

Supplementary Information

for

Palladium Catalyzed Aryl C–H Amination with O₂ via In Situ Formation of Peroxide- Based Oxidant(s) from Dioxane

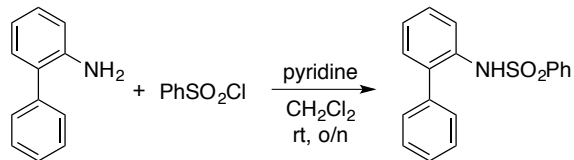
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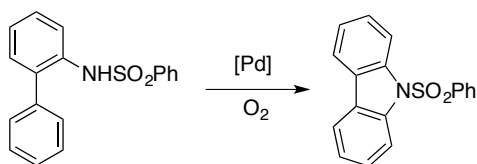
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1. *N*-Benzenesulfonyl-2-aminobiphenyl and carbazole



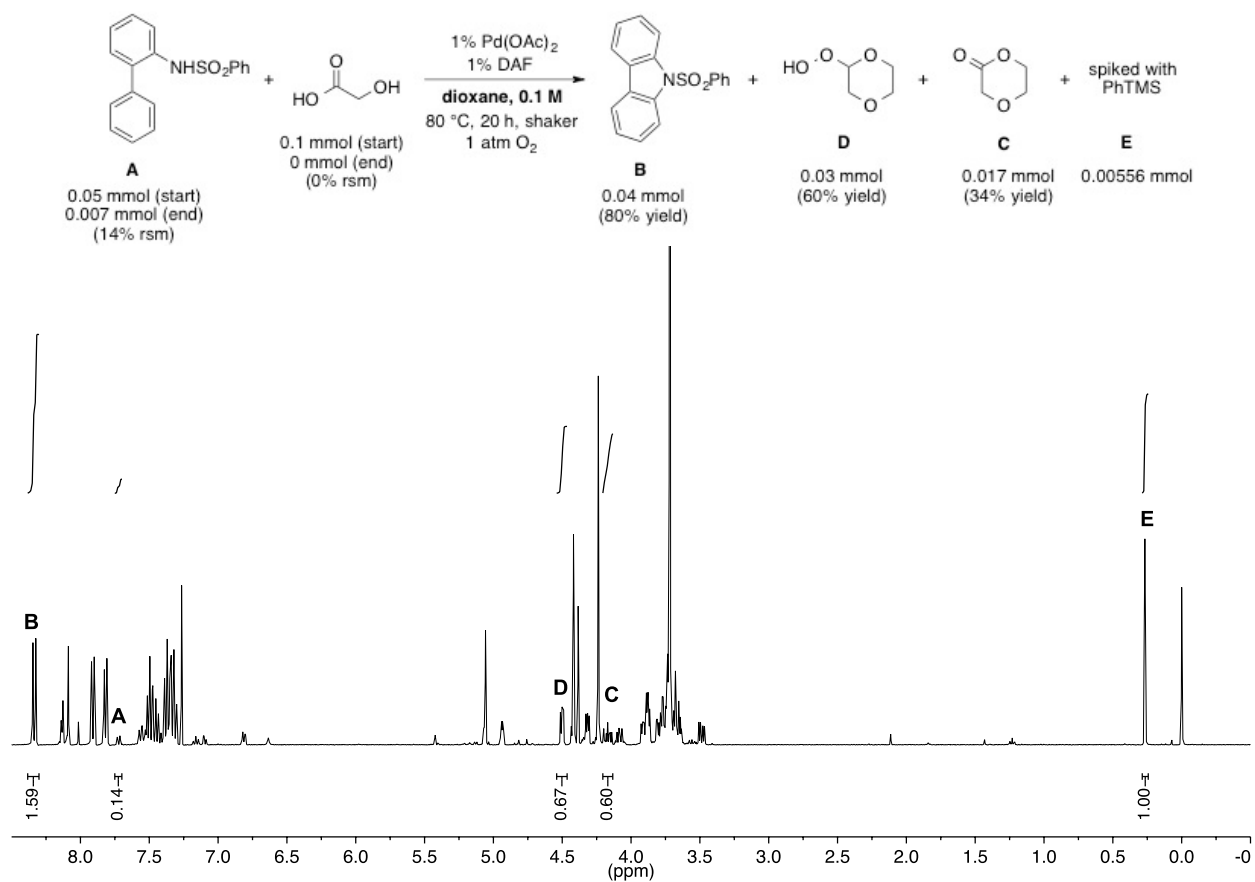
***N*-Benzenesulfonyl-2-aminobiphenyl:** A 250 ml round-bottomed flask was charged with 2-aminobiphenyl (1.5 g, 8.86 mmol, 1 equiv) and dissolved in 88 ml of dichloromethane (0.1 M). Pyridine (3.58 ml, 44.3 mmol, 5 equiv) and benzenesulfonyl chloride (1.71 ml, 13.3 mmol, 1.5 equiv) were added via syringe. The reaction mixture was allowed to stir under air for 16 hours. The reaction mixture was diluted with dichloromethane, washed 3x with water, dried over MgSO₄ and concentrated. Purification on silica with hexanes : ethyl acetate (4:1) afforded the product (2.51 g, 93%) as an off-white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.61 – 7.51 (m, 3H), 7.45 – 7.29 (m, 6H), 7.16 (td, *J* = 7.5, 1.2 Hz, 1H), 7.09 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.81 (dd, *J* = 7.7, 1.8 Hz, 2H), 6.58 (s, 1H).



