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Immobilization of Pd Catalysts on Mesoporous Silica for Amine- and Copper-Free Sonogashira Coupling Reactions

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Abstract: Immobilization of catalysts on solid supports is a promising approach to combine the advantages of heterogeneous and homogeneous catalysts. $Pd(PPh_3)_2Cl_2$, known as an extremely active homogeneous catalyst for the Sonogashira coupling reaction, has been immobilized on high-surface-area MCF (mesocellular foams)–type mesoporous silica powder modified with 3-aminopropyltriethoxysilane and subsequently with diphenylphosphine. The functionalized MCF-type silica and supported catalysts have been characterized by x-ray photoelectron spectroscopy (XPS), fourier transform infrared spectroscopy (FTIR), elemental analysis, nitrogen sorption porosimetry, and scanning electron microscopy (SEM). Such supported Pd catalysts have proven to be useful recyclable reagents for copper- and amine-free Sonogashira coupling reactions of haloaromatic compounds with terminal alkynes.

Keywords: Mesoporous silica; Pd catalyst immobilization; Sonogashira coupling

INTRODUCTION

The Sonogashira reaction was originally reported in 1975.[1] Over the past few decades, this palladium-catalyzed coupling of terminal acetylenes with aryl and vinyl halides has emerged as one of the most important and widely used carbon–carbon bond-forming reactions in organic

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synthesis.[2] The Sonogashira reaction also provides a powerful method for the preparation of conjugated oligomers and polymers,[3] which show interesting optical[4] and electronic properties.[5] Typical procedures for the Sonogashira reaction utilize palladium as a catalyst, an amine as a base, a phosphine as a ligand for palladium, and Cu(I) as a co-catalyst.[1,6] In addition, Cu(I) mediates homocoupling of terminal alkynes in the presence of oxidative agents or air.[7] To address this issue, a number of modifications such as copper-free or amine- and copper-free systems have been used. Most recently, ligand-, amine- and copper-free Sonogashira reactions in dimethylformamide (DMF) have been reported.[8] Typically, the expensive palladium complex catalyst is used homogeneously, which makes the recovery of the metal tedious.[9] The immobilization of transition-metal catalysts on insoluble supports has received considerable attention in recent years as a method of combining the practical advantages of heterogeneous and homogeneous catalysts.[10] Heterogenization allows for easy handling, retrieving, and recycling of the catalyst, while homogenization offers excellent catalytic activity.[11] Polymer-supported palladium-catalyzed coupling reactions have been reported[12], however applications that involve the Sonogashira reaction have been less widely investigated[13,14] and usually employ a polystyrene-based support medium.[15] Recently, nanosized Pd(0)[9] and silica-based supported Pd-complex catalyst for Sonogashira reaction have been reported.[16] No information on the source of silica or the materials properties of the supported Pd catalyst were given. As to our knowledge, use of mesoporous silica as the catalyst support for Sonogashira reaction has not been reported.

Since the discovery of a new family of mesoporous silicas (MCM-41) in 1992, ordered mesoporous silicas have been widely investigated because of their high surface area, ordered pore structure of varying morphologies, and controllable pore size, compared with conventional microporous silica gels.[17] Such properties make these mesoporous materials very attractive for applications as catalyst supports, sensors, and sorbents.[18] One of the most extensively studied member of the mesoporous materials has been SBA-15, which combines large ordered mesopores (up to 30 nm in diameter) and micro- and relatively thick walls.[19] Adding a sufficient amount of 1,3,5-trimethylbenzene (TMB) induces a phase transformation from SBA-15-type mesoporous silicas to MCFs (mesocellular foams) composed of uniformly sized, large micron-size spherical cells that are interconnected by uniform windows. The pores constitute a 3D channel system, which makes MCF silicas promising candidates for flow-through supports in heterogeneous catalysis. Recently, we have reported the preparation of polymer nano-encapsulated monoliths with improved mechanical properties using templated mesoporous silica.[20,21]

