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A phosphine-free heterogeneous coupling of acyl chlorides with terminal alkynes catalyzed by an MCM-41-immobilized palladium complex

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The phosphine-free heterogeneous coupling of acyl chlorides with terminal alkynes was achieved in triethylamine at 50 °C in the presence of a 0.2 mol% 3-(2-aminoethylamino)propyl-functionalized MCM-41-immobilized palladium complex [MCM-41-2N-Pd(OAc)$_2$], yielding a variety of ynones in good to excellent yields. This novel heterogeneous palladium catalyst can be conveniently prepared from commercially available and cheap reagents and recycled by a simple filtration of the reaction solution, and used for at least 10 consecutive trials without any decrease in activity. Our system not only avoids the use of phosphine ligands, but also solves the basic problem of palladium catalyst recovery and reuse.

Introduction

The utilization of ynones is a common strategy in the synthesis of many biologically-active compounds and heterocyclic derivatives.[1] Traditionally, ynones are generally prepared *via* the coupling reaction of acyl chlorides with lithium acetylides;[2] however, this method lacks chemical selectivity in the presence of other electrophiles and functional groups such as hydroxyls, acids, amines, aldehydes, ketones, *etc.* also have to be protected prior to the reaction. Recently, an alternative coupling of acyl chlorides with terminal alkynes catalyzed by palladium catalysts has received much attention since this reaction can proceed under mild conditions with a wide range of functional groups on alkynes and enhanced chemoselectivity.[3] Among these successful examples for the construction of synthetically useful ynones, homogeneous palladium complexes such as $PdCl_2(PPh_3)_2$ and $Pd(OAc)_2$ are usually used as catalysts for the coupling reactions. However, the problem with homogeneous catalysis is the difficulty to separate the expensive palladium catalyst from the reaction mixture and the impossibility to reuse it in consecutive reactions. From the viewpoints of economical and environmental concern, easy separation of catalysts and products for the recycling of the catalyst is very important. In contrast, heterogeneous catalysts can be easily separated from the reaction mixture by simple filtration and reused in successive reactions provided that the active sites have not become deactivated. Heterogeneous catalysis also helps to minimize wastes derived from reaction workup, contributing to the development of green chemical processes.[4] Hence, heterogenization of such homogeneous palladium catalysts used for the synthesis of ynones is very valuable.

Recently, Likhar *et al.* reported the coupling reaction of acyl chlorides with terminal alkynes catalyzed by Pd/C in toluene and found that the catalyst could be reused for five cycles with a 15% leaching of palladium.[5] Bakherad *et al.* described the acylation of acyl chlorides with terminal alkynes catalyzed by a polystyrene-supported phosphine palladium(0) complex [PS-dpp-Pd(0)].[6] This heterogeneous phosphine palladium catalyst exhibited high catalytic activity and good reusability, but its preparation requires use of expensive 1,2-bis(diphenylphosphino)ethane (dppe). Recent developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support for immobilization of homogeneous catalysts.[7] MCM-41 has a regular pore diameter of *ca.* 5 nm and a specific surface area >700 $m^2\ g^{-1}$.[8] Its large pore size allows passage of large molecules such as organic reactants and metal complexes through the pores to reach the surface of the channel.[9] To date, some palladium complexes on the functionalized MCM-41 support have been prepared and successfully used in carbon–carbon bond formation reactions such as Heck reaction,[10] Suzuki–Miyaura reaction,[11] Sonogashira reaction,[12] and Stille reaction.[13] Recently, Tsai *et al.* reported that the nanosized MCM-41 anchored palladium bipyridyl complex can also catalyze efficiently the coupling of acyl chlorides with terminal alkynes in the presence of a catalytic amount of PPh_3.[14] However, the procedure for preparing this supported palladium catalyst is rather complicated due to the use of expensive and not readily available 4,4′-bis(bromomethyl)-2,2′-bipyridine, moreover, the catalyst exhibited very low activity without the addition of PPh_3 and only 2% GC yield was obtained. Therefore, the development of phosphine-free, readily available heterogeneous

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palladium catalysts having a high activity and good stability is a topic of enormous importance. In continuing our efforts to develop practical synthetic pathways for organic transformations, our new approach, described in this paper, was to design and synthesize a 3-(2-aminoethylamino)propyl-functionalized MCM-41-immobilized palladium complex, which was used as an effective, phosphine-free palladium catalyst for the coupling of acyl chlorides with terminal alkynes.

Results and discussion

Although phosphine ligands stabilize palladium and influence its reactivity, the simplest and cheapest palladium catalysts are of course phosphine-free systems, specifically when used at low loading. It is known that the catalysts containing phosphine ligands are unstable at higher temperatures.[15] Furthermore, the procedure for preparing the polymer-immobilized phosphine palladium complexes is rather complicated since the synthesis of the supported phosphine ligands requires multistep sequences. A novel MCM-41-immobilized bidentate nitrogen palladium(II) complex [MCM-41-2N-Pd(OAc)$_2$] was conveniently synthesized from commercially available and inexpensive 3-(2-aminoethylamino)propyltrimethoxysilane *via* immobilization on MCM-41, followed by reaction with palladium acetate in acetone (Scheme 1). The X-ray powder diffraction (XRD) analysis of the MCM-41-2N-Pd(OAc)$_2$ indicated that, in addition to an intense diffraction peak (100), two higher order peaks (110) and (200) with lower intensities were also detected, and therefore the chemical bonding procedure did not diminish the structural ordering of the MCM-41.