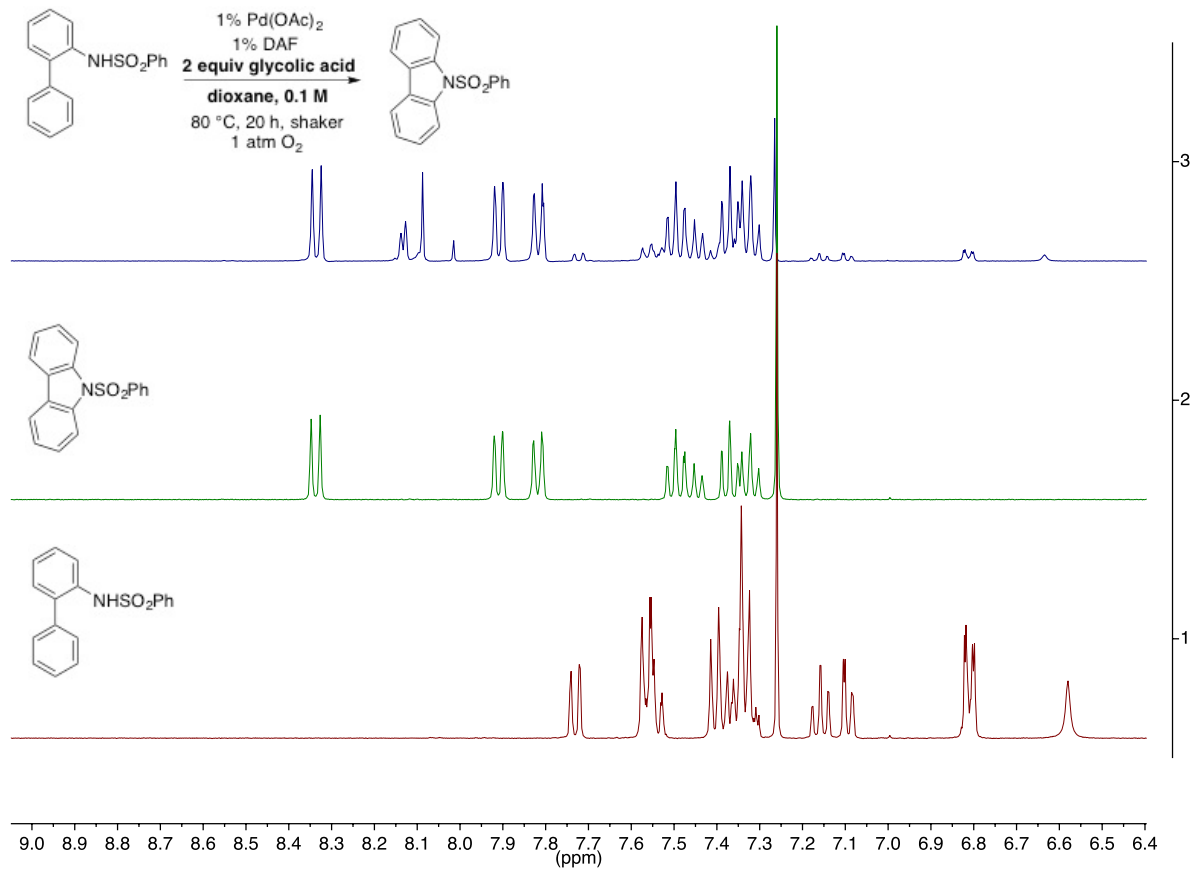
***N*-Benzenesulfonyl-carbazole:** The carbazole was obtained from the palladium catalyzed aerobic oxidation reactions and was isolated as a white solid with purification on silica using a hexanes : ethyl acetate solvent system (5:1). ¹H NMR (400 MHz, CDCl₃) δ 8.34 (dt, *J* = 8.5, 0.8 Hz, 2H), 7.91 (dt, *J* = 7.7, 1.0 Hz, 2H), 7.82 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.50 (ddd, *J* = 8.6, 7.4, 1.3 Hz, 2H), 7.47 – 7.42 (m, 1H), 7.37 (td, *J* = 7.5, 1.0 Hz, 2H), 7.32 (t, *J* = 7.9 Hz, 2H).