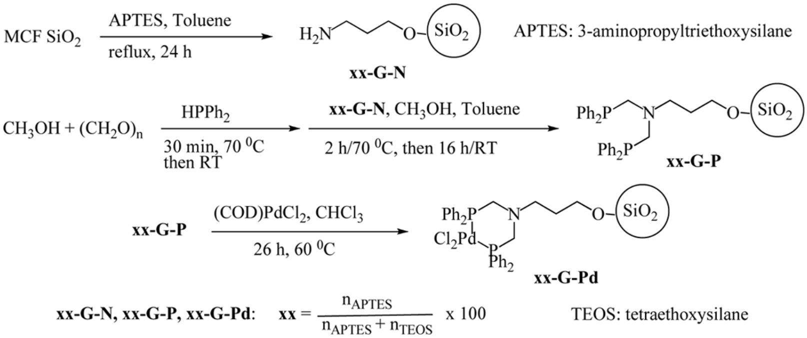
Herein, we report for the first-time immobilization of Pd catalyst on powder MCF-type mesoporous silica, and we demonstrate its use in copper- and amine-free Sonogashira reactions of phenyl acetylene with various aryl iodides and bromides. The corresponding coupling products are obtained in good yields, and the supported catalysts can be recovered and recycled without significant decrease in reactivity.

RESULTS AND DISCUSSION

Preparation of the Supported Catalysts

Scheme 1 summarizes the procedure for the preparation of Pd catalysts supported on MCF silica powders. The latter have been synthesized according to Stucky's method.[22]

Modified MCFs with different amine content (**xx-G-N**) were synthesized by introducing controlled amounts of APTES.[23] "xx" denotes the content of the amine groups present in the amine-modified MCF silica and is defined as $xx = 100 \times n_{APTES}/(n_{APTES} + n_{TEOS})$, where TEOS is tetraethoxysilane. Diphenylphosphine ligands were introduced into the **xx-G-N** surface via the Mannich reaction.[24] Supported Pd catalysts **xx-G-Pd** were prepared via ligand metathesis of (COD)PdCl$_2$ (COD: 1,5-cyclooctadiene) with **xx-G-P**.[15]



Scheme 1. Preparation of supported catalysts based on MCF silica.

Materials Characterization

Characterization of the chemical identity of the materials was conducted by XPS, FTIR, and elemental analysis, while the porous structure of the supported catalyst was probed by nitrogen sorption porosimetry.

XPS

The incorporation of APTES on the MCF silica surface was confirmed by X-ray photoelectron spectroscopy (XPS), as shown in Fig. 1. Pure

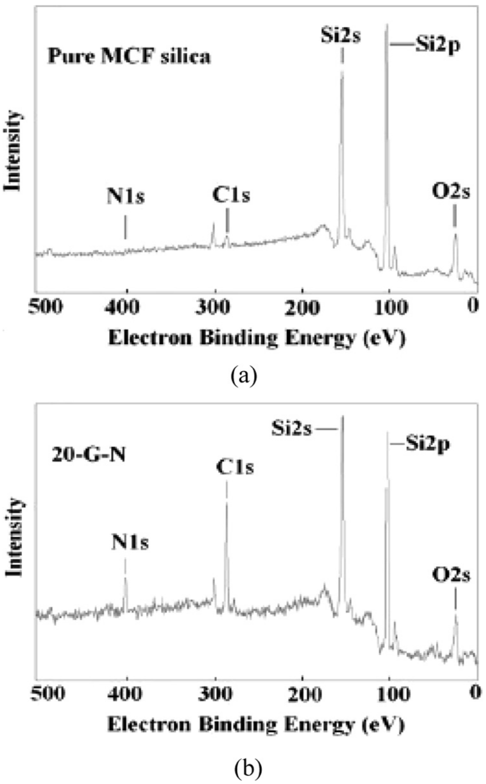


Figure 1. X-ray photoelectron spectra of pure MCF silica (a) and **20-G-N**(b).

