Support information for Dalton Transactions

Rapid one–pot synthesis of magnetically separable Fe_3O_4–Pd nanocatalysts: a highly reusable catalyst for the Suzuki–Miyaura coupling reaction

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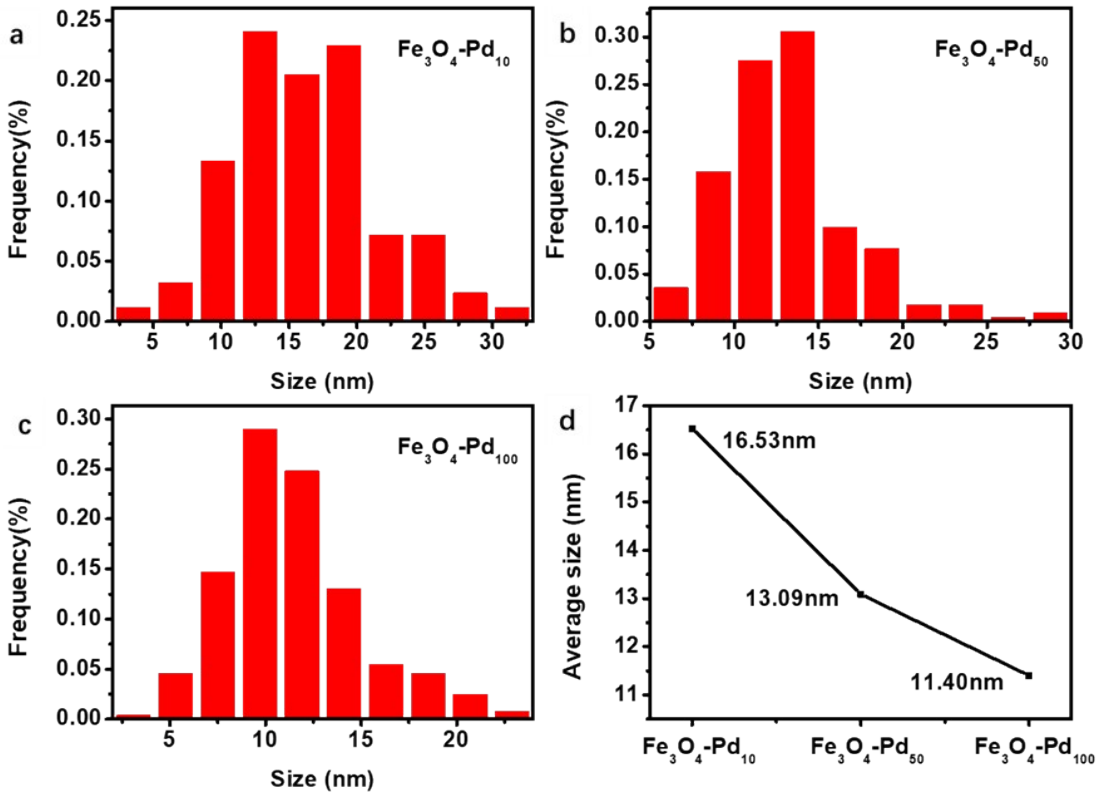


Fig. S1. The size distribution of (a,b,c) Fe_3O_4-Pd_n ,and (d) their average size summary graph.

