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MCM-41-supported bidentate phosphine palladium(0) complex: a highly active and recyclable catalyst for the Sonogashira reaction of aryl iodides

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Abstract—The first MCM-41-supported bidentate phosphine palladium(0) complex has been prepared. This complex is a highly efficient catalyst for Sonogashira reaction and can be reused at least 10 times without any decrease in activity.

1. Introduction

The Sonogashira reaction, the palladium-catalyzed cross-coupling of terminal alkynes with aryl and vinyl halides, is one of the most important, powerful, and versatile tools in organic synthesis and has been widely applied to diverse areas such as natural product synthesis and material science.[1] The reaction generally proceeds in the presence of a homogeneous palladium catalyst, which makes the catalyst recovery a tedious operation and might result in unacceptable palladium contamination of the product. From the standpoint of green chemistry, the development of more environmentally benign conditions for the reaction, for example, the use of a heterogeneous palladium catalyst would be desirable.[2] So far, cross-linked polystyrene or silica-supported palladium catalysts have been used for Sonogashira reaction.[3] Unfortunately, they often result in lower catalytic activity compared with their soluble counterparts. In addition, the activity of the recycled catalysts gradually decreases because the palladium species leaches from the supporting polymer or silica gel. To overcome these limitations, a novel methodology for creating insoluble and highly active catalysts is needed. Our approach was guided by three imperatives: the support should be easily accessible (1), starting from readily available and cheap reagents (2). The ligand anchored on the support should be air stable at room temperature, which should allow its storage in normal bottles with unlimited shelf life (3). Recent developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support for immobilization of homogeneous catalysts.[4] MCM-41 has a regular pore diameter of ca. 5 nm and a specific surface area $>700\ m^2\ g^{-1}$.[5] 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.[6–8] It is generally believed that high surface area of heterogeneous catalyst results in high catalytic activity. Considering the fact that MCM-41 support has an extremely high surface area and the catalytic palladium species is anchored on the inner surface of the mesopore of MCM-41 support, we expect that MCM-41-supported palladium catalyst will exhibit high activity and good reusability. To date, a few palladium complexes on functionalized MCM-41 support have been prepared and successfully used in organic reactions.[9–13] However, to the best of our knowledge, there has been no general study of Sonogashira coupling reaction catalyzed by a MCM-41-supported phosphine palladium complex described to date. In this paper, we wish to report the synthesis of the first MCM-41-supported bidentate phosphine palladium(0) complex [abbreviated as MCM-41-2P-Pd(0)] and its catalytic properties in the Sonogashira coupling reaction.

2. Results and discussion

Over the last few years, the *N*,*N*-bis(diphenylphosphinomethyl)amino-functionality has been used for the preparation of dendrimer bound and supramolecular homogeneous catalysts.[14] Just recently insoluble versions of this chelating phosphine ligand have been applied in Rh-catalyzed hydroformylation and Rh-catalyzed hydrogenation.[15] The first MCM-41-supported bidentate phosphine palladium(0) complex [MCM-41-2P-Pd(0)] was conveniently synthesized

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from commercially available and cheap γ-aminopropyltriethoxysilane via immobilization on MCM-41, followed by reacting with diphenylphosphinomethanol, which resulted from adduct formation between diphenylphosphine and paraformaldehyde, and palladium chloride and then the reduction with hydrazine monohydrate (Scheme 1).

XRD patterns of the parent MCM-41 and the modified materials MCM-41-2P and MCM-41-2P-Pd(0) are displayed in Figure 1. Small angle X-ray powder diffraction of the parent MCM-41 gave peaks corresponding to hexagonally ordered mesoporous phases. For MCM-41-2P and MCM-41-2P-Pd(0), the (100) reflection of the parent MCM-41 with decreased intensity was remained after functionalization, while the (110) and (200) reflections became weak and diffused, which could be due to contrast matching between the silicate framework and organic moieties, which are located inside the channels of MCM-41. These results indicated that the basic structure of the parent MCM-41 was not damaged in the whole process of catalyst preparation.

