Supporting Information

Synthesis of complex 4a

$PdCl_2$ (33 mg, 0.186 mmol) was dissolved in HCl (conc, 35% aq., 1 mL). The resulting mixture was stirred until the $PdCl_2$ was completely dissolved (*ca.* 10 min.). A few drops of NaOH (15% aq.) were added until a pale precipitate of $Pd(OH)_2$ just begun to form. The ligand **7a** (50 mg, 0.22 mmol) was dissolved in methanol (2.5 mL) and the resulting solution was added to the solution of H_2PdCl_4. The initially dark solution gradually became paler and a yellow precipitate was formed. Stirring was continued for 2-3 hours after which the precipitate was collected by filtration and washed with H_2O and MeOH. The obtained yellow powder was dried *in vacuo* to yield 55 mg of **4a** (73%). Crystals suitable for X-ray analysis were grown from a concentrated solution of **4a** in DMSO. Mp: decomposes. ^{1}H NMR (DMSO-d_6): Major rotamer (*ca.* 84%) 9.79 (d, 1H, *J* = 9.8 Hz), 8.88 (d, 2H, *J* = 6.1 Hz), 8.19 (t, 2H, *J* = 7.3 Hz), 7.59 (m, 2H), 7.35 (d, 1H, *J* = 9.8 Hz), 2.26 (s, 3H). Minor rotamer (*ca.* 14%) 9.63 (1H), 8.90 (2H), 8.08 (2H), 7.90 (2H), 7.57 (2H), 6.30 (1H), 2.03 (3H). ^{13}C NMR (DMSO-d_6): 170.1, 154.3, 153.6, 141.1, 125.1, 121.6, 58.5, 22.7. IR (KBr): 3320, 3074, 3113, 1692, 1604, 1519, 1477, 1466, 1441, 1363, 1282, 1252, 1211, 1161, 1097, 1038, 766, 658, 640, 543. Elemental analysis calcd for $C_{13}H_{12}Cl_2N_3OPd$ (Mw = 404 g mol^{-1}): C 38.69; H 3.00; N 10.41. Found: C 38.54; H 3.18; N 10.04.

Synthesis of complex 4b

$PdCl_2$ (48 mg, 0.27 mmol) was dissolved in HCl (conc, 35% aq., 1.5 mL). The resulting mixture was stirred until the $PdCl_2$ was completely dissolved (ca 10 min.). A few drops of NaOH (15% aq.) were added until a pale precipitate of $Pd(OH)_2$ just begun to form. The ligand **7b** (100 mg, 0.32 mmol) was dissolved in methanol (2.5 ml) and the resulting solution was added to the solution of H_2PdCl_4. The initially dark solution gradually became paler and a yellow precipitate was formed. Stirring was continued for 2-3 hours after which the precipitate was collected by filtration and washed with H_2O and MeOH. The pale yellow powder obtained was dried *in vacuo* to yield 123 mg of **4b** (94%). The NMR-spectrum of **4b** shows the presence of two rotamers (major and minor) in the approximate ratio 3:1. ^{1}H NMR (DMSO-d_6): 8.95 (d, 2H, *J* = 6.1 Hz, minor), 8.86 (d, 2H, *J* = 4.9 Hz, major), 8.19 (m, 2H, major), 8.10 (m, 2H, minor), 7.91 (m, 1H), 7.68 (d, 2H, *J* = 7.3 Hz), 7.57 (t, 2H, *J* = 6.1 Hz), 7.14 (d, 1H, *J* = 11.0 Hz, major), 6.80 (d, 1H, *J* = 7.3 Hz, minor), 6.43 (d, 1H, *J* = 7.3 Hz), 3.51 (m, 1H), 1.90-1.00 (m, 10H). ^{13}C NMR (DMSO-d_6): 156.4, 156.0, 155.4, 154.0, 153.6, 153.4, 141.1, 140.8, 127.0, 125.2, 124.9, 121.4, 61.3, 59.9, 48.3, 32.3, 25.2, 24.3. IR (KBr): 3372, 3347, 3112, 3077, 3041, 2928, 2871, 2850, 1674, 1605, 1548, 1468, 1440, 1337, 1282, 1236, 1220, 1147, 1165, 1037, 985, 778, 633, 550. Elemental analysis calcd for $C_{18}H_{22}Cl_2N_4OPd$ (Mw = 487.72 g mol^{-1}): C 44.33; H 4.55; N 11.49 (Cl 14.54, O 3.28, Pd 21.82). Found: C 44.35; H 4.52; N 11.13.

