An Efficient and Recyclable Magnetic-Nanoparticle-Supported Palladium Catalyst for the Suzuki Coupling Reactions of Organoboronic Acids with Alkynyl Bromides

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Abstract: A highly active, air- and moisture-stable and easily recoverable magnetic-nanoparticle-supported palladium catalyst has been developed for the Suzuki cross-coupling reaction of organoboron derivatives with alkynyl bromides. In the presence of palladium catalyst (0.5 mol%), organoboron derivatives including aromatic and aliphatic boronic acids, potassium aryltrifluoroborates, and sodium tetraphenylborate reacted smoothly with 1-bromo-2-substituted acetylenes to generate the corresponding cross-coupling products in good to excellent yields in ethanol. In addition, it is possible to recover and reuse the supported palladium catalyst at least 16 times without significant loss of its catalytic activity.

Key words: palladium catalyst, Suzuki coupling reaction, organoboronic acids, alkynyl bromides, magnetic nanoparticles

The palladium-catalyzed carbon–carbon cross-coupling of organometallic nucleophiles with organoelectrophiles is an important synthetic reaction in modern organic synthesis.[1] However, most organometallic compounds are sensitive to air and moisture, or toxic, and often will not tolerate functional groups, which may be important in complex syntheses. Constituting one of the few organometallic reagents that tolerate a wide range of functional groups, boronic acids are conveniently available and generally environmentally benign. In addition, they are inert to air and moisture, and resistant to heat.

The Suzuki coupling reaction of organoboronic acids with C_{sp2}–X bonds has become a mainstay of modern synthetic organic chemistry for the preparation of biaryl compounds.[2] It has also been applied to the synthesis of natural products, agrochemicals, pharmaceuticals, polymers, and other materials.[3] Since its invention, the development of efficient catalytic systems for the Suzuki coupling reaction has attracted much attention. Classic Suzuki coupling reactions generally employ palladium catalysts along with phosphine ligands in the presence of a base.[2e,4] However, the expensive palladium complexes tend to be difficult to manipulate and recover.

In the past decades, significant progress in this area has been achieved with a variety of homogeneous palladium catalysts.[2e,5] However, homogeneous catalysis suffers from the problematic separation of the expensive catalyst. Furthermore, homogeneous catalysis might result in heavy metal contamination of the desired isolated product. These problems are of particular environmental and economic concern in large-scale syntheses. Heterogeneous catalysts, especially expensive and/or toxic heavy metal complexes could be an attractive solution to this problem.[2c,6] There has been considerable interest in the development of supported catalytic systems that can be efficiently recycled and reused whilst keeping the inherent catalytic activity. Various inorganic and organic supports have been explored, such as silica,[7] ionic liquids,[8] and polymers.[9]

Magnetic nanoparticles have been studied widely for various biological and medical applications,[10] and most recently, they have emerged as smart and promising supports with great industrial potential for immobilization. This is because magnetic-nanoparticle-supported catalysts can be easily separated from the reaction medium by an external permanent magnet, which achieves simple separation of the catalysts without filtration.[11]

As one of the substrates for the Suzuki reactions, organoelectrophiles, which contain C_{sp2}–X bonds (such as aryl and alkenyl halides), C_{sp2}–OTf and C_{sp3}–OTf (aryl and alkyl triflates) bonds, and even C_{sp3}–X bonds (alkyl halides) were employed to couple with organoboron derivatives in the Suzuki reactions.[12] In contrast, organic halides possessing C_{sp}–X bonds are rarely used as organoelectrophiles due to the formation of a mixture of cross-coupling and homo-coupling products.[13]

In continuation of our efforts to develop economical and eco-friendly synthetic pathways for organic transformations from the viewpoint of green chemistry, we wish to report here the synthesis of a simple, highly active, air- and moisture-stable and magnetically recoverable palladium-catalyzed Suzuki cross-coupling reaction of organoboron compounds, such as aryl- and alkylboronic acids, potassium aryltrifluoroborates and sodium tetraphenylborate with alkynyl bromides with C_{sp}–Br bonds to generate the corresponding cross-coupling products in good to ex-