Elemental analyses and X-ray photoelectron spectroscopy (XPS) were used to characterize the MCM-41-supported bidentate phosphine palladium(0) complex. The phosphine and palladium content of the MCM-41-2P-Pd(0) was determined to be 1.15 and 0.52 mmol/g, respectively, and the P:Pd mole ratio of this complex was 2.21. The XPS data for MCM-41-2P, MCM-41-2P-Pd(II), MCM-41-2P-Pd(0), and $PdCl_2$ are listed in Table 1. It can be seen that the binding energies of N_{1s}, Si_{2p}, and O_{1s} of MCM-41-2P-Pd(II) are similar to those of MCM-41-2P, and the binding energy of Cl_{2p} of MCM-41-2P-Pd(II) is similar to that of $PdCl_2$. However, the difference of $Pd_{3d5/2}$ binding energies between MCM-41-2P-Pd(II) and $PdCl_2$ is 1.2 eV. The difference of P_{2p} binding energies between MCM-41-2P-Pd(II) and MCM-41-2P is 0.5 eV. These results suggest that a coordination bond between P and Pd is formed in the MCM-41-2P-Pd(II). The binding energy (336.2 eV) of $Pd_{3d5/2}$ of MCM-41-2P-Pd(0) was lower than the binding energy (336.9 eV) of $Pd_{3d5/2}$ of MCM-41-2P-Pd(II). The $Pd_{3d5/2}$ binding energy depends strongly on the nature of the ligands. Consequently, it is impossible to identify the reduced complex as a zerovalent one on the basis of its $Pd_{3d5/2}$ binding energy only. However, the binding energy of Cl_{2p} in the MCM-41-2P-Pd(0) cannot be detected, the shift (lower) of $Pd_{3d5/2}$ binding energy together with the change in color (from yellow to brown) suggests that the reduction of the starting palladium(II) complex to the lower valent state has taken place. The MCM-41-2P-Pd(0) complex catalyst formed is stable in air, but for prolonged storage it is better stored under an atmosphere of argon in which case no decomposition and deactivation are noted over the period of six months at room temperature.

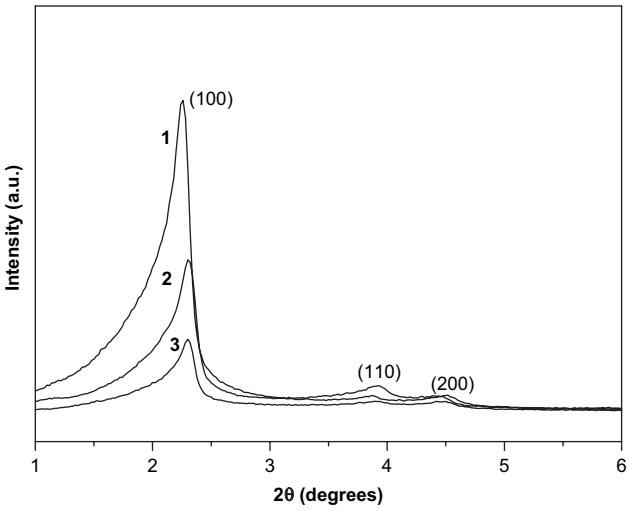
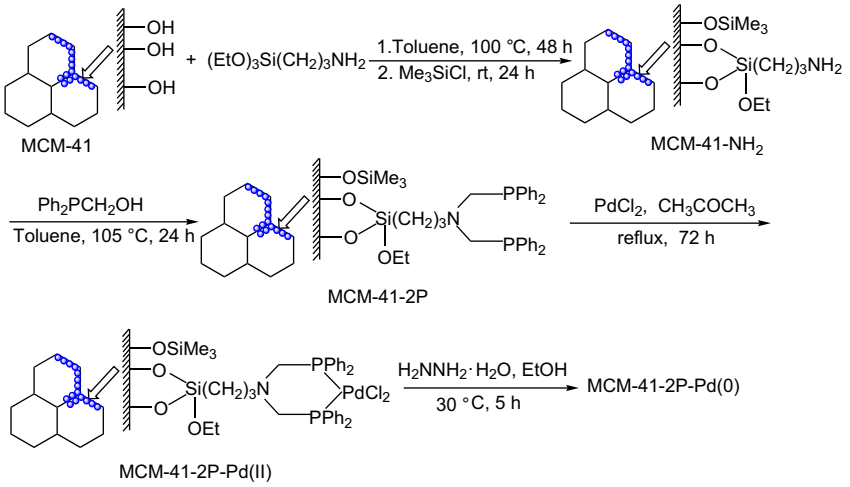


Figure 1. XRD profiles of the parent MCM-41 (**1**), MCM-41-2P (**2**), and MCM-41-2P-Pd(0) (**3**).

