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Preparation and Reactivation of Heterogeneous Palladium Catalysts and Applications in Sonogashira, Suzuki, and Heck Reactions in Aqueous Media

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A new type of heterogeneous palladium catalyst, PdMgAl-LDH, was facilely prepared by the immobilization of Pd^{2+} species in the layers of a Mg-Al layered double hydroxide (LDH) with co-precipitation, and then fully characterized by using powder XRD, thermogravimetric differential thermal analysis, TEM, energy-dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy techniques. These catalysts can efficiently catalyze copper-free Sonogashira, Suzuki and Heck coupling reactions of various aryl iodides, bromides, and chlorides in aqueous media under phosphine-ligand- and organic-base-free conditions. These catalysts feature easy recovery through simple filtration and could be reused at least six times without a marked loss in activity. Notably, they can be facilely reactivated by a combination of nitrolysis with co-precipitation. The basic LDH skeletons could effectively stabilize the Pd^0 species created in situ and donate electron density to the Pd^0 center to facilitate the oxidative addition of aryl halides, thus the PdMgAl-LDH catalysts are stable during catalysis.

1. Introduction

Palladium-catalyzed Sonogashira, Suzuki, and Heck reactions are powerful tools for the formation of carbon–carbon bonds in modern organic synthesis and can boost greater diversity in natural products, biological molecules, and functional materials.[1] In general, homogeneous Pd catalysts are used with various phosphine ligands, which results in several limitations, such as a lack of catalyst reuse and residual heavy metals in the final products.[2] However, the application of heterogeneous Pd catalysts could avoid such limitations.[3] A popular strategy is to immobilize Pd species onto a suitable solid support, such as activated carbon,[4] metal oxide,[5] silica,[6] zeolite,[7] or organic polymers.[8] These catalysts could be applied to promote some coupling reactions, but their preparation and reactivation are laborious and difficult. In particular, the loss of Pd species from the solid supports is a serious issue. Thus, it is essential to develop well-defined heterogeneous Pd catalysts

that feature high catalytic performance and facile preparation and regeneration.

Recently, layered double hydroxides (LDHs), a class of 2D anionic clays composed of positively charged brucite-like layers with an interlayer region that consists of charge-compensating anions and solvent molecules,[9] were shown to be a promising support for heterogeneous catalysts, largely because of their high dispersion, preferential orientation, abundant basic sites as potential donors, and high catalytic performance.[10] To date, a majority of LDH-based heterogeneous Pd catalysts have been prepared through two strategies: 1) insertion of Pd species into the interlayer region of the LDH to give a Pd/MgAl-LDH catalyst (Figure 1a)[11] or 2) by implanting Pd species into the layers of the LDH through bonding to create a PdMgAl-LDH catalyst (Figure 1b).[12] Choudary et al.[11a] reported that the Pd/MgAl-LDH catalyst can catalyze the Heck reaction of aryl chlorides under high temperature or microwave radiation in the presence of an organic base. Ruiz et al.[11b] demonstrated that the Pd/MgAl-LDH catalyst exhibits high catalytic performance in the Suzuki reaction. Moreover, Corma et al.[11c] developed a family of PdCu/MgAl(O) catalysts

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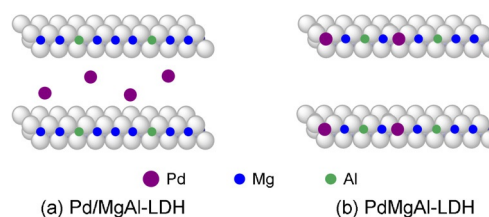[+] These authors contributed equally to this work

Figure 1. The structures of two types of LDH-based Pd catalysts: a) Pd/MgAl-LDH and b) PdMgAl-LDH.

that were prepared through wetness impregnation of calcined MgAl-LDH with Cu^{2+} and Pd^{2+} nitrates, and found that these catalysts have good activity in the Sonogashira reaction. However, these catalysts are still difficult to prepare and inefficient to reactivate.

Currently, few PdMgAl-LDH catalysts (Figure 1b) have been developed and applied in coupling reactions.[12] Sivasanker et al.[12a] reported that the PdMgAl-LDH catalyst, obtained by a co-precipitation method, was only used for the Heck reaction in the presence of an organic base and at high temperature. Ruiz et al.[12b,c] synthesized the PdMgAl-LDH catalyst in the same way and used it to catalyze the Suzuki reaction, which gave less than 10% conversion. Liu et al.[12d] reported that a Pd^{2+}-doped colloidal LDH catalyst, obtained by delamination of glycinate-intercalated PdMgAl-LDH, showed high efficiency in the Heck reaction, but was difficult to recycle.

Our strategy is to implant Pd species in the layers of an LDH to create PdMgAl-LDH catalysts because they can efficiently avoid the loss of Pd during the catalytic process. Herein, we present a series of PdMgAl-LDH catalysts that can efficiently catalyze the Sonogashira, Suzuki, and Heck reactions of aryl halides in greener media under P-ligand- and organic-base-free conditions. Moreover, they can be easily prepared by co-precipitation and reactivated by a combination of nitrolysis and co-precipitation.

2. Results and Discussion

2.1. Preparation and Characterization of Catalysts

PdMgAl-LDH and MgAl-LDH (Pd-free) catalysts were facilely prepared by co-precipitation with a double-drop technique.[13] Given the stability of the brucite layers, two PdMgAl-LDH catalysts, PdMgAl-LDH-1 (0.50% Pd w/w) and PdMgAl-LDH-2 (2.58% Pd w/w), were synthesized and characterized by using powder XRD, thermogravimetric differential thermal analysis (TG-DTA), TEM, energy-dispersive X-ray spectroscopy (EDX), FTIR, and X-ray photoelectron spectroscopy (XPS) techniques. Additionally, two Pd/MgAl-LDH catalysts, Pd/MgAl-LDH-1 (0.56% Pd w/w) and Pd/MgAl-LDH-2 (2.64% Pd w/w) were prepared by exchanging proportional $PdCl_4^{2-}$ ions into the interlayer region of the MgAl-LDH.[14]

From powder XRD patterns of the PdMgAl-LDH catalysts, both PdMgAl-LDH-1 (Figure 2a) and PdMgAl-LDH-2 (Figure 2b) exhibit typical diffraction peaks similar to MgAl-LDH (Figure 2c),[15] although the ionic radius of Pd^{2+} is different from that of Mg^{2+}. Because LDH has a hexagonal structure, lattice parameters a and c indicate the average distance between metal ions within the layers and the separation of the neighboring layer centers, respectively,[16a] and can be calculated from the (110) and (003) reflections of the XRD spectra (Figure 2) based on $a = 2d_{110}$ and $c = 3d_{003}$. Parameters a and c of the PdMgAl-LDH catalysts are slightly larger than those of MgAl-LDH and increase as the amount of Pd is increased (Table S1, see the Supporting Information). The increase in parameter a results from larger Pd^{2+} ions (0.086 nm) in the octahedral coordination site[16b] compared with Mg^{2+}. The increase
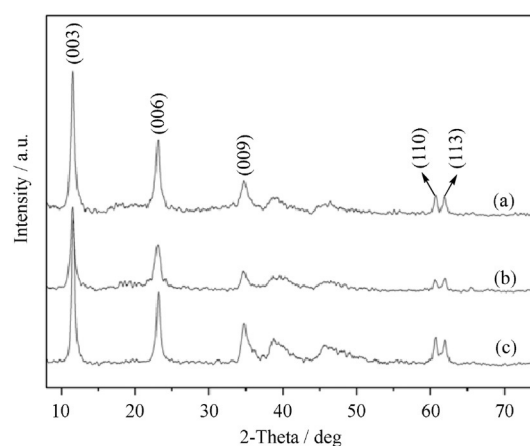

Figure 2. Powder XRD patterns of a) PdMgAl-LDH-1, b) PdMgAl-LDH-2, and c) MgAl-LDH.

in parameter c may be ascribed to the distortion of the structure caused by the larger Pd^{2+} ions, which affects the layer thickness.[16c] These results confirmed that Pd^{2+} ions were successfully implanted in the layers of MgAl-LDH. The XRD patterns and a and c parameters of the Pd/MgAl-LDH catalysts (Figure S1, Table S2) are consistent with results reported previously,[14] which indicated that $PdCl_4^{2-}$ was successfully exchanged into the interlayer region of the MgAl-LDH.

The TG-DTA results of PdMgAl-LDH-1, PdMgAl-LDH-2, and MgAl-LDH are shown in Figure 3. All compounds showed obvious weight loss in two consecutive endothermic stages.[17] The destructive temperatures of PdMgAl-LDH-1 (Figure 3a) and PdMgAl-LDH-2 (Figure 3b) at the second weight-loss process are distinctly ahead of MgAl-LDH (Figure 2c), presumably due to the structural distortion caused by the larger Pd^{2+} ions. This is in agreement with the results from the powder XRD analysis.