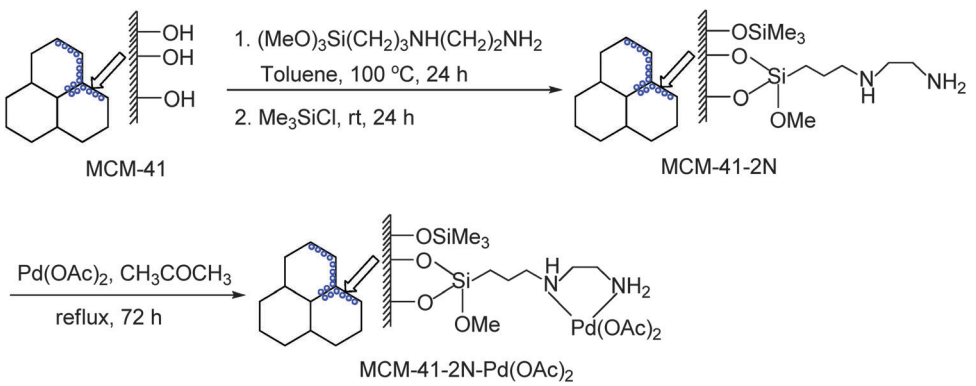
Elemental analyses and X-ray photoelectron spectroscopy (XPS) were used to characterize the MCM-41-immobilized bidentate nitrogen palladium(II) complex. The N : Pd mole ratio of the MCM-41-2N-Pd(OAc)$_2$ was determined to be 6.22. The XPS data for MCM-41-2N-Pd(OAc)$_2$, MCM-41-2N, Pd(OAc)$_2$ and metal Pd are listed in Table 1. It can be seen that the binding energies of Si_{2p} and O_{1s} of MCM-41-2N-Pd(OAc)$_2$ are similar to those of MCM-41-2N. However the difference of N_{1s} binding energies between MCM-41-2N-Pd(OAc)$_2$ and MCM-41-2N is 1.2 eV. The binding energy of $Pd_{3d5/2}$ in MCM-41-2N-Pd(OAc)$_2$ is 0.7 eV less than that in Pd(OAc)$_2$, but 2.1 eV larger than that in metal Pd. These results show that a coordination bond between N and Pd is formed in MCM-41-2N-Pd(OAc)$_2$.

Table 1 XPS data for MCM-41-2N-Pd(OAc)$_2$, MCM-41-2N, Pd(OAc)$_2$ and metal Pd[a]

Sample	$Pd_{3d5/2}$	N_{1s}	Si_{2p}	O_{1s}
MCM-41-2N-Pd(OAc)$_2$	337.5	400.8	103.3	533.1
MCM-41-2N		399.6	103.2	533.2
Pd(OAc)$_2$	338.2			
Metal Pd	335.4			

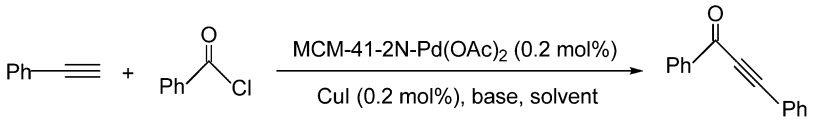
[a] The binding energies are referenced to C_{1s} (284.6 eV) and the energy differences were determined with an accuracy of ±0.2 eV.

In order to test the catalytic activity of the MCM-41-2N-Pd(OAc)$_2$, the coupling reactions of terminal alkynes with acyl chlorides were investigated. The reaction of phenylacetylene with benzoyl chloride (1.1 equiv.) was chosen as a model reaction, and the influences of various reaction parameters such as solvent, base, and palladium catalyst quantity on the reaction were tested. The results are summarized in Table 2. Among the temperatures evaluated [25, 50 and 80 °C], 50 °C was found to be the most effective. The decrease in yield upon enhancing the temperature may be due to the oxidative homocoupling of terminal alkynes in the presence of CuI. We then turned our attention to investigate the effect of solvents on the coupling reaction. Among the solvents evaluated such as toluene, DME, THF, dioxane and Et_3N, Et_3N was the best choice. The coupling reaction was completely blocked as inorganic bases such as K_2CO_3 and Cs_2CO_3 were used, presumably due to the poor solubility of these salts in organic solvents (entries 8 and 9). When Et_3N was used as both base and solvent, the coupling reaction proceeded very smoothly at 50 °C to afford the desired coupling product in an excellent yield (entry 2). The amount of supported palladium catalyst was also screened, and 0.2 mol% loading of palladium was found to be optimal; a lower yield was observed and a longer reaction time was required when the amount of the catalyst was decreased (entry 11). Increasing the amount of palladium catalyst could shorten the reaction time, but did not increase the yield of 1,3-diphenylpropynone (entry 12). CuI as co-catalyst had to be added to the reaction system to obtain a satisfactory result (entry 13), the role of CuI should be the conversion of terminal alkynes to the



Scheme 1 Preparation of MCM-41-2N-Pd(OAc)$_2$.