Table 1. XPS data for MCM-41-2P, MCM-41-2P-Pd(II), MCM-41-2P-Pd(0) and $PdCl_2$[a]

Sample	$Pd_{3d5/2}$	P_{2p}	N_{1s}	Si_{2p}	O_{1s}	Cl_{2p}
MCM-41-2P-Pd(0)	336.2	131.9	399.4	103.2	533.1	
MCM-41-2P-Pd(II)	336.9	131.7	399.2	103.3	533.0	199.3
MCM-41-2P		132.2	399.3	103.2	533.1	
$PdCl_2$	338.1					199.2

[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.



Scheme 1.

In order to evaluate the catalytic activity of the first MCM-41-supported bidentate phosphine palladium(0) complex [MCM-41-2P-Pd(0)], the Sonogashira reactions of terminal alkynes with aryl iodides were studied. The reactions were performed under conditions similar to those used in the corresponding homogeneous reactions. The influences of bases, solvents, and amounts of the catalyst on catalytic property of the MCM-41-2P-Pd(0) complex were investigated by using coupling reaction of iodobenzene with 1-hexyne. The results are shown in Table 2. It was found that among the bases tested, piperidine proved to be the most efficient. Among the solvents used, piperidine was also the best choice. Increasing the amount of palladium catalyst could shorten the reaction time, but did not increase the yield of 1-phenyl-1-hexyne (entry 12). The low palladium concentration usually led to a long period of reaction, which was consistent with our experimental results (entries 13 and 14). Taken together, excellent result was obtained when the coupling reaction was carried out with 0.5 mol % of MCM-41-2P-Pd(0) and 5 mol% of CuI in piperidine at room temperature (entry 9).

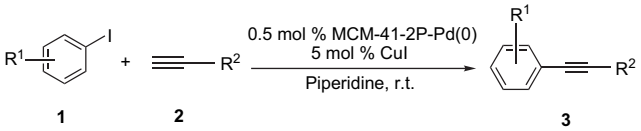
To examine the scope for this coupling reaction, a variety of terminal alkynes were coupled with various aryl iodides in piperidine in the presence of a catalytic amounts of MCM-41-2P-Pd(0) and CuI at room temperature (Scheme 2). The experimental results are summarized in Table 3. As shown in Table 3, the Sonogashira coupling reactions of aryl iodides with a variety of terminal alkynes proceeded smoothly under very mild conditions giving the corresponding coupling products in excellent yields. The coupling reaction of aryl iodides with terminal alkynes catalyzed by polystyrene-supported phosphine palladium complex was also very high yielding, but it was necessary to pre-soak the catalyst with a large amount of solvent and a higher temperature (60 °C) was required.[3f] The optimized catalyst system was quite general and tolerant of a range of functional groups. For the electron-deficient aryl iodides, the coupling reactions were rapidly completed within 1.5 h, and the others required slightly longer reaction times. The coupling reactions of phenyl bromide with terminal alkynes were very slow under the same conditions giving traces of cross-coupling products after 24 h of reaction time and the coupling reactions of phenyl chloride with terminal alkynes did not occur at all. To further illustrate that bromoarenes were inert in the reaction system, the coupling reaction of 4-nitrobromobenzene with phenylacetylene was performed at 100 °C, it was found that only trace of 1-(4-nitrophenyl)-2-phenylethyne was obtained and considerable amount of homocoupling product of phenylacetylene was formed. The similar observation was made by other groups using heterogeneous palladium catalysts in Sonogashira reactions.[3] In all reactions, only 0.5 mol% of MCM-41-2P-Pd(0) based on the aryl iodides was used, the molar turnover numbers (TON) were larger than those in the corresponding coupling reaction catalyzed by other heterogeneous catalysts reported.[3]