MCF silica (Fig. 1a) shows the presence of peaks at binding energies of 285, 151, 103, and 23 eV corresponding to C1s, Si2s, Si2p, and O2s, respectively. A new peak at 398 eV corresponding to N1 s is seen on **20-G-N** (Fig. 1b). Also the higher intensity peak at 285 eV corresponding to C1s (Fig. 1b) supports the conversion of Si-OH to Si-O-$(CH_2)_3$-NH_2 group.

FTIR

The incorporation of the amine group in the MCF silica can be further confirmed by a weak peak in the FTIR spectrum of **20-G-N** at 681 cm^{-1} corresponding to N-H bend (Fig. 2b). It has been reported that pure silica has three strong peaks at about 3747, 3680, and 3545 cm^{-1}.[25,26] However, these peaks are masked by a broad –OH peak

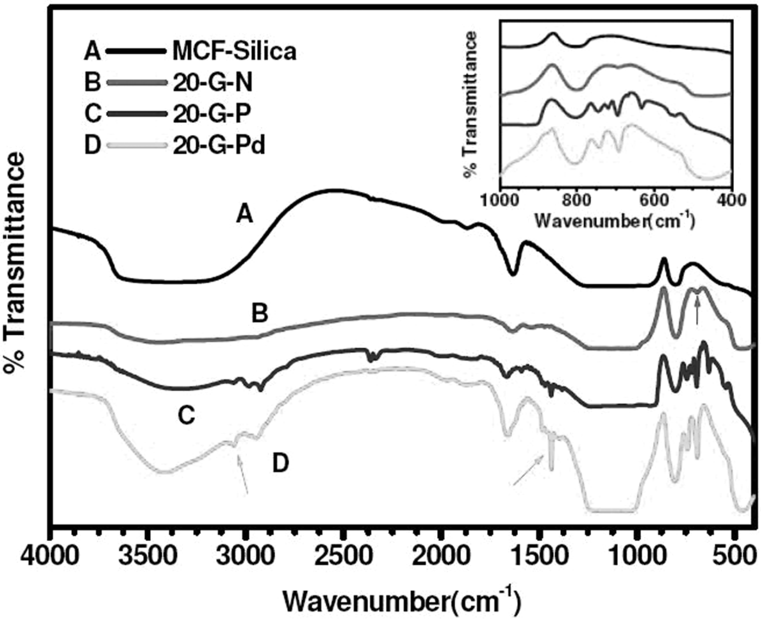
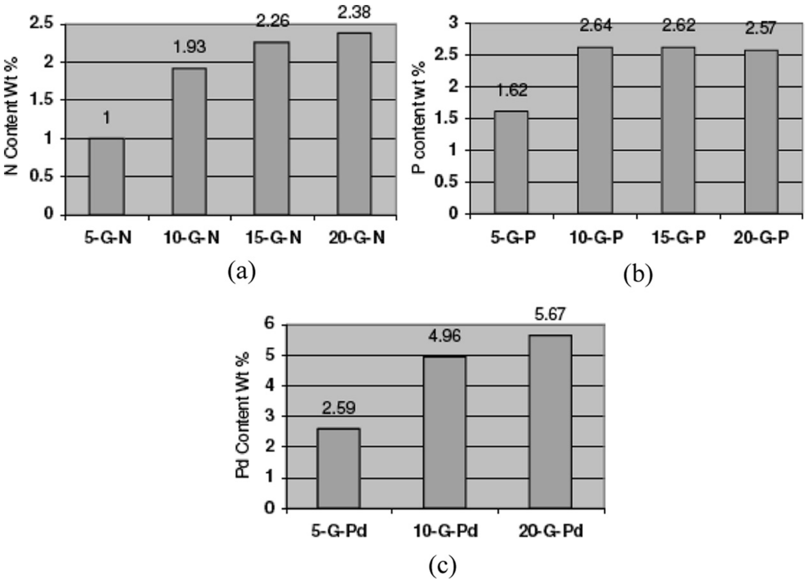


Figure 2. IR spectra of MCF silica (a) and functionalized MCF silicas **20-G-N** (b), **20-G-P** (c), and **20-G-Pd** (d).

due to the hygroscopic nature of this material.[27] Compared with the pure MCF silica, the increase in the width of this broad peak at ~3500 cm^{-1} may be due to the symmetric N-H stretch at 3346 cm^{-1}.[25] The presence of the phenyl groups from the diphenylphosphine ligands in the **20-G-P** and **20-G-Pd** samples can be confirmed from the peaks at 3057 cm^{-1} (aromatic C-H stretch), 1437 cm^{-1} (C=C aromatic ring stretch), and in the 600–760 cm^{-1} region (out-of-plane ring C=C and C-H bends) as seen in Fig. 2c and 2d.

