Supplementary information for

Phosphine-stabilized Pd nanoparticles supported on silica as highly active catalyst for Suzuki-Miyaura cross-coupling reaction

Debojeet Sahu and Pankaj Das

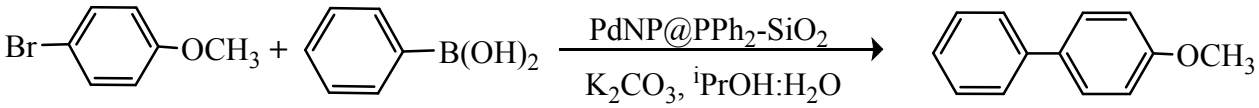
Department of Chemistry, Dibrugarh University, Dibrugarh-786004, Assam, India.

Table S1 Textural data of the silica-based materials.

Materials	Surface area* (m^2/g)	Pore volume* (cm^3/g)	Pore diameter* (nm)
PPh_2-SiO_2	181	0.24	3.81
PdNP @PPh_2-SiO_2	100	0.19	3.70

*Determined by BET method.

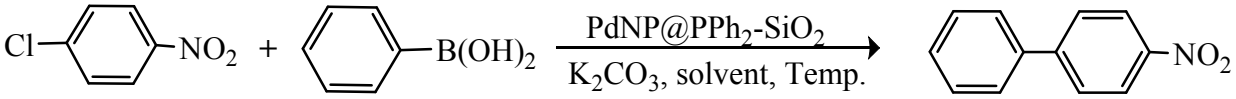
Table S2 Optimization of temperature and catalyst quantity for Suzuki-Miyaura cross coupling reaction of *p*-bromoanisole with phenylboronic acid.[a]



Entry	Catalyst (mol%)	Temp (°C)	Time (h)	Yield (%)[b]
1	0.5	100	2.0	100
2	0.5	80	2.0	100
3	0.5	60	3.0	100
4	0.5	RT	6.0	16
5	0.3	60	3.0	100
6	0.1	60	3.5	100
7	0.05	60	6.0	86
8	0.01	60	6.0	60

[a]Reaction conditions: 0.5 mmol *p*-bromoanisole, 0.75 mmol phenylboronic acid, 1.5 mmol K_2CO_3, 6 mL $^iPrOH:H_2O$ (1:1).
[b]GC yield.

Table S3 Optimization of reaction conditions for Suzuki-Miyaura cross coupling of *p*-chloronitrobenzene with phenylboronic acid.[a]



Entry	Solvent	Catalyst (mol%)	Temp (^oC)	Time (h)	Yield (%)[b]
1	^{i}PrOH-H_2O	0.1	60	6	17
2	^{i}PrOH-H_2O	0.3	80	8	28
3	^{i}PrOH-H_2O	0.5	100	8	31
4	^{i}PrOH	0.5	100	8	56
5	DMF	0.5	100	5	96
6	DMF-H_2O	0.5	100	5	61
7	Toluene	0.5	100	5	64
8	THF	0.5	100	5	41
9	DMF	0.2	100	6	64
10	DMF	0.1	100	6	43

[a]Reaction conditions: 0.5 mmol *p*-chloronitrobenzene, 0.75 mmol phenylboronic acid, 1.5 mmol K_2CO_3.
[b]GC yield.

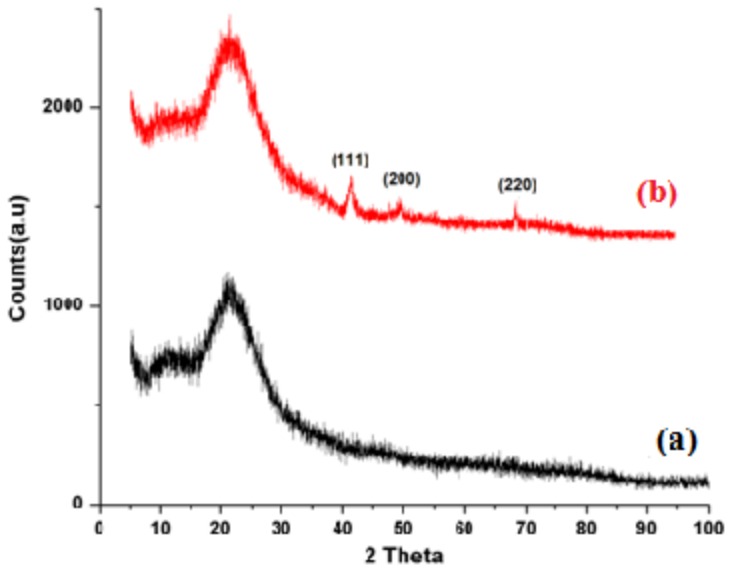


Fig. S1 The powder XRD patterns of (a) PPh_2-SiO_2 and (b) PdNP@PPh_2-SiO_2.

