

Electronic Supporting Information file

Palladium nanoparticles on carbon nanotubes as catalysts of cross-coupling reactions

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S1. Preparation of catalysts

S1.1 Purification of carbon nanostructures

Carbon nanostructures were purchased from a range of commercial suppliers and treated prior to use in an attempt to remove any residual metal catalyst from synthesis: SWNT (Helix SWNT from Helix Material Solutions, made by arc discharge), DWNT (Nanocyl 2100 from Nanocyl, made by CVD), MWNT (Baytubes C150P from Bayer Material Science, made by CVD) and GNF (Pyrograf PR19 from Applied Science Inc., made by CVD). In a typical procedure: carbon nanostructures (50 mg) were dispersed in concentrated hydrochloric acid (25 mL) and bath sonicated for 30 minutes at room temperature. The suspension was diluted with deionised water (500 mL), filtered under vacuum (0.2 μm , PTFE membrane), successively washed with deionised water (750 mL) and methanol (500 mL) and finally dried under vacuum to yield a black solid.

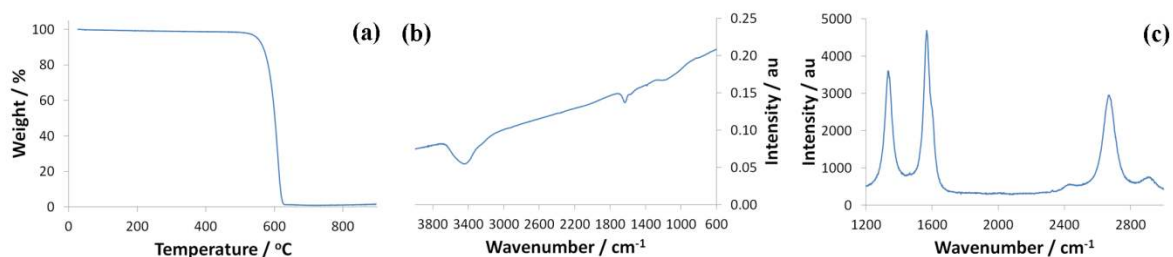


Figure S1. (a) Thermogravimetric analysis, (b) infrared and (c) Raman spectroscopic analysis of MWNT following treatment in hydrochloric acid. TGA indicates a low percentage of functional groups (1.8% weight loss prior to the oxidation of carbon nanotubes at 610 °C) and a low quantity of residual metal subsequent to carbon nanotube oxidation (1.3 % at 800 °C). The $\nu_{\text{C=C}}$ stretching vibration at 1635 cm^{-1} of carbon nanotubes in the IR spectrum is the only significant spectroscopic feature observed and confirms the low number of vibrationally active functional groups (e.g. $-\text{COOH}$, $-\text{OH}$, $=\text{CO}$). The band at 3400 cm^{-1} is associated with atmospheric water. The $I_{\text{D}}/I_{\text{G}}$ ratio of 0.7 indicates a moderate number of defects, however the lack of functional groups observed through TGA and IR spectroscopy suggests these defects are not associated with functionality but rather structural dislocations in the graphitic lattice.

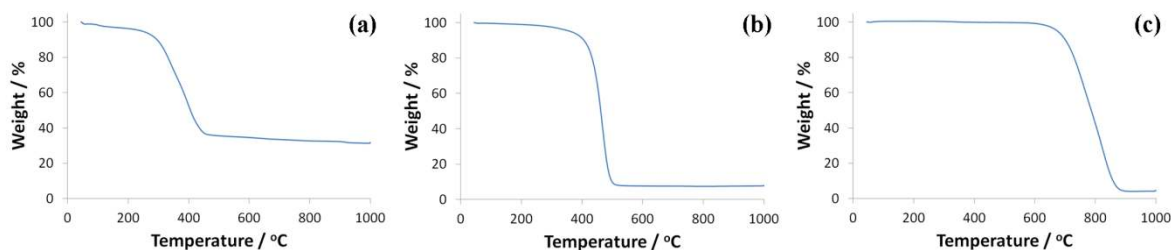


Figure S2. TGA analysis of (a) SWNT, (b) DWNT and (c) GNF following treatment in hydrochloric acid.

S1.2 Preparation of palladium nanoparticles

S1.2.1 PdNP@Salk

PdNP@Salk were prepared following a method analogous to that outlined by Zamborini *et al.*^[S1] To a solution of potassium tetrachloropalladate (150 mg, 0.46 mmol, 1 eq.) in deionised water (25 mL) was added a solution of tetraoctylammonium bromide (375 mg, 0.69 mmol, 1.5 eq.) in toluene (125 mL) and the combined biphasic mixture was vigorously stirred for 20 minutes at room temperature. The aqueous layer was separated and discarded, to the organic phase was added dodecanethiol (110 μ L, 0.46 mmol, 1 eq.) and the combined mixture was stirred for 10 minutes at room temperature. To this organic solution, a further solution of sodium borohydride (175 mg, 4.6 mmol, 10 eq.) in deionised water (10 mL) was rapidly added and the combined mixture stirred for 20 hours at room temperature. The aqueous layer was separated and discarded, the organic phase retained and washed with deionised water (2 x 50 mL) and the solvent removed under vacuum. To the crude brown solid was added a mixture of toluene (~2 mL) and ethanol (200 mL) and the product precipitated at -20 °C overnight. The obtained solid was collected by vacuum filtration (0.2 μ m, PTFE membrane), successively washed with ethanol (250 mL) and acetone (250 mL) and finally dried under vacuum to yield a dark brown solid (105 mg).

