Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Heck, Suzuki and Sonogashira Cross-Coupling Reactions using ppm Level of SBA-16 Supported Pd-Complex

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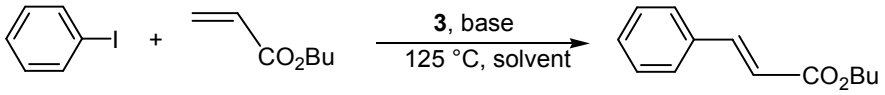
Supplementary material

Table 1: Structural information of the SBA-16 supported Pd complex **3**

Sample	Surface area	Pore diameter	Pore volume	Functional group
SBA-16	820 m^2/g	5.13 nm	0.73 cm^3/g	-
1	655 m^2/g	3.97 nm	0.43 cm^3/g	0.7 mmol/g
2	520 m^2/g	3.55 nm	0.35 cm^3/g	0.4 mmol/g
3	465 m^2/g	3.10 nm	0.28 cm^3/g	0.25 mmol/g

Table 2. Heck coupling of iodobenzene with methyl acrylate[a]



Entry	Solvent (1:1)	Base	**3** (mol%)	Time (h)	Yield (%)[b]
1	DMA:H_2O	Na_2CO_3	1.5	0.8	100
2	DMA:H_2O	Na_2CO_3	1.0	1.5	98(96)[c]
3	DMA:H_2O	Na_2CO_3	0.3	2	90
4	DMA:H_2O	Na_2CO_3	0.1	2.5	81
5	DMA:H_2O	Na_2CO_3	0.05	4	95
6	DMA:H_2O	Na_2CO_3	0.01	5	89(85)[c]
7	DMA:H_2O	K_2CO_3	1.0	1.5	95
8	DMA:H_2O	NaOMe	1.0	1.5	95
9	DMA:H_2O	Na_2PO_4	1.0	1.5	93
10	DMA:H_2O	K_2PO_4	1.0	1.5	92
11	DMSO:H_2O	Na_2CO_3	1.0	1.5	95
12	NMP:H_2O	Na_2CO_3	1.0	1.5	94
13	DMF:H_2O	Na_2CO_3	1.0	1.5	96
14	Dodacane:H_2O	Na_2CO_3	1.0	6	82

[a] All reactions were carried using 1 mmol of iodobenzene, 1.3 mmol of butyl acrylate, a catalytic amount of **3** and 2 mmol of base in 2 mL of solvent. [b] GC yield determined using *n*-decane as an internal standard and based on the amount of iodobenzene employed. [c] Isolated yield.

(E)-3-Phenylacrylic acid n-butyl ester ***4a*** *[1]:* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 16.0 Hz, 1 H), 7.53-7.51 (m, 2 H), 7.39-7.36 (m, 3 H), 6.46 (d, *J* = 16.05 Hz, 1 H), 4.21 (t, *J* = 6.9 Hz, 2 H), 1.72-1.67 (m, 2 H), 1.47-1.40 (sextet, *J* = 7.45 Hz, 2 H), 0.96 (t, *J* = 7.45 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 167.07, 144.51, 134.45, 130.16, 1128.84, 128.02, 118.28, 64.39, 30.75, 19.17, 13.72. EI-MS *m/z* = 204 (M^+).

(E)-3-(4′-tolyl)acrylic acid n-butyl ester ***4b*** *[1]:* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.67 (d, *J* = 16.05 Hz, 1 H), 7.43 (d, *J* = 8.10 Hz, 2 H), 7.19 (d, *J* = 8.05 Hz, 2 H), 6.40 (d, *J* = 16.0 Hz, 1 H), 4.20 (t, *J* = 6.3 Hz, 2 H), 2.36 (s, 3 H), 1.71-1.65 (m, 2 H), 1.47-1.40 (m, 2 H), 0.94 (t, *J* = 7.45 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 167.28, 144.52 140.58, 131.73, 129.57, 128.02, 117.18, 64.32,

30.77, 21.42, 19.18, 13.73. EI-MS *m/z* = 218 (M^+).

