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_2Cl_2) (lit.,[18] 120.7-121.5 ˚C). Found: C, 91.60; H, 7.63. $C_{14}H_{14}$ requires C, 92.30; H, 7.69%. **2d**: isolated yield 69% based on **1d**, mp 80 ˚C (from EtOH/H_2O) (lit.,[19] 93-94.5 ˚C). Found: C, 57.82; H, 2.90; F, 39.28. $C_{14}H_8F_6$ requires C, 57.93; H, 2.75; F, 39.31%. δ_H ($CDCl_3$; Me_4Si) 7.69 (8H, m, ArH) (lit.,[20] 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, $k_{obs} = 3.8 \times 10^{-2}$ min^{-1}, $r^2 = 0.999$ for 5 observations; 2.0 M, $k_{obs} = 3.98 \times 10^{-2}$ min^{-1}, $r^2 = 0.999$ for 5 observations; and 2.5 M, $k_{obs} = 4.3 \times 10^{-2}$ min^{-1}, $r^2 = 0.997$ for 5 observations); *(ii)* catalyst loading (5 experiments using 0.25 g of 5% w/v Pd, $k_{obs} = 0.33 \times 10^{-2}$ min^{-1}, $r^2 = 0.999$ for 7 observations; 0.5 g 5% w/v Pd, $k_{obs} = 0.75 \times 10^{-2}$ min^{-1}, $r^2 = 0.973$ for 7 observations; 0.75 g 5% Pd, $k_{obs} = 1.46 \times 10^{-2}$ min^{-1}, $r^2 = 0.88$ for 7 observations; 1.0g of 5% w/v Pd, $k_{obs} = 3.67 \times 10^{-2}$ min^{-1}, $r^2 = 0.996$ for 6 observations); and 1.5 g of 5% w/v Pd, $k_{obs} = 4.09 \times 10^{-2}$ min^{-1}, $r^2 = 0.97$ for 6 observations); *(iii)* Zn loading (4 experiments using 0.02 mol Zn, $k_{obs} = 1.1 \times 10^{-2}$ min^{-1}, $r^2 = 0.973$ for 5 observations; 0.045 mol, $k_{obs} = 3.8 \times 10^{-2}$ min^{-1}, $r^2 = 0.999$ for 5 observations; 0.05 mol, $k_{obs} = 5.7 \times 10^{-2}$ min^{-1}, $r^2 = 0.97$ for 5 observations; and 0.06 mol, $k_{obs} = 8.9 \times 10^{-2}$ min^{-1}, $r^2 = 0.91$ for 4 observations); and *(iv)* reaction temperature (4 experiments at 60 ˚C, $k_{obs} = 1.47 \times 10^{-2}$ min^{-1}, $r^2 = 0.993$ for 7 observations; 80 ˚C, $k_{obs} = 2.48 \times 10^{-2}$ min^{-1}, $r^2 = 0.998$ for 7 observations; 100 ˚C, $k_{obs} = 3.67 \times 10^{-2}$ min^{-1}, $r^2 = 0.996$ for 7 observations; and 120 ˚C, $k_{obs} = 8.22 \times 10^{-2}$ min^{-1}, $r^2 = 0.986$ for 7 observations).

References:

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