Electronic Supporting Information file

Palladium nanoparticles in catalytic carbon nanoreactors: the effect of confinement on Suzuki-Miyaura reactions

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S1. Preparation of the catalysts

S1.1. Preparation of PdNP@GNF catalysts

S.1.1.1. Preparation of PdNP@GNF-I

PdNP@GNF-I was prepared by modification of the method described by Tessonnier *et al.*[S1] A solution of potassium tetrachloropalladate (0.766 mg, 0.0023 mmol) in deionised water (0.2 mL) was added dropwise to graphitised nanofibres (5 mg, GNF, heated for 1 hour at 450 °C in air) and the resulting paste-like solid stirred at room temperature for 2 days. The obtained solid was heated in air at 350 °C for 2 hours, then in a tube furnace under an atmosphere of hydrogen/argon (10/90) at 400 °C for 2 hours and finally cooled at room temperature under an inert atmosphere of argon to yield a black solid (4.6 mg).

S.1.1.2. Preparation of PdNP@GNF-II

PdNP@GNF-II was prepared by modification of the method described by Endo *et al.*[S2] Graphitised nanofibres (5 mg, heated for 1 hour at 450 °C in air) in deionised water (1 mL) were bath sonicated for 15 min and added of a solution of potassium tetrachloropalladate (0.766 mg, 0.0023 mmol) in deionisdeioniseed water (0.2 mL). The resulting suspension was heated at 90 °C with stirring for 6 hours, then heated in a tube furnace under an atmosphere of hydrogen/argon (10/90) at 400 °C for 3 hours and finally cooled at room temperature under an atmosphere of argon to yield a black solid (4.6 mg).

S.1.1.3. Preparation of PdNP@GNF-III

PdNP@GNF-III was prepared by modification of the method described by Gu *et al.*[S3] Palladium *bis*(acetylacetonate) (1.43 mg, 0.0047 mmol) and graphitised nanofibres (10 mg, heated for 1 hour at 450 °C in air) were mixed in a glass vacuum pyrolysis tube. The sample was sealed under vacuum (1×10^{-5} mbar) and heated in a furnace at 500 °C for 2 hours. The obtained black solid was then heated in a tube furnace under an atmosphere of hydrogen/argon (10/90) at 300 °C for 3 hours and finally cooled down at room temperature under an inert atmosphere of argon to yield a black solid (4.2 mg).

S.1.1.4. Preparation of PdNP@GNF-IV

PdNP@GNF-IV was prepared by modifications of the methods described by Zamborini *et al.*[S4] and Solomonsz *et al.*[S5]

Nanoparticle preparation: to a solution of potassium tetrachloropalladate (150 mg, 0.46 mmol, 1.0 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 min at room temperature. The aqueous layer was separated and discarded, to the organic phase was added dodecanethiol (110 µL, 0.46 mmol, 1.0 eq.) and the combined mixture was stirred for 10 min at room temperature. To this organic solution, a further solution of sodium borohydride (175 mg, 4.6 mmol, 10.0 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 × 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 µm, 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).

Nanoreactor preparation: to a solution of palladium nanoparticles (0.3 mg) in *n*-hexane (5 mL) was added graphitised nanofibres (5 mg, heated for 1 hour at 450 °C in air) and the combined mixture was bath sonicated for 15 min at room temperature. The obtained suspension was transferred to a steel autoclave (10 mL volume) equipped with a magnetic stirrer bar and mixed with carbon dioxide (40 °C, 4000 psi) for 18 hours. During the experiment, the carbon dioxide pressure was cycled between 1000 and 4000 psi, three times. Ethanol (15 mL) was added and the suspension probe sonicated (probe diameter 3 mm, frequency 20 KHz, power 130 W) for 25 min at room temperature. The resultant suspension was filtered through a membrane filter (0.2 µm, PTFE), washed successively with acetone (50 mL), chloroform (50 mL), *n*-hexane (50 mL) and acetone (100 mL) and finally dried under vacuum to yield a black solid (3.9 mg).

S1.2. Preparation of PdNP@CNS catalysts

PdNP@CNS were prepared by modification of the method described by Zhi *et al.*[S6] In a typical experiment, a solution of potassium tetrachloropalladate (3.83 mg, 0.0117 mmol) in deionised water (1 mL) was added dropwise to carbon nanostructures (25 mg, CNS, heated in air for: 1 hour at 450 °C, 12 min at 550 °C or 30 min at 380 °C for GNF, MWNT or SWNT respectively). The combined dispersion was stirred at room temperature for 1 hour and then dried at room temperature under vacuum for 15 hours. The obtained solid was heated in a tube furnace under an atmosphere of hydrogen/argon (10/90) at 400 °C for 3 hours and finally cooled at room temperature under an inert atmosphere of argon to yield a black solid.

S1.3. Preparation of PdNP/CNS catalysts

PdNP/CNS were prepared by modification of the method described by Zhi *et al.*[S6] In a typical experiment, a solution of potassium tetrachloropalladate (3.83 mg, 0.0117 mmol) in deionised water (1 mL) was added dropwise to carbon nanostructures (25 mg of as-received GNF, MWNT or SWNT). The combined dispersion was stirred at room temperature for 1 hour and then dried at room temperature under vacuum for 15 hours. The obtained solid was heated in a tube furnace under an atmosphere of hydrogen/argon (10/90) at 400 °C for 3 hours and finally cooled at room temperature under an inert atmosphere of argon to yield a black solid.