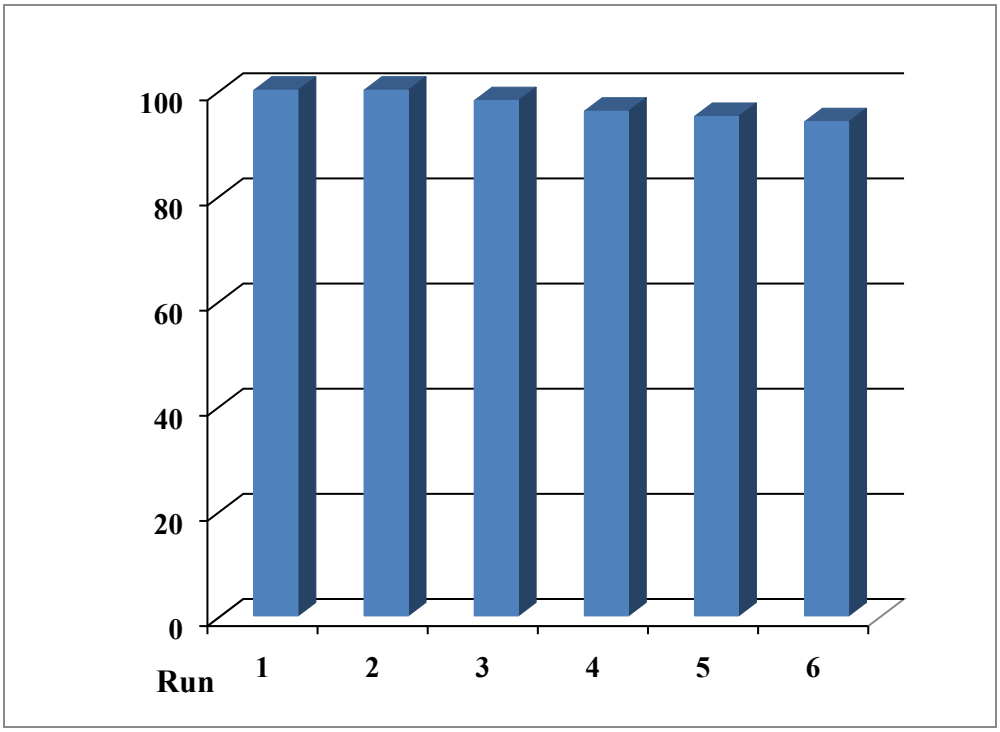


Fig. S2 Bar diagram showing the recyclability of the coupling reaction between *p*-bromoanisole and phenylboronic acid using PdNP@PPh_2-SiO_2.

^{1}H NMR and mass spectral data of the coupling products:

4-Methoxybiphenyl (Table 1, entry 1 and Table 2, entry 7): ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.56 (tt, *J* = 1.5 and 4.7 Hz, 4H), 7.42 (t, *J* = 7.4 and 7.8, 2H), 7.29 (tt, *J* = 6.9Hz , 1H), 6.98 (d, *J* = 8.5 Hz, 2H), 3.85(s, 3H, CH_3); GC-MS (m/z): 184 (M^+)

Biphenyl (Table 1, entry 2 and Table 2, entry 4): ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.60 (d, *J* = 7.6 Hz, 4H), 7.45 (t, *J* = 6.8 Hz, 4H), 7.36 (t, *J* = 7.2 Hz, 2H); GC-MS (m/z): 153.8 (M^+)

Biphenyl-4-carbaldehyde (Table 1, entry 3 and Table 2, entry 5): ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 10.05 (s, 1H, CH=O), 7.95 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.38-7.50 (m, 3H); GC-MS (m/z): 181.9 (M^+)

4-Methylbiphenyl (Table 1, entry 4): ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.57 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 8 Hz, 2H), 7.42 (t, *J* = 7.6 and 8.0 Hz, 2H), 7.36 (dd, *J* = 6.2 and 4 Hz, 1H), 7.25 (d, *J* = 8 Hz, 2H), 2.39 (s, 3H, CH_3); GC-MS (m/z): 167.9 (M^+)

Biphenyl-2-carbaldehyde (Table 1, entry 5): ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 9.78 (s, 1H, CHO), 7.92 (d, *J* = 8.2 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.53-7.44 (m, 5H), 7.36-7.39 (m, 2H); GC-MS (m/z): 182.1 (M^+)

