SUPPORTING INFORMATION

Synthesis of Oximes 10:[1] Hydroxylamine hydrochloride (3.06 g, 44 mmol), anhydrous sodium acetate (3.6 g, 44 mmol) and water (50 mL) were heated at 60 ºC for 1h. Then, a methanolic (10 mL) solution of the appropriate ketone (22 mmol) was added and the mixture was stirred overnight at the same temperature. The resulting solution was cooled to room temperature and the corresponding oximes were filtered off, whased with water and purified by recrystallization. Yields were in all cases above 90% and the purity of the products was determined by ^{1}H NMR and found to be >98%.

Synthesis of Palladacycles 11:[2] To a solution of Li_2PdCl_4 (2.62 g, 10 mmol) in methanol (20 mL), a methanolic solution (10 mL) of the corresponding oxime (10 mmol) and sodium acetate (0.82 g, 10 mmol) was added. Then, the solution was stirred for 2 to 3 days at room temperature, the mixture was filtered and after adding water (10 mL), the corresponding cyclopalladated complexes precipitated. The solid was filtered off (G-4), dried under vacuum and used in the catalytic processes. Yields and physical properties are summarized in Table 1.

Selected data for **11a**: mp = 139-141 ºC; IR (KBr, cm^{-1}) 3373, 1645, 1569, 1435, 1340, and 1024; ^{1}H NMR (300 MHz, DMSO-d^6) δ_H (ppm) 6.69 (4 H, m), 7.09 (4 H, m), 7.35-8.10 (10 H, m).

Selected data for **11c**: mp = 135-137 ºC; IR (KBr, cm^{-1}) 3390, 1607, 1579, 1559, 1344, 1253, 1233, 1177 and 1026; ^{1}H NMR (300 MHz, DMSO-d^6) δ_H (ppm) 3.71, 3.83 (12 H, 2s, 6H each), 6.71 (4 H, m), 7.08-7.25 (5 H, m with d at 7.10, *J* = 8.6 Hz), 7.30-7.55 (5 H, m with d at 7.43, *J* = 8.6 Hz).

Representative Procedure for Heck Couplings: To a solution in NMP (3 mL) of the palladacycle **11a** (0.066 mg, 10^{-2} mol% Pd), phenyl iodide (228 μL, 2 mmol), Et_3N (391 μL, 2.8 mmol) and methyl acrylate (216 μL, 2.4 mmol) were added. The reaction mixture was vigorously stirred and heated to 110 ºC for 1.5 h. The solvent was evaporated and the

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[1] Hutchins, R. D.; Adams, J.; Rutledge, M. C. *J. Org. Chem.* **1995**, *60*, 7396-7405.

[2] Onoue, H.; Minami, K.; Nakagawa, K. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3480-3485.

crude reaction mixture was extracted with water and EtOAc (3x20 mL). The organic phases were dried, evaporated and the resulting crude product was purified by flash chromatography (hexane/ether) yielding 298 mg of methyl cinnamate (92 % yield, >99% pure by GC analysis).

Representative Procedure for Heck Couplings under Jeffery´s Conditions: To a solution in DMF (5 mL) of the catalyst **11a** (3.35 mg, 0.5 mol% Pd), *p*-bromoacetophenone (406 mg, 2 mmol), NaOAc (230 mg, 2.8 mmol), Bu_4NBr (129 mg, 20 mol%) and methyl acrylate (216 µL, 2.4 mmol) were added. The reaction mixture was vigorously stirred and heated to 135 ºC for 5 h. The reaction was extracted with water and EtOAc (3x20 mL) and the organic phases washed with water (5x20 mL). The organic extracts were dried, evaporated and the resulting crude product was purified by flash chromatography (hexane/ether) yielding 314 mg of methyl cinnamate (97 % yield, >99% pure by GC analysis).

Representative Procedure for Sonogashira Reactions: To a stirred solution of iodobenzene (228 µL, 2 mmol), **11e** (0.66 mg, 0.1 mol% Pd) and CuI (19 mg, 5 mol%) in pyrrolidine (4 mL), phenyl acetylene was added (268 µL, 2.4 mmol). After stirring during 2 h at 90 ºC, the solvent was evaporated and the resulting crude mixture was extracted with water and EtOAc (3x20 mL). The organic phases were dried, evaporated and the resulting crude product was purified by flash chromatography (hexane/ether) yielding 242 mg of diphenylacetylene (68 % yield, >99% pure by GC analysis).

Representative Procedure for Stille Couplings: A toluene solution (3 mL) of *p*-bromoacetophenone (50.75 mg, 0.25 mmol), Me_3SnPh (70.42 µL, 0.38 mmol) and palladacycle **11e** (2.52 mg, 3 mol% Pd) was stirred at 110 ºC for 5 h. The solvent was evaporated and the resulting crude mixture was extracted with water and EtOAc (3x20 mL). The organic phases were dried, evaporated and the resulting crude product was purified by flash chromatography (hexane/ether) yielding 46.6 mg of 4-acetylbiphenyl (95 % yield, >99% pure by GC analysis).

Representative Procedure for Suzuki Reactions: A toluene solution (7 mL) containing **11e** (0.67 mg, 0.1 mol % Pd), *p*-bromoactetophenone (406 mg, 2.0 mmol), $PhB(OH)_2$ (377 mg, 3.0 mmol) and K_2CO_3 (553 mg, 4.0 mmol) was heated to 110 ºC with stirring for 0.5 h. The solvent was evaporated and the resulting crude mixture was extracted with water and EtOAc (3x20 mL). The organic extracts were dried, evaporated and the resulting crude product was purified by recrystallization (EtOAc/pentane) yielding 372 mg of 4-acetylbiphenyl (95 % yield, >99% pure by GC analysis).

Representative Procedure for Ullmann-type Couplings: A DMF solution (5 mL) containing phenyl iodide (228 μL, 2 mmol), hydroquinone (110 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol) and **11e** (13.4 mg, 2 mol% Pd) was heated and stirred at 110 ºC for 2h. The reaction mixture was filtered through a thin pad of silica (hexane/ether) and the solvents evaporated to yield 262 mg of pure biphenyl (85% yield, >99% pure by GC analysis).