TEM images of PdMgAl-LDH catalysts and MgAl-LDH are shown in Figure 4. The expected hexagonal-plate-like nature of the crystallites is obviously apparent in each sample, and the diameters ranged from 60 to 80 nm. The TEM images of PdMgAl-LDH-1 (Figure 4a) and PdMgAl-LDH-2 (Figure 4b) are
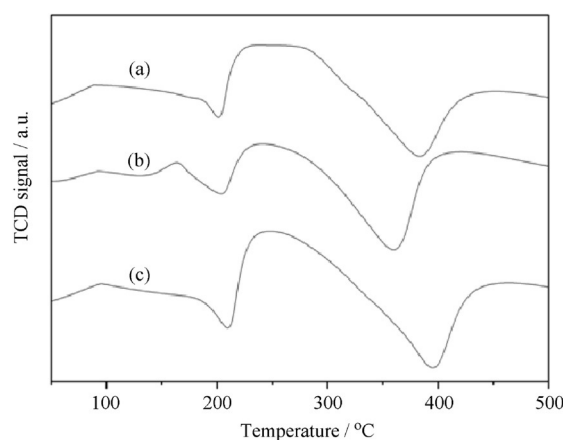

Figure 3. Differential thermal analysis (DTA) curves for a) PdMgAl-LDH-1, b) PdMgAl-LDH-2, and c) MgAl-LDH.
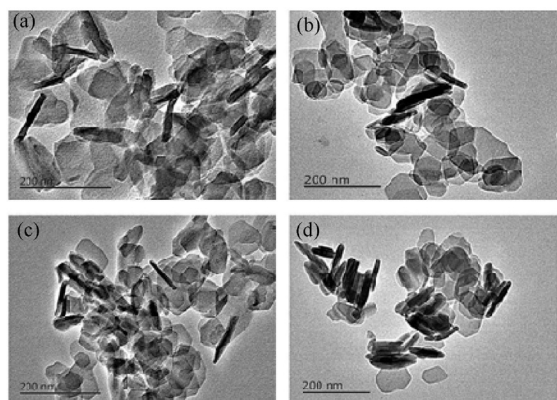
Figure 4. TEM images of a) PdMgAl-LDH-1, b) PdMgAl-LDH-2, c) MgAl-LDH, and d) PdMgAl-LDH-1R.

similar to that of MgAl-LDH (Figure 4c), which indicates that the morphology is well retained after a small amount of Mg is replaced by Pd species in the MgAl-LDH layers. This was also confirmed by the EDX spectrum (Figure S2). The FTIR spectra of PdMgAl-LDH-1 and PdMgAl-LDH-2 are similar to that of MgAl-LDH in the 400 to 4000 cm^{-1} region (Figure 5), and show typical bands for hydrotalcite with intercalated carbonate counterions.[12b, 18]
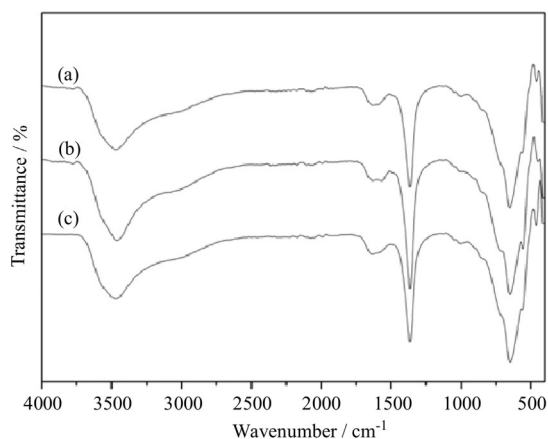

Figure 5. FTIR spectra for a) PdMgAl-LDH-1, b) PdMgAl-LDH-2, and c) MgAl-LDH.

To assess the Pd oxidation state in the PdMgAl-LDH catalysts, XPS analyses were carried out for PdMgAl-LDH-1 and PdMgAl-LDH-1$_1$ (after one run). The binding energies of Pd 3d$_{5/2}$ and 3d$_{3/2}$ for PdMgAl-LDH-1 were 337.5 and 342.8 eV, respectively (Figure S3 a), which indicated that the implanted Pd is in the II state.[19] Note that the XPS signal of Pd 3d$_{3/2}$ is weak due to the low loading of palladium. Moreover, the binding energy of Pd 3d$_{5/2}$ in PdMgAl-LDH-1 (337.5 eV) is different from that in Pd/MgAl-LDH (337.1 eV[11a]) and Pd(OH)$_2$ (336.8 eV; Figure S4).[19]

In brief, two PdMgAl-LDH catalysts, with Pd loadings of 0.50 and 2.58%, respectively, were prepared and fully characterized.

Pd^{2+} ions were successfully immobilized in the brucite layers and show morphology similar to that of MgAl-LDH.

2.2. Catalyst Evaluation

To examine their catalytic activity, the prepared PdMgAl-LDH catalysts were applied to Sonogashira, Suzuki, and Heck coupling reactions. In view of its environmental safety and compatibility with the PdMgAl-LDH catalysts, we tried water as the reaction solvent.

2.2.1. Application in the Sonogashira Reaction

The Sonogashira reaction is a powerful method to create a carbon–carbon bond between a terminal alkyne and an aryl or vinyl halide by using a palladium catalyst and a copper co-catalyst; however, the latter could result in a homocoupling product upon oxidation. To avoid this byproduct, a copper-free Sonogashira reaction has been developed.[20] Therefore, the PdMgAl-LDH catalysts were first applied in a copper-free Sonogashira reaction.

To optimize the coupling conditions, we used bromobenzene and phenylacetylene as model substrates (Table 1). First, a coupling reaction was conducted in water at 80 °C for 24 h with PdMgAl-LDH-1 (0.20 mol% Pd) as the catalyst and K$_2$CO$_3$ (200 mol%) as the base, which gave a 47% yield of diphenylacetylene (Table 1, entry 1). However, with sodium ascorbate (NaVc) as the reducing agent, the reaction gave diphenylacetylene in 89% yield (Table 1, entry 2) under identical conditions. This may be ascribed to the fact that Pd^{2+} in PdMgAl-LDH-1 was reduced to Pd^0 in situ by NaVc, which accelerated the oxidative addition of Pd^0 to the C—Br bond.[21] This reduction was also confirmed by using XPS analysis (Figure S3 b). The binding

Table 1. Optimization of Sonogashira reactions catalyzed by using PdMgAl-LDH-1.[a]

Entry	Base	Additive[b]	Pd [mol%]	T [h]	Yield [%][c]
1	K$_2$CO$_3$	none	0.20	24	47[d]
2	K$_2$CO$_3$	none	0.20	24	89
3	K$_2$CO$_3$	CTAB	0.20	12	93
4	K$_2$CO$_3$	TBAB	0.20	15	89
5	K$_2$CO$_3$	TPAB	0.20	16	87
6	K$_2$CO$_3$	TEBAC	0.20	16	85
7	K$_2$CO$_3$	CTAB	0.30	10	95
8	K$_2$CO$_3$	CTAB	0.10	24	72
9	K$_2$CO$_3$	CTAB	0.20	12	65[e]
10	Na$_2$CO$_3$	CTAB	0.20	12	85
11	K$_3$PO$_3$	CTAB	0.20	12	82
12	Et$_3$N	CTAB	0.20	16	87
13	pyridine	CTAB	0.20	16	89

[a] Reagents and conditions: bromobenzene (1.00 mmol), phenylacetylene (1.10 mmol), base (2.00 mmol), NaVc (0.01 mmol), additive (0.10 mmol), and H$_2$O (3 mL). [b] TBAB = tetrabutylammonium bromide, TPAB = tetrapropylammonium bromide, TEBAC = benzyltriethylammonium chloride. [c] Isolated yield. [d] NaVc-free. [e] Reaction at 60 °C.

energies of Pd were 335.4 ($3d_{5/2}$) and 340.7 eV ($3d_{3/2}$), and were assigned to the Pd^0 species.[19]

We found that the use of some tetraalkylammonium salts as an additive could facilitate the coupling reaction (Table 1, entries 3–6); cetyltrimethylammonium bromide (CTAB) was the best additive for the coupling reaction (Table 1, entry 3). We presume that CTAB may act as both a phase-transfer catalyst and an interlayer regulator of the PdMgAl-LDH because the powder XRD analysis (Figure S5) indicated that CTAB was partly incorporated into the interlayer region of PdMgAl-LDH, which extended the interlayer separation from 0.765 to 2.386 nm (Table S1, entry 5) and allowed the substrates to enter the interlayer region more easily.