S1.2.2 PdNP@Nalk

PdNP@Nalk were prepared following a method analogous to that outlined by Mazumder *et al.*^[S2] To palladium acetylacetonate (75 mg, 0.25 mmol, 1 eq.) was added oleylamine (15 mL, 45.6 mmol, 185.4 eq.) and the combined mixture stirred under an inert atmosphere of argon for 10 minutes at 60 °C. To this was added *via* syringe a solution of boron *tert*-butylamine complex (300 mg, 3.4 mmol, 13.8 eq.) in oleylamine (4 mL) and the mixture was stirred under an argon atmosphere for 1 hour at 90 °C. After cooling to room temperature, ethanol (150 mL) was added and the product was isolated by centrifugation (2 x 8000 rpm, 8 minutes) and vacuum filtration (0.2 μ m, PTFE membrane), successively washed with ethanol (250 mL) and ethyl acetate (250 mL) and finally dried under vacuum to yield a dark brown solid (14 mg).

S1.2.3 PdNP@DMAP

PdNP@DMAP were prepared following a method analogous to that outlined by Flanagan *et al.*^[S3] To a solution of potassium tetrachloropalladate (41 mg, 0.13 mmol, 1 eq.) in deionised water (3 mL) was added a bath sonicated solution of 4-dimethylaminopyridine (83.3 mg, 0.68 mmol, 5.4 eq.) in

deionised water (9 mL) and the combined mixture was vigorously stirred for 20 minutes at room temperature. To this was added an aqueous solution of sodium borohydride (1.1 mL, 1% w/v in deionised water) and the mixture was stirred for a further 20 minutes at room temperature. After stirring, the suspension was filtered through a cotton wool plug and stored as a liquid at 5°C consistent with literature protocol.^[S3]

S1.3 Preparation of MWNT/PdNP catalysts using an *ex situ* approach

S1.3.1 MWNT/PdNP-1 (MWNT/PdNP@Salk)

The *ex situ* preparation of composite catalysts was conducted following a method analogous to that described by Rance *et al.*^[S4] To a suspension of PdNP@Salk (5.0 mg) in *n*-hexane (10 mL) was added MWNT (10.0 mg) and the combined dispersion bath sonicated for 1 hour at room temperature. The product was isolated by vacuum filtration (0.2 µm, PTFE membrane), washed with *n*-hexane (50 mL) and dried under vacuum to yield a black solid (12.6 mg).

Analogous procedures were used to prepare the following catalysts:

Table S1. Synthesis and designation of CNS/PdNP@Salk catalysts.

Entry	Catalyst	Mass _{PdNP} / mg	Mass _{CNS} / mg	Volume _{<i>n</i>-hexane} / mL	Mass _{CNS/PdNP} / mg
1	SWNT/PdNP-1	25	50	50	62.4
2	DWNT/PdNP-1	25	50	50	63.2
3	MWNT/PdNP-1	5	10	10	12.6
4	MWNT/PdNP-1*	0.4	20	10	17.0
5	GNF/PdNP-1	25	50	50	52.4

S.1.3.2 MWNT/PdNP-2 (MWNT/PdNP@Nalk)

To a suspension of PdNP@Nalk (5.0 mg) in *n*-hexane (5 mL) was added MWNT (10.0 mg) and the combined dispersion bath sonicated for 1 hour at room temperature. The product was isolated by vacuum filtration (0.2 µm, PTFE membrane), washed with *n*-hexane (50 mL) and finally dried under vacuum to yield a black solid (10.5 mg).

S.1.3.3 MWNT/PdNP-3 (MWNT/PdNP@DMAP)

To an aqueous solution of PdNP@DMAP (5.0 mL) diluted with deionised water (5.0 mL) was added MWNT (10.0 mg) and the combined dispersion bath sonicated for 1 hour at room temperature. The product was isolated by vacuum filtration (0.2 µm, PTFE membrane), successively washed with deionised water (50 mL) and chloroform (50 mL) and finally dried under vacuum to yield a black solid (8.3 mg).

S1.4 Preparation of MWNT/PdNP catalysts using an *in situ* approach

S1.4.1 MWNT/PdNP-4 (MWNT/PdNP)

MWNT/PdNP-4 was prepared according to the method outlined by Corma *et al.*^[S5] To a solution of palladium diacetate (2 mg, 0.01 mmol) in anhydrous tetrahydrofuran (4 mL), purified by syringe filtration (0.2 µm, PTFE membrane) in an attempt to remove any insoluble palladium species, was added MWNT (20 mg) and the combined dispersion bath sonicated for 4 minutes at room temperature, then stirred for 4 hours at 70 °C. After cooling to room temperature, the product was isolated by vacuum filtration (0.2 µm, PTFE membrane), washed with anhydrous tetrahydrofuran (100 mL) and finally dried under vacuum to yield a black solid (19.0 mg).

