

Supporting information

Efficient parts-per-million α -Fe₂O₃ nanocluster/graphene oxide catalyst for Suzuki–Miyaura coupling reactions and 4-nitrophenol reduction in aqueous solution

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1. General data

All solvents and chemicals were used as purchased.

-**Milli-Q water** (18.2 M Ω) was used for all the nanoparticle preparations. Prior to the synthesis, the Schlenk flask was washed with a solution of aqua regia (HCl/HNO₃ = 3:1 v/v) to remove any traces of metal residue.

-**NMR spectra** were recorded at 25 °C with a Bruker AC 200, or 300 (200 or 300 MHz). All the chemical shifts are reported in parts per million (δ , ppm) with reference to Me₄Si for the ¹H and ¹³C NMR spectra.

-**UV-vis. absorption spectra** were measured with a Perkin-Elmer Lambda 19 UV-vis. spectrometer.

- **Transmission Electron Microscopy (TEM)** images were recorded at Laboratoire de Chimie de Coordination (LCC), CNRS, 205 Route de Narbonne, 31077 Toulouse Cedex, France), and CIC bioma GUNE, Unidad Biosuperficies, Paseo Miramon No 182, Edif "C" 20009 Donostia-San Sebastian, Spain. A TEM JEOL JEM 1400 (120 kV) and a high-resolution TEM JEOL JEM 2100F (200 kV) that was equipped with a PGT X-ray analyzer were used for size and composition analysis. Size was calculated based on at least 100 NPs.

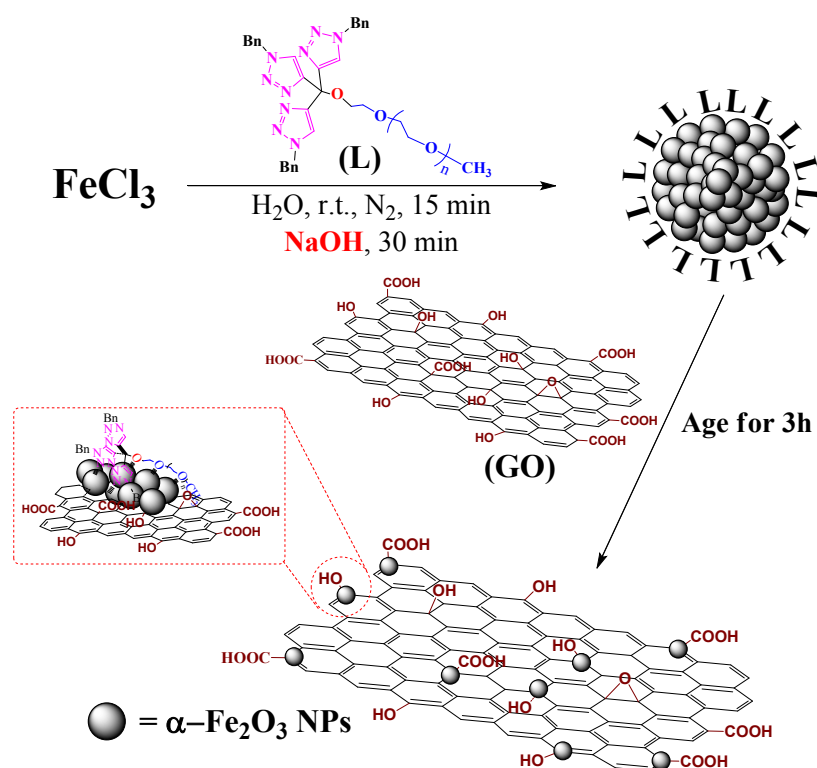
- **X-ray photoelectron spectra (XPS):**

System: SPECS SAGE HR, X-Ray source: Mg K α non-monochromatic, operated at 12.5 kV and 250 W. Take off angle 90°, at ~10⁻⁸ Torr. Pass energy for survey spectra 30 eV, 15 eV for narrow scans. Analysis: spectra are calibrated to CC carbon 285 eV. Analysis consisted of Shirley background subtraction. Peaks are fitted with symmetrical Gaussian-Lorentzian (GL) line shapes. Sample is dispersed on silica substrate and evaporated prior to measurement.

- **Flash column chromatography** was performed using silica gel (300-400 mesh).

1. Synthesis of the catalyst $\alpha\text{-Fe}_2\text{O}_3$ /graphene oxide, 1

The catalyst **1** was synthesized in water under N_2 (Scheme S1). Typically, in a dried Schlenk flask, 7.66 mg of tris-trz-PEG ligand was solubilized in 5 mL H_2O , 0.5 mL FeCl_3 (1 mg/mL) and was injected to the Schlenk. The mixture was stirring for 30 min, then the freshly prepared NaOH solution (2.47 mg in 1.5 mL H_2O) was injected into the Schlenk, and the mixture was allowed to stir for 30 min. Graphene oxide was then directly injected, and the catalyst was aged for 3 hours. The catalyst was then collected and dried *in vacuo* at 50 °C overnight. The catalyst was then stored under N_2 for the characterizations and catalytic applications.