Typical Procedure for Heck Reactions in DMF

A 10 mL round-bottom flask was charged with palladium catalyst **4** (10^{-3}-10^{-2} mol%), aryl halide (2 mmol), alkene (2.4 mmol), tri-n-butylamine (2.8 mmol) and DMF (4 mL). For bromobenzene and *p*-chlorostyrene K_2CO_3 (2.8 mmol) as base and tetrabutylammonium bromide (0.4 mmol) as additive were used. The mixture was

heated at 140 or 160 ºC and stirred during the reaction time. The reaction progress was analysed by GLC. The mixture was cooled to room temperature and was diluted with EtOAc (20 mL), washed with 2M HCl and water. The organic phase was dried over $MgSO_4$, concentrated in vacuo and purified by flash chromatography on silica gel.

Typical Procedure for Heck Reactions of Iodobenzene with Alkenes in Water

A 15 mL ace pressure tube was charged with palladium catalyst **4b** (10^{-3}-0.1 mol% Pd), iodobenzene (1 mmol), alkene (1.5 mmol), diisopropylamine (3 mmol) and water (2 mL). The mixture was heated at 140 ºC and stirred during the reaction time. The reaction progress was analysed by GLC. The mixture was cooled to room temperature and was extracted with EtOAc (3 x 15 mL), dried over $MgSO_4$, concentrated in vacuo and purified by flash chromatography on silica gel.

Typical Procedure for Heck Reactions of Iodobenzene and Bromobenzene with Alkenes in NMP/H_2O

A 10 mL round-bottom flask was charged with palladium catalyst **4b** (10^{-3} mol%), iodobenzene (1 mmol), alkene (1.5 mmol), diisopropylamine (3 mmol) and a 3:1 mixture of NMP and water (2 mL). In the case of bromobenzene tetrabutylammonium bromide (0.5 mmol) was added. The mixture was heated at 160 ºC and stirred in air during the reaction time. The reaction progress was analyzed by GLC. The mixture was cooled to room temperature and was extracted with water and EtOAc (3 x 15 mL), dried over $MgSO_4$, concentrated in vacuo and purified by flash chromatography on silica gel.

Typical Procedure for Heck Reactions of Bromobenzene or Chlorobenzene with Alkenes in NMP/H_2O

A 10 mL round-bottom flask was charged with palladium catalyst **4b** (10^{-2} mol%), bromo- or chlorobenzene (1 mmol), alkene (1.5 mmol), diisopropylamine (3 mmol) and a 3:1 mixture of NMP and water (2 mL). The mixture was heated at 140 ºC or 160ºC and stirred in air during the reaction time. The reaction progress was analyzed by GLC. The mixture was cooled to room temperature and was extracted with water and EtOAc (3 x 15 mL), dried over $MgSO_4$, concentrated in vacuo and purified by flash chromatography on silica gel.

Typical Procedure for Suzuki Couplings of Aryl Bromides and Chlorides with Phenylboronic Acid in Aqueous DMF

A 10 mL round-bottom flask was charged with palladium catalyst **4b** (1-10^{-3} mol%), aryl bromide (1 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2 mmol) and a mixture 95:5 of DMF/water (2 mL). The mixture was heated at 110 or 130 ºC and stirred in air during the reaction time. The reaction progress was analyzed by GLC. The mixture was cooled to room temperature and was extracted with EtOAc (3 x 15 mL), dried over $MgSO_4$, concentrated in vacuo and purified by flash chromatography on silica gel.