S1.4.2 MWNT/PdNP-5 (MWNT/PdNP)

MWNT/PdNP-5 was prepared according to the method outlined by Yang *et al.*^[S6] To a solution of palladium dichloride (2 mg, 0.02 mmol, 1 eq.) in deionised water (5 mL) was added MWNT (20 mg) and the combined dispersion bath sonicated for 4 minutes at room temperature. To this was slowly added dropwise a solution of sodium borohydride (4.3 mg, 0.11 mmol, 6.7 eq.) in deionised water (3 mL) and the combined mixture stirred for 12 hours at room temperature. The product was isolated by vacuum filtration (0.2 µm, PTFE membrane), successively washed with deionised water (100 mL) and methanol (100 mL) and finally dried under vacuum to yield a black solid (18.7 mg).

S1.4.3 MWNT/PdNP-6 (MWNT/PdNP@SDS)

MWNT/PdNP-6 was prepared according to the method outlined by Karousis *et al.*^[S7] To MWNT (20 mg) was added an aqueous solution of sodium *n*-dodecylsulfate (288 mg, 1 mmol, 22.2 eq.) in deionised water (20 mL) and the combined dispersion bath sonicated for 20 minutes at room temperature. To this was added palladium diacetate (10 mg, 0.05 mmol, 1 eq.) and the mixture stirred for 6 hours at 100 °C. After cooling to room temperature, the product was isolated by vacuum filtration (0.2 µm, PTFE membrane), extensively washed with deionised water (3 L) and finally dried under vacuum to yield a black solid (13.0 mg).

S2. Characterisation of catalysts

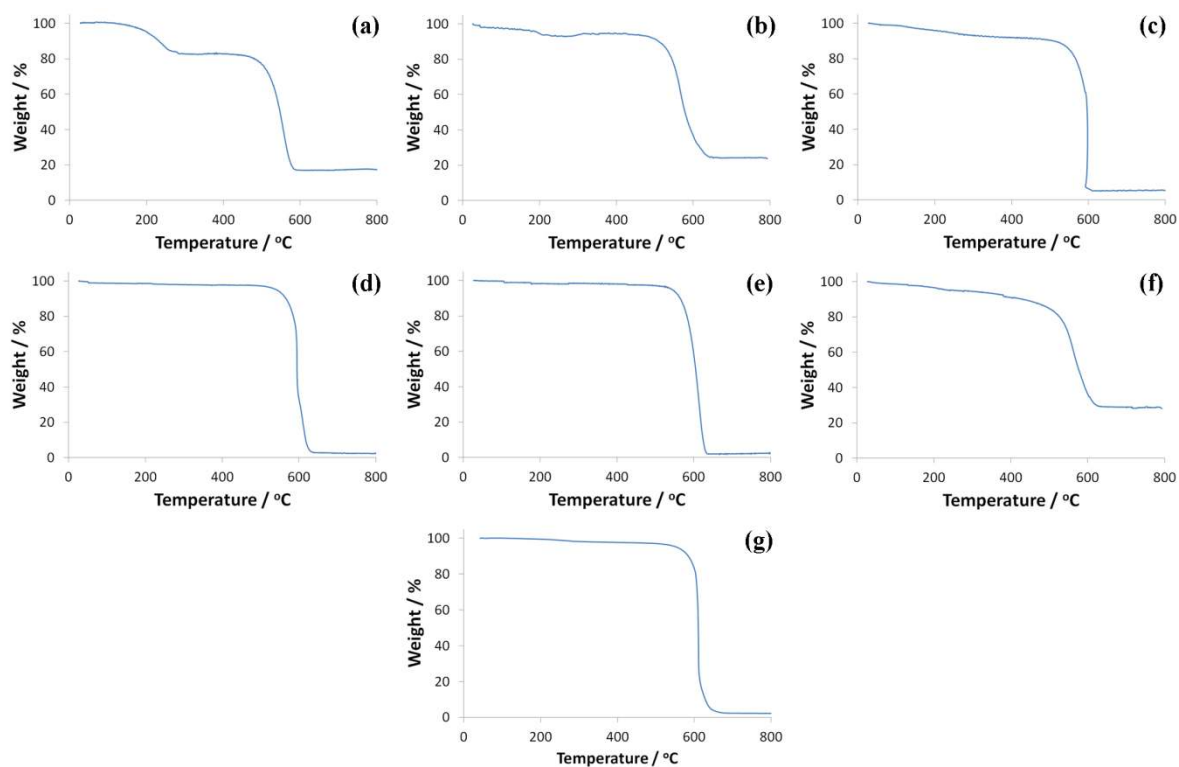


Figure S3. TGA of the MWNT/PdNP catalysts: (a) MWNT/PdNP-1, (b) MWNT/PdNP-2, (c) MWNT/PdNP-3, (d) MWNT/PdNP-4, (e) MWNT/PdNP-5, (f) MWNT/PdNP-6 and (g) MWNT/PdNP-1*.