The novel MCM-41-supported bidentate phosphine palladium(0) catalyst can be easily recovered by simple filtration. We also examined the reuse of the catalyst by using the coupling reaction of iodobenzene with 1-hexyne. 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. However, when the reaction of iodobenzene with 1-hexyne was performed even with 0.5 mol % of MCM-41-2P-Pd(0), the catalyst could be recycled 10 times without any loss of activity. The reaction promoted by the 10 th recycled catalyst gave **3n** in 96% yield (Table 4, entry 2). The average yield of **3n** in consecutive reactions promoted by the 1–10 times recycled catalyst was 97% (entry 3). The result is important from a practical point of view. The

Table 2. Sonogashira reaction of iodobenzene with 1-hexyne in the presence of several bases and solvents[a]

Entry	Base	Solvent	MCM-41-2P-Pd(0) (mol%)	Time (h)	Yield[b] (%)
1	Et_3N	Toluene	0.5	10	76
2	Et_3N	DMF	0.5	6	81
3	Et_3N	Dioxane	0.5	7	80
4	Et_3N	Et_3N	0.5	3	85
5	$BuNH_2$	DMF	0.5	7	82
6	$BuNH_2$	Dioxane	0.5	6	78
7	$BuNH_2$	$BuNH_2$	0.5	3	86
8	Piperidine	DMF	0.5	5	88
9	Piperidine	Piperidine	0.5	2	98
10	Pyrrolidine	DMF	0.5	5	86
11	Pyrrolidine	Pyrrolidine	0.5	2	94
12	Piperidine	Piperidine	1.0	1	96
13	Piperidine	Piperidine	0.1	7	92
14	Piperidine	Piperidine	0.05	24	88

[a] All reactions were performed using 1.0 mmol of iodobenzene, 1.5 mmol of 1-hexyne, 0.05 mmol of CuI, and 3.0 mmol of base in 3 mL of solvent at room temperature under Ar.
[b] Isolated yield based on the iodobenzene used.



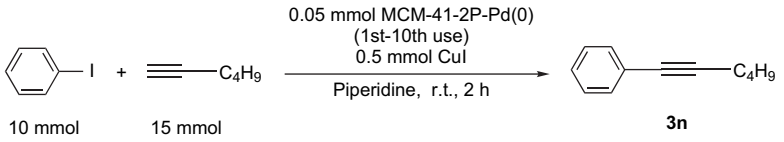
Scheme 2.

Table 3. Sonogashira reactions of terminal alkynes with aryl iodides[a]

Entry	R^1	R^2	Time (h)	Product	Yield[b] (%)
1	H	Ph	2	**3a**	94
2	4-CH_3	Ph	2.5	**3b**	95
3	4-Cl	Ph	1.5	**3c**	97
4	4-O_2N	Ph	1.5	**3d**	95
5	3-O_2N	Ph	1.5	**3e**	98
6	4-CH_3CO	Ph	1.5	**3f**	96
7	2-CF_3	Ph	2.5	**3g**	89
8	3-CN	Ph	2	**3h**	95
9	H	Me_3Si	2	**3i**	96
10	4-CH_3O	Me_3Si	3	**3j**	93
11	4-Cl	Me_3Si	1.5	**3k**	97
12	H	CH_3OCH_2	2	**3l**	94
13	4-Cl	CH_3OCH_2	1.5	**3m**	95
14	H	n-C_4H_9	2	**3n**	98
15	4-O_2N	n-C_4H_9	1.5	**3o**	97
16	3-CN	n-C_4H_9	2	**3p**	95
17	2-CF_3	n-C_4H_9	2.5	**3q**	90
18	H	4-$CH_3OC_6H_4$	2	**3r**	94
19	4-CH_3	4-BrC_6H_4	2.5	**3s**	93

[a] All reactions were performed using 1.0 mmol of **1**, 1.5 mmol of **2**, 0.005 mmol of MCM-41-2P-Pd(0), and 0.05 mmol of CuI in 3 mL of piperidine at room temperature under Ar.
[b] Isolated yield based on **1** used.