2,5-dimethoxybiphenyl (Table 1, entry 6): ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.56 (d, *J* = 3.2 Hz, 2H), 7.43 (t, *J* = 7.2 and 8 Hz, 2H), 7.35 (t, *J* = 7.2 and 7.6 Hz, 1H), 7.15 (d, *J* = 2.8 Hz, 1H), 6.95 (s, 1H), 6.88 (d, *J* = 2.8 Hz, 1H), 3.87 (s, 3H, CH_3), 3.83 (s, 3H, CH_3); GC-MS (m/z): 214 (M^+)

4-Benzoylbiphenyl (Table 1, entry 7): ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.90 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8 Hz, 2H), 7.60 (t, *J* = 7.6 and 7.2 Hz, 1H), 7.52-7.46 (m, 4H), 7.41 (t, *J* = 7.6 Hz, 1H);

5-Phenylpyrimidine (Table 1, entry 8): ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 9.36 (s, 1H), 9.05 (s, 2H), 8.17 (d, *J* = 6.8 Hz, 2H), 7.58-7.44 (m, 3H); GC-MS (m/z): 155.8 (M^+)

3-methyl-2-phenylthiophene (Table 1, entry 9): ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.46 (d, *J* = 6.8 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.30 (dd, *J* = 6.4 and 7.2 Hz, 1H), 7.18 (d, *J* = 5.2 Hz, 1H), 6.91 (d, *J* = 4.8 Hz, 1H), 2.31 (s, 3H, CH_3); GC-MS (m/z): 173.9 (M^+)

4-Methoxy-4'-methylbiphenyl (Table 1, entry 10): ^{1}H NMR (400 MHz, $CDCl_3$) 7.50 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8 Hz, 2H), 7.22 (d, *J* = 8 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 3.86(s, 3H, O-CH_3), 2.39 (s, 3H, CH_3); GC-MS (m/z): 199.9 (M^+)

3-Nitrobiphenyl (Table 1, entry 11 and Table 2, entry 2): ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 8.44 (s, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.59-7.63 (m, 3H), 7.48-7.53 (m, 2H), 7.45 (t, *J* = 7.2 Hz, 1H); GC-MS (m/z): 200 (M^+)

4-Nitrobiphenyl (Table 2, entry 1): ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 8.30 (d, J = 8.8 Hz, 2H), 7.73 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 7.2 Hz, 2H), 7.52-7.43 (m, 3H); GC-MS (m/z): 200 (M^+)

2-Nitrobiphenyl (Table 2, entry 3): ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.95 (d, J = 8.4 Hz, 1H), 7.72 (t, J = 7.6 Hz,1H), 7.57 (t, J = 7.6 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.48-7.43 (m, 3H), 7.37 (d, J = 7.8 Hz, 2H); GC-MS (m/z): 200 (M^+)

4-Acetylbiphenyl (Table 2, entry 6): ^{1}H NMR (500 MHz, $CDCl_3$): δ(ppm) 8.06 (d, 2H, J = 8.5 Hz), 7.71 (d, 2H, J = 8.5 Hz), 7.66 (d, 2H, J = 7 Hz), 7.5 (t, 2H, J = 7 and 8 Hz), 7.43(t, 1H, J = 7 Hz), 2.66 (s, 3H, CH_3); GC-MS (m/z): 196 (M^+)

4-Biphenylmethanol (Table 2, entry 8): ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.66-7.62 (m, 4H), 7.45-7.39 (m, 4H), 7.35-7.32 (m, 1H), 4.50 (s, 2H, CH_2), 3.02 (s, 1H, OH); GC-MS (m/z): 183.8 (M^+)

3-Biphenylmethanol (Table 2, entry 9): ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 7.82 (s, 1H), 7.63-7.55 (m, 2H), 7.46-7.42 (m, 3H), 7.32-7.28 (m, 3H), 4.52 (s, 2H, CH_2), 2.90 (s, 1H, OH); GC-MS (m/z): 183.4 (M^+)

4-methyl-4'-nitrobiphenyl (Table 2, entry 10): ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.28 (d, 2H, J = 8.6 Hz), 7.75 (d, 2H, J = 8.6 Hz), 7.58 (d, 2H, J = 7.4 Hz), 7.46 (d, 2H, J = 7.4 Hz), 2.41 (s, 3H, CH_3); GC-MS (m/z): 213.1 (M^+)

4-chloro-4'-nitrobiphenyl (Table 2 entry 11) ^{1}H NMR (500 MHz, $CDCl_3$): δ(ppm) 8.32 (d, 2H, J = 10 Hz), 7.73 (d, 2H, J = 9 Hz), 7.58 (d, 2H, J = 8.5 Hz), 7.49 (d, 2H, J = 8.5 Hz); GC-MS (m/z): 233 (M^+)