(E)-3-(4′-Methoxyphenyl)acrylic acid n-butyl ester ***4c*** *[1]:* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 16.0 Hz, 1 H), 7.48 (d, *J* = 8.6 Hz, 2 H), 6.90 (d, *J* = 8.5 Hz, 2 H), 6.32 (d, *J* = 16.0 Hz, 1 H), 4.19 (t, *J* = 7.0 Hz, 2 H), 3.83 (s, 3 H), 1.71-1.65 (m, 2 H), 1.45-1.41 (sextet, *J* = 7.5 Hz, 2 H), 0.96 (t, *J* = 7.5 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 167.42, 161.29, 144.17, 129.66, 127.20, 115.76, 114.28, 64.23, 55.33, 30.79, 19.18, 13.73. EI-MS *m/z* = 234 (M^+).

(E)-3-(4′-Nitrophenyl)acrylic acid n-butyl ester ***4d*** *[1]:* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.25 (d, *J* = 8.55 Hz, 2 H), 7.72-7.66 (m, 3 H), 6.58 (d, *J* = 16.0 Hz, 1 H), 4.24 (t, *J* = 6.3 Hz, 2 H), 1.73-1.67 (m, 2 H), 1.48-1.42 (m, 2 H), 0.97 (t, *J* = 7.7 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.10, 148.47, 141.56, 140.59, 128.60, 124.14, 122.61, 64.90, 30.68, 19.15, 13.70. EI-MS *m/z* = 249 (M^+).

(E)-3-(4-Acetylphenyl)acrylic acid n-butyl ester ***4e*** *[1]:* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 8.0 Hz, 2 H), 7.71 (d, *J* = 16.5 Hz, 1 H), 7.621 (d, *J* = 8.0 Hz, 2 H), 6.54 (d, *J* = 16.05 Hz, 1 H), 4.22 (t, *J* = 6.9 Hz, 2 H), 2.61 (s, 3 H), 1.72-1.67 (m, 2 H), 1.46-1.42 (m, 2 H), 0.97 (t, *J* = 7.45 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 197.28, 166.55, 142.93, 138.79, 137.94, 128.82, 128.08, 120.82, 64.65, 30.71, 26.64, 19.15, 13.70. EI-MS *m/z* = 246 (M^+).

(E)-3-(4′-Trifluoromethylphenyl)acrylic acid n-butyl ester ***4f*** *[1]:* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 15.0 Hz, 1 H), 7.65-7.61 (m, 4 H), 6.52 (d, *J* = 16.0 Hz, 1 H), 4.23 (t, *J* = 6.7 Hz, 2 H), 1.72-1.64 (m, 2 H), 1.48-1.40 (sextet, *J* = 7.5 Hz, 2 H), 0.97 (t, *J* = 7.45 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.48, 142.63, 137.83, 131.81 (q, *J* = 23.2 Hz), 128.13, 125.86 (q, *J* = 3.57 Hz), 124.89, 122.72, 120.86, 64.69, 30.71, 19.15, 13.69. EI-MS *m/z* = 272 (M^+).

n-Butyl trans-3-(3-pyridinyl)acrylate ***4g*** *[2]:* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.75 (s, 1 H), 8.61-8.60 (m, 1 H), 7.84 (d, *J* = 7.5 Hz, 1 H), 7.68 (d, *J* = 16.1 Hz, 1 H), 7.34-7.32 (m, 1 H), 6.53 (d, *J* = 16.1 Hz, 1 H), 4.23 (t, *J* = 7.0 Hz, 2 H), 1.72-1.67 (quint, *J* = 6.5 Hz, 2 H), 1.47-1.40 (sextet, *J* = 7.5 Hz, 2 H), 0.97 (t, *J* = 7.5 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) 166.37, 150.93, 149.68, 140.78, 134.16, 130.21, 123.69, 120.48, 64.68, 30.69, 19.15, 13.70. EI-MS *m/z* = 205 (M^+).