Table 2 Reaction condition screening for the coupling reaction of phenylacetylene with benzoyl chloride[a]



Entry	Solvent	Base	Temp. (°C)	Time (h)	Yield[b] (%)
1	Et_3N	Et_3N	25	24	25
2	Et_3N	Et_3N	50	6	92
3	Et_3N	Et_3N	80	4	86
4	Toluene	Et_3N	50	24	23
5	Dioxane	Et_3N	50	24	19
6	DME	Et_3N	50	24	7
7	THF	Et_3N	50	24	21
8	THF	K_2CO_3	50	24	0
9	THF	Cs_2CO_3	50	24	0
10	THF	DBU	50	24	15
11[c]	Et_3N	Et_3N	50	15	85
12[d]	Et_3N	Et_3N	50	3	91
13[e]	Et_3N	Et_3N	50	24	9

[a] Reaction conditions: phenylacetylene (1.0 mmol), benzoyl chloride (1.1 mmol), MCM-41-2N-Pd(OAc)$_2$ (0.2 mol%), CuI (0.2 mol%), base (2.0 mmol) in solvent (3.0 mL) under Ar. [b] Isolated yield. [c] 0.1 mol% of palladium catalyst was used. [d] 0.5 mol% of palladium catalyst was used. [e] Without CuI.

corresponding alkynyl copper(I). Thus, the optimized reaction conditions for this coupling reaction are the MCM-41-2N-Pd(OAc)$_2$ (0.2 mol%), CuI (0.2 mol%) in Et_3N with Et_3N as base at 50 °C under Ar for 6 h (entry 2).

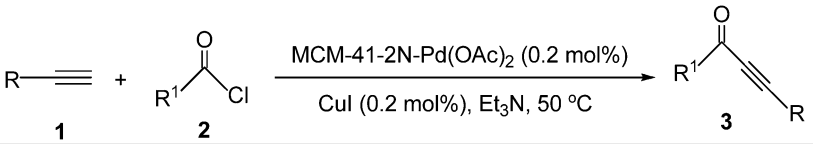
With these promising results in hand, we started investigating the scope of both terminal alkynes and acyl chlorides under the optimized conditions, and the results are summarized in Table 3. As shown in Table 3, the coupling reactions of phenylacetylene with a variety of aromatic acyl chlorides proceeded smoothly under mild conditions affording the corresponding ynones **3a–d** in excellent yields (entries 1–4). The coupling reactions of heteroaryl chlorides such as furan-2-carbonyl chloride and thiophene-2-carbonyl chloride with phenylacetylene gave the corresponding ynones **3e** and **3f** in 90% and 87% yields, respectively (entries 5 and 6). The reaction of substituted phenylacetylenes such as 4-methylphenylacetylene with benzoyl chloride also gave the desired coupled product **3g** in an excellent yield (entry 7). In order to compare the catalytic activity of this heterogeneous palladium catalyst with a homogeneous one, Pd(OAc)$_2$/$H_2NCH_2CH_2NH_2$ (1 : 1) was used as the catalyst for the reaction of phenylacetylene with benzoyl chloride. Under identical conditions, a 79% yield of **3a** was isolated, indicating that a higher activity was obtained after heterogenization of the palladium catalyst as compared with its homogeneous counterpart. A possible explanation for the higher activity observed for the MCM-41-2N-Pd(OAc)$_2$ complex is that the chemical bonding between metal complexes and functional groups of the MCM-41 support maintains the isolated nature of metal complexes, which can influence the catalytic performance in a manner that the analogous homogeneous complex does not exhibit high activity in solution.[16] It is generally believed that high surface area of heterogeneous catalyst results in high catalytic activity. In addition, the MCM-41 support has an extremely high surface area, which also plays an important role in enhancing the catalytic activity. We also compared the reactivity of the MCM-41-2N-Pd(OAc)$_2$ with that of some commercially available heterogeneous palladium catalysts such as Pd/C (from Aldrich). The reaction of benzoyl chloride (1.1 equiv.) with phenylacetylene in the presence of 0.2 mol% of Pd/C (10 wt%) and 0.2 mol% of CuI in Et_3N at 50 °C for 6 h gave a 75% yield of **3a**.

The optimized reaction conditions were also applied to the coupling of aliphatic terminal alkynes such as 1-hexyne, 1-octyne, and 3-methoxypropyne with a variety of aromatic acyl chlorides and heteroaroyl chlorides; the results are also summarized in Table 3. Various electron-donating and electron-withdrawing groups such as –OCH_3, –CH_3, –NO_2, and –Cl on aromatic acyl chlorides were well tolerated to give the desired ynones **3h–u** in good to excellent yields (entries 8–21). (Trimethylsilyl)acetylene was also coupled with a variety of aromatic acyl chlorides to afford the corresponding 1-aryl-3-(trimethylsilyl)propynones **3v–y** in high yields (entries 22–25).

The method provides a quite general route for the synthesis of ynones having various functionalities. The results above prompted us to investigate the coupling reaction of aliphatic acyl chlorides with terminal alkynes, but aliphatic acyl chlorides were not reactive under the conditions optimized for aromatic acyl chlorides. For example, the reaction of acetyl chloride (2 equiv.) with phenylacetylene in Et_3N in the presence of 1 mol% of MCM-41-2N-Pd(OAc)$_2$ and 1 mol% of CuI was carried out at 50 °C for 24 h, and no desired ynone was detected. A similar observation was made by Bakherad *et al.* in the coupling reaction of acyl chlorides with terminal alkynes catalyzed by a polystyrene-supported phosphine palladium(0) complex.[6]

In order to determine whether the catalysis was due to the MCM-41-2N-Pd(OAc)$_2$ complex or to a homogeneous palladium complex that comes off the support during the reaction and then returns to the support at the end, we performed the hot filtration test.[17] We focused on the coupling reaction of phenylacetylene with benzoyl chloride. We filtered off the MCM-41-2N-Pd(OAc)$_2$ complex after 2 h of reaction time and allowed the filtrate to react further. The catalyst filtration was performed at the reaction temperature (50 °C) in order to avoid possible

Table 3 Heterogeneous coupling reaction of terminal alkynes with acyl chlorides[a]



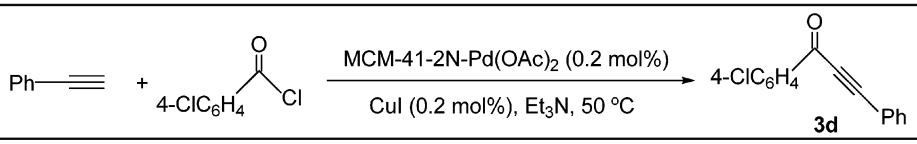
Entry	R	R^1	Time (h)	Product	Yield[b] (%)
1	Ph	Ph	6	**3a**	92
2	Ph	4-$CH_3C_6H_4$	6	**3b**	90
3	Ph	4-$CH_3OC_6H_4$	6	**3c**	96
4	Ph	4-ClC_6H_4	3	**3d**	93
5	Ph	2-Furyl	6	**3e**	90
6	Ph	2-Thienyl	6	**3f**	87
7	4-$CH_3C_6H_4$	Ph	6	**3g**	91
8	*n*-C_4H_9	Ph	10	**3h**	89
9	*n*-C_4H_9	4-$CH_3C_6H_4$	10	**3i**	88
10	*n*-C_4H_9	4-$CH_3OC_6H_4$	10	**3j**	85
11	*n*-C_4H_9	4-ClC_6H_4	6	**3k**	89
12	*n*-C_4H_9	4-$NO_2C_6H_4$	3	**3l**	87
13	*n*-C_4H_9	2-Furyl	9	**3m**	90
14	*n*-C_6H_{13}	Ph	9	**3n**	91
15	*n*-C_6H_{13}	4-$CH_3C_6H_4$	9	**3o**	92
16	*n*-C_6H_{13}	4-$CH_3OC_6H_4$	9	**3p**	88
17	*n*-C_6H_{13}	4-ClC_6H_4	7	**3q**	93
18	*n*-C_6H_{13}	2-Furyl	6	**3r**	91
19	*n*-C_6H_{13}	2-Thienyl	6	**3s**	88
20	CH_3OCH_2	Ph	12	**3t**	78
21	CH_3OCH_2	4-$CH_3C_6H_4$	12	**3u**	75
22	Me_3Si	Ph	12	**3v**	92
23	Me_3Si	4-$CH_3C_6H_4$	12	**3w**	87
24	Me_3Si	4-$CH_3OC_6H_4$	12	**3x**	89
25	Me_3Si	4-ClC_6H_4	10	**3y**	91

[a] Reaction conditions: **1** (1.0 mmol), **2** (1.1 mmol), MCM-41-2N-Pd$(OAc)_2$ (0.2 mol%), CuI (0.2 mol%) in Et_3N (3.0 mL) at 50 °C under Ar. [b] Isolated yield.

recoordination or precipitation of soluble palladium upon cooling. We found that, after this hot filtration, no further reaction was observed. We also ascertained the Pd-content in the filtrate by ICP analysis, and only 0.2 ppm of palladium was found in the clear solution. This result suggests that the palladium catalyst remains on the support at elevated temperatures during the reaction and points to a process of heterogeneous nature.

For a heterogeneous transition-metal catalyst, it is important to examine its ease of separation, good of recoverability and reusability. This heterogeneous palladium catalyst can be easily recovered by a simple filtration of the reaction solution. We also investigated the possibility to reuse the catalyst by using the coupling reaction of 4-chlorobenzoyl chloride with phenylacetylene. After carrying out the reaction, the catalyst was separated by simple filtration and washed with 3 N HCl, EtOH, and Et_2O. After being air-dried, it could be reused directly without further purification. The recovered palladium catalyst was used in the next run under identical conditions, and almost consistent activity was observed for ten consecutive cycles (Table 4, entries 1–10). Fig. 1 shows the time course of the coupling reaction of 4-chlorobenzoyl chloride with phenylacetylene using the fresh and the fourth recycled catalysts. As

Table 4 Coupling reaction of 4-chlorobenzoyl chloride with phenylacetylene catalyzed by the recycled catalyst[a]



Cycle	Yield[b] (%)	Cycle	Yield[b] (%)
1	93	2	93
3	92	4	92
5	91	6	92
7	91	8	90
9	89	10	90

[a] Reaction conditions: phenylacetylene (1.0 mmol), 4-chlorobenzoyl chloride (1.1 mmol), MCM-41-2N-Pd$(OAc)_2$ (0.2 mol%), CuI (0.2 mol%) in Et_3N (3.0 mL) at 50 °C for 3 h under Ar. [b] Isolated yield.

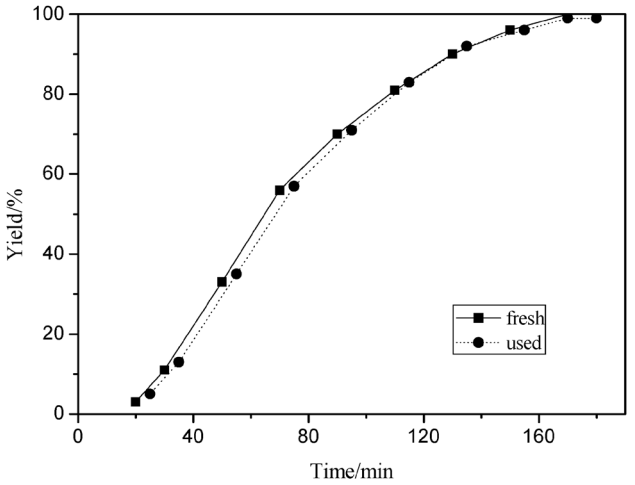


Fig. 1 Plot of GC yield *versus* time for the coupling reaction of 4-chlorobenzoyl chloride with phenylacetylene using the fresh and the fourth recycled catalysts.

Table 5 Textural parameters of the fresh and the 10th recycled catalysts

Palladium catalyst	Surface area[a]/ (m^2 g^{-1})	Pore volume[b]/ (cm^3 g^{-1})	Diameter[c]/ (nm)
Fresh catalyst	577.3	0.46	2.1
10th recycled catalyst	575.6	0.45	2.0

[a] BET surface area. [b] Single point total pore volume. [c] Pore diameter according to the maximum of the BJH pore size distribution.

shown in Fig. 1, for the fourth recycled catalyst, the induction period and the reaction rate in the fourth run did not change significantly compared with that of the fresh one indicating the excellent stability and recyclability of the catalytic system. In addition, palladium leaching in the supported catalyst was also determined. The palladium content of the recycled catalyst was determined by ICP analysis to be 0.27 mmol g^{-1} after ten consecutive runs, and no palladium had been lost from the MCM-41 support. By comparing the data on the porosity of the fresh and the 10th recycled catalysts (Table 5), it is clear that the mesoporous structure of MCM-41 remains intact during the reaction procedure, indicating that MCM-41 is a very stable material in dry Et_3N medium.

From a mechanistic point of view, the Pd(II) will be reduced to Pd(0) first and then a oxidative addition, transmetallation, reductive elimination pathway could be the possible mechanism. So, the structure of the recycled catalyst should be $(N\hat{}N)_2Pd(0)$. In general, the continuous recycle of resin-supported palladium catalysts is difficult owing to leaching of the palladium species from the polymer supports, which often reduces their activity within a five-recycle run. The high stability and excellent reusability of the catalyst should result from the chelating action of the bidentate 2-aminoethylamino ligand on palladium and the mesoporous structure of the MCM-41 support. The result is important from a practical point of view. The high catalytic activity, excellent reusability and the easy accessibility of the MCM-41-2N-$Pd(OAc)_2$ complex make it a highly attractive heterogeneous palladium catalyst for the parallel solution phase synthesis of diverse libraries of compounds.

Conclusion

In summary, we have developed a novel, phosphine-free, practical and economic catalyst system for the coupling reaction of terminal alkynes with acyl chlorides by using an MCM-41-immobilized bidentate nitrogen palladium complex as a catalyst in Et_3N. This novel heterogeneous palladium catalyst can be very conveniently prepared by a simple two-step procedure from commercially available and cheap reagents and recycled by a simple filtration of the reaction solution and used for at least 10 consecutive trials without any decrease in activity. The heterogeneous coupling reaction of terminal alkynes with acyl chlorides catalyzed by the MCM-41-2N-$Pd(OAc)_2$ complex provides a better and practical procedure for the synthesis of a variety of ynone compounds.

Experimental

General comments

All chemicals were reagent grade and used as purchased. All solvents were dried and distilled before use. The products were purified by flash chromatography on silica gel. A mixture of EtOAc and hexane was generally used as the eluent. All coupling products were characterized by comparison of their spectra and physical data with authentic samples. IR spectra were determined on a Perkin-Elmer 683 instrument. ^1H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer with TMS as an internal standard in $CDCl_3$ as the solvent. ^{13}C NMR spectra (100 MHz) were recorded on a Bruker Avance 400 MHz spectrometer in $CDCl_3$ as solvent. The palladium content was determined using inductively coupled plasma atom emission Atomscan16 (ICP-AES, TJA Corporation). The BET surface area and pore analysis were performed on an ASAP2010 (micromeritics) by N_2 physical adsorption–desorption at 77.4 K. The X-ray powder diffraction data were obtained on a Damx-rA (Rigaka). X-ray photoelectron spectra were recorded on XSAM 800 (Kratos). Microanalyses were carried out using a Yanaco MT-3 CHN microelemental analyzer. GC analysis was performed on an SRI 8610C equipped with a fused silica capillary column. The mesoporous material MCM-41 was easily prepared according to a literature procedure.[18]

Preparation of MCM-41-2N

A solution of 1.54 g of 3-(2-aminoethylamino)propyltrimethoxysilane in 18 mL of dry chloroform was added to a suspension of 2.2 g of the MCM-41 in 180 mL of dry toluene. The mixture was stirred for 24 h at 100 °C. Then the solid was filtered and washed with $CHCl_3$ (2 × 20 mL), and dried under vacuum at 160 °C for 5 h. The dried white solid was then soaked in a solution of 3.1 g of Me_3SiCl in 100 mL of dry toluene at room temperature under stirring for 24 h. Then the solid was filtered, washed with acetone (3 × 20 mL) and diethyl ether (3 × 20 mL), and dried under vacuum at 120 °C for 5 h to obtain 3.49 g of hybrid material MCM-41-2N. The nitrogen content was found to be 1.84 mmol g^{-1} by elemental analysis.

Preparation of MCM-41-2N-Pd(OAc)$_2$

In a small Schlenk tube, 2.03 g of the above-functionalized MCM-41 (MCM-41-2N) was mixed with 0.137 g (0.61 mmol) of $Pd(OAc)_2$ in 50 mL of dry acetone. The mixture was refluxed for 72 h under an argon atmosphere. The solid product was filtered by suction, washed with acetone, distilled water and acetone successively and dried at 70 °C/26.7 Pa under Ar for 5 h to give 2.12 g of a light yellow palladium complex [MCM-41-2N-$Pd(OAc)_2$]. The nitrogen and palladium contents were found to be 1.68 mmol g^{-1} and 0.27 mmol g^{-1}, respectively.

General procedure for the synthesis of ynones

An oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with MCM-41-2N-$Pd(OAc)_2$ (8 mg, 0.002 mmol Pd), aromatic acyl chloride (1.1 mmol), and terminal alkyne (1.0 mmol) followed by anhydrous Et_3N (3 mL) under Ar. The reaction mixture was stirred in an oil bath at 50 °C for 3–12 h. The mixture was cooled to room temperature, diluted with diethyl ether (30 mL) and filtered. The MCM-41-2N-$Pd(OAc)_2$ complex was washed with 3 N HCl (2 × 5 mL), EtOH (2 × 5 mL), and Et_2O (2 × 5 mL) and reused in the next run. The filtrate was washed with water (2 × 10 mL) and dried over anhydrous magnesium sulfate. The solvent was removed and the residue was purified by flash column chromatography on silica gel (hexane–ethyl acetate = 10 : 1).

1,3-Diphenylpropynone 3a [Table 3, entry 1][3a]. White solid, mp 43–44 °C. IR (KBr): ν_{max}/cm^{-1} 2203, 1636, 1603, 1288, 1013, 761. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.23 (d, J = 7.6 Hz, 2H), 7.70 (d, J = 7.2 Hz, 2H), 7.64 (t, J = 7.2 Hz, 1H), 7.55–7.41 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.1, 136.9, 134.2, 133.1, 130.9, 129.6, 128.7, 128.6, 120.1, 93.2, 86.9.

1-(4-Methylphenyl)-3-phenylpropynone 3b [Table 3, entry 2][19]. White solid, mp 86–87 °C. IR (KBr): ν_{max}/cm^{-1} 2198, 1636, 1604, 1288, 1211, 1013, 761, 690. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.12 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.48 (t, J = 6.8 Hz, 1H), 7.42 (t, J = 7.2 Hz, 2H), 7.31 (d, J = 7.6 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.7, 145.2, 134.7, 133.0, 130.7, 129.7, 129.4, 128.7, 120.3, 92.6, 87.0, 21.8.

1-(4-Methoxyphenyl)-3-phenylpropynone 3c [Table 3, entry 3][3a]. White solid, mp 98–99 °C. IR (KBr): ν_{max}/cm^{-1} 2201, 1634, 1602, 1316, 1210, 1014, 762, 693. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.21 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 7.2 Hz, 2H), 7.49 (t, J = 6.8 Hz, 1H), 7.43 (t, J = 7.2 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 176.7, 164.5, 133.0, 132.0, 130.6, 130.3, 128.7, 120.4, 113.9, 92.4, 87.2, 55.6.

1-(4-Chlorophenyl)-3-phenylpropynone 3d [Table 3, entry 4][3a]. White solid, mp 106–107 °C. IR (KBr): ν_{max}/cm^{-1} 2200, 1654, 1585, 1303, 1207, 1170, 1091, 752, 682. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.17 (d, J = 7.6 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.51–7.44 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 176.7, 140.8, 135.3, 133.1, 131.0, 130.9, 129.0, 128.8, 119.9, 93.7, 86.6.

1-(Furan-2-yl)-3-phenylpropynone 3e [Table 3, entry 5][3a]. Brown solid, mp 49–50 °C. IR (KBr): ν_{max}/cm^{-1} 2201, 1713, 1634, 1567, 1463, 1395, 1312, 1161, 1043, 1008, 758, 689. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.70–7.64 (m, 3H), 7.52–7.41 (m, 4H), 6.61 (t, J = 1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 164.8, 153.3, 148.0, 133.1, 130.9, 128.7, 120.9, 120.0, 112.7, 91.9, 86.3.

3-Phenyl-1-(thiophen-2-yl)propynone 3f [Table 3, entry 6][14]. Brown solid, mp 54–55 °C. IR (KBr): ν_{max}/cm^{-1} 2199, 1725, 1614, 1489, 1410, 1359, 1308, 1230, 1082, 1053, 966, 758, 725. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.01 (d, J = 4.0 Hz, 1H), 7.73 (d, J = 4.8 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.51–7.40 (m, 3H), 7.19 (t, J = 4.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.8, 145.0, 135.2, 135.0, 133.1, 130.9, 128.7, 128.3, 120.0, 91.7, 86.5.

1-Phenyl-3-(4-methylphenyl)propynone 3g [Table 3, entry 7][14]. White solid, mp 66–67 °C. IR (KBr): ν_{max}/cm^{-1} 2194, 1629, 1604, 1316, 1295, 1209, 1009, 816, 697. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.22 (d, J = 8.4 Hz, 2H), 7.69–7.49 (m, 5H), 7.23 (d, J = 8.0 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.1, 141.6, 137.0, 134.0, 133.1, 129.6, 129.5, 128.6, 117.0, 93.8, 86.8, 21.8.

1-Phenylhept-2-yn-1-one 3h [Table 3, entry 8][6]. Pale yellow oil. IR (film): ν_{max}/cm^{-1} 2959, 2201, 1643, 1597, 1449, 1313, 1267, 1175, 911, 702. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.14 (d, J = 8.0 Hz, 2H), 7.60 (t, J = 7.2 Hz, 1H), 7.50–7.45 (m, 2H), 2.51 (t, J = 6.8 Hz, 2H), 1.69–1.61 (m, 2H), 1.54–1.48 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.3, 136.9, 133.9, 129.6, 128.5, 96.9, 79.7, 29.9, 22.1, 18.9, 13.6.

1-(4-Methylphenyl)hept-2-yn-1-one 3i [Table 3, entry 9][6]. Pale yellow oil. IR (film): ν_{max}/cm^{-1} 2959, 2199, 1643, 1605, 1269, 1177, 910, 742. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.03 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 2.50 (t, J = 7.2 Hz, 2H), 2.43 (s, 3H), 1.70–1.64 (m, 2H), 1.53–1.47 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.0, 144.9, 134.6, 129.7, 129.2, 96.3, 79.7, 29.9, 22.1, 21.8, 18.9, 13.6.

1-(4-Methoxyphenyl)hept-2-yn-1-one 3j [Table 3, entry 10][6]. Pale yellow oil. IR (film): ν_{max}/cm^{-1} 2959, 2201, 1639, 1599, 1508, 1317, 1259, 1167, 1029, 911, 845, 759. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.11 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 3.89 (s, 3H), 2.50 (t, J = 6.6 Hz, 2H), 1.68–1.64 (m, 2H), 1.54–1.48 (m, 2H), 0.96 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.1, 164.3, 132.0, 130.3, 113.7, 96.0, 79.6, 55.6, 29.9, 22.1, 18.9, 13.6.

1-(4-Chlorophenyl)hept-2-yn-1-one 3k [Table 3, entry 11][6]. Pale yellow oil. IR (film): ν_{max}/cm^{-1} 2961, 2201, 1650, 1587, 1485, 1401, 1264, 1171, 1091, 911, 847, 748. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.07 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 2.52 (t, J = 7.2 Hz, 2H), 1.69–1.63 (m, 2H), 1.53–1.46 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.0, 140.5, 135.3, 131.0, 128.9, 97.5, 79.4, 29.8, 22.1, 18.9, 13.6.

1-(4-Nitrophenyl)hept-2-yn-1-one 3l [Table 3, entry 12][6]. Yellow oil. IR (film): ν_{max}/cm^{-1} 2960, 2201, 1653, 1603, 1528, 1344, 1320, 1261, 1105, 912, 850, 711. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.33 (d, J = 8.8 Hz, 2H), 8.29 (d, J = 8.8 Hz, 2H), 2.55 (t, J = 7.2 Hz, 2H), 1.72–1.66 (m, 2H), 1.55–1.48 (m, 2H), 0.98 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 176.1, 150.8, 141.1, 130.4, 123.8, 99.5, 79.4, 29.7, 22.1, 19.0, 13.5.

1-(Furan-2-yl)hept-2-yn-1-one 3m [Table 3, entry 13][19]. Pale yellow oil. IR (film): ν_{max}/cm^{-1} 2960, 2210, 1635, 1566, 1463, 1394, 1302, 1171, 1124, 1017, 884, 827, 765. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.64 (d, J = 0.8 Hz, 1H), 7.31 (d, J = 3.2 Hz, 1H), 6.57–6.55 (m, 1H), 2.47 (t, J = 7.0 Hz, 2H), 1.66–1.58 (m, 2H), 1.52–1.46 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.1, 153.3, 147.7, 120.5, 112.5, 95.6, 79.0, 29.7, 22.0, 18.8, 13.5.

1-Phenylnon-2-yn-1-one 3n [Table 3, entry 14][14]. Pale yellow oil. IR (film): ν_{max}/cm^{-1} 2931, 2201, 1646, 1598, 1450, 1313, 1265, 1175, 909, 702. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.14 (d, J = 8.0 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 2.50 (t, J = 7.2 Hz, 2H), 1.72–1.64 (m, 2H), 1.52–1.33 (m, 6H), 0.91 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.2, 137.0, 133.8, 129.5, 128.5, 96.9, 79.7, 31.2, 28.6, 27.8, 22.5, 19.2, 14.0.

1-(4-Methylphenyl)non-2-yn-1-one 3o [Table 3, entry 15][20]. Pale yellow oil. IR (film): ν_{max}/cm^{-1} 2931, 2199, 1645, 1605, 1465, 1309, 1268, 1176, 1107, 741. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.03 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 2.49 (t, J = 7.2 Hz, 2H), 2.43 (s, 3H), 1.69–1.64 (m, 2H), 1.51–1.33 (m, 6H), 0.91 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.9, 144.8, 134.7, 129.7, 129.2, 96.3, 79.8, 31.2, 28.6, 27.8, 22.5, 21.7, 19.2, 14.0.

1-(4-Methoxyphenyl)non-2-yn-1-one 3p [Table 3, entry 16][20]. Pale yellow oil. IR (film): ν_{max}/cm^{-1} 2933, 2200, 1643, 1599, 1464, 1316, 1257, 1167, 1029, 845, 759. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.11 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H), 2.48 (t, J = 7.2 Hz, 2H), 1.69–1.63 (m, 2H), 1.49–1.32 (m, 6H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.0, 164.3, 131.9, 130.4, 113.7, 96.0, 79.6, 55.6, 31.3, 28.7, 27.8, 22.5, 19.2, 14.1.

1-(4-Chlorophenyl)non-2-yn-1-one 3q [Table 3, entry 17]. Pale yellow oil. IR (film): ν_{max}/cm^{-1} 2931, 2201, 1649, 1587, 1263, 1091, 1014, 846, 747. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.07 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 2.50 (t, J = 7.2 Hz, 2H), 1.69–1.63 (m, 2H), 1.49–1.31 (m, 6H), 0.91 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 176.8, 140.4, 135.4, 130.9, 128.8, 97.4, 79.4, 31.2, 28.6, 27.7, 22.5, 19.2, 14.0. Anal. calcd for $C_{15}H_{17}OCl$: C, 72.41; H, 6.89. Found: C, 72.18; H, 6.64.

1-(Furan-2-yl)non-2-yn-1-one 3r [Table 3, entry 18][21]. Pale yellow oil. IR (film): ν_{max}/cm^{-1} 2931, 2210, 1634, 1566, 1463, 1395, 1302, 1171, 1016, 765. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.64 (s, 1H), 7.31 (d, J = 3.6 Hz, 1H), 6.57–6.55 (m, 1H), 2.46 (t, J = 7.0 Hz, 2H), 1.69–1.61 (m, 2H), 1.48–1.32 (m, 6H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.1, 153.3, 147.7, 120.5, 112.4, 95.6, 79.0, 31.2, 28.6, 27.7, 22.5, 19.1, 14.0.

1-(Thiophen-2-yl)non-2-yn-1-one 3s [Table 3, entry 19][21]. Pale yellow oil. IR (film): ν_{max}/cm^{-1} 2931, 2230, 1629, 1515, 1411, 1358, 1279, 1041, 728. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.90–7.88 (m, 1H), 7.69–7.67 (m, 1H), 7.16–7.13 (m, 1H), 2.48 (t, J = 7.0 Hz, 2H), 1.68–1.61 (m, 2H), 1.49–1.26 (m, 6H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.1, 145.1, 134.9, 134.8, 128.2, 95.5, 79.3, 31.2, 28.6, 27.7, 22.5, 19.1, 14.0.

4-Methoxy-1-phenylbut-2-yn-1-one 3t [Table 3, entry 20][22]. Pale yellow oil. IR (film): ν_{max}/cm^{-1} 2934, 2227, 1723, 1651, 1598, 1450, 1314, 1263, 1175, 1105, 701. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.15 (d, J = 7.6 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 4.41 (s, 2H), 3.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.5, 136.3, 134.4, 129.6, 128.7, 90.0, 84.2, 59.8, 58.3.

4-Methoxy-1-(*p*-tolyl)but-2-yn-1-one 3u [Table 3, entry 21]. Pale yellow oil. IR (film): ν_{max}/cm^{-1} 2928, 2227, 1645, 1605, 1450, 1310, 1266, 1178, 1105, 740. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.04 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 4.39 (s, 2H), 3.50 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.2, 145.5, 134.1, 129.8, 129.4, 89.4, 84.4, 59.8, 58.2, 21.9. Anal. calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.34; H, 6.64.

1-Phenyl-3-(trimethylsilyl)propynone 3v [Table 3, entry 22][23]. Pale yellow oil. IR (film): ν_{max}/cm^{-1} 2963, 2153, 1645, 1598, 1254, 1036, 1018, 848, 701. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.15 (d, J = 7.6 Hz, 2H), 7.65 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 0.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.8, 136.5, 134.2, 129.7, 128.6, 100.8, 100.6, −0.7.

1-(4-Methylphenyl)-3-(trimethylsilyl)propynone 3w [Table 3, entry 23]. Pale yellow oil. IR (film): ν_{max}/cm^{-1} 2962, 2154, 1644, 1605, 1259, 1175, 1036, 1016, 848, 741. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.04 (d, J = 8.4 Hz, 2H), 7.28 (t, J = 8.4 Hz, 2H), 2.44 (s, 3H), 0.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.1, 146.0, 134.9, 130.5, 130.0, 101.6, 100.6, 22.5, 0.0. Anal. calcd for $C_{13}H_{16}OSi$: C, 72.20; H, 7.46. Found: C, 72.32; H, 7.29.

1-(4-Methoxyphenyl)-3-(trimethylsilyl)propynone 3x [Table 3, entry 24][23]. Pale yellow oil. IR (film): ν_{max}/cm^{-1} 2961, 2252, 1637, 1598, 1257, 1165, 1026, 910, 846, 734. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.12 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H), 0.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.0, 165.2, 132.7, 130.6, 114.5, 102.1, 100.2, 56.2, 0.0.

1-(4-Chlorophenyl)-3-(trimethylsilyl)propynone 3y [Table 3, entry 25]. Pale yellow oil. IR (film): ν_{max}/cm^{-1} 2963, 2155, 1651, 1587, 1252, 1170, 1092, 1034, 846, 747. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.08 (d, J = 8.4 Hz, 2H), 7.47 (t, J = 8.4 Hz, 2H), 0.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.1, 141.5, 135.6, 131.7, 129.7, 102.0, 101.1, 0.0. Anal. calcd for $C_{12}H_{13}OSiCl$: C, 60.88; H, 5.54. Found: C, 60.62; H, 5.31.

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