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 $Pd_2(dba)_3$ (2 mg, 0.0011 mmol) and (*S*)-BINAP (6 mg, 0.01 mmol) in dry toluene (1 mL) and allowed to stirr 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 ^{1}H-NMR integration of an identical sample indicating a 1-to-1 response in the TIC between monocyclized product and dicyclized product. **Compound 6:** IR ($CHCl_3$) 1658, 1552 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{22}H_{18}O_2$ calculated 314.1306, found 314.1303; MS for D incorporation m/z 315 (80), 300 (100); HRMS for D incorporation $C_{22}H_{17}DO_2$ calculated 315.1370, found 315.1369. **Compound 8:** IR ($CHCl_3$) 1651, 1591 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) 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 $C_{22}H_{16}O_2$ calculated 312.1151, found 312.1124.