Furthermore, the bases, catalyst loadings, and reaction temperature were also screened. Of the bases tested (Table 1, entries 2 and 10–13), K_2CO_3 was found to be the most efficient base and resulted in a 93% yield. If the loading of the catalyst was changed to 0.30 mol%, the yield did not increase significantly (Table 1, entry 7), whereas a decrease in the catalyst loading to 0.10 mol% gave only a 72% yield (Table 1, entry 8). When the temperature was decreased from 80 to 60 °C, the yield of product reduced from 93 to 65% (Table 1, entry 9), so the reaction temperature was maintained at 80 °C.

To expand the scope of the reaction, we investigated the copper-free Sonogashira coupling of various aryl halides and terminal alkynes under the optimized conditions; the results are shown in Table 2. In most cases the desired products were obtained in excellent yields with both aryl iodides and aryl bromides and the reactions proceeded rapidly (1–15 h). In particular, aryl bromides with an electron-rich or -deficient group could proceed smoothly to give the desired products in 92 to 95% yields (Table 2, entries 9–12). In view of the steric hindrance, the products were obtained in moderate yields with 2-bromotoluene (82%, Table 2, entry 13) and 2-bromo-*p*-xylene (80%, Table 2, entry 14) as the starting materials. Moreover, the coupling of 4-bromopyridine and 5-bromopyrimidine also gave the products in 91 and 92% yields (Table 2, entries 15 and 16).

The copper-free Sonogashira reactions of some aryl chlorides were also studied (Table 3). We found that the reaction of chlorobenzene and phenylacetylene proceeded sluggishly and gave a lower yield under the same conditions (Table 3, entry 1). Remarkably, the yield was greatly improved when the loading of Pd was increased (1.00 mol%) with PdMgAl-LDH-2 in place of PdMgAl-LDH-1 (Table 3, entry 2). However, addition of a catalytic amount of Na_2H_2EDTA as a chelating ligand notably shortened the reaction time (Table 3, entry 5) compared with other ligands, such as L-proline (Table 3, entry 3) and glycine (Table 3, entry 4). This may be ascribed to the fact that the ligand binds to the Pd^0 species and facilitates oxidative addition to the C–Cl bond.[21] Different aryl halides were used to assess the scope of the copper-free Sonogashira reaction and all gave moderate yields (Table 3, entries 5–10).

For comparison, catalysts PdMgAl-LDH-1,2 and Pd/MgAl-LDH-1,2 were used to catalyze the same model reaction (Table 4). We found that the activity of PdMgAl-LDH-1 was slightly lower than that of Pd/MgAl-LDH-1, which can be ascribed to the different locations of the Pd species in these cat-

Table 2. Scope of Sonogashira reactions catalyzed by PdMgAl-LDH-1.[a]

$$Ar-X(Br, I) + R-\!\!\!\equiv \xrightarrow[K_2CO_3, \text{ CTAB}, H_2O, 80\ ^\circ C]{\text{PdMgAl-LDH-1(0.20 mol\%), NaVc}} Ar-\!\!\!\equiv\!\!\!-R$$

Entry	Aryl bromide/iodide	Alkyne	T [h]	Yield [%][b]
1	I-substituted benzene	phenyl alkyne	1	94
2	Br-substituted benzene	phenyl alkyne	12	93
3	I-substituted benzene	HO-alkyne	1.5	92
4	Br-substituted benzene	HO-alkyne	10	93
5	I-substituted benzene	alkyl alkyne	1.5	87
6	Br-substituted benzene	alkyl alkyne	12	85
7	I-substituted benzene	Fc-alkyne	2	96
8	Br-substituted benzene	Fc-alkyne	15	93
9	O_2N-phenyl-Br	phenyl alkyne	10	95
10	(O=)phenyl-Br	phenyl alkyne	10	94
11	Me-phenyl-Br	phenyl alkyne	14	92
12	MeO-phenyl-Br	phenyl alkyne	14	93
13	Me-(2-)phenyl-Br	phenyl alkyne	14	82
14	Br, Me, Me-xylyl	phenyl alkyne	14	80
15	N-pyridyl-Br	phenyl alkyne	12	91
16	N,N-pyrimidyl-Br	phenyl alkyne	12	92

[a] Reagents and conditions: aryl halide (1.00 mmol), terminal alkyne (1.10 mmol), K_2CO_3 (2.00 mmol), NaVc (0.01 mmol), CTAB (0.10 mmol), and H_2O (3 mL). [b] Isolated yield.

alysts. Similarly, parallel results were obtained for the reaction of chlorobenzene with phenyl acetylene catalyzed by PdMgAl-LDH-2 (Table 3, entry 5) and Pd/MgAl-LDH-2 (Table 3, entry 11), respectively. Pd in the PdMgAl-LDH catalysts is implanted in the layers of the LDH, whereas Pd in the Pd/MgAl-LDH catalysts is found in the interlayer region of the LDH. This difference means that it is more difficult for aryl halide molecules to reach the Pd^0 species in PdMgAl-LDH than in Pd/MgAl-LDH.

To verify that the catalytic activity originated from Pd species implanted in the LDH layers rather than Pd species leached into solution, the Sonogashira reaction of bromobenzene and phenylacetylene in the presence of PdMgAl-LDH-1 was conducted. Two parallel reactions were stirred at 80 °C for 4 h, then the catalyst was removed from the solution by simple filtration. In one reaction the conversion was found to be 48%, whereas the other reaction was continued with the filtrate for a further 8 h; the conversion was found to be almost unchanged. ICP-MS analysis of the filtrate indicated that only

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Table 3. Sonogashira reactions of aryl chlorides with phenylacetylene catalyzed by MgAl-LDH-2.[a]

$$Ar-Cl + \text{(phenylacetylene)} \xrightarrow[\substack{K_2CO_3, \text{ CTAB, additive,} \\ H_2O, 80\,^\circ C}]{\substack{PdMgAl\text{-}LDH\text{-}2(1.00\ mol\%), \\ NaVc}} \text{(product)}-Ar$$

Entry	Aryl chloride	Additive	T [h]	Yield [%][b]
1	⬡—Cl	none	72	45[c]
2	⬡—Cl	none	72	75
3	⬡—Cl	L-proline	48	72
4	⬡—Cl	glycine	48	75
5	⬡—Cl	Na_2H_2EDTA	48	82
6	O_2N—⬡—Cl	Na_2H_2EDTA	36	85
7	(O=)⬡—Cl	Na_2H_2EDTA	36	79
8	H_2N—⬡—Cl	Na_2H_2EDTA	48	84
9	Me—⬡—Cl	Na_2H_2EDTA	48	81
10	MeO—⬡—Cl	Na_2H_2EDTA	48	76
11	⬡—Cl	Na_2H_2EDTA	36	84[d]

[a] Reagents and conditions: aryl chloride (1.00 mmol), phenyl acetylene (1.10 mmol), K_2CO_3 (2.00 mmol), NaVc (0.05 mmol), CTAB (0.10 mmol), additive (0.10 mmol), and H_2O (3 mL). [b] Isolated yield. [c] PdMgAl-LDH-1 (0.20 mol% Pd). [d] Pd/MgAl-LDH-2 (1.00 mol% Pd).

Table 4. Comparison of the Sonogashira reaction between bromobenzene and phenylacetylene, catalyzed by various catalysts.[a]

$$\text{⬡}-Br + \text{(phenylacetylene)} \xrightarrow[\substack{K_2CO_3, \text{ CTAB, } H_2O, 80\,^\circ C}]{\substack{cat.(0.20\ mol\%), NaVc}} \text{(product)}$$

Catalyst	T [h]	Yield [%][b]	TON[c]	TOF[d]
PdMgAl-LDH-1	12	93	465	38.8
Pd/MgAl-LDH-1	8	92	460	57.5

[a] Reagents and conditions: bromobenzene (1.00 mmol), phenyl acetylene (1.10 mmol), K_2CO_3 (2.00 mmol), NaVc (0.01 mmol), CTAB (0.10 mmol), and H_2O (3 mL). [b] Isolated yield. [c] TON = turnover number = mmol of product per mmol of Pd catalyst. [d] TOF = TON/time.