Table 4. Sonogashira reaction of iodobenzene with 1-hexyne catalyzed by recycled catalyst



Entry	Catalyst cycle	Isolated yield (%)	TON
1	First	98	196
2	Tenth	96	192
3	First to tenth consecutive	av 97	Total of 1940

possible reasons without palladium leaching from the MCM-41-2P-Pd(0) catalyst may be (1) the heterogeneous MCM-41-2P-Pd(0) catalyst was a highly stable phosphine palladium complex due to the chelating action of the bidentate phosphine ligand on palladium. (2) The catalytic palladium species was anchored on the inner surface of the mesopore of MCM-41 support; so there was no strong complexing and solvolytic action of the solvent. (3) Cleavages of the Si–O and P–Pd bonds of MCM-41-2P-Pd(0) were not so easy since the coupling reaction was performed at room temperature. The high catalytic activity, excellent reusability, and the easy accessibility of the MCM-41-2P-Pd(0) make the catalyst a highly attractive supported palladium catalyst for the parallel solution phase synthesis of diverse libraries of compounds.

3. Conclusions

In summary, we have developed a new reusable heterogeneous catalyst, MCM-41-2P-Pd(0), prepared from commercially available and cheap γ-aminopropyltriethoxysilane via amino-functionalization of MCM-41, followed by reacting with diphenylphosphinomethanol and palladium chloride and then the reduction with hydrazine monohydrate. It efficiently catalyzed the heterogeneous Sonogashira coupling reaction of terminal alkynes with aryl iodides and can be reused 10 times without any decrease in its catalytic activity. The advantages of our heterogeneous catalytic system over others are as follows: (1) the heterogeneous MCM-41-2P-Pd(0) catalyst can be conveniently prepared from commercially available reagents; (2) the reaction conditions are very mild, i.e., only 0.5 mol% palladium catalyst and room temperature; (3) excellent performance and reusability of the catalyst.

4. Experimental

4.1. Materials

All chemicals were reagent grade and used as purchased. The mesoporous material MCM-41 was prepared according to the literature procedure.[16] All reactions were performed under an inert atmosphere of dry argon using distilled dried solvents. 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. ^{1}H NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with TMS as an internal standard and $CDCl_3$ as a solvent. ^{13}C NMR spectra were recorded on a Bruker AC-P400 (100 MHz) spectrometer in $CDCl_3$ as solvent. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyzer. X-ray powder diffraction patterns were obtained on Damx-rA (Rigaka). X-ray photoelectron spectra were recorded on XSAM 800 (Kratos).

4.2. Preparation of MCM-41-NH_2

A solution of γ-aminopropyltriethoxysilane (2.20 g, 10 mmol) in dry chloroform (18 mL) was added to a suspension of the mesoporous support MCM-41 (2.80 g) in dry toluene (180 mL). The mixture was stirred for 48 h at 100 °C. Then the solid was filtered and washed with $CHCl_3$ (2×20 mL), and dried in vacuum at 160 °C for 5 h. The dried white solid was then soaked in a solution of Me_3SiCl (4.36 g, 40 mmol) in dry toluene (150 mL) 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 in vacuum at 120 °C for 5 h to obtain 3.54 g of hybrid material MCM-41-NH_2. The nitrogen content was found to be 1.27 mmol/g by elemental analysis.

4.3. Preparation of MCM-41-2P

A Schlenk flask was charged with paraformaldehyde (0.701 g, 23.3 mmol), dry MeOH (20 mL), and diphenylphosphine (4.340 g, 23.3 mmol). The reaction mixture was heated to 60 °C under Ar until the white suspension formed a colorless solution. After removal of MeOH in vacuo the remaining viscous oil was diluted in dry toluene (20 mL). This solution was added to a suspension of MCM-41-NH_2 (3.020 g) in dry toluene (60 mL) and the reaction mixture was heated to 105 °C under Ar for 24 h. In the cooler regions of the flask, the water/toluene azeotrope separated indicating the reaction progress. After cooling to room temperature, the solid product was collected by filtration under Ar, washed with dry toluene (4×30 mL), CH_2Cl_2/THF (1:1) (2×30 mL), CH_2Cl_2 (2×30 mL), and dried in vacuo (100 °C) for 5 h to give 4.08 g of the light yellow MCM-41-2P. The nitrogen and phosphine contents were found to be 0.76 and 1.44 mmol/g, respectively.