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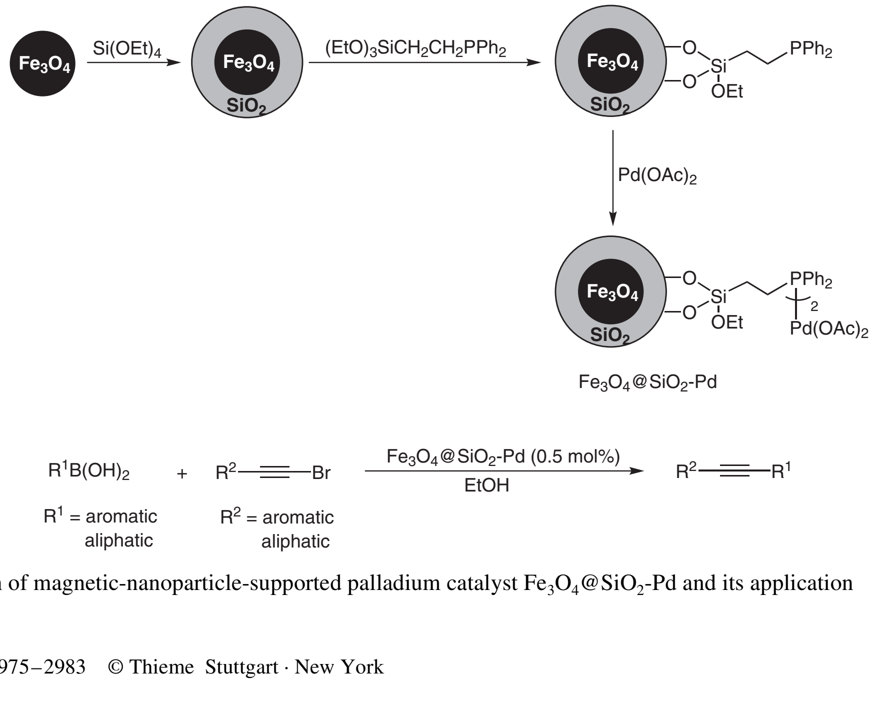
cellent yields in ethanol (Scheme 1). Moreover, easy catalyst recovery and excellent recycling efficiency of the catalyst make it an ideal system for the reaction, and it is possible to recover and reuse the grafted catalysts at least 16 times without significant loss of its catalytic activity.

The magnetic-nanoparticle-supported palladium catalyst $Fe_3O_4@SiO_2$-Pd was prepared according to the synthetic route listed in Scheme 1. The silica-coated Fe_3O_4 [$Fe_3O_4@SiO_2$] was prepared following the literature procedures.[11b,c,14] Commercially available Fe_3O_4 nanoparticles with average diameter of 10 nm after sonication, were coated with a thin layer of silica using a sol-gel method to generate silica-coated Fe_3O_4 [$Fe_3O_4@SiO_2$]. TEM images of the $Fe_3O_4@SiO_2$ show the core-shell structure of the particles, and the silica coating, which has a uniform thickness of ca. 10 nm. Next, the phosphine ligand can be anchored easily onto the surface of $Fe_3O_4@SiO_2$ using 2-(diphenylphosphino)ethyltriethoxysilane in anhydrous toluene at 120 °C for 24 hours, with a loading of 0.18 mmol of phosphine per gram, which was quantified via CHN microanalyses based on the carbon content determination. Subsequently, the supported palladium catalyst, $Fe_3O_4@SiO_2$-Pd was obtained by dissolving palladium(II) acetate in tetrahydrofuran and treating it with the above phosphine-functionalized $Fe_3O_4@SiO_2$. The generated $Fe_3O_4@SiO_2$-Pd was found to have a loading of 0.049 mmol of palladium per gram determined via inductively coupled plasma (ICP) analysis. XRD measurements of $Fe_3O_4@SiO_2$-Pd exhibit diffraction peaks corresponding to the typical spinel maghemite structure and the diffraction peak of the layered amorphous silica was not obvious, and no peaks characteristic for palladium(0) nanoparticles were observed, which proves the excellent dispersion of the palladium sites on the magnetic nanoparticles. The energy dispersive X-ray (EDX) analysis showed the presence of palladium with a loading of 0.056 mmol/g in $Fe_3O_4@SiO_2$-Pd (see Supporting Information).

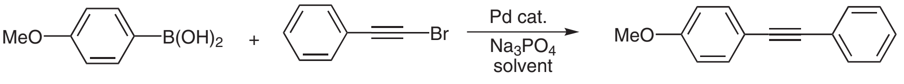
For optimization of the Suzuki coupling reaction conditions, the reaction of 4-methoxyphenylboronic acid (**1a**) with 1-bromo-2-phenylacetylene (**2a**) was chosen as a model reaction for the exploration in the presence of the magnetic-nanoparticle-supported palladium catalyst $Fe_3O_4@SiO_2$-Pd. The results are summarized in Table 1. Initially, our investigation was focused on the effect of solvent on the model reaction. As shown in Table 1, among the solvents tested, ethanol was the most suitable reaction media for the model reaction carried out in the presence of $Fe_3O_4@SiO_2$-Pd (0.5 mmol%) and Na_3PO_4 (2.0 equiv) at room temperature for 12 hours (Table 1). Methanol, isopropanol, acetonitrile, *N*,*N*-dimethylformamide, 1,4-dioxane, tetrahydrofuran, dimethyl sulfoxide, toluene, and hexane were inferior and generated the desired cross-coupling product **3a** in 90, 78, 66, 54, 62, 71, 58, 30, and 17% yield, respectively (Table 1, entries 2–10). Unfortunately, no cross-coupling product was isolated when the reaction was carried out in water (Table 1, entry 11). For the model reaction using nanoparticle-supported palladium catalyst derived from $PdCl_2$, $Pd(dba)_3$, or $Pd(OTFA)_2$ instead of $Pd(OAc)_2$, the yields of **3a** obtained were comparable with that of the yield of **3a** by using nanoparticle-supported palladium catalyst derived from $Pd(OAc)_2$ (Table 1, entries 12–14 vs 1). The effects of other palladium sources, such as $PdCl_2$, $Pd(OAc)_2$, $Pd(PPh_3)_2Cl_2$, and $Pd(PPh_3)_4$ on the model reaction were also examined under the present reaction conditions and the results are also summarized in Table 1. The coupling reaction could be catalyzed by $PdCl_2$, $Pd(OAc)_2$, $Pd(PPh_3)_2Cl_2$, or $Pd(PPh_3)_4$, but their catalytic activity is inferior to that of $Fe_3O_4@SiO_2$-Pd (Table 1, entries 15–18 vs 1). The amount of $Fe_3O_4@SiO_2$-Pd catalyst was also screened and the experimental data indicated that the reaction was complete when 0.5 mol% loading of palladium was used at room temperature for 12 hours.

