Supplementary Information

General procedure for preparation of XL-Pd plugs:

To a suspension of palladium acetate (4.6 mg, 0.021 mmol, 0.005 eq) in 1,4-dioxane (50 mL) were added 25 aminomethyl polystyrene resin plugs (PL-AMS StratoSpheres Plugs™, 4.125 mmol, 0.165 mmol/plug) and the reaction mixture was stirred for 10 min at 80 °C then 7 h at room temperature. The 25 resulting brown plugs were removed from solution with tweezers, washed successively with 1,4-dioxane (5 × 30 mL), dichloromethane (5 × 30 mL) and diethyl ether (5 × 30 mL). The Pd-loaded plugs were added to 10% hydrazine hydrate in 1,4-dioxane (30 mL). After 1 h at room temperature under magnetic stirring, the 25 resulting black plugs were removed from solution with tweezers and washed successively with 1,4-dioxane (5 × 30 mL), dichloromethane (5 × 30 mL) and diethyl ether (5 × 30 mL). The entrapped Pd-plugs (4.125 mmol, 0.165 mmol/plug) were treated with a solution of triethylamine (1.725 mL, 12.375 mmol, 3.0 eq) and succinyl chloride (227 μL, 2.063 mmol, 0.5 eq) in dry dichloromethane (50 mL) and the reaction mixture was stirred for 4 h at room temperature. The resulting black plugs were removed from solution with tweezers and washed successively with dichloromethane (5 × 30 mL), diethyl ether (5 × 30 mL) and 1,4-dioxane (5 × 30 mL). The Plugs were then subjected to Soxhlet extraction in 1,4-dioxane for 72 h, washed with diethyl ether (5 × 30 mL) and dried in a vacuum oven at 40 °C for 4 weeks to give XL-Pd plugs. **Pd analysis**: 0.04% Pd.

TEM analysis:

Sample resin plugs (XL-Pd plugs) were embedded in Spurr resin and polymerised at 60 °C for 18 h. 100 nm sections were cut on a Reichhert OMU3 ultramicrotome using a diamond knife and the sections were viewed on a Hitachi H7000 Transmission Electron Microscope.

General procedure for Suzuki-Miyaura coupling of aryl iodides:

To a solution of the aryl iodide (1.0 mmol) in DMF (5 mL) were added phenylboronic acid (183 mg, 1.5 mmol, 1.5 eq), K_2CO_3 (207 mg, 1.5 mmol, 1.5 eq) and 1 Pd-plug catalyst (30 μmol, 3 mol %). The reaction mixture was heated at 115 °C under magnetic stirring. The Pd plug was removed from solution with tweezers, washed with DCM (10 × 6 mL) and dried in the vacuum oven at room temperature for 48 h. The reaction mixture was diluted in DCM (100 mL) and washed with 1M HCl (pH 7). The aqueous phase was extracted with DCM (3 × 50 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to yield final product.

4-Methoxybiphenyl (Table 2, entry 1):

Obtained as a white solid (167 mg, 91%). $\mathbf{R_f}$ (Hexane/EtOAc 95/5): 0.50; **mp**: 79-81 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.58-7.53 (m, 4H, Ar + Ar'), 7.44-7.40 (m, 2H, Ar'), 7.33-7.29 (m, 1H, Ar'), 6.99 (d, 2H, J = 8.8 Hz, Ar), 3.86 (s, 3H, CH_3O); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ_C 159.3, 141.0, 134.0, 128.9, 128.3, 126.9, 126.8, 114.4, 55.5; **MS** (EI): m/z (%) 184 ($[M]^{+\cdot}$, 100), 169 (42), 152 (6), 141 (26), 115 (31), 92 (11), 89 (7).

4-(Trifluoromethyl)biphenyl (Table 2, entry 2):

Obtained as a white solid (180 mg, 81%). $\mathbf{R_f}$ (Hexane): 0.53; **mp**: 66-68 °C; **^{1}H NMR** ($CDCl_3$, 250 MHz): δ_H 7.69 (s, 4H, Ar), 7.63-7.57 (m, 2H, Ar'), 7.52-7.37 (m, 3H, Ar'); **^{13}C NMR** ($CDCl_3$, 63 MHz): δ_C 144.7, 139.7, 129.0, 128.2, 127.4, 127.2, 125.7, 125.6; **MS** (EI): m/z (%) 222 ($[M]^{+\cdot}$, 100), 203 (40), 183 (12), 172 (22), 153 (70), 152 (74), 102 (10), 86 (17), 77 (10), 76 (15).