S2. Characterisation of the catalysts

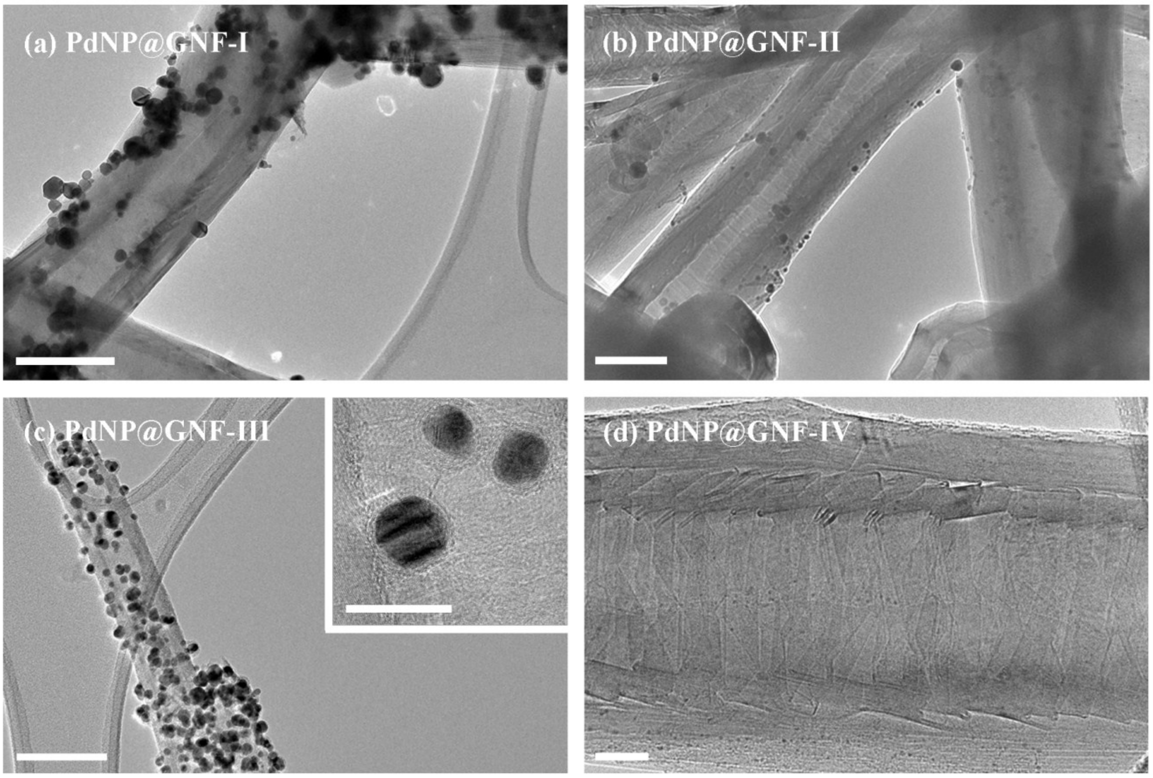


Fig. S1 Supplementary transmission electron microscopy (TEM) analysis of: (a) PdNP@GNF-I, (b) PdNP@GNF-II, (c) PdNP@GNF-III and (d) PdNP@GNF-IV. Inset in (c) indicates that palladium nanoparticles are coated with semi-graphitic carbon shells that will prohibit access of reactants to the catalytic surface. Scale bar in inset (c) is 20 nm. Scale bars are (a-c) 100 and (d) 20 nm.

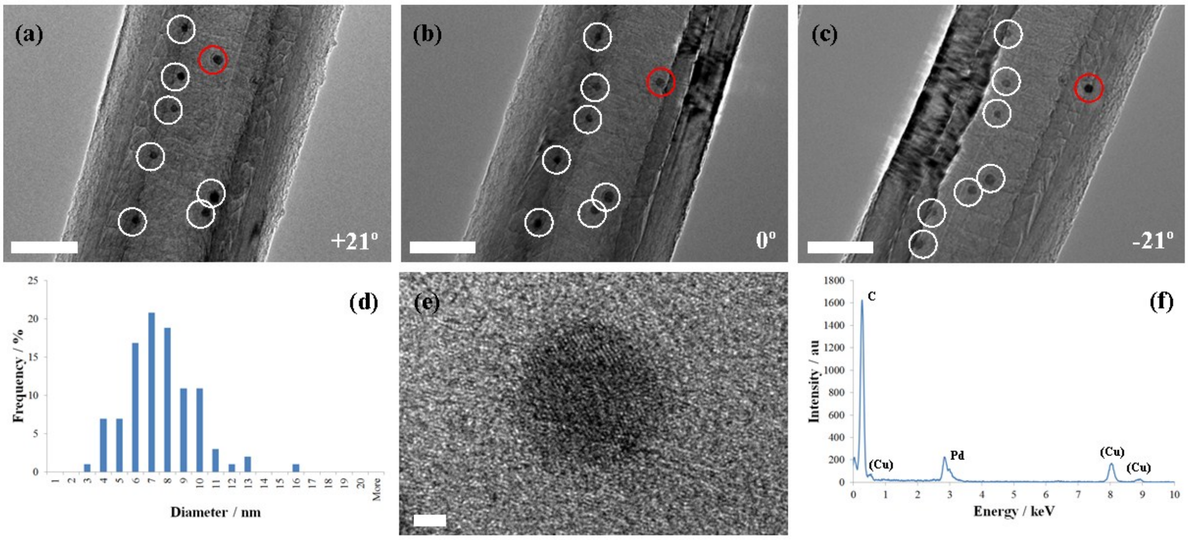


Fig. S2 Supplementary TEM imaging and analysis of PdNP@GNF. The tilt series (a)-(c) represents typical analysis undertaken to approximate the location of PdNP (either inside or outside of the nanoreactor). The sample is tilted around the nanofibre growth axis; those PdNP that remain between the two internal walls must be inside the nanoreactor (white circles); those PdNP that move beyond the limits of the internal walls must be outside the nanoreactor (red circles). By analysing multiple nanofibres within the specimen, it is possible to afford a semi-quantitative description of PdNP positions (±5%). The histogram (d) represents the distribution of sizes of PdNP. HR-TEM (e) reveals the semi-crystalline nature of nanoparticles with a clear d spacing of 2.24 Å, which precisely matches the spacing between Pd(111) crystallographic planes. The elemental composition of PdNP@GNF 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 (a-c) 50 and (e) 2 nm.