Next, the effect of base on the model reaction was examined at room temperature by using 0.5 mol% of



Scheme 1 Preparation of magnetic-nanoparticle-supported palladium catalyst $Fe_3O_4@SiO_2$-Pd and its application

Table 1 Effect of Solvents and Palladium Catalysts on the Suzuki Reaction[a]



1a **2a** **3a**

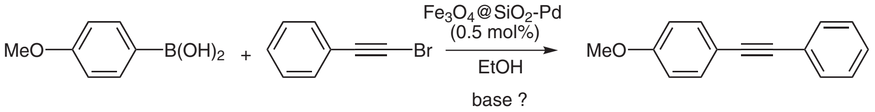
Entry	Catalyst	Solvent	Yield (%)[b]
1	Fe_3O_4@SiO_2-Pd	EtOH	96
2	Fe_3O_4@SiO_2-Pd	MeOH	90
3	Fe_3O_4@SiO_2-Pd	*i*-PrOH	78
4	Fe_3O_4@SiO_2-Pd	MeCN	66
5	Fe_3O_4@SiO_2-Pd	DMF	54
6	Fe_3O_4@SiO_2-Pd	1,4-dioxane	62
7	Fe_3O_4@SiO_2-Pd	THF	71
8	Fe_3O_4@SiO_2-Pd	DMSO	58
9	Fe_3O_4@SiO_2-Pd	toluene	30
10	Fe_3O_4@SiO_2-Pd	hexane	17
11	Fe_3O_4@SiO_2-Pd	H_2O	0
12	Fe_3O_4@SiO_2-Pd[c]	EtOH	95
13	Fe_3O_4@SiO_2-Pd[d]	EtOH	93
14	Fe_3O_4@SiO_2-Pd[e]	EtOH	97
15	$PdCl_2$	EtOH	28
16	$Pd(OAc)_2$	EtOH	36
17	$Pd(PPh_3)_2Cl_2$	EtOH	40
18	$Pd(PPh_3)_4$	EtOH	51

[a] Reaction conditions: 4-methoxyphenylboronic acid (1 mmol), 1-bromo-2-phenylacetylene (1 mmol), Pd catalyst (0.005 mmol), and Na_3PO_4 (2 mmol) in solvent (2 mL) at r.t. for 12 h.
[b] Isolated yields.
[c] Fe_3O_4@SiO_2-Pd derived from $PdCl_2$.
[d] Fe_3O_4@SiO_2-Pd derived from $Pd(dba)_3$.
[e] Fe_3O_4@SiO_2-Pd derived from $Pd(OTFA)_2$.

Fe_3O_4@SiO_2-Pd as catalyst in ethanol. Sodium phosphate was found to be the most effective base. Other bases, such as sodium carbonate, potassium phosphate, potassium carbonate, cesium carbonate, triethylamine, and sodium acetate were substantially less effective (Table 2, entries 1–7); and *tert*-butoxide and sodium hydroxide were no longer the effective bases in the model reaction due to their strong basicity. It should be noted that the cross-coupling of the model substrates could not occur in the absence of a suitable base.

With the optimized reaction conditions [0.50 mol% loading of Fe_3O_4@SiO_2-Pd, Na_3PO_4 as base, EtOH as solvent, r.t.], we examined the scope of the supported-palladium catalyzed Suzuki coupling reactions of arylboronic acids and alkynyl bromides on a series of different substrates. The results are listed in Table 3. At the beginning of the search for the organoboron substrate scope, 1-bromo-2-phenylacetylene (**2a**) was used as one of the model substrate and a variety of organoboronic acids were examined for the coupling reactions (Table 3, entries 1–13). As can be seen from Table 3, the reactivity of both aromatic and alkenylboronic acids was observed, in which aromatic boronic acids were much more reactive than the alkenyl one (Table 3, entries 1–12 vs 13). Aromatic boronic acids with electron-donating groups (such as Me, MeO, and *t*-Bu) or electron-withdrawing groups (such as F, Cl, Br, and I) on the aromatic rings, as well as 1-naphthaleneboronic acid, reacted with 1-bromo-2-phenylacetylene (**2a**) completely and generated the corresponding cross-coupling products in excellent yields. In most cases, almost quantitative yields were obtained (Table 3, entries 1–12). It is important to note that the location of the substituents on the aromatic rings in arylboronic acids had little effect on the reaction, or even on the *ortho*-position (Table 3, entries 9–