(E)-N-Isopropyl-cinnamamide ***4h****:* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 15.5 Hz, 1 H), 7.48-7.47 (m, 2 H), 7.36-7.33 (m, 3 H), 6.39 (d, *J* = 16.6 Hz, 1 H), 5.62 (brs, 1 H), 4.26-4.19 (m, 1 H), 1.22 (d, *J* = 6.3 Hz, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 164.98, 140.63, 134.91, 129.48, 128.74, 127.68, 121.06, 41.54, 22.81. EI-MS *m/z* = 189 (M^+).

(E)-N-isopropyl-3-(p-tolyl)acrylamide ***4i****:* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.48 (d, *J* = 15.5 Hz, 1 H), 7.39 (d, *J* = 8.0 Hz, 2 H), 7.16 (d, *J* = 7.45 Hz, 2 H) 6.32 (d, *J* = 15.45 Hz, 1 H), 5.46 (brs, 1 H), 4.25-4.19 (m, 1 H), 2.35 (s, 3 H), 1.22 (d, *J* = 6.3 Hz, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.15, 140.63, 139.77, 132.15, 129.48, 127.66, 119.97, 41.50, 22.85, 21.36. EI-MS *m/z* = 203 (M^+).

(E)-N-isopropyl-3-(4-methoxyphenyl)acrylamide ***4j****:* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.58 (d, *J* = 16.05 Hz, 1 H),7.43 (d, *J* = 8.6 Hz, 2 H), 6.86 (d, *J* = 8.6 Hz, 2 H), 6.26 (d, *J* = 16. 0 Hz, 1 H), 5.56 (brs, 1 H), 4.25-4.18 (m, 1 H), 3.81 (s, 3 H), 1.22 (d, *J* = 6.85 Hz, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.31, 160.72, 140.22, 129.20, 127.62, 118.69, 114.17, 55.30, 41.46, 22.84. EI-MS *m/z* = 219 (M^+).

(E)-Stilbene ***4k*** *[2]:* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.51 (d, *J* = 7.4 Hz, 4 H), 7.36-7.33 (m, 4 H), 7.27-7.25 (m, 2 H), 7.10 (d, *J* = 11.5 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 137.38, 128.65, 127.6, 126.49. EI-MS *m/z* = 180 (M^+).

(E)-1-Styryl-4-(trifluoromethyl)benzene ***4l*** *[2]:* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.60 (m, 4 H), 7.54 (d, *J* = 7.7 Hz, 2 H), 7.38 (t, *J* = 7.4 Hz, 2 H), 7.30 (t, *J* = 7.5 Hz, 1 H), 7.21 (d, *J* = 16.5 Hz, 1 H), 7.13 (d, *J* = 16.5 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 136.62, 131.19, 128.78, 128.27, 127.11, 126.76, 126.56, 125.63 (q, *J* = 3.57 Hz, C-F), 123.12. EI-MS *m/z* = 248 (M^+).

(E)-4-Methylstilbene ***4m*** *[2]:* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.51 (d, *J* = 8.0 Hz, 2 H), 7.42 (d, *J* = 7.5 Hz, 2 H), 7.34 (t, *J* = 8.0 Hz, 2 H), 7.25-7.22 (m, 1 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 7.07 (d, *J* = 4.05 Hz, 2 H), 2.36 (s, 3 H).^{13}C NMR (125 MHz, $CDCl_3$) δ: 137.51, 134.54, 129.38, 128.64, 127.69, 127.39, 126.37, 21.23. EI-MS *m/z* = 194 (M^+).

(E)-4-Methoxystilbene ***4n*** *[2]:* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.49-7.44 (m, 4 H), 7.34 (t, *J* = 7.5 Hz, 2 H), 7.26-7.21 (m, 1 H), 7.08 (d, *J* =16.0 Hz, 1 H), 6.99 (d, *J* = 16.5 Hz, 1 H), 6.90 (d, *J* = 5.0 Hz, 2 H), 3.82 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.30, 137.64, 130.14, 128.63, 128.20, 127.70, 127.20, 126.61, 126.23, 114.13, 55.31. EI-MS *m/z* = 210 (M^+).