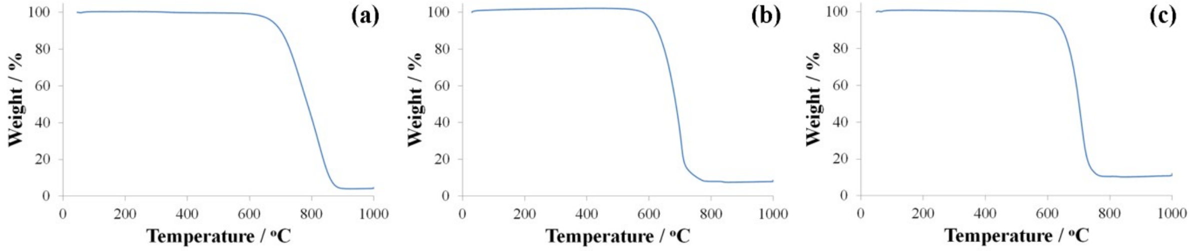


Fig. S3 Representative TGA analysis of (a) GNF, (b) PdNP@GNF and (c) PdNP/GNF.

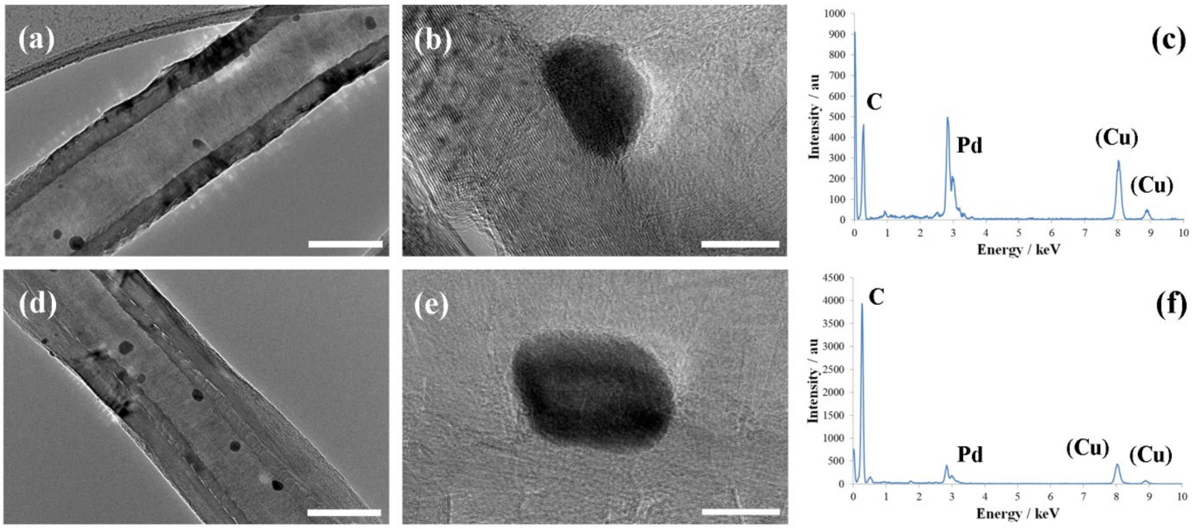


Fig. S4 Characterisation of PdNP@GNF after (a-c) one and (d-f) five cycles of catalysis. TEM indicates that PdNP undergo a process of growth subsequent to catalysis (d_{NP} = 21.1±9.8 nm after one cycle) but critically remain within the internal channel of GNF. No significant further growth is observed after this initial cycle (21.8±14.8 nm after five cycles) highlighting the stability of the catalytic nanoreactor. HR-TEM (b,e) highlights retention of the semi-crystallinity of nanoparticles subsequent to catalysis. The elemental composition of PdNP@GNF was confirmed by measurement of d-spacing and energy dispersive X-ray analysis (f). Scale bars are (a,d) 100 and (b,e) 10 nm.