Table 2 Effect of Bases on the Suzuki Reaction[a]



1a **2a** **3a**

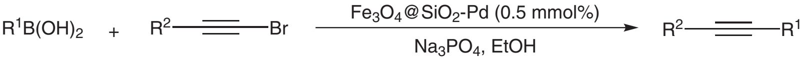
Entry	Base	Yield (%)[b]
1	Na_3PO_4	96
2	Na_2CO_3	93
3	K_3PO_4	90
4	K_2CO_3	87
5	Cs_2CO_3	81
6	Et_3N	62
7	NaOAc	37

[a] Reaction conditions: 4-methoxyphenylboronic acid (1 mmol), 1-bromo-2-phenylacetylene (1 mmol), Fe_3O_4@SiO_2-Pd catalyst (102 mg, containing 0.005 mmol of Pd), and base (2 mmol) in EtOH (2 mL) at r.t. for 12 h.

[b] Isolated yields.

11). It is noteworthy that the reactivity of C_{sp}–Br in 1-bromo-2-phenylacetylene is more than that of C_{sp2}–Br in 4-bromophenylboronic acid, and that of C_{sp2}–I in 4-iodophenylboronic acid (Table 3, entries 7 and 8). Fortunately, the cross-coupling reaction involving alkenylboronic acid also gave the desired product in 77% isolated yield (Table 3, entry 13). As an alternative to organoboronic acids and esters, organotrifluoroborate salts have emerged as a new class of air-stable boron derivatives, facile to prepare, easy to handle, and feasible to utilize in a number of organic transformations.[15] When the reaction of potassium aryltrifluoroborates with **2a** was performed under the present reaction conditions, as expected, excellent yield of the desired product was obtained (Table 3, entry 14). In addition, as a stable and commercially available borate source, sodium tetraphenylborate[16] was also coupled with **2a** completely to generate the corresponding product in 93% yield (Table 3, entry 15).

Table 3 Fe_3O_4@SiO_2-Pd-Catalyzed Suzuki Coupling Reactions of Organoboronic Acids with Alkynyl Bromides[a]



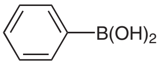
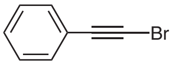
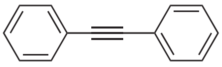
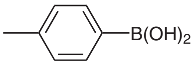
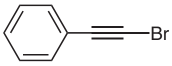
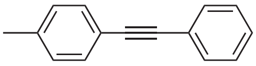
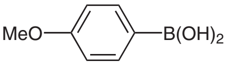
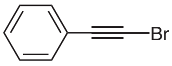
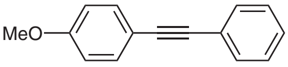
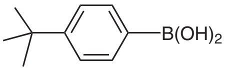
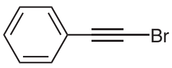
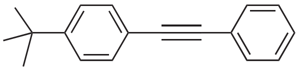
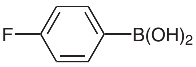
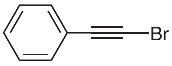
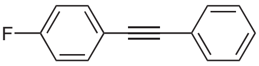
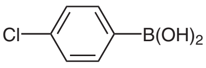
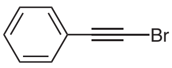
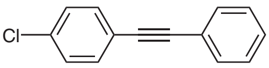
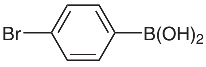
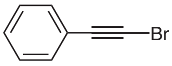
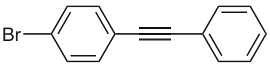
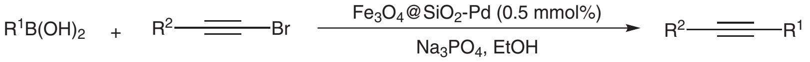
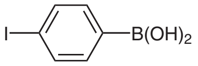
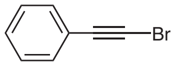
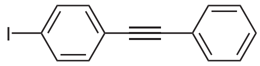
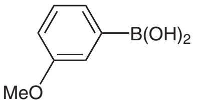
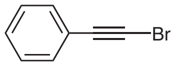
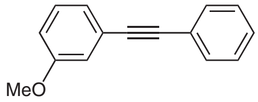
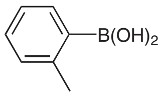
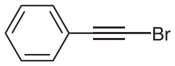
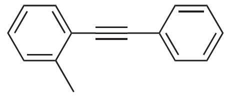
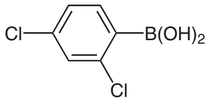
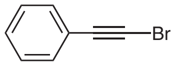
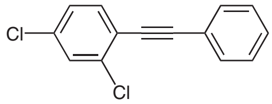
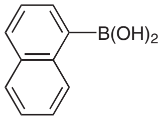
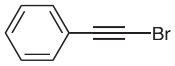
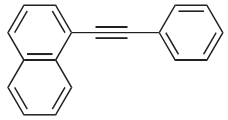
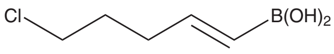
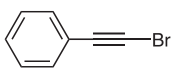
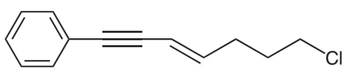
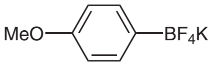
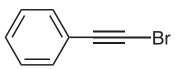
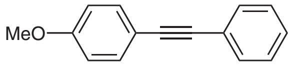
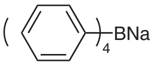
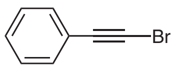
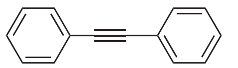
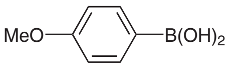
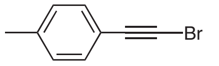
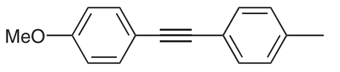
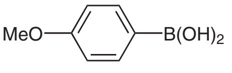
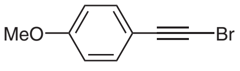
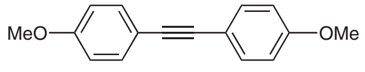
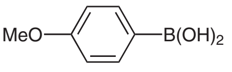
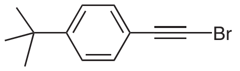
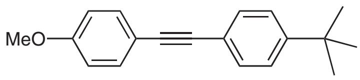
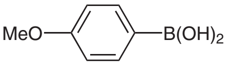
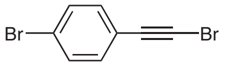
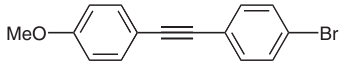
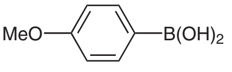
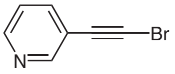
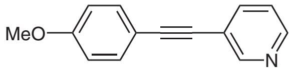
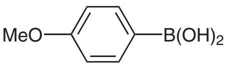
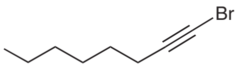
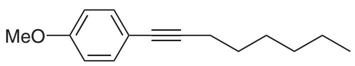
Entry	Arylboronic acid	Alkynyl bromide	Product	Yield (%)[b]
1				96
2				97
3				96
4				93
5				89
6				91
7				90