4-Nitrobiphenyl (Table 2, entry 3):

Obtained as a pale yellow solid (198 mg, 99%). $\mathbf{R_f}$ (Hexane/EtOAc 95/5): 0.39; **mp**: 108-110 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 8.30 (d, 2H, J = 8.8 Hz, Ar), 7.74 (d, 2H, J = 8.8 Hz, Ar), 7.63 (dd, 2H, J = 8.8, 1.5 Hz, Ar'), 7.53-7.43 (m, 3H, Ar'); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ_C 147.8, 147.3, 138.9, 129.3, 129.1, 127.9, 127.5, 124.2; **MS** (EI): m/z (%) 199 ($[M]^{+\cdot}$, 61), 169 (78), 152 (100), 141 (19), 115 (14), 77 (19).

4-Methylbiphenyl (Table 2, entry 4):

Obtained as a white solid (153 mg, 91%). $\mathbf{R_f}$ (Hexane): 0.44; **mp**: 50-52 °C; **^{1}H NMR** ($CDCl_3$, 250 MHz): δ_H 7.55-7.51 (m, 2H, Ar'), 7.45 (d, 2H, J = 8.0 Hz, Ar), 7.40-7.33 (m, 2H, Ar'), 7.30-7.22 (m, 1H, Ar'), 7.19 (d, 2H, J = 8.0 Hz, Ar), 2.33 (s, 3H, CH_3); **^{13}C NMR** ($CDCl_3$, 63 MHz): δ_C 141.1, 138.3, 136.9, 129.4, 128.7, 126.9, 126.8, 21.0; **MS** (EI): m/z (%) 168 ($[M]^{+\cdot}$, 100), 167 (92), 153 (55), 152 (67), 139 (22), 115 (37), 91 (32), 89 (19), 83 (35), 77 (18).

Biphenyl (Table 2, entry 5):

Obtained as a white solid (133 mg, 86%). $\mathbf{R_f}$ (Hexane): 0.47; **mp**: 64-66 °C; **^{1}H NMR** ($CDCl_3$, 250 MHz): δ_H 7.68-7.63 (m, 4H), 7.54-7.46 (m, 4H), 7.44-7.36 (m, 2H); **^{13}C NMR** ($CDCl_3$, 63 MHz): δ_C 141.2, 128.7, 127.2, 127.1; **MS** (EI): m/z (%) 154 ($[M]^{+\cdot}$, 100), 153 (89), 152 (99), 139 (12), 128 (30), 115 (31), 102 (21), 89 (10), 77 (49), 76 (66).

General procedure for Sonogashira-Hagihara coupling of aryl iodides:

To a solution of the aryl iodide (1.0 mmol) in DMF (5 mL) were added phenyl acetylene (165 μL, 1.5 mmol, 1.5 eq), K_2CO_3 (207 mg, 1.5 mmol, 1.5 eq) and 1 Pd-plug catalyst (30 μmol, 3 mol %). The reaction mixture was heated at 115 °C under magnetic stirring. The Pd plug was removed from solution with tweezers, washed with DCM (10 × 6 mL) and dried in the vacuum oven at room temperature for 48 h. The reaction mixture was diluted in DCM (100 mL) and washed with 1M HCl (pH 7). The aqueous phase was extracted with DCM (3 × 50 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to yield final product.

1-Methoxy-4-[2-phenyl-1-ethynyl]benzene (Table 2, entry 1):

Obtained as an off-white solid (160 mg, 77%). $\mathbf{R_f}$ (Hexane/EtOAc 95/5): 0.44; **mp**: 88-90 °C; **^{1}H NMR** ($CDCl_3$, 250 MHz): δ_H 7.54-7.44 (m, 4H, Ar + Ar'), 7.35-7.32 (m, 3H, Ar'), 6.89 (d, 2H, J = 9.0 Hz, Ar), 3.83 (s, 3H, CH_3O); **^{13}C NMR** ($CDCl_3$, 63 MHz): δ_C 159.6, 133.0, 131.4, 128.6, 128.3, 123.6, 115.3, 114.0, 89.3, 88.0, 55.3; **MS** (EI): m/z (%)

208 ([M]$^{+\cdot}$, 100), 193 (74), 179 (16), 166 (25), 165 (83), 164 (18), 152 (27), 139 (24), 115 (16), 89 (17).