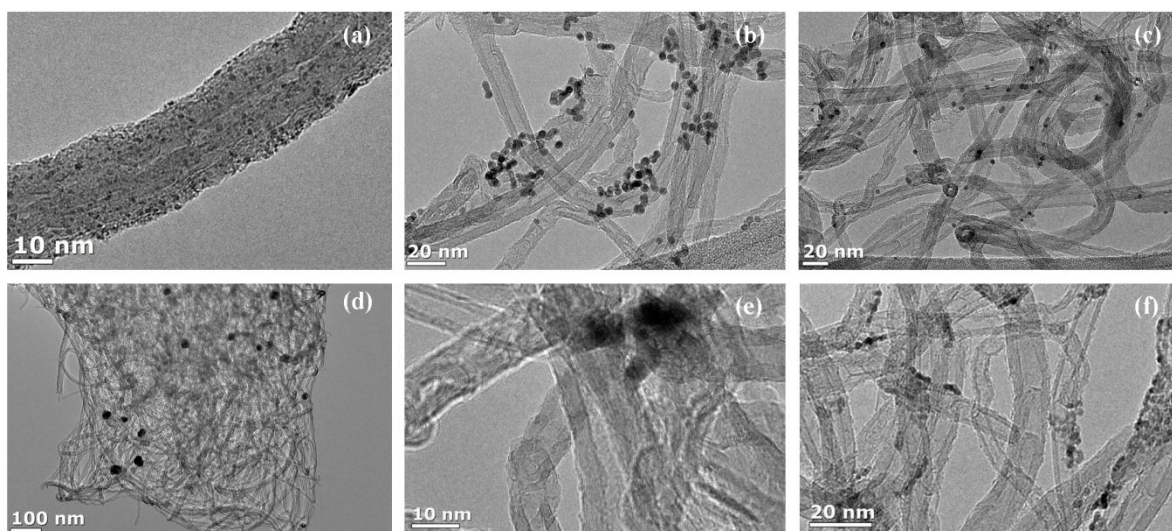


Figure S4. Further TEM analysis of the MWNT/PdNP catalysts: (a) MWNT/PdNP-1, (b) MWNT/PdNP-2, (c) MWNT/PdNP-3, (d) MWNT/PdNP-4, (e) MWNT/PdNP-5 and (f) MWNT/PdNP-6.

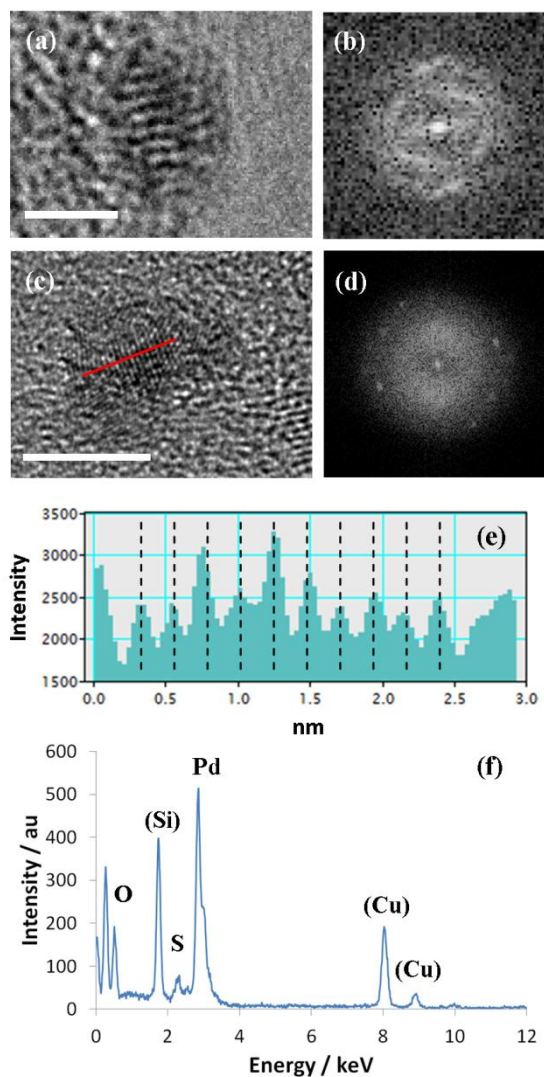


Figure S5. High resolution TEM (a,c) and optical diffractograms (b,d) of MWNT/PdNP-1 and MWNT/PdNP-2 respectively. HR-TEM reveals the semi-crystalline nature of small nanoparticles with a clear d spacing of 2.23 Å, which precisely matches the spacing between Pd(111) crystallographic planes. The optical diffractogram in (b) highlights the lack of crystalline ordering in very small ($d_{\text{NP}} = 1.1$ nm) nanoparticles in MWNT/PdNP-1, however three crystallographic spacings between atomic layers are clearly evident in slightly larger nanoparticles of MWNT/PdNP-2 ($d_{\text{NP}} = 3.5$ nm) as indicated by the presence of 6 clear spots in the diffractogram generated by Fourier transform (d). The periodicity of lattice spacing is further evident in the histogram profile of MWNT/PdNP-2 (e) generated from an intensity profile along the red line in (c). The elemental composition of MWNT/PdNP-1 was confirmed by energy dispersive X-ray analysis (f). The presence of copper peak is related to the TEM column assembly and grid material. Scale bars are 2 (a) and 5 nm (c) respectively.