Table 3 $Fe_3O_4@SiO_2$-Pd-Catalyzed Suzuki Coupling Reactions of Organoboronic Acids with Alkynyl Bromides[a] (continued)



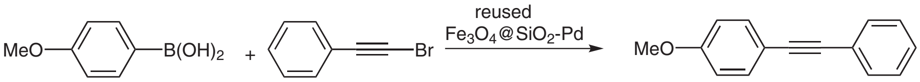
Entry	Arylboronic acid	Alkynyl bromide	Product	Yield (%)[b]
8				90
9				94
10				93
11				90
12				96
13				77
14				94
15				93
16				95
17				98
18				93
19				93
20				92
21				73

[a] Reaction conditions: alkynyl bromide (1 mmol), organoboron compound (1 mmol), $Fe_3O_4@SiO_2$-Pd catalyst (102 mg, containing 0.005 mmol of Pd), and Na_3PO_4 (2 mmol) in EtOH (2 mL) at r.t. for 12 h.

[b] Isolated yields.

Next, a series of 1-bromo-2-substituted acetylenes were surveyed for the scope of C_{sp}–Br substrates and the results in Table 3 indicate that 2-aryl- and 2-alkylethynyl bromides, including 1-bromo-2-(4-methylphenyl)acetylene, 1-bromo-2-(4-methoxyphenyl)acetylene, 1-bromo-2-(*tert*-butylphenyl)acetylene, 1-bromo-2-(4-bromophenyl)acetylene, 1-bromo-2-(*m*-pyridyl)acetylene, and 1-bromo-2-hexylacetylene displayed high reactivity to 4-methoxyphenylboronic acid under the present reaction conditions and good to excellent yields of desired cross-coupling products were obtained (Table 3, entries 16–21). It is evident that the reactivity of 1-bromo-2-arylacetylenes was more than that of 1-bromo-2-alkylacetylenes (Table 3, entries 3, and 16–20 vs 21). For 1-bromo-2-arylacetylenes, the presence of electron-donating groups (MeO, Me, and *t*-Bu), electron-withdrawing groups (Br), and their location on the benzene rings also had little effect on the reactions (Table 3, entries 16–19).