Table 5. Changes in Pd loading in two catalysts after five cycles of Sonogashira reactions.[a]

$$\text{⬡}-Br + \text{(phenylacetylene)} \xrightarrow[\substack{K_2CO_3, \text{ CTAB, } H_2O, 80\,^\circ C}]{\substack{cat.(0.20\ mol\%), NaVc}} \text{(product)}$$

Catalyst	Pd [%] (w/w)		
	Fresh catalyst	Used catalyst	Leached Pd
PdMgAl-LDH-1	0.50	0.48	0.02
Pd/MgAl-LDH-1	0.56	0.44	0.12

[a] Reagents and conditions: bromobenzene (1.00 mmol), phenyl acetylene (1.10 mmol), K_2CO_3 (2.00 mmol), NaVc (0.01 mmol), CTAB (0.10 mmol), and H_2O (3 mL).

With a viable protocol in hand, we propose a plausible mechanism for the copper-free Sonogashira reaction mediated by PdMgAl-LDH (Figure 6), which proceeds similarly to that in homogeneous catalysis and involves a typical Pd^0/Pd^{II} cycle.[22] The cycle is initiated by the creation of Pd^0 species I, followed by oxidative addition with aryl halide to II, in which the basic layers of the LDH increase the electron density around the Pd center to accelerate oxidative addition.[11a,23] Then, coordination with the terminal alkyne leads to III with a subsequent deprotonation to give IV, which undergoes reductive elimination to yield the final product and restart the catalytic cycle.
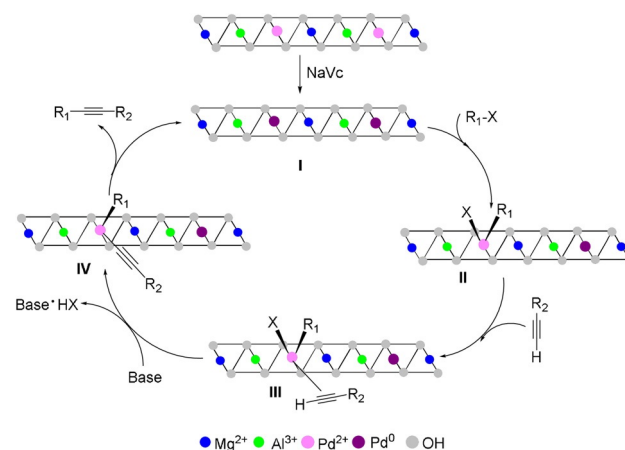
Figure 6. A plausible mechanism for the PdMgAl-LDH-catalyzed copper-free Sonogashira reaction.

2.2.2. Application in the Suzuki Reaction

To extend the application scope, the PdMgAl-LDH catalysts were then applied in the Suzuki coupling reaction. Most conditions optimized for the copper-free Sonogashira reaction were used directly and the results are shown in Table 6. Similar to the Sonogashira reaction, if 0.20 mol% Pd loading of PdMgAl-LDH-1 was used, aryl iodides and aryl bromides with either electron-rich (Table 6, entries 7,8) or electron-deficient groups (Table 6, entries 5–6 and 9–10) gave the coupling products in yields of 91 to 96% over 2 to 15 h. As expected, with 1.00 mol% Pd in PdMgAl-LDH-2 and with Na_2H_2EDTA as the ligand, the desired products were obtained from aryl chlorides

about 0.005% of the total Pd had leached into the solution. These results strongly confirmed that coupling reactions catalyzed by PdMgAl-LDH proceed heterogeneously.

Next, the degree of leaching of Pd from two different catalysts, PdMgAl-LDH-1 and Pd/MgAl-LDH-1, was tested after the fifth Sonogashira reaction cycle of bromobenzene with phenyl acetylene. In all cases, the catalyst was exhaustively removed by filtration and the amount of Pd species leached into solution was determined by using ICP-MS. As shown in Table 5, PdMgAl-LDH-1 is a very stable catalyst that leached only 0.02% Pd after five cycles.

Table 6. Evaluation of the PdMgAl-LDH-1 catalyst applied to Suzuki reactions of aryl halides with aryl boronic acid.[a]

$$Ar-X(Cl, Br, I) + Ar'-B(OH)_2 \xrightarrow[\text{K}_2\text{CO}_3, \text{CTAB, H}_2\text{O, 80 °C}]{\text{PdMgAl-LDH-1(0.20 mol\%), NaVc}} Ar-Ar'$$

Entry	Aryl halide	Arylboronic acid	T [h]	Yield [%][b]
1	⟨benzene⟩—I	⟨benzene⟩—B(OH)$_2$	2	93
2	⟨benzene⟩—Br	⟨benzene⟩—B(OH)$_2$	12	90
3	⟨benzene⟩—I	Me—⟨benzene⟩—B(OH)$_2$	2	96
4	⟨benzene⟩—Br	Me—⟨benzene⟩—B(OH)$_2$	10	94
5	O$_2$N—⟨benzene⟩—Br	⟨benzene⟩—B(OH)$_2$	8	96
6	(O=)C—⟨benzene⟩—Br	⟨benzene⟩—B(OH)$_2$	8	93
7	Me—⟨benzene⟩—Br	⟨benzene⟩—B(OH)$_2$	15	91
8	MeO—⟨benzene⟩—Br	⟨benzene⟩—B(OH)$_2$	15	93
9	⟨pyridine N⟩—Br	⟨benzene⟩—B(OH)$_2$	10	93
10	⟨pyrimidine⟩—Br	⟨benzene⟩—B(OH)$_2$	10	95
11	⟨benzene⟩—Cl	⟨benzene⟩—B(OH)$_2$	48	80[c]
12	O$_2$N—⟨benzene⟩—Cl	⟨benzene⟩—B(OH)$_2$	32	86[c]
13	(O=)C—⟨benzene⟩—Cl	⟨benzene⟩—B(OH)$_2$	36	84[c]
14	Me—⟨benzene⟩—Cl	⟨benzene⟩—B(OH)$_2$	48	78[c]
15	MeO—⟨benzene⟩—Cl	⟨benzene⟩—B(OH)$_2$	48	76[c]

[a] Reagents and conditions: aryl halide (1.00 mmol), arylboronic acid (1.10 mmol), K$_2$CO$_3$ (2.00 mmol), NaVc (0.01 mmol), CTAB (0.10 mmol), and H$_2$O (3 mL). [b] Isolated yield. [c] PdMgAl-LDH-2 (1.00 mol% Pd), NaVc (0.05 mmol), and Na$_2$H$_2$EDTA (0.10 mmol).

Table 7. Evaluation of the PdMgAl-LDH-1 catalyst applied to Heck reactions of aryl halides with alkenes.[a]

$$Ar-X(Cl, Br, I) + R\diagup \xrightarrow[\text{K}_2\text{CO}_3, \text{CTAB, H}_2\text{O/DMF, 100 °C}]{\text{PdMgAl-LDH-1(0.20 mol\%), NaVc}} Ar\diagup R$$

Entry	Aryl halide	Alkene	T [h]	Yield [%][b]
1	⟨benzene⟩—I	⟨styrene⟩	5	92
2	⟨benzene⟩—Br	⟨styrene⟩	16	90
3	⟨benzene⟩—I	⟨CO$_2$Me acrylate⟩	4	93
4	⟨benzene⟩—Br	⟨CO$_2$Me acrylate⟩	12	91
5	O$_2$N—⟨benzene⟩—Br	⟨styrene⟩	10	94
6	NC—⟨benzene⟩—Br	⟨styrene⟩	10	93
7	Me—⟨benzene⟩—Br	⟨styrene⟩	16	92
8	MeO—⟨benzene⟩—Br	⟨styrene⟩	16	94
9	⟨benzene⟩—Cl	⟨styrene⟩	48	67[c]
10	O$_2$N—⟨benzene⟩—Cl	⟨styrene⟩	36	75[c]
11	Me—⟨benzene⟩—Cl	⟨styrene⟩	48	69[c]
12	MeO—⟨benzene⟩—Cl	⟨styrene⟩	48	62[c]

[a] Reagents and conditions: aryl halide (1.00 mmol), acrylate or styrene (1.10 mmol), K$_2$CO$_3$ (2.00 mmol), NaVc (0.01 mmol), CTAB (0.10 mmol), and H$_2$O/DMF (2:1, 3 mL). [b] Isolated yield. [c] PdMgAl-LDH-2 (1.00 mol% Pd), NaVc (0.05 mmol) and Na$_2$H$_2$EDTA (0.10 mmol).

in yields of 76 to 86% (Table 6, entries 11–13). This is markedly different from the result reported previously,[12b] in which the reaction of bromobenzene and phenylboronic acid catalyzed by PdMgAl-LDH obtained through co-precipitation by using a single-drop method only gave a 10% yield. However, the yield of the same reaction catalyzed by our catalyst was 90% (Table 6, entry 2). This can be attributed to the fact that our catalyst was prepared through co-precipitation by using a double-drop technique, which gives higher catalytic activity. Additionally, sodium ascorbate and CTAB play a vital role in the present protocol.