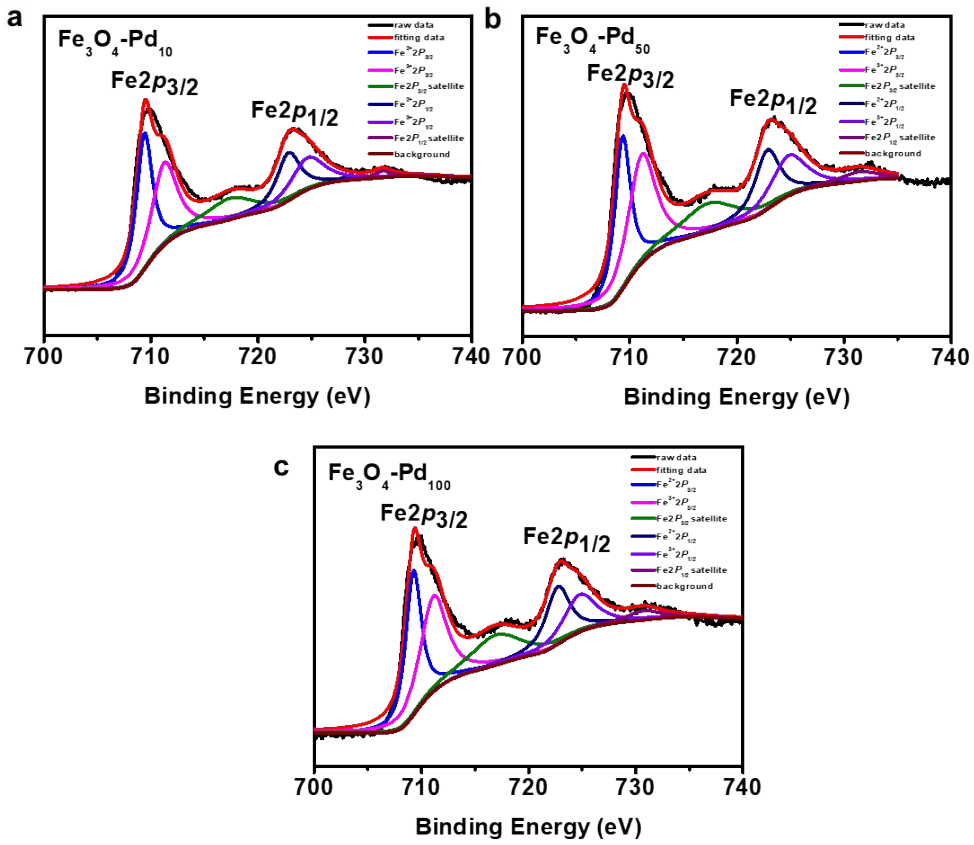
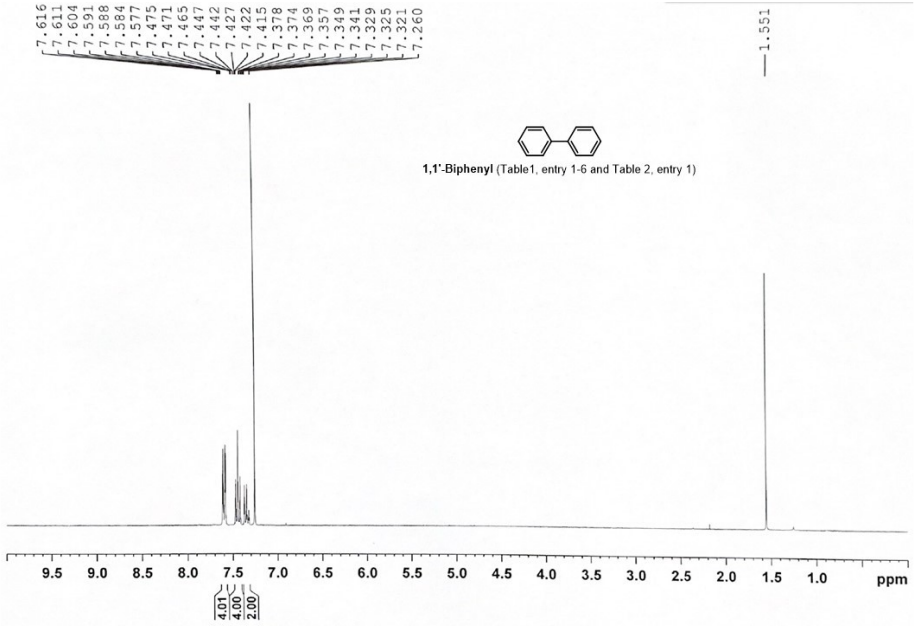


Fig. S2. Deconvolution of high-resolution XPS spectra for the Fe2p in the (a) Fe_3O_4-Pd_{10}, (b) Fe_3O_4-Pd_{50}, and (c) Fe_3O_4-Pd_{100}.