4.4. Preparation of MCM-41-2P-Pd(0) complex

To a solution of $PdCl_2$ (0.216 g, 1.22 mmol) in acetone (50 mL) was added the MCM-41-2P (2.01 g). The reaction mixture was refluxed under Ar for 72 h. The product was allowed to cool, then filtered. The yellow solid was washed

with distilled water (3×30 mL) and acetone (3×30 mL), then stirred with hydrazine monohydrate (1.6 g) and EtOH (25 mL) at 30 °C under Ar for 5 h. The resulting product was filtered, washed with EtOH (3×25 mL) and Et_2O (3×25 mL), and dried under vacuum at 60 °C to give 1.93 g of the brown MCM-41-2P-Pd(0). The nitrogen, phosphine, and palladium content was 0.58, 1.15, and 0.52 mmol/g, respectively.

4.5. General procedure for the Sonogashira coupling reaction

Aryl iodide (1.0 mmol), MCM-41-2P-Pd(0) (10 mg, 0.005 mmol Pd), piperidine (3 mL), and CuI (0.05 mmol) were added to a flask under Ar, and the resulting mixture was stirred at room temperature for 5 min. To this suspension was added terminal alkyne (1.5 mmol), and the reaction mixture was stirred at room temperature for 1.5–3 h. The mixture was diluted with Et_2O (40 mL). The MCM-41-2P-Pd(0) catalyst was separated from the mixture by filtration, washed with distilled water (2×10 mL), EtOH (3×10 mL), and Et_2O (2×10 mL) and reused in the next run. The ethereal solution was washed with water (2×10 mL) and dried over $MgSO_4$. The solvent was removed under vacuum, and the residue was purified by flash chromatography on silica gel to give the desired product.

4.5.1. PhC≡CPh (3a).[17] White solid, 60–61 °C. IR (KBr): ν (cm^{-1}) 3063, 1599, 1492, 756, 689. ^1H NMR (400 MHz, $CDCl_3$): δ 7.55–7.52 (m, 4H), 7.37–7.32 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.6, 128.4, 128.3, 123.3, 89.4.

4.5.2. 4-$CH_3C_6H_4C$≡CPh (3b).[17] White solid, 73–74 °C. IR (KBr): ν (cm^{-1}) 3029, 2918, 2859, 2215, 1594, 1509, 818, 690. ^1H NMR (400 MHz, $CDCl_3$): δ 7.53–7.51 (m, 2H), 7.42 (d, J=8.0 Hz, 2H), 7.36–7.27 (m, 3H), 7.14 (d, J=8.0 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 131.6, 131.5, 129.1, 128.3, 128.1, 123.5, 120.2, 89.6, 88.7, 21.5.

4.5.3. 4-ClC_6H_4C≡CPh (3c).[18] White solid, 82–83 °C. IR (KBr): ν (cm^{-1}) 3048, 2213, 1587, 1495, 831, 730, 687. ^1H NMR (400 MHz, $CDCl_3$): δ 7.54–7.51 (m, 2H), 7.46 (d, J=8.4 Hz, 2H), 7.36–7.31 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.3, 132.8, 131.6, 128.7, 128.5, 128.4, 122.9, 121.8, 90.3, 88.2.

4.5.4. 4-$O_2NC_6H_4C$≡CPh (3d).[17] Yellow solid, 120–121 °C. IR (KBr): ν (cm^{-1}) 3082, 2217, 1592, 1511, 1495, 858, 765, 690. ^1H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J=8.8 Hz, 2H), 7.67 (d, J=8.8 Hz, 2H), 7.58–7.55 (m, 2H), 7.41–7.37 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 132.3, 131.8, 130.3, 129.3, 128.5, 123.7, 122.1, 94.7, 87.5.

4.5.5. 3-$O_2NC_6H_4C$≡CPh (3e).[18] Yellow solid, 69–70 °C. IR (KBr): ν (cm^{-1}) 3081, 2210, 1597, 1530, 1517, 1347, 810, 759, 692. ^1H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 8.19–8.16 (m, 1H), 7.82 (d, J=7.6 Hz, 1H), 7.57–7.51 (m, 3H), 7.40–7.37 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 137.2, 131.8, 129.4, 129.1, 128.5, 126.4, 125.2, 122.9, 122.2, 92.0, 86.9.