2.2.3. Application in the Heck Reaction

To extend the application scope, we also assessed the Heck olefination of various aryl halides mediated by PdMgAl-LDH catalysts in the presence of K$_2$CO$_3$ in H$_2$O/DMF (2:1 v/v; Table 7). Satisfyingly, all aryl halides with iodide, bromide, and chloride were converted into the corresponding products in

yields of 62 to 94%. These results are better than those reported previously,[12a] and some reactions were conducted under relatively mild conditions.

In summary, heterogeneous PdMgAl-LDH catalysts were successfully applied for copper-free Sonogashira, Suzuki, and Heck reactions of various aryl halides with good-to-excellent yields in most cases. The chemical structures of all target products were identified by using IR, ^{1}H, ^{13}C NMR spectroscopies and HRMS (see the Supporting Information).

2.3. Catalyst Reusability

Reusability is an important feature for heterogeneous catalysts. To assess the reusability of PdMgAl-LDH, repeated model Sonogashira, Suzuki, and Heck reactions were carried out. In all cases, the catalyst could be recovered easily from the terminated reaction mixture by filtration or centrifugation. The recovered catalyst was washed with hot EtOH before it was used for the next cycle under the same conditions. As shown in Figure 7, the catalyst can be recycled six times without a marked loss in catalytic activity. Additionally, the morphology of PdMgAl-LDH-1 used in the Sonogashira reaction was monitored by using TEM analysis. The results revealed that there
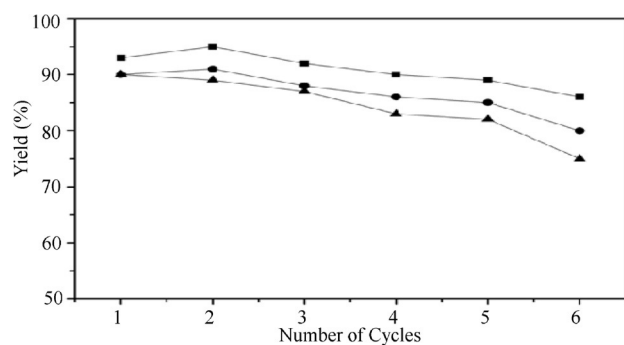
Figure 7. Reusability of PdMgAl-LDH-1 in the Sonogashira (■), Suzuki (●), and Heck (▲) coupling reactions.

was no obvious aggregation of Pd species in the catalyst after the fifth cycle; however, the Pd species essentially cluster together after the tenth cycle (Figure S6), which is the key reason for catalyst deactivation.

2.4. Catalyst Reactivation

For practical applications of a promising heterogeneous catalyst, easy reactivation is very significant because deactivation is inevitable. In fact, it is very difficult to reactivate the original morphology and catalytic activity of most heterogeneous Pd catalysts. However, we have successfully developed a technique that can efficiently reactivate the deactivated PdMgAl-LDH catalyst, in which deactivated PdMgAl-LDH-1 (after ten cycles) was washed thoroughly with hot EtOH to remove organic contaminants, then the amount of Pd was determined by using ICP-MS, followed by a co-precipitation process to produce the PdMgAl-LDH-1R catalyst.

The morphology of PdMgAl-LDH-1R is almost the same as the original PdMgAl-LDH-1 catalyst, as identified by using powder XRD (Figure S7) and TEM (Figure 4d) analyses. Moreover, ICP-MS data revealed that the PdMgAl-LDH-1R catalyst contained 0.44% Pd (w/w) and only 0.02% Pd was lost in the reactivation procedure.

The catalytic performance of the PdMgAl-LDH-1R catalyst was evaluated in copper-free Sonogashira, Suzuki, and Heck reactions (Table 8) and is very similar to the original PdMgAl-LDH-1 catalyst in all cases. This confirmed that our reactivation method for PdMgAl-LDH catalysts is reliable and facile.

3. Conclusions

Two new heterogeneous catalysts, PdMgAl-LDH-1 and PdMgAl-LDH-2, were prepared by a co-precipitation method with the double-drop technique and characterized by using powder XRD, TG-DTA, TEM, EDS, and XPS techniques. The catalysts can efficiently catalyze copper-free Sonogashira, Suzuki, and Heck reactions for diverse aryl iodides, bromides, and chlorides with K_2CO_3 base in aqueous media. The Pd species within the PdMgAl-LDH layers are stable enough to be cycled in at least six consecutive runs with high catalytic performance.

Table 8. Evaluation of the PdMgAl-LDH-1R catalyst applied to Sonogashira, Suzuki, and Heck reactions.[a]

Reaction	PhY	T [h]	Yield [%][b]
Sonogashira	(phenylacetylene)	12	92 (93)
Suzuki	(phenylboronic acid) B(OH)$_2$	12	89 (90)
Heck	(styrene)	16	88 (90)

[a] Reagents and conditions: bromobenzene (1.00 mmol), PhY (1.10 mmol), K_2CO_3 (2.00 mmol), NaVc (0.01 mmol), CTAB (0.10 mmol), and H_2O (3 mL). Note: for Heck reaction, H_2O/DMF (2:1 v/v, 3 mL) and 100 °C. [b] Isolated yield, data in parentheses refer to yields obtained with PdMgAl-LDH-1.

Furthermore, these catalysts are easy to prepare and reactivate, and showed low loss of Pd species.

Experimental Section

General Information

All chemical reagents were purchased and used without further purification. H_2O was boiled for 3 h to remove oxygen. DMF was distilled under reduced pressure over CaH_2. All reactions were carried out under an N_2 atmosphere by using standard Schlenk techniques. The powder XRD patterns were recorded by using a Bruker D8 Advance X-ray diffractometer. The DTA analyses were recorded by using a thermogravimetric analysis instrument (SDTQ 600). The TEM images were obtained by using TEM apparatus (JEM-2100). FTIR spectra were recorded by using a Bruker Alpha FT-IR spectrophotometer. The ICP-MS data were recorded by using an IRIS Advantage Radial instrument under standard conditions. ^1H and ^{13}C NMR spectra were recorded by using a BRUKER ADVANCE 300 spectrometer. Mass spectrometric data were collected by using a maXis UHR-TOF mass spectrometer. Melting points were measured by using a Yanaco MP-500 micro melting point apparatus and are uncorrected.

General Procedure for the Preparation of Catalysts

Solution A, which contained Mg, Al, and Pd nitrates in an appropriate ratio, and solution B, which contained proportional NaOH and Na_2CO_3 bases, were made up. Solutions A and B were then simultaneously added dropwise to stirred, deionized H_2O (9 mL) at such a rate that the pH of the reaction mixture was maintained at 9.5. The mixing process was performed at RT. The resulting slurry was aged for 13 h at 100 °C, then the precipitate was filtered, washed fully with deionized H_2O, and dried for 24 h at 100 °C to give the PdMgAl-LDH catalyst.

PdMgAl-LDH-1 (0.50% Pd w/w)

Pd(NO$_3$)$_2$·2H$_2$O (0.027 g, 0.10 mmol), Mg(NO$_3$)$_2$·6H$_2$O (4.590 g, 17.90 mmol), and Al(NO$_3$)$_3$·9H$_2$O (2.251 g, 6.00 mmol) were dissolved in deionized H_2O (10 mL) to give solution A, to which

0.10 mol L^{-1} HNO$_3$ (1 mL) was added to avoid hydrolysis of palladium nitrate. NaOH (1.540 g, 38.50 mmol) and Na$_2$CO$_3$ (1.272 g, 12.00 mmol) were dissolved in deionized H$_2$O (11 mL) to form mixed-base solution B. Then, following the general procedure, PdMgAl-LDH-1 was prepared as a grey solid (yield: 1.954 g, 0.50% Pd w/w).

PdMgAl-LDH-2 (2.58% Pd w/w)

Following the same procedure as for PdMgAl-LDH-1, Mg(NO$_3$)$_2$·6H$_2$O (4.487 g, 17.50 mmol) and Pd(NO$_3$)$_2$·2H$_2$O (0.133 g, 0.50 mmol) were used to give PdMgAl-LDH-2 as a dark-grey solid (yield: 2.012 g, 2.58% Pd w/w).

General Procedure for the Reactivation of PdMgAl-LDH

The deactivated catalyst was first washed twice with hot EtOH to remove organic contaminants, then dried and used in the reactivation procedure.

Deactivated PdMgAl-LDH-1 (2.000 g, 0.46% Pd w/w, as confirmed by ICP) was treated with 20% HNO$_3$ (11 mL) and heated to give transparent solution A. NaOH (3.200 g, 80.00 mmol) and Na$_2$CO$_3$ (1.272 g, 12.00 mmol) were dissolved in deionized H$_2$O (11 mL) to create mixed-base solution B. Then, following the general procedure for the preparation of the catalysts, PdMgAl-LDH-1R was obtained as a grey solid (yield: 1.966 g, 0.44% Pd w/w).

