

Optimization of Palladium-Catalyzed Polycyclizations: Suppression of Competing Hydride Transfer from Tertiary Amines with Dabco™ and an Unexpected Hydride Transfer from 1,4-Dioxane.

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Supporting Material

A typical experimental procedure is as follows: The catalyst solution was prepared by dissolving Pd₂(dba)₃ (2 mg, 0.0011 mmol) and (*S*)-BINAP (6 mg, 0.01 mmol) in dry toluene (1 mL) and allowed to stir for 30 minutes under argon. Triflate **2** (30 mg, 0.065 mmol) was dissolved in dry toluene (1 mL) and Dabco™ (36 mg, 0.325 mmol) was added. This solution was added to the catalyst solution and placed in a preheated oil bath at 110°C for 3 d under Ar. The solution was cooled to RT and diluted with diethyl ether (10 mL) and filtered through a silica gel plug. The resulting solution was concentrated *in vacuo* and purified by preparative thin layer chromatography (3:1 hexanes:ethyl acetate) to afford a mixture of the monocyclized and dicyclized product (based on GC ratios, monocyclized: 1 mg, 0.0032 mmol, 5%; dicyclized: 16 mg, 0.0512 mmol, 79%). Various solvent systems were attempted but failed to chromatographically separate the monocyclized product from the dicyclized product. Product ratios were determined by GC integration. Response factors for integration of the TIC were based upon ¹H-NMR integration of an identical sample indicating a 1-to-1 response in the TIC between monocyclized product and dicyclized product. **Compound 6**: IR (CHCl₃) 1658, 1552 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) 1.40 (s, 6H), 5.44 (d, J = 1.0 Hz, 1H), 5.90 (d, J = 1.0 Hz, 1H), 7.34-7.60 (m, 8H), 7.72 (s, 1H), 8.35 (ddd, J = 0.64 Hz, 1.50 Hz, 7.82 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) 29.5, 38.6, 119.1, 126.2, 126.4, 126.5, 126.7, 126.8, 126.9, 128.4, 128.6, 128.9, 131.2, 132.7, 139.5, 140.0, 146.7, 151.5, 173.4; MS m/z 314 (86), 299 (100); HRMS C₂₂H₁₈O₂ calculated 314.1306, found 314.1303; MS for D incorporation m/z 315 (80), 300 (100); HRMS for D incorporation C₂₂H₁₇DO₂ calculated 315.1370, found 315.1369. **Compound 8**: IR (CHCl₃) 1651, 1591 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) 1.55 (s, 3H), 2.62-2.76 (m, 1H), 3.15 (dd, J = 6.41 Hz, 16.49 Hz, 1H), 6.25 (dd, J = 2.39 Hz, 6.67 Hz, 1H), 7.34-7.60 (m, 8H), 7.70 (s, 1H), 8.41 (ddd, J=0.60, 1.45, 7.78 Hz, 1H). MS m/z 312 (100), 297 (31), 284 (50), 269 (40); HRMS C₂₂H₁₆O₂ calculated 312.1151, found 312.1124.