1-(2-Phenyl-1-ethynyl)-4-(trifluoromethyl)benzene (Table 2, entry 2):

Obtained as a white solid (214 mg, 87%). **R_f** (Hexane): 0.18; **mp**: 99-101 °C; **^{1}H NMR** ($CDCl_3$, 250 MHz): δ_H 7.64-7.57 (m, 6H, Ar + Ar'), 7.42-7.38 (m, 3H, Ar'); **^{13}C NMR** ($CDCl_3$, 63 MHz): δ_C 131.8, 131.7, 129.9 (J = 32.7 Hz), 128.8, 128.4, 127.1, 125.2 (J = 14.8 Hz), 124.0 (J = 272.2 Hz), 122.6, 91.7, 88.0; **MS** (EI): m/z (%) 246 ([M]$^{+\cdot}$, 100), 227 (62), 207 (16), 202 (38), 196 (48), 176 (60), 151 (29), 123 (41), 98 (76), 85 (20), 75 (21).

1-Nitro-4-[2-phenyl-1-ethynyl]benzene (Table 2, entry 3):

Obtained as a bright yellow solid (205 mg, 92%). **R_f** (Hexane/EtOAc 95/5): 0.43; **mp**: 114-115 °C; **^{1}H NMR** ($CDCl_3$, 250 MHz): δ_H 8.21 (d, 2H, J = 9.0 Hz, Ar), 7.66 (d, 2H, J = 9.0 Hz, Ar), 7.59-7.54 (m, 2H, Ar'), 7.41-7.38 (m, 3H, Ar'); **^{13}C NMR** ($CDCl_3$, 63 MHz): δ_C 146.9, 132.2, 131.8, 130.2, 129.2, 128.5, 123.6, 122.0, 94.7, 87.5; **MS** (EI): m/z (%) 223 ([M]$^{+\cdot}$, 100), 202 (22), 193 (25), 177 (24), 176 (49), 165 (23), 151 (24), 105 (29), 88 (10), 77 (17).

1-Methyl-4-[2-phenyl-1-ethynyl]benzene (Table 2, entry 4):

Obtained as a white solid (169 mg, 88%). **R_f** (Hexane): 0.37; **mp**: 67-69 °C; **^{1}H NMR** ($CDCl_3$, 250 MHz): δ_H 7.58-7.53 (m, 2H, Ar'), 7.46 (d, 2H, J = 8.0 Hz, Ar), 7.37-7.34 (m, 3H, Ar'), 7.18 (d, 2H, J = 8.0 Hz, Ar), 2.39 (s, 3H, CH_3); **^{13}C NMR** ($CDCl_3$, 63 MHz): δ_C 138.3, 131.5, 131.5, 129.1, 128.3, 128.0, 123.4, 120.1, 89.5, 88.7, 21.5; **MS** (EI): m/z (%) 192 ([M]$^{+\cdot}$, 100), 191 (62), 176 (5), 165 (24), 139 (8), 115 (10), 96 (8), 83 (7).

1,2-Diphenylethyne (Table 2, entry 5):

Obtained as an off-white solid (151 mg, 85%). **R_f** (Hexane): 0.40; **mp**: 68-70 °C; **^{1}H NMR** ($CDCl_3$, 250 MHz): δ_H 7.59-7.52 (m, 4H), 7.40-7.35 (m, 6H); **^{13}C NMR** ($CDCl_3$, 63 MHz): δ_C 131.6, 128.3, 128.2, 123.2, 89.3; **MS** (EI): m/z (%) 178 ([M]$^{+\cdot}$, 100), 177

(36), 176 (74), 165 (7), 152 (46), 151 (35), 150 (21), 126 (26), 102 (11), 89 (36), 88 (15), 77 (14), 76 (39), 75 (16).