General Procedure for Sonogashira Reactions

CTAB (0.10 mmol), sodium ascorbate (0.01 mmol or 0.05 mmol), and H$_2$O (3 mL) were added to a mixture of aryl halide (1.00 mmol), terminal alkyne (1.10 mmol), K$_2$CO$_3$ (2.00 mmol), and PdMgAl-LDH-1 (0.043 g, 0.20 mol% Pd) or PdMgAl-LDH-2 (0.041 g, 1.00 mol% Pd) in a 25 mL round-bottom flask The resulting mixture was stirred at 80 °C under an N$_2$ atmosphere. After completion, the mixture was cooled to RT and diluted with ethyl acetate, then the slurry was ultrasonicated to remove the product from the catalyst surface. The catalyst was separated by centrifugation, and the centrifugate was washed with brine, dried over anhydrous MgSO$_4$, and the final products were purified by using flash column chromatography (hexane/ethyl acetate) to obtain the desired purity.

General Procedure for Suzuki Reactions

A mixture of aryl halide (1.00 mmol), arylboronic acid (1.10 mmol), K$_2$CO$_3$ (2.00 mmol), PdMgAl-LDH-1 (0.043 g, 0.20 mol% Pd) or PdMgAl-LDH-2 (0.041 g, 1.00 mol% Pd), CTAB (0.10 mmol), sodium ascorbate (0.01 mmol or 0.05 mmol), and H$_2$O (3 mL) was placed in a 25 mL round-bottom flask and stirred at 80 °C under an N$_2$ atmosphere. After completion, the reaction mixture was cooled to RT and diluted with ethyl acetate, then the slurry was ultrasonicated to remove the product from the catalyst surface. The catalyst was separated by using centrifugation, and the centrifugate was washed with brine, dried over anhydrous Mg$_2$SO$_4$, concentrated under reduced pressure, and purified by using flash column chromatography (hexane/ethyl acetate) to give the desired product.

General Procedure for Heck Reactions

A mixture of aryl halide (1.00 mmol), acrylate or styrene (1.10 mmol), K$_2$CO$_3$ (2.00 mmol), PdMgAl-LDH-1 (0.043 g, 0.20 mol% Pd) or PdMgAl-LDH-2 (0.041 g, 1.00 mol% Pd), CTAB (0.10 mmol), sodium ascorbate (0.01 mmol or 0.05 mmol) in DMF/H$_2$O (3 mL, 1:2) was placed in a 25 mL round-bottom flask and stirred at 100 °C under an N$_2$ atmosphere. After completion, the reaction mixture was cooled to RT and diluted with ethyl acetate, then the slurry was ultrasonicated to remove the product from the catalyst surface. The catalyst was separated by centrifugation, and the centrifugate was washed with brine, dried over anhydrous MgSO$_4$, and the crude product was purified by using flash column chromatography (hexane/ethyl acetate) to obtain the desired purity.

Diphenylacetylene

White solid; eluent: ethyl acetate/hexane (1:20), R_f = 0.6; m.p.: 58–59 °C; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): ä = 7.58–7.55 (m, 4H; ArH), 7.39–7.30 ppm (m, 6H; ArH); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): ä = 131.66, 128.39, 128.29, 123.37, 89.47 ppm; IR (neat): $\tilde{I}_{max}$ = 1596, 1492, 748, 681 cm^{-1}; HRMS (APCI): m/z calcd for C$_{14}$H$_{11}$ [M+H]$^+$: 179.0861; found: 179.0865.

2-Methyl-4-phenylbut-3-yn-2-ol

Yellow oil; eluent: ethyl acetate/hexane (1:3), R_f = 0.5; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): ä = 7.43–7.40 (m, 2H; ArH), 7.39–7.29 (m, 3H; ArH), 2.01 (s, 1H; -OH), 1.62 ppm (s, 6H; -CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): ä = 131.63, 128.22, 122.76, 93.82, 82.14, 65.60, 31.49 ppm; IR (neat): $\tilde{I}_{max}$ = 3271, 2207, 1596, 1486, 753, 690 cm^{-1}; HRMS (ESI): m/z calcd for C$_{11}$H$_{13}$O [M+H]$^+$: 161.0966; found: 161.0970.

1-n-Propyl-2-phenylacetylene

Yellow oil; eluent: ethyl acetate/hexane (1:20), R_f = 0.5; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): ä = 7.42–7.39 (m, 2H; ArH), 7.32–7.28 (m, 3H; ArH), 2.40 (t, J = 6.90 Hz, 2H; -CH$_2$), 1.71–1.59 (m, 2H; -CH$_2$), 1.06 ppm (t, J = 7.35 Hz, 3H; -CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): ä = 131.53, 128.14, 127.42, 124.13, 90.21, 80.71, 22.21, 21.38, 13.50 ppm; IR (neat): $\tilde{I}_{max}$ = 2235, 1598, 1498, 753, 689 cm^{-1}; HRMS (APCI): m/z calcd for C$_{11}$H$_{13}$ [M+H]$^+$: 145.1017; found: 145.1021.

1-Ferrocenyl-2-phenylacetylene

Orange solid; eluent: ethyl acetate/hexane (1:15), R_f = 0.6; m.p.: 117–119 °C; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): ä = 7.53–7.49 (m, 2H; ArH), 7.36–7.32 (m, 3H; ArH), 4.53 (s, 2H; FcH), 4.27 ppm (s, 7H; FcH); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): ä = 131.43, 128.30, 127.68, 123.98, 88.33, 85.76, 71.50, 70.09, 68.93, 65.44 ppm; IR (neat): $\tilde{I}_{max}$ = 2196, 1593, 1488, 690, 751 cm^{-1}; HRMS (APCI): m/z calcd for C$_{18}$H$_{15}$Fe [M+H]$^+$: 287.0523; found: 287.0528

4-Nitrophenyl-2-phenylacetylene

Pale yellow solid; eluent: ethyl acetate/hexane (1:10), R_f = 0.6; m.p.: 118–119 °C; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): ä = 8.22 (d, J = 8.40 Hz, 2H; ArH), 7.67 (d, J = 8.40 Hz, 2H; ArH), 7.57–7.55 (m, 2H; ArH), 7.41–7.39 ppm (m, 3H; ArH); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): ä = 147.02, 132.25, 131.84, 130.26, 129.26, 128.53, 123.61, 122.13,

94.70, 87.55 ppm; IR (neat): $\tilde{I}_{max}=2207$, 1586, 1508, 1339, 853, 756, 685 cm^{-1}; HRMS (ESI): m/z calcd for C$_{14}$H$_{10}$NO$_2$ [M+H]$^+$: 224.0712; found: 224.0715.

4-Phenylethynylacetophenone

White solid; eluent: ethyl acetate/hexane (1:10), R_f=0.5; m.p.: 94–96 °C; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\ddot{a}=7.96$ (d, $J=8.40$ Hz, 2H; ArH), 7.63 (d, $J=8.40$ Hz, 2H; ArH), 7.59–7.56 (m, 2H; ArH), 7.40–7.38 (m, 3H; ArH), 2.63 ppm (s, 3H; -CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): $\ddot{a}=197.24$, 136.23, 131.7, 131.74, 128.80, 128.43, 128.26, 122.68, 92.70, 88.60, 26.57 ppm; IR (neat): $\tilde{I}_{max}=2216$, 1674, 1594, 1515, 830, 754, 688 cm^{-1}; HRMS (ESI): m/z calcd for C$_{16}$H$_{13}$O [M+H]$^+$: 221.0966; found: 221.0962.

4-Phenylethynylaniline

Brown solid; eluent: ethyl acetate/hexane (1:3), R_f=0.5; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\ddot{a}=7.54$–7.51 (m, 2H; ArH), 7.38–7.31 (m, 5H; ArH), 6.66 (d, $J=8.40$ Hz, 2H; ArH), 3.83 ppm (s, 2H; -NH$_2$); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): $\ddot{a}=146.66$, 132.96, 131.36, 128.25, 127.64, 123.96, 114.75, 112.69, 90.14, 87.34 ppm; IR (neat): $\tilde{I}_{max}=3472$, 3375, 2207, 1611, 1508, 822, 751, 685 cm^{-1}; HRMS (ESI): m/z calcd for C$_{14}$H$_{12}$N [M+H]$^+$: 194.0970; found: 194.0972.