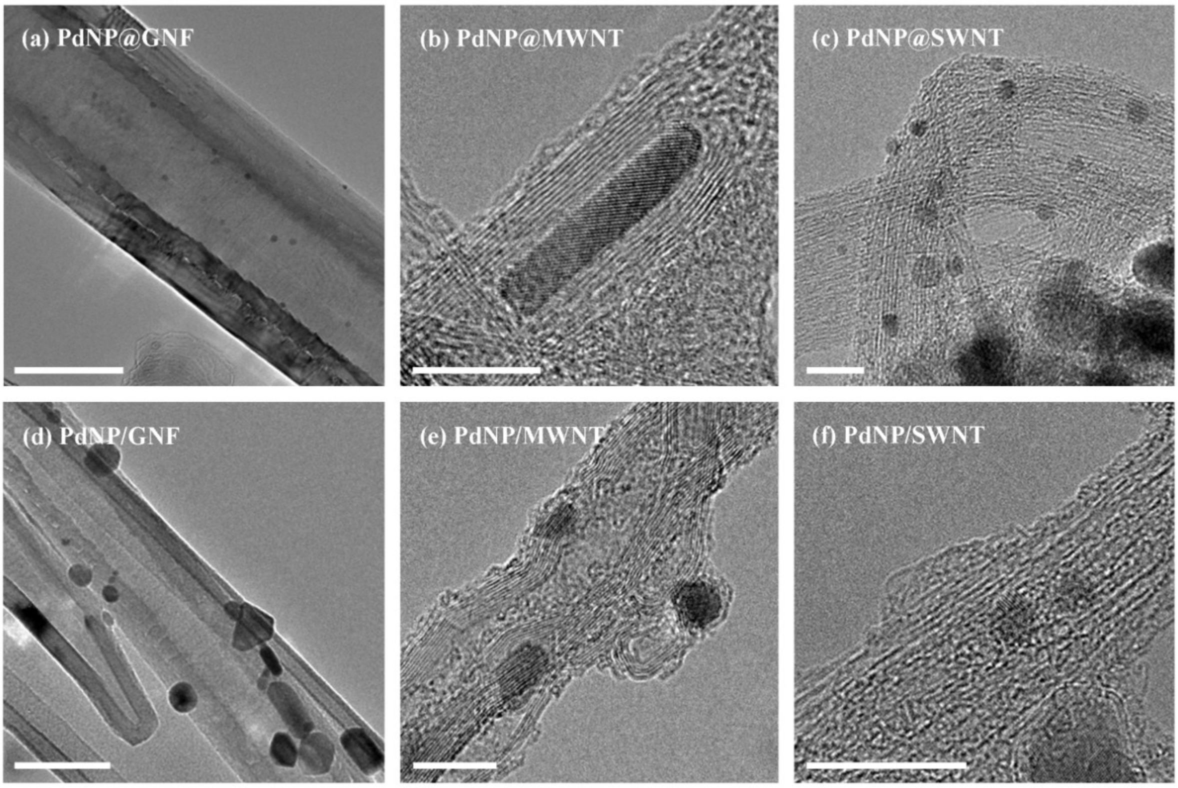


Fig. S5 TEM analysis of the catalytic nanoreactors: (a) PdNP@GNF, (b) PdNP@MWNT and (c) PdNP@SWNT and supported catalysts: (d) PdNP/GNF, (e) PdNP/MWNT and (f) PdNP/SWNT. Selective deposition of PdNP on the carbon nanostructure (CNS) outer surface shows particle diameter increasing on increasing the CNS diameter in (d-f). Scale bars are (a,d) 100 and (b-c,e-f) 10 nm.

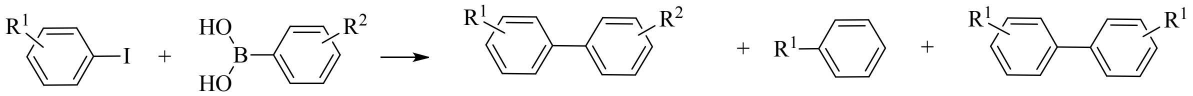
Table S1. Structural characterisation of the PdNP-carbon nanostructure catalysts by transmission electron microscopy (TEM) and thermogravimetric analysis (TGA): d_{CNSint} and d_{CNSext} refer to the interior and exterior diameters of carbon nanostructures respectively, d_{NP} refers to the mean nanoparticle diameter as determined by TEM; T_{oxid} and Pd_{900} refer to the temperature of primary oxidation and the percentage of residual palladium metal at 900 °C respectively as determined by TGA.

Entry	**Catalyst**	**TEM analysis**			**TGA analysis**		
		d_{CNSint} / nm	**d_{CNSext} / nm**	**d_{NP} / nm**	**T_{oxid} / °C**	**Pd_{900} / %**	**loading**
1	PdNP@GNF	52.7±16.2	132.8±37.0	7.0±2.2	705	7.8	mid
2	PdNP/GNF			25.8±16.1	710	10.8	mid
3	PdNP@MWNT	4.1±1.8	15.4±6.7	3.9±0.4[a] 12.9±9.4[b]	469	10.0	mid
4	PdNP/MWNT			6.1±2.6	474	14.2	mid
5	PdNP@SWNT	1.4±0.3		3.9±1.0	383	12.1	mid
6	PdNP/SWNT			3.9±0.9	385	12.2	mid

[a] dimension perpendicular to the nanotube growth axis. [b] dimension parallel to the nanotube growth axis.

S3. Catalytic assessment

S3.1. The Suzuki-Miyaura reaction



1a: R^1 = 4-NO_2
b: R^1 = 3-NO_2
c: R^1 = 2-NO_2
d: R^1 = H
e: R^1 = 4-NH_2

2a: R^2 = H
b: R^2 = 4-CH_3
c: R^2 = 3-CH_3
d: R^2 = 2-CH_3
e: R^2 = 3-OCH_3

3aa: R^1 = 4-NO_2, R^2 = H
ab: R^1 = 4-NO_2, R^2 = 4-CH_3
ac: R^1 = 4-NO_2, R^2 = 3-CH_3
ad: R^1 = 4-NO_2, R^2 = 2-CH_3
ae: R^1 = 4-NO_2, R^2 = 3-OCH_3
ba: R^1 = 3-NO_2, R^2 = H
ca: R^1 = 2-NO_2, R^2 = H
db: R^1 = H, R^2 = 4-CH_3
eb: R^1 = 4-NH_2, R^2 = 4-CH_3

4

5a: R^1 = 4-NO_2
b: R^1 = 3-NO_2

Scheme S1. The palladium catalysed reactions of aryl iodides **1** and boronic acids **2** leading to the products of Suzuki-Miyaura cross-coupling **3**, dehalogenation **4** and Ullmann coupling **5**.

To **1a-e** (0.041-0.056 mmol, 1.0 eq.), **2a-e** (0.053-0.075 mmol, 1.3 eq.), sodium acetate (0.9-17.2 mg, 0.094-0.13 mmol, 2.3 eq.) and the catalyst (0.2-4.7 mg, 2 mol %) in a two-necked round-bottomed flask was added *via cannula* a degassed solution of methanol (5 mL) and the resulting suspension stirred under an inert atmosphere of argon at 70 °C. After cooling to room temperature, the dispersion was filtered through a PTFE membrane filter (pore diameter 0.2 μm) and concentrated under vacuum. The products in the crude mixture were identified by ^{1}H NMR spectroscopy and isolated by flash column chromatography on a silica gel (ccsg).

4-nitrobiphenyl **3aa** White solid. R_f = 0.50 (petroleum ether/ethyl acetate, 9/1); ^{1}H NMR (300 MHz, $CDCl_3$, δ_H): 8.31 (dt, J = 9.0, 2.1 Hz, 2H; 2 × Ar H), 7.75 (dt, J = 9.0, 2.1 Hz, 2H; 2 × Ar H), 7.64 (dt, J = 6.9, 1.8 Hz, 2H; 2 × Ar H), 7.54-7.43 (m, 3H, 3 × Ar H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_C): 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*: [M^+] calculated for $C_{12}H_9NO_2$, 199.0633; found, 199.0689. Data consistent with literature reports.[S7]

