Materials and Instrumentation.

All the reagents and solvents were purchased from Sinopharm Chemical Reagent Co. Ltd and without any pretreatment except divinyl benzene. Reaction yields were analyzed by gas chromatography (GC, Agilent Tecnologies). The state of palladium was determined by X-ray diffractometer (XRD, Bruker). The size and morphology of magnetic nanoparticles were observed using transmission electron microscopy (TEM, HITACHI). Magnetic content of nanoparticles was analyzed by thermogravimetric analyser (TG, SHIMADZU). The magnetization measurements were performed at room temperature using a vibrating sample magnetometer (Mpms XL-7, Quantum Design). The BET analysis was performed on surface area analyzer (Quantachrome Instruments). The ^{1}H NMR of the compounds was recorded on a 400MHz Bruker Avance spectrometer. Elementary analysis of dried samples was implemented by using vario EL III (elementar). Palladium amount on the carriers was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES, SHIMADZU). The BET analysis was performed on surface area analyzer (Quantachrome Instruments). Analysis adsorptive: N2 (77k). Pretreatment method: the dried sample was suffered vacuum degassing at 90 ^{o}C for 8 h. Relative pressure was ranged from 0.1 to 0.35, and we selected six test points.

Preparation of ferrofluid[1]

$FeCl_3 \cdot 6H_2O$ (24g) was dissolved in 200 mL distilled water in a three necked flask. Then, it was bubbled with nitrogen for 30 min. 17g $FeSO_4 \cdot 7H_2O$ was then added into the flask. After it dissolved, 60 mL ammonium hydroxide was added under fast stirring and 4 g of oleic acid follow added. The reactants was heated to 90 °C and kept for 3 hours under nitrogen atmosphere. Then, the black precipitate was obtained by magnetic separation. It was washed with distilled water and ethanol for several times than dried under vacuum at 40 °C for 48 h. The obtained coated magnetite nanoparticles were dispersed in the cyclohexane to form to a ferrofluid with a magnetite content of 14 wt%.

Preparation of polymer magnetic nanoparticles

A mixture of 14 mL ferrofluid and 0.3 g hexadecane was added into 24 g water containing 0.7 g SDS. This mixture was stirred for 1 h followed by sonication for 10 min to form a miniemulsion. Another mixture of 2.4 g styrene, 0.6 g divinyl benzene and 120 mg hexadecane was added into a surfactant solution containing 36 mg SDS dissolved in 12 g water. After 1h of stirring, the mixture was subjected to sonication for 10 min to prepare styrene miniemulsion. After cyclohexane was carefully evaporated at 80 °C, the monomer miniemulsion was added and co-sonicated for 10 minutes in an ice-cooled bath. Then, 15 mg KPS was added to start the polymerization at 80 °C for 24h. The processes mentioned above were all carried out with continuous stirring at 300 rpm.

Preparation of NHC ligand[2]

2,6-Diisopropylaniline (0.05 mmol) and glyoxal were dispersed in MeOH (20 mL). Then, this mixture was stirred for 12 h at room temperature. After a yellowish mixture appeared, NH_4Cl (5.35 g, 0.1 mol) was added followed by 37% aq formaldehyde (8 mL, 0.1 mol). The mixture was diluted with MeOH (200 mL) and the resulting mixture was refluxed for 1 h. H_3PO4

(7mL, 85%) was added over a period of 5 min. The resulting mixture was then stirred at reflux for a further 8 h. Dark residue was obtained after the solvent was evaporated. Some ice was added into the residue and NaOH solution was employed to adjust pH value to 9. Resulting mixture was extracted with diethyl ether for three times (3×50 mL). The organic phases were combined and washed with water and brine. The pure products were separated by careful chromatographic fractionation on silica gel (pe-troleum ether/EtOAc=3/1).

Preparation of Supported-Pd Catalysts with polymer magnetic nanoparticles

A mixture of 1 g magnetic chloromethyl nanoparticles (MCNS) and 0.63 mmol 1-Arylimidazoles were stirred at 90 °C for 24 h in 100 mL toluene. After magnetic separation, the precipitate was washed by DMF for several times and sufficiently dried (calculated loading:0.21 mmol/g, according to the result analyzed by element analyzer). These achieved particles (1 g) were then dispersed into DMSO. After $Pd(OAc)_2$ (0.63 mmol) were added, this mixture was reacted at 50 °C for 12 h. The mixture was cooled to room temperature and magnetic separation was performed to obtain the magnetic palladium catalyst 1. The catalyst was washed with water (5×20 mL) and methanol (5×20 mL) subsequently.