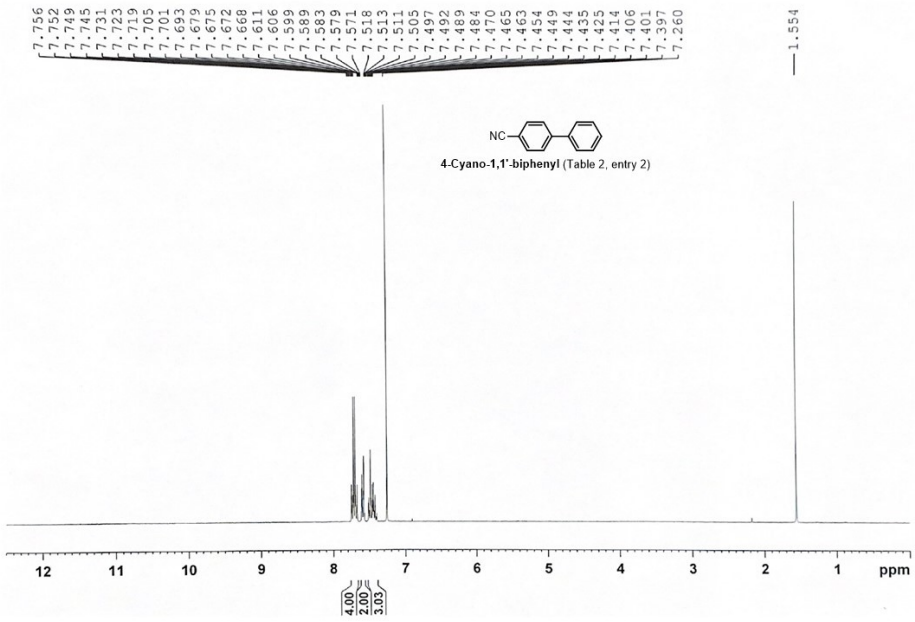
1,1’-Biphenyl (Table 2, entry 1)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62-7.58 (m, 4H), 7.48-7.42 (m, 4H), 7.38-7.32 (m, 2H)



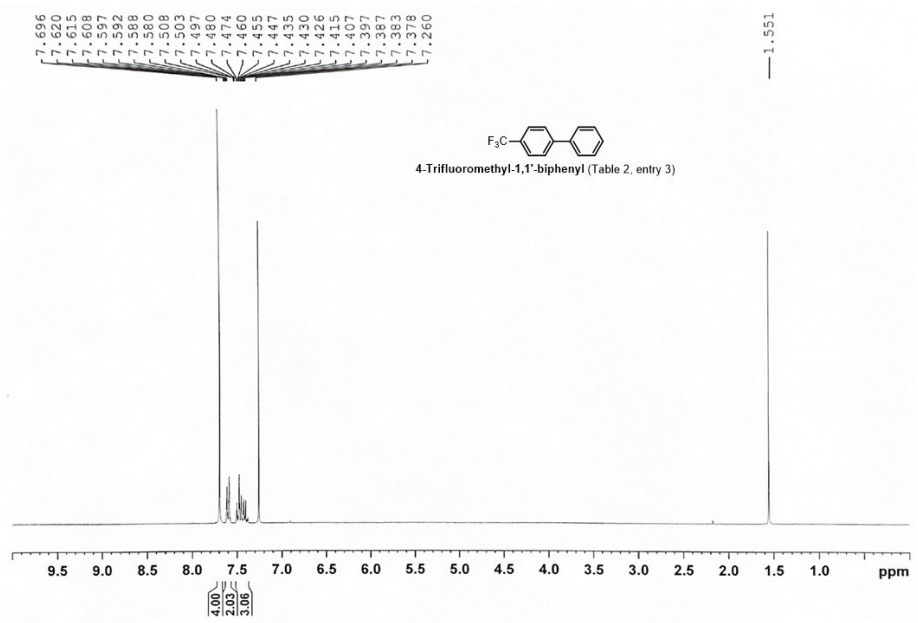
4-Cyano-1,1’-biphenyl (Table 2, entry 2)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76-7.67 (m, 4H), 7.61-7.57 (m, 2H), 7.52-7.40 (m, 3H)