Scheme S1. Synthesis of the catalyst $\alpha\text{-Fe}_2\text{O}_3$ /graphene oxide, 1.

2. XPS of α -Fe₂O₃/GO catalyst

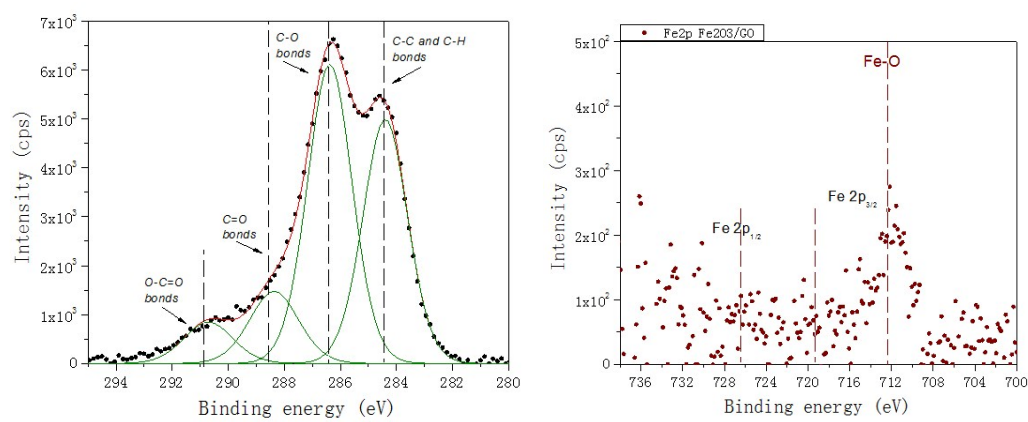


Figure S2. XPS of the catalyst 1. C 1s spectrum (left) and Fe2p (right).

3. Procedures for 4-nitrophenol reduction and Suzuki–Miyaura coupling reactions

4-Nitrophenol reduction

Generally, 4-NP (1 equiv.) was mixed with 81 equiv. NaBH_4 in water under air at 20 °C. The color of the solution changed from light yellow to dark yellow due to the formation of the 4-nitrophenolate ion. Then a solution containing the catalyst was added into the mixture; the solution quickly lost its dark yellow color with time, and the progress of the reaction was measured by UV-vis. spectroscopy rapidly in a scanning range of 250–500 nm (40 s for each run). For the recycling study, the catalyst was recovered by centrifugation and washed, then re-dispersed in water. The reaction was then conducted following the above-mentioned procedure.

Kinetics

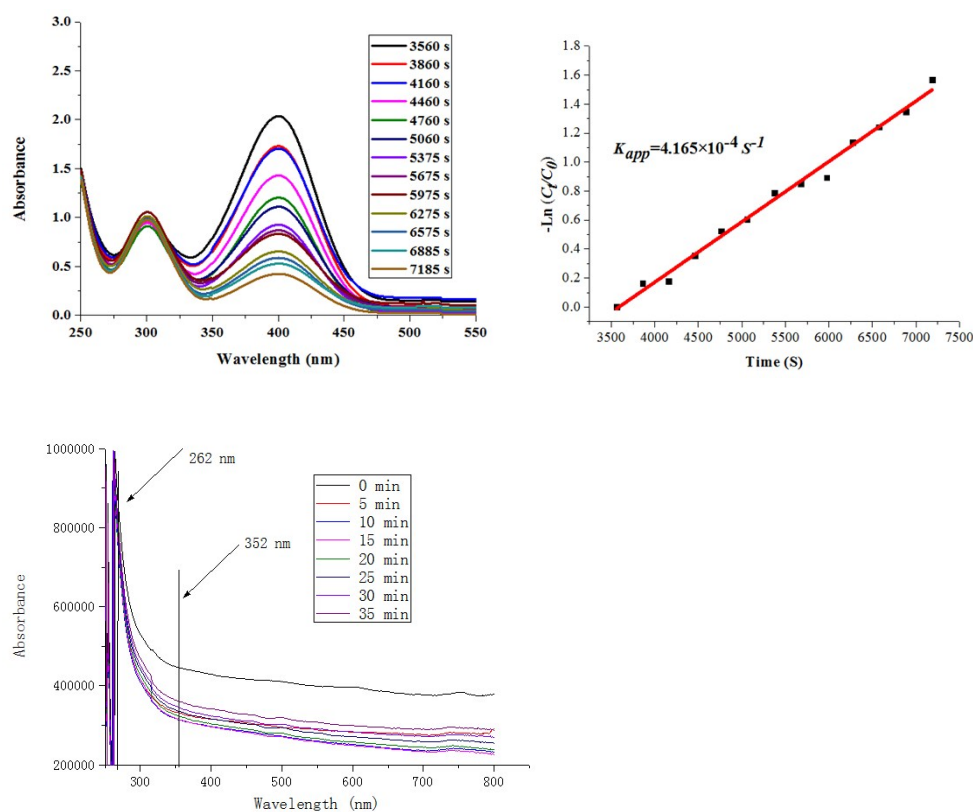
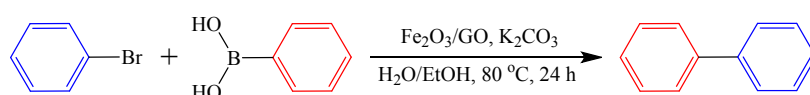