Typical Procedure for Suzuki Couplings of Aryl Bromides and Chlorides with Phenylboronic Acid in Water

A 10 mL round-bottom flask was charged with palladium catalyst **4b** ($1\text{-}10^{-3}$ mol%), aryl bromide (1 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2 mmol) and water (2.5 mL). In the case of aryl chlorides tetrabutylammonium bromide (0.5-1 mmol) was added. The mixture was heated at 100 ºC and stirred in air during the reaction time. The reaction progress was analyzed by GLC. The mixture was cooled to room temperature and was extracted with EtOAc (3 x 15 mL), dried over $MgSO_4$, concentrated in vacuo and purified by flash chromatography on silica gel.

Typical Procedure for Suzuki Couplings of Aryl Bromides with Phenylboronic Acid in Aqueous MeOH

A 10 mL round-bottom flask was charged with palladium catalyst **4b** ($1\text{-}10^{-3}$ mol%), aryl bromide (1 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2 mmol) and a mixture 3/1 of MeOH/water (2 mL). The mixture was stirred at room temperature in air during the reaction time. The reaction progress was analyzed by GLC. The mixture was extracted with EtOAc (3 x 15 mL), dried over $MgSO_4$, concentrated in vacuo and purified by flash chromatography on silica gel.

Typical Procedure for Sonogashira Couplings of Aryl Iodides and Bromides with Alkynes in Water

A 10 mL round-bottom flask was charged with palladium catalyst **4b** (0.1-0.5 mol%), aryl halide (1 mmol), alkyne (1.5 mmol), pyrrolidine (2 mmol), tetrabutylammonium bromide (1 mmol) and water (2.5 mL). The mixture was heated at 100 ºC and stirred in air during the reaction time. The reaction progress was analyzed by GLC. The mixture was cooled to room temperature and was extracted with EtOAc (3 x 15 mL), dried over $MgSO_4$, concentrated in vacuo and purified by flash chromatography on silica gel.

Typical Procedure for Sonogashira Couplings of Aryl Iodides and Bromides with Alkynes in NMP

A 10 mL round-bottom flask was charged with palladium catalyst **4b** (0.1-0.5 mol%), aryl halide (1 mmol), alkyne (1.5 mmol), tetrabutylammonium acetate (2 mmol) and NMP (3 mL). The mixture was heated at 110 ºC and stirred in air during the reaction time. The reaction progress was analyzed by GLC. The mixture was cooled to room temperature and was extracted with water and EtOAc (3 x 15 mL), dried over $MgSO_4$, concentrated in vacuo and purified by flash chromatography on silica gel.

HECK COUPLING PRODUCTS

Butyl cinnamate (Comercially available): ^{1}H RMN ($CDCl_3$): δ_H = 0.97 (t, 3H, *J* = 7.3 Hz, CH_2CH_3), 1.40-1.48 (m, 2H, $CH_2CH_2CH_3$), 1.70 (q, 2H, *J* = 7.3 Hz, $CH_2CH_2CH_2$), 4.21 (t, 2H, *J* = 7.3 Hz, OCH_2CH_2), 6.44, 7.68 (2d, 2H, *J* = 16.2 Hz, CH=CH), 7.37-7.39 (m, 3H, ArH) and 7.51-7.54 (m, 2H, ArH); *m/z* (%) 204 (M^+, 11), 149 (10), 148 (63), 147 (53), 132 (11), 131 (100), 104 (11), 103 (50), 102 (14), 77 (30) and 51 (10).

tert-Butyl cinnamate (Comercially available)

Cinnamic acid (Comercially available): ^{1}H RMN ($CDCl_3$): δ_H = 6.45 (d, 1H, *J* = 16.1, CH=CH), 7.35-7.45 (m, 3H, ArH), 7.51-7.54 (m, 2H, ArH), 7.79 (d, 1H, *J* = 16.1), 11.8 (s ancho, 1H, OH); ^{13}C RMN ($CDCl_3$): δ_C = 117.3 (CH=CH), 128.3, 128.9, 130.7, 134 (4xArC), 147.1 (CH=CH), 172.7 (COOH); *m/z* (%) 148 (M^+, 76), 147 (M^+-1, 100), 131 (21), 103 (52), 102 (27), 91 (24) and 77 (37).