General procedure for Heck-Mizoroki coupling of aryl iodides:

To a solution of the aryl iodide (1.0 mmol) in DMF (5 mL) were added styrene (172 μL, 1.5 mmol, 1.5 eq), K_2CO_3 (207 mg, 1.5 mmol, 1.5 eq) and 1 Pd-plug catalyst (10 μmol, 1 mol %). The reaction mixture was heated at 115 °C under magnetic stirring. The Pd plug was removed from solution with tweezers, washed with DCM (10 × 6 mL) and dried in the vacuum oven at room temperature for 48 h. The reaction mixture was diluted in DCM (100 mL) and washed with 1M HCl (pH 7). The aqueous phase was extracted with DCM (3 × 50 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to yield final product.

1-Methoxy-4-[2-phenyl-1-ethenyl]benzene (Table 2, entry 1):

Obtained as an off-white solid (191 mg, 91%). $\mathbf{R_f}$ (Hexane/EtOAc 95/5): 0.41; **mp**: 130-132 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.50-7.43 (m, 4H, Ar + Ar'), 7.34 (t, 2H, J = 7.6 Hz, Ar'), 7.23 (t, 1H, J = 7.6 Hz, Ar'), 7.06 (d, 1H, J = 16.3 Hz, C*H*=CH), 6.97 (d, 1H, J = 16.3 Hz, C*H*=CH), 6.89 (d, 2H, J = 8.8 Hz, Ar), 3.82 (s, 3H, CH_3O); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ_C 159.5, 137.8, 130.3, 128.8, 128.4, 127.9, 127.4, 126.8, 126.4, 114.3, 55.5; **MS** (EI): m/z (%) 210 ($[M]^{+\cdot}$, 100), 195 (29), 179 (20), 165 (64), 152 (29), 105 (16), 89 (18).

1-(2-Phenyl-1-ethenyl)-4-(trifluoromethyl)benzene (Table 2, entry 2):

Obtained as a white solid (235 mg, 95%). $\mathbf{R_f}$ (Hexane): 0.41; **mp**: 130-132 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.66-7.64 (m, 4H, Ar + Ar'), 7.57 (d, 2H, J = 7.5 Hz, Ar), 7.42 (t, 2H, J = 7.5 Hz, Ar'), 7.36-7.29 (m, 1H, Ar'), 7.23 (d, 1H, J = 16.3 Hz, C*H*=CH), 7.15 (d, 1H, J = 16.3 Hz, C*H*=CH); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ_C 141.0, 136.8, 131.4, 129.0, 128.4, 127.3, 126.9, 126.7, 125.8, 125.8; **MS** (EI): m/z (%) 248 ($[M]^{+\cdot}$, 78), 227 (14), 179 (100), 178 (83), 152 (13), 105 (16), 89 (12).

1-Nitro-4-[2-phenyl-1-ethenyl]benzene (Table 2, entry 3):

Obtained as a yellow solid (219 mg, 97%). **R_f** (Hexane/EtOAc 95/5): 0.33; **mp**: 151-153 °C); **^{1}H NMR** ($CDCl_3$, 250 MHz): δ_H 8.15 (d, 2H, *J* = 8.8 Hz, Ar), 7.56 (d, 2H, *J* = 8.8 Hz, Ar), 7.49 (d, 2H, *J* = 7.5 Hz, Ar'), 7.38-7.25 (m, 3H, Ar'), 7.21 (d, 1H, *J* = 16.3 Hz, C*H*=CH), 7.07 (d, 1H, *J* = 16.3 Hz, C*H*=CH); **^{13}C NMR** ($CDCl_3$, 63 MHz): δ_C 146.7, 143.8, 136.1, 133.3, 128.9, 128.8, 127.0, 126.8, 126.2, 124.1; **MS** (EI): m/z (%) 225 ($[M]^{+\cdot}$, 93), 179 (40), 178 (100), 152 (35), 115 (10), 89 (18), 76 (21).