Table 4 Reuse of Fe_3O_4@SiO_2-Pd Catalyst for the Model Suzuki Reaction[a]



Cycle	Yield (%)[b]	Cycle	Yield (%)[b]
1	96	9	94
2	96	10	95
3	96	11	95
4	95	12	94
5	96	13	93
6	95	14	93
7	96	15	92
8	95	16	92

[a] Reaction conditions: 4-methoxyphenylboronic acid (1 mmol), 1-bromo-2-phenylacetylene (1 mmol), reused Fe_3O_4@SiO_2-Pd catalyst (102 mg, containing 0.005 mmol of Pd), and Na_3PO_4 (2 mmol) in EtOH (2 mL) at r.t. for 12 h.

[b] Isolated yields.

The magnetic-nanoparticle-supported palladium catalyst Fe_3O_4@SiO_2-Pd was tested for recoverability and reusability. After the reaction, Fe_3O_4@SiO_2-Pd was recovered by magnetic separation, washed with ethanol (2 mL), water (2 mL), ethanol (2 mL), and diethyl ether (2 mL), respectively, dried in air and reused for the next reaction. For the model reactions of Suzuki coupling, results in Table 4 indicate that Fe_3O_4@SiO_2-Pd catalyst can be recovered and reused for 16 consecutive trials without significant loss of its activity. In addition, palladium leaching in the supported catalyst was also determined. ICP analysis of the ethanol solution (3 mL) of the Suzuki reaction showed that the palladium content was less than 0.20 ppm. It was found that more than 99.64 wt% of palladium was recovered after the Suzuki reaction. To investigate the heterogeneity of the catalyst systems, filtration test was performed. However, no additional amount of the desired product was obtained for the model reaction by adding substrates to the filtrate obtained from the separation of the immobilized palladium catalyst after the reaction. The heterogeneous character of the catalytically active species is confirmed in this reaction.

In summary, an efficient and recyclable magnetic-nanoparticle-supported palladium catalyst for the Suzuki coupling reactions of organoboron derivatives with alkynyl bromides to form 1,2-disubstituted acetylenes have been developed. In the presence of Fe_3O_4@SiO_2-Pd (0.5 mol%), organoboron compounds, including aryl and alkenyl boronic acids, potassium aryltrifluoroborates, and sodium tetraphenylborate reacted smoothly with 1-bromo-2-substituted acetylenes to generate the corresponding cross-coupling products in good to excellent yields. This methodology provides an efficient, alternative and environmentally friendly process for the synthesis of symmetric and nonsymmetric 1,2-disubstituted acetylenes through Suzuki coupling reaction of organoboron derivatives with ethynyl bromides by using a recyclable magnetic-nanoparticle-supported palladium catalyst. The supported catalyst Fe_3O_4@SiO_2-Pd could be reused for 16 consecutive cycles without significant loss of catalytic activity through a simple magnetic separation. Further investigation on the application of magnetic-nanoparticle-supported catalysts in organic synthesis is still underway in our laboratory.

All ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance FT-NMR spectrometer (400 MHz or 100 MHz, respectively). Chemical shifts are given as δ values with reference to TMS as internal standard. The C, H, and N analyses were performed with a Vario El III elementar apparatus. The Pd content was determined by a Jarrell-Ash 1100 ICP analysis. Transmission electron micrograph (TEM) images were obtained on a Jeol-2010 transmission electron microscope. X-ray diffraction (XRD) measurements were carried out using a Bruker D8 Advance X-ray powder diffractmeter. IR spectra were recorded on a Nicolet 6700 FT-IR spectrophotometer using KBr pellets. Products were purified by flash chromatography on 200–300 mesh silica gel. All the reactions were carried out under an air atmosphere, and the chemicals were purchased from commercial suppliers and were used without purification prior to use.

Silica-Coated Magnetic Nanoparticles Fe_3O_4@SiO_2

Fe_3O_4 (0.50 g, with an average diameter of 20 nm, purchased from Aldrich) was diluted with deionized H_2O (7 mL) and propan-2-ol (30 mL), and the mixture was sonicated for approximately 30 min (the average diameter of Fe_3O_4 was about 10 nm according to the TEM image). To this well dispersed magnetic nanoparticle solution, $NH_3{\cdot}H_2O$ (2 mL) followed $(EtO)_4Si$ (2 g) slowly added and stirred for further 4 h at r.t. The material was washed repeatedly with H_2O until the solution was neutral, then the solid material was magnetically separated, washed with EtOH (3 mL) and Et_2O (3 mL), respectively, and dried under vacuum.

IR (KBr): 3396 (O–H), 1080 cm^{-1} (Si–O).

Phosphine-Functionalized Fe_3O_4@SiO_2

2-(Diphenylphosphino)ethyltriethoxysilane (0.38 g) dissolved in anhyd toluene (5 mL) was added to a suspension of Fe_3O_4@SiO_2

(0.50 g) in anhyd toluene (30 mL). The mixture was then shaken at 100 °C under a N_2 atmosphere for 24 h. The solid material, Fe_3O_4@SiO_2-P, was magnetically separated, washed repeatedly with toluene (3 × 2 mL) and CH_2Cl_2 (3 × 2 mL) to remove unanchored species, and dried under vacuum. The loading of phosphine in phosphine-functionalized Fe_3O_4@SiO_2 was quantified via CHN microanalyses and found to be 0.18 mmol·g^{-1} based on the carbon content determination.