4-methyl-4'-nitrobiphenyl **3ab** White solid. R_f = 0.17 (petroleum ether/dichloromethane, 9/1); ^{1}H NMR (300 MHz, $CDCl_3$, δ_H): 8.29 (dt, J = 9.0, 2.1 Hz, 2H; 2 × Ar H), 7.73 (dt, J = 9.0, 2.1 Hz, 2H; 2 × Ar H), 7.54 (dt, J = 8.1, 1.8 Hz, 2H; 2 × Ar H), 7.31 (dp, J = 7.8, 0.6, 2H; 2 × Ar H), 2.44 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ_C): 147.6 (C), 146.9 (C), 139.1 (C), 135.9 (C), 129.9 (CH), 127.5 (CH), 127.2 (CH), 124.1 (CH), 21.2 (CH_3); HRMS (EI) *m/z*: [M^+] calculated for $C_{13}H_{11}NO_2$, 213.0790; found, 213.0787. Data consistent with literature reports.[S8]

3-methyl-4'-nitrobiphenyl **3ac** White solid. R_f = 0.19 (petroleum ether/dichloromethane, 9/1); ^{1}H NMR (300 MHz, $CDCl_3$, δ_H): 8.30 (dt, J = 9.0, 2.1 Hz, 2H; 2 × Ar H), 7.74 (dt, J = 9.0, 2.1 Hz, 2H; 2 × Ar H), 7.46-7.36 (m, 3H, 3 × Ar H), 7.30-7.25 (dh, J = 7.2, 0.9 Hz, 1H; Ar H), 2.46 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ_C): 147.8 (C), 147.0 (C), 138.9 (C), 138.8 (C), 129.7 (CH), 129.0 (CH), 128.1 (CH), 127.8 (CH), 124.5 (CH), 124.0 (CH), 21.5 (CH_3); HRMS (EI) *m/z*: [M^+] calculated for $C_{13}H_{11}NO_2$, 213.0790; found, 213.0796. Data consistent with literature reports.[S7]

2-methyl-4’-nitrobiphenyl **3ad** White solid. R_f = 0.19 (petroleum ether/dichloromethane, 9/1); ^{1}H NMR (300 MHz, CDCl$_3$, δ_H): 8.30 (dt, *J* = 9.0, 2.1 Hz, 2H; 2 × Ar H), 7.50 (dt, *J* = 9.0, 2.1 Hz, 2H; 2 × Ar H), 7.36-7.21 (m, 4H, 4 × Ar H), 2.28 (s, 3H, C*H$_3$*); ^{13}C NMR (75 MHz, CDCl$_3$, δ_C): 148.8 (C), 146.9 (C), 139.6 (C), 135.1 (C), 130.7 (CH), 130.1 (CH), 129.4 (CH), 128.5 (CH), 126.1 (CH), 123.4 (CH), 20.3 (*C*H$_3$); HRMS (EI) *m/z*: [M$^+$] calculated for $C_{13}H_{11}NO_2$, 213.0790; found, 213.0786. Data consistent with literature reports.[S9]

3-methoxy-4’-nitrobiphenyl **3ae** White solid. R_f = 0.14 (petroleum ether/dichloromethane, 7/3); ^{1}H NMR (300 MHz, CDCl$_3$, δ_H): 8.30 (dt, *J* = 9.0, 2.1 Hz, 2H; 2 × Ar H), 7.74 (dt, *J* = 9.0, 2.1 Hz, 2H; 2 × Ar H), 7.42 (t, *J* = 8.1 Hz, 1H; Ar H), 7.21 (ddd, *J* = 7.5, 1.8, 0.9 Hz, 1H; Ar H), 7.15 (t, *J* = 2.4 Hz, 1H; Ar H), 7.00 (ddd, *J* = 8.4, 2.7, 0.9 Hz, 1H; Ar H), 3.89 (s, 3H, OC*H$_3$*); ^{13}C NMR (75 MHz, CDCl$_3$, δ_C): 160.1 (C), 147.5 (C), 147.1 (C), 140.2 (C), 130.2 (CH), 127.8 (CH), 124.0 (CH), 119.8 (CH), 114.1 (CH), 113.2 (CH), 55.4 (O*C*H$_3$); HRMS (ESI) *m/z*: [M + Na]$^+$calculated for $C_{13}H_{11}NO_3Na$, 252.0637; found, 252.0633. Data consistent with literature reports.[S10]

3-nitrobiphenyl **3ba** White solid. R_f = 0.19 (petroleum ether/dichloromethane, 9/1); ^{1}H NMR (300 MHz, CDCl$_3$, δ_H): 8.47 (t, *J* = 2.1 Hz, 1H; Ar H), 8.22 (dq, *J* = 8.4, 1.2 Hz, 1H; Ar H), 7.94 (dq, *J* = 7.9, 0.9 Hz, 1H; Ar H), 7.67-7.62 (m, 2H, 2 × Ar H), 7.60 (s, 1H, Ar H), 7.55-7.41 (m, 3H, 3 × Ar H); ^{13}C NMR (75 MHz, CDCl$_3$, δ_C): 148.7 (C), 142.9 (C), 138.7 (C), 133.0 (CH), 129.7 (CH), 129.2 (CH), 128.5 (CH), 127.2 (CH), 122.0 (CH), 122.0 (CH); HRMS (EI) *m/z*: [M$^+$] calculated for $C_{12}H_9NO_2$, 199.0633; found, 199.0639. Data consistent with literature reports.[S7]

2-nitrobiphenyl **3ca** Pale yellow solid. R_f = 0.15 (petroleum ether/dichloromethane, 9/1); ^{1}H NMR (300 MHz, CDCl$_3$, δ_H): 7.87 (dd, *J* = 8.1, 1.2 Hz, 1H; Ar H), 7.63 (td, *J* = 7.5, 1.2 Hz, 1H; Ar H), 7.53-7.41 (m, 5H, 5 × Ar H), 7.36-7.31 (m, 2H, 2 × Ar H); ^{13}C NMR (75 MHz, CDCl$_3$, δ_C): 149.3 (C), 137.4 (C), 136.4 (C), 132.3 (CH), 132.0 (CH), 128.7 (CH), 128.6 (CH), 128.1 (CH), 127.9 (CH), 124.1 (CH); HRMS (EI) *m/z*: [M$^+$] calculated for $C_{12}H_9NO_2$, 199.0633; found, 199.0624. Data consistent with literature reports.[S11]