1-Methyl-4-[2-phenyl-1-ethenyl]benzene (Table 2, entry 4):

Obtained as an off-white solid (189 mg, 97%). **R_f** (Hexane): 0.34; **mp**: 115-117 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.52 (d, 2H, *J* = 7.8 Hz, Ar'), 7.43 (d, 2H, *J* = 8.0 Hz, Ar), 7.37 (t, 2H, *J* = 7.8 Hz, Ar'), 7.26 (m, 1H, Ar'), 7.19 (d, 2H, *J* = 8.0 Hz, Ar), 7.12 (d, 1H, *J* = 16.4 Hz, C*H*=C*H*), 7.07 (d, 1H, *J* = 16.4 Hz, C*H*=C*H*), 2.38 (s, 3H, CH_3); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ_C 137.7, 137.7, 134.7, 129.5, 128.8, 127.9, 127.5, 126.6, 126.5, 21.4; **MS** (EI): m/z (%) 194 ($[M]^{+\cdot}$, 100), 179 (81), 178 (64), 152 (9), 115 (15), 96 (40), 89 (12).

1,2-Diphenylethene (Table 2, entry 5):

Obtained as a white solid (171 mg, 95%). **R_f** (Hexane): 0.34; **mp**: 122-124 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.57-7.54 (m, 4H, Ar), 7.42-7.38 (m, 4H, Ar), 7.32-7.28 (m, 2H, Ar), 7.15 (s, 2H, C*H*=CH); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ_C 137.5, 128.9, 128.8, 127.8, 126.7; **MS** (EI): m/z (%) 180 ($[M]^{+\cdot}$, 100), 179 (88), 178 (58), 165 (33), 152 (13), 89 (43).

Various Heck-Mizoroki reactions with a range of substrates:

The general procedure for Heck-Mizoroki coupling gave:

1,2-Diphenylethene (Table 3, entry 1):

Obtained as a white solid (165 mg, 92%). **R_f** (Hexane/EtOAc 9/1): 0.83; **mp**: 118-120 °C; **^{1}H NMR** ($CDCl_3$, 300 MHz): δ_H 7.54-7.50 (m, 4H, Ar), 7.39-7.32 (m, 4H, Ar), 7.29-

7.23 (m, 2H, Ar), 7.12 (s, 2H, C*H*=CH); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ_C 137.5, 128.8, 127.7, 126.6; **MS** (EI): m/z (%) 180 ($[M]^{+\cdot}$, 89), 179 (95), 178 (96), 165 (100), 152 (85), 89 (80).

4-[2-Phenyl-1-ethenyl]pyridine (Table 3, entry 2):

Obtained as a white solid (176 mg, 97%). **R_f** (Hexane/EtOAc 8/2): 0.09; **mp**: 127-129 °C; **^{1}H NMR** ($CDCl_3$, 300 MHz): δ_H 8.54 (d, 2H, *J* = 3.7 Hz, Ar'), 7.50 (dd, 2H, *J* = 1.2, 8.1 Hz, Ar), 7.38-7.28 (m, 5H, Ar + Ar'), 7.25 (d, 1H, *J* = 16.3 Hz, C*H*=CH), 6.96 (d, 1H, *J* = 16.3 Hz, C*H*=CH); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ_C 150.2, 144.6, 136.2, 133.2, 128.9, 128.8, 127.1, 126.0, 120.9; **MS** (EI): m/z (%) 181 ($[M]^{+\cdot}$, 81), 180 (100), 152 (31), 89 (16).

Methyl 4-[2-(4-methoxyphenyl)-1-ethenyl]benzoate (Table 3, entry 3):

Obtained as a white solid (178 mg, 93%). **R_f** (Hexane/EtOAc 9/1): 0.28; **mp**: 87-88 °C; **^{1}H NMR** ($CDCl_3$, 300 MHz): δ_H 7.62 (d, 1H, *J* = 16.0 Hz, C*H*=CH), 7.43 (d, 2H, *J* = 8.8 Hz, Ar), 6.86 (d, 2H, *J* = 8.8 Hz, Ar), 6.28 (d, 1H, *J* = 16.0 Hz, C*H*=CH), 3.78 (s, 3H, CH_3O), 3.76 (s, 3H, CH_3O); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ_C 167.7, 161.4, 144.5, 129.7, 127.1, 115.3, 114.3, 55.3, 51.5; **MS** (EI): m/z (%) 192 ($[M]^{+\cdot}$, 72), 161 (100), 133 (36), 118 (18), 102 (8), 89 (31).