Figure S3. UV-vis. spectra for the reduction of 4-NP by NaBH_4 catalyzed by **1** (top left) and $-\ln(C_t/C_0)$ vs. reaction time for this reaction (top right). High-resolution UV-vis. spectra of the reduction of 4-NP by NaBH_4 catalyzed by **1** (bottom). The spectra did not change during the reaction, and no peaks at 352 nm and at 262 nm that corresponded to Fe(0) were observed.

Suzuki–Miyaura coupling reactions

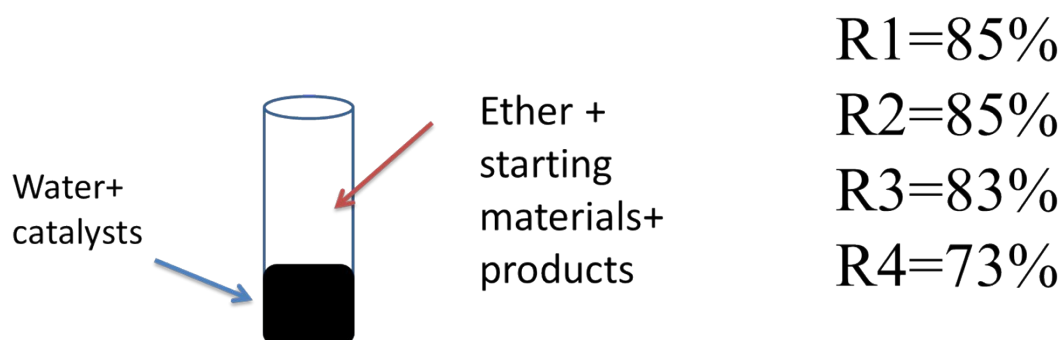
A dry Schlenk flask was charged with K_2CO_3 (2 equiv.), phenylboronic acid (1.5 equiv.), and bromobenzene (1 equiv.). The catalyst **1** was then successively added, and the solvents H_2O and EtOH were added in order to make a total of 2 mL of solvent (volume ratio of H_2O /EtOH: 1/1). The suspension was then allowed to stir under N_2 for 24 hours at $80^\circ C$. After the reaction, the Schlenk flask was cooled to r.t., the mixture was extracted three times with diethyl ether (Et_2O , 3×10 mL), the organic phase was dried over Na_2SO_4 , and the solvent was removed *in vacuo*. In parallel, the reaction was checked using TLC in only petroleum ether as eluent. The crude product was checked by 1H NMR in order to calculate the conversion. The purification by flash chromatography column was conducted with silica gel as the stationary phase and petroleum ether as the mobile phase.

Table S1. Optimization of the Suzuki–Miyaura coupling reactions.



Catalyst	Solvent	Conversion	Yield
α - Fe_2O_3 /GO	H_2O /DMF (1mL: 1 mL)	0	0
α - Fe_2O_3 /GO	H_2O /ethylene glycol (1mL:1 mL)	0	0
α - Fe_2O_3 /GO	H_2O/EtOH (1:1, 2 mL)	100%	87%
α - Fe_2O_3 /GO	H_2O /EtOH (1:1, 20 mL)	0	0
GO	H_2O/EtOH (1:1, 2 mL)	0 (1st); 0 (2nd); 0 (3rd).	0
α - Fe_2O_3	H_2O/EtOH (1:1, 2 mL)	0	0