Elemental Analysis

Elemental analysis data for modified MCFs are given graphically in Fig. 3 and reveal the presence of N in **xx-G-N**, P in **xx-G-P**, and Pd in **xx-G-Pd**, showing that the amine functionality, the diphenylphosphine ligand, and Pd metal ions were successfully introduced on the MCF silica surface. Figure 3 indicates also that the amount of N, P, and subsequently the Pd content in the supported catalysts all level off at ~**10-G-(N, P, or Pd)**. Therefore, in this study, we chose **5-G-Pd** and **10-G-Pd** for testing the catalytic activity toward Sonogashira coupling reactions.



(a) (b)

(c)

Figure 3. Elemental analysis data: Nitrogen content in amine-modified MCF silica (a), phosphorus content in modified MCF silica with phosphine ligand (b), and palladium content in supported catalysts (c).

Nitrogen Sorption Porosimetry

A typical N sorption isotherm is shown in Fig. 4. The shape is characteristic for a mesoporous material with a Type IV isotherm and a H1 hysteresis loop. Table 1 summarizes the structural properties of APTES-functionalized MCF silica (**xx-G-N**) in comparison with pure MCF silica, characterized by N_2 adsorption. As expected, the introduction of the organic fragment leads to a somewhat decreased surface area and pore volume.

Scanning Electron Microscopy (SEM)

SEMs of MCF silica at all stages of modification look identical, confirming that modification does not affect the microscopic structure of the catalyst. Figure 5 shows typical SEM images at two different magnifications (A: 5,000× ; B: 45,000×) of a sample terminally modified with Pd (**5-G-Pd**) where the macroporosity of the MCF-type silica is clearly evident (A) as well as the texture on the surface (B) that leads to the mesopores.

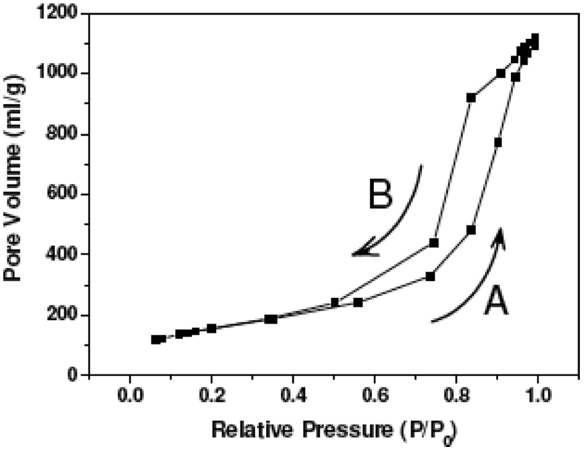


Figure 4. N_2 sorption isotherms of an APTES-functionalized MCF silica sample: (A) adsorption; (B) Desorption.

Supported Catalysts in Sonogashira Reactions

Catalyst Comparison

We examined the catalytic activity of **5-G-Pd** and **10-G-Pd** in the Sonogashira coupling reaction of phenylacetylene with 1-bromo-4-nitrobenzene (Table 2, entry 1). The catalyst loading was 5 mol% Pd relative to the aryl halide substrate. The disappearance of phenylacetylene was monitored as a function of time using gas chromatography (GC). Results show that after 3 h, ~80% of phenylacetylene had reacted using either **5-G-Pd** or **10-G-Pd** as a catalyst, suggesting that both **5-G-Pd** and **10-G-P** have similar catalytic activity. Therefore, for economic reasons, we chose **5-G-Pd** as the supporting catalyst for all of the subsequent Sonogashira reactions in this study (Table 2).