To prepare catalyst 2, the modification of MCNS with 1-Arylimidazoles was carried out with the above steps. Then, modified nanoparticles (1 g) was added in a mixture of 3-Chloropyridine (10 mL) and K_2CO_3 (1.93 g, 14 mmol) followed by the addition of $PdCl_2$ (47 mg, 210 μmol). After 15 min of ultrasonic dispersion, the mixture was stirred at 80 °C for 24 h. The mixture was cooled to room temperature and washed with DCM for several times with the help of magnetic separation.

Preparation of the dispersion of Nano Palladium particles[3]

First, a solution of disodium tetrachloropalladate was obtained by dissolving 17.7 mg palladium chloride and 11.7 mg sodium chloride in 10 mL DI water. These chemicals of 45.6 mg anhydrous sodium citrate, 25 mg tannic acid and 8.7 mg potassium carbonate were dissolved into 20 mL DI water and heated to 80 ^oC to prepare the reducing agent. Then 1 mL of disodium tetrachloropalladate solution was diluted with 79 mL DI water in a 250 mL conical flask, the solution was heated to 80 ^oC, too. The formation of Pd NPs was apparent upon addition of the reducing agent to the diluted solution with stirring at 1200 rpm. A dark coffee-brown color was observed and this solution was then heated to boil with continued stirring for 5 min. The solution was cooled to room temperature to obtain a dispersion of the Pd NPs.

Animation of MCNS

The chloromethyl magnetic nanoparticles (2 g, MCNS) were directly dispersed in 25 mL DMF under sonification for 10 min. After the mixture was stirred overnight to swelling, 5 mL of ethylenediamine was added in. The mixture was kept at 80 ^oC for 3 h with continuing stirring (250 rpm). The modified MCNS were obtained by magnetic separation and washed with DMF (20 mL×3) and H_2O (20 mL×3) in turns. The element analyzer shows the ethylenediamine loading amount was 0.4 mmol/g.

Preparation of MCNS supported nano-palladium[4]

To prepare these composite, 1g of modified MCNS was taken in 50 mL ethanol, then, 200 mL of palladium nanoparticles dispersion was added in. The mixture was shaken for 6 h on a circumferential shake table at room temperature under enclosed condition. The product was gained by magnetic separation and washed with distilled water for several times. The amount of palladium of the composite was characterized by ICP-AES.

General Procedures for Suzuki Cross-Coupling Reactions Catalyzed by Catalyst 1

After 2 mg of catalyst 1 was ultrasoinc dispersed in 15 mL ethanol for 15 min, aryl halide reagent (2 mmol) and arylboronic acid (2.4 mmol) was added. K_2CO_3 (6 mmol) was dissolved in 5 mL water and added in. The reaction mixture was stirred at 70 °C for 12h. The catalyst recovery was performed with magnetic separation. Then, the products were extracted for three times by chloroform (3×5 mL). The organic phases were dried with anhydric $MgSO_4$. Hexadecane was added into the mixture as the internal standard for GC analysis.

General Procedures for Suzuki Cross-Coupling Reactions Catalyzed by Catalyst 2

50 mg of catalyst 2 and K_2CO_3 (3mmol) were dispersed in DMF (10 mL) with the help of sonication. Then, aryl halide reagent (1 mmol) and arylboronic acid (2 mmol) were added in. After the mixture was subjected to sonication for 15 min, it was stirred at 100 °C for 12h. The catalyst was recovered by magnetic separation. After the solvent was removed, the products were dispersed in 15 mL chloroform and analyzed by GC as the same procedure above.

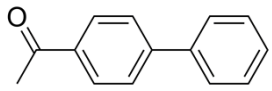
Procedures of Reusability Test of Catalyst 1

100mg of catalyst 1 (1 mol%) was ultrasonic dispersed in 15ml ethanol. Then, 4'-Bromoacetophenone (2 mmol) and phenylboronic acid (2.4 mmol) was added. After K_2CO_3 (6 mmol) was dissolved in 5 mL disitilled water, it was added into the mixture. After 12 h of the reaction at 70 °C, magnetic separation was performed to recover the catalyst while hot. The product was extracted by chloroform (3×5 mL). Then, the organic phases were dried over $MgSO_4$. Hexadecane was added into the mixture as an internal standard for the analysis by GC. The collected catalyst was dried and repeated used.