4.5.6. 4-$CH_3COC_6H_4C$≡CPh (3f).[17] White solid, 98–99 °C. IR (KBr): ν (cm^{-1}) 3080, 2922, 2218, 1680, 1604, 1265, 833, 693. ^1H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J=8.0 Hz, 2H), 7.61 (d, J=8.0 Hz, 2H), 7.55 (d, J=2.4 Hz, 2H), 7.38–7.36 (m, 3H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 136.2, 131.8, 131.7, 128.8, 128.5, 128.3, 128.2, 122.7, 92.7, 88.6, 26.6.

4.5.7. 2-$CF_3C_6H_4C$≡CPh (3g). Colorless liquid. IR (neat): ν (cm^{-1}) 3066, 2925, 2222, 1605, 1497, 1320, 756, 690. ^1H NMR (400 MHz, $CDCl_3$): δ 7.70–7.66 (m, 2H), 7.59–7.51 (m, 3H), 7.44–7.35 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.7, 131.7, 131.4, 128.8, 128.4, 127.9, 125.9, 125.0, 122.8, 122.2, 121.6, 94.9, 85.4. Anal. Calcd for $C_{15}H_9F_3$: C, 73.19; H, 3.66. Found: C, 73.02; H, 3.39.

4.5.8. 3-NCC_6H_4C≡CPh (3h).[18] White solid, 71–72 °C. IR (KBr): ν (cm^{-1}) 3050, 2228, 2207, 1600, 1490, 891, 760, 680. ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (t, J=1.2 Hz, 1H), 7.72–7.69 (m, 1H), 7.58–7.51 (m, 3H), 7.43 (t, J=7.6 Hz, 1H), 7.39–7.33 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.7, 134.9, 131.8, 131.4, 129.3, 129.0, 128.5, 124.9, 122.3, 118.2, 112.9, 91.9, 87.0.

4.5.9. PhC≡$CSiMe_3$ (3i).[19] Colorless liquid. IR (neat): ν (cm^{-1}) 3080, 2159, 1598, 1488, 1250, 864, 757, 690. ^1H NMR (400 MHz, $CDCl_3$): δ 7.48–7.45 (m, 2H), 7.31–7.29 (m, 3H), 0.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.0, 128.5, 128.2, 123.1, 105.1, 94.1, 0.01.

4.5.10. 4-$CH_3OC_6H_4C$≡$CSiMe_3$ (3j).[19] Colorless liquid. IR (neat): ν (cm^{-1}) 2156, 1606, 1508, 1249, 834, 756, 699. ^1H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, J=8.8 Hz, 2H), 6.81 (d, J=8.8 Hz, 2H), 3.81 (s, 3H), 0.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 133.5, 115.3, 113.8, 105.2, 92.5, 55.3, 0.08.

4.5.11. 4-ClC_6H_4C≡$CSiMe_3$ (3k).[19] Colorless liquid. IR (neat): ν (cm^{-1}) 3030, 2159, 1590, 1488, 1250, 844, 759, 685. ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J=8.4 Hz, 2H), 7.26 (d, J=8.4 Hz, 2H), 0.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.6, 133.2, 128.6, 121.7, 103.9, 95.4, −0.07.

4.5.12. PhC≡CCH_2OCH_3 (3l). Colorless liquid. IR (neat): ν (cm^{-1}) 2930, 2237, 1599, 1490, 1357, 757, 691. ^1H NMR (400 MHz, $CDCl_3$): δ 7.46–7.44 (m, 2H), 7.32–7.30 (m, 3H), 4.32 (s, 2H), 3.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.8, 128.4, 128.3, 122.7, 86.4, 84.9, 60.4, 57.7. Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.84. Found: C, 81.93; H, 6.61.

4.5.13. 4-ClC_6H_4C≡CCH_2OCH_3 (3m). Colorless liquid. IR (neat): ν (cm^{-1}) 3056, 2241, 1592, 1489, 1355, 828. ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J=8.4 Hz, 2H), 7.29 (d, J=8.4 Hz, 2H), 4.31 (s, 2H), 3.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.5, 133.0, 128.7, 121.1, 85.9, 85.3, 60.4, 57.8. Anal. Calcd for $C_{10}H_9OCl$: C, 66.50; H, 4.98. Found: C, 66.24; H, 4.79.