(E)-4-Styrylbenzonitrile ***4o*** *[2]:* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.63 (d, *J* = 8.15 Hz, 2 H), 7.57 (d, *J* = 6.5 Hz, 2 H), 7.53 (d, *J* = 7.45 Hz, 2 H), 7.38 (m, 2 H), 7.31 (t, *J* = 7.45 Hz, 1 H), 7.23 (t, *J* = 16.6 Hz, 1 H), 7.10 (d, *J* = 16.6 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 141.81, 136.26, 132.46, 132.38, 128.84, 128.62, 126.89, 126.83, 126.70, 119.00, 110.56. EI-MS *m/z* = 205 (M^+).

General procedure for the Sonogashira reaction

Aryl halide (1 mmol), phenylacetylene (1.2 mol equiv), piperidine (2 mol equiv) and the Pd-complex **3** 0.8 mg, 0.02 mol%, 200 mol ppm) was stirred at 80 °C for 2 h monitoring periodically by GC analysis. The reaction mixture was cold at room temperature and diluted with EtOAc and the immobilized Pd-complex was separated by filtration. The organic layer was washed by H_2O and dried over $MgSO_4$. Solvent was evaporated under reduced pressure and the residue was purified by short column chromatography on silica gel eluted with *n*-hexane/EtOAc to afford the corresponding coupling products in up to 96% yield.

Diphenylacetylene ***6a*** *[3]:* ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.52-7.47 (m, 4H), 7.35-7.28 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 131.5, 128.1, 128.1, 123.2, 89.6. EI-MS *m/z* = 178 (M^+).

Phenyl-p-tolyacetylene ***6b*** *[3]:* ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.51-7.49 (m, 2 H), 7.42 (d, *J* = 7.89 Hz, 2 H), 7.32-7.26 (m, 3 H), 7.12 (d, *J* = 7.88 Hz, 2 H), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 138.2, 131.4, 129.2, 128.3, 128.3, 123.4, 120.3, 89.7, 88.6, 21.5. EI-MS *m/z* = 192 (M^+).

4-Methoxyphenyl-phenylacetylene ***6c*** *[3]:* ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.51-7.47 (m, 4 H), 7.35-7.31 (m, 3 H), 6.85 (dd, *J* = 8.78, 2.2 Hz, 2 H), 3.83 (s, 3 H).^{13}C NMR ($CDCl_3$, 125 MHz) δ: 159.3, 133.2, 131.2, 128.4, 127.8, 123.6, 115.4, 114.0, 89.4, 88.1, 55.2. EI-MS *m/z* = 208 (M^+).

4-Acetylphenyl-phenylacetylene ***6d*** *[3]:* ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.92 (d, *J* = 8.49Hz, 2 H), 7.60 (d, *J* = 8.49 Hz, 2 H), 7.55-7.53 (m, 2H), 7.37-7.34 (m, 3 H), 2.59 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 197.2, 136.3, 131.9, 131.7, 128.9, 128.6, 128.1, 128.1, 122.5, 92.8, 88.4, 26.7. EI-MS *m/z* = 220 (M^+).

4-Cyanophenyl-phenylacetylene ***6e*** *[4]:* ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.66-7.59 (m, 4 H), 7.57-7.54 (m, 2 H), 7.41-7.38 (m, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 132.1, 131.7, 129.2, 128.6, 128.3, 122.3, 118.6, 111.5, 93.8, 87.8. EI-MS *m/z* = 203 (M^+).

4-Nitrophenyl-phenylacetylene ***6f*** *[3]:* ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.20 (d, *J* = 8.92 Hz, 2 H), 7.65 (d, *J* = 8.90 Hz, 2 H), 7.57-7.54 (m, 2 H), 7.41-7.37 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 147.1, 132.1, 131.9, 130.3, 129.3, 128.6, 123.8, 122.1, 94.8, 87.6. EI-MS *m/z* = 223 (M^+).

General procedure for the Suzuki reaction

A mixture of aryl halide (1 mmol), boronic acid (1.1 mol equiv), K_2CO_3 (2 mol equiv), and the Pd-complex **3** (0.4 mg, 0.01 mol%, 100 mol ppm) in aqueous ethanol (1:1) was stirred at 90 ºC for 6 h. The reaction was monitored with GC until the complete consumption of the aryl halide. The Pd-complex **3** was separated by filtration and the reaction mixture was diluted with H_2O and ether. The organic layer was dried over $MgSO_4$ and then evaporated under reduced pressure. The residue was purified by short column chromatography on silica gel to give the corresponding coupling product in up to 94% isolated yield.