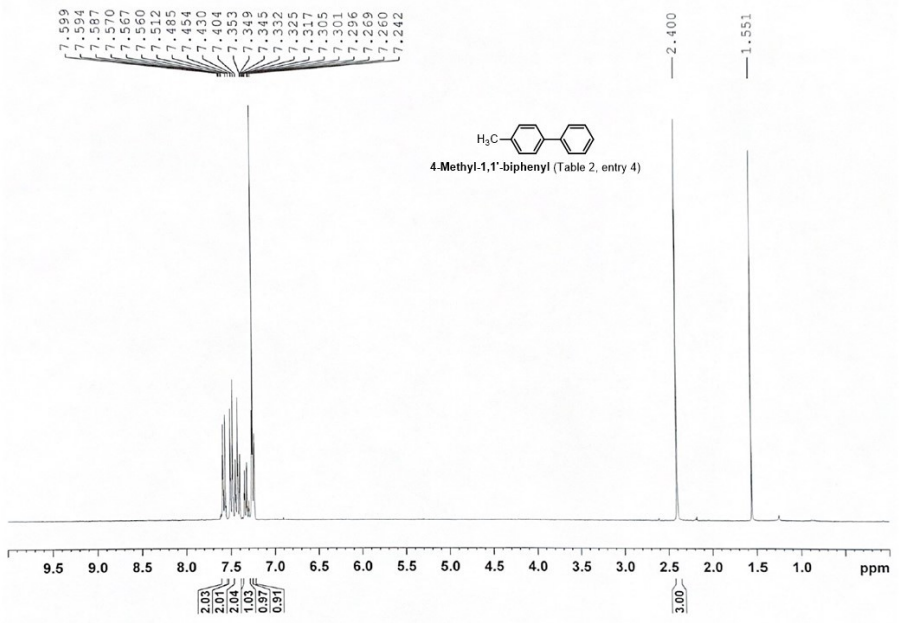
4-Trifluormethyl-1,1’-biphenyl (Table 2, entry 3)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (s, 4H), 7.62-7.58 (m, 2H), 7.51-7.38 (m, 3H)



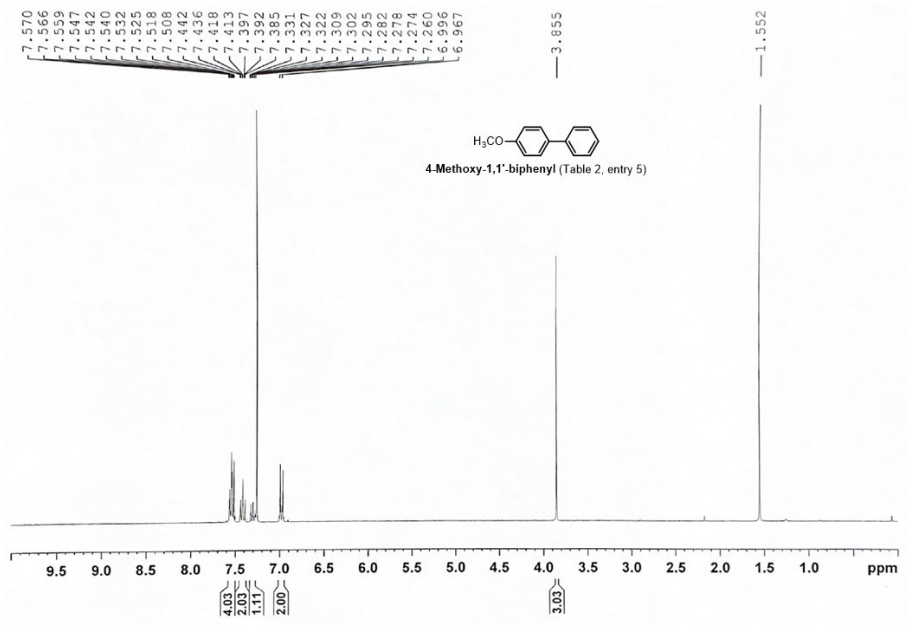
4-Methyl-1,1’-biphenyl (Table 2, entry 4)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60-7.56 (m, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.35-7.30 (m, 1H), 7.26 (d, 2H), 2.40 (s, 3H)