4.5.14. PhC≡$C(CH_2)_3CH_3$ (3n).[17] Colorless liquid. IR (neat): ν (cm^{-1}) 3056, 2960, 2870, 2237, 1598, 1499, 752, 690. ^1H NMR (400 MHz, $CDCl_3$): δ 7.40–7.38 (m, 2H),

7.29–7.26 (m, 3H), 2.41 (t, J=7.2 Hz, 2H), 1.62–1.56 (m, 2H), 1.53–1.46 (m, 2H), 0.95 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.6, 128.2, 127.5, 124.2, 90.4, 80.6, 30.9, 22.0, 19.1, 13.7.

4.5.15. 4-$O_2NC_6H_4C{\equiv}C(CH_2)_3CH_3$ (3o).[17] Yellow liquid. IR (neat): ν (cm^{-1}) 3081, 2934, 2873, 2230, 1594, 1519, 854. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J=8.8 Hz, 2H), 7.52 (d, J=8.8 Hz, 2H), 2.46 (t, J=7.2 Hz, 2H), 1.63–1.57 (m, 2H), 1.51–1.46 (m, 2H), 0.96 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 132.3, 131.2, 123.5, 96.8, 79.3, 30.5, 22.1, 19.3, 13.6.

4.5.16. 3-$NCC_6H_4C{\equiv}C(CH_2)_3CH_3$ (3p). Colorless liquid. IR (neat): ν (cm^{-1}) 3069, 2958, 2873, 2232, 1597, 1478, 896, 798, 683. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 1H), 7.60–7.53 (m, 2H), 7.39 (t, J=7.6 Hz, 1H), 2.42 (t, J=7.2 Hz, 2H), 1.61–1.56 (m, 2H), 1.50–1.45 (m, 2H), 0.96 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.7, 135.0, 130.7, 129.1, 125.7, 118.3, 112.6, 93.4, 78.5, 30.5, 22.0, 19.1, 13.7. Anal. Calcd for $C_{13}H_{13}N$: C, 85.26; H, 7.10. Found: C, 85.02; H, 6.91.

4.5.17. 2-$CF_3C_6H_4C{\equiv}C(CH_2)_3CH_3$ (3q). Colorless liquid. IR (neat): ν (cm^{-1}) 3075, 2961, 2875, 2235, 1604, 1491, 1450, 765. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J=7.6 Hz, 1H), 7.52 (d, J=7.6 Hz, 1H), 7.44 (t, J=7.6 Hz, 1H), 7.34 (t, J=7.6 Hz, 1H), 2.45 (t, J=7.2 Hz, 2H), 1.62–1.57 (m, 2H), 1.52–1.46 (m, 2H), 0.95 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.9, 131.6, 131.3, 127.2, 125.7, 125.0, 122.4, 96.7, 77.5, 30.5, 21.9, 19.3, 13.6. Anal. Calcd for $C_{13}H_{13}F_3$: C, 69.05; H, 5.75. Found: C, 68.87; H, 5.58.

4.5.18. 4-$CH_3OC_6H_4C{\equiv}CPh$ (3r).[17] White solid, 58–59 °C. IR (KBr): ν (cm^{-1}) 3024, 2212, 1602, 1498, 1245, 835, 750, 690. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.43 (m, 4H), 7.32–7.29 (m, 3H), 6.86–6.83 (m, 2H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 133.0, 131.4, 128.3, 127.9, 123.4, 115.5, 113.9, 89.4, 88.1, 55.2.

4.5.19. 4-$CH_3C_6H_4C{\equiv}CC_6H_4Br$-4 (3s).[17] White solid, 157–158 °C. IR (KBr): ν (cm^{-1}) 3026, 2920, 2859, 2216, 1594, 1509, 818. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.34 (m, 6H), 7.14 (d, J=8.0 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 132.9, 131.6, 131.5, 129.1, 122.5, 122.3, 120.0, 90.6, 87.7, 21.5.

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