Recycling: biphasic method



5 Spectra of the reaction products of the Suzuki–Miyaura coupling reactions

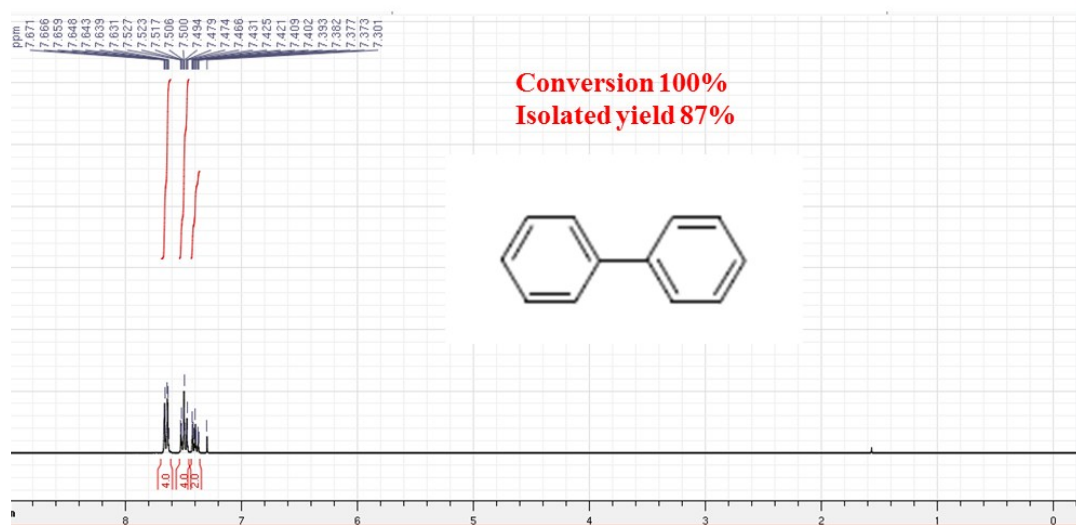


Figure S4. ^1H NMR (CDCl_3 , 300 MHz) spectrum of biphenyl: δ_{ppm} 7.60-7.64 (m, 4H), 7.46 (t, $J = 7.5$ Hz, 4H), 7.37 (t, $J = 7.4$ Hz, 2H).

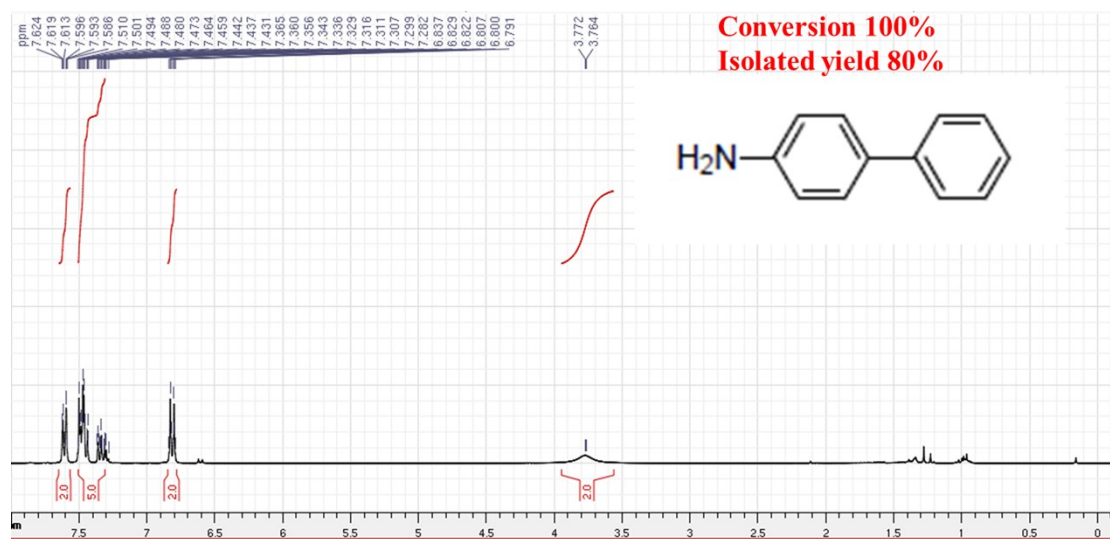


Figure S5. ^1H NMR (CDCl_3 , 300 MHz) spectrum of biphenyl-4-ylamine. δ_{ppm} 7.55 (d, $J = 7.2$ Hz, 2H), 7.37-7.45 (m, 4H), 7.22-7.31 (m, 1H), 6.76 (d, $J = 8.4$ Hz, 2H), 3.71 (bs, 2H).