4-methylbiphenyl **3db** White solid. R_f = 0.33 (petroleum ether); ^{1}H NMR (300 MHz, CDCl$_3$, δ_H): 7.58 (dt, *J* = 7.2, 1.2 Hz, 2H; 2 × Ar H), 7.51 (dt, *J* = 8.1, 1.8 Hz, 2H; 2 × Ar H), 7.44 (tt, *J* = 6.9, 1.8 Hz, 2H; 2 × Ar H), 7.33 (tt, *J* = 7.5, 1.5 Hz, 1H; Ar H), 7.26 (dt, *J* = 6.3, 1.8 Hz, 2H; 2 × Ar H), 2.41 (s, 3H, C*H$_3$*); ^{13}C NMR (75 MHz, CDCl$_3$, δ_C): 141.2 (C), 138.4 (C), 137.0 (C), 129.5 (CH), 128.7 (CH), 127.0 (CH), 127.0 (CH), 21.1 (*C*H$_3$); HRMS (EI) *m/z*: [M$^+$] calculated for $C_{13}H_{12}$, 168.0939; found, 168.0941. Data consistent with literature reports.[S8]

4-amino-4’-methylbiphenyl **3eb** Yellow solid. R_f = 0.34 (dichloromethane); ^{1}H NMR (300 MHz, CDCl$_3$, δ_H): 7.47-7.36 (m, 4H, 4 × Ar H), 7.21 (d, *J* = 8.4 Hz, 2H; 2 × Ar H), 6.76 (d, *J* = 8.4 Hz, 2H; 2 × Ar H), 3.75 (br s, 2H, N*H$_2$*), 2.38 (s, 3H, C*H$_3$*); ^{13}C NMR (75 MHz, CDCl$_3$, δ_C): 145.5 (C), 138.3 (C), 135.9 (C), 131.6 (C), 129.4 (CH), 127.8 (CH), 126.2 (CH), 115.4 (CH), 21.0 (*C*H$_3$); HRMS (ESI) *m/z*: [M + H]$^+$ calculated for $C_{13}H_{14}N$, 184.1126; found, 184.1123. Data consistent with literature reports.[S8]

Table S2. Comparison of the selectivity and activity of PdNP-CNS catalysts in the Suzuki-Miyaura cross-coupling of 1-iodo-4-nitrobenzene **1a** and phenylboronic acid **2a**.[a]

Entry	**Catalyst**	***t* / h**	**Conversion / %** [b]	**Selectivity for 3aa (4:5a) / %** [b]
1	PdNP@GNF	24	83	87 (10:3)
2	PdNP/GNF	24	78	80 (17:3)
3	PdNP@MWNT	24	77	91 (6:2)
4	PdNP/MWNT	24	88	86 (12:2)
5	PdNP@SWNT	24	95	83 (14:3)
6	PdNP/SWNT	24	97	89 (7:4)

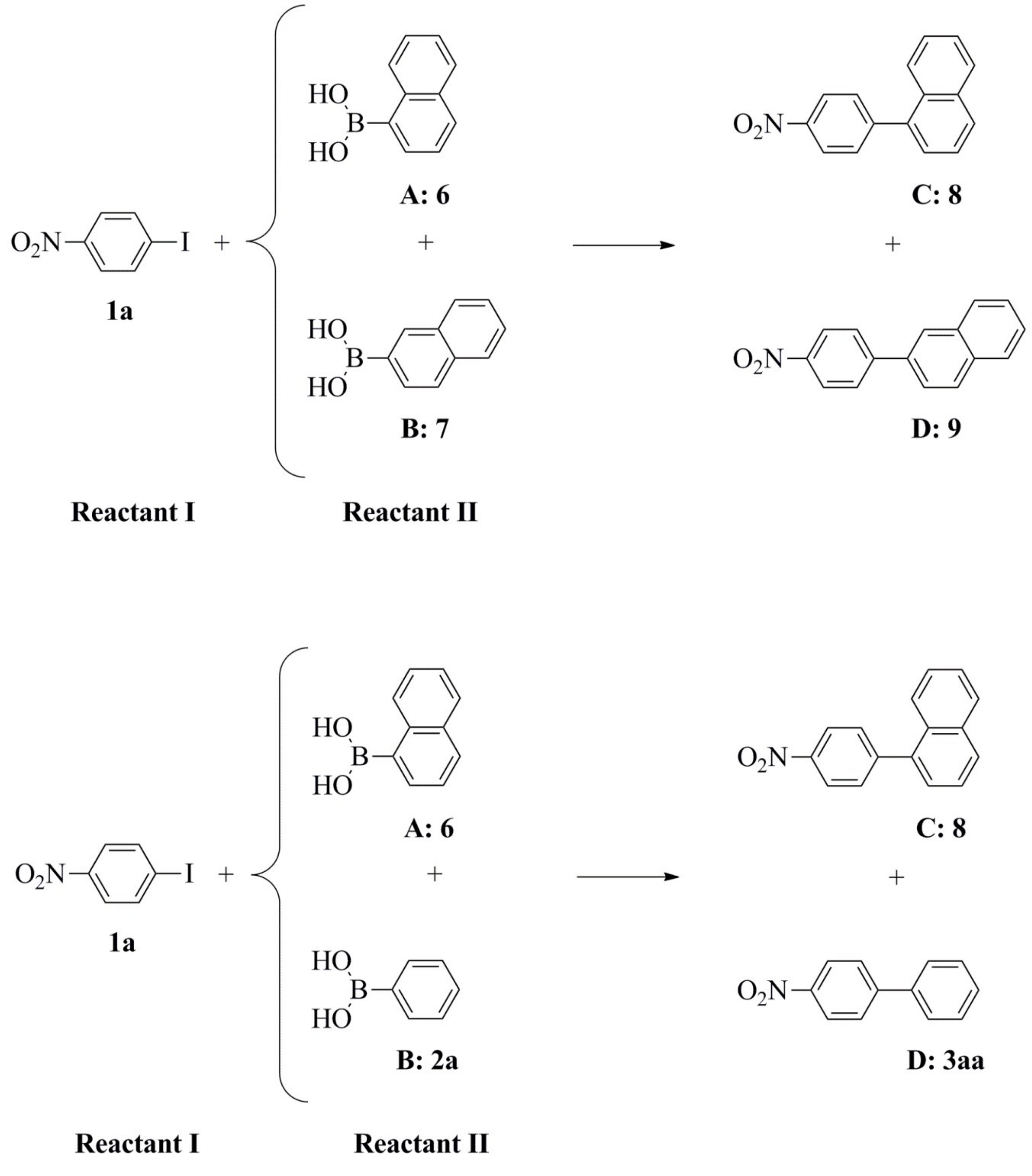
[a] Standard conditions: 1-iodo-4-nitrobenzene **1a** (0.056 mmol, 1.0 eq.), phenylboronic acid **2a** (0.075 mmol, 1.3 eq.), sodium acetate (0.13 mmol, 2.3 eq.), catalyst (2 mol %), methanol (5 mL), 70 ^{o}C, 24 h; [b] conversion and selectivity for 4-nitrobiphenyl **3aa**, nitrobenzene **4** and 4,4'-dinitrobiphenyl **5a**, as the products of cross-coupling, dehalogenation and Ullmann coupling respectively, were determined by ^{1}H NMR spectroscopy of the crude mixture.