4-Chloroestilbene (Comercially available): ^{1}H RMN ($CDCl_3$): δ_H = 7.04-7.49 (m, 11H, ArH); ^{13}C RMN ($CDCl_3$): δ_C = 126.5, 127.3, 127.6, 127.8, 128.7, 128.8, 129.3, 133.1, 135.8, 136.9; *m/z* (%) 216 (M^++2, 26), 215 (M^++1, 14), 214 (M^+, 79), 180 (13), 179 (93), 178 (100), 177 (16), 176 (19), 152 (14), 151 (10), 89 (20) and 76 (18).

SUZUKI COUPLING PRODUCTS

4-Phenylacetophenone (Comercially available): Colourless solid; M.p. 123 ºC; R_f 0.55 (Hexane/AcOEt: 3/1); IR (KBr): = 1680 (C=O) and 1601 (ArC) cm^{-1}; ^{1}H RMN ($CDCl_3$): δ_H = 8.03-8.00 (m, 2H, ArH), 7.69-7.66 (m, 2H, ArH), 7.63-7.60 (m, 2H, ArH), 7.49-7.38 (m, 3H, ArH) and 2.62 (s, 3H, CH_3); ^{13}C RMN ($CDCl_3$): δ_C = 197.7 (CO), 145.7, 139.8, 135.8 (ArC), 129.0, 128.9, 128.3, 127.3, 127.2 (ArCH) and 26.6 (CH_3); *m/z* (%): 196 (M^+, 45), 181 (M^+-15, 100), 153 (36), 152 (54), 151 (20) and 76 (65).

4-Phenylphenol (Comercially available): Colourless solid; M.p. 166 ºC; R_f 0.40 (Hexane/AcOEt: 3/1); IR (KBr): = 3404 (OH), 1610 and 1523 (ArC) cm^{-1}; ^{1}H RMN (acetone-d_6): δ_H = 8.44 (s, 1H, OH), 7.57 (d, *J* = 7.3 Hz, 2H, ArH), 7.50 (d, *J* = 8.6 Hz, 2H, ArH), 7.42-7.37 (m, 2H, ArH), 7.29-7.24 (m, 1H, ArH) and 6.93 (d, *J* = 8.6 Hz, 2H, ArH); ^{13}C RMN (acetone-d_6): δ_C = 158.0, 141.8, 133.1 (ArC), 129.5, 128.8, 127.2, 127.1 and 116.5 (ArCH); *m/z* (%): 170 (M^+, 100), 141 (24), 115 (26) and 85 (9).

4-Phenylaniline (Comercially available): Colourless solid; M.p. 51 ºC; R_f 0.31 (Hexane/AcOEt: 3/1); IR (KBr): = 3424, 3382, 3300, 3206 (N-H) and 1617 (ArC) cm^{-1}; ^{1}H RMN ($CDCl_3$): δ_H = 7.55-7.37 (m, 7H, ArH), 6.76 (d, *J* = 8.6 Hz, 2H, ArH) and 3.71 (br s, 2H, NH_2); ^{13}C RMN ($CDCl_3$): δ_C = 145.9, 141.2, 131.6 (ArC), 128.7, 128.1, 126.4, 126.3 and 115.4 (ArCH); *m/z* (%): 169 (M^+, 100) and 84(12).

N,N-Dimethyl-4-phenylaniline : Colourless solid; ^{1}H RMN ($CDCl_3$): δ_H = 7.56-7.48 (m, 4H, ArH), 7.30-7.21 (m, 3H, ArH), 6.80 (d, *J* = 8.9 Hz, 2H, ArH), 2.97 (s,

6H, N(CH_3)$_2$); ^{13}C RMN ($CDCl_3$): $_C$ = 149.9, 141.2, 129.2, 128.6, 127.7, 126.3, 126, 112,8 (ArC), 40,6 [ArN(CH_3)$_2$)]; *m/z* (%): 197 (M^+, 100), 196 (M^+-1, 73), 181 (M^+-15, 15), 153 (15), 154 (28), 98 (16)

SONOGASHIRA COUPLING PRODUCTS

1-(4-Chlorophenyl)-2-phenylacetylene (Comercially available): M.p.: 81 ºC; IR (KBr): = 3048 cm^{-1}; ^{1}H RMN ($CDCl_3$): $_H$ = 7.32-7.37 (m, 5H, Ar*H*) and 7.45-7.55 (m, 4H, Ar*H*); ^{13}C RMN ($CDCl_3$): $_C$ = 88.3, 90.3 (C C), 121.8, 123.0, 128.4, 128.5, 128.7, 131.6, 132.8 and 134.3 (ArC); *m/z* (%) 214 (M^++2, 32), 213 (M^++1, 16), 212 (M^+, 100), 176 (41), 151 (15), 150 (11), 106 (10) and 88 (11).