***tert*-Butyl 4-[2-(4-methoxyphenyl)-1-ethenyl]benzoate (Table 3, entry 4):**

Obtained as a yellow oil (151 mg, 79%). **R_f** (Hexane/EtOAc 9/1): 0.43; **^{1}H NMR** ($CDCl_3$, 300 MHz): δ_H 7.53 (d, 1H, *J* = 15.9 Hz, C*H*=CH), 7.42 (d, 2H, *J* = 8.7 Hz, Ar), 6.85 (d, 2H, *J* = 8.7 Hz, Ar), 6.23 (d, 1H, *J* = 15.9 Hz, C*H*=CH), 3.77 (s, 3H, CH_3O), 1.52 (s, 9H, (CH_3)$_3$CO); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ_C 166.6, 161.2, 143.2, 138.2, 129.5, 127.4, 117.7, 116.4, 114.3, 80.1, 55.3, 28.2; **MS** (EI): m/z (%) 234 ($[M]^{+\cdot}$, 6), 178 (39), 161 (17), 133 (5), 118 (3), 89 (5).

4-[2-(4-Methoxyphenyl)-1-ethenyl]pyridine (Table 3, entry 5):

Obtained as a yellow solid (205 mg, 97%). **R_f** (Hexane/EtOAc 8/2): 0.07; **mp**: 133-135 °C; **^{1}H NMR** ($CDCl_3$, 300 MHz): δ_H 8.53 (d, 2H, *J* = 5.75 Hz, Ar'), 7.45 (d, 2H, *J* = 8.7

Hz, Ar), 7.30 (d, 2H, *J* = 5.75 Hz, Ar'), 7.22 (d, 1H, *J* = 16.3 Hz, C*H*=CH), 6.90 (d, 2H, *J* = 8.7 Hz, Ar), 6.84 (d, 1H, *J* = 16.3 Hz, C*H*=CH); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ_C 160.2, 150.2, 145.0, 132.8, 129.0, 128.5, 123.8, 120.7, 114.4, 55.4; **MS** (EI): m/z (%) 211 ($[M]^{+\cdot}$, 100), 196 (15), 180 (18), 152 (7), 89 (10).

1-Methoxy-4-[2-phenyl-1-ethenyl]benzene (Table 3, entries 6 and 7):

Obtained as a white solid (for X = I: 191 mg, 91%, for X = Br: 8 mg, 4%). **R_f** (Hexane/EtOAc 9/1): 0.58; **mp**: 131-133 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.43-7.36 (m, 4H, Ar + Ar'), 7.27 (t, 2H, *J* = 7.3 Hz, Ar'), 7.21-7.13 (m, 1H, Ar'), 6.99 (d, 1H, *J* = 16.3 Hz, C*H*=CH), 6.90 (d, 1H, *J* = 16.3 Hz, C*H*=CH), 6.82 (d, 2H, *J* = 8.8 Hz, Ar), 3.75 (s, 3H, CH_3O); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ_C 159.5, 137.8, 130.3, 128.8, 128.4, 127.9, 127.4, 126.8, 126.4, 114.3, 55.5; **MS** (EI): m/z (%) 210 ($[M]^{+\cdot}$, 100), 195 (19), 179 (13), 165 (50), 152 (27), 105 (9), 89 (11).

Recycling test of XL-Pd plugs in Suzuki-Miyaura reactions:

Synthesis of 4-nitrobiphenyl

To a solution of 4-nitro bromobenzene (202 mg, 1.0 mmol) in *N,N'*-dimethylformamide (4 mL) were added phenylboronic acid (183 mg, 1.5 mmol, 1.5 eq), K_2CO_3 (415 mg, 3.0 mmol, 3.0 eq) and 1 XL-Pd plug catalyst (0.1 mmol, 0.1 eq). The reaction mixture was heated at 80 °C and stirred for 48 h. The Pd plug was removed from solution with tweezers, washed with dichloromethane (10 × 6 mL) and dried in a vacuum oven at 40 °C for 48 h before its reuse in next cycle. The reaction mixture was diluted with dichloromethane (100 mL) and washed with 1M HCl (pH 7). The aqueous phase was extracted with dichloromethane (3 × 50 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Hexane) to yield a pale yellow solid [183 mg, 92% (1st use), 192 mg, 96% (2nd use), 174 mg, 87% (3rd use), 184 mg, 92% (4th use)]. **R_f** (Hexane/EtOAc 9/1): 0.60; **mp**: 111-113 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 8.28 (d, 2H, *J* = 8.8 Hz, Ar), 7.72 (d, 2H, *J* = 8.8 Hz, Ar), 7.64-7.61 (m, 2H, Ar'), 7.53-7.43 (m,