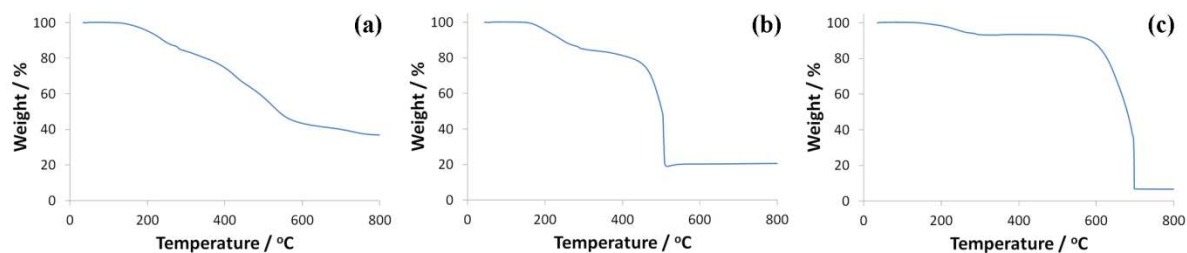
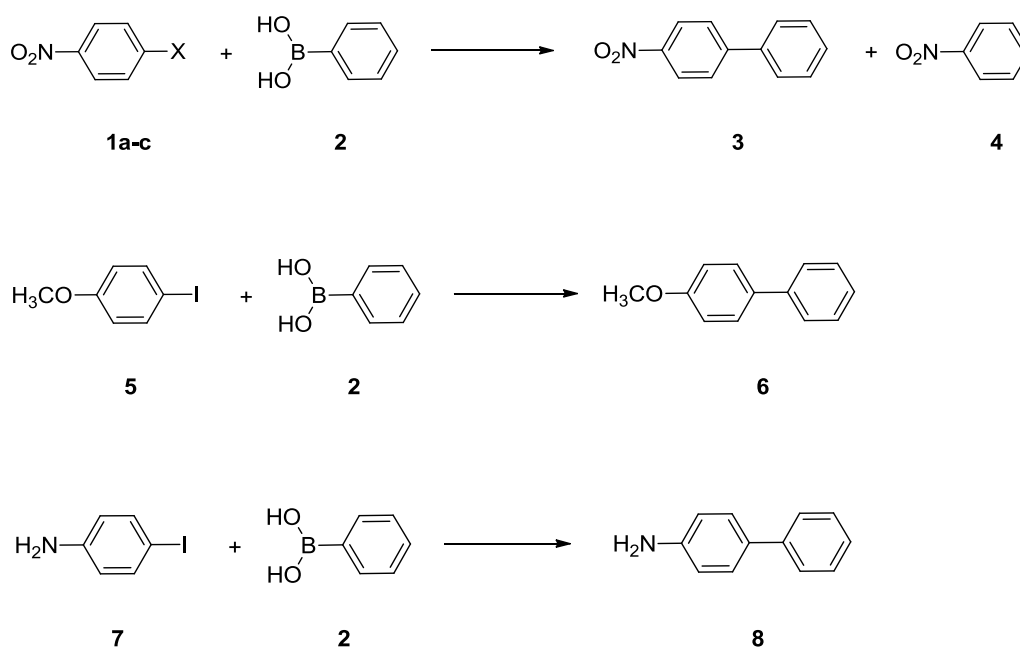


Figure S6. TGA of the CNS/PdNP-1 catalysts: (a) SWNT/PdNP-1, (b) DWNT/PdNP-1 and (c) GNF/PdNP-1.

S3. Catalytic assessment

S3.1 The Suzuki-Miyaura reaction



Scheme S1. The Suzuki-Miyaura reaction.

S3.1.1 Preparation of 4-nitro-1,1'-biphenyl **3**

To 1-halo-4-nitrobenzene **1** (0.04 – 0.50 mmol, 1.0 eq.), phenylboronic acid **2** (0.05 – 0.6 mmol, 1.2 eq.), sodium acetate (0.09 – 1.20 mmol, 2.4 eq.) and the catalyst (0.075 – 5 mol %) in a two-necked round-bottomed flask was added *via cannula* a degassed solution of methanol (10 – 15 mL) and the resulting mixture stirred under an inert atmosphere of argon at 70°C. The progress of the reaction was monitored by thin layer chromatography. After cooling to room temperature, the catalyst was separated from the dispersion by vacuum filtration (0.2 μ m PTFE membrane), washed with methanol (50 mL), dried under vacuum and reused in subsequent reactions. The obtained filtrate was concentrated under vacuum and the products in the crude mixture identified by ^1H NMR spectroscopy and isolated by flash chromatography (silica, petroleum ether / ethyl acetate, 95 / 5) as a white solid (0

– 100 %). $R_f = 0.50$ (petroleum ether / ethyl acetate, 9 / 1); $^1\text{H NMR}$ (300 MHz) $\delta_{\text{H}}/\text{ppm}$ 8.31 (dt, 2H, $J = 8.8, 1.9$ Hz), 7.74 (dt, 2H, $J = 8.8, 1.9$ Hz), 7.63 (dt, 2H, $J = 8.4, 1.9$ Hz), 7.53-7.41 (m, 3H); $^{13}\text{C NMR}$ (75 MHz) $\delta_{\text{C}}/\text{ppm}$ 147.6 (C), 147.0 (C), 138.7 (C), 129.1 (CH), 128.9 (CH), 127.8 (CH), 127.3 (CH), 124.1 (CH); HRMS (EI) m/z : calculated for $\text{C}_{12}\text{H}_9\text{NO}_2 = 199.0633$, found = 199.0689 $[\text{M}]^+$.