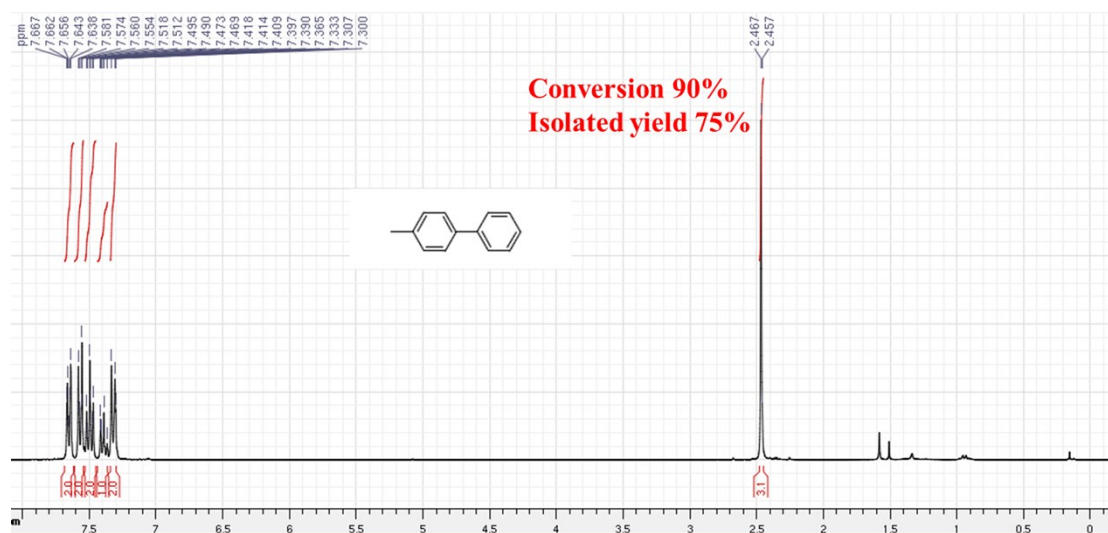


Figure S6. ^1H NMR (CDCl_3 , 300 MHz) spectrum of 4-methyl-biphenyl. δ_{ppm} 7.58-7.61 (m, 2H), 7.51 (d, $J = 8.1$ Hz, 2H), 7.43 (t, $J = 7.4$ Hz, 2H), 7.33 (t, $J = 7.4$ Hz, 1H) 7.26 (d, $J = 7.8$ Hz, 2H), 2.41 (s, 3H).

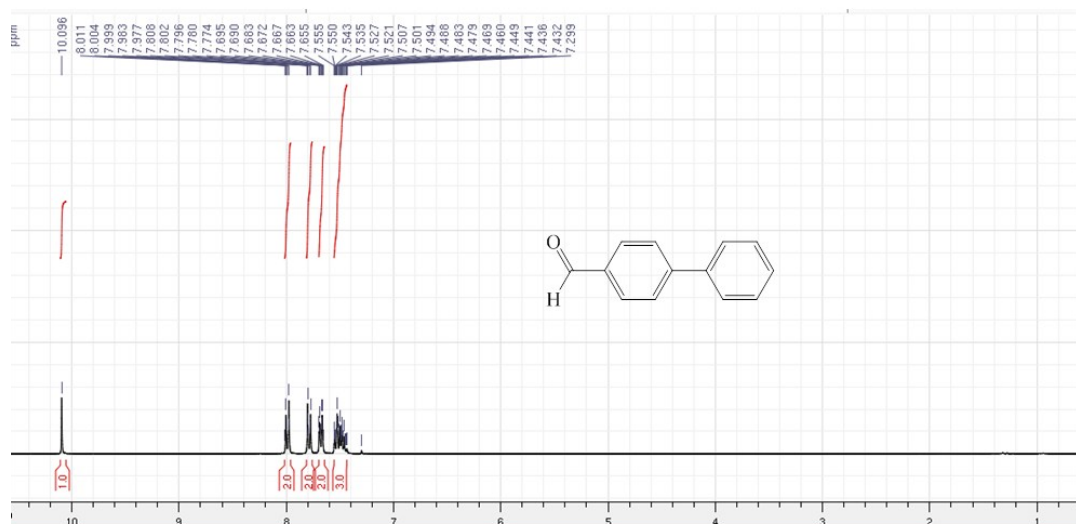


Figure S7. ¹H NMR (CDCl₃, 300 MHz) spectrum of biphenyl-4-carbaldehyde. δ_{ppm} 10.09 (s, 1H), 7.93 (d, $J = 8.4$ Hz, 2H), 7.73 (d, $J = 8.4$ Hz, 2H), 7.60-7.64 (m, 2H), 7.37-7.50 (m, 3H).