3H, Ar'); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ_C 147.6, 147.1, 138.8, 129.2, 129.0, 127.8, 127.4, 124.1; **MS** (EI): m/z (%) 199 ($[M]^{+\cdot}$, 50), 169 (57), 152 (100).

Recycle test of XL-Pd plugs in Sonogashira-Hagihara reactions:

Synthesis of 1-nitro-4-(2-phenyl-1-ethynyl)benzene

To a solution of 4-nitro bromobenzene (202 mg, 1.0 mmol) in *N,N'*-dimethylformamide (4 mL) were added phenyl acetylene (165 μL, 1.5 mmol, 1.5 eq), K_2CO_3 (415 mg, 3.0 mmol, 3.0 eq) and 1 XL-Pd plug catalyst (0.1 mmol, 0.1 eq). The reaction mixture was heated at 80 °C and stirred for 48 h. The Pd plug was removed from solution with tweezers, washed with dichloromethane (10 × 6 mL) and dried in a vacuum oven at 40 °C for 48 h before its reuse in next cycle. The reaction mixture was diluted in dichloromethane (100 mL) and washed with 1M HCl (pH 7). The aqueous phase was extracted with dichloromethane (3 × 50 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Hexane) to yield a bright yellow solid [162 mg, 73% (1st use), 165 mg, 74% (2nd use), 163 mg, 73% (3rd use), 160 mg, 72% (4th use)]. **R_f** (Hexane/EtOAc 9/1): 0.64; **mp**: 117-119 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 8.22 (t, 2H, J = 8.0 Hz, Ar), 7.66 (t, 2H, J = 8.0 Hz, Ar), 7.58-7.54 (m, 2H, Ar'), 7.41-7.38 (m, 3H, Ar'); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ_C 147.1, 132.4, 132.0, 130.4, 129.4, 128.7, 123.8, 122.3, 94.9, 87.7; **MS** (EI): m/z (%) 223 ($[M]^{+\cdot}$, 100), 193 (83), 176 (95).

Recycle test of XL-Pd plugs in Heck-Mizoroki reactions:

Synthesis of 1,2-diphenylethene

To a solution of iodobenzene (112 μL, 1.0 mmol) in *N,N'*-dimethylformamide (5 mL) were added styrene (172 μL, 1.5 mmol, 1.5 eq), K_2CO_3 (207 mg, 1.5 mmol, 1.5 eq) and 1 XL-Pd plug catalyst (1 μmol, 0.001 eq). The reaction mixture was heated at 115 °C and stirred for 48 h. The Pd plug was removed from solution with tweezers, washed with dichloromethane (10 × 6 mL) and dried in the vacuum oven at 40 °C for 48 h. The reaction mixture was diluted in dichloromethane (100 mL) and washed with 1M HCl (pH

7). The aqueous phase was extracted with dichloromethane (3 × 50 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Hexane, Hexane/EtOAc 95/05) to yield an off-white solid [165 mg, 92% (1st use), 149 mg, 83% (2nd use), 146 mg, 81% (3rd use), 142 mg, 79% (4th use)]. **R_f** (Hexane/EtOAc 9/1): 0.83; **mp**: 118-120 °C; **^{1}H NMR** ($CDCl_3$, 300 MHz): δ_H 7.54-7.50 (m, 4H, Ar), 7.39-7.32 (m, 4H, Ar), 7.29-7.23 (m, 2H, Ar), 7.12 (s, 2H, C*H*=CH); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ_C 137.5, 128.8, 127.7, 126.6; **MS** (EI): m/z (%) 180 ($[M]^{+\cdot}$, 89), 179 (95), 178 (96), 165 (100), 152 (85), 89 (80).