (6.9 mg, 0.025 mmol) was placed in a reaction flask. Toluene (3 mL), ^tBu₃P (1.0 M hexane solution, 0.05 mL, 0.05 mmol) and a solution of Cp*allyl (8.8 mg, 0.05 mmol) in toluene (2 mL) were added dropwise. The solution was stirred for 10 min at 0 °C. Benzaldehyde (**1a**, 53 mg, 0.5 mmol) and Et₃B (1.0 M hexane solution, 1.0 mL, 1.0 mmol) were then added. After being stirred for 24 h at the same temperature, the resulting mixture was poured into 3.0 M hydrochloric acid (10 mL). Extraction with hexane/ethyl acetate (5:1) followed by silica gel column purification afforded 1-phenyl-1-propanol (**3a**, 63 mg, 0.47 mmol) in 93% yield.

General Procedure for Butylation of Benzaldehyde (**1a**)

With a glovebox, Ni(cod)₂ (11 mg, 0.040 mmol) and Cs₂CO₃ (489 mg, 1.5 mmol) were placed in a reaction flask. Toluene (10 mL) and ^tBu₃P (1.0 M hexane solution, 0.096 mL, 0.096 mmol) were added. The resulting suspension was stirred for 10 min at 0 °C. Benzaldehyde (**1a**, 53 mg, 0.5 mmol) and ⁿBu₃B (1.0 M THF solution, 1.5 mL, 1.5 mmol) were then added and the mixture was allowed to warm to room temperature. After being stirred for 24 h at the same temperature, the reaction was quenched with 1.0 M hydrochloric acid (10 mL). Extraction with hexane/ethyl acetate (5:1) and concentration gave the crude product. The crude product obtained was oxidized with treatment of aqueous H₂O₂ (30%, 0.8 mL) and aqueous NaOH (6.0 M, 0.5 mL) in EtOH/THF (1.2 mL:2 mL) at reflux for 1 h. After aqueous sodium thiosulfate was added, extraction and purification provided 1-phenyl-1-pentanol (**3b**, 71 mg, 0.43 mmol) in 86% yield.

Characterization Data.

^1H NMR spectral data for all products are shown below. Except for **3k** and **3l**, all compounds are known.

11-Hydroxy-2-tridecanone (3k): IR (NUJOL) 3261, 2849, 1672, 1707, 1464, 1364, 1205, 1169, 1132, 1115, 989, 943, 868, 719 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.51–3.55 (m, 1H), 2.43 (t, $J = 7.5$ Hz, 2H), 2.14 (s, 3H), 1.40–1.59 (m, 10H), 1.30 (bs, 7H), 0.95 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 9.87, 23.82, 25.60, 29.13, 29.31, 29.40, 29.61, 29.86, 30.14, 36.91, 43.79, 73.32, 209.43.

Methyl 6-hydroxyoctanoate (3l): IR (neat) 3433, 2937, 287, 1740, 1460, 1439, 1366, 1200, 1173, 111, 1097, 968 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.68 (s, 3H), 3.52–3.57 (m, 1H), 2.34 (t, $J = 7.5$ Hz, 2H), 1.62–1.70 (m, 2H), 1.36–1.55 (m, 7H), 0.95 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 9.86, 24.88, 25.19, 30.18, 34.00, 36.46, 51.49, 73.00, 174. Found: C, 61.97; H, 10.15%. Calcd for $\text{C}_9\text{H}_{18}\text{O}_3$: C, 62.04; H, 10.41%.