Table 1. Structural properties of APTES-functionalized and pure MCF silica samples

Samples	S_{BET} (m^2/g)	Pore volume (cc/g)	Pore size, (nm)
MCF silica	570	1.69	11.9
5-G-N	459	1.59	13.8
10-G-N	367	1.2	13.1
15-G-N	386	1.3	13.4
20-G-N	445	1.45	13.0

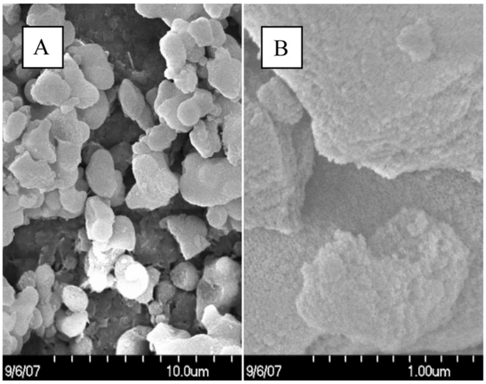
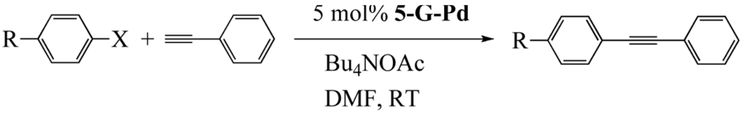


Figure 5. Typical SEM images of **5-G-Pd** samples (see Table 2) using a Hitachi S4700 FESEM, at 10.0 kV and a 5.7-mm focal distance at two different magnifications: (A) 5,000×; (B) 45,000×.

Reactivity and Recycling Ability

We investigated the Sonogashira reaction using a representative group of aryl iodides and bromides with phenylacetylene. The results are shown in Table 2. For reporting reaction yields, products were isolated, purified on preparative silica-gel thin-layer-chromatographic (TLC) plates, and characterized by NMR. The electron-neutral, electron-rich aryl iodides

Table 2. Sonogashira coupling reaction of aryl halides with phenylacetylene



Entry	R	X	Reaction time (h)	Product yield (%)[a]
1	-NO_2	-Br	5	72
2	-CN	-Br	5	68
3	-H	-I	5	62
4	-Me	-I	5	67
5[b]	-Me	-I	5	64
6[c]	-Ph	-Br	4	74

[a] Isolated yields.

[b] Using $Pd(PPh_3)_2Cl_2$ as a homogeneous catalyst.

[c] Reaction was carried out at 80°C, with a molar ratio of phenylacetylene to aryl halide equal to 2.

Table 3. Recycling of the immobilized catalyst **5-G-Pd**[a]

Cycle	Yield (%)[b]
1	67
2	73
3	66

[a] Under the conditions of entry 4, Table 2.
[b] Isolated yields.

(entries 3 and 4, Table 2) and electron-poor aryl bromides (entries 1 and 2, Table 2) reacted with phenylacetylene well, generating the corresponding cross-coupling products. The reaction of electron-rich aryl bromide (entry 6, Table 2) with phenylacetylene generates the product in good yield at higher reaction temperature (80°C) when the molar ratio of the phenylacetylene to aryl bromide is increased from 1 to 2.

The catalytic activity of **5-G-Pd** was compared with that of homogeneous catalyst $Pd(PPh_3)_2Cl_2$ in the coupling reaction of 4-iodotoluene with phenylacetylene (entries 4 and 5, Table 2). Interestingly, **5-G-Pd** exhibited a slightly higher activity than the homogeneous catalyst.

The recycling ability of the **5-G-Pd** catalyst was also investigated under the conditions of entry 4, Table 2. Thus, after the completion of the reaction, the catalyst was recovered by filtration, rinsed with Et_2O, dried in vacuo at room temperature, and stored in a desiccator. In 2 to 3 days, a new reaction was performed with fresh solvent and reactants under the same conditions. The product yields are shown in Table 3 after each cycle. The results indicate the supported **5-G-Pd** catalyst is a highly efficient reusable reagent for copper- and amine-free Sonogashira reactions.