S3.1.2 Preparation of 4-methoxy-1,1'-biphenyl **6**

An analogous procedure was used for the preparation of 4-methoxy-1,1'-biphenyl **6**, using 1-iodo-4-methoxybenzene **5**, as a white solid (90 % conversion in 48 hr with 100 % selectivity determined by $^1\text{H NMR}$ spectroscopy). $R_f = 0.25$ (petroleum ether / dichloromethane, 19 / 1); $^1\text{H NMR}$ (300 MHz) $\delta_{\text{H}}/\text{ppm}$ 7.59 (m, 4H), 7.46 (t, 2H, $J = 9.0$ Hz), 7.36 (m, 1H), 7.02 (dt, 2H, $J = 8.7, 2.1$ Hz), 3.89 (s, 3H); $^{13}\text{C NMR}$ (75 MHz) $\delta_{\text{C}}/\text{ppm}$ 159.1 (C), 140.8 (C), 133.7 (C), 128.7 (CH), 128.1 (CH), 126.7 (CH), 126.6 (CH), 114.2 (CH), 55.3 (CH); HRMS (EI) m/z : calculated for $\text{C}_{13}\text{H}_{12}\text{O} = 184.0888$, found = 184.0889 $[\text{M}]^+$.

S3.1.3 Preparation of 4-amino-1,1'-biphenyl **8**

An analogous procedure was used for the preparation of 4-amino-1,1'-biphenyl **8**, using 1-iodo-4-aminobenzene **7**, as a yellow/orange solid (74 % conversion in 98 hr with 100 % selectivity determined by $^1\text{H NMR}$ spectroscopy). $R_f = 0.25$ (petroleum ether / ethyl acetate, 6 / 1); $^1\text{H NMR}$ (300 MHz) $\delta_{\text{H}}/\text{ppm}$ 7.57 (dt, 2H, $J = 8.4, 2.4$ Hz), 7.44 (m, 4H), 7.30 (m, 1H), 6.79 (dt, 2H, $J = 8.4, 2.4$ Hz), 3.75 (bs, 2H); $^{13}\text{C NMR}$ (75 MHz) $\delta_{\text{C}}/\text{ppm}$ 145.8 (C), 141.1 (C), 131.6 (C), 128.6 (CH), 128.0 (CH), 126.4 (CH), 126.2 (CH), 115.4 (CH); HRMS (ESI) m/z : calculated for $\text{C}_{12}\text{H}_{12}\text{N} = 170.0970$, found = 170.0968 $[\text{M}+\text{H}]^+$.

Table S2. The versatility of MWNT/PdNP-1 in the cross coupling of 4-substituted aryl iodides with phenylboronic acid **2**, where R refers to the substituent in the 4-position of the aryl iodide (**1c**, **5** and **7** where R = NO_2 , OCH_3 and NH_2 respectively).

Entry	R	t / hr	Conversion / % ^a	TOF / $\text{mol mol}^{-1} \text{hr}^{-1b}$	Selectivity / % ^a
1	NO_2	4	100	12.5	80
2	OCH_3	48	90	1.0	100
3	NH_2	98	74	0.3	100

^a determined by $^1\text{H NMR}$ spectroscopy; ^b based on total metal loading.

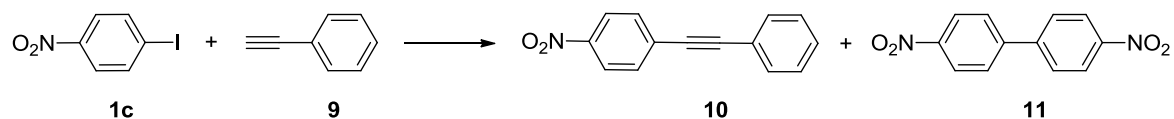
S3.1.4 Comparison of the carbon supports

Table S3. Comparison of the selectivity, activity and recyclability of CNS/PdNP-1 catalysts in the Suzuki-Miyaura cross-coupling of 1-iodo-4-nitrobenzene **1c** and phenylboronic acid **2**.