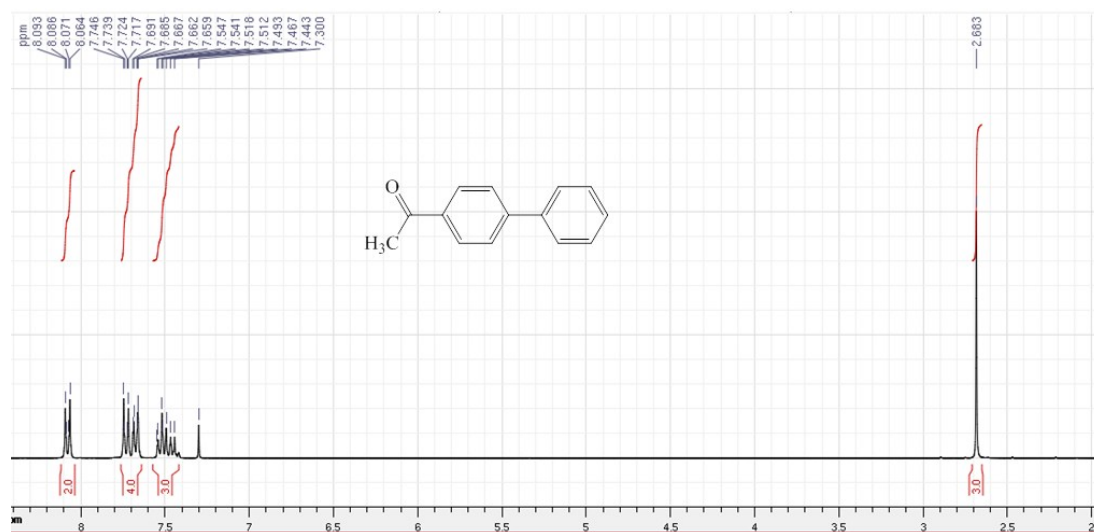


Figure S8. ¹H NMR (CDCl₃, 300 MHz) spectrum of 1-biphenyl-4-yl-ethanone. δ_{ppm} 8.02 (d, $J = 8.4$ Hz, 2H), 7.60-7.69 (m, 4H), 7.36-7.49 (m, 3H), 2.68 (s, 3H).

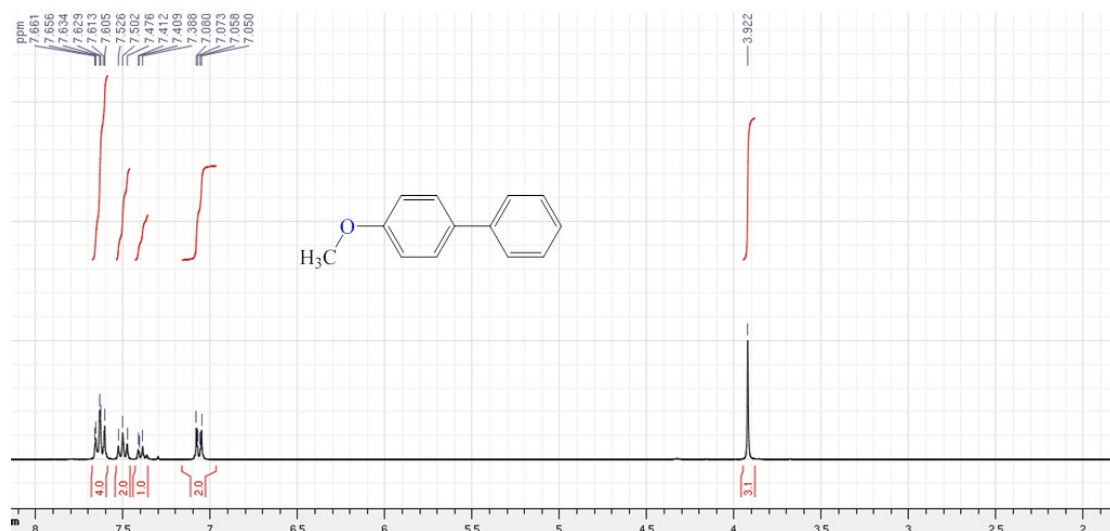


Figure S9. ¹H NMR (CDCl₃, 300 MHz) spectrum of 4-methoxy-biphenyl. δ_{ppm} 7.55-7.60 (m, 4H), 7.44 (t, $J = 7.7$ Hz, 2H), 7.33 (t, $J = 7.4$ Hz, 1H), 7.05-7.07 (m, 2H), 3.92 (s, 3H).