4-Methylphenyl-2-phenylacetylene

White solid; eluent: ethyl acetate/hexane (1:20), R_f=0.5; m.p.: 68–70 °C; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\ddot{a}=7.55$–7.51 (m, 2H; ArH), 7.43 (d, $J=8.10$ Hz, 2H; ArH), 7.37–7.33 (m, 3H; ArH), 7.16 (d, $J=8.10$ Hz, 2H; ArH), 2.37 ppm (s, 3H; -CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): $\ddot{a}=138.41$, 131.58, 131.53, 129.14, 128.34, 128.10, 123.53, 120.24, 89.60, 88.76, 21.53 ppm; IR (neat): $\tilde{I}_{max}=2917$, 2210, 1584, 1500, 814, 752, 687 cm^{-1}; HRMS (APCI): m/z calcd for C$_{15}$H$_{13}$ [M+H]$^+$:193.1017; found: 193.1022.

4-Methoxyphenyl-2-phenylacetylene

White solid; eluent: ethyl acetate/hexane (1:15), R_f=0.5; m.p.: 56–58 °C; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\ddot{a}=7.55$–7.48 (m, 4H; ArH), 7.37–7.33 (m, 3H; ArH), 6.90 (d, $J=9.00$ Hz, 2H; ArH), 3.85 ppm (s, 3H; -CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): $\ddot{a}=159.65$, 133.07, 131.47, 128.32, 127.94, 123.64, 115.43, 114.02, 89.39, 88.08, 55.32 ppm; IR (neat): $\tilde{I}_{max}=2931$, 2207, 1595, 1501, 832, 751, 687 cm^{-1}; HRMS (APCI): m/z calcd for C$_{15}$H$_{13}$O [M+H]$^+$: 209.0966; found: 209.0970.

3-Methylphenyl-2-phenylacetylene

Colorless oil; eluent: ethyl acetate/hexane (1:20), R_f=0.6; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\ddot{a}=7.58$–7.51 (m, 3H; ArH), 7.41–7.36 (m, 3H; ArH), 7.26–7.16 (m, 3H; ArH), 2.54 ppm (s, 3H; -CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): $\ddot{a}=140.22$, 131.88, 131.55, 129.50, 128.39, 128.34, 128.20, 125.62, 123.61, 123.07, 93.39, 88.39, 20.78 ppm; IR (neat): $\tilde{I}_{max}=2919$, 2214, 1597, 1491, 750, 686 cm^{-1}; HRMS (APCI): m/z calcd for C$_{15}$H$_{13}$ [M+H]$^+$: 193.1017; found: 193.1014.

2,5-Dimethylphenyl-2-phenylacetylene

Pale yellow solid; eluent: ethyl acetate/hexane (1:20), R_f=0.5; m.p.: 80–82 °C; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\ddot{a}=7.56$–7.55 (m, 2H; ArH), 7.38–7.36 (m, 4H; ArH), 7.15 (d, $J=7.80$ Hz, 1H; ArH), 7.07 (d, $J=7.80$ Hz, 1H; ArH), 2.50 (s, 3H; -CH$_3$), 2.34 ppm (s, 3H; -CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): $\ddot{a}=137.12$, 135.06, 132.34, 131.53, 129.39, 129.24, 128.36, 128.11, 123.70, 122.80, 92.98, 88.59, 20.78, 20.25 ppm; IR (neat): $\tilde{I}_{max}=2915$, 2203, 1594, 1485, 810, 895, 749, 684 cm^{-1}; HRMS (APCI): m/z calcd for C$_{16}$H$_{15}$ [M+H]$^+$: 207.1174; found: 207.1178.

4-(Phenylethynyl)pyridine

Pale yellow solid; eluent: ethyl acetate/hexane (1:3), R_f=0.6; m.p.: 93–95 °C; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\ddot{a}=8.62$ (d, $J=6.00$ Hz, 2H; PyH), 7.59–7.56 (m, 2H; PyH), 7.41–7.39 ppm (m, 5H; ArH); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): $\ddot{a}=149.66$, 131.90, 131.52, 129.24, 128.52, 125.81, 122.12, 94.04, 86.68 ppm; IR (neat): $\tilde{I}_{max}=2214$, 1577, 1533, 1406, 754, 689 cm^{-1}; HRMS (ESI): m/z calcd for C$_{13}$H$_{10}$N [M+H]$^+$: 180.0813; found: 180.0815.

5-(Phenylethynyl)pyrimidine

Yellow oil; eluent: ethyl acetate/hexane (1:3), R_f=0.5; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\ddot{a}=9.14$ (s, 1H; PyrimH), 8.86 (s, 2H; PyrimH), 7.57–7.54 (m, 2H; ArH), 7.40–7.35 ppm (m, 3H; ArH); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): $\ddot{a}=158.63$, 156.71, 131.80, 129.39, 128.57, 121.80, 119.96, 96.35, 82.31 ppm; IR (neat): $\tilde{I}_{max}=2212$, 1598, 1482, 1408, 759, 687 cm^{-1}; HRMS (ESI): m/z calcd for C$_{12}$H$_9$N$_2$ [M+H]$^+$: 181.0766; found: 181.0761.

Biphenyl

White solid; eluent: ethyl acetate/hexane (1:20), R_f=0.6; m.p.: 69–70 °C; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\ddot{a}=7.61$ (d, $J=6.90$ Hz, 4H; ArH), 7.46 (t, $J=7.35$ Hz, 4H; ArH), 7.36 ppm (t, $J=7.35$ Hz, 2H; ArH); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): $\ddot{a}=141.30$, 128.80, 127.30, 127.22 ppm; IR (neat): $\tilde{I}_{max}=1569$, 1470, 723, 688 cm^{-1}; HRMS (APCI): m/z calcd for C$_{12}$H$_{11}$ [M+H]$^+$: 155.0861; found: 155.0866.

4-Methylbiphenyl

White solid; eluent: ethyl acetate/hexane (1:20), R_f=0.5; m.p.: 46–48 °C; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\ddot{a}=7.63$ (d, $J=7.20$ Hz, 2H; ArH), 7.54 (d, $J=8.10$ Hz, 2H; ArH), 7.47 (t, $J=7.50$ Hz, 2H; ArH), 7.36 (t, $J=7.35$ Hz, 1H; ArH), 7.30 (d, $J=8.10$ Hz, 2H; ArH), 2.44 ppm (s, 3H; -CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): $\ddot{a}$ 141.24, 138.43, 137.06, 129.54, 128.77, 127.23, 127.04, 21.16 ppm; IR (neat): $\tilde{I}_{max}=2912$, 1600, 1478, 821, 749, 685 cm^{-1}; HRMS (APCI): m/z calcd for C$_{13}$H$_{13}$ [M+H]$^+$: 169.1017; found: 169.1013.

4-Nitrobiphenyl

Pale yellow solid; eluent: ethyl acetate/ hexane (1:15), R_f=0.5; m.p.: 114–116 °C; ^{1}H NMR (300 MHz, [D$_6$]DMSO, TMS): $\ddot{a}=8.30$ (d, $J=9.00$ Hz, 2H; ArH), 7.96 (d, $J=8.70$ Hz, 2H; ArH), 7.80–7.77 (m, 2H; ArH), 7.56–7.45 ppm (m, 3H; ArH); ^{13}C NMR (75 MHz, [D$_6$]DMSO, TMS): $\ddot{a}=147.15$, 147.09, 138.29, 129.68, 129.50, 128.30, 127.71, 124.52 ppm; IR (neat): $\tilde{I}_{max}=1591$, 1506, 1396, 847, 733, 691 cm^{-1}; HRMS (ESI): m/z calcd for C$_{12}$H$_{10}$NO$_2$ [M+H]$^+$: 200.0712; found: 200.0717.

4-Phenylacetophenone

White solid; eluent: ethyl acetate/hexane (1:10); $R_f = 0.5$; m.p.: 120–122 °C; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\ddot{a} = 8.06$ (d, $J = 8.40$ Hz, 2 H; ArH), 7.71 (d, $J = 8.10$ Hz, 2 H; ArH), 7.65 (d, 2 H; $J = 6.90$ Hz, 2 H; ArH), 7.40–7.52 (m, 3 H; ArH), 2.66 ppm (s, 3 H; -CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): $\ddot{a} = 197.75$, 145.81, 139.90, 135.89, 128.97, 128.93, 128.25, 127.29, 127.24, 26.67 ppm; IR (neat): $\tilde{I}_{max} = 2919$, 1672, 1592, 1477, 835, 759, 683 cm^{-1}; HRMS (ESI): m/z calcd for C$_{14}$H$_{13}$O [M+H]$^+$: 197.0966; found: 197.0961.