Entry	Catalyst	Cycle	<i>t</i> / hr	Conversion / % ^a	TOF / mol mol ⁻¹ hr ⁻¹ ^b	Selectivity 3 : 4 / % ^a
1	SWNT/PdNP-1	1	16	100	3.1	90 : 10
2		2	16	85	2.7	80 : 20
3		3	16	95	3.0	81 : 19
4		4	16	84	2.6	100 : 0
5		5	16	97	3.0	100 : 0
6	DWNT/PdNP-1	1	16	100	3.1	86 : 14
7		2	16	92	2.9	90 : 10
8		3	16	71	2.2	82 : 18
9		4	16	89	2.8	89 : 11
10		5	16	84	2.6	82 : 18
16	GNF/PdNP-1	1	16	100	3.1	84 : 16
17		2	16	88	2.8	83 : 17
18		3	16	81	2.5	88 : 12
19		4	16	83	2.6	100 : 0
20		5	16	86	2.7	78 : 22

^a determined by ¹H NMR spectroscopy; ^b based on total metal loading.

S3.2 The Sonogashira reaction

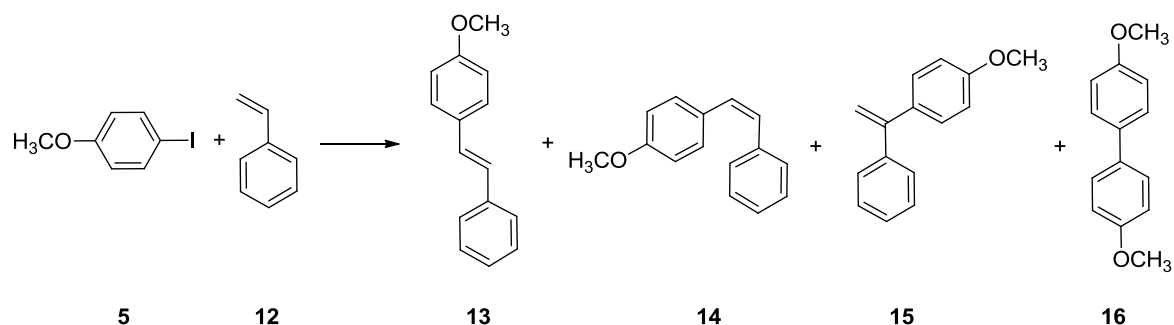


Scheme S2. The Sonogashira reaction.

Preparation of 1-nitro-4-(phenylethynyl)benzene **10**

To 1-iodo-4-nitrobenzene **1c** (0.3 mmol, 1 eq.), phenylacetylene **9** (0.4 mmol, 1.3 eq.), triethylamine (0.6 mmol, 2 eq.) and the catalyst (2 mol %) in a two-necked round-bottomed flask was added *via cannula* a degassed solution of deuterated benzene (2.5 mL) and the combined mixture heated under an inert atmosphere of argon for 48 hours at 50°C. After cooling to room temperature, the catalyst was removed by filtration and the solution concentrated under vacuum. The product was isolated by flash chromatography (silica, petroleum ether / dichloromethane, 4 / 1) as a pale yellow solid (99 % conversion with 92 % selectivity for 1-nitro-4-(phenylethynyl)benzene **10** and 8 % for 4,4'-dinitro-1,1'-biphenyl **11** determined by ¹H NMR spectroscopy). *R_f* = 0.30 (petroleum ether/ dichloromethane, 4/1); ¹H NMR (300 MHz) δ_H/ppm 8.21 (dt, 2H, *J* = 9.0, 2.1 Hz), 7.65 (dt, 2H, *J* = 9.0, 2.1 Hz), 7.57 (m, 2H), 7.40 (m, 3H); ¹³C NMR (75 MHz) δ_C/ppm 146.9 (C), 132.2 (CH), 131.8 (CH), 130.1 (C), 129.2 (CH), 128.5 (CH), 123.5 (CH), 122.0 (C), 94.6 (C), 87.5 (C); HRMS (ESI) *m/z* calculated for C₁₄H₁₀NO₂ 224.0712, found 224.0711 [M+H]⁺.

S3.3 The Heck reaction



Scheme S3. The Heck reaction.

Preparation of (E)-1-methoxy-4-styrylbenzene 13

To 1-iodo-4-methoxybenzene **5** (0.3 mmol, 1 eq.), styrene **12** (0.4 mmol, 1.3 eq.), triethylamine (0.6 mmol, 2 eq.) and the catalyst (2 mol %) in a two-necked round-bottomed flask was added *via cannula* a degassed solution of deuterated benzene (2.5 mL) and the combined mixture heated under an inert atmosphere of argon for 6 days at 80°C. After cooling to room temperature, the catalyst was removed by filtration and the solution concentrated under vacuum. The product was isolated by flash chromatography (silica, petroleum ether / dichloromethane, 9 / 1) as a white solid (93 % conversion with 75 % selectivity for (*E*)-1-methoxy-4-styrylbenzene **13**, 6 % for (*Z*)-1-methoxy-4-styrylbenzene **14**, 7 % for 1-methoxy-4-(1-phenylethenyl)benzene **15** and 12 % for 4,4'-dimethoxy-1,1'-biphenyl **16** by ¹H NMR spectroscopy). *R*_f = 0.18 (petroleum ether / dichloromethane, 9 / 1); ¹H NMR (300 MHz) δ_H/ppm 7.51 (m, 4H), 7.38 (t, 2H, *J* = 7.5 Hz), 7.28 (m, 1H), 7.11 and 7.01 (2d, 2H, *J* = 16.4 Hz), 6.94 (d, 2H, *J* = 8.7 Hz), 3.86 (s, 3H); ¹³C NMR (75 MHz) δ_C/ppm 159.3 (C), 137.6 (C), 130.1 (C), 128.6 (CH), 128.2 (CH), 127.7 (CH), 127.2 (CH), 126.6 (CH), 126.2 (CH), 114.1 (CH), 55.3 (CH); HRMS (ESI) *m/z* calculated for C₁₅H₁₅O 211.1117, found 211.1125 [M+H]⁺.

