Supporting Information

Ni- or Cu-Catalyzed Cross-Coupling Reaction of Alkyl Fluorides with Grignard Reagents

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Typical Experimental Procedures and Analytical Data of Products.

n-Undecane

Into a 20 mL pyrex glass vessel were placed 1-fluorooctane (264 mg, 2 mmol) and ⁿPrMgBr (0.93 M in THF, 2.8 mL, 2.6 mmol) under N₂. The system was closed and cooled to -78 °C. Then 1,3-butadiene (4.48 mL at 20 °C under 1 atm, 0.2 mmol) was introduced through a septum using a syringe into the vessel, which showed slightly reduced pressure. The system was opened to an atmospheric pressure of N₂ and a catalytic amount of CuCl₂ (8.0 mg, 0.06 mmol) was added. The system was closed again, warmed to 25 °C and stirred for 6 h. A saturated aqueous NH₄Cl solution (10 mL) was added, and the product was extracted with ether (10 mL). The organic layer was dried over MgSO₄, and evaporated to give n-undecane (94% GC yield).

1,1-Diphenyl-1-nonene (1).

A mixture of 1,1-diphenyl-6-fluoro-1-hexene (254 mg, 1 mmol) and ⁿPrMgBr (0.93 M in THF, 1.4 mL, 1.3 mmol) was cooled to -78 °C and 1,3-butadiene (2.24 mL at 20 °C under 1 atm, 0.1 mmol) was introduced. After adding CuCl₂ (4.0 mg, 0.03 mmol) at -78 °C, the solution was stirred for 6 h at 25 °C. Similar workup as mentioned above afforded a colorless product (98% NMR yield). IR (neat): 2924, 2853, 1598, 1493, 1443, 1073, 1029, 761, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.38-7.16 (m, 10H), 6.08 (t, *J* = 7.5 Hz, 1H), 2.10 (dt, *J* = 7.3, 7.5 Hz, 2H), 1.52-1.39 (m, 2H), 1.28-1.23 (m, 8H), 0.86 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 142.7, 141.9, 141.1, 140.1, 130.2, 129.8, 127.9, 127.8, 127.0, 126.6, 126.5, 31.9, 30.1, 29.9, 29.3, 22.8, 14.3; MS (EI) *m/z* (relative intensity, %) 278 (M⁺, 73), 193 (100), 180 (57), 115 (36), 91 (17); HRMS calcd for C₂₁H₂₆ 278.2034, found 278.2030; Anal. Calcd for: C, 90.59; H, 9.41. Found: C, 90.37; H, 9.32.

1,1-Diphenyl-6-fluoro-1-hexene

A THF solution (20 mL) of *p*-TsF (*p*-toluenesulfonyl fluoride, 1.741 g, 10 mmol) and 1,1-diphenyl-1-hexene-6-ol¹ (1.261 g, 5 mmol) was added to a THF solution of TBAF·3H₂O (tetrabutylammonium fluoride, 1 M, 15 mL, 15 mmol) at 25 °C in the presence of molecular sieves

4A (12 g).² After stirring at reflux for 17 h, the reaction mixture was filtered and the residue was washed with EtOAc. The combined washings were evaporated to give a colorless oil. Purification by silica gel column chromatography with hexane/ether 98:2 afforded 430.2 mg (34%) of 1,1-diphenyl-6-fluoro-1-hexene. IR (neat): 2960, 2860, 1597, 1494, 1443, 1073, 1031 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.32-7.08 (m, 10H), 6.07 (t, $J = 7.5$ Hz, 1H), 4.39 (dt, $J_{\text{H-F}} = 47.1$ Hz, $J_{\text{H-H}} = 6.0$ Hz, 2H), 2.16 (q, $J = 7.5$ Hz, 2H), 2.19-1.52 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 142.4, 142.0, 140.0, 129.7, 129.1, 128.0, 127.9, 127.0, 126.8, 126.7, 83.9(d, $^1J_{\text{C-F}} = 163$ Hz), 30.1(d, $^2J_{\text{C-F}} = 20.0$ Hz), 29.3, 25.6; MS (EI) m/z (relative intensity, %) 254 (M^+ , 52), 193 (100), 178 (29), 115 (53), 91 (18); HRMS calcd for $\text{C}_{18}\text{H}_{19}\text{F}$ 254.1471, found 254.1469; Anal. Calcd for $\text{C}_{18}\text{H}_{19}\text{F}$: C, 85.00; H, 7.53. Found: C, 84.73; H, 7.54.

(1) Biellmann, J. F.; Ducep, J. B.; Schmitt, J. L. *Tetrahedron* **1976**, 32, 1061-1064.

(2) Shimizu, M.; Nakahara, Y.; Yoshioka, H. *Tetrahedron Lett.* **1985**, 26, 4207-4210.