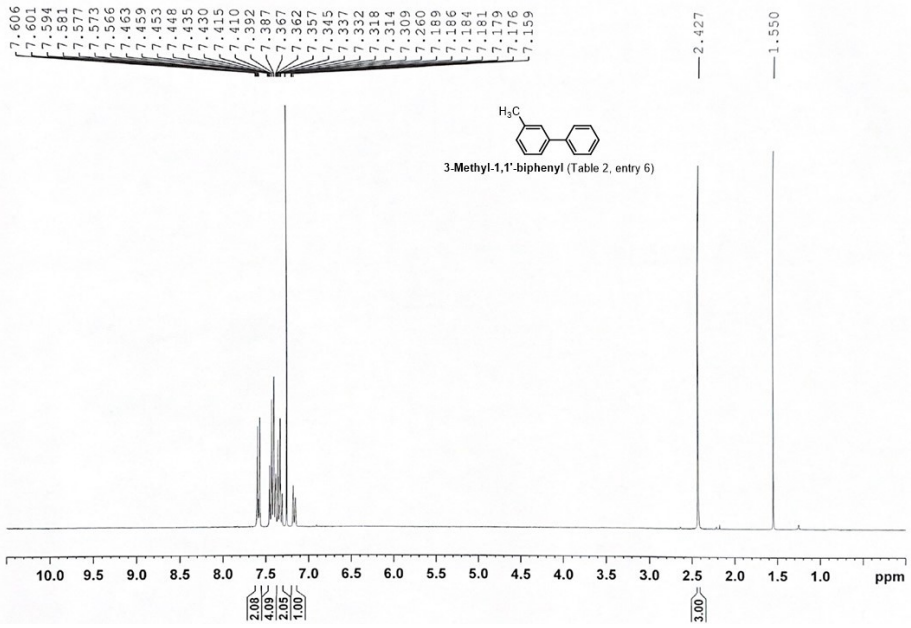
4-Methoxy-1,1’-biphenyl (Table 2, entry 5)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57-7.51 (m, 4H), 7.44-7.39 (m, 2H), 7.33-7.27 (m, 1H), 6.98 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H)



3-Methyl-1,1’-biphenyl (Table 2, entry 6)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61-7.57 (m, 2H), 7.46-7.31 (m, 6H), 7.19-7.16 (m, 1H), 2.43 (s, 3H)



2-Methyl-1,1’-biphenyl (Table 2, entry 7)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45-7.39 (m, 2H), 7.37-7.31 (m, 3H), 7.28-7.22 (m, 4H), 2.28 (s, 3H)