S3.2. Recyclability of the catalysts

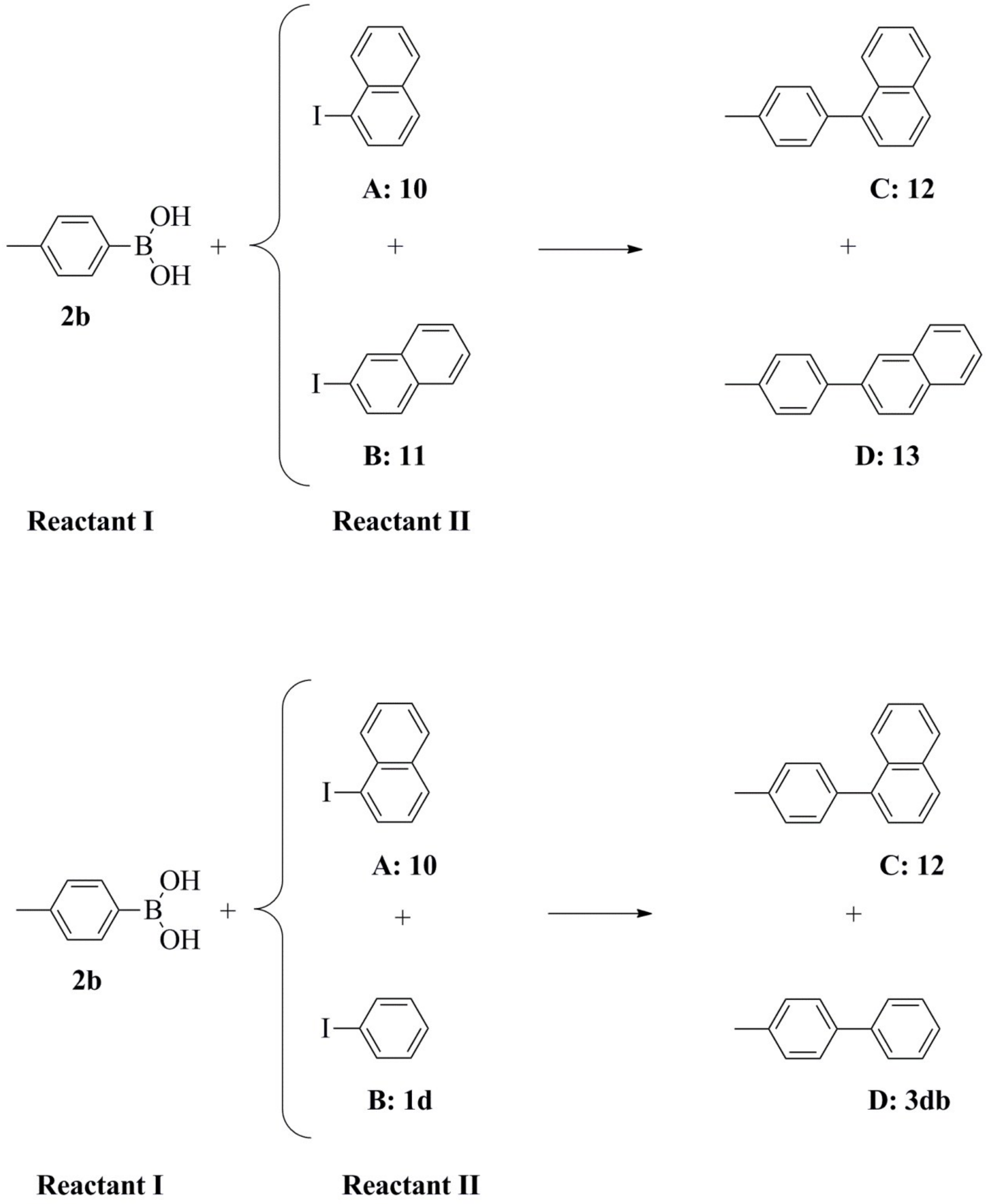
To 1-iodo-4-cyanobenzene (0.12 mmol, 1.0 eq.), phenylboronic acid **2a** (0.23 mmol, 1.3 eq.), sodium acetate (0.41 mmol, 2.3 eq.) and the catalyst (2 mol %) in a two-necked round-bottomed flask was added *via cannula* a degassed solution of methanol (15 mL) and the resulting suspension stirred under an inert atmosphere of argon at 70 °C for 16 hours. After cooling to room temperature, the catalyst was collected by vacuum filtration (0.2 μm pore diameter PTFE membrane), washed with methanol (10 mL), dried under vacuum and reused in subsequent reactions. The obtained filtrate was concentrated under vacuum and the products in the crude mixture were identified by ^{1}H NMR spectroscopy and isolated by flash column chromatography on a silica gel (ccsg).