CONCLUSIONS

The Pd complexes were first immobilized on the high surface area of MCF silica, and the resulting materials were used as catalysts for Sonogashira reactions. For this, $-NH_2$ groups were successfully introduced on the mesoporous surfaces of MCF silica by grafting with APTES. The $-NH_2$ group content can be controlled by adjusting the amount of APTES, but it has an upper limit of 2.38 wt% N content of the modified silica. The $-PPh_2$ ligand and the Pd were successfully introduced on the amine-modified MCF silica surface to yield supported catalysts, which proved to be highly efficient reusable catalysts for copper- and amine-free Sonogashira reactions. It is noted that the activity of **5-G-Pd** is comparable to that of homogeneous Pd catalysts.

The Sonogashira reaction should be considered as a model, or a point of departure for a new generation of flow-through monolithic catalysts that will include acids and bases for classic C-C forming reactions such as Michael additions and oxidative as well as chiral catalyses.

EXPERIMENTAL

General

Starting materials and solvents were purchased from Aldrich, Fluka, or Acros and were used without further purification. Melting points were uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian Inova 400 NMR spectrometer and are reported as parts per million (ppm) with the NMR solvent serving as a reference. Infrared spectra were recorded on a Nicolet Magna IR model 750 spectrometer. Gas chromatographic (GC) analyses were conducted on a Hewlett-Packard HP5890 series II chromatograph equipped with a HP-1 (15 m × 0.25 mm × 0.25 mm film; Hewlett-Packard) capillary column using 1,3,5-trimethyl benzene (TMB) as an internal standard and nitrogen as a carrier gas. The injection temperature was 300°C and the detection temperature was 325°C. The GC column was initially maintained at 100°C for 1 min, and its temperature was gradually increased to 250°C at a rate of 30°C/min. The column temperature was maintained at 250°C for 5 min. Elemental analysis was performed by Prevalere Life Sciences, Inc. (Whitesboro, N.Y.).

Preparation of MCF (Mesocellular Foam) Silica[22]

Poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) triblock copolymer ($EO_{20}PO_{70}EO_{20}$, Pluronic P_{123}, $M_{av} = 5800$, Aldrich, 2.0 g, 0.4 mmol) was dissolved in 75 mL of aqueous HCl (1.6 M, 120 mmol) at 40°C, followed by the sequential addition of NH_4F (23 mg, 0.6 mmol) and 1,3,5-trimethylbenzene (TMB, 2.0 g, 17 mmol). After 1 h at 35–40°C, tetraethoxysilane (TEOS, 4.4 g, 21 mmol) was added. After 20 h at 35–40°C, the cloudy mixture was kept at 100°C for 24 h without stirring. The filtered precipitate was dried in air and then calcined at 500°C for 12 h in air to yield a white powder (MCF silica).

Preparation of Amine-Modified MCF Silica[23]

To prepare **5-G-N**, which means amine-grafted MCF silica with APTES/(APTES + TEOS) molar ratio equal to 0.05, APTES (0.52 mL, 2.19 mmol) was added dropwise to a suspension of MCF silica (2.50 g) in anhydrous toluene (65 mL), under an N_2 atmosphere. The resulting mixture was refluxed at 115°C for 24 h. After cooling, the suspension was filtered, and the solid residue was washed successively with methanol, acetone, and hexane (3 × 40 mL, each). The resulting solid was dried under vacuum at room temperature, giving a white powder.

Preparation of PPh_2-Modified MCF Silica from Amine-Modified MCF Silica[24]

To prepare **5-G-P**, diphenylphosphine (5.86 g, 31.46 mmol) was added, under an N_2 atmosphere, to a solution of paraformaldehyde (0.71 g, 23.60 mmol) in degassed anhydrous methanol (30 mL). The mixture was stirred at 70°C for 30 min and then cooled to room temperature, followed by the addition of **5-G-N** (2.00 g, 1.57 mmol with respect to NH_2) in degassed methanol (15 mL) and toluene (60 mL). The reaction mixture was stirred at 70°C for 2 h and then at room temperature for 16 h. The product was isolated by filtration under an N_2 atmosphere and washed with methanol (100 mL). The residual solvent was removed in vacuo, and the product was stored under N_2.