IR (KBr): 3396 (O–H), 2923, 2862 (C–H), 1517, 1469 (C=C_{arom}), 1080 cm^{-1} (Si–O).

Fe_3O_4@SiO_2-Pd

To a sealable reaction tube, $Pd(OAc)_2$ (11.2 mg, 0.05 mmol) and THF (5 mL) were added. The solution was shaking at r.t. under N_2 atmosphere for 10 min, and then 1 g of the above phosphine-functionalized magnetic nanoparticles Fe_3O_4@SiO_2-P was added. The mixture was shaken at r.t. for 4 h, then the solid catalyst was magnetically separated, the solid washed thoroughly with THF (4 × 2.5 mL), and dried under vacuum at 50 °C for 3 h. The Fe_3O_4@SiO_2-Pd catalyst was obtained with a loading of Pd 0.049 mmol·g^{-1} determined via inductively-coupled plasma (ICP) analysis.

IR (KBr): 3396 (O–H), 2978, 2895 (C–H), 1649, 1520 (C=C_{arom}), 1080 cm^{-1} (Si–O).

Catalytic Suzuki Reactions; General Procedure

A mixture of alkynyl bromide (1 mmol), organoboron compound (1 mmol), Na_3PO_4 (2 mmol), Fe_3O_4@SiO_2-Pd catalyst (102 mg, containing 0.005 mmol of Pd), and EtOH (2 mL) was stirred at r.t. for 4 h. The reaction solution was vacuum-filtered and washed with EtOH (3 mL) and Et_2O (3 mL), concentrated, and the residue was purified by flash chromatography on silica gel (eluent: PE–EtOAc, 9:1) to obtain the desired product (Table 3).

Diphenylacetylene[17]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.52 (m, 4 H), 7.33–7.31 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.58, 128.31, 128.22, 123.24, 89.36.

Phenyl-*p*-tolyacetylene[17]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.51 (m, 2 H), 7.42 (d, *J* = 8.0 Hz, 2 H), 7.34–7.32 (m, 3 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 2.35 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.35, 131.52, 131.47, 129.09, 128.28, 128.04, 123.45, 120.16, 89.54, 88.70, 21.48.

(4-Methoxyphenyl)phenylacetylene[17]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.52 (m, 2 H), 7.37–7.32 (m, 3 H), 7.25–7.23 (m, 1 H), 7.14–7.11 (m, 1 H), 7.06 (t, *J* = 1.2 Hz, 1 H), 6.95–6.90 (m, 1 H), 3.82 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.32, 131.61, 129.39, 128.33, 124.16, 123.16, 116.30, 114.93, 89.28, 89.17, 55.27.

(4-*tert*-Butylphenyl)phenylacetylene[18]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.51 (m, 2 H), 7.47 (d, *J* = 8.0 Hz, 2 H), 7.37–7.30 (m, 5 H), 1.32 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.50, 131.56, 131.32, 128.28, 128.04, 125.33, 123.51, 120.23, 89.52, 88.71, 34.77, 31.17.

(4-Fluorophenyl)phenylacetylene[19]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.48 (m, 4 H), 7.35–7.32 (m, 3 H), 7.05–7.00 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.45 (d, *J* = 247.9 Hz), 133.44 (d, *J* = 8.3 Hz), 132.47, 131.52, 128.32, 123.05, 119.31 (d, *J* = 3.6 Hz), 115.60 (d, *J* = 21.9 Hz), 89.02, 88.28.

(4-Chlorophenyl)phenylacetylene[20]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.51 (m, 2 H), 7.50–7.44 (m, 2 H), 7.37–7.30 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.23, 132.79, 131.58, 128.67, 128.47, 128.38, 122.90, 121.76, 90.29, 88.22.

(4-Bromophenyl)phenylacetylene[20]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.50 (m, 2 H), 7.48–7.45 (m, 5 H), 7.39–7.36 (m, 2 H), 7.35–7.31 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.99, 131.58, 131.56, 128.47, 128.37, 122.89, 122.44, 122.22, 90.49, 88.29.

(4-Iodophenyl)phenylacetylene[21]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 8.2 Hz, 2 H), 7.52–7.50 (m, 2 H), 7.35–7.32 (m, 3 H), 7.23 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.48, 133.05, 131.57, 128.48, 128.36, 122.87, 122.76, 94.09, 90.77, 88.43.

(3-Methoxyphenyl)phenylacetylene[17]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.54 (m, 1 H), 7.53–7.52 (m, 1 H), 7.37–7.34 (m, 4 H), 7.14–7.12 (m, 1 H), 7.07–7.06 (m, 1 H), 6.91–6.88 (m, 1 H), 3.83 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.34, 132.49, 131.62, 129.39, 128.33, 124.25, 124.17, 123.17, 116.32, 114.94, 89.28, 89.17, 55.29.