1-(4-Methoxyphenyl)-2-phenylacetylene (Comercially available): R_f: 0.15 (Hexane); M.p.: 51-53 ºC; IR (KBr): = 3053, 2216, 1246 and 1028 cm^{-1}; ^{1}H RMN ($CDCl_3$): $_H$ = 3.81 (s, 3H, CH_3), 6.87 (d, 2H, *J* = 8.5 Hz, Ar*H*), 7.31-7.34 (m, 3H, Ar*H*) and 7.45-7.52 (m, 4H, Ar*H*); ^{13}C RMN ($CDCl_3$): $_C$ = 55.3 (C-O), 88.0, 89.3 (C C), 114.0, 115.3, 123.6, 127.9, 128.3, 131.4, 133.0 and 159.6 (ArC); *m/z* (%) 209 (M^++1, 16), 208 (M^+, 100), 193 (53), 165 (53), 164 (19), 163 (15) and 139 (16).

2-(4-Methoxyphenyl)-1-ethynyl(trimethyl)silane: R_f: 0.18 (hexane); IR (KBr): (film) = 3038, 3001, 2154 (C C), 1249 and 1036 cm^{-1}; ^{1}H RMN ($CDCl_3$): $_H$ = 1.12 (s, 21H, 3 C*H*(CH_3)$_2$), 3.80 (s, 3H, OCH_3), 6.81 (d, 2H, *J* = 8.5 Hz, ArH) and 7.41 (d, 2H, *J* = 8.5 Hz, Ar*H*); ^{13}C RMN ($CDCl_3$): $_C$ = 11.4 (CH_3), 18.7 (CH), 55.3 (OCH_3), 88.6, 107.1 (C C), 113.8, 115.8, 133.5 and 159.6 (ArC); *m/z* (%) 288 (M^+), 246 (22), 245 (M^+-43, 100), 217 (24), 203 (47), 189 (53), 176 (13), 175 (79), 161 (11), 159 (14), 135 (10) and 94 (19).

1-(4-Chlorophenyl)-2-butylacetylene: ^{1}H RMN ($CDCl_3$): $_H$ = 0.93 (t, 3H, *J* = 7.1 Hz, CH_2CH_3), 1.42-1.60 (m, 4H, CH_2CH_2), 2.38 (t, 2H, *J* = 6.8 Hz, C CCH_2), 7.22 and 7.29 (2d, 4H, *J* = 8.4 Hz, Ar*H*); ^{13}C RMN ($CDCl_3$): $_C$ =13.6 (CH_3), 19, 22, 30.7 (3xCH_2), 79.5, 91.4 (C C), 122.6, 128.4, 132.7, 133.3 (ArC); *m/z* (%) 194 (M^++2, 13), 194 (M^+, 38), 179 (12), 177 (39), 163 (28), 157 (26), 151 (42), 150 (14), 149 (100), 138 (11), 136 (22), 129 (62), 128 (38), 127 (34), 125 (11), 116 (12), 115 (51), 114 (31), 113 (20), 75 (10) and 63 (15).

1-(4-Methylphenyl)-2-phenylacetylene (Comercially available): ^{1}H RMN ($CDCl_3$): $_H$ = 2.37 (s, 3H, CH_3), 7.15 (d, 2H, *J* = 7.8 Hz, ArH) and 7.32-7.53 (m, 7H, ArH); ^{13}C RMN ($CDCl_3$): $_C$ = 21.5 (CH_3), 88.6, 89.5 (C C), 120.2, 123.5, 128, 128.3, 129.1, 131.4, 131.5 and 138.4 (ArC); *m/z* (%) 193 (M^++1, 15), 192 (M^+, 100), 191 (44), 190 (11), 189 (23) and 165 (16).