S4. Characterisation of catalysts after catalysis

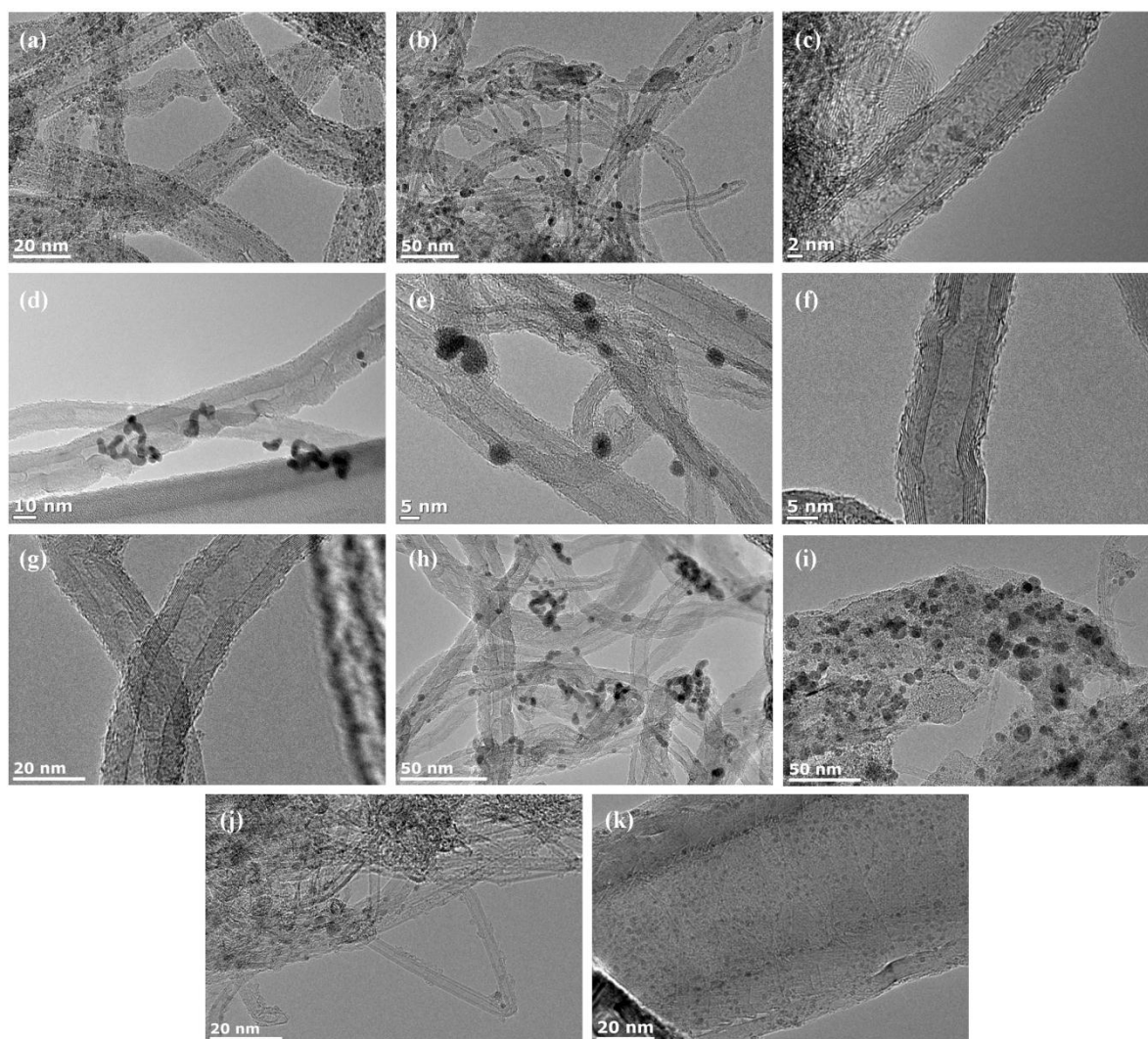


Figure S7. (a)-(k) TEM of the CNS/PdNP catalysts subsequent to catalysis: (a) MWNT/PdNP-1 with **1a**; (b) MWNT/PdNP-1 with **1b**; (c) MWNT/PdNP-1 with **1c**; (d) MWNT/PdNP-2 with **1c**; (e) MWNT/PdNP-3 with **1c**; (f) MWNT/PdNP-4 with **1c**; (g) MWNT/PdNP-5 with **1c**; (h) MWNT/PdNP-6 with **1c**; (i) SWNT/PdNP-1 with **1c**; (j) DWNT/PdNP-1 with **1c** and (k) GNF/PdNP-1 with **1c**.

S5. References

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