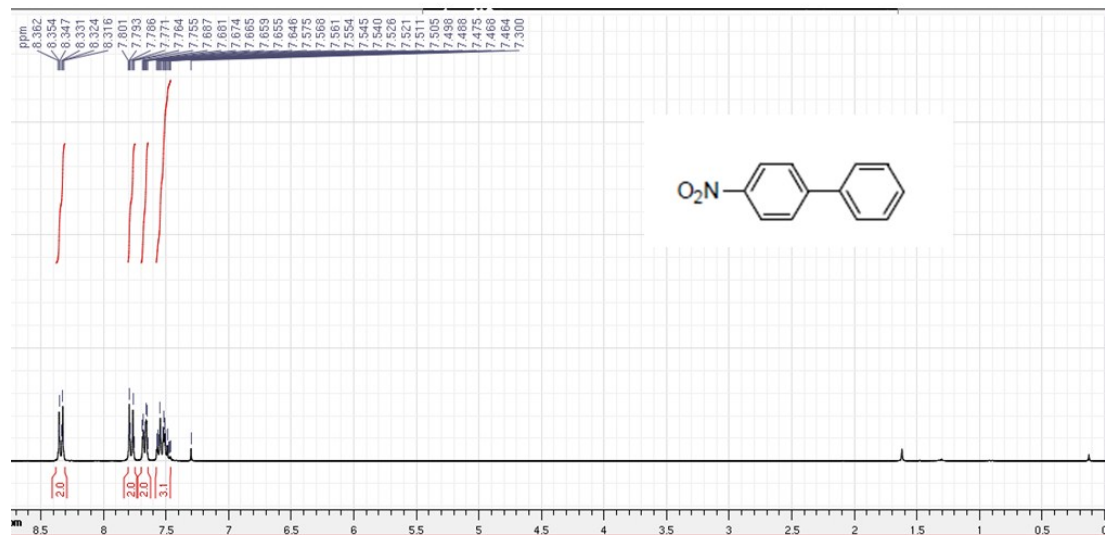


Figure S10. ¹H NMR (CDCl₃, 300 MHz) spectrum of 4-nitro-biphenyl. δ_{ppm} 8.31-8.36 (m, 2H), 7.70-7.74 (m, 2H), 7.59-7.63 (m, 2H), 7.46-7.52 (m, 3H)

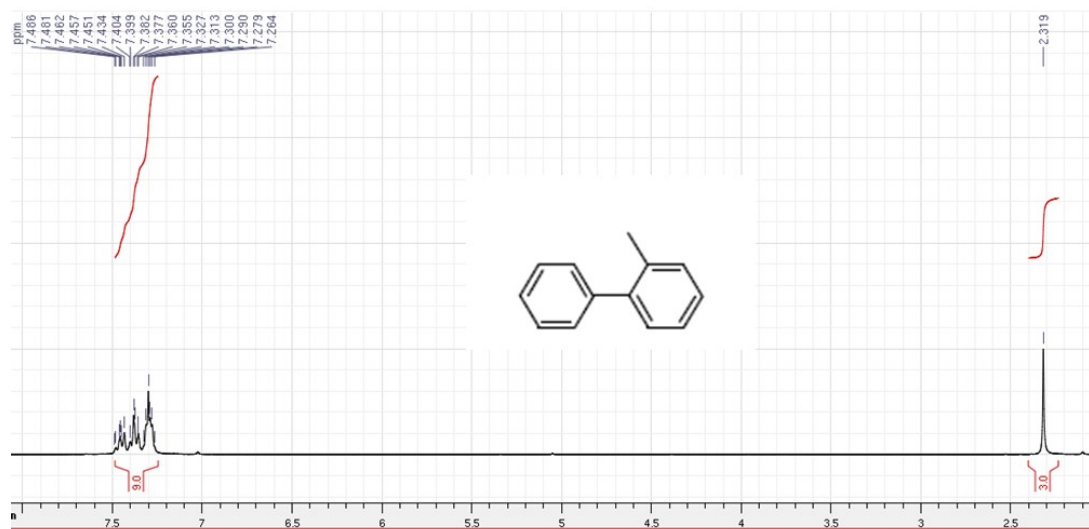


Figure S11. ¹H NMR (CDCl₃, 300 MHz) spectrum of 2-methyl-biphenyl. δ_{ppm} 7.26-7.49 (m, 9H), 2.32 (s, 3H).

6 XPS of α -Fe₂O₃/GO catalyst after reaction and Hot filtration test

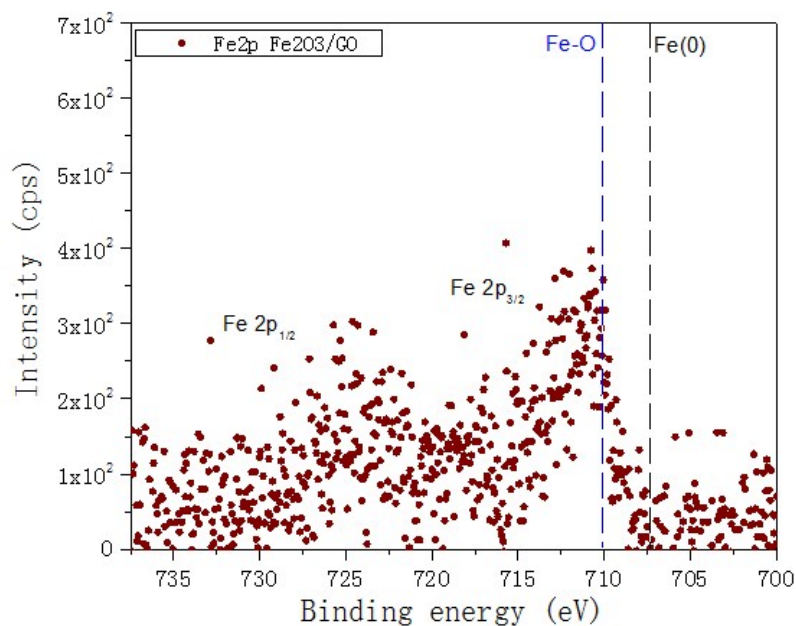


Figure S12. XPS Fe2p spectrum of the catalyst **1** after Suzuki reaction in the presence of large amount of solvent (H₂O:EtOH = 10 mL:10mL).