2. Typical crude ^1H NMR spectrum and isolation of autoxidation byproducts

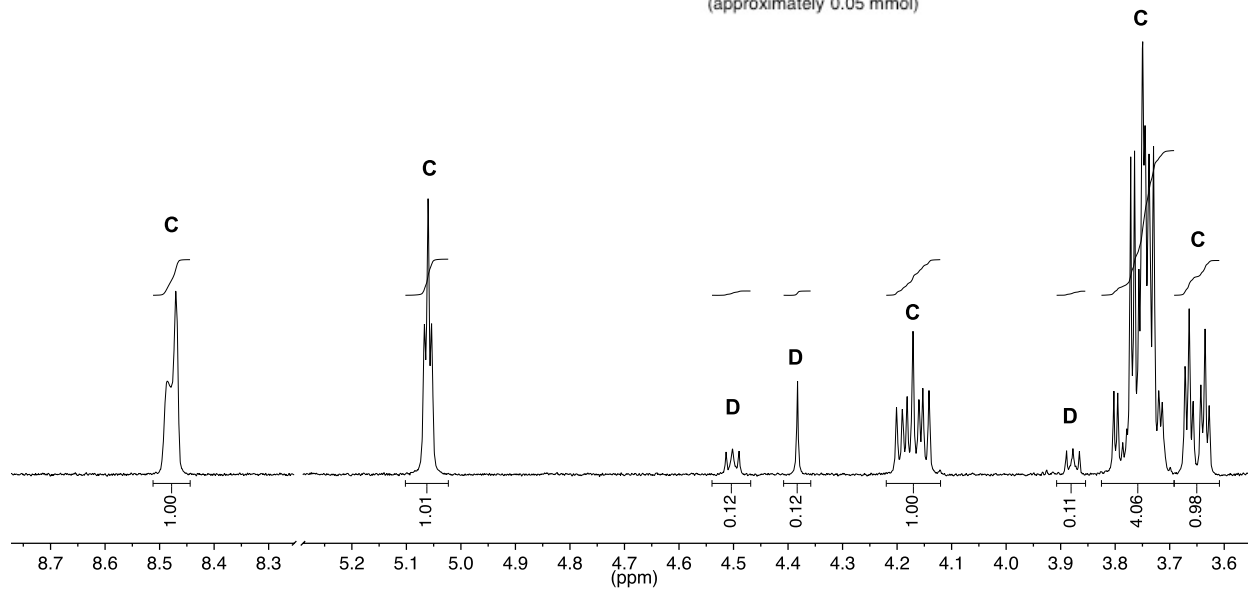
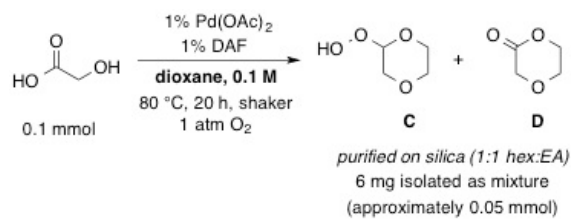
Crude ^1H NMR after the reaction was carried out according to the general procedure above:



Crude ^1H NMR spectrum with comparison to product and starting material spectra:



Isolated 1,4-dioxan-2-hydroperoxide and 1,4-dioxan-2-one:



Crude ^1H NMR spectrum with comparison to 1,4-dioxan-2-hydroperoxide and 1,4-dioxan-2-one:

