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Highly-efficient and recyclable nanosized MCM-41 anchored palladium bipyridyl complex-catalyzed coupling of acyl chlorides and terminal alkynes for the formation of ynones

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ABSTRACT

A highly-efficient and practical method for the formation of ynones from a variety of acyl chlorides and terminal alkynes catalyzed by a nanosized MCM-41 anchored palladium bipyridyl complex is described herein. Aroyl, heteroaroyl, and alkyl acyl chlorides were easily coupled with terminal alkynes, giving good to high isolated yields in the presence of a very low catalyst loading (0.002–0.1 mol % Pd) in Et_3N or diisopropylethylamine at 50 °C. Furthermore, the reaction scale was up to 150 mmol for a single batch reaction, providing the potential for practically synthetic application. After centrifugation, the supported catalyst was able to be recycled and reused several times with only a slight decrease in activity.

1. Introduction

Ynones are useful synthetic intermediates for the preparation of many biologically-active compounds and heterocyclic derivatives.[1,2] Among many synthetic strategies, the coupling reaction of acyl chlorides and terminal alkynes catalyzed by palladium catalysts has received much attention of late. This reaction can be achieved under mild conditions with a wide range of functional groups on alkynes and enhanced chemoselectivity.[3] In spite of the synthetic elegance of the construction of synthetically useful ynones, these palladium-catalyzed reactions are usually carried out in a homogeneous phase, which makes the catalysts difficult to recover and reuse in subsequent reactions. Hence, facile separation of catalysts and products for the recycling of the catalysts is rather important from the viewpoints of economical and environmental concern. For these reasons, heterogenization of such homogeneous catalysts used for ynone formation is very valuable.

Recently, Likhar's group reported that acyl chlorides could be coupled with terminal alkynes in the presence of 1 mol % Pd/C under refluxing toluene and the catalyst could be reused for five cycles with a 15% leaching of Pd.[4] On the other hand, recent developments in ordered mesoporous silica (OMS) materials such as MCM-41 and SBA-15 lend these materials very well to their use as solid supports for the purpose of heterogenization of homogeneous catalysts.[5] The uniform pore size and large surface area of OMS allow simple grafting of transition-metal complexes to the wall and the catalysis of organic reactions in the nanopores. Recently, several palladium complexes have been immobilized on OMS for employment as heterogeneous catalysts for carbon–carbon bond-forming reactions, such as the Mizoroki–Heck reaction,[6] Suzuki–Miyaura reaction,[7] Sonogashira coupling,[8] Kumada–Tamao–Corriu reaction,[9] Migita–Kosugi–Stille reaction,[10] and ketone formation.[11] We have reported previously that nanosized MCM-41–Pd (Fig. 1) is an excellent heterogeneous catalyst for carbon–carbon bond cross–coupling reactions due to its short and highly-connected wormhole-like channels, which allow easy exchange of reactants and products throughout the nanochannels.[6g,9,11] Thus, a very low catalyst loading can be used in the reaction without encountering the saturation phenomenon. As a part of our continuing efforts in the development of a recyclable catalyst for carbon–carbon bond-forming reactions, we report herein the coupling of various acyl chlorides and terminal alkynes catalyzed by nanosized MCM-41–Pd (denoted as NS-MCM-41–Pd) for the formation of ynones. This reaction not only uses a very low catalyst loading (0.002–0.1 mol % Pd) in each batch, but also the reaction scale can be up to 150 mmol, making it useful for practically synthetic application (Scheme 1).

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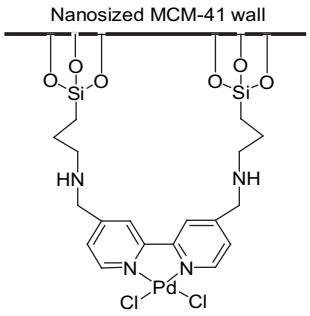
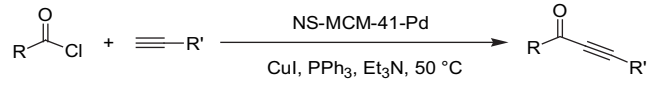


Figure 1. Nanosized MCM-41–Pd.



R = aryl, heteroaryl, alkyl
R' = aryl, alkyl, alkenyl

Scheme 1. NS-MCM-41–Pd-catalyzed coupling of acyl chlorides with terminal alkynes.

2. Results and discussion

NS-MCM-41–Pd was prepared according to our previous procedures.[6g,9] After the grafting of the palladium bipyridyl complex onto NS-MCM-41, the surface area and pore diameter decreased from 705 m^2/g and 2.5 nm to 588 m^2/g and 2.3 nm, respectively, and the amount of Pd complex anchored on the wall of MCM-41 was estimated to be 0.15 mmol/g by ICP-MASS analysis. As shown in Table 1, our initial goal was to optimize the reaction conditions for the coupling of benzoyl chloride **1a** (1.3 equiv) and phenylacetylene **2a** (1.0 equiv) in the presence of 0.02 mol % Pd (as in NS-MCM-41–Pd). When the reaction was conducted in common organic solvents such as THF, toluene, DME, and 1,4-dioxane with Et_3N as a base, low GC yields were obtained (entries 1–4). The coupling reaction was completely blocked as inorganic bases such as KOH and K_2CO_3 were employed, presumably owing to the poor solubility of these salts in organic solvents (entries 5–6). When Et_3N was used as both solvent and base, the reaction showed high activity and afforded near-quantitative yield at 50 °C in 0.5 h (entry 7). However, only a 10% yield of **3a** was obtained when the reaction was conducted at room temperature (entry 8), and both PPh_3 and CuI had to be added to the reaction system to obtain satisfactory results (entries 9–10). In order to compare the activity of this heterogeneous catalyst, NS-MCM-41–Pd, with a homogeneous one, $PdCl_2$(bpy) was used as the catalyst for the same reaction. Under identical conditions, a 66% yield of **3a** was isolated, indicating that higher catalytic activity was obtained after heterogenization of the palladium catalyst as compared with the homogeneous counterpart (entry 11).

Table 1
Optimization of reaction conditions for the coupling of benzoyl chloride **1a** with phenylacetylene **2a**[a]

Entry	Base	Solvent	Temperature (°C)	Yield[b] (%)
1	Et_3N	THF	50	21
2	Et_3N	Toluene	50	14
3	Et_3N	DME	50	3
4	Et_3N	1,4-Dioxane	50	21
5	K_2CO_3	THF	50	0
6	KOH	THF	50	0
7	Et_3N	Et_3N	50	99 (92)
8	Et_3N	Et_3N	rt	10
9[c]	Et_3N	Et_3N	50	2
10[d]	Et_3N	Et_3N	50	7
11[e]	Et_3N	Et_3N	50	78 (66)

[a] Reaction conditions: benzoyl chloride (19.5 mmol), phenylacetylene (15 mmol), NS-MCM-41–Pd (0.02 mol %), PPh_3 (0.04 mol %), CuI (0.04 mol %), base (30 mmol), and solvent (20 mL) for 0.5 h.
[b] GC yields. Isolated yields are shown in parentheses.
[c] Without PPh_3.
[d] Without CuI.
[e] $PdCl_2$(bpy) was used as the catalyst.

After the optimized conditions had been found, a variety of acyl chlorides were coupled with phenylacetylene (Table 2, the products were denoted as **3** when aromatic terminal alkynes were used). First, we increased the ratio of phenylacetylene to Pd to 50 000 by scaling up the alkyne to 150 mmol. To our delight, the reaction was completed in 36 h and resulted in a 93% isolated yield (entry 1). This result shows its potential for practically synthetic application. Not only aryl acyl chlorides but also heteroaryl chlorides coupled with phenylacetylene smoothly in the presence of low amount of NS-MCM-41–Pd within a short reaction time to give high product yields when both aroyl and heteroaroyl chlorides were used as the substrates (entries 2–7). Under similar conditions, we also studied the reactivity of alkyl acyl chlorides in the presence of 0.02 mol % of the Pd catalyst: **1h**–**1j** coupled with phenacetylene effectively, resulting in the formation of the corresponding products at yields of between 86 and 94% (entries 8–10). In the case of valeroyl chloride, **1k**, a bulky diisopropylethylamine was employed instead of Et_3N to avoid direct reaction of the amine with the linear aliphatic acyl chloride,[3f,12] whereupon a good isolated yield of **3k** was obtained (entry 11).

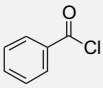
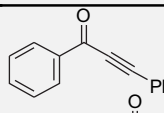
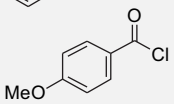
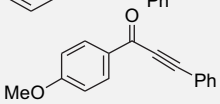
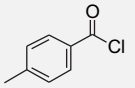
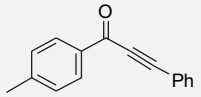
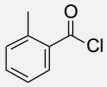
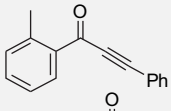
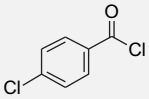
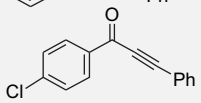
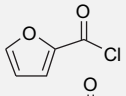
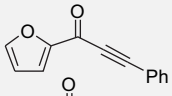
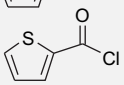
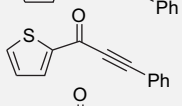
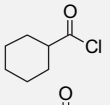
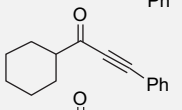
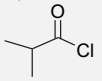
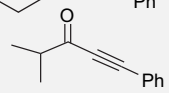
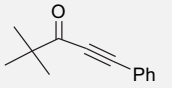
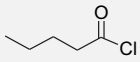
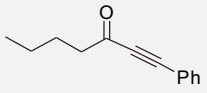
Next, a variety of substituted aromatic terminal alkynes were used to couple with acyl chlorides in the presence of 0.02 mol % NS-MCM-41–Pd (Table 3). The *para*-substituted phenylacetylenes, such as 4-ethynylanisole **2b** and 4-ethynylchlorobenzene **2c**, reacted with various aroyl and alkyl acyl chlorides very efficiently, giving the corresponding products, **3l**–**3s**, in high yields within short reaction time (entries 1–8). Terminal alkynes **2d**–**2h** also coupled with acyl chlorides smoothly under the same conditions (entries 9–19), and even reaction with *ortho*-substituted alkynes **2d**, **2e**, and **2h** proceeded with yields almost at the same level as the *para*-substituted alkynes (entries 9–11). However, the reaction rate when employing the larger 9-ethynylphenanthrene **2i** was smaller owing to the difficulty of diffusion of the bulky reactant in the catalyst-containing nanopores (entry 20).

The utility of this coupling reaction for aliphatic terminal alkynes was also evaluated (Table 4, the products were denoted as **4** when aliphatic terminal alkynes were used). Compared with that of aromatic terminal alkynes, the coupling of acyl chlorides with aliphatic terminal alkynes proceeded at relatively lower rates. When a higher catalyst loading (0.1 mol %) was applied, however, both aroyl and alkyl acyl chlorides coupled with aliphatic terminal alkynes to give the corresponding products **4a**–**4i** in good to high yields (entries 1–9).

In order to determine whether catalysis was due to NS-MCM-41–Pd itself or to the leached palladium in solution, a hot filtration experiment was performed.[6–11] We performed a coupling reaction of 4-methoxybenzoyl chloride **1b** and phenylacetylene **2a** catalyzed by 0.01 mol % of NS-MCM-41–Pd (Table 2, entry 2). After 1 h of reaction, the reaction mixture was promptly filtered through a dried Celite pad under nitrogen at the reaction temperature to remove any undissolved fine particles. The clear filtrate was analyzed by GC and a yield of 53% was obtained; the solution was then stirred at 50 °C, and we observed that the clear filtrate showed no further activity for the coupling reaction, even upon stirring for an additional 12 h. We ascertained the Pd-content in the filtrate by ICP-MASS, and only 0.3 ppm of palladium was found in the clear solution. This indicated that the catalytic activity indeed was resulted from the grafted palladium complex.

One of the purposes for the designing of this heterogeneous catalyst is to enable recycling of the catalyst for use in subsequent

Table 2
NS-MCM-41–Pd-catalyzed coupling of acyl chlorides **1** with phenylacetylene **2a**[a]

Entry	Acyl chloride	[Pd] (mol %)	Time (h)	Product	Yield[b] (%)
1[c]	 **1a**	0.002	36	 **3a**	93
2	 **1b**	0.01	6	 **3b**	96
3	 **1c**	0.01	6	 **3c**	85
4	 **1d**	0.01	6	 **3d**	87
5	 **1e**	0.02	1	 **3e**	77
6	 **1f**	0.02	6	 **3f**	90
7	 **1g**	0.02	6	 **3g**	88
8	 **1h**	0.02	0.5	 **3h**	94
9	 **1i**	0.02	1	 **3i**	86
10	 **1j**	0.02	9	 **3j**	86
11[d]	 **1k**	0.1	24	 **3k**	58

[a] Reaction conditions: in Et_3N at 50 °C. [acyl chloride]:[phenylacetylene]=1.3:1. [NS-MCM-41–Pd]:[PPh_3]:[CuI]=1:2:2.
[b] Isolated yields.
[c] 150 mmol of phenylacetylene was used.
[d] Diisopropylethylamine was used as both base and solvent.

reactions. For the recycle experiment, we used cyclohexanecarbonyl chloride **1h** and phenylacetylene **2a** as the representative reactants in the presence of 0.1 mol % NS-MCM-41–Pd to study the recyclability of this heterogeneous catalyst (see Section 4.3). After a reaction time of 0.5 h at 50 °C, the mixture from the first-run reaction was centrifuged and the solid obtained was washed alternately with 3 N HCl and THF twice. After drying under vacuum, the recovered NS-MCM-41–Pd was then re-used in the same reaction under identical conditions. We found that the product yield decreased slightly from 98 to 90% over four recycling runs (Scheme 2). This slight decrease in the activity of NS-MCM-41–Pd indicated a high stability upon workup and excellent recyclability of this mesoporous supported catalyst. After our analysis of this recovered catalyst by ICP-MASS, the amount of Pd in the catalyst is still 0.15 mmol/g. The slight decrease of activity is presumably due to the gradual deactivation of the catalyst in the nanopores.

3. Conclusion

In conclusion, we have shown that NS-MCM-41–Pd is a highly-efficient and recyclable catalyst for the coupling of a variety of acyl chlorides and terminal alkynes leading to the formation of ynones. The catalyst can be easily recycled by centrifugation and reused several times with only a slight decrease in activity. Furthermore, this method involves reactants on a large scale (up to 150 mmol) with a very low catalyst loading (0.002–0.1 mol % Pd), rendering it suitable for practically synthetic application of very high yield. Further studies are in progress to develop new carbon–carbon bond-forming reactions catalyzed with this recyclable catalytic system.

4. Experimental

4.1. General

All reactions involving air- and moisture-sensitive conditions were carried out in a dry nitrogen atmosphere. The chemicals were purchased from commercial suppliers and were used without further purification. THF, 1,4-dioxane, DME, and toluene were distilled from sodium benzophenone ketyl. Et_3N and diisopropylethylamine were dried over KOH and then distilled. 4,4′-Bis(bromomethyl)-2,2′-bipyridine,[13] $PdCl_2(PhCN)_2$,[14] and nanosized MCM-41[15] were prepared according to known procedures. The detailed procedure for the preparation of NS-MCM-41–Pd was reported in our previously published paper.[6g,9] Melting points were recorded using

Table 3
NS-MCM-41–Pd-catalyzed coupling of acyl chlorides with aromatic terminal alkynes[a]

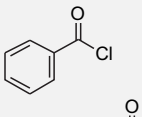
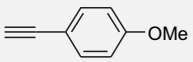
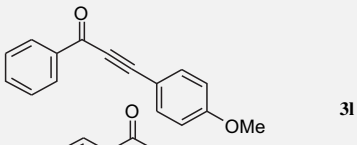
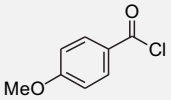
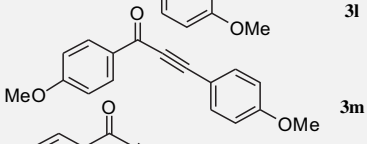
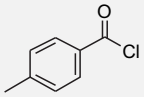
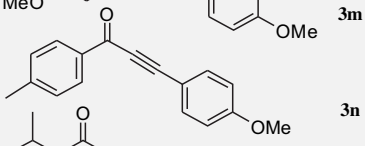
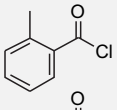
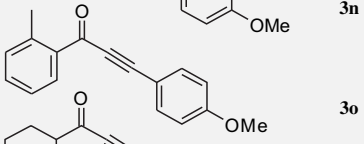
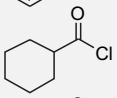
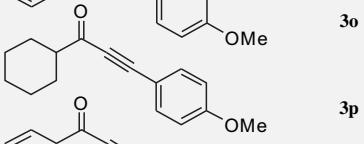
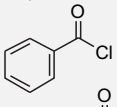
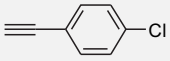
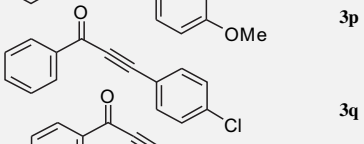
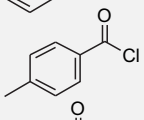
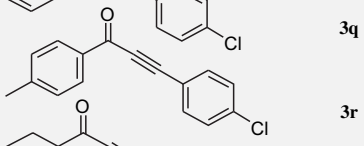
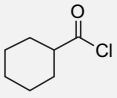
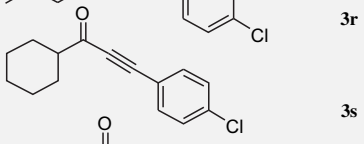
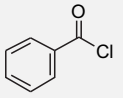
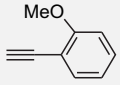
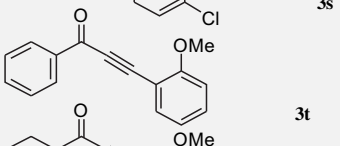
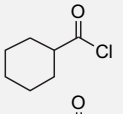
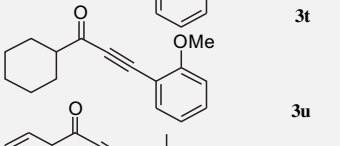
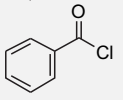
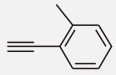
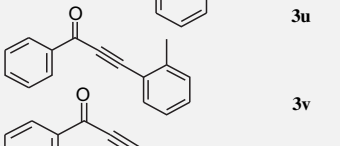
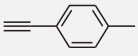
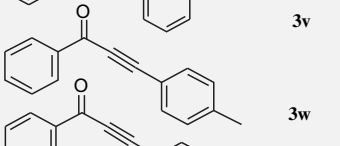
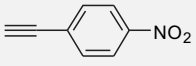
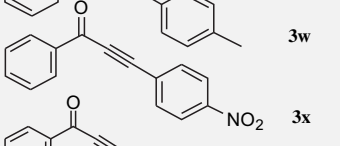
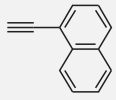
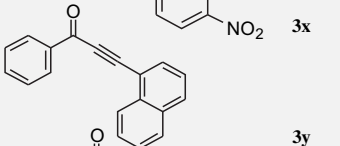
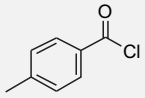
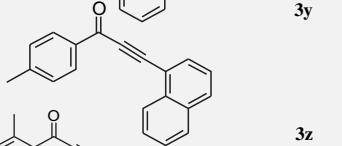
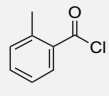
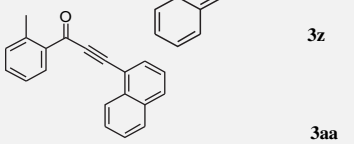
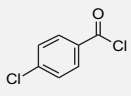
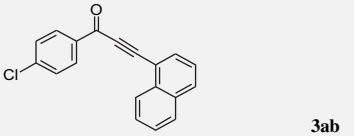
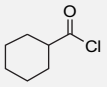
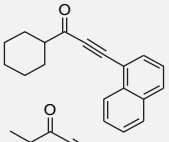
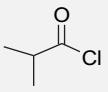
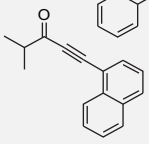
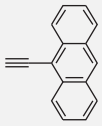
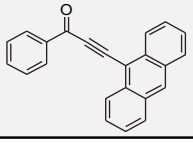
Entry	Acyl chloride	Alkyne	[Pd] (mol %)	Time (h)	Product	Yield[b] (%)
1	 **1a**	 **2b**	0.02	3	 **3l**	90
2	 **1b**	**2b**	0.02	3	 **3m**	88
3	 **1c**	**2b**	0.02	3	 **3n**	80
4	 **1d**	**2b**	0.02	1	 **3o**	85
5	 **1h**	**2b**	0.02	1	 **3p**	91
6	 **1a**	 **2c**	0.02	3	 **3q**	92
7	 **1c**	**2c**	0.02	3	 **3r**	95
8	 **1h**	**2c**	0.02	1	 **3s**	85
9	 **1a**	 **2d**	0.02	6	 **3t**	90
10	 **1h**	**2d**	0.02	3	 **3u**	83
11	 **1a**	 **2e**	0.02	6	 **3v**	85
12	**1a**	 **2f**	0.02	3	 **3w**	88
13	**1a**	 **2g**	0.02	3	 **3x**	74
14	**1a**	 **2h**	0.02	3	 **3y**	93
15	 **1c**	**2h**	0.02	3	 **3z**	91
16	 **1d**	**2h**	0.02	3	 **3aa**	84
17	 **1e**	**2h**	0.02	3	 **3ab**	87

Table 3 (*continued*)

Entry	Acyl chloride	Alkyne	[Pd] (mol %)	Time (h)	Product	Yield[b] (%)
18	 **1h**	**2h**	0.02	3	 **3ac**	85
19	 **1i**	**2h**	0.02	1	 **3ad**	88
20	**1i**	 **2i**	0.02	9	 **3ae**	25

[a] Reaction conditions: in Et_3N at 50 °C. [acyl chloride]:[terminal alkyne]=1.3:1. [NS-MCM-41–Pd]:[PPh_3]:[CuI]=1:2:2.
[b] Isolated yields.

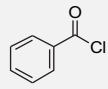
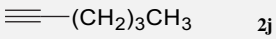
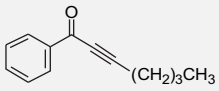
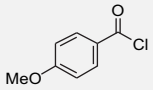
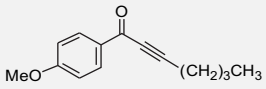
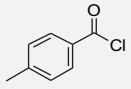
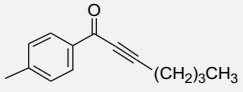
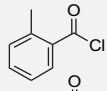
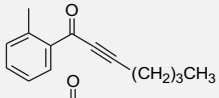
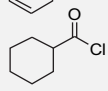
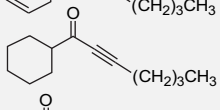
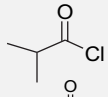
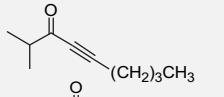
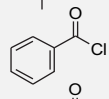
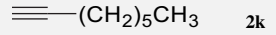
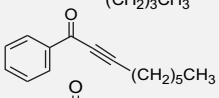
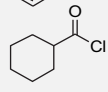
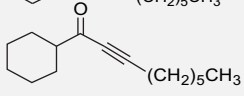
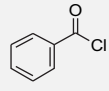
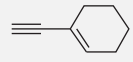
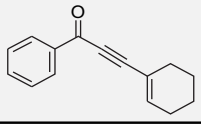
melting point apparatus and were uncorrected. All ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ or C_6D_6 solutions at 25 °C on Varian 200 NMR spectrometers. GC analysis was performed on an SRI 8610C equipped with a fused silica capillary column.

4.2. General procedure for the coupling of acid chlorides and terminal alkynes

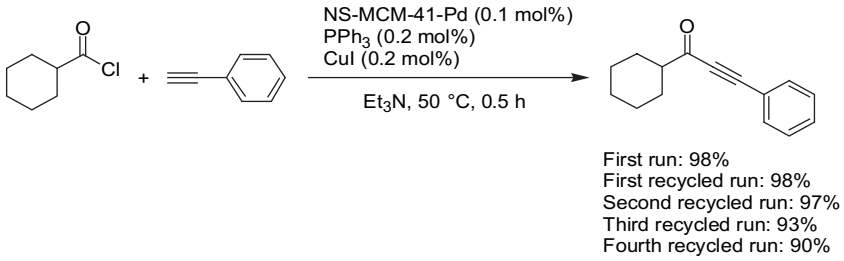
Under a nitrogen atmosphere, a Schlenk tube was charged with NS-MCM-41–Pd (20 mg, 0.003 mmol, in the case of 0.02 mol % catalyst loading), PPh_3 (1.6 mg, 0.006 mmol), CuI (1.1 mg, 0.006 mmol), Et_3N (20 mL), terminal alkyne (15 mmol), and acyl chloride (19.5 mmol), then the reaction mixture was stirred at 50 °C for the indicated reaction time period (see Tables 2–4). After cooling to room temperature, the resulting solution was passed through a short silica gel column using EtOAc as the eluent to remove the ammonium salt. The solvent was then removed in a vacuum and the desired product was purified by silica gel column chromatography.

*4.2.1. 1,3-Diphenylpropynone (**3a**).* Yellow liquid.[3e] ^1H NMR ($CDCl_3$, 200 MHz) δ 8.24 (d, J=8.3 Hz, 2H), 7.70 (d, J=7.7 Hz, 2H), 7.43–7.65

Table 4
NS-MCM-41–Pd-catalyzed coupling of acyl chlorides with aliphatic terminal alkynes[a]

Entry	Acyl chloride	Alkyne	[Pd] (mol %)	Time (h)	Product	Yield[b] (%)
1	 **1a**	 **2j**	0.1	6	 **4a**	86
2	 **1b**	**2j**	0.1	12	 **4b**	75
3	 **1c**	**2j**	0.1	12	 **4c**	79
4	 **1d**	**2j**	0.1	6	 **4d**	88
5	 **1h**	**2j**	0.1	3	 **4e**	82
6	 **1i**	**2j**	0.1	3	 **4f**	78
7	 **1a**	 **2k**	0.1	6	 **4g**	98
8	 **1h**	**2k**	0.1	6	 **4h**	63
9	 **1a**	 **2l**	0.1	6	 **4i**	84

[a] Reaction conditions: in Et_3N at 50 °C. [acyl chloride]:[terminal alkyne]=1.3:1. [NS-MCM-41–Pd]:[PPh_3]:[CuI]=1:2:2.
[b] Isolated yields.



Scheme 2. Recycling studies of the NS-MCM-41–Pd-catalyzed coupling of cyclohexanecarbonyl chloride with phenylacetylene.

(m, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 177.2, 136.3, 133.6 (2C), 132.6, 130.3, 129.1 (2C), 128.2 (2C), 128.1, 119.7, 92.9, 86.7.

*4.2.2. 1-(4-Methoxyphenyl)-3-phenylpropynone (**3b**).* Pale yellow solid. Mp 99–100 °C (lit.[16] 100–101 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.18 (d, J=8.8 Hz, 2H), 7.66 (d, J=8.0 Hz, 2H), 7.39–7.47 (m, 3H), 6.97 (d, J=8.8 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 175.2, 163.2, 131.6 (2C), 130.6 (2C), 129.3, 128.9, 127.3 (2C), 119.1, 112.6 (2C), 90.9, 85.7, 54.3.

*4.2.3. 3-Phenyl-1-p-tolylpropynone (**3c**).* Pale yellow solid. Mp 87–88 °C (lit.[17] 86–88 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.07 (d, J=8.2 Hz, 2H), 7.63 (d, J=7.2 Hz, 2H), 7.21–7.40 (m, 5H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 177.4, 145.1, 134.5, 132.8 (2C), 130.5, 129.5 (2C), 129.2 (2C), 128.5 (2C), 120.1, 92.4, 86.9, 21.7.

*4.2.4. 3-Phenyl-1-o-tolylpropynone (**3d**).* Yellow liquid.[18] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.30 (d, J=7.6 Hz, 1H), 7.64–7.69 (m, 3H), 7.26–7.52 (m, 5H), 2.68 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 178.2, 139.1, 134.4, 131.9, 131.6 (2C), 130.9, 129.3 (2C), 127.3 (2C), 124.6, 119.1, 90.5, 87.2, 20.7.

*4.2.5. 1-(4-Chlorophenyl)-3-phenylpropynone (**3e**).* Pale yellow solid. Mp 105–106 °C (lit.[16] 107–108 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.16 (d, J=8.8 Hz, 2H), 7.70 (d, J=7.9 Hz, 2H), 7.52–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 176.4, 140.6, 135.3, 132.9 (2C), 130.8, 130.7 (2C), 128.8 (2C), 128.6 (2C), 119.8, 93.5, 86.5.

*4.2.6. 1-Furan-2-yl-3-phenylpropynone (**3f**).* Brown solid. Mp 50–51 °C (lit.[2a] 49–51 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.64–7.71 (m, 3H), 7.38–7.50 (m, 4H), 6.62 (dd, J=3.8, 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 164.7, 153.2, 147.9, 132.9 (2C), 130.8, 128.6 (2C), 120.8, 119.9, 112.6, 91.8, 86.2.

*4.2.7. 3-Phenyl-1-thiophen-2-yl-propynone (**3g**).* Brown solid. Mp 55–56 °C (lit.[3g] 53–54 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.00–8.03 (m, 1H), 7.65–7.75 (m, 3H), 7.38–7.49 (m, 3H), 7.17–7.21 (m, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 169.6, 144.8, 135.1, 134.9, 132.9 (2C), 130.7, 128.6 (2C), 128.2, 119.8, 91.6, 86.4.

*4.2.8. 1-Cyclohexyl-3-phenylpropynone (**3h**).* Yellow liquid.[2a] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.60 (d, J=7.6 Hz, 2H), 7.36–7.49 (m, 3H), 2.44–2.57 (m, 1H), 2.03–2.09 (m, 2H), 1.20–1.87 (m, 8H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 189.9, 131.6 (2C), 129.2, 127.2 (2C), 118.9, 89.9, 85.9, 50.9, 27.1 (2C), 24.5, 24.1 (2C).

*4.2.9. 4-Methyl-1-phenylpent-1-yn-3-one (**3i**).* Yellow liquid.[2a] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.60 (d, J=7.9 Hz, 2H), 7.34–7.46 (m, 3H), 2.77 (hep, J=6.8 Hz, 1H), 1.27 (d, J=6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 191.3, 132.4 (2C), 130.2, 128.4 (2C), 119.7, 91.1, 86.5, 42.7, 17.1 (2C).

*4.2.10. 4,4-Dimethyl-1-phenylpent-1-yn-3-one (**3j**).* Yellow liquid.[2a] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.56–7.61 (m, 2H), 7.38–7.46 (m, 3H), 1.28 (s, 9H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 193.9, 132.8 (2C), 130.4, 128.5 (2C), 120.2, 92.1, 85.9, 44.8, 26.1 (3C).

*4.2.11. 1-Phenylhept-1-yn-3-one (**3k**).* Yellow liquid.[19] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.56–7.61 (m, 2H), 7.33–7.46 (m, 3H), 2.67 (t, J=7.4 Hz, 2H), 1.66–1.81 (m, 2H), 1.26–1.49 (m, 2H), 0.95 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 187.9, 132.8 (2C), 130.5, 128.5 (2C), 120.1, 90.4, 87.8, 45.2, 29.2, 22.1, 13.7.

*4.2.12. 3-(4-Methoxyphenyl)-1-phenylpropynone (**3l**).* Pale yellow solid. Mp 81–83 °C (lit.[16] 81–82 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.20 (d, J=8.4 Hz, 2H), 7.46–7.65 (m, 5H), 6.90 (d, J=8.4 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 177.8, 161.6, 136.9, 134.9 (2C), 133.7, 129.3 (2C), 128.4 (2C), 114.3 (2C), 111.7, 94.2, 86.8, 55.3.

*4.2.13. 1,3-Bis-(4-methoxyphenyl)propynone (**3m**).* Pale yellow solid. Mp 73–75 °C (lit.[20] 72–77 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.20 (d, J=8.8 Hz, 2H), 7.99 (d, J=8.8 Hz, 2H), 7.64 (d, J=8.3 Hz, 2H), 6.96 (d, J=8.3 Hz, 2H), 3.90 (s, 3H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 176.5, 164.2, 161.4, 134.8 (2C), 131.6 (2C), 128.5, 119.6, 114.3 (2C), 113.7 (2C), 93.2, 86.7, 55.3, 55.2.

*4.2.14. 3-(4-Methoxyphenyl)-1-p-tolylpropynone (**3n**).* Pale yellow solid. Mp 93–94 °C (lit.[20] 93.5–94.5 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.09 (d, J=8.4 Hz, 2H), 7.62 (d, J=8.4 Hz, 2H), 7.28 (d, J=8.2 Hz, 2H), 6.91 (d, J=8.4 Hz, 2H), 3.84 (s, 3H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 177.6, 161.5, 144.8, 134.9 (2C), 129.5 (2C), 129.2 (2C), 128.6, 114.3 (2C), 111.9, 93.6, 86.8, 55.3, 21.7.

*4.2.15. 3-(4-Methoxyphenyl)-1-o-tolylpropynone (**3o**).* Yellow liquid. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.39 (d, J=8.4 Hz, 1H), 7.85–7.38 (m, 5H), 7.04 (d, J=8.4 Hz, 2H), 3.98 (s, 3H), 2.79 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 179.7, 161.4, 140.0, 135.9, 134.7 (2C), 132.7, 132.5, 131.9, 128.7, 125.7, 114.3 (2C), 92.8, 88.3, 55.3, 21.7. HRMS Calcd for $C_{17}H_{14}O_2$: 250.0994; found: 250.0986.

*4.2.16. 1-Cyclohexyl-3-(4-methoxyphenyl)propynone (**3p**).* Yellow liquid.[21] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.51 (d, J=8.6 Hz, 2H), 6.78 (d, J=8.6 Hz, 2H), 3.82 (s, 3H), 2.41–2.52 (m, 1H), 2.01–2.06 (m, 2H), 1.29–1.77 (m, 8H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 189.9, 160.2, 133.6 (2C), 113.0 (2C), 110.6, 91.1, 85.8, 54.0, 50.9, 27.1 (2C), 24.6, 24.1 (2C).

*4.2.17. 3-(4-Chlorophenyl)-1-phenylpropynone (**3q**).* Pale yellow solid. Mp 107–108 °C (lit.[16] 105–106 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.21 (d, J=8.4 Hz, 2H), 7.49–7.69 (m, 5H), 7.41 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 177.5, 137.1, 136.6, 134.1 (3C), 129.4 (2C), 129.0 (2C), 128.5 (2C), 118.5, 91.5, 87.5.

*4.2.18. 3-(4-Chlorophenyl)-1-p-tolylpropynone (**3r**).* Pale yellow solid. Mp 135–137 °C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.08 (d, J=8.2 Hz, 2H), 7.60 (d, J=8.6 Hz, 2H), 7.39 (d, J=8.6 Hz, 2H), 7.30 (d, J=8.2 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 177.2, 154.2, 136.9, 134.4,

134.1 (2C), 129.5 (2C), 129.3 (2C), 128.9 (2C), 118.6, 90.0, 87.6, 21.7; Anal. Calcd for $C_{16}H_{11}ClO$: C, 75.45, H, 4.35; Found: C, 75.44, H, 4.84.

*4.2.19. 3-(4-Chlorophenyl)-1-cyclohexylpropynone (**3s**).* Pale yellow solid. Mp 50–52 °C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.51 (d, J=8.6 Hz, 2H), 7.37 (d, J=8.6 Hz, 2H), 2.43–2.57 (m, 1H), 2.02–2.08 (m, 2H), 1.19–1.84 (m, 8H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 190.9, 136.7, 134.0 (2C), 128.9 (2C), 118.6, 89.6, 78.8, 52.2, 28.2 (2C), 25.7, 25.3 (2C); Anal. Calcd for $C_{15}H_{15}ClO$: C, 73.02, H, 6.13; Found: C, 72.58, H, 6.21.

*4.2.20. 3-(2-Methoxyphenyl)-1-phenylpropynone (**3t**).* Pale yellow solid. Mp 74–75 °C (lit.[22] 72–73.5 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.32 (d, J=7.0 Hz, 2H), 7.42–7.67 (m, 5H), 6.94–7.04 (m, 2H), 3.98 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 177.9, 161.7, 137.1, 134.8, 133.7, 132.5, 129.6 (2C), 128.4 (2C), 120.6, 110.8, 109.4, 91.2, 90.5, 55.8.

*4.2.21. 1-Cyclohexyl-3-(2-methoxyphenyl)propynone (**3u**).* Yellow liquid. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.51 (d, J=8.5 Hz, 2H), 7.36 (d, J=8.5 Hz, 2H), 7.26–7.29 (m, 2H), 3.92 (s, 3H), 2.45–2.56 (m, 1H), 2.02–2.18 (m, 2H), 1.26–1.80 (m, 8H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 191.3, 161.4, 134.7, 132.2, 120.4, 110.7, 109.3, 91.3, 88.7, 55.7, 55.3, 28.3 (2C), 25.8, 25.3 (2C). HRMS Calcd for $C_{16}H_{18}O_2$: 242.1307; found: 242.1319.

*4.2.22. 1-Phenyl-3-o-tolylpropynone (**3v**).* Yellow liquid.[23] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.24 (d, J=8.2 Hz, 2H), 7.48–7.68 (m, 5H), 7.28–7.37 (m, 2H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 177.6, 141.9, 136.8, 133.8, 133.4, 130.6, 129.7, 129.2 (2C), 128.4 (2C), 125.7, 119.8, 91.9, 90.6, 20.6.

*4.2.23. 1-Phenyl-3-p-tolylpropynone (**3w**).* Pale yellow solid. Mp 68–69 °C (lit.[16] 67–68 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.21 (d, J=8.0 Hz, 2H), 7.51–7.62 (m, 5H), 7.22 (d, J=8.0 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 177.8, 141.4, 136.9, 133.9, 132.9 (2C), 129.5 (2C), 129.3 (2C), 128.5 (2C), 116.9, 93.7, 86.7, 21.7.

*4.2.24. 3-(4-Nitrophenyl)-1-phenylpropynone (**3x**).* Orange solid. Mp 146–148 °C (lit.[16] 148–150 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.31 (d, J=9.0 Hz, 2H), 8.21 (d, J=7.0 Hz, 2H), 7.85 (d, J=9.0 Hz, 2H), 7.51–7.72 (m, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 177.3, 148.5, 136.3, 134.6, 133.6 (2C), 129.5 (2C), 128.7 (2C), 126.7, 123.7 (2C), 89.8, 89.1.

*4.2.25. 3-Naphthalen-1-yl-1-phenylpropynone (**3y**).* Pale yellow solid.[3e] Mp 81–83 °C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.41 (d, J=8.4 Hz, 1H), 8.31 (d, J=8.0 Hz, 2H), 7.93–7.97 (m, 2H), 7.87 (d, J=8.4 Hz, 1H), 7.48–7.67 (m, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 177.2, 136.5, 133.7, 133.2, 132.7, 132.6, 131.1, 129.2 (2C), 128.3 (2C), 128.2, 127.3, 126.5, 125.4, 124.8, 117.3, 91.5, 91.3.

*4.2.26. 3-Naphthalen-1-yl-1-p-tolylpropynone (**3z**).* Pale yellow solid. Mp 80–81 °C (lit.[24] 78–80 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.42 (d, J=8.0 Hz, 1H), 8.20 (d, J=8.2 Hz, 2H), 7.88–7.99 (m, 3H), 7.48–7.69 (m, 3H), 7.35 (d, J=8.2 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 178.6, 145.1, 134.7, 133.5, 133.1, 132.9, 131.2, 129.6 (2C), 129.3 (2C), 128.5, 127.6, 126.8, 125.7, 125.1, 117.8, 91.7, 90.8, 21.8.

*4.2.27. 3-Naphthalen-1-yl-1-o-tolylpropynone (**3aa**).* Pale yellow solid. Mp 72–73 °C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.37–8.44 (m, 2H), 7.86–7.97 (m, 3H), 7.28–7.67 (m, 6H), 2.72 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 179.5, 140.3, 135.8, 133.6, 132.9, 132.7, 132.1, 131.8, 131.1, 128.4, 127.5, 126.7, 125.8, 125.7, 124.9, 124.8, 117.8, 93.1, 90.1, 21.8. HRMS Calcd for $C_{20}H_{14}O$: 270.1045; found: 270.1040.

*4.2.28. 1-(4-Chlorophenyl)-3-naphthalen-1-ylpropynone (**3ab**).* Pale yellow solid. Mp 116–117 °C (lit.[17] 115–116 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.39 (d, J=8.2 Hz, 1H), 8.24 (d, J=8.6 Hz, 2H), 7.91–8.11 (m, 3H), 7.57–7.75 (m, 5H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 176.4, 140.6, 135.4, 133.5, 133.2, 133.1, 131.6, 130.7 (2C), 128.9 (2C), 128.5, 127.7, 126.9, 125.6, 125.1, 117.4, 91.9, 91.3.

*4.2.29. 1-Cyclohexyl-3-naphthalen-1-ylpropynone (**3ac**).* Pale yellow solid. Mp 55–56 °C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.30 (d, J=8.2 Hz, 1H), 7.80–7.96 (m, 3H), 7.23–7.67 (m, 3H), 2.48–2.61 (m, 1H), 2.10–2.15 (m, 2H), 1.23–1.87 (m, 8H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 191.1, 136.5, 133.5, 132.9, 131.1, 128.4, 127.5, 126.7, 125.6, 125.1, 117.7, 91.9, 89.5, 52.4, 28.4 (2C), 25.8, 25.4 (2C). HRMS Calcd for $C_{19}H_{18}O$: 262.1358; found: 262.1350.

*4.2.30. 4-Methyl-1-naphthalen-1-ylpent-1-yn-3-one (**3ad**).* Yellow liquid. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.33 (d, J=8.0 Hz, 1H), 7.84–7.98 (m, 3H), 7.44–7.65 (m, 3H), 2.88 (hep, J=6.8 Hz, 1H), 1.35 (d, J=6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 190.6, 132.3, 131.8, 130.1, 129.6, 127.2, 126.3, 125.6, 124.4, 123.8, 116.4, 90.3, 88.5, 41.9, 16.9 (2C). HRMS Calcd for $C_{16}H_{14}O$: 222.1045; found: 222.1040.

*4.2.31. 3-Anthracen-9-yl-1-phenylpropynone (**3ae**).* Yellow solid. Mp 113–116 °C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.64 (d, J=9.0 Hz, 2H), 8.60 (s, 1H), 8.28–8.41 (m, 5H), 8.06 (d, J=8.4 Hz, 2H), 7.52–7.78 (m, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 177.8, 137.3, 133.9 (2C), 131.1, 130.9 (2C), 129.6 (2C), 128.9 (2C), 128.7 (2C), 127.9 (2C), 127.1, 126.1 (2C), 115.9 (2C), 113.4, 98.2, 90.3. HRMS Calcd for $C_{23}H_{14}O$: 306.1045; found: 306.1054.

*4.2.32. 1-Phenylhept-2-yn-1-one (**4a**).* Pale yellow liquid.[2a] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.09–8.11 (m, 2H), 7.42–7.58 (m, 3H), 2.47 (d, J=7.2 Hz, 2H), 1.45–1.82 (m, 4H), 0.93 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 177.4, 136.3, 133.3, 129.1 (2C), 127.9 (2C), 96.6, 79.5, 30.1, 22.4, 19.2, 13.9.

*4.2.33. 1-(4-Methoxyphenyl)hept-2-yn-1-one (**4b**).* Pale yellow liquid.[25] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.11 (d, J=8.6 Hz, 2H), 6.95 (d, J=8.6 Hz, 2H), 3.88 (s, 3H), 2.50 (t, J=6.8 Hz, 2H), 1.41–1.74 (m, 4H), 0.97 (t, J=7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 176.7, 164.1, 131.7 (2C), 130.2, 113.6 (2C), 95.7, 79.5, 55.4, 29.8, 21.9, 18.7, 13.4.

*4.2.34. 1-p-Tolylhept-2-yn-1-one (**4c**).* Pale yellow liquid.[25] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.01 (d, J=8.0 Hz, 2H), 7.25 (d, J=7.8 Hz, 2H), 2.47 (t, J=6.8 Hz, 2H), 2.40 (s, 3H), 1.42–1.68 (m, 4H), 0.94 (t, J=7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 177.6, 144.6, 134.5, 129.4 (2C), 128.9 (2C), 95.9, 79.6, 29.7, 21.9, 21.5, 18.7, 13.3.

*4.2.35. 1-o-Tolylhept-2-yn-1-one (**4d**).* Pale yellow liquid.[25] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.17 (d, J=7.6 Hz, 1H), 7.19–7.41 (m, 3H), 2.60 (s, 3H), 2.45 (t, J=7.1 Hz, 2H), 1.41–1.66 (m, 4H), 0.93 (t, J=7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 179.8, 140.1, 135.7, 132.9, 132.4, 131.9, 125.6, 95.2, 81.1, 29.8, 21.9, 21.7, 18.7, 13.4.

*4.2.36. 1-Cyclohexylhept-2-yn-1-one (**4e**).* Pale yellow liquid.[2a] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.38 (d, J=6.8 Hz, 2H), 1.22–1.99 (m, 15H), 0.93 (t, J=7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 191.3, 94.6, 80.0, 52.1, 29.7, 28.2 (2C), 25.7, 25.3 (2C), 21.8, 18.5, 13.3.

*4.2.37. 2-Methylnon-4-yn-3-one (**4f**).* Pale yellow liquid.[2a] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.62 (hep, J=7.0 Hz, 1H), 2.38 (t, J=6.9 Hz, 2H), 1.16–1.62 (m, 4H), 1.18 (d, J=7.0 Hz, 6H), 0.93 (t, J=7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 192.0, 94.9, 79.7, 42.9, 29.7, 21.8, 18.5, 17.9 (2C), 13.3.

*4.2.38. 1-Phenylnon-2-yn-1-one (**4g**).* Pale yellow liquid.[25] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.12–8.17 (m, 2H), 7.43–7.64 (m, 3H), 2.51 (t, J=6.8 Hz, 2H), 1.61–1.75 (m, 2H), 1.29–1.75 (m, 6H), 0.91 (t, J=6.6 Hz,

3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 177.5, 136.5, 133.4, 129.0 (2C), 128.0 (2C), 96.3, 79.3, 30.9, 28.2, 27.4, 22.1, 18.8, 13.6.

*4.2.39. 1-Cyclohexylnon-2-yn-1-one (**4h**).* Pale yellow liquid.[26] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.33–2.40 (m, 3H), 1.22–1.99 (m, 18H), 0.90 (t, J=7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 191.5, 94.8, 80.1, 52.2, 31.1, 28.4, 28.2 (2C), 27.7, 25.7, 25.3 (2C), 22.4, 18.9, 13.9.

*4.2.40. 3-Cyclohex-1-enyl-1-phenylpropynone (**4i**).* Pale yellow liquid.[3e] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.14 (d, J=8.2 Hz, 2H), 7.44–7.60 (m, 3H), 6.59 (m, 1H), 2.20–2.30 (m, 4H), 1.63–1.74 (m, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 177.8, 142.5, 136.8, 133.6, 129.2 (2C), 128.3 (2C), 118.9, 95.5, 85.0, 28.2, 26.0, 21.8, 20.9.

4.3. Experimental procedure for the recycling of NS-MCM-41–Pd

This procedure was conducted as described above: cyclohexanecarbonyl chloride (19.5 mmol), phenylacetylene (15 mmol), PPh_3 (7.9 mg, 0.03 mmol), CuI (5.7 mg, 0.03 mmol), NS-MCM-41-Pd (100 mg, 0.015 mmol), and Et_3N (20 mL) were used in this case, and the reaction time for each cycle was fixed at 0.5 h at 50 °C. After the reaction, the catalyst was collected by centrifugation, washed alternately with 3 N HCl aqueous solution and THF twice (20 mL for each wash), and dried in vacuum overnight. The recovered catalyst was then re-used in the same reaction under identical conditions. The product in each cycle was isolated from the collected solution by the usual workup procedures.

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