In the Fe 2p spectrum, the Fe 2p_{3/2} peak position is around 710.5 eV and is related to Fe-O bonds; no signal of Fe(0) is found, suggesting that the α -Fe₂O₃ is not reduced in the present condition.

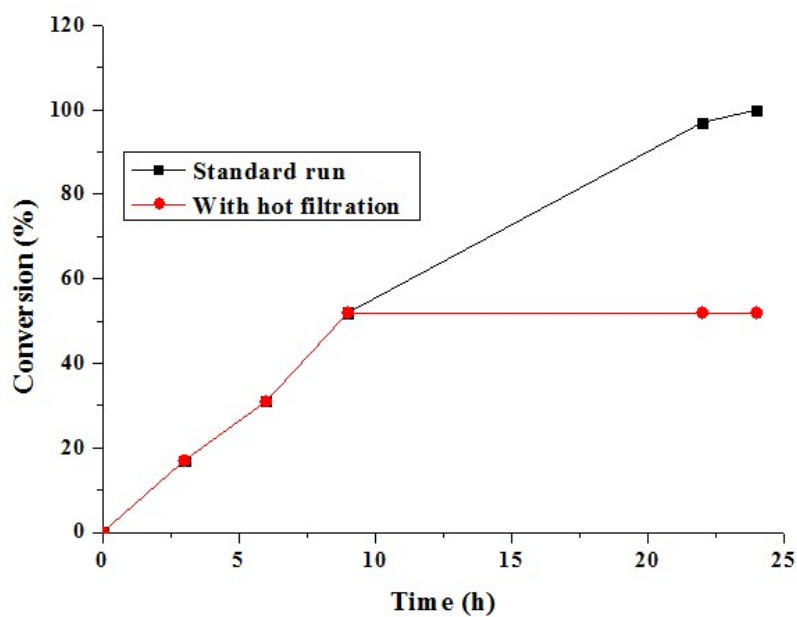
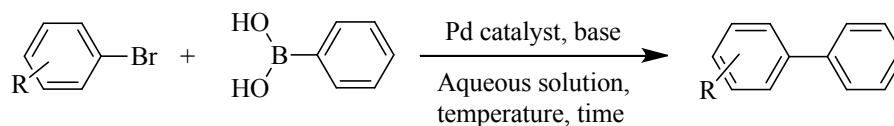


Figure S13. Hot filtration test of the standard Suzuki reaction in the presence of α -Fe₂O₃/graphene oxide catalyst.

7 Comparative table with literature

Table S1: Comparison table of Suzuki-Miyaura coupling of bromoarenes using the conventional Pd catalysts. The reactions have been conducted with various catalysts at different temperatures in aqueous solvents.



R ^{ref}	catalyst	Temp. (°C)	TON	TOF (h ⁻¹)
4-H ^{S1}	α -Fe ₂ O ₃ nanocluster/GO	80	5800	242.7
4-OMe ^{S1}	α -Fe ₂ O ₃ nanocluster/GO	80	5200	208
4-OMe ^{S2}	Pd-SDS	100	38	456
4-Me ^{S3}	Pd-PEG	25	90	45
4-NO ₂ ^{S4}	Pd-1/FSG	100	990	123
4-OMe ^{S5}	Fe ₃ O ₄ -Pd	50	144	12
4-OMe ^{S6}	pEVPBr-Pd	90	340	38
4-OMe ^{S7}	Pd-PS	100	50	10
4-COMe ^{S8}	HAP-Pd ⁰	100	139	23
4-OMe ^{S9}	Pd@PNIPAM	90	300	30
4-Me ^{S10}	Pd _x - ([PW ₁₁ O ₃₉] ⁷⁻) _y	80	89	7
4-OMe ^{S11}	Pd-block-co-poly	90	310	31
4-Me ^{S12}	PS-PdONPs	80	59	59
4-OMe ^{S13}	Pd@PMO-IL	75	475	95
4-NH ₂ ^{S14}	Pd-XH-15-SBA	90	96	7
4-OMe ^{S15}	Pd ²⁺ -G0	80	386	99
4-Me ^{S16}	Pd(0)/Al ₂ O ₃ -ZrO ₂	60	45	12

8 Reference

S1 Present work

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