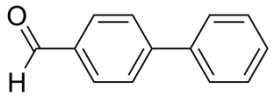
Procedures of leaking Pd analyzing

After the magnetic separation of these catalysts, the product was heated 400 °C for 3 h in a muffle. Then 1 ml HCl (37 wt%) and 0.5 ml HNO_3 65 wt%) were added into the ash to dissolve the Pd. After the reaction for 24 h on circumferential shake table, some distill water was added and the supernatant was analyzed by ICP-AES.

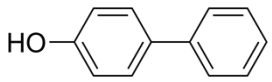
1H NMR data of some products:


4-Acetylbiphenyl

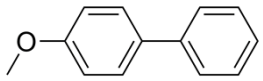
^{1}H NMR (400 MHz, $CDCl_3$): δ= 2.61 (s, 3H), 7.39 (m, 1H), 7.44 (m, 2H), 7.57 (d, 2H), 7.67 (d, 2H), 8.03 (d, 2H).


4-Biphenylcarboxaldehyde

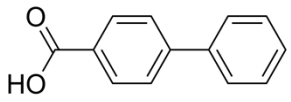
^{1}H NMR (400 MHz, $CDCl_3$): δ=7.48 (m, 3H), 7.74 (d, 2H), 7.91 (d, 2H), 8.00 (d, 2H), 10.04 (s, 1H).


4-Hydroxybiphenyl

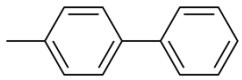
^{1}H NMR (400 MHz, $CDCl_3$): δ= 4.82 (s, 1H), 6.89 (d, 2H), 7.29 (q, 1H), 7.42 (m, 4H), 7.55 (d, 2H).


4-Methoxybiphenyl

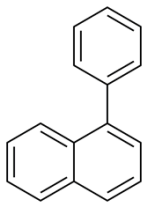
^{1}H NMR (400 MHz, $CDCl_3$): δ=3.84(s, 3H), 6.97(d, 2H), 7.24(t, 1H), 7.40(t, 2H), 7.52(d, 4H)


4-Biphenylcarboxylic Acid

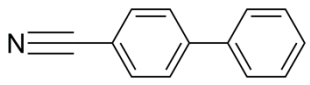
^{1}H NMR (400 MHz, DMSO-d): δ=7.42 (q, 1H), 7.50 (q, 2H), 7.72 (d, 2H), 7.81 (d, 2H), 8.03 (d, 1H), 13 (d, 1H).


4-Methylbiphenyl

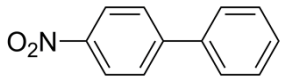
^{1}H NMR (400 MHz , $CDCl_3$): δ=2.41 (s, 3H), 7.25 (d, 2H), 7.33 (q, 1H), 7.46 (q, 2H), 7.54 (d, 2H), 7.64 (d, 2H).


1-Phenylnaphthalene

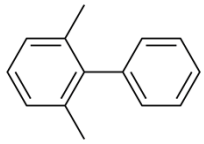
^{1}H NMR (400MHz, $CDCl_3$) δ=7.38(t, 3H), 7.44(m, 6H), 7.84(d, 1H), 7.87(d, 1H), 7.89(t, 2H)


4-Cyanobiphenyl

^{1}H NMR (400 MHz, CDCl3): δ=7.51 (m, 3H), 7.75 (d, 2H), 7.91 (m, 4H).

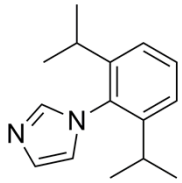

4-Nitrobiphenyl

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.53 (m, 3H), 7.79 (d, 2H), 7.96 (d, 2H), 8.30 (d, 2H).



2,6-Dimethyl-1,1'-biphenyl

^{1}H NMR (400 MHz, $CDCl_3$): δ=2.03(s, 6H), 7.14(q, 4H), 7.10(m, 5H), 7.31(m, 1H), 7.40(m, 2H).



1-(2,6-diisopropylphenyl)-1H-imidazole

^{1}H NMR (400MHz, $CDCl_3$): δ=1.14(d, 12H), 2.40(m, 2H), 6.94(s, 1H), 7.26(d, 3H), 7.43(dd, 1H), 7.47(dd, 1H).

[1] W. Zheng, F. Gao, H. Gu, *J. Magn. Magn. Mater.* 2005, **288**, 403-410.

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[4] J. A. Johnson, J. J. Makis, K. A. Marvin, S. E. Rodenbusch, K. J. Stevenson, *J. Phys. Chem. C.* 2013, **117**, 22644−22651.