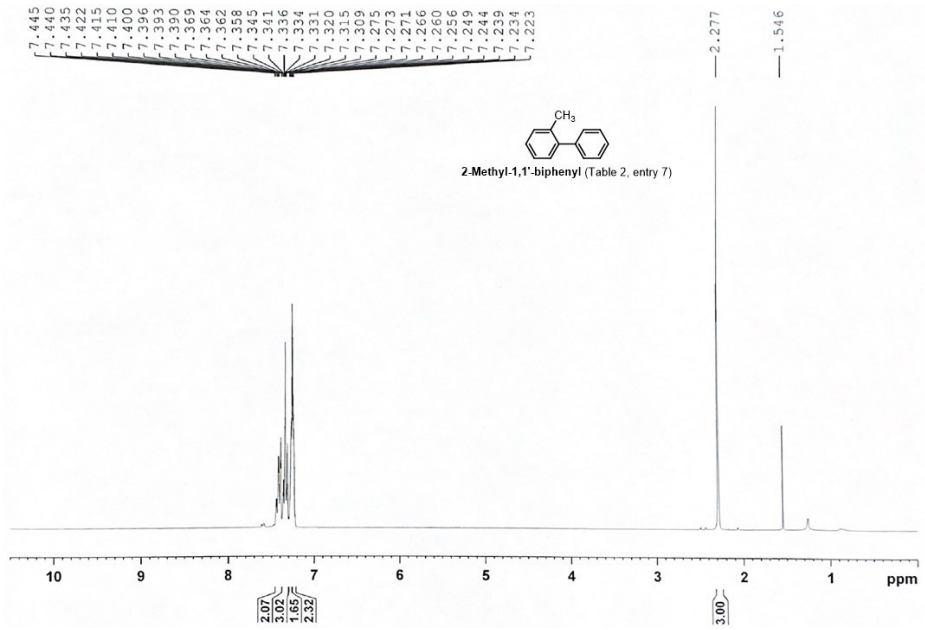


Fig. S3 The ^{1}H NMR spectra recorded to identify the products for Table 2.

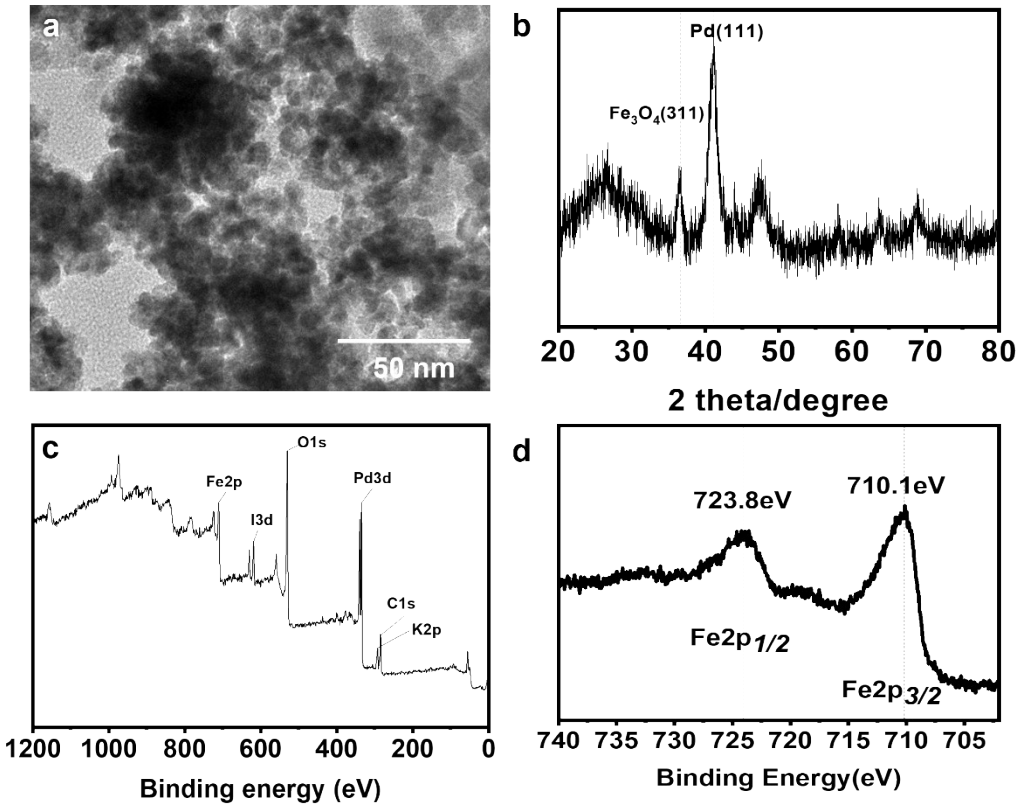


Fig. S4. (a) TEM, (b) XRD, (c) a survey XPS spectrum, and (d) fine XPS spectra of Fe 2p analyses of the Fe_3O_4-Pd_{50} after 10 reaction cycles.