4-Methoxybiphenyl

White solid; eluent: ethyl acetate/hexane (1:12); $R_f = 0.5$; m.p.: 86–87 °C; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\ddot{a} = 7.60$–7.55 (m, 4 H; ArH), 7.45 (t, $J = 7.50$ Hz, 2 H; ArH), 7.33 (t, $J = 7.20$ Hz, 1 H; ArH), 7.02 (d, $J = 8.70$ Hz, 2 H; ArH), 3.88 ppm (s, 3 H; -CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): $\ddot{a} = 159.19$, 140.86, 133.81, 128.72, 128.16, 126.74, 126.66, 114.24, 55.34 ppm; IR (neat): $\tilde{I}_{max} = 2961$, 1600, 1518, 831, 755, 683 cm^{-1}; HRMS (APCI): m/z calcd for C$_{13}$H$_{13}$O [M+H]$^+$: 185.0966; found: 185.0969.

4-Phenylpyridine

Pale yellow solid; eluent: ethyl acetate/hexane (1:1); m.p.: 77–78 °C; ^{1}H NMR (300 MHz, [D$_6$]DMSO, TMS): $\ddot{a} = 8.64$ (d, $J = 6.00$ Hz, 2 H; PyH), 7.80 (d, $J = 6.00$ Hz, 2 H; PyH), 7.71–7.69 (m, 2 H; PyH), 7.56–7.45 ppm (m, 3 H; ArH); ^{13}C NMR (75 MHz, [D$_6$]DMSO, TMS): $\ddot{a} = 150.68$, 147.45, 137.63, 129.67, 129.64, 127.24, 121.66 ppm; IR (neat): $\tilde{I}_{max} = 1581$, 1474, 755, 678 cm^{-1}; HRMS (ESI): m/z calcd for C$_{11}$H$_{10}$N [M+H]$^+$: 156.0813; found: 156.0809.

5-Phenylpyrimidine

Pale yellow solid; eluent: ethyl acetate/hexane (2:3); $R_f = 0.5$; m.p.: 50–52 °C; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\ddot{a} = 9.22$ (s, 1 H; PyrimH), 8.97 (s, 2 H; PyrimH), 7.61–7.45 ppm (m, 5 H; ArH); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): $\ddot{a} = 157.49$, 154.91, 134.36, 134.29, 129.44, 129.02, 127.00 ppm; IR (neat): $\tilde{I}_{max} = 1577$, 1497, 1408, 760, 693 cm^{-1}; HRMS (APCI): m/z calcd for C$_{10}$H$_9$N$_2$ [M+H]$^+$: 157.0766; found: 157.0762.

(E)-1,2-Diphenylethene

White solid; eluent: hexane; $R_f = 0.5$; m.p.: 126–127 °C; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\ddot{a} = 7.53$ (d, $J = 7.20$ Hz, 4 H; ArH), 7.37 (t, $J = 7.35$ Hz, 4 H; ArH), 7.26 (t, $J = 7.20$ Hz, 2 H; ArH), 7.12 ppm (s, 2 H; CH=CH); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): $\ddot{a} = 137.39$, 128.75, 128.73, 127.66, 126.56 ppm; IR (neat): $\tilde{I}_{max} = 3021$, 2923, 1595, 1498, 757, 684 cm^{-1}; HRMS (APCI): m/z calcd for C$_{14}$H$_{13}$ [M+H]$^+$: 181.1017; found: 181.1020

Methyl Cinnamate

Pale yellow solid; eluent: ethyl acetate/hexane (1:10); $R_f = 0.6$; m.p.: 34–36 °C; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\ddot{a} = 7.70$ (d, $J = 16.20$ Hz, 1 H; CH=CH), 7.54–7.51 (m, 2 H; ArH), 7.39–7.37 (m, 3 H; ArH), 6.45 (d, $J = 15.90$ Hz, 1 H; CH=CH), 3.81 ppm (s, 3 H; CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): $\ddot{a} = 167.43$, 144.88, 134.42, 130.30, 128.91, 128.08, 117.84, 51.70 ppm; IR (neat): $\tilde{I}_{max} = 3065$, 2923,1711, 1632, 1489, 769, 713 cm^{-1}; HRMS (APCI): m/z calcd for C$_{10}$H$_{11}$O$_2$ [M+H]$^+$: 163.0759; found: 163.0763.

(E)-4-Nitrophenyl-2-styrene

Pale yellow solid; eluent: ethyl acetate/hexane (1:15); $R_f = 0.5$; m.p.: 159–160 °C; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\ddot{a} = 8.22$ (d, $J = 9.0$ Hz, 2 H; ArH), 7.64 (d, $J = 8.70$ Hz, 2 H; ArH), 7.55 (d, $J = 7.20$ Hz, 2 H; ArH), 7.43–7.33 (m, 3 H; ArH), 7.28 (d, $J = 16.20$ Hz, 1 H; CH=CH), 7.15 ppm (d, $J = 16.20$ Hz, 1 H; CH=CH); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): $\ddot{a} = 146.81$, 143.87, 136.21, 133.34, 128.92, 128.87, 127.05, 126.88, 126.31, 124.16 ppm; IR (neat): $\tilde{I}_{max} = 3077$, 2934, 1593, 1504, 1335, 832, 765, 691 cm^{-1}; HRMS (ESI): m/z calcd for C$_{14}$H$_{12}$NO$_2$ [M+H]$^+$: 226.0868; found: 226.0863.

(E)-4-Styrylbenzonitrile

White solid; eluent: ethyl acetate/hexane (1:12); $R_f = 0.5$; m.p.: 115–117 °C; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\ddot{a} = 7.64$ (d, $J = 8.10$ Hz, 2 H; ArH), 7.59 (d, $J = 8.40$ Hz, 2 H; ArH), 7.54 (d, $J = 7.50$ Hz, 2 H; ArH), 7.41–7.29 (m, 3 H; ArH), 7.22 (d, $J = 16.20$ Hz, 1 H; CH=CH), 7.09 ppm (d, $J = 16.50$ Hz, 1 H; CH=CH); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): $\ddot{a} = 141.87$, 136.32, 132.51, 132.45, 128.88, 128.66, 126.93, 126.89, 126.76, 119.04, 110.63 ppm; IR (neat): $\tilde{I}_{max} = 3024$, 2924, 2222, 1596, 1497, 823, 756, 690 cm^{-1}; HRMS (ESI): m/z calcd for C$_{15}$H$_{12}$N [M+H]$^+$: 206.0970; found: 206.0966.

(E)-4-Methylphenyl-2-styrene

White solid; eluent: ethyl acetate/hexane (1:20); $R_f = 0.6$; m.p.: 121–123 °C; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\ddot{a} = 7.51$ (d, $J = 6.90$ Hz, 2 H; ArH), 7.42 (d, $J = 8.10$ Hz, 2 H; ArH), 7.35 (t, $J = 7.35$ Hz, 2 H; ArH), 7.26–7.24 (m, 1 H; ArH), 7.17 (d, $J = 7.80$ Hz, 2 H; ArH), 7.08 (s, 2 H; CH=CH), 2.36 ppm (s, 3 H; CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): $\ddot{a} = 137.55$, 134.59, 129.42, 128.67, 127.74, 127.42, 126.45, 126.42, 21.27 ppm; IR (neat): $\tilde{I}_{max} = 3020$, 2915, 1587, 1502, 804, 752, 686 cm^{-1}; HRMS (APCI): m/z calcd for C$_{15}$H$_{15}$ [M+H]$^+$: 195.1174; found: 195.1176.

(E)-4-Methoxylphenyl-2-styrene

White solid; eluent: ethyl acetate/hexane (1:20); $R_f = 0.5$; m.p.: 135–137 °C; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\ddot{a} = 7.49$ (t, $J = 9.15$ Hz, 4 H; ArH), 7.36 (t, $J = 7.50$ Hz, 2 H; ArH), 7.24–7.22 (m, 1 H; ArH), 7.09 (d, $J = 16.20$ Hz, 1 H; CH=CH), 6.99 (d, $J = 16.50$ Hz, 1 H; CH=CH), 6.92 (d, $J = 8.70$ Hz, 2 H; ArH), 3.85 ppm (s, 3 H; CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): $\ddot{a} = 159.34$, 137.68, 130.18, 128.65, 128.24, 127.72, 127.22, 126.65, 126.26, 114.16, 55.34 ppm; IR (neat): $\tilde{I}_{max} = 3056$, 2918, 1595, 1503, 814, 750, 686 cm^{-1}; HRMS (APCI): m/z calcd for C$_{15}$H$_{15}$O [M+H]$^+$: 211.1123; found: 211.1119.

Conflict of Interest

The authors declare no conflict of interest.

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