Phenyl-*o*-tolyacetylene[18]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.48 (m, 3 H), 7.34–7.29 (m, 3 H), 7.21–7.20 (m, 2 H), 7.16–7.13 (m, 1 H), 2.50 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.11, 132.44, 131.79, 131.46, 129.42, 128.30, 128.11, 125.54, 123.51, 122.98, 93.33, 88.33, 20.69.

(2,4-Dichlorophenyl)phenylacetylene[17]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59–7.56 (m, 2 H), 7.48 (d, *J* = 8.4 Hz, 1 H), 7.46 (d, *J* = 2.0 Hz, 1 H), 7.39–7.36 (m, 3 H), 7.23 (dd, *J* = 2.0, 8.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.63, 134.46, 133.71, 131.70, 129.28, 128.82, 128.39, 126.95, 122.57, 121.83, 95.44, 85.20.

1-(Phenylethynyl)naphthalene[18]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, *J* = 8.4 Hz, 1 H), 7.73 (t, *J* = 9.2 Hz, 2 H), 7.66 (d, *J* = 7.2 Hz, 1 H), 7.56–7.54 (m, 2 H), 7.49 (t, *J* = 8.0 Hz, 1 H), 7.42 (t, *J* = 7.2 Hz, 1 H), 7.34 (t, *J* = 7.2 Hz, 1 H), 7.31–7.25 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.22, 133.16, 131.63, 130.33, 128.73, 128.40, 128.35, 128.28, 126.74, 126.39, 126.18, 125.25, 123.35, 120.84, 94.29, 87.50.

7-Chloro-1-phenylhept-3-en-1-yne[22]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.41 (m, 2 H), 7.33–7.30 (m, 3 H), 6.24–6.16 (m, 1 H), 5.77 (d, *J* = 16.4 Hz, 1 H), 3.57 (t, *J* = 6.8 Hz, 2 H), 2.34 (q, *J* = 3.6, 10.8 Hz, 2 H), 1.95–1.88 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.54, 131.41, 128.27, 128.03, 123.32, 111.07, 88.46, 87.80, 44.10, 31.42, 30.17.

4-Methyl-4′-methoxydiphenylacetylene[23]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 9.2 Hz, 2 H), 7.40 (d, *J* = 8.0 Hz, 2 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 3.82 (s, 3 H), 2.36 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.46, 138.00, 132.95, 131.32, 129.06, 120.48, 115.58, 113.95, 88.63, 88.17, 55.27, 21.47.

Bis(4-methoxyphenyl)acetylene[17]

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.44 (d, *J* = 8.8 Hz, 4 H), 6.85 (d, *J* = 8.8 Hz, 4 H), 3.78 (s, 6 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 159.31, 132.80, 115.63, 113.89, 87.91, 55.18.

1-*tert*-Butyl-4-[(4-methoxyphenyl)ethynyl]benzene[24]

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.47–7.43 (m, 4 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 6.86 (d, *J* = 8.8 Hz, 2 H), 3.79 (s, 3 H), 1.31 (s, 9 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 159.45, 151.12, 132.96, 131.14, 125.27, 120.54, 115.61, 113.93, 88.66, 88.15, 55.22, 34.71, 31.15.

1-Bromo-4-[(4-methoxyphenyl)ethynyl]benzene[25]

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.47–7.45 (m, 4 H), 7.36 (d, *J* = 8.4 Hz, 2 H), 6.88 (d, *J* = 8.4 Hz, 2 H), 3.83 (s, 3 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 159.77, 133.05, 132.83, 131.54, 122.56, 122.03, 114.96, 114.03, 90.53, 87.03, 55.29.

3-[(4-Methoxyphenyl)ethynyl]pyridine[23]

^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.75 (s, 1 H), 8.51 (dd, *J* = 1.6, 4.8 Hz, 1 H), 7.77–7.74 (m, 1 H), 7.47 (d, *J* = 8.4 Hz, 2 H) 7.25–7.21 (m, 1 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 3.80 (s, 3 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 159.88, 151.95, 148.06, 138.04, 133.04, 122.84, 120.65, 114.42, 113.96, 92.65, 84.61, 55.13.

1-(4-Methoxylphenyl)oct-1-yne[17]

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.32 (d, *J* = 8.8 Hz, 2 H), 6.81 (d, *J* = 8.8 Hz, 2 H), 3.80 (s, 3 H), 2.38 (t, *J* = 7.2 Hz, 2 H), 1.61–1.55 (m, 2 H), 1.48–1.41 (m, 2 H), 1.34–1.29 (m, 4 H), 0.90 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 158.95, 132.83, 116.28, 113.78, 88.80, 80.20, 55.23, 31.38, 28.84, 28.61, 22.56, 19.41, 14.05.

Recycling of the Supported Palladium Catalyst

In Suzuki coupling reactions, the possibility of recycling the recovered catalyst was investigated using 1-bromo-2-phenylacetylene and 4-methoxyphenylboronic acid as substrates. After each round, the supported catalyst was magnetic separated, and washed thoroughly with Et$_2$O (3 × 2 mL), then dried, and used directly for the next run.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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