Preparation of Supported Pd Catalyst from PPh_2 Modified MCF Silica[15]

To prepare **5-G-Pd**, (COD)$PdCl_2$ (0.161 g, 0.565 mmol, 1.2 equiv.) was added to diphenylphosphine modified MCF silica **5-G-P** (1.80 g, 0.94 mmol based on P), dispersed in degassed $CHCl_3$ (100 mL). The reaction mixture was heated to 60°C for 26 h. After cooling to room temperature, the solid was collected by filtration under N_2, washed successively with $CHCl_3$ (4 × 40 mL), EtOH (1 × 40 mL), and CH_2Cl_2 (3 × 40 mL), and dried in vacuo.

Typical Procedure for the Sonogashira Reaction using 5-G-Pd[8]

An oven-dried three-necked flask equipped with a magnetic stirring bar was charged with Bu_4NOAc (452 mg, 1.5 mmol), **5-G-Pd** (202 mg, 0.050 mmol), and 1-bromo-4-nitrobenzene (202 mg, 1.0 mmol). The flask was capped with a rubber septum, and then anhydrous DMF (3 mL) and TMB (0.162 g, 1.35 mmol) were successively added. After 5 min of stirring, phenylacetylene (0.154 mL, 1.4 mmol) was added. Stirring was continued at room temperature under nitrogen (reaction times are shown in Table 2). The reaction mixture was diluted with water (10 mL) and the solid catalyst **5-G-Pd** was removed by filtration. The filtrate was extracted with diethyl ether (4 × 10 mL). The combined ether layers were dried over anhydrous Na_2SO_4, filtered, concentrated, and purified on preparative silica gel plates (20 × 20 cm, 1000 μ, Analtech) using methylene chloride/hexane (20/80; v/v) as eluent. All coupling product yields are shown in Table 2.

Coupling Product Characterization

1-Nitro-(4-phenylethynyl)benzene (Table 2, entry 1): mp 118–119°C (lit.[28] 119°C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, 2H, $J = 8.98$ Hz), 7.65 (d, 2H, $J = 8.98$ Hz), 7.56–7.53 (m, 2 H), 7.40–7.37 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 132.2, 131.7, 130.1, 129.2, 128.4, 123.5, 121.9, 94.6, 87.5.

Diphenylethyne-4-carbonitrile (Table 2, entry 2): mp 105–106°C (lit.[29] mp 106–108°C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.61 (m, 4H), 7.48–7.44 (m, 2H), 7.39–7.36 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.1, 132.1, 131.6, 128.7, 128.1, 128.0, 122.0, 118.4, 111.2, 93.6, 87.6.

Diphenylacetylene (Table 2, entry 3): mp 59–60°C (lit.[28] mp 60°C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.50 (m, 4H), 7.35–7.31 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.6, 128.3, 128.2, 123.3, 89.4.

4-(Phenylethynyl)toluene (Table 2, entries 4 and 5): mp 70–71°C (lit.[28] mp 70°C);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.56 (m, 2H), 7.48 (d, 2H, $J = 7.9$ Hz), 7.40–7.34 (m, 3H), 7.19 (d, 2 H, $J = 7.9$ Hz), 2.40 (s, 3H),; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 131.5, 131.4, 129.1, 128.3, 128.0, 123.4, 120.1, 89.5, 88.7, 21.4.

4-(Phenylethynyl)-1,1′-biphenyl (Table 2, entry 6): mp 161–163°C (lit.[9]mp 163–164°C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.58 (m, 6H), 7.54–7.52 (m, 4H), 7.37–7.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 140.2, 132.1, 131.7, 131.7, 128.7, 128.5, 128.1, 127.1, 126.7, 123.2, 122.1, 90.0, 89.2.

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