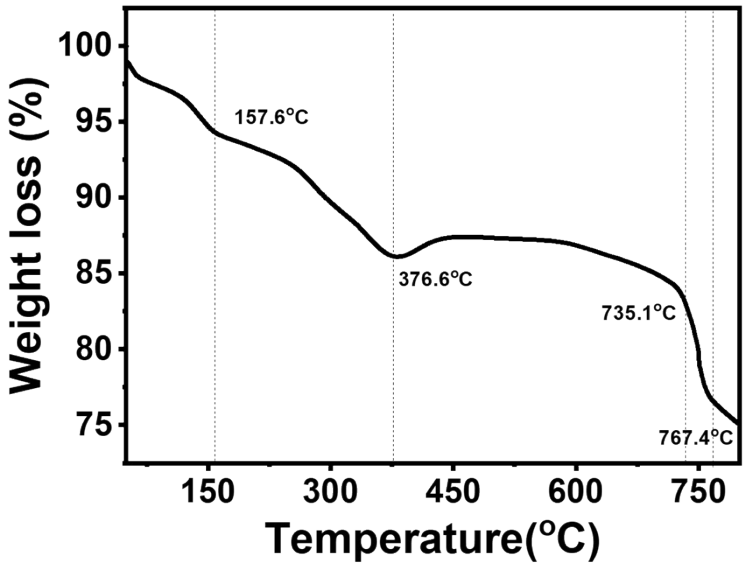
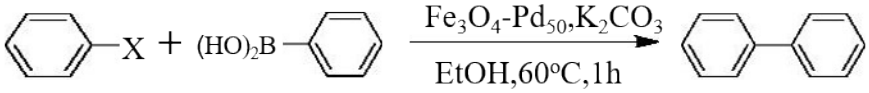


Fig. S5. The thermogravimetric analysis (TGA) of Fe_3O_4-Pd_{50} after 10 cycles. It was carried out at a temperature range of 50 – 800 °C at heating rate of 10°C /min under N_2 atmosphere.

Table S1. The Suzuki reactions of aryl halides with phenylboronic acid using the Fe_3O_4-Pd_{50} catalyst[a].



Entry	Aryl halide	Yield(%)[b]
1	X=I	100.0[c]
2	X=Br	7.5
3	X=Cl	/

[a]Isolated yield by column chromatography.

[b]Reaction condition: aryl halide (1.0 mmol), pheylboronic(1.5 mmol),K_2CO_3 (2.0mmol), ethanol (6.0 mL), Fe_3O_4-Pd_{50} catalyst (Pd content in Fe_3O_4-Pd_{50} is: 1.0 mol%; 0.01mmol), and 60°C, 1h.

Table S2: The Suzuki-Miyaura coupling reactions between iodobenzene and phenylboronic acid using the Fe_3O_4-Pd_{50}, Pd, and Fe_3O_4 as catalysts.[a]

Entry	Cat.	Cat. Mass	Yield(%)
1	Fe_3O_4-Pd_{50}	Pd content in cat.: 0.01mmol	99.9[b]
2	Pd	0.01mmol	>80[c]
3	Fe_3O_4	0.01mmol	-[c]

[a]Reaction condition: iodobenzene (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), ethanol (6.0 mL), catalyst (1mol%), 60°C, 360 rpm, 1 atm, and 1 h.

[b]GC yield.

[c]Isolated yield by column chromatography.

Table S3: ICP data of the Fe_3O_4-Pd_{50} after 10 reaction cycles.

Name	Molar fraction of metal (%)			
	Pd	Fe	(Fe+Pd)	Fe/Pd ratio
Fe_3O_4-Pd_{50}-after 10 cycles	25.4	15.6	4.1	85.45%