4-Methoxybiphenyl ***5a*** *[5]:* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.83 (s, 3 H), 6.97 (d, *J* = 8.6 Hz, 2 H), 7.30 (t, *J* = 8.0 Hz, 1 H), 7.42 (t, *J* = 8.0 Hz, 2 H), 7.51-7.55 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 55.2, 114.2, 126.7, 128.1, 128.2, 128.7, 133.7, 140.8, 159.1; FTIR (cm^{-1}): 3032, 3010, 2836, 1609, 1518, 1485, 1440, 1291, 1261, 1245, 1215, 1043, 833, 746, 719, 697; MS-EI, m/z 184 (M^+).

4-Methylbiphenyl ***5b*** *[5]:* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.39 (s, 3 H), 7.25 (d, *J* = 8.0 Hz, 2 H), 7.31 (t, *J* = 7.4 Hz, 1 H), 7.42 (t, *J* = 7.4 Hz, 2 H), 7.49 (d, *J* = 8.0 Hz, 2 H), 7.58 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 21.0, 126.9, 127.0, 128.6, 129.4, 137.0, 138.3, 141.1; FTIR (cm^{-1}): 3031, 2920, 2859, 1601, 1518, 1486, 1445, 1216, 1111, 1038, 1007, 821, 746, 696; MS-EI, m/z 168 (M^+).

Biphenyl-4-ol ***5c*** *[5]:* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.96 (brs, 1 H), 6.62 (d, *J* = 8.6 Hz, 2 H), 6.91 (d, *J* = 8.6 Hz, 1 H), 7.30 (t, *J* = 7.4 Hz, 1 H), 7.41 (t, *J* = 7.4 Hz, 1 H), 7.47-7.54 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 115.6, 126.6, 128.3, 128.7, 134.0, 140.7, 155.3; FTIR (cm^{-1}): 3362, 3019, 1582, 1485, 1257, 1213, 1171, 1006, 822, 742, 698, 667; MS-EI, m/z 170 (M^+).

Biphenyl-4-amine ***5d*** *[5]:* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.66 (brs, 2 H), 6.45 (d, *J* = 8.6 Hz, 2 H), 6.75 (d, *J* = 8.6 Hz, 1 H), 7.26 (t, *J* = 7.4 Hz, 1 H), 7.37-7.42 (m, 4 H), 7.52 (d, *J* = 7.4 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 115.3, 117.2, 126.3, 127.9, 128.6, 131.5, 135.4, 137.8, 141.0, 145.9; FTIR (cm^{-1}): 3452, 3368, 3215, 3025, 2922, 1617, 1588, 1484, 1297, 1177, 1058, 1000, 814, 751, 689; MS-EI, m/z 169 (M^+).

4,4'-dimethylbiphenyl ***5e*** *[5]:* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.38 (s, 6 H), 7.23 (dd, *J* = 8.0, 1.7 Hz, 4 H), 7.47 (dd, *J* = 8.0, 1.7 Hz, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 21.0, 126.7, 129.4, 136.6, 138.2; FTIR (cm^{-1}): 3032, 2924, 2854, 1500, 1214, 1111, 1002, 803, 746, 668; MS-EI, m/z 182 (M^+).

4-Acetyl- 1,1'-biphenyl ***5f*** *[5]:* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.64 (s, 3 H), 7.47 (t, *J* = 7.4, Hz, 2 H), 7.62-7.69 (m, 5 H), 8.04 (d, *J* = 8.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 26.6, 127.2, 128.1, 128.9, 129.7, 135.8, 137.9, 139.8, 145.7, 197.7; FTIR (cm^{-1}): 3073, 3001, 1676, 1591, 1485, 1391, 1357, 1262, 1179, 1076, 1005, 958, 835, 754, 690; MS-EI, m/z 196 (M^+).

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