4-cyanobiphenyl White solid. $R_f = 0.17$ (petroleum ether/dichloromethane, 2/1); ^{1}H NMR (300 MHz, $CDCl_3$, δ_H): 7.72 (qt, $J = 6.0$, 2.4 Hz, 4H; 4 × Ar H), 7.62-7.58 (m, 2H, 2 × Ar H), 7.53-7.41 (m, 3H, 3 × Ar H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_C): 145.7 (C), 139.2 (C), 132.6 (CH), 129.1 (CH), 128.6 (CH), 127.7 (CH), 127.2 (CH), 118.9 (C), 110.9 (C); HRMS (EI) *m/z*: [M^+] calculated for $C_{13}H_9N$, 179.0735; found, 179.0730. Data consistent with literature reports.[S12]

S3.3. The competitive Suzuki-Miyaura reaction



Scheme S2. The competitive Suzuki-Miyaura reactions of two aromatic boronic acids with a common aryl iodide.



Scheme S3. The competitive Suzuki-Miyaura reactions of two aryl iodides with a common aromatic boronic acid.

To **Reactant I** (0.065 mmol, 1.0 eq.), **Reactant II** (**A**: 0.065 mmol, 1.0 eq. + **B**: 0.065 mmol, 1.0 eq.), sodium acetate (0.15 mmol, 2.3 eq.) and the catalyst (2 mol %) in a two-necked round-bottomed flask was added *via cannula* a degassed solution of methanol (5 mL) and the resulting suspension stirred under an inert atmosphere of argon at 70 °C for 24 hours. After cooling to room temperature, the dispersion was filtered through a PTFE membrane filter (pore diameter 0.2 μm) and concentrated under vacuum. The products in the crude mixture were identified by ^{1}H NMR spectroscopy and isolated by flash column chromatography on a silica gel (ccsg).

1-(4-nitrophenyl)naphthalene **8** White solid. R_f = 0.14 (petroleum ether/dichloromethane, 9/1); ^{1}H NMR (300 MHz, $CDCl_3$, δ_H): 8.38 (dt, *J* = 9.0, 2.1 Hz, 2H; 2 × Ar H), 7.95 (dt, *J* = 9.0, 2.1 Hz, 2H; 2 × Ar H), 7.82-7.76 (m, 1H, Ar H), 7.69 (dt, *J* = 8.7, 2.1 Hz, 2H; 2 × Ar H), 7.62-7.42 (m, 4H, 4 × Ar H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_C): 147.7 (C), 147.2 (C), 137.8 (C), 133.8 (C), 130.9 (CH), 129.0 (CH), 127.1 (CH), 126.7 (CH), 126.2 (CH), 125.3 (CH), 125.1 (CH), 123.6 (CH); HRMS (EI) *m/z*: [M$^+$] calculated for $C_{16}H_{11}NO_2$, 249.0790; found, 249.0782. Data consistent with literature reports.[S13]

2-(4-nitrophenyl)naphthalene **9** White solid. R_f = 0.10 (petroleum ether/dichloromethane, 9/1); ^{1}H NMR (300 MHz, $CDCl_3$, δ_H): 8.36 (dt, *J* = 9.0, 2.1 Hz, 2H; 2 × Ar H), 8.11 (s, 1H, Ar H), 8.00-7.86 (m, 5H, 5 × Ar H), 7.75 (dd, *J* = 8.4, 1.8 Hz, 1H; Ar H), 7.60-7.53 (m, 2H, 2 × Ar H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_C): 147.6 (C), 147.1 (C), 136.0 (C), 133.5 (C), 133.2 (C), 129.0 (CH), 128.4 (CH), 128.0 (CH), 127.7 (CH), 126.9 (CH), 126.8 (CH), 124.9 (CH), 124.2 (CH); HRMS (EI) *m/z*: [M$^+$] calculated for $C_{16}H_{11}NO_2$, 249.0790; found, 249.0785. Data consistent with literature reports.[S14]

1-(4-methylphenyl)naphthalene **12** White solid. R_f = 0.45 (petroleum ether/dichloromethane, 9/1); ^{1}H NMR (300 MHz, $CDCl_3$, δ_H): 7.95-7.89 (m, 2H, 2 × Ar H), 7.86 (d, *J* = 7.5 Hz, 1H; Ar H), 7.55-7.39 (m, 6H, 6 × Ar H), 7.31 (d, *J* = 7.5 Hz, 2H; 2 × Ar H), 2.47 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ_C): 140.2 (C), 137.8 (C), 136.9 (C), 133.8 (C), 131.7 (C), 130.7 (CH), 129.9 (CH), 129.0 (CH), 128.2 (CH), 127.4 (CH), 126.7 (CH), 126.1 (CH), 125.9 (CH), 125.7 (CH), 125.4 (CH), 21.2 (CH_3); HRMS (EI) *m/z*: [M$^+$] calculated for $C_{17}H_{14}$, 218.1096; found, 218.1104. Data consistent with literature reports.[S15]

2-(4-methylphenyl)naphthalene **13** White solid. R_f = 0.44 (petroleum ether/dichloromethane, 9/1); ^{1}H NMR (300 MHz, $CDCl_3$, δ_H): 8.07 (s, 1H, Ar H), 7.83-7.74 (m, 4H, 4 × Ar H), 7.64 (dt, *J* = 8.1, 2.1 Hz, 2H; 2 × Ar H), 7.46-7.34 (m, 2H, 2 × Ar H), 7.22 (d, *J* = 7.8 Hz, 2H; 2 × Ar H), 2.30 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ_C): 138.5 (C), 138.2 (C), 137.2 (C), 133.7 (C), 132.5 (C), 129.6 (CH), 128.3 (CH), 128.1 (CH), 127.6 (CH), 127.2 (CH), 126.2 (CH), 125.8 (CH), 125.5 (CH), 125.4 (CH), 21.1 (CH_3); HRMS (EI) *m/z*: [M$^+$] calculated for $C_{17}H_{14}$, 218.1096; found, 218.1092. Data consistent with literature reports.[S16]

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