

**Supporting Information** for the article: **On the mechanism of palladium-catalyzed coupling of haloaryls to biaryls in water with zinc** / S. Mukhopadhyay *et al.*

**Synthesis of 2b and 2d.** The substituted biphenyls 4,4'-dimethylbiphenyl **2b** and 4,4'-ditrifluoromethylbiphenyl **2d** were similarly prepared. **2b**: isolated yield 51% based on **1b**, mp 119 °C (from CH<sub>2</sub>Cl<sub>2</sub>) (lit.,<sup>18</sup> 120.7-121.5 °C). Found: C, 91.60; H, 7.63. C<sub>14</sub>H<sub>14</sub> requires C, 92.30; H, 7.69%. **2d**: isolated yield 69% based on **1d**, mp 80 °C (from EtOH/H<sub>2</sub>O) (lit.,<sup>19</sup> 93-94.5 °C). Found: C, 57.82; H, 2.90; F, 39.28. C<sub>14</sub>H<sub>8</sub>F<sub>6</sub> requires C, 57.93; H, 2.75; F, 39.31%.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>; Me<sub>4</sub>Si) 7.69 (8H, m, ArH) (lit.,<sup>20</sup> 7.67).

**Experimental procedure for kinetic studies.** Example: 44 mmol **1a**, 45 mmol Zn; 125 mmol NaOH, 5% Pd/C, 1 g (1.0 mol% Pd relative to **1a**), and 1.5 g PEG-400 (8.4 mol% relative to **1a**) were mixed in water (50 ml total reaction volume) at 100 °C in an autoclave. Reaction progress was monitored by GC. The following parameters were studied: (i) initial substrate concentration, using xylene as the diluting organic solvent (3 experiments at 1.76 M,  $k_{\text{obs}} = 3.8 \times 10^{-2} \text{ min}^{-1}$ ,  $r^2 = 0.999$  for 5 observations; 2.0 M,  $k_{\text{obs}} = 3.98 \times 10^{-2} \text{ min}^{-1}$ ,  $r^2 = 0.999$  for 5 observations; and 2.5 M,  $k_{\text{obs}} = 4.3 \times 10^{-2} \text{ min}^{-1}$ ,  $r^2 = 0.997$  for 5 observations); (ii) catalyst loading (5 experiments using 0.25 g of 5% w/v Pd,  $k_{\text{obs}} = 0.33 \times 10^{-2} \text{ min}^{-1}$ ,  $r^2 = 0.999$  for 7 observations; 0.5 g 5% w/v Pd,  $k_{\text{obs}} = 0.75 \times 10^{-2} \text{ min}^{-1}$ ,  $r^2 = 0.973$  for 7 observations; 0.75 g 5% Pd,  $k_{\text{obs}} = 1.46 \times 10^{-2} \text{ min}^{-1}$ ,  $r^2 = 0.88$  for 7 observations; 1.0g of 5% w/v Pd,  $k_{\text{obs}} = 3.67 \times 10^{-2} \text{ min}^{-1}$ ,  $r^2 = 0.996$  for 6 observations); and 1.5 g of 5% w/v Pd,  $k_{\text{obs}} = 4.09 \times 10^{-2} \text{ min}^{-1}$ ,  $r^2 = 0.97$  for 6 observations); (iii) Zn loading (4 experiments using 0.02 mol Zn,  $k_{\text{obs}} = 1.1 \times 10^{-2} \text{ min}^{-1}$ ,  $r^2 = 0.973$  for 5 observations; 0.045 mol,  $k_{\text{obs}} = 3.8 \times 10^{-2} \text{ min}^{-1}$ ,  $r^2 = 0.999$  for 5 observations; 0.05 mol,  $k_{\text{obs}} = 5.7 \times 10^{-2} \text{ min}^{-1}$ ,  $r^2 = 0.97$  for 5 observations; and 0.06 mol,  $k_{\text{obs}} = 8.9 \times 10^{-2} \text{ min}^{-1}$ ,  $r^2 = 0.91$  for 4 observations); and (iv) reaction temperature (4 experiments at 60 °C,  $k_{\text{obs}} = 1.47 \times 10^{-2} \text{ min}^{-1}$ ,  $r^2 = 0.993$  for 7 observations; 80 °C,  $k_{\text{obs}} = 2.48 \times 10^{-2} \text{ min}^{-1}$ ,  $r^2 = 0.998$  for 7 observations; 100 °C,  $k_{\text{obs}} = 3.67 \times 10^{-2} \text{ min}^{-1}$ ,  $r^2 = 0.996$  for 7 observations; and 120 °C,  $k_{\text{obs}} = 8.22 \times 10^{-2} \text{ min}^{-1}$ ,  $r^2 = 0.